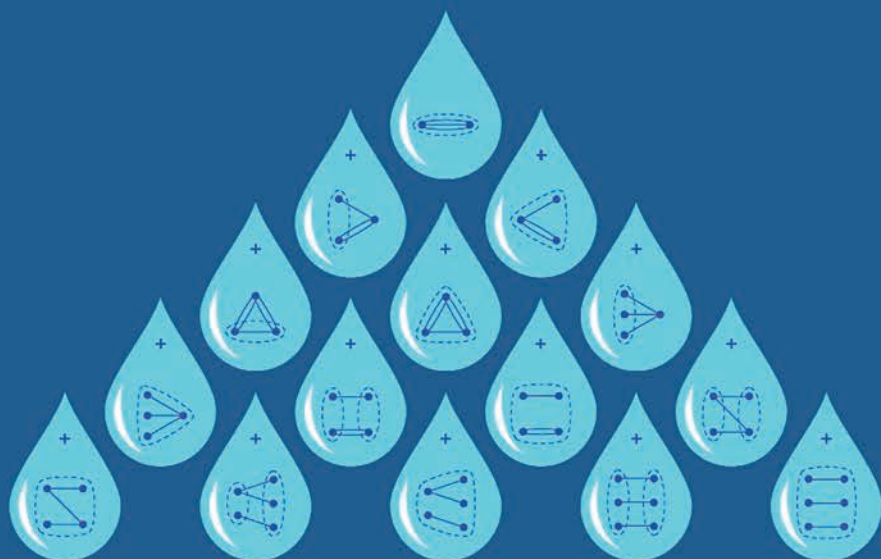


Ihor YUKHNOVSKII
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STATISTICAL THEORY OF CLASSICAL EQUILIBRIUM SYSTEMS



NATIONAL ACADEMY
OF SCIENCES OF UKRAINE
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FOR CONDENSED MATTER PHYSICS
OF THE NAS OF UKRAINE

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ПРОЄКТ
«УКРАЇНСЬКА НАУКОВА КНИГА
ІНОЗЕМНОЮ МОВОЮ»

КИЇВ
АКАДЕМПЕРІОДИКА
2025

Ihor YUKHNOVSKII
Myroslav HOLOVKO

**STATISTICAL
THEORY
OF CLASSICAL
EQUILIBRIUM
SYSTEMS**

*PROJECT
«UKRAINIAN SCIENTIFIC BOOK
IN A FOREIGN LANGUAGE»*

KYIV
AKADEMPERIODYKA
2025

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*Approved for publication by the Scientific Council of the Yukhnovskii Institute
for Condensed Matter Physics of the National Academy of Sciences of Ukraine
(April 9, 2025, Protocol No. 49)*

*The publication was funded within the framework of the Targeted
Complex Program of the NAS of Ukraine “Scientific Bases of Functioning
and Providing for Conditions for the Development of the Scientific
and Publishing Complex of the NAS of Ukraine”*

Yukhnovskii I.R.

Y91 Statistical Theory of Classical Equilibrium Systems/
I.R. Yukhnovskii, M.F. Holovko; NAS of Ukraine, Yukhnovskii
Institute for Condensed Matter Physics of the NAS of Ukraine. —
2nd ed., English, revised and supplemented. — Kyiv: Akademp-
riodyka, 2025. — 444 p.

ISBN 978-966-360-558-6

The monograph, first published by Naukova Dumka in 1980, provides a systematic presentation of the statistical theory of classical equilibrium systems. It is among the first works devoted to the microscopic theory of the liquid state and may be regarded as an advanced textbook. A broad class of systems representing gases, liquids, and solutions is analyzed from a unified standpoint. The theory describes interacting particles in an extended phase space that includes both individual coordinates and collective variables characterizing density fluctuations. The ion-molecular approach developed for electrolyte solutions treats interactions between ions and solvent molecules on an equal basis, revealing fundamentally different mechanisms of electrostatic screening. Spatially inhomogeneous systems are examined in detail as well.

UDC 531.19

ISBN 978-966-360-558-6

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EDITORIAL PREFACE TO THE SECOND EDITION

In 1980, the monograph *Statistical Theory of Classical Equilibrium Systems* by Ihor Yukhnovskii and Myroslav Holovko appeared under the imprint of “Naukova Dumka”. This book was among the first worldwide to summarise the achievements of that time in developing a consistent microscopic theory of dense fluids. It presented the main results achieved by Professor Yukhnovskii’s research laboratory over the previous two decades. The theory was grounded to a large extent in the ideas of Mykola Bogolyubov, whose influence profoundly shaped Yukhnovskii’s scientific outlook. Myroslav Holovko was one of Yukhnovskii’s first students and eventually became the leading figure in the group’s research on simple and molecular liquids and electrolyte solutions.

The principal axis of the monograph is in the development and application of the collective variables method to classical equilibrium fluids. This original approach, as a tool of microscopic statistical theory, is focused on the description of thermodynamic, structural and electric properties of systems of interacting particles that follow from the calculation of the partition function or, equivalently, from the pair distribution functions. Within this methodology, the authors develop the idea of applying different statistical treatments to the short-range and long-range contributions of the total interparticle interaction. The proposed approaches make it possible to obtain formally exact and physically meaningful results for simple fluids, molecular systems with different intramolecular structures, fluid mixtures, ionic melts and electrolyte solutions. Moreover, the method is formulated *ab ovo* to model fluids under the influence of an external field, which allows one to describe various surface phenomena. In particular, for ion-molecular systems with multipole electrostatic interaction, the authors constructed cluster expansions for the Helmholtz free energy and for the pair distribution functions of species in terms of the screened potentials. For

ionic and ion-dipole model of electrolyte solutions the effective interaction between ions results in the Debye screened potential, whereas the ion-solute and solute-solute screening involves the dielectric function. It allows the use of the dipole and/or quadrupole moments of molecules to fit the magnitude of solvent effects in solution, besides the parameters characterizing the ionic solutes. These results form the essence of a consistent and successful microscopic theory of electrolyte solutions. It has been applied to describe the phenomenon of ion solvation in terms of the structural and thermodynamic properties of aqueous and non-aqueous electrolytes. A more sophisticated reference system treatment of short-range interparticle interactions, aimed at extending the methodology to dense fluids, has also been elaborated in the monograph. This version of the theory yields optimised cluster expansions that directly benefit from the results of the integral equations of the liquid state theory. It is worth mentioning that the extension of the screened potential concept within the collective variables approach has been elaborated in more recent research to explore solid electrolytes.

The reference system treatment of short-range interactions requires tools capable of accurately describing the internal structure and shape of molecules. The authors provided an extensive review addressing this problem. In particular, the authors discuss the scaled particle theory for hard-body systems of arbitrary convex shapes, later successfully extended to the adsorption of fluids in partly quenched disordered materials. For inhomogeneous ion-molecular mixtures, the method of collective variables, combined with two versions of the treatment of short-range interactions, made it possible to describe a range of interfacial properties. In the problem of a fluid electrolyte in contact with a solid surface, the effect of electrostatic images on the density profiles has been elucidated. On the other hand, the reference system approach allowed the description of trends in the behaviour of the electric double-layer capacitance. We would like to note that recent developments have explored and analysed the relationship between the collective variables method and the density functional and field theoretical approaches at a fundamental level. Much less attention has been paid to the problems of phase behaviour and phase transitions in the systems under consideration. The problems of fluid crystallisation, liquid–vapour phase transition and interfacial structure, as well as liquid–liquid phase behaviour, have been either considered only briefly or omitted. The authors acknowledged in their introduction to the first edition that these issues would require separate volumes to be written. We share their view on this matter.

The scope of the book does not include a detailed comparison between theoretical results and experimental findings. Nevertheless, numerous examples of such studies can be found in more recent literature following the publication of the monograph, particularly for electrolyte solutions, fluids of polymers and macromolecules, adsorption isotherms, contact angle calculations, and proper-

ties of the electric double layer. It is worth mentioning that several problems discussed in the monograph have significantly influenced research in computer simulations within this field over the past decades. At the time the monograph was written, such studies were still in their infancy compared with current developments, which have advanced greatly with the progress of computational technology and facilities.

The monograph is of interest to theoreticians working in the field of the statistical physics of liquids. It provides both fundamental concepts and practical tools for theoretical chemists, particularly in chemical engineering and electrochemistry. In addition, it may attract the attention of biologists interested in physicochemical and interdisciplinary applications.

The monograph has long served as a research and advanced pedagogical tool for many theoretical physicists working on liquid-state theory across the former USSR. The original text was written in Russian, which was not the native language of either author. Indeed, the authors of nearly all scientific monographs in the natural sciences under the communist regime in Ukraine faced a dilemma: either to compromise and publish their work in Russian — a choice encouraged at all administrative levels and generally regarded as supportive of scientific development, or to insist on their legal right to publish in Ukrainian — thereby significantly limiting the potential dissemination of their work. Publishing in English was, in practice, not considered a viable option at all. Nevertheless, the monograph was cited in English-language scientific journals, although such citations often contained errors arising from the language barrier. Since the full text of the book remained inaccessible to English-speaking readers, physicists from abroad repeatedly inquired over the years whether an English edition would eventually appear.

Taking into account all the circumstances outlined above, a group of enthusiasts came together with the aim to produce English translation of the monograph by I. Yukhnovskii and M. Holovko. We are convinced that, even 45 years after its original publication, this book has not lost its relevance. Moreover, readers are likely to find particular interest in the last, new chapter of the book written by one of the co-authors — Myroslav Holovko. He reflects on some aspects of subsequent evolution of the theory of liquids since the original edition was published.

In addition, this English-language edition may be of special interest to scholars of the history of science and could serve as the foundation for a dedicated series of rare reprints by the National Academy of Sciences of Ukraine, tentatively titled the *Classics of Ukrainian Physical Science*.

Finally, it is worth noting that the 1st of September 2025 marks the centenary of the birth of Academician Ihor Yukhnovskii. He passed away shortly before reaching the age of 99, remaining active and deeply engaged with developments in Ukraine and the wider world until the very end. He continued his

work as a theoretical physicist, having returned, after many years in politics, to his lifelong passion — statistical physics. With his passing, Ukraine lost a renowned scientist, the founder of the Lviv school of statistical physics and a recognized architect of the Ukrainian modern statehood. It is therefore our honour to dedicate this English-language edition of the monograph *Statistical Theory of Classical Equilibrium Systems* to the memory of this remarkable and distinguished individual.

In conclusion, we would like to extend our sincere gratitude to all colleagues from the Yukhnovskii Institute for Condensed Matter Physics of the NAS of Ukraine who actively contributed to the preparation of this edition: *O. Patsahan*, *M. Tokarchuk*, *A. Trokhymchuk*, *M. Dudka*, *I. Kravtsiv*, as well as *R. Romanik*, *Y. Honchar*, *D. Yaremchuk*, *M. Kopcha*, *I.-M. Ilenkov*, and *O. Kalyuzhnyi* for their assistance with text translation, formula typesetting, and proofreading; *O. Velychko* for digitizing and replotting the figures; *H. Butovych* for drawing diagrams; and *A. Shvaika* for his valuable advice and guidance on the technical aspects of preparing the edition. Many enthusiasts took part in the preparation of this book, and the editorial offers its heartfelt thanks to every one of them. We sincerely hope this edition will find its readers.

AUTHOR'S PREFACE TO THE SECOND EDITION

Since the previous edition of this book was published, 45 years have passed. In fact, considering that the manuscript was submitted to the publisher in 1977, and accounting for the time it took to write, more than 50 years have elapsed. During this period, statistical-mechanical research on classical systems of interacting particles has undergone significant further development and found new areas of application. In the intervening years, the concept of soft matter emerged in the research group of the French scientist P.-G. de Gennes, and it has since taken a prominent place in the physics of condensed matter [1]. This term now encompasses a wide range of systems that were traditionally associated with the fields of chemistry and biology. These include, first and foremost, the objects of liquid state physics, liquids and solutions.

In a narrower sense, the term soft matter is sometimes equated with complex fluids, which are typically characterized by the presence of particles or structures of mesoscopic dimensions. Examples of complex fluids include polymers, polyelectrolytes, liquid crystals, colloidal and micellar systems, and microemulsions. The category of soft matter also includes gels, membranes, various biological systems, fluids in porous media, and other similar systems.

In his 1991 Nobel lecture [2], de Gennes identified two key characteristics of soft matter: complexity and flexibility (softness). The complexity of soft matter is manifested, above all, in the lack of simple and intuitive models of its structure — unlike, for example, the ideal gas model for gases or the crystalline lattice for solid-state crystals.

The relatively weak attractive interactions in soft matter systems enhance thermal fluctuations, making their structure inherently probabilistic. As a result, understanding and inter-

preting the properties of soft matter necessarily requires the use of statistical physics methods.

Like solids, soft matter is characterized by relatively high bulk compressibility. However, due to the presence of thermal fluctuations and structural irregularity, it exhibits a very low shear modulus. As a result, soft matter possesses significant flexibility, which fundamentally accounts for its softness. It can easily change shape, a feature that, in the case of liquids, manifests as fluidity. More generally, as de Gennes noted, this is reflected in the presence of a large response function. Overall, the softness of soft matter gives rise to the remarkable richness and uniqueness of its properties, which are rarely observed in other types of condensed systems. These include, in particular, the complexity of its phase behaviour and the extraordinary features of its dynamic properties.

A striking example is found in biological structures such as proteins and membranes, which, owing to the low dimensionality of their architecture, exhibit extreme sensitivity to fluctuations — resulting in a wide variety of conformational transitions.

Over the past 50 years, a number of monographs have been published that explore the development of statistical-mechanical methods for studying the properties of classical models of interacting particles and their applications in the theory of simple liquids and solutions. Among these, we should first highlight the unique book by Hansen and McDonald [3], which has been reissued multiple times in recent years. Perturbation theories for the thermodynamic properties of simple fluids and solids are presented in the book by Solana [4]. Also worth mentioning is the foundational two-volume monograph by Gray and Gubbins [5, 6] devoted to the theory of molecular fluids, as well as the monograph by Rowlinson and Widom [7] on the molecular theory of capillarity. We also note the recent monograph by Hirata [8], dedicated to the study of fluctuations in biological systems with explicit consideration of the aqueous environment. Since the first edition of the present monograph, the theory of classical systems of interacting particles has also seen rapid development in the field of computer simulation methods. Excellent textbooks on this subject have appeared [9, 10]. It is worth noting that comparing theoretical predictions with computational results enables one to assess the validity of the theoretical approximations used.

In the previous edition, we already noted the usefulness of splitting into the intermolecular interaction potential into short- and long-range parts and applying different approximations to describe them. In the present edition, we have added a new sixth chapter based on the original research of the authors conducted after the publication of the first edition. As mentioned in the introduction to the first edition, short-range interactions are of repulsive nature, vary rapidly with distance, and primarily determine the entropic and

structural properties of the system. The long-range interactions vary more smoothly and their contribution is mainly energetic. The emergence and development of soft matter physics necessitated a separation of intermolecular interaction potentials into three parts. Alongside short- and long-range interactions, it became necessary to isolate strongly attractive interactions at intermediate distances. These interactions are often referred to as associative, and they are responsible for the formation of various associates in the system, such as dimers, polymers, network-like, solvation, and more complex structures.

A significant contribution to the extension of the theory of simple liquids to the case of associative fluids was made in M. Wertheim's works [11–14], which demonstrated that, due to their steric saturation, associative interactions require a combination of cluster expansions in both density and activity. This led to the development of the multidensity formalism. Our group at the Yukhnovskii Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine also made important contributions to the development of this formalism. Unfortunately, we are not able to discuss these studies in more detail here.

We hope that the material from this research will become the subject of a separate monograph. In the present edition, we have only added Chapter 6 based on the original research carried out after the first edition of this monograph.

The additional chapter consists of two sections. In the first section, an integral equation is formulated for the pair distribution function of systems with long-range and short-range interactions, and it is shown that the cluster expansions for the pair distribution function obtained in Chapter 2 can be derived iteratively from this integral equation. It is demonstrated that the diagrammatic expressions for the pair distribution function and the free energy from Chapter 2 are easily generalized to the case in which short-range interactions are treated as the reference system, through a simple change in diagrammatic notation. In the second section, these results are extended to include associative interactions.

In the new edition, a three-part numbering system for equations has been adopted. The first digit corresponds to the chapter, the second to the section within the chapter, and the third to the equation number within that section.

In conclusion, I would like to express my gratitude to I. Yukhnovskii, my teacher and mentor, for nearly 60 years of collaboration, beginning in 1965. I have learned a great deal from him. The idea of writing this monograph, as well as its reissue, belonged to I. Yukhnovskii. During the process of writing and republishing it, I was able to organize and consolidate my knowledge of the statistical theory of liquids and solutions. Unfortunately, in March of last year,

I. Yukhnovskii passed away, and the responsibility for finalizing the content of the new edition was left to me alone.

I would like to thank the managing editors and editorial board, the language editor, and the reviewers for their helpful advice and support, as well as the staff of the Yukhnovskii Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine for their assistance in preparing the book for publication. In particular, I wish to thank O. Pizio for initiating the reissue of the book in English, T. Patsahan for organizing the translation and typesetting of the new edition, and I. Kravtsiv for help with the translation and typesetting of the preface to the second edition, the last two chapters, and various additional edits.

Myroslav HOLOVKO
May, 2025

PREFACE TO THE FIRST EDITION

Classical system of interacting particles, e.g., atoms, molecules or ions, is the microscopic model of a substance in all of the three aggregation states, namely solid, liquids and gas. The objective of the equilibrium statistical theory is to describe thermodynamic and structural properties of a system at given external conditions and at a given interparticle interaction. Commonly, it has a different shape at large and small distances between particles.

The short-range interactions are repulsive. They rapidly change with the distance and yield the main contribution into the entropic and structural properties of the system. The long-range interactions change more smoothly and their contribution is mostly energetic. The short-range and long-range interactions are characterized by different parameters and require different means of describing them within approximate calculations.

An idea to use different methods for the description of short-range and long-range interactions was formulated by van der Waals more than 150 years ago. However, only in the last two decades substantial achievements have been reached in realization of this idea. This became possible due to the construction of the theory for systems with solely short-range interactions and subsequent development of a consistent method to take into account the long-range interactions from such a starting point. This permitted to construct the theory of liquid state that for years was less developed compared to the theories of solid state and of gases.

However, these successes have not been sufficiently well described in the literature. In the majority of works, e.g., in the monographs of I.Z. Fisher, Ref. [15], of Rice and Grey, Ref. [16], and in the book by Croxton, Ref. [17], the principal attention is focused on the results of approximate integral equations that undoubtedly play an important role within the present development of statistical theory of equilibrium systems, but do not provide a reliable description of the contribution from the long-

range interactions. Recent collections of review articles, Refs. [18–21], describe several important issues of the state of art of statistical theory of classical equilibrium systems. Nevertheless, they do not provide an entirely consistent and systematic description of the problem.

In this monograph, it is attempted to give a systematic description of the statistical theory of equilibrium classical systems using the idea of van der Waals from the very beginning. Presentation of the material is done mathematically rigorously as much as possible and in a systematic manner by using an original method of collective variables. In order to describe the system, an extended phase space is used. For the simplest system of monoatomic particles, it consists of their Cartesian coordinates and modes of waves of density oscillations, the so-called collective variables. The short-range interactions are described using the Cartesian coordinates whereas the space of collective variables is used to describe the long-range interactions. A transformation to the space of these variables is performed within a specific procedure developed in Refs. [22] and [23].

Mathematical apparatus of the collective variables method represent our tools to consider a wide set of problems of the statistical theory of equilibrium systems of interacting particles. This method permeates the problems under study in this book as a whole.

The book consists of five chapters. In the first chapter we present principal issues concerned with equilibrium thermodynamics and statistical physics necessary for further developments. The theory of interparticle interactions and Mayer cluster expansions are given briefly. A few remarks concerning integral equations and computer simulations are provided as well.

The principal chapter is the second one. It describes the collective variables method. A transformation from the coordinate space to the representation of collective variables is given in very detail. The method is illustrated by the calculations of the configuration partition function of one-component system of particles that interact via the long-range interactions solely. The short-range interaction effects are taken into account next by functional differentiation.

The results obtained within such a procedure generalize Mayer cluster expansions for systems with strong long-range interactions. These series contain the screened potential rather than the initial long-range interactions. In the case of systems with Coulomb forces, the screened potential coincides with the well known expression by Debye.

In order to describe dense systems, one needs to identify the model with short-range interactions at the beginning and then, using it as a “background”, take the long-range interactions into account. This version of the procedure within the collective variables method is given in the second chapter too. Transformation into the collective variable space in this case is performed by using the Jacobian of transition that follows from averaging the transition function

over the system with short-range interactions. The results obtained generalize cluster expansions mentioned above, but involve the free energy and the distribution functions of the model with short-range interactions, rather than bare short-range interactions. The terms of these series for the free energy represent different approximations with accounted for the long-range interactions. In particular, the first term corresponds to the van der Waals theory whereas the second one, to the random phase approximation. The third and the following terms describe contributions coming from the pair, three-particle and further correlations. All the terms, besides the first one, include screened potentials rather than the initial long-range interactions.

In order to enhance the convergence of the cluster series, the optimization procedure of Weeks, Chandler and Andersen, Refs. [24–29], is used. Its essence is due to the ambiguity of splitting the total interaction into two terms in the physically inaccessible region of small interparticle distances. This procedure leads to the integral equation of the mean spherical type for the screened potential. The relation between the series obtained within the collective variables method and of other procedures, like the Bogolyubov theory for expansions by plasma parameter for Coulomb systems, high-temperature perturbation theory, gamma-ordering and other diagrammatic expansions are discussed.

In the following three chapters, theoretical results are applied to the description of different particular systems. Namely, our explanations refer to the systems with augmenting complexity. Specifically, in the third chapter the mono-atomic systems are considered. The theory for systems with most simple short-range potential, i.e., for a model of hard spheres is presented. Next, the problems arising due to the separation of the total potential into the short-range and long-range contributions are discussed using a simple system with Lennard-Jones potential as an example. A model with realistic repulsion and different contributions to the free energy and structural properties are considered there as well. This kind of results are generalized to many-component systems and are applied to the description of mono-atomic ionic systems.

The fourth chapter is devoted to the description of polyatomic molecular systems. General methodology for the description of systems with non-central interparticle interaction is provided. The problems due to account for orientational degrees of freedom are solved using an expansion of orientation-dependent functions into a series of generalized spherical harmonics. Separately, the approach based on atom-atom potentials is considered. In order to describe molecular systems with purely repulsive interactions, two models, such as the model of hard ellipsoids and reference model of interacting sites, are studied in detail. These results are then used to investigate molecular systems with electrostatic interaction and ion-molecular mixtures.

The fifth chapter deals with spatially inhomogeneous systems. There, the theory is generalized for the systems in the external field. Besides, the surface properties of condensed systems are described.

Evidently, this monograph does not represent a comprehensive description of the modern state of statistical theory of equilibrium systems. It is restricted to classical systems for which the quantum effects do not play a substantial role. Thus, it refers to the majority of real substances with the exception of helium and hydrogen at low temperatures. On the other hand, the systems under study with pair-wise interaction are considered at the level of models. Therefore, much attention is focused on the comparison of theoretical results with computer experiment rather than with real experiment. In this book the theory for out of equilibrium systems is not considered, not much attention is paid the phase transitions and critical state. The principal issues refer solely to liquid and gaseous state of matter.

A construction of the method of collective variable has been accompanied by collaboration. In particular, importance of the work by Zubarev, Ref. [22], has been pointed out by Parasiuk. An idea and the way of including the effects of short-range forces via functional differentiation, together with the long-range interactions, has been proposed by Bogolyubov.

This chapter contains the basic concepts and relationships of the equilibrium thermodynamics and statistical physics. The theory of intermolecular interactions is briefly outlined, and a review of the Mayer cluster expansions is presented.

1.1. Basic concepts

1.1.1. Characteristic functions

The description of equilibrium processes within the framework of thermodynamics reduces to the determination of the internal parameters of a system as single-valued functions of a certain number of its external parameters. For simple one-component systems, the external parameters are two variables selected from the subsets of extensive (volume V and entropy S) and intensive parameters (temperature T and pressure P). Equilibrium processes in such systems obey the second law of thermodynamics

$$dE = TdS - PdV, \quad (1.1.1)$$

where the variables S and V are external, and E , T , and P are internal parameters. A complete thermodynamic description of the system is provided if all internal parameters are known as functions of the external ones. Therefore, in addition to equation (1.1.1), two more equations are required. According to the first law of thermodynamics, the internal energy E completely determines the state of the system, thus dE is an exact differential. Two additional equations follow from (1.1.1),

$$T = \left(\frac{\partial E}{\partial S} \right)_V, \quad P = - \left(\frac{\partial E}{\partial V} \right)_S. \quad (1.1.2)$$

They determine all three internal parameters E , T , and P , which describe the equilibrium processes that occur in a simple system upon arbitrary changes in S and V . The quantity E is called a characteristic function of the variables S and V .

It describes the work, $-dE = P dV$, performed by the system during an adiabatic process with $T dS = 0$.

In general, a characteristic function is a function that, together with its derivatives, completely characterizes the state and processes in an equilibrium system. For each complete set of independent variables there is its own characteristic function. In particular, for the system considered above with two external variables, there are four characteristic functions. Formally, they are all obtained from the main equation (1.1.1) by applying the Legendre transformation. Adding the differential $d(PV)$ to both sides of (1.1.1), one obtains the enthalpy, $H = H(S, P)$,

$$H = E + PV, \quad dH = TdS + VdP, \quad (1.1.3)$$

that describes the latent heat, $T dS$, during isobaric process $V dP = 0$.

Subtracting the differential $d(TS)$ from both sides of (1.1.1), one arrives at the free energy, $F(T, V) = E - TS$,

$$dF = -SdT - PdV. \quad (1.1.4)$$

F is equal to the maximum amount of energy that the system can expend to perform work in an isothermal process $dT = 0$, freely replenished by an inflow of heat from the heat reservoir without changing its quality. Finally, subtracting the differential $d(TS) - d(PV)$ from both sides of (1.1.1), one obtains the thermodynamic potential

$$\Phi(P, T) = E - TS + PV = F + PV, \quad d\Phi = -SdT + VdP, \quad (1.1.5)$$

which describes isothermal-isobaric processes.

For systems with more than two degrees of freedom, the characteristic functions also depend on other external parameters. Thus, in the case of a multicomponent system containing M types of particles with N_a particles of each type $\left(\sum_{a=1}^M N_a = N\right)$, the differentials of all characteristic functions include an additional term $\sum_{a=1}^M \mu_a dN_a$, where μ_a is the chemical potential of particles of type a .

The use of characteristic functions forms the basis for the thermodynamic description of equilibrium systems. Knowing the appropriate characteristic function for a given complete set of independent variables makes possible to determine all macroscopic characteristics of the system and thermodynamic processes occurring in it.

The free energy plays a special role between the characteristic functions. It is expressed directly through the partition function $Z(T, V)$, and therefore

serves as the fundamental function to construct the statistical theory of equilibrium systems,

$$F = -k_{\text{B}}T \ln Z(T, V), \quad (1.1.6)$$

where k_{B} is the Boltzmann constant.

Knowing the free energy and using (1.1.4), one can obtain the entropy,

$$S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad (1.1.7)$$

the equation of state,

$$P = - \left(\frac{\partial F}{\partial V} \right)_T, \quad (1.1.8)$$

and the chemical potentials of species,

$$\mu_a = \left(\frac{\partial F}{\partial N_a} \right)_{T, V, N_b, \dots}. \quad (1.1.9)$$

From these equations all other thermodynamic functions of the system follow by simple differentiation and integration.

1.1.2. Partition function of the classical system

The partition function is generally defined as the trace of the statistical operator $\exp(-\beta H_N)$ over the eigenvalues of the complete set of quantum states,

$$Z = \text{Sp} \exp(-\beta H_N), \quad (1.1.10)$$

where $\beta^{-1} = k_{\text{B}}T$ and H_N is the total Hamiltonian of a system of N interacting particles. Such particles may include electrons and nuclei, which form atoms, molecules, and ions. Therefore, the trace operation in (1.1.10) denotes summation over all possible states of all nuclei and electrons. However, since atomic nuclei are much heavier than electrons, the description of electronic and nuclear motion is treated differently. The motion of electrons obeys laws of quantum mechanics and leads to the formation of atoms, molecules, or ions. If in (1.1.10) the trace is taken only over electronic states, one arrives at a new statistical operator,

$$\exp(-\beta \tilde{H}_N) = \text{Sp}_e \exp(-\beta H_N) \quad (1.1.11)$$

with an effective Hamiltonian $\tilde{H}_N$, which depends on the nuclear coordinates, as well as on temperature and density. In fact, $\tilde{H}_N$ is the operator of the local free energy of the nuclei subsystem.

The motion of nuclei is quasi-classical and characterizes the motion of molecules. The number of degrees of freedom of an individual molecule of type a is equal to $3X_a$, where X_a is the number of nuclei in the molecule. Of all the degrees of freedom, the first three describe the translational motion of the centre of mass of the molecule. The other three for non-linear molecules and

two for linear molecules are rotational degrees of freedom. The remaining degrees of freedom are internal and can be usually classified as vibrational and internal rotational. All the degrees of freedom, except for vibrational ones, for most substances at not very low temperatures can be described using the methods of classical mechanics. Oscillatory (vibrational) motions should be treated quantum mechanically. However, in an ample interval of temperatures (except for temperatures at which thermal dissociation of molecules is possible), oscillations can be neglected, considering the oscillatory degrees of freedom as the “frozen” ones. Therefore, from now on we will consider $\tilde{H}_N$ to be a classical function that depends on momenta and coordinates. $\tilde{H}_N$ consists of the kinetic energy of individual motions, denoted by K_N , and the potential energy U_N of intermolecular interactions,

$$\tilde{H}_N = K_N + U_N, \quad (1.1.12)$$

where U_N depends on the coordinates of centre of mass of molecules and relative nuclear coordinates, and K_N depends on their conjugated momenta. The partition function of the classical system of N particles, consisting of M species with N_a particles in each of them, has the form,

$$Z_N = \frac{1}{\prod_a N_a!} \frac{1}{\prod_a h^{q_a N_a}} \int \exp\{-\beta \tilde{H}_N\} (d\mathbf{p})(d\Gamma), \quad (1.1.13)$$

where

$$(d\mathbf{p}) = \prod_{a=1}^M \prod_{i=1}^{N_a} d\mathbf{p}_i, \quad (d\Gamma) = \prod_{a=1}^M \prod_{i=1}^{N_a} d\Gamma_i, \quad d\Gamma_i = d\mathbf{R}_i d\Xi_i^a.$$

Here, $d\mathbf{R}_i$ is the volume element; $d\Xi_i^a$ is the element of the configuration space of the orientation and internal degrees of freedom of the i -th molecule in the a -th species; $d\mathbf{p}_i$ is element of the phase space of the set of all momenta canonically conjugated to the variables Γ_i ; q_a is a number of molecule degrees of freedom in the a -th species; h is the Planck's constant, and $\sum_{a=1}^M N_a = N$.

The integrals in (1.1.13) on momenta and coordinates are separated, and the expression for the partition function can be rewritten as product,

$$Z_N = Z_N^{\text{id}} Q_N, \quad (1.1.14)$$

where

$$Z_N^{\text{id}} = \frac{V^N \prod_a \Xi_a^{N_a}}{\prod_a N_a! h^{q_a N_a}} \int \exp\{-\beta K_N\} (d\mathbf{p}) \quad (1.1.15)$$

is the partition function of the ideal system, which corresponds to the real system in the absence of interactions; $\Xi_a = \int d\Xi_i^a$; and

$$Q_N = \frac{1}{V^N \prod_a \Xi_a^{N_a}} \int \exp\{-\beta U_N\} (d\Gamma) \quad (1.1.16)$$

is the configuration integral. Its value is determined by the character of intermolecular interaction forces in the system. In particular, for a system of non-interacting particles $U_N = 0$ and $Q_N = 1$.

The momentum integration in (1.1.15) is almost always performed analytically. Thus, for a system of monoatomic molecules, ($K_N = \sum_{a,i} p_i^2/2m_a$),

$$\begin{aligned} Z_N^{\text{id}} &= \frac{V^N}{\prod_a N_a! h^{3N}} \prod_{a=1}^M \left[\int_0^\infty \exp\left(-\frac{p^2}{2m_a k_B T}\right) 4\pi p^2 dp \right]^{N_a} = \\ &= \frac{V^N}{\prod_a N_a! \lambda_a^{3N_a}}, \end{aligned} \quad (1.1.17)$$

where m_a is the mass of molecule in the a -th species and $\lambda_a = h(2\pi m_a k_B T)^{-1/2}$ is the de Broglie thermal wavelength.

The calculation of the configuration integral (1.1.16) is a more complicated problem. The potential energy U_N in general is the sum of an infinite number of terms,

$$U_N = \sum_{a,i} u_a(\Gamma_i) + \sum_{a,b; i < j} u_{a,b}(\Gamma_i, \Gamma_j) + \sum_{a,b,c; i < j < l} u_{a,b,c}(\Gamma_i, \Gamma_j, \Gamma_l) + \dots \quad (1.1.18)$$

The first term describes the energy of the system in the external field, the second one describes the energy of pair interaction, the next term corresponds to the energy of three-particle interactions, etc. Even in the case of a system of monoatomic particles with the pair interaction,

$$U_N = \sum_{a,b} \sum_{i < j} u_{a,b}(|\mathbf{R}_i - \mathbf{R}_j|), \quad (1.1.19)$$

the potential energy U_N depends essentially on the coordinates of all interacting particles, such that Q_N does not decompose into the product of integrals over the coordinates of individual molecules.

The external parameters of Z_N in (1.1.13) are the temperature T , system volume V and densities of particles of species, N_a/V , $a = 1, \dots, M$. Meanwhile, the experiment most often corresponds to isobaric-isothermal conditions of thermodynamic processes. These processes, as it follows from (1.1.5), are described by the thermodynamic potential, $\Phi(P, T)$, following from the isobaric-isothermal partition function, $Z_N(P, T)$,

$$\Phi(P, T) = -k_B T \ln Z_N(P, T). \quad (1.1.20)$$

In this case, $Z_N(P, T)$ is related to $Z_N(V, T)$ by the integral Laplace transform

$$Z_N(P, T) = \int_0^\infty Z_N(V, T) e^{-\beta P V} dV. \quad (1.1.21)$$

The partition function defined according to (1.1.10), (1.1.13) and (1.1.21) corresponds to the canonical Gibbs ensemble and describes systems with a fixed number of particles. Thermodynamically open systems are described in a grand canonical ensemble, the initial function of which is a grand partition function that, in the case of one-component systems, has the form,

$$\Xi(z, T, V) = \sum_{N=0}^{\infty} z^N Z_N(T, V), \quad (1.1.22)$$

where $z = e^{\beta\mu}$ and μ are an absolute activity and chemical potential, respectively; and $Z_N(T, V)$ is the partition function of the system of N particles, determined according to (1.1.10).

The calculation of the partition function is one of the central problems of the statistical theory of equilibrium systems of interacting particles. Knowing Z_N as a function of T , V and densities of particles in all the species by according to (1.1.6) one can find the free energy, next by using (1.1.7)–(1.1.9) all thermodynamic properties of the system can be determined. From expression (1.1.22) for a grand partition function, one can find the average number of particles,

$$\langle N \rangle = \frac{\sum_{N \geq 0} N z^N Z_N(T, V)}{\sum_{N \geq 0} z^N Z_N(T, V)} = z \frac{\partial}{\partial z} \ln \Xi(z, T, V). \quad (1.1.23)$$

The logarithm of the partition function leads to the equation of state,

$$\frac{PV}{k_B T} = \ln \Xi(z, T, V). \quad (1.1.24)$$

Excluding the activity z from the last two equations, the equation of state can be expressed in terms of the variables $\langle N \rangle$, T , and V . The equation of state thus obtained, of course, coincides with (1.1.8) found from the partition function $Z_N(T, V)$.

1.1.3. Distribution functions

Complete information about the thermodynamic state of a system can also be obtained from the distribution functions introduced into statistical physics by Bogolyubov, Born, Green, Kirkwood, and Yvon [30–32]. For simplicity, we restrict ourselves to the consideration of a one-component system of particles having only translational degrees of freedom. Initial expression for the introduction of distribution functions is the n -particle Gibbs distribution function,

$$F_N = \frac{1}{Q_N} \exp(-\beta U_N), \quad (1.1.25)$$

where

$$Q_N = \frac{1}{V^N} \int \exp(-\beta U_N) (d\Gamma)$$

is the configuration integral of the system, and $(d\Gamma) = \prod_{i=1}^N d\mathbf{R}_i$.

By integrating over the coordinates of $N - n$ particles in the expression (1.1.25), we arrive at the definition of the n -particle distribution function,

$$\frac{F_n}{V^n} = \frac{1}{V^N Q_N} \int \exp(-\beta U_N) d\mathbf{R}_{n+1} \dots d\mathbf{R}_N, \quad (1.1.26)$$

which describes the probability density of finding n particles at certain fixed coordinates whereas the coordinates of all other, $N - n$, particles are arbitrary. By the definition, the distribution functions are normalised,

$$\frac{1}{V} \int F_{n+1} d\mathbf{R}_{n+1} = F_n, \quad \frac{1}{V} \int F_1 d\mathbf{R}_1 = 1. \quad (1.1.27)$$

The n -particles distribution functions satisfy the system of the Bogolyubov chain of integro-differential equations. Indeed, assuming that $U_N = \sum_{i < j} u_2(|\mathbf{R}_i - \mathbf{R}_j|)$ and differentiating (1.1.26) by the coordinate of one of the particles, one gets,

$$\nabla_1 F_n + \beta (\nabla_1 U_n) F_n + \frac{N}{V} \int \nabla_1 u_2(|\mathbf{R}_1 - \mathbf{R}_{n+1}|) F_{n+1} d\mathbf{R}_{n+1} = 0, \quad (1.1.28)$$

where $U_n = \sum_{1 \leq i < j \leq n} u_2(|\mathbf{R}_i - \mathbf{R}_j|)$ is the potential energy of the set of n -particles.

Among all distribution functions, the singlet (one-particle) and pair distribution (two-particle) functions play a special role. The singlet distribution function, $F_1(R)/V$, is the simplest one of the n -particle ones. It describes the probability density of finding a particle at a point $\mathbf{R}$ in a unit volume, all other particles are in arbitrary location. For crystalline systems, $F_1(R)$ is a periodic function with sharp maxima at the sites of lattice. For isotropic systems (gases and liquids) $F_1(R) = 1$, such that all points of volume V are equiprobable.

The pair distribution function $F_2(\mathbf{R}_1, \mathbf{R}_2)$ describes the probability density of the arrangement of two particles, one at the point $\mathbf{R}_1$ and the other at the point $\mathbf{R}_2$, with all other particles at arbitrary coordinates. For isotropic systems, the pair distribution function depends only on the distance between them,

$$F_2(\mathbf{R}_1, \mathbf{R}_2) = F_2(|\mathbf{R}_1 - \mathbf{R}_2|) = F_2(R), \quad (1.1.29)$$

where $R = |\mathbf{R}_1 - \mathbf{R}_2|$. The deviation of $F_2(R)$ from unity is due to intermolecular interaction and is an important characteristic of the system structure.

The pair distributions function can be obtained experimentally, as it enters the expression describing the diffraction of X -rays, electrons or neutrons [33]. The cross section of single coherent scattering, $\mathbf{m}_2(k)$, equals to

$$\mathbf{m}_2(k) = 1 + 4\pi \frac{N}{V} \int_0^\infty [F_2(R) - 1] \frac{\sin(kR)}{kR} R^2 dR, \quad (1.1.30)$$

where k is the value of the momentum transferred to the scattered particle, $\mathbf{m}_2(k)$ is the structure factor of the system experimentally available.

Distribution functions are also important for the thermodynamic description. For systems with pair interactions, all thermodynamic properties can be obtained using only a pair function. Namely, the internal energy is

$$E = N \left[\frac{3}{2} k_B T + \frac{1}{2} \frac{N}{V} \int u_2(R) F_2(R) dR \right]. \quad (1.1.31)$$

By differentiating the configuration integral over volume (in the case of potential $u_2(R)$ that does not depend on the particles density), the virial equation of state can be obtained,

$$P = \frac{N}{V} \left[k_B T - \frac{2}{3} \pi \frac{N}{V} \int_0^\infty \frac{\partial u_2(R)}{\partial R} F_2(R) R^2 dR \right]. \quad (1.1.32)$$

The square fluctuation of the number of particles in a spatially homogeneous system, as well as the isothermal compressibility $\chi_T = -(1/V)(\partial V/\partial P)_T$, are expressed through the pair distribution function,

$$\begin{aligned} \frac{N}{V} k_B T \chi_T &= k_B T \left(\frac{\partial \rho}{\partial P} \right)_T = \\ &= 1 + 4\pi \frac{N}{V} \int_0^\infty [F_2(R) - 1] R^2 dR = \mathbf{m}_2(k=0), \end{aligned} \quad (1.1.33)$$

where $\rho = N/V$ is the particles number density. This is a general relation that does not depend on the assumption made previously about the pairwise nature of the intermolecular interactions.

Thus, in statistical physics there are two methods for describing equilibrium, spatially homogeneous systems. The first method is based on determining the pair distribution function $F_2(R)$, and the second one — is to calculate the configuration integral Q_N . Both methods are equivalent, because knowing the pair distribution function, one can determine the configuration integral,

$$Q_N = \exp \left\{ - \int_0^1 d\xi \frac{N^2}{2V} \int \beta u_2(R) F_2(R, \xi) dR \right\}, \quad (1.1.34)$$

where ξ is the parameter for switching on the interaction. On the other hand, functional differentiation of the configuration integral by the interaction potential (see Chapter 2), yields the pair distribution function as follows,

$$\frac{1}{V}F_2(R) = -\frac{1}{2\beta} \frac{\delta \ln Q_N}{\delta u_2(R)}. \quad (1.1.35)$$

The calculation of the configuration integral and the pair distribution function can be considered as the principal objectives for the construction of the statistical theory of equilibrium systems. The presentation of rigorous methods for their calculation comprise the content of the proposed monograph. However, before proceeding to the presentation of these methods, it is necessary to discuss intermolecular interactions in order to specify the expression for the potential energy, U_N .

1.2. Intermolecular interactions

Both the chemical nature of molecules and its interactions are of electromagnetic origin and, if we neglect the small relativistic effects, they are determined exclusively by the Coulomb interaction of the electrons and nuclei that form the molecules. Finding the potential energy of intermolecular interactions U_N — the initial function for our further calculations — according to (1.1.11) and (1.1.12) is connected with the determination of the effective Hamiltonian $\tilde{H}_N$.

We do not aim at disclosing these formulas very consistently. Assuming that the electronic energy of each particle is much larger than the thermal energy $k_B T$, one can proceed from the usual quantum-mechanical formulation of the problem when studying the effective Hamiltonian $\tilde{H}_N$. It reduces to the solution of the Schrödinger equation for the electrons and nuclei of all molecules of the system. In the adiabatic approximation, the electron problem at fixed positions of the nuclei first is solved. It leads to the potential energy U_N as a function of the nuclear coordinates.

It is commonly assumed that the potential energy U_N can be represented as a series (1.1.18). For spatially homogeneous systems, the first term is absent, the second term describes the sum of pair interactions of molecules, the next one corresponds to three-particle interactions, etc. Pair interactions play the most important role and can be found by solving a quantum mechanical problem for two isolated molecules. Accordingly, the three-particle interactions require solving a problem for three molecules, etc.

Neglecting multi-particle interactions, one considers the expression (1.1.19) for the function U_N , in which the potential energy of the interaction of two molecules $U_{ab}(|\mathbf{R}_1 - \mathbf{R}_2|) = u_{ab}(R)$ is called the interaction potential. If the potential depends only on the mutual distance between the molecules,

then such interactions are called central interactions. When describing molecular systems, it is usually assumed that intramolecular interactions are much stronger than intermolecular interactions, such that the molecules can be considered as rigid. In this case, the potential energy, U_N , depends not only on the coordinates of the centres of mass of the molecules, but also on their orientation. Such interactions are called non-central ones.

To determine the intermolecular interaction potentials is not an easy task. The difficulties are primarily due to the lack of satisfactory methods that give reliable results at all intermolecular distances. For example, the conventional quantum mechanical perturbation theory well describes long-range interactions but encounters serious difficulties in accounting for exchange and correlation effects that play an important role in the interval of small and intermediate distances.

So far, intermolecular interactions at large distances have been best studied, when the exchange effects for electrons can be neglected and quantum mechanical perturbation theory can be used. Let us consider these interactions in more detail. Suppose the Hamiltonian describing the interaction of two molecules of species a and b has the following form,

$$H = h_a + h_b + v_{ab}, \quad (1.2.1)$$

where h_a and h_b are the Hamiltonians of separated molecules of the same type,

$$v_{ab} = e^2 \left\{ \sum_{\mu_1=1}^{X_a} \sum_{\mu_2=1}^{X_b} \frac{Z_{\mu_1} Z_{\mu_2}}{|\mathbf{r}_{\mu_1} - \mathbf{r}_{\mu_2}|} - \sum_{\mu_1=1}^{X_a} \sum_{\nu_2=1}^{Y_b} \frac{Z_{\mu_1}}{|\mathbf{r}_{\mu_1} - \mathbf{r}_{\nu_2}|} - \sum_{\nu_1=1}^{Y_a} \sum_{\mu_2=1}^{X_b} \frac{Z_{\mu_2}}{|\mathbf{r}_{\nu_1} - \mathbf{r}_{\mu_2}|} + \sum_{\nu_1=1}^{Y_a} \sum_{\nu_2=1}^{Y_b} \frac{1}{|\mathbf{r}_{\nu_1} - \mathbf{r}_{\nu_2}|} \right\} \quad (1.2.2)$$

is the electrostatic interactions between electrons and nuclei of molecules; eZ_μ is a charge of the μ -th nucleus; $\mathbf{r}_\nu$ and $\mathbf{r}_\mu$ are coordinates of the corresponding nuclei and electrons, respectively. After switching to the coordinates of the mass centres of the molecules ($\mathbf{R}_1$ and $\mathbf{R}_2$) and the relative coordinates of the nuclei and electrons ($\mathbf{l}_\mu$ and $\mathbf{l}_\nu$), using the translation operator $e^{\mathbf{l}\Delta}$, which shifts [34] the argument of the function $f(R)$ by $\mathbf{l}$, $e^{\mathbf{l}\Delta}f(R) = f(|\mathbf{R} + \mathbf{l}|)$, one can obtain,

$$v_{ab} = Q_a(\nabla)Q_b(-\nabla)\frac{1}{R_{12}}, \quad (1.2.3)$$

where

$$\begin{aligned} Q_a(\nabla) &= e \left[\sum_{\mu=1}^{X_a} Z_\mu e^{\mathbf{l}_\mu \nabla} - \sum_{\nu=1}^{Y_a} e^{\mathbf{l}_\nu \nabla} \right], \\ Q_b(-\nabla) &= e \left[\sum_{\mu=1}^{X_b} Z_\mu e^{-\mathbf{l}_\mu \nabla} - \sum_{\nu=1}^{Y_b} e^{-\mathbf{l}_\nu \nabla} \right]. \end{aligned} \quad (1.2.4)$$

The operators $Q_a(\nabla)$ and $Q_b(-\nabla)$ have the dimension of charges and hereafter they will be referred to as the generalized operator of charges.

Let $|0\rangle$ be the ground state eigenvector and $|s\rangle$ be the eigenvector corresponding to the s th excited state of the Hamiltonian of two non-interacting molecules $H_0 = h_a + h_b$, where $h_a|0, a\rangle = E_{0,a}|0, a\rangle$, $h_b|0, b\rangle = E_{0,b}|0, b\rangle$, $E_0 = E_{0,a} + E_{0,b}$, $|0\rangle = |0, a\rangle|0, b\rangle$. In order to find the potential $u_{ab}(R)$, which appears in (1.1.19), at large distances R , we can use the quantum perturbation theory for the Hamiltonian (1.2.1). One gets:

$$u_{ab}(R) = \langle 0|H|0\rangle - E_0 = \langle 0|v_{ab}|0\rangle + \sum_{s \neq 0} \frac{|\langle 0|v_{ab}|s\rangle|^2}{E_0 - E_s} + \dots \quad (1.2.5)$$

The first term in (1.2.5), $u_{ab}^{(\text{el})} = \langle 0|v_{ab}|0\rangle = \langle 0|Q_a(\nabla)|0\rangle\langle 0|Q_b(-\nabla)|0\rangle(1/R)$ describes the electrostatic interaction between two molecules. After expanding the exponential functions in (1.2.4) into series, the generalized charges, averaged over the ground state, can be written as follows,

$$\begin{aligned} \langle 0|Q_a(\nabla)|0\rangle &= ez_a + \mathbf{p}_a^{(1)}\nabla + \frac{1}{3}\mathbf{p}_a^{(2)}\widehat{\nabla\nabla} + \dots, \\ \langle 0|Q_b(-\nabla)|0\rangle &= ez_b - \mathbf{p}_b^{(1)}\nabla + \frac{1}{3}\mathbf{p}_b^{(2)}\widehat{\nabla\nabla} + \dots \end{aligned} \quad (1.2.6)$$

The action of these operators in (1.2.5) leads to the multipole expansion of $u_{ab}^{(\text{el})}(R)$ in terms of inverse powers of the intermolecular distance,

$$\begin{aligned} u_{ab}^{(\text{el})}(R) &= \frac{e^2 z_a z_b}{R} - ez_a(\mathbf{p}_b^{(1)}\nabla)\frac{1}{R} + ez_b(\mathbf{p}_a^{(1)}\nabla)\frac{1}{R} - \\ &- (\mathbf{p}_a^{(1)}\nabla)(\mathbf{p}_b^{(1)}\nabla)\frac{1}{R} + \frac{1}{3}ez_a(\mathbf{p}_b^{(2)}:\widehat{\nabla\nabla})\frac{1}{R} + \dots \end{aligned} \quad (1.2.7)$$

The first term $e^2 z_a z_b / R$ describes the Coulomb interaction between two ions with valencies of $z_a = \sum_{\mu=1}^{X_a} Z_\mu - Y_a$, $z_b = \sum_{\mu=1}^{X_b} Z_\mu - Y_b$. For molecules

$z_a = z_b = 0$. The second term $ez_a(\mathbf{p}_b^{(1)}\nabla)/R = ez_a p_b^{(1)} \cos \vartheta_b / R^2$ describes the interaction between an ion and a polar molecule with a dipole moment $p_a^{(1)} = e\langle 0|\sum_{\mu} Z_\mu \mathbf{l}_\mu - \sum_{\nu} \mathbf{l}_\nu|0\rangle$. The next term describes the electrostatic interaction between two polar molecules,

$$-(\mathbf{p}_a^{(1)}\nabla)(\mathbf{p}_b^{(1)}\nabla)\frac{1}{R} = \frac{p_a^{(1)} p_b^{(1)}}{R^3} [2 \cos \theta_a \cos \theta_b - \sin \theta_a \sin \theta_b \cos(\phi_a - \phi_b)]$$

where (θ, ϕ) are the polar orientations of the dipole moment vector relative to the axis $\mathbf{R}$. The term,

$$\frac{1}{3}ez_a(\mathbf{p}_b^{(2)}:\widehat{\nabla\nabla})\frac{1}{R} = ez_a p_b^{(2)} \frac{(3 \cos^2 \theta_b - 1)}{R^3}$$

describes the interaction between an ion and a molecule with a quadrupole moment

$$\mathbf{p}^{(2)} = \frac{1}{2}e\langle 0 | \sum_{\mu} Z_{\mu}(3\widehat{\mathbf{l}}_{\mu}\mathbf{l}_{\mu} - \mathbf{l}_{\mu}^2) - \sum_{\nu} (3\widehat{\mathbf{l}}_{\nu}\mathbf{l}_{\nu} - \mathbf{l}_{\nu}^2) | 0 \rangle,$$

and so on.

In the second order of perturbation theory in (1.2.5), dependent on the excited state function chosen, two new types of interactions can appear. If $|s\rangle = |0, a\rangle|s, b\rangle$ or $|s\rangle = |s, a\rangle|0, b\rangle$ for the case of large R , the so-called induction interactions arise. If $|s\rangle = |s, a\rangle|s, b\rangle$, then the resulting interaction is known as a dispersion interaction. Expanding the exponential functions in (1.2.4) into series, we get,

$$\begin{aligned} u_{ab}^{(\text{ind})} = & - \left[\frac{ez_a^2\alpha_b}{2R^2} + \frac{1}{R^5}(2ez_ap_a^{(1)}\alpha_b \cos\theta_a + 2ez_bp_b^{(1)}\alpha_a \cos\theta_b) \right] + \\ & + \frac{1}{2R^6} \left[(p_a^{(1)})^2\alpha_b(3\cos^2\theta_a + 1) + (p_b^{(1)})^2\alpha_a(3\cos^2\theta_b + 1) + \dots \right], \quad (1.2.8) \\ u_{ab}^{(\text{disp})} = & - \frac{c'_{ab}}{R^6} - \frac{c_{ab}}{R^8} - \dots, \end{aligned}$$

where

$$\begin{aligned} c'_{ab} = & e^4 \sum_{s \neq 0} \frac{|\langle 0, a | \sum_{\mu} Z_{\mu}\mathbf{l}_{\mu} - \sum_{\nu} \mathbf{l}_{\nu} | s, a \rangle|^2 \langle 0, b | \sum_{\mu} Z_{\mu}\mathbf{l}_{\mu} - \sum_{\nu} \mathbf{l}_{\nu} | s, b \rangle}{E_{sa} - E_{0a} + E_{sb} - E_{0b}} = \\ & = \frac{3}{\pi} \int_0^{\infty} \alpha_a(i\omega)\alpha_b(i\omega)d\omega \simeq \frac{3}{2} \frac{I_a I_b}{I_a + I_b} \alpha_a \alpha_b, \\ c_{ab} = & \frac{1}{4}e^4 \sum_{s \neq 0} \left[|\langle 0, a | \sum_{\mu} Z_{\mu}(3\widehat{\mathbf{l}}_{\mu}\mathbf{l}_{\mu} - \mathbf{l}_{\mu}^2) - \sum_{\nu} (3\widehat{\mathbf{l}}_{\nu}\mathbf{l}_{\nu} - \mathbf{l}_{\nu}^2) | s, a \rangle|^2 \times \right. \\ & \times |\langle 0, b | \sum_{\mu} Z_{\mu}\mathbf{l}_{\mu} - \sum_{\nu} \mathbf{l}_{\nu} | s, b \rangle|^2 + \\ & + |\langle 0, a | \sum_{\mu} Z_{\mu}\mathbf{l}_{\mu} - \sum_{\nu} \mathbf{l}_{\nu} | s, a \rangle|^2 |\langle 0, b | \sum_{\mu} Z_{\mu}(3\widehat{\mathbf{l}}_{\mu}\mathbf{l}_{\mu} - \mathbf{l}_{\mu}^2) - \\ & - \sum_{\nu} (3\widehat{\mathbf{l}}_{\nu}\mathbf{l}_{\nu} - \mathbf{l}_{\nu}^2) | s, b \rangle|^2 \left. \right] (E_{sa} - E_{0a} + E_{sb} - E_{0b})^{-1}, \\ & \alpha_a(i\omega) = \frac{1}{2}e^2 \sum_{s \neq 0} |\langle 0, a | \sum_{\mu} Z_{\mu}\mathbf{l}_{\mu} - \sum_{\nu} \mathbf{l}_{\nu} | s, a \rangle|^2 \times \\ & \times [(E_{sa} - E_{0a} + i\omega)^{-1} + (E_{sa} - E_{0a} - i\omega)^{-1}]. \quad (1.2.9) \end{aligned}$$

$\alpha(i\omega)$ is the dynamic dipolar polarisability of molecule in the a th species; $\alpha_a = \alpha_a(\omega = 0)$ is the static dipolar polarisability; and I_a has the value of the order of an ionization energy of the molecule.

Unlike electrostatic interactions, which can lead to both repulsion and attraction depending on the mutual orientation of the molecules, the induction and dispersion interactions lead solely to attraction. Another specific feature of these interactions compared to electrostatic ones, is their multi-particle nature.

For example, applying the perturbation theory (1.2.5) to three molecules leads to three-particle induction and dispersion interactions. Induction interactions arise only if one of the particles is an ion or has a non-zero multipole moment. Dispersion interactions are universal, they are characteristic of all molecules and describe intermolecular attraction, which was first taken into account by van der Waals when deriving the equation of state. Therefore, they are also known as van der Waals interactions.

Thus, at large distances, the interaction potential of two isolated molecules can be represented as the sum of electrostatic, dispersion, and induction terms,

$$u_{ab}^{(\text{long})} = u_{ab}^{(\text{el})} + u_{ab}^{(\text{ind})} + u_{ab}^{(\text{disp})}. \quad (1.2.10)$$

The relative contribution of different types of interactions depends on the distances, mutual orientation of the molecules, and their chemical nature. Typically, the role of induction interactions¹ is less significant than that of dispersion interactions, even for highly polar molecules [35].

Calculation of interactions at small distances is more complicated due to the importance of exchange effects and the inapplicability of the expansions used above for the quantities (1.2.4). Usually, the Hartree–Fock method leads to satisfactory results in the region of small distances. In this case, if the particles do not form covalent bonds, strong repulsive forces act between them at small distances.

Among the new effective methods suitable for describing interactions over a wide range of intermolecular distances, the approach of Gordon and Kim [36, 37] should be mentioned, in which the results of quantum statistical theory of the electron gas are used to describe the interaction of atoms (or ions) with closed electron shells (see, for example, [38]). The interaction potential of two atoms belonging to a and b species is represented as follows,

$$u_{ab}(R) = u_{ab}^{(1)}(R) + u_{ab}^{(2)}(R), \quad (1.2.11)$$

where

$$\begin{aligned} u_{ab}^{(1)}(R) = & \frac{e^2 Z_a Z_b}{R} + \int \frac{\rho_a(l_1) \rho_b(l_2)}{|\mathbf{R} + \mathbf{l}_1 - \mathbf{l}_2|} d\mathbf{l}_1 d\mathbf{l}_2 - \\ & - e Z_a \int \frac{\rho_b(l_2)}{|\mathbf{R} - \mathbf{l}_2|} d\mathbf{l}_2 - e Z_b \int \frac{\rho_a(l_1)}{|\mathbf{R} - \mathbf{l}_1|} d\mathbf{l}_1 \end{aligned} \quad (1.2.12)$$

is the Coulomb part of the interaction ($\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$),

$$\begin{aligned} u_{ab}^{(2)}(R) = & \int d\mathbf{l} \{ \rho_{ab}(|\mathbf{l} - \mathbf{R}_1|, |\mathbf{l} - \mathbf{R}_2|) E_e[\rho_{ab}(|\mathbf{l} - \mathbf{R}_1|, |\mathbf{l} - \mathbf{R}_2|)] - \\ & - \rho_a(|\mathbf{l} - \mathbf{R}_1|) E_e[\rho_a(|\mathbf{l} - \mathbf{R}_1|)] - \rho_b(|\mathbf{l} - \mathbf{R}_2|) E_e[\rho_b(|\mathbf{l} - \mathbf{R}_2|)] \} \end{aligned} \quad (1.2.13)$$

denotes a correlational part of the potential, being particularly important in the potential well range. Here, eZ_a and eZ_b are the charges of the atomic

¹However, this does not apply to multiparticle induction interactions.

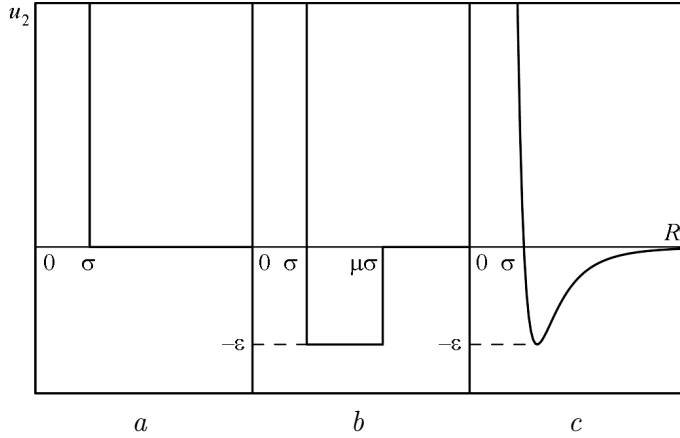


Fig. 1. Examples of some simple model potentials: *a* — hard-sphere; *b* — square-well; *c* — Lennard-Jones

nuclei; $\rho_a(l)$ and $\rho_b(l)$ are the electronic densities of the atoms, which are usually taken in the Hartree—Fock approximation; $E_e[\rho(r)]$ is the energy of the electron gas with density $\rho(r)$; $\rho_{ab}(\mathbf{r}_1, \mathbf{r}_2) = \rho_a(\mathbf{r}_1) + \rho_b(\mathbf{r}_2)$ is the total electron density of two atoms. The results obtained in this manner are in good agreement with experimental data, but the Gordon and Kim approach does not take into account dispersion and induction interactions, nor the effects of electron density redistribution, which are important in the formation of, for example, chemical bonds.

In practice, the interaction potential is usually given a certain functional form containing certain parameters that are determined by processing the experimental data. Such potentials are called model potentials. The requirements for model potentials are that they should accurately reflect real interactions and should be convenient for calculations. It is usually assumed that,

$$u_{ab}(R) = u_{ab}^{(\ell)}(R) + u_{ab}^{(sh)}(R). \quad (1.2.14)$$

There are many model potentials, some of which will be discussed below. The simplest model potential is the potential of a hard spheres of diameter σ (see Fig. 1, *a*),

$$u_2(R) = \begin{cases} 0, & R > \sigma, \\ \infty, & R < \sigma, \end{cases} \quad (1.2.15)$$

which in a very simplified way reflects the nature of short-range repulsive interactions. To account for long-range attractive forces, a square-well model is often used (see Fig. 1, *b*). However, the most common is the Lennard-Jones potential (Fig. 1, *c*),

$$u_2(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right], \quad (1.2.16)$$

where σ represents the particle size; ϵ is the depth of the potential well (when $R = \sigma$, one has $u_2(\sigma) = 0$, but $u_2(\sqrt[6]{2}\sigma) = -\epsilon = \min u_2(R)$ if $R = \sqrt[6]{2}\sigma$). In recent decades, due to the development of electronic computing techniques, more complex potentials have been used [35, 39].

When describing the interaction of ions or polar molecules, the contributions due to electrostatic interactions are usually added to the potentials discussed above. Examples of the simplest potentials describing the interaction of polar molecules are the Keesom potential

$$u_2(R) = \begin{cases} \infty, & R < \sigma, \\ -\frac{p^2}{R^3}u^{112}(\Omega_1, \Omega_2), & R > \sigma, \end{cases} \quad (1.2.17)$$

and Stockmayer

$$u_2(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] - \frac{p^2}{R^3}u^{112}(\Omega_1, \Omega_2) \quad (1.2.18)$$

potentials, in which $u^{112}(\Omega_1, \Omega_2) = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)$.

Thermodynamic and structural properties of interacting systems are functionally dependent on the thermodynamic and molecular parameters that are included in the interaction potentials. Thermodynamic variables include temperature T , volume V , particle concentrations N_a/V , N_b/V , etc. Molecular parameters are associated with individual particle characteristics and the forces of their interaction, such as the particle size σ_{ab} , potential well depth ϵ_{ab} , electron charge (e), and other constants contained in the interaction potentials. The expressions for thermodynamic functions also include universal physical constants: the Boltzmann constant k_B , the Planck's constant h , etc.

All these quantities can be grouped into certain combinations that have the dimension of length or energy. Certain ratios between them lead to dimensionless system parameters, the degree of smallness of which can be used to judge the applicability of the corresponding model or the legitimacy of using a particular mathematical apparatus [34]. The condition of stability of "classical" particles requires that the consideration should be carried out at temperatures below the ionization energy (for molecules — below the dissociation energy as well), whereas the condition for the classical description of particle systems is the smallness of the de Broglie thermal wave $\lambda = [h^2/2\pi m k_B T]^{1/2}$ compared to the particle size σ and to the average distance between particles $\langle R \rangle$, where $[4\pi \langle R \rangle^3]/3 = V/N$. We assume that these conditions are satisfied in what follows. The conditions above imply that our description refers to the temperature interval restricted from the left by the statistical degeneracy condition, i.e., $\lambda \ll \langle R \rangle$ or

$$\frac{3}{2}k_B T \gg \frac{h^2}{m} \left(\frac{N}{V} \right)^{-2/3} \left(\frac{3}{4\pi} \right)^{1/3},$$

and from the right by the ionization point, i.e., $k_B T \ll E_{\text{ion}}$, along the temperature axis.

For a simple one-component system of non-polar particles, there are two independent parameters: reduced density $\rho^* = (N/V)\sigma^3$ and temperature $T^* = k_B T/\epsilon$. For more complex systems, there are also other parameters. Thermodynamic and structural functions expressed in dimensionless variables will be universal functions of these parameters for all systems with the same form of interaction potentials. This statement is known as the law of corresponding states and substantially simplifies the construction of the theory of many-particle systems.

1.3. Mayer cluster expansions

One of the first approaches of calculating the configuration integral (1.1.16) is the method of cluster expansions in terms of the density powers, developed by Mayer [40]. Although in its original form, this theory is applicable only in the case of dilute gas systems with short-range interaction, it has served as a starting point for many theoretical constructions.

1.3.1. Virial expansions

The method of Mayer's cluster expansions is based on the extraction of contributions coming from the groups of two, three, and more particles in the configuration integral. Assuming that the potential energy is equal to the sum of pair interactions, the Gibbs function for N particles can be represented as a product,

$$\exp\{-\beta U_N\} = \prod_{i < j} [1 + f(R_{ij})], \quad (1.3.1)$$

where $f(R_{ij}) = \exp\{-\beta u_2(R_{ij})\} - 1$ is the Mayer function. For typical potentials of intermolecular interactions, $u_2(R)$, the Mayer function is equal to minus one for distances smaller than the size of the molecule; it is positive in the potential well region and rapidly tends to zero with increasing distance.

In the Mayer theory, the expression (1.3.1) is expanded into the series,

$$\prod_{i < j} [1 + f(R_{ij})] = 1 + \sum_{i < j} f(R_{ij}) + \sum_{i < j} \sum_{l < m} f(R_{ij}) f(R_{lm}) + \dots, \quad (1.3.2)$$

each term of which is the product of a certain number of Mayer functions. To analyse this series, we will use the diagram technique. Each molecule is represented by a circle, from which the lines corresponding to the Mayer functions emerge. The set of molecules connected in this way forms a group or cluster, the size of which is determined by the number of connected circles. As a result, the terms of the series (1.3.2) are represented as products of different groups or

clusters. In general, N molecules can be split into m_l groups, each containing l molecules, and for this method of partitioning $\sum_{l=1}^N l m_l = N$. For each group, a cluster integral can be introduced,

$$b_l = \frac{1}{Vl!} \int \sum \prod f(R_{ij}) \prod_{i=1}^l d\mathbf{R}_i, \quad (1.3.3)$$

where the summation is performed over all possible products of Mayer functions for a cluster of l particles. An important property of the cluster integrals is their independence of the system volume as $V \rightarrow \infty$. The rigorous proof of this statement can be found in works [41, 42].

In terms of cluster integrals, the configuration integral of the system can be represented as,

$$Q_N = \frac{1}{V^N} \sum \prod_{l=1}^N (l! V b_l)^{m_l},$$

where the summation is performed over all possible groups and ways of dividing molecules into groups. Since there are $N! [\prod (l!)^{m_l} m_l!]^{-1}$ ways to split N molecules into m_l different groups, each containing l molecules, then

$$Q_N = \frac{N!}{V^N} \sum_{\{m_l\}} \prod_{l=1}^N \frac{(V b_l)^{m_l}}{m_l!}, \quad (1.3.4)$$

where the summation is performed over all possible groups which satisfy the condition $N = \sum_l l m_l$. Taking this condition into account significantly complicates the calculations. To circumvent this difficulty, it is convenient to consider a grand canonical partition function $\Xi(z, T, V)$ instead of (1.3.4),

$$\Xi(z, T, V) = \sum_{N=0}^{\infty} z^N Z_N = \sum_{N=0}^{\infty} \frac{V^N}{N!} \left(\frac{z}{\lambda^3} \right)^N Q_N \quad (1.3.5)$$

in which the absolute activity z should be defined in such a way that the mean value $\langle N \rangle$ in (1.3.5) coincided with a fixed N in (1.3.4):

$$N = \langle N \rangle = z \frac{\partial \ln \Xi}{\partial z}.$$

Substituting expression (1.3.4) into (1.3.5) one obtains,

$$\Xi = \sum_{N=0}^{\infty} \zeta^N \sum_{\{m_l\}} \prod_{l=1}^{\infty} \frac{(V b_l)^{m_l}}{m_l!} = \prod_{l=1}^{\infty} \sum_{m_l=0}^{\infty} \frac{1}{m_l!} (V b_l \zeta^l)^{m_l} = \exp \left\{ V \sum_{l=0}^{\infty} b_l \zeta^l \right\}, \quad (1.3.6)$$

where $\zeta = z/\lambda^3$ is the fugacity, and

$$z \frac{\partial \ln \Xi}{\partial z} = V \sum_{l=1}^{\infty} l b_l \zeta^l = N, \quad \frac{N}{V} = \sum_{l=1}^{\infty} l b_l \zeta^l. \quad (1.3.7)$$

Using (1.3.6), the equation of state can be obtained,

$$\beta PV = \ln \Xi = V \sum_{l=1}^{\infty} b_l \zeta^l. \quad (1.3.8)$$

Next, instead of ζ , one should use (1.3.7) to elucidate the dependence on density and temperature.

A number of terms in the cluster integrals (1.3.3) can be written more simply if we introduce the concept of irreducible cluster integrals. An irreducible cluster includes only those diagrams in which at least two independent lines extend from each vertex. The exception is a group of two molecules, which is also considered irreducible. Each irreducible group corresponds to irreducible cluster integral,

$$\beta_n = \frac{1}{n!} \frac{1}{V} \int \sum_{1 \leq i < j \leq n+1} \prod f(R_{ij}) d\mathbf{R}_1 \dots d\mathbf{R}_{n+1},$$

where the summation is performed over all possible products of Mayer functions for an irreducible group of $(n+1)$ particles. The β_n integrals are irreducible because they cannot be reduced to simpler ones. Some terms of cluster integrals are expressed through products of irreducible integrals. Thus, for example, in b_3 there are terms of the type $\int f(R_{12})f(R_{31})d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 = V\beta_1^2$. By breaking down each group into a set of irreducible groups, the cluster integrals can be represented as a sum of products of irreducible integrals $b_l = \frac{1}{l!} \sum_n \prod (n! \beta_n)^{p_n}$,

where the summation is performed over all irreducible groups and all possible ways of splitting the group of l particles into irreducible groups with the condition $\sum_n^{l-1} n p_n = l - 1$. Since there are

$$\frac{l!}{l^2} \prod_{n=1}^{l-1} \left(\frac{l}{n!} \right)^{p_n} \frac{1}{p_n!}$$

such ways in general, then

$$b_l = \frac{1}{l!} \sum_{\{p_n\}} \prod_{n=1}^{l-1} \frac{1}{p_n!} (l \beta_n)^{p_n}, \quad (1.3.9)$$

where the summation is performed over all possible irreducible groups consistent with the condition $\sum_{n=1}^{l-1} n p_n = l - 1$ (for more details, see [40]).

Inverting the series (1.3.7), the fugacity can be represented as a series in terms of density powers,

$$\zeta = \rho - 2b_2\rho^2 + (8b_2^2 - 3b_3)\rho^3 + \dots$$

or by expressing the cluster integrals according to (1.3.9) as irreducible cluster integrals, as follows:

$$\zeta = \rho \left[1 - \beta_1\rho + \frac{1}{2}\beta_1^2\rho^2 - \beta_2\rho^2 + \dots \right] = \rho \exp \left\{ - \sum_{n \geq 1} \beta_n \rho^n \right\}. \quad (1.3.10)$$

From the relations (1.3.7), (1.3.8), and (1.3.10) it follows that

$$\beta P = \sum_{l \geq 1} b_l \zeta^l = \int_0^\zeta d\zeta \frac{1}{\zeta} \sum_{l \geq 1} l b_l \zeta^l = \int_0^\rho d\rho \left[1 - \sum_{n \geq 1} n \beta_n \rho^n \right],$$

and then

$$\beta P \frac{1}{\rho} = 1 - \sum_{n \geq 1} \frac{n}{n+1} \beta_n \rho^n = 1 + \sum_{n \geq 2} \rho^{n-1} \tilde{B}_n. \quad (1.3.11)$$

The resulting expression is known as a virial expansion, and the coefficients $\tilde{B}_n = -n\beta_n/(n+1)$ in (1.3.11) are called the cluster coefficients. The first nontrivial cluster coefficient $\tilde{B}_2$, can be measured experimentally and is one of the sources of knowledge about intermolecular interactions. The value of the second cluster coefficient is determined only by pair interactions, however the third coefficient includes contributions from three-particle interactions. Following the methodology outlined above, when accounting for three-particle interactions in the third cluster coefficient, one obtains an additional term,

$$\begin{aligned} \Delta \tilde{B}_3 &= \frac{1}{6} \rho^3 \int \exp \{ -\beta [u_2(R_{12}) + u_2(R_{32}) + u_2(R_{13})] \} \\ &\quad \times [\exp \{ -\beta u_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \} - 1] d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3. \end{aligned}$$

A comparison of theoretical results with experiments for noble gases clearly indicates the need to take into account three-particle interactions (see, for example, [18]).

Free energy of the system is $F = N\mu - PV$ where $\mu = k_B T \ln(\xi \lambda^3)$ is a chemical potential. According to (1.3.10) and (1.3.11)

$$F = F_{\text{id}} - N k_B T \sum_{n \geq 1} \rho^n \frac{\beta_n}{n+1} = F_{\text{id}} - k_B T \sum_{n \geq 2} B_n, \quad (1.3.12)$$

where $F_{\text{id}} = N k_B T \ln [\rho \lambda^3 - 1]$ is the free energy of an ideal gas. The quantities $B_n = \rho^{n-1} \beta_{n-1}/(nN)$ are called the virial coefficients of the free energy. For

a more concise and attractive visual representation, the virial coefficients are drawn using diagrams. Each vertex of the diagram corresponds to a factor ρ and an integration operation over $d\mathbf{R}$, and each line corresponds to a Mayer function, such that $\bullet = \rho \int d\mathbf{R}$ and $\text{---} = f(R)$.

In diagrammatic notation

$$B_2 = \frac{1}{2} \bullet \text{---} \bullet, \quad B_3 = \frac{1}{2 \cdot 3} \triangle, \\ B_4 = \frac{1}{2 \cdot 4} \left[\square + 2 \begin{array}{c} \bullet \text{---} \bullet \\ | \quad | \\ \bullet \text{---} \bullet \end{array} + \frac{1}{3} \begin{array}{c} \bullet \text{---} \bullet \\ / \quad \backslash \\ \bullet \text{---} \bullet \end{array} \right], \dots$$

Although the description of a system based on the virial expansion is quite simple and appealing, it has a number of serious drawbacks, the main ones being the unsatisfactory description of long-range interactions and poor convergence of the virial series at high densities. For example, the second virial coefficient provides a poor description of the behaviour of real gases at moderate densities, and the virial series diverges for high densities. Namely, the second virial coefficient for the potential $u_2(R) = \alpha/R^\delta$ is equal [30]:

$$B_2 = \frac{1}{2} \frac{N^2}{V} 4\pi \int_0^\infty [\exp(-\beta u_2(R)) - 1] R^2 dR = \\ = \frac{2}{3} \pi \frac{N^2}{V} (\beta\alpha)^{\frac{3}{\delta}} \Gamma\left(1 - \frac{3}{\delta}\right),$$

where $\Gamma(x)$ is the gamma function. The latter diverges for $\delta \leq 3$, which leads to divergence of the virial coefficients as well. Hereinafter, such potentials will be called strongly long-range interactions, while the potentials with $\delta > 3$ are weakly long-range interactions. For these potentials the virial coefficients do not diverge, however the virial series exhibit poor convergence. To describe dense systems, it is necessary to at least approximately sum up the virial series. In close similarity to the considerations above, let us consider virial expansions for a pair distributions function, for which it is easier to classify and perform summation of the diagrams.

1.3.2. Classification and summation of diagrams

Functionally differentiating the expression for the free energy with respect to the interaction potential according to (1.1.35), the virial expansion for a pair distribution function can be obtained,

$$F_2(R) = e^{-\beta u_2(R)} \left[1 + \sum_{n \geq 1} F_2^{(n+2)}(R) \right], \quad (1.3.13)$$

where $F_2^{(n+2)}(R)$ is the $(n+2)$ th virial coefficient of a pair distribution function and $R = |\mathbf{R}_1 - \mathbf{R}_2|$ as before. In the diagrammatic notation adopted above, one has

$$F_2^{(3)}(R) = \text{diagram of two open circles connected by a single line}, \quad F_2^{(4)}(R) = \text{diagram of two open circles connected by two parallel lines} + 2 \times \text{diagram of two open circles connected by two lines forming a triangle with a filled vertex} + \frac{1}{2} \times \text{diagram of two open circles connected by two lines forming a square with two filled vertices} + \frac{1}{2} \times \text{diagram of two open circles connected by two lines forming a square with two filled vertices and a diagonal} + \dots, \quad (1.3.14)$$

where the open circles denote fixed coordinates of two molecules, and the filled circles are field vertices over which integration is performed.

The diagrams of the pair distribution function differ only by their structure. The topological analysis leads to their classification and partial summation [43, 44]. First of all, it is necessary to distinguish between the irreducible diagrams and diagrams with parallel links. The latter are expressed as products of corresponding irreducible diagrams. For example, the diagram  of

the fourth virial coefficient equals to the square of the diagram .

Summing up the diagrams with parallel links across the virial expansions leads to an exponential form of the sum of solely irreducible diagrams

$$\begin{aligned} F_2(R) &= \exp \left\{ -\beta u_2(R) + \sum_{n \geq 1} \tilde{F}_2^{(n+2)}(R) \right\} = \\ &= \exp \{ -\beta u_2(R) + w_2(R) \} = \exp \{ -\beta \psi(R) \}, \end{aligned} \quad (1.3.15)$$

where $\tilde{F}_2^{(n+2)}(R)$ is the sum of all irreducible diagrams of the $(n+2)$ -th virial coefficient. The quantity $\psi_2(R)$ is commonly referred to as the potential of mean force.

By substituting $e^{-\beta u_2(R)} = 1 + f(R)$ in (1.3.15), the pair distribution function can be represented as:

$$F_2(R) = 1 + N_2(R) + c_2(R), \quad (1.3.16)$$

where

$$N_2(R) = \text{diagram of two open circles connected by a single line} + \text{diagram of two open circles connected by two parallel lines} + \text{diagram of two open circles connected by two lines forming a triangle with a filled vertex} + \dots$$

is a set of diagrams with nodal vertices, the removal of which leads to the splitting the diagram into two independent parts;

$$c_2(R) = \text{diagram of two open circles connected by a single line} + \text{diagram of two open circles connected by two lines forming a triangle with a filled vertex} + \frac{1}{2} \times \text{diagram of two open circles connected by two lines forming a square with two filled vertices} + \dots$$

is a set of diagrams without nodal vertices.

All diagrams with nodal vertices are irreducible, but there are also irreducible diagrams without nodal vertices. This set is formed by the elementary diagrams,

$$w_2(R) = N_2(R) + E_2(R), \quad (1.3.17)$$

where

$$E_2(R) = \frac{1}{2} \text{ (diagram 1) } + \frac{1}{2} \text{ (diagram 2) }$$

is the sum of all elementary diagrams.

Among the elementary diagrams, a set of basis elementary diagrams can be distinguished, in which at least three lines emerge from each field vertex and at least two lines from each vertex with fixed coordinates of molecules. The sum of elementary diagrams is reduced to the sum of only basis diagrams by replacing the line $f(R)$ by $F_2(R) - 1$. Collecting the diagrams in $N_2(R)$ by the number of nodal vertices, one arrives at integral equation,

$$h_2(R_{12}) = c_2(R_{12}) + N_2(R_{12}) = c_2(R_{12}) + \rho \int h_2(R_{13})c_2(R_{32})d\mathbf{R}_3, \quad (1.3.18)$$

known as the Ornstein—Zernike equation (OZ) [17, 18]. Here, $h_2(R) = F_2(R) - 1$, and $c_2(R)$ are called the pair correlation function and the direct correlation function, respectively. According to (1.3.15)—(1.3.17), one has

$$\begin{aligned} c_2(R) &= h_2(R) - w_2(R) + E_2(R) = \\ &= h_2(R) - \beta u_2(R) - \ln F_2(R) + E_2(R). \end{aligned} \quad (1.3.19)$$

1.3.3. Integral equations

The obtained integral equation (1.3.18) is exact, but it is not closed, since its solution requires knowledge of the direct correlation function $c_2(R)$, the expression (1.3.19) for which contains an infinite series $E_2(R)$. By making certain assumptions about the function $E_2(R)$, the integral equation can be closed and leads to an approximate relationship between the pair distribution function and the pair interaction potential expressed in the form of integral equation. Assuming that $E_2(R) = 0$, one obtains the so-called hypernetted-chain approximation (HNC). According to (1.3.19),

$$c_2^{(\text{HNC})}(R) = h_2(R) - \beta u_2(R) - \ln F_2(R). \quad (1.3.20)$$

On the other hand, assuming that the class of elementary diagrams $E_2(R)$ cancels the set of diagrams with parallel bonds, i.e. $E_2(R) + e^{w_2(R)} - 1 - w_2(R) = 0$, we arrive at the Percus—Yevick integral equation (PY). Since $w_2(R) = \beta u_2(R) + \ln F_2(R)$ according to (1.3.15), it follows from (1.3.19),

$$c_2^{(\text{PY})}(R) = F_2(R) \{1 - \exp[-\beta u_2(R)]\}. \quad (1.3.21)$$

This relation determines the direct correlation function with certain accuracy only at small distances. For example, for hard-sphere potential,

$$e^{-\beta u_2(r)} = \begin{cases} 0, & R < \sigma, \\ 1, & R > \sigma, \end{cases} \quad (1.3.22)$$

and $c_2^{(\text{PY})}(R) = 0$ for $R > \sigma$. In the hypernetted-chain approximation, the direct correlation function has a long-range part given by,

$$d_2^{(\text{HNC})}(R) = e^{\beta u_2(R)} F_2(R) - 1 - \ln F_2(R) - \beta u_2(R). \quad (1.3.23)$$

As a generalization of (1.3.20) and (1.3.21), the Rowlinson approximation can be obtained,

$$c_2(R) = c_2^{(\text{PY})}(R) + \alpha d_2^{(\text{HNC})}(R). \quad (1.3.24)$$

The parameter α is determined by the requirement of thermodynamic self-consistency of the pair distribution function. It is clear that when $\alpha = 0$, then $c_2(R) = c_2^{(\text{PY})}(R)$ and for $\alpha = 1$, one has $c_2(R) = c_2^{(\text{HNC})}(R)$.

The Bogolyubov chain of equations (1.1.28) with chain breaking based on certain approximations for a higher-order distribution functions is also used to obtain integral equations. Assuming, for example, additivity of the mean force potential, one arrives at the superposition approximation for the three-particle distribution function,

$$F_2(R_{12}, R_{13}, R_{32}) = F_2(R_{12}) F_2(R_{13}) F_2(R_{32}). \quad (1.3.25)$$

Although the approximation (1.3.25) itself is not bad, its application to truncate the Bogolyubov chain leads to significant inaccuracies for the pair distribution function.

The higher-order superposition approximation [15] can also be used to close the Bogolyubov chain sequence,

$$\begin{aligned} F_4(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) = \\ = \frac{F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_4) F_3(\mathbf{R}_1, \mathbf{R}_3, \mathbf{R}_4) F_3(\mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4)}{F_2(R_{12}) F_2(R_{13}) F_2(R_{14}) F_2(R_{32}) F_2(R_{24}) F_2(R_{34})}, \end{aligned} \quad (1.3.26)$$

which, however, significantly complicates the calculation. Nevertheless, in order to obtain more accurate equations, one should proceed from a higher distribution functions. They, like the pair distribution function, can be found by functional differentiation of the expression for free energy (see Chapter 2). Thus, the three-particle distribution function after selective summation of diagrams is represented as,

$$F_3(R_{12}, R_{13}, R_{23}) = F_2(R_{12}) F_2(R_{13}) F_2(R_{23}) e^{w_2(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)}, \quad (1.3.27)$$

where $w_2(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ is a set of diagrams with three fixed vertices that are not directly connected. At least three lines $h_2(R)$ emerge from each field vertex. After replacing $F_2(R)$ by $1 + h_2(R)$ in (1.3.27), one can obtain a diagrammatic

expression for the three-body correlation function,

$$h_3(R_{12}, R_{13}, R_{32}) = F_3(R_{12}, R_{13}, R_{32}) - F_2(R_{12}) - F_2(R_{13}) - F_2(R_{32}) + 2$$

and introduce the direct correlation function $c_3(R_{12}, R_{13}, R_{32})$ related to $h_3(R_{12}, R_{13}, R_{32})$ via one of four equivalent manners [46], for example:

$$\begin{aligned} h_3(R_{12}, R_{13}, R_{32}) = & c_3(R_{12}, R_{13}, R_{32}) + h_2(R_{12})h_2(R_{13}) + \\ & + h_2(R_{12})h_2(R_{23}) + h_2(R_{13})h_2(R_{23}) + \\ & + \rho \int d\mathbf{R}_4 h_2(R_{14})h_2(R_{24})h_2(R_{34}) + \\ & + \rho \int d\mathbf{R}_4 h_2(R_{34})c_3(R_{12}, R_{14}, R_{24}) + \\ & + \rho \int d\mathbf{R}_4 h_2(R_{24})c_3(R_{13}, R_{14}, R_{34}) + \\ & + \rho \int d\mathbf{R}_4 h_2(R_{14})c_3(R_{23}, R_{34}, R_{24}) + \\ & + \rho^2 \int d\mathbf{R}_4 d\mathbf{R}_5 h_2(R_{15})h_2(R_{34})c_3(R_{24}, R_{25}, R_{45}) + \\ & + \rho^2 \int d\mathbf{R}_4 d\mathbf{R}_5 h_2(R_{25})h_2(R_{34})c_3(R_{14}, R_{15}, R_{45}) + \\ & + \rho^2 \int d\mathbf{R}_4 d\mathbf{R}_5 h_2(R_{15})h_2(R_{14})c_3(R_{35}, R_{34}, R_{45}) + \\ & + \rho^3 \int d\mathbf{R}_4 d\mathbf{R}_5 d\mathbf{R}_6 h_2(R_{15})h_2(R_{26})h_2(R_{34})c_3(R_{45}, R_{46}, R_{56}). \end{aligned} \quad (1.3.28)$$

This equation represents a three-particle analogue of equation (1.3.18).

By repeating the calculations outlined at the beginning of this section, Wertheim [47] obtained integral equations in the hypernetted-chain approximation (HNCA) and in the Percus—Yevick approximation (PYA) for the three-body function. Similarly, integral equations can be obtained for a higher-order distribution functions. Another way of obtaining integral equations for higher-order functions is the method proposed by Verlet [48], which accounts for higher-order terms in the functional Taylor series for generating functionals. It should be noted that there exist several exact relations for higher-order correlation functions. These are, first of all, the chain of equations (1.1.28). Besides, they include the Baxter relations [49] for direct correlation functions,

$$\frac{\partial}{\partial \rho} c_n(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n) = \int c_{n+1}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{n+1}) d\mathbf{R}_{n+1} \quad (1.3.29)$$

and others. Taking them into account is undoubtedly important when describing a system.

The main types of integral equations for the distribution functions have only been briefly considered. The lines of research within integral equations is sufficiently detailed in the literature (see, for example, [3, 17, 18]).

Knowing the pair distribution function, the thermodynamic description of the system can be developed using any of the three expressions (1.1.31)–(1.1.33). It is clear that for an accurate pair distribution function, the value of any thermodynamic quantity does not depend on which of the formulas (1.1.31)–(1.1.33) it can be obtained from. This is an important requirement for the thermodynamic self-consistency of the pair distribution function. However, the approximate nature of integral equations usually leads to a strong thermodynamic inconsistency of the results obtained using them, which represents a serious drawback of the method of integral equations. Like Mayer cluster expansions, the integral equations described above equally take into account the interactions at both large and small distances, and thus are poorly suited for the combined description of short- and long-range interactions that are very different in nature.

1.3.4. Methods of computer simulation

There are two types of approximations in the statistical description of real interacting systems. One is related to modelling the system under consideration. We have already noted the complex nature of the calculation of the potential energy U_N and the model character of the system with two-particle interaction $u_2(R)$. The second type of approximation is related to the approximate nature of the statistical description of the chosen model. Therefore, serious difficulties arise in the experimental verification of the results of the theory, since without additional information it is impossible to determine to what extent and by which approximation the theoretical and experimental data deviations are caused.

New opportunities in statistical theory arose in connection with the development of computer technology. As a result, an intermediate link appeared between theory and experiment, which was called a computer experiment or simulation. In essence, there are two types of such “experiment” based on the Monte Carlo (MC) and the molecular dynamics (MD) methods. The first one consists in a direct numerical calculation of statistical averages, while the second method is related to a numerical solution of equations of motion for a system of many particles. Each method has its advantages and disadvantages. Thus, MD enables the study of non-equilibrium properties, whereas MC methods are well-suited for evaluating thermodynamic properties that are challenging to obtain using MD (see [3, 9, 10, 15, 51–53]).

For systems with given interactions, both methods lead to rigorous numerical results and allow one to estimate their accuracy. Thus, knowing the results of a computer simulation for a system with a specified interaction, it is always possible to check how accurate a particular theoretical description of the system is. As computational capabilities grow, the role of computer simulations inevitably increase.

Nevertheless, the development of computer methods does not diminish the role of analytical approaches. On the contrary, the comparison of computer and analytical results allows us to identify the limits of applicability of the existing theories, stimulating the development of new analytical methods. In particular, a comparison of the results of computer simulations with those obtained using the integral equations discussed above shows that the theory quite well describes the systems with short-range interactions. However, the methods of integral equations are poorly adapted to simultaneously take into account both short- and long-range interactions.

In classical systems, the interaction of many particles can be attributed to two types, i.e., the short-range interactions at small distances and the long-range ones at large distances. The presence of different types of interaction requires the development of the methods that allow one to describe their contributions in different ways. The short-range interactions characterize a mutual impenetrability of classical particles that leads to a decrease of the volume accessible for the particles. The long-range interactions extend to large distances and, as a result, collective phenomena arise in the system usually manifesting themselves in the propagation of elastic fluctuations and in the screening of interparticle interactions.

Two main directions are distinguished in the development of the methods for the description of collective motions in the systems of interacting particles. In the first one, using the canonical transformation, the transformation is made to the collective coordinates and momenta which describe the collective oscillations or the elementary excitations corresponding to them. Since in this case the collective coordinates and momenta are not ordinary variables, the transformation to them is accompanied by additional conditions keeping fixed the total number of degrees of freedom of the system. This direction was developed for the use of new variables in the equations of motion and was used in the description of plasma, in the theory of solids, in the theory of the nucleus as well as for other systems (see, for example, [38, 54, 55]).

The second direction is connected with the work of Zubarev [22]. Here, for the first time, the transformation from a finite set of individual coordinates to a set of the so-called collective variables was performed rigorously from the mathematical point of view by using the Jacobian of the transformation in the configuration integral of the system of charges. Due to the development of this formalism, the method of collective variables was developed which made it possible to solve one of the main prob-

lems of the statistical theory of equilibrium systems, i.e., the problem of different ways of describing the short- and long- range interactions. This chapter is devoted to the presentation of the grounds of the method of collective variables, including their systematic introduction, obtaining both an analytical expression for the Jacobian of the transformation and the transformation function associated with it, calculating the free energy and the distribution functions of the simplest one-component system of interacting particles. A generalization of the method for more complex systems will be discussed in the following chapters.

2.1. Representation of collective variables

Collective variables describe the collective motions in the system and they are determined depending on the specific properties of the system. We restrict our considerations to simple one-component systems for which the collective variables are defined as the Fourier components of the operator of the deviation of the density of the number of particles from the average value. The transformation from the coordinate representation of the functions to the representation of the collective variables is performed in the following way. First, the operator $\hat{n}(\mathbf{R})$ is introduced, which describes the deviation of a number of particles from the average value, then the functions are represented as power series of the Fourier transform $\hat{\rho}_{\mathbf{k}}$ of the operator $\hat{n}(\mathbf{R})$. Finally, we write an integral transformation of the type of the Cauchy integrals in which the Fourier transforms $\hat{\rho}_{\mathbf{k}}$ are replaced by the collective variables, and a rigorous definition of the set of the collective variables is given.

2.1.1. Operator of the deviation of the particle density from the average value

Let us consider a one-component system of N particles in a volume V , the average density $\rho = N/V$. We define $\hat{n}(\mathbf{R})$ as the operator for the deviation of the number of particles from its average value in a unit volume around the point $R(x, y, z)$:

$$\hat{n}(\mathbf{R}) = \sum_{i=1}^N \delta(x - x_i) \delta(y - y_i) \delta(z - z_i) - \frac{N}{V},$$

where (x, y, z) are coordinates of the points $\mathbf{R}$, (x_i, y_i, z_i) are coordinates of the particle i , $\delta(x - x_i)$ is the Dirac delta-function¹. In what follows, a product of

¹The Dirac delta function is a generalized function and formally

$$\delta(x - x_i) = \begin{cases} \infty, & x = x_i, \\ 0, & x \neq x_i, \end{cases}$$

three delta-functions will be denoted as $\delta(\mathbf{R} - \mathbf{R}_i) = \delta(x - x_i)\delta(y - y_i)\delta(z - z_i)$, and for $\hat{n}(\mathbf{R})$

$$\hat{n}(\mathbf{R}) = \sum_{i=1}^N \delta(\mathbf{R} - \mathbf{R}_i) - \frac{N}{V}. \quad (2.1.1)$$

The integral $\int_G \hat{n}(\mathbf{R}) d\mathbf{R} = N_G - NG/V$ is equal to a deviation of the number of particles in the volume G from their average value; for a whole volume of the system $\int_V \hat{n}(\mathbf{R}) d\mathbf{R} = 0$. Here, $d\mathbf{R} = dx dy dz$ is a volume element. Imposing periodicity boundary conditions on the system, we present $\hat{n}(\mathbf{R})$ as a Fourier series

$$\hat{n}(\mathbf{R}) = \sum_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}} \frac{\sqrt{N}}{V}, \quad (2.1.2)$$

where $\sum_{\mathbf{k}} = \sum_{k_x} \sum_{k_y} \sum_{k_z}$, $k_i = \frac{2\pi}{L} n_i$, $i = x, y, z$; n_i is an integer, $V = L^3$ is the volume of the system which is equal to the volume of periodicity of all its properties. The Fourier transform $\hat{\rho}_{\mathbf{k}}$ has the form

$$\hat{\rho}_{\mathbf{k}} = \frac{1}{\sqrt{N}} \int \hat{\rho}_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{R}) d\mathbf{R} = \frac{1}{\sqrt{N}} \sum_{i=1}^N \exp(i\mathbf{k}\mathbf{R}_i) - \sqrt{N} \delta_{\mathbf{k},0}. \quad (2.1.3)$$

the properties of $\delta(x - x_i)$ are determined on a set of the main functions $\varphi(x)$

$$\begin{aligned} \int_{-\infty}^{\infty} -\infty^{\infty} \varphi(x) \delta(x - x_i) dx &= \varphi(x_i), \\ \int_{-\infty}^{\infty} \delta(x - x_i) dx &= 1, \quad \int_G \delta(x - x_i) dx = \begin{cases} 1, & x_i \in G, \\ 0, & x_i \notin G. \end{cases} \end{aligned}$$

In the three-dimensional case, $\delta(\mathbf{R} - \mathbf{R}_i) = \delta(x - x_i)\delta(y - y_i)\delta(z - z_i)$, an integral representation of a δ -function is as follows: $\delta(\mathbf{R} - \mathbf{R}_i) = \sum_{\mathbf{k}} \frac{1}{V} \exp[i\mathbf{k}(\mathbf{R} - \mathbf{R}_i)]$, the sum runs over a set of discrete values of the vector $\mathbf{k}$, in the case of continuous $\mathbf{k}$ $\delta(\mathbf{R} - \mathbf{R}_i) = \frac{1}{(2\pi)^3} \int \exp[2\pi i \mathbf{k}(\mathbf{R} - \mathbf{R}_i)] d\mathbf{k}$. Next,

$$\int \delta(\mathbf{R} - \mathbf{R}_i) d\mathbf{R} = \sum_{\mathbf{k}} \int \frac{1}{V} \exp[i\mathbf{k}(\mathbf{R} - \mathbf{R}_i)] d\mathbf{R} = \sum_{\mathbf{k}} \delta_{\mathbf{k},0} e^{i\mathbf{k}\mathbf{R}_i} = \sum_{\mathbf{k}} \delta_{\mathbf{k},0} = 1,$$

where $\delta_{\mathbf{k},0} = 1/V \int e^{i\mathbf{k}\mathbf{R}} d\mathbf{R}$ is the Kronecker symbol for a discrete argument, $\delta_{\mathbf{k},0} = \delta_{k_x,0} \delta_{k_y,0} \delta_{k_z,0}$,

$$\delta_{\mathbf{k},0} = \begin{cases} 1, & k = 0, \\ 0, & k \neq 0. \end{cases}$$

Being a function of $\mathbf{R}_1, \dots, \mathbf{R}_N$, $\hat{\rho}_{\mathbf{k}}$ is complex and symmetric with respect to permutation of the coordinates of the particles. In this case, $\hat{\rho}_{\mathbf{k}=0} = \int \hat{n}(\mathbf{R}) d\mathbf{R} = 0$ regardless of the values of $\mathbf{R}_1, \dots, \mathbf{R}_N$.

The real part of $\hat{\rho}_{\mathbf{k}}$ and the coefficient of its imaginary part are, respectively,

$$\hat{\rho}_{\mathbf{k}}^c = \frac{1}{\sqrt{N}} \sum_{j=1}^N \cos(\mathbf{k} \mathbf{R}_j), \quad \hat{\rho}_{\mathbf{k}}^s = \frac{1}{\sqrt{N}} \sum_{j=1}^N \sin(\mathbf{k} \mathbf{R}_j), \quad \text{where } \mathbf{k} \neq 0. \quad (2.1.4)$$

The following relations hold

$$\hat{\rho}_{\mathbf{k}}^c = \hat{\rho}_{-\mathbf{k}}^c, \quad \hat{\rho}_{\mathbf{k}}^s = -\hat{\rho}_{-\mathbf{k}}^s, \quad \hat{\rho}_{\mathbf{k}} = \hat{\rho}_{-\mathbf{k}}^*. \quad (2.1.5)$$

Each function (2.1.3), (2.1.4) has a certain value of the vector $\mathbf{k}$, which also plays the role of an index. The arithmetic mean values of $\hat{\rho}_{\mathbf{k}}^c$, $\hat{\rho}_{\mathbf{k}}^s$, $\hat{\rho}_{\mathbf{k}}$ and their products are found from the relations

$$\begin{aligned} V^{-N} \int \hat{\rho}_{\mathbf{k}}(d\mathbf{R}) &= \sqrt{N} \delta_{\mathbf{k},0} = 0, \quad \text{because } \mathbf{k} \neq 0, \\ V^{-N} \int \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2}(d\mathbf{R}) &= \delta_{\mathbf{k}_1+\mathbf{k}_2,0}, \\ V^{-N} \int \hat{\rho}_{\mathbf{k}_1}^c \hat{\rho}_{\mathbf{k}_2}^c(d\mathbf{R}) &= \frac{1}{2} [\delta_{\mathbf{k}_1+\mathbf{k}_2,0} + \delta_{\mathbf{k}_1-\mathbf{k}_2,0}], \\ V^{-N} \int \hat{\rho}_{\mathbf{k}_1}^s \hat{\rho}_{\mathbf{k}_2}^s(d\mathbf{R}) &= \frac{1}{2} [\delta_{\mathbf{k}_1+\mathbf{k}_2,0} - \delta_{\mathbf{k}_1-\mathbf{k}_2,0}], \\ V^{-N} \int \hat{\rho}_{\mathbf{k}_1}^c \hat{\rho}_{\mathbf{k}_2}^s(d\mathbf{R}) &= 0. \end{aligned} \quad (2.1.6)$$

Here, $\int \dots(d\mathbf{R})$ is a $3N$ -dimensional integral $\int_V \dots \int_V d\mathbf{R}_1 \dots d\mathbf{R}_N$. In (2.1.2)–(2.1.5), the factor $N^{-1/2}$ is introduced for a normalisation, $V^{-1} \int \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}}(d\mathbf{R}) = 1$. We find for the density correlation

$$\int \hat{n}(\mathbf{R}') \hat{n}(\mathbf{R} - \mathbf{R}') d\mathbf{R} = \frac{N}{V} \sum_{\mathbf{k} \neq 0} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} e^{-i\mathbf{k} \mathbf{R}}. \quad (2.1.7)$$

2.1.2. Fourier transform of functions

Consider functions $F(\mathbf{R}_1, \dots, \mathbf{R}_N)$ which are symmetric with respect to permutation of the particle coordinates $\mathbf{R}_1, \dots, \mathbf{R}_N$ and which belong to the class L_2 . Present $F(\mathbf{R}_1, \dots, \mathbf{R}_N)$ as a function of either $\hat{\rho}_{\mathbf{k}}$ or $\hat{\rho}_{\mathbf{k}}^c$, $\hat{\rho}_{\mathbf{k}}^s$. More precisely, for $F(\mathbf{R}_1, \dots, \mathbf{R}_N)$ we take the functions of the additive and binary types

$$\Psi(\mathbf{R}_1, \dots, \mathbf{R}_N) = \sum_{j=1}^N \Phi_1(\mathbf{R}_j), \quad v(\mathbf{R}_1, \dots, \mathbf{R}_N) = \sum_{1 \leq i < j \leq N} \Phi_2(\mathbf{R}_i, \mathbf{R}_j).$$

The first function can present, for example, the energy of particles in the presence of an external field, the second function presents the energy of the pair interactions. According to the definition (2.1.1) of the operator $\hat{n}(\mathbf{R})$,

$$\begin{aligned}\Psi(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \frac{N}{V} \int \Phi_1(\mathbf{R}) d\mathbf{R} + \int \Phi_1(\mathbf{R}) \hat{n}(\mathbf{R}) d\mathbf{R}, \\ v(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \frac{1}{2} \sum_{i,j=1}^N \Phi_2(R_{ij}) - \frac{1}{2} N \Phi_2(0) = \int \frac{1}{2} \Phi_2(R_{12}) \times \\ &\times \hat{n}(\mathbf{R}_1) \hat{n}(\mathbf{R}_2) d\mathbf{R}_1 d\mathbf{R}_2 + \frac{1}{2} \frac{N^2}{V} \int \Phi_2(r) d\mathbf{R} - \frac{1}{2} N \Phi_2(0).\end{aligned}\quad (2.1.8)$$

Instead of $\hat{n}(\mathbf{R})$, we substitute its Fourier expansion (2.1.2). Then,

$$\begin{aligned}\Psi(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \sum_{\mathbf{k}} \frac{\sqrt{N}}{V} \mu(\mathbf{k}) \hat{\rho}_{\mathbf{k}} + \frac{N}{V} \mu(0), \\ v(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \frac{1}{2} \frac{N}{V} \sum_{\mathbf{k}} \nu(k) \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}} + \frac{1}{2} \frac{N^2}{V} \nu(0) - \frac{1}{2} N \Phi_2(0),\end{aligned}\quad (2.1.9)$$

where $\mu(\mathbf{k})$ and $\nu(\mathbf{k})$ are Fourier transforms of $\Phi_1(\mathbf{R})$ and $\Phi_2(\mathbf{R})$, respectively; $\mu(\mathbf{k}) = \int \Phi_1(\mathbf{R}) e^{-i\mathbf{k}\mathbf{R}} d\mathbf{R}$ and $\nu(\mathbf{k}) = \int \Phi_2(\mathbf{R}) e^{-i\mathbf{k}\mathbf{R}} d\mathbf{R}$. In the case when the potential energy of the pair interaction is a spatially homogeneous function, $\Phi_2(\mathbf{R}_i, \mathbf{R}_j) = \Phi_2(|\mathbf{R}_i - \mathbf{R}_j|)$, the Fourier transform $\nu(\mathbf{k}) = \nu(-\mathbf{k})$ and we have for $v(\mathbf{R}_1, \dots, \mathbf{R}_N)$

$$v(\mathbf{R}_1, \dots, \mathbf{R}_N) = \frac{N}{V} \sum' \nu(k) [(\hat{\rho}_{\mathbf{k}}^c)^2 + (\hat{\rho}_{\mathbf{k}}^s)^2] + \frac{1}{2} \frac{N^2}{V} \nu(0) - \frac{1}{2} N \Phi_2(0). \quad (2.1.10)$$

Here, the prime means that the sum over $\mathbf{k}$ is performed in the upper semi-space.

In equations (2.1.9)–(2.1.10), the functions of an additive type are presented as series containing, respectively, the first and second powers of the Fourier transform of the operator $\hat{n}(\mathbf{R})$. An arbitrary symmetric function $F(\mathbf{R}_1, \dots, \mathbf{R}_N)$ which belongs to the class L_2 is written as a power series

$$\begin{aligned}F(\mathbf{R}_1, \dots, \mathbf{R}_N) &= f_0 + \sum_{\mathbf{k}} f_1(\mathbf{k}) \hat{\rho}_{\mathbf{k}} + \sum_{\mathbf{k}_1, \mathbf{k}_2} f_2(\mathbf{k}_1, \mathbf{k}_2) \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} + \dots \\ &\dots + \sum_{\mathbf{k}_1, \dots, \mathbf{k}_N} f_N(\mathbf{k}_1, \dots, \mathbf{k}_N) \hat{\rho}_{\mathbf{k}_1} \dots \hat{\rho}_{\mathbf{k}_N}.\end{aligned}\quad (2.1.11)$$

In the spatially homogeneous case, the coefficients $f_i(\mathbf{k}_1, \dots, \mathbf{k}_i)$ contain the Kronecker symbols $\delta_{\mathbf{k}_1 + \dots + \mathbf{k}_i, 0}$.

2.1.3. Analytical functional

In the complex plane of $\hat{\rho}_{\mathbf{k}}$, we find the contour C containing all the points of the Fourier transform $\hat{\rho}_{\mathbf{k}} = 1/\sqrt{N} \sum_{i=1}^N \exp(i\mathbf{k}\mathbf{R}_i)$ taken for all possible $\mathbf{R}_1, \dots, \mathbf{R}_N$ in the volume V . We consider in a similar way the complex plane of $\hat{\rho}_{\mathbf{k}}$ for the functions $\hat{\rho}_{\mathbf{k}}^c$ whose values are located along the real axis from $-\sqrt{N}$ to $\sqrt{N}$ as well as the complex region of $\hat{\rho}_{\mathbf{k}}$ for $\hat{\rho}_{\mathbf{k}}^s$, the values of which are also located along the real axis on the segment from $-\sqrt{N}$ to $\sqrt{N}$. Let us introduce the Cauchy integrals along the contour C . Since, according to (2.1.9) and (2.1.11), $\Psi(\mathbf{R}_1, \dots, \mathbf{R}_N)$, $v(\mathbf{R}_1, \dots, \mathbf{R}_N)$ and $F(\mathbf{R}_1, \dots, \mathbf{R}_N)$ are power functions of $\hat{\rho}_{\mathbf{k}}$, then from the Cauchy integral theorem

$$\begin{aligned} \Psi(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \oint_C \dots \oint_C \left[\frac{\sqrt{N}}{V} \sum_{\mathbf{k}} \mu(k) \rho_{\mathbf{k}} + \frac{N}{V} \mu(0) \right] \prod_{\mathbf{k}} \frac{1}{\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}} \frac{1}{2\pi i} d\rho_{\mathbf{k}}, \\ v(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \oint_C \dots \oint_C \left[\frac{1}{2} \frac{N}{V} \sum_{\mathbf{k}} \nu(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \frac{1}{2} \frac{N^2}{V} \nu(0) - \right. \\ &\quad \left. - \frac{1}{2} N \Phi_2(0) \right] \prod_{\mathbf{k}} \frac{1}{\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}} \frac{1}{2\pi i} d\rho_{\mathbf{k}}, \end{aligned} \quad (2.1.12)$$

$$\begin{aligned} F(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \oint_C \dots \oint_C \left[f_0 + \sum_{\mathbf{k}} f_1(\mathbf{k}) \rho_{\mathbf{k}} + \sum_{\mathbf{k}_1, \mathbf{k}_2} f_2(\mathbf{k}_1, \mathbf{k}_2) \rho_{\mathbf{k}_1} \rho_{\mathbf{k}_2} + \dots \right. \\ &\quad \left. \dots + \sum_{\mathbf{k}_1, \dots, \mathbf{k}_N} f_N(\mathbf{k}_1, \dots, \mathbf{k}_N) \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_N} \right] \prod_{\mathbf{k}} \frac{1}{\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}} \frac{1}{2\pi i} d\rho_{\mathbf{k}}, \end{aligned}$$

where $\frac{1}{2\pi i} \oint_C \frac{1}{\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}} d\rho_{\mathbf{k}} = 1$.

Now we define the phase space of the collective variables. In the general case, the collective variable is considered as a complex variable $\rho_{\mathbf{k}}$ related to the Fourier transform $\hat{\rho}_{\mathbf{k}}$ by the relation

$$\hat{\rho}_{\mathbf{k}} = \frac{1}{2\pi i} \oint_C \frac{\rho_{\mathbf{k}}}{\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}} d\rho_{\mathbf{k}}. \quad (2.1.13)$$

Then, the relationships (2.1.12) describe the transformation from $\mathbf{R}_1, \dots, \mathbf{R}_N$ to the $\dots \rho_{\mathbf{k}} \dots$ -representation. We call the function

$$\Psi(\rho) = \frac{\sqrt{N}}{V} \sum_{\mathbf{k}} \mu(k) \rho_{\mathbf{k}} + \frac{N}{V} \mu(0) \quad (2.1.14)$$

a ρ -representation of an additive function of the $\Psi(\mathbf{R}_1, \dots, \mathbf{R}_N)$ type. According to (2.1.9), the ρ -representation for a pair distribution function has the form

$$v(\rho) = \frac{1}{2} \frac{N}{V} \sum_{\mathbf{k}} \nu(\mathbf{k}) (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1) + \frac{1}{2} \frac{N^2}{V} \nu(0), \quad (2.1.15)$$

here the substitution $\frac{N}{2} \Phi_2(0) = \frac{1}{2} \frac{N}{V} \sum_{\mathbf{k}} \nu(\mathbf{k})$ is made.

In general,

$$\begin{aligned} F(\rho) = & f_0 + \sum_{\mathbf{k}} f_1(\mathbf{k}) \rho_{\mathbf{k}} + \sum_{\mathbf{k}_1, \mathbf{k}_2} f_2(\mathbf{k}_1, \mathbf{k}_2) \rho_{\mathbf{k}_1} \rho_{\mathbf{k}_2} + \dots \\ & \dots + \sum_{\mathbf{k}_1, \dots, \mathbf{k}_N} f_N(\mathbf{k}_1, \dots, \mathbf{k}_N) \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_N}. \end{aligned} \quad (2.1.16)$$

Taking into account (2.1.14)–(2.1.16), we write the relation (2.1.12) in the general form characterizing the transformation from the $\mathbf{R}_1, \dots, \mathbf{R}_N$ -representation to the $\dots \rho_{\mathbf{k}} \dots$ -representation

$$\begin{aligned} \Psi(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \oint_C \dots \oint_C \Psi(\rho) \mathcal{R}(\rho) \prod_{\mathbf{k}} d\rho_{\mathbf{k}}, \\ v(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \oint_C \dots \oint_C v(\rho) \mathcal{R}(\rho) \prod_{\mathbf{k}} d\rho_{\mathbf{k}}, \\ F(\mathbf{R}_1, \dots, \mathbf{R}_N) &= \oint_C \dots \oint_C F(\rho) \mathcal{R}(\rho) \prod_{\mathbf{k}} d\rho_{\mathbf{k}}, \end{aligned} \quad (2.1.17)$$

where $\mathcal{R}(\rho)$ is a resolvent of the transformation

$$\mathcal{R}(\rho) = \prod_{\mathbf{k}} \frac{1}{2\pi i} \frac{1}{\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}}. \quad (2.1.18)$$

Our aim here is not to study the properties of the resolvent $\mathcal{R}(\rho)$ and the general forms (2.1.17). In this book we consider the physical systems of particles subject to singlet and pair potentials, and the pair potentials are spatially homogeneous functions with respect to the coordinates of the centres of mass of the particles. Therefore, we reduce the relations (2.1.13)–(2.1.18) to the form that is more convenient to study such physical systems. According to (2.1.10), the spatially homogeneous potential of pair interactions is a quadratic form with respect to the Fourier transforms $\hat{\rho}_{\mathbf{k}}^c$ and $\hat{\rho}_{\mathbf{k}}^s$, which are real functions of particle coordinates. Based on (2.1.13), we define a set of the real collective variables $\rho_{\mathbf{k}}^c, \rho_{\mathbf{k}}^s$

$$\hat{\rho}_{\mathbf{k}}^c = \frac{1}{2\pi i} \oint_C \frac{\rho_{\mathbf{k}}}{\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}^c} d\rho_{\mathbf{k}}, \quad \hat{\rho}_{\mathbf{k}}^s = \frac{1}{2\pi i} \oint_C \frac{\rho_{\mathbf{k}}}{\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}^s} d\rho_{\mathbf{k}}. \quad (2.1.19)$$

Since both integrals are of the same type, we study the first of them in detail. The poles of the function under the integral are located along the real axis at the points corresponding to the given values of $\frac{1}{\sqrt{N}} \sum_i \cos(\mathbf{k}\mathbf{R}_i)$. The coordinate $\mathbf{R}_i$ of the i -th particle takes all values inside the volume V in such a way that the points $\rho_{\mathbf{k}}^c$ tightly cover a segment of the real axis $\rho_{\mathbf{k}}$ from $-\infty$ to ∞ , except for a coordinate origin. Thus, the contour C in (2.1.19) can be deformed by reducing it to a rectangle elongated along the real axis, each of the two sides of which is equal to $2\sqrt{N} + 2C$, C is an arbitrary positive number, and the other two sides being 2Δ long each, where Δ is a small value. The contour integral is equal to the sum of four integrals. Presenting $\rho_{\mathbf{k}}$ as $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}^c + i\rho_{\mathbf{k}}^s$, we have

$$\begin{aligned} \hat{\rho}_{\mathbf{k}}^c = & \frac{1}{2\pi i} \oint_C \frac{\rho_{\mathbf{k}} d\rho_{\mathbf{k}}}{\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}^c} = \frac{1}{2\pi i} \left[\int_{-\sqrt{N}-C-i\Delta}^{\sqrt{N}+C-i\Delta} \frac{\rho_{\mathbf{k}}^c - i\Delta}{\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c - i\Delta} d\rho_{\mathbf{k}}^c + \right. \\ & + \int_{-\sqrt{N}-C-i\Delta}^{\sqrt{N}+C-i\Delta} \frac{\rho_{\mathbf{k}}^c - i\Delta}{\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c - i\Delta} d\rho_{\mathbf{k}}^c + i \int_{\sqrt{N}+C-i\Delta}^{\sqrt{N}+C+i\Delta} \frac{\sqrt{N} + C + i\rho_{\mathbf{k}}^s}{\sqrt{N} + C - \hat{\rho}_{\mathbf{k}}^c + i\rho_{\mathbf{k}}^s} d\rho_{\mathbf{k}}^s + \\ & \left. + i \int_{-\sqrt{N}-C+i\Delta}^{-\sqrt{N}-C-i\Delta} \frac{-\sqrt{N} - C + i\rho_{\mathbf{k}}^s}{-\sqrt{N} - C - \hat{\rho}_{\mathbf{k}}^c + i\rho_{\mathbf{k}}^s} d\rho_{\mathbf{k}}^s \right]. \end{aligned} \quad (2.1.20)$$

The third and forth integrals disappear in the limit $\Delta \rightarrow 0$, we use the relationship

$$\lim_{\Delta \rightarrow 0} \frac{1}{\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c \mp i\Delta} = \mathcal{P} \frac{1}{\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c} \pm i\pi\delta(\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c),$$

to the other parts, $\mathcal{P}$ is a symbol of the principal value.

As a result, for (2.1.20) we obtain

$$\hat{\rho}_{\mathbf{k}}^c = \int_{-\infty}^{\infty} \rho_{\mathbf{k}}^c \delta(\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c) d\rho_{\mathbf{k}}^c. \quad (2.1.21)$$

This trivial relationship of the analytic functional type defines the real collective variable $\rho_{\mathbf{k}}^c$ corresponding to the Fourier transform $\hat{\rho}_{\mathbf{k}}^c$. The real collective variable $\rho_{\mathbf{k}}^s$ is defined in a similar way

$$\hat{\rho}_{\mathbf{k}}^s = \int_{-\infty}^{\infty} \rho_{\mathbf{k}}^s \delta(\rho_{\mathbf{k}}^s - \hat{\rho}_{\mathbf{k}}^s) d\rho_{\mathbf{k}}^s. \quad (2.1.22)$$

We introduce the phase space of independent variables $\dots, \rho_{\mathbf{k}}^c, \dots, \dots, \rho_{\mathbf{k}}^s, \dots$, corresponding to the Fourier transforms $\hat{\rho}_{\mathbf{k}}^c$ and $\hat{\rho}_{\mathbf{k}}^s$, defined by the equations

(2.1.21)–(2.1.22). According to equalities (2.1.5), a set of the variables $\rho_{\mathbf{k}}^c$ and $\rho_{\mathbf{k}}^s$ is determined by the range of the index $\mathbf{k}$, which takes all values in the upper semi-space, except for the points of the semi-plane $k_z = 0$, $k_x < 0$, for the points of the semi-axis $k_y \leq 0$ and the coordinate origin $\mathbf{k} = 0$. This region will be denoted by Ω . Under deformation of each contour in (2.1.17) the resolvent $\mathcal{R}(\rho)$ (see (2.1.18)) transforms into a product of δ -functions, which we call the transformation function from the set of variables $\mathbf{R}_1, \dots, \mathbf{R}_N$ to the set of variables $\rho_{\mathbf{k}}^c$ and $\rho_{\mathbf{k}}^s$. We denote the transformation function by $J(\rho R)$:

$$J(\rho R) = \prod'_{\mathbf{k}} \delta(\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c) \delta(\rho_{\mathbf{k}}^s - \hat{\rho}_{\mathbf{k}}^s). \quad (2.1.23)$$

The prime means that the product over $\mathbf{k}$ takes the values in the region Ω . Instead of the equations (2.1.21)–(2.1.22) we write

$$\hat{\rho}_{\mathbf{k}}^c = \int \rho_{\mathbf{k}}^c J(\rho R) (d\rho), \quad \hat{\rho}_{\mathbf{k}}^s = \int \rho_{\mathbf{k}}^s J(\rho R) (d\rho), \quad (2.1.24)$$

where $(d\rho)$ is a volume element of the phase space of the collective variables,

$$(d\rho) = \prod'_{\mathbf{k}} d\hat{\rho}_{\mathbf{k}}^c d\hat{\rho}_{\mathbf{k}}^s. \quad (2.1.25)$$

The integrals over each $\rho_{\mathbf{k}}^c$, $\rho_{\mathbf{k}}^s$ are taken within the range $(-\infty, \infty)$. For an arbitrary function $F(\mathbf{R}_1, \dots, \mathbf{R}_N)$, analytical with respect to the Fourier transforms $\rho_{\mathbf{k}}^c$, $\rho_{\mathbf{k}}^s$ or $\rho_{\mathbf{k}}$, one can write its collective variable representation in the form of an analytical functional:

$$F(\mathbf{R}_1, \dots, \mathbf{R}_N) = \int F(\rho) J(\rho R) (d\rho). \quad (2.1.26)$$

Now, we consider the functions of the additive and binary types in detail.

$$\Psi(\mathbf{R}_1, \dots, \mathbf{R}_N) = \sum_{i=1}^N \Phi_1(R_i) = \int \Psi(\rho) J(\rho R) (d\rho), \quad (2.1.27)$$

where $\Psi(\rho) = \sum_{\mathbf{k}} \frac{\sqrt{N}}{V} \mu(\mathbf{k}) \rho_{\mathbf{k}} + \frac{N}{V} \mu(0)$, $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}^c - i\rho_{\mathbf{k}}^s$, $\rho_{\mathbf{k}}^c = \rho_{-\mathbf{k}}^c$, $\rho_{\mathbf{k}}^s = -\rho_{-\mathbf{k}}^s$. As a result,

$$\Psi(\rho) = \frac{\sqrt{N}}{V} \sum'_{\mathbf{k}} [\mu(\mathbf{k}) (\rho_{\mathbf{k}}^c - i\rho_{\mathbf{k}}^s) + \mu(-\mathbf{k}) (\rho_{\mathbf{k}}^c + i\rho_{\mathbf{k}}^s)] + \frac{N}{V} \mu(0). \quad (2.1.28)$$

For the pair distribution functions (see (2.1.12)),

$$v(\mathbf{R}_1, \dots, \mathbf{R}_N) = \sum_{1 \leq i < j \leq N} \Phi_2(\mathbf{R}_{ij}) = \int v(\rho) J(\rho R) (d\rho). \quad (2.1.29)$$

$v(\rho)$ is a $\rho_{\mathbf{k}}^c, \rho_{\mathbf{k}}^s$ -representation of the function $v(\mathbf{R}_1, \dots, \mathbf{R}_N)$:

$$\begin{aligned} v(\rho) &= \frac{1}{2} \sum_{\mathbf{k}} \frac{N}{V} [\nu(\mathbf{k}) + \nu(-\mathbf{k})] [(\rho_{\mathbf{k}}^c)^2 + (\rho_{\mathbf{k}}^s)^2 - 1] + \frac{N^2}{2V} \nu(0) = \\ &= \frac{1}{2} \sum_{\mathbf{k}} \frac{N}{V} \nu(\mathbf{k}) (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1) + \frac{1}{2} \frac{N^2}{V} \nu(0). \end{aligned} \quad (2.1.30)$$

In the case of spatially homogeneous functions for which $\nu(\mathbf{k}) = \nu(-\mathbf{k})$,

$$v(\rho) = \sum_{\mathbf{k}}' \frac{N}{V} \nu(k) [(\rho_{\mathbf{k}}^c)^2 + (\rho_{\mathbf{k}}^s)^2 - 1] + \frac{1}{2} \frac{N^2}{V} \nu(0). \quad (2.1.31)$$

Thus, the transformation is made from the Cartesian coordinate representation $\mathbf{R}_1, \dots, \mathbf{R}_N$ to the representation of the collective variables. It is associated with two successive transformations, i.e., the usual Fourier transform and the construction of an analytic functional using the transformation function $J(\rho R)$.

2.1.4. Jacobian of the transformation from the (R) -phase space to the (ρ) -phase space

Let us transform the integral $\int v(\mathbf{R}_1, \dots, \mathbf{R}_N) d\mathbf{R}_1, \dots, d\mathbf{R}_N$, where $v(\mathbf{R}_1, \dots, \mathbf{R}_N)$ is a symmetric function belonging to the class L_2 , to the variables $\rho_{\mathbf{k}}^c, \rho_{\mathbf{k}}^s$.

According to the general rules

$$\frac{1}{V^N} \int v(\mathbf{R}_1, \dots, \mathbf{R}_N) d\mathbf{R}_1, \dots, d\mathbf{R}_N = \int v(\rho) J(\rho) (d\rho), \quad (2.1.32)$$

where $J(\rho)$ is the Jacobian of the transformation. To determine $J(\rho)$, we substitute for $v(\mathbf{R}_1, \dots, \mathbf{R}_N)$ in the left-hand side its ρ -representation

$$v(\mathbf{R}_1, \dots, \mathbf{R}_N) = \int v(\rho) J(\rho R) (d\rho).$$

Rearranging the order of integration over (R) and (ρ) , we obtain

$$\frac{1}{V^N} \int v(\rho) \left[\int J(\rho R) d\mathbf{R}_1, \dots, d\mathbf{R}_N \right] (d\rho) = \int v(\rho) J(\rho) (d\rho).$$

Hence, due to the arbitrariness of $v(\rho)$, there follows the definition of the Jacobian of the transformation to a set of the collective variables, introduced in this form for the first time by Zubarev [22]:

$$\begin{aligned} J(\rho) &= \frac{1}{V^N} \int J(\rho R) d\mathbf{R}_1, \dots, d\mathbf{R}_N = \\ &= \frac{1}{V^N} \int \prod_{\mathbf{k}}' \delta(\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c) \delta(\rho_{\mathbf{k}}^s - \hat{\rho}_{\mathbf{k}}^s) d\mathbf{R}_1, \dots, d\mathbf{R}_N. \end{aligned} \quad (2.1.33)$$

Note that this expression coincides with the usual definition of the Jacobian of the transformation. As the simplest example, we consider the transformation from the system of the Cartesian coordinates to the system of the polar coordinates, determined by the transformation $x = r \cos \varphi$, $y = r \sin \varphi$ or $r = \sqrt{x^2 + y^2}$, $\varphi = \arctan(y/x)$.

First, we construct the transformation function $J(x, y; r, \varphi)$ and then, according to the definition (2.1.33), we find the Jacobian of the transformation from the Cartesian to the polar coordinates:

$$\begin{aligned} J(r, \varphi) &= \int \delta\left(\varphi - \arctan \frac{y}{x}\right) \delta\left(r - \sqrt{x^2 + y^2}\right) dx dy = \\ &= \int \delta\left(\varphi - \arctan \frac{y}{x}\right) \frac{\delta\left(y - \sqrt{r^2 - x^2}\right)}{y/\sqrt{x^2 + y^2}} dx dy = \\ &= \int r \delta\left(\varphi - \arctan \frac{\sqrt{r^2 - x^2}}{x}\right) \frac{dx}{\sqrt{r^2 - x^2}} = \\ &= r \int \frac{\delta(x - r \cos \varphi)}{\left|\frac{d}{dx} \arctan \frac{\sqrt{r^2 - x^2}}{x}\right|} \frac{dx}{\sqrt{r^2 - x^2}} = r. \end{aligned}$$

For further specific calculations, it is necessary to have an explicit expression for the transformation Jacobian $J(\rho)$. It can be easily obtained if in (2.1.33) we pass to the integral form for the δ -functions. Then,

$$\begin{aligned} J(\rho) &= \frac{1}{V^N} \int \exp \left\{ 2\pi i \sum_{\mathbf{k}}' [\omega_{\mathbf{k}}^c (\rho_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^c) + \omega_{\mathbf{k}}^s (\rho_{\mathbf{k}}^s - \hat{\rho}_{\mathbf{k}}^s)] \right\} (d\omega)(d\mathbf{R}) = \\ &= \frac{1}{V^N} \int \exp \left\{ \pi i \sum_{\mathbf{k}} \omega_{\mathbf{k}} (\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}) \right\} (d\omega)(d\mathbf{R}), \end{aligned} \quad (2.1.34)$$

where $(d\omega) = \prod_{\mathbf{k}} d\omega_{\mathbf{k}}^c d\omega_{\mathbf{k}}^s$; $(d\mathbf{R}) = d\mathbf{R}_1, \dots, d\mathbf{R}_N$. For convenience, we introduced complex quantities $\omega_{\mathbf{k}} = \omega_{\mathbf{k}}^c + i\omega_{\mathbf{k}}^s$, $\omega_{-\mathbf{k}} = \omega_{\mathbf{k}}^c - i\omega_{\mathbf{k}}^s$. Perform the integration over all $(d\mathbf{R})$ in (2.1.34). Using the exponential form for the integrand, we obtain

$$\begin{aligned} J(\rho) &= \int \exp \left\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \frac{(-i\pi)^2}{2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \mathfrak{M}_2(\mathbf{k}_1, \mathbf{k}_2) \omega_{\mathbf{k}_1} \omega_{\mathbf{k}_2} + \dots \right. \\ &\quad \left. + \frac{(-i\pi)^n}{n!} \frac{N}{\sqrt{N^n}} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \omega_{\mathbf{k}_1}, \dots, \omega_{\mathbf{k}_n} + \dots \right\} (d\omega). \end{aligned} \quad (2.1.35)$$

In mathematical statistics, such a series is called a cumulant series [56], and the quantities $\mathfrak{M}_n$ are called cumulants. The latter, like moments, are

introduced to describe statistical distributions. Formally, the moments and the cumulants of a random variable X are defined by the equality

$$\langle e^{\xi X} \rangle = \sum_{n \geq 0} \frac{\xi^n}{n!} \langle X^n \rangle = \exp \left(\sum_{n \geq 1} \frac{\xi^n}{n!} \mathfrak{M}_n \right), \quad (2.1.36)$$

where $\langle A \rangle$ is the average value of A with respect to some distribution; $\langle X^n \rangle$ is the n -th moment; $\mathfrak{M}_n$ is the n -th cumulant of this distribution. There are exact relationships between the cumulants and the moments in the literature. All cumulants, except for the first one, are invariant with respect to a variation of the initial value of the variable, that is the reason for their other name, Thiele's semi-invariants, since they were first introduced by Thiele.

Definition (2.1.36) can also be generalized to the multidimensional case [57]. For N variables $X_1, X_2, \dots, X_N$

$$\begin{aligned} \left\langle \exp \left(\sum_{j=1}^N \xi_j X_j \right) \right\rangle &= \sum_{\nu_1, \dots, \nu_N} \left(\prod_{j=1}^N \frac{1}{\nu_j!} \xi_j^{\nu_j} \right) \langle X_1^{\nu_1} \dots X_N^{\nu_N} \rangle = \\ &= \exp \left\{ \sum'_{\nu_1, \dots, \nu_N} \left(\prod_{j=1}^N \frac{1}{\nu_j!} \xi_j^{\nu_j} \right) \langle X_1^{\nu_1} \dots X_N^{\nu_N} \rangle_c \right\}, \end{aligned} \quad (2.1.37)$$

where $\langle X_1^{\nu_1} \dots X_N^{\nu_N} \rangle$ is a usual average, $\langle X_1^{\nu_1} \dots X_N^{\nu_N} \rangle_c$ is a cumulant average. The prime at the sum excludes the case $\nu_1 = \nu_2 = \dots = \nu_N = 0$. Each cumulant of the n -th order is expressed in terms of the moments of the n -th and lower orders. And vice versa, each moment of the n -th order is expressed in terms of the cumulants of the n -th and lower orders. In particular,

$$\begin{aligned} \langle X_1 \rangle_c &= \langle X_1 \rangle, \quad \langle X_1 X_2 \rangle_c = \langle X_1 X_2 \rangle - \langle X_1 \rangle \langle X_2 \rangle, \\ \langle X_1 X_2 X_3 \rangle_c &= \langle X_1 X_2 X_3 \rangle - [\langle X_1 \rangle \langle X_2 X_3 \rangle + \langle X_2 \rangle \langle X_1 X_3 \rangle + \\ &\quad + \langle X_3 \rangle \langle X_1 X_2 \rangle] + 2 \langle X_1 \rangle \langle X_2 \rangle \langle X_3 \rangle. \end{aligned} \quad (2.1.38)$$

By definition, a cumulant is equal to zero if it is possible to distinguish a statistically independent subgroup among its variables.

In (2.1.34), the exponential is averaged over an ideal distribution of non-interacting particles, so that for the quantities $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ introduced in (2.1.35) we have

$$\frac{N}{\sqrt{N^n}} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = \langle \hat{\rho}_{\mathbf{k}_1} \dots \hat{\rho}_{\mathbf{k}_n} \rangle_c = \frac{N}{\sqrt{N^n}} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0}. \quad (2.1.39)$$

It should be noted that here the Kronecker symbol denotes an irreducible closed sum of n vectors. The sum of vectors $\mathbf{k}_1 + \dots + \mathbf{k}_n$ has the closed form if

$\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ and the sum of n vectors is irreducible if it cannot be split in the sums equal to zero of the number of vectors less than n . For example, in the irreducible closed sum $\mathbf{k}_1 + \mathbf{k}_2 + \dots + \mathbf{k}_4 = 0$ there should be no cases $\mathbf{k}_1 + \mathbf{k}_2 = 0$ or $\mathbf{k}_3 + \mathbf{k}_4 = 0$. We also remind that in (2.1.35) none of $\mathbf{k}$ is equal to zero.

Denoting briefly

$$D_n(\omega) = \frac{(-i\pi)^n}{n!} \frac{N}{\sqrt{N^n}} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \omega_{\mathbf{k}_1}, \dots, \omega_{\mathbf{k}_n},$$

we present the Jacobian of the transformation (2.1.35) as follows:

$$J(\rho) = \int \exp \left\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \sum_{n \geq 2} D_n(\omega) \right\} (d\omega). \quad (2.1.40)$$

However, it is often necessary to have an expression for $J(\rho)$ as an explicit function of ρ . In particular, calculating the configuration integral, we need a form $J(\rho)$ that contains an approximate Gaussian distribution as a zero approximation. To this end, in (2.1.40) we replace all the functions $D_n(\omega)$ for $n > 3$ with the operators

$$\hat{D}_n \left(\frac{\partial}{\partial \rho} \right) = \frac{(-1)^n}{\sqrt{N^n}} N \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \frac{\partial^n}{\partial \rho_{\mathbf{k}_1} \dots \partial \rho_{\mathbf{k}_n}} \quad (2.1.41)$$

and present $J(\rho)$ in the form:

$$J(\rho) = \exp \left[\sum_{n \leq 3} \hat{D}_n \left(\frac{\partial}{\partial \rho} \right) \right] \int \exp \left\{ i\pi \sum'_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} - \frac{\pi^2}{2} \sum'_{\mathbf{k}} \mathfrak{M}_2(k) \omega_{\mathbf{k}} \omega_{-\mathbf{k}} \right\} (d\omega).$$

In the above integral, the integration variables can be separated and

$$\begin{aligned} & \int \exp \left\{ i\pi \sum'_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right\} \exp \left\{ -\frac{\pi^2}{2} \sum'_{\mathbf{k}} \mathfrak{M}_2(k) \omega_{\mathbf{k}} \omega_{-\mathbf{k}} \right\} (d\omega) = \\ & = \int \exp \left\{ \sum'_{\mathbf{k}} \left[(2\pi i \omega_{\mathbf{k}}^c \rho_{\mathbf{k}}^c - \pi^2 (\omega_{\mathbf{k}}^c)^2) + (2\pi i \omega_{\mathbf{k}}^s \rho_{\mathbf{k}}^s - \pi^2 (\omega_{\mathbf{k}}^s)^2) \right] \right\} \times \\ & \times \prod'_{\mathbf{k}} d\omega_{\mathbf{k}}^c d\omega_{\mathbf{k}}^s = \prod'_{\mathbf{k}} \frac{1}{\pi \mathfrak{M}_2(k)} \exp \left\{ -\sum'_{\mathbf{k}} \left[(\rho_{\mathbf{k}}^c)^2 + (\rho_{\mathbf{k}}^s)^2 \right] \frac{1}{\mathfrak{M}_2(k)} \right\}. \end{aligned} \quad (2.1.42)$$

For the Jacobian of the transformation, we obtain [23]

$$J(\rho) = \exp \left(\sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right) J_G(\rho), \quad (2.1.43)$$

where

$$J_G(\rho) = \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \left[\frac{1}{\mathfrak{M}_2(k)} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \ln(\pi \mathfrak{M}_2(k)) \right] \right\}$$

is the Gaussian approximation of the Jacobian. Expression (2.1.43) will be our working formula. Acting on $J_G(\rho)$ with the operators $\hat{D}_n(\partial/\partial\rho)$, we obtain an exponential form

$$J(\rho) = \exp \left\{ a_0 - \frac{1}{2} \sum_{\mathbf{k}} a_2 \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{1}{3!} \frac{1}{\sqrt{N}} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} a_3 \rho_{\mathbf{k}_1} \rho_{\mathbf{k}_2} \rho_{\mathbf{k}_3} \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, 0} - \right. \\ \left. - \frac{1}{4!} \frac{1}{N} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} a_4 \rho_{\mathbf{k}_1} \rho_{\mathbf{k}_2} \rho_{\mathbf{k}_3} \rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4, 0} - \dots \right\}, \quad (2.1.44)$$

where the sums over $\mathbf{k}$ are closed and irreducible, just like the sums over $\mathbf{k}$ in the operators $\hat{D}_n(\partial/\partial\rho)$. Coefficients $a_0, a_2, a_3, \dots$ are expressed through single integrals

$$a_0 \simeq N \ln 2Q, \quad Q = \int_0^\infty f(\omega) d\omega, \\ f(\omega) = \exp \left\{ -\pi^2 \mathfrak{M}_2 \omega^2 + \frac{(i\pi)^3}{3!} \mathfrak{M}_3 \omega^3 - \frac{(i\pi)^4}{4!} \mathfrak{M}_4 \omega^4 + \dots \right\}, \\ a_2 \simeq \pi^2 \left[\frac{1}{Q} \int_0^\infty \omega^2 f(\omega) d\omega - \frac{1}{Q^2} \left[\int_0^\infty \omega f(\omega) d\omega \right]^2 \right], \\ a_3 \simeq \pi^3 \left\{ \frac{1}{Q} \int_0^\infty \omega^3 f(\omega) d\omega - \frac{3}{Q^2} \left[\int_0^\infty \omega^2 f(\omega) d\omega \right] \left[\int_0^\infty \omega f(\omega) d\omega \right] + \right. \\ \left. + 2 \left[\frac{1}{Q} \int_0^\infty \omega f(\omega) d\omega \right]^3 \right\}, \text{ etc.}$$

In this book, the form (2.1.44) is used only to interpret the collective motions in an equilibrium spatially homogeneous system².

²We suggest the reader to derive (2.1.44). To this end, one should divide the variables under the integral in (2.1.35) using the unitary transformation $\omega_{\mathbf{k}} = \int \omega(\mathbf{R}) e^{i\mathbf{k}\mathbf{R}} (d\mathbf{R})$, then integrate over all $\omega(\mathbf{R})$ and obtain (2.1.44); see also [58], where this transformation is done for the spin systems.

2.1.5. Orthonormality conditions of $J(\rho R)$

Our purpose now is to consider the properties of the transformation function $J(\rho R)$, to find an explicit expression for the collective variable and to carry out the inverse transformation from the (ρ) -representation to the $(\mathbf{R})$ -representation.

According to the definition (2.1.23), $J(\rho R)$ depends on $\mathbf{R}_1, \dots, \mathbf{R}_N$, entering the Fourier transforms $\hat{\rho}_{\mathbf{k}}^c$ and $\hat{\rho}_{\mathbf{k}}^s$, as well as depends on the collective variables $\rho_{\mathbf{k}}^c$ and $\rho_{\mathbf{k}}^s$. Two sets of variables $\dots \rho_{\mathbf{k}}^c \dots$, $\dots \rho_{\mathbf{k}}^s \dots$ and $\mathbf{R}_1, \dots, \mathbf{R}_N$, on which the transformation function $J(\rho R)$ is defined, can be considered alternately as sets of parameters, and independent variables (for example, once $\dots \rho_{\mathbf{k}}^c \dots$ and $\dots \rho_{\mathbf{k}}^s \dots$ can be considered as parameters then $\mathbf{R}_1, \dots, \mathbf{R}_N$ are independent variables or, vice versa, $\mathbf{R}_1, \dots, \mathbf{R}_N$ are parameters and $\dots \rho_{\mathbf{k}}^c \dots$ and $\dots \rho_{\mathbf{k}}^s \dots$ are independent variables). In particular, the presentation of the transformation function in the form $J(\rho R)$ means that $\dots \rho_{\mathbf{k}}^c \dots$, $\dots \rho_{\mathbf{k}}^s \dots$ are considered as parameters and $\mathbf{R}_1, \dots, \mathbf{R}_N$ are independent variables. Going through all possible parameter values $\dots \rho_{\mathbf{k}}^c \dots$, $\dots \rho_{\mathbf{k}}^s \dots$ we obtain a system of functions $\{J(\rho R)\}$. This is a complete system of functions, because, as it was shown above, it is possible to obtain a $F(\rho)$ -representation for each symmetric function $F(\mathbf{R}_1, \dots, \mathbf{R}_N)$ from class L_2 . It is also necessary to have an expression for the system of inverse functions $[J(\rho R)]^{-1}$ that allows one to carry out the inverse transformation from the $\dots \rho_{\mathbf{k}}^c \dots$, $\dots \rho_{\mathbf{k}}^s \dots$ -representation called below a (ρ) -representation to the $\mathbf{R}_1, \dots, \mathbf{R}_N$ -representation, which we briefly call a $(\mathbf{R})$ -representation.

Now we turn to the study of the properties of orthonormality of the system of the functions $J(\rho R)$. First, we show the validity of the relationship

$$J(\rho R)J(\rho' R) = \delta(\rho - \rho')J(\rho R), \quad (2.1.45)$$

where $\delta(\rho - \rho')$ is the product of δ -functions; $\delta(\rho - \rho') = \prod_{\mathbf{k}} \delta(\rho_{\mathbf{k}}^c - \rho_{\mathbf{k}}'^c) \delta(\rho_{\mathbf{k}}^s - \rho_{\mathbf{k}}'^s)$. We multiply both sides of equation (2.1.45) by an arbitrary function $\mu(\rho)\mu(\rho')$ and integrate over all (ρ) and (ρ') . For the left-hand side, we obtain

$$\int (d\rho)(d\rho') J(\rho R)J(\rho' R) \mu(\rho)\mu(\rho') = \mu(\hat{\rho})\mu(\hat{\rho}'),$$

and for the right-hand side

$$\int (d\rho)(d\rho') \delta(\rho - \rho') J(\rho R) \mu(\rho)\mu(\rho') = \int \mu(\rho)\mu(\rho) J(\rho R) (d\rho) = \mu(\hat{\rho})\mu(\hat{\rho}),$$

which proves the validity of (2.1.45).

Integrating both parts of (2.1.45) over $(d\mathbf{R})$, we obtain the first important relationship for the transformation functions

$$\int J(\rho R)J(\rho' R) (d\mathbf{R}) = \delta(\rho - \rho')J(\rho). \quad (2.1.46)$$

It indicates that two transformation functions, the former of which corresponds to a set of the parameters (ρ) , and the latter corresponds to a set of the parameters (ρ') , are mutually orthogonal if $(\rho') \neq (\rho)$ and if they are normalised with the weight $J(\rho)$. Using the equation (2.1.46), one can obtain explicit expressions for the functions $F(\rho)$ in (2.1.26).

First, we write an explicit expression for the collective variables. We multiply both sides of each integral in (2.1.24) by $J(\rho R)$ and integrate over $(d\mathbf{R})$ using (2.1.46). Then,

$$\rho_{\mathbf{k}}^c = \frac{1}{J(\rho)} \int \hat{\rho}_{\mathbf{k}}^c J(\rho R)(d\mathbf{R}), \quad \rho_{\mathbf{k}}^s = \frac{1}{J(\rho)} \int \hat{\rho}_{\mathbf{k}}^s J(\rho R)(d\mathbf{R}). \quad (2.1.47)$$

Now we multiply both sides of (2.1.26) by $J(\rho' R)$, integrate over all $d\mathbf{R}$ exactly as it was in the case (2.1.47). As a result, we find

$$F(\rho) = \frac{1}{J(\rho)} \int F(\mathbf{R}_1, \dots, \mathbf{R}_N) J(\rho R)(d\mathbf{R}). \quad (2.1.48)$$

In particular, for the functions of the binary type we get (see (2.1.31))

$$v(\rho) = \frac{1}{J(\rho)} \int \frac{1}{2} \sum_{1 \leq i < j \leq N} \Phi_2(R_{ij}) J(\rho R)(d\mathbf{R}). \quad (2.1.49)$$

The inverse transformation from the ρ - to $\mathbf{R}$ -representation is connected to the relationship which is inverse to the equation (2.1.46). We multiply both sides of (2.1.48) by $J(\rho R')$ and integrate over all $(d\rho)$. Then, according to (2.1.26), in the left-hand side we obtain the initial function $F(\mathbf{R}'_1, \dots, \mathbf{R}'_N)$ and in the right-hand side we obtain the integrals

$$\frac{1}{J(\rho)} \int F(\mathbf{R}_1, \dots, \mathbf{R}_N) J(\rho R) J(\rho R')(d\mathbf{R})(d\rho).$$

The above expression is equal to $F(\mathbf{R}'_1, \dots, \mathbf{R}'_N)$ under condition

$$\int \frac{1}{J(\rho)} J(\rho R) J(\rho R')(d\rho) = \delta(\mathbf{R}_1 - \mathbf{R}'_1) \dots \delta(\mathbf{R}_N - \mathbf{R}'_N). \quad (2.1.50)$$

As a result, the function inverse to $J(\rho R)$ has the form:

$$J^{-1}(\rho R) = \frac{1}{J(\rho)} J(\rho R). \quad (2.1.51)$$

This implies that the transformation from the $(\mathbf{R})$ -representation to the (ρ) -representation is not a unitary transformation.

For a full product in (2.1.52) we have

$$\frac{\prod_{\mathbf{k}}' \delta(\hat{\rho}_{\mathbf{k}} - \hat{\rho}'_{\mathbf{k}})}{\int (dR) \prod_{\mathbf{k}}' \delta(\hat{\rho}_{\mathbf{k}} - \hat{\rho}'_{\mathbf{k}})} = \frac{\sum_m A(\mathbf{r}_m) \delta(\mathbf{R} - \mathbf{r}_m)}{\sum_m A(\mathbf{r}_m)}, \quad (2.1.55)$$

where $A(\mathbf{r}_m) = \prod_{\mathbf{k} \notin K} \delta(\hat{\rho}_{\mathbf{k}} - \hat{\rho}'_{\mathbf{k}})|_{\mathbf{R}=\mathbf{r}_m}$.

Roots of two types should be distinguished among the roots $\mathbf{r}_m$: the roots $\mathbf{r}_m$ being the roots of equations (2.1.54) for all values of $\mathbf{k}$, and the roots $\mathbf{r}_m$, which are the roots of (2.1.54) only for $\mathbf{k}$ of the subsystem K or for $\mathbf{k}$ belonging to a subset of equations larger than K , but not for all $\mathbf{k}$. For the $\mathbf{r}_m$ of the first type, all δ -functions in $A(\mathbf{r}_m)$ tend to infinity, for the $\mathbf{r}_m$ of the second type, some δ -functions (or all) in $A(\mathbf{r}_m)$ are equal to zero. Therefore, in the equation (2.1.55), in the numerator and denominator in the sums over m , only the terms corresponding to the roots $\mathbf{r}_m$ of the first type remain. Let us show that the roots of the first type can only be the roots $\mathbf{r}_m = P(\mathbf{R}'_1, \dots, \mathbf{R}'_N)$, where P is a permutation symbol. Squaring each of the equations (2.1.54) and summing over all $\mathbf{k}$, we get

$$\sum_i \sum_j [\delta(\mathbf{R}_i - \mathbf{R}_j) + \delta(\mathbf{R}'_i - \mathbf{R}'_j) - \delta(\mathbf{R}_i - \mathbf{R}'_j) - \delta(\mathbf{R}'_i - \mathbf{R}_j)] = 0. \quad (2.1.56)$$

There are three possible cases here:

1. Each of the δ -functions in (2.1.56) vanishes. This leads to trivial roots.
2. None of $\mathbf{R}_i$ coincides with $\mathbf{R}'_i$. In this case, the left-hand side of (2.1.56) reduces to the sum $\sum_{i,j} [\delta(\mathbf{R}_i - \mathbf{R}_j) + \delta(\mathbf{R}'_i - \mathbf{R}_j)] = \infty$ and the system (2.1.54) is not satisfied.

3. A number of the vectors $\mathbf{R}_i$ coincide with $\mathbf{R}'_i$.

Let us assume that in the set $\mathbf{R}_1, \dots, \mathbf{R}_N$, we have N_{t_1} equal vectors, each equal to $\mathbf{R}_{t_1}$, N_{t_2} equal vectors, each equal to $\mathbf{R}_{t_2}$, ..., N_{p_1} equal vectors, each equal to $\mathbf{R}_{p_1}$, N_{p_2} equal vectors, each equal to $\mathbf{R}_{p_2}$, etc., and the condition $\sum_t N_t + \sum_p N_p = N$ holds. We collect equal vectors and denote their numbers from the set $\mathbf{R}_1, \dots, \mathbf{R}_N$ as $N'_{t_1}, N'_{t_2}, \dots, N_{p_1}, N_{p_2}, \dots$ in such a way that $\sum_t N'_t + \sum_{p'} N'_p = N$. Let N_{t_1} vectors from the set $\mathbf{R}_1, \dots, \mathbf{R}_N$ coincide with N'_{t_1} vectors from the set $\mathbf{R}'_1, \dots, \mathbf{R}'_N$, N_{t_2} vectors from the set $\mathbf{R}_1, \dots, \mathbf{R}_N$ coincide with N'_{t_2} vectors in the set $\mathbf{R}'_1, \dots, \mathbf{R}'_N$, but the vectors with the indices p from

both sets do not coincide. Then, we have for (2.1.56)

$$\delta(0) \left[\sum_t N_t^2 + \sum_p N_p^2 + \sum_t N_t'^2 + \sum_{p'} N_{p'}'^2 - 2 \sum_t N_t N_t' \right] = 0$$

(strictly speaking $\delta(0)$ should be replaced with the limit transformation) or

$$\delta(0) \left[\sum_t (N_t - N_t')^2 + \sum_p N_p^2 + \sum_{p'} N_{p'}'^2 \right] = 0,$$

that it is possible under conditions $N_p = 0$, $N_{p'}' = 0$, and $N_t = N_t'$. Thus, it is proved that the only roots of the system of the equations (2.1.53), (2.1.54) are such $\mathbf{r}_t(\mathbf{R}_1, \dots, \mathbf{R}_N)$ for which

$$\mathbf{R}_i = P(\mathbf{R}_i'), \quad i = 1, 2, \dots, N. \quad (2.1.57)$$

It remains to show that

$$\frac{\sum_i A(\mathbf{r}_i) \delta(\mathbf{R} - \mathbf{r}_i)}{\sum_i A(\mathbf{r}_i)} = \prod_{i=1}^N \delta(\mathbf{R}_i - \mathbf{R}_i'). \quad (2.1.58)$$

For $\mathbf{r}_t$, we take only the roots of type (2.1.57) which satisfy the full system of the equations (2.1.54). A sum symbol over t means now the summation over permutations performed within the set $\mathbf{R}_1', \dots, \mathbf{R}_N'$. Since all $A(\mathbf{r}_t)$ are equal in this case, we obtain for (2.1.55)

$$\frac{\sum_t A(\mathbf{r}_t) \delta(\mathbf{R} - P\mathbf{R}')}{\sum_t A(\mathbf{r}_t)} = \frac{\sum_P \prod_i \delta(\mathbf{R}_i - P(\mathbf{R}_i'))}{\sum_P 1} = \prod_{i=1}^N \delta(\mathbf{R}_i - \mathbf{R}_i'). \quad (2.1.59)$$

(Reducing the fraction by $A(\mathbf{r}_t)$, we have not given consecutive calculations.) The validity of equality (2.1.58) is proved. It is important that in order to obtain the condition (2.1.56), summation over all values of $\mathbf{k}$ in (2.1.54) was performed.

2.1.6. Physical meaning of the collective variables

Let us start with the physical meaning of the Fourier transform $\hat{\rho}_{\mathbf{k}} = 1/\sqrt{N} \sum_{i=1}^N \exp(i\mathbf{k}\mathbf{R}_i)$ or of its real and imaginary parts, respectively, $\hat{\rho}_{\mathbf{k}}^c = 1/\sqrt{N} \sum_{i=1}^N \cos(\mathbf{k}\mathbf{R}_i)$, $\hat{\rho}_{\mathbf{k}}^s = 1/\sqrt{N} \sum_{i=1}^N \sin(\mathbf{k}\mathbf{R}_i)$.

Let the set of variables $\mathbf{R}_1, \dots, \mathbf{R}_N$ characterize an instantaneous position of the system particles at time $t = 0$. After a certain interval of time Δt ,

the coordinate of the i -th particle will be $\mathbf{R}_i(\Delta t) = \mathbf{R}_i - \boldsymbol{\nu}_i \Delta t$. Therefore, $\hat{\rho}_{\mathbf{k}}(\Delta t) = 1/\sqrt{N} \sum_{i=1}^N \exp(i\mathbf{k}(\mathbf{R}_i - \boldsymbol{\nu}_i \Delta t))$, where $\boldsymbol{\nu}_i$ is the velocity of the i -th particle at time $t = 0$. Thus, a fluctuating sound wave occurs in the system, the nodes of which correspond to a uniform distribution of particles. The quantity $\hat{\rho}_{\mathbf{k}}$ is the stationary phase or mode of this wave [24]. It follows from this that the collective variable $\rho_{\mathbf{k}}$ connected with $\hat{\rho}_{\mathbf{k}}$ by the relationship (2.1.13) also has the meaning of the mode of the fluctuation wave with the wave vector $\mathbf{k}$. The quantities $\rho_{\mathbf{k}}^c$ and $\rho_{\mathbf{k}}^s$, determined by the relationship (2.1.24), are modes of cosine and sine fluctuation waves, respectively.

Formally, $\rho_{\mathbf{k}}^c$ and $\rho_{\mathbf{k}}^s$ are real numbers and become fluctuation modes only in the presence of the transformation function $J(\rho R)$. Therefore, the appropriateness of mapping of the system into the phase space of the collective variables depends on the degree of accuracy with which the transformation function $J(\rho R)$ and the transformation Jacobian $J(\rho)$ are calculated. For example, considering the system as a set of independent random fluctuations, according to the central theorem of the theory of probability, we arrive at the Gaussian form of the Jacobian of the transformation [54]. Therefore, the approximation based on the Gaussian form of the transformation Jacobian is known as the random phase approximations (RPA). The consideration of the higher-order terms in an exact Jacobian (2.1.43) means taking into account the correlations between waves with different wavevectors. The calculations performed for the three-dimensional Ising model make it possible to separate the variables in the integrals for the Jacobian of the transformation and to calculate $J(\rho)$ with the highest accuracy.

Nevertheless, there is no sense in introducing collective variables for all systems. This depends on the nature of the system as well as on the nature of the interparticle interactions. As it was already noted, the representation of collective variables is possible only if the interaction potential belongs to the class L_2 . In real systems, the intermolecular interactions are carried out by two types of forces, i.e., by the short-range interactions at small distances and by the long-range interactions at large distances. Therefore, the total interaction potential can always be formally split into two parts

$$u_2(R) = \varphi_2(R) + \Phi_2(R), \quad (2.1.60)$$

where $\varphi_2(R)$ and $\Phi_2(R)$ are its short- and long-range parts.

A general property of the short-range interactions is strong repulsion at small distances, determined primarily by the geometric shape and size of the molecules. Such a potential can be successfully modelled by a hard-sphere type potential, which, however, does not belong to the functions of class L_2 . Consequently, the short-range interactions are not represented on the set of collective variables.

The long-range interactions change more smoothly with the distance, having an electrostatic character at large distances for ions and polar molecules as well as a van der Waals character in the case of nonpolar molecules. If the interaction potential $u_2(R)$ is known, one can always select its long-range part $\Phi(R)$ belonging to the functions of class L_2 . In this case, $\Phi_2(R)$ accurately describes the potential $u_2(R)$, starting from the region of the large distances up to the distances of the order of the particle sizes, where it can be sufficiently smoothed to belong to the class L_2 and have a representation of the collective variables. The short-range part of the potential, $\varphi_2(R)$, continuously supplements the potential $\Phi_2(R)$ to the total potential $u_2(R) = \varphi_2(R) + \Phi_2(R)$. In this case, of course, an exact theory should not depend on the form of the long-range potential in the region of the short distances.

2.2. Method of collective variables

We start with the use of collective variables to the calculation of the configuration integral by considering the simplest one-component system with a pair central interaction $u_2(R)$. According to (1.1.16), the configuration integral

$$Q_N = \frac{1}{V^N} \int (d\mathbf{R}) e^{-\beta U_N}, \quad (2.2.1)$$

where U_N is the potential energy of the intermolecular interactions. According to (2.1.60),

$$U_N = U_0(R) + v(R), \quad (2.2.2)$$

where $U_0(R) = \sum_{i<j} \varphi_2(R_{ij})$ and $v(R) = \sum_{i<j} \Phi_2(R_{ij})$ are the short- and long-range parts of the potential energy of the system.

Let there exist a representation of the collective variables for $v(R)$

$$v(R) = \int (d\rho) v(\rho) J(\rho R), \quad (2.2.3)$$

where

$$v(\rho) = \frac{1}{2} \frac{N}{V} \sum_{\mathbf{k}} \nu(k) (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1) + \frac{1}{2} \frac{N^2}{V} \nu(0);$$

$\rho_{\mathbf{k}} = \rho_{\mathbf{k}}^c + i\rho_{\mathbf{k}}^s$; $\rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^*$; $\rho_{\mathbf{k}}^c$ and $\rho_{\mathbf{k}}^s$ are the collective variables; $(d\rho) = \prod_{\mathbf{k}} d\rho_{\mathbf{k}}^c d\rho_{\mathbf{k}}^s$; $\nu(k) = \int \Phi_2(R) e^{-i\mathbf{k}\mathbf{R}} (d\mathbf{R})$ is the Fourier transform of the potential $\Phi_2(R)$. Since $e^{-\beta v(R)}$ is an analytic function, it can be presented as an analytic functional³

$$e^{-\beta v(R)} = \int e^{-\beta v(\rho)} J(\rho R) (d\rho). \quad (2.2.4)$$

³It is easy to verify the validity of this equality in such a formal way. We expand $e^{-\beta v(R)}$

Substituting (2.2.2) into (2.2.1) and using (2.2.4), we arrive at the initial expression in the method of collective variables for the configuration integral

$$Q_N = \frac{1}{V^N} \int_{(V)} \int_{(\rho)} e^{-\beta U_0(R)} e^{-\beta v(\rho)} J(\rho R) (d\rho) (dR). \quad (2.2.5)$$

Here, the integration is performed in the extended phase space of the Cartesian coordinates $\mathbf{R}_1, \dots, \mathbf{R}_N$ and the collective variables instead of a usual phase space of the Cartesian coordinates. Thus, one of the main problems of the statistical theory of the equilibrium systems about the different description of the short- and long-range interactions is solved here in a rather natural way. The long-range interactions, associated with the collective properties of the system, are described in the phase space of the collective variables, while the short-range interactions, which characterize the interactions of individual particles, are described in the phase space of the coordinates of the particles.

Two ways of constructing the theory depending on the sequence of the short- and long-range interactions being taken into account. In the first one, the configuration integral of the system is calculated taking into account only the long-range interactions. Then, on its ground, the short-range interactions are taken into account using the functional differentiation [61]. In the second variant, the configuration integral of the system with the short-range interactions is calculated. Then, the function of the transformation to the collective variables is averaged over the system with the short-range interactions and the long-range interactions are taken into account. First, consider the former way, which leads to simpler and more illustrative cluster expansions, valid for the systems with a low density of the particles. The results obtained in this way, as we shall see below, are useful for the cases where it is possible to elucidate the role of the long-range interactions. Moreover, having understood these, it will be easier to understand a second more complicated way, which is more preferable when considering dense systems. Thus, we calculate the configuration integral of the system, in which there are only long-range interactions, thereby revealing the method of integration over the collective variables.

in the series

$$e^{-\beta v(R)} = \sum_{n \geq 0} \frac{(-1)^n}{n!} [\beta v(R)]^n = \sum_{n \geq 0} \frac{(-1)^n}{n!} \beta^n \left[\int (d\rho) J(\rho R) v(R) \right]^n;$$

according to (2.1.45),

$$\prod_{s=1}^n J(\rho_s R) = \prod_{s=2}^n \delta(\rho_s - \rho_1) J(\rho_1 R)$$

and

$$e^{-\beta v(R)} = \sum_{n \geq 0} \int (d\rho) J(\rho R) \frac{(-1)^n}{n!} [\beta v(\rho)]^n = \int (d\rho) J(\rho R) e^{-\beta v(\rho)},$$

As a result, we obtain (2.2.4).

2.2.1. Configuration integral of a system with the long-range interactions

Let us set $U_N(R)$ equal to zero in (2.2.5). Then, instead of Q_N we have $Q_N^{(\ell)}$ which is the configuration integral of the system with the long-range interactions. Integration over $(d\mathbf{R})$ refers only to the transformation function and leads to the Jacobian $J(\rho)$, as a result

$$Q_N^{(\ell)} = \int e^{-\beta v(\rho)} J(\rho) (d\rho). \quad (2.2.6)$$

Here, the configuration integral is completely determined on the phase space of variables (ρ) . Let us first consider the issue of the physical interpretation of the integrand. Instead of $v(\rho)$ we substitute in (2.2.6) the expression (2.1.30) and instead of $J(\rho)$ – the expression (2.1.43), then

$$Q_N^{(\ell)} = \exp \left[-\frac{1}{2} N \alpha(0) + \frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k}) \right] \int \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} (\alpha(\mathbf{k}) + a_2) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \right. \\ \left. - \frac{1}{3!} \frac{1}{\sqrt{N}} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} a_3 \rho_{\mathbf{k}_1} \rho_{\mathbf{k}_2} \rho_{\mathbf{k}_3} \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, 0} - \right. \\ \left. - \frac{1}{4!} \frac{1}{N} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} a_4 \rho_{\mathbf{k}_1} \rho_{\mathbf{k}_2} \rho_{\mathbf{k}_3} \rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4, 0} - \dots \right] (d\rho), \quad (2.2.7)$$

where $\alpha(\mathbf{k}) = \beta \frac{N}{V} \nu(\mathbf{k})$.

The first term in the exponential under the integral describes stationary harmonic oscillations of the density. From the point of view of correlations of the particle motions, here we have such a case of pair interactions in which two particles exchange the momentum $\mathbf{k}$. In this case, each particle gives a momentum $\mathbf{k}$ and receives a momentum $-\mathbf{k}$, without the change of the total momentum of the system $\mathbf{p} = 0$. The terms

$\sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} a_3 \rho_{\mathbf{k}_1} \rho_{\mathbf{k}_2} \rho_{\mathbf{k}_3}$ give rise to anharmonic oscillations encompassing the correlations of two- and three-particle types. In any three-particle correlations, the first particle gives the momentum $\mathbf{k}_1$ to the second particle, the second particle gives the momentum $\mathbf{k}_2$ to the third particle, and the third particle gives the momentum $\mathbf{k}_3$ to the first particle. As a result, each particle deviates from its previous position in such a way that the centre of mass of the three particles remains unchanged

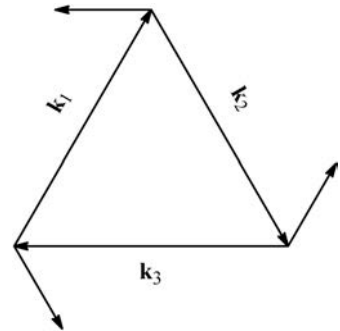


Fig. 1. Wave vector triangle illustrating the momentum exchange in a three-particle correlation, with $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$

because $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$. In the diagram shown in Fig. 1, the vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ form a triangle. The arrows indicate the direction of the particle displacement. In the case of a two-particle interaction, there is such a statistical alternative process, in which one particle transmits to another particle first the momentum $\mathbf{k}_1$, then the momentum $\mathbf{k}_2$ and takes on back the momentum $\mathbf{k}_3$, performing certain displacements so that the centre of mass of the two particles remains unchanged.

Next, we have the term $\sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} a_4 \rho_{\mathbf{k}_1} \rho_{\mathbf{k}_2} \rho_{\mathbf{k}_3} \rho_{\mathbf{k}_4}$, which characterizes more complex anharmonic interactions of fluctuating waves. Here, from the point of view of the particle interactions, there are statistical correlations in groups of two-, three-, and four particles. Thus, the subsequent terms of the series in the exponential function in (2.2.7) describe the involvement of the particles in increasingly complex collective motions, each of which conserves a total momentum of the system $\mathbf{p} = 0$.

Let us now proceed with the calculation of $Q_N^{(\ell)}$. The collective motions described above are especially intense in the systems with long-range interactions between particles. Among the emerging elastic density oscillations, the most important are harmonic oscillations that generate the screening of the interactions. Accordingly, we must present the configuration integral in the form of a sum of derivatives of a generating functional built on harmonic density oscillations. To this end, we substitute into (2.2.6) instead of $J(\rho)$ the expression (2.1.43), in which free harmonic oscillations of the density are completely distinguished, and the sums over the vectors $\mathbf{k}$ in the operators $\hat{D}_n(\partial/\partial\rho)$ are irreducible, i.e., they do not include the terms with “paired” $\mathbf{k}$ -vector derivatives of the type $\partial^2/\partial\rho_{\mathbf{k}}\partial\rho_{-\mathbf{k}}$, which can be associated with the harmonic motion.

The configuration integral is written as follows:

$$Q_N^{(\ell)} = \int \exp\left[-\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k})(\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - 1) - \frac{1}{2}N\alpha(0)\right] \times \\ \times \exp\left[\sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho)\right] J_G(\rho)(d\rho). \quad (2.2.8)$$

In a zero approximation, the operator $\exp\left[\sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho)\right]$ is replaced by a unit. We obtain the configuration integral of the harmonic density oscillations

$$Q_N^{(\ell)} = \int \exp\left[-\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k})(\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - 1) - \frac{1}{2}N\alpha(0)\right] J_G(\rho)(d\rho) = \\ = \frac{1}{\pi} \exp\left[\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k}) - \frac{1}{2}N\alpha(0)\right] \prod'_{\mathbf{k}} \left\{ \int \exp[-[\alpha(\mathbf{k}) + 1](\rho_{\mathbf{k}}^c)^2](d\rho_{\mathbf{k}}^c) \times \right.$$

$$\begin{aligned}
 & \times \int \exp[-[\alpha(\mathbf{k}) + 1](\rho_{\mathbf{k}}^s)^2](d\rho_{\mathbf{k}}^s) \Big\} = \\
 & = \exp \left[\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k}) - \frac{1}{2} N \alpha(0) \right] \prod'_{\mathbf{k}} \frac{1}{1 + \alpha(\mathbf{k})}. \quad (2.2.9)
 \end{aligned}$$

As it is noted, the results obtained using the Gaussian form of the Jacobian of the transformation are known as the random phase approximation (RPA). Consequently, the result (2.2.9) corresponds to the random phase approximation of the configuration integral.

Let us now use a full Jacobian in the formula (2.2.8). We present $J(\rho)$ as follows:

$$J(\rho) = (1 + B_1'' + B_2'' + B_1'' + B_3'' + \dots) J_G(\rho), \quad (2.2.10)$$

where

$$\begin{aligned}
 B_1'' &= \hat{D}_3 + \hat{D}_4 + \hat{D}_5 + \dots, \\
 B_2'' &= \frac{1}{2} [\hat{D}_3 \hat{D}_3 + \hat{D}_4 \hat{D}_4 + \dots + 2(\hat{D}_3 \hat{D}_4 + \hat{D}_3 \hat{D}_5 + \dots + \hat{D}_4 \hat{D}_5 + \dots)], \\
 B_3'' &= \frac{1}{3!} [\hat{D}_3 \hat{D}_3 \hat{D}_3 + 3(\hat{D}_3 \hat{D}_3 \hat{D}_4 + \dots) + 6(\hat{D}_3 \hat{D}_4 \hat{D}_5 + \dots) + \hat{D}_4 \hat{D}_4 \hat{D}_4 + \dots].
 \end{aligned}$$

Acting on $J_G(\rho)$, the operators $\hat{D}_n(\partial/\partial\rho)$ and their products, lead to the formation of different products of $\rho_{\mathbf{k}_1}, \rho_{\mathbf{k}_2}, \dots$. Since $v(\rho)$ and $J_G(\rho)$ are even functions of the collective variables, the result of integration in (2.2.8) is not equal to zero, if the terms of type $\rho_{\mathbf{k}}\rho_{-\mathbf{k}}$ are singled out. Since in the operators $\hat{D}_n(\partial/\partial\rho)$ all the sums over $\mathbf{k}$ are closed and irreducible, we do not obtain even products of $\rho_{\mathbf{k}}$ of the indicated type from the linear terms in $\hat{D}_n$ (see (2.2.10)). They appear only in the paired, triple, etc., products of $\hat{D}_n$. For example, having paired the derivatives in the product of two operators $\hat{D}_3$, we obtain

$$\begin{aligned}
 \frac{1}{2} \hat{D}_3 \hat{D}_3 J_G(\rho) &= \frac{3!}{2} \frac{N^2}{3!3!} \frac{1}{N^3} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} \frac{\partial^3}{\partial \rho_{\mathbf{k}_1} \partial \rho_{\mathbf{k}_2} \partial \rho_{\mathbf{k}_3}} \frac{\partial^3}{\partial \rho_{-\mathbf{k}_1} \partial \rho_{-\mathbf{k}_2} \partial \rho_{-\mathbf{k}_3}} J_G(\rho) = \\
 &= \frac{1}{2} \frac{N^2}{V} \frac{1}{3!} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} \frac{1}{N^3} \int (\rho_{\mathbf{k}_1} \rho_{-\mathbf{k}_1} - 1)(\rho_{\mathbf{k}_2} \rho_{-\mathbf{k}_2} - 1)(\rho_{\mathbf{k}_3} \rho_{-\mathbf{k}_3} - 1) \times \\
 &\quad \times J_G(\rho) \exp[i(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3)\mathbf{R}](d\mathbf{R}). \quad (2.2.11)
 \end{aligned}$$

Similar transformations occur with the other terms of the series (2.2.10) which are called the pairing of the operators. It is convenient to perform the pairing of the operators using the diagrammatic method. Let each operator $\hat{D}_n$ be denoted by a black circle from which n lines emerge. In the product of two operators $\hat{D}_n$, the lines can be connected in $3!$ ways so that the expression (2.2.11) can be graphically represented as

$$\frac{1}{2} \text{---} \text{---} \text{---} J_G(\rho) = \frac{1}{2} \text{---} \text{---} J_G(\rho). \quad (2.2.12)$$

Thus, a graphical pairing in the products of the operators consists in constructing the diagrams from these operators without free bonds, taking into account the number of all possible bonds between the lines. For example, for $\frac{1}{2}\hat{D}_4\hat{D}_5\hat{D}_5J_G(\rho)$, we have

$$\frac{1}{2} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} J_G(\rho) = \frac{1}{2 \cdot 3} \cdot 3 \cdot \begin{array}{c} \triangle \\ \triangle \end{array} J_G(\rho).$$

A segment connecting two vertices corresponds to each pairing, i.e., to the result of the action of the derivative $\partial^2/\partial\rho_{\mathbf{k}}\partial\rho_{-\mathbf{k}}$ on $J_G(\rho)$ (to the multiplier $(\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - 1)$). The number of segments is equal to the number of pairings and it indicates the number of sums over $\mathbf{k}$, and the number of vertices corresponds to the number of the operators which are paired. The number of segments outgoing from each vertex is equal to the order of the operator $\hat{D}_n$ at this vertex, i.e., n . Each vertex corresponds to a multiplier

$$(-1)^n \frac{N}{V} \frac{1}{\sqrt{N^n}} \int \exp[i(\mathbf{k}_1 + \dots + \mathbf{k}_n)\mathbf{R}] d\mathbf{R},$$

where n is the order of the operator $\hat{D}_n$ standing at the vertex. It should also be borne in mind that the beginning of the segment corresponds to $\mathbf{k}$, and its end corresponds to $-\mathbf{k}$. In the diagram as a whole, for each number of lines connecting any two vertices, there is an inverse factorial of this number, equal to the number of ways the two vertices can be connected. Having written the right-hand side of (2.2.12) in an analytical form, we arrive at the expression (2.2.11). The remaining products of the operators in (2.2.10) are performed in the same way.

The series B''_n in (2.2.10) after pairing will be denoted by B_n . Since no even products $\rho_{\mathbf{k}}\rho_{-\mathbf{k}}$ arise from the action of linear operators B''_1 , we immediately set $B'_1 = 0$. From the series B''_2 only the products $\hat{D}_n\hat{D}_m$ with $n = m$ can be paired so that

$$B'_2 = \frac{1}{2} (\begin{array}{c} \text{---} \text{---} \end{array} + \begin{array}{c} \text{---} \text{---} \end{array} + \dots). \quad (2.2.13)$$

From the series B''_3 , we can pair only the products of such operators $\hat{D}_n\hat{D}_m\hat{D}_l$, for which $m + n + l$ is an even number; $m + n > l$ and $|m - n| < l$ for all $m, n, l \geq 3$. Therefore,

$$B'_3 = \frac{1}{2 \cdot 3} [3\hat{D}_3\hat{D}_3\hat{D}_4 + 6(\hat{D}_3\hat{D}_4\hat{D}_5 + \hat{D}_3\hat{D}_5\hat{D}_6 + \dots) + \hat{D}_4\hat{D}_4\hat{D}_4 + 3\hat{D}_5\hat{D}_5\hat{D}_6 + 6(\hat{D}_5\hat{D}_6\hat{D}_7 + \dots) + \dots].$$

It turns out that after the pairing of the operators, all diagrams of these series can be constructed starting from only the two lowest diagrams $3 \cdot \begin{array}{c} \triangle \\ \triangle \end{array}$

and . All other diagrams in B'_3 are obtained from these two diagrams by completing in them the sides that have two lines each:

$$B'_3 = \frac{1}{2 \cdot 3} \left\{ 3 \left[\text{triangle with 2 lines} + \text{triangle with 3 lines} + \dots + 2 \left(\text{triangle with 2 lines} + \text{triangle with 3 lines} + \dots \right) \right] + \right. \\ \left. + \text{triangle with 2 lines} + \text{triangle with 3 lines} + \dots + 3 \left[\text{triangle with 2 lines} + \dots + 2 \left(\text{triangle with 2 lines} + \dots \right) + \dots \right] \right\}. \quad (2.2.14)$$

The coefficients for the diagrams are the same as for the operators, since each product of three operators corresponds to one diagram.

For the products of four and more operators, the disconnected diagrams also arise in addition to the connected diagrams. Thus, the disconnected diagrams can be formed from the products of the operators $\frac{1}{4!} \hat{D}_3^4$, $\frac{1}{4!} \hat{D}_3^4 \hat{D}_4$, $\frac{1}{2 \cdot 3} \hat{D}_3^2 \hat{D}_4^2$, $\frac{1}{2} \left(\text{double line} \right)^2$, $\left(\text{double line} \right) \left(\frac{1}{2} \text{triangle with 2 lines} \right)$, $\frac{1}{2} \left(\text{double line} \right) \left(\frac{1}{3} \text{triangle with 2 lines} \right)$. All disconnected diagrams are the products that arise from the sum of the connected diagrams by expanding the exponential function. Finally, after pairing the operators, the transformation function can be presented as follows:

$$J(\rho) = \exp(B'_2 + B'_3 + \dots) J_G(\rho), \quad (2.2.15)$$

where the series B'_n are constructed only from the connected diagrams.

We now substitute (2.2.15) in (2.2.8). According to the notation, each segment in the diagrams B'_n corresponds to the function $(\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1)$. However, in the integral (2.2.8) the function can be obtained by differentiating the expression $\exp \left(-\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k}) (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1) \right)$ with respect to $-\alpha(\mathbf{k})$. Consequently, each segment in all diagrams can be associated with a parametric derivative $(\partial)/(\partial \alpha(\mathbf{k}))$. Then, the whole series $B'_2 + B'_3 + \dots$ in the exponential function in (2.2.15) is replaced by a series of the operators $\hat{B}'_2 + \hat{B}'_3 + \dots$. The exponential operator can be moved in front of the integral over $(d\rho)$. Integration over the collective variables in (2.2.8) leads to the result

$$Q_N^{(\ell)} = \exp[\hat{B}'_2 + \hat{B}'_3 + \dots] \exp \left[\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k}) - \frac{1}{2} N \alpha(0) \right] \prod'_{\mathbf{k}} \frac{1}{1 + \alpha(\mathbf{k})} = \\ = \exp[\hat{B}'_2 + \hat{B}'_3 + \dots] Q_G^{(\ell)}, \quad (2.2.16)$$

in which the configuration integral of elastic harmonic oscillations of the density, $Q_G^{(\ell)}$, serves as a generating functional of the complete configuration integral. The action of each derivative with respect to $\alpha(\mathbf{k})$ is written as

$$-\frac{\partial}{\partial \alpha(\mathbf{k})} Q_G^{(\ell)} = -\frac{\alpha(\mathbf{k})}{1 + \alpha(\mathbf{k})} Q_G^{(\ell)}.$$

As a result, each line of the diagrams B'_n in (2.2.16) can be associated with the function $-\frac{\alpha(k)}{1+\alpha(k)}$ and we can consider the integration over the collective variables fulfilled. For the configuration integral we get

$$Q_N^{(\ell)} = \exp[B'_2 + B'_3 + \dots] \prod'_{\mathbf{k}} \frac{1}{1+\alpha(\mathbf{k})} \exp \left[\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k}) - \frac{1}{2} N \alpha(0) \right], \quad (2.2.17)$$

where $B'_2 + B'_3 + \dots$ is the sum of the diagrams (2.2.13), (2.2.14), etc., in which each line is associated with the function $-\frac{\alpha(k)}{1+\alpha(k)}$.

For a more compact representation of (2.2.17), in each diagram an inverse Fourier transform is performed. Moreover, in the limit $N \rightarrow \infty$, $V \rightarrow \infty$, all irreducible sums over $\mathbf{k}$ can be replaced by ordinary sums. For example, for a diagram  from B'_3 , we have

$$\begin{aligned} \text{Diagram} &= \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \frac{N}{\sqrt{N^3}} \frac{N}{\sqrt{N^5}} \frac{N}{\sqrt{N^4}} \left[-\frac{\alpha(k_1)}{1+\alpha(k_1)} \right] \dots \left[-\frac{\alpha(k_6)}{1+\alpha(k_6)} \right] \times \\ &\times \frac{1}{2!} \frac{1}{3!} \frac{1}{V^3} \int \exp[i(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) \mathbf{R}_1] d\mathbf{R}_1 \int \exp[-i(\mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_4 - \mathbf{k}_5 - \mathbf{k}_6) \mathbf{R}_2] d\mathbf{R}_2 \times \\ &\times \int \exp[-i(\mathbf{k}_4 + \mathbf{k}_5 + \mathbf{k}_6 + \mathbf{k}_1) \mathbf{R}_3] d\mathbf{R}_3 = \\ &= \frac{N^3}{V^3} \int \frac{1}{2} (g(k) e^{i\mathbf{k} \cdot \mathbf{R}_{12}})^2 \frac{1}{3!} (g(k) e^{i\mathbf{k} \cdot \mathbf{R}_{32}})^3 (g(k) e^{i\mathbf{k} \cdot \mathbf{R}_{31}}) d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 = \\ &= \frac{N^3}{V^2} \int \frac{1}{2} g^2(R_{12}) \frac{1}{3!} g^3(R_{32}) g(R_{13}) d\mathbf{R}_{12} d\mathbf{R}_{13}, \end{aligned}$$

where $g(k) = -\frac{1}{N} \frac{\alpha(k)}{1+\alpha(k)} = -\frac{1}{V} \beta \frac{\nu(k)}{1+\beta \frac{N}{V} \nu(k)}$ or in the coordinate representation

$$g(R) = \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}} = -\frac{1}{V} \beta \sum_{\mathbf{k}} \frac{\nu(k) e^{i\mathbf{k} \cdot \mathbf{R}}}{1+\beta \frac{N}{V} \nu(k)}. \quad (2.2.18)$$

The function $g(R)$ describes the screening effect of the system on the interaction between two particles. Therefore, we will henceforth call $g(R)$ the screened potential. According to (2.2.18), the screened potential satisfies the integral equation

$$g(R_{12}) = -\beta \Phi_2(R_{12}) - \beta \frac{1}{V} \int \Phi_2(R_{13}) g(R_{32}) d\mathbf{R}_3. \quad (2.2.19)$$

which is consistent with the Ornstein–Zernike equation (1.3.13) if $c(R) = -\beta \Phi_2(R)$. In this case, the pair correlation function $h_2(R) = g(R)$.

After integration over the collective variables, the structure of the diagrams B'_n does not change except that each vertex of the diagram and each its side connecting two vertices with m lines correspond to $\bullet = \frac{N}{V} \int d\mathbf{R}$ and $\overline{\bullet\bullet\bullet\bullet} = \frac{1}{m!} g^m(r)$. The diagrams in B'_n are easy to sum up. As a result,

$$\begin{aligned} B'_2 &= \frac{1}{2} \left(\frac{N}{V} \right)^2 \int \left[\frac{1}{3!} g^3(R_{12}) + \frac{1}{4!} g^4(R_{12}) + \dots \right] d\mathbf{R}_1 d\mathbf{R}_2 = \\ &= \frac{1}{2} \frac{N^2}{V} \int \left\{ \exp[g(R)] - 1 - g(R) - \frac{1}{2} g^2(R) \right\} d\mathbf{R}, \end{aligned} \quad (2.2.20)$$

$$\begin{aligned} B'_3 &= \frac{1}{2 \cdot 3} \frac{N^3}{V^3} \int \left\{ \left[e^{g(R_{12})} - 1 - g(R_{12}) \right] \left[e^{g(R_{13})} - 1 - g(R_{13}) \right] \times \right. \\ &\quad \times \left[e^{g(R_{23})} - 1 - g(R_{23}) \right] + 3g(R_{12}) \left[e^{g(R_{13})} - 1 - g(R_{13}) \right] \times \\ &\quad \left. \times \left[e^{g(R_{23})} - 1 - g(R_{23}) \right] \right\} d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3, \end{aligned} \quad (2.2.21)$$

and etc.

Having known the configuration integral, according to (1.1.14) and (1.1.6), we find the partition function and the long-range part of the free energy, respectively. Substituting (2.2.20)–(2.2.21) into (2.2.17), we have for the free energy

$$F^{(\ell)} = F_{\text{id}} + F_{\text{HTA}} + F_{\text{RPA}} - \frac{1}{\beta} (B'_2 + B'_3 + \dots), \quad (2.2.22)$$

where $F_{\text{id}} = -\frac{1}{\beta} \ln Z_N^{(\text{id})}$ is the ideal part of the free energy which corresponds to a system of non-interacting particles;

$$F_{\text{HTA}} = \frac{1}{2\beta} N \alpha(0) = \frac{1}{2} \frac{N^2}{V} \int \Phi_2(R) d\mathbf{R} \quad (2.2.23)$$

is the average value of the energy of long-range interactions with an homogeneous distribution of particles. Expression (2.2.23) does not depend on temperature and, thus, the restriction of the series expansion (2.2.22) by this term corresponds to the high-temperature approximation (HTA) for $F^{(\ell)}$. The term

$$F_{\text{RPA}} = -\frac{1}{2\beta} \sum'_k [\alpha(k) - \ln(1 + \alpha(k))] \quad (2.2.24)$$

is related to taking into account only the Gaussian part of the Jacobian of the transformation and, thus, corresponds to the random phase approximation for

$F^{(\ell)}$. This expression can also be represented as

$$\begin{aligned} F_{\text{RPA}} &= -\frac{1}{2\beta} \int_0^1 d\xi \sum'_k \alpha(k) \frac{\xi \alpha(k)}{1 + \xi \alpha(k)} = \\ &= \frac{1}{2} \frac{N^2}{V} \int d\mathbf{R} \int_0^1 d\xi \Phi_2(R) g(R, \xi), \end{aligned} \quad (2.2.25)$$

where the screened potential $g(R, \xi)$ differs from (2.2.18) by replacing $\nu(k)$ with $\xi \nu(k)$. Therefore, F_{RPA} has a meaning of the work on the screening of the system.

Next, there are cluster integrals $B'_2, B'_3, \dots$ in (2.2.22) given by the equations (2.2.20)–(2.2.21), which will be called herein below the second, third, ... cluster coefficients. Unlike the Mayer expressions, all integrals begin with the diagrams having at least three lines $g(R)$ outgoing from a vertex. All diagrams having at least one vertex with two lines are included in screening automatically: one part of the screening is included in F_{RPA} , and another part is included in the cluster coefficients $B'_2, B'_3, \dots$.

In the literature (see, for example, [63]), another method for obtaining the expansion (2.2.22) is described, which is based on the use of the Mayer cluster expansions. Expanding the Mayer function $f(R) = e^{-\beta \Phi_2(R)} - 1 = \sum_{n \geq 1} \frac{1}{n!} (-\beta \Phi_2(R))^n$, the Mayer series (1.1.12) are rearranged using the diagrammatic technique especially developed for this purpose in such a way that a final expression for the free energy is represented by the series (2.2.22). In this case, F_{HTA} corresponds to the first term in the second cluster coefficient of the Mayer expansion. To obtain F_{RPA} , one should consider a sum of the ring diagrams

$$F_{\text{RPA}} = -\frac{1}{2\beta} \left[\frac{1}{2} \text{---} \bullet \text{---} \bullet + \frac{1}{3} \text{---} \bullet \text{---} \bullet \text{---} \bullet + \frac{1}{4} \text{---} \bullet \text{---} \bullet \text{---} \bullet \text{---} \bullet + \dots \right], \quad (2.2.26)$$

where the dashed line corresponds to the potential $-\beta \Phi_2(R)$. Using the Fourier transform of the function $-\beta \Phi_2(R) = -\beta \frac{1}{V} \sum_k \nu(k) e^{i\mathbf{k} \cdot \mathbf{R}}$, the series expansion (2.2.26) is summed up into the expression that coincides with (2.2.24).

The diagrams of the chain type $\circ \text{---} \circ + \text{---} \circ \text{---} \circ + \text{---} \circ \text{---} \circ \text{---} \circ + \dots$ are distinguished among the other diagrams and their summation leads to the screened potential (2.2.18). Collecting the diagrams according to the number of vertices, we arrive at the cluster expansion (2.2.22), in which all diagrams with two-, three-vertices, etc. are collected in the cluster integrals $B'_2, B'_3, \dots$. However,

the implementation of the entire procedure is associated with a number of cumbersome diagrammatic transformations.

Within the method of collective variables, these difficulties do not arise. This is a quite clear and strict non-diagrammatic method of obtaining cluster expansions (2.2.22). Using the formalism of the method of collective variables, one can rather easily obtain the cluster integrals of sufficiently high multiplicity. Calculations in the phase space of collective variables using a simple method of Gaussian moments automatically lead to the screening of the interactions.

The screened potential depends on the temperature and density of the system as well as on a specific form of the long-range potential. One can distinguish two types of screening depending on $\nu(k)$ being the Fourier transform of $\Phi_2(R)$. If $\nu(k) > 0$ (this case corresponds to repulsion), the screening leads to a decrease in the interaction of particles compared to the initial potential. If $\nu(k) < 0$ (this case corresponds to attraction), the method of Gaussian moments used here is valid if in (2.2.18) $1 - \beta N/V \nu(k) > 0$. The point at which $1 - \beta N/V \nu(k) = 0$ is critical and in the vicinity of this point, the cluster expansions (2.2.22) are not applicable.

In the next chapters, various specific systems will be considered. Here, we focus on a simple model often used to describe plasma, namely, a classical electron gas. In this case, $F_{\text{HTA}} = 0$ which is equivalent to the introduction of an external compensating field maintaining the electroneutrality of the system. For the Coulomb interaction potential of electrons $\nu(k) = \int \Phi_2(R) e^{-i\mathbf{k} \cdot \mathbf{R}} d\mathbf{R} = 4\pi e^2/k^2$ and according to (2.2.24), F_{RPA} coincides with the well-known expression for the free energy of the charged particle system:

$$F_{\text{RPA}} = -\frac{V}{4\pi^2\beta} \int_0^\infty \left[\beta \frac{N}{V} \nu(k) - \ln(1 + \beta \frac{N}{V} \nu(k)) \right] k^2 dk = -\frac{V}{4\pi\beta} \frac{\kappa^3}{3}, \quad (2.2.27)$$

where $\kappa = (4\pi\beta e^2 N/V)^{1/2}$. The quantity κ^{-1} is known as the Debye length and characterizes the radius of the effective interaction of the charged particles. Indeed, according to (2.2.18),

$$g(R) = -\frac{1}{(2\pi)^3} \beta \int \frac{\nu(k) e^{i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k}}{1 + \beta \frac{N}{V} \nu(k)} = -\beta \frac{e^2}{R} e^{-\kappa R}. \quad (2.2.28)$$

As one can see, the screening leads to the replacement of the potential $1/R$ with the potential $1/Re^{-\kappa R}$, the presence of which in the cluster integrals $B'_2, B'_3, \dots$ eliminates the divergences which appear at large distances in the case of the ordinary Mayer expansions.

Thus, the application of the method of collective variables leads to cluster expansions, which, unlike Mayer expansions, do not contain divergences

for long-range potentials. For an electron gas, there are no divergences even at small distances. However, in the case of the potential $\Phi_2(R) < 0$ corresponding to attraction, the cluster integrals can diverge at small distances (for example, for the system of the positively and negatively charged particles). To eliminate this divergence, the short-range interactions must be taken into account. Let us go back to the original problem of calculating the configuration integral (2.2.5). There is an extended phase space of the collective variables and the individual coordinates of particles under the integral in (2.2.5). Assuming that the potential energy of short-range interaction is equal to zero, we performed integration in the phase space of collective variables, in which long-range interactions are described, and we obtain the expression (2.2.22) for the free energy. Now, we need short-range interactions to take into account. Before solving this problem, let us make a short digression and find distribution functions from an expression for the free energy.

2.2.2. Distribution functions in a system with long-range interactions

As it is known [31, 32], the free energy is a generating functional for the construction of a set of the distribution functions. The free energy variation δF corresponding to a variation in interaction potential $\delta u_2(R_{12})$ is equal to

$$\delta F = \frac{1}{V^N Q_N} \int e^{-\beta U_N} \delta u_2(\mathbf{R}_1, \mathbf{R}_2) (d\mathbf{R}). \quad (2.2.29)$$

Due to the spatially homogeneity of the system,

$$\delta F = \frac{1}{Q_N V^{N-1}} \int e^{-\beta U_N} \delta u_2(R_{12}) d\mathbf{R}_{12} d\mathbf{R}_{13} \dots d\mathbf{R}_{1N}.$$

The quantity

$$\frac{\delta F}{\delta u_2(R_{12})} = \frac{1}{Q_N V^{N-1}} \int e^{-\beta U_N} d\mathbf{R}_{12} d\mathbf{R}_{13} \dots d\mathbf{R}_{1N} = \frac{F_2(R_{12})}{V}. \quad (2.2.30)$$

is the functional derivative of the free energy with respect to the pair potential $u_2(R_{12})$ and determines the pair distribution function $F_2(R_{12})$.

The three-particle distribution function is equal to

$$\frac{F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)}{V^3} = \frac{1}{Q_N V^N} \int e^{-\beta U_N} d\mathbf{R}_4 \dots d\mathbf{R}_N. \quad (2.2.31)$$

In the case of a spatially homogeneous system, the three-particle distribution function depends on the two relative coordinates

$$\frac{F_3(\mathbf{R}_{12}, \mathbf{R}_{13})}{V^2} = \frac{1}{Q_N V^{N-1}} \int e^{-\beta U_N} d\mathbf{R}_{14} \dots d\mathbf{R}_{1N}. \quad (2.2.32)$$

The above expression arises from the double functional derivative of the free energy or from the first functional derivative of the pair distribution function (2.2.30) with respect to the potential $u_2(R_{13})$

$$\begin{aligned} \frac{\delta^2 F}{\delta u_2(R_{12})\delta u_2(R_{13})} &= -\beta \frac{1}{Q_N V^{N-1}} \int e^{-\beta U_N} d\mathbf{R}_{14} \dots d\mathbf{R}_{1N} - \\ &\quad - \beta \frac{1}{Q_N V^{N-1}} \int e^{-\beta U_N} d\mathbf{R}_{13} \dots d\mathbf{R}_{1N} \times \\ &\quad \times \frac{1}{Q_N V^{N-1}} \int e^{-\beta U_N} d\mathbf{R}_{12} d\mathbf{R}_{14} \dots d\mathbf{R}_{1N}. \end{aligned} \quad (2.2.33)$$

Comparing the above expression with (2.2.32), we have

$$-\frac{1}{\beta} \frac{\delta^2 F}{\delta u_2(R_{12})\delta u_2(R_{13})} = \frac{F_3(\mathbf{R}_{12}, \mathbf{R}_{13})}{V^2} - \frac{F_2(R_{12})}{V} \frac{F_2(R_{13})}{V}. \quad (2.2.34)$$

For the higher-order functional derivatives, we get

$$\begin{aligned} \frac{(-\beta)^{-m+2} \delta^{m-1} F}{\delta u_2(R_{12})\delta u_2(R_{13}) \dots \delta u_2(R_{1m})} &= \frac{F_m(\mathbf{R}_{12}, \mathbf{R}_{13}, \dots, \mathbf{R}_{1m})}{V^{m-1}} - \\ &- \sum_{j=2}^m \frac{F_2(R_{1j})}{V} \frac{1}{V^{m-2}} F_{m-1}(\mathbf{R}_{12}, \dots, \mathbf{R}_{1j-1}, \mathbf{R}_{1j+1}, \dots, \mathbf{R}_{1m}) + \\ &+ (-1)^m \frac{F_2(R_{12})}{V} \frac{F_2(R_{13})}{V} \dots \frac{F_2(R_{1m})}{V}. \end{aligned} \quad (2.2.35)$$

Let us proceed with the calculation of the distribution functions of the system with long-range interactions. For the free energy, we take the expression (2.2.22), where $u_2(R)$ has the form $\Phi_2(R)$. Using (2.2.30), we first find an expression for $F_2^{(\ell)}(R)$. For each term in (2.2.22), we have

$$\frac{\delta F_{\text{id}}}{\delta \Phi_2(R)} = 0, \quad \frac{\delta F_{\text{HTA}}}{\delta \Phi_2(R)} = \frac{1}{V}$$

and, according to (2.2.24),

$$\frac{\delta F_{\text{RPA}}}{\delta \Phi_2(R)} = -\frac{1}{\beta} \frac{\delta}{\delta \Phi_2(R)} \left[\frac{1}{2} \sum_k [\alpha(k) - \ln(1 + \alpha(k))] \right],$$

where $\alpha(k) = N/V \beta \nu(k)$. Instead of $\nu(k)$ one can write

$$\nu(k) = \int \Phi_2(R) e^{-i\mathbf{k} \cdot \mathbf{R}} d\mathbf{R} = \frac{1}{2N(N-1)} \sum_{i \neq j} \int \Phi_2(R_{ij}) e^{-i\mathbf{k} \cdot \mathbf{R}_{ij}} d\mathbf{R}_{ij}.$$

Then

$$\frac{\delta\alpha(k)}{\delta\Phi_2(R)} = \beta \frac{1}{VN} e^{i\mathbf{k}\cdot\mathbf{R}}. \quad (2.2.36)$$

As a result,

$$\frac{\delta F_{\text{RPA}}}{\delta\Phi_2(R)} = -\frac{1}{\beta} \sum'_k \left[1 - \frac{1}{1 + \alpha(k)} \right] \beta \frac{1}{VN} e^{i\mathbf{k}\cdot\mathbf{R}} = \frac{1}{V} g(R), \quad (2.2.37)$$

where $g(R)$ is the screened potential.

We now pass to the functional derivative of the cluster coefficients, each of which depends on $g(R)$. Therefore,

$$\begin{aligned} & \frac{\delta(B'_2 + B'_3 + \dots)}{\delta\Phi_2(R_{12})} = \\ &= \frac{1}{2} \sum_{i \neq j} \int \int \frac{\delta(B'_2 + B'_3 + \dots)}{\delta g(R_{ij})} \frac{\delta g(R_{ij})}{\delta\Phi_2(R_{12})} d\mathbf{R}_i d\mathbf{R}_j. \end{aligned} \quad (2.2.38)$$

We can easily find the derivatives with respect to the screened potential. According to (2.2.20) and (2.2.21),

$$\begin{aligned} \frac{\delta B_2}{\delta g(R_{ij})} &= \frac{1}{V} \left[e^{g(R_{ij})} - 1 - g(R_{ij}) \right], \\ \frac{\delta B_3}{\delta g(R_{ij})} &= \frac{1}{V^2} \sum_l \int \left\{ \left[e^{g(R_{il})} - 1 - g(R_{il}) \right] \times \right. \\ &\quad \times \left[e^{g(R_{jl})} - 1 - g(R_{jl}) \right] \left[e^{g(R_{ij})} - 1 \right] + \\ &\quad + \left[e^{g(R_{il})} - 1 - g(R_{il}) \right] \left[e^{g(R_{jl})} - 1 - g(R_{jl}) \right] + \\ &\quad \left. + 2g(R_{il}) \left[e^{g(R_{jl})} - 1 - g(R_{jl}) \right] \left[e^{g(R_{ij})} - 1 \right] \right\} d\mathbf{R}_l, \text{ and etc.} \end{aligned} \quad (2.2.40)$$

These expressions must be multiplied by the derivative $\delta g(R)/\delta\Phi_2(R)$. To find it, we use the integral equation (2.2.19). Varying the functions $\Phi_2(R)$ and $g(R)$ in (2.2.19), we obtain the equation for $\delta g(R)$:

$$\begin{aligned} & \delta g(R_{ij}) + \sum_l \frac{1}{V} \int \delta g(R_{lj}) \beta \Phi_2(R_{il}) d\mathbf{R}_l = \\ &= -\beta \delta\Phi_2(R_{ij}) - \beta \sum_l \frac{1}{V} \int \delta\Phi_2(R_{il}) g(R_{lj}) d\mathbf{R}_l. \end{aligned}$$

The Green function $G(R)$ of this equation

$$G(R_{ij}) + \beta \sum_l \frac{1}{V} \int \Phi_2(R_{il}) G(R_{lj}) d\mathbf{R}_l = \delta(\mathbf{R}_{ij})$$

has the Fourier transform $G(k) = -(1 + \alpha(k))^{-1} = -1 + \frac{\alpha(k)}{1 + \alpha(k)}$ and it is equal to

$$G(R_{ij}) = -\delta(\mathbf{R}_{ij}) - \frac{N}{V}g(R_{ij}). \quad (2.2.41)$$

Using the above expression for $G(R_{ij})$, we can write for the variation $\delta g(R_{ij})$

$$\begin{aligned} \delta g(R_{ij}) &= -\sum_l \int \delta(\mathbf{R}_{il}) \left[-\beta \delta \Phi_2(R_{lj}) - \right. \\ &\quad \left. -\beta \sum_m \frac{1}{V} \int \delta \Phi_2(R_{lm}) g(R_{mj}) d\mathbf{R}_m \right] d\mathbf{R}_l - \\ &\quad -\frac{N}{V} \sum_l \int g(R_{il}) \left[-\beta \delta \Phi_2(R_{lj}) - \right. \\ &\quad \left. -\sum_m \frac{1}{V} \int \beta \delta \Phi_2(R_{lm}) g(R_{mj}) d\mathbf{R}_m \right] d\mathbf{R}_l = \\ &= \beta \delta \Phi_2(R_{ij}) + \beta \frac{1}{V} \sum_m \int \delta \Phi_2(R_{lm}) g(R_{mj}) d\mathbf{R}_m + \\ &\quad + \sum_l \beta \frac{1}{V} \int g(R_{il}) \delta \Phi_2(R_{lj}) d\mathbf{R}_l + \\ &\quad + \sum_{l,m} \frac{1}{V^2} \int g(R_{im}) \beta \delta \Phi_2(R_{ml}) g(R_{lj}) d\mathbf{R}_m d\mathbf{R}_l. \end{aligned}$$

In order to take the derivative $\delta g(R_{ij})/\delta \Phi_2(R_{12})$ it is necessary to distinguish the cases $i = 1, j = 2$; $i = 1, j \neq 2$; $i \neq 1, i \neq 2, j \neq 1, j \neq 2$ and their various permutations. To combine everything into one formula, we write $\delta g(R_{ij})$ as a complete functional

$$\begin{aligned} \delta g(R_{ij}) &= \beta \sum_{s,t} \delta_{is} \delta_{jt} \int \delta(\mathbf{R}_i - \mathbf{R}_s) \delta(\mathbf{R}_j - \mathbf{R}_t) \left\{ \delta \Phi_2(R_{st}) + \right. \\ &\quad + \sum_m \frac{1}{V} \int [\delta \Phi_2(R_{sm}) g(R_{mt}) + g(R_{sm}) \delta \Phi_2(R_{mt})] d\mathbf{R}_m + \\ &\quad \left. + \sum_{l,m} \frac{1}{V^2} \int g(R_{sm}) \delta \Phi_2(R_{ml}) g(R_{lt}) d\mathbf{R}_m d\mathbf{R}_l \right\} d\mathbf{R}_s d\mathbf{R}_t. \quad (2.2.42) \end{aligned}$$

The functional derivative is taken with respect to $\Phi_2(\mathbf{R}_1, \mathbf{R}_2)$ which, in turn, depends on $\mathbf{R}_1$ and $\mathbf{R}_2$:

$$\begin{aligned} \frac{\delta g(\mathbf{R}_i, \mathbf{R}_j)}{\delta \Phi_2(\mathbf{R}_1, \mathbf{R}_2)} &= \delta_{i1} \delta_{j2} \delta(\mathbf{R}_i - \mathbf{R}_1) \delta(\mathbf{R}_j - \mathbf{R}_2) + \delta_{i2} \delta_{j1} \delta(\mathbf{R}_i - \mathbf{R}_2) \delta(\mathbf{R}_j - \mathbf{R}_1) + \\ &\quad + \frac{1}{V} [\delta_{i1} \delta(\mathbf{R}_i - \mathbf{R}_1) g(R_{2j}) + \delta_{i2} \delta(\mathbf{R}_i - \mathbf{R}_2) g(R_{1j}) + \delta_{j2} \delta(\mathbf{R}_j - \mathbf{R}_2) g(R_{i1}) + \\ &\quad + \delta_{j1} \delta(\mathbf{R}_j - \mathbf{R}_1) g(R_{i2})] + \frac{1}{V^2} [g(R_{i1}) g(R_{2j}) + g(R_{i2}) g(R_{j1})]. \quad (2.2.43) \end{aligned}$$

The Kronecker symbols refer to the particle numbers. Substituting (2.2.39) and (2.2.43) into (2.2.38), we find

$$\begin{aligned}
 \frac{\delta(-\frac{1}{\beta}B'_2)}{\delta\Phi_2(R_{12})} &= \frac{1}{2} \sum_{i \neq j} \int \left[e^{g(R_{ij})} - 1 - g(R_{ij}) \right] \left\{ \delta_{i1} \delta_{j2} \delta(\mathbf{R}_i - \mathbf{R}_1) \delta(\mathbf{R}_j - \mathbf{R}_2) + \right. \\
 &\quad + \delta_{i2} \delta_{j1} \delta(\mathbf{R}_i - \mathbf{R}_2) \delta(\mathbf{R}_j - \mathbf{R}_1) - \frac{1}{V} \left[\delta_{i1} \delta(\mathbf{R}_i - \mathbf{R}_1) g(R_{2j}) + \right. \\
 &\quad + \delta_{i2} \delta(\mathbf{R}_i - \mathbf{R}_2) g(R_{1j}) + \delta_{j2} \delta(\mathbf{R}_j - \mathbf{R}_2) g(R_{i1}) + \delta_{j1} \delta(\mathbf{R}_j - \mathbf{R}_1) g(R_{i2}) \left. \right] + \\
 &\quad \left. + \frac{1}{V^2} \left[g(R_{i1}) g(R_{2j}) + g(R_{i2}) g(R_{j1}) \right] \right\} d\mathbf{R}_i d\mathbf{R}_j = \\
 &= - \left\{ e^{g(R_{12})} - 1 - g(R_{12}) + \sum_j \frac{1}{V} \int \left[(e^{g(R_{1j})} - 1 - g(R_{1j})) g(R_{j2}) + \right. \right. \\
 &\quad \left. \left. + g(R_{1j}) (e^{g(R_{j2})} - 1 - g(R_{j2})) \right] d\mathbf{R}_j + \right. \\
 &\quad \left. + \sum_{i,j} \frac{1}{V^2} \int g(R_{1i}) \left(e^{g(R_{ij})} - 1 - g(R_{ij}) \right) g(R_{j2}) d\mathbf{R}_i d\mathbf{R}_j \right\}. \quad (2.2.44)
 \end{aligned}$$

As one can see, in accordance with the previously accepted diagrammatic notation, the functional derivative of the second cluster coefficient generates the terms which do not contain field vertices and the terms having one and two field vertices. As it is seen from (2.2.43), their appearance is connected with the properties of the functional derivative $\frac{\delta g(R_{ij})}{\delta\Phi_2(R_{12})}$. The functional derivative of the third cluster coefficient leads to the appearance of the terms with one, two and three field vertices. Using (2.2.43) and (2.2.40), we obtain

$$\begin{aligned}
 \frac{1}{2} \sum_{i,j} \int \frac{\delta(B'_3)}{\delta g(R_{ij})} \frac{\delta g(R_{ij})}{\delta\Phi_2(R_{12})} d\mathbf{R}_i d\mathbf{R}_j &= \frac{1}{V^2} \left[A_3(R_{12}) + \right. \\
 &\quad + \frac{1}{V} \sum_l \int [g(R_{1l}) A_3(R_{l2}) + A_3(R_{1l}) g(R_{l2})] d\mathbf{R}_l + \\
 &\quad \left. + \frac{1}{V^2} \sum_{l,m} \int g(R_{1l}) A_3(R_{lm}) g(R_{m2}) d\mathbf{R}_l d\mathbf{R}_m \right], \quad (2.2.45)
 \end{aligned}$$

where

$$\begin{aligned}
 A_3(R_{12}) &= \frac{1}{V} \sum_t \int \left\{ \left[e^{g(R_{12})} - 1 \right] \left[e^{g(R_{1t})} - 1 - g(R_{1t}) \right] \times \right. \\
 &\quad \times \left[e^{g(R_{t2})} - 1 - g(R_{t2}) \right] + g(R_{12}) \left[e^{g(R_{1t})} - 1 \right] \left[e^{g(R_{t2})} - 1 - g(R_{t2}) \right] + \\
 &\quad + g(R_{12}) \left[e^{g(R_{1t})} - 1 - g(R_{1t}) \right] \left[e^{g(R_{t2})} - 1 \right] + \\
 &\quad \left. + \left[e^{g(R_{1t})} - 1 - g(R_{1t}) \right] \left[e^{g(R_{t2})} - 1 - g(R_{t2}) \right] \right\} d\mathbf{R}_t.
 \end{aligned}$$

Expressions with the same number of field vertices are topologically equivalent and they can be summarized. To obtain a pair distribution function with an accuracy of a one-field vertex, one should take into account the full expression for functional derivatives of F_{HTA} and F_{RPA} , the terms without field vertices, the terms with a one-field vertex of the functional derivative of the second cluster coefficient and, finally, the terms with a one-field vertex of the functional derivative of the third cluster coefficient⁴.

From the expressions (2.2.37), (2.2.44), and (2.2.45) we select all the terms containing two fixed vertices and at most a one-field vertex. We see that the contributions F_{HTA} and F_{RPA} are completely cancelled by the corresponding terms of the second cluster coefficient, and the expression with a one-field vertex of the second cluster coefficient cancels the corresponding term in the last terms for $A_3(R_{12})$ in (2.2.45).

Thus, for a pair distribution function, we get

$$\begin{aligned} F_2^{(\ell)}(\mathbf{R}_1, \mathbf{R}_2) = & e^{g(R_{12})} \left\{ 1 + \frac{N}{V} \int \left[e^{g(R_{13})} - 1 - g(R_{13}) \right] \left[e^{g(R_{32})} - \right. \right. \\ & \left. \left. - 1 - g(R_{32}) \right] d\mathbf{R}_3 + \frac{N}{V} \int g(R_{13}) \left[e^{g(R_{32})} - 1 - g(R_{32}) \right] d\mathbf{R}_3 + \right. \\ & \left. + \frac{N}{V} \int \left[e^{g(R_{13})} - 1 - g(R_{13}) \right] g(R_{32}) d\mathbf{R}_3 + \dots \right\}. \end{aligned} \quad (2.2.46)$$

The higher-order distribution functions can be found in the same way. In particular, we have for $1/V^2 F_3^{(\ell)}(\mathbf{R}_{12}, \mathbf{R}_{13})$ up to terms that do not contain field vertices

$$\begin{aligned} -\beta V^3 \frac{\delta^2 F^{(\ell)}}{\delta \Phi_2(R_{12}) \delta \Phi_2(R_{13})} = & \exp[g(R_{12}) + g(R_{13}) + g(R_{23})][1 + \dots] - \\ & - \exp[g(R_{12}) + g(R_{13})][1 + \dots]. \end{aligned}$$

According to (2.2.34),

$$F_3^{(\ell)}(\mathbf{R}_{12}, \mathbf{R}_{13}) = \exp[g(R_{12}) + g(R_{13}) + g(R_{23})][1 + \dots], \quad (2.2.47)$$

which agrees with the superposition approximation (1.3.25) up to the third cluster coefficient. However, the consideration of the diagrams with a one-field vertex leads to an expression for the three-particle distribution function that differs from the superpositional form.

As in the previous subsection, to illustrate the results obtained, we turn to the classical electron gas model. For this system, in the case of low density, as shown by Bogolyubov [31, 32], there is a small parameter called a plasma

⁴The functional derivative of the fourth cluster coefficient contains the terms with two-, three-, and four-field vertices.

carried out through n successive steps, at each step the equation (2.2.49) is used and, as a result, a one field vertex is added to the right-hand side at each step. Thus, the function $h_2^{(n)}(R)$ will contain the diagrams starting with $\frac{1}{(n+1)!}g^{(n+1)}(R)$ and ending with the diagrams with $2n$ field vertices ([64], see also [65, 66]). In particular,

$$v^*h_2^{(1)}(R) = \frac{1}{2}g^2(R) + \frac{1}{2}\left(\text{diagram 1} + \text{diagram 2} + \text{diagram 3}\right), \quad (2.2.50)$$

where $\text{—} = g(R)$ is the screened potential.

Comparing this result with the expression (2.2.46), we see that the n -th approximation with respect to the plasma parameter contains contributions to the free energy from different cluster coefficients, starting from the second cluster coefficient and ending with the $(2n+2)$ -th one. To get the cluster expansion (2.2.46) it is necessary in the expansion in powers of the plasma parameter to collect all the diagrams in terms of the number of field vertices and sum them up. It should be noted that in the expansion in powers of the plasma parameter, the divergent diagrams appear starting from the second order. In the cluster expansion (2.2.46) grouped by the correlations, there are no divergences for the electron gas. However, the divergences appear when the system consists of oppositely charged particles. In order to eliminate them, the short-range interactions must be taken into account.

2.2.3. Free energy accounting for short-range interactions

The short-range interactions will be taken into account using the method of functional differentiation. Consider the full configuration integral (2.2.5) and represent it in the form:

$$\begin{aligned} Q_N &= \frac{1}{V^N} \int \prod_{1 \leq i < j \leq N} [1 + f(R_{ij})] e^{\beta v(R)} (d\mathbf{R}) = \\ &= \frac{1}{V^N} \int \prod_{1 \leq i < j \leq N} [1 + f(R_{ij})] J(\rho R) e^{\beta v(\rho)} (d\rho) (d\mathbf{R}), \end{aligned} \quad (2.2.51)$$

where $f(R_{ij}) = \exp[-\beta\varphi_2(R_{ij})] - 1$ is the Mayer function for the short-range interaction, Q_N is a linear functional of the functions $f(R_{ij})$, and the free energy determined according to (1.1.6) can be represented as a series in the Mayer functions

$$\begin{aligned} F &= (F)_{f=0} + \sum_{1 \leq i < j \leq N} \int f(R_{ij}) \left[\frac{\delta F}{\delta f(R_{ij})} \right]_{f=0} d\mathbf{R}_i d\mathbf{R}_j + \\ &+ \sum_{i,j,l,m} \int f(R_{ij}) f(R_{lm}) \left[\frac{\delta^2 F}{\delta f(R_{ij}) \delta f(R_{lm})} \right]_{f=0} d\mathbf{R}_i d\mathbf{R}_j d\mathbf{R}_l d\mathbf{R}_m + \end{aligned}$$

$$\begin{aligned}
 & + \sum_{i,j,l,m,n,s} \int f(R_{ij})f(R_{lm})f(R_{ns}) \left[\frac{\delta^3 F}{\delta f(R_{ij})\delta f(R_{lm})\delta f(R_{ns})} \right]_{f=0} \times \\
 & \times d\mathbf{R}_i d\mathbf{R}_j d\mathbf{R}_l d\mathbf{R}_m d\mathbf{R}_n d\mathbf{R}_s + \dots
 \end{aligned} \tag{2.2.52}$$

It should be noted that there are only single derivatives with respect to each of $f(R_{ij})$. In the obtained expansion, the groups of two-, three-, four-, etc. particles connected by the functions $f(R_{ij})$ are formed. Since all groups of two particles are included in the second term of (2.2.52), we proceed with the functional derivatives connecting the groups of three particles. To this end, one should take such functional derivatives

$$\frac{\delta^2 F}{\delta f(R_{ij})\delta f(|\mathbf{R}'_i - \mathbf{R}_l|)}, \quad \frac{\delta^3 F}{\delta f(R_{ij})\delta f(|\mathbf{R}'_i - \mathbf{R}_l|)\delta f(|\mathbf{R}'_j - \mathbf{R}'_l|)}.$$

The differentiation procedure is fully consistent with the one given in the previous paragraph (see the formulas leading to (2.2.43)). Each time, before taking the functional derivative with respect to $f(R_{ij})$, one must first have the functional containing the integration with respect to $d\mathbf{R}_i$ and $d\mathbf{R}_j$. Therefore, in (2.2.52), we obtain an expression containing one δ -function and integrals $\int \delta(\mathbf{R}_i - \mathbf{R}'_i) \dots d\mathbf{R}_i d\mathbf{R}_j d\mathbf{R}'_i d\mathbf{R}_l$ for the terms with the second derivative. Integration over the δ -function contracts $\mathbf{R}'_i$ into the point $\mathbf{R}_i$. For the considered third-order derivative, we get six integrals and three δ -functions $\int \delta(\mathbf{R}_i - \mathbf{R}'_i)\delta(\mathbf{R}_j - \mathbf{R}'_j)\delta(\mathbf{R}_l - \mathbf{R}'_l) \dots d\mathbf{R}_i d\mathbf{R}'_i d\mathbf{R}_j d\mathbf{R}'_j d\mathbf{R}_l d\mathbf{R}'_l$. The integration leads to three integrals over the vertices $\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_l$. Therefore, one can use a simple rule in the functional expansion: when the first-order derivative with respect to $f(R_{ij})$ is taken, the integrals over $\mathbf{R}_i$ and $\mathbf{R}_j$, are removed; then, when the second-order derivative with respect to $f(R_{il})$ is taken, the integral over $\mathbf{R}_l$ is removed; finally, when it is also necessary to take the third-order derivative with respect to $f(R_{jl})$, then it is taken not as a functional derivative but as an ordinary derivative. A similar rule is used for the higher-order derivatives.

For each derivative in (2.2.52) one can write a set of equalities

$$\left[\frac{\delta \dots F}{\delta f(R_{12})} \right]_{f=0} = \left[\frac{\delta \dots F}{\delta(-\beta\varphi_2(R_{12}))} \right]_{\varphi_2=0} = \frac{\delta \dots F^{(\ell)}}{\delta(-\beta\Phi_2(R_{12}))}. \tag{2.2.53}$$

In general, for the n -order derivative, we have

$$\left[\frac{\delta^n F}{\delta f(R_{12})\delta f(R_{13})\dots\delta f(R_{1n})} \right]_{f=0} = (-\beta)^{-n} \frac{\delta^n F^{(\ell)}}{\delta\Phi_2(R_{12})\delta\Phi_2(R_{13})\dots\delta\Phi_2(R_{1n})}.$$

Applying both the established rule for the multiple functional differentiation and the replacement of functions in the derivatives (2.2.53), the expan-

sion (2.2.52) can be written in the form of cluster expansions

$$\begin{aligned}
 F = F^{(\ell)} + \sum_{1 \leq i < j \leq N} \int f(R_{ij}) \frac{\delta F^{(\ell)}}{\delta(-\beta \Phi_2(R_{ij}))} d\mathbf{R}_i d\mathbf{R}_j + \\
 + \sum_{1 \leq i < j < l \leq N} \int \left\{ f(R_{ij}) f(R_{il}) \frac{\delta^2 F^{(\ell)}}{\delta(-\beta \Phi_2(R_{ij})) \delta(-\beta \Phi_2(R_{il}))} + \right. \\
 \left. + f(R_{ij}) f(R_{il}) f(R_{jl}) \frac{\delta^3 F^{(\ell)}}{\delta(-\beta \Phi_2(R_{ij})) \delta(-\beta \Phi_2(R_{il})) \delta(-\beta \Phi_2(R_{jl}))} \right\} \times \\
 \times d\mathbf{R}_i d\mathbf{R}_j d\mathbf{R}_l + \dots
 \end{aligned} \tag{2.2.54}$$

Instead of the functional derivatives, we substitute their values in the terms of distribution functions found in the previous subsection

$$\begin{aligned}
 -\beta(F - F^{(\ell)}) = \sum_{1 \leq i < j \leq N} \int f(R_{ij}) \frac{1}{V} F_2^{(\ell)}(R_{ij}) d\mathbf{R}_i + \\
 + \sum_{1 \leq i < j < l \leq N} \int \left\{ f(R_{ij}) f(R_{il}) \left[\frac{F_3^{(\ell)}(R_{ij}, R_{il})}{V^2} - \frac{F_2^{(\ell)}(R_{ij})}{V} \frac{F_2^{(\ell)}(R_{il})}{V} \right] + \right. \\
 \left. + f(R_{ij}) f(R_{il}) f(R_{jl}) \frac{F_3^{(\ell)}(R_{ij}, R_{il})}{V^2} \right\} d\mathbf{R}_i d\mathbf{R}_j d\mathbf{R}_l + \dots
 \end{aligned} \tag{2.2.55}$$

Here, we restrict our consideration to the approximation containing three field vertices. This means that for $F^{(\ell)}$ in (2.2.55), one should take into account the expression up to the third cluster coefficient, for $F_2^{(\ell)}$ — the approximation up to one field vertex, and for $F_3^{(\ell)}$ — the approximation without field vertices. There are such approximations in (2.2.22), (2.2.46) and (2.2.47). We substitute them into (2.2.55). We write each function $f(R_{ij})$ as $\exp[-\beta \varphi_2(R_{ij})] - 1$. After all reductions, we get

$$F = F_{\text{id}} + F_{\text{HTA}} + F_{\text{RPA}} - \frac{1}{\beta} (B_2 + B_3 + \dots), \tag{2.2.56}$$

where F_{id} is an ideal part of the free energy; expressions for F_{HTA} and F_{RPA} are given by expressions (2.2.23) and (2.2.24), and for B_2 and B_3 , we have

$$B_2 = \frac{1}{2} \frac{N^2}{V} \int [\Psi(R_{12}) - g(R_{12}) - \frac{1}{2} g^2(R_{12})] d\mathbf{R}_{12}, \tag{2.2.57}$$

$$\begin{aligned}
 B_3 = \frac{1}{3 \cdot 2} \frac{N^3}{V^2} \int \{ [\Psi(R_{12}) - g(R_{12})] [\Psi(R_{13}) - g(R_{13})] [\Psi(R_{23}) - g(R_{23})] + \\
 + 3g(R_{12}) [\Psi(R_{13}) - g(R_{13})] [\Psi(R_{23}) - g(R_{23})] \} d\mathbf{R}_{12} d\mathbf{R}_{13},
 \end{aligned} \tag{2.2.58}$$

where $\Psi(R_{12}) = \exp[-\beta\varphi_2(R_{12}) + g(R_{12})] - 1$; B_2 , B_3 are the second and third cluster coefficients of the free energy, respectively, in the presence of short-range and long-range interactions. The behaviour of the function $\Psi(R)$ at large distances is determined by a decrease of the screened potential $g(R)$, while the convergence at small distances is provided by a short-range potential. Therefore, the requirement to the potential $\varphi_2(R)$ is the presence at $R = 0$ of a positive pole of a higher order than $\Phi_2(0)$ if $\Phi_2(R)$ corresponds to attraction.

Comparing the expressions (2.2.56) and (2.2.22), we see that the structure of the series for the free energy F is determined by the free energy without allowance for short-range forces $F^{(\ell)}$. Cluster coefficients B'_n and B_n differ only in replacing the Boltzmann factors $e^{g(R)}$ with $\exp[-\beta\varphi_2(R) + g(R)]$. It should be noted that the resulting cluster expansions for the free energy are not common virial expansions in powers of the density, because the screened potential $g(R)$ also depends on the density of the system. The cluster expansions (2.2.56) coincide with the ordinary virial expansions only in the case of the systems with a purely short-range interaction, i.e., when $g(R) = 0$.

2.2.4. Structure of cluster expansions

For a more compact presentation of the cluster coefficients, we introduce the following diagrammatic notation: --- for the function $\Psi(R)$, $\text{---} \mid \text{---}$ for the function $\Psi(R) - g(R)$, --- for the potential $g(R)$, $\bullet$ for the field vertex $N/V \int d\mathbf{R}$. Using these notations, the second and the third cluster coefficients can be written as follows:

$$B_2 = \frac{1}{2} \left(\text{---} \mid \text{---} - \frac{1}{2} \text{---} \text{---} \right), \quad B_3 = \frac{1}{2 \cdot 3} \left(\text{---} \triangle \text{---} + 3 \text{---} \triangle \text{---} \right). \quad (2.2.59)$$

The higher-order cluster coefficients can also be found using the method described earlier. In particular, the cluster integrals for B_4 can be obtained by completing the connections in such simplest diagrams:

$$\frac{1}{4!} \left\{ 6 \text{---} \square \text{---} + 12 \text{---} \square \text{---} + 3 \text{---} \square \text{---} + 12 \text{---} \square \text{---} + 12 \text{---} \square \text{---} + \right. \\ \left. + 24 \text{---} \square \text{---} + 6 \text{---} \square \text{---} + \text{---} \square \text{---} \right\}. \quad (2.2.60)$$

They are obtained by pairing the products of four operators (see Subsection 2.2.1), starting with the lowest-order diagrams and until the diagram with a symmetrical ring is obtained. The coefficients on the diagrams indicate the number of configurations that differ only by the numbering of particles. Next, for the ring diagrams, the sides with double links are completed, and for the rest, in addition, internal links are constructed. If the lowest-order diagram

in a certain type of the diagrams has all nodes formed by three links (or all nodes formed by a larger number of links, but the same for each node), then all links are completed. Having performed the inverse Fourier transform and the summation, double and single bonds pass to $e^{g(R)} - 1 - g(R)$ and $e^{g(R)} - 1$, respectively, and having taken into account the short-range forces, they pass to $\Psi(R) - g(R)$ and $\Psi(R)$. Thus, in the diagrammatic notation

$$B_4 = \frac{1}{2 \cdot 4} \left[\begin{array}{c} \text{square with 4 links} \\ + 2 \left(\text{square with 3 links} + \text{square with 3 links} \right) \\ + 2 \left(\text{square with 2 links} \right) \\ + 4 \left(\text{square with 1 link} \right) \\ + 2 \left(\text{square with 4 links} \right) \\ + \frac{1}{3} \left(\text{square with 4 links} \right) \end{array} \right]. \quad (2.2.61)$$

The higher-order cluster coefficients are found similarly. In [67] the following expression was obtained for the fifth cluster coefficient:

$$B_5 = \frac{1}{5!} \left\{ \begin{array}{l} 12 \left[\text{pentagon with 5 links} + 5 \left(\text{pentagon with 4 links} + \text{pentagon with 4 links} \right) \right] + 60 \left[\text{pentagon with 4 links} + \right. \\ \left. + \text{pentagon with 3 links} + 2 \left(\text{pentagon with 3 links} + \text{pentagon with 3 links} \right) + \text{pentagon with 2 links} + 2 \left(\text{pentagon with 2 links} + \right. \right. \\ \left. \left. + \text{pentagon with 1 link} + \text{pentagon with 1 link} \right) + 2 \left(\text{pentagon with 1 link} \right) \right] + 10 \left[\text{pentagon with 4 links} + 6 \left(\text{pentagon with 3 links} + \right. \right. \\ \left. \left. + \text{pentagon with 2 links} + \text{pentagon with 2 links} + \text{pentagon with 2 links} \right) + 2 \left(\text{pentagon with 1 link} \right) + 10 \left[\text{pentagon with 4 links} + \right. \right. \\ \left. \left. + 6 \left(\text{pentagon with 3 links} + \text{pentagon with 3 links} + \text{pentagon with 3 links} + \text{pentagon with 3 links} \right) + 2 \left(\text{pentagon with 2 links} \right) + \right. \\ \left. + 60 \left[\text{pentagon with 4 links} + 2 \left(\text{pentagon with 3 links} + \text{pentagon with 3 links} + \text{pentagon with 3 links} \right) + \text{pentagon with 2 links} + \right. \right. \\ \left. \left. + \text{pentagon with 1 link} \right] + 30 \left[\text{pentagon with 4 links} + 2 \left(\text{pentagon with 3 links} \right) + 30 \left[\text{pentagon with 4 links} + \right. \right. \\ \left. \left. + 2 \left(\text{pentagon with 3 links} \right) \right] + 15 \left(\text{pentagon with 4 links} \right) + 10 \left(\text{pentagon with 4 links} \right) + \text{pentagon with 4 links} \right] \end{array} \right\}. \quad (2.2.62)$$

Thus, the main task of this section is fulfilled, i.e., the high-order cluster expansion for the free energy is found for the systems of particles interacting by

means of short- and long-range forces. It remains to define the pair distribution function.

2.2.5. Pair distribution function accounting for short-range interactions

If the free energy is known, one can find the distribution functions taking short-range interactions into account. Substantially, it does not matter which type of the potential, the long-range $\Phi_2(R)$ or short-range $\varphi_2(R)$ potential, is used for the functional differentiation. The free energy is an explicit functional of the short-range potential $\varphi_2(R)$ and an implicit functional of the long-range potential $\Phi_2(R)$. Therefore, differentiation with respect to $\varphi_2(R)$ is simpler. In the diagram notations adopted earlier, this derivative with respect to $\varphi_2(R)$ reduces to the replacement of the two-field vertices denoted with black circles by the two vertices denoted with white circles as well as to the replacement of the thick line connecting them by the factor $\exp[-\beta\varphi_2(R) + g(R)]$.

As a result,

$$F_2(R) = \exp[-\beta\varphi_2(R) + g(R)][1 + \sum_{n \geq 1} F_2^{n+2}(R)], \quad (2.2.63)$$

where $F_2^{n+2}(R)$ is the $(n+2)$ -th cluster coefficient of the pair distribution function. In particular,

$$\begin{aligned} F_2^{(3)}(R) &= \text{triangle diagram} - \text{triangle diagram}, \\ F_2^{(4)}(R) &= \text{square diagram} - \text{square diagram} - \text{square diagram} + \text{square diagram} + \text{square diagram} - \text{square diagram} + \\ &+ \text{square diagram} - \text{square diagram} + \frac{1}{2} (\text{diagonal square} - \text{diagonal square} - \text{diagonal square} + \text{diagonal square} + \text{diagonal square}), \\ F_2^{(5)}(R) &= \text{pentagon diagram} - \text{pentagon diagram} - \text{pentagon diagram} - \text{pentagon diagram} + \text{pentagon diagram} + \\ &+ \text{pentagon diagram} + \text{pentagon diagram} - \text{pentagon diagram} - \text{pentagon diagram} + \text{pentagon diagram} + \text{pentagon diagram} - \\ &- \text{pentagon diagram} - \text{pentagon diagram} + \text{pentagon diagram} + \text{pentagon diagram} - \text{pentagon diagram} - \text{pentagon diagram} - \\ &- \text{pentagon diagram} + \text{pentagon diagram} - \text{pentagon diagram} - \text{pentagon diagram} + \text{pentagon diagram} + \text{pentagon diagram} - \\ &- \text{pentagon diagram} + \text{pentagon diagram} - \text{pentagon diagram} - \text{pentagon diagram} - \text{pentagon diagram} + \text{pentagon diagram} + \end{aligned}$$

$$\begin{aligned}
& + \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} - \\
& - \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} - \\
& - \text{diagram} + \text{diagram} - \text{diagram} + \frac{1}{2} \left(\text{diagram} - \text{diagram} + \text{diagram} + \right. \\
& + \text{diagram} + \text{diagram} + \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} + \\
& + \text{diagram} + \text{diagram} + \text{diagram} - \text{diagram} - \text{diagram} + \text{diagram} + \\
& + \text{diagram} - \text{diagram} - \text{diagram} + \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} - \\
& - \text{diagram} + \text{diagram} + \text{diagram} - \text{diagram} - \text{diagram} + \text{diagram} \left. \right) + \\
& + \text{diagram} - \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} - \text{diagram} - \\
& - \text{diagram} + \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} - \text{diagram} - \\
& - \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} + \text{diagram} + \frac{1}{3!} \left(\text{diagram} - \right. \\
& - \text{diagram} \left. \right) + \frac{1}{2} \left(\text{diagram} - \text{diagram} + \text{diagram} - \text{diagram} \right) + \frac{1}{3!} \text{diagram}.
\end{aligned}
\tag{2.2.64}$$

As in the case of ordinary virial expansions (1.3.13), the pair distribution function represents a set of diagrams, each of which has two fixed vertices connected to field vertices in different ways. When the order of the cluster coefficient increases, the number of diagrams increases rapidly. Distinguishing the class of irreducible diagrams, the pair distribution function can be represented as the exponential of the potential of the mean force:

$$F_2(R) = \exp[-\beta\varphi_2(R) + g(R) + \sum_{n \geq 1} \tilde{F}_2^{n+2}(R)] =$$

$$= \exp[-\beta\varphi_2(R) + g(R) + w_2(R)], \quad (2.2.65)$$

where $\tilde{F}_2^{n+2}(R)$ is a set of irreducible diagrams of the $(n+2)$ -th cluster coefficient. In particular, $\tilde{F}_2^3(R) = F_2^3(R)$, $\tilde{F}_2^4(R)$ differs from $F_2^4(R)$ only in that it does not contain the last diagram in brackets in expression (2.2.64) for $F_2^4(R)$, etc. The importance of the exponential form consists in its positive definiteness for all distances, regardless of the nature of intermolecular interactions.

Let us focus on some general regularities in the structure of the free energy diagrams. Among the diagrams there are symmetrical ones which are reminiscent of Mayer diagrams. The entire set of symmetrical diagrams (built only with thick lines) will be divided into two parts. In the first part of the diagrams, at least three lines emerge from each vertex. They all are $\Psi(R)$, i.e., the thick lines without dashes crossing the lines. Each diagram of the second part has at least one vertex, from which only two thick lines with crossing emerge. A certain number of asymmetric diagrams with thin lines is necessarily added to such a diagram in the cluster coefficient and no more than one thin line emerges from each vertex in this case. This is due to the fact that in the Jacobian of the transformation $J(\rho)$, the pairing of the operators $\hat{D}_n$ is carried out starting with $\hat{D}_3$. The resulting structure of cluster expansions is determined by the form of the Jacobian of the transformation.

The lines emerging from the vertices of the diagrams will be called bonds. The bond is a thin line for $g(R)$, a thick line for $\Psi(R)$ or a thick line with crossing for $\Psi(R) - g(R)$. Each bond connects vertices in a diagram. The simplest diagrams in (2.2.65) are the chain diagrams corresponding to ring diagrams of free energy. As it was noted above, the free energy includes all kinds of ring diagrams built on bonds so that no more than one thin line emerges from each field vertex. When a pair distribution function is obtained as a result of the functional differentiation, the ring is broken, and the factors accompanying the ring diagrams are reduced. Thus, the pair distribution function includes chain diagrams based on the bonds $\Psi(R) - g(R)$ and $g(R)$ so that two thin lines do not emerge of the same vertex. We form a sum of the chain diagrams

$$w_2^{(1)}(R) = \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \text{diagram 4} + \text{diagram 5} + \text{diagram 6} + \text{diagram 7} + \text{diagram 8} + \text{diagram 9} + \dots \quad (2.2.66)$$

To build them, one can use the following simple rule. To get all chain diagrams of the $(n+2)$ -th cluster coefficient of the pair distribution function, we need to take the sum of all chains of the $(n+1)$ coefficient, replacing one of the fixed vertices (for example, only the right-hand vertex) with a field vertex having an additional bond $\bullet \text{---} \text{---} \circ$, and to take the sum of all chains of the n -th cluster

coefficient with a similar replacement of one vertex of the fixed vertices with a field vertex adding the bond $\bullet \text{---} \text{---} \bullet \text{---} \circ$ to it.

As in the case of Mayer expansions, a set of diagrams for $w_2(R)$ (see (2.2.66)) can be presented in a form similar to (1.3.17)

$$g(R) + w_2(R) = N_2(R) + E_2(R), \quad (2.2.67)$$

where $E_2(R)$ is a set of elementary diagrams, which, as in the Mayer case, are reduced to the sum of only basic diagrams, built on the bonds $h_2(R) = F_2(R) - 1 = \text{---} \text{---} \text{---}$, $N_2(R)$ is a set of diagrams having at least one nodal vertex⁵.

Similar as in the case of Mayer expansions,

$$N_2(R) = h_2(R) - c_2(R), \quad (2.2.68)$$

where $c_2(R)$ is the direct correlation function, defined by the Ornstein—Zernike equation (1.3.18).

After presentation of the pair and direct correlation functions in the form

$$\begin{aligned} h_2(r) &= g(R) + \delta h(R) \\ c_2(R) &= -\beta\Phi(R) + \delta c(R), \end{aligned} \quad (2.2.69)$$

the pair distribution function can be presented in the form

$$F_2(R) = \exp[-\beta\varphi(R) + g(R) + \delta h(R) - \delta c(R) + E(R)]. \quad (2.2.70)$$

This expression has the form of an integral equation. In Chapter 6 we will show that an iterative procedure of solving this equation automatically leads to cluster expressions for the pair distribution function considered in this paragraph.

2.3. Reference system approach to short-range interactions

In the previous section, the method of collective variables is described in detail, the influence of short-range interactions is discussed using a functional expansion in terms of the Mayer functions of short-range forces. The latter were introduced mainly to eliminate the divergence in cluster integrals at small distances and were actually described using the Mayer expansion in powers of the density, that is inapplicable at high densities. When the density increases, the average distance between particles decreases, which leads to an increase in the role of short-range interactions.

The thermodynamic and structural properties of one-component systems are characterized by two independent parameters, i.e., the reduced density

⁵Recall that the node is the vertex that divides the diagram into two independent parts, and the fixed vertices belong to different parts in this case.

ρ^* and the temperature T^* . The experimental data [45, 68] indicate that the main factor determining the structure of dense systems, such as liquids, is its density. Since short-range interactions are of a strongly repulsive character, corresponding distribution functions have a weak dependence on the temperature. Therefore, it can be assumed that the short-range interactions make the main contribution to the structural properties of the system. This conclusion is actually reflected in the van der Waals equation (see Chapter 3), and it forms the foundation of the modern theory of classical systems.

The short-range interactions describe the sizes of molecules. Therefore, at small distances in the entire range of temperatures and densities, the pair distribution function of the system is equal to zero, regardless of the specific form of the long-range interactions (see, for example, (1.3.13)). It is clear that when constructing approximate theories describing the system in a wide range of densities, one should first select a system with a short-range interaction and only then take into account long-range interactions. Such an approach is at the heart of the second variant of the calculation of the configuration integral in the method of collective variables we proposed in Subsection 2.2.1. After integration in the space of Cartesian coordinates, we present the configuration integral (2.2.5) in the form:

$$Q_N = Q_0 \int (d\rho) J(\rho) e^{-\beta v(\rho)}, \quad (2.3.1)$$

where $Q_0 = 1/V^N \int (d\mathbf{R}) e^{-\beta U_0(R)}$ is the configuration integral of the system with short range interactions,

$$J(\rho) = \frac{1}{Q_0 V^N} \int (d\mathbf{R}) e^{-\beta U_0(R)} J(\rho R) \quad (2.3.2)$$

is the Jacobian of the transformation obtained as a result of averaging the transformation function over a system with a short-range interaction. The main point in this approach consists in the short-range interactions being taken into account playing a basic role with respect to the long-range interactions. Therefore, a system with short-range interactions is usually called a basis system or a reference system. The system forms some ideal structure based on which all events related to the long-range interactions take place. The final formulas of the proposed approach include the free energy and the distribution functions of a reference system, which makes it possible to use more powerful methods for the description of short-range interactions than the Mayer expansions in powers of density (for example, the results of computer simulations, solutions of integral equations, etc.). Averaging the transformation function to the collective variables over the reference system automatically ensures the contribution of short-range forces to the screening of long-range interactions.

2.3.1. Jacobian of the transformation

Using the expression (2.1.23) for the transformation function, we have for the Jacobian of the transformation according to (2.3.2)

$$J(\rho) = \frac{1}{Q_0 V^N} \int (d\omega) \exp \left\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right\} \int (d\mathbf{R}) e^{-\beta U_0(\mathbf{R})} \exp \left\{ -i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} \right\}, \quad (2.3.3)$$

where as before $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}^c - i\rho_{\mathbf{k}}^s$, $\rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^c + i\rho_{\mathbf{k}}^s$, $\omega_{\mathbf{k}} = \omega_{\mathbf{k}}^c + i\omega_{\mathbf{k}}^s$, $\omega_{-\mathbf{k}} = \omega_{\mathbf{k}}^c - i\omega_{\mathbf{k}}^s$, $\hat{\rho}_{\mathbf{k}} = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{i\mathbf{k} \cdot \mathbf{R}_j}$, ($\mathbf{k} \neq 0$), $(d\omega) = \prod'_{\mathbf{k}} d\omega_{\mathbf{k}}^c d\omega_{\mathbf{k}}^s$. The second integral in (2.3.3) is the Fourier transform $J(\rho)$; denoting it as $J(\omega)$, we obtain

$$J(\rho) = \int \exp \left\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right\} J(\omega) (d\omega), \quad (2.3.4)$$

$$J(\omega) = \frac{1}{Q_0 V^N} \int e^{-\beta U_0(\mathbf{R})} \exp \left\{ -i\pi \sum'_{\mathbf{k}} \omega_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} \right\} (d\mathbf{R}). \quad (2.3.5)$$

Just as it was done in (2.1.35), we represent $J(\omega)$ in the exponential form

$$J(\omega) = \exp \left\{ \sum_{n \geq 2} D_n(\omega) \right\}, \quad (2.3.6)$$

where

$$D_n(\omega) = \frac{(-i\pi)^n}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \omega_{\mathbf{k}_1}, \dots, \omega_{\mathbf{k}_n} \frac{N}{\sqrt{N}^n} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n), \quad (2.3.7)$$

$$\frac{N}{\sqrt{N}^n} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = \langle \hat{\rho}_{\mathbf{k}_1}, \dots, \hat{\rho}_{\mathbf{k}_n} \rangle_c. \quad (2.3.8)$$

The cumulant of the n -th order $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$, averaged over $\exp \left\{ -i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} \right\}$ in the expression for $J(\omega)$, has a physical meaning of the n -particle structural factor of the system with a short-range interaction. Indeed, according to (2.1.38)

$$\begin{aligned} \langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \rangle_c &= \frac{1}{N} \left[\sum_j \langle e^{i(\mathbf{k}_1 + \mathbf{k}_2) \mathbf{R}_j} \rangle_c + \sum_{i \neq j} \langle e^{i\mathbf{k}_1 \mathbf{R}_i + i\mathbf{k}_2 \mathbf{R}_j} \rangle_c \right] = \\ &= \mathfrak{M}_2(\mathbf{k}_1) \delta_{\mathbf{k}_1 + \mathbf{k}_2, 0}, \end{aligned} \quad (2.3.9)$$

where $\mathfrak{M}_2(k) = 1 + \frac{N}{V} h_2^{(0)}(k)$ is a two-particle structure factor of the system with a short-range interaction, defined by the formula (1.1.33). Similarly (2.3.9),

$$\langle \hat{\rho}_{\mathbf{k}_1} \hat{\rho}_{\mathbf{k}_2} \hat{\rho}_{\mathbf{k}_3} \rangle_c = \frac{N}{\sqrt{N}^3} \mathfrak{M}_3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, 0}, \quad (2.3.10)$$

where

$$\mathfrak{M}_3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = 1 + \frac{N}{V} [h_2^{(0)}(k_1) + h_2^{(0)}(k_2) + h_2^{(0)}(k_3)] + \frac{N^2}{V^2} h_3^{(0)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$$

is the three-particle structure factor of the system with short-range forces, $h_2^{(0)}(k)$ and $h_3^{(0)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$ are the Fourier transforms of the correlation functions $h_2(R)$ and $h_3(R_{12}, R_{13}, R_{32})$, respectively (see Section 1.3).

To investigate the general properties of the cumulants $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$, we introduce some auxiliary external field $\varphi(R) = \sum_j \sum_{\mathbf{k}} \varphi(\mathbf{k}) e^{-i\mathbf{k}\mathbf{R}_j}$ into the potential energy $U_0(R)$ by considering the function $U_\varphi = U_0 + \varphi$ instead of $U_0(R)$ so that $(U_\varphi)_{\varphi=0} = U_0$ and $(Q_\varphi)_{\varphi=0} = Q_0$. Then,

$$N\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = (-\beta)^{-n} \left[\frac{\delta^n \ln Q_\varphi}{\delta \varphi(k_1), \dots, \delta \varphi(k_n)} \right]_{\varphi=0}. \quad (2.3.11)$$

Each cumulant consists of sums of the Fourier transforms of the correlation functions which, in turn, consist of the Fourier transforms of the distribution functions. It is easy to get an idea of the general expression for $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ by writing (2.3.11) as follows:

$$N\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = (-\beta)^{-n} \left[\frac{\delta^{n-1}}{\delta \varphi(k_2), \dots, \delta \varphi(k_n)} \frac{1}{Q_\varphi} \sum_j \int e^{-i\mathbf{k}_1 \mathbf{R}_j} e^{-\beta U_\varphi} \right]_{\varphi=0}.$$

If we take only the derivative of the numerator, we get a sum of the distribution functions $\frac{N}{V} F_1(\mathbf{k}_1 + \dots + \mathbf{k}_n) + \frac{1}{2} \frac{N(N-1)}{V^2} \sum_{n_1 \geq 1, n-n_1 \geq 1} C_n^{n_1} F_2(\mathbf{k}_1 + \dots + \mathbf{k}_{n_1}, \mathbf{k}_{n_1+1} + \dots + \mathbf{k}_n) + \dots + \frac{N \dots (N-n+1)}{V^n} F_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$, each of which is the beginning of the corresponding correlation function in the full expression for $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$; $C_n^{n_1} = \frac{n!}{(n-n_1)!n_1!}$. Instead of the functions $h_m(\mathbf{k}_1, \dots, \mathbf{k}_m)$ we will use hereafter the correlation functions

$$\begin{aligned} \mu_m(\mathbf{k}_1, \dots, \mathbf{k}_m) &= \frac{N(N-1) \dots (N-m+1)}{V^m} F_m(\mathbf{k}_1, \dots, \mathbf{k}_m) - \\ &- \sum_{j=1}^m \mu_1(\mathbf{k}_j) \mu_{m-1}(\mathbf{k}_1, \dots, \mathbf{k}_m) - \frac{1}{2} \sum_{i,j=1}^m \mu_2(\mathbf{k}_i, \mathbf{k}_j) \mu_{m-2}(\mathbf{k}_1, \dots, \mathbf{k}_m) - \\ &- \dots - \sum_{(1 \leq i_1, \dots, i_{m_1} \leq m)}' \frac{1}{m_1!} \mu_{m_1}(\mathbf{k}_{i_1}, \dots, \mathbf{k}_{i_{m_1}}) \mu_{m-m_1}(\mathbf{k}_1, \dots, \mathbf{k}_m) \times \\ &\times \left(1 - \frac{1}{2} \delta_{m,2m_1} \right) - \dots - \mu_1(\mathbf{k}_1) \dots \mu_1(\mathbf{k}_m), \end{aligned} \quad (2.3.12)$$

where $m_1 = 1/2(m - 1)$ for odd m and $m_1 = 1/2m$ for even m . The form $\frac{\mathbf{k}_i \mathbf{k}_j}{(\mathbf{k}_1, \dots, \mathbf{k}_m)}$ means that the arguments $\mathbf{k}_i, \mathbf{k}_j$ are excluded from a set of the arguments $\mathbf{k}_1, \dots, \mathbf{k}_m$. The prime on the summation means that the indices $i_1, i_2, \dots$ cannot be the same. The general expression for the cumulant $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ will be as follows:

$$\begin{aligned} N\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) &= \mu_1(\mathbf{k}_1 + \dots + \mathbf{k}_n) + \\ &+ \frac{1}{2} \sum_{n_1 \geq 1, n-n_1 \geq 1} C_n^{n_1} \mu_2(\mathbf{k}_1 + \dots + \mathbf{k}_{n_1}, \mathbf{k}_{n_1+1} + \dots + \mathbf{k}_n) + \\ &+ \frac{1}{3!} \sum_{n_1 \geq 1, n_2 \geq 1, n-n_1-n_2 \geq 1} C_n^{n_1} C_{n-n_1}^{n_2} \mu_3(\mathbf{k}_1 + \dots + \mathbf{k}_{n_1}, \mathbf{k}_{n_1+1} + \\ &+ \dots + \mathbf{k}_{n_1+n_2}, \mathbf{k}_{n_1+n_2+1} + \dots + \mathbf{k}_n) + \dots + \mu_n(\mathbf{k}_1, \dots, \mathbf{k}_n). \end{aligned} \quad (2.3.13)$$

In a spatially homogeneous case, the sum $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ is closed; the sum $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ will be closed irreducible, if it does not decompose into the sums equal to zero of the order lower than n ; the sum $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ is closed reducible if it splits into the sums equal to zero of the order lower than n , i.e., $\mathbf{k}_1 + \mathbf{k}_2 = 0$ and $\mathbf{k}_3 + \mathbf{k}_4 + \mathbf{k}_6 = 0$, $\mathbf{k}_6 + \dots + \mathbf{k}_n = 0$. When the sums $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ are reducible, there occurs a partial or complete reduction of the correlation functions that make up the cumulant $\mathfrak{M}_n$. To present correctly $\mathfrak{M}_n$ in this case, instead of the “collecting” binomial coefficients $C_n^{m_1}, C_{n-n_1}^{m_2}, \dots$ all combinations should be written down. Therefore, instead of the formula (2.3.13), we write

$$\begin{aligned} N\mathfrak{M}(\mathbf{k}_1, \dots, \mathbf{k}_n) &= \mu_1(\mathbf{k}_1 + \dots + \mathbf{k}_n) = \\ &= \frac{1}{2} \sum_{n_1 \geq 1, (n-n_1) \geq 1} \sum_{(1 \leq i_1 < i_2 < \dots < i_{n_1} \leq n)} \mu_2(\mathbf{k}_1, \dots, \mathbf{k}_{i_{n_1}}, \mathbf{k}_{i_{n_1}+1} + \dots + \mathbf{k}_{i_n}) + \frac{1}{3!} \times \\ &\times \sum_{\substack{n_1 \geq 1, n_2 \geq 1 \\ n-n_1-n_2 \geq 1}} \sum_{\substack{(1 \leq i_1 < i_2 < \dots < i_{n_1} \leq n) \\ (i_{n_1}+1 < \dots < i_{n_1+n_2}) \\ (i_{n_1+n_2}+1 < \dots < i_n)}} \mu_3(\mathbf{k}_1, \dots, \mathbf{k}_{i_{n_1}}, \mathbf{k}_{i_{n_1}+1} + \dots + \mathbf{k}_{i_{n_1}+i_{n_2}}, \mathbf{k}_{i_{n_1}+i_{n_2}+1} + \dots + \mathbf{k}_{i_n}) + \\ &+ \dots + \mu_n(\mathbf{k}_1, \dots, \mathbf{k}_n). \end{aligned} \quad (2.3.14)$$

Let us study the properties of the cumulants containing the reducible sums. First, consider the Fourier transforms of the distribution functions and of the correlation functions entering the cumulants. By definition of the n -th distribution function,

$$\frac{F_n(\mathbf{k}_1, \dots, \mathbf{k}_n)}{V^n} = \frac{1}{Q_0 V^N} \int e^{-\beta U_0(R)} \exp\{i(\mathbf{k}_1 \mathbf{R}_1 + \dots + \mathbf{k}_n \mathbf{R}_n)\} (d\mathbf{R}). \quad (2.3.15)$$

The Fourier transform $F_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ has the property

$$\frac{F_n(\mathbf{k}_1, \dots, \mathbf{k}_m, 0, \dots, 0)}{V^n} = \frac{F_m(\mathbf{k}_1, \dots, \mathbf{k}_m)}{V^m}. \quad (2.3.16)$$

Taking into account this property, according to (2.3.12)

$$\mu_n(0, \mathbf{k}_2, \dots, \mathbf{k}_n) = -(n-1)\mu_{n-1}(\mathbf{k}_2, \dots, \mathbf{k}_n). \quad (2.3.17)$$

We use these equation to prove two properties of the cumulants.

Theorem 1. *Cumulant $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = 0$ if any $\mathbf{k}_i = 0$, $i = 1, 2, \dots, n$.*

Proof. Let $\mathbf{k}_1 = 0$. Let us prove that in the sum (2.3.14) all terms are successively cancelled. The first term $\mu_1(\mathbf{k}_2 + \dots + \mathbf{k}_n)$ cancels out with the terms $1/2[\mu_2(0, \mathbf{k}_2 + \dots + \mathbf{k}_n) + \mu_2(\mathbf{k}_2 + \dots + \mathbf{k}_n, 0)] = -\mu_1(\mathbf{k}_2 + \dots + \mathbf{k}_n)$ from the second sum. All the other terms in the second sum cancel out with such terms from the third sum

$$\begin{aligned} & 3 \frac{1}{3!} \sum_{n_2 \geq 1, n-1-n_2 \geq 1} C_{n-1}^{n_2} \mu_3(0, \mathbf{k}_2 + \dots + \mathbf{k}_{n_2+1}, \mathbf{k}_{n_2+2} + \dots + \mathbf{k}_n) - \\ & - \sum_{n_2 \geq 1, n-1-n_2 \geq 1} C_{n-1}^{n_2} \mu_2(\mathbf{k}_2 + \dots + \mathbf{k}_{n_2+1}, \mathbf{k}_{n_2+2} + \dots + \mathbf{k}_n). \end{aligned} \quad (2.3.18)$$

The number of terms in (2.3.18) is $C_{n-1}^1 + \dots + C_{n-1}^{n-2} = 2^{n-1} - 2$. The total number of terms in the second sum (2.3.13) is $1/2[C_n^1 + \dots + C_n^{n-1}] = 2^{n-1} - 1$.

We have shown how all terms μ_1 and μ_2 are cancelled in $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$. Proceeding with this process, we make sure that in the next to last sum, the terms $\mu_{n-1}(0 + \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4, \dots, \mathbf{k}_n) + \mu_{n-1}(\mathbf{k}_2, 0 + \mathbf{k}_3, \mathbf{k}_4, \dots, \mathbf{k}_n) + \dots + \mu_{n-1}(\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4, \dots, \mathbf{k}_n + 0) = (n-1)\mu_{n-1}(\mathbf{k}_2, \dots, \mathbf{k}_n)$ remain which are equal to $\mu_n(0, \mathbf{k}_2, \dots, \mathbf{k}_n)$. Thus, all terms in (2.3.14) and (2.3.13) cancel each other and $\mathfrak{M}_n(0, \mathbf{k}_2, \dots, \mathbf{k}_n) = 0$. $\square$

Now, let any of $\mathbf{k}_i$ in $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ be not equal to zero, but the closed sum $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ is reducible and decomposes into sums equal to zero. In this case, the cumulant $\mathfrak{M}_n$ differs from zero, but the number of terms is reduced.

We introduce a definition: we assume that $\mu_1(\mathbf{k}_1 + \dots + \mathbf{k}_n)$ has one argument $\mathbf{k}_1 + \dots + \mathbf{k}_n$ (one vertex), the function $\mu_2(\mathbf{k}_1 + \dots + \mathbf{k}_{n_1}, \mathbf{k}_{n_1+1} + \dots + \mathbf{k}_n)$ has two arguments (two vertices), μ_3 has three arguments (three vertices), etc. If the sum $\mathbf{k}_1 + \dots + \mathbf{k}_n$ is reducible, then the reduction of the argument occurs.

Let $\mathbf{k}_1 + \mathbf{k}_2 = 0$, $\mathbf{k}_3 + \mathbf{k}_4 + \dots + \mathbf{k}_n = 0$. Let us give examples of the correlation functions with the complete or partial reduction of one or several arguments.

The examples of the complete reduction: $\mu_2(\mathbf{k}_1 + \mathbf{k}_2, \mathbf{k}_3 + \dots + \mathbf{k}_n) = \mu_2(0, 0) = -N$; $\mu_3(\mathbf{k}_1 + \mathbf{k}_2, \mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_5 + \dots + \mathbf{k}_n) = \mu_3(0, \mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_5 + \dots + \mathbf{k}_n) = -2\mu_2(\mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_5 + \dots + \mathbf{k}_n)$; $\mu_m(\mathbf{k}_1 + \mathbf{k}_2, \mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_5, \dots, \mathbf{k}_n) = \mu_m(0, \mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_5, \dots, \mathbf{k}_n) = -(m-1)\mu_{m-1}(\mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_5, \dots, \mathbf{k}_n)$.

The examples of the functions with the partial reduction: $\mu_2(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, \mathbf{k}_4 + \dots + \mathbf{k}_n) = \mu_2(\mathbf{k}_3, \mathbf{k}_4 + \dots + \mathbf{k}_n)$; $\mu_3(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_5, \mathbf{k}_6 + \dots + \mathbf{k}_n) = \mu_3(\mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_5, \mathbf{k}_6 + \dots + \mathbf{k}_n)$.

Theorem 2. *If the closed sum $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ in the cumulant $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ is reducible, i.e., if it splits into two or several closed irreducible sums, then all the correlation functions with the partial or complete reduction of the arguments in (2.3.13) and (2.3.14) are mutually cancelled.*

Proof. Let $\mathbf{k}_1 + \dots + \mathbf{k}_{n_1} = 0$ in $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ for $n_1 \leq n - n_1$. The proof consists of the following points:

1. The function $\mu_1(\mathbf{k}_1 + \dots + \mathbf{k}_n) = \mu_1(\mathbf{k}_{n_1+1} + \dots + \mathbf{k}_n)$ is cancelled by the function $\mu_2(\mathbf{k}_1 + \dots + \mathbf{k}_{n_1}, \mathbf{k}_{n_1+1} + \dots + \mathbf{k}_n) = -\mu_1(\mathbf{k}_{n_1+1} + \dots + \mathbf{k}_n)$.

2. The partial cancellation of the functions ranging from μ_2 to μ_{n-n_1-2} occurs because μ_{n-n_1-2} has $n - n_1 - 2$ arguments and, therefore, none of them can contain the sum of the n_1 vectors $\mathbf{k}_1 + \dots + \mathbf{k}_n$.

3. Assume that there is a reduction in the corresponding correlation functions ranging from the first one to the μ_{n-n_1} function. At the same time, the functions μ_i having a partial reduction of the argument are cancelled by those μ_{i+1} functions having a complete reduction of the arguments.

4. In the sum of the correlation functions μ_{n-n_1+1} in (2.3.14), there is a single term in which the argument $\mu_{n-n_1+1}(\mathbf{k}_1 + \dots + \mathbf{k}_{n_1}, \mathbf{k}_{n_1+1}, \dots, \mathbf{k}_n)$ is completely canceled. This term will cancel all those $(n - n_1)$ functions μ_{n-n_1} , for which a partial reduction of the argument occurs $\mu_{n-n_1}(\mathbf{k}_1 + \dots + \mathbf{k}_{n_1} + \mathbf{k}_{n_1+1}, \mathbf{k}_{n_1+2}, \dots, \mathbf{k}_n) + \mu_{n-n_1}(\mathbf{k}_{n_1+1}, \mathbf{k}_1 + \dots + \mathbf{k}_{n_1} + \mathbf{k}_{n_1+2} + \dots + \mathbf{k}_n) + \dots + \mu_{n-n_1}(\mathbf{k}_{n_1+1}, \mathbf{k}_{n_1+2}, \dots, \mathbf{k}_n + \mathbf{k}_1 + \dots + \mathbf{k}_{n_1})$.

The theorem is proved. $\square$

Thus, only the cumulants $\mathfrak{M}_n$ with the irreducible sums over $\mathbf{k}$ contain the function $\mu_1(\mathbf{k}_1 + \dots + \mathbf{k}_n)$, and the cumulants with the reducible sums over $\mathbf{k}_1 + \dots + \mathbf{k}_n$ begin with μ_2 . In the case $U_0(R) = 0$, all $\mu_n = 0$ for $n > 1$, and $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0}$ with the irreducible sum $\mathbf{k}_1 + \dots + \mathbf{k}_n$ in agreement with (2.2.39). It should be noted that $U_0(R) = 0$ means the transition to the model of non-interacting particles. Therefore, the results of the previous section were obtained for the system of an ideal gas as the reference system. Hereafter, the cumulants with a reducible sum $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ will be called reducible, and the cumulants with an irreducible sum $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ will be called irreducible.

Having clarified the structure of the cumulants, we write, using (2.3.6), the original expression for the Jacobian (2.3.4)

$$J(\rho) = \int \exp \left\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \sum_{n \geq 2} D_n(\omega) \right\} (d\omega), \quad (2.3.19)$$

where $D_n(\omega)$ and the cumulants $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ are given in (2.3.7) and (2.3.14), respectively. Integrating in (2.3.19) over $(d\omega)$, we find $J(\rho)$ as an explicit function of (ρ) . To get $J(\rho)$ in the form that includes the Gaussian distribution as a zero approximation, we replace in (2.3.19) all functions $D_n(\omega)$

for $n \geq 3$ by the operators

$$\hat{D}(\partial/\partial\rho) = \frac{N}{\sqrt{N^n}} (-1)^n \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \frac{\partial^n}{\partial \rho_{\mathbf{k}_1}, \dots, \partial \rho_{\mathbf{k}_n}}.$$

Then, the integration over $(d\omega)$ is carried out as in (2.1.42). As a result, the form of the Jacobian of the transformation coincides with (2.1.43):

$$J(\rho) = \exp \left\{ \sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right\} J_G(\rho), \quad (2.3.20)$$

where $J_G(\rho) = \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \left[\frac{1}{\mathfrak{M}_2(\mathbf{k})} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \ln(\pi \mathfrak{M}_2(\mathbf{k})) \right] \right\}$ is the Gaussian approximation of the Jacobian.

2.3.2. Calculation of the configuration integral

Let us start with the calculation of the configuration integral (2.3.1). Substituting Eq. (2.1.30) for $v(\rho)$ and Eq. (2.3.20) for $J(\rho)$, we have

$$\begin{aligned} Q_N = Q_0 \int \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \alpha(k) [\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1] - \frac{1}{2} N \alpha(0) \right\} \times \\ \times \exp \left\{ \sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right\} J_G(\rho) (d\rho). \end{aligned} \quad (2.3.21)$$

Expanding the exponential $\exp \left\{ \sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right\}$, we get in zero approximation⁶

$$\begin{aligned} Q_G = Q_0 \int \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \alpha(k) [\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1] - \frac{1}{2} N \alpha(0) \right\} J_G(\rho) (d\rho) = \\ = Q_0 \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \alpha(k) - \frac{1}{2} N \alpha(0) \right\} \prod'_{\mathbf{k}} [1 + \alpha(k) \mathfrak{M}_2(\mathbf{k})]^{-1}. \end{aligned} \quad (2.3.22)$$

The following expression for the free energy corresponds to the Gaussian approximation of the configuration integral:

$$F = F_{\text{id}} - \frac{1}{\beta} \ln Q_G = F_0 + F_{\text{HTA}} + F_{\text{RPA}}, \quad (2.3.23)$$

where $F_0 = F_{\text{id}} - \frac{1}{\beta} \ln Q_0$ is the free energy of the reference system with short-range interactions;

$$\begin{aligned} F_{\text{HTA}} &= \frac{1}{2\beta} \left[N \alpha(0) + \sum_{\mathbf{k}} \alpha(k) [\mathfrak{M}_2(\mathbf{k}) - 1] \right] = \\ &= \frac{1}{2} \frac{N^2}{V} \int F_2^0(R) \Phi_2(R) (d\mathbf{R}) \end{aligned} \quad (2.3.24)$$

⁶Under condition $1 + \alpha(k) \mathfrak{M}_2(\mathbf{k}) > 0$.

is a mean value of the energy of long-range interactions, averaged over the reference system; $F_2^0(R)$ is a pair distribution function of the reference system. The expression (2.3.24), as well as the corresponding expression (2.2.23), does not almost depend on the temperature (the temperature dependence arises only through the pair distribution function $F_2^0(R)$). Therefore, we call this approximation the high-temperature approximation (HTA).

Finally, the last term associated with the Gaussian part in (2.3.20) corresponds to the random phase approximation:

$$F_{\text{RPA}} = -\frac{1}{2\beta} \sum_{\mathbf{k}}' \left[\alpha(k) \mathfrak{M}_2(\mathbf{k}) - \ln[1 + \alpha(k) \mathfrak{M}_2(\mathbf{k})] \right]. \quad (2.3.25)$$

Like (2.2.24), it can also be represented in the form (2.2.25):

$$\begin{aligned} F_{\text{RPA}} &= -\frac{1}{2\beta} \int_0^1 d\xi \sum_{\mathbf{k}}' \alpha(k) \mathfrak{M}_2(\mathbf{k}) \xi \alpha(k) \mathfrak{M}_2(\mathbf{k}) [1 + \xi \alpha(k) \mathfrak{M}_2(\mathbf{k})]^{-1} = \\ &= \frac{1}{2} \frac{N^2}{V} \int d\mathbf{R} \int_0^1 d\xi \Phi_2(R) g(R, \xi), \end{aligned} \quad (2.3.26)$$

where

$$\begin{aligned} g(R) &= \sum_{\mathbf{k}} g(\mathbf{k}) e^{i\mathbf{k}\mathbf{R}} = -\frac{1}{V} \beta \sum_{\mathbf{k}} \frac{\mathfrak{M}_2(\mathbf{k}) \nu(k) \mathfrak{M}_2(\mathbf{k})}{1 + \alpha(k) \mathfrak{M}_2(\mathbf{k})} e^{i\mathbf{k}\mathbf{R}}, \\ g(\mathbf{k}) &= -\frac{1}{N} \frac{\alpha(k) \mathfrak{M}_2(\mathbf{k}) \mathfrak{M}_2(\mathbf{k})}{1 + \alpha(k) \mathfrak{M}_2(\mathbf{k})}. \end{aligned} \quad (2.3.27)$$

The function $g(R)$ is a new screened potential which differs from that given in (2.2.18) by the contribution of the short-range forces. Screened potential (2.3.27) satisfies the Ornstein–Zernike integral equation (1.3.18) if in the latter one sets

$$c_2(R) = c_2^0(R) - \beta \Phi_2(R), \quad h_2(R) = h_2^0(R) + g(R), \quad (2.3.28)$$

where $c_2^0(R)$ and $h_2^0(R)$ are the direct and the pair correlation functions of the reference system, respectively. They are also related by the equation (1.3.18). The screened potential $g(R, \xi)$ differs from $g(R)$ only by replacing $\nu(k)$ with $\xi \nu(k)$.

We now take into account the operator part of the Jacobian of the transformation (2.3.20). We start by introducing the sum of the operators $\hat{D}(\partial/\partial\rho)$

$$\sum_{n \geq 3} \hat{D}(\partial/\partial\rho) = \sum_{n \geq 3} \hat{D}^{(1)}(\partial/\partial\rho) + \sum_{n \geq 4} \hat{D}^{(2)}(\partial/\partial\rho), \quad (2.3.29)$$

$$\hat{D}_n^{(1)}(\partial/\partial\rho) = \frac{(-1)^n}{n! \sqrt{N^{n-2}}} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_n \\ (\text{irreducible})}} \mathfrak{M}_n^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n) \frac{\partial^n}{\partial \rho_{\mathbf{k}_1} \dots \partial \rho_{\mathbf{k}_n}}, \quad (2.3.30)$$

$$\hat{D}_n^{(2)}(\partial/\partial\rho) = \frac{(-1)^n}{n!\sqrt{N^{n-2}}} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_n \\ \text{(reducible)}}} \mathfrak{M}_n^{(2)}(\mathbf{k}_1, \dots, \mathbf{k}_n) \frac{\partial^n}{\partial\rho_{\mathbf{k}_1}, \dots, \partial\rho_{\mathbf{k}_n}}, \quad (2.3.31)$$

$\mathfrak{M}_n^{(1)}$ and $\mathfrak{M}_n^{(2)}$ are the corresponding parts of the cumulants with irreducible and reducible sums over $\mathbf{k}$, respectively.

As in the previous paragraph, we expand $\exp\left\{\sum_{n \geq 3} \hat{D}(\partial/\partial\rho)\right\}$ in (2.3.21)

into a series and then the operators $\hat{D}(\partial/\partial\rho)$ are paired. Each pairing corresponds to the operator $\partial^2/\partial\rho_{\mathbf{k}}\partial\rho_{-\mathbf{k}}$, whose action on $J_G(\rho)$ leads to the appearance of the factor $\mathfrak{M}_2^{-1}(\mathbf{k})[\mathfrak{M}_2^{-1}(\mathbf{k})\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - 1]$. If we replace $\rho_{\mathbf{k}}\rho_{-\mathbf{k}}$ with $1 - \partial/\partial\alpha(k)$ the integration over the collective variables can be considered complete. The operator $1 - \partial/\partial\alpha(k)$ acts on Q_G in such a way that, according to (2.3.22), each pairing of the operators corresponds to the expression

$$\tilde{g}(k) = -\frac{1}{N} \frac{\alpha(k)}{1 + \alpha(k)\mathfrak{M}_2(\mathbf{k})}, \quad (2.3.32)$$

in which the numerator differs from the Fourier transform of the screened potential (2.3.27). For the construction of cluster expansions, first we take the screened potential

$$\tilde{g}(R) = -\frac{1}{N} \sum_{\mathbf{k}} \frac{\alpha(k)e^{i\mathbf{k}R}}{1 + \alpha(k)\mathfrak{M}_2(\mathbf{k})}, \quad (2.3.33)$$

as a basis and then we show how these expansions can be modified to be built on the potential (2.3.27). The operator part of the Jacobian of the transformation is considered in three steps. In the first step, we obtain the main topological diagrams corresponding to the cluster integrals found in the previous section without taking short-range forces into account. In the second step, we include those terms from $\sum_{n \geq 4} \hat{D}_n^{(2)}$, which, due to the inclusion of the short-range forces,

correct the expressions for the cluster integrals obtained in the first step but do not change their structure. Finally, in the third step, we take into account all those terms from $\sum_{n \geq 4} \hat{D}_n^{(2)}$ that are not considered in the first two steps.

If in (2.3.29) we omit the operators containing $\mathfrak{M}_n^{(2)}$ and use the first term for $\mathfrak{M}_n^{(1)}$ in (2.3.14), we obtain the cluster expansions found in the previous section for the configuration integral of a system with long-range interactions

$$Q_N \approx Q_G \exp[B'_2 + B'_3 + \dots], \quad (2.3.34)$$

where Q_G can be found from the expression (2.3.22), and $B'_2, B'_3, \dots$ are the cluster coefficients built on the screened potential (2.3.33) and for which the expressions (2.2.20), (2.2.21), ... are obtained.

We now use the full expression of $\mathfrak{M}_n^{(1)}$ for the operators $\hat{D}_n^{(1)}(\partial/\partial\rho)$. Again, we obtain the cluster expansions having the same structure as in (2.3.34), but each vertex becomes complex. To illustrate this we use the first term in B'_2 (2.3.34) as an example

$$-\frac{N^2}{2V^2} \frac{1}{3!} \int g^3(R_{12}) d\mathbf{R}_1 d\mathbf{R}_2. \quad (2.3.35)$$

The appearance of this term is discussed in detail in the previous paragraph. Now, in (2.2.11), we replace the Kronecker symbol $\delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, 0}$ with the full cumulants $\mathfrak{M}_3^{(1)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$. As a result, the expression (2.3.35) is replaced with a more general expression

$$\begin{aligned} \frac{1}{2 \cdot 3!} \int q^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) q^{(3)}(\mathbf{R}'_1, \mathbf{R}'_2, \mathbf{R}'_3) \tilde{g}(|\mathbf{R}_1 - \mathbf{R}'_1|) \times \\ \times \tilde{g}(|\mathbf{R}_2 - \mathbf{R}'_2|) \tilde{g}(|\mathbf{R}_3 - \mathbf{R}'_3|) d\mathbf{R}_1 d\mathbf{R}'_1 \dots d\mathbf{R}'_3, \end{aligned} \quad (2.3.36)$$

where

$$\begin{aligned} q^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = \frac{N}{V} \delta(\mathbf{R}_1 - \mathbf{R}_3) \delta(\mathbf{R}_1 - \mathbf{R}_2) + \delta(\mathbf{R}_1 - \mathbf{R}_2) \mu_2(|\mathbf{R}_1 - \mathbf{R}_3|) + \\ + \dots + \delta(\mathbf{R}_2 - \mathbf{R}_3) \mu_2(|\mathbf{R}_1 - \mathbf{R}_2|) + \mu_3(R_{12}, R_{13}, R_{23}) \end{aligned} \quad (2.3.37)$$

is a complex three-particle density.

Introducing the complex n -particle density

$$\begin{aligned} q^{(n)}(\mathbf{R}^n) = q^{(n)}(\mathbf{R}_1, \dots, \mathbf{R}_n) = \frac{N}{V} \prod_{i=2}^n \delta(\mathbf{R}_1 - \mathbf{R}_i) + \\ + \mu_2(|\mathbf{R}_1 - \mathbf{R}_2|) \prod_{i=3}^n \delta(\mathbf{R}_1 - \mathbf{R}_i) + \dots + \mu_n(\mathbf{R}_1, \dots, \mathbf{R}_n), \end{aligned} \quad (2.3.38)$$

the second cluster coefficient can be represented as

$$\begin{aligned} -\beta B_2 = \frac{1}{2} \sum_{n \geq 3} \frac{1}{n!} \int q^{(n)}(\mathbf{R}^{(n)}) q^{(n)}(\mathbf{R}'^{(n)}) \times \\ \times \prod_{i=1}^n \tilde{g}(\mathbf{R}_i - \mathbf{R}'_i) d\mathbf{R}^{(n)} d\mathbf{R}'^{(n)}, \end{aligned} \quad (2.3.39)$$

where $d\mathbf{R}^{(n)} = d\mathbf{R}_1, \dots, d\mathbf{R}_n$, $d\mathbf{R}'^{(n)} = d\mathbf{R}'_1, \dots, d\mathbf{R}'_n$.

Similar results can be obtained for the higher-order cluster coefficients. According to the n -particle density $q^{(n)}(\mathbf{R}^{(n)})$, we introduce the notion of the n -order field vertex. The operation $\int d\mathbf{R}^{(n)} q^{(n)}(\mathbf{R}^{(n)})$, $n \geq 3$ is called a n -order field vertex. The operation $N/V \int d\mathbf{R}$, as before, is called a zero-order vertex. Thus, if we restrict ourselves in the Jacobian $J(\rho)$ to the irreducible

cumulants, we obtain a cluster expansion (2.3.34) for free energy, in which the cluster integrals and the corresponding diagrams have a topological structure of the expressions as that obtained in the previous section. However, the composite field vertices appear instead of simple vertices. Next, in (2.3.21), we consider the operators $\hat{D}_n^{(2)}$ with the reducible cumulants.

First, we supplement the expansion (2.3.34) with the diagrams which are topologically equivalent from the point of view of the arrangement structure of the functions $\tilde{g}(R)$. We start with diagrams with two field vertices corresponding to the expression (2.3.39) for the second cluster coefficient. The cumulants $\mathfrak{M}_n^{(2)}$, unlike $\mathfrak{M}_n^{(1)}$, begin with μ_2 . The function μ_2 has two arguments and the diagram built on this function has two field vertices.

Let us perform detailed calculations of the first term B'_2 for which there are equations (2.3.35) and (2.3.36). The expression (2.3.35) corresponds to the result of the action of the first term of the operator $\hat{D}_6^{(2)}$

$$\frac{1 \cdot 5 \cdot 3 \cdot 4}{6!} \frac{1}{N^3} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} \mu_2(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3) \times \\ \times \frac{\partial^2}{\partial \rho_{\mathbf{k}_1} \partial \rho_{-\mathbf{k}_1}} \frac{\partial^2}{\partial \rho_{\mathbf{k}_2} \partial \rho_{-\mathbf{k}_2}} \frac{\partial^2}{\partial \rho_{\mathbf{k}_3} \partial \rho_{-\mathbf{k}_3}},$$

in which the derivatives with respect to the collective variables are fully paired. The coefficient $5 \cdot 3$ is equal to the number of pairs by two types $\mathbf{k}_1, -\mathbf{k}_1$, $\mathbf{k}_2, -\mathbf{k}_2$, $\mathbf{k}_3, -\mathbf{k}_3$, which can be performed in the product of six sums over $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4, \mathbf{k}_5, \mathbf{k}_6$, and the factor 4 is equal to the number of the correlation functions $\mu_2(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3)$ included in $\mathfrak{M}_6^{(2)}$. Matching each derivative with the result of its action, we finally obtain

$$\frac{N^2}{2V^2} \frac{1}{3 \cdot 2} \int \tilde{g}^3(R_{12}) [F_2^0(R_{12}) - 1] d\mathbf{R}_1 d\mathbf{R}_2,$$

where $F_2^0(R_{12})$ is the pair distribution function of the reference system. Similar calculations can be carried out for the other terms of B_2 . Thus, sets of paired operators

$$\frac{1}{2} [\hat{D}_3^{(1)} \hat{D}_3^{(1)} + \dots + \hat{D}_n^{(1)} \hat{D}_n^{(1)} + \dots], \quad (2.3.40)$$

forming the second cluster coefficient (2.3.39) correspond to the sum of the operators

$$\hat{D}_6^{(2)} + \hat{D}_8^{(2)} + \dots + \hat{D}_{2n}^{(2)} + \dots, \quad (2.3.41)$$

with fully paired derivatives with respect to the collective variables in each $\hat{D}_{2n}^{(2)}$. However, in this case, (2.3.41) includes more terms than it is necessary to establish the correspondence with (2.3.40). Thus, we first combine the

main terms in (2.3.40) with the corresponding terms in (2.3.41). The terms in (2.3.40)

$$\frac{1}{2} \sum_{n \geq 3} \frac{1}{n!} \frac{1}{N^n} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mu_1(\mathbf{k}_1 + \dots + \mathbf{k}_n) \mu_1(-\mathbf{k}_1 - \mathbf{k}_2 - \dots - \mathbf{k}_n) \times \\ \times \frac{\partial^2}{\partial \rho_{\mathbf{k}_1} \partial \rho_{-\mathbf{k}_1}} \dots \frac{\partial^2}{\partial \rho_{\mathbf{k}_n} \partial \rho_{-\mathbf{k}_n}} \quad (2.3.42)$$

correspond to the terms in (2.3.41)

$$\sum_{n \geq 3} \frac{(2n-1)!!}{(2n)!} \frac{1}{N^n} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} 2^{n-1} \mu_2(\mathbf{k}_1 + \dots + \mathbf{k}_n, -\mathbf{k}_1 - \mathbf{k}_2 - \dots - \mathbf{k}_n) \times \\ \times \frac{\partial^2}{\partial \rho_{\mathbf{k}_1} \partial \rho_{-\mathbf{k}_1}} \dots \frac{\partial^2}{\partial \rho_{\mathbf{k}_n} \partial \rho_{-\mathbf{k}_n}}. \quad (2.3.43)$$

The action of this operator leads to the expression

$$\frac{N^2}{2V^2} \int [F_2^0(R_{12}) - 1] \sum_{n \geq 3} \frac{1}{n!} (-1)^n \tilde{g}^n(R_{12}) d\mathbf{R}_1 d\mathbf{R}_2. \quad (2.3.44)$$

Summing up the result of the action of operators (2.3.42) and (2.3.43), we arrive at the following expression for the second cluster coefficient:

$$B_2 = \frac{N^2}{2V^2} \int F_2^0(R_{12}) \left[e^{\tilde{g}(R_{12})} - 1 - \tilde{g}(R_{12}) - \frac{1}{2!} \tilde{g}^2(R_{12}) \right] d\mathbf{R}_1 d\mathbf{R}_2. \quad (2.3.45)$$

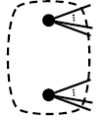
This formula establishes the correspondence between the terms from (2.3.40) which are proportional to the product $\mu_1 \mu_1$, and the first terms from (2.3.41), which are proportional to μ_2 . For the other terms in (2.3.40), there are also corresponding terms in (2.3.41). Taking them into account leads to the formation of composite vertices. The formula (2.3.45) is very interesting. The pair distribution function of short-range interactions leaves its mark on the entire pair correlation caused by the long-range interactions.

In (2.3.42) and (2.3.43), only the first terms for each operator are considered in (2.3.40) and (2.3.41). A similar situation arises for more complex correlations. In this case, the calculations are rather cumbersome; to make them more visual, we use the following diagrammatic representations. The function $\mu_1(\mathbf{k}_1 + \dots + \mathbf{k}_n)$ is matched with the vertex from which n rays are emitted:

$$\mu_1(k_1 + \dots + k_n) = \begin{array}{c} \diagup \\ \diagdown \end{array}.$$

We match the function $\mu_2(\mathbf{k}_1 + \dots + \mathbf{k}_{n_1}, \mathbf{k}_{n_1+1} + \dots + \mathbf{k}_n)$ with two vertices outlined by a dashed closed contour, from which n_1 rays and $n - n_1$ rays are

emitted, respectively:



A segment representing two paired rays is matched to the two paired values $\mathbf{k}$ and $-\mathbf{k}$. The thin line connecting the two vertices represents a screened potential $\tilde{g}(R)$. The set of n lines $\tilde{g}(R)$ connecting two field vertices is associated with the inverse factorial $1/n!$. In addition, each field vertex corresponds to the integral $N/V \int d\mathbf{R}$. A rectangle with two vertices inside represents the pair distribution function $F_2^0(R_{12})$: $F_2^0(R_{12}) = \boxed{\bullet \bullet}$, $F_3^0(R_1, R_2, R_3) = \boxed{\bullet \bullet \bullet}$ represents the ternary distribution function, etc.

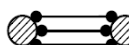
According to the notation for the sum of expressions obtained as a result of the action of the operators (2.3.42) and (2.3.43), the equation (2.3.45) can be represented diagrammatically

$$\begin{aligned} \frac{1}{2}(\text{diagram 1} + \text{diagram 2} + \dots) + \frac{1}{2}(\text{diagram 3} + \text{diagram 4} + \dots) = \\ = \frac{1}{2}(\boxed{\text{diagram 1}} + \boxed{\text{diagram 2}} + \dots). \end{aligned} \quad (2.3.46)$$

Now consider the diagrams for composite vertices. We restrict ourselves to the first term of the second cluster coefficient. The diagrammatic representations of the integrals (2.3.36) have the following form⁷:

$$\begin{aligned} \frac{1}{2} \left\{ \text{diagram 1} + \frac{1}{2} \left[\text{diagram 2} + \text{diagram 3} \right] + \frac{1}{3!} \left[\text{diagram 4} + \text{diagram 5} \right] + \text{diagram 6} + \right. \\ \left. + \text{diagram 7} + \frac{1}{2} \left[\text{diagram 8} + \text{diagram 9} \right] + \frac{1}{3!} \left[\text{diagram 10} \right] \right\}. \end{aligned} \quad (2.3.47)$$

Each diagram in (2.3.47) can be matched with a diagram resulting from the action of the operator $\hat{D}_6^{(2)}$. These diagrams contain correlation functions, the order of which is equal to the sum of the orders of the correlation functions included in the corresponding diagrams in (2.3.47). Thus, one should add to

⁷Here one could introduce a complex vertex of the type  and write the sum of all diagrams (2.3.36) by one diagram  (see (2.3.92)).

(2.3.47) the series of the following diagrams:

$$\begin{aligned}
 & \frac{1}{2} \left\{ \text{diagram 1} + \frac{1}{2} \left[\text{diagram 2} + \text{diagram 3} \right] + \frac{1}{3!} \left[\text{diagram 4} + \text{diagram 5} \right] + \right. \\
 & \left. + \frac{1}{2} \left[\text{diagram 6} + \text{diagram 7} + \text{diagram 8} \right] + \frac{1}{4 \cdot 3!} \left[\text{diagram 9} \right] \right\}. \quad (2.3.48)
 \end{aligned}$$

Having added the formulas (2.3.47) and (2.3.48), we obtain a new complete expression which should be written instead of $\frac{N^2}{2V^2} \int \tilde{g}^3(R_{12}) d\mathbf{R}_1 d\mathbf{R}_2$ in the second cluster coefficient

$$\begin{aligned}
 & \frac{1}{2} \left\{ \text{diagram 1} + 2 \left[\text{diagram 2} + \text{diagram 3} \right] + \frac{2}{3!} \left[\text{diagram 4} + \text{diagram 5} \right] + \left[\text{diagram 6} + \right. \right. \\
 & \left. + \frac{1}{2} \left[\text{diagram 7} \right] + \left[\text{diagram 8} + \frac{1}{2} \left[\text{diagram 9} \right] + \left[\text{diagram 10} + \frac{1}{2} \left[\text{diagram 11} \right] + \right. \right. \\
 & \left. \left. + \frac{1}{3!} \left[\text{diagram 12} + \frac{1}{4} \left[\text{diagram 13} \right] \right] \right] \right\}.
 \end{aligned}$$

The first diagram has already been studied, and the other diagrams are more complex. For example, the second addend has the following analytical form:

$$\int \left[\mu_3(\mathbf{R}_1, \mathbf{R}'_1, \mathbf{R}_2) + \frac{N}{V} \mu_2(\mathbf{R}_1, \mathbf{R}'_1) \right] \frac{1}{2} \tilde{g}^2(R_{12}) \tilde{g}(|\mathbf{R}'_1 - \mathbf{R}_2|) d\mathbf{R}_1 d\mathbf{R}'_1 d\mathbf{R}_2.$$

The function $\mu_3(\mathbf{R}_1, \mathbf{R}'_1, \mathbf{R}_2) + \frac{N}{V} \mu_2(\mathbf{R}_1, \mathbf{R}'_1) = \frac{N^3}{V^3} [F_3(\mathbf{R}_1, \mathbf{R}'_1, \mathbf{R}_2) - F_2(R_{12}) - F_2(\mathbf{R}'_1, \mathbf{R}_2) + 1]$ reduces to $\frac{N}{V} \mu_2(\mathbf{R}_1, \mathbf{R}'_1)$ in the asymptotic case $\mathbf{R}_2 \rightarrow \infty$ and to zero when $\mathbf{R}_1$ or $\mathbf{R}'_1$ increases. For $\mathbf{R}_2 - \mathbf{R}'_1 \rightarrow 0$ it is proportional to $F_2(\mathbf{R}'_1, \mathbf{R}_2) - 1$. Similar reasoning is valid for the remaining terms arising from (2.3.41) and, in general, for B_2 . Summing up the calculation of the second cluster coefficient, we write B_2 in the form:

$$B_2 = \frac{1}{2} \left\{ \text{diagram 1} + \left(\text{diagram 2} - \text{diagram 3} \right) + \left(\text{diagram 4} - \text{diagram 5} \right) + \right.$$

$$\begin{aligned}
 & + \frac{1}{2} \left[\left(\text{diagram 1} - \text{diagram 2} \right) + \frac{1}{2} \left(\text{diagram 3} - \text{diagram 4} \right) \right] + \\
 & + \left(\text{diagram 5} + \frac{1}{2} \text{diagram 6} \right) + \frac{2}{3} \left(\text{diagram 7} + \text{diagram 8} \right) + \\
 & + \left(\text{diagram 9} + \frac{1}{2} \text{diagram 10} \right) + \frac{1}{3!} \left(\text{diagram 11} + \frac{1}{4} \text{diagram 12} \right) + \dots \Big\}, \quad (2.3.49)
 \end{aligned}$$

where

$$\begin{aligned}
 \text{---} &= e^{\tilde{g}(R)} - 1, \\
 \text{---} \perp &= e^{\tilde{g}(R)} - 1 - \tilde{g}(R), \\
 \text{---} \# &= e^{\tilde{g}(R)} - 1 - \tilde{g}^2(R).
 \end{aligned}$$

The above described is also true for the third cluster coefficient. When considering B_3 , we restrict ourselves to the most important points. Equation (2.2.14) gives the initial topological expression, which corresponds to the sum of the diagrams with three vertices and thin lines $\tilde{g}(R)$ connecting them. Simultaneously, three or more lines emerge from each vertex. Take one of these diagrams and bring it to a new form taking into account the complex vertices and the corresponding terms in the reducible cumulants. Let this be a diagram



. To build all the diagrams corresponding to it, consider the sum of paired operators $\frac{1}{3!} 3\hat{D}_3^{(1)}\hat{D}_3^{(1)}\hat{D}_1^{(1)} + 2\frac{1}{2}[\hat{D}_3^{(1)}\hat{D}_7^{(2)} + \hat{D}_4^{(1)}\hat{D}_6^{(2)}] + \hat{D}_{10}^{(2)}$ where the three-vertex term is taken in the term $\hat{D}_{10}^{(2)}$ with fully paired derivatives. In the diagrammatic representation, we have

$$\begin{aligned}
 & \frac{1}{2} \left[\left(\leftarrow + \dots \right) \left(\leftarrow + \dots \right) \left(\leftarrow + \dots \right) \right] + \left[\left(\leftarrow + \dots \right) \left(\text{diagram 1} + \dots \right) \right] + \\
 & + \left[\left(\text{diagram 2} + \dots \right) \left(\text{diagram 3} + \dots \right) \right] + \left[\left(\text{diagram 4} + \dots \right) \right], \quad (2.3.50)
 \end{aligned}$$

where dots denote the diagrams arising from the first diagram by complicating the vertices⁸.

⁸For example, $\left\{ \leftarrow + \dots \right\} = \left\{ \leftarrow + 3 \left(\text{diagram 1} \right) + \left(\text{diagram 2} \right) \right\}$.

Having made pairing, we have

$$\frac{1}{2} \left[\text{triangle} + \dots \right] + \left[\text{triangle with dashed line} + \dots \right] + \frac{1}{2} \left[\text{triangle with dashed line} + \dots \right] + \frac{1}{2} \text{triangle with dashed line} + \dots \quad (2.3.51)$$

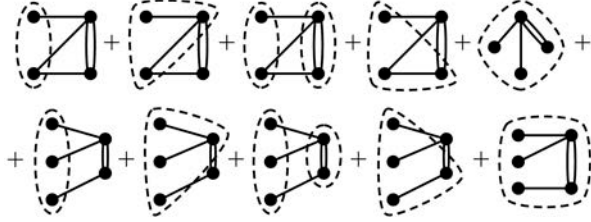
Taking into account that

$$\begin{aligned} \mu_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) &= \frac{N(N-1)(N-2)}{V^3} F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - \\ &- \mu_2(\mathbf{R}_1, \mathbf{R}_2) \mu_1(\mathbf{R}_3) - \mu_2(\mathbf{R}_1, \mathbf{R}_3) \mu_1(\mathbf{R}_2) - \\ &- \mu_2(\mathbf{R}_2, \mathbf{R}_3) \mu_1(\mathbf{R}_1) - \mu_1(\mathbf{R}_1) \mu_1(\mathbf{R}_2) \mu_1(\mathbf{R}_3), \end{aligned}$$

and summing up all four diagrams, explicitly written in (2.3.51), we obtain

$$\boxed{\text{triangle}} + \dots \quad (2.3.52)$$

The dots in (2.3.51) and (2.3.52) denote summation of the diagrams containing composite vertices. For example, complicating the left-hand vertex is equal to the sum of the diagrams



Summing up the calculation of the third cluster coefficient, we write down its principal value

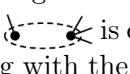
$$\begin{aligned} B_3^{(1)} &= \boxed{\text{triangle with internal lines}} + 3 \boxed{\text{triangle with internal lines}} = \\ &= \frac{1}{6} \frac{N^2}{2V^2} \int F_3^0(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \left[\left(e^{\tilde{g}(R_{12})} - 1 - \tilde{g}(R_{12}) \right) \times \right. \\ &\quad \times \left(e^{\tilde{g}(R_{13})} - 1 - \tilde{g}(R_{13}) \right) \left(e^{\tilde{g}(R_{23})} - 1 - \tilde{g}(R_{23}) \right) + \\ &\quad + 3\tilde{g}(R_{12}) \left(e^{\tilde{g}(R_{13})} - 1 - \tilde{g}(R_{13}) \right) \times \\ &\quad \left. \times \left(e^{\tilde{g}(R_{23})} - 1 - \tilde{g}(R_{23}) \right) \right] d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3. \end{aligned} \quad (2.3.53)$$

Complicating the vertices means rearranging the cluster series and adding to the lower-order cluster coefficients the diagrams containing more field vertices than in the given cluster coefficient. In particular, the diagrams with three field vertices in (2.3.49) could be added to the diagrams (2.3.53) for the third cluster coefficient.

Let us finally pass to the third step of the calculation of the configuration integral. In this step, the terms not taken into account before in the reducible cumulants $\mathfrak{M}_n^{(2)}$ will be considered. We start with the terms containing the functions μ_2 . Here, we have not taken into account the correlation functions μ_2 , in which at least one vertex consists of the sum of only two vectors $\mathbf{k}$, for example, $\mathbf{k}_1 + \mathbf{k}_2$, and at least for one of them, for example, $\mathbf{k}_2$, there is a paired vector $-\mathbf{k}_2$ in another vertex. The corresponding terms have the following diagrammatic representation:

$$\text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \dots + \text{---} \text{---} \text{---} + \dots + \quad (2.3.54)$$

plus the diagrams resulting from the replacement of simple vertices with composite vertices containing the same number of thin lines and, accordingly, the correlation functions of higher-order.

The first diagram in (2.3.54) arises under the action of the operator $\hat{D}_4^{(2)}(\partial/\partial\rho)$, more precisely, the operator $\sum_{\mathbf{k}_1, \mathbf{k}_2} \frac{3 \cdot 2}{4!} \frac{1}{N^2} \mu_2(\mathbf{k}_1 + \mathbf{k}_2, -\mathbf{k}_1 - \mathbf{k}_2) \times \frac{\partial^2}{\partial \rho_{\mathbf{k}_1} \partial \rho_{-\mathbf{k}_1}} \frac{\partial^2}{\partial \rho_{\mathbf{k}_2} \partial \rho_{-\mathbf{k}_2}} \text{---}$ leads to the diagram in $\hat{D}_4^{(2)}$. Since μ_3 and μ_4 are taken into account in $\hat{D}_4^{(2)}$, this leads to the diagrams  and , corresponding to the first diagram (2.3.54), but having composite field vertices. The second diagram in (2.3.54) arises under the action of the operator $\hat{D}_5^{(2)}$. The diagram  is contained in the operator $\hat{D}_2^{(6)}$, etc. Further, there are terms beginning with the functions μ_3 in a set of the diagrams which were not taken into account before:

$$\text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \dots + \text{---} \text{---} \text{---} + \dots + \quad (2.3.55)$$

plus the diagram containing the same number of lines $\tilde{g}(R)$, but having more complex vertices and, accordingly, more complex correlation functions.

Then, there are diagrams starting with μ_4 :

$$\text{---} \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} \text{---} + \dots + \text{---} \text{---} \text{---} \text{---} + \dots + \quad (2.3.56)$$

plus the diagrams with the same number of lines $\tilde{g}(R)$, but with more complex vertices, etc.

All mentioned diagrams are chain diagrams. Among them there are “ring” diagrams

$$\text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \dots \equiv \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \dots + \text{---} \text{---} \text{---} + \dots, \quad (2.3.57)$$

in which all derivatives are paired, and the diagrams

$$\begin{aligned} & \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \dots + \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \dots + \text{---} \text{---} \text{---} + \\ & + \dots + \text{---} \text{---} \text{---} + \dots + \text{---} \text{---} \text{---} + \dots + \text{---} \text{---} \text{---} + \dots, \quad (2.3.58) \end{aligned}$$

which, in addition to the paired derivatives, contain free ends. The number of the latter can be three, as in $\hat{D}_3^{(1)}$, or four as in $\hat{D}_4^{(1)}$, etc. Regardless of the number of free ends, all diagrams are topologically similar. There are also diagrams of a mixed type in addition to the diagrams (2.3.57) and (2.3.58), for example $\text{---} \text{---} \text{---}$, containing the elements of the chain diagrams as well as the pairs of the field vertices with two or more thin lines between the vertices.

Although the chain- and mixed-type diagrams do not arise under the action of the operators $\hat{D}_n^{(1)}(\partial/\partial\rho)$, they can be added to the cluster coefficients considered previously. The fully paired diagrams (2.3.57) are added in (2.3.56) to the second, third, etc. cluster coefficients, respectively. The diagrams (2.3.58) with unpaired ends first should be paired with $\hat{D}_n^{(1)}$ as well as between themselves. Depending on the number of the field vertices that have arisen, they must be added to the corresponding cluster coefficient. As a result, collecting all paired diagrams into groups according to the number of the field vertices, regardless of the type of functions connecting these vertices, we arrive at a cluster expansion for the free energy:

$$F = F_0 + F_{\text{HTA}} + F_{\text{RPA}} - \frac{1}{\beta}(B_2 + B_3 + \dots), \quad (2.3.59)$$

where F_{HTA} and F_{RPA} are given in (2.3.24) and (2.3.25), respectively, and

$$\begin{aligned} B_2 = \frac{1}{2} \frac{N^2}{V} \int \left[F_2^0(R) \left(e^{g(R)} - 1 - g(R) - \frac{1}{2}g^2(R) \right) + \right. \\ \left. + \frac{1}{2}g^2(R)h_2^0(R) \right] d\mathbf{R} \end{aligned} \quad (2.3.60)$$

is the second cluster coefficient,

$$B_3 = \frac{N^3}{6V^2} \int \left\{ F_3^0(R_{12}, R_{13}, R_{23}) \left[e^{g(R_{12})} - 1 + 2g(R_{12}) \right] \left[e^{g(R_{13})} - 1 - g(R_{13}) \right] \times \right.$$

$$\begin{aligned}
 & \times \left[e^{g(R_{23})} - 1 - g(R_{23}) \right] + 3[F_3^0(R_{12}, R_{13}, R_{23}) - F_2^0(R_{13})F_2^0(R_{32})] \times \\
 & \times \left[e^{g(R_{13})} - 1 \right] \left[e^{g(R_{32})} - 1 \right] + h_3^0(R_{12}, R_{13}, R_{23})g(R_{12})g(R_{13})g(R_{23}) + \\
 & + 3[F_3^0(R_{12}, R_{13}, R_{23}) - F_2^0(R_{32})]g(R_{12})g(R_{13}) \left[e^{g(R_{23})} - 1 - g(R_{23}) \right] \Big\} \times \\
 & \times d\mathbf{R}_{12}d\mathbf{R}_{13}. \tag{2.3.61}
 \end{aligned}$$

Comparing (2.3.60) and (2.3.61) with (2.3.45) and (2.3.53), we see that the second cluster coefficient in (2.3.60), when compared with (2.3.45), has only one additional term describing a ring diagram from $\hat{D}_4^{(2)}$. However, the number of additional terms increases sharply starting from the third cluster coefficient. The first term in (2.3.61) represents the diagrams determining the topology of the third cluster coefficient, the second term represents the diagrams which determine the second cluster coefficient with one composite vertex, the third term is related to chain diagrams of the ring type, and the fourth term represents the chain diagrams which are paired with the operators $\hat{D}_n^{(1)}$ in such a way that the diagrams have three field vertices.

2.3.3. Discussion of the obtained results

Comparing the cluster expansions (2.2.56) and (2.3.59), we see that they have the same structure, but the expressions for individual terms are different. Instead of F_{id} in (2.2.56) and (2.3.59), we have F_0 , free energy of the reference system. For the high-temperature approximation F_{HTA} , instead of averaging in (2.2.23) over the ideal distribution, the average in (2.3.24) is performed over the reference system. There are also some significant differences in the structure of the viral coefficients. The main difference is that the distribution functions of the reference system enter (2.3.60) and (2.3.61) as multipliers that simultaneously include all the coordinates of the functions describing the long-range correlations. For example, the second cluster coefficient in (2.3.60) contains the product $F_2^0(R)(e^{g(R)} - 1 - g(R) - \frac{1}{2}g^2(R))$, which due to the presence of $F_2^0(R)$, vanishes at small distances. At the same time, in (2.2.57), there is an expression $e^{-\beta\varphi_2(R)+g(R)} - 1 - g(R) - \frac{1}{2}g^2(R)$ in which the contribution from the last two terms at small distances can be overestimated. This is undoubtedly an important advantage of formulas (2.3.60) and (2.3.61) that eliminates the necessity for various artificial methods of regularization at small distances. However, in (2.3.60) and (2.3.61), there are also a number of diagrams that are “non-standard” from the point of view of the topology of cluster expansions. These are the terms associated with the composite field vertices and the chain diagrams.

A characteristic feature of the expansions (2.3.59) as compared with (2.2.56) is the presence of two screened potentials. The former, (2.3.27), describes the work of screening (2.3.26), and the latter, (2.3.33), is the basis for constructing the cluster coefficients (2.3.60) and (2.3.61). Since the Fourier transforms of these screened potentials differ only in their numerators, to pair the operators $\hat{D}_n(\partial/\partial\rho)$ in order to obtain the expression (2.3.27), we represent them in the form [69, 70]:

$$\begin{aligned} \hat{D}_n(\partial/\partial\rho) = & \frac{(-1)^n}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \frac{N}{\sqrt{N^n}} \tilde{\mathfrak{M}}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \times \\ & \times \prod_{i=1}^n \mathfrak{M}_2(\mathbf{k}_i) \frac{\partial^n}{\partial \rho_{\mathbf{k}_1}, \dots, \partial \rho_{\mathbf{k}_n}}. \end{aligned} \quad (2.3.62)$$

In this case, the cumulants $\mathfrak{M}_2(k)$ are included in the pairing, and the multi-particle cumulants $\tilde{\mathfrak{M}}_n$ are replaced with

$$\tilde{\mathfrak{M}}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = \mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \left[\prod_{i=1}^n \mathfrak{M}_2(k_i) \right]^{-1}. \quad (2.3.63)$$

Now, the cluster coefficients will be constructed on the screened potential (2.2.27), but the new cumulants $\tilde{\mathfrak{M}}_n^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n)$ being taken into account, makes it complicated to construct cluster expansions. In accordance with (2.3.63), we set for the irreducible part of the cumulants

$$\tilde{\mathfrak{M}}_n^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0} [1 + \Delta \tilde{\mathfrak{M}}_n^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n)], \quad (2.3.64)$$

where $\Delta \tilde{\mathfrak{M}}_n^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \mathfrak{M}_n^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n) \left[\prod_{i=1}^n \mathfrak{M}_2(k_i) \right]^{-1} - 1$.

In particular,

$$\begin{aligned} \Delta \tilde{\mathfrak{M}}_3^{(1)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = & \rho^2 [h_3^0(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) - h_2^0(\mathbf{k}_1) h_2^0(\mathbf{k}_2) - \\ & - h_2^0(\mathbf{k}_1) h_2^0(\mathbf{k}_3) - h_2^0(\mathbf{k}_2) h_2^0(\mathbf{k}_3) - \rho h_2^0(\mathbf{k}_1) h_2^0(\mathbf{k}_2) h_2^0(\mathbf{k}_3)] \times \\ & \times [1 - \rho(h_2^0(\mathbf{k}_1) + h_2^0(\mathbf{k}_2) + h_2^0(\mathbf{k}_3)) + \rho^2(h_2^0(\mathbf{k}_1) h_2^0(\mathbf{k}_2) + \dots) + \dots]. \end{aligned}$$

In the simplest approximation, known as the convolution approximation [71], $\Delta \tilde{\mathfrak{M}}_n^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n) = 0$. In this approximation, in the diagrams corresponding to $\hat{D}_n^{(1)}$ all field vertices are simple vertices. Since $\Delta \tilde{\mathfrak{M}}_n^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n)$ is taken into account, this leads to the complication of the vertices.

When considering the reduced cumulants, as before, we divide the correlation functions into two groups: $\tilde{\mathfrak{M}}_n^{(2)} = \tilde{\mathfrak{M}}_{n,1}^{(2)} + \tilde{\mathfrak{M}}_{n,2}^{(2)}$. The first group includes those correlation functions that, without changing the structures of cluster

coefficients, introduce the corresponding distribution functions under the integrals. The order of the distribution functions is determined by the number of fixed vertices of the integrand. The second group includes the correlation functions that lead to the formation of the chain diagrams. In both groups, the part corresponding to the convolution approximation which does not lead to the complication of field vertices is distinguished. We start with the diagrams of the first type. For the second cluster coefficient, we need the correlation functions $\mu_2(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3), \dots, \mu_2(\mathbf{k}_1 + \dots + \mathbf{k}_n, -\mathbf{k}_1 - \dots - \mathbf{k}_n)$ which are included in $\tilde{\mathfrak{M}}_{n,2}^{(2)}$ for $n \geq 3$.

For the third cluster coefficient, both the correlation functions μ_2 with partially paired arguments $\mu_2(\mathbf{k}_1 + \mathbf{k}'_1 + \mathbf{k}'_2, -\mathbf{k}'_1 - \mathbf{k}'_2 + \mathbf{k}_3 + \mathbf{k}_3), \dots, \mu_2(\mathbf{k}_1 + \mathbf{k}'_1 + \dots + \mathbf{k}_n, -\mathbf{k}'_1 - \dots - \mathbf{k}'_n + \mathbf{k}_3 + \mathbf{k}_3)$ and the correlation functions $\mu_3(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_1 + \mathbf{k}_4 + \mathbf{k}_5, -\mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4 - \mathbf{k}_5)$ with fully paired arguments are necessary. The general rule for the selection of the first type of diagrams consists in singling out the correlation functions from $\tilde{\mathfrak{M}}_n^{(2)}$ having at least the sum of three vectors $\mathbf{k}$ in each vertex. Therefore, this selection starts with $\tilde{\mathfrak{M}}_6^{(2)}$. Thus, for $\tilde{\mathfrak{M}}_{6,1}^{(2)}$, we set

$$\begin{aligned} \tilde{\mathfrak{M}}_{6,1}^{(2)}(\mathbf{k}_1, \dots, \mathbf{k}_6) = & \frac{1}{2} C_6^3 3 \mu_2(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_1 + \mathbf{k}_4 + \mathbf{k}_5) \delta_{\mathbf{k}_1 + \mathbf{k}_6, 0} + \\ & + \frac{1}{2} C_6^3 \cdot 2 \cdot 3 \mu_2(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3) \times \\ & \times \delta_{\mathbf{k}_1 + \mathbf{k}_4, 0} \delta_{\mathbf{k}_2 + \mathbf{k}_5, 0} + \Delta \tilde{\mathfrak{M}}_{6,1}^{(2)}, \end{aligned} \quad (2.3.65)$$

where $\Delta \tilde{\mathfrak{M}}_{6,1}^{(2)}$ is the part of $\tilde{\mathfrak{M}}_{6,1}^{(2)}$ that remains.

Similarly, $\tilde{\mathfrak{M}}_{7,1}^{(2)}$ and $\tilde{\mathfrak{M}}_{8,1}^{(2)}$ can be represented. The cumulants $\tilde{\mathfrak{M}}_{9,1}^{(2)}, \tilde{\mathfrak{M}}_{10,1}^{(2)}, \tilde{\mathfrak{M}}_{11,1}^{(2)}$ are expressed through μ_2 and μ_3 . In general, the cumulants $\tilde{\mathfrak{M}}_{3m,1}^{(2)}, \tilde{\mathfrak{M}}_{3m+1,1}^{(2)}, \tilde{\mathfrak{M}}_{3m+2,1}^{(2)}$ are expressed in terms of $\mu_2, \mu_3, \dots, \mu_m$. For example,

$$\begin{aligned} \tilde{\mathfrak{M}}_{10,1}^{(2)}(\mathbf{k}_1, \dots, \mathbf{k}_{10}) = & \frac{3 \cdot 7}{2} C_{10}^2 \mu_2(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_1 + \mathbf{k}_5 + \dots + \mathbf{k}_{10}) \delta_{\mathbf{k}_1 + \mathbf{k}_4, 0} + \dots + \\ & + \frac{5}{2} \cdot 5 C_{10}^5 \mu_2(\mathbf{k}_1 + \dots + \mathbf{k}_5, -\mathbf{k}_1 + \mathbf{k}_7 + \dots + \mathbf{k}_{10}) \delta_{\mathbf{k}_1 + \mathbf{k}_6, 0} + \\ & + \frac{1}{2} 3 \cdot 6 \cdot 7 C_{10}^3 \mu_2(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_6 + \dots + \mathbf{k}_{10}) \delta_{\mathbf{k}_1 + \mathbf{k}_4, 0} \delta_{\mathbf{k}_2 + \mathbf{k}_5, 0} + \dots + \\ & + \frac{5 \cdot 4}{2} C_{10}^5 C_5^2 \mu_2(\mathbf{k}_1 + \dots + \mathbf{k}_5, -\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_8 + \dots + \mathbf{k}_{10}) \delta_{\mathbf{k}_1 + \mathbf{k}_6, 0} \delta_{\mathbf{k}_2 + \mathbf{k}_7, 0} + \dots + \\ & + \frac{5!}{2} C_{10}^5 \mu_2(\mathbf{k}_1 + \dots + \mathbf{k}_5, -\mathbf{k}_1 - \dots - \mathbf{k}_5) \delta_{\mathbf{k}_1 + \mathbf{k}_6, 0} \delta_{\mathbf{k}_5 + \mathbf{k}_{10}, 0} + \dots + \\ & + 4 C_{10}^3 C_7^3 \mu_3(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_1 + \mathbf{k}_5 + \mathbf{k}_6, -\mathbf{k}_5 + \mathbf{k}_8 + \dots + \mathbf{k}_{10}) \times \\ & \times \delta_{\mathbf{k}_1 + \mathbf{k}_4, 0} \delta_{\mathbf{k}_5 + \mathbf{k}_7, 0} + \dots \end{aligned} \quad (2.3.66)$$

Since the correlation functions of the first type considered in detail in the previous subsection are taken into account, this leads to the cluster coefficients of the form (2.3.60) but with a screened potential (2.3.27) and the complication of vertices due to $\Delta\tilde{\mathfrak{M}}_n^{(1)}$ and $\Delta\tilde{\mathfrak{M}}_{n,1}^{(1)}$. Consider now the correlation functions of the second type associated with the formation of the chain diagrams. The cumulants of the second type begin with $\tilde{\mathfrak{M}}_{4,2}^{(2)}$, for which, according to (2.3.63), we set

$$\tilde{\mathfrak{M}}_{4,2}^{(2)}(\mathbf{k}_1, \dots, \mathbf{k}_4) = C_4^2 \mu_2(\mathbf{k}_1 + \mathbf{k}_2, -\mathbf{k}_1 - \mathbf{k}_2) + \Delta\tilde{\mathfrak{M}}_{4,2}^{(2)}(\mathbf{k}_1, \dots, \mathbf{k}_4). \quad (2.3.67)$$

We can obtain similar expressions for the higher-order cumulants, for example,

$$\begin{aligned} \tilde{\mathfrak{M}}_{6,2}^{(2)}(\mathbf{k}_1, \dots, \mathbf{k}_6) = \\ = \frac{4 \cdot 2}{3!} C_6^2 C_4^2 \mu_3(-\mathbf{k}_1 + \mathbf{k}_2, -\mathbf{k}_2 + \mathbf{k}_3, -\mathbf{k}_3 + \mathbf{k}_1) + \Delta\tilde{\mathfrak{M}}_{6,2}^{(2)}, \text{ etc.} \end{aligned}$$

If the diagrams of the second type are attributed to the cluster coefficients, collecting all paired diagrams according to the number of the field vertices, we again arrive at the cluster expansion for the free energy (2.3.59). However, the cluster coefficients are now constructed on the screened potential (2.3.27). In this case, the expression for the second cluster coefficient is given by formula (2.3.60), but the structure of the higher-order cluster coefficients is changed. In particular, in the expression (2.3.61) for the third cluster coefficient, the factor $F_3^0(R_{12}, R_{13}, R_{23}) - [F_2^0(R_{13}) + F_2^0(R_{32})][F_2^0(R_{12}) - 1] - 1$ appears in the second term instead of the factor $F_3^0(R_{12}, R_{13}, R_{23}) - F_2^0(R_{13})F_2^0(R_{32})$. Even more significant changes occur in the higher-order cluster coefficients. However, there is now the same screened potential (2.3.27) everywhere.

If the free energy is known, using the functional differentiation according to (2.2.31), we find the pair distribution function. Using the expressions (2.3.23), (2.3.26), and (2.3.60) we find for the terms of the series (2.3.59)

$$\frac{\delta F_0}{\delta \Phi_2(R)} = 0, \quad \frac{\delta F_{\text{HTA}}}{\delta \Phi_2(R)} = \frac{1}{V} F_2^0(R), \quad \frac{\delta F_{\text{RPA}}}{\delta \Phi_2(R)} = \frac{1}{V} g(R). \quad (2.3.68)$$

The derivative of the cluster coefficients is determined by the rule (2.2.38). In particular, the derivative of the second cluster coefficient with respect to the screened potential is equal to

$$\frac{\delta B_2}{\delta g(R)} = \frac{1}{V} F_2^0(R) \left[e^{g(R)} - 1 - g(R) \right] \frac{1}{V} g(R) [F_2^0(R) - 1]. \quad (2.3.69)$$

According to (2.2.38), this expression must be multiplied by the derivative $\frac{\delta g(R_{ij})}{\delta \Phi_2(R_{12})}$. Since the screened potential satisfies the Ornstein–Zernike equation with the correlation functions (2.3.28), using the method presented in

Subsection 2.2.2, we find the expression similar to (2.2.43)

$$\begin{aligned}
 -\frac{\delta g(R_{ij})}{\delta \Phi_2(R_{12})} &= \delta(R_{1j})\delta(R_{2i})\delta_{1j}\delta_{2i} + \delta(R_{1i})\delta(R_{2j})\delta_{1i}\delta_{2j} + \\
 + \frac{1}{V} &[\delta(R_{1i})\delta_{1i}h_2(R_{2j}) + \delta(R_{2i})\delta_{2i}h_2(R_{1j}) + \delta(R_{1j})\delta_{1j}h_2(R_{2i}) + \\
 &+ \delta(R_{2j})\delta_{2j}h_2(R_{1i})] + \frac{1}{V^2}[\dots], \tag{2.3.70}
 \end{aligned}$$

where $h_2(R) = F_2^0(R) - 1 + g(R)$. Hence, we find the cluster coefficient up to the second-order

$$-\frac{1}{\beta} \frac{\delta B_2}{\delta \Phi_2(R_{12})} = \frac{1}{V} [F_2^0(R)e^{g(R)} - 1 - g(R)] + g(R)[F_2^0(R) - 1].$$

Collecting this term together with (2.3.68), according to (2.2.31), we have

$$F_2(R) = F_2^0(R)e^{g(R)}[1 + \dots]. \tag{2.3.71}$$

So far, our description has been somewhat formal. The reference system includes that part of the interaction for which the representation in terms of the collective variables does not exist. Any model can act as a reference system, depending on the specific physical situation, but its properties should be known. The simplest example of the system with a short-range interaction is the model of hard spheres, the properties of which have been sufficiently studied to date. It allows one to use this system as a basis for the description of more realistic systems.

To be specific, we consider a system with a pair interaction⁹.

$$u_2(R) = \Phi_2(R) + \varphi_2(R) = \begin{cases} \infty, & \sigma > R, \\ \Phi_2(R), & \sigma \leq R, \end{cases} \tag{2.3.72}$$

where σ is a diameter of hard spheres (see (1.2.15)).

Obviously, for such an interaction, the long-range part $\Phi_2(R)$ is not uniquely determined for $R < \sigma$ and, in this region, it can be chosen quite arbitrarily, provided that the potential energy $\sum_{i < j} \Phi_2(R_{ij})$ has a collective variables representation. Since the physical properties of the system should not depend on this choice, it can be used to improve the convergence of cluster expansions (2.3.59).

It should be noted that expression (2.3.59) is a formally exact infinite series, the structure of which does not depend on the method of separating

⁹The relation of this model to a system with a more real interaction is discussed in Chapter 3.

short-range and long-range interactions. Nevertheless, each term of the series, except for the first two terms, is an explicit functional of the screened potential, the value of which depends on the Fourier image of the potential $\Phi_2(R)$. It is clear that different choices of $\Phi_2(R)$ for $R < \sigma$ will correspond to different screened potentials and, thus, to different values of F_{RPA} and cluster coefficients. The value of the cluster coefficients and the convergence of the series (2.3.59) are affected, to a certain extent, by the behaviour of the integrands at small distances. For the part of the integrands containing the distribution functions of the reference system as multipliers, the behaviour of the screened potentials at small distances does not affect the cluster coefficients. However, the remaining part of the cluster coefficients depends on the form of $g(R)$ at small distances. Minimizing the functional F_{RPA} with respect to $\Phi_2(R)$ in the region $R < \sigma$, we arrive at the condition for the optimum separation of interactions, for the first time formulated by Andersen and Chandler [25, 26]:

$$\frac{V \delta F_{\text{RPA}}}{\delta \Phi_2(R)} = g(R) = 0, \quad R < \sigma. \quad (2.3.73)$$

The series (2.3.59) constructed on such a screened potential is called the optimized cluster expansion, and the corresponding terms of the series are called the optimized random phase approximation (ORPA) and the optimized cluster coefficients, respectively. Of course, condition (2.3.73) does not guarantee the convergence of the series, but it does ensure a separation of the interactions for which the convergence is optimal.

It has already been noted that if we pass to the functions (2.3.28), the screened potential will satisfy the Ornstein–Zernike equation (1.3.18). Since $F_2^0(R) = 0$ for $R < \sigma$, the requirement for optimum separation of interactions means that

$$F_2^0(R) + g(R) = 1 + h_2(R) = 0, \quad R < \sigma. \quad (2.3.74)$$

The above condition is for the system that includes a short-range interaction of the hard sphere type regardless of specific forms of the long-range potential. If we use the Percus–Yevick approximation for the description of hard spheres, according to which $c_2^0(R) = 0$ for $R > \sigma$ (see (1.3.22), then for $c_2(R)$ in (2.3.28), we can put

$$c_2(R) = -\beta \Phi_2(R), \quad R \geq \sigma. \quad (2.3.75)$$

The Ornstein–Zernike equation under conditions (2.3.74) and (2.3.75) has a closed form. The description of the system based on this closed equation is known as the mean spherical approximation (MSA). As we see, this approximation determines the screened potential at the level of the optimum separation of interactions. When $\sigma \rightarrow 0$, the MSA equation passes into (2.2.19), whence it follows that the screened potential given by the equation (2.2.19) corresponds to the system of the point particles with long-range interactions. The

MSA equation that determines $g(R)$ is quite helpful. To date, exact analytical results have been obtained for several interesting systems, which will be discussed in the following chapters. However, even in the case when an analytical solution is unknown, the condition (2.3.73) greatly simplifies the numerical solution since it reduces to finding a stationary point of the functional of the type F_{RPA} [26].

It should be noted that for many systems the direct correlation function, apart from the region of the critical point, indeed has the asymptotic form (2.3.75) at large distances [72, 73]. Therefore, if we supplement the approximation (2.3.75) with some short-range function $c_2^{\text{sh}}(R)$, then a more precise expression can be presented for the direct correlation function [74, 75]:

$$c_2(R) = c_2^{\text{sh}}(R) - \beta\Phi_2(R), \quad R \geq \sigma. \quad (2.3.76)$$

As usual, $c_2^{\text{sh}}(R)$ is approximated by one or more functions of the Yukawa potential type with the parameters found from the conditions of thermodynamic self-consistency. Such a description is known as the generalized mean spherical approximation (GMSA).

Comparing the cluster expansions (2.2.22) and (2.3.59), one can note in (2.3.59) the presence of the “non-standard” diagrams from the point of view of general topology of the cluster coefficients. These are the terms corresponding to the cumulants $\tilde{\mathfrak{M}}_{n,2}^{(2)}$. They can be excluded from consideration by renormalising the screened potential [76]. According to the partition we made above, $\tilde{\mathfrak{M}}_n = \tilde{\mathfrak{M}}_n^{(1)} + \tilde{\mathfrak{M}}_{n,1}^{(2)} + \tilde{\mathfrak{M}}_{n,2}^{(2)}$, $\hat{D}_n = \hat{D}_n^{(1)} + \hat{D}_{n,1}^{(2)} + \hat{D}_{n,2}^{(2)}$, where $\tilde{\mathfrak{M}}_n^{(1)}$ is included in $\hat{D}_n^{(1)}$, $\tilde{\mathfrak{M}}_{n,1}^{(2)}$ is included in $\hat{D}_{n,1}^{(2)}$, and $\tilde{\mathfrak{M}}_{n,2}^{(2)}$ is included in $\hat{D}_{n,2}^{(2)}$. If we now represent the Jacobian of the transformation in the form

$$J(\rho) = \exp \left\{ \sum_{n \geq 3} \hat{D}_n^{(1)}(\partial/\partial\rho) + \sum_{n \geq 6} \hat{D}_{n,1}^{(2)}(\partial/\partial\rho) \right\} J_0(\rho) \quad (2.3.77)$$

including $\hat{D}_{n,2}^{(2)}$ in the zero distribution

$$\begin{aligned} J_0(\rho) = \int (d\omega) \exp \bigg\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} - \frac{\pi^2}{2} \sum_{\mathbf{k}} \omega_{\mathbf{k}} \omega_{-\mathbf{k}} \bigg[\mathfrak{M}_2(k) - \\ - \frac{\pi^2}{2} \frac{1}{N} \sum_{\mathbf{k}_1} \mathfrak{M}_{4,2}^{(2)}(\mathbf{k} + \mathbf{k}_1, -\mathbf{k} - \mathbf{k}_1) \omega_{\mathbf{k}_1} \omega_{-\mathbf{k}_1} + \\ + \frac{\pi^4}{3} \frac{1}{N^2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \mathfrak{M}_{6,2}^{(2)}(-\mathbf{k} + \mathbf{k}_1, -\mathbf{k}_1 + \mathbf{k}_2, -\mathbf{k}_2 + \mathbf{k}) \times \\ \times \omega_{\mathbf{k}_1} \omega_{-\mathbf{k}_1} \omega_{\mathbf{k}_2} \omega_{-\mathbf{k}_2} + \dots \bigg] \bigg\}, \end{aligned} \quad (2.3.78)$$

then “non-standard” diagrams do not appear in the cluster coefficients. All of them are included in the renormalisation of the screened potential. Denoting by $M_2(k)$ the mean value of the expression in square brackets (2.3.78), we obtain

$$\begin{aligned} M_2(k) = & \mathfrak{M}_2(k) - \frac{\pi^2}{2} \frac{1}{N} \sum_{\mathbf{k}_1} \mathfrak{M}_{4,2}^{(2)}(\mathbf{k} + \mathbf{k}_1, -\mathbf{k} - \mathbf{k}_1) \langle \omega_{\mathbf{k}_1} \omega_{-\mathbf{k}_1} \rangle + \\ & + \frac{\pi^4}{3} \frac{1}{N^2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \mathfrak{M}_{6,2}^{(2)}(-\mathbf{k} + \mathbf{k}_1, -\mathbf{k}_1 + \mathbf{k}_2, -\mathbf{k}_2 + \mathbf{k}) \times \\ & \times \langle \omega_{\mathbf{k}_1} \omega_{-\mathbf{k}_1} \omega_{\mathbf{k}_2} \omega_{-\mathbf{k}_2} \rangle + \dots, \end{aligned} \quad (2.3.79)$$

for $J_0(\rho)$ we use the approximate form

$$J_0(\rho) = \int (d\omega) \exp \left\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} - \frac{1}{2} \pi^2 \sum_{\mathbf{k}} \omega_{\mathbf{k}} \omega_{-\mathbf{k}} M_2(k) \right\}, \quad (2.3.80)$$

which differs from $J_G(\rho)$ only by replacing $\mathfrak{M}_2(k)$ with $M_2(k)$.

Using the expression (2.3.77) for the calculation of the configuration integral (2.3.21), we arrive at the cluster expansions (2.3.59), which do not contain “non-standard” diagrams. At the same time, the term $-1/\beta \sum_{\mathbf{k}} \alpha(k)[M_2(k) - \mathfrak{M}_2(k)]$ is added to F_{HTA} given in (2.3.24) and $M_2(k)$ instead of $\mathfrak{M}_2(k)$ appears in the expression (2.3.25) for F_{RPA} . New screened potential

$$G(R) = -\frac{1}{N} \sum_{\mathbf{k}} \frac{\alpha(k) M_2(k) M_2(k)}{1 + \alpha(k) M_2(k)} e^{i\mathbf{k}\mathbf{R}} \quad (2.3.81)$$

also differs from (2.3.27) by replacing $\mathfrak{M}_2(k)$ by $M_2(k)$. To get this screened potential in the cluster coefficients, it is necessary to introduce $\tilde{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ instead of $\tilde{\mathfrak{M}}_n$ determined in (2.3.63), i.e.,

$$\tilde{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = \frac{\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)}{\prod_{i=1}^n M_2(k_i)}. \quad (2.3.82)$$

As a result, for the cluster coefficients we obtain the expressions

$$B_2 = \frac{1}{2} \frac{N^2}{V} \int F_2^0(R) \left[e^{G(R)} - 1 - G(R) - \frac{1}{2} G^2(R) \right] d\mathbf{R} \quad (2.3.83)$$

plus the diagrams with the composite vertices,

$$\begin{aligned} B_3 = & \frac{1}{3} \frac{N^3}{2V^2} \int F_3^0(R_{12}, R_{13}, R_{23}) \left[e^{G(R_{12})} - 1 + 2G(R_{12}) \right] \times \\ & \times \left[e^{G(R_{13})} - 1 - G(R_{13}) \right] \left[e^{G(R_{23})} - 1 - G(R_{23}) \right] d\mathbf{R}_{12} d\mathbf{R}_{13} d\mathbf{R}_{23} \end{aligned} \quad (2.3.84)$$

plus the diagrams with the composite vertices, etc.

In this case, the complexity of the vertices is caused by $\Delta\tilde{M}_n^{(1)} = \tilde{M}_n^{(1)} - 1$. The method of renormalisation of the screened potential is a reliable means of expanding the range of applicability of cluster expansions since, as we will see below, the chain diagrams included in the renormalisation can play an important role in describing various specific systems. Calculations of the Fourier transform of the screened potential $G(R)$ can be performed using successive approximations. It is obvious that the number of the terms required for $M_2(k)$ depends on the ratio of the parameters of short-range and long-range interactions. Instead of $1 + \alpha(k)M_2(k)$, one can introduce the dielectric function

$$\varepsilon(k) = 1 + \alpha(k)M_2(k). \quad (2.3.85)$$

Consider, for example, such two approximations: a zero approximation

$$\varepsilon(k) \simeq 1 + \alpha(k)\mathfrak{M}_2(k), \quad (2.3.86)$$

in which all chain diagrams are neglected, and the first approximation (according to the number of the field vertices taken into account in $M_2(k)$):

$$\varepsilon(k) \simeq 1 + \alpha(k) \left[\mathfrak{M}_2(k) - \frac{1}{2N^2} \sum_{\mathbf{k}_1} \mu_2(\mathbf{k} + \mathbf{k}_1, -\mathbf{k} - \mathbf{k}_1) \tilde{g}(k_1) \right], \quad (2.3.87)$$

where $\tilde{g}(k) = -\frac{1}{N} \frac{\alpha(k)}{1 + \alpha(k)\mathfrak{M}_2(k)}$. Since $\frac{1}{2N^2} \sum_{\mathbf{k}_1} \mu_2(\mathbf{k} + \mathbf{k}_1, -\mathbf{k} - \mathbf{k}_1) \tilde{g}(k_1) = \frac{N^2}{V} \int h_2^0(R) \tilde{g}(R) e^{i\mathbf{k}\mathbf{R}} d\mathbf{R}$, then in the considered approximation

$$\varepsilon(k) \simeq 1 + \alpha(k) \left[\mathfrak{M}_2(k) - \frac{1}{2} \frac{N}{V} \int h_2^0(R) \tilde{g}(R) e^{i\mathbf{k}\mathbf{R}} d\mathbf{R} \right]. \quad (2.3.88)$$

Thus, taking into account the high-order cluster coefficients, it is also necessary to calculate the dielectric function or the screened potential.

Before focusing on the specific systems, we discuss the general possibilities of the obtained cluster expansions. In the low density limit, the expansions (2.2.56) and (2.3.59) are equivalent, and since (2.2.56) is a generalization of the Mayer expansion to the case of the systems with long-range interactions, both expansions are fairly accurate in the region of low densities. The expansion (2.3.59) is also sufficiently accurate in the region of high densities since the higher-order cluster coefficients can be neglected as a result of screening at high densities.

In conclusion, let us compare the expansion (2.3.59) with the other forms of the cluster expansions known in the literature. We arrive at one of them by representing the interaction potential in the form $u(R) = \varphi_2(R) + \xi\Phi_2(R)$ and by expanding the free energy of the system in a series in powers of ξ . Since

the configuration integral of a system with short-range interactions depends only weakly on temperature, in this case, the expansion yields a series in the inverse temperature β . This form of the cluster expansion is proposed by Zwanzig [77, 78] (see also [79]) and is known as the high-temperature expansion. To obtain this expansion, we use the expression (2.2.55), in which we change the notation. We replace the distribution functions $F_n^{(l)}$ with the distribution functions of the reference system $F_n^0(R_1, \dots, R_n)$ and the Mayer functions of short-range interactions with the Mayer functions of long-range interactions $f^{(l)}(R) = e^{-\beta \xi \Phi_2(R)} - 1$. Then,

$$\begin{aligned} F = F_0 - \frac{1}{\beta} \frac{N^2}{2V} \int f^{(l)}(R) F_2^0(R) d\mathbf{R} - \frac{N^3}{6\beta V^3} \int [3f^{(l)}(R_{12})f^{(l)}(R_{13}) \times \\ \times [F_3^0(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - F_2^0(R_{12})F_2^0(R_{13})] + f^{(l)}(R_{12})f^{(l)}(R_{13})f^{(l)}(R_{23}) \times \\ \times F_3^0(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)] d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 + \dots \end{aligned} \quad (2.3.89)$$

Expanding the Mayer functions $f^{(l)}(R)$ in a series in ξ and collecting the terms in powers of ξ , we arrive at the desired expansion

$$F = F_0 + \xi \sum_{n \geq 1} (\xi \beta)^{n-1} F^{(n)}, \quad (2.3.90)$$

where

$$\begin{aligned} F^{(1)} &= \frac{1}{2} \frac{N^2}{V} \int F_2^0(R) \Phi_2(R) d\mathbf{R}, \\ F^{(2)} &= -\frac{1}{4} \frac{N^2}{V} \int F_2^0(R) \Phi_2^2(R) d\mathbf{R} - \frac{N^3}{2V^3} \int \Phi_2(R_{12}) \Phi_2(R_{13}) \times \\ &\times [F_3^0(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - F_2^0(R_{12})F_2^0(R_{13})] d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 - \\ &- \frac{1}{8} \frac{N^4}{V^4} \int \Phi_2(R_{12}) \Phi_2(R_{34}) [F_4^0(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) - \\ &- F_2^0(R_{12})F_2^0(R_{34})] d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 d\mathbf{R}_4, \text{ etc.} \end{aligned}$$

As one can see, the calculation of $F^{(2)}$ leads to complicated integrals, which are expressed by high-order distribution functions. In addition, due to the lack of screening, the series is inapplicable for the systems with strong interactions. It can also converge poorly at low temperatures. Nevertheless, it is quite accurate at high temperatures for the systems with weakly long-range interactions. The expansions (2.3.90) and (2.3.59) coincide up to the first two terms. Therefore, expansion (2.3.59) is also reasonably accurate at high temperatures. However, screening ensures a better convergence of the series (2.3.59) and, as a result, its applicability to the systems with strong long-range interactions.

We arrive at one more form of the cluster expansions by representing the interaction potential in the form [80–82]

$$u_2(R) = \varphi_2(R) + \gamma^\nu \Phi_2(\gamma R), \quad (2.3.91)$$

where ν is the space dimension; γ is the ratio of the radius of short-range forces to the radius of long-range forces. For example, for the system of charged particles, γ is a plasma parameter equal to the ratio of the average distance between particles to the Debye length $\gamma^3 = v^* = V/N\kappa^3$.

The Mayer cluster expansion (1.3.13) is taken as an initial one to build the γ -expansion. In this case, each Mayer function is represented in the form: $f(R) = f_0(R) + [1 + f_0(R)] \sum_{n \geq 1} \frac{1}{n!} [-\beta \gamma^3 \Phi_2(\gamma R)]^n$, where $f_0(R) = e^{-\beta \varphi_2(R)} - 1$.

Collecting the terms in powers of γ in the resulting series, we arrive at the expansion [83, 84]:

$$\hat{\mu}_2(R) = \hat{\mu}_2^{\text{sh}}(R) + \mu_2^{(\ell)}(R) = \frac{N}{V} \left[\delta(\mathbf{R}) + \frac{N}{V} (F_2(R) - 1) \right].$$

In the diagrammatic representation, $\hat{\mu}_2(R)$ has the form:

$$\begin{aligned} \hat{\mu}_2(R) = & \text{diagram 1} + \text{diagram 2} + \frac{1}{2} \left[\text{diagram 3} + \text{diagram 4} + \right. \\ & \left. + \text{diagram 5} + \text{diagram 6} \right] + \dots, \end{aligned} \quad (2.3.92)$$

where each large vertex corresponds to the function $\hat{\mu}_n^{\text{sh}}(R_1, \dots, R_n)$, which coincides with the expression for the n -particle density (2.3.38) if one replaces the correlation functions of the reference system with $\hat{\mu}_n^{\text{sh}}(R_1, \dots, R_n)$. The number of small vertices surrounding each large vertex corresponds to the order of its correlation function $\hat{\mu}_n^{\text{sh}}(\mathbf{R}_1, \dots, \mathbf{R}_n)$. Each small field vertex corresponds to the operation $\bullet = \int d\mathbf{R}$, the open vertex is fixed. Each line is the screened potential, the expression for which coincides with (2.3.32) if instead of $\mathfrak{M}_2(k)$ we put the Fourier transform $V/N\hat{\mu}_2^{\text{sh}}$. The expression for $V/N\hat{\mu}_2^{\text{sh}}$ as well as for $M_2(k)$ is presented as an infinite series. Therefore, to obtain a series in powers of γ in (2.3.92), one should expand each function $\hat{\mu}_n^{\text{sh}}(\mathbf{R}_1, \dots, \mathbf{R}_n)$ in a series in γ . In particular, $\text{diagram 1} = \hat{\mu}_2^0(R) + O(\gamma^3)$.

In the absence of short-range interactions, all complex vertices become simple, and the expression (2.3.92) coincides with a usual expansion in powers of the plasma parameter (2.2.52). Thus, collecting in (2.3.92) all the terms in a number of large vertices we arrive at the cluster expansion for the pair distribution function which corresponds to that obtained above using the renormalisation of the screened potential (if we do not use the representation (2.3.82)).

The expansion (2.3.92) corresponds to the series of the free energy

$$F = F_0 + \frac{1}{2} \frac{N^2}{V} \int \Phi_2(R) d\mathbf{R} - \frac{1}{2} \gamma^3 \sum_{\mathbf{k}} [\alpha(k) - \ln[1 + \alpha(k)\mathfrak{M}_2(k)]] + O(\gamma^6), \quad (2.3.93)$$

from which in the limit $\gamma \rightarrow 0$, we have the exact result [80, 81, 85]

$$F = F_0 + \frac{N^2}{2V} a, \quad a = \int \Phi_2(R) d\mathbf{R}. \quad (2.3.94)$$

corresponding to an idealized case of the system with the infinite radius of infinitely weak interaction (i.e., strong long-range, but small in magnitude). From (2.3.94), the van der Waals equation of state follows automatically (see the next chapter).

The issue of the number of terms taken into account in (2.3.59) must be considered in each case separately, depending on the range of parameters and the specificity of a particular system.

It is interesting to note that the second term in the series (2.3.59) according to Bogolyubov—Gibbs inequality [86] (see also [41, 87]) determines an exact upper limit for the free energy

$$F - F_0 \leq F_{\text{HTA}}. \quad (2.3.95)$$

There should be also noted a thermodynamic inconsistency of the GMSA approximation in the general case. However, as it was recently shown by Høye and Stell [88], the expression for the pair distribution function

$$F_2(R) = F_2^0(R)[1 + g(R)] + \frac{1}{2} g^2(R), \quad (2.3.96)$$

corresponding to the first two terms in the exponential (2.3.70) leads to a thermodynamic consistency of the expressions obtained based on the expressions for the internal energy (1.1.31) and for the virial equation of state (1.1.32).

In conclusion of this Chapter, we note the application of the collective variables method in the theory of critical phenomena and second-order phase transitions, as proposed by the first author of this monograph. The foundation of the developed theory lies in the fact that fluctuations in the number of particles in the critical region become infinitely large. Since mean-squared fluctuations in the number of particles are expressed in terms of the pair correlation function according to equation (1.1.33), the Ornstein—Zernike equation implies that the divergence of these fluctuations in the critical region leads to

the following condition for the direct correlation function $c_2(R)$:

$$1 - 4\pi \frac{N}{V} \int_0^\infty c_2(R) R^2 dR = 0, \quad (2.3.97)$$

which results in a Coulomb-like divergence of the pair correlation function $h(R)$.

Given the formal similarity between the Ornstein–Zernike equation (1.3.18) and equation (2.2.19) for the screened potential $g(R)$, obtained using the the Jacobian $J(\rho)$ in the Gaussian approximation $J_G(\rho)$, it was concluded that the Gaussian distribution in the Jacobian must be replaced by the distribution which includes, at the very least, the fourth-order terms. To compute it in the form of equation (2.1.40), it is necessary to include, in addition to the $D_2(\omega)$ terms, the terms $D_n(\omega)$ with $n \leq 4$.

For improved accuracy, one should proceed to a sixth-order distribution, including the terms $D_n(\omega)$ with n up to $n \leq 6$. The theory developed in this way is presented in the monographs [89, 90].

This chapter deals with simple one-atom systems. The intermolecular interaction in such systems is central and has a repulsive character at small distances and a smooth long-range interaction at large ones. This allows us to directly use the results of the previous chapter for their description. First, a model of hard spheres is considered, which plays an important role in the description of monatomic systems. Further, the cluster expansions obtained in the method of collective variables are used to describe systems with van der Waals interaction. Then, the results obtained are generalized to the multicomponent case and, in conclusion, monoatomic ionic systems are considered.

3.1. Hard-sphere system

Hard spheres represent the simplest nontrivial reference system and are widely used in describing the equilibrium and non-equilibrium properties of matter beginning from van der Waals and Maxwell. The interaction between two hard spheres with a diameter σ is described by the pair potential (1.2.15), which takes into account the presence of strongly repulsive forces due to the internal electronic structure of molecules.

In recent years, our knowledge of the hard sphere system has expanded considerably. Much information about the thermodynamic properties of the system has been obtained using the scaled particle theory (SPT). Exact expressions for the thermodynamic and structural functions of a one-dimensional system of hard rods were known as early as the 1930s. In 1963, Wertheim [91, 92] and Thiele [93] found an analytical solution of the Percus—Yevick equation in the three-dimensional case, which gave almost exact information about the equation of state and the pair distribution function in the region of low and medium densities. Comparison of these results with the data of a computer simulation made it possible to parametrize them in such a way that they turned out to be suitable for higher densities. With

the help of a computer simulation in the hard sphere model, a phase transition closely related to the crystallization of real systems was discovered.

3.1.1. General properties. Exact relations

Hard spheres in the description of monatomic systems play the role of an ideal model, corresponding to their high-temperature limit. Indeed, for the potential (1.2.15), the Mayer function,

$$f(R) = \exp[-\beta u_2(R)] - 1 = \begin{cases} 0, & R \geq \sigma, \\ -1, & R < \sigma. \end{cases} \quad (3.1.1)$$

As a result, neither the configuration integral nor the distribution functions of the system depend on temperature. The thermodynamic and structural properties are determined by only one variable — the reduced density η , which is equal to $(1/6)\pi(N/V)\sigma^3$ in the three-dimensional case ($V = L^3$), $(1/4)\pi(N/V)\sigma^2$ in the two-dimensional case ($V = L^2$), and $(N/V)\sigma$ in the one-dimensional case ($V = L$).

The density of the system η is limited from above by a certain maximum value $\eta_{\max}$, which corresponds to the densest packing of spheres. Determining the maximum density of geometric figures in space is one of the main problems of combinatorial geometry [94]. For spheres in the three-dimensional case, $\eta_{\max} = 1/6\pi\sqrt{2} \sim 0.74048$, in the two-dimensional case, $1/6\pi\sqrt{3} \sim 0.9069$, and in the one-dimensional case, 1. Close packing also corresponds to the maximum coordination number, defined as the greatest number of spheres that can simultaneously be in contact with a given sphere. In the three-dimensional case it is equal to 12, in the two-dimensional case to 6, and in one-dimensional to 2. However, it should be noted that although there are no crystal structures with a density greater than $\eta_{\max}$, there is no rigorous evidence that $\eta_{\max}$ is indeed the maximum allowable density. Moreover, recent studies (see, for example, the article by Bernal and King in Ref. [18]) indicate the possibility of the formation of disordered structures with a local density exceeding $\eta_{\max}$.

In the region of low densities, the thermodynamic and structural functions of the system can be represented as series in powers of η , known as virial expansions. The terms of these series, the virial coefficients, play an important role, since when assessing the accuracy of any approximate theory, one should check how correctly it reproduces the virial coefficients. Thus, the first diagram in (1.3.13) corresponds to the third virial coefficient for the pair distribution function

$$F_2^{(3)}(R_{12}) = \text{diagram} = \frac{N}{V} \int d\mathbf{R}_3 f(R_{13}) f(R_{32}),$$

where $f(R)$ is Mayer function equal to (3.1.1). Here, integration is carried out over the third particle. Calculating such integrals, a transition to a bipolar coordinate system is usually made. As a result,

$$F_2^{(3)}(r) = 12\eta \frac{1}{r} \int_0^\infty f(s) s ds \int_{|s-r|}^{s+r} f(t) t dt,$$

where $r = R/\sigma$. The integral is determined by the volume of intersection of two spheres with a diameter σ , whose centres are located at a distance R [95]

$$F_2^{(3)}(R_{12}) = \begin{cases} 12\eta \frac{1}{r} \int_{r-1}^1 s ds \int_{r-s}^s t dt = 3\eta(r^3 - 12r + 16), & r < 2, \\ 0, & r \geq 2. \end{cases} \quad (3.1.2)$$

Diagrams of the fourth virial coefficient having nodal vertices are found similarly. However, the calculation of elementary diagrams is more complex. To date, we know the analytical expression only for the first one [96, 97].

Knowing the virial coefficients for a pair distribution function, one-time integration finds the virial coefficients for the free energy or the equation of state. Thus, the second virial coefficient

$$B_2 = -\frac{1}{2} \frac{N}{V} \int_0^\sigma (-1) 4\pi R^2 dR = 4\eta,$$

the third

$$B_3 = -\frac{1}{3} \frac{N}{V} \int_0^\sigma (-1) F_2^{(3)}(R) 4\pi R^2 dR = 10\eta^2,$$

the fourth $B_4 \sim 17.365\eta^3$, etc. The virial expansion can be extrapolated to the region of high densities using the Padé approximants. For the equation of state, such an approximant, taking into account the first six terms of the virial series, has the following form [98]

$$\frac{PV}{N} \beta - 1 = \frac{4\eta + 1.016112\eta^2 + 1.109056\eta^3}{1 - 2.245972\eta + 1.301008\eta^2}. \quad (3.1.3)$$

Due to the potential (1.2.15), for a system of hard spheres there exists a number of rigorous relations. First of all, it follows from equation (1.1.31) that the internal energy of a system of hard spheres coincides with the internal energy of an ideal gas $E = (3/2)Nk_B T$, since the pair distribution function $F_2(R)$ due to the presence of the Boltzmann factor $\exp[-\beta u_2(R)]$ is equal to zero for $R < \sigma$, while the potential $u_2(R)$ is zero for $R \geq \sigma$.

It follows from equation (1.1.32) that the pressure in the system of hard spheres is completely determined by the so-called contact value of the pair distribution function $F_2(\sigma+)$, i.e., its value at the point $R = \sigma$ at $R \rightarrow \sigma$ from above. Indeed, the function

$$\exp[-\beta u_2(R)] = \begin{cases} 0, & R < \sigma, \\ 1, & R \geq \sigma. \end{cases}$$

For its derivative we have

$$\frac{d}{dR} \exp[-\beta u_2(R)] = \delta(R - \sigma). \quad (3.1.4)$$

It follows from the definition of the pair distribution function (1.1.26) that the function

$$y_2(R) = e^{\beta u_2(R)} F_2(R)$$

is finite and continuous for all values of R . Rewriting equation (1.1.32) in the form

$$\begin{aligned} \frac{PV}{N} \beta &= 1 - \frac{4\pi}{6} \beta \frac{N}{V} \int_0^\infty \frac{du_2(R)}{dR} F_2(R) R^3 dR = \\ &= 1 + \frac{2}{3} \pi \frac{N}{V} \int_0^\infty y_2(R) \frac{d}{dR} [e^{-\beta u_2(R)}] R^3 dR, \end{aligned}$$

according to (3.1.4) we obtain

$$\frac{PV}{N} \beta = 1 + \frac{2}{3} \pi \frac{N}{V} y_2(\sigma) \sigma^3 = 1 + 4\eta F_2(\sigma+) \quad (3.1.5)$$

since function $y_2(R)$ is continuous.

Let us consider this function more in detail. For $R \geq \sigma$, $y_2(R) = F_2(R)$, but in contrast to $F_2(R)$, function $y_2(R) \neq 0$ for $R < \sigma$. In particular, at $R = 0$ according to the definition of the radial distribution function (1.1.26),

$$\begin{aligned} y_2(0) &= \lim_{R_{12} \rightarrow 0} [e^{\beta u_2(R_{12})} F_2(R_{12})] = \lim_{R_{12} \rightarrow 0} \frac{1}{V^{N-2} Q_N} \times \\ &\times \int \exp \left\{ -\beta \sum_{i=3}^N [u_2(R_{i1}) + u_2(R_{i2})] - \beta \sum_{3 \leq i < j \leq N}^N u_2(R_{ij}) \right\} d\mathbf{R}_3 \dots d\mathbf{R}_N = \\ &= \frac{1}{V^{N-2} Q_N} \int \exp \left\{ -2\beta \sum_{i=3}^N u_2(R_{i1}) - \beta \sum_{3 \leq i < j \leq N}^N u_2(R_{ij}) \right\} d\mathbf{R}_3 \dots d\mathbf{R}_N. \end{aligned}$$

Since for hard sphere potential $2u_2(R) = u_2(R)$, then

$$y_2(0) = \frac{1}{V^{N-2} Q_N} \int \exp \left\{ -\beta \sum_{2 \leq i < j \leq N}^N u_2(R_{ij}) \right\} d\mathbf{R}_3 \dots d\mathbf{R}_N = \frac{Q_{N-1}}{Q_N},$$

where Q_{N-1} is the configuration integral of the system of $N - 1$ particles. According to Eqs. (1.1.6), (1.1.9) and (1.1.14),

$$\mu - \mu_{\text{id}} = -\frac{1}{\beta} \frac{\partial \ln Q_N}{\partial N} = \frac{1}{\beta} \ln \frac{Q_{N-1}}{Q_N},$$

where μ_{id} is the ideal part of the chemical potential. Thus, at $R = 0$, function $y_2(R)$ is determined by the chemical potential of the system

$$y_2(0) = \exp\{\beta(\mu - \mu_{\text{id}})\}. \quad (3.1.6)$$

Each sphere with diameter σ excludes the centres of all other spheres from the region with radius σ and can be considered as a spherical cavity with radius σ . The function $y_2(R)$ can be interpreted as a pair distribution function of two cavities. The absence of the Boltzmann multiplier $\exp[-\beta u_2(R)]$ in the definition of the function $y_2(R)$ means that the two cavities interact only indirectly. Therefore, unlike hard spheres, they can approach at a distance $R < \sigma$. At $R = 0$, both cavities coincide, forming one cavity. Therefore, according to (3.1.6), $\mu - \mu_{\text{id}}$ has the meaning of work on the formation of a spherical cavity with radius σ in the system.

By analogy, it is possible to introduce a higher-order cavity distribution functions. In particular,

$$y_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = e^{\beta[u_2(R_{12})+u_2(R_{13})+u_2(R_{23})]} F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3).$$

Substituting this expression into the equation of Bogolyubov (1.1.28), we obtain a chain of equations for the cavity distribution functions. Since,

$$\frac{\partial}{\partial \mathbf{R}_1} F_2(R_{12}) = e^{-\beta u_2(R_{12})} \frac{\partial}{\partial \mathbf{R}_1} y_2(R_{12}) - \beta F_2(R_{12}) \frac{\partial u_2(R_{12})}{\partial \mathbf{R}_1},$$

the equation (1.1.28) for a pair distribution function can be written in the form

$$\frac{\partial}{\partial \mathbf{R}_1} y_2(R_{12}) = \frac{N}{V} \int d\mathbf{R}_3 y_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) e^{-\beta u_2(R_{23})} \frac{\partial}{\partial \mathbf{R}_1} e^{-\beta u_2(R_{13})}, \quad (3.1.7)$$

but according to (3.1.4)

$$\frac{\partial}{\partial \mathbf{R}_1} e^{-\beta u_2(R_{13})} = -\frac{\mathbf{R}_{13}}{R_{13}} \frac{d}{dR_{13}} e^{-\beta u_2(R_{13})} = -\frac{\mathbf{R}_{13}}{R_{13}} \delta(R_{13} - \sigma).$$

Similarly, we also present the derivative

$$\frac{\partial}{\partial \mathbf{R}_1} e^{-\beta u_2(R_{13})} = -\frac{\mathbf{R}_{12}}{R_{12}} \frac{d}{dR_{12}} y_2(R_{12}).$$

Substituting these expressions into (3.1.7) and multiplying both parts by $\mathbf{R}_{12}/R_{12}$, we get

$$\frac{\partial}{\partial R_{12}} y_2(R_{12}) = -\frac{N}{V} \int \frac{\mathbf{R}_{12}\mathbf{R}_{13}}{R_{12}R_{13}} y_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) e^{-\beta u_2(R_{23})} \delta(R_{13} - \sigma) d\mathbf{R}_3.$$

At $\mathbf{R}_{12} \rightarrow 0$, $\mathbf{R}_{23} \rightarrow \mathbf{R}_{13}$, $y_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \rightarrow y_2(R_{12})y_2(R_{13})$ and

$$\left[\frac{\partial}{\partial R_{12}} \ln y_2(R_{12}) \right]_{R_{12}=0} = -\frac{N}{V} \int \cos \theta y_2(R_{13}) e^{-\beta u_2(R_{13})} \delta(R_{13} - \sigma) d\mathbf{R}_3,$$

whence we have the final expression

$$\sigma \left[\frac{\partial}{\partial R} \ln y_2(R) \right]_{R=0} = -6\eta y_2(\sigma). \quad (3.1.8)$$

Equations (3.1.5), (3.1.6) and (3.1.8) are exact. Expression (3.1.6) was first obtained by Hoover and Poirier [99], and (3.1.8) by Meeron and Siegert [100].

Before we begin describing the three-dimensional system of hard spheres, we will study its general properties using the example of an exactly solvable one-dimensional model.

3.1.2. One-dimensional system

The problem of describing a one-dimensional system with short-range interactions is solved exactly. This solution is of great interest for two reasons. On the one hand, its analysis allows us to evaluate the suitability of approximate methods, and on the other hand, the one-dimensional model has the characteristic features of systems with a hard core.

Let us consider a certain one-dimensional system of particles located on a line of length V . To take into account the effects of the wall, it is usually assumed [15] that the wall behaves like two additional particles fixed at points $R = 0$ and $R = V$, respectively. Due to the short-range nature of the interaction, each particle can interact only with two neighbouring particles located on the line V . Therefore, the total potential energy of the system is

$$U_N = u_2(R_1) + \sum_{j=1}^{N-1} u_2(R_{j+1} - R_j) + u_2(V - R_N).$$

Since the particles cannot move off the line, they can be numbered by choosing one particular from the N possible symmetrical arrangements, for example $0 < R_1 < R_2 < \dots < R_N < V$. The configuration integral of the system

$$Q_N = \frac{N!}{V^N} \int_0^V e^{-\beta u_2(V-R_N)} dR_N \int_0^{R_N} e^{-\beta u_2(R_N-R_{N-1})} dR_{N-1} \dots \int_0^{R_2} e^{-\beta u_2(R_1)} dR_1.$$

Considering the sequence of functions

$$\chi_1(R) = e^{-\beta u_2(R)},$$

$$\chi_m(R) = \int_0^R \chi(R') \chi_{m-1}(R - R') dR', \quad m \geq 2,$$

where each function $\chi_m(R)$ is obtained by the convolution transformation of the previous functions $\chi_{m-1}(R)$ and $\chi(R)$, for the non-normalised configuration integral $Q'_N = V^N 1/N! Q_N$ according to (3.1.8), we have $Q'_N = \chi_{N+1}(V)$. Using the Laplace transform we obtain

$$\int_0^\infty e^{-sR} Q'_N(T, V) dV = [\Omega(s)]^{N+1}, \quad (3.1.9)$$

where

$$\Omega(s) = \int_0^\infty e^{-sR} e^{-\beta u_2(R)} dR$$

and $\text{Re } s > 0$. From here, by definition (1.1.21), we find the partition function of the isobaric-isothermal ensemble

$$Z_N(P, T) = N! \frac{Z_{\text{id}}}{V^N} [\Omega(s = \beta P)]^N,$$

and according to (1.1.20), the thermodynamic potential

$$\Phi(P, T) = -\frac{1}{\beta} \ln Z_N(P, T) = \frac{1}{\beta} N \ln \left[\frac{1}{\lambda} \Omega(s = \beta P) \right],$$

where

$$Z_{\text{id}} = \frac{1}{N!} \left(\frac{V}{\lambda} \right)^N$$

is the ideal part of the partition function, λ is the de Broglie thermal wavelength.

Differentiating $\Phi(P, T)$ with respect to P , we arrive at the equation of state

$$V = \left(\frac{\partial \Phi}{\partial P} \right)_T = -\frac{1}{\beta} N \left(\frac{\partial}{\partial P} \ln \Omega(s = \beta P) \right)_T. \quad (3.1.10)$$

For a system of rigid rods (one-dimensional “spheres”)

$$\Omega(s) = \int_0^\infty e^{-sR} dR = \frac{1}{s} e^{-s\sigma}$$

and according to (3.1.10)

$$\frac{V}{N} = \frac{1}{\beta P} + \sigma,$$

from which follows the equation of state obtained by Tonks,

$$\beta P \sigma = \frac{\eta}{1 - \eta}, \quad (3.1.11)$$

where $\eta = N/V\sigma$.

From (3.1.9), using the inverse Laplace transform, we find an expression for the configuration integral

$$Q_N(V) = \frac{N!}{V^N} \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{sV} [\Omega(s)]^{N+1} ds,$$

where $c > 0$ is chosen so that the integration path lies to the right of all the poles of the integrand. Since the function $e^{-\beta u_2(R)}$ is bounded, the integration path can be replaced by a closed contour that encloses the origin and all the poles of the integrand. Then,

$$Q_N = \frac{N!}{V^N} \frac{1}{2\pi i} \oint e^{sV} [\Omega(s)]^{N+1} ds. \quad (3.1.12)$$

The evaluation of such integrals is usually carried out by the saddle point method. As is known [101], for $N \rightarrow \infty$ the integral

$$\frac{1}{2\pi i} \oint g(s) e^{Nf(s)} ds \simeq g(s_0) e^{Nf(s_0)} [2\pi N f''(s_0)]^{-1/2},$$

where s_0 is a saddle point, which is determined by the equation $f'(s_0) = 0$. In the case under consideration, $g(s) = 1$ and

$$f(s) = s \frac{V}{N+1} + \ln \Omega(s),$$

so that in the limit $N \rightarrow \infty$,

$$Q_N(V) = \frac{1}{V^N} N! e^{s_0 V} [\Omega(s_0)]^{N+1},$$

where for s_0 , we have the equation

$$\frac{V}{N} + \left[\frac{\partial}{\partial s} \ln \Omega(s) \right]_{s=s_0} = 0.$$

By comparing this expression with (3.1.10), we find $s_0 = \beta P$, whence

$$Q_N(V) = \frac{N!}{V^N} e^{\beta P V} [\Omega(s = \beta P)]^{N+1}. \quad (3.1.13)$$

Let us now proceed to the calculation of the distribution functions. Using δ -functions, expression (1.1.26) for the n -particle distribution function can be represented as [102]

$$F_n(R_1, \dots, R_n) = \frac{1}{Q_N V^{N-n} N^n} \int (dR) e^{-\beta U_N} \times \\ \times \sum_{i_1 \neq i_2 \neq \dots \neq i_n} \delta(R_{i_1} - R_1) \dots \delta(R_{i_n} - R_n). \quad (3.1.14)$$

For a singlet function, due to the short-range nature of the interaction,

$$F_1(R) = \frac{V}{N} \sum_{j=1}^N \frac{Q'_{j-1}(R) Q'_{N-j}(V-R)}{Q'_N(V)},$$

where

$$Q'_{j-1}(R) = \frac{R^{j-1}}{(j-1)!} Q_{j-1}(R)$$

is the non-normalised configuration integral of the system $(j-1)$ of particles located on a segment of length R ; $Q'_{N-j}(V-R)$ and $Q'_N(V)$ are similar configuration integrals for the system $(N-j)$ and N of particles located, respectively, on segments of length $V-R$ and V . Using relations (3.1.12) and (3.1.13), we find

$$F_1(R) = \frac{V}{N} \sum_{j=1}^N \frac{e^{-\beta PR}}{\Omega^j(s = \beta P)} \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{sR} [\Omega(s)]^j ds. \quad (3.1.15)$$

This function describes the density distribution of particles at a distance R from a particle fixed at a point $R = 0$, and is thus in fact a pair distribution function $F_2(R)$ for an infinite chain. For hard rods

$$\Omega(s) = \frac{1}{s} e^{-s\sigma}, \\ \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{1}{s^j} e^{s(R-j\sigma)} ds = \begin{cases} \frac{R-j\sigma}{(j-1)!}, & R \geq j\sigma, \\ 0, & R < j\sigma. \end{cases}$$

Substituting these expressions into (3.1.15) and excluding the pressure according to formula (3.1.11), we obtain the following expression for the pair distribution function of an infinite chain of hard rods:

$$F_2(r) = \sum_{j=1}^{\infty} \frac{H(r-j)}{1-\eta} \left[\frac{\eta}{1-\eta} (r-j) \right]^{j-1} \times \\ \times \frac{1}{(j-1)!} \exp \left[-\frac{\eta}{1-\eta} (r-j) \right], \quad (3.1.16)$$

where

$$r = R/\sigma \quad \text{and} \quad H(x) = \begin{cases} 0, & x < 0, \\ 1, & x > 0 \end{cases}$$

is the Heaviside step function.

A distinctive feature of the obtained expression for a pair distribution function is its discrete piecewise continuous nature. The function is defined differently in each region $n < r < n + 1$, where n is a positive integer. In the region $0 < r < 1$, as it should be, $F_2(r) = 0$. For $1 < r < 2$,

$$F_2(r) = \frac{1}{1-\eta} \exp \left[-\frac{\eta}{1-\eta}(r-1) \right],$$

for $2 < r < 3$,

$$F_2(r) = \frac{1}{1-\eta} \exp \left[-\frac{\eta}{1-\eta}(r-1) \right] + \eta \frac{(r-2)}{(1-\eta)^2} \exp \left[-\frac{\eta}{1-\eta}(r-2) \right],$$

etc.

It is important to note the oscillatory nature of the behaviour of $F_2(r)$, associated with the emergence of short-range order in the system. With increasing density η , the amplitude of the oscillations increases and they occupy an increasingly larger region. The purely geometric and “density” origin of the short-range order is visible [15]. Expression (3.1.16) for the pair distribution function was first obtained by Frenkel [45]. We suggest the reader to independently verify the thermodynamic self-consistency of this expression.

Knowing the pair distribution function, from the Ornstein–Zernike equation one can determine the corresponding direct correlation function $c_2(r)$ [48]. To do this, one must first find the Fourier transform of the pair correlation function,

$$h_2(k) = \frac{1}{V} \int_{-\infty}^{\infty} [F_2(r) - 1] e^{ikr} dr,$$

and from it the Fourier transform of the direct correlation function

$$c_2(k) = \frac{h_2(k)}{1 + \frac{N}{V} h_2(k)}.$$

Having performed these calculations, we obtain

$$c_2(r) = \begin{cases} -\frac{(1-\eta)r}{(1-\eta)^2}, & r < 1, \\ 0, & r > 1. \end{cases} \quad (3.1.17)$$

As we see, the Percus–Yevick approximation (1.3.22) for a system of rigid rods is exact ($c_2(r) = 0$ for $r > 1$). Indeed, Wertheim [92] obtained expression (3.1.17) from the Percus–Yevick equation.

According to the scheme considered above, in accordance with (3.1.14), we can also find higher-order distribution functions [103]. In this case, the n -particle function

$$F_n(R_1, \dots, R_n) = \prod_{j=1}^{n-1} F_2(R_{j+1} - R_j),$$

where $R_1 < R_2 < \dots < R_n$. In particular, the three-particle distribution function

$$F_3(R_1, R_2, R_3) = F_2(R_{12})F_2(R_{23}),$$

where $R_1 < R_2 < R_3$. This result is quite interesting. It follows that the usual superposition approximation (1.3.25) is obviously incorrect in the one-dimensional case, while the higher-order superposition approximation (1.3.26) is exact.

3.1.3. Scaled particle theory

According to (3.1.5), the equation of state, and hence other thermodynamic properties of a system of hard spheres, are completely determined by the contact value of the pair distribution function. The use of this idea underlies the scaled particle theory (SPT) proposed by Reiss, Frisch and Lebowitz [104]. The essence of the method consists in introducing a new particle into the system — a hard sphere of diameter σ , which is called a scaled particle. The contact value of the pair distribution function of two spheres with diameters σ and σ' , respectively, is denoted by $G(\lambda)$ and is the central function of the method. In particular, $G(\lambda = \sigma) = F_2(\sigma+)$. The presence of an additional hard sphere is equivalent to the existence in the system of a cavity of radius λ , from which the centers of all other molecules are excluded. This cavity is called the λ -sphere.

Considering the scaled particle as a molecule of the soluble substance and the remaining particles as a solvent, the work of forming a λ -sphere can be interpreted as the free energy of solvation of the scaled particle (see also Section 3.3 of this chapter). This work $W(\lambda)$ is equal to the change in the free energy of the system upon the introduction of the scaled particle

$$W(\lambda) = -\frac{1}{\beta} \ln \frac{\int (d\mathbf{R}) \exp \left\{ -\beta \left[U_N + \sum_{i=1}^N u_2(|\mathbf{R} - \mathbf{R}_i|) \right] \right\}}{\int (d\mathbf{R}) \exp(-\beta U_N)} =$$

$$= \mu(\lambda) - \mu_{\text{id}}(\lambda), \quad (3.1.18)$$

where $(d\mathbf{R}) = \prod_{i=1}^N d\mathbf{R}_i$,

$$U_N = \sum_{1 \leq i < j \leq N} u_2(R_{ij})$$

is the potential energy of the system,

$$u_2(|\mathbf{R} - \mathbf{R}_j|, \lambda) = \begin{cases} 0, & |\mathbf{R} - \mathbf{R}_j| > \lambda, \\ \infty, & |\mathbf{R} - \mathbf{R}_j| < \lambda, \end{cases}$$

is the potential of interaction of the j -th molecule with the scaled particle; and $\mu(\lambda)$ is the chemical potential of the scaled particle; $\mu_{\text{id}}(\lambda)$ is its ideal part. Expression (3.1.18) can be represented as an infinite series

$$\begin{aligned} e^{-\beta W(\lambda)} &= 1 + \rho \int f(R) d\mathbf{R} + \frac{1}{2} \rho^2 \int f(R_{12}) f(R_{13}) F_2(R_{23}) d\mathbf{R}_2 d\mathbf{R}_3 + \\ &+ \dots = \sum_{n \geq 0} \frac{1}{n!} \rho^n \int \prod_{j=1}^n f(|\mathbf{R} - \mathbf{R}_j|) F_n(R_1, \dots, R_n) d\mathbf{R}_1 \dots d\mathbf{R}_n, \end{aligned} \quad (3.1.19)$$

where $F_n(R_1, \dots, R_n)$ is n -particle distribution functions of the system, and

$$f(|\mathbf{R} - \mathbf{R}_j|) = \exp\{-\beta u_2(|\mathbf{R} - \mathbf{R}_j|, \lambda)\} - 1 = \begin{cases} -1, & (|\mathbf{R} - \mathbf{R}_j|) < \lambda, \\ 0, & (|\mathbf{R} - \mathbf{R}_j|) > \lambda. \end{cases}$$

The terms of the series (3.1.19) consistently take into account the presence of one, two, n molecules in the λ -sphere. For $\lambda < 1/2\sigma$, the scaled particle should be considered a point, i.e., $\sigma' = 0$. It forms a cavity of radius $\lambda = 1/2\sigma$, so that in the region $\lambda \leq 1/2\sigma$, in the λ -sphere there cannot be more than one molecular center. In this case, all terms of the series (3.1.19), except for the first two, are identically equal to zero and

$$e^{-\beta W(\lambda)} = 1 - \frac{4}{3} \pi \lambda^3 \rho, \quad \lambda \leq \frac{1}{2} \sigma. \quad (3.1.20)$$

In the region $1/2\sigma \leq \lambda \leq 1/3\sigma$ in the λ -sphere, there may be centres of two molecules and it becomes necessary to take into account the third term of the series (3.1.19). However, in this case it is necessary to know the pair distribution function of the system

$$\begin{aligned} e^{-\beta W(\lambda)} &= 1 - \frac{4}{3} \pi \lambda^3 \rho + 2\pi \rho^2 \int_0^{2\lambda} F_2(R) \left\{ \frac{4}{3} \pi \lambda^3 \left[1 - \frac{3}{4} \left(\frac{R}{\lambda} \right) + \right. \right. \\ &\quad \left. \left. + \frac{1}{16} \left(\frac{R}{\lambda} \right)^3 \right] \right\} R^2 dR, \quad \frac{1}{2} \sigma \leq \lambda \leq \frac{1}{\sqrt{3}} \sigma, \end{aligned} \quad (3.1.21)$$

where the expression in brackets is the integral $\int f(|\mathbf{R} - \mathbf{R}_1|) f(|\mathbf{R} - \mathbf{R}_2|) d\mathbf{R}$, equal to the total volume of two spheres of radius λ , whose centers are at a distance R . Its calculation is similar to the third virial coefficient, (3.1.2).

The work $W(\lambda)$ is uniquely related to the central function $G(\lambda)$. Considering λ as an interaction inclusion parameter, according to (3.1.18), we have

$$W(\lambda) = \frac{N}{V} \int_0^\lambda d\lambda' \int d\mathbf{R} \frac{\partial u_2(R, \lambda')}{\partial \lambda'} F_2(R, \lambda'),$$

where $F_2(R, \lambda)$ is the pair distribution function of one of the hard spheres and the scaled particle; $u_2(R, \lambda)$ is the potential of their interaction. Since

$$\frac{\partial u_2(R, \lambda)}{\partial \lambda} F_2(R, \lambda) = -\frac{1}{\beta} \frac{\partial}{\partial \lambda} \left[e^{-\beta u_2(R, \lambda)} \right] y_2(R, \lambda) = -\frac{1}{\beta} \delta(R - \lambda) y_2(R, \lambda),$$

then, after integration over $d\mathbf{R}$

$$W(\lambda) = \frac{N}{V} \frac{1}{\beta} \int_0^\lambda G(\lambda') 4\pi \lambda'^2 d\lambda', \quad (3.1.22)$$

where $G(\lambda) = y_2(R = \lambda, \lambda) = F_2(R = \lambda+, \lambda)$. From here

$$G(\lambda) = \frac{\beta}{4\pi \lambda^2 N/V} \frac{\partial W(\lambda)}{\partial \lambda}. \quad (3.1.23)$$

According to (3.1.20) for $\lambda \leq 1/2\sigma$ we have the exact expression

$$G(\lambda) = \left[1 - \frac{4}{3} \pi \lambda^3 \frac{N}{V} \right]^{-1}. \quad (3.1.24)$$

In the region of large λ , when the cavity reaches macroscopic dimensions, we can put $dW = PdV + \gamma d\Sigma$, where γ is the surface tension; Σ and V are the surface area and volume of the λ -sphere, respectively. From here, according to (3.1.23),

$$G(\lambda) = \beta \frac{V}{N} \left[P + 2\gamma \frac{1}{\lambda} \right].$$

At $\lambda \rightarrow \infty$ according to (3.1.5) we have the following relationship:

$$G(\infty) = \beta \frac{V}{N} P = 1 + 4\eta G(\sigma), \quad (3.1.25)$$

where $\eta = 1/6\pi N/V\sigma^3$. It is usually assumed that $\gamma(\lambda) = \gamma_0[1 + \mathfrak{R}_0\sigma/\lambda]$, where γ_0 is the surface tension at $\lambda \rightarrow \infty$; $\mathfrak{R}_0$ is the radius of curvature of the surface. Thus, for large λ , we can assume

$$G(\lambda) = \beta \frac{V}{N} \left[P + 2\gamma_0 \frac{1}{\lambda} + 4\gamma_0 \mathfrak{R}_0 \frac{\sigma}{\lambda^2} \right]. \quad (3.1.26)$$

Of course, the coefficients γ_0 and $\mathfrak{R}_0$ cannot be measured for microscopic values of λ . Let us assume, following [104], that relation (3.1.26) is valid in the entire region of $\lambda > 1/2\sigma$, i.e.,

$$G(\lambda) = \beta \frac{P}{\rho} + A \frac{\sigma}{\lambda} + B \left(\frac{\sigma}{\lambda} \right)^2, \quad \lambda > \frac{1}{2}\sigma, \quad (3.1.26a)$$

where $A = 2\gamma_0\beta 1/\rho\sigma$, $B = 4\gamma_0\mathfrak{R}_0\beta 1/\rho\sigma^2$, $\rho = N/V$. Hence, taking into account (3.1.24) and (3.1.25), we obtain,

$$\beta \frac{PV}{N} = \frac{1 + 4\eta(A + B)}{1 - 4\eta},$$

$$G(\lambda) = \begin{cases} \left[1 - 8\eta \left(\frac{\lambda}{\sigma} \right)^3 \right]^{-1}, & \lambda < \frac{1}{2}\sigma, \\ \frac{1 + 4\eta(A + B)}{1 - 4\eta} + \frac{A}{\lambda} + \frac{B}{\lambda^2}, & \lambda > \frac{1}{2}\sigma. \end{cases}$$

The expressions for A and B are found from the continuity conditions of the functions $G(\lambda)$ and $\partial G(\lambda)/\partial\lambda$ at point $\lambda = 1/2\sigma$. As a result,

$$A = -\frac{3}{2}\eta \frac{1 + \eta}{(1 - \eta)^3}, \quad B = \frac{3}{4}\eta^2 \frac{1}{(1 - \eta)^3},$$

wherefrom we get

$$\beta \frac{PV}{N} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}, \quad F_2(\sigma+) = G(\sigma) = \frac{4 - 2\eta + \eta^2}{4(1 - \eta)^3}. \quad (3.1.27)$$

An undoubted advantage of the scaled particle theory is the possibility of obtaining analytical expressions for the surface tension γ_0 and the surface curvature $\mathfrak{R}_0$:

$$\gamma_0 = -\frac{9}{2\pi} \frac{\eta^2}{\beta\sigma^2} \frac{1 + \eta}{(1 - \eta)^3}, \quad \mathfrak{R}_0 = \frac{1}{4} \left[1 - \frac{1 - \eta}{1 + \eta} \right]. \quad (3.1.28)$$

The fact that $\gamma_0 < 0$ is not surprising, since in the system of hard spheres there are no attractive forces.

Later in work [105] the scaled particle theory was generalized to one- and two-dimensional systems. Since in the one-dimensional case at $\lambda = 1/2\sigma$ no more than two molecules from opposite sides of the λ -sphere can interact with the scaled particle, $G(\lambda)$ at $\lambda > 1/2\sigma$ does not depend on λ . Therefore, $G(\infty) = G(\sigma)$ and in accordance with a relation of type (3.1.25) we arrive at equation (3.1.11), which, as is known, is exact.

In the two-dimensional case, instead of (3.1.20) and (3.1.24) in the region $\lambda < 1/2\sigma$ we have $\exp[-\beta W(\lambda)] = 1 - \pi\rho\lambda^2$ and $G(\lambda) = [1 - \pi\rho\lambda^2]^{-1}$. For region $\lambda > 1/2\sigma$, assuming $G(\lambda) = \beta PV/N + A\sigma/\lambda$ similarly to (3.1.26),

from a relation of type (3.1.25) and the continuity condition of $G(\lambda)$ at point $\lambda = 1/2\sigma$ we find

$$\beta \frac{PV}{N} = \frac{1}{(1-\eta)^2}, \quad A = \frac{1}{2} \left[\frac{1}{1-\eta} - \frac{1}{(1-\eta)^2} \right],$$

where $\eta = (1/4)\pi\sigma^2(N/V)$.

Let us return again to the three-dimensional case and study the properties of the function $G(\lambda)$. First of all, let us verify the continuity of $G(\lambda)$ and its derivative at point $\lambda = 1/2\sigma$. According to (3.1.21) and (3.1.23),

$$G\left(\lambda = \frac{1}{2}\sigma\right) = \frac{1}{1-\eta}, \quad (3.1.29)$$

$$\left[\frac{\partial}{\partial \lambda} G(\lambda) \right]_{\lambda=\frac{1}{2}\sigma} = \frac{1}{\sigma} \frac{6\eta}{(1-\eta)^2}. \quad (3.1.30)$$

We also arrive at similar results based on (3.1.24). However, the second derivative of the function $G(\lambda)$ at point $\lambda = 1/2\sigma$ has a jump proportional to $G(\sigma)$:

$$\begin{aligned} \left[\frac{\partial^2 G(\lambda)}{\partial \lambda^2} \right]_{\lambda=\frac{1}{2}\sigma-} &= \frac{6\eta(4-\eta)}{\sigma^2(1-\eta)^3}, \\ \left[\frac{\partial^2 G(\lambda)}{\partial \lambda^2} \right]_{\lambda=\frac{1}{2}\sigma+} &= \left[\frac{\partial^2 G(\lambda)}{\partial \lambda^2} \right]_{\lambda=\frac{1}{2}\sigma-} - \frac{48\eta}{\sigma^2(1-\eta)} G(\sigma). \end{aligned} \quad (3.1.31)$$

At $\lambda = \sigma/\sqrt{3}$, the λ -sphere can contain the centers of three molecules. An analysis similar to that given above shows that at this point, the function $G(\lambda)$ and its first three derivatives are continuous, but the fourth derivative has a discontinuity proportional to the contact value of the ternary distribution function. As λ increases, the number of molecules whose centers can be in the λ -sphere continues to increase. Thus, at $\lambda = \sigma$ it reaches twelve. In this case, the order of the discontinuous derivative increases by two when passing from one singular point to the next.

Thus, the function $G(\lambda)$ is non-analytic at points $\lambda = \sigma/2, \sigma/\sqrt{3}, \dots$, i.e., when in the λ -sphere one more particle can be placed in addition to the existing ones. Thus, at a distance from $\sigma/2$ to σ , the function $G(\lambda)$ is non-analytic at least at twelve points. The discontinuities of the derivatives are due to the processes associated with the introduction of new particles into the cavity. However, since $G(\lambda)$ has discontinuities for its higher derivatives, in the scaled particle theory it is considered that it can be approximated with a good degree of accuracy by a well-chosen analytical function. As the latter, one can propose the expression

$$G(\lambda) = \sum_{n \geq 0} G_n \lambda^{-n}, \quad (3.1.32)$$

that generalizes the above expression (3.1.26).

For $G(\lambda)$ we have four exact relations (3.1.25), (3.1.29), (3.1.30), (3.1.31), with the help of which we can determine the first four coefficients of expansion (3.1.32). However, using the form $G(\lambda) = \sum_{n=0} G_n \lambda^{-n}$ instead of (3.1.26)

leads to much worse results, even incapable of reproducing the exact value of the second virial coefficient. The presence of terms in $G(\lambda)$ proportional to λ^{-3} , according to (3.1.22) for $W(\lambda)$ leads to the emergence of a logarithmic term. Therefore, we should put $G_3 = 0$. Similarly, in the two-dimensional case $G_2 = 0$ [106]. Considering the thermodynamic cycle for the formation of a cavity in the system, Tully-Smitt and Reiss [107] obtained another condition for the function $G(\lambda)$

$$\eta \frac{\partial G(\sigma)}{\partial \eta} + 2G(\sigma) - \frac{1}{4(1-\eta)} = 6\eta \int_{1/2}^1 \lambda^2 \frac{\partial G(\lambda)}{\partial \lambda} d\lambda + 6 \int_{1/2}^1 \lambda^2 G(\lambda) d\lambda. \quad (3.1.33)$$

Assuming $G_3 = 0$, using (3.1.33) and other exact conditions, the authors found that $G_4 = 0$ too. This leads to one of the best asymptotic formulas

$$G(\lambda) = G_0 + \frac{1}{\lambda} G_1 + \frac{1}{\lambda^2} G_2 + \frac{1}{\lambda^5} G_5.$$

Based on the works [107, 108], Table 1 was compiled, which summarizes the results obtained by the approximation of type (3.1.32) and the exact relations (3.1.25), (3.1.29)–(3.1.31), and (3.1.33). To assess the accuracy of the various approximations, the obtained values of the first virial coefficients in the expansion of $G(\sigma) = a_0 + a_1\eta + a_2\eta^2 + a_3\eta^3 + \dots$ are given. For comparison, the exact values of the coefficients found by formula (3.1.3) are also given. As can be seen, the best results are obtained by the approximation of type (3.1.26), supplemented by the term $\lambda^{-5}G_5$. It is interesting to note that the very simple approximation $G(\lambda) = G_0 + \lambda^{-1}G_1$ also leads to good results.

Cotter and Stillinger [109], having analysed the expansion (3.1.19) in the region $1/2\sigma \leq \lambda \leq 1/3\sigma$, proposed in the two-dimensional case an asymptotic expression for $\lambda \geq 1/\sqrt{3}\sigma$

$$G(\lambda) = G_0 + \frac{1}{\lambda} G_1 + \frac{1}{(\lambda - \lambda_3)^3} G_3 + \frac{1}{(\lambda - \lambda_4)^4} G_4. \quad (3.1.34)$$

To determine the constants G_n and λ_n , various exact conditions are used, also including the continuity of $G(\lambda)$ and its first three derivatives at the point $\lambda = 1/\sqrt{3}\sigma$. In subsequent works by Reiss and his co-workers [108, 110], the scaled particle theory received a new justification and further development on the basis of statistical thermodynamics of curved surfaces.

Conceptually close to the scaled particle theory under consideration is Andrew's approach [111], which started from expression (3.1.18). Assuming that

N particles of the system occupy their most probable configurations corresponding to the equilibrium temperature and density of the system, and the $(N + 1)$ -th particle of size $\lambda = \sigma$ wanders between them, the author considers the quantity $\exp[-\beta W(\sigma)]$ as the product of two terms. The first is the probability that R , a randomly chosen coordinate of the $(N + 1)$ -th particle, is not located inside one of the N hard spheres. This probability is equal to $1 - \eta$, i.e., a fraction of the total volume not occupied by the hard spheres. The second term is the probability that there is no other particle in a sphere of radius σ centred at point R . Since there really is not a single particle in a sphere of radius $1/2\sigma$, there must be no other particle in the volume $(4/3)\pi\sigma^3 - (1/6)\pi\sigma^3 = (7/6)\pi\sigma^3$. The probability that all N molecules are outside this volume is equal to the N -th power of the probability that none of them is in it. This probability is equal to the ratio of the volume $(7/6)\pi\sigma^3$ to the total free volume of the sys-

Table 1. Comparison of different asymptotic expressions for $G(\sigma)$ obtained via the scaled particle theory

Asymptotic expression for $G(\lambda)$	Exact conditions applied	$G(\sigma)$	Virial coefficients			
			a_0	a_1	a_3	a_4
$G_0 + \frac{1}{\lambda}G_1 + \frac{1}{\lambda^2}G_2$	(3.1.29), (3.1.30), (3.1.25) or (3.1.33)	$\frac{4 - 2\eta + \eta^2}{4(1 - \eta)^3}$	1	2.5	4.7484	7.7544
$G_0 + \frac{1}{\lambda}G_1 + \frac{1}{\lambda^2}G_2 + \frac{1}{\lambda^3}G_3$	(3.1.29)–(3.1.31), (3.1.25)	$\frac{2 + \eta}{2(1 - \eta)^2} + \frac{3}{2} \frac{7 + 2\eta}{2 + \eta} \times (20 - 15\eta + 8\eta^2)^{-1}$	1.4125	2.75304	4.0644	—
$G_0 + \frac{1}{\lambda}G_1 + \frac{1}{\lambda^2}G_2 + \frac{1}{\lambda^4}G_4$	(3.1.29), (3.1.30), (3.1.33), (3.1.25)	$\frac{4 - 2\eta + \eta^2}{4(1 - \eta)^3}$	1	2.5	4.7484	7.7544
$G_0 + \frac{1}{\lambda}G_1 + \frac{1}{\lambda^2}G_2 + \frac{1}{\lambda^4}G_4$	(3.1.29)–(3.1.31), (3.1.25)	$\frac{2 + \eta}{2(1 - \eta)^2} + \frac{7}{16} \frac{\eta^2}{1 - \eta} \times \left(1 - \frac{23}{24}\eta + \frac{7}{12}\eta^2\right)^{-1}$	1	2.5	4.4374	6.3569
$G_0 + \frac{1}{\lambda}G_1 + \frac{1}{\lambda^2}G_2 + \frac{1}{\lambda^5}G_5$	(3.1.29)–(3.1.31), (3.1.25)	$\frac{2 + \eta}{2(1 - \eta)^2} + \frac{93}{192} \frac{\eta^2}{1 - \eta} \times \left(1 - \frac{117}{94}\eta + \frac{57}{96}\eta^2\right)^{-1}$	1	2.5	4.4856	6.5664
$G_0 + \frac{1}{\lambda}G_1$	(3.1.29), (3.1.25)	$\frac{(1 - \frac{1}{2}\eta)}{(1 - \eta)(1 - 2\eta)}$	1	2.5	5.5	10
Exact values according to (3.1.3)	—	—	1	2.50	4.5912	7.0632

tem $V(1 - \omega\eta)$, where ω is some average fraction of the volume in units of η occupied by the molecules. Thus,

$$e^{-\beta W(\sigma)} = (1 - \eta) \left[1 - \frac{7/6\pi\sigma^3}{V(1 - \omega\eta)} \right]^N = (1 - \eta) \exp \left[- \frac{7\eta}{1 - \omega\eta} \right]. \quad (3.1.35)$$

The choice of $\omega = 29/14$ provides the exact value of the fourth virial coefficient, $\omega = 3\sqrt{2}/\pi$ corresponds to close packing. Of course, ω could be replaced by some function $\omega(\eta)$, e.g., a polynomial.

Attempts have also been made to apply the scaled particle theory to the calculation of a pair distribution function. The most successful work in this regard is Ref. [112], in which an integral equation was found that is exact in the one-dimensional case, but contains a ternary function in the three-dimensional case. A successful approximation was proposed for the latter, but no analytical solution was obtained.

3.1.4. Percus—Yevick approximation

The Percus—Yevick equation is the only one for which an analytical solution has been found in the three-dimensional case of hard spheres. In addition, as noted in Subsection 3.1.2 this equation is exact in the one-dimensional case. Let us dwell on this approximation more in detail.

According to (1.3.22), for a system of hard spheres in the Percus—Yevick approximation

$$\begin{aligned} F_2(R) &= e^{-\beta u_2(R)} y_2(R) = \begin{cases} 0, & R < \sigma, \\ y_2(R), & R > \sigma, \end{cases} \\ c_2(R) &= [e^{-\beta u_2(R)} - 1] y_2(R) = \begin{cases} 0, & R < \sigma, \\ -y_2(R), & R \geq \sigma. \end{cases} \end{aligned} \quad (3.1.36)$$

After substituting (3.1.36) into the Ornstein—Zernike equation (1.3.18), we arrive at the equation

$$y_2(r) = 1 + \frac{N}{V} \int_{R' < \sigma} y_2(R') d\mathbf{R}' - \frac{N}{V} \int_{R' < \sigma, |\mathbf{R} - \mathbf{R}'| > \sigma} y_2(R') y_2(|\mathbf{R} - \mathbf{R}'|) d\mathbf{R}'$$

or after the transformation to a bipolar coordinate system and dimensionless variables $r = R/\sigma$,

$$\begin{aligned} y_2(r) &= 1 + 24\eta \int_0^1 y_2(r') r'^2 dr' - 12\eta \frac{1}{r} \int_0^1 y_2(u) u du \times \\ &\quad \times \int_{|r-v|}^{r+v} H(v-1) y_2(v) v dv, \end{aligned} \quad (3.1.37)$$

where

$$H(x) = \begin{cases} 0, & x < 0, \\ 1, & x \geq 0, \end{cases}$$

is the Heaviside step function, $\eta = \frac{1}{6}\pi\frac{N}{V}\sigma^3$.

As noted at the beginning of this section, the function $y_2(r)$ is finite and continuous for all r . From equation (3.1.27), in particular, we have

$$y_2(0) = 1 + 24\eta \int_0^1 y_2(r)r^2 dr = 1 - 24\eta \int_0^1 c_2(r)r^2 dr = \beta \left(\frac{\partial P}{\partial \rho} \right)_T, \quad (3.1.38)$$

which also follows from the Ornstein–Zernike equation and from the expression for compressibility (1.1.33).

The main difficulty in solving the equation (3.1.37) is that it defines the function $y_2(r)$ in the domain $r \leq n$ if the latter is defined for $r \leq n + 1$. The solution of such problems by the Wiener–Hopf method is very effective (see, for example [113, 114]). Therefore, following the work of Baxter [115], we transform the Ornstein–Zernike equation in the approximation (3.1.36) to a form in which the correlation functions $h_2(r)$ and $c_2(r)$ are determined only by the value of $h_2(r)$ for $r < 1$.

Using the Fourier transform, the Ornstein–Zernike equation (1.3.18) can be represented as

$$\mathbf{m}_2(k) = 1 + \frac{N}{V}h_2(k) = \left[1 - \frac{N}{V}c_2(k) \right]^{-1}, \quad (3.1.39)$$

where

$$c_2(k) = \frac{4\pi}{k} \int_0^\infty c_2(R) \sin(kR) R dR, \quad h_2(k) = \frac{4\pi}{k} \int_0^\infty h_2(R) \sin(kR) R dR \quad (3.1.40)$$

are the Fourier components of the direct and pair correlation functions, respectively, and $\mathbf{m}_2(k)$ is the structural factor of the system.

Since $c_2(R) = 0$ for $R > \sigma$, the integration in the expression for $c_2(k)$ is actually carried out in the interval from 0 to σ . For the value inverse to the structure factor, by integrating by parts, from (3.1.39) we find

$$A(k) = \mathbf{m}_2^{-1}(k) = 1 - 4\pi\frac{N}{V} \int_0^\sigma S(R) \cos(kR) dR, \quad (3.1.41)$$

where

$$S(R) = \int_R^\sigma t c_2(t) dt. \quad (3.1.42)$$

Similarly to (3.1.42), the function $h_2(k)$ can be represented as

$$h_2(k) = 4\pi \int_0^\infty I(R) \cos(kR) dR = 2\pi \int_{-\infty}^\infty I(|R|) e^{ikR} dR, \quad (3.1.43)$$

where

$$I(R) = \int_R^\infty t h_2(t) dt. \quad (3.1.44)$$

In the Wiener–Hopf method, an analytic continuation of the Fourier transforms with respect to the transformation variable from the real axis to the complex plane is performed. Since, according to (3.1.33), $A(k=0) = \beta(\partial P/\partial \rho)_T < \infty$, $h_2(k) < \infty$ for all $\text{Re } k$. In accordance with (3.1.39), $A(k)$ has no zeros in the entire real region k and, according to (3.1.41), uniformly tends to unity as $|\text{Re } k| \rightarrow \infty$. Thus, along the real axis there is a strip $|\text{Im } k| < \varepsilon$ in which $A(k)$ has no zeros. Since in (3.1.41) the integration is carried out over a finite interval, $A(k)$ is an analytic function in the entire complex plane k . The function $\ln A(k)$ is also analytic in the strip $|\text{Im } k| < \varepsilon$ and uniformly tends to zero as $|\text{Re } k| \rightarrow \infty$. Therefore, according to the Cauchy theorem, for k inside the strip $|\text{Im } k| < \varepsilon$, the function $\ln A(k)$ can be represented as a sum of two terms,

$$\begin{aligned} \ln A(k) = \ln Q(k) + \ln P(k) &= \frac{1}{2\pi i} \int_{-i\varepsilon-\infty}^{-i\varepsilon+\infty} \frac{\ln Q(k')}{k' - k} dk' - \\ &- \frac{1}{2\pi i} \int_{i\varepsilon-\infty}^{i\varepsilon+\infty} \frac{\ln P(k')}{k' - k} dk'. \end{aligned} \quad (3.1.45)$$

In this case, the function $\ln Q(k)$ is analytic, has no zeros for $\text{Im } k > -\varepsilon$ and tends to zero as $\text{Im } k \rightarrow \infty$. Similarly, the function $\ln P(k)$ is analytic, has no zeros for $\text{Im } k < \varepsilon$ and tends to zero as $\text{Im } k \rightarrow -\infty$. Since $A(k)$ is an even function of k , $\ln P(k) = \ln Q(-k)$ and

$$A(k) = Q(k)Q(-k). \quad (3.1.46)$$

This is the Wiener–Hopf factorization.

Let us first consider the function $Q(k)$. For $|\text{Re } k| \rightarrow \infty$ in the strip $|\text{Im } k| < \varepsilon$, the function $\ln Q(k) \rightarrow 0$. Therefore, the function $1 - Q(k)$ has an inverse Fourier representation and one can write

$$\frac{1}{2\pi} \int_{-\infty}^\infty dk e^{-ikR} [1 - Q(k)] = 2\pi \frac{N}{V} q(R). \quad (3.1.47)$$

Since for real k the function $Q(-k)$ is the complex conjugate of $Q(k)$, then $q(R)$ is a real function of R . As $\text{Im } k \leq 0$, the function $Q(k)$ tends to unity if k tends to infinity. Then, for $R < 0$, closing the integration contour in (3.1.47) in the upper half-plane, we have $q(R) = 0$.

Based on (3.1.46), we define the analytic continuation of $Q(k)$ to the lower half-plane

$$Q(k) = \frac{A(k)}{Q(-k)}, \quad (3.1.48)$$

since $A(k)$ is everywhere analytic; $Q(-k)$ is an analytic function and has no zeros for $\text{Im } k < \varepsilon$. Since $Q(-k) \rightarrow 1$ for $\text{Im } k \rightarrow -\infty$, the functions $Q(k)$ and $A(k)$ for $\text{Im } k \rightarrow -\infty$ behave identically. According to (3.1.41), for $\text{Im } k \rightarrow -\infty$, the function $A(k) \sim \exp(ik\sigma)$, and so does $Q(k) \sim \exp(ik\sigma)$. Therefore, for $R > \sigma$, closing the integration contour in (3.1.47) in the lower half-plane, we have $q(R) = 0$. Thus, it is shown that

$$q(R) = 0, \text{ if } R < 0 \text{ or } R > \sigma. \quad (3.1.49)$$

Using the inverse Fourier transform from (3.1.47) we find

$$Q(k) = 1 - 2\pi \frac{N}{V} \int_0^\sigma e^{ikR} q(R) dR. \quad (3.1.50)$$

Using now relations (3.1.39), (3.1.41), (3.1.46) and (3.1.50), we can express the correlation functions $c_2(R)$ and $h_2(R)$ in terms of $q(R)$. Substituting (3.1.41) and (3.1.50) into (3.1.46), multiplying this result by $\exp(-ikR)$ and integrating over dk from $-\infty$ to ∞ , we express the function $S(R)$ in terms of $q(R)$:

$$S(R) = q(R) - 2\pi \frac{N}{V} \int_R^\sigma dt q(t) q(t - R), \quad 0 < R < \sigma. \quad (3.1.51)$$

Similarly, the expression for $I(R)$ is found through $q(R)$. According to (3.1.39) and (3.1.46)

$$Q(k) \left[1 + \frac{N}{V} h_2(k) \right] = Q^{-1}(-k). \quad (3.1.52)$$

Multiplying (3.1.52) by $\exp(-ikR)$, we integrate over k from $-\infty$ to ∞ . The contribution of the right-hand side for $R > 0$ is zero, since the integration contour can be closed in the lower half-plane, where $Q(-k)$ is analytic, has no zeros, and tends to unity at infinity. Therefore, for all $R > 0$,

$$I(R) = q(R) + 2\pi \frac{N}{V} \int_0^\sigma dt q(t) I(|R - t|), \quad (3.1.53)$$

where according to (3.1.49) $q(R) = 0$ for $R > \sigma$. From equations (3.1.51) and (3.1.42) it follows that $q(R) \rightarrow 0$ at $R \rightarrow \sigma-$, which thus ensures the continuity of $q(R)$ at the point $R = \sigma$.

Differentiating (3.1.51) and (3.1.53) with respect to R and taking into account that $q(\sigma) = 0$, we arrive at a set of equations into which the Ornstein–Zernike equation is transformed if $c_2(R) = 0$ for $R > \sigma$,

$$Rc_2(R) = -q'(R) + 2\pi \frac{N}{V} \int_R^\sigma dt q'(t) q(|t - R|), \quad 0 < R < \sigma, \quad (3.1.54)$$

$$Rh_2(R) = -q'(R) + 2\pi \frac{N}{V} \int_0^R dt (R - t) h_2(|R - t|) q(t), \quad R > 0, \quad (3.1.55)$$

where $q'(R) = d/dR q(R)$.

For a system of hard spheres $h_2(R) = -1$ for $R < \sigma$. Therefore, from equation (3.1.55) for $R < \sigma$ after switching to dimensionless variables, we obtain the following,

$$q'(r) = \lambda_1 + \lambda_2 r, \quad (3.1.56)$$

where

$$\lambda_1 = 2\pi \frac{N}{V} \sigma^3 \int_0^1 t q(t) dt, \quad \lambda_2 = 1 - 2\pi \frac{N}{V} \sigma^3 \int_0^1 q(t) dt. \quad (3.1.57)$$

Integrating (3.1.56) with respect to r and using the condition $q(r) = 0$ for $r > 1$, we obtain

$$q(r) = \lambda_1(r - 1) + \frac{1}{2}\lambda_2 = (r^2 - 1). \quad (3.1.58)$$

Substituting (3.1.58) into (3.1.57) leads to a system of two linear equations for λ_1 and λ_2 ,

$$\lambda_1 = -\frac{3}{2} \frac{\eta}{(1 - \eta)^2}, \quad \lambda_2 = \frac{1 + 2\eta}{(1 - \eta)^2}. \quad (3.1.59)$$

Since the function $q(r)$ is now known, from equation (3.1.54) we find the function $c_2(r)$,

$$-c_2(r) = \begin{cases} \lambda_2^2 - 6\eta(\lambda_1 + \lambda_2)^2 r + \frac{1}{2}\eta\lambda_2^2 r^3, & r < 1, \\ 0, & r \geq 1. \end{cases} \quad (3.1.60)$$

The value of $c_2(r)$ at the point $r = 1$ in accordance with (3.1.36) determines the contact value of the pair distribution function,

$$\begin{aligned} F_2(\sigma+) = -c_2(\sigma-) = y_2(\sigma) &= \lambda_2^2 - 6\eta(\lambda_1 + \lambda_2)^2 + \frac{1}{2}\eta\lambda_2^2 = \\ &= \lambda_1 + \lambda_2 = \frac{1 + \frac{1}{2}\eta}{(1 - \eta)^2}. \end{aligned} \quad (3.1.61)$$

Hence, according to (3.1.5),

$$\beta \frac{P_v}{\rho} = 1 + 4\eta F_2(\sigma+) = \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2}, \quad (3.1.62)$$

where “ v ” means that the equation of state is obtained from the virial expression (1.1.32). According to the known direct correlation function, according to (1.1.33) and in accordance with (3.1.38), we obtain

$$\beta \left(\frac{\partial P}{\partial \rho} \right)_T = 1 - 24\eta \int_0^1 c_2(r) r^2 dr = y_2(0) = -c_2(0) = \lambda_2^2. \quad (3.1.62a)$$

Hence, we find the second expression for the equation of state

$$\beta \frac{P_c}{\rho} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}, \quad (3.1.63)$$

where “ c ” means that this expression is obtained on the basis of the expression for the compressibility (1.1.33). It is noteworthy that this result coincides with expression (3.1.27), which we obtained by the scaled particle theory. However, this does not mean that these two methods are equivalent. Expressions (3.1.62) and (3.1.63) were first obtained by Wertheim [91] and Thiele [93] by direct integration of equation (3.1.37). Both formulas give exact values of the second and third virial coefficients, but different values of the fourth, and higher virial coefficients. The fact that $P_v \neq P_c$, testifies to the thermodynamic non-self-consistency of the Percus–Yevick equation in the case under consideration. Carnahan and Starling [116], having analysed expressions $Z_c = \beta P_c / \rho$ and $Z_v = \beta P_v / \rho$ and compared them with (3.1.3), arrived at the semi-empirical formula

$$Z_{CS} = \frac{1}{3}[2Z_c + Z_v] = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (3.1.64)$$

In Table 2 there are presented the virial series corresponding to Z_v , Z_c , Z_{CS} in comparison with the exact results obtained in accordance with (3.1.3). As one can see, the exact values of the virial coefficients are between Z_c and Z_v . The virial coefficients obtained according to the formula (3.1.64) almost coincide with their exact values. Comparing with the results of the computer simulation, it turned out

Table 2. Comparison of approximate virial expansions for the equation of state of the hard-sphere model

$Z = \frac{1}{\rho} \beta P$	Virial expansion
Z_c	$1 + 4\eta + 10\eta^2 + 19\eta^3 + 31\eta^4 + 46\eta^5 + \dots$
Z_v	$1 + 4\eta + 10\eta^2 + 16\eta^3 + 22\eta^4 + 28\eta^5 + \dots$
Z_{CS}	$1 + 4\eta + 10\eta^2 + 18\eta^3 + 28\eta^4 + 40\eta^5 + \dots$
(3.1.3)	$1 + 4\eta + 10\eta^2 + 18.36\eta^3 + 28.2\eta^4 + 39.5\eta^5 + \dots$

that the formula (3.1.64) with sufficient accuracy describes the system up to the crystallization point. Taking into account (3.1.5), the contact value of the pair distribution function that corresponds to formula (3.1.64), reads

$$F_2^{\text{CS}}(\sigma+) = \frac{4 - 2\eta}{4(1 - \eta)^3}. \quad (3.1.65)$$

Integrating (3.1.64) by density, we come to the corresponding expression for free energy of the system,

$$\frac{F - F_{\text{id}}}{N} \beta = \frac{4\eta - 3\eta^2}{(1 - \eta)^2}. \quad (3.1.66)$$

Knowing the direct correlation function (3.1.60), according to the formula (3.1.39), we find the structure factor of the system [117]

$$\begin{aligned} \mathbf{m}_2(k) &= \left[1 - \frac{N}{V} c_2(k) \right]^{-1}, \\ -\frac{N}{V} c_2(k) &= 24\eta \frac{1}{k^6} \left\{ \lambda_2^2 k^3 [\sin k - k \cos k] - 6\eta(\lambda_1 + \lambda_2)^2 k^2 \times \right. \\ &\quad \times [2k \sin k - (k^2 - 2) \cos k - 2] - \\ &\quad \left. - \frac{1}{2} \eta \lambda_2^2 [(k^4 - 12k^2 + 24) \cos k - 4k \sin k (k^2 - 6) - 24] \right\}, \end{aligned} \quad (3.1.67)$$

where k is measured in units of σ^{-1} .

Knowing the function $q(R)$, from the equation (3.1.55) one can find the pair distribution function $F_2(R)$. It is determined sequentially, first in the distance range $\sigma < R < 2\sigma$, then for $2\sigma < R < 3\sigma$, etc. It is interesting to note that, having differentiated the expression (3.1.55) three times, the integral equation can be converted into differential one [118].

To solve the equation (3.1.55), we use the Laplace transform. First substituting the expressions (3.1.56) and (3.1.58) into (3.1.55), and then multiplying the obtained result by $\exp(-sr)$ and integrating over dr , we get

$$\begin{aligned} \mathcal{F}_2(s) &= \frac{e^{-s}}{s^2} [\lambda_2 + s(\lambda_1 + \lambda_2)] \left\{ 1 - 12\eta \left[\frac{\lambda_1 + \lambda_2}{s^2} (1 - s - e^{-s}) + \right. \right. \\ &\quad \left. \left. + \lambda_2 \frac{1}{s^2} \left(1 - s + \frac{1}{2} s^2 - e^{-s} \right) \right] \right\}^{-1}, \end{aligned} \quad (3.1.68)$$

where $\mathcal{F}(s) = \int_0^\infty F_2(r) e^{-sr} r dr$ is the Laplace transform of the pair distribution function.

Substituting instead of λ_1 , and λ_2 their values (3.1.59), using the inverse Laplace transform, we come for the pair distribution function to the expression first received by Wertheim [91, 92],

$$F_2^{\text{PY}}(r) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{sL(s)e^{sr}}{12\eta[L(s) + S(s)e^s]} ds, \quad (3.1.69)$$

where

$$\begin{aligned} L(s) &= 12\eta \left[\left(1 + \frac{1}{2}\eta\right) s + (1 + 2\eta) \right], \\ S(s) &= (1 - \eta)^2 s^3 + 6\eta(1 - \eta)s^2 + 18\eta^2 s - 12\eta(1 + 2\eta). \end{aligned} \quad (3.1.70)$$

The integration contour in (3.1.69) passes on the right of all poles of the integrand. Since the denominator has no zeros in the right half-plane for $r < 1$, closing the integration contour with a large semicircle in the right half-plane, we have $F_2(r) = 0$ for $r < 1$. For $r > 1$ integration contour is closed in the left half-plane. At the same time, the integrand function has an infinite number of poles. The contribution of the pole $s = 0$ gives $F_2(r) = 1$ for $r > 1$. The remaining poles are complex and conjugate in pairs. A pair of poles $s = x \pm iy$ with the smallest real part determines the asymptotic behaviour of the pair distribution function at $R \rightarrow \infty$ [119]

$$F_2(r) \rightarrow 1 + 2|\gamma| \frac{1}{r} e^{-xr} \cos(yr + \arg \gamma), \quad (3.1.71)$$

where

$$\gamma = \frac{sL(s)}{12\eta[L'(s) + (S(s) + S(s))e^s]}$$

is the residue at the point $s = x \pm iy$. It should be noted that an expression of the type (3.1.71) was also obtained by Fisher [15] when studying the asymptotics of the pair distribution function in the superposition approximation. To obtain a closed-form expression for the pair distribution function, the denominator of the integrand is expanded into a series in powers of $L(s)/S(s)$. The integration contour is chosen such that $|S(s)| > |L(s)\exp(-s)|$. As a result, we obtain

$$F_2(r) = \frac{1}{24\pi\eta ir} \sum_{n \geq 1} (-1)^{n-1} \oint e^{s(r-n)} \left[\frac{L(s)}{S(s)} \right]^n s ds. \quad (3.1.72)$$

Each of these integrals is equal to zero for $r < n$, since the contour can be closed in the right half-plane, where the integrand has no poles. For $r > n$, the contour is closed in the left half-plane, and the contributions of all zeros

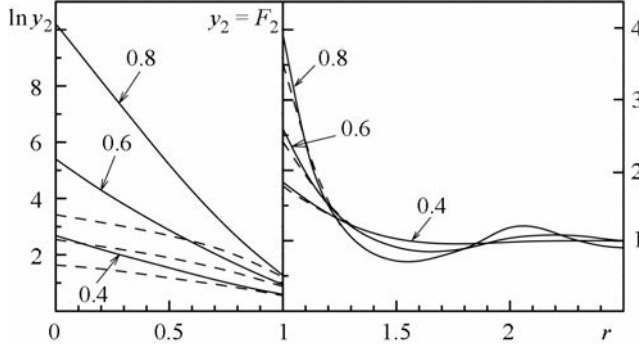


Fig. 3. Distance dependence of the pair distribution function $y_2(r) = e^{\beta u(r)} \times F_2(r) F_2(r)$ for different reduced densities $\rho^* = 0.4, 0.6, 0.8$. Distance range $r < 1$ (left-hand side, logarithmic scale) and $r > 1$ (right-hand side)

of the function $S(s)$ are taken into account. As a result,

$$F_2(r) = \frac{1}{r} \sum_{n \geq 1} \frac{(-12\eta)^{n-1}}{(n-1)!} H(r-n) \times \sum_{l=0}^2 \lim_{s \rightarrow s_l} \frac{d^{n-1}}{ds^{n-1}} (s - s_l)^n s \left[\frac{L(s)}{S(s)} \right]^n e^{s(r-n)}, \quad (3.1.73)$$

where $H(x)$ is the Heaviside step function,

$$s_l = \frac{2\eta}{1-\eta} [-1 + x_+ j^l + x_- j^{-l}]$$

are the roots of the equation $S(s)=0$, $j = \exp(2/3\pi i)$, $x_{\pm} = [f \pm \sqrt{f^2 + 1/8}]^{1/3}$ and $f = (3 + 3\eta - \eta^2)/(4\eta^2)$.

Such a form of the pair distribution function closely resembles expression (3.1.16) in the one-dimensional case. The function $F_2(r)$ is defined differently for each region $n < r < n + 1$. In the interval $1 < r < 2$ it has the form [91],

$$F_2(r) = \frac{1}{r} \frac{1}{(1-\eta)^2} \sum_{l=0}^2 A_l e^{s_l(r-1)}, \quad (3.1.74)$$

where

$$A_l = \frac{1}{3} \sum_{m=0}^2 H_m j^{lm}, \quad H_0 = 1 + \frac{1}{2}\eta, \\ H_1 = -\frac{1}{4\eta} \left(f^2 + \frac{1}{8} \right)^{-1/2} \left[x_-^2 (1 - 3\eta - 4\eta^2) + x_+ \left(1 - \frac{5}{2}\eta \right) \right], \\ H_2 = -\frac{1}{4\eta} \left(f^2 + \frac{1}{8} \right)^{-1/2} \left[x_+^2 (1 - 3\eta - 4\eta^2) + x_- \left(1 - \frac{5}{2}\eta \right) \right].$$

An analytical expression for the region $r \leq 5$ is presented in [120]. In Refs. [121, 122], the pair distribution function has been tabulated for various density values up to $r \leq 6$. The pair distribution function in the Percus—Yevick approximation for three different values of the reduced density $\rho^* = N/V\sigma^3$ is shown in Fig. 3 with a dashed line. As in the one-dimensional case, the pair distribution function exhibits an oscillatory nature, reflecting the short-range order in the system. With increasing density, the oscillations become more pronounced, extending over a larger region. At the same time, the second and higher maxima shift toward smaller r . For $\rho^* \geq 1.18$, the pair distribution function takes on negative values, which contradicts its physical meaning. Additionally, as the density increases, the discrepancy between the results of the Percus—Yevick approximation and computer simulations also grows.

3.1.5. Semi-empirical parametrization of expressions for correlation functions

Verlet and Weiss [123] pointed out three main shortcomings of expression (3.1.72), which become significant with increasing system density: 1) The Percus-Yevick expression for the pair distribution function $F_2(r)$ is underestimated in the region $R \sim \sigma$; 2) The oscillations of $F_2(r, \eta)$ at large R lead to an overestimation of the principal maximum of the structure factor; 3) There is a slight phase difference between the oscillations of the exact and the Percus—Yevick distribution functions.

It was also noted that the first maximum of the pair distribution function is not located at $R = \sigma$, as predicted by the Percus—Yevick equation, but slightly further. To address these shortcomings, Verlet and Weiss parametrized the Percus—Yevick expression for the pair distribution function, representing it in the form:

$$F_2\left(\frac{R}{\sigma}, \eta\right) = \begin{cases} 0, & R < \sigma, \\ F_2^{\text{PY}}\left(\frac{R}{\sigma}, \eta'\right) + \frac{A}{R} e^{-m(R-\sigma)} \cos[m(R-\sigma)], & R > \sigma, \end{cases} \quad (3.1.75)$$

The parameters A and m are chosen such that the equation of state, derived from the virial formula, and the compressibility formula coincide with each other and with expression (3.1.64), which is considered exact. The parameter $\sigma' < \sigma$ is introduced to slightly adjust the phase of the oscillations of $F_2^{\text{PY}}(r)$. Verlet and Weiss proposed an empirical relationship,

$$\left(\frac{\sigma'}{\sigma}\right)^3 = 1 - \frac{1}{16}\eta. \quad (3.1.76)$$

The main drawback of the Percus—Yevick approximation is associated with neglecting the long-range part $d_2(R)$ in the exact expression (1.3.19) for

the direct correlation function

$$c_2(R) = \left[e^{-\beta u_2(R)} - 1 \right] y_2(R) + d_2(R),$$

which leads to qualitatively incorrect results for $y_2(R)$ in the region of small R . According to (3.1.38), $y_2(0)$ in the Percus—Yevick approximation is determined by the value of the systems isothermal compressibility, whereas, according to the exact formula (3.1.6), the value of $y_2(0)$ is determined by the excess chemical potential. In the Carnahan—Starling approximation, using the exact relations (3.1.6) and (3.1.8), we find,

$$\begin{aligned} \ln y_2(0) &= \frac{1}{k_B T} (\mu - \mu_{\text{id}}) = \frac{8\eta - 9\eta^2 + 3\eta^3}{(1 - \eta)^3}, \\ \left(\frac{\partial \ln y_2(R)}{\partial R} \right)_{R=0} &= -6\eta y_2(\sigma) = -3\eta \frac{2 - \eta}{(1 - \eta)^3}. \end{aligned} \quad (3.1.77)$$

Therefore, for $R < \sigma$, Henderson and Grundke [124] approximated the expression for $\ln y_2(R)$ with a cubic polynomial,

$$\ln y_2(R) = \sum_{n=0}^3 a_n R^n. \quad (3.1.78)$$

The coefficients a_0 and a_1 of the cubic polynomial are defined by relations (3.1.77), while coefficients a_2 and a_3 are determined from the conditions of continuity of $y_2(R)$ and $\partial y_2(R)/\partial R$ at $R = \sigma$. For $R \geq \sigma$, function $y_2(R) = F_2(R)$, which is defined by expression (3.1.75). Fig. 3 presents the curves of the function $y_2(R)$ for three different values of density $\rho^* = (N/V)\sigma^3$. The solid line represents $y_2(R)$ based on formulas (3.1.75) and (3.1.78), while the dashed line corresponds to the Percus—Yevick approximation. As shown in the figure, the Percus—Yevick approximation is sufficiently accurate in the region of large R , but underestimates the value of the pair distribution function at $R \approx \sigma$. As density increases, the discrepancy between the exact value and the Percus—Yevick value $F_2(\sigma+)$ grows. In the region $R < \sigma$, the Percus—Yevick approximation for $y_2(R)$ is completely incorrect.

Using the numerical Fourier transform based on the Ornstein—Zernike equation, Henderson and Grundke determined the direct correlation function corresponding to expression (3.1.75). These results, obtained for the same density values as in Fig. 3, are presented in Fig. 4. The solid curve represents the exact results, while the dashed curve corresponds to the Percus—Yevick results according to (3.1.60). At $R = \sigma$, the function $c_2(R)$ exhibits a discontinuity, the magnitude of which is determined by $F_2(\sigma+)$ due to the continuity of the function $h_2(R) - c_2(R)$. Unlike the Percus—Yevick approximation, in the region $R > \sigma$, direct correlation function $c_2(R) \neq 0$, and at higher densities a second maximum appears near $R \sim 1.3\sigma$. For $R < \sigma$, as shown in the figure,

the Percus–Yevick approximation underestimates the value of $c_2(R)$. Henderson and Grundke proposed the following semi-empirical expression:

$$c_2(R) = \begin{cases} c_2^{\text{PY}}(R/\sigma, \eta) \left[1 - 0.127 \left(\frac{N}{V} \sigma^3 \right)^2 \right], & R < \sigma, \\ \frac{B}{R} \exp \left[20 \left(1 - \frac{R}{\sigma} \right) \right], & R > \sigma, \end{cases} \quad (3.1.79)$$

where the value of the constant B is chosen from the condition of the discontinuity of the function $c_2(R)$ at $R = \sigma$. For the long-range part of the direct correlation function, an expression was proposed in Ref. [124],

$$\ln d_2(R) = \sum_{n=0}^3 b_n R^n \quad (3.1.80)$$

and approximated values of the coefficients b_n were found. It is worth noting that in the Percus–Yevick approximation, $d_2(R) = 0$. Finally, in the work by Waisman [125], an analytical solution to the Ornstein–Zernike equation was obtained in the mean spherical approximation for the Yukawa potential. These results correspond to the choice of $c_2(R)$ in the form (3.1.79) and can also be used for parametrizing the correlation functions of hard sphere systems.

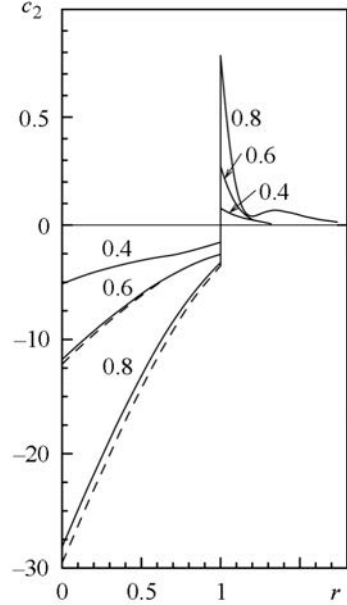


Fig. 4. Radial dependence of the direct correlation function $c_2(r)$ for various reduced densities $\rho^* = 0.4, 0.6, 0.8$

3.1.6. Phase transition in the hard-sphere systems

An important feature of hard sphere systems is the phase transition between the disordered (vapour) phase, which is stable at low densities, and the ordered (crystalline) phase, which is stable at high densities. This transition was observed through computer simulations at densities around $2/3\eta_{\text{max}}$ in both two-dimensional and three-dimensional systems, but it is absent in the one-dimensional case. During the transition, dense crystalline structures are formed. In the two-dimensional case, this is a flat hexagonal lattice, while in the three-dimensional case, it is either a cubic or hexagonal lattice, both of which have the same packing density.

Computer simulations show that for the equation of state of hard spheres, there are two distinct branches — one for the crystalline state and the other for the amorphous liquid and vapour states. This result is shown in Fig. 5, taken

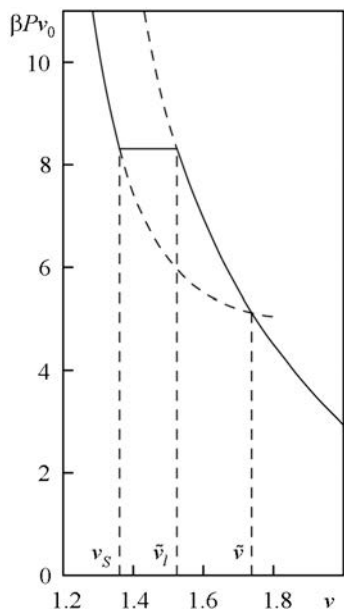


Fig. 5. Equation of state for the hard-sphere system as function of $v = v/v_0$ ($v_0 = \sigma^3/\sqrt{2}$) obtained from computer simulations [18]. Two distinct branches correspond to the disordered fluid phase and the ordered crystalline phase. The horizontal line represents the coexistence region, while dashed extensions of the solid curves indicate metastable states

from the study by Alder and Hoover [18]. The horizontal line in the figure corresponds to the phase boundary, and the dashed extensions of the solid curves for the crystalline and liquid–vapour states represent metastable states. This pattern indicates the absence of any critical point for the vapour (or liquid)—solid phase transition, similar to the critical point for the vapour–liquid phase transition (see the next section). If the crystalline branch is continued, it intersects with the second branch at some point corresponding to the density $\rho = \tilde{\rho} = 1/v$. Although this result was not obtained in the computer simulations, it is clear that starting from the density $\rho \geq \tilde{\rho}$, the system can exhibit a metastable crystalline phase. The formation of a stable crystalline phase occurs at a density $\rho > \tilde{\rho}$, where the chemical potentials of both phases are equal. While the theory of the crystalline state is beyond the scope of this book, we briefly discuss the behaviour of the system at the point $\rho = \tilde{\rho}$.

In the vapour (as well as in the liquid) phase, the system is spatially homogeneous. This means that the singlet distribution function $F_1(\mathbf{R}) = 1$, and the pair distribution function $F_2(\mathbf{R}_1, \mathbf{R}_2) = F_2(R_{12})$ and characterizes the short-range order of the molecular arrangement. The transition to the crystalline state is associated with the formation of a regular arrangement of molecules at macroscopic distances, i.e., with the emergence of long-range order. The system then becomes spatially heterogeneous, and the singlet distribution function $F_1(\mathbf{R})$ must possess all the symmetry properties of the corresponding lattice. Spatially inhomogeneous systems will be discussed in detail in Chapter 5. In this context, according to (5.1.17), the pair distribution

function of the system,

$$F_2(\mathbf{R}_1, \mathbf{R}_2) = [1 + h_2(\mathbf{R}_1, \mathbf{R}_2)]F_1(\mathbf{R}_1)F_1(\mathbf{R}_2). \quad (3.1.81)$$

If we now identify the function $1 + h_2(\mathbf{R}_1, \mathbf{R}_2)$ with the pair distribution function of the vapour system $F_2(R_{12})$, then after substituting (3.1.81) into the equation of Bogolyubov (1.1.28), we obtain,

$$\nabla_1 \ln F_1(\mathbf{R}_1) = -\beta \frac{N}{V} \int d\mathbf{R}_2 F_1(\mathbf{R}_2) F_2(R_{12}) \nabla_1 u_2(R_{12}). \quad (3.1.82)$$

This equation, in the context of the crystallization problem, was discussed by Tyablikov [126], and for the hard sphere system, it was thoroughly examined in the works of Raveché and Stuart [127–129]. For convenience, let us express (3.1.82) in the form,

$$\nabla_1 \ln |1 + h_1(\mathbf{R}_1)| = -\beta \frac{N}{V} \nabla_1 \int d\mathbf{R}_2 h_1(\mathbf{R}_2) \Psi(R_{12}), \quad (3.1.83)$$

where $h_1(\mathbf{R}) = F_1(\mathbf{R}) - 1$, and function $\Psi(R_{12})$ is determined according to relation,

$$\nabla_1 \Psi(R_{12}) = F_2(R_{12}) \nabla_1 u_2(R_{12}). \quad (3.1.84)$$

In accordance with the normalisation condition (1.1.27)

$$\lim_{V \rightarrow \infty} \frac{1}{V} \int d\mathbf{R} h_1(\mathbf{R}) = 0. \quad (3.1.85)$$

Equation (3.1.83) has a trivial solution $h_1(\mathbf{R}) = 0$, corresponding to the spatially homogeneous phase. Let us examine the conditions under which a non-trivial solution $h_1(\mathbf{R}) \neq 0$ arises. According to (3.1.83)

$$1 + h_1(\mathbf{R}_1) = C(h_1) \left\{ -\beta \frac{N}{V} \int d\mathbf{R}_2 h_1(\mathbf{R}_2) \Psi(R_{12}) \right\}, \quad (3.1.86)$$

where the constant $C(h_1)$ is determined from the normalisation condition (3.1.85)

$$1 = C(h_1) \lim_{V \rightarrow \infty} \frac{1}{V} \int d\mathbf{R}_1 \left\{ -\beta \frac{N}{V} \int d\mathbf{R}_2 h_1(\mathbf{R}_2) \Psi(R_{12}) \right\}. \quad (3.1.87)$$

According to the theory of nonlinear integral equations [130], the value of the parameter $(\beta N/V)$ at which a solution $h_1(R) \neq 0$ arises, is found as the eigenvalue of the homogeneous equation,

$$w(\mathbf{R}_1) = -\beta \frac{N}{V} \int d\mathbf{R}_2 w(\mathbf{R}_2) \Psi(R_{12}), \quad (3.1.88)$$

where according to (3.1.87)

$$\lim_{V \rightarrow \infty} \frac{1}{V} \int d\mathbf{R} w(R) = 0. \quad (3.1.89)$$

It should be noted that the linearization of equation (3.1.86) into (3.1.88) is not a linearization with respect to the density $\rho = N/V$, but rather with respect to the trivial solution $h_1(\mathbf{R}) = 0$.

The function $h_1(\mathbf{R})$, describing the crystalline ordering, must possess the following properties:

1. For a given crystalline structure defined by the lattice vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ (see, for example, Ref. [131]), $h_1(\mathbf{R} + \mathbf{a}l + \mathbf{b}m + \mathbf{c}n) = h_1(\mathbf{R})$, i.e., $h_1(\mathbf{R})$ is a periodic function with the lattices period.

2. For all elements $\mathbf{\Gamma}$ of the point group of the given lattice, $h_1(\mathbf{\Gamma R}) = h_1(\mathbf{R})$, i.e., $h_1(\mathbf{R})$ is invariant under all rotations and reflections that map the lattice onto itself.

3. According to the normalisation condition (3.1.85),

$$\frac{1}{w} \int h_1(\mathbf{R}) d\mathbf{R} = 0,$$

where the integration is carried out over w that is the volume of the elementary cell of the crystal. This implies that the function $h_1(\mathbf{R})$ has maxima at all (and only) points corresponding to the lattice nodes.

In the case of hard spheres, according to (3.1.84),

$$\Psi(R_{12}) = -\frac{1}{\beta} F_2(\sigma+) H(R_{12} - \sigma), \quad (3.1.90)$$

where $F_2(\sigma+)$ is the contact value of the pair distribution function, $H(x)$ is the Heaviside step function. In this case, for equation (3.1.88), we have the following expression,

$$w(\mathbf{R}_1) = -\frac{N}{V} F_2(\sigma+) \int_{R_2 \leq \sigma} d\mathbf{R}_2 w(\mathbf{R}_1 - \mathbf{R}_2). \quad (3.1.91)$$

Expanding the function $w(\mathbf{R})$ into a Fourier series as

$$w(\mathbf{R}) = \sum_{h,l,k} \alpha_{hllk} e^{i\mathbf{GR}},$$

where $\alpha_{000} = 0$, and $\mathbf{G} = \mathbf{A}h + \mathbf{B}k + \mathbf{C}l$, with $\mathbf{A}, \mathbf{B}, \mathbf{C}$ being the reciprocal lattice vectors, then from equation (3.1.91), we obtain:

$$-\rho F_2(\sigma+) \int_{R_2 \leq \sigma} d\mathbf{R}_2 e^{i\mathbf{GR}_2} = 1. \quad (3.1.92)$$

Hence, by specifying the type of lattice with the vector $\mathbf{G}$ and using the previously determined value $F_2(\sigma+) = y_2(\sigma)$, one can determine the density $\rho_0 = \tilde{\rho}$ at which a crystalline solution corresponding to the given lattice may emerge. It is clear that the system can make transit into this new state only if it corresponds to a lower free energy than the spatially homogeneous phase. Raveché and Stuart [129] used equation (3.1.92) to determine the density $\tilde{\rho}$ at which densely packed crystalline structures arise in a system of hard spheres. Their results are quite significant; however, the fact that a crystalline solution was found in the one-dimensional case indicates the necessity of improving the approximation $1 + h_2(\mathbf{R}_1, \mathbf{R}_2) = F_2(R_{12})$ adopted in equation (3.1.81).

Thus, the system of hard spheres naturally unifies the models of an ideal gas and a densely packed crystalline lattice, which it represents as limiting cases at low and high densities, respectively. It is clear that this model should serve as a fundamental starting point for describing monoatomic systems over a wide range of densities.

3.2. System with van der Waals interactions

Let us now proceed to the description of more realistic systems, in which, along with short-range repulsion, there also act van der Waals attractive forces. Taking these into account leads to a temperature dependence of the configuration integral and the distribution functions. Consequently, the free energy depends on two variables — the density $\eta = \frac{\pi N}{6V}\sigma^3$ and the temperature $T^* = \frac{k_B T}{\epsilon}$ — in such a way that in the limit $T^* \rightarrow \infty$, it reduces to the free energy of hard spheres.

The characteristic features of this system were predicted over a century and a half ago by van der Waals based on the equation of state he proposed. To derive this equation, it is sufficient to retain only the first two terms in the expansion (2.3.59). As previously noted, such an approximation is exact in the limit of weak but strongly long-range interactions. Using the hard-sphere system as a reference and assuming for it

$$\frac{P_0 V}{N} \beta = \frac{1}{1 - 4\eta}, \quad F_2^0(R) = H(R - \sigma), \quad (3.2.1)$$

we obtain

$$P = \frac{N k_B T}{V - Nb} - \frac{N^2}{V^2} a, \quad (3.2.2)$$

where

$$a = -2\pi \int_0^\infty \Phi_2(R) R^2 dR, \quad b = 4\eta \frac{V}{N}.$$

This is precisely the van der Waals equation.

Despite its simplicity, equation (3.2.2) was the first to reveal the fundamental properties of the spatially homogeneous phase of matter, namely: 1. the phenomenon of condensation; 2. the existence of metastable states; 3. the presence of a critical point, above which the distinction between liquid and vapour disappears. When supplemented by the condition of equal chemical potentials, equation (3.2.2) also describes the two-phase region.

However, the approximations in (3.2.1) are not sufficiently rigorous. The first is exact only in the one-dimensional case, while the second corresponds to the limit of low densities, which is justified in the case of weak, long-range interactions. Instead of (3.2.1), one should use more accurate results obtained in the previous section. Furthermore, Van der Waals attractive forces are neither weak nor strongly long-range, which necessitates considering higher-order terms in the expansion (2.3.59).

3.2.1. Choice of the reference system. Relation to the hard-sphere model

For simple models with a square-well-type potential, it is natural to choose the hard-sphere model as the reference system. Setting aside such simple model systems, we proceed directly to describing systems with more realistic interactions, for which the choice of the reference system is not so straightforward. This choice is directly related to the method of separation of the original potential into short-range and long-range components. The question of the form of the potential of the reference system, as well as the choice of the splitting point of the original potential, is ambiguous. As noted in the previous chapter, among all possible ways of splitting interactions, there exists an optimum method that ensures the best convergence of cluster expansions. Let us examine this issue more in detail using the example of a simple model with the Lennard-Jones potential in the form:

$$u_2(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

or in dimensionless variables $T^* = k_B T / \epsilon$ and $r = R / \sigma$,

$$\beta u_2(R) = \frac{4}{T^*} \left[\frac{1}{r^{12}} - \frac{1}{r^6} \right] \quad (3.2.3)$$

where ϵ characterizes the depth of the potential well, and σ corresponds to the effective diameter of the particles.

When this potential is split into short-range $\varphi_2(R)$ and long-range $\Phi_2(R)$ parts, such that $u_2(R) = \varphi_2(R) + \Phi_2(R)$, the repulsive part of the potential is included in $\varphi_2(R)$, and the attractive part is included in $\Phi_2(R)$. Fig. 6 shows three different methods of such a separation. In the first method (Fig. 6, a),

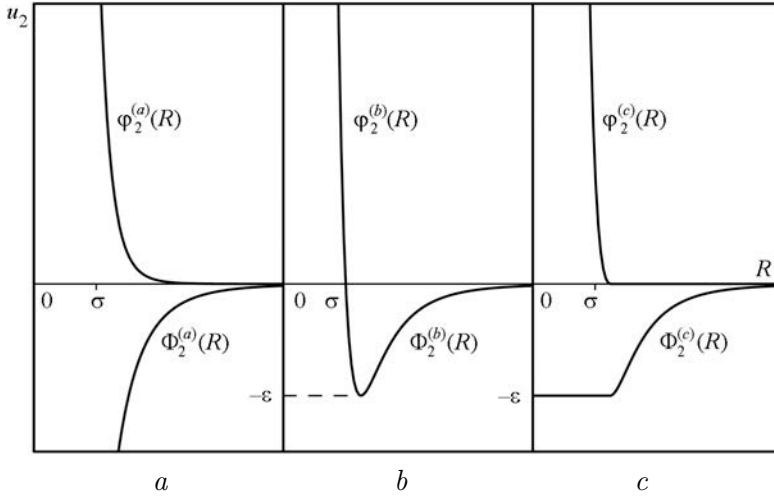


Fig. 6. Three different separation schemes of the Lennard-Jones pair potential $u_2(R)$ into short-range repulsive $\varphi_2(R)$ and long-range attractive $\Phi_2(R)$ components: *a* — separation by McQuarrie and Katz, *b* — by Barker—Henderson, and *c* — the Weeks—Chandler—Andersen (WCA) separation, where the splitting point is chosen at the minimum of the potential $R_0 = 2^{1/6}\sigma$

proposed by McQuarrie and Katz [132], the first term in (3.2.3) is considered short-range, and the second term is considered long-range. In the second method (Fig. 6, *b*), used in the work of Barker and Henderson [133], the positive part of the potential is taken as $\varphi_2(R)$, and the negative part as $\Phi_2(R)$. In the third method (Fig. 6, *c*), proposed by Weeks, Chandler, and Andersen [134], the point of separation is chosen at the minimum of the potential $R_0 = \sqrt[6]{2}\sigma$, where the force acting on a molecule due to another molecule is zero, because $(\partial u_2(R)/\partial R)_{R=R_0} = 0$. Thus, this method of separation corresponds more to the separation of interaction forces rather than interaction potentials. It is important that with this choice, the long-range part of the potential changes quite smoothly, especially at small distances. Of course, none of the proposed methods is optimum in the sense discussed in the previous chapter. However, numerical calculations [123] convincingly show that the third method significantly improves the convergence of cluster expansions, while the first method converges very slowly. In what follows, unless otherwise specified, we adhere to the third method of dividing the interactions.

To apply the cluster expansions (2.3.59), it is necessary to know the free energy and at least the pair distribution function of the reference system. Thus, there arises the task of describing a system with the potential $\varphi_2(R)$. This potential is of a purely repulsive nature, so the corresponding Mayer function $f_0(R) = \exp[-\beta\varphi_2(R)] - 1$ smoothly changes from -1 at small distances to 0 at large distances. As a result of a strong repulsive character of the potential

$\varphi_2(R)$, the function $f_0(R)$ almost coincides with the Mayer function of hard spheres $f_d(R) = \exp[-\beta\varphi_2^{(d)}(R)] - 1$, where $\varphi_2^{(d)}(R)$ is the interaction potential of hard spheres with diameter d . A small difference exists only around $R \sim \sigma$. Therefore, it can be hoped that with a good choice of diameter d , the reference system can be approximated by the corresponding system of hard spheres, the thermodynamic and structural properties of which are well known to us. A rigorous analysis of the relationship between the hard sphere model and the system with real repulsion was carried out by Andersen, Weeks, and Chandler [29]. They represented the free energy of the reference system in the form of the following functional series:

$$F_0 = F_d + \sum_{1 \leq i < j \leq N} \int d\mathbf{R}_i d\mathbf{R}_j \left(\frac{\delta F_0}{\delta f_0(R_{ij})} \right)_{f_0=f_d} \Delta f(R_{ij}) + \frac{1}{2} \sum_{i,j,l,m} \int d\mathbf{R}_i d\mathbf{R}_j d\mathbf{R}_l d\mathbf{R}_m \left(\frac{\delta^2 F_0}{\delta f_0(R_{ij}) \delta f_0(R_{lm})} \right)_{f_0=f_d} \times \Delta f(R_{ij}) \Delta f(R_{lm}) + \dots, \quad (3.2.4)$$

where F_d is the free energy of hard spheres with diameter d , and $\Delta f(R) = f_0(R) - f_d(R)$.

The functional derivatives correspond to the hard sphere system. The first derivative in (3.2.4), according to (2.2.30), is equal to

$$\left(\frac{\delta F_0}{\delta f_0(R)} \right)_{f_0=f_d} = \frac{1}{\beta V^2} y_2^{(d)}(R),$$

where

$$y_2^{(d)}(R) = e^{\beta\varphi_2^{(d)}(R)} F_2^{(d)}(R),$$

and $F_2^{(d)}(R)$ is the pair distribution function of hard spheres. The second derivative

$$\begin{aligned} \left(\frac{\delta^2 F_0}{\delta f_0(R_{ij}) \delta f_0(R_{lm})} \right)_{f_0=f_d} &= \frac{1}{\beta V^5} \int d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 \delta(\mathbf{R}_{12} - \mathbf{R}_{ij}) \times \\ &\times \delta(\mathbf{R}_{13} - \mathbf{R}_{lm}) \delta_{im} y_2^{(d)}(R_{12}) y_2^{(d)}(R_{13}) j_3^{(d)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) + \\ &+ \frac{1}{4\beta V^6} \int d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 d\mathbf{R}_4 \delta(\mathbf{R}_{12} - \mathbf{R}_{ij}) \delta(\mathbf{R}_{34} - \mathbf{R}_{lm}) \times \\ &\times y_2^{(d)}(R_{12}) y_2^{(d)}(R_{34}) j_4^{(d)}(\mathbf{R}_1, \dots, \mathbf{R}_4). \end{aligned} \quad (3.2.5)$$

One can show [29] that

$$\begin{aligned} j_3^{(d)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) &= h_2^{(d)}(R_{23}) + \\ &+ F_2^{(d)}(R_{23}) \left[\frac{F_3^{(d)}(R_1, R_2, R_3)}{F_2^{(d)}(R_{12}) F_2^{(d)}(R_{13}) F_2^{(d)}(R_{32})} - 1 \right], \end{aligned}$$

in the superposition approximation, $j_3^{(d)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = h_2^{(d)}(R_{23})$. The expression for $j_4^{(d)}(\mathbf{R}_1, \dots, \mathbf{R}_4)$ is more complex since it contains $F_2^{(d)}(R)$, $F_3^{(d)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$, and $F_4^{(d)}(\mathbf{R}_1, \dots, \mathbf{R}_4)$. However, in the superposition approximation:

$$\begin{aligned} j_4^{(d)}(\mathbf{R}_1, \dots, \mathbf{R}_4) = & h_2^{(d)}(R_{13})h_2^{(d)}(R_{24}) + h_2^{(d)}(R_{14})h_2^{(d)}(R_{23}) + \\ & + h_2^{(d)}(R_{13})h_2^{(d)}(R_{23})h_2^{(d)}(R_{24}) + h_2^{(d)}(R_{13})h_2^{(d)}(R_{14})h_2^{(d)}(R_{24}) + \\ & + h_2^{(d)}(R_{13})h_2^{(d)}(R_{14})h_2^{(d)}(R_{33}) + h_2^{(d)}(R_{14})h_2^{(d)}(R_{23})h_2^{(d)}(R_{24}) + \\ & + h_2^{(d)}(R_{13})h_2^{(d)}(R_{14})h_2^{(d)}(R_{23})h_2^{(d)}(R_{24}). \end{aligned}$$

Now, the series (3.2.4) can be rewritten in the form,

$$\begin{aligned} \beta \frac{F - F_0}{N} = & \frac{1}{2}\rho^2 \int d\mathbf{R} B_d(R) + \frac{1}{2}\rho^3 \int d\mathbf{R}_{12} d\mathbf{R}_{13} B_d(R_{12}) B_d(R_{13}) \times \\ & \times j_3^{(d)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) + \frac{1}{8}\rho^4 \int d\mathbf{R}_{12} d\mathbf{R}_{13} d\mathbf{R}_{14} B_d(R_{12}) B_d(R_{34}) \times \\ & \times j_4^{(d)}(\mathbf{R}_1, \dots, \mathbf{R}_4) + \dots, \end{aligned} \quad (3.2.6)$$

The introduced function

$$B_d(R) = y_2^{(d)}(R)[f_0(R) - f_d(R)] \quad (3.2.7)$$

is nonzero only in a small region $|R - d| \leq \xi d$, where $f_0 \neq f_d$. For the hard-sphere system, $\xi = 0$, so the parameter ξ serves as a measure of the “softness” of the potential. Since the n -th functional derivative in the expansion (3.2.4) includes n functions $B_d(R)$, the series (3.2.6) represents an expansion of the free energy of the reference system in powers of ξ . We choose the size of the hard spheres based on the condition

$$\int d\mathbf{R} B_d(R) = 0. \quad (3.2.8)$$

This causes the first term in series (3.2.6) to vanish, while the discarded terms are of order $O(\xi^4)$ rather than $O(\xi^2)$, as would be the case with any

other choice. Indeed, let us consider the integral $\int_0^\infty B_d(R) F(R, s) R^2 dR$, where

$F(R, s)$ is an arbitrary smooth function of R , also depending on other variables s , over which no integration is performed. It is clear that, since $B_d(R) \neq 0$ only in the region $|R - d| < \xi d$, this integral is of order $O(\xi)$. But according to (3.2.6)

$$\int_0^\infty B_d(R) F(R, s) R^2 dR = \int_0^\infty [F(R, s) - F(d, s)] B_d(R) R^2 dR,$$

and since $F(R, s)$ is a smooth function of R , the expression in brackets is also of order $O(\xi)$. Therefore, the integral under consideration is of order $O(\xi^2)$. Using these arguments, we conclude that the second and third terms in (3.3.98) are of order $O(\xi^4)$. Thus,

$$F_0 = F_d[1 + O(\xi^4)], \quad (3.2.9)$$

where diameter d is determined according to (3.2.8).

Thus, a direct connection has been established between the thermodynamic properties of the hard-sphere system and a system with a real repulsive potential. The diameter d is determined from (3.2.8) and depends on both density and temperature. This dependence must undoubtedly be taken into account when deriving other thermodynamic quantities from the free energy.

Equation (3.2.8) can be approximately solved in an analytical form [135]. To achieve this, let us represent it in the form

$$12\eta \int_0^\infty y_2^{(d)} \Delta f(r) r^2 dr = 0,$$

where $r = R/\sigma$ and $\eta = \pi/6 N/V \sigma^3$. Since $\Delta f(r) \neq 0$ only in the region $R \simeq d\xi$, the smooth function $r^2 y_2^{(d)}(r)$ can be expanded into a series around the point $r = 1$,

$$r^2 y_2^{(d)}(r) = \gamma_0 + \gamma_1(r - 1) + \frac{1}{2}\gamma_2(r - 1)^2 + \dots, \quad (3.2.10)$$

where γ_0 is expressed through the contact value of the pair distribution function of hard spheres and, according to (3.1.65), $\gamma_0 = (1 - \eta/2)/(1 - \eta)^3$. Verlet and Weis also obtained semi-empirical expressions for γ_1 and γ_2 . Taking into account the first term in (3.2.10), it leads to the equation

$$12\eta \int_0^\infty \gamma_0 \Delta f(r) dr = 0,$$

from which for the diameter of hard spheres we obtain,

$$d = d_{\text{BH}} = \int_0^\infty [1 - e^{-\beta\varphi_2(R)}] dR. \quad (3.2.11)$$

This expression was first derived in the work of Barker and Henderson [133]. Taking into account the second term in (3.2.10) leads to the expression

$$d = d_{\text{BH}}[1 + \Psi\delta], \quad (3.2.12)$$

where

$$\Psi = \frac{1}{2} \frac{\gamma_1}{\gamma_0}, \quad \delta = \int_0^\infty \left[\frac{R}{d_{\text{BH}}} - 1 \right]^2 \frac{d}{dR} [e^{-\beta\varphi_2(R)}] dR.$$

The value of the diameter depends on temperature (mainly through d_{BH}) and density (through Ψ). As the temperature increases, d_{BH} decreases, leading to a reduction in d . From a physical perspective, this is understandable because, with increasing temperature, configurations with higher potential energy become more probable, corresponding to smaller intermolecular distances. As the density increases, Ψ decreases, which also results in a decrease in d . This is also intuitive since, with increasing density, the pressure in the system rises, causing the system to become more compressed [29].

By functional differentiation of the free energy, one can obtain the pair distribution function. However, instead of the pair distribution function, it is more convenient to consider the function $y_2^0(R)$. Functionally differentiating expression (3.2.6), we obtain:

$$\begin{aligned} y_2^0(R) = y_2^{(d)}(R) & \left[1 + 2\rho \int d\mathbf{R}_{12} d\mathbf{R}_{13} \delta(\mathbf{R}_{12} - \mathbf{R}) \times \right. \\ & \times B_d(R_{13}) j_3^{(d)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) + \frac{1}{2} \rho^2 \int d\mathbf{R}_{12} d\mathbf{R}_{13} d\mathbf{R}_{14} \delta(\mathbf{R}_{12} - \mathbf{R}) \times \\ & \left. \times B_d(R_{34}) j_4^{(d)}(\mathbf{R}_1, \dots, \mathbf{R}_4) + \dots \right]. \end{aligned} \quad (3.2.13)$$

Unlike the free energy, in this case, it is not possible to choose d in such a way that the term with the first functional derivative becomes zero for all R . However, if we use the same value for the diameter d as we did earlier for the free energy, it can be shown that

$$y_2^0(R) = y_2^{(d)}(R) [1 + O(\xi^2)] \quad (3.2.14)$$

or

$$F_2^0(R) = e^{-\beta\varphi_2(R)} y_2^{(d)}(R) [1 + O(\xi^2)]. \quad (3.2.15)$$

This relation establishes a direct connection between the structural properties of a system with real repulsive interactions and the hard sphere system. It is interesting to note that the expression (3.2.9) for the free energy is more accurate than (3.2.15) for the pair distribution function. Therefore, thermodynamic quantities (internal energy, pressure, etc.), derived from the free energy, are more accurate than those found from the pair distribution function. Of course, when higher-order terms are considered in (3.2.15), the results will be identical.

The considered scheme is applicable to any short-range repulsive potential. In particular, in Ref. [29], it was successfully used to describe a system

with the potential $\varphi_2(R) = \epsilon(\sigma/R)^{12}$, as well as the reference system with the Lennard-Jones potential using for the separation of pair interaction the method proposed by Weeks, Andersen, and Chandler (see Fig. 6, *b*). The obtained results for thermodynamic properties and the pair distribution function are in good agreement with the results from computer simulations across nearly the entire range of the temperatures and densities considered.

3.2.2. Cluster expansions

Let us proceed to the analysis of cluster expansions for the model with the Lennard-Jones potential. We begin with the high-temperature approximation (HTA), which corresponds to the van der Waals approach of accounting for attractive forces. According to (2.3.24)

$$\frac{F - F_0}{N}\beta = \frac{1}{2}\rho \int F_2^0(R)\Phi_2(R)d\mathbf{R}, \quad F_2(R) = F_2^0(R), \quad (3.2.16)$$

where F_0 and $F_2^0(R)$ are free energy and pair distribution function of the reference system.

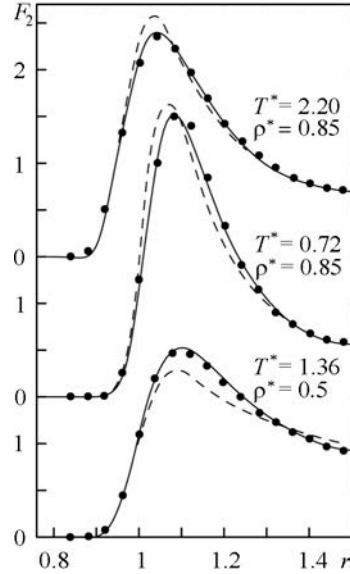
Although the high-temperature approximation completely neglects the contribution of long-range forces to the systems structure, comparison with computer simulations shows that expressions (3.2.16) are sufficiently accurate not only in the high-temperature region but also in the high-density region for all temperatures, including the triple point, where all three phases (crystalline, vapour, and liquid) coexist.

Table 3. The value of the free energy $\frac{1}{N}\beta F$ for a system with the Lennard-Jones potential

T^*	$\rho\sigma^3$	MC	PY	HTA	ORPA
2.74	0.6	-0.34	-0.33	-0.33	-0.34
	0.7	0.01	0.01	0.01	0.00
	0.8	0.43	0.43	0.41	0.41
	0.9	0.93	0.95	0.92	0.92
	1.0	0.59	1.61	1.56	1.56
1.35	0.6	-1.77	-1.75	-1.74	-1.76
	0.7	-1.65	-1.62	-1.63	-1.64
	0.8	-1.41	-1.37	-1.41	-1.42
	0.9	-1.02	-0.99	-1.02	-1.03
1.15	0.6	-2.29	-2.28	-2.26	-2.29
	0.7	-2.25	-2.23	-2.24	-2.25
	0.8	-2.06	-2.06	-2.09	-2.10
	0.9	-1.79	-1.74	-1.77	-1.77
0.75	0.6	-4.24	—	-4.18	-4.25
	0.7	-4.53	-4.50	-4.51	-4.54
	0.8	-4.69	-4.63	-4.69	-4.71

Table 3, taken from [136], presents the values of free energy obtained within the approximation (3.2.16) for various values of reduced temperature T^* and reduced density ρ^* . For comparison, the table also includes exact results obtained using the Monte Carlo simulation (MC), as well as the results derived from the numerical solution of the Percus—Yevick equation (PY) based on expression (1.1.31) for internal energy. As seen from the table, the high-temperature approximation (HTA) provides the

Fig. 7. Pair distribution function $F_2(r)$ of the Lennard-Jones fluid for three thermodynamic states [136]. Symbols correspond to the computer simulation data, while dashed and solid lines represent the high-temperature approximation and the optimized cluster expansion results, respectively



dominant contribution to the systems free energy and, in the high-density region, leads to significantly better results than the Percus—Yevick approximation.

Fig. 7, also taken from Ref. [136], presents the pair distribution function for three thermodynamic states. The solid curve with symbols represents the results of computer simulations. The dashed curve corresponds to the pair distribution function obtained in the high-temperature approximation. As seen from the figure, the high-temperature approximation provides the dominant contribution. At high densities, the structure of the system is mainly determined by short-range interactions.

As density and temperature decrease, the need arises to account for higher-order terms in expansion (2.3.59). Higher-order approximations, instead of the potential $\Phi_2(R)$, include the screened potential $g(R)$. Calculating the screened potential, it is reasonable to approximate the short-range potential $\varphi_2(R)$ with the potential of hard spheres of diameter d . This does not introduce a significant error for potentials with strong repulsion. In this case, as noted in Chapter 2, the optimization procedure reduces to solving the variational problem $\delta F / \delta \Phi_2(R) = 0$ for the unphysical region $R < d$.

Fig. 8 presents the screened potentials obtained numerically in Ref. [137] at $T^* = 1.15$ for three different densities: $\rho^* = 0.50$ and $\rho^* = 0.85$. At $\rho^* = 0$, $g(R) = \beta\Phi_2(R)$, and as the density increases, the role of long-range forces diminishes. In the high-density region, even at low temperatures, $|g(R)| \ll 1$. Thus, due to screening, the effect of long-range forces is weakened, and short-range interactions play a dominant role. This explains the success of the high-

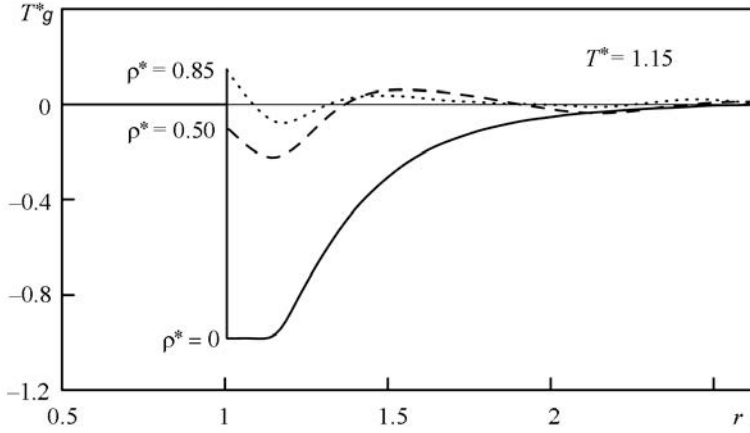


Fig. 8. Screened effective interaction potential $T^*g(r)$ for a Lennard-Jones system at reduced temperature $T^* = 1.15$ and three densities $\rho^* = 0, 0.5, 0.85$

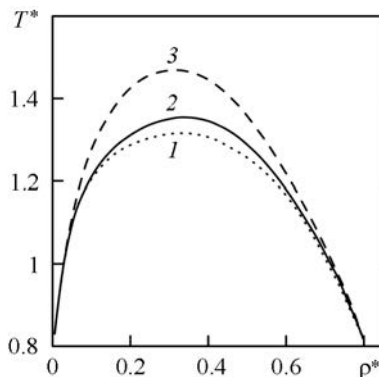
temperature approximation in the high-density region. However, at low and moderate densities, long-range interactions remain significant.

Accounting for the third term in expression (2.3.59) for the free energy leads to an optimized random phase approximation (ORPA). For the pair distribution function, this corresponds to the expression $F_2(R) = F_2^0(R) + g(R)$. Due to the small magnitude of the screened potential at high temperatures and at large densities, the high-temperature approximation naturally retains its accuracy. The values of the obtained free energy using this approximation are also presented in Table 3. As seen from the table, the inclusion of F_{ORPA} significantly improves the results of the high-temperature approximation in the range of moderate densities but does not significantly contribute at high densities.

Accounting for the fourth term in expression (2.3.59) leads to an approximation of the second cluster coefficient. The corresponding expression for the pair distribution function is $F_2(R) = F_2^0(R) \exp(g(R))$, which is exact in the low-density limit since for $\rho^* \rightarrow 0$, $g(R) \rightarrow -\beta\Phi_2(R)$. In Fig. 7, the pair distribution function in the second cluster coefficient approximation is shown as a solid line. In this approximation, the function perfectly agrees with the results of computer simulations.

In studies [27, 28], numerical differentiation was used to determine the values of internal energy and pressure. These values, obtained based on the free energy, agree with simulation data, as does the free energy itself. Importantly, the results obtained using the second cluster coefficient approximation by different methods are thermodynamically self-consistent with high accuracy [137]. Nevertheless, as noted earlier, the cluster expansion (2.3.59) becomes invalid near the critical point, where strong long-range correlations arise, making interactions between different collective modes significant. In this region, the

Fig. 9. Coexistence curves for the liquid and vapour phases of a Lennard-Jones fluid. Curve 1 shows experimental data for argon. Curve 2 represents the theoretical prediction by Sung and Chandler [137] based on the equation of state with the second cluster coefficient approximation and chemical potential matching. Curve 3 is calculated using a high-temperature approximation



Gaussian form of the Jacobian fails to correctly describe the singularities at the critical point. Clearly, the van der Waals equation, which is also based on expansion (2.3.59), does not provide a correct description of the critical behaviour either.

Sung and Chandler [137], based on the second cluster coefficient approximation, attempted to determine the coexistence curve of the liquid and vapour phases. They used the equation of state supplemented by the equality of the chemical potentials of the coexisting phases. The results are presented in Fig. 9. Since the second cluster coefficient approximation is quite accurate in the regions of high and low densities, the low-temperature part of their obtained curve correctly represents the exact phase diagram of the system. The authors suggest that the second cluster coefficient approximation is accurate at least for $T^* \leq 1.15$. As the temperature increases, the behaviour of the system near the critical point becomes important. The obtained curve 2 cannot be directly compared with exact results because computer simulations methods struggle to describe long-range correlations present at the critical point. Therefore, Sung and Chandler compared curve 2 with the experimental coexistence curve of argon (curve 1). As seen in the figure, the curves differ only near the critical point. Also shown in the figure is curve 3, obtained using the high-temperature approximation. However, in terms of accuracy, this approximation is significantly less reliable than the second cluster coefficient. Near the critical point, the thermodynamic self-consistency of the second cluster coefficient approximation breaks down. In particular, the isothermal compressibility, derived from the free energy, correctly diverges to infinity at the critical point. However, the compressibility obtained from the pair distribution function using (1.1.33) remains finite. This indicates that the second cluster coefficient approximation becomes invalid in the vicinity of the critical point. To describe the system near the critical point, the approach should be based, as in the theory of second-order phase transitions [58], on a non-Gaussian form of the fluctuation distribution. This requires introducing the Jacobian for the transformation to collective variables.

Table 4. Critical parameters for a system with Lennard-Jones potential

Method	T_c^*	ρ_c^*	P_c^*	$Z_c = \frac{1}{\rho_c} \beta_c P_c$
MD	1.32–1.36	0.32–0.36	0.13–0.17	0.30–0.36
ORPA + B_2	1.35	0.35	0.15	0.32
SP(v)	1.45	0.40	0.26	0.44
SP(c)	1.58	0.40	0.30	0.48
PY(v)	1.25	0.29	0.11	0.30
PY(c)	1.32	0.28	0.13	0.36
PY(E)	1.34	0.34	0.14	0.31
HNC(v)	1.25	0.26	0.12	0.35
HNC(c)	1.39	0.28	0.15	0.38
PY II (v)	1.36	0.36	0.15	0.31
Experimental values for Argon	1.26	0.316	0.117	0.293

Table 4, taken from [136], presents the values of the critical parameters $P_c^* = 1/\epsilon P_c \sigma^3$, $T_c^* = k_B T_c / \epsilon$, and $\rho_c^* = \rho_c \sigma^3$, obtained by Sung and Chandler using the second cluster coefficient approximation. For comparison, the table also includes critical parameters determined using molecular dynamics (MD) simulations, as well as results based on integral equations: the superposition approximation (SP) with the virial equation (v), the equation for compressibility, the Percus–Yevick equation (PY) in three approximations (c, v, E), the hypernetted-chain approximation (HNC), and the second-order Percus–Yevick equation. Additionally, experimental values for argon are provided for comparison. As seen from the table, the critical parameters derived from the second cluster coefficient approximation are within the accuracy range of computer simulation results and the second-order Percus–Yevick equation. The discrepancy between theoretical and experimental values is attributed to the model nature of the potential.

We previously noted that when describing real systems (even noble gases), it becomes necessary to account for many-particle interactions, at least three-particle interactions. In principle, the description of a real system can be reduced to the description of a hypothetical system with an effective two-particle interaction $u_2^{\text{ef}}(R)$. By expanding, for example, the configuration integral of the real system into a series using Mayer functions, it can be shown [138] that

$$\begin{aligned}
 u_2^{\text{ef}}(R) = u_2(R_{12}) - \frac{1}{\beta} \ln \left[1 + \frac{N}{V} \int \frac{F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)}{F_2(R_{12})} \times \right. \\
 \left. \times [e^{-\beta u_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)} - 1] d\mathbf{R} + \dots \right], \quad (3.2.17)
 \end{aligned}$$

where $F_2(R)$, $F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ are the distribution functions of the system with potential $u_2(R)$.

The description of a system with the potential $u_2^{\text{ef}}(R)$ follows the previously outlined scheme for the Lennard-Jones potential. However, if higher-order interactions need to be accounted for in the series expansion, determining $u_2^{\text{ef}}(R)$ becomes no less complicated than computing the configuration integral in the presence of many-particle interactions.

One of the authors attempted [139] to derive the expressions for effective potentials by screening them with many-particle interactions. This approach allowed for an approximate relation describing the variation of the potential well depth as a function of the system density. Nevertheless, for the description of dense systems, the screening of interactions must be carried out based on a fundamental consideration of short-range forces.

It should also be noted that the inclusion of many-particle van der Waals interactions can be performed using the formalism of macroscopic electrodynamics. However, this requires the knowledge of a dielectric function $\varepsilon(\mathbf{k}, \omega)$ or, more generally, the Green function describing the fluctuations of the electromagnetic fields in the system [140].

The results obtained in this section can also be used to describe liquid metals. The latter consist of electrons and free ions. Averaging the statistical operator over the electronic subsystem, according to (1.1.11), leads to the consideration of only the ionic subsystem with an effective interionic interaction. The electrons fully screen the Coulomb interionic repulsion, providing an effective attraction at shorter distances. Calculations by Ashcroft and Lekner [117] show that the primary contribution to the structural factors of simple metals comes from hard spheres. Interestingly, for the second term in the expansion (2.3.59), which corresponds to the mean electrostatic energy of the Coulomb interaction between ions with the compensation energy subtracted according to the condition of overall charge neutrality of the system,

$$F_{\text{HTA}}^{(1)} = \frac{1}{2} \frac{N^2}{V} \int \frac{e^2 z^2}{R} [F_2^0(R) - 1] d\mathbf{R},$$

a rather simple expression can be obtained [141]. Namely, using the Laplace transform of the hard-sphere pair distribution function

$$\mathcal{F}(s) = \int_0^\infty F_2^0(R) e^{-sR} R dR$$

one obtains

$$F_{\text{HTA}}^{(1)} = 2\pi e^2 z^2 \frac{N^2}{V} \lim_{s \rightarrow 0} \left[\mathcal{F}(s) - \frac{1}{s^2} \right],$$

from which, in the Percus—Yevick approximation, according to (3.1.69), we obtain:

$$F_{\text{HTA}}^{(1)} = -N \frac{e^2 z^2}{\sigma} \frac{12\eta}{1+2\eta} \left[\frac{1}{2} - \frac{1}{10}\eta + \frac{1}{20}\eta^2 \right], \quad (3.2.18)$$

where z is the valency of the ion.

3.3. Multicomponent systems

Herein before we analysed the systems consisting of particles of one species (one-component systems). Now let us consider the systems consisting of particles of several different species. Those are various mixtures (solutions, melts, alloys, etc.), which contrary to one-component systems have additional thermodynamic degrees of freedom, related to concentrations of various components. For example, in a two-component system besides usual variables T and V (or other pair) there is another variable — concentration of one of the components $x_a = \frac{N_a}{N_a + N_b}$, where N_a and N_b is the number of particles of corresponding species a and b . In this case, the concentration of the other component $x_b = 1 - x_a = \frac{N_b}{N_a + N_b}$. It is worth noting that concentration of the particles of species a $x_a = N_a/N$, where $N = \sum_a N_a$, is an independent variable only in the case when no chemical reactions take place involving this species.

The existence of additional degrees of freedom significantly increases the diversity of phase states, which can take place in multicomponent systems. In the current chapter we consider mixtures of simple monoatomic systems while the results obtained earlier are generalized for multicomponent case.

3.3.1. General relations

Thermodynamic description of multicomponent systems, as well as one-component ones, is based on the use of characteristic state functions. While defining those functions, as was mentioned at the beginning of the book, one should add the term $\sum_{a=1}^M \mu_a dN_a$, where μ_a is chemical potential of particles of species a ; N_a is the number of particles of species a ; M is the number of components in the system. For the thermodynamic potential, one has

$$d\Phi = -SdT + VdP + \sum_{a=1}^M \mu_a dN_a. \quad (3.3.1)$$

Since Φ is homogeneous function on the number of particles, then

$$\Phi = \sum_{a=1}^M N_a \mu_a. \quad (3.3.2)$$

Subtracting from the first equation the derivative of the second equation, we can obtain the famous Gibbs—Duhem equation

$$-SdT + VdP - \sum_{a=1}^M N_a d\mu_a = 0. \quad (3.3.3)$$

When pressure and temperature are constant

$$\sum_{a=1}^M x_a d\mu_a = 0. \quad (3.3.4)$$

The equation (3.3.4) defines the character of concentration changes in the system. The difference between chemical potentials for particles of a species does not depend on the reference value. Thus, any standard relation can be chosen. Usually, the high-dilution limit is adopted as the reference case, which corresponds to the limit $x_a = N_a/N \rightarrow 0$. Thermodynamic description is performed based on the activity coefficients $f_a = \exp\{-\beta\Delta\mu_a\}$ or osmotic coefficients $\chi = P/P^0$, where $\Delta\mu_a = \mu_a - \mu_a^0$; μ^0 is the value of chemical potential in the reference state; P^0 is pressure in the reference state. Both quantities are normalised so that for $x_a \rightarrow 0$, $f_a \rightarrow 1$, $\chi \rightarrow 1$.

The problem of describing multicomponent systems does not consist in describing the thermodynamic functions, but in describing only the functions of mixing, which define the changes in thermodynamic properties upon mixing. For example, in the case of some observable X , the function of mixing would be

$$X^{(m)} = X - \sum_a x_a X_a, \quad (3.3.5)$$

where X_a is the value of observable X for subsystem consisting of particles of species a in the absence of other components. The difference of the function of mixing and its ideal part is described by the system of excess functions

$$X^{(\text{exc})} = X^{(m)} - X_{\text{id}}^{(m)}, \quad (3.3.6)$$

calculation of which is the main objective in the theory of multicomponent systems.

Structure and character of thermal motion in multicomponent systems is similar to that in one-component system, the difference is in complexity of

the problem arising due to multiplicity of parameters specific to each component. In the core of modern treatment of multicomponent systems, as well as one-component ones, is the use of distribution functions. The n -particle distribution function for species $a_1, a_2, \dots, a_n$ (see (1.1.26)) has the form

$$F_{a_1, \dots, a_n}(\mathbf{R}_1, \dots, \mathbf{R}_n) = \frac{1}{V^{N-n} Q_N} \int e^{-\beta U_N} (d\mathbf{R})_{a_1, \dots, a_n}, \quad (3.3.7)$$

where $(d\mathbf{R})_{a_1, \dots, a_n}$ means the integration over all particles, except n fixed particles. The existence of particles of different species significantly increases the number of distribution functions. For example, in the case of a binary mixture, instead of one there are three pair distribution functions $F_{aa}(R)$, $F_{ab}(R)$, $F_{bb}(R)$. In general case of M -sorts system there will be $1/2M(M+1)$ different pair distribution functions. For the system with pair interaction, all thermodynamic properties are determined by the set of pair distribution functions $F_{ab}(R)$. For the internal energy one has

$$E = \frac{3}{2} N k_B T + \frac{1}{2} \sum_{a,b} \frac{N_a N_b}{V} \int F_{ab}(R) u_{ab}(R) d\mathbf{R}. \quad (3.3.8)$$

After differentiation of configuration integral over V , one can obtain a virial equation of state

$$P = \frac{N}{V} k_B T - \frac{1}{6} \sum_{a,b} \frac{N_a N_b}{V^2} \int F_{ab}(R) \frac{\partial u_{ab}(R)}{\partial R} d\mathbf{R}. \quad (3.3.9)$$

From fluctuation relations it can be seen that

$$\frac{1}{\beta} \left(\frac{\partial N_a}{\partial \mu_b} \right)_{T, V, \mu_a, \dots} = N_a \delta_{ab} + \frac{N_a N_b}{V^2} \int |F_{ab}(R) - 1| d\mathbf{R}, \quad (3.3.10)$$

which generalizes the expression in (1.1.33) for the one-component case. It is straightforward to generalize also (1.1.34) and (1.1.35), connecting pair distribution functions and configuration integral

$$Q_N = \exp \left\{ \sum_{a,b} \frac{N_a N_b}{2V} \int_0^1 d\xi \int d\mathbf{R} u_{ab}(R) F_{ab}(R, \xi) \right\}, \quad (3.3.11)$$

$$\frac{1}{V^2} F_{ab}(R) = -\frac{1}{\beta} \frac{\delta \ln Q_N}{\delta u_{ab}(R)}. \quad (3.3.12)$$

In principle, the description of a multicomponent system can be reduced to some hypothetical one-component system with effective pair interaction potential $u_2^{\text{ef}}(R)$. However, the problem of finding such $u_2^{\text{ef}}(R)$ is no less complicated, than the original one. Usually the potential $u_2^{\text{ef}}(R)$ is constructed on the basis

of some intuitive considerations. For example, in the approximation of mean potential $u_2^{\text{ef}}(R) = \sum_{a,b} x_a u_{ab}(R)$. For the systems with van der Waals interactions in van der Waals approximation one may consider a one-component system with particle size $\sigma = \left(\sum_{a,b} x_a x_b \sigma_{ab}^3 \right)^{1/3}$ and depth of the potential well $\epsilon = \frac{1}{\sigma^3} \left(\sum_{a,b} x_a x_b \epsilon_{ab} \sigma_{ab}^3 \right)$. There also exist other choices for $u_2^{\text{ef}}(R)$. However, they do not bear a strictly controllable character, distort a real picture of changes of concentration.

Another approach in a one-component description is connected with the exclusion of one of subsystems and lies in the core of osmotic theory of solutions [95, 142]. Let us consider it more in detail. To this end, we consider a two-component system with the dominance in the concentration for one of them. The system for which concentration is dominant is usually called a solvent, and the other a solute. Solvent can be excluded from explicit consideration and theory can be presented in the form in which only solute particles are considered explicitly. Let us average the Gibbs function of entire system over the configuration space of solvent

$$\frac{1}{\int e^{-\beta U_s} d\Gamma_s} \int e^{-\beta U} d\Gamma_s = e^{-\beta W}, \quad (3.3.13)$$

where U_s is potential energy of interaction between molecules of solvent; U is potential energy of interaction of all particles.

As a result, the description of the equilibrium properties of the system reduces to calculating the configuration integral only for the solute particles, with the substitution of their potential in vacuum by W — the free energy of interaction in the pure solvent. However, the determination of the former is not a simple problem. For example, in the case of pair intermolecular interactions

$$U = \sum_{i<j} u(R_{ij}) + \sum_{i,j} u_s(R_{ij}) + \sum_{i<j} u_{ss}(R_{ij}), \quad U_s = \sum_{i<j} u_{ss}(R_{ij}),$$

where $u(R)$ is the interaction potential of two solute particles; $u_s(R)$ is the interaction potential of solute particle with solvent molecule; $u_{ss}(R)$ is the interaction potential between two solvent molecules.

According to (3.3.13), the determination of W involves integration over the configuration space of the solvent, $d\Gamma_s = \prod_{i=1}^{N_s} d\Gamma_i$, where $d\Gamma_i$ is the element of the configuration space corresponding to the i -th solvent molecule; N_s is the

number of solvent molecules. Expression in (3.3.13) can be rewritten in the following form

$$e^{-\beta W} = \frac{e^{-\beta \sum_{i<j} u(R_{ij})}}{\int e^{-\beta U_s} d\Gamma_s} \int \prod_{j=1}^{N_s} [1 + f_j] e^{-\beta U_s} d\Gamma_s,$$

where $f_j = \exp \left[-\beta \sum_i u_s(R_{ij}) \right] - 1$ is the Mayer function of the j -th molecule of the solvent in the field of all particles of solute. Expanding the product $\prod_j [1 + f_j]$ in a series, one can obtain

$$e^{-\beta W} = \exp \left\{ -\beta \sum_{i<j} u(R_{ij}) \right\} \left\{ 1 + \sum_i \frac{1}{V} \int f_j d\Gamma_j + \frac{1}{V^2} \sum_{i<j} \int f_i f_j \times \right. \\ \left. \times F_{ij} d\Gamma_i d\Gamma_j + \frac{1}{V^3} \sum_{i<j<l} \int f_i f_j f_l F_{ijl} d\Gamma_i d\Gamma_j d\Gamma_l + \dots \right\},$$

where $F_{ij}, F_{ijl}, \dots$ is a set of distribution functions of the solvent, unperturbed by the particles of solute. After switching from distribution functions to correlation functions $h_{ij} = F_{ij} - 1$, $h_{ijl} = F_{ijl} - F_{ij} - F_{jl} - F_{il} + 2, \dots$ one has

$$W = \sum_{i<j} u(R_{ij}) - \frac{1}{\beta} \left\{ \sum_i \frac{1}{V} \int f_j d\Gamma_j + \sum_{i<j} \frac{1}{V^2} \int f_i f_j h_{ij} d\Gamma_i d\Gamma_j + \dots \right\}. \quad (3.3.14)$$

This is an expression for free energy of interaction in the medium we sought. It consists of the potential energy of interaction in the absence of the medium and the terms which describe indirect interactions via medium, the structure of which is taken into account by correlation functions $h_{ij}, h_{ijl}, \dots$. The expression (3.3.14) after switching from $f_j = \prod_i [1 + f_s(R_{ij})] - 1$ to ordinary

Mayer functions $f_s(R) = \exp\{-\beta u_s(R)\} - 1$ can be split into a set of terms

$$W = \sum_i w(i) + \sum_{i<j} w(ij) + \sum_{i<j<l} w(ijl) + \dots, \quad (3.3.15)$$

where

$$w(i) = -\beta \left[\sum_j \frac{1}{V} \int f_s(R_{ij}) d\Gamma_j + \sum_{j,l} \frac{1}{V^2} \int f_s(R_{ij}) f_s(R_{il}) \times \right. \\ \left. \times h_{jl}(R_{jl}) d\Gamma_j d\Gamma_l + \dots \right],$$

$$w(ij) = u(R_{ij}) - \frac{1}{\beta} \left[\sum_l \frac{1}{V} \int f_s(R_{il}) f_s(R_{jl}) d\Gamma_l + \dots \right] \text{ etc.}$$

With the help of diagrams, these results can be represented in a compact form. Let us denote Mayer functions with lines, and correlation functions with ovals. The number of vertex inside the oval determines the degree of correlation function. Those vertices corresponding to $N_s/V \int d\Gamma_j$, are denoted with black filled circles, the open circles are fixed coordinates of solute particles. Then,

$$\begin{aligned} w(i) &= -\frac{1}{\beta} \left[\text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \dots \right], \\ w(ij) &= u(R_{ij}) - \frac{1}{\beta} \left[\text{diagram 4} + \text{diagram 5} + \text{diagram 6} + \dots \right], \\ w(ijl) &= -\frac{1}{\beta} \left[\text{diagram 7} + \text{diagram 8} + \text{diagram 9} + \text{diagram 10} + \dots \right], \dots \end{aligned} \quad (3.3.16)$$

Let us figure out the physical meaning of the obtained results. The singlet terms describe the changes in free energy upon the introduction of one solute particle in the regime of a dilute solution. This energy is also referred to as the solvation free energy. Since it does not depend on the coordinates of the solute particles, it is also independent of their concentration, and together with the ideal part, it determines the reference value of the chemical potential $w_a = \mu_a^0 - \mu_a^{\text{id}}$, where μ_a^0 is the chemical potential of the reference state; μ_a^{id} is its ideal part.

Thus, dependence of the properties of solution on concentration in accordance with McMillan—Mayer theory [143] is determined by potential of mean force of solute particles in the dilute regime. Additionally, pair terms $w(ij)$ (potential of the mean force between two particles i and j in dilute regime) describing pair interactions between two particle in a solvent, and three-particle terms $w(ijl)$ (potential of mean force of three particles with subtraction of the pair potentials) — three-particle interactions, etc.

For dilute systems, one can use only the first two terms in (3.3.15). However, as the concentration increases, the role of multi-particle interactions becomes more significant. As a result, this method is useful only in the region of small concentrations, and the description of the system in a wide range of concentrations requires the generalization of previously discussed methods to the multicomponent systems.

Generalisation of Mayer cluster expansion method in the case of multicomponent systems is not difficult. The reader may be sure that the topological structure of diagrams (1.3.12)—(1.3.14) will not change. Only the notation is affected: to every field vertex there is a corresponding operation

$\bullet = \sum_a \frac{N_a}{V} \int d\mathbf{R}$, and every line corresponds to Mayer function $\text{---} = f_{ab}(\mathbf{R}) = e^{-\beta u_{ab}(\mathbf{R})} - 1$. As in the one-component case, one can perform partial summation of the diagrams, obtain approximated integral equation, etc. The generalization mostly consist in substituting the $\frac{N}{V}$ by operation $\sum_a \frac{N_a}{V}$. For example, the Ornstein–Zernike equation (1.3.18) in the case of multicomponent system becomes

$$h_{ab}(\mathbf{R}) = c_{ab}(\mathbf{R}) + \sum_c \frac{N_c}{V} \int d\mathbf{R}' c_{ac}(\mathbf{R}') h_{cb}(|\mathbf{R} - \mathbf{R}'|), \quad (3.3.17)$$

where $h_{ab}(\mathbf{R}) = F_{ab}(\mathbf{R}) - 1$; $c_{ab}(\mathbf{R})$ is direct correlation function of two particles of species a and b . The other relations, discussed in Chapter 1, can be generalized accordingly.

3.3.2. Extension of the collective variables method

In the multicomponent systems there are fluctuations of the number density of the particles of every species, which are usually interpreted as fluctuations of density of all particles and fluctuations of concentrations. Therefore, in order to describe multicomponent systems it is reasonable to introduce collective variables for each species of particles. In accordance with method discussed in Chapter 2, let us introduce the operator of the number density deviation from its mean value for the a species of particles

$$\hat{n}_a(\mathbf{R}) = \sum_{i=1}^{N_a} \delta(\mathbf{R} - \mathbf{R}_i) - \frac{N_a}{V}, \quad (3.3.18)$$

or via the Fourier transform

$$\hat{n}_a(\mathbf{R}) = \frac{\sqrt{N_a}}{V} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}} \hat{\rho}_{\mathbf{k},a}, \quad \mathbf{k} \neq 0, \quad (3.3.19)$$

where $\hat{\rho}_{\mathbf{k},a} = \frac{1}{\sqrt{N_a}} \sum_{j=1}^{N_a} e^{-i\mathbf{k}\mathbf{R}_j}$; $\mathbf{k} \neq 0$ is a shorthand notation for Fourier transform of $\hat{n}_a(\mathbf{R})$ operator. Similarly to the one-component case, $\hat{\rho}_{\mathbf{k},a} = \hat{\rho}_{\mathbf{k},a}^c + \hat{\rho}_{\mathbf{k},a}^s$, where $\hat{\rho}_{\mathbf{k},a}^c = \frac{1}{\sqrt{N_a}} \sum_{j=1}^{N_a} \cos(\mathbf{k}\mathbf{R}_j)$, $\hat{\rho}_{\mathbf{k},a}^s = \frac{1}{\sqrt{N_a}} \sum_{j=1}^{N_a} \sin(\mathbf{k}\mathbf{R}_j)$. Also the following relations hold

$$\hat{\rho}_{\mathbf{k},a} = \hat{\rho}_{-\mathbf{k},a}^*, \quad \frac{1}{V} \int (d\mathbf{R}) \hat{\rho}_{\mathbf{k}_1,a} \hat{\rho}_{\mathbf{k}_2,b} = \delta_{ab} \delta_{\mathbf{k}_1 + \mathbf{k}_2, 0}.$$

Suppose that interaction in the system is a pairwise additive property and the interaction potential of two species of particles a and b is

$$u_{ab}(R) = \Phi_{ab}(R) + \varphi_{ab}(R), \quad (3.3.20)$$

where $\Phi_{ab}(R)$ is long-range part of the potential; $\varphi_{ab}(R)$ is its short-range part. Expanding the long-range part of potential energy of the system into Fourier series

$$v(\mathbf{R}) = \sum_{a,b} \sum_{i < j} \Phi_{ab}(R_{ij}) = \sum_{a,b} \sum_{i < j} \sum_k \frac{\nu_{ab}(k)}{V} e^{i\mathbf{k}\mathbf{R}_{ij}},$$

and presenting it in the following form

$$v(\mathbf{R}) = \frac{1}{2\beta} \sum_{a,b} \sum_{\mathbf{k}} \alpha_{ab}(k) [\hat{\rho}_{\mathbf{k},a} \hat{\rho}_{-\mathbf{k},b} - \delta_{ab}] + \frac{1}{2\beta} \sum_{a,b} \sqrt{N_a N_b} \alpha_{ab}(k=0), \quad (3.3.21)$$

where $\alpha_{ab}(k) = 1/V\beta\sqrt{N_a N_b}\nu_{ab}(k)$, $\nu_{ab}(k) = \int d\mathbf{R} e^{i\mathbf{k}\mathbf{R}} \Phi_{ab}(R)$ is the Fourier transform of the potential $\Phi_{ab}(R)$.

Generalizing the calculations, presented in Chapter 2 for one-component system, let us write down $v(R)$ as analytic functional

$$v(R) = \int v(\rho) J(\rho R) (d\rho), \quad (3.3.22)$$

where $(d\rho) = \prod_a \prod_{\mathbf{k}}' d\rho_{\mathbf{k},a}$;

$$v(\rho) = \frac{1}{2\beta} \sum_{a,b} \sum_{\mathbf{k}}' \alpha_{ab}(k) [\rho_{\mathbf{k},a} \rho_{-\mathbf{k},b} - \delta_{ab}] + \frac{1}{2\beta} \sum_{a,b} \sqrt{N_a N_b} \alpha_{ab}(\mathbf{k}=0)$$

is representation of collective variables for function $v(R)$; $J(\rho R) = \prod_{a=1}^M \prod_{\mathbf{k}}' \delta(\rho_{\mathbf{k},a} - \hat{\rho}_{\mathbf{k},a})$ is the transformation Jacobian to collective variables, which is equal to the product of transformation functions for each species:

$$J(\rho R) = \prod_{a=1}^M J(\rho_a, R_a), \quad (3.3.23)$$

where $J(\rho_a, R_a) = \prod_{\mathbf{k}}' \delta(\rho_{\mathbf{k},a} - \hat{\rho}_{\mathbf{k},a})$.

Using the representation of collective variables, for configuration integral one has:

$$Q_N = \frac{1}{V^N} \int (d\mathbf{R}) e^{-\beta U_N} = \frac{1}{V^N} \int (d\mathbf{R}) \int (d\rho) J(\rho R) \exp\{-\beta v(\rho)\} \times \\ \times \exp(-\beta U_0(R)), \quad (3.3.24)$$

where $U_0(R) = \sum_{a,b} \sum_{i < j} \varphi_{ab}(R_{ij})$ is potential energy of short-range interactions.

Similarly to one-component systems case, let us first consider the long-range part of configuration integral

$$Q_N^{(\ell)} = \frac{1}{V^N} \int (d\mathbf{R}) (d\rho) J(\rho R) e^{-\beta v(\rho)}. \quad (3.3.25)$$

The integration in coordinate space is relevant to the transformation function and leads to the following Jacobian

$$J(\rho) = \frac{1}{V^N} \int (d\mathbf{R}) J(\rho R), \quad (3.3.26)$$

which, according to (3.3.23), can be represented as a product $J(\rho) = \prod_{a=1}^M J(\rho_a)$,

where $J(\rho_a)$ is the Jacobian of the transformation of variables only for particles of species a . This Jacobian is discussed in detail in Chapter 2 and, according to (2.1.40), it has the following form

$$J(\rho) = \prod_a \int (d\omega_a) \exp \left[\sum_{n \geq 2} D_n(\omega_a) \right] \exp \left[i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k},a} \rho_{\mathbf{k},a} \right],$$

where

$$(d\omega_a) = \prod_{\mathbf{k}}' d\omega_{\mathbf{k},a}, \quad D_n(\omega_a) = \frac{(-i\pi)^n}{n!} \frac{N_a}{\sqrt{N_a^n}} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \omega_{\mathbf{k}_1,a} \dots \omega_{\mathbf{k}_n,a} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0},$$

sum $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$ is irreducible. Hence,

$$J(\rho) = \int (d\omega) \exp \left\{ \sum_{n \geq 2} D_n(\omega) + i\pi \sum_{\mathbf{k},a} \omega_{\mathbf{k},a} \rho_{\mathbf{k},a} \right\}, \quad (3.3.27)$$

where $D_n(\omega) = \sum_a D_n(\omega_a)$; $(d\omega) = \prod_a \prod_{\mathbf{k}}' d\omega_{\mathbf{k},a}$.

Far from the critical point, the Jacobian can be represented as follows:

$$J(\rho) = \exp \left\{ \sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right\} J_G(\rho), \quad (3.3.28)$$

where $J_G(\rho) = \exp \left\{ -1/2 \sum_{\mathbf{k}}' \left[\sum_a \rho_{\mathbf{k},a} \rho_{-\mathbf{k},a} + \ln \pi \right] \right\}$ is the Gaussian part of the Jacobian,

$$\hat{D}_n(\partial/\partial\rho) = \frac{(-1)^n}{n!} \sum_a \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \frac{N_a}{\sqrt{N_a^n}} \frac{\partial^n}{\partial \rho_{\mathbf{k}_1,a} \dots \partial \rho_{\mathbf{k}_n,a}} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0}.$$

This expression is the generalization of (2.1.43) for the case of multicomponent systems.

The calculation method of long-range part in configuration integral (3.3.25) is the same as in one-component case. According to (3.3.26)–(3.3.27)

$$Q_N^{(\ell)} = \exp \left\{ -\frac{1}{2} \sum_{a,b} \sqrt{N_a N_b} \alpha_{ab}(k=0) \right\} \int \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \sum_{a,b} \alpha_{ab}(k) \times \right. \\ \left. \times [\rho_{\mathbf{k},a} \rho_{-\mathbf{k},b} - \delta_{ab}] \right\} \exp \left\{ \sum_{n \geq 3} \hat{D}_n(\partial/\partial \rho) \right\} J_G(\rho) (d\rho).$$

The calculation of $Q_N^{(\ell)}$ can be performed with Gaussian density measures. The operator part of the Jacobian of the transformation can be expanded into a series, and operators can be paired. As a result, to each pair $\partial^2/\partial \rho_{\mathbf{k},a} \partial \rho_{-\mathbf{k},b}$ there corresponds multiplicative factor $[\rho_{\mathbf{k},a} \rho_{-\mathbf{k},b} - \delta_{ab}]$, which can be replaced by derivative $-\partial/\partial \alpha_{ab}(k)$ from $\exp \left\{ -\frac{1}{2} \sum_{a,b} \sum_{\mathbf{k}} \alpha_{ab}(k) [\rho_{\mathbf{k},a} \rho_{-\mathbf{k},b} - \delta_{ab}] \right\}$. All derivatives $-\partial/\partial \alpha_{ab}(k)$ can be written before the integral sign. The integration over the rest of collective variables leads to the configuration integral in the random phase approximation

$$Q_G^{(\ell)} = \int \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \sum_{a,b} \alpha_{ab}(k) [\rho_{\mathbf{k},a} \rho_{-\mathbf{k},b} - \delta_{ab}] - \right. \\ \left. - \frac{1}{2} \sum_{\mathbf{k}}' \left[\sum_a \rho_{\mathbf{k},a} \rho_{-\mathbf{k},a} + \ln \pi \right] \right\} (d\rho) = \\ = \exp \left\{ \frac{1}{2} \sum_{\mathbf{k}}' \left[\sum_a \alpha_{aa}(k) - \ln \det(\mathbf{1} + \boldsymbol{\alpha}(k)) \right] \right\}, \quad (3.3.29)$$

where the matrix $\mathbf{1} + \boldsymbol{\alpha}(k)$ consists of matrix elements $\delta_{ab} + \alpha_{ab}(k)$.

Taking into account the derivatives $-\partial/\partial \alpha_{ab}(k)$, one can perform cluster expansions, which are structurally similar to that in one-component case, only now for each vertex corresponds the operation $\sum_a N_a/V \int d\mathbf{R}$, and the basis for the expansion is a screened potential

$$g_{ab}(R) = \frac{1}{\sqrt{N_a N_b}} \sum_{\mathbf{k}}' \left[\frac{1 + \delta_{ab}}{2} \frac{\partial}{\partial \alpha_{ab}(k)} \ln \det(\mathbf{1} + \boldsymbol{\alpha}(k)) - \delta_{ab} \right] e^{i\mathbf{k}\mathbf{R}} = \\ = V^2 \frac{\delta \ln Q_G}{\delta \Phi_{ab}(R)}, \quad (3.3.30)$$

where coefficient $\frac{1 + \delta_{ab}}{2}$ takes into account the symmetry of the matrix $\boldsymbol{\alpha}(k)$ relative to the interchange between $\alpha_{ab}(k)$ and $\alpha_{ba}(k)$. Similarly to the one-component case, the screened potential satisfies equations (3.3.17), if in the latter we assume $c_{ab}(R) = -\beta \Phi_{ab}(R)$ and $h_{ab}(R) = g_{ab}(R)$.

The calculations for short-range interaction in the framework of functional derivatives is similar to a one-component case. As a result, one can obtain the following expression of the free energy:

$$F = F_{\text{id}} + F_{\text{HTA}} + F_{\text{RPA}} - \frac{1}{\beta}(B_2 + B_3 + \dots), \quad (3.3.31)$$

where F_{id} is ideal part of free energy;

$$F_{\text{HTA}} = \frac{1}{2\beta} \sum_{a,b} \sqrt{N_a N_b} \alpha_{ab}(k=0) = \frac{1}{2} \sum_{a,b} \frac{N_a N_b}{V} \int \Phi_{ab}(R) d\mathbf{R}$$

is mean value of long-range part of energy;

$$F_{\text{RPA}} = -\frac{1}{2\beta} \sum_{\mathbf{k}}' \left[\sum_a \alpha_{aa}(k) - \ln \det(\mathbf{1} + \boldsymbol{\alpha}(k)) \right]$$

is free energy in the random phase approximation;

$$B_2 = \sum_{a,b} \frac{N_a N_b}{2V} \int \left[\exp(g_{ab}(R) - \beta\varphi_{ab}(R)) - 1 - g_{ab}(R) - \frac{1}{2}g_{ab}^2(R) \right] d\mathbf{R}$$

is the second cluster coefficient; B_3 is the third cluster coefficient, etc.

Using functional differentiation according to (3.3.12), one can obtain an expression for the pair distribution functions

$$F_{ab}(R) = \exp[g_{ab}(R) - \beta\varphi_{ab}(R)] \left[1 + \sum_{n \geq 1} F_{ab}^{(n+2)}(R) \right], \quad (3.3.32)$$

where $F_{ab}^{(n+2)}(R)$ – $(n+2)$ -th cluster coefficient for pair distribution function. Topological structure of diagrams is the same as in a one-component case. The generalization is relevant only to the notation

$$\begin{aligned} \text{---}\text{+}\text{---} &= \exp[g_{ab}(R) - \beta\varphi_{ab}(R)] - 1 - g_{ab}(R), \\ \text{---} &= \exp[g_{ab}(R) - \beta\varphi_{ab}(R)] - 1, \\ \text{---} &= g_{ab}(R), \quad \bullet = \sum_a \frac{N_a}{V} \int d\mathbf{R}. \end{aligned} \quad (3.3.33)$$

There is also classification of diagrams, and partial summation leads to similar integral equations.

3.3.3. Reference system approach to short-range interactions

Let us consider short-range interactions as the reference system. After the integration over $(d\mathbf{R})$ in (3.3.24), the configuration integral can be represented in the following form

$$Q_N = Q_0 \int \exp\{-\beta v(\rho)\} J(\rho) (d\rho), \quad (3.3.34)$$

where $Q_0 = 1/V^N \int e^{-\beta U_0(R)} (d\mathbf{R})$ is configuration integral of the system with short-range interactions;

$$J(\rho) = \frac{1}{V^N Q_0} \int (d\mathbf{R}) e^{-\beta U_0(R)} J(\rho, R) \quad (3.3.35)$$

is the Jacobian of the transformation averaged over short-range system.

The calculation of $J(\rho)$ is performed similarly to the one-component case via cumulant technique. As a result,

$$J(\rho) = \int (d\omega) \exp \left[i\pi \sum_{\mathbf{k}} \sum_{\sigma} \omega_{\mathbf{k},a} \rho_{\mathbf{k},a} \right] \exp \left[\sum_{n \geq 2} D_n(\omega) \right], \quad (3.3.36)$$

$$D_n(\omega) = \frac{(-i\pi)^n}{n!} \sum_{a_1, \dots, a_n} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \omega_{\mathbf{k}_1 a_1} \dots \omega_{\mathbf{k}_n a_n} \times \\ \times \frac{N_{a_1}}{\sqrt{N_{a_1} \dots N_{a_n}}} \mathbf{m}_{a_1, \dots, a_n}(\mathbf{k}_1, \dots, \mathbf{k}_n),$$

where $\frac{N_{a_1}}{\sqrt{N_{a_1} \dots N_{a_n}}} \mathbf{m}_{a_1, \dots, a_n}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \langle \hat{\rho}_{\mathbf{k}_1 a_1} \dots \hat{\rho}_{\mathbf{k}_n a_n} \rangle_c$ is n -th cumulant of multicomponent system, which has a physical meaning of n -particle structure factor for particles of species $a_1, \dots, a_n$, similarly to the one-component case (see Section 2.3). In particular, for two particles of the species a and b $\mathbf{m}_{ab}(\mathbf{k}) = \delta_{ab} + N_b/V h_{ab}^0(k)$, where $h_{ab}^0(k)$ is the Fourier transform of the correlation function $h_{ab}^0(R) = F_{ab}^0(R) - 1$. Let us introduce auxiliary external field $\varphi = \sum_{a,j} \sum_{\mathbf{k}} \varphi_a(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}_j}$ and instead of Q_0 let us consider configuration integral

$$Q_\varphi = \frac{1}{V^N} \int (d\mathbf{R}) \exp[-\beta(U_0 + \varphi)].$$

Generalizing the definition (2.3.11) for the case of multicomponent systems, one has

$$N_{a_1} \mathbf{m}_{a_1 \dots a_n}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \frac{1}{V^N} (-\beta)^{-n} \left(\frac{\delta^n \ln Q_\varphi}{\delta \varphi_{a_1}(\mathbf{k}_1) \dots \delta \varphi_{a_n}(\mathbf{k}_n)} \right)_{\varphi=0} = \\ = \left[(-\beta)^{-n+1} \frac{\delta^{n-1}}{\delta \varphi_{a_2}(\mathbf{k}_2) \dots \delta \varphi_{a_n}(\mathbf{k}_n)} \frac{1}{Q_\varphi V^N} \sum_{1 \leq j \leq N_{a_1}} \int e^{-i\mathbf{k}_j \cdot \mathbf{R}_j} \times \right. \\ \left. \times e^{-\beta[U_0 + \varphi]} (d\mathbf{R}) \right]_{\varphi=0}.$$

The derivatives from the numerator lead to the sum of the distribution functions

$$\begin{aligned} & \frac{N_{a_1}}{V} F_{a_1}(\mathbf{k}_1 + \dots + \mathbf{k}_n) \delta_{a_1 a_2} \dots \delta_{a_1 a_n} + \frac{1}{2} \frac{N_{a_1}(N_{a_2} - \delta_{a_1 a_2})}{V^2} \times \\ & \times \sum_{n_1 \geq 1} C_n^{n_1} F_{a_1 a_2}(\mathbf{k}_1 + \dots + \mathbf{k}_{n_1}, \mathbf{k}_{n_1+1} + \dots + \mathbf{k}_n) \times \\ & \times \delta_{a_1 a_3} \dots \delta_{a_1 a_{n_1}} \delta_{a_2 a_{n_1+1}} \dots \delta_{a_2 a_n} + \dots + \\ & + \frac{N_{a_1}(N_{a_2} - \delta_{a_1 a_2}) \dots (N_{a_n} - \delta_{a_1 a_n} - \dots - \delta_{a_{n-1} a_n})}{V^n} \times \\ & \times F_{a_1, \dots, a_n}(\mathbf{k}_1, \dots, \mathbf{k}_n). \end{aligned}$$

The derivatives from the denominator change every distribution function with a corresponding correlation function $\mu_{a_1, \dots, a_n}(\mathbf{k}_1, \dots, \mathbf{k}_n)$. As a result

$$\begin{aligned} N_{a_1} \mathbf{m}_{a_1, \dots, a_n}(\mathbf{k}_1, \dots, \mathbf{k}_n) &= \frac{1}{1!} \mu_{a_1}(\mathbf{k}_1 + \dots + \mathbf{k}_n) \delta_{a_1 a_2} \dots \delta_{a_1 a_n} + \\ &+ \sum_{\substack{n_1 \geq 1 \\ n - n_1 \geq 1}} \frac{1}{2} \sum_{\substack{1 \leq i_2 < \dots < i_{n_1} \leq n \\ i_{n_1+1} < \dots < i_n}} \mu_{a_{i_1} a_{i_{n_1+1}}}(\mathbf{k}_{i_1} + \dots + \mathbf{k}_{i_{n_1}}, \mathbf{k}_{i_{n_1+1}} + \dots + \\ &+ \mathbf{k}_{i_n}) \delta_{a_{i_1} a_{i_2}} \dots \delta_{a_{i_1} a_{i_n}} \delta_{a_{i_{n_1+1}} a_{i_{n_1+2}}} \dots \delta_{a_{i_{n_1+1}} a_{i_n}} + \dots + \\ &+ \mu_{a_1 \dots a_n}(\mathbf{k}_1, \dots, \mathbf{k}_n), \end{aligned} \quad (3.3.37)$$

which is the generalization of the formula in (2.3.14). Two theorems, proven in the previous chapter, are also valid in the current multicomponent case.

In the expression for the Jacobian (3.3.36), one can perform substitution $i\pi\omega_{\mathbf{k},a} = \partial/\partial\rho_{\mathbf{k},a}$ within $D_n(\omega)$ for $n \geq 3$, and then carry out the integration over all $(d\omega)$. As a result

$$J(\rho) = \exp\left\{\sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho)\right\} J_G(\rho), \quad (3.3.38)$$

where

$$\begin{aligned} \hat{D}_n(\partial/\partial\rho) &= \frac{(-1)^n}{n!} \sum_{\substack{a_1, \dots, a_n \\ \mathbf{k}_1, \dots, \mathbf{k}_n}} \frac{N_{a_1}}{\sqrt{N_{a_1} \dots N_{a_n}}} \mathbf{m}_{a_1 \dots a_n}(\mathbf{k}_1, \dots, \mathbf{k}_n) \times \\ &\times \frac{\partial^n}{\partial \rho_{\mathbf{k}_1 a_1} \dots \partial \rho_{\mathbf{k}_n a_n}}; \\ J_G(\rho) &= \int (d\omega) \exp\left\{i\pi \sum_{\mathbf{k}, a} \omega_{\mathbf{k}, a} \rho_{\mathbf{k}, a} - \right. \\ &\left. - \frac{\pi^2}{2} \sum_{\mathbf{k}}' \sum_{a, b} \frac{N_a}{\sqrt{N_a N_b}} \mathbf{m}_{ab}(k) \omega_{\mathbf{k}a} \omega_{\mathbf{k}b}\right\}. \end{aligned}$$

The expression in the exponent under integration in $J_G(\rho)$ is a diagonal form with respect to $\mathbf{k}$, but it is not such with respect to species. In order to carry out the integration, let us perform the change of variables from $\omega_{\mathbf{k},a}$ to $\omega'_{\mathbf{k},a}$, which diagonalize the form $\sum_{a,b} \omega_{\mathbf{k},a} \omega_{-\mathbf{k},b} \tilde{\mathbf{m}}_{ab}(k)$, where

$$\tilde{\mathbf{m}}_{ab}(k) = \frac{N_a}{\sqrt{N_a N_b}} \mathbf{m}_{ab}(k) = \delta_{ab} + \frac{1}{V} \sqrt{N_a N_b} h_{ab}^0(k)$$

is the symmetrized two-particle structure factor. Determining $\omega_{\mathbf{k},a} = \sum_c \gamma_{ac} \omega'_{\mathbf{k},c}$, so that $\sum_{a,b} \tilde{\mathbf{m}}_{ab}(k) \omega_{\mathbf{k},a} \omega_{-\mathbf{k},b} = \sum_{a,b,c,d} \tilde{\mathbf{m}}_{ab}(k) \gamma_{ac} \gamma_{bd} \omega'_{\mathbf{k},c} \omega'_{-\mathbf{k},d}$. For the form to be diagonal in new variables, coefficients of transformation should satisfy $\sum_{a,b} \tilde{\mathbf{m}}_{ab}(k) \gamma_{ac} \gamma_{bd} = \delta_{cd}$. This means that $\det \gamma = [\det \tilde{\mathbf{m}}(k)]^{-1/2}$, where

γ is the matrix composed of elements γ_{ab} ; $\tilde{\mathbf{m}}(k)$ is the matrix composed of elements $\tilde{\mathbf{m}}_{ab}(k)$. After integration over $(d\omega)$ in $J_G(\rho)$, one can obtain the following

$$J_G(\rho) = \exp \left\{ -\frac{1}{2} \sum_{a,b} [\tilde{\mathbf{m}}^{-1}(k)]_{ab} \rho_{\mathbf{k},a} \rho_{-\mathbf{k},b} \right\} \prod'_{\mathbf{k}} [\pi \det \tilde{\mathbf{m}}(k)]^{-1/2}, \quad (3.3.39)$$

where $[\tilde{\mathbf{m}}^{-1}(k)]_{ab}$ are elements of the inverse of the matrix $\tilde{\mathbf{m}}(k)$, $[\tilde{\mathbf{m}}^{-1}(k)]_{ab} = \frac{1 + \delta_{ab}}{2} \frac{\partial}{\partial \tilde{\mathbf{m}}_{ab}(k)} \ln \det \tilde{\mathbf{m}}(k)$; the coefficient $\frac{1 + \delta_{ab}}{2}$ takes into account the symmetry of the elements $\tilde{\mathbf{m}}_{ab}(k)$ relatively to the interchange of the species indices.

Substituting (3.3.38) and (3.3.21) into (3.3.34) for the configuration integral, one obtains

$$\begin{aligned} Q_N = Q_0 \int (d\rho) \exp \left\{ \sum_{n \geq 3} \hat{D}_n(\partial/\partial \rho) \right\} \exp \left\{ -\frac{1}{2} \sum'_{\mathbf{k}} \sum_{a,b} [(\alpha_{ab}(k) + \right. \\ \left. + [\tilde{\mathbf{m}}^{-1}(k)]_{ab}) \rho_{\mathbf{k},a} \rho_{-\mathbf{k},b} - \delta_{ab} \alpha_{ab}(k) + \ln(\pi \det \tilde{\mathbf{m}}(k)) - \right. \\ \left. - \sqrt{N_a N_b} \alpha_{ab}(k=0)] \right\}. \end{aligned} \quad (3.3.40)$$

Similarly to the one-component system case, taking into account the Gaussian part of the Jacobian leads to the random phase approximation for the free energy, and taking into account the operator part — to cluster expansions. Let us first consider the random phase approximation. Leaving aside the operator part in (3.3.40), one obtains

$$\begin{aligned} Q_G = Q_0 \exp \left\{ \frac{1}{2} \sum_{\mathbf{k}} \sum_a \alpha_{aa}(k) - \sum_{a,b} \sqrt{N_a N_b} \alpha_{ab}(k=0) \right\} \times \\ \times \prod_{\mathbf{k}} [\pi \det \tilde{\mathbf{m}}(k)]^{-1/2} \int \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \sum_{a,b} [\alpha_{ab}(k) + (\tilde{\mathbf{m}}^{-1}(k))_{ab}] \rho_{\mathbf{k},a} \rho_{-\mathbf{k},b} \right\}. \end{aligned}$$

Integration over collective variables is performed similarly to that over $(d\omega)$. As a result

$$Q_G = Q_0 \exp \left\{ \frac{1}{2} \sum_{\mathbf{k}} \sum_a \alpha_{aa}(\mathbf{k}) - \sum_{a,b} \sqrt{N_a N_b} \alpha_{ab}(\mathbf{k}=0) \right\} \times \\ \times \prod_{\mathbf{k}}' [\pi \det \tilde{\mathbf{m}}(\mathbf{k})]^{-1/2} \sqrt{\pi (\det [\boldsymbol{\alpha}(\mathbf{k}) + \tilde{\mathbf{m}}^{-1}(\mathbf{k})])^{-1}},$$

where the matrix $\boldsymbol{\alpha}(\mathbf{k})$ consists of elements $\alpha_{aa}(\mathbf{k})$. Since $\det[\tilde{\mathbf{m}}(\mathbf{k})] \det[\boldsymbol{\alpha}(\mathbf{k}) + \tilde{\mathbf{m}}^{-1}(\mathbf{k})] = \det[\mathbf{1} + \boldsymbol{\alpha}(\mathbf{k})\tilde{\mathbf{m}}(\mathbf{k})]$, hence

$$Q_G = Q_0 \exp \left\{ \frac{1}{2} \sum_{\mathbf{k}} \sum_a \alpha_{aa}(\mathbf{k}) - \sum_{a,b} \sqrt{N_a N_b} \alpha_{ab}(\mathbf{k}=0) \right\} \times \\ \times \prod_{\mathbf{k}}' [\det[\mathbf{1} + \boldsymbol{\alpha}(\mathbf{k})\tilde{\mathbf{m}}(\mathbf{k})]]^{-1/2}. \quad (3.3.41)$$

The expression for the free energy will accordingly take the form

$$F_G = F_0 + F_{\text{HTA}} + F_{\text{RPA}} = -\frac{1}{\beta} \ln Q_G, \quad (3.3.42)$$

where $F_0 = -\frac{1}{\beta} \ln Q_0$ is a free energy of a system with short-range interaction:

$$F_{\text{HTA}} = \frac{1}{2\beta} \sum_{\mathbf{k}} \sum_{a,b} [\mathbf{m}_{ab}(\mathbf{k}) - \delta_{ab}] \alpha_{ab}(\mathbf{k}) + \frac{1}{2\beta} \sum_{a,b} \sqrt{N_a N_b} \alpha_{ab}(\mathbf{k}=0) = \\ = \frac{1}{2} \sum_{a,b} \frac{N_a N_b}{V} \int \Phi_{ab}(R) F_{ab}^0(R) d\mathbf{R} \quad (3.3.43)$$

is the system-averaged value of the long-range part of the system's energy, corresponding to the high-temperature approximation for the free energy:

$$F_{\text{RPA}} = -\frac{1}{2\beta} \sum_{\mathbf{k}} \left\{ \sum_{a,b} \alpha_{ab}(\mathbf{k}) \mathbf{m}_{ab}(\mathbf{k}) - \ln \det [\mathbf{1} + \boldsymbol{\alpha}(\mathbf{k})\tilde{\mathbf{m}}(\mathbf{k})] \right\} \quad (3.3.44)$$

is the random phase approximation for the free energy.

As in the one-component case, expression (3.3.44) can be represented in the form

$$F_{\text{RPA}} = \frac{1}{2} \sum_{a,b} \frac{N_a N_b}{V} \int d\mathbf{R} \int_0^1 d\xi \Phi_{ab}(R) g_{ab}(R, \xi), \quad (3.3.45)$$

where

$$g_{ab}(R) = \frac{1}{\sqrt{N_a N_b}} \sum_{\mathbf{k}} \left[\frac{1 + \delta_{ab}}{2} \frac{\partial}{\partial \alpha_{ab}(\mathbf{k})} \ln \det [\mathbf{1} + \boldsymbol{\alpha}(\mathbf{k})\tilde{\mathbf{m}}(\mathbf{k})] - \right. \\ \left. - \tilde{\mathbf{m}}_{ab}(\mathbf{k}) \right] e^{i\mathbf{k}\mathbf{R}} = -\beta V^2 \frac{\delta F_{\text{RPA}}}{\delta \Phi_{ab}(R)} \quad (3.3.46)$$

is the screened potential. The expression $g_{ab}(R, \xi)$ differs from $g_{ab}(R)$ only by replacing $\alpha(k)$ with $\xi\alpha(k)$.

The screened potentials (3.3.46) satisfy the set of integral equations (3.3.17) if we assume

$$h_{ab}(R) = h_{ab}^0(R) + g_{ab}(R), \quad c_{ab}(R) = c_{ab}^0(R) - \beta\Phi_{ab}(R). \quad (3.3.47)$$

In the particular case of describing short-range interactions by hard spheres of size σ_{ab} under imposed conditions

$$1 + h_{ab}(R) = 0, \quad R < \sigma_{ab}; \quad c_{ab}^0(R) = 0, \quad R > \sigma_{ab} \quad (3.3.48)$$

we obtain the mean spherical approximation for the multicomponent system. The first condition is exact and corresponds to the optimum separation of short-range and long-range interactions, and the second condition corresponds to the Percus–Yevick approximation for hard spheres.

To account for the operator part of the Jacobian $\exp \left[\sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right]$, the transformation terms are expanded into a series, and the operators $\hat{D}_n(\partial/\partial\rho)$ are paired. Each pair corresponds to an operator $\frac{1}{\sqrt{N_a N_b}} \frac{\partial^2}{\partial \rho_{\mathbf{k},a} \partial \rho_{-\mathbf{k},b}}$ which gives the result equal to

$$\frac{1}{\sqrt{N_a N_b}} \sum_{c,d} [\tilde{\mathbf{m}}^{-1}(k)]_{ac} [\tilde{\mathbf{m}}^{-1}(k)]_{bd} \rho_{\mathbf{k},d} \rho_{-\mathbf{k},c} - [\tilde{\mathbf{m}}^{-1}(k)]_{ab}.$$

Then, a substitution of $\rho_{\mathbf{k},d} \rho_{-\mathbf{k},c}$ for $\delta_{cd} - \partial/\partial\alpha_{cd}$ is made.

As a result, each pair corresponds to the expression

$$g_{ab}(k) = \frac{1}{\sqrt{N_a N_b}} \left\{ \sum_{c,d} [\tilde{\mathbf{m}}^{-1}(k)]_{ac} [\tilde{\mathbf{m}}^{-1}(k)]_{bd} \times \right. \\ \left. \times \frac{\partial}{\partial \alpha_{cd}(k)} \ln \det[1 - \alpha(k) \tilde{\mathbf{m}}(k)] - [\tilde{\mathbf{m}}^{-1}(k)]_{ab} \right\}, \quad (3.3.49)$$

related to the screened potential (3.3.46) by the relation:

$$g_{ab}(R) = \frac{1}{\sqrt{N_a N_b}} \sum_k \sum_{c,d} \tilde{\mathbf{m}}_{ac}(k) \tilde{\mathbf{m}}_{bd}(k) g_{cd}(k) e^{i\mathbf{k}R}. \quad (3.3.50)$$

The further calculation of the configuration integral follows the derivations described in the previous chapter for the one-component case. The operators $\hat{D}_n(\partial/\partial\rho)$ are split into two parts, $\hat{D}_n(\partial/\partial\rho) = \hat{D}_n^{(1)}(\partial/\partial\rho) + \hat{D}_n^{(2)}(\partial/\partial\rho)$, which contain cumulants with irreducible and reducible sums over k , respectively. The construction of the cluster expansions is done in three steps. First,

the irreducible part of $\hat{D}_n^{(1)}(\partial/\partial\rho)$ is taken into account, leading to cluster expansions similar to those obtained in the previous section, but with more complex vertices. In the second step, the terms are considered that do not change the structure of the $\hat{D}_n^{(2)}(\partial/\partial\rho)$ diagram, but only contribute to the group integrals of the short-range interaction distribution functions. Here, the Fourier transform of the screened potential is defined by expression (3.3.49). In the third step, the remaining parts of the operators $\hat{D}_n^{(2)}(\partial/\partial\rho)$ are taken into account, leading to additional terms for the cluster coefficients. These can also be used to renormalise the screened potential. Finally, we find the cluster expansion for the free energy, analogous to equation (2.3.59),

$$F = F_0 + F_{\text{HTA}} + F_{\text{RPA}} - \frac{1}{\beta} (B_2 + B_3 + \dots). \quad (3.3.51)$$

The cluster coefficients $B_2, B_3, \dots$ have the same structure as in the one-component case, except that each field vertex now corresponds to the operation $\sum_a N_a/V \int d\mathbf{R}$.

As in the one-component case, to obtain the screened potential (3.3.50) during the pairing of operators, the irreducible part of the cumulants should be rewritten in the form

$$\mathbf{m}_{a_1 \dots a_n}^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \tilde{\mathbf{m}}_{a_1 \dots a_n}^{(1)}(\mathbf{k}_1, \dots, \mathbf{k}_n) \sum_{a'_1 \dots a'_n} \mathbf{m}_{a_1 a'_1}(k_1) \dots \mathbf{m}_{a_n a'_n}(k_n).$$

Then, each pairing will correspond to operation $\frac{1}{\sqrt{N_a N_b}} \sum_{a' b'} \mathbf{m}_{a a'}(k) \mathbf{m}_{b b'}(k) \times \partial^2/\partial\rho_{\mathbf{k}, a'} \partial\rho_{-\mathbf{k} b'}$, which ultimately leads to the screened potential (3.3.50). If the renormalisation of the screened potentials is not carried out, the cluster expansion (3.3.51) coincides with the result of Andersen and Chandler [26], where the first terms are given by the expressions (3.3.43) and (3.3.44), and the second cluster coefficient is:

$$B_2 = \frac{1}{2} \sum_{a, b} \frac{N_a N_b}{V} \int \left\{ F_{ab}^0(R) \left[e^{g_{ab}(R)} - 1 - g_{ab}(R) - \frac{1}{2} g_{ab}^2(R) \right] + \frac{1}{2} g_{ab}^2(R) [F_{ab}^0(R) - 1] \right\} d\mathbf{R}. \quad (3.3.52)$$

Functional differentiation of the free energy expression with respect to the interaction potentials, gives the pair distribution functions. As in the one-component case,

$$\frac{\delta F_0}{\delta \Phi_{ab}(R)} = 0, \quad \frac{\delta F_{\text{HTA}}}{\delta \Phi_{ab}(R)} = \frac{1}{V^2} F_{ab}^0(R), \quad \frac{\delta F_{\text{RPA}}}{\delta \Phi_{ab}(R)} = \frac{1}{V^2} g_{ab}(R).$$

To differentiate the cluster coefficients, the variations $\delta g_{ab}(R)$ should be expressed by $\delta \Phi_{ab}(R)$. According to the equation (3.3.47) $\delta \Phi_{ab}(R) = \frac{1}{\beta}[\delta c_{ab}^0(R) - \delta c_{ab}(R)]$, $\delta g_{ab}(R) = \delta h_{ab}(R) - \delta h_{ab}^0(R)$. Since functions $h_{ab}(R)$ and $c_{ab}(R)$ are related by the set of equations (3.3.17), for the derivative $\delta g_{cd}(R)/\delta \Phi_{ab}(R)$, we obtain an expression analogous to (2.3.70). As a result, for the pair distribution function in the approximation of the second cluster coefficient, we get:

$$F_{ab}(R) = F_{ab}^0(R) e^{g_{ab}(R)}[1 + \dots]. \quad (3.3.53)$$

3.3.4. Hard-sphere system

As in the one-component case, the simplest non-trivial reference system is a hard sphere model. The interaction between two spheres of type a and b is given by:

$$\varphi_{ab}(R) = \begin{cases} 0, & R > \sigma_{ab}, \\ \infty, & R < \sigma_{ab}, \end{cases} \quad (3.3.54)$$

where $\sigma_{ab} = r_a + r_b$; r_a and r_b are the radii of the corresponding spheres, so that $\sigma_{ab} = 1/2(\sigma_{aa} + \sigma_{bb})$.

The configuration integral and distribution functions of the considered system do not depend on temperature, but only on the reduced density $\eta = \frac{1}{6}\pi \frac{N}{V} \sum_a x_a \sigma_{aa}^3$, the concentration of components $x_a = N_a/N$, and the size ratio of spheres of different types. In a multicomponent system, hard spheres of different sizes can be packed more densely than in the one-component case. In particular, smaller spheres can fill the voids between larger spheres. Therefore, the maximum density $\eta_{\max}$ depends on the concentration x_a and the size ratio of spheres of different types.

According to (3.3.8) the internal energy of the system coincides with the internal energy of an ideal gas, as in the one-component case. From the virial equation of state, it follows that the pressure in the system is completely determined by the contact values of the pair distribution functions $F_{ab}(\sigma_{ab}+)$. Since $d/dR e^{-\beta\varphi_{ab}(R)} = \delta(R - \sigma_{ab})$, then according to (3.3.9)

$$\beta \frac{PV}{N} = 1 + \frac{2}{3}\pi \frac{N}{V} \sum_{a,b} x_a x_b F_{ab}(\sigma_{ab}+) \sigma_{ab}^3. \quad (3.3.55)$$

Let us look at the behaviour of the function $y_{ab}(R) = e^{\beta\varphi_{ab}(R)} F_{ab}(R)$ in the region of small distances. Since for $R \leq |\sigma_{aa} - \sigma_{bb}|$, a smaller sphere is completely inside the larger sphere, we can express $y_{ab}(R)$ in this region as the ratio of the configuration integral of the system without the particle inside the

sphere to the full configuration integral of the entire system. Hence,

$$y_{ab}(R \leq |\sigma_{aa} - \sigma_{bb}|) = \begin{cases} \exp\{\beta[\mu_a - \mu_a^{(\text{id})}]\}, & \sigma_{aa} \leq \sigma_{bb}, \\ \exp\{\beta[\mu_b - \mu_b^{(\text{id})}]\}, & \sigma_{aa} \geq \sigma_{bb}, \end{cases} \quad (3.3.56)$$

where μ_a is the chemical potential of particles of type a ; $\mu_a^{(\text{id})}$ is its ideal part.

Generalizing equation (3.1.7) to the multi-component case, we obtain

$$\frac{\partial}{\partial \mathbf{R}_1} y_{ab}(R_{12}) = \sum_c \frac{N_c}{V} \int d\mathbf{R}_3 y_{acb}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) e^{-\beta\varphi_{cb}(R_{32})} \frac{\partial}{\partial \mathbf{R}_1} e^{-\beta\varphi_{ac}(R_{13})}.$$

Since $\partial/\partial \mathbf{R}_1 e^{-\beta\varphi_{ac}(R_{13})} = -\mathbf{R}_{13}/R_{13} \delta(R_{13} - \sigma_{ac})$, we have

$$\begin{aligned} \frac{\partial}{\partial R_{12}} y_{ab}(R_{12}) &= - \sum_c \frac{N_c}{V} \int d\mathbf{R}_3 \frac{\mathbf{R}_{12}\mathbf{R}_{13}}{R_{12}R_{13}} y_{abc}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) e^{-\beta\varphi_{cb}(R_{32})} \times \\ &\quad \times \delta(R_{13} - \sigma_{ac}). \end{aligned}$$

In region $R < |\sigma_{aa} - \sigma_{bb}|$, the smaller sphere is inside the larger one, so

$$y_{abc}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = y_{ab}(R_{12}) y_{bc}(R_{23}), \quad \mathbf{R}_{13} \rightarrow \mathbf{R}_{23} \delta_{ab},$$

hence it follows that

$$\left[\frac{\partial}{\partial R} \ln y_{ab}(R) \right]_{R \leq |\sigma_{aa} - \sigma_{bb}|} = -\pi \delta_{ab} \sum_c \frac{N_c}{V} \sigma_{bc}^2 y_{cb}(\sigma_{cb}). \quad (3.3.57)$$

The relations (3.3.56) and (3.3.57) are generalized expressions of (3.1.6) and (3.1.8) and were first derived by Grundke and Henderson [144].

Let us generalize the methods we have discussed so far to describe hard spheres. We start with the scaling particle method. Following the work [145], we introduce a scaling particle into the system with radius r . The contact value of the pair distribution function for the introduced particle and the particle of type a is denoted by $G_a(r + r_a)$, where $r_a = 1/2\sigma_{aa}$ is the radius of the sphere of type a . Generalizing the relation (3.1.23) for the $W(r)$ of the introduction of a particle with radius r , we have

$$\beta \frac{\partial W(r)}{\partial r} = 4\pi \frac{N}{V} \sum_a x_a G_a(r + r_a) (r + r_a)^2. \quad (3.3.58)$$

For a point particle, there is an exact relation

$$G_a(r + r_a) = \left[1 - \frac{4}{3} \pi \frac{N}{V} \sum_b x_b (r + r_b)^3 \right]^{-1}, \quad r \leq 0. \quad (3.3.59)$$

Similarly to the one-component case, for $r \geq 0$, we assume:

$$G_a(r + r_a) = \frac{P_a V}{N_a} \beta + \frac{A_a}{r + r_a} + \frac{B_a}{(r + r_a)^2}, \quad r \geq 0, \quad (3.3.60)$$

where P_a is the partial pressure of particles of type a . In the limit as $r \rightarrow \infty$, according to (3.3.60) and (3.3.55)

$$\lim_{r \rightarrow \infty} \sum_a x_a G_a(r + r_a) = \beta \frac{PV}{N} = 1 + \frac{2}{3} \pi \frac{N}{V} \sum_{a,b} x_a x_b G_{ab}(r_a + r_b) \sigma_{ab}^3, \quad (3.3.61)$$

whence

$$\frac{P_a V}{N_a} \beta = \frac{1 + \frac{2}{3} \pi \frac{N}{V} \sum_b x_b \sigma_{ab} (A_a \sigma_{ab} + B_a)}{1 - \frac{2}{3} \pi \frac{N}{V} \sum_b x_b \sigma_{ab}^3}. \quad (3.3.62)$$

The constants A_a and B_a are determined from the continuity conditions for the functions $G_a(r + r_a)$ and $\partial/\partial r G_a(r + r_a)$ at the point $r = 0$:

$$\begin{aligned} A_a &= -2\beta \frac{P_a V}{N_a} r_a + \frac{2r_a}{1 - \eta} + \frac{\rho s_m r_a^2}{(1 - \eta)^2}, \\ B_a &= \beta \frac{P_a V}{N_a} r_a^2 - \frac{r_a^2}{(1 - \eta)} - \frac{\rho s_m r_a^3}{(1 - \eta)^2}, \end{aligned} \quad (3.3.63)$$

where $s_m = \pi \sum_a x_a \sigma_{aa}^2$; $\rho = \frac{N}{V}$; $\eta = \frac{1}{6} \pi \frac{N}{V} \sum_a x_a \sigma_{aa}^3$.

Substituting the equation (3.3.63) into (3.3.62) and using the fact that $P = \sum_a P_a$, we find the equation of state

$$\frac{PV}{N} \beta = \frac{1}{1 - \eta} + \frac{\rho s_m r_m}{(1 - \eta)^2} + \frac{\rho^2}{12\pi} \frac{s_m^3}{(1 - \eta)^3}, \quad (3.3.64)$$

where $r_m = 1/2 \sum_a x_a \sigma_{aa}$.

According to (3.3.60), for the contact value of the pair distribution function, we obtain

$$\begin{aligned} F_{ab}(\sigma_{ab}+) &= G_b(r_a + r_b) = G_a(r_b + r_a) = \frac{1}{1 - \eta} + \\ &+ \frac{s_m \rho}{(1 - \eta)^2} \frac{r_a r_b}{r_a + r_b} + \frac{1}{3} \frac{s_m^2 \rho^2}{(1 - \eta)^3} \left(\frac{r_a r_b}{r_a + r_b} \right)^2. \end{aligned} \quad (3.3.65)$$

From formula (3.3.58), we get the expression for the solvation free energy of the scaling particle

$$\beta W(r) = -\ln(1 - \eta) + \frac{\rho s_m r}{1 - \eta} + \left[\frac{4\pi \rho r_m}{1 - \eta} + \frac{1}{2} \frac{s_m^2 \rho^2}{(1 - \eta)^2} \right] r^2 + \frac{3}{4} \pi \beta P r^3. \quad (3.3.66)$$

Let us proceed further to generalize the results obtained in Section 3.1 of this chapter for the Percus—Yevick approximation to the multicomponent case. For a mixture of hard spheres in the Percus—Yevick approximation

$$\begin{aligned} F_{ab}(R) &= e^{-\beta\varphi_{ab}(R)} y_{ab}(R) = \begin{cases} 0, & R < \sigma_{ab}, \\ y_{ab}(R), & R > \sigma_{ab}, \end{cases} \\ c_{ab}(R) &= \left[e^{-\beta\varphi_{ab}(R)} - 1 \right] y_{ab}(R) = \begin{cases} -y_{ab}(R), & R < \sigma_{ab}, \\ 0, & R > \sigma_{ab}, \end{cases} \end{aligned} \quad (3.3.67)$$

As in the one-component case, we obtain a set of equations

$$\begin{aligned} y_{ab}(R) &= 1 + \sum_c \frac{N_c}{V} \int_{(R' < \sigma_{ac})} y_{ac}(R') d\mathbf{R}' - \\ &- \sum_c \frac{N_c}{V} \int_{(R' < \sigma_{ac}, |\mathbf{R} - \mathbf{R}'| > \sigma_{cb})} y_{ac}(R') y_{cb}(|\mathbf{R} - \mathbf{R}'|) d\mathbf{R}', \end{aligned} \quad (3.3.68)$$

from which it follows that

$$\begin{aligned} y_{ab}(0) &= 1 + \sum_c \frac{N_c}{V} \int_{(R' < \sigma_{ac})} y_{ac}(R') d\mathbf{R}' = \\ &= 1 - \sum_c \frac{N_c}{V} \int c_{ac}(R) d\mathbf{R} = \beta \frac{\partial P}{\partial \rho_a}. \end{aligned} \quad (3.3.69)$$

in accordance with (3.3.10) and (3.3.17).

As in the one-component case, to solve equation (3.3.68), we will use the Baxter method, which was generalized in [146] for the multicomponent case. Using the Fourier transform, the set of equations (3.3.17) can be represented as:

$$[\mathbf{1} + \mathbf{h}(k)][\mathbf{1} - \mathbf{c}(k)] = \mathbf{1}, \quad (3.3.70)$$

where $\mathbf{h}(k)$ and $\mathbf{c}(k)$ are matrices with elements

$$\begin{aligned} h_{ab}(k) &= \frac{4\pi}{k} \sqrt{\rho_a \rho_b} \int_0^\infty h_{ab}(R) \sin(kR) R dR, \\ c_{ab}(k) &= \frac{4\pi}{k} \sqrt{\rho_a \rho_b} \int_0^\infty c_{ab}(R) \sin(kR) R dR. \end{aligned} \quad (3.3.71)$$

$\mathbf{1}$ is the identity matrix, $\rho_a = N_a/V$, $\rho_b = N_b/V$.

By integrating the Fourier components, we represent them in the form:

$$h_{ab}(k) = 4\pi\sqrt{\rho_a\rho_b} \int_0^\infty I_{ab}(R) \cos(kR) dR, \quad (3.3.72)$$

$$I_{ab}(R) = \int_R^\infty h_{ab}(t) t dt,$$

$$c_{ab}(k) = 4\pi\sqrt{\rho_a\rho_b} \int_0^\infty S_{ab}(R) \cos(kR) dR, \quad (3.3.73)$$

$$S_{ab}(R) = \int_R^\infty c_{ab}(t) t dt.$$

Due to the finiteness of $\mathbf{h}(k)$ and $\mathbf{c}(k)$, the matrix $\mathbf{1} - \mathbf{c}(k)$ has no zeros for all real k . Since $C_{ab}(R) = 0$ for $R > \sigma_{ab}$, the integration in (3.3.73) is carried out over a finite interval, making the elements of the matrix $\mathbf{c}(k)$ analytic functions throughout the entire k -plane. The symmetric matrix $\mathbf{1} - \mathbf{c}(k)$, whose elements are even functions of k , can be represented as

$$\mathbf{1} - \mathbf{c}(k) = \mathbf{Q}^T(-k)\mathbf{Q}(k), \quad (3.3.74)$$

where $\mathbf{Q}^T(k)$ is the transpose of the matrix $\mathbf{Q}(k)$. To each element $Q_{ab}(k)$, we associate a function $q_{ab}(R)$ such that

$$Q_{ab}(k) = \delta_{ab} - 2\pi\sqrt{\rho_a\rho_b} \int_{\lambda_{ab}}^{\sigma_{ab}} q_{ab}(R) e^{ikR} dR. \quad (3.3.75)$$

Substituting (3.3.73) and (3.3.75) into (3.3.74), we confirm that (3.3.74) holds if for $\lambda_{ab} \leq R \leq \sigma_{ab}$

$$S_{ab}(|R|) = q_{ab}(R) - 2\pi \sum_c \rho_c \int q_{ac}(t) q_{cb}(R+t) dt, \quad (3.3.76)$$

where the integration over t is carried out over the interval $\lambda_{ac} < t < \min[\sigma_{ac}, \sigma_{cb} - R]$, and $\lambda_{ab} = 1/2|\sigma_{aa} - \sigma_{bb}|$.

The matrix $\mathbf{Q}(k)$ consists of analytic functions that have no zeros in the region $\text{Im } k > 0$. Since $\det \mathbf{Q}(k) \neq 0$ for $\text{Im } k > 0$, $\mathbf{Q}(k)$ can be extended into the lower half-plane. According to (3.3.70) and (3.3.74)

$$\mathbf{Q}(k)[\mathbf{1} + \mathbf{h}(k)] = [\mathbf{Q}^T(-k)]^{-1}, \quad (3.3.77)$$

According to (3.3.75), as $\text{Im } k \rightarrow -\infty$, $Q_{ab}(k) \sim \delta_{ab} - \frac{2\pi}{ik} \sqrt{\rho_a \rho_b} e^{ik\lambda_{ab}} q_{ab}(\lambda_{ab})$ and thus,

$$\mathbf{Q}(-k) = \mathbf{P}^{-1}(k) \mathbf{Y}(k) \mathbf{P}(k), \quad (3.3.78)$$

where $P_{ab}(k) = \delta_{ab} \exp(i 1/2 k \sigma_{aa})$ and $\mathbf{Y}(k) = \mathbf{1} + \mathbf{O}(1/k)$. Hence, as $\text{Im } k \rightarrow -\infty$, the right-hand side of (3.3.77) approaches $e^{ik\lambda_{ab}}$. Multiplying both sides of (3.3.77) by e^{-ikR} and integrating over k from $-\infty$ to ∞ . For $R > \lambda_{ab}$, the integration contour for the right-hand side of (3.3.77) can be closed in the lower half-plane, where $\mathbf{Q}^T(-k)$ is analytic and has no zeros, making this integral equal to zero. Substituting (3.3.72) and (3.3.75) into (3.3.77), for $R > \lambda_{ab}$, we obtain:

$$I_{ab}(|R|) = q_{ab}(R) + 2\pi \sum_c \rho_c \int_{\lambda_{ac}}^{\sigma_{ac}} dt q_{ac}(t) I_{cb}(|R-t|). \quad (3.3.79)$$

For $R > \sigma_{ab}$, $q_{ab}(R) = 0$. From equation (3.3.76), it follows that as $R \rightarrow \sigma_{ab}$, $q_{ab}(R) = 0$, ensuring the continuity of $q_{ab}(R)$ at $R = \sigma_{ab}$. For $R < \lambda_{ab}$, $q_{ab}(R) = 0$. Again, from equation (3.3.76), we obtain $q_{ab}(\lambda_{ab}) = q_{ba}(\lambda_{ba}) = 0$.

By differentiating (3.3.76) and (3.3.79) with R , we arrive at a set of equations, which transforms (3.3.17) under the condition that $c_{ab}(R) = 0$ for $R > \sigma_{ab}$

$$R h_{ab}(R) = -q'_{ab}(R) + 2\pi \sum_c \frac{N_c}{V} \int_{\lambda_{ac}}^{\sigma_{ac}} dt (R-t) q_{ac}(t) h_{cb}(|R-t|) \quad (3.3.80)$$

for $R > \lambda_{ab}$ and

$$R c_{ab}(R) = -q'_{ab}(R) + 2\pi \sum_c \frac{N_c}{V} \int dt q_{ac}(t) q'_{cb}(R+t) \quad (3.3.81)$$

for $\lambda_{ab} < R < \sigma_{ab}$, where $q'_{ab} = d/dR q_{ab}(R)$. The integration in (3.3.81) is carried out over the interval $\lambda_{ac} < t < \min[\sigma_{ac}, \sigma_{cb} - R]$.

For a system of hard spheres, $h_{ab}(R) = -1$ for $R < \sigma_{ab}$. Therefore, according to (3.3.80), for $\lambda_{ab} < R < \sigma_{ab}$, we have:

$$q'_{ab}(R) = \alpha_a R + \beta_a, \quad (3.3.82)$$

where

$$\alpha_a = 1 - \sum_c \rho_c \int_{\lambda_{ac}}^{\sigma_{ac}} dt q_{ac}(t), \quad \beta_a = \sum_c \rho_c \int_{\lambda_{ac}}^{\sigma_{ac}} t dt q_{ac}(t). \quad (3.3.83)$$

Integrating (3.3.82) and considering that $q_{ab}(R) = 0$ for $R \geq \sigma_{ab}$, we obtain:

$$q_{ab}(R) = \frac{1}{2} \alpha_a (R^2 - \sigma_{ab}^2) + \beta_a (R - \sigma_{ab}), \quad (3.3.84)$$

where $\lambda_{ab} < R < \sigma_{ab}$.

Substituting (3.3.84) into (3.3.83) leads to a system of two linear equations for α_a and β_a :

$$\alpha_a = \frac{1}{1-\eta} + \frac{1}{2} \frac{\rho s_m \sigma_{aa}}{(1-\eta)^2}, \quad \beta_a = -\frac{1}{4} \frac{s_m \rho \sigma_{aa}^2}{(1-\eta)^2}. \quad (3.3.85)$$

Substituting (3.3.84) into (3.3.81), we obtain:

$$\begin{aligned} -c_{ab}(R) &= -c_{ba}(R) = \\ &= \begin{cases} a_{ab}, & R \leq \lambda_{ab}, \\ a_{ab} + \frac{1}{R} [b_{ab}(R - \lambda_{ab})^2 + 4\lambda_{ab}d_{ab} \times \\ \times (R - \lambda_{ab})^3 + d_{ab}(R - \lambda_{ab})^4], & \lambda_{ab} \leq R \leq \sigma_{ab}, \\ 0, & R \geq \sigma_{ab}, \end{cases} \end{aligned} \quad (3.3.86)$$

where

$$\begin{aligned} a_{ab} &= \begin{cases} a_{aa}, & \sigma_{aa} \leq \sigma_{bb}, \\ a_{bb}, & \sigma_{aa} \geq \sigma_{bb}, \end{cases} \quad d_{ab} = \frac{\pi}{12} \sum_c \frac{N_c}{V} a_{cc}, \quad a_{aa} = \alpha_a^2, \quad (3.3.87) \\ -b_{ab} &= \frac{\eta}{(1-\eta)^2} \frac{\sigma_{ab}}{\sigma_{aa}^2} + \frac{\rho s_m}{(1-\eta)^3} \frac{\sigma_{ab}}{\sigma_{aa}} + \frac{1}{4} \frac{\rho^2 s_m^2 \sigma_{ab}}{(1-\eta)^4} - \\ &- \frac{1}{4} \frac{\rho s_m}{(1-\eta)^2} \frac{\sigma_{bb}}{\sigma_{aa}} + \frac{\pi}{12} \rho \sigma_{aa} (\sigma_a + 3\lambda_{ab}) (1-\eta)^{-2} \times \\ &\times \left[1 + 2\rho s_m r_m (1-\eta)^{-1} + \frac{1}{4\pi} \rho^2 s_m^3 (1-\eta)^{-2} \right]. \end{aligned} \quad (3.3.88)$$

According to (3.3.67), $c_{ab}(R)$ at $R = \sigma_{ab}$ defines the contact values of the pair distribution functions

$$\begin{aligned} F_{ab}(\sigma_{ab}+) &= -c_{ab}(\sigma_{ab}-) = y_{ab}(\sigma_{ab}) = \frac{1}{1-\eta} - \frac{\sigma_{bb}}{\sigma_{aa}} \frac{\beta_a}{\sigma_{ab}} = \\ &= \frac{1}{1-\eta} + \frac{1}{4} \frac{\sigma_{aa} \sigma_{bb}}{\sigma_{ab}} \frac{\rho s_m}{(1-\eta)^2}. \end{aligned} \quad (3.3.89)$$

According to (3.3.69) and (3.3.87), $\beta \partial P / \partial \rho_a = a_{aa}$, from which it follows:

$$\beta \frac{P_c}{\rho} = \frac{1}{1-\eta} + \frac{\rho s_m r_m}{(1-\eta)^2} + \frac{\rho^2}{12\pi} \frac{s_m^3}{(1-\eta)^3}, \quad (3.3.90)$$

where c indicates that the equation of state is derived from the compressibility formula (3.3.10). As in the one-component case, (3.3.90) coincides with the expression (3.3.64), previously obtained using the scaled particle theory.

Substituting (3.3.89) into (3.3.55), we find the virial equation of state:

$$\beta \frac{P_v}{\rho} = \beta \frac{P_c}{\rho} - \frac{\eta}{12\pi} \frac{\rho^2 s_m^3}{(1-\eta)^3}. \quad (3.3.91)$$

As in the one-component case, the results of computational experiments agree well with the Carnahan–Starling approximation

$$\begin{aligned} Z_{\text{CS}} &= \frac{P_{\text{CS}}\beta}{\rho} = \frac{1}{3}\beta\frac{1}{\rho} [2P_c + P_v] = \beta\frac{1}{\rho}P_c - \frac{\rho^2}{36\pi} \frac{\eta s_m^3}{(1-\eta)^3} = \\ &= \frac{1}{1-\eta} + \frac{\rho s_m r_m}{(1-\eta)^2} + \frac{\rho^2}{12\pi} \frac{s_m^3}{(1-\eta)^3} \left[1 - \frac{1}{3}\eta\right]. \end{aligned} \quad (3.3.92)$$

The excess functions calculated using this formula are also in good agreement with computer simulation data. Moreover, the excess part of the thermodynamic potential, $\Phi_{\text{exc}} < 0$, indicates the absence of any phase transitions in the system, except, of course, for crystalline ordering. This implies that hard spheres mix in any quantities and proportions without phase separation. For the excess volume, $V_{\text{exc}} < 0$ as well, except possibly in the regions of high pressure [147]. This highlights a significant structural difference between one-component and multicomponent systems of hard spheres.

Using the known functions $q_{ab}(R)$ from equation (3.3.80), the pair distribution functions $F_{ab}(R)$ can be determined. Perram [118] transformed (3.3.80) into a system of differential equations and proposed a simple numerical algorithm for its solution. As in the one-component case, substituting expressions (3.3.82) and (3.3.84) into (3.3.80), multiplying both sides of the resulting equation by e^{-sR} , and integrating with respect to dR , we obtain:

$$\begin{aligned} \sum_c \mathcal{F}_{ac}(s) [\delta_{cb} - \rho_c \tilde{q}_{cb}(s)] &= \frac{1}{s^2} e^{-s\sigma_{ab}} \left[\alpha_b + \frac{s}{1-\eta} \left(\sigma_{ab} + \right. \right. \\ &\quad \left. \left. + \frac{1}{4}\rho \frac{s_m}{1-\eta} \sigma_{aa}\sigma_{bb} \right) \right], \end{aligned} \quad (3.3.93)$$

where $\mathcal{F}_{ab}(s) = \int_0^\infty F_{ab}(R) e^{-sR} R dR$ are the Laplace transforms of the pair distribution functions:

$$\begin{aligned} \tilde{q}_{ab}(s) &= \int_{\lambda_{ba}}^\infty q_{ab}(R) e^{-sR} dR = e^{-s\lambda_{ab}} \left\{ \frac{1}{s^2} [1 - s\sigma_{aa} - e^{-s\sigma_{aa}}] \left[\frac{\sigma_{ab}}{1-\eta} + \right. \right. \\ &\quad \left. \left. + \frac{1}{4}\rho s_m \frac{\sigma_{aa}\sigma_{bb}}{(1-\eta)^2} \right] + \frac{\alpha_b}{s^3} \left[1 - s\sigma_{aa} + \frac{1}{2}s^2\sigma_{aa}^2 - e^{-s\sigma_{aa}} \right] \right\}. \end{aligned}$$

Solving the set of equations (3.3.93), we obtain

$$\begin{aligned} \mathcal{F}_{ab}(s) &= \frac{e^{-s\sigma_{ab}}}{s^2(1-\eta)D(s)} \left\{ s \left[\sigma_{ab} + \frac{1}{4}\rho \frac{s_m\sigma_{aa}\sigma_{bb}}{1-\eta} \right] + 1 + \frac{3\eta}{1-\eta} + \right. \\ &\quad \left. + \frac{1}{s} \frac{\pi}{1-\eta} \sum_c \frac{N_c}{V} \lambda_{ac}\lambda_{cb} [1 - s\sigma_{cc} - e^{-s\sigma_{cc}}] \right\}, \end{aligned} \quad (3.3.94)$$

where

$$D(s) = 1 - \frac{1}{s^3} \frac{2\pi}{1-\eta} \left(1 + \frac{3\eta}{1-\eta}\right) \sum_c \frac{N_c}{V} \left[1 - s\sigma_{cc} + \frac{1}{2}s^2\sigma_{cc}^2 - e^{-s\sigma_{cc}}\right] - \\ - \frac{1}{s^2} \frac{2\pi}{1-\eta} \left\{ \sum_c \frac{N_c}{V} [1 - s\sigma_{cc} - e^{-s\sigma_{cc}}] \left[\sigma_{cc} \left(1 + \frac{1}{4}\rho \frac{s_m\sigma_{cc}}{1-\eta}\right) + \right. \right. \\ \left. \left. + \frac{1}{s^2} \frac{\pi}{4} (1-\eta)^{-1} \sum_d \frac{N_d}{V} \lambda_{cd}^2 (1 - s\sigma_{dd} - e^{-s\sigma_{dd}}) \right] \right\}.$$

Hence, using the inverse Laplace transform, the functions $F_{ab}^{\text{PY}}(R)$ can be obtained. These results for a binary system were first derived by Lebowitz [148] and were later generalized in [149]. As in one-component systems, expressions for the pair distribution functions can be represented in an analytical form similar to (3.1.72) [150].

The Percus–Yevick approximation tends to underestimate the pair distribution function values in the region of the first maximum. Generalizing expression (3.1.75), we can represent the pair distribution function as follows

$$F_{ab}(R) = e^{-\beta\varphi_{ab}(R)} \left[y_{ab}^{(\text{PY})}(R, \{\sigma'\}) + \frac{A_{ab}}{R} e^{-X_{ab}} \cos X_{ab} \right], \quad (3.3.95)$$

where $X_{ab} = m_{ab}(R - \sigma_{ab})$; $\{\sigma'\}$ represents the set of all functions $\sigma'_{ab} = \left(1 - \frac{1}{16}\eta\right)^{1/3} \sigma_{ab}$. As in the one-component case, a correction term is introduced here to adjust the contact values of the pair distribution functions, σ'_{ab} adjusts the phases of oscillations.

Expression (3.3.95) contains $1/2M(M+1)$ constants A_{ab} and m_{ab} , which, however, cannot be determined from the condition of thermodynamic self-consistency of the pressure due to an insufficient number of relations. Grundke and Henderson [144] noted that, since the contact values of the pair distribution functions found in the Percus–Yevick (PY) approximation (3.3.89) define P_v , and the contact values (3.3.65), obtained using the scaled particle theory, define P_c , it follows from (3.3.92) that

$$F_{ab}^{(\text{CS})}(\sigma_{ab}+) = \frac{1}{3} \left[F_{ab}^{(\text{PY})}(\sigma_{ab}+) + 2F_{ab}^{(\text{SPT})}(\sigma_{ab}+) \right]. \quad (3.3.96)$$

Considering this relationship to be exact, we can determine the constants A_{ab} . The constants m_{ab} are determined from the condition of thermodynamic self-consistency of the chemical potentials, obtained from the virial formula and equations for compressibility. In Fig. 10, taken from [144], the pair distribution functions for a binary mixture of hard spheres are shown with $\eta = 0.5068$, $\sigma_{bb}/\sigma_{aa} = 3$, and $x_a = x_b = 0.5$. The solid curves correspond to (3.3.95), while the dashed curves represent the Percus–Yevick approximation. The points mark the results from a computer simulation for $F_{ab}(\sigma_{ab}+)$.

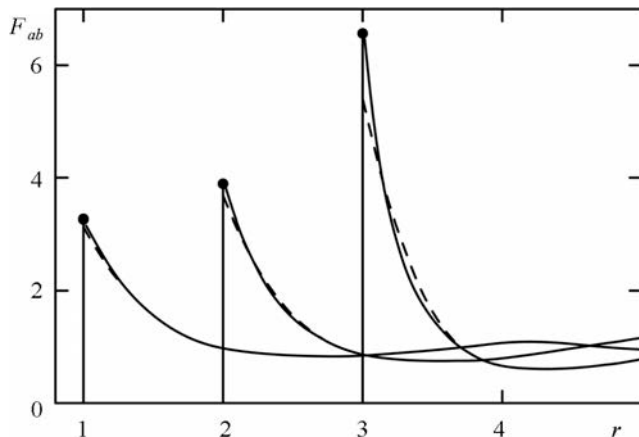


Fig. 10. Pair distribution function $F_{ab}(r)$ for a binary hard-sphere mixture with packing fraction $\eta = 0.5068$, size ratio $\sigma_{bb}/\sigma_{aa} = 3$, and equal composition $x_a = x_b = 0.5$. Solid curves correspond to expression (3.3.95); dashed lines correspond to the Percus–Yeick approximation; dots show simulation results

The Percus–Yeick approximation leads to qualitatively incorrect results for $y_{ab}(R) = e^{\beta\varphi_{ab}(R)}F_{ab}(R)$ in the region $R < \sigma_{ab}$. Specifically, according to (3.3.69), when $R = 0$, we have $y_{ab}^{(PY)}(0) = \beta\partial P/\partial\rho_a$, which contradicts the exact formula (3.3.56). As in the one-component case, based on the exact relations (3.3.56) and (3.3.57), the function $y_{ab}(R)$ in the region $R < \sigma_{ab}$ can be approximated by a cubic polynomial. The coefficients of this polynomial are determined using (3.3.56), (3.3.57), and the conditions for the continuity of the functions $y_{ab}(R)$ and their derivatives at $R = \sigma_{ab}$ [144].

Up until now, it has been assumed that hard spheres have additive sizes, so that $\sigma_{ab} = \frac{1}{2}[\sigma_{aa} + \sigma_{bb}] = r_a + r_b$. However, in real systems, due to the redistribution of electron density between interacting particles, the repulsion potential may significantly differ from that of hard spheres with additive sizes. Non-additivity of hard spheres is also introduced when describing a reference system with real repulsion using the hard-sphere model (see the next section). In [151], the solution to the Percus–Yeick equation for a binary mixture of hard spheres with non-additive sizes was considered, such that $\sigma_{ab} = \frac{1}{2}(\sigma_{aa} + \sigma_{bb}) + \alpha$, where α characterizes the deviation from additivity. The results of this work show that for hard spheres with non-additive sizes, the Percus–Yeick approximation in one-dimensional systems is no longer exact. For the three-dimensional case, a general solution was not obtained. In [152], a solution was found for a simplified model where $\sigma_{aa} = \sigma_{bb} = 0$ and $a > 0$. This system with such interactions was proposed by Widom and Rowlinson [153] as an isomorphic model for describing the critical point. For this model, in the Percus–Yeick approximation, phase separation was found, but the behaviour of the system at the critical point in this approximation exhibits to a classical van der Waals-like character. Bergman [154] used the scale particle theory to describe this model, which significantly improved the descrip-

tion, as the results obtained in the one-dimensional case almost coincide with the exact results.

3.3.5. Accounting for long-range interactions

The consideration of long-range interactions in a multicomponent system is analogous to the one-component case. The starting point is the cluster expansion (3.3.51) for the free energy. The high-temperature approximation, corresponding to the first two terms of the series (3.3.51), is sufficiently accurate for high temperatures and in the van der Waals limit of weak long-range interactions. However, unlike the one-component case, it does not yield satisfactory results in the region of high densities.

In a multicomponent system, depending on the intensity of the attractive forces, a phase separation or a complex formation may occur. For instance, if the molecular sizes are identical and the attraction between molecules of different components exceeds the attraction between molecules of the same component, the system exhibits a tendency toward a complex formation. Conversely, if the attraction within the same component is stronger, a phase separation tends to occur.

Thus, long-range interactions can create significant structural effects that are neglected in the high-temperature approximation. For this reason, in the case of multicomponent systems and at high densities, it becomes necessary to account for the higher-order terms in series (3.3.51).

In [155], the simplest model was considered — a binary mixture of hard spheres and hard spheres with a square-well potential. Thermodynamic properties of the system, calculated within the second cluster coefficient approximation, agreed satisfactorily with the results of computer simulations, except in the critical region where the thermodynamic self-consistency of the theory breaks down.

For systems with more realistic interactions, as in the one-component case, the choice and description of the reference system becomes crucial. Let us consider, as an example, a simple mixture of particles interacting via the Lennard-Jones potential $U_{ab}(R) = 4\epsilon_{ab} \left[\left(\frac{\sigma_{ab}}{R} \right)^{12} - \left(\frac{\sigma_{ab}}{R} \right)^6 \right]$, for which it is commonly assumed that $\sigma_{ab} = \frac{1}{2}(\sigma_{aa} + \sigma_{bb})$, $\epsilon_{ab} = \sqrt{\epsilon_{aa}\epsilon_{bb}}$. Among all possible methods of separating interactions, as in the one-component case, the separation by the Weeks—Chandler—Andersen scheme (see Fig. 6, c) [156, 157] provides the best convergence of the cluster expansions, which gives

$$\begin{aligned} u_{ab}(R) &= \varphi_{ab}(R) + \Phi_{ab}(R), \\ \varphi_{ab}(R) &= \begin{cases} u_{ab}(R) + \epsilon_{ab}, & R \leq \sqrt[6]{2}\sigma_{ab}, \\ 0, & R > \sqrt[6]{2}\sigma_{ab}, \end{cases} \\ \Phi_{ab}(R) &= \begin{cases} -\epsilon_{ab}, & R \leq \sqrt[6]{2}\sigma_{ab}, \\ u_{ab}(R), & R > \sqrt[6]{2}\sigma_{ab}. \end{cases} \end{aligned} \quad (3.3.97)$$

The reference system with potentials $\varphi_{ab}(R)$ can be approximated by a model of hard spheres with sizes d_{ab} . Generalizing the relations (3.2.8)–(3.2.15), we get

$$F_0 = F_d [1 + O(\xi^4)], \quad F_{ab}^0(R) = e^{-\beta\varphi_{ab}(R)} y_{ab}^{(d)}(R) [1 + O(\xi^2)], \quad (3.3.98)$$

where F_d and $y_{ab}^{(d)}(R)$ correspond to the system of hard spheres with sizes d_{ab} ; ξ is the “softness” parameter of the potentials $\varphi_{ab}(R)$. The sizes of the hard spheres are determined from the conditions

$$\sum_{a,b} x_a x_b \int dR y_{ab}^{(d)}(R) [e^{-\beta\varphi_{ab}(R)} - e^{-\beta\varphi_{ab}^{(d)}(R)}] = 0, \quad (3.3.99)$$

where $\varphi_{ab}^{(d)}(R)$ are the potentials of hard spheres with sizes d_{ab} . Expanding the function $y_{ab}^{(d)}(R)R^2$ in (3.3.99) around the point $R = d_{ab}$ into a series $R^2 y_{ab}^{(d)}(R)/d_{ab} = \gamma_{ab}^{(0)} + \gamma'_{ab}(R - d_{ab}) + \dots$, we obtain the expression generalizing (3.2.12),

$$d_{ab} \approx d_{ab}^{\text{BH}} [1 + \Psi_{ab} \delta_{ab}], \quad (3.3.100)$$

where $d_{ab}^{\text{BH}} = \int_0^\infty [e^{-\beta\varphi_{ab}(R)} - 1] dR$ is the Barker–Henderson expression for the hard sphere diameters; $\Psi_{ab} = \frac{1}{2} \gamma'_{ab} \frac{1}{\gamma_{ab}^{(0)}}$; $\delta_{ab} = \int_0^\infty dR [\frac{R}{d_{ab}^{\text{BH}}} - 1]^2 \frac{d}{dR} \times \times (e^{-\beta\varphi_{ab}(R)})$. Equation (3.3.100) leads to independent values for all diameters d_{ab} . Clearly, in general, $d_{ab} \neq \frac{1}{2}[d_{aa} + d_{bb}]$, although the original sizes σ_{ab} may be additive. The non-additivity of the spheres can play an important role, since even small changes in the sizes of the spheres lead to significant changes in thermodynamic quantities [156].

When considering the long-range part of the interaction, the high-temperature approximation is insufficient in most cases, and there arises a need to account for higher-order terms in the series. The latter, instead of the potentials $\Phi_{ab}(R)$, involve screened potentials $g_{ab}(R)$. When the short-range potentials $\varphi_{ab}(R)$ are replaced with hard-sphere potentials $\varphi_{ab}^d(R)$, the optimum separation of interactions in the calculation of $g_{ab}(R)$ reduces to solving the variational problem $\frac{\delta F}{\delta \varphi_{ab}^d(R)} = 0$ for $R \leq d_{ab}$.

As in the one-component case, the cluster expansions (3.3.51) can also be used to describe liquid metal alloys. In particular, the generalization of formula (3.2.18) for alloys was found in work [158]. But here too, apparently, there is a need to account for higher-order terms in the series (3.3.51).

3.4. Ionic systems

A special class consists of systems of charged particles, which differ from the systems discussed earlier due to the long-range Coulomb nature of the interaction at large distances. Among them, electron-ion and purely ionic systems are distinguished. The former primarily includes metallic systems, as well as electron-ion plasma. Their description involves an explicit accounting for the electronic subsystem, for which, due to the small mass of the electron, quantum effects play an important role. Ions have significantly larger masses, so the description of ionic systems is mostly classical. Ionic systems include ionic melts, as well as the ionic subsystem of electrolyte solutions.

Of all the classical systems, the theory of charged particles, presumably, has the largest number of works devoted to it. This interest is driven both by the practical significance of such systems and by the specificity of its features associated with Coulomb interaction. The long-range nature of the latter leads to strong interparticle correlations, causing the system to acquire unique collective properties. These manifest themselves primarily in the screening of interparticle interactions and the existence of longitudinal density oscillations of the electric charge, known as plasma waves. In this case, the screening radius coincides with the amplitude of the plasma oscillations. Screening plays a fundamental role in all properties of the system, ensuring, in particular, the self-consistency of its thermodynamic limit. The presence of plasma waves leads to a natural way of describing the system within the framework of the collective variables method, corresponding to these oscillations.

3.4.1. Fundamental properties of the system. Dielectric formalism

The equilibrium ionic system is overall electrically neutral, so its total charge

$$e \sum_{a=1}^M N_a z_a = 0, \quad (3.4.1)$$

where z_a is the valence of the ion of type a .

Like neutral particles, ions have a certain electron-nuclear structure, so in addition to Coulomb forces, other types of interactions also take place. The interaction potential between two ions of type a and b consists of two parts

$$u_{ab}(R) = \Phi_{ab}(R) + \varphi_{ab}(R), \quad (3.4.2)$$

where $\Phi_{ab}(R) = \frac{e^2 z_a z_b}{\varepsilon R}$ is Coulomb potential; $\varphi_{ab}(R)$ is non-Coulomb part; ε is dielectric permittivity of the medium in which the ions are located. As in the case of neutral particles, the non-Coulomb part of the potential has long-range and short-range terms.

Considering a system with the interaction $\varphi_{ab}(R)$ as a reference system, according to the Bogolyubov—Gibbs inequality (2.3.95), we arrive at the upper bound for the free energy of the system

$$F - F_0 \leq F_{\text{HTA}} = \sum_{a,b} \frac{N_a N_b}{2V} \int \Phi_{ab}(R) F_{ab}^0(R) d\mathbf{R}, \quad (3.4.3)$$

where F_0 and $F_{ab}^0(R)$ are the free energy and pair distribution functions of the reference system, respectively. In particular, for a system with identical potentials $\varphi_{ab}(R)$ for all ions, $F_{\text{HTA}} = 0$, so that $F - F_0 \leq 0$.

Another important inequality, derived by Onsager [159], establishes the lower bound for the free energy

$$F - F_0 \geq - \sum_a N_a u_a^{(\text{el})}, \quad (3.4.4)$$

where $u_a^{(\text{el})}$ is the electrostatic self-energy of an ion of type a . In particular, for charged hard spheres, $u_a^{(\text{el})} = \frac{e^2 z_a^2}{\varepsilon \sigma_{aa}}$, where σ_{aa} is the size of the ion of type a . Inequality (3.4.4) follows from the fact that the total electrostatic energy of the system, which is the sum of the Coulomb interaction energy and the electrostatic self-energy of the ions, is always a positive-definite quantity (see also [160, 161]). The set of inequalities (3.4.3) and (3.4.4) actually establishes the existence of the thermodynamic limit for the ionic system. Inequality (3.4.4) also defines the dependence of the free energy on the intensity of the Coulomb interaction in the strongly non-ideal limit $\beta e^2 \rightarrow \infty$.

To establish general relations, we use electrostatic concepts and introduce the dielectric function $\varepsilon(k)$. The interaction potential between two ions with charges ez_a and ez_b , located at a distance R in the system, is

$$w_{ab}^{(\text{el})}(R) = \sum_k \frac{1}{V} \frac{\nu(k)}{\varepsilon(k)} \frac{e^2 z_a z_b}{\varepsilon} e^{i\mathbf{k}\mathbf{R}}, \quad (3.4.5)$$

where $\nu(k) = 4\pi/k^2$ is the Fourier transform of the Coulomb potential, and $w_{ab}^{(\text{el})}(R)$ is the electrostatic part of the potential of mean force of two ions placed in a medium with dielectric permittivity ε . Expressions for the effective interaction potentials were derived in the previous section. Generalising these results to the case of a multicomponent medium does not present significant difficulties. In this case, the form of the diagrammatic expressions (3.3.16) remains unchanged, with only notations being modified. In particular: (i) each field vertex corresponds to the operation $\sum_a \frac{N_a}{V} \int d\mathbf{R}$, (ii) each line corresponds to the Mayer function $f_{ab}(R) = e^{-\beta u_{ab}(R)} - 1$, (iii) each oval corresponds to the correlation function $h_{a_1, \dots, a_n}(R_1, \dots, R_n)$. Thus, for the effective

interaction potential between two particles of types a and b :

$$w_{ab}(R) = u_{ab}(R) - \frac{1}{\beta} \left[\text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \dots \right]. \quad (3.4.6)$$

Expanding the Mayer functions into a series of powers ez_a and ez_b , and restricting ourselves to linear terms, we obtain the expression for the dielectric function introduced in accordance with (3.4.5):

$$\frac{\varepsilon}{\varepsilon(k)} = 1 - \frac{\varkappa^2}{k^2} - \frac{4\pi}{k^2} \sum_{a,b} \frac{N_a N_b}{V^2} \frac{e^2 z_a z_b}{\varepsilon} \beta \int_0^\infty \frac{\sin(kR)}{kR} F_{ab}(R) 4\pi R^2 dR, \quad (3.4.7)$$

where $\varkappa^2 = 4\pi\beta e^2 / \varepsilon \sum_a N_a / V z_a^2$ is the square of the inverse Debye length.

Since the ionic system is a conductor, the limiting relation [162] $\lim_{k \rightarrow 0} \varepsilon(k) = \infty$ holds. Or, according to (3.4.7):

$$\lim_{k \rightarrow 0} \frac{1}{k^2} \left[\varkappa^2 + 4\pi \sum_{a,b} \frac{N_a N_b}{V^2} \frac{e^2 z_a z_b}{\varepsilon} \beta \int_0^\infty \frac{\sin(kR)}{kR} F_{ab}(R) 4\pi R^2 dR \right] = 1. \quad (3.4.8)$$

Expanding $\sin(kR)$ into a series, we arrive at the following conditions imposed on the pair distribution functions of the system:

$$\varkappa^2 + 4\pi\beta \sum_{a,b} \frac{N_a N_b}{V^2} \frac{e^2 z_a z_b}{\varepsilon} \int_0^\infty F_{ab}(R) 4\pi R^2 dR = 0, \quad (3.4.9)$$

$$1 + \frac{2}{3}\pi\beta \sum_{a,b} \frac{N_a N_b}{V^2} \frac{e^2 z_a z_b}{\varepsilon} \int_0^\infty F_{ab}(R) 4\pi R^4 dR = 0, \quad (3.4.10)$$

first obtained by Stillinger and Lovett [163]. To clarify their physical meaning, we introduce the quantity

$$\zeta_a(R) = \sum_b \frac{N_b}{V} e z_b F_{ab}(R), \quad (3.4.11)$$

describing the density of the electric charge at a distance R from an ion with charge ez_a . The condition (3.4.9) can be rewritten as

$$ez_a + \int \zeta_a(R) d\mathbf{R} = 0. \quad (3.4.12)$$

Thus, as a result of the interaction, around each ion with charge ez_a , a peculiar ion “atmosphere” is formed with charge density $\zeta_a(R)$, in which there is

an excess charge of the opposite sign. According to (3.4.12), the charge of each ion is completely compensated by its atmosphere. Therefore, equality (3.4.12) is called the condition of local electroneutrality of the system. Of course, it is stricter than the usual condition of electroneutrality (3.4.1) and, in particular, determines the asymptotic behaviour of the correlation functions as $R \rightarrow \infty$. The condition (3.4.12) was first used by Debye and Hückel [164], as well as in the works of G.A. Martynov [165, 166].

The second condition (3.4.10) defines the behaviour of the ion “atmosphere”. According to (3.4.11)

$$4\pi\beta \sum_a \frac{N_a e z_a}{V \varepsilon} \int \zeta_a(R) R^2 d\mathbf{R} + 6 = 0. \quad (3.4.13)$$

An important consequence following from this is the prediction of the oscillatory nature of the ion “atmosphere” in the region of high densities. For example, for a two-component system of charged hard spheres with sizes σ and equal valencies $z_+ = -z_-$, such that $N_+ = N_- = \frac{1}{2}N$, the conditions (3.4.9)–(3.4.10) take the form

$$\begin{aligned} 4\pi \frac{N}{2V} \int_{\sigma}^{\infty} [F_{+-}(R) - F_{++}(R)] R^2 dR &= 1, \\ 4\pi \frac{N}{2V} \int_{\sigma}^{\infty} [F_{+-}(R) - F_{++}(R)] R^4 dR &= \frac{6}{\varkappa^2}. \end{aligned} \quad (3.4.14)$$

Noticing that for $R \geq \sigma$, $R^4 \geq R^2 \sigma^2$, we find that for $\zeta_+(R) = \frac{N}{2V} [F_{+-}(R) - F_{++}(R)] < 0$, we get $\frac{6}{\varkappa^2} \geq \sigma^2$, or $\varkappa^2 \sigma^2 \leq 6$. This means that for $x = \varkappa \sigma \geq \sqrt{6}$, the density of the ion “atmosphere” around the positive ion cannot be negative for all $R \geq \sigma$ and, thus, has an oscillatory nature.

The proof above of the relations (3.4.9)–(3.4.10) is, of course, not sufficiently rigorous, although these conditions appear to be exact. In the work [167], it is shown that for the conditions (3.4.9)–(3.4.10) to hold, it is necessary that the direct correlation functions $c_{ab}(R)$ should be given by $c_{ab}(R) = -\beta \Phi_{ab}(R) + c_{ab}^{(sh)}(R)$, where $c_{ab}^{(sh)}(R)$ is the short-range part that decays at large distances faster than $1/R$ and has no singularities at $R = 0$.

The average electrostatic potential of the i -th ion of type a at an arbitrary point R

$$\Psi_a(|\mathbf{R} - \mathbf{R}_i|) = \frac{e z_a}{\varepsilon |\mathbf{R} - \mathbf{R}_i|} + \Psi'_a(|\mathbf{R} - \mathbf{R}_i|) \quad (3.4.15)$$

consists of the potential of the ion’s own field $\frac{e z_a}{\varepsilon |\mathbf{R} - \mathbf{R}_i|}$ and the field of the ion “atmosphere”:

$$\Psi'_a(|\mathbf{R} - \mathbf{R}_i|) = \int \frac{\zeta_a(|\mathbf{R}_i - \mathbf{R}_j|)}{\varepsilon |\mathbf{R} - \mathbf{R}_j|} d\mathbf{R}_j = \sum_b \frac{N_b}{V} \int \frac{e z_b F_{ab}(\mathbf{R}_{ij})}{\varepsilon |\mathbf{R} - \mathbf{R}_i|} d\mathbf{R}_i. \quad (3.4.16)$$

The electrostatic part of the free energy, due to Coulomb interaction, can be expressed in terms of the dielectric function (3.4.7) or the electrostatic potential (3.4.16).

According to (3.3.11)

$$\begin{aligned} F - F_0 &= \frac{1}{2} \sum_a N_a e z_a \int_0^1 d\xi \Psi'_a(\xi) = \\ &= -\frac{V}{2\beta} \sum_k \int_0^1 \frac{1}{\xi} d\xi \left[\frac{\chi^2(\xi)}{k^2} + \frac{\varepsilon}{\varepsilon(k, \xi)} - 1 \right], \end{aligned} \quad (3.4.17)$$

where $\Psi'_a = \Psi'_a(R=0)$; ξ is the parameter of Coulomb interaction inclusion; F_0 is the free energy of the system when $\Phi_{ab}(R) = 0$.

It should be noted that the functions introduced above, $\varepsilon(k)$, $\zeta_a(R)$, and $\Psi_a(R)$, are fully determined by the pair distribution functions of the system. However, specifying any of them does not unambiguously define the distribution functions. In particular, arbitrary terms $\tilde{F}_{ab}(R)$, for which $\sum_b N_b/V e z_b \tilde{F}_{ab}(R) = 0$, can be added to the pair distribution functions $F_{ab}(R)$ without changing the functions $\varepsilon(k)$, $\zeta_a(R)$, and $\Psi_a(R)$, and, consequently, the electrostatic part of the free energy.

The expression (3.4.16) can be written as an equation

$$\nabla^2 \Psi_a(R) = -\frac{4\pi}{\varepsilon} \left[\sum_b \frac{N_b}{V} e z_b F_{ab}(R) + e z_a \delta(R) \right], \quad (3.4.18)$$

or due to (3.4.11)

$$\nabla^2 \Psi_a(R) = -\frac{4\pi}{\varepsilon} [\zeta_a(R) + e z_a \delta(R)],$$

which is the standard Poisson equation for the electrostatic potential of the ion. Expressing the pair distribution functions through the potentials of the mean force $F_{ab}(R) = e^{-\beta w_{ab}(R)}$, the equation (3.4.18) can be rewritten as

$$\nabla^2 \Psi_a(R) = -\frac{4\pi}{\varepsilon} \left[\sum_b \frac{N_b}{V} e z_b e^{-\beta w_{ab}(R)} + e z_a \delta(R) \right]. \quad (3.4.19)$$

This equation is exact, but since the dependence of the mean force potential $w_{ab}(R)$ on the electrostatic potential $\Psi_a(R)$ is unknown, it is not closed. Therefore, when using it, certain approximations are due to be made, the validity of which can only be evaluated based on a more consistent approach. In particular, if in (3.4.19) we set $w_{ab}(R) = e z_b \Psi_a(R)$, we arrive at the Poisson–Boltzmann equation, first used to describe ionic systems by Debye and Hückel [164].

3.4.2. Application of the collective variables method

To describe the ionic system, one can use cluster expansions (3.3.31), as well as introduce new collective variables corresponding to longitudinal oscillations of the electric charge density. For convenience, let us introduce dimensionless charges $\lambda_a = \frac{ez_a}{\sqrt{\sum_a N_a e^2 z_a^2}}$, normalised in such a way that $\sum_a N_a \lambda_a^2 = 1$. Since, according to (3.4.1), $\sum_a N_a \lambda_a = 0$, the operator for the deviation of the charge density from its mean value

$$\hat{n}(\mathbf{R}) = \sum_{a=1}^M \sum_{j=1}^{N_a} \lambda_a \delta(\mathbf{R} - \mathbf{R}_j) = \frac{1}{V} \sum_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}}, \quad \mathbf{k} \neq 0,$$

where $\hat{\rho}_{\mathbf{k}} = \sum_{a=1}^M \lambda_a \sum_{j=1}^{N_a} e^{-i\mathbf{k}\mathbf{R}_j}$, $\mathbf{k} \neq 0$.

Expanding the Coulomb part of the potential energy in a Fourier series, we can represent it as an analytic functional

$$U^{(\text{el})}(R) = \sum_{a,b} \sum_{i < j} \Phi_{ab}(R_{ij}) = \int U^{(\text{el})}(\rho) J(\rho R) (d\rho),$$

where $U^{(\text{el})}(\rho) = \frac{1}{2\beta} \sum_{\mathbf{k}} \alpha(k) (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1) + U^{(\text{el})}(\mathbf{k} = 0)$ is representation of collective variables for the function $U^{(\text{el})}(R)$; $\alpha(k) = \beta \nu(k) \frac{1}{\varepsilon} \sum_a \frac{N_a}{V} e^2 z_a^2 = \frac{\varkappa^2}{k^2}$; $\nu(k) = \frac{4\pi}{k^2}$ is the Fourier transform of the Coulomb potential; $\varkappa^2 = 4\pi\beta \frac{1}{\varepsilon} \sum_a \frac{N_a}{V} \times e^2 z_a^2$ is the square of the quantity inverse to the Debye length; $U^{(\text{el})}(\mathbf{k} = 0) = \frac{1}{2\beta} \sum_{a,b} N_a N_b \lambda_a \lambda_b \alpha(\mathbf{k} = 0) = 0$ due to (3.4.1); $(d\rho) = \prod_{\mathbf{k}}' d\rho_{\mathbf{k}}$; $J(\rho R) = \prod_{\mathbf{k}}' \delta(\rho_{\mathbf{k}} - \hat{\rho}_{-\mathbf{k}})$ is the transformation function to collective variables. Since in the one-component case $\lambda_a = \frac{1}{\sqrt{N}}$, by generalizing the results of the previous chapter, we arrive at the cluster expansion (3.3.31) for the free energy, where the screened potentials

$$\begin{aligned} g_{ab}(R) &= - \sum_{\mathbf{k}} \lambda_a \lambda_b \frac{\alpha(k)}{1 + \alpha(k)} e^{i\mathbf{k}\mathbf{R}} = \\ &= -\beta \frac{e^2 z_a z_b}{\varepsilon} \frac{4\pi}{V} \sum_{\mathbf{k}} (\varkappa^2 + k^2)^{-1} e^{i\mathbf{k}\mathbf{R}} = -\beta e^2 z_a z_b \frac{1}{\varepsilon R} e^{-\varkappa R}. \end{aligned} \quad (3.4.20)$$

According to (3.4.1), $F_{\text{HTA}}^{(\ell)} = 0$, and $-\beta F_{\text{RPA}}^{(\ell)} = \frac{V}{4\pi} \frac{\varkappa^3}{3}$, which corresponds to the result obtained by Debye and Hückel [164] based on the linearized Poisson–Boltzmann equation. This result is rather accurate in the low-density limit. The subsequent terms are cluster coefficients describing the correlation corrections, whose magnitudes increase with density. As noted earlier, the series (3.3.31) is not an expansion in terms of a small parameter. Each cluster coefficient contains an infinite summation over the plasma parameter. To determine the order of the cluster coefficients in the low-density limit, the exponential $e^{g_{ab}(R)}$ needs to be expanded into a series, and the first non-zero term must be estimated. The results obtained in this manner are presented in Table 5, taken from [63]. The estimation of the order of cluster coefficients leads to different results for symmetric ($z_+ = -z_-$) and asymmetric ($z_+ \neq z_-$) electrolytes. In the first case, according to (3.4.1), $\sum_a N_a z_a^3 = 0$, while in the second case, $\sum_a N_a z_a^3 \neq 0$.

The approximation of the second cluster coefficient is the most extensively studied. In the simplest case of a system of hard spheres with diameters σ_{ab} :

$$B_2 = 2\pi \sum_{a,b} \frac{N_a N_b}{V} \sigma_{ab}^3 K(x_{ab}, \beta_{ab}^*), \quad (3.4.21)$$

where $x_{ab} = \varkappa \sigma_{ab}$; $\beta_{ab}^* = -\beta \frac{e^2 z_a z_b}{\varepsilon \sigma_{ab}}$

$$K(x, \beta^*) = \int_1^\infty \exp \left[\frac{\beta^*}{r} e^{-xr} \right] r^2 dr - \int_0^\infty \left[1 + \beta^* \frac{1}{2} e^{-xr} + \frac{1}{2} \beta^{*2} \frac{1}{r^2} e^{-2xr} \right] r^2 dr. \quad (3.4.22)$$

The quantity $\beta e^2 \frac{1}{\varepsilon} |z_a z_b|$ in β_{ab}^* is known as the Bjerrum radius. For oppositely charged ions, it characterizes the distances at which the Coulomb attraction energy exceeds the thermal energy, making it possible for ionic complexes

Table 5. Order in density for the first coefficients of cluster expansions for ionic systems

Case	B_2	B_3	B_4	B_5	B_6	B_7
$\sum_a \rho_a z_a^3 \neq 0$	$\rho^2 \ln \rho$	$\rho^{5/2}$	$\rho^{5/2}$	ρ^3	ρ^3	$\rho^{7/2}$
$\sum_a \rho_a z_a^3 = 0$	ρ^2	$\rho^3 \ln \rho$	ρ^3	$\rho^{7/2}$	$\rho^{7/2}$	ρ^4

to form at smaller distances. The function $K(x, \beta^*)$ has been studied by many researchers. In the region of small β^* , the lower exponent of the first integral can be expanded into a series [63]. As a result:

$$K(x, \beta^*) = -\frac{1}{3} + \beta^* \frac{1}{x} \left[e^{-x} + \frac{1}{x} (e^{-x} - 1) \right] + \frac{1}{4x} \beta^{*2} (e^{-2x} - 1) + \sum_{m \geq 3} \frac{1}{m!} \beta^{*m} E_{m-2}(mx), \quad (3.4.23)$$

where $E_m(x) = \int_1^\infty e^{-xt} t^{-m} dt$. At $m = 1$, $E_1(x) = -\text{Ei}(-x)$, where $\text{Ei}(x) = \int_{-\infty}^x \frac{1}{t} e^t dt$ is exponential integral with asymptotics $\text{Ei}(x) = C + \ln|x| + x + \frac{1}{2 \cdot 2!} x^2 + \dots + \frac{1}{n \cdot n!} x^n + \dots$, $C = 0.5772$ — where C is Euler's constant. For $m \geq 2$

$$E_m(x) = \frac{1}{(m-1)!} \left[(-1)^m x^{m-1} \text{Ei}(-x) + e^{-x} \sum_{k=0}^{m-2} (-x)^k (m-2-k)! \right].$$

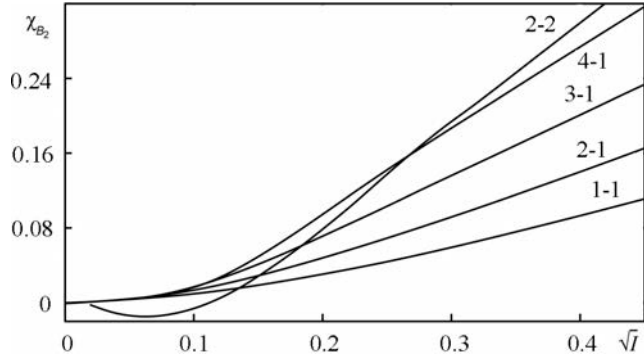
In the work [168], the integration region in (3.4.22) is divided into three intervals: $(0, 1)$, $(1, |\beta^*|)$ and $(|\beta^*|, \infty)$. When $1 < |\beta^*| < \kappa^{-1}$, in the interval $(1, |\beta^*|)$, the upper exponential is expanded instead of the lower one. This leads to the multiplication in (3.4.21) of σ_{ab}^3 by $|\beta_{ab}|^3$, and in (3.4.23), to the substitution $|\beta^*| \rightarrow 1$, $x \rightarrow x|\beta^*|$, resulting in the emergence of a new term

$$\begin{aligned} \frac{1}{|\beta^*|^3} \int_1^{|\beta^*|} r^2 dr \exp \left\{ \frac{\beta^*}{r} - \beta^* x + \frac{1}{2} \beta^* x^2 r + \dots \right\} \approx \\ \approx e^{\beta^* x} \left[E_4 \left(\frac{\beta^*}{|\beta^*|} \right) - E_4(\beta^*) \right]. \end{aligned}$$

The function $K(x, \beta^*)$ was most thoroughly studied in the works of Kelbg and his collaborators ([169, 170], as well as [171]). By isolating the logarithmic terms in (3.4.23), they represented $K(x, \beta^*)$ as a series in powers of the parameter $x\beta^*$:

$$\begin{aligned} K(x, \beta^*) = \left[K_0(\beta^*) - \frac{1}{6} \beta^{*2} \ln x \right] \left[1 - x\beta^* + \frac{5}{8} (x\beta^*)^2 \right] + \\ + \frac{1}{6} \beta^{*3} \left[x\beta^* \left(1 - \ln \frac{4}{3} \right) + \frac{5}{8} (x\beta^*)^2 \left(\frac{31}{20} - \ln \frac{5}{3} \right) \right] - \\ - \frac{1}{8\beta^*} e^{\beta^*} (\beta^* x)^2 + O[(\beta^* x)^3], \quad (3.4.24) \end{aligned}$$

Fig. 11. Contribution of the second virial coefficient to the osmotic coefficients of charged hard-sphere systems modelling the electrolyte solutions. The results are shown for different valence combinations at $T = 25\text{ }^\circ\text{C}$, particle diameter $\sigma = 4.2\text{ \AA}$, and as a function of the ionic strength $I = \sum N_a z_a^2 / N$



where $K_0(\beta^*) = \frac{1}{6}\beta^{*3} \left[\text{Ei}(\beta^*) - \ln |\beta^*| - 2C + \frac{11}{6} \right] - \frac{1}{6}e^{\beta^*} (2 + \beta^* + \beta^{*2})$. In the work [63], the function $\frac{x^2}{\beta^*} K(x, \beta^*)$ is tabulated for the intervals $0.02 \leq x \leq 2.6$; $-30 \leq \beta^* \leq 10$.

The approximation of the second cluster coefficient has been applied by several authors in the description of the thermodynamic properties of electrolyte solutions. The studies by Kelbg [172, 173] of the osmotic coefficients of tetra-alkyl ammonium salts indicate a significant role of short-range interactions. Depending on the depth of the potential well, both positive and negative deviations from the Debye approximation were obtained. Investigations of the thermodynamic properties of aqueous solutions of 2-2-valent electrolytes have shown that, in the region of low concentrations, the contribution of the second cluster coefficient can exceed the contribution of the Debye term [174, 175]. This leads to an anomalous behaviour of the thermodynamic quantities, which is also observed experimentally. This effect is illustrated in Fig. 11, taken from the work [175], where the contribution of the second cluster coefficient to the osmotic coefficients of a system of charged hard spheres with a radius $\sigma = 4.2\text{ \AA}$ and different valencies under conditions, corresponding to aqueous electrolyte solutions at $25\text{ }^\circ\text{C}$, plotted as a function of the ionic strength $I = \sum_a \frac{N_a}{N} z_a^2$, is shown.

However, it should be noted that the Debye expression $-\beta F_{\text{RPA}} = -V/4\pi\kappa^3/3$ does not provide the correct limit (3.4.4) as $\beta e^2 \rightarrow \infty$. Therefore, the application of cluster expansions (3.3.31) is limited to the region of small Bjerrum radii. As the density or the Bjerrum radius increases, the series (3.3.31) must be resummed, leading to the integral equations. In the one-component case, this reduces to an equation of the type (2.2.69). Generalization to the multicomponent case does not pose significant difficulties and merely requires substituting the operation $N/V \int d\mathbf{R}$ by $\sum_a N_a/V \int d\mathbf{R}$.

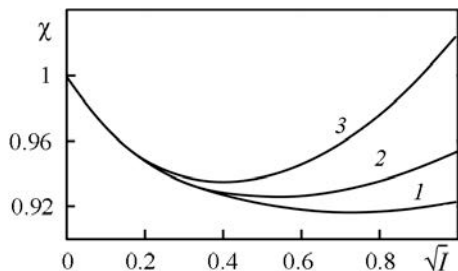


Fig. 12. Osmotic coefficient χ as a function of ionic strength $I = \sum N_a z_a^2 / N$ for a model of monovalent charged hard spheres with diameter $\sigma = 3.9 \text{ \AA}$, representing aqueous NaCl at 25°C . Curve 1: second cluster approximation; curve 2: experimental data; curve 3: hypernetted-chain approximation

The application of integral equations in the description of ionic systems was discussed in detail in the works of Rasaiah and Friedman [176, 177]. A comparison of their results with those from computer simulations shows [178, 179] that the hypernetted-chain approximation (HCA) is quite accurate. The Percus–Yevick–Allnatt (PYA) approximation leads to worse results. In the case of 2-2-valent electrolytes, the hypernetted-chain approximation, like the second cluster coefficient approximation, results in an anomalous behaviour of thermodynamic properties in the region of low concentrations. However, a comparison of the second cluster coefficient approximation and the hypernetted-chain approximation shows that, as the density increases, the former leads to significantly underestimated results. Figure 12, taken from [180], shows the osmotic coefficients as a function of the ionic strength $I = \sum_a N_a / N z_a^2$ for monovalent

charged hard spheres with a radius $\sigma = 3.9 \text{ \AA}$. This model corresponds to an aqueous solution of NaCl at 25°C . Curve 1, obtained using the second cluster coefficient approximation, agrees quite well with the experimental curve 2, and it seems that taking higher cluster coefficients into account should lead to even better agreement. However, curve 3, obtained using the hypernetted-chain approximation, is much higher than curve 2. This result is quite interesting, as it highlights the difficulties encountered by researchers when attempting to interpret the experimental data based on approximate results from model systems. Clearly, in this case, the contradiction between the theoretical and experimental results is due to the model itself.

The hypernetted-chain approximation (HCA) is quite accurate, but it is rather complicated, and its solution is only possible using numerical methods.

3.4.3. Reference system approach to short-range interactions

Application of the reference approach to account for short-range interaction leads to simpler results. In this case, we arrive at cluster expansions (3.3.51), and specific expressions for screened potentials depend both on the nature of short-range interactions and on the method of separating interactions. Thus, assuming that long-range interactions have a

Coulomb nature for all distances, in the case where short-range interactions are the same for all types of ions due to the electroneutrality condition (3.4.1) $\det [1 + \alpha(k)m_2(k)] = 1 + \kappa^2/k^2$ which leads to expression (3.4.20) for screened potentials. In this case, again $F_{\text{HTA}} = 0$, $F_{\text{RPA}} = -V/4\pi\beta\kappa^3/3$, which, as noted, does not provide the correct limit (3.4.4) as $\beta e^2 \rightarrow \infty$. Thus, the cluster expansions (3.3.51) with the used method of separation of interactions are directly applicable only in the region of small values of the Bjerrum radius. Nevertheless, they can serve as a basis for constructing interpolation expressions that satisfy condition (3.4.4) and are thus valid in the region of low temperatures (large values of the Bjerrum radius).

For concreteness, let us dwell more in detail on the simplest model of symmetric electrolytes — a system of charged hard spheres of equal size σ . In this case, expanding in cluster coefficients of the exponent $e^{g_{ab}(R)}$, expression (3.3.51) for the free energy can be represented as a series in powers of the parameter $x = \kappa\sigma$ [181]

$$-\beta \frac{F - F_0}{V} \sigma^3 = \frac{x^3}{12\pi} [1 + A_1 x + A_2 x^2 + A_3 x^3 + \dots]. \quad (3.4.25)$$

After the transformation to dimensionless variables $r = R/\sigma$, we have:

$$\begin{aligned} A_1 &= \frac{3}{4} \int_0^\infty h_2^0(r) dr, & A_2 &= -\frac{3}{2} \int_0^\infty h_2^0(r) r dr, \\ A_3 &= \frac{3}{2} \int_0^\infty h_2^0(r) r^2 dr - \frac{1}{2} \int_0^\infty dr \int_0^\infty du \int_{|r-u|}^{r+u} dv h_3^0(t, u, v), \end{aligned}$$

where A_1 , A_2 and the first term of A_3 arises from the term $\sum_{a,b} \frac{N_a N_b}{2V} \frac{1}{2} \int g_{ab}^2(R) h_2^0(R) d\mathbf{R}$ in the second cluster coefficient, and the second term in A_3 arises from the corresponding term of the third cluster coefficient $h_2^0(r)$ and $h_3^0(r, u, v)$ are the corresponding correlation functions of hard spheres.

It is clear that series (3.4.25), like the original cluster expansion (3.3.51), does not satisfy condition (3.4.4). Nevertheless, on its basis, as Stell and Wu [182] showed, it is possible to construct a Padé approximant that ensures the fulfillment of condition (3.4.4):

$$-\beta \frac{F - F_0}{V} \sigma^3 = \frac{x^3}{12\pi} \frac{1 + a_1 x}{1 + a_2 x + a_3 x^2}, \quad (3.4.26)$$

where

$$a_1 = \frac{A_1^3 - 2A_1 A_2 + A_3}{A_1^2 - A_2}, \quad a_2 = \frac{A_3 - A_1 A_2}{A_1^2 - A_2}, \quad a_3 = \frac{A_2^2 - A_1 A_3}{A_1^2 - A_2}.$$

A similar expression has also been proposed for the internal energy [183]. The disadvantage of expression (3.4.26) is that it does not lead to the anomalous behaviour of the thermodynamic properties of aqueous solutions of 2-2-valent electrolytes noted in the previous section. Hence, in the work [184] it was proposed to supplement (3.4.26) with a part of the expression for the second coefficient, found by taking into account short-range forces using the method of functional differentiation. According to (3.4.21):

$$-\beta \frac{F - F_0}{V} \sigma^3 = \frac{x^3}{12\pi} \frac{1 + a_1 x}{1 + a_2 x + a_3 x^2} + 2\pi \sum_{a,b} \rho_a \rho_b \tilde{K}(x, \beta_{ab}^*), \quad (3.4.27)$$

where

$$\begin{aligned} \tilde{K}(x, \beta_{ab}^*) &= \int_1^\infty \left[\exp \left\{ \frac{1}{r} \beta^* e^{-xr} \right\} - 1 - \frac{1}{r} \beta^* e^{-xr} - \frac{1}{r^2} \beta^{*2} e^{-2xr} \right] r^2 dr = \\ &= \sum_{m \geq 3} \frac{1}{m!} \beta^{*m} E_{m-2}(mx). \end{aligned}$$

Since $\beta e^2 \rightarrow \infty$ $\tilde{K}(x, \beta^*) \rightarrow 0$, expression (3.4.27) ensures that condition (3.4.4) is satisfied, and the presence of the second term in (3.4.27) leads to the correct behaviour of the thermodynamic properties in the region of low densities. Singling out the second term (3.4.27) in the second cluster coefficient (which was obtained taking in short range interactions using reference approach), we see that none of its terms are included in (3.4.26), which justifies the validity of expression (3.4.27).

The extension of the applicability domain of the cluster expansions (3.3.51) is also associated with a more consistent separation of short- and long-range interactions. This problem was discussed in general in Chapter 2 and was studied in great detail in the works of Andersen and Chandler [25, 26] in relation to the model of charged hard spheres. Until now, we have assumed that the long-range interaction $\Phi_{ab}(R)$ is Coulombic for all distances R . This led us to the screened potentials (3.4.20). Assuming the long-range potential in the region $R < \sigma$ to be equal to zero, for the screened potentials we arrive at a new expression

$$g_{ab}(R) = -\beta \frac{4\pi}{V} \sum_k \frac{e^2 z_a z_b}{\varepsilon} \frac{\cos(k\sigma)}{k^2 + \varkappa^2 \cos(k\sigma)} e^{i\mathbf{k}\mathbf{R}}, \quad (3.4.28)$$

which corresponds to the second Debye–Hückel approximation [164]. Finding these screened potentials is carried out using residue theory and is reduced to solving the transcendental equation $z^2 + x^2 \cos z = 0$, where $z = k\sigma$, $x = \varkappa\sigma$. Numerical studies [185, 186] show that in the region $x < 1.03$ this equation has two complex solutions z_1 and z_2 , while $x \rightarrow 0$ $z_1 \rightarrow ix$,

$z_2 \rightarrow i\infty$. The remaining roots are also complex with an infinitely large imaginary part. Therefore, in the region of small densities for $R > \sigma$, we can set $g_{ab}(R) = -\beta A_a e z_b \frac{1}{R} e^{-\kappa R} = -\beta e^2 z_a z_b \frac{1}{\varepsilon R} \frac{e^x}{1+x} e^{-\kappa R}$, where A_a is determined from condition (3.4.12). With increasing density, starting from $x \simeq 0.5$, z_2 is also important, and for $x = 1.03$, $z_1 = z_2$. For $x > 1.03$, all roots are complex and the screened potential, in accordance with (3.4.13), acquires an oscillating character. Thus, the screened potentials (3.4.28), compared with (3.4.20), provide a qualitatively correct behaviour of the system.

However, the best convergence of the cluster expansions (3.3.51) is achieved by the optimum separation of interactions, which, in the Percus—Yevick description of hard spheres, is reduced to solving the integral equation of the mean spherical approximation. For a system of charged hard spheres in the mean spherical approximation, the set of equations (3.3.17) is closed by the conditions

$$h_{ab}(R) = -1, \quad R < \sigma_{ab}, \quad c_{ab}(R) = -\beta \frac{e^2 z_a z_b}{\varepsilon R}, \quad R > \sigma_{ab}. \quad (3.4.29)$$

Let us first consider the simplest model of a binary system of monovalent charged hard spheres of identical size. In this case, from the distribution functions $F_{++}(R) = F_{--}(R)$ and $F_{+-}(R) = F_{-+}(R)$ we can pass to the functions $F_2^0(R) = 1/2[F_{++}(R) + F_{+-}(R)]$ and $G(R) = 1/2[F_{+-}(R) - F_{++}(R)]$, where in the mean spherical approximation, $F_2^0(R)$ is the pair distribution function of hard spheres, while $G(R) = g(R) = -g_{++}(R) = g_{+-}(R)$. In this case, system (3.3.17) breaks down into a set of two equations, the first of which coincides with the Percus—Yevick equation for hard spheres of size σ and density $\eta = \frac{1}{6}\pi \frac{N}{V} \sigma^3$, and determines $F_2^0(R)$. The second equation:

$$\begin{aligned} g(R) &= c(R) - \rho \int c(R') g(|\mathbf{R} - \mathbf{R}'|) d\mathbf{R}', \\ g(R) &= 0, \quad R < \sigma; \quad c(R) = -\beta \frac{1}{\varepsilon R} e^2, \quad R > \sigma \end{aligned} \quad (3.4.30)$$

defines the function $g(R)$; $N_+ = N_- = 1/2N$, $\rho = N/V$.

The function $c(R)$ can be written as $c(R) = c_0(R) - \beta \frac{e^2}{\varepsilon R}$, where $c_0(R) = 0$ for $R > \sigma$. To ensure correctness of the calculations, we set $c(R) - c_0(R) = -\beta \frac{e^2}{\varepsilon R} e^{-\alpha R}$ assuming that the limit $\alpha \rightarrow 0$ is taken in the final results.

Using the Fourier transform, equation (3.4.30) can be represented as:

$$[1 - \rho g(k)] \left[1 + \rho c_0(k) - \frac{4\pi}{\varepsilon} \frac{\beta \rho e^2}{(k^2 + \alpha^2)} \right] = 1, \quad (3.4.31)$$

where

$$g(k) = \frac{4\pi}{k} \int_0^{\infty} R dR g(R) \sin(kR) = 4\pi \int_0^{\infty} I(R) \cos(kR) dR, \quad (3.4.32)$$

$$c_0(k) = \frac{4\pi}{k} \int_0^{\infty} R dR c_0(R) \sin(kR) = 4\pi \int_0^{\infty} S(R) \cos(kR) dR, \quad (3.4.33)$$

$$I(R) = \int_R^{\infty} R g(R) dR, \quad S(R) = \int_R^{\infty} R c_0(R) dR. \quad (3.4.34)$$

By repeating the reasoning used in deriving relation (3.1.47), we obtain

$$1 + \rho c_0(k) - 4\pi\beta \frac{1}{\varepsilon} \rho \frac{e^2}{k^2 + \alpha^2} = Q(k)Q(-k). \quad (3.4.35)$$

The function $Q(k)$, analytic in the domain $\text{Im } k > 0$, can be associated with the function $q(R)$, defined according to (3.1.47). In this case, $q(R) = 0$ for $R < 0$. Analytic continuation of the function $Q(k)$ into the lower half-plane is given by the relation $Q(k) = \left[1 + \rho c_0(k) - 4\pi\beta \rho \frac{1}{\varepsilon} \frac{e^2}{k^2 + \alpha^2} \right] Q^{-1}(-k)$. Since $c_0(R)$ is finite and equal to zero in the region $R > \sigma$, then for the $R > \sigma$ $q(R) = Ae^{-\alpha R}$, where $2\pi\rho A = -\varkappa$, $\varkappa = (4\pi\beta\rho e^2/\varepsilon)^{1/2}$ is the inverse Debye length. Using the inverse Fourier transform from (3.1.47), we find

$$Q(k) = 1 - 2\pi\rho \int_0^{\sigma} q(R) e^{ikR} dR + \varkappa \int_{\sigma}^{\infty} e^{-\alpha R} e^{ikR} dR. \quad (3.4.36)$$

We substitute (3.4.33) and (3.4.36) into (3.4.35), multiply the resulting expression by e^{-ikR} , and integrate over dk . As a result, in the region $0 < R < \sigma$ we obtain

$$S(R) - \beta e^2 \frac{1}{\varepsilon \alpha} e^{-\alpha R} = -q(R) + 2\pi\rho \int_0^{\infty} q(t+R)q(t) dt. \quad (3.4.37)$$

According to (3.4.31) and (3.4.35)

$$[1 - \rho g(k)]Q(k) = Q^{-1}(-k). \quad (3.4.38)$$

We multiply (3.4.38) by e^{-ikR} and integrate over dk . For $R > 0$, the contribution of the right-hand side is zero, and as a result

$$I(R) = -q(R) + 2\pi\rho \int_0^{\infty} dt q(t) I(|R-t|). \quad (3.4.39)$$

Differentiating (3.4.37) and (3.4.39) with respect to R taking into account that for $R > \sigma$, $2\pi\rho q(R) = -\kappa e^{-\alpha R}$, and after taking the limit $\alpha \rightarrow 0$ we arrive at a set of equations for the functions $g(R)$ and $c_0(R)$:

$$Rg(R) = q'(R) + 2\pi\rho \int_0^\sigma dt(R-t)q(t)g(|R-t|) + \kappa I(|R-\sigma|), \quad R > 0, \quad (3.4.40)$$

$$Rc_0(R) = q'(R) + 2\pi\rho \int_R^\sigma dtq(t)q'(R-t) + 2\pi\rho q(R)q(0) + \kappa q(\sigma-R) + \frac{1}{4\pi\rho}\kappa^2, \quad 0 < R < \sigma, \quad (3.4.41)$$

where $q'(R) = \frac{d}{dR}q(R)$.

Since in the region $R < \sigma$ $g(R) = 0$, from (3.4.40) we have:

$$q'(R) = -\kappa I \equiv -\kappa \int_0^\infty Rg(R)dR, \quad (3.4.42)$$

hence

$$q(R) = I\kappa R - a \quad (3.4.43)$$

From the continuity of $q(R)$ at the point $R = \sigma$ we find

$$\kappa I\sigma + a = \frac{1}{2\pi\rho}\kappa. \quad (3.4.44)$$

The second equation is obtained from (3.4.41). Due to the finiteness of $c_0(R)$ the left-hand side of (3.4.41) at $R = 0$ is equal to zero, so that $q'(0) + \pi\rho q^2(0) = 0$ or, according to (3.4.42) and (3.4.43)

$$\kappa I = -\pi\rho a^2. \quad (3.4.45)$$

From (3.4.45) and (3.4.44) we find

$$2\pi\rho a\sigma \equiv 2\Gamma\sigma = \sqrt{1+2x} - 1, \quad (3.4.46)$$

$$2\pi\rho I\sigma \equiv B = \frac{1}{x} \left(1 + x - \sqrt{1+2x}\right) = \Gamma\sigma [1 + \Gamma\sigma]^{-1},$$

where $x = \kappa\sigma$.

Knowing $q(R)$ from (3.4.41) we find

$$c_0(R) = \beta \frac{e^2}{\varepsilon\sigma} \left[2B - B^2 \frac{R}{\sigma} \right], \quad R < \sigma. \quad (3.4.47)$$

From equation (3.4.40) we immediately have

$$g(\sigma+) = \frac{\Gamma^2}{\pi\rho\sigma} = \beta \frac{e^2}{\varepsilon\sigma} \left[\frac{2\Gamma}{\kappa} \right]^2, \quad (3.4.48)$$

and using the Laplace transform we find an expression for the screened potential

$$g(R) = \frac{1}{2\pi i R} \int_{c-i\infty}^{c+i\infty} \frac{\Gamma^2}{\pi \rho} \frac{e^{sR} s ds}{(s^2 + 2\Gamma s + 2\Gamma^2)e^{s\sigma} - 2\Gamma^2}. \quad (3.4.49)$$

By direct substitution $g(R) = 1/2[F_{+-}(R) - F_{++}(R)]$ we make sure that the expression found for the screened potential satisfies conditions (3.4.14). The behaviour of potential (3.4.49) is qualitatively the same as (3.4.28). Its calculation is also reduced to finding the poles of the integrand function. Numerical studies [187] show that in the region $x < 1.229$, the integrand has two real poles, and at $x \rightarrow 0$ $s_1 \rightarrow -2\Gamma$, $s \rightarrow -\infty$, the remaining poles are complex with an infinitely large real part. Therefore, in the region of small x , the screened potential has the standard Debye form only with $\varkappa$ replaced by 2Γ :

$$g(R) = \beta \frac{e^2}{\varepsilon R} \left(\frac{2\Gamma}{\varkappa} \right)^2 \exp\{-2\Gamma(R - \sigma)\}, \quad R > \sigma, \quad (3.4.50)$$

where Γ is defined according to (3.4.46). An important feature of the new screening radius is that, in the low-density region, it coincides with the Debye length ($2\Gamma \rightarrow \varkappa$ at $x \rightarrow 0$), and in the region of high densities it changes proportionally to the square root of the Debye length ($2\Gamma\sigma \rightarrow \sqrt{2}x$ at $x \gg 1$). In the entire region x $2\Gamma < \varkappa$.

As x increases, the second pole s_2 also becomes important, and at $x = 1.229$, $s_1 = s_2$, while at $x > 1.229$ all poles are complex and the screened potential acquires an oscillating character. In this case, as in the calculation of the integral (3.1.69) for the pair distribution function of hard spheres, the denominator of the integrand (3.4.49) can be expanded in a series in powers of $\frac{2\Gamma^2}{s^2 + 2\Gamma s + 2\Gamma^2}$, representing the screened potential in the form

$$g(R) = \frac{1}{2\pi i R} \frac{1}{2\pi \rho} \sum_{n \gg 1} \oint \left[\frac{2\Gamma^2}{s^2 + 2\Gamma s + 2\Gamma^2} \right]^n e^{s(R-n\sigma)} s ds. \quad (3.4.51)$$

Each of these integrals, as in the case of (3.1.72), is equal to zero for $R < n\sigma$. For $R > n\sigma$, integration contour is closed in the left half-plane and the contribution of all the zeros of the function $s^2 + 2\Gamma s + 2\Gamma^2$ is taken into account. In particular, in the region $\sigma < R < 2\sigma$ we have

$$g(R) = \frac{\Gamma^2}{\pi \rho R} e^{-\Gamma(R-\sigma)} \sqrt{2} \cos \left[\Gamma(R - \sigma) + \frac{\pi}{4} \right]. \quad (3.4.52)$$

Knowing the screened potential, we proceed by describing the thermodynamic and structural properties of the system. In the case under consideration, ac-

cording to (3.3.8) and (3.3.9)

$$\frac{E - E_{\text{id}}}{Nk_{\text{B}}T} = \frac{1}{4}\kappa^2 \int_0^\infty [F_{++}(R) - F_{+-}(R)] R dR, \quad (3.4.53)$$

$$\beta \frac{PV}{N} = 1 + \frac{1}{3} \frac{E - E_{\text{id}}}{Nk_{\text{B}}T} + \text{contact}, \quad (3.4.54)$$

where

$$\text{contact} = 2\eta [F_{++}(\sigma+) + F_{+-}(\sigma+)]. \quad (3.4.55)$$

According to (3.4.1) $F_{\text{HTA}} = 0$. In the approximation of the ORPA $g(R) = -\frac{1}{2}|F_{++}(R) - F_{+-}(R)|$ and according to (3.4.42), (3.4.46), (3.4.53)

$$\frac{E - E_{\text{id}}}{Nk_{\text{B}}T} = -\beta \frac{e^2}{\varepsilon} \frac{\Gamma}{1 + \Gamma\sigma}. \quad (3.4.56)$$

Since in the approximation of the ORPA $\frac{1}{2}[F_{+-}(R) + F_{++}(R)] = F_2^0(R)$, according to (3.4.54)

$$\frac{P - P_0}{N} V \beta = \frac{1}{3} \frac{E - E_{\text{id}}}{Nk_{\text{B}}T} = -\frac{1}{3} \beta e^2 \frac{1}{\varepsilon} \frac{\Gamma}{(1 + \Gamma\sigma)}. \quad (3.4.57)$$

Using formula (3.3.45), we find the expression for free energy

$$\begin{aligned} \frac{\beta F_{\text{ORPA}}}{Nk_{\text{B}}T} &= -\beta \frac{e^2}{\varepsilon} \int_0^1 \frac{\Gamma(\xi) d\xi}{1 + \Gamma(\xi)\sigma} = \frac{\Gamma^3}{3\pi\rho} + \frac{E - E_{\text{id}}}{Nk_{\text{B}}T} = \\ &= -\frac{1}{12\pi\sigma^3\rho} [6x + 3x^2 + 2 - 2(1 + 2x)^{3/2}]. \end{aligned} \quad (3.4.58)$$

It is important to note that the expression obtained has the correct limit corresponding to (3.4.4). When $\beta e^2 \rightarrow \infty$ $\frac{1}{N} \beta F_{\text{ORPA}} \rightarrow -\beta \frac{e^2}{\varepsilon\sigma}$. Differentiating expression (3.4.58) with respect to V , we arrive at the equation of state:

$$\frac{(P - P_0)}{N} \beta V = -\frac{\Gamma^3}{3\pi\rho}. \quad (3.4.59)$$

The discrepancy between (3.4.59) and (3.4.57) is due to the thermodynamic non-self-consistency of the random phase approximation.

According to the law of corresponding states, the thermodynamic and structural properties of the system under consideration are completely determined by two parameters $\eta = \frac{1}{6}\pi \frac{N}{V}\sigma^3$ and $\beta^* = \beta e^2 \frac{1}{\varepsilon\sigma}$. The first parameter is the dimensionless density, and the second is the quantity being inverse to the dimensionless temperature. For example, the parameter $x^2 = \kappa^2 \sigma^2 = 24\eta\beta^*$

mentioned earlier. Table 6, compiled on the basis of works [26, 183, 184, 188], presents the values of $-\frac{1}{V}\beta(E - E_{\text{id}})$, obtained by different methods for different thermodynamic states. The first corresponds to an aqueous solution of a 1–1-valent electrolyte at an ion concentration of 2 mol/L, the second to a 2–2-valent solution at the concentration of 0.0625 mol/L, the third to the concentration of 2 mol/L, the fourth to 2–2-valent solution at an ion concentration of 1 mol/L in a medium with a dielectric constant of $\varepsilon = 45$, and the fifth to a molten salt.

As can be seen from the table, expression (3.4.56) (ORPA) agrees well with the results of the MC simulation and thus makes the main contribution to the value of $E - E_{\text{id}}$. It is clear that in the region of low densities at β^* , corresponding to an aqueous solution of a 2–2-valent electrolyte, (3.4.56) does not lead to an anomalous behaviour. However, taking into account the second cluster coefficient (ORPA + B_2) ensures excellent agreement with the results of computer simulations [26]. As can be seen from the table, the computer simulation results are between the data of the HNC and ORPA + B_2 . The approximation (3.4.56) is considerably, especially in the region of high densities, if we take into account the term of the second cluster coefficient $LB_2 = \sum_{a,b} \frac{N_a N_b}{2V} \int \frac{1}{2} g_{ab}^2(R) [F_{ab}^0(R) - 1] dR$ (approximation ORPA + LB_2)

[184]. It is clear that in the region of low densities this approximation will not provide a description of the anomalous behaviour. Very simple formulas (3.4.26) and (3.4.27) also lead to satisfactory results [188]. Other thermodynamic quantities obtained on the basis of internal energy (equation of state, compressibility, etc.) also agree well with the data of the computer simulation [184].

A key property of the system under consideration is the critical point, identified in [184, 189] as well as in [190, 191] using the MC method. In thermodynamic analysis, the latter is determined from the conditions

Table 6. Excess values of internal energy $\frac{1}{V}\beta(E - E_{\text{id}})$ for a symmetric system of charged hard spheres

No.	$\rho^* = \frac{N}{V}\sigma^3$	$\beta^* = \beta \frac{e^2}{\varepsilon\sigma}$	ORPA (3.4.56)	ORPA+ + B_2	ORPA+ + LB_2	HNC	Padé F (3.4.26)	Padé $F + B_2$ (3.4.27)	MC
1	0.1819	1.68	0.6362	—	0.6505	0.6460	0.6375	0.6375	0.6511
2	0.00558	6.81	1.455	2.062	1.456	1.7371	1.452	1.599	1.900
3	0.17755	6.81	3.380	3.579	—	3.396	3.225	3.255	3.522
4	0.006796	12.0	5.550	—	5.592	—	—	—	5.832
5	0.6690	35.476	25.28	—	26.37	—	—	—	26.54

given in [79]:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0, \quad (3.4.60)$$

which, together with the equation of state $P = P(V, T)$ determine the critical values of density ρ_c^* and the temperature $T_c^* = 1/\beta_c^*$. The values of the critical parameters are presented in Table 7, compiled on the basis of works [184, 189, 190].

The critical point under discussion is associated with the ordering of ions and marks the onset of the formation of a structure characteristic of ionic crystals. In order to trace the nature of structural transformations with a change in density and temperature, we turn to pair distribution functions. In the approximation of the second cluster coefficient for the contact value of pair distribution functions according to (3.1.61) and (3.4.48) we have [69]:

$$F_{ab}(\sigma+) = \frac{1 + \frac{1}{2}\eta}{(1 - \eta)^2} \exp \left\{ -\beta \frac{e^2 z_a z_b}{\varepsilon \sigma} \left(\frac{2\Gamma}{\varkappa} \right)^2 \right\}, \quad (3.4.61)$$

from which it is evident that at low densities $\eta \rightarrow 0$ $2\Gamma \rightarrow \varkappa$, and the main contribution to $F_{ab}(R)$ is due to Coulomb interactions. As the density increases, the role of Coulomb forces decreases $\left(-\frac{2\Gamma}{\varkappa} \rightarrow 0\right)$ and at the same time the role of short-range interactions increases. Due to Coulomb forces, the value of $F_{ab}(\sigma+)$ increases for ions of the opposite sign and decreases for equally charged ions.

The role of Coulomb forces also increases with increasing inverse temperature, β^* . We have already noted that the oscillatory nature of the ionic “atmosphere” following from conditions (3.4.14) arises at least for $x > \sqrt{6}$. It is clear that the occurrence of oscillations can be associated with both an increase in the density η and inverse temperature β^* . “Ionic” oscillations, superimposed on oscillations caused by the geometric packing of hard spheres, lead to a qualitative change in the structure of the system. As the results of a computer simulation [191] show, in the region of small values of β^* and η , the distribution functions have a monotonous dependence on R . An increase of β^* leads to the emergence of a new structure, expressed by the appearance of antiphase oscillations for $F_{++}(R)$ and $F_{+-}(R)$, that increase with

Table 7. Values of critical parameters for a symmetrical system of charged hard spheres

Approximation	ORPA (3.4.56)	Padé F (3.4.26)	Padé $F + B_2$	MC
ρ_c^*	0.013	0.0098	0.0096	0.16
$T_c^* = \frac{1}{\beta_c^*}$	0.0782	0.0745	0.0832	0.095
$Z_c = \frac{1}{\rho_c} \beta_c P_c$	0.098	0.091	0.38	0.59

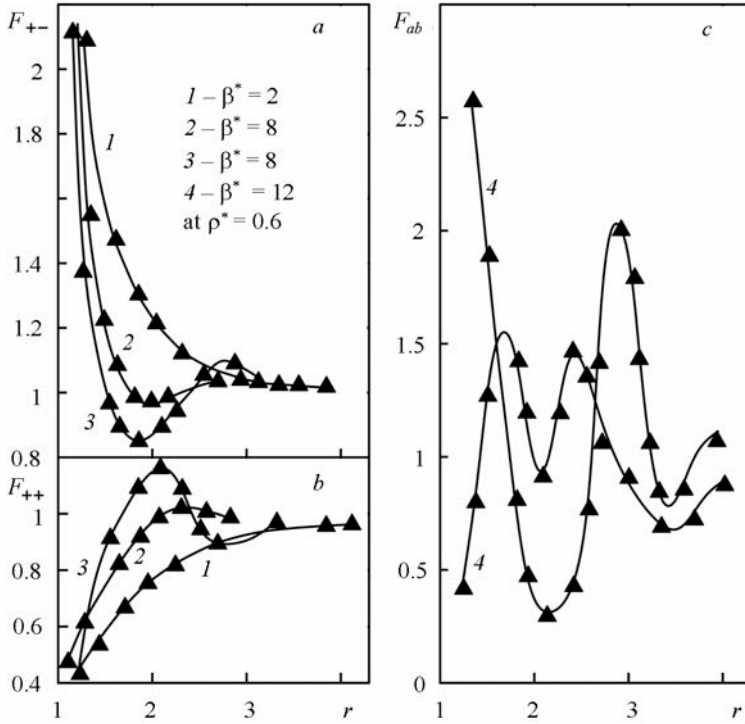


Fig. 13. Radial distribution functions $F_{+-}(r)$ and $F_{++}(r)$ for a model of charged hard spheres at fixed density $\rho^* = 0.6$ and various inverse temperatures $\beta^* = 2, 6, 8, 12$

an increase of β^* . In the region $\beta^* > \beta_c^*$, the first minimum and the second maximum of the function $F_{+-}(R)$ become more pronounced, and at the location of the first maximum of $F_{++}(R)$, a sharp dip appears, separating two prominent maxima. This picture of structural changes is clearly illustrated in Fig. 13, which shows the pair distribution functions of the charged hard sphere model for various thermodynamic states, as presented in [191].

As already noted, instead of the functions $F_{++}(R)$ and $F_{+-}(R)$ we can introduce the functions:

$$\begin{aligned} F_s(R) &= \frac{1}{2} [F_{++}(R) + F_{+-}(R)], \\ F_D(R) &= \frac{1}{2} [F_{+-}(R) - F_{++}(R)], \end{aligned} \quad (3.4.62)$$

which respectively describe the distribution of density and charge in the system. In this case, system (3.3.17) breaks down into a set of two independent equations for $F_s(R)$ and $F_D(R)$. In [184, 192], an attempt was made to parametrise these functions based on the GMSA. Assuming that for $R > \sigma$:

$$c_s(R) = K_s \frac{1}{R} e^{-\alpha_s R}, \quad c_D(R) = -\beta \frac{e^2}{\epsilon R} + K_D \frac{1}{R} e^{-\alpha_D R}, \quad (3.4.63)$$

obtained an analytical solution of the Ornstein–Zernike equations with the conditions $h_s(R) = -1$, $h_D(R) = 0$ when $R < \sigma$. The constants K and α are expressed in terms of internal energy, isothermal compressibility, and contact values $F_s(\sigma+)$, $F_D(\sigma+)$. According to (3.4.54) $F_s(\sigma+)$ is expressed in terms of pressure, so that the first three quantities are considered thermodynamic and for them it is possible to use the results discussed earlier. When determining $F_D(\sigma+)$ it is possible to use the approximation (3.4.61) for the function $F_{++}(\sigma+)$ and put

$$F_D(\sigma+) = F_s(\sigma+) - F_2^0(\sigma+) \exp \left[-\beta \frac{e^2}{\varepsilon \sigma} \left(\frac{2\Gamma}{\sigma} \right)^2 \right].$$

We examined in sufficient detail the most advanced ionic system, namely a symmetric binary mixture of charged hard spheres of equal size. These results of solving the equation of the mean spherical approximation were obtained for the first time by Weisman and Lebowitz [193, 194]. Blum [195] found a solution to the equation of the mean spherical approximation in the general case of an arbitrary number of ions of different sizes and valences. The solution method proposed by him is based on a generalization of Baxter's method [146], used in the previous paragraph when solving the Perkus–Yevick equation for a mixture of hard spheres. In accordance with (3.4.28), for the Fourier forms of the direct correlation functions, it is possible to put $c_{ab}(k) = c_{ab}^0(k) -$

$-\frac{4\pi}{\varepsilon} \beta \frac{e^2 z_1 z_b}{k^2 + \alpha^2}$, where $\alpha \rightarrow 0$; $c_{ab}^0(R) = 0$ for $R > \sigma_{ab}$. The matrix $1 - c(k)$, appearing in (3.3.71) can be presented in the form (3.3.75), but at the same time $q_{ab}(R) \neq 0$ when $R > \sigma_{ab}$, so that the expression (3.3.76) for $Q_{ab}(k)$ will

contain an additional term $2\pi \sqrt{\rho_a \rho_b} q_{ab}(\sigma_{ab}) \int_{\sigma_{ab}}^{\infty} \exp(ikR - \alpha R) dR$ ($\alpha \rightarrow 0$). As

a result for the functions $I_{ab}(R)$ and $S_{ab}(R)$, determined according to (3.3.73), (3.3.74), we arrive at the set of equations (3.3.80), (3.3.77), in which, however, the integration is now carried out within the limits $\lambda_{ac} < t < \infty$. Since for $R < \sigma_{ab}$ $h_{ab}(R) = -1$, it immediately follows from the equation for $I_{ab}(R)$ that in the region $\lambda < R < \sigma$ $q_{ab}(R)$, as in the case of hard spheres, is quadratic polynomial R , the coefficients of which are found from the equation for $I_{ab}(R)$ and the conditions of continuity and symmetry of the functions $q_{ab}(R)$ at the point $R = \sigma_{ab}$. As in the symmetric case, all thermodynamic and structural properties are determined by the screening radius 2Γ , which is found from the equation

$$4\Gamma^2 = \frac{4\pi\beta e^2}{\varepsilon} \sum_a \rho_a X_a^2, \quad (3.4.64)$$

where

$$X_a = \left(z_a - \frac{\pi}{2} \frac{\sigma_{aa}^2}{1 - \eta} P_M \right) (1 + \Gamma \sigma_{aa})^{-1};$$

$$P_M = \frac{\sum_a \rho_a \sigma_{aa} z_a (1 + \Gamma \sigma_{aa})^{-1}}{1 + \frac{\pi}{2} (1 - \eta)^{-1} \sum_a \rho_a \sigma_{aa}^3 (1 + \Gamma \sigma_{aa})^{-1}};$$

$$\eta = \frac{1}{6} \pi \sum_a \rho \sigma_{aa}^3; \quad \rho_a = \frac{N_a}{V}.$$

It is clear that in the case of a symmetric system of the same size, the solution (3.4.64) coincides with the expression (3.4.46).

Based on the solution found in [149, 196], equations for the screened potentials and thermodynamic functions were obtained in the ORPA approximation. In particular, a simple expression is derived for the contact value of the screened potentials

$$g_{ab}(\sigma_{ab}+) = -\beta \frac{e^2 X_a X_b}{\varepsilon \sigma_{ab}}. \quad (3.4.65)$$

For internal energy

$$\begin{aligned} \frac{E - E_{\text{id}}}{V k_B T} = & -\beta \frac{e^2}{\varepsilon} \left[\Gamma \sum_a \rho_a z_a^2 (1 + \Gamma \sigma_{aa})^{-1} + \right. \\ & \left. + \frac{\pi}{2} \frac{P_M^2}{1 - \eta} \left(1 + \frac{\pi}{2} \frac{1}{1 - \eta} \sum_a \frac{\sigma_a^3}{1 + \Gamma \sigma_{aa}} \right) \right], \end{aligned} \quad (3.4.66)$$

from which follows the expression for the free energy

$$\frac{F_{\text{ORPA}}}{N k_B T} = \frac{E - E_{\text{id}}}{N k_B T} + \frac{\Gamma^3}{3\pi\rho}, \quad (3.4.67)$$

which in form coincides with (3.4.58).

Expression (3.4.66) consists of two terms. The first of them corresponds to (3.4.56), the second depends on the difference in the sizes of the ions and disappears if all the ions have the same size ($P_M = 0$ according to (3.4.1)). Ions of different sizes have different screening capabilities, and large ions have a lower capability than small ones, since their sizes do not allow them to approach the central ion. In [197], the limiting case of a binary mixture of charged hard spheres and point ions was considered. It should be noted that in this case, for pair distribution functions, one must proceed from the exponential form, since, for example, the approximate ORPA leads to a negative value of the pair distribution function of point ions in the region of small distances. The very large contact values $F_{+-}(1/2\sigma+)$ obtained in this work using the MC simulation and the absence of clear ordering for point ions indicate the formation of polymer-like ionic chains in the system with a coordination number close to two. Similar polymerization by means of hydrogen bonding is observed, for example, in hydrogen fluoride.

In this chapter, the previously developed methods are applied to the description of polyatomic molecular systems. First, a general description scheme is considered. In this context, the method of collective variables is generalized, and the properties of model systems with purely repulsive interactions are studied, which, as in the monoatomic case, play a fundamental role in describing real molecular systems. Then, the obtained results are applied to the description of molecular systems with electrostatic interactions and mixed ion-molecular systems.

4.1. Systems with non-central interactions

Each polyatomic molecule possesses $3X_a$ degrees of freedom, where X_a is the number of atoms in a molecule of type a . Of these degrees of freedom, the first three are translational, another three (for non-linear molecules) or two (for linear molecules) are rotational, and the remaining ones are typically classified as internal (vibrational or internal rotational) degrees of freedom. The presence of rotational and internal degrees of freedom is a significant distinguishing feature of molecular systems compared to the previously considered monoatomic systems.

4.1.1. General relations for molecular systems

The position of a molecule, in addition to the usual specification of the centre of mass, is also characterized by coordinates corresponding to the remaining degrees of freedom. For rotational degrees of freedom, this is a set of angles Ω , which describe the orientation of the molecule in space. In the case of a linear molecule, these are two angles $\Omega = (\vartheta, \varphi)$ which characterize the orientation of the molecular axis. For a non-linear molecule, three Euler angles $\Omega = (\alpha, \beta, \gamma)$ are used, defining the mutual orientation of two Cartesian coordinate systems with a common origin. In this case, one of them is associated with the molecule fixed in it, and the second is fixed in space (see, for example, [35, 198]).

At the core of the statistical description of molecular systems, both molecular and monoatomic, there lies computation of the configuration integral

$$Q_N = \frac{1}{V^N} \int e^{-\beta U_N} (d\Gamma) \quad (4.1.1)$$

and the distribution function

$$F_n(\Gamma_1, \dots, \Gamma_n) = \frac{1}{Q_N V^{N-n}} \int e^{-\beta U_N} d\Gamma_{n+1} \dots d\Gamma_N, \quad (4.1.2)$$

where U_N is the total potential energy of the system, which will subsequently be equal to $\sum_{a,b} \sum_{i < j} u_{ab}(\Gamma_i, \Gamma_j)$; $u_{ab}(\Gamma_i, \Gamma_j)$ is the interaction potential of two

molecules; $(d\Gamma) \equiv \prod_a \prod_i d\Gamma_i$; $d\Gamma_i = d\mathbf{R}_i d\Xi_i$; $d\Xi_i$ is the element of the configuration space of rotational and internal degrees of freedom of the i -th molecule, normalised to unity. When considering only translational and rotational degrees of freedom, $d\Omega_i = \frac{1}{4\pi} \sin \vartheta_i d\vartheta_i d\varphi_i$ for linear molecules, and $d\Omega_i = \frac{1}{8\pi^2} \sin \beta_i d\alpha_i d\beta_i d\gamma_i$ for non-linear molecules.

The presence of new variables in (4.1.2) compared to (1.1.26) expands the concept of distribution functions. The latter now acquires the meaning of the probability density of placing complexes of n particles with a fixed configuration. For a molecular system, similar relations to (1.1.27), (1.1.28) also hold, but in the latter, the element $d\mathbf{R}$ needs to be replaced by $d\Gamma$. By differentiating the Gibbs function with respect to orientation or another coordinate of a single particle, a new system of integro-differential equations between distribution functions can be obtained [15]. To describe molecular systems, it is also possible to introduce distribution functions only in the coordinate space

$$F_n(\mathbf{R}_1, \dots, \mathbf{R}_n) = \int d\Xi_1 \dots d\Xi_n F_n(\Gamma_1, \dots, \Gamma_n) \quad (4.1.3)$$

or only in the space of orientational and internal coordinates

$$F_n(\Xi_1, \dots, \Xi_n) = \frac{1}{V^n} \int d\mathbf{R}_1 \dots d\mathbf{R}_n F_n(\Gamma_1, \dots, \Gamma_n). \quad (4.1.4)$$

For molecular systems, the relations (3.3.6)–(3.3.10) are also easily generalized, linking pair distribution functions to the thermodynamic properties of the system

$$E - E_{\text{id}} = \frac{1}{2} \sum_{a,b} \frac{N_a N_b}{V^2} \int F_{ab}(\Gamma_1, \Gamma_2) u_{ab}(\Gamma_1, \Gamma_2) d\Gamma_1 d\Gamma_2, \quad (4.1.5)$$

$$P - P_{\text{id}} = -\frac{1}{6} \sum_{a,b} \frac{N_a N_b}{V^3} \int F_{ab}(\Gamma_1, \Gamma_2) \frac{\partial u_{ab}(\Gamma_1, \Gamma_2)}{\partial R_{12}} R_{12} d\Gamma_1 d\Gamma_2, \quad (4.1.6)$$

$$\frac{1}{\beta} \left(\frac{\partial N_a}{\partial \mu_b} \right)_{T,V,\mu_a,\dots} = N_a \delta_{ab} + \frac{N_a N_b}{V^2} \int [F_{ab}(\Gamma_1, \Gamma_2) - 1] d\Gamma_1 d\Gamma_2, \quad (4.1.7)$$

$$Q_N = \exp \left\{ \beta \sum_{a,b} \frac{N_a N_b}{2V^2} \int_0^1 d\xi \int u_{ab}(\Gamma_1, \Gamma_2) F_{ab}(\Gamma_1, \Gamma_2 \xi) d\Gamma_1 d\Gamma_2 \right\}, \quad (4.1.8)$$

$$F_{ab}(\Gamma_1, \Gamma_2) = -V^2 \frac{1}{\beta} \frac{\delta \ln Q_N}{\delta u_{ab}(\Gamma_1, \Gamma_2)}.$$

The description of molecular systems can be reduced to a certain hypothetical monoatomic system with effective interactions. For this purpose, the Gibbs distribution function must be averaged over orientational and internal coordinates. This procedure is analogous to the one considered in the previous chapter on the osmotic theory of solutions and also leads to effective many-particle interactions. The role of the latter increases as the contribution of orientational and internal degrees of freedom grows, which significantly limits the possibility of a monoatomic description. Therefore, let us now proceed with generalization of the previously described methods to molecular systems.

The generalization of Mayer's virial expansions follows naturally with a simple reinterpretation of diagrammatic notation. Each line corresponds to Mayer's function $f_{ab}(\Gamma_i, \Gamma_j) = e^{-\beta u_{ab}(\Gamma_i, \Gamma_j)} - 1$, and each field vertex represents the operator $\sum_a N_a/V \int d\Gamma$. Partial summation of diagrams leads to the generalization of the previously considered integral equations. In particular, for the Ornstein–Zernike equation, we obtain

$$h_{ab}(\Gamma_1, \Gamma_2) = c_{ab}(\Gamma_1, \Gamma_2) + \sum_c \frac{N_c}{V} \int d\Gamma_3 c_{ac}(\Gamma_1, \Gamma_3) h_{cb}(\Gamma_3, \Gamma_2), \quad (4.1.9)$$

where $h_{ab}(\Gamma_1, \Gamma_2) = F_{ab}(\Gamma_1, \Gamma_2) - 1$ is the pair correlation function of two molecules of types a and b , while $c_{ab}(\Gamma_1, \Gamma_2)$ is the corresponding direct correlation function.

4.1.2. Systems with non-central interaction. Expansion in spherical functions

For many molecular systems, intramolecular interactions are much stronger than intermolecular interactions, so molecules can be considered sufficiently rigid, neglecting internal degrees of freedom. Such molecules possess only rotational and translational degrees of freedom. For simplicity, we consider one-component systems in the following discussion.

Due to the noncentral nature of intermolecular interactions, the potential $u_2(R, \Omega_1, \Omega_2)$ depends both on the relative position of the molecules R and on their mutual orientations Ω_1, Ω_2 . The latter are defined relative to the axis coinciding with the centre of intermolecular interactions. However, since in (4.1.1) and (4.1.2), differentiation is performed independently of the orientations of the molecules and their axes¹, when constructing the statistical description, it is often necessary to separate these orientations. This problem can generally be solved by expanding the orientation-dependent functions in a series of generalized spherical functions $D_{\mu\nu}^l(\Omega)$. These are the eigenfunctions of the rotation operator, and their properties are well known (see, for example, [35, 198, 199]). Let us briefly review some of these properties, which will be needed later.

The function $D_{\mu\nu}^l(\Omega)$ is represented as the product of three factors, each of which depends only on one of the Euler angles

$$D_{\mu\nu}^l(\Omega) = e^{l\mu\alpha} d_{\mu\nu}^l(\beta) e^{i\nu\gamma}, \quad (4.1.10)$$

where $d_{\mu\nu}^l(\beta)$ is a real function expressed in terms of Jacobi polynomials with the argument $\cos \beta$; the index l takes all non-negative integer values; μ, ν vary within the range from $-l$ to $+l$. If at least one of the indices μ, ν is zero, then $D_{\mu\nu}^l(\Omega)$ reduces to the standard spherical functions $Y_{l\mu}(\Omega)$

$$\begin{aligned} D_{\mu 0}^l(\alpha, \beta, 0) &= \sqrt{\frac{4\pi}{(2l+1)}} Y_{l\mu}(\beta, \alpha), \\ D_{0\nu}^l(0, \beta, \gamma) &= (-1)^\nu \sqrt{\frac{4\pi}{(2l+1)}} Y_{l\nu}(\beta, \gamma), \\ D_{00}^l(0, \beta, 0) &= P_l(\cos \beta), \end{aligned} \quad (4.1.11)$$

where $P_l(\cos \beta)$ is the Legendre polynomial.

At fixed l , the functions $D_{\mu\nu}^l(\Omega)$ form a $(2l+1)$ -dimensional unitary matrix

$$D_{\mu\nu}^l(\Omega) = (-1)^{\nu-\mu} D_{-\mu, -\nu}^{*l}(\Omega); \quad \sum_{\mu} D_{\mu\nu}^{*l}(\Omega) D_{\mu\nu'}^l(\Omega) = \frac{\delta_{\nu\nu'}}{2l+1}. \quad (4.1.12)$$

The functions $D_{\mu\nu}^l(\Omega)$ are orthogonal to each other:

$$\int D_{\mu\nu}^l(\Omega) D_{\mu'\nu'}^{*l}(\Omega) d\Omega = \frac{\delta_{\mu\mu'} \delta_{\nu\nu'}}{(2l+1)}, \quad (4.1.13)$$

with $\int d\Omega = \frac{1}{8\pi^2} \int_0^\pi \sin \beta d\beta \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma$.

¹In the spherical coordinate system $d\mathbf{R} = 4\pi R^2 dR d\Omega_{\mathbf{R}}$, where $\Omega_{\mathbf{R}}$ is the orientation of the vector $\mathbf{R}$.

For the sum of two successive rotations, $\Omega = \Omega_1 + \Omega_2$, we have the following addition formula:

$$D_{\mu\nu}^l(\Omega) = \sum_{\nu'=-l}^l D_{\mu\nu'}^l(\Omega_1) D_{\nu'\nu}^l(\Omega_2). \quad (4.1.14)$$

which, in the case of $\mu = \nu = 0$ reduces to the standard addition formula for spherical functions

$$P_l(\cos \vartheta) = \frac{4\pi}{2l+1} \sum_{\nu} Y_{l\nu}(\vartheta_1 \varphi_1) Y_{l\nu}^*(\vartheta_2 \varphi_2). \quad (4.1.15)$$

with $\cos \vartheta = \cos \vartheta_1 \cos \vartheta_2 + \sin \vartheta_1 \sin \vartheta_2 \cos(\varphi_1 - \varphi_2)$.

The product of two spherical functions $D_{\mu\nu}^l(\Omega)$ with the same arguments is expressed as a linear combination

$$D_{\mu_1\nu_1}^{l_1}(\Omega) D_{\mu_2\nu_2}^{l_2}(\Omega) = \sum_{l=|l_2-l_1|}^{l_1+l_2} \begin{pmatrix} l_1 & l_2 & l \\ \mu_1 & \mu_2 & \mu \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ \nu_1 & \nu_2 & \nu \end{pmatrix} D_{\mu\nu}^{*l}(\Omega) \quad (4.1.16)$$

and vice versa

$$D_{\mu\nu}^l(\Omega) = (2l+1) \sum_{\mu_1, \nu_1} \begin{pmatrix} l_1 & l_2 & l \\ \mu_1 & \mu_2 & \mu \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ \nu_1 & \nu_2 & \nu \end{pmatrix} D_{\mu_1\nu_1}^{l_1}(\Omega) D_{\mu_2\nu_2}^{l_2}(\Omega), \quad (4.1.17)$$

where $\begin{pmatrix} l_1 & l_2 & l \\ \mu_1 & \mu_2 & \mu \end{pmatrix}$ are the so-called Clebsch–Gordan coefficients or Wigner’s $3j$ -symbols. They are nonzero only if the conditions $\mu_1 + \mu_2 + \mu = 0$ and $|l_2 - l_1| \leq l \leq l_1 + l_2$ are satisfied. The latter inequality is often referred to as the triangle relation and is denoted as $\Delta(l_1 l_2 l)$. The $3j$ -symbols satisfy orthogonality conditions

$$\begin{aligned} \sum_{\mu_1, \mu_2} \begin{pmatrix} l_1 & l_2 & l_3 \\ \mu_1 & \mu_2 & \mu_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ \mu_1 & \mu_2 & \mu \end{pmatrix} &= \frac{\delta_{l_3 l} \delta_{\mu_3 \mu}}{2l+1}, \\ \sum_{l, \mu} (2l+1) \begin{pmatrix} l_1 & l_2 & l \\ \mu_1 & \mu_2 & \mu \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ \mu'_1 & \mu'_2 & \mu \end{pmatrix} &= \delta_{\mu_1 \mu'_1} \delta_{\mu_2 \mu'_2}. \end{aligned} \quad (4.1.18)$$

More detailed information on the functions $D_{\mu\nu}^l(\Omega)$ and $3j$ -symbols can be found in the specialized literature [198].

The set of functions $D_{\mu\nu}^l(\Omega)$ forms a complete system of functions, permitting any function $\Phi(R, \Omega_1, \Omega_2)$ integrable over the domain of variation of Ω_1 and Ω_2 to be represented as a series

$$\Phi(R, \Omega_1, \Omega_2) = \sum_{l_1 l_2 \mu_1 \mu_2 \nu_1 \nu_2} \Phi_{\mu_1 \mu_2 \nu_1 \nu_2}^{l_1 l_2}(R) D_{\mu_1 \nu_1}^{l_1}(\Omega_1) D_{\mu_2 \nu_2}^{l_2}(\Omega_2) \quad (4.1.19)$$

with coefficients

$$\begin{aligned} \Phi_{\mu_1\mu_2\nu_1\nu_2}^{l_1l_2}(R) &= (2l_1 + 1)(2l_2 + 1) \int \Phi(R, \Omega_1, \Omega_2) \times \\ &\times D_{\mu_1\nu_1}^{*l_1}(\Omega_1) D_{\mu_2\nu_2}^{*l_2}(\Omega_2) d\Omega_1 d\Omega_2. \end{aligned}$$

This approach to describing systems with non-central interactions was proposed by Steele [200]. The orientations Ω_1 and Ω_2 in (4.1.19) are defined relative to the axis $\mathbf{R}$ connecting the centres of mass of the two considered molecules. By employing the addition formulas (4.1.14), one can transform to independent orientations and thereby separate the orientations of the particles from the orientations of their axes. In the work of Jepsen and Friedman [201], the expansion

$$\begin{aligned} \Phi(R, \Omega_1, \Omega_2) &= \sum_{m,n,l=0}^{\infty} \sum_{\substack{|\mu,\mu'|\leq m \\ |\nu,\nu'|\leq n,\lambda\leq l}} \Phi_{\mu\mu'\nu\nu'\lambda}^{mnl}(R) \times \\ &\times D_{\mu\mu'}^m(\Omega_1) D_{\nu\nu'}^n(\Omega_2) D_{\lambda 0}^l(\Omega_R), \end{aligned} \quad (4.1.20)$$

was used, in which the orientations Ω_1 and Ω_2 are separated from the orientation of Ω_R . Depending on the symmetry of the system under consideration, not all the terms in the expansion (4.1.20) may be equally important. Blum and Torruella [202] noted that in the spatially homogeneous case, the function $\Phi(R_{12}, \Omega_1, \Omega_2)$ satisfies the following symmetry conditions: 1) translational invariance; 2) rotational invariance; 3) invariance under the permutation of two identical molecules; 4) invariance with respect to the symmetry group of individual molecules. The complete group of all possible symmetry transformations is given by the direct product of the above subgroups. According to group theory [203], the projection operator for a fully invariant representation is

$$\hat{P}_h = \frac{1}{h} \sum_s \hat{Q}_s, \quad (4.1.21)$$

where h is the number of subgroup elements, and summation is carried out over all symmetry operations $\hat{Q}_s$ of this subgroup. Let us consider the primary conditions imposed on the expansion coefficients in (4.1.20) by the listed types of symmetry.

1. Translational invariance implies that the function $\Phi(R_{12}, \Omega_1, \Omega_2)$ depends only on the difference $R_{12} = |\mathbf{R}_2 - \mathbf{R}_1|$, which was used in writing the expansion (4.1.20).

2. Rotational invariance means that in the absence of orientational ordering in the system, the function $\Phi(R_{12}, \Omega_1, \Omega_2)$ is a true scalar and depends only on the relative orientations of the two molecules Ω_{12} and $\Omega_{\mathbf{R}_{12}}$. In this case,

$\hat{O}_s$ is the rotation operator. Applying the projection operator $\hat{P}_h$ to (4.1.20), and using (4.1.14), we obtain²

$$\begin{aligned} \Phi(R_{12}, \Omega_1, \Omega_2) &= \sum_{m,n,l} \sum_{\mu\mu'\nu\nu'\lambda} \Phi_{\mu\mu'\nu\nu'\lambda}^{mnl}(R_{12}) \times \\ &\times \sum_{\mu''\nu''\lambda''} \int d\Omega D_{\mu\mu'}^m(\Omega) D_{\nu\nu'}^n(\Omega) D_{\lambda\lambda'}^l(\Omega) D_{\mu''\mu''}^m(\Omega_1) \times \\ &\times D_{\nu''\nu''}^n(\Omega_2) D_{\lambda''0}^l(\Omega_R) \end{aligned}$$

According to (4.1.17) and (4.1.13),

$$\int d\Omega D_{\mu\mu''}^m(\Omega) D_{\nu\nu''}^n(\Omega) D_{\lambda\lambda''}^l(\Omega) = \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} \begin{pmatrix} m & n & l \\ \mu'' & \nu'' & \lambda'' \end{pmatrix}. \quad (4.1.22)$$

This allows us to express (4.1.20) in an invariant form as

$$\Phi(R_{12}, \Omega_1 \Omega_2) = \sum_{mnl} \sum_{\mu'\nu'} \Phi_{\mu'\nu'}^{mnl}(R_{12}) \Psi_{\mu'\nu'}^{mnl}(\Omega_1 \Omega_2 \Omega_{R_{12}}), \quad (4.1.23)$$

where

$$\begin{aligned} \Phi_{\mu'\nu'}^{mnl}(R_{12}) &= \sum_{\mu\nu\lambda} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} \varphi_{\mu\mu'\nu\nu'\lambda}^{mnl}(R_{12}), \\ \Psi_{\mu'\nu'}^{mnl}(\Omega_1, \Omega_2, \Omega_{R_{12}}) &= \sum_{\mu\nu\lambda} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} D_{\nu\mu'}^m(\Omega_1) D_{\nu\nu'}^n(\Omega_2) D_{\lambda 0}^l(\Omega_{R_{12}}) \end{aligned} \quad (4.1.24)$$

are rotationally invariant.

It is easy to verify the invariance of this expression by changing the orientation reference frame using (4.1.14):

$$\begin{aligned} \Phi(R_{12}, \Omega_1, \Omega_2) &= \sum_{mnl} \sum_{\mu'\nu'} \Phi_{\mu'\nu'}^{mnl}(R_{12}) \times \\ &\times \sum_{\mu\nu\lambda} \sum_{\mu''\nu''\lambda''} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} D_{\mu\mu''}^m(\Omega) D_{\nu\nu''}^n(\Omega) \times \\ &\times D_{\lambda\lambda''}^l(\Omega) D_{\mu''\mu'}^m(\Omega_1) D_{\nu''\nu'}^n(\Omega_2) D_{\lambda''0}^l(\Omega_{R_{12}}) = \\ &= \sum_{mnl\mu'\nu'} \Phi_{\mu'\nu'}^{mnl}(R) \Psi_{\mu'\nu'}^{mnl}(\Omega_1 \Omega_2 \Omega_{R_{12}}), \end{aligned}$$

since from the properties of the functions $D_{\mu\nu}^l(\Omega)$ and the $3j$ -symbols, it follows that

$$\sum_{\mu\nu\lambda} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} D_{\nu\mu''}^m(\Omega) D_{\nu\nu''}^n(\Omega) D_{\lambda\lambda''}^l(\Omega) = \begin{pmatrix} m & n & l \\ \mu'' & \nu'' & \lambda'' \end{pmatrix}. \quad (4.1.25)$$

²Since the rotation group is continuous $\frac{1}{h} \sum_s = d\Omega$.

3. Invariance under the permutation of two molecules means that $\Phi(R_{12}, \Omega_1, \Omega_2) = \Phi(R_{21}, \Omega_2, \Omega_1)$. Since $\Omega_{R_{12}} = -\Omega_{R_{21}}$ and $D_{\lambda 0}^l(-\Omega_R) = (-1)^l \times D_{\lambda 0}^l(\Omega_R)$ using the symmetry properties of $3j$ -symbols [198], we obtain

$$\Phi_{\mu'\nu'}^{mnl}(R_{12}) = (-1)^{m+n} \Phi_{\nu'\mu'}^{mnl}(R_{12}). \quad (4.1.26)$$

Furthermore, for a real function $\Phi(R_{12}, \Omega_1, \Omega_2)$, we have

$$|\Phi_{\mu'\nu'}^{mnl}(R)|^* = (-1)^{m+n+l+u+\nu} \Phi_{-u', -\nu'}^{mnl}(R). \quad (4.1.27)$$

4. Since the symmetry of a molecule reduces the number of functions $D_{\mu\nu}^l(\Omega)$ needed to define its orientation, the number of terms in expansion (4.1.23) also decreases. To illustrate this, consider some molecular tensor $\mathbf{T}$. Its polar components $T_\nu^n(\Omega)$, defined in a fixed coordinate system, are related to the components $T_\nu^n(0)$ defined relative to the fixed molecular axis, by the relation

$$T_\nu^n(\Omega) = \sum_{\nu'} D_{\nu\nu'}^{nl}(\Omega) T_{\nu'}^n(0). \quad (4.1.28)$$

The action of a symmetry operator $\hat{S}$ of a molecule does not change the tensor components, so that $T_\nu^n(0) = \hat{S} T_\nu^n(0)$ or according to (4.1.28)

$$T_\nu^n(\Omega) = \sum_{\nu'} D_{\nu\nu'}^n(\Omega) \left[\hat{S} T_{\nu'}^n(0) \right] = \sum_{\nu'} \left[D_{\nu\nu'}^n(\Omega) \hat{S}^{-1} \right] T_{\nu'}^n(0), \quad (4.1.29)$$

and thus reduces to the action on generalized spherical functions.

Molecular symmetry groups are discrete and can be obtained by various combinations of rotation $\hat{\mathfrak{R}}$ and inversion $\hat{I}$ operations [200, 202]

$$\begin{aligned} D_{\lambda\lambda'}^l(\Omega) \hat{\mathfrak{R}} &= \sum_{\lambda''} D_{\lambda\lambda''}^l(\Omega) D_{\lambda''\lambda'}^l(D_{\hat{\mathfrak{R}}}) \\ D_{\lambda\lambda'}^l(\Omega) \hat{I} &= \sum_{\lambda''} D_{\lambda\lambda''}^l(\Omega) (-1)^l \delta_{\lambda'\lambda''}. \end{aligned} \quad (4.1.30)$$

All molecular symmetry operations are combinations of various elements of point groups. The identity transformation operator $\hat{E}^1$ is the simplest. Next come rotation and reflection elements. Suppose a molecule has a symmetry axis of order h . The rotation operation about this axis, usually denoted as $\hat{C}_h$, leads to the following condition for the components of the tensor $\mathbf{T}$:

$$\frac{1}{h} \sum_{s=0}^{h-1} \exp\left(2\pi i \frac{s\mu}{h}\right) T_\mu^m = \begin{cases} T_\mu^m, & \mu = kh, k = 0, 1, 2, \dots, \\ 0, & \mu \neq kh. \end{cases}$$

Therefore, when the operation $\hat{C}_h$ is present, only terms with μ and ν that are multiples of h appear in the expansion (4.1.23). In particular, for linear molecules, $\mu = \nu = 0$.

Table 8. Exact relationships for the coefficients of the invariant expansion (4.1.23) for some simple molecular systems

Symmetry group	Example molecules	Conditions for indices and components $\Phi_{\mu\nu}^{mnl}(R)$
C_{2v}	H ₂ O, SO ₂	μ, ν even; $\Phi_{\mu\nu}^{mnl}(R) = \Phi_{\pm\mu\pm\nu}^{mnl}(R)$
C_{3v}	NH ₃ , CH ₃ Cl	μ, ν multiples of 3; $\Phi_{\mu\nu}^{mnl}(R) = (-1)^{\mu+\nu} \Phi_{-\nu-\mu}^{mnl}(R)$
C_{2h}	trans-C ₂ H ₂ Cl ₂	m, μ even
D_{3d}	C ₂ H ₆	μ multiple of 3, m even; $\Phi_{\mu\nu}^{mnl}(R) = (-1)^m \Phi_{\mu\nu}^{mnl}(R)$
D_{6h}	C ₆ H ₆	m even, μ multiple of 6; $\Phi_{\mu\nu}^{mnl}(R) = \Phi_{-\mu\nu}^{mnl}(R)$
$C_{\infty v}$	HCl, CO	$\mu = \nu = 0$
$D_{\infty v}$	H ₂ , CO ₂	$\mu = \nu = 0; m, n, l$ even

Next, consider a double rotation about an axis perpendicular to the z -axis, forming an angle φ with the x -axis. The representation of this symmetry element is $\hat{O}(C_2^\varphi) = (-1)^m e^{2\mu\varphi i} \delta_{\mu,-\mu'}$. For $\varphi = 0$, we arrive at conditions for the coefficients

$$\begin{aligned} \Phi_{\mu\nu}^{mnl}(R) &= (-1)^m \Phi_{-\mu,\nu}^{mnl}(R) = (-1)^n \Phi_{\mu,-\nu}^{mnl}(R) = \\ &= (-1)^{m+n} \Phi_{-\mu,-\nu}^{mnl}(R). \end{aligned}$$

Consider the reflection operation $\hat{\sigma}_{zx}$ with respect to the zx -plane of a molecule. It can be represented as a rotation by an angle π around the y -axis followed by an inversion. In this case $\hat{O}(\sigma_{zx}) = (-1)^\mu \delta_{\mu,-\mu'}$. Similarly, for a plane forming an angle φ with the zx -plane $\hat{O}(\sigma_\varphi) = (-1)^\mu e^{2\mu\varphi i} \delta_{\mu,-\mu'}$ and for the horizontal plane $\hat{O}(\sigma_{xy}) = (-1)^{m+\mu} \delta_{\mu\mu'}$. The consideration of representations for elements of higher symmetry is more complex and is beyond the scope of this discussion. More detailed coverage of these topics can be found in specialized literature.

The projection operator $\hat{P}_s$ for each molecule can be represented as a sum of simple elements. For example, for a water molecule with C_{2v} symmetry, $\hat{P}_s = \frac{1}{4} [\hat{E} + \hat{C}_2 + \hat{\sigma}_{zx} + \hat{\sigma}_{zy}]$. For illustration, Table 8, compiled based on [202], presents exact relations for some simple molecules derived from their symmetry.

Using the invariant expression (4.1.23) for the pair distribution function and interaction potential, the relations (4.1.5)–(4.1.7) in the one-sort case can be represented as:

$$\begin{aligned} E - E_{\text{id}} &= 2\pi\rho^2 \sum_{\substack{mnl, \\ \mu\nu}} \int_0^\infty R^2 dR F_{\mu\nu}^{mnl}(R) [u_{\mu\nu}^{mnl}(R)]^* \frac{1}{(2m+1)(2n+1)(2l+1)}, \\ P - P_{\text{id}} &= -\frac{2}{3}\pi\rho^2 \sum_{\substack{mnl, \\ \mu\nu}} \int_0^\infty R^3 dR F_{\mu\nu}^{mnl}(R) \left[\frac{\partial u_{\mu\nu}^{mnl}(R)}{\partial R} \right]^* \times \end{aligned}$$

$$\times \frac{1}{(2m+1)(2n+1)(2l+1)},$$

$$\frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right)_T = 1 + 4\pi\rho \int_0^\infty [F_{00}^{000}(R) - 1] R^2 dR, \quad (4.1.31)$$

where $F_{\mu\nu}^{mnl}(R)$ and $u_{\mu\nu}^{mnl}(R)$ are components in the expansion (4.1.23) for the pair distribution function and interaction potential, respectively; $\rho = N/V$.

4.1.3. Extension of the collective variables method

A system with non-central interactions, in addition to fluctuations in particle number density, is also characterized by fluctuations in their orientations. Suppose the interaction in the system has a pairwise-additive nature with an intermolecular interaction potential

$$u_2(R_{12}, \Omega_1 \Omega_2) = \varphi_2(R_{12}, \Omega_1 \Omega_2) + \Phi_2(R_{12}, \Omega_1 \Omega_2), \quad (4.1.32)$$

where $\varphi_2(R_{12}, \Omega_1 \Omega_2)$ is the short-range part of the potential; $\Phi_2(R_{12}, \Omega_1 \Omega_2)$ is the long-range part.

Expand the function $\Phi_2(R_{12}, \Omega_1 \Omega_2)$ into a Fourier series. To do this, we present it in the form (4.1.23) and use the relation

$$\begin{aligned} e^{i\mathbf{k}\mathbf{R}} &= \sum_{l=0}^{\infty} (2l+1) i^l j_l(kR) P_l(\cos \widehat{\mathbf{k}\mathbf{R}}) = \\ &= \sum_{l \geq 0} (2l+1) i^l j_l(kR) \sum_{\lambda=-l}^l D_{\lambda 0}^l(\Omega_{\mathbf{k}}) D_{\lambda 0}^{*l}(\Omega_{\mathbf{R}}), \end{aligned} \quad (4.1.33)$$

where $j_l(\mathbf{k}\mathbf{R})$ is the spherical Bessel function of order l ; $\widehat{\mathbf{k}\mathbf{R}}$ is the angle between the vectors $\mathbf{k}$ and $\mathbf{R}$; $\Omega_{\mathbf{k}}$ is the orientation of the vector $\mathbf{k}$ in a fixed reference frame. As a result, we obtain

$$\Phi_2(R, \Omega_1 \Omega_2) = \frac{1}{V} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}} \sum_{\substack{mnl, \\ \mu\nu}} \Phi_{\mu\nu}^{mnl}(k) \Psi_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_{\mathbf{k}}), \quad (4.1.34)$$

where $\Phi_{\mu\nu}^{mnl}(k) = 4\pi i^l \int_0^\infty R^2 dR j_l(kR) \Phi_{\mu\nu}^{mnl}(R)$; $\Phi_{\mu\nu}^{mnl}(R)$ are the components

in the expansion (4.1.23) for $\Phi_2(R, \Omega_1 \Omega_2)$; $\Psi_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_{\mathbf{k}})$ is determined by expression (4.1.24) with $\Omega_{\mathbf{R}}$ replaced by $\Omega_{\mathbf{k}}$.

Using the relation

$$\sum_{\lambda} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} D_{\lambda 0}^l(\Omega_{\mathbf{k}}) = \sum_{\lambda} \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} D_{\lambda \mu}^m(\Omega_{\mathbf{k}}) D_{\lambda \nu}^{*n}(\Omega_{\mathbf{k}}), \quad (4.1.35)$$

which follows from (4.1.17) and the orthogonality properties of the $3j$ -symbols, the long-range part of the potential energy of the system can be represented as

$$v(R, \Omega) = \sum_{i < j} \Phi_2(R_{ij}, \Omega_i, \Omega_j) = \frac{1}{2\beta} \sum_k' \left[\sum_{\substack{mnl \\ \mu\nu\lambda}} \alpha(k, mnl\mu\nu\lambda) \times \right. \\ \left. \times \hat{\rho}_{\mu\nu}^m(k) \hat{\rho}_{\nu\lambda}^{*n}(k) - \gamma(k) \right] + \sum_{i < j} \frac{1}{V} \int \Phi_2(R_{ij}, \Omega_i, \Omega_j) d\mathbf{R}_{ij}, \quad (4.1.36)$$

where

$$\hat{\rho}_{\mu\lambda}^m(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{j=1}^N \sum_{\mu'=-m}^m D_{\mu\mu'}^m(\Omega_j) D_{\mu'\lambda}^m(\Omega_{\mathbf{k}}) e^{i\mathbf{k}\mathbf{R}_j}, \quad \mathbf{k} \neq 0, \quad (4.1.37)$$

$$\alpha(k, mnl\mu\nu\lambda) = \beta \frac{N}{V} \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} \Phi_{\mu\nu}^{mnl}(k);$$

$$\gamma(k) = \sum_{\substack{mnl \\ \mu\nu\lambda}} \alpha(k, mnl\mu\nu\lambda) \frac{1}{N} \sum_j \sum_{\mu'\nu'} D_{\mu\mu'}^m(\Omega_j) D_{\nu\nu'}^n(\Omega_j) \times \\ \times D_{\mu'\lambda}^m(\Omega_{\mathbf{k}}) D_{\nu'\lambda}^n(\Omega_{\mathbf{k}}) = \sum_{\substack{mnl \\ \mu\nu\lambda}} \alpha(k, mnl\mu\nu\lambda) \frac{\delta_{mn}\delta_{\mu\nu}}{(2m+1)}, \quad (4.1.38)$$

according to (4.1.14) and the definition of $\Phi_{\mu\nu}^{mnl}(k)$.

The last term in (4.1.36) corresponds to $k = 0$ and can be represented as a series:

$$\int \Phi_2(R, \Omega_i, \Omega_j) d\mathbf{R} = \sum_{l \geq 0} a_l P_l(\cos \vartheta_{ij}), \quad (4.1.39)$$

where ϑ_{ij} is the angle between the axes of the two molecules; $P_l(\cos \vartheta)$ is the Legendre polynomial;

$$a_l = \int \Phi_2(R, \Omega_i, \Omega_j) P_l(\cos \vartheta_{ij}) d\mathbf{R} d\Omega_i d\Omega_j.$$

The consideration of term (4.1.39) may generally lead to molecular orientational ordering since, for orientationally disordered systems, due to rotational invariance, $a_l = 0$ for $l \neq 0$.

Summarizing the arguments presented in Chapter 2, we represent $v(R, \Omega)$ in the form of an analytical functional

$$v(R, \Omega) = \int v(\rho) J(\rho, R\Omega) (d\rho), \quad (4.1.40)$$

where

$$v(\rho) = \frac{1}{2\beta} \sum_{\mathbf{k}}' \sum_{\substack{mnl \\ \mu\nu\lambda}} \alpha(k, mnl\mu\nu\lambda) \left[\rho_{\mu\lambda}^m(\mathbf{k}) (\rho_{\nu\lambda}^n(\mathbf{k}))^* - \frac{\delta_{mn}\delta_{\mu\nu}}{2m+1} \right] +$$

$$+ \frac{N}{2\beta} \alpha (k = 0, m = n = l = 0)$$

represents the collective variables for the functions $v(R, \Omega)$; $J(\rho, R\Omega) = \prod'_{\mathbf{k}} \prod_{m, \mu\lambda} \delta(\rho_{\mu\lambda}^m(\mathbf{k}) - \hat{\rho}_{\mu\lambda}^m(\mathbf{k}))$ is the transformation function to collective variables; $(d\rho) = \prod'_{\mathbf{k}} \prod_{m, \mu\lambda} d\rho_{\mu\lambda}^m(\mathbf{k})$. Using the representation of collective variables for the configuration integral (4.1.1), we obtain

$$Q_N = \frac{1}{V^N} \int (d\mathbf{R}) (d\Omega) (d\rho) J(\rho, R\Omega) e^{-\beta U_0(R\Omega)} e^{-\beta v(\rho)}, \quad (4.1.41)$$

where

$$(d\mathbf{R}) = \prod_{i=1}^N d\mathbf{R}_i, \quad (d\Omega) = \prod_{i=1}^N d\Omega_i, \quad U_0(R, \Omega) = \sum_{i < j} \varphi_2(R_{ij}, \Omega_i \Omega_j)$$

is the potential energy of short-range forces.

As in the monoatomic case, we first calculate the configuration integral of the system without short-range interactions

$$Q_N^{(\ell)} = Q_{\text{HTA}}^{(\ell)} \int (d\rho) \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \sum_{\substack{mnl \\ \mu\nu\lambda}} \alpha(k, mnl\mu\nu\lambda) \times \right. \\ \left. \times \left[\rho_{\mu\lambda}^m(\mathbf{k}) \rho_{\nu\lambda}^{*n}(\mathbf{k}) - \frac{\delta_{mn}\delta_{\mu\nu}}{(2m+1)} \right] \right\} J(\rho), \quad (4.1.42)$$

where

$$Q_{\text{HTA}}^{(\ell)} = \int (d\Omega) \exp \left\{ -\beta \frac{1}{V} \sum_l a_l \sum_{i < j} P_l(\cos \vartheta_{ij}) \right\}$$

is the high-temperature part of the configuration integral;

$$J(\rho) = \frac{1}{V^N Q_{\text{HTA}}^{(\ell)}} \int (d\mathbf{R}) (d\Omega) \exp \left\{ -\beta \frac{1}{V} \sum_l a_l \sum_{i < j} P_l(\cos \vartheta_{ij}) \right\} J(\rho, R\Omega)$$

is the Jacobian of the transformation to collective variables.

Considering $\rho_{\mu\lambda}^m(\mathbf{k})$ as species collective variables, we obtain³

$$J(\rho) = \int (d\omega) \exp \left[\sum_{n \geq 2} D_n(\omega) \right] \exp \left[i\pi \sum'_{\mathbf{k}} \sum_{m\mu\lambda} \omega_{\mu\lambda}^m(\mathbf{k}) \rho_{\mu\lambda}^m(\mathbf{k}) \right] \quad (4.1.43)$$

where

$$(d\omega) = \prod_{\mathbf{k}} \prod_{m\mu\lambda} d\omega_{\mu\lambda}^m(\mathbf{k});$$

³We hope that the reader will not confuse the quantities $D_n(\omega)$ and $\hat{D}_n(\partial/\partial\rho)$ with the functions $D_{\mu\nu}^n(\Omega)$.

$$\begin{aligned}
D_n(\omega) &= \frac{1}{n!} (-i\pi)^n \frac{N}{\sqrt{N^n}} \sum_{\substack{\{\mathbf{k}_s m_s \mu_s \mu'_s \lambda_s\} \\ (1 \leq s \leq n)}} \int \prod_{s=1}^n D_{\mu'_s \mu_s}^{m_s}(\Omega) F_1(\Omega) d\Omega \times \\
&\quad \times D_{\mu'_s \lambda_s}^{m_s}(\Omega \mathbf{k}_s) \omega_{\mu_s \lambda_s}^{m_s}(\mathbf{k}_s) \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0}, \\
F_1(\Omega_1) &= \frac{1}{Q_{\text{HTA}}^{(\ell)}} \int d\Omega_2 \dots d\Omega_N \exp \left\{ -\beta \frac{1}{V} \sum_l a_l \sum_{i < j} P_l(\cos \vartheta_{ij}) \right\} \quad (4.1.44)
\end{aligned}$$

is the singlet distribution function in the high-temperature approximation. For orientationally disordered systems $F_1(\Omega) = 1$, and according to (4.1.12) and (4.1.13)

$$D_2(\omega) = -\frac{\pi^2}{2} \sum_{\mathbf{k}} \sum_{m\mu\lambda} \omega_{\mu\lambda}^m(\mathbf{k}) \omega_{\mu\lambda}^{*m}(\mathbf{k}) \frac{1}{(2m+1)}.$$

The further calculation of the configuration integral fully follows the methodology developed earlier in Chapter 3 for multicomponent monoatomic systems. In (4.1.43), for all $D_n(\omega)$, starting from $n \geq 3$, the replacement $i\pi\omega_{\mu\lambda}^m(\mathbf{k}) = \partial/\partial\rho_{\mu\lambda}^m(\mathbf{k})$ is performed, and integration over $(d\omega)$ is carried out. This leads to the Jacobian of the transformation taking the well-known form:

$$J(\rho) = \exp \left[\sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right] J_G(\rho),$$

where

$$\begin{aligned}
J_G(\rho) &= \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \sum_{m\mu\lambda} \left[(2m+1) \rho_{\mu\lambda}^m(\mathbf{k}) (\rho_{\mu\lambda}^m(\mathbf{k}))^* + \ln \left(\frac{\pi}{2m+1} \right) \right] \right\}, \\
\hat{D}_n(\partial/\partial\rho) &= \frac{(-1)^n}{n!} \frac{N}{\sqrt{N^n}} \sum_{\substack{\{\mathbf{k}_s m_s \mu_s \mu'_s \lambda_s\} \\ (1 \leq s \leq n)}} \int d\Omega \prod_{s=1}^n D_{\mu'_s \mu_s}^{m_s}(\Omega) \times \\
&\quad \times D_{\mu'_s \lambda_s}^{m_s}(\Omega \mathbf{k}_s) \frac{\partial^n}{\partial \rho_{\mu_s \lambda_s}^{m_s}(\mathbf{k}_s)} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0}. \quad (4.1.45)
\end{aligned}$$

Then, the exponent $\exp \left[\sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right]$ is expanded into a series and the operator pairing is performed. As a result of integrating over the collective variables in (4.1.42), for the long-range part of the free energy, we arrive at the well-known cluster expansion

$$F^{(\ell)} = F_{\text{id}} + F_{\text{HTA}} + F_{\text{RPA}} - 1/\beta(B_2^{(\ell)} + B_3^{(\ell)} + \dots), \quad (4.1.46)$$

where $F_{\text{HTA}} = \frac{N^2}{2V} \int \Phi_2(R, \Omega_1 \Omega_2) d\mathbf{R} d\Omega_1 d\Omega_2$ is the average value of the long-range part of interaction;

$$F_{\text{RPA}} = -\frac{1}{2\beta} \sum_{\mathbf{k}}' \{ \text{Sp} \tilde{\alpha}(k) - \ln \det [1 + \tilde{\alpha}(k)] \}, \quad (4.1.47)$$

where the matrix $\tilde{\alpha}(k)$ consists of elements $\tilde{\alpha}(k, mnl\mu\nu\lambda) = \frac{\alpha(k, mnl\mu\nu\lambda)}{\sqrt{(2m+1)(2n+1)}}$.

The cluster coefficients $B_2^{(\ell)}, B_3^{(\ell)}, \dots$ have the same structure as in the monoatomic case (see (2.2.22)), but now each field vertex corresponds to $N/V \int d\mathbf{R} d\Omega$ ⁴, and the screened potential

$$g(R, \Omega_1 \Omega_2) = \frac{1}{N} \sum_{\mathbf{k}}' e^{i\mathbf{k}\mathbf{R}} \sum_{\substack{mnl \\ \mu\nu\mu'\nu'\lambda}} D_{\mu\mu'}^m(\Omega_1) D_{\nu\nu'}^n(\Omega_2) D_{\mu'\lambda}^m(\Omega_{\mathbf{k}}) D_{\nu'\lambda}^{*n}(\Omega_{\mathbf{k}}) \times \\ \times \left[\frac{\partial}{\partial \tilde{\alpha}(k, mnl\mu\nu\lambda)} \ln \det(1 + \tilde{\alpha}(k)) - \delta_{mn} \delta_{\mu\nu} \right]. \quad (4.1.48)$$

Using the expression (4.1.33) for the exponent $e^{i\mathbf{k}\mathbf{R}}$, the expression (4.1.48) can be rewritten in an invariant form

$$g(R, \Omega_1 \Omega_2) = \sum_{\substack{mnl \\ \mu\nu}} g_{\mu\nu}^{mnl}(R) \Psi_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}),$$

where

$$g_{\mu\nu}^{mnl}(R) = \frac{V}{N} 4\pi i^l (2l+1) \frac{1}{(2\pi)^3} \int_0^\infty j_l(kR) k^2 dk \sum_{\lambda} \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} \times \\ \times \left[\frac{\partial \ln \det[1 + \tilde{\alpha}(k)]}{\partial \tilde{\alpha}(k, mnl\mu\nu\lambda)} - \delta_{mn} \delta_{\mu\nu} \right]. \quad (4.1.49)$$

The inclusion of short-range interactions using the functional-differentiation method does not change the structure of expansion (4.1.46) and, as before, only leads to replacing the cluster coefficients in the Boltzmann factors $e^{g(R, \Omega_1 \Omega_2)}$ with $\exp[g(R, \Omega_1 \Omega_2) - \beta\varphi_2(R, \Omega_1 \Omega_2)]$.

4.1.4. Reference system approach to short-range interactions

Restricting the description to orientationally disordered systems, after integrating in (4.1.41) over $(d\mathbf{R})$ and $(d\Omega)$, the configuration integral takes the form:

$$Q_N = Q_0 \int (d\rho) J(\rho) e^{-\beta v(\rho)}, \quad (4.1.50)$$

where $Q_0 = \frac{1}{V^N} \int (d\mathbf{R}) (d\Omega) e^{-\beta U_0(R\Omega)}$ is the configuration integral of the system with short-range interactions;

$$J(\rho) = \frac{1}{V^N Q_0} \int (d\mathbf{R}) (d\Omega) e^{-\beta U_0(R, \Omega)} J(\rho, R, \Omega) \quad (4.1.51)$$

⁴Or in a more general case $\bullet = N/V \int F_1(\Omega) d\Omega d\mathbf{R}$, while $\tilde{\alpha}(k, mnl\mu\nu\lambda) = \alpha(k, mnl\mu\nu\lambda) \int D_{\mu\lambda}^m(\Omega) D_{\nu\lambda}^n(\Omega) F_1(\Omega) d\Omega$.

is the Jacobian of the transformation to collective variables in the basic count of short-range interactions.

Using the integral representation of the δ -functions, the transformation Jacobian can be expressed in the exponential form (4.1.43), in which, however,

$$D_n(\omega) = \frac{(-i\pi)^n}{n!} \frac{N}{\sqrt{N^n}} \sum_{\substack{\{\mathbf{k}_s, m_s, \mu_s, \mu'_s, \lambda_s\} \\ (1 \leq s \leq n)}} \int \mathbf{m}_n(\mathbf{k}_1, \dots, \mathbf{k}_n, \Omega_1, \dots, \Omega_n) \times \\ \times \prod_{s=1}^n D_{\mu_s \mu'_s}^{m_s}(\Omega_s) D_{\mu'_s \lambda_s}^{m_s}(\Omega_{\mathbf{k}_s}) \omega_{\mu_s \lambda_s}^{m_s}(\mathbf{k}_s) d\Omega_s,$$

where the n -th cumulant $\mathbf{m}_n(\mathbf{k}_1, \dots, \mathbf{k}_n, \Omega_1, \dots, \Omega_n)$ represents the n -particle structure factor for a system of n molecules with orientations $\Omega_1, \dots, \Omega_n$. In particular, $\mathbf{m}_2(\mathbf{k}, -\mathbf{k}, \Omega_1, \Omega_2) = \delta_{\Omega_1 \Omega_2} + \rho h_2^0(\mathbf{k}, \Omega_1 \Omega_2)$, where $h_2^0(k, \Omega_1 \Omega_2) \dots \Omega_1$ is the Fourier transform of the pair correlation function with fixed molecular orientations Ω_1 and Ω_2 . To explicitly extract the orientational dependence, we represent the cumulant $\mathbf{m}_2(k, \Omega_1 \Omega_2)$ in the invariant form (4.1.23)

$$\mathbf{m}_2(k, \Omega_1 \Omega_2) = \sum_{\substack{mnl \\ \mu\nu}} \mathbf{m}_{\mu\nu}^{mnl}(k) \Psi_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_{\mathbf{k}}). \quad (4.1.52)$$

Then, after integrating over orientations according to (4.1.13) and (4.1.22), we obtain:

$$D_2(\omega) = -\frac{\pi^2}{2} \sum_{\mathbf{k}} \sum_{\substack{mnl \\ \mu\nu\lambda}} \mathbf{m}_{\mu\nu}^{mnl}(k) \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} \frac{\omega_{\mu\nu}^m(\mathbf{k}) \omega_{\nu\lambda}^{*n}(\mathbf{k})}{(2m+1)(2n+1)}. \quad (4.1.53)$$

In the absence of short-range forces, $\mathbf{m}_2(k, \Omega_1 \Omega_2) = \delta_{\Omega_1 \Omega_2}$ and we return to the result (4.1.45). In the particular case of central short-range interactions $\mathbf{m}_2(k, \Omega_1 \Omega_2) = \delta_{\Omega_1 \Omega_2} + \frac{N}{V} h_2^0(k)$ and

$$D_2(\omega) = -\frac{\pi^2}{2} \sum_{\mathbf{k}}' \left[\omega_{00}^0(\mathbf{k}) \omega_{00}^{*0}(\mathbf{k}) \mathbf{m}_2(k) + \sum_{\substack{m, \mu, \lambda \\ (m \neq 0)}} \frac{\omega_{\mu\lambda}^m(\mathbf{k}) \left(\omega_{\mu\lambda}^m(\mathbf{k}) \right)^*}{(2m+1)} \right],$$

where $\mathbf{m}_2(k) = 1 + N/V h_2^0(k)$ is the usual structure factor of short-range interactions.

A further calculation of the Jacobian (4.1.51) follows the derivations presented in Chapter 3 for multicomponent monoatomic systems, so we again obtain

$$J(\rho) = \exp \left[\sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right] J_G(\rho),$$

where

$$J_G(\rho) = \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}}' \sum_{\substack{mnl \\ \mu\nu\lambda}} \left[\rho_{\mu\lambda}^n(\mathbf{k}) (\rho_{\nu\lambda}^n(\mathbf{k}))^* (\tilde{\mathbf{m}}_2^{-1}(k))_{\mu\nu\lambda}^{mnl} + \ln(\pi \det \tilde{\mathbf{m}}_2(k)) \right] \right\}; \quad (4.1.54)$$

$$\begin{aligned} \hat{D}_n(\partial/\partial\rho) &= \frac{(-1)^n}{n!} \frac{N}{\sqrt{N^n}} \sum_{\substack{\{\mathbf{k}_s, m_s, \mu_s, \mu'_s, \lambda_s\} \\ (1 \leq s \leq n)}} \int \mathbf{m}_n(\mathbf{k}_1, \dots, \mathbf{k}_n, \Omega_1, \dots, \Omega_n) \times \\ &\times \prod_{s=1}^n D_{\mu_s \mu'_s}^{m_s}(\Omega_s) D_{\mu'_s \lambda_s}^{m_s}(\Omega_{\mathbf{k}_s}) \frac{\partial^n}{\partial \rho_{\mu_s \lambda_s}^{m_s}} d\Omega_s. \end{aligned} \quad (4.1.55)$$

The matrix $\tilde{\mathbf{m}}_2(k)$ consists of matrix elements $\tilde{\mathbf{m}}_{\mu\nu\lambda}^{mnl}(k) = \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} \times \frac{\mathbf{m}_{\mu\nu\lambda}^{mnl}(k)}{(2m+1)(2n+1)}$; $(\tilde{\mathbf{m}}_2^{-1}(k))_{\mu\nu\lambda}^{mnl}$ is the matrix element of the inverse matrix to $\tilde{\mathbf{m}}_2(k)$.

Substituting the obtained transformation Jacobian into expression (4.1.50) for the configuration integral, and after integrating over the collective variables, we arrive at the standard cluster expansion for the free energy of the system

$$F = F_0 + F_{\text{HTA}} + F_{\text{RPA}} - \frac{1}{\beta} (B_2 + B_3 + \dots), \quad (4.1.56)$$

where F_0 is the free energy of the reference system:

$$F_{\text{HTA}} = \frac{N^2}{V} \int \Phi^2(R, \Omega_1 \Omega_2) F_2^0(R, \Omega_1 \Omega_2) d\mathbf{R} d\Omega_1 d\Omega_2 \quad (4.1.57)$$

is the average value of the long-range interaction energy, averaged over the reference system with short-range interactions:

$$F_{\text{RPA}} = -\frac{1}{2\beta} \sum_k' \{Sp[\tilde{\alpha}(k) \tilde{\mathbf{m}}_2(k)] - \ln \det[1 + \tilde{\alpha}(k) \tilde{\mathbf{m}}_2(k)]\} \quad (4.1.58)$$

is the random phase approximation; $B_2, B_3, \dots$ are the cluster coefficients, which have the same structure as in the case of systems with central interactions, except that now each field vertex corresponds to the operation $\frac{N}{V} \int d\mathbf{R} d\Omega$ and the screened potential is

$$\begin{aligned} g(R, \Omega_1 \Omega_2) &= \frac{1}{N} \sum_{\mathbf{k}}' e^{i\mathbf{k}\mathbf{R}} \sum_{\substack{m, n, l \\ \mu, \nu, \mu', \nu', \lambda}} D_{\mu\mu'}^m(\Omega_1) D_{\nu\nu'}^n(\Omega_2) D_{\mu'\lambda}^m(\Omega_{\mathbf{k}}) D_{\nu'\lambda}^{*n}(\Omega_{\mathbf{k}}) \times \\ &\times \left[\frac{\partial}{\partial \tilde{\alpha}(k, mnl\mu\nu\lambda)} \ln \det[1 + \tilde{\alpha}(k) \tilde{\mathbf{m}}_2(k)] - \tilde{\mathbf{m}}_2(k, mnl\mu\nu\lambda) \right]. \end{aligned} \quad (4.1.59)$$

Using expression (4.1.34) for the exponent $e^{i\mathbf{k}\mathbf{R}}$, the screened potential can be represented in an invariant form

$$g(R, \Omega_1 \Omega_2) = \sum_{\substack{mnl \\ \mu\nu}} g_{\mu\nu}^{mnl}(R) \Psi_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}),$$

where

$$g_{\mu\nu}^{mnl}(R) = \frac{V}{N} \frac{4\pi i^l}{(2\pi)^3} \int_0^\infty j_l(kR) k^2 dk \sum_{\lambda} \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} \times \\ \times \left[\frac{\partial}{\partial \tilde{\alpha}(k, mnl\mu\nu\lambda)} \ln \det [1 + \tilde{\alpha}(k) \tilde{\mathbf{m}}_2(k)] - \tilde{\mathbf{m}}_2(k, mnl\mu\nu\lambda) \right]. \quad (4.1.60)$$

By functional differentiation of the free energy, the expression for the pair distribution function is obtained. Its structure, taking into account the diagrammatic modifications mentioned above, also coincides with the corresponding results for monoatomic systems.

4.1.5. Screened potential

As in the case of systems with central interactions, finding the screened potential reduces to solving the Ornstein—Zernike equation

$$h_2(R_{12}, \Omega_1 \Omega_2) = c_2(R_{12}, \Omega_1 \Omega_2) + \\ + \frac{N}{V} \int d\mathbf{R}_3 d\Omega_3 h_2(R_{13} \Omega_1 \Omega_3) c_2(R_{23} \Omega_2 \Omega_3), \quad (4.1.61)$$

where

$$h_2(R, \Omega_1 \Omega_2) = h_2^0(R, \Omega_1 \Omega_2) + g(R, \Omega_1 \Omega_2); \\ c_2(R, \Omega_1 \Omega_2) = c_2^0(R, \Omega_1 \Omega_2) - \beta \Phi_2(R, \Omega_1 \Omega_2), \quad (4.1.62)$$

where $c_2^0(R, \Omega_1 \Omega_2)$ is the direct correlation function of short-range interactions, and $h_2^0(R, \Omega_1 \Omega_2)$ is the corresponding pair correlation function.

As before, optimal convergence of cluster expansions is ensured by a method of interaction separation in which $g(R, \Omega_1 \Omega_2) = 0$ in the region of short-range interactions. In particular, when choosing $\varphi_2(R, \Omega_1 \Omega_2)$ as a hard-sphere potential with diameter σ in the Percus—Yevick approximation for the reference system ($c_2^0(R, \Omega_1 \Omega_2) = 0$ for $R > \sigma$), we arrive at the equation for the screened potential in the mean spherical approximation.

The Ornstein—Zernike equation has its own specificity related to integration over the coordinates of centre of mass and the orientations of a third particle. Using invariant expressions

$$h_2(R, \Omega_1 \Omega_2) = \sum_{\substack{mnl \\ \mu\nu}} h_{\mu\nu}^{mnl}(R) \Psi_{\mu\nu}^{mnl}(\Omega_1, \Omega_2, \Omega_{\mathbf{R}}), \\ c_2(R, \Omega_1 \Omega_2) = \sum_{\substack{mnl \\ \mu\nu}} c_{\mu\nu}^{mnl}(R) \Psi_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}), \quad (4.1.63)$$

Blum [204, 205] transformed equation (4.1.61) in such a way that it reduced to a set of equations, which is solved analogously to the case of central interactions. Let us examine this more in detail.

Substitute (4.1.63) into (4.1.61) and perform the Fourier transform. For this purpose, multiply both sides of the resulting equation by $e^{i\mathbf{k}\mathbf{R}_{12}}$, use expression (4.1.34), and integrate over $d\mathbf{R}_{12}$. As a result, we obtain

$$\begin{aligned} & \sum_{\substack{mnl, \\ \mu\nu}} \left[h_{\mu\nu}^{mnl}(k) - c_{\mu\nu}^{mnl}(k) \right] \Psi_{\mu\nu}^{mnl}(\Omega_1, \Omega_2, \Omega_{\mathbf{k}}) = \\ & = \frac{N}{V} \int d\Omega_3 \sum_{\substack{m_1 n_1 l_1 \\ \mu_1 \nu_1}} \sum_{\substack{m_2 n_2 l_2 \\ \mu_2 \nu_2}} h_{\mu_1 \nu_1}^{m_1 n_1 l_1}(k) c_{\mu_2 \nu_2}^{m_2 n_2 l_2}(k) \Psi_{\mu_1 \nu_1}^{m_1 n_1 l_1}(\Omega_1 \Omega_3 \Omega_{\mathbf{k}}) \times \\ & \quad \times \Psi_{\mu_2 \nu_2}^{m_2 n_2 l_2}(\Omega_3, \Omega_2, \Omega_{\mathbf{k}}), \end{aligned} \quad (4.1.64)$$

where

$$\begin{aligned} h_{\mu\nu}^{mnl}(k) &= 4\pi i^l \int_0^\infty R^2 dR j_l(kR) h_{\mu\nu}^{mnl}(R), \\ c_{\mu\nu}^{mnl}(k) &= 4\pi i^l \int_0^\infty R^2 dR j_l(kR) c_{\mu\nu}^{mnl}(R). \end{aligned} \quad (4.1.65)$$

After integration over $d\Omega_3$, we obtain

$$\begin{aligned} & \frac{N}{V} \sum_{\substack{n_1 l_1 l_2 \\ \nu_1 \nu_l \lambda_1 \lambda_2}} \frac{(-1)^{\nu_1 - \nu_l'}}{(2n_l + 1)} \begin{pmatrix} m & n_1 & l_1 \\ \mu & \nu_1 & \lambda_1 \end{pmatrix} \begin{pmatrix} n_1 & n_2 & l_2 \\ -\nu_1 & \nu & \lambda_2 \end{pmatrix} h_{\mu' \nu_l}^{m n_1 l_1}(k) c_{-\nu_1 \nu}^{n_1 n l_2}(k) \times \\ & \times D_{\lambda_1 0}^{l_1}(\Omega_{\mathbf{k}}) D_{\lambda_2 0}^{l_2}(\Omega_{\mathbf{k}}) = \sum_{\lambda} \left[h_{\mu' \nu'}^{mnl}(k) - c_{\mu' \nu'}^{mnl}(k) \right] \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} D_{\lambda 0}^l(\Omega_{\mathbf{k}}). \end{aligned}$$

To eliminate the remaining orientational dependence, we multiply both sides of this equation by $D_{\lambda 0}^{*l}(\Omega_{\mathbf{k}})$ and integrate over $d\Omega_{\mathbf{k}}$. As a result, we obtain

$$\begin{aligned} & \frac{N}{V} \sum_{n_1 l_1 l_2} \frac{(2l+1)}{(2n_1+1)} (-1)^{m+n+n_1} \left\{ \begin{matrix} l_2 & l_1 & l \\ m & n & n_1 \end{matrix} \right\} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \sum_{\nu_l'=-n_1}^{n_1} (-1)^{\nu_l'} \times \\ & \times h_{\mu' \nu_l'}^{m n_1 l_1}(k) c_{-\nu_l' \nu'}^{n_1 n l_2}(k) = h_{\mu' \nu'}^{mnl}(k) - c_{\mu' \nu'}^{mnl}(k), \end{aligned} \quad (4.1.66)$$

where

$$\begin{aligned} \left\{ \begin{matrix} l_1 & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{matrix} \right\} &= \sum_{\mu_1 \mu_2 \mu_4} \text{sgn} \left(\sum_{i=1}^6 (l_i - \mu_i) \right) \begin{pmatrix} l_1 & l_2 & l_3 \\ -\mu_1 & -\mu_2 & -\mu_3 \end{pmatrix} \times \\ & \times \begin{pmatrix} l_1 & l_5 & l_6 \\ \mu_1 & -\mu_5 & \mu_6 \end{pmatrix} \begin{pmatrix} l_4 & l_2 & l_6 \\ \mu_4 & \mu_2 & -\mu_6 \end{pmatrix} \begin{pmatrix} l_4 & l_5 & l_3 \\ -\mu_4 & \mu_5 & \mu_3 \end{pmatrix} \end{aligned}$$

are the so-called Racah coefficients or Wigner's $6j$ -symbols [198, 199]. The $6j$ -symbols are nonzero only if the triangle relations $\Delta(l_1 l_2 l_3)$, $\Delta(l_1 l_5 l_6)$, $\Delta(l_4 l_2 l_6)$, $\Delta(l_4 l_5 l_3)$ are satisfied.

Equation (4.1.66) can also be rewritten in another form if the ambiguity of expansions (4.1.64) is utilized. Indeed, in general, one can assume

$$h_2(R, \Omega_1 \Omega_2) = \sum_{\substack{mnl, \\ \mu\nu}} \hat{h}_{\mu\nu}^{mnl}(R) \hat{\Psi}_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_R), \quad (4.1.67)$$

$$\hat{h}_{\mu\nu}^{mnl}(R) = \frac{1}{f^{mnl}} h_{\mu\nu}^{mnl}(R), \quad \hat{\Psi}_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_R) = f^{mnl} \Psi_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_R),$$

where $f^{mnl} \neq 0$ are arbitrary constants that depend only on m, n, l . Similarly, for $c_2(R, \Omega_1 \Omega_2) = \sum_{\substack{mnl, \\ \mu\nu}} \hat{c}_{\mu\nu}^{mnl}(R) \hat{\Psi}_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_R)$, and thus, for the Fourier transforms

$$h(k, \Omega_1 \Omega_2) = \sum_{\substack{mnl, \\ \mu\nu}} \hat{h}_{\mu\nu}^{mnl}(k) \hat{\Psi}_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_{\mathbf{k}}),$$

$$c(k, \Omega_1 \Omega_2) = \sum_{\substack{mnl, \\ \mu\nu}} \hat{c}_{\mu\nu}^{mnl}(k) \hat{\Psi}_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_{\mathbf{k}}). \quad (4.1.68)$$

Now, the equation (4.1.66) can be represented in the form

$$\hat{h}_{\mu\nu}^{mnl}(k) - \hat{c}_{\mu\nu}^{mnl}(k) = \sum_{l_2 l_1 n_1} \hat{Z}_{mnn_1}^{l_2 l_1 l} \sum_{\nu_1=-n_1}^{n_1} \hat{h}_{\mu\nu_1}^{mn_1 l_1}(k) (-1)^{\nu_1} \hat{c}_{-\nu_1 \nu}^{n_1 n l_2}(k), \quad (4.1.69)$$

where

$$\hat{Z}_{mnn_1}^{l_2 l_1 l} = \frac{f^{mn_1 l_1} f^{n_1 n l_2}}{f^{mnl}} \operatorname{sgn}(m+n+n_1) \frac{2l+1}{2n_1+1} \left\{ \begin{matrix} l_2 & l_1 & l \\ m & n & n_1 \end{matrix} \right\} \left(\begin{matrix} l_2 & l_1 & l \\ 0 & 0 & 0 \end{matrix} \right).$$

Blum put $f^{mnl} = \sqrt{(2m+1)(2n+1)}$. At the same time

$$\begin{aligned} \hat{Z}_{mnn_1}^{l_2 l_1 l} &= (2l+1) \operatorname{sgn}(m+n+n_1) \left\{ \begin{matrix} l_2 & l_1 & l \\ m & n & n_1 \end{matrix} \right\} \left(\begin{matrix} l_2 & l_1 & l \\ 0 & 0 & 0 \end{matrix} \right) = \\ &= (2l+1) \sum_{\chi} (-1)^{\chi} \left(\begin{matrix} n_1 & n & l_2 \\ \chi & -\chi & 0 \end{matrix} \right) \left(\begin{matrix} m & n_1 & l_1 \\ \chi & -\chi & 0 \end{matrix} \right) \left(\begin{matrix} m & n & l \\ \chi & -\chi & 0 \end{matrix} \right). \end{aligned} \quad (4.1.70)$$

The last equality follows from the properties of $3j$ - and $6j$ -symbols.

Next, we introduce the functions

$$H_{\mu\nu, \chi}^{mn}(k) = \sum_{l=|m-n|}^{m+n} \left(\begin{matrix} m & n & l \\ \chi & -\chi & 0 \end{matrix} \right) \hat{h}_{\mu\nu}^{mnl}(k),$$

$$C_{\mu\nu, \chi}^{mn}(k) = \sum_{l=|m-n|}^{m+n} \left(\begin{matrix} m & n & l \\ \chi & -\chi & 0 \end{matrix} \right) \hat{c}_{\mu\nu}^{mnl}(k), \quad (4.1.71)$$

Hence, according to (4.1.18),

$$\begin{aligned}\hat{h}_{\mu\nu}^{mnl}(k) &= (2l+1) \sum_{\chi} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} H_{\mu\nu,\chi}^{mnl}(k), \\ \hat{c}_{\mu\nu}^{mnl}(k) &= (2l+1) \sum_{\chi} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} C_{\mu\nu,\chi}^{mnl}(k).\end{aligned}\tag{4.1.72}$$

Now, the equation (4.1.69) can be rewritten in the form

$$H_{\mu\nu,\chi}^{mn}(k) - C_{\mu\nu,\chi}^{mn}(k) = \frac{N}{V} \sum_{n_1\nu_1} (-1)^{\nu_1+\chi} H_{\mu\nu_1,\chi}^{mn_{11}}(k) C_{-\nu_1\nu,\chi}^{m_{11}n}(k)$$

or, more concisely, in a matrix form

$$\mathbf{H}_{\chi}(k) - \mathbf{C}_{\chi}(k) = (-1)^{\chi} \frac{N}{V} \mathbf{H}_{\chi}(k) \mathbf{P} \mathbf{C}_{\chi}(k),\tag{4.1.73}$$

where $\mathbf{P}$ is the identity diagonal matrix corresponding to the factor $(-1)^{\nu_1}$.

It is clear that solving this set of equations with consideration of (4.1.63) leads to expression (4.1.59) for the screened potential. However, fulfilling the condition of optimal interaction separation requires a transformation to coordinate space. In this regard, we introduce new functions $C_{\mu\nu}^{mnl}(r)$ and $H_{\mu\nu}^{mnl}(r)$, which are defined differently for even and odd l :

$$\hat{h}_{\mu\nu}^{mnl}(k) = \begin{cases} 4\pi \int_0^{\infty} r^2 dr j_0(kr) H_{\mu\nu}^{mnl,e}(r) & \text{for even } l, \\ 4\pi i \int_0^{\infty} r^2 dr j_1(kr) H_{\mu\nu}^{mnl,o}(r) & \text{for odd } l, \end{cases}\tag{4.1.74}$$

$$\hat{c}_{\mu\nu}^{mnl}(k) = \begin{cases} 4\pi \int_0^{\infty} r^2 dr j_0(kr) C_{\mu\nu}^{mnl,e}(r) & \text{for even } l, \\ 4\pi i \int_0^{\infty} r^2 dr j_1(kr) C_{\mu\nu}^{mnl,o}(r) & \text{for odd } l, \end{cases}\tag{4.1.75}$$

Hence, according to (4.1.65),

$$\begin{aligned}H_{\mu\nu}^{mnl}(r) &= \int_0^{\infty} R^2 dR \Theta_l(R, r) \hat{h}_{\mu\nu}^{mnl}(R), \\ C_{\mu\nu}^{mnl}(r) &= \int_0^{\infty} R^2 dR \Theta_l(R, r) \hat{c}_{\mu\nu}^{mnl}(R),\end{aligned}\tag{4.1.76}$$

where

$$\Theta_l(R, r) = \begin{cases} i^l \frac{2}{\pi} \int_0^\infty k^2 dk j_l(kR) j_0(kr) & \text{for even } l, \\ i^{l-1} \frac{2}{\pi} \int_0^\infty k^2 dk j_l(kR) j_1(kr) & \text{for odd } l. \end{cases} \quad (4.1.77)$$

Equations (4.1.76) represent a specific integral transformation of the functions $\hat{h}_{\mu\nu}^{mnl}(R)$ and $\hat{c}_{\mu\nu}^{mnl}(R)$. Due to the orthogonality of spherical Bessel functions,

$$\frac{2}{\pi} \int_0^\infty k^2 dk j_l(kR) j_l(kr) = \frac{1}{R^2} \delta(R - r) \text{ as defined in (4.1.77)}$$

$$\int_0^\infty \Theta_l(x, y) \Theta_l(z, y) y^2 dy = \frac{1}{xz} \delta(x - z). \quad (4.1.78)$$

and thus, the transformations (4.1.76) correspond to the inverse transformations

$$\hat{h}_{\mu\nu}^{mnl}(R) = (-1)^l \int_0^\infty r^2 dr \Theta_l(R, r) H_{\mu\nu}^{mnl}(r),$$

$$\hat{c}_{\mu\nu}^{mnl}(R) = (-1)^l \int_0^\infty r^2 dr \Theta_l(R, r) C_{\mu\nu}^{mnl}(r), \quad (4.1.79)$$

To calculate $\Theta_l(R, r)$, following Edelman and Deutsch [206], we use the integral representation of the function $j_l(kR)$

$$j_l(kR) = \frac{1}{2i^l} \int_{-1}^1 e^{ikRx} P_l(x) dx, \quad (4.1.80)$$

where $P_l(x)$ is the Legendre polynomial.

Substitute $j_0(kr) = \frac{\sin(kr)}{kr}$, $j_1(kr) = \frac{1}{kr} \left[\frac{\sin kr}{kr} - \cos kr \right]$ into (4.1.77), and use expression (4.1.80) instead of $j_l(kR)$. Change the order of integration and, at the same time, to ensure the convergence of the integrals, introduce the factor $\lim_{\varepsilon \rightarrow 0} e^{-k\varepsilon}$. For even l , we obtain

$$\Theta_l^\varepsilon(R, r) = \lim_{\varepsilon \rightarrow 0} \frac{1}{\pi r} \int_{-1}^1 P_l(x) dx \int_0^\infty k \sin(kr) e^{ik(Rx+i\varepsilon)} dk.$$

Since

$$\frac{1}{iR} \frac{d}{dx} \int_0^\infty dk \sin(kr) e^{ik(xR+i\varepsilon)} = \frac{1}{2iR} \frac{d}{dx} \left[\frac{1}{xR+r+i\varepsilon} - \frac{1}{xR-r+i\varepsilon} \right]$$

by integrating by parts, we obtain

$$\begin{aligned} \Theta_l^e(R, r) = \lim_{\varepsilon \rightarrow 0} \frac{1}{2\pi i r R} \left[P_l(x) \left(\frac{1}{xR+r+i\varepsilon} - \frac{1}{xR-r+i\varepsilon} \right) \right]_{-1}^1 - \\ - \int_{-1}^1 P_l'(x) \left(\frac{1}{xR+r+i\varepsilon} - \frac{1}{xR-r+i\varepsilon} \right) dx \right], \end{aligned}$$

where $P_l'(x) = \frac{d}{dx} P_l(x)$. Since $P_l(-x) = (-1)^l P_l(x)$, applying the identity

$$\lim_{\varepsilon \rightarrow 0} \frac{1}{R+r+i\varepsilon} = \mathcal{P} \left(\frac{1}{r+R} \right) - i\pi \delta(R+r),$$

where $\mathcal{P}$ is the principal value symbol, for even l we obtain

$$\begin{aligned} \Theta_l^e(R, r) = \frac{1}{Rr} \left\{ \delta(R-r) - \delta(R+r) - \int_0^1 P_l'(x) [\delta(xR-r) - \right. \\ \left. - \delta(xR+r)] \right\} = \frac{1}{Rr} \left[\delta(R-r) - \frac{1}{R} H(R-r) P_l' \left(\frac{r}{R} \right) \right], \end{aligned}$$

where $H(R-r)$ is the Heaviside step function.

A similar expression is obtained for odd l . We suggest that the reader independently derives the corresponding calculations, resulting in

$$\Theta_l(R, r) = \frac{1}{Rr} \left[\delta(R-r) - \frac{1}{R} H(R-r) P_l' \left(\frac{r}{R} \right) \right]. \quad (4.1.81)$$

Let us now return to relations (4.1.74) and (4.1.75). By integrating them by parts, they can be represented in the form:

$$\hat{h}_{\mu\nu}^{mnl}(k) = \begin{cases} 4\pi \int_0^\infty dr \cos kr \int_r^\infty t dt H_{\mu\nu}^{mnl,e}(t) & \text{for even } l, \\ 4\pi i \int_0^\infty r dr \sin kr \int_r^\infty t dt H_{\mu\nu}^{mnl,o}(t) & \text{for odd } l, \end{cases} \quad (4.1.82)$$

$$\hat{c}_{\mu\nu}^{mnl}(k) = \begin{cases} 4\pi \int_0^\infty dr \cos kr \int_r^\infty dt C_{\mu\nu}^{mnl,e}(t) & \text{for even } l, \\ 4\pi i \int_0^\infty r dr \sin kr \int_r^\infty dt C_{\mu\nu}^{mnl,o}(t) & \text{for odd } l, \end{cases} \quad (4.1.83)$$

Next, we distinguish between even and odd l in expressions (4.1.71) for $\hat{H}_{\mu\nu,\chi}^{mn}(k)$ and $\hat{C}_{\mu\nu,\chi}^{mn}(k)$:

$$\begin{aligned} H_{\mu\nu,\chi}^{mn}(k) &= \sum_{(\text{even } l)} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \hat{h}_{\mu\nu}^{mnl}(k) + \sum_{(\text{odd } l)} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \hat{h}_{\mu\nu}^{mnl}(k) = \\ &= 4\pi \int_0^\infty dr \left[\cos(kr) \int_r^\infty dt \bar{H}_{\mu\nu,\chi}^{mn,e}(t) + i \sin(kr) r \int_r^\infty dt \bar{H}_{\mu\nu,\chi}^{mn,o}(t) \right], \end{aligned} \quad (4.1.84)$$

$$C_{\mu\nu,\chi}^{mn}(k) = 4\pi \int_0^\infty dr \left[\cos(kr) \int_r^\infty dt \bar{C}_{\mu\nu,\chi}^{mn,e}(t) + i \sin(kr) r \int_r^\infty dt \bar{C}_{\mu\nu,\chi}^{mn,o}(t) \right], \quad (4.1.85)$$

where

$$\begin{aligned} \bar{H}_{\mu\nu,\chi}^{mn,e}(r) &= \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} H_{\mu\nu}^{mnl,e}(r) \quad \text{for even } l, \\ \bar{H}_{\mu\nu,\chi}^{mn,o}(r) &= \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} H_{\mu\nu}^{mnl,o}(r) \quad \text{for odd } l, \end{aligned} \quad (4.1.86)$$

and similarly for $\bar{C}_{\mu\nu,\chi}^{mn,e}(r)$ and $\bar{C}_{\mu\nu,\chi}^{mn,o}(r)$.

After some straightforward transformations, we obtain

$$\begin{aligned} H_{\mu\nu,\chi}^{mn}(k) &= \int_0^\infty dr \left[e^{ikr} I_{\mu\nu,\chi}^{mn,+}(r) + e^{-ikr} I_{\mu\nu,\chi}^{mn,-}(r) \right], \\ C_{\mu\nu,\chi}^{mn}(k) &= \int_0^\infty dr \left[e^{ikr} S_{\mu\nu,\chi}^{mn,+}(r) + e^{-ikr} S_{\mu\nu,\chi}^{mn,-}(r) \right], \end{aligned} \quad (4.1.87)$$

where

$$\begin{aligned} I_{\mu\nu,\chi}^{mn,\pm}(r) &= 2\pi \int_r^\infty dt \left[\bar{H}_{\mu\nu,\chi}^{mn,e}(t) \pm r \bar{H}_{\mu\nu,\chi}^{mn,o}(t) \right], \\ S_{\mu\nu,\chi}^{mn,\pm}(r) &= 2\pi \int_r^\infty dt \left[\bar{C}_{\mu\nu,\chi}^{mn,e}(t) \pm r \bar{C}_{\mu\nu,\chi}^{mn,o}(t) \right]. \end{aligned} \quad (4.1.88)$$

Let us now return to the Ornstein—Zernike equation, presented in the form (4.1.73). By multiplying both sides of equation (4.1.88) by $\mathbf{P}$, we represent it in the form

$$\left[1 + (-1)^\chi \frac{N}{V} \mathbf{H}_\chi(k) \mathbf{P}\right] \left[1 - (-1)^\chi \frac{N}{V} \mathbf{C}_\chi(k) \mathbf{P}\right] = 1 \quad (4.1.89)$$

which coincides with Baxters form (3.3.70) for multicomponent systems with central interactions. Since $\det \mathbf{P} = 1$, by definition, all elements of the matrix $\mathbf{H}(k)$ are finite in the real domain of k , and the matrix

$$\mathbf{A}_\chi(k) = 1 - (-1)^\chi \frac{N}{V} \mathbf{C}_\chi(k) \mathbf{P} \quad (4.1.90)$$

has no singularities for all $\text{Re } k$. Thus, Wiener—Hopf factorization for $\mathbf{A}_\chi(k)$ is possible.

The only difference from the case of a multicomponent monoatomic system here is that the matrices $\mathbf{H}_\chi^\pm(k)$ and $\mathbf{C}_\chi^\pm(k)$ are not symmetric under the transformation $k \rightarrow -k$. Nevertheless, by definition (4.1.86)—(4.1.88) and according to (4.1.76)

$$\mathbf{I}_\chi^\pm(r) = (\mathbf{I}_{-\chi}^\mp(r))^T, \quad \mathbf{S}_\chi^\pm(r) = (\mathbf{S}_{-\chi}^\mp(r))^T,$$

where T denotes the transposed matrix. Therefore,

$$\mathbf{A}_\chi(-k) = \mathbf{P} \mathbf{A}_{-\chi}^T(k) \mathbf{P} = \tilde{\mathbf{A}}_{-\chi}(k) \quad (4.1.91)$$

and, since $\mathbf{A}_\chi(k)$ has no singularities along the real axis, similar to the case of (3.3.74), we have

$$\mathbf{A}_\chi(k) = \mathbf{Q}_\chi(k) \tilde{\mathbf{Q}}_{-\chi}(-k). \quad (4.1.92)$$

This is the Wiener—Hopf factorization for equation (4.1.89). In particular, if $\mathbf{S}_\chi^\pm(r) = 0$ for $r > \sigma$, the matrix $\mathbf{Q}_\chi(k)$ can be associated with the matrix $q_\chi(r)$, defined by the equation

$$\mathbf{Q}_\chi(k) = 1 - (-1)^\chi \frac{N}{V} \int_0^\sigma dr e^{ikr} \mathbf{q}_\chi(r). \quad (4.1.93)$$

Using (4.1.87), (4.1.92), (4.1.93), and the analytical properties of the function $\mathbf{Q}_\chi(k)$, we obtain

$$\begin{aligned} \mathbf{S}_\chi^+(r) &= \mathbf{q}_\chi(r) \mathbf{P} - (-1)^\chi \frac{N}{V} \int_r^\sigma dt \mathbf{q}_\chi(t) \hat{\mathbf{q}}_{-\chi}(t-r) \mathbf{P}, \\ \mathbf{S}_\chi^-(r) &= \tilde{\mathbf{q}}_{-\chi}(r) \mathbf{P} - (-1)^\chi \frac{N}{V} \int_r^\sigma dt \mathbf{q}_\chi(t-r) \tilde{\mathbf{q}}_{-\chi}(t) \mathbf{P}. \end{aligned} \quad (4.1.94)$$

Since the matrix $\mathbf{Q}_{-\chi}(-k)$ has no singularities in the lower half-plane,

$$\begin{aligned}\mathbf{I}_{\chi}^{+}(r) &= \mathbf{q}_{\chi}(r) \mathbf{P} + (-1)^{\chi} \frac{N}{V} \left[\int_0^r dt \mathbf{I}_{\chi}^{+}(r-t) \mathbf{P} \mathbf{q}_{\chi}(t) + \right. \\ &\quad \left. + \int_r^{\sigma} dt \mathbf{I}_{\chi}^{-}(t-r) \mathbf{P} \mathbf{q}_{\chi}(t) \right] \mathbf{P}, \\ \mathbf{I}_{\chi}^{-}(r) &= \tilde{\mathbf{q}}_{-\chi}(r) \mathbf{P} + (-1)^{\chi} \frac{N}{V} \left[\int_0^r dt \mathbf{q}_{-\chi}(t) \mathbf{I}_{\chi}^{-}(r-t) + \right. \\ &\quad \left. + \int_r^{\sigma} dt \mathbf{q}_{-\chi}(t) \mathbf{I}_{\chi}^{+}(t-r) \right].\end{aligned}\tag{4.1.95}$$

Hence, if the form of the matrix $\mathbf{I}_{\chi}^{\pm}(r)$ is known for $r < \sigma$, we can determine $\mathbf{q}_{\chi}(r)$ and, according to (4.1.94), $\mathbf{C}_{\chi}^{\pm}(r)$ hereby solving the Ornstein–Zernike equation for the system with non-central interactions.

In conclusion, we note the general nature of the cluster expansions (4.1.56) obtained in this section. The results are easily generalized if it is necessary to account for other degrees of freedom of the molecules. To achieve this, it is sufficient to replace the element $d\Omega d\mathbf{R}$ with a more general element $d\Gamma$ throughout. In this case, when introducing collective variables, the interaction potential decomposes into eigenfunctions of all types of the considered individual motions of molecules. In particular, when considering vibrational degrees of freedom, in addition to expanding the interaction potential into a Fourier series and a series in spherical functions, it is also necessary to expand it in terms of Hermite polynomials.

4.2. Simple molecular systems

Before proceeding to the description of various molecular systems, let us first consider simple model systems with purely repulsive interactions. Similar to how the simplest nontrivial reference system for monoatomic molecules is the model of hard spheres, for nonspherical molecules, such a system is the model of hard convex particles. Another approach to describing molecular systems involves the use of site-site potentials.

4.2.1. Model of hard convex bodies.

Application of the scaled particle theory

A particle (or body) is convex if it completely contains the line segment connecting any two of its points. Each convex body is characterized by a set of three quantities: its intrinsic volume v_0 , surface area s_0 , and mean

curvature r_0 . According to differential geometry

$$\begin{aligned} v_0 &= \frac{1}{3} \int \left(\mathbf{r} \left[\frac{\partial \mathbf{r}}{\partial \vartheta} \frac{\partial \mathbf{r}}{\partial \varphi} \right] \right) d\vartheta d\varphi, \quad s_0 = \int \left(\mathbf{u} \left[\frac{\partial \mathbf{r}}{\partial \vartheta} \frac{\partial \mathbf{r}}{\partial \varphi} \right] \right) d\vartheta d\varphi, \\ r_0 &= \frac{1}{4\pi} \int \left(\mathbf{r} \left[\frac{\partial \mathbf{u}}{\partial \vartheta} \frac{\partial \mathbf{u}}{\partial \varphi} \right] \right) d\vartheta d\varphi, \end{aligned} \quad (4.2.1)$$

where $\mathbf{u}(\vartheta, \varphi)$ is the unit vector in the direction of the normal to the tangent plane, and $\mathbf{r}(\vartheta, \varphi)$ is the vector from the centre of the convex body to the contact point; ϑ, φ are the polar angles. The values of v_0, s_0, r_0 for some bodies are given in Table 9, taken from [136].

The interaction in a system of convex bodies depends only on ζ — the shortest distance between the surfaces of two molecules. For hard bodies, the intermolecular interaction potential

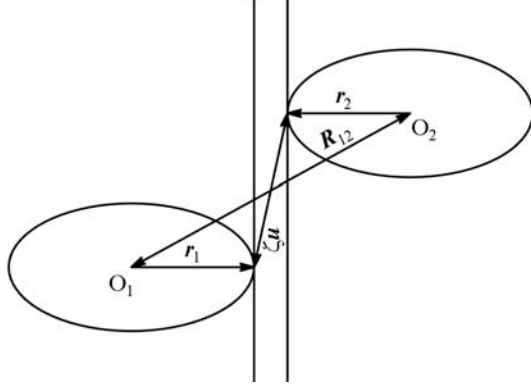
$$u_2(\zeta) = \begin{cases} 0, & \zeta > 0, \\ \infty, & \zeta < 0. \end{cases} \quad (4.2.2)$$

Thus, as in the case of hard spheres, the configuration integral and distribution functions do not depend on temperature. However, the thermodynamic and structural properties of the system are now determined by two parameters.

Table 9. Values of the geometric measures r_0, s_0, v_0 for convex bodies

Molecule shape	Size	r_0	s_0	v_0
Sphere	Radius a	a	$4\pi a^2$	$\frac{4}{3}\pi a^3$
Rectangular parallelepiped	Vertices lengths l_1, l_2, l_3	$\frac{1}{4}(l_1 + l_2 + l_3)$	$2(l_1 l_2 + l_2 l_3 + l_1 l_3)$	$l_1 l_2 l_3$
Regular tetrahedron	Side l	$\frac{3l}{2\pi} \arctan \sqrt{2}$	$\sqrt{3}l^2$	$\frac{1}{12}\sqrt{2}l^3$
Cylinder	Length l , radius a	$\frac{1}{4}(l + \pi a)$	$2\pi a(l + a)$	$\pi a^2 l$
Elongated (cigar-shaped) spherocylinder	Length l , radius a	$\frac{1}{4}l + a$	$2\pi a(l + 2a)$	$\pi a^2 \left(l + \frac{4}{3}a \right)$
Elongated ellipsoid of revolution	Major semiaxis a	$\frac{a}{2} \left(1 + \frac{1-\varepsilon^2}{2\varepsilon} \ln \frac{1+\varepsilon}{1-\varepsilon} \right)$	$2\pi b^2 \left(1 + \frac{1}{\varepsilon \sqrt{1-\varepsilon^2}} \arcsin \varepsilon \right)$	$\frac{4}{3}\pi a b^2$
Oblate ellipsoid of revolution	Minor semiaxis b $\left(\varepsilon^2 = \frac{a^2 - b^2}{a^2} \right)$	$\frac{b}{2} \left(1 + \frac{1}{\varepsilon} \frac{\arcsin \varepsilon}{\sqrt{1-\varepsilon^2}} \right)$	$2\pi a^2 \left(1 + \frac{1-\varepsilon^2}{2\varepsilon} \ln \frac{1+\varepsilon}{1-\varepsilon} \right)$	$\frac{4}{3}\pi a^2 b$

Fig. 14. Schematic representation of the contact between two convex bodies. The relative position vector $\mathbf{R}_{12}$ is expressed via the local surface vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ and the unit normal vector $\mathbf{u}$ at the point of contact



One is $\eta = N/Vv_0$, which is related to the system's density, and the other is $\alpha = \frac{r_0 s_0}{3v_0}$ which characterizes the shape of the molecule. The maximum density $\eta_{\max}$, corresponding to dense packing, depends on α . In addition to the phase transition associated with crystallization, the system may also exhibit another type of phase transition related to orientational ordering. For hard spheres $\alpha = 1$. With α increasing, the orientational transition initially occurs in the crystalline region; however, it may also take place in the disordered phase, corresponding to a liquid-crystalline ordering. Both phase transitions occur only in two- and three-dimensional cases.

The features of interactions in a system of convex bodies allow for the simplification of some of the general relations presented at the beginning of this chapter. First, due to translational invariance, we can transform to the relative coordinates $\mathbf{R}_{12}, \Omega_{12}$. Since $\mathbf{R}_{12} = \mathbf{r}_1(\vartheta, \varphi) + \mathbf{r}_2(\vartheta, \varphi) + \zeta \mathbf{u}(\vartheta, \varphi)$ (see Fig. 14), it follows that $d\mathbf{R}_{12} = \left(\mathbf{u} \left[\frac{\partial \mathbf{R}_{12}}{\partial \vartheta} \times \frac{\partial \mathbf{R}_{12}}{\partial \varphi} \right] \right) d\zeta d\vartheta d\varphi$. Substituting this expression into formulas (4.1.5)–(4.1.7), for a one-component system, we obtain

$$E - E_{\text{id}} = \frac{1}{2} \frac{N^2}{V} \int_0^\infty d\zeta \int d\Omega d\vartheta d\varphi u_2(\zeta) F_2(\zeta, \vartheta, \varphi, \Omega) \left(\mathbf{u} \left[\frac{\partial \mathbf{R}_{12}}{\partial \vartheta} \frac{\partial \mathbf{R}_{12}}{\partial \varphi} \right] \right). \quad (4.2.3)$$

Taking into account that $\mathbf{R}_{12} \frac{\partial u_2(\zeta)}{\partial \mathbf{R}_{12}} = \frac{\partial u_2(\zeta)}{\partial \zeta} (\mathbf{R}_{12} \mathbf{u})$, for the equation of state, we have

$$P - P_{\text{id}} = -\frac{1}{6} \frac{N^2}{V^2} \int_0^\infty d\zeta \int d\Omega d\vartheta d\varphi F_2(\zeta, \vartheta, \varphi, \Omega) \frac{\partial u_2(\zeta)}{\partial \zeta} \left(\mathbf{R}_{12} \left[\frac{\partial \mathbf{R}_{12}}{\partial \vartheta} \frac{\partial \mathbf{R}_{12}}{\partial \varphi} \right] \right). \quad (4.2.4)$$

For hard convex bodies with the interaction potential (4.2.2), the energy is given by $E = E_{\text{id}}$, and the pressure is determined by the contact value of

the pair distribution function at fixed orientations, i.e., $F_2(\zeta = 0+, \vartheta\varphi\Omega)$. Indeed, assuming $F_2(\zeta, \vartheta\varphi\Omega) = e^{-\beta u_2(\zeta)} y_2(\zeta, \vartheta\varphi\Omega)$ and taking into account that $-\beta \frac{\partial u_2(\zeta)}{\partial \zeta} e^{-\beta u_2(\zeta)} = \delta(\zeta)$, we obtain

$$P - P_{\text{id}} = -\frac{1}{6} \frac{N^2}{V^2} \frac{1}{\beta} \int F_2(0+, \vartheta\varphi\Omega) \left(\mathbf{r}_{12} \left[\frac{\partial \mathbf{r}_{12}}{\partial \vartheta} \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right] \right) d\vartheta d\varphi d\Omega, \quad (4.2.5)$$

where $\mathbf{r}_{12} = \mathbf{r}_1(\vartheta, \varphi) + \mathbf{r}_2(\vartheta, \varphi)$.

The introduced function $y_2(\zeta, \vartheta\varphi\Omega)$, as in the case of hard spheres, represents the distribution function of two cavities. In the limit $N/V \rightarrow 0$, we have $y_2(\zeta, \vartheta\varphi\Omega) \rightarrow 1$ and from (4.2.5), we obtain the expression for the second virial coefficient

$$B_2 = \frac{1}{2} \frac{N}{V} v_{O+O} = \eta(1 + 3\alpha), \quad (4.2.6)$$

where

$$v_{O+O} = \frac{1}{3} \int \left(\mathbf{r}_{12} \left[\frac{\partial \mathbf{r}_{12}}{\partial \vartheta} \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right] \right) d\vartheta d\varphi d\Omega = 2v_0 + 2r_0 s_0$$

is the volume of a convex body formed as a result of the rotation of one molecule around another in such a way that they are constantly in contact. Since for all convex bodies $\alpha > 1$, the second virial coefficient of nonspherical bodies is always larger than that of hard spheres with the same volume. Finding higher-order virial coefficients is a more complex problem, and currently, the third virial coefficient of a fluid of spheroids was calculated by direct integration using the method of 2-point measures of convex body geometry [207, 208]. However, the expression (4.2.5) suggests the possibility of generalizing the approach developed in the previous section using the scaled particle theory. This problem was addressed in the works of Gibbons [209] and Boublik [210].

According to the general scaled particle theory, we introduce a small auxiliary body that is congruent to the remaining molecules. Let the distance between its centre of mass and the centre of mass of one of the molecules in the system be $\mathbf{R}_{12}(\lambda) = \lambda \mathbf{r}_1 + \mathbf{r}_2 + \zeta \mathbf{u}$, where the parameter λ characterizes the size of the introduced particle. The work $W(\lambda)$ required for the introduction of this scaled particle is equal to its free energy of solvation. Proceeding as in the derivation of (3.1.19), we obtain

$$e^{-\beta W(\lambda)} = 1 + \frac{N}{V} \int_0^\infty d\zeta \int d\Omega d\vartheta d\varphi [H(\zeta) - 1] \left(\mathbf{u} \left[\frac{\partial \mathbf{R}_{12}(\lambda)}{\partial \vartheta} \frac{\partial \mathbf{R}_{12}(\lambda)}{\partial \varphi} \right] \right) + \dots,$$

where $H(\zeta) = \begin{cases} 0, & \zeta < 0, \\ 1, & \zeta > 0 \end{cases}$ is the Heaviside step function.

In the region $\lambda \leq 0$, the scaled particle becomes point-like, and we arrive at the exact relation $e^{-\beta W(\lambda)} = 1 - \frac{N}{V} \vartheta_{\lambda O+O}$, where $\vartheta_{\lambda O+O} = \int d\Omega d\vartheta d\varphi \times$

$\times \left(\mathbf{u} \left[\frac{\partial \mathbf{R}_{12}(\lambda)}{\partial \vartheta} \frac{\partial \mathbf{R}_{12}(\lambda)}{\partial \varphi} \right] \right) = \lambda^3 v_0 + \lambda^2 s_0 r_0 + \lambda r_0 s_0 + v_0$ represents the volume of the body formed as a result of the rotation of one of the molecules around the scaled particle in such a way, that they are constantly in contact; $\mathbf{r}_{12}(\lambda) = \lambda \mathbf{r}_1 + \mathbf{r}_2$. As a result

$$-\beta W(\lambda) = \ln[1 - \eta(1 + \lambda^3 + 3\alpha\lambda^2 + 3\alpha\lambda)], \quad \lambda \leq 0, \quad (4.2.7)$$

where $\eta = \frac{N}{V} v_0$.

When injecting a particle identical to the others, $W(\lambda = 1) = \mu - \mu_{\text{id}}$, where μ is the chemical potential of the system. It is easy to verify that

$$\mu - \mu_{\text{id}} = \frac{N}{V} \int_0^1 d\xi \int_0^\infty d\zeta \int d\vartheta d\varphi d\Omega u_2(\zeta) F_2(\zeta, \vartheta\varphi\Omega, \xi) \left(\mathbf{u} \left[\frac{\partial \mathbf{R}_{12}}{\partial \vartheta} \times \frac{\partial \mathbf{R}_{12}}{\partial \varphi} \right] \right).$$

As a parameter for incorporating interactions, one can use λ . When $\lambda = 1$, the introduction of a scaled particle consists of two stages. First, a point particle ($\lambda = 0$) is introduced, and then its size is gradually increased from zero to one. Since, according to (4.2.7), for a point particle $-\beta W(\lambda)_{\lambda=0} = \ln(1 - \eta)$, then

$$\begin{aligned} \mu - \mu_{\text{id}} &= -\frac{1}{\beta} \ln(1 - \eta) + \\ &+ \frac{N}{V} \int_0^1 d\lambda \int_0^\infty d\zeta \int d\vartheta d\varphi d\Omega \frac{\partial u_2(\zeta)}{\partial \lambda} F_2(\zeta, \vartheta\varphi\Omega, \lambda) \left(\mathbf{u} \left[\frac{\partial \mathbf{R}_{12}(\lambda)}{\partial \vartheta} \frac{\partial \mathbf{R}_{12}(\lambda)}{\partial \varphi} \right] \right). \end{aligned}$$

Taking into account that

$$\frac{\partial u_2(\zeta)}{\partial \lambda} = -\frac{\partial u_2(\zeta)}{\partial \zeta}(\mathbf{r}_1, \mathbf{u}), \quad \frac{\partial u_2(\zeta)}{\partial \zeta} e^{-\beta u_2(\zeta)} = -\frac{1}{\beta} \delta(\zeta),$$

we have

$$\begin{aligned} \beta(\mu - \mu_{\text{id}}) &= -\ln(1 - \eta) + \frac{N}{V} \int_0^1 d\lambda \int d\vartheta d\varphi d\Omega F_2(0+, \vartheta\varphi\Omega, \lambda) \times \\ &\times \left(\mathbf{r}_1 \left[\frac{\partial \mathbf{r}_{12}(\lambda)}{\partial \vartheta} \frac{\partial \mathbf{r}_{12}(\lambda)}{\partial \varphi} \right] \right). \end{aligned} \quad (4.2.8)$$

It is clear that at injecting a particle of size λ

$$\beta W(\lambda) = \frac{N}{V} \int_0^\lambda d\lambda' \int d\vartheta d\varphi d\Omega F_2(0+, \vartheta\varphi\Omega, \lambda') \left(\mathbf{r}_1 \left[\frac{\partial \mathbf{r}_{12}(\lambda')}{\partial \vartheta} \frac{\partial \mathbf{r}_{12}(\lambda')}{\partial \varphi} \right] \right). \quad (4.2.9)$$

Define the function $G(\lambda)$

$$\begin{aligned} & \int d\vartheta d\varphi d\Omega F_2(0+, \vartheta\varphi\Omega, \lambda) \left(\mathbf{r}_1 \left[\frac{\partial \mathbf{r}_{12}(\lambda)}{\partial \vartheta} \frac{\partial \mathbf{r}_{12}(\lambda)}{\partial \varphi} \right] \right) = \\ & = G(\lambda) \int d\vartheta d\varphi d\Omega \left(\mathbf{r}_1 \left[\frac{\partial \mathbf{r}_{12}(\lambda')}{\partial \vartheta} \frac{\partial \mathbf{r}_{12}(\lambda')}{\partial \varphi} \right] \right) = \\ & = G(\lambda) [3\lambda^2 v_0 + 2\lambda s_0 r_0 + r_0 s_0], \end{aligned} \quad (4.2.10)$$

where $G(\lambda)$ is the orientation-averaged contact value of the pair distribution function of the scaled particle and one of the molecules in the system.

Now, according to (4.2.5) and (4.2.8),

$$\beta \frac{(P - P_{id})}{N} V = \frac{1}{2} \frac{N}{V} G(1) v_{O+O} = \eta(1 + 3\alpha)G(1), \quad (4.2.11)$$

$$\beta(\mu - \mu_{id}) = -\ln(1 - \eta) + 3\eta \int_0^1 d\lambda G(\lambda)(\lambda^2 + 2\alpha\lambda + \alpha), \quad (4.2.12)$$

and thus, the function $G(\lambda)$, defined in the interval $0 \leq \lambda \leq 1$, fully determines the thermodynamic properties of the system.

There exists a unique relationship between the functions $W(\lambda)$ and $G(\lambda)$. According to (4.2.9) and (4.2.10)

$$\beta \frac{\partial W(\lambda)}{\partial \lambda} = 3\eta(\lambda^2 + 2\alpha\lambda + \alpha)G(\lambda), \quad \lambda \geq 0. \quad (4.2.13)$$

Let us now determine the exact relations that these functions satisfy. In the region $\lambda \leq 0$, there exists an exact expression (4.2.7). Due to the continuity of $W(\lambda)$ and its first two derivatives at $\lambda = 0$

$$G(\lambda = 0) = \frac{1}{1 - \eta}, \quad \left(\frac{\partial G(\lambda)}{\partial \lambda} \right)_{\lambda=0} = \frac{3\eta\alpha}{(1 - \eta)^2}. \quad (4.2.14)$$

Another condition follows from the asymptotic behaviour of $G(\lambda)$ as $\lambda \rightarrow \infty$ and equation (4.2.11):

$$\beta \frac{PV}{N} = G(\infty) = 1 + \eta(1 + 3\alpha)G(1). \quad (4.2.15)$$

For $\lambda \geq 1$, T. Boublik [210] proposed an approximation expression

$$G(\lambda) = \beta \frac{PV}{N} + \frac{A\alpha(1 + \lambda)}{\lambda^2 + 2\alpha\lambda + \alpha} + \frac{B\alpha}{\lambda^2 + 2\alpha\lambda + \alpha}, \quad (4.2.16)$$

where, according to (4.2.15)

$$\beta \frac{PV}{N} = \frac{1 + \alpha\eta(2A + B)}{1 - (1 + 3\alpha)\eta}. \quad (4.2.17)$$

Coefficients A and B are found from the conditions (4.2.14)

$$A = -\frac{3\alpha\eta}{(1-\eta)^2} - \frac{6\alpha^2\eta^2}{(1-\eta)^3}, \quad B = \frac{3\alpha^2\eta^2}{(1-\eta)^3},$$

from which it follows

$$G(1) = \frac{1}{1-\eta} + \frac{3\alpha(1+\alpha)}{1+3\alpha} \frac{\eta}{(1-\eta)^2} + \frac{3\alpha^2}{1+3\alpha} \frac{\eta^2}{(1-\eta)^3}, \quad (4.2.18)$$

$$\beta \frac{PV}{N} = \frac{1}{1-\eta} + \frac{3\alpha\eta}{(1-\eta)^2} + \frac{3\alpha^2\eta^2}{(1-\eta)^3}. \quad (4.2.19)$$

According to formula (4.2.12), we obtain the expression for the chemical potential

$$\begin{aligned} \beta(\mu - \mu_{id}) = & -\ln(1-\eta) + (1+6\alpha) \frac{\eta}{1-\eta} + \\ & + \left(\frac{9}{2}\alpha + 3\right) \alpha \frac{\eta^2}{(1-\eta)^2} + \frac{3\alpha^2\eta^3}{(1-\eta)^3}. \end{aligned} \quad (4.2.20)$$

We suggest the reader to independently verify that for $\alpha = 1$, the obtained results coincide with the corresponding expressions for hard spheres found in the previous chapter. When generalizing these results to two-dimensional systems, Boublik [211] assumed

$$G(\alpha) = \beta \frac{PV}{N} + \frac{A\pi\alpha_2}{\alpha_2 + \pi\lambda},$$

where $\alpha_2 = \frac{\pi r_0^2}{s_0}$.

Since $G(\lambda = 0) = \frac{1}{1-\eta_2}$, where $\eta_2 = \frac{N}{V}s_0$, using the condition of continuity of $G(\lambda)$ at $\lambda = 0$ and the asymptotic expression analogous to (4.2.15), we find

$$\beta \frac{PV}{N} = \frac{1 + (\alpha_2 - 1)\eta_2}{(1-\eta_2)^2}, \quad A = -\frac{\alpha_2\eta_2}{(1-\eta_2)^2}. \quad (4.2.21)$$

The results obtained above were also generalized in works [209, 210] for multicomponent systems of hard convex bodies. Let us introduce a multicomponent system of hard convex bodies with a scaling particle congruent to molecules of type a . As in the one-component case, we consider the function $G_{ab}(\lambda)$, which corresponds to the orientation-averaged contact value of the pair distribution function of the scaling particle and a molecule of type b :

$$\begin{aligned} & \int F_{ab}(0+, \vartheta\varphi\Omega, \lambda) \left(\mathbf{r}_a \left[\frac{\partial \mathbf{r}_{ab}(\lambda)}{\partial \vartheta} \frac{\partial \mathbf{r}_{ab}(\lambda)}{\partial \varphi} \right] \right) d\vartheta d\varphi d\Omega = \\ & = G_{ab}(\lambda) \int \left(\mathbf{r}_a \left[\frac{\partial \mathbf{r}_{ab}(\lambda)}{\partial \vartheta} \frac{\partial \mathbf{r}_{ab}(\lambda)}{\partial \varphi} \right] \right) d\vartheta d\varphi d\Omega = \\ & = G_{ab}(\lambda) [3\lambda^2 v_a + 2\lambda s_a r_b + r_a s_b], \end{aligned} \quad (4.2.22)$$

where $\mathbf{r}_{ab}(\lambda) = \lambda \mathbf{r}_a + \mathbf{r}_b$; v_a, s_a, r_a are the quantities characterizing a molecule of type a and are defined according to (4.2.1)⁵. Generalizing expressions (4.2.11) and (4.2.12) to the multicomponent case, we obtain

$$\beta \frac{(P - P_{\text{id}})}{N} V = \frac{1}{6} \sum_{a,b} \frac{N_a N_b}{V^2} [G_{ab}(\lambda = 1)(3v_a + 2s_a r_b + r_a s_b) + G_{ba}(\lambda = 1)(3v_b + 2r_a s_b + s_a r_b)], \quad (4.2.23)$$

$$\begin{aligned} \beta(\mu_a - \mu_a^{\text{id}}) = & -\ln(1 - \eta) + \sum_b \frac{N_b}{V} \int_0^1 d\lambda G_{ab}(\lambda) [3\lambda^2 v_a + \\ & + 2\lambda s_a r_b + r_a s_b] d\lambda, \quad \eta = \sum_a \frac{N_a}{V} v_a. \end{aligned} \quad (4.2.24)$$

For the work of embedding the scaling particle in the region $\lambda \leq 0$, we have the exact relation

$$\beta W_a(\lambda) = -\ln \left(1 - \sum_b \frac{N_b}{V} v_{\lambda a+b} \right), \quad (4.2.25)$$

where $v_{\lambda a+b} = \lambda^3 v_a + \lambda^2 s_a r_b + \lambda r_a s_b + v_b$. For $\lambda \geq 0$

$$\beta W_a(\lambda) = \sum_b \frac{N_b}{V} \int_0^\lambda d\lambda' G_{ab}(\lambda') [3\lambda'^2 v_a + 2\lambda' s_a r_b + r_a s_b]. \quad (4.2.26)$$

From the continuity conditions of the function $W_a(\lambda)$ and its first two derivatives at $\lambda = 0$, we obtain the following exact relations:

$$G_{ab}(\lambda = 0) = \frac{1}{1 - \eta}, \quad \left(\frac{\partial G_{ab}(\lambda)}{\partial \lambda} \right)_{\lambda=0} = \frac{r_a s_m}{(1 - \eta)^2}, \quad (4.2.27)$$

where $s_m = \sum_a \frac{N_a}{V} s_a$.

The other exact relations are derived from the invariance of the expression $F_{ab}(0+, \vartheta \varphi \Omega, \lambda = 1) \left(\mathbf{u} \left[\frac{\partial r_{ab}}{\partial \vartheta} \frac{\partial r_{ab}}{\partial \varphi} \right] \right)$ relative to the permutation of species indices, as well as from the asymptotic behaviour of $G_{ab}(\lambda)$ at $\lambda \rightarrow \infty$: $G_{ab}(\infty) = \beta \frac{P_a V}{N_a}$, where P_a is the partial pressure of component a . Using these relations allows $G_{ab}(\lambda)$ to be determined via a three-parameter interpolation formula of

⁵We hope that the reader will not confuse the mean curvature radius r_a with the radius vector $\mathbf{r}_a$.

the type (4.2.16). Omitting detailed derivations (which are provided in [210]), we present the final results:

$$G_{ab}(\lambda = 1) = A_{ab} + \frac{B_{ab}(s_a r_b + r_a s_b)}{3v_a + 2s_a r_b + r_a s_b} + \frac{C_{ab} r_a s_b}{3v_a + 2s_a r_b + r_a s_b}, \quad (4.2.28)$$

where

$$\begin{aligned} A_{ab} &= \frac{1}{1-\eta} + \frac{s_b(r_m - t_m) + t_b s_m}{(1-\eta)^2} + \frac{1}{3} \frac{s_b q_m s_m}{(1-\eta)^3}; \\ B_{ab} &= -\frac{2s_b(r_m - t_m) + \left(2t_b - \frac{r_a^2 s_b}{r_b s_a}\right) s_m}{(1-\eta)^2} - \frac{2}{3} \frac{s_b q_m s_m}{(1-\eta)^3}; \\ C_{ab} &= \frac{s_b(r_m - t_m) + \left(t_b - \frac{r_a^2 s_b}{r_b s_a}\right) s_m}{(1-\eta)^2} + \frac{1}{3} \frac{s_b q_m s_m}{(1-\eta)^3}; \\ t_a &= 4\pi \frac{r_a^2}{s_a}; \quad q_a = r_a^2; \quad r_m = \sum_a \frac{N_a}{V} r_a; \quad t_m = \sum_a \frac{N_a}{V} t_a; \quad q_m = \sum_a \frac{N_a}{V} q_a. \end{aligned}$$

For the equation of state, according to (4.2.23), we have

$$\beta \frac{PV}{N} = \frac{1}{1-\eta} + \frac{r_m s_m}{\rho(1-\eta)^2} + \frac{q_m s_m^2}{3\rho(1-\eta)^3} \quad (4.2.29)$$

and for the chemical potential, according to (4.2.24)

$$\begin{aligned} \beta(\mu_a - \mu_a^{\text{id}}) &= -\ln(1-\eta) + \frac{r_a s_m + s_a r_m + v_a \rho}{1-\eta} + \\ &+ \frac{r_a^2 s_m^2 + 2v_a s_m r_m}{(1-\eta)^2} + \frac{1}{3} \frac{v_a s_m^2 q_m}{(1-\eta)^3}, \end{aligned} \quad (4.2.30)$$

where $\rho = \sum_a \frac{N_a}{V}$. It is easy to verify that the presented results coincide with the expressions found above for the one-component case, as well as with the results obtained in the previous chapter for a mixture of hard spheres.

For more precise results, one can follow the work [212] and use the Carnahan—Starling approximation (3.1.64). Let us first compare expressions (3.1.27) and (3.1.65) for the contact value of the pair distribution function of hard spheres. Representing expression (3.1.27) in the form $G(1) = \frac{1}{1-\eta} + \frac{3}{2} \frac{\eta}{(1-\eta)^2} + \frac{3}{4} \frac{\eta^2}{(1-\eta)^3}$, we see that it transforms to (3.1.65) provided the last term is multiplied by 2/3. Having verified that this rule also holds for hard convex body mixtures, Boublik extended it to mixtures of hard convex bodies. As a result, $G_{ab}(\lambda = 1)$ again takes the form (4.2.28), but with

the last terms of the coefficients A_{ab}, B_{ab}, C_{ab} multiplied by $2/3$. This form of $G_{ab}(\lambda = 1)$ leads to the equation of state

$$\beta \frac{PV}{N} = \frac{1}{1 - \eta} + \frac{r_m s_m}{\rho(1 - \eta)^2} + \frac{q_m s_m^2}{9\rho} \frac{(3 - \eta)}{(1 - \eta)^3}, \quad (4.2.31)$$

which generalizes the Carnahan—Starling equation to the case of a mixture of hard convex bodies. In the one-component case

$$\beta \frac{PV}{N} = [1 + (3\alpha - 2)\eta + (3\alpha^2 - 3\alpha + 1)\eta^2 - \alpha^2\eta^3](1 - \eta)^{-3}. \quad (4.2.32)$$

Cotter and Martire [213], applying the scaled particle theory to describe hard elongated spherocylinders, used two scaling parameters. One, λ , is associated with the length of the “scaled” spherocylinder, and the other, γ , with its diameter. For the work of insertion $W(\lambda, \gamma)$, in the volume $\lambda \geq 0, \gamma \geq 0$ they used the following interpolation expression

$$\begin{aligned} -\beta W(\lambda, \gamma) = & A + B\gamma + C\lambda + D\gamma\lambda + E\gamma^2 - \\ & - \frac{1}{4}\pi\gamma^2\sigma^2\beta P \left(l\lambda + \frac{2}{3}\sigma\gamma \right), \end{aligned} \quad (4.2.33)$$

where the coefficients are determined from the continuity conditions of the function $W(\lambda, \gamma)$ and its derivatives at the point $\lambda = 0, \gamma = 0$. As a result, they obtained an expression for the equation of state

$$\beta \frac{PV}{N} = \left[1 + \frac{3x^2 - 3x + 2}{3x - 1}\eta + \frac{3x^3 + 3x^2 - 3x + 1}{(3x - 1)^2}\eta^2 \right] (1 - \eta)^{-1}, \quad (4.2.34)$$

where the parameter $x = 1 + l/\sigma$ is related to α via $\alpha = \frac{x(x+1)}{3x+1}$; l is the length of the spherocylinder; σ is its diameter.

Table 10. Equation of state for hard spherocylinders at $x = 3$

η	$\frac{1}{\rho}\beta P$			
	MC	(4.2.19)	(4.2.32)	(4.2.34)
0.30	5.4	5.96	5.77	5.51
0.3474	6.86	8.13	7.8	7.4
0.35	7.17	8.28	7.93	7.51
0.393	8.98	11.11	10.5	9.95
0.40	9.6	11.67	11.0	10.42
0.45	13.0	16.75	15.5	14.67

In Table 10, taken from work [214], formulas (4.2.19), (4.2.32), and (4.2.34) are compared with the results obtained using the Monte Carlo method for spherocylinders at $x = 3$. As seen from the table, the results of equation (4.2.32) are better than those of (4.2.19). However, the best results for this model are given by equation (4.2.34), although its deviation from computational data increases significantly with density, reaching 13% at $\eta = 0.45$.

In recent years, the model of hard elongated spherocylinders has attracted particular attention due to the discovery in this system of a phase transition associated with the emergence of long-range orientational order. This transition was first observed by Onsager for hard rods ($l \rightarrow \infty$, $\sigma \rightarrow 0$, $l^2\sigma = \text{const}$). In works [213, 215, 216], based on the scaled particle method, the equation of state for partially ordered spherocylinders with fixed orientation was considered. In this context, for the introduction of the scaled particle with orientation Ω , the following expression was used ($\lambda \geq 0$, $\gamma \geq 0$)

$$-\beta W(\lambda, \gamma, \Omega) = \frac{Q}{1 + \alpha} + A + B\gamma + C\lambda + D\gamma\lambda + E\gamma^2 - \frac{\pi}{4}\gamma^2\sigma^2\beta P\left(l\lambda + \frac{2}{3}\sigma\gamma\right), \quad (4.2.35)$$

which differs from (4.2.33) by the first term $Q/(l + \alpha)$. The coefficients of this expansion are also determined from the continuity conditions of the function $W(\lambda, \gamma, \Omega)$ and its derivatives but, unlike (4.2.33), depend on the orientation of the molecules. Minimization of the free energy with respect to orientations leads to an integral equation for the unit function $F_1(\Omega)$, which has a trivial solution $F_1(\Omega) = 1$. However, at high densities, a second thermodynamically stable solution appears, corresponding to the ordered phase.

4.2.2. Application of site-site potentials. Reference system approach to interacting sites

Another approach to describing molecular systems relates to the application of site-site potentials. Since any molecule consists of a certain number of atoms bound to each other by chemical bonds, it can be considered as a set of force centres located at the atomic nuclei. In this case, intermolecular interaction is represented as the sum of site-site potentials

$$u_{ab}(\Gamma_1, \Gamma_2) = \sum_{\alpha, \beta} u_{\alpha\beta}(r_{\alpha\beta}), \quad (4.2.36)$$

where summation is carried out over all force centres α , β of interacting molecules of types a and b . The site-site interaction potential $u_{\alpha\beta}(r_{\alpha\beta})$ depends only on the interatomic distances $r_{\alpha\beta} = |\mathbf{R}_{12} + \mathbf{l}_\alpha - \mathbf{l}_\beta|$ where $\mathbf{l}_\alpha$, $\mathbf{l}_\beta$ are the relative coordinates of the force centres (Fig. 15). In addition to atoms, these force centres may also include specific atomic groups or, in the case of molecules with a particular electron density distribution (such as water), additional force centres may be introduced.

The approach based on the application of site-site potentials has been known for a long time [35, 217], and has recently undergone further development in the works of Chandler and his collaborators [218–224] and others. The

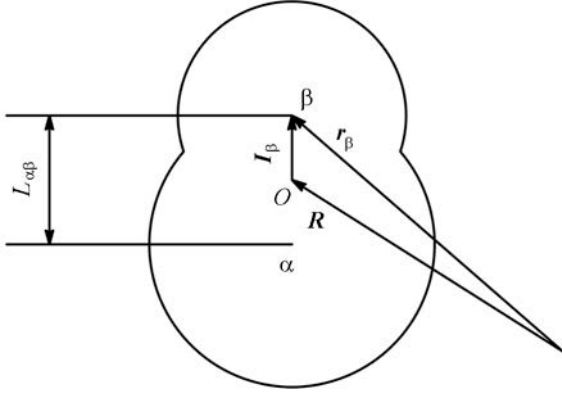


Fig. 15. Schematic representation of the atom-atom interaction model between two molecules. The total intermolecular potential is expressed as the sum over pair atomic potentials $u_{\alpha\beta}(r_{\alpha\beta})$, where $r_{\alpha\beta}$ depends on the relative position vectors of the interaction centres

foundation of these studies lies in the use of site-site distribution functions

$$\begin{aligned} F_{\alpha,\beta}(r_{12}) &= \int d\Gamma_1 d\Gamma_2 F_{ab}(\Gamma_1, \Gamma_2) \delta(\mathbf{r}_\alpha - \mathbf{r}_1) \delta(\mathbf{r}_\beta - \mathbf{r}_2) = \\ &= -\frac{V^2}{\beta} \frac{\delta \ln Q_n}{\delta u_{\alpha\beta}(r_{12})}, \end{aligned} \quad (4.2.37)$$

describing the probability density distribution of the force centres of two different molecules. These functions depend only on the interatomic distances, making them simpler compared to conventional molecular functions $F_{ab}(\Gamma_1, \Gamma_2)$. Moreover, the set of functions $F_{\alpha\beta}(r)$ fully describes all thermodynamic and structural properties of the system.

For simplicity, we will further limit our consideration to a one-component system of rigid molecules, each containing X force centres. In this case, the quantities $\mathbf{l}_\alpha, \mathbf{l}_\beta, \dots$ are characteristic molecular constants, and $d\Gamma = d\mathbf{R}d\Omega$. For $1 \leq n \leq X$ various force centres, one can introduce the intramolecular distribution functions

$$G_{\alpha_1, \dots, \alpha_n}^{(n/X)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \prod_{(1 \leq i < j \leq n)} (1 - \delta_{\alpha_i \alpha_j}) \int d\mathbf{R} d\Omega \prod_{i=1}^n \delta(\mathbf{r}_{\alpha_i} - \mathbf{r}_i), \quad (4.2.38)$$

describing the density distribution of the force centres of a molecule. The Kronecker delta symbols $\delta_{\alpha_i \alpha_j}$ in front indicate that the function $G_{\alpha_1, \dots, \alpha_n}^{(n/X)}$ is nonzero only if all force centres are distinct. For $n = 2$, we obtain the distribution function of two force centres

$$\begin{aligned} G_{12}^{(2/X)}(r_{12}) &= \int d\mathbf{R} d\Omega \delta(\mathbf{R} + \mathbf{l}_1(\Omega) - \mathbf{r}_1) \delta(\mathbf{R} + \mathbf{l}_2(\Omega) - \mathbf{r}_2) = \\ &= \int d\Omega \delta(\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{l}_1(\Omega) + \mathbf{l}_2(\Omega)) = \frac{1}{4\pi L_{12}^2} \delta(r_{12} - L_{12}), \end{aligned} \quad (4.2.39)$$

where $L_{12} = |\mathbf{l}_1 - \mathbf{l}_2|$, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

With the help of the introduced function, we have for an arbitrary function $F(r_{\alpha_1}, \dots, r_{\alpha_n})$

$$\begin{aligned} \int d\mathbf{R} d\Omega F(\mathbf{r}_{\alpha_1}, \dots, \mathbf{r}_{\alpha_n}) &= \int d\mathbf{r}_1 \dots d\mathbf{r}_n \int d\mathbf{R} d\Omega F(\mathbf{r}_{\alpha_1}, \dots, \mathbf{r}_{\alpha_n}) \times \\ &\times \prod_{i=1}^n \delta(\mathbf{R} + \mathbf{l}_{\alpha_i}(\Omega) - \mathbf{r}_i) = \int d\mathbf{r}_1 \dots d\mathbf{r}_n F(\mathbf{r}_1, \dots, \mathbf{r}_n) \times \\ &\times G_{\alpha_1, \dots, \alpha_n}^{(n/X)}(\mathbf{r}_1, \dots, \mathbf{r}_n). \end{aligned} \quad (4.2.40)$$

Representing the Mayer's functions

$$f(R, \Omega_1 \Omega_2) = \exp(-\beta u_2(R, \Omega_1 \Omega_2)) - 1$$

as a series

$$\begin{aligned} f(R, \Omega_1 \Omega_2) &= \prod_{\alpha, \beta} [1 + f_{\alpha\beta}(r)] - 1 = \sum_{\alpha\beta} f_{\alpha\beta}(r) + \\ &+ \frac{1}{2} \sum_{\alpha, \alpha'} \sum_{\beta, \beta'} f_{\alpha\beta}(r) f_{\alpha'\beta'}(r') + \dots, \end{aligned} \quad (4.2.41)$$

substituting them into the Mayer expansion (1.3.13) for $F_2(R, \Omega_1 \Omega_2)$ and then into (4.2.37) for $F_{\alpha\beta}(r)$ while taking (4.2.40) into account, we arrive at the Mayer expansion for site-site distribution functions, expressed as $f_{\alpha\beta}(r) = \exp\{-\beta u_{\alpha\beta}(r)\} - 1$, and intramolecular distribution functions $G_{\alpha_1, \dots, \alpha_n}^{(n/X)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$. For the diagrammatic representation of these expansions, we introduce the following notations. Each line , corresponds to the

Mayer function $f_{\alpha\beta}(r)$, each field vertex $\bullet$ represents the operation $\sum_{\alpha=1}^X \int d\mathbf{r}_\alpha$ and the white vertex corresponds to a fixed force centre. We also introduce complex vertices, which will be associated with intramolecular functions:

$$\text{Diagram of a complex vertex with two shaded lobes labeled alpha and beta} = G_{\alpha\beta}^{(2/X)}(r), \text{Diagram of a complex vertex with three shaded lobes labeled alpha, beta, and gamma} = G_{\alpha\beta\gamma}^{(3/X)}(r_\alpha, r_\beta, r_\gamma), \dots \quad (4.2.42)$$

Each field vertex, including complex ones, from which at least two lines emerge, corresponds to the factor $\rho = N/V$. This factor corresponds to a complex vertex only if it does not contain a single light vertex, i.e., all vertices surrounding it are field vertices.

As a result, for the function $F_{\alpha\beta}(r)$ or its corresponding correlation function $h_{\alpha\beta}(r) = F_{\alpha\beta}(r) - 1$ we arrive at an infinite set of diagrams constructed in all possible ways on the links $f_{\alpha\beta}(r)$, connecting simple and complex vertices

with $n \leq X$ of simple vertices. Two of these simple vertices will be light and correspond to fixed force centres α and β

$$h_{\alpha\beta}(\mathbf{r}) = \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \frac{1}{2} \text{diagram 4} + \text{diagram 5} + \text{diagram 6} + \frac{1}{2} \text{diagram 7} + \frac{1}{2} \text{diagram 8} + \dots \quad (4.2.43)$$

As in the case of monoatomic systems, by excluding diagrams with parallel connections, the distribution function $F_{\alpha\beta}(r)$ can be represented in an exponential form in terms of the mean force potential. Grouping diagrams by the number of nodal vertices, we arrive at the generalized Ornstein–Zernike equation

$$h_{\alpha\beta}(r_{\alpha\beta}) = \sum_{\gamma\lambda} \int d\mathbf{r}_\lambda d\mathbf{r}_\gamma S_{\alpha\gamma}(r_{\alpha\gamma}) c_{\gamma\lambda}(r_{\gamma\lambda}) S_{\lambda\beta}(r_{\lambda\beta}) + \\ + \frac{N}{V} \sum_{\gamma\lambda} \int d\mathbf{r}_\lambda d\mathbf{r}_\gamma S_{\alpha\gamma}(r_{\alpha\gamma}) c_{\gamma\lambda}(r_{\gamma\lambda}) h_{\lambda\beta}(r_{\lambda\beta}), \quad (4.2.44)$$

where $S_{\alpha\gamma}(r) = \delta_{\alpha\gamma}\delta(r) + G_{\alpha\gamma}^{(2/X)}(r)$, $c_{\gamma\lambda}(r)$ is the direct correlation function, which equals the sum of diagrams that do not contain nodal vertices. For monoatomic systems $G_{\alpha\gamma}^{(2/X)}(r) = 0$ and equation (4.2.44) reduces to the usual Ornstein—Zernike equation (1.3.18). Naturally, as in the one-component case, equation (4.2.44) should be considered as the definition of the functions $c_{\alpha\beta}(r)$. The Fourier transform of the function $S_{\alpha\beta}(r)$

$$S_{\alpha\beta}(k) = \int d\mathbf{r} e^{i\mathbf{k}\mathbf{r}} S_{\alpha\beta}(r) = \int d\Omega e^{i\mathbf{k}(\mathbf{l}_\alpha - \mathbf{l}_\beta)} = \frac{\sin(k|\mathbf{r}_\alpha - \mathbf{l}_\beta|)}{k|\mathbf{l}_\alpha - \mathbf{l}_\beta|} \quad (4.2.45)$$

is the internal structural factor of the molecule.

Using the Fourier components

$$h_{\alpha\beta}(k) = \int d\mathbf{r} h_{\alpha\beta}(r) e^{i\mathbf{k}\mathbf{r}}, \quad c_{\alpha\beta}(k) = \int d\mathbf{r} c_{\alpha\beta}(r) e^{i\mathbf{k}\mathbf{r}}$$

the equation (4.2.44) can be represented as

$$\mathbf{h}(k) = \mathbf{S}(k)\mathbf{c}(k)\mathbf{S}(k) + \rho\mathbf{S}(k)\mathbf{c}(k)\mathbf{h}(k), \quad (4.2.46)$$

where the matrices $\mathbf{h}(k)$, $\mathbf{c}(k)$, $\mathbf{S}(k)$ consist of the matrix elements $h_{\alpha\beta}(k)$, $c_{\alpha\beta}(k)$, $S_{\alpha\beta}(k)$, correspondingly. From equation (4.2.46), we find

$$\mathbf{h}(k) = \mathbf{S}(k)\mathbf{c}(k) [1 - \rho\mathbf{S}(k)\mathbf{c}(k)]^{-1} \mathbf{S}(k), \quad (4.2.47)$$

where $(\mathbf{1} - \rho \mathbf{S}(k) \mathbf{c}(k))^{-1}$ is the matrix inverse of $\mathbf{1} - \rho \mathbf{S}(k) \mathbf{c}(k)$.

Let us extend the method of collective variables to systems with site-site interactions. Following the general methodology outlined in Chapter 2, we consider the density of force centres of type α at an arbitrary point $\mathbf{r}$ [218]

$$\rho_\alpha(\mathbf{r}) = \sum_{j=1}^N \delta(\mathbf{r}_j^\alpha - \mathbf{r}).$$

For an isotropic system, the average value of this density is

$$\langle \rho_\alpha(\mathbf{r}) \rangle = \frac{1}{VN} \int (d\mathbf{R})(d\Omega) \rho_\alpha(\mathbf{r}) = \frac{N}{V} = \rho.$$

The operator of the deviation of the density of force centres from its average value is

$$\hat{n}_\alpha(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho.$$

Using the Fourier expansion, we find

$$\hat{n}_\alpha(\mathbf{r}) = \sum_{\mathbf{k}} \frac{\sqrt{N}}{V} \hat{\rho}_\alpha(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}}, \quad k \neq 0 \quad (4.2.48)$$

where $\hat{\rho}_\alpha(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{i\mathbf{k}\mathbf{r}_j^\alpha} - \sqrt{N} \delta_{\mathbf{k},0}$ is the Fourier transform of the operator $\hat{n}_\alpha(\mathbf{r})$, describing the fluctuation of the density of force centres, since $\hat{\rho}_\alpha(\mathbf{k} = 0) = 0$.

Let the interatomic interaction potential be represented as the sum of two terms

$$u_{\alpha\beta}(r) = \varphi_{\alpha\beta}(r) + \Phi_{\alpha\beta}(r), \quad (4.2.49)$$

where $\varphi_{\alpha\beta}(r)$ is its short-range part, and $\Phi_{\alpha\beta}(r)$ is the long-range part. Assuming that the potential $\Phi_{\alpha\beta}(r)$ has a Fourier expansion, we represent the long-range part of the potential energy as an analytical functional

$$v(r) = \frac{1}{2} \sum_{i,j} \sum_{\alpha\beta} (1 - \delta_{\alpha\beta} \delta_{ij}) \Phi_{\alpha\beta}(r_{ij}) = \int (d\rho) v(\rho) J(\rho r), \quad (4.2.50)$$

where

$$v(\rho) = \frac{1}{2} \frac{N}{V} \sum_{\mathbf{k}}' \sum_{\alpha\beta} \nu_{\alpha\beta}(k) [\rho_\alpha(\mathbf{k}) \rho_\beta(-\mathbf{k}) - S_{\alpha\beta}(k)] + \frac{1}{2} \frac{N^2}{V} \sum_{\substack{\alpha,\beta \\ X}} \nu_{\alpha\beta}(\mathbf{k} = 0)$$

is the representation of collective variables; $J(\rho r) = \prod_{\alpha=1}^X \prod_{\mathbf{k}}' \delta(\rho_\alpha(\mathbf{k}) - \hat{\rho}_\alpha(\mathbf{k}))$ is the function of the transformation to collective variables; $(d\rho) = \prod_{\alpha=1}^X \prod_{\mathbf{k}}' d\rho_\alpha(\mathbf{k})$; $\nu_{\alpha\beta}(k) = \int \Phi_{\alpha\beta}(r) e^{i\mathbf{k}\mathbf{r}} d\mathbf{r}$ is the Fourier transform of the long-range potential.

The configuration integral (4.1.1) can now be presented in the form

$$Q_N = \frac{1}{V^N} \int (d\mathbf{R})(d\Omega) e^{-\beta U_0(R, \Omega)} \exp \left\{ -\frac{1}{2} \sum_{\alpha\beta} \frac{N^2}{V} \beta \nu_{\alpha\beta}(k=0) \right\} \times \\ \times \exp \left\{ -\frac{1}{2} \sum'_{\mathbf{k}} \sum_{\alpha\beta} \alpha_{\alpha\beta}(k) [\rho_{\alpha}(\mathbf{k}) \rho_{\beta}(-\mathbf{k}) - S_{\alpha\beta}(k)] \right\} J(\rho r)(d\rho), \quad (4.2.51)$$

where $\alpha_{\alpha}(k) = \beta \frac{N}{V} \nu_{\alpha\beta}(k)$, $U_0(R, \Omega) = \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} (1 - \delta_{\alpha\beta} \delta_{ij}) \varphi_{\alpha\beta}(r_{ij})$ is the short-range part of the potential energy.

As a result of integration in (4.2.51) over $d\mathbf{R}$ and $d\Omega$, we have

$$Q_N = Q_0 \int (d\rho) J_{U_0}(\rho) \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \sum_{\alpha\beta} \alpha_{\alpha\beta}(k) [\rho_{\alpha}(\mathbf{k}) \rho_{\beta}(-\mathbf{k}) - S_{\alpha\beta}(k)] - \right. \\ \left. -\frac{1}{2} \sum_{\alpha\beta} \frac{N^2}{V} \beta \nu_{\alpha\beta}(k=0) \right\}, \quad (4.2.52)$$

where $Q_0 = \frac{1}{V^N} \int (d\mathbf{R})(d\Omega) e^{-\beta U_0(R, \Omega)}$ is the configuration integral for a system with short-range interaction;

$$J_{U_0}(\rho) = \frac{1}{V_N Q_0} \int (d\mathbf{R})(d\Omega) J(\rho R) e^{-\beta U_0(R, \Omega)} \quad (4.2.53)$$

is the Jacobian of the transformation with the weight function $\exp\{-\beta U_0(R)\}$

In the absence of the short-range interactions, $U_0(R) = 0$,

$$Q_N^{(\ell)} = \frac{1}{V^N} \int (d\mathbf{R})(d\Omega) e^{-\beta v(R, \Omega)} = \exp \left\{ -\frac{1}{2} \beta \frac{N^2}{V} \sum_{\alpha\beta} \nu_{\alpha\beta}(0) \right\} \times \\ \times \int (d\rho) J(\rho) \exp \left\{ -\frac{1}{2} \sum_{\alpha\beta} \sum'_{\mathbf{k}} \alpha_{\alpha\beta}(k) [\rho_{\alpha}(\mathbf{k}) \rho_{\beta}(-\mathbf{k}) - S_{\alpha\beta}(k)] \right\}, \quad (4.2.54)$$

where $J(\rho)$ is the usual Jacobian of the transformation, which is represented as

$$J(\rho) = \int (d\omega) \exp \left\{ \sum_{n \geq 2} D_n(\omega) \right\} \exp \left\{ i\pi \sum'_{\mathbf{k}} \sum_{\alpha} \omega_{\alpha}(\mathbf{k}) \rho_{\alpha}(\mathbf{k}) \right\},$$

where

$$(d\omega) = \prod_{\alpha=1}^X \prod'_{\mathbf{k}} d\omega_{\alpha}(\mathbf{k}), \\ D_n(\omega) = \frac{(-i\pi)^n}{n!} \frac{N}{\sqrt{N^n}} \sum_{\substack{\{k_j, \alpha_j\} \\ (1 \leq j \leq n)}} \int d\Omega \prod_{j=1}^n e^{ik_j l_{\alpha_j}(\Omega)} \omega_{\alpha_j}(\mathbf{k}_j) \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0},$$

or, after integration over orientations,

$$D_n(\omega) = \frac{(-i\pi)^n}{n!} \frac{N}{\sqrt{N^n}} \sum_{\substack{\{k_j, \alpha_j\} \\ (l \leq j \leq n)}} S_{\alpha_1, \dots, \alpha_n}(\mathbf{k}_1, \dots, \mathbf{k}_n) \times \\ \times \omega_{\alpha_1}(\mathbf{k}_1) \dots \omega_{\alpha_n}(\mathbf{k}_n) \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0}$$

where $S_{\alpha_1, \dots, \alpha_n}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \int d\Omega \prod_{j=1}^n e^{i\mathbf{k}_j \mathbf{l}_{\alpha_j}(\Omega)}$ are the n -particle intramolecular structure factors. In particular, $D_2(\omega) = -\frac{\pi^2}{2} \sum_{\mathbf{k}} \sum_{\alpha\beta} \omega_{\alpha}(\mathbf{k}) \omega_{\beta}(-\mathbf{k}) S_{\alpha\beta}(k)$, where $S_{\alpha\beta}(\mathbf{k}) = \int d\Omega \exp\{i\mathbf{k}(\mathbf{l}_{\alpha} - \mathbf{l}_{\beta})\} = \sin[k|\mathbf{l}_{\alpha} - \mathbf{l}_{\beta}|]/[k|\mathbf{l}_{\alpha} - \mathbf{l}_{\beta}|]$ is the two-particle structure factor of a molecule.

The calculation of the Jacobian is carried out as in the case of multispecies monoatomic systems. As a result, we arrive at the standard form

$$J(\rho) = \exp \left\{ \sum_{n \geq 3} D_n(\partial/\partial\rho) \right\} J_G(\rho),$$

in which we have

$$J_G(\rho) = \exp \left\{ -\frac{1}{2} \sum'_{\mathbf{k}} \left[\sum_{\alpha, \beta} \rho_{\alpha}(\mathbf{k}) \rho_{\beta}(-\mathbf{k}) [\mathbf{S}^{-1}(k)]_{\alpha\beta} \right] + \ln(\pi \det \mathbf{S}(k)) \right\}, \quad (4.2.55)$$

$$\hat{D}_n(\partial/\partial\rho) = \frac{(-1)^n}{n!} \frac{N}{\sqrt{N^n}} \sum_{\substack{\{k_j, \alpha_j\} \\ l \leq j \leq n}} S_{\alpha_1, \dots, \alpha_n}(\mathbf{k}_1, \dots, \mathbf{k}_n) \times \\ \times \frac{\partial^n}{\partial \rho_{\alpha_1}(\mathbf{k}_1) \dots \partial \rho_{\alpha_n}(\mathbf{k}_n)} \delta_{\mathbf{k}_1, \dots, \mathbf{k}_n, 0},$$

where $\mathbf{S}(k)$ is the matrix consisting of the matrix elements $S_{\alpha\beta}(k)$; $(\mathbf{S}^{-1}(k))_{\alpha\beta}$ are the matrix elements of the matrix inverse of $\mathbf{S}(k)$.

The integration in (4.2.54) over the collective variables is carried out according to the previously described methodology and leads to a cluster expansion

$$Q_N^{(\ell)} = Q_{\text{HTA}}^{(\ell)} Q_{\text{RPA}}^{(\ell)} \exp \left[B_2^{(\ell)} + B_3^{(\ell)} + \dots \right], \quad (4.2.56)$$

where $Q_{\text{HTA}}^{(\ell)} = \exp \left\{ -\beta \frac{N^2}{2V} \sum_{\alpha\beta} \int d\mathbf{r} \Phi_{\alpha\beta}(r) \right\}$ is the high-temperature part of the configuration integral for a system without short-range forces:

$$Q_{\text{RPA}}^{(\ell)} = \exp \left\{ \frac{1}{2} \sum'_{\mathbf{k}} [\text{Sp}(\boldsymbol{\alpha}(k) \mathbf{S}(k)) - \ln \det[1 + \boldsymbol{\alpha}(k) \mathbf{S}(k)]] \right\}, \quad (4.2.57)$$

where the matrix $\boldsymbol{\alpha}(k)$ consists of elements $\alpha_{\alpha\beta}(k)$.

The cluster coefficients $B_2^{(\ell)}, B_3^{(\ell)}, \dots$ have a well-known form (2.2.20), (2.2.21) and are constructed based on the screened potential

$$g(R, \Omega_1 \Omega_2) = -\frac{1}{N} \sum_{\alpha\beta} \sum_{\mathbf{k}} [\boldsymbol{\alpha}(k)(\mathbf{1} + \boldsymbol{\alpha}(k)\mathbf{S}(k))^{-1}]_{\alpha\beta} e^{i\mathbf{k}r_{\alpha\beta}}, \quad (4.2.58)$$

where $[\boldsymbol{\alpha}(k)(\mathbf{1} + \boldsymbol{\alpha}(k)\mathbf{S}(k))^{-1}]_{\alpha\beta}$ is the matrix element for the product of the matrix $\boldsymbol{\alpha}(k)$, and of the matrix inverse of $\mathbf{1} + \boldsymbol{\alpha}(k)\mathbf{S}(k)$.

The consideration of short-range interactions using the method of functional differentiation does not alter the general structure of the expansion (4.2.56) and leads only to the replacement of the virial coefficients in the Boltzmann factors $e^{g(R, \Omega_1, \Omega_2)}$ by $\exp \left[g(R, \Omega_1, \Omega_2) - \beta \sum_{\alpha, \beta} \varphi_{\alpha\beta} \right]$. Using a functional differentiation, we obtain an expression for the distribution function, which also has a known structure. Functional differentiation of the configuration integral with respect to the intermolecular interaction potential, according to (4.2.37), leads to an expression for site-site distribution functions $F_{\alpha\beta}(r)$. Their cluster expansions are constructed based on the site-site screened potential

$$g_{\alpha\beta}(r) = \frac{1}{N} \sum_{\mathbf{k}} \left\{ \frac{\partial \ln \det[\mathbf{1} + \boldsymbol{\alpha}(k)\mathbf{S}(k)]}{\partial \alpha_{\alpha\beta}(k)} - S_{\alpha\beta}(k) \right\} e^{i\mathbf{k}r}, \quad (4.2.59)$$

the expression for which, as can be easily verified, coincides with the solution of equation (4.2.47) if we set $c_{\alpha\beta}(r) = -\beta\Phi_{\alpha\beta}(r)$.

Let us proceed to the basis consideration of short-range interactions. In this case, the Jacobian of the transformation is given by expression (4.2.53). Representing it, as usual, in exponential form

$$J(\rho) = \int (d\omega) \exp \left[\sum_{n \geq 2} D_n(\omega) + \sum_{\alpha} \sum_{\mathbf{k}} i\pi\omega_{\alpha}(\mathbf{k})\rho_{\alpha}(\mathbf{k}) \right],$$

where

$$D_n(\omega) = \frac{1}{n!} (-i\pi)^n \frac{N}{\sqrt{N^n}} \sum_{\substack{\{\mathbf{k}_j, \alpha_j\} \\ 1 \leq j \leq n}} \mathbf{m}_{\alpha_1, \dots, \alpha_n}(\mathbf{k}_1, \dots, \mathbf{k}_n) \omega_{\alpha_1}(\mathbf{k}_1) \dots \omega_{\alpha_n}(\mathbf{k}_n);$$

$\mathbf{m}_{\alpha_1, \dots, \alpha_n}(\mathbf{k}_1, \dots, \mathbf{k}_n)$ is the n -th cumulant, equal to the n -particle atomic structure factor of a molecular system with short-range interactions. In particular, $\mathbf{m}_{\alpha\beta}(k) = S_{\alpha\beta}(k) + \rho h_{\alpha\beta}^0(k)$, where $h_{\alpha\beta}^0(k)$ is the Fourier transform of the correlation function $h_{\alpha\beta}^0(r) = F_{\alpha\beta}^0(r) - 1$.

Further calculation of the configuration integral repeatedly follows the steps we have already performed and ultimately leads to a cluster expansion for the free energy

$$F = F_0 + F_{\text{HTA}} + F_{\text{RPA}} - \frac{1}{\beta} (B_2 + B_3 + \dots), \quad (4.2.60)$$

with F_0 being the free energy for a system with short-range interaction;

$$F_{\text{HTA}} = \frac{1}{2} \frac{N^2}{V} \sum_{\alpha, \beta} \int F_{\alpha\beta}^0(r) \Phi_{\alpha\beta}(r) d\mathbf{r}, \quad (4.2.61)$$

$$F_{\text{RPA}} = -\frac{1}{2\beta} \sum_k \{ \text{Sp}[\boldsymbol{\alpha}(k)\mathbf{m}(k)] - \ln \det[\mathbf{1} + \boldsymbol{\alpha}(k)\mathbf{m}(k)] \}.$$

The matrix $\mathbf{m}(k)$ consists of matrix elements $\mathbf{m}_{\alpha\beta}(k)$; $B_2, B_3, \dots$ are the cluster coefficients, the structure of which was discussed in detail in Chapter 2. For site-site screened potentials, we obtain the expression

$$g_{\alpha\beta}(r) = \frac{1}{N} \sum_{\mathbf{k}} \left[\frac{\partial \ln \det(\mathbf{1} + \boldsymbol{\alpha}(k)\mathbf{m}(k))}{\partial \alpha_{\alpha\beta}(k)} - \mathbf{m}_{\alpha\beta}(k) \right] e^{i\mathbf{k}r}, \quad (4.2.62)$$

which satisfies equation (4.2.47), if in the latter we set $c_{\alpha\beta}(r) = c_{\alpha\beta}^0(r) - \beta \Phi_{\alpha\beta}(r)$, $h_{\alpha\beta}(r) = h_{\alpha\beta}^0(r) + g_{\alpha\beta}(r)$, where $c_{\alpha\beta}^0(r)$ is the direct correlation function of the system with short-range interactions. Under this optimal separation of the interactions, the condition $g_{\alpha\beta}(r) = 0$ holds in the region of short-range interactions. In the particular case where the short-range intermolecular interactions have a central character,

$$\mathbf{m}_{\alpha\beta}(k) = S_{\alpha\beta}(k) + \rho S_{\alpha}(k) S_{\beta}(-k) h_2^0(k), \quad (4.2.63)$$

where $S_{\alpha}(k) = \int d\Omega e^{i\mathbf{k}l_{\alpha}(\Omega)} = \frac{\sin kl_{\alpha}}{kl_{\alpha}}$; $h_2^0(k)$ is the Fourier-image of the correlation function for short-range forces.

To apply the obtained results, it is necessary to know the free energy and the distribution function of the reference system. It is clear that the simplest nontrivial reference model is a system in which atoms interact as hard spheres

$$\varphi_{\alpha\beta}(r) = \begin{cases} 0, & r > \sigma_{\alpha\beta}, \\ \infty, & r < \sigma_{\alpha\beta}, \end{cases} \quad (4.2.64)$$

where $\sigma_{\alpha\beta}$ is the diameter of the sphere for the interaction between the force centre α of one molecule and force centre β of another molecule. A system of molecules with such interactions was named the reference interaction site model (RISM) in works [218, 222]. Although the diameters $\sigma_{\alpha\beta}$ are not necessarily additive, it is usually assumed that $\sigma_{\alpha\beta} = 1/2(\sigma_{\alpha\alpha} + \sigma_{\beta\beta})$, which allows this model to be considered as a system of molecules composed of X hard spheres that may partially overlap but are rigidly connected to each other (see Fig. 15).

In the case of molecules whose shape is close to spherical, their description within the reference model can be reduced to the model of hard spheres with an

effective diameter. To determine this diameter, the condition (3.2.8) is usually used, which in the context of the considered case is written in the form [157]

$$\int \left[\exp \{ -\beta \varphi_2(R, \Omega_1 \Omega_2) \} - \exp \{ -\beta \varphi_2^{(d)}(R) \} \right] y_2^{(d)}(R) d\mathbf{R} d\Omega_1 d\Omega_2 = 0, \quad (4.2.65)$$

where $\varphi_2(R, \Omega_1 \Omega_2) = \sum_{\alpha\beta} \varphi_{\alpha\beta}(r_{\alpha\beta})$ is the short-range interaction potential; $\varphi_2^{(d)}(R)$ is the hard-sphere potential with an effective diameter d ; $y_2^{(d)}(R) = e^{\beta \varphi_2^{(d)}(R)} F_2^{(d)}(R)$; $F_2^{(d)}(R)$ is the hard-sphere distribution function.

The condition (4.2.65) serves as an equation for determining the diameter d . When $y_2^{(d)}(R) = 1$, it satisfies the requirement that molecules and hard spheres occupy the same volume. This leads to a fairly simple estimate of the diameter of hard spheres as $\frac{1}{6}\pi d^3 = v_0$, where v_0 is the volume of a single molecule. In the particular case of a homodimeric molecule composed of two spheres of diameter σ at a distance L , we obtain $v_0 = \frac{1}{6}\pi\sigma^3 \left[1 + \frac{3}{2}L^* - \frac{1}{3}L^{*3} \right]$, from which $d = \sigma \left[1 + \frac{3}{2}L^* - \frac{1}{3}L^{*3} \right]^{1/3}$, $L^* = L/\sigma$. However, for large L and more complex molecules, this approach leads to incorrect results since the entire molecule cannot be considered a hard sphere. Therefore, we describe the reference system in terms of interacting sites. First, we highlight some generic properties of this model.

The pair distribution function $F_{\alpha\beta}(r) = e^{-\beta\varphi_{\alpha\beta}(r)} y_{\alpha\beta}(r)$, same as in the case of hard spheres, has a discontinuity at $r = \sigma_{\alpha\beta}(r)$:

$$F_{\alpha\beta}(r) = \begin{cases} 0, & r < \sigma_{\alpha\beta}, \\ y_{\alpha\beta}(r), & r > \sigma_{\alpha\beta}. \end{cases} \quad (4.2.66)$$

From the continuity of the function $c_{\alpha\beta}(r) - h_{\alpha\beta}(r)$, it follows that the function $c_{\alpha\beta}(r)$ also has a discontinuity at the point $r = \sigma_{\alpha\beta}(r)$, whose magnitude is $y_{\alpha\beta}(\sigma)$.

By definition, the function $y_{\alpha\beta}(r)$ is continuous, but it has kinks associated with the contribution of intramolecular functions (4.2.38). To verify this, let us consider the set of diagrams for the function $y_{\alpha\beta}(r)$, which can be represented as follows

$$I_{\alpha\gamma\beta}(r) = \int d\mathbf{r}' G_{\alpha\gamma}^{(2/X)}(r') f_{\gamma\beta}(|\mathbf{r} - \mathbf{r}'|) J_{\alpha\gamma\beta}(r, |\mathbf{r} - \mathbf{r}'|, r'), \quad (4.2.67)$$

where $f_{\gamma\beta}(r) = \begin{cases} 0, & r > \sigma_{\gamma\beta}, \\ -1, & r < \sigma_{\gamma\beta} \end{cases}$, are the Mayer function, $J_{\alpha\gamma\beta}(r, |\mathbf{r} - \mathbf{r}'|, r')$ is

the set of diagrams forming a continuous function of $r, |\mathbf{r} - \mathbf{r}'|, r'$. By differentiating $I_{\alpha\gamma\beta}(r)$ with respect to r , and accounting for (4.2.39), we see that

the function

$$\begin{aligned} \frac{\partial I_{\alpha\gamma\beta}(r)}{\partial r} = & -\frac{1}{r}I_{\alpha\gamma\beta}(r) + \frac{(1-\delta_{\alpha\gamma})}{2rL_{\alpha\gamma}} \left\{ (r+L_{\alpha\gamma})f_{\gamma\beta}(r+L_{\alpha\gamma}) \times \right. \\ & \times J_{\alpha\gamma\beta}(L_{\alpha\gamma}, r+L_{\alpha\gamma}, r) - (r-L_{\alpha\gamma})f_{\gamma\beta}(|r-L_{\alpha\gamma}|)J_{\alpha\gamma\beta}(L_{\alpha\gamma}, |r-L_{\alpha\gamma}|, r) + \\ & \left. + \int_{|r-L_{\alpha\gamma}|}^{r+L_{\alpha\gamma}} f_{\gamma\alpha}(x) \frac{\partial}{\partial x} [J_{\alpha\gamma\beta}(L_{\alpha\gamma}, x, r)] dx \right\} \end{aligned}$$

has discontinuities at the points $r = |\sigma_{\beta\gamma} \pm L_{\alpha\gamma}|$. Therefore, at these points, both $I_{\alpha\gamma\beta}(r)$, and $y_{\alpha\gamma}(r)$ exhibit cusps. Similarly, one can verify the presence of cusps at $r = |\sigma_{\alpha\gamma} \pm L_{\gamma\beta}|$. In some special cases the function $y_{\alpha\beta}(r)$ may exhibit cusps in other points as well [225].

The pair distribution function $F_{\alpha\beta}(r)$ also exhibits cusps, at least at points $r = \sigma_{\alpha\gamma} + L_{\gamma\beta}$, $\sigma_{\beta\gamma} + L_{\gamma\alpha}$ and $|\sigma_{\alpha\gamma} - L_{\gamma\beta}|$, $|\sigma_{\beta\gamma} - L_{\gamma\alpha}|$, provided these distances exceed $\sigma_{\alpha\beta}$. From the Ornstein–Zernike equation, we conclude that cusps at these points also appear in the direct correlation function $c_{\alpha\beta}(r)$. They arise from terms of the form $\int G_{\alpha\gamma}^{(2/X)}(r')h_{\gamma\beta}(|\mathbf{r} - \mathbf{r}'|)d\mathbf{r}'$. Since $h_{\gamma\beta}(r) = -1$ for $r < \sigma_{\gamma\beta}$, the function $c_{\alpha\beta}(r)$ must necessarily have cusps at $r = |\sigma_{\alpha\gamma} - L_{\gamma\beta}|$, $|\sigma_{\beta\gamma} - L_{\gamma\alpha}|$, if these distances are not larger than $\sigma_{\alpha\beta}$. The presence of cusps in region $r > \sigma_{\alpha\beta}$ is not entirely clear, since in this region the cusps arising from the aforementioned terms may cancel out with the corresponding terms of the function $h_{\alpha\beta}(r)$.

Let us consider two limiting cases: 1. When all $L_{\alpha\beta} \rightarrow \infty$, the intramolecular functions vanish, and the system transforms into an ordinary mixture of hard spheres of X different types with an equal concentration of N/V . 2. When all $L_{\alpha\beta} \rightarrow 0$, the system reduces to a one-component system of hard spheres with diameter σ_{11} and density N/V . In this case, all the Mayer functions $f_{\alpha\beta}(r)$, except for $f_{11}(r)$, are zero, and the correlation functions satisfy the following simple relation $h_{\alpha\beta}(k) = S_{\alpha 1}(k)S_{\beta 1}(k)h_2(k)$, where $h_2(k)$ is the Fourier transform of the correlation function for a system of hard spheres with diameter σ and density N/V . For the direct correlation function, the corresponding expression is $c_{\alpha\beta}(r) = \delta_{\alpha 1}\delta_{\beta 1}c_2(r)$, where $c_2(r)$ is the direct correlation function of the hard sphere system with diameter σ and density N/V .

By analogy with the Percus–Yevick equation for systems with central interactions, following Chandler and Andersen [222], we assume

$$c_{\alpha\beta}(r) = f_{\alpha\beta}(r)y_{\alpha\beta}(r). \quad (4.2.68)$$

For systems with potential (4.2.64), this corresponds to $c_{\alpha\beta}(r) = 0$ for $r > \sigma_{\alpha\beta}$, which, together with the exact relation $F_{\alpha\beta}(r) = 0$ for $r < \sigma_{\alpha\beta}$ closes

the Ornstein–Zernike equation (4.2.44) and thus leads to a set of integral equations for describing the reference model of interacting sites. However, the variational analysis of the approximation (4.2.68) performed by Chandler [219] shows that it neglects an entire class of diagrams. At the same time, the function $y_{\alpha\beta}(r)$ in each order in density takes into account an infinite set of diagrams, which are in fact absent in the exact expansion. Thus, the Chandler–Andersen equation, unlike those previously considered in the description of monoatomic systems, remains inaccurate even at low densities. Nevertheless, the solution to this equation has the following important properties: 1) it leads to discontinuities and cusps in the function $F_{\alpha\beta}(r)$ at the same points as the exact function $F_{\alpha\beta}(r)$; 2) in the limit $L_{\alpha\beta} \rightarrow \infty$, the functions $F_{\alpha\beta}(r)$ coincide with the distribution functions of hard spheres, found in the Percus–Yevick approximation; 3) in the limit $L_{\alpha\beta} \rightarrow 0$, $h_{\alpha\beta}(k) = S_{\alpha 1}(k)S_{\beta 1}(k)h_2^{(\text{PY})}(k)$, where $h_2^{(\text{PY})}(k)$ is the Fourier-component of the pair correlation function of the hard-sphere system in the Percus–Yevick approximation. Thus, the Chandler–Andersen equation leads to correct behaviour of the distribution function in both limiting cases $L_{\alpha\beta} \rightarrow \infty$ and $L_{\alpha\beta} \rightarrow 0$, transforming into the Percus–Yevick equation, which, as is known, is quite precise for a system with strong repulsive interactions. This allows considering approximation (4.2.68) as a successful interpolation formula throughout the entire region $0 < L_{\alpha\beta} < \infty$.

In real systems, the repulsion potential is softer than (4.2.64), resulting in a smoother behaviour of the function $F_{\alpha\beta}(r)$ at points of discontinuity and cusps. To establish a connection between a system with real repulsion and the reference model of interacting sites, we use the Weeks–Chandler–Andersen method, presented in the previous chapter for describing systems with van der Waals interactions. For the hard sphere sizes $d_{\alpha\beta}$, we obtain the set of equations

$$\int d\mathbf{r} B_{\alpha\beta}^{(d)}(r) = 0, \quad (4.2.69)$$

where the function $B_{\alpha\beta}^{(d)}(r) = y_{\alpha\beta}^{(d)}(r)[e^{-\beta\varphi_{\alpha\beta}(r)} - e^{-\beta\varphi_{\alpha\beta}^{(d)}(r)}]$ is non-zero only in the region $|r - d_{\alpha\beta}| \leq \xi d_{\alpha\beta}$, where $e^{-\beta\varphi_{\alpha\beta}(r)} \neq e^{-\beta\varphi_{\alpha\beta}^{(d)}(r)}$. The parameter ξ is a measure of “softness” of a real repulsive potential $\varphi_{\alpha\beta}(r)$. Here, $y_{\alpha\beta}^{(d)}(r)$ is the function $y_{\alpha\beta}(r)$ for the hard-sphere system with the potential $\varphi_{\alpha\beta}^{(d)}(r) =$
 $= \begin{cases} 0, & r > d_{\alpha\beta}, \\ \infty, & r < d_{\alpha\beta}. \end{cases}$ Since $y_{\alpha\beta}^{(d)}(r)$ exhibits cusps, we present it in the form

$$y_{\alpha\beta}^{(d)}(r) = y_{\alpha\beta}^{(c)}(r) + y_{\alpha\beta}^{(s)}(r),$$

where $y_{\alpha\beta}^{(s)}(r)$ is a smooth function for all r , and $y_{\alpha\beta}^{(c)}(r)$ includes cusps present in $y_{\alpha\beta}^{(d)}(r)$. Suppose that $y_{\alpha\beta}^{(d)}(r)$ possesses cusps only in the points $r = |\sigma_{\alpha\gamma} \pm L_{\gamma\beta}|$,

$|\sigma_{\beta\gamma} \pm L_{\gamma\alpha}|$. Then, $y_{\alpha\beta}^{(c)}(r)$ can be represented in the form [225]

$$y_{\alpha\beta}^{(c)}(r) = \sum_{j=1}^X \int d\mathbf{r}' \left\{ A_{\alpha\gamma\beta} G_{\alpha\gamma}^{(2/X)}(r') f_{\gamma\beta}^{(d)}(|\mathbf{r} - \mathbf{r}'|) + A_{\alpha\gamma\beta} f_{\alpha\gamma}(r') G_{\gamma\beta}^{(2/X)}(|\mathbf{r} - \mathbf{r}'|) \right\}, \quad (4.2.70)$$

where $f_{\alpha\beta}^{(d)}(r) = e^{-\beta\varphi_{\alpha\beta}^{(d)}(r)} - 1$. The constants $A_{\alpha\gamma\beta}$ are defined by the relations

$$\lim_{\varepsilon \rightarrow 0} \left\{ y'_{\alpha\beta}{}^{(d)}(L_{\alpha\gamma} + d_{\gamma\beta} + \varepsilon) - y'_{\alpha\beta}{}^{(d)}(L_{\alpha\gamma} + d_{\gamma\beta} - \varepsilon) \right\} = A_{\alpha\gamma\beta} d_{\gamma\beta} [2L_{\alpha\gamma}(L_{\alpha\gamma} + d_{\gamma\beta})]^{-1}, \quad (4.2.71)$$

where $y'_{\alpha\beta}(r) = \frac{\partial}{\partial r} y_{\alpha\beta}(r)$.

Since with this definition of $y_{\alpha\beta}^{(c)}(r)$ the function $y_{\alpha\beta}^{(s)}(r) = y_{\alpha\beta}^{(d)}(r) - y_{\alpha\beta}^{(c)}(r)$ is smooth, just as in monoatomic systems, we set

$$y_{\alpha\beta}^{(s)}(r) = y_{\alpha\beta(d)}^{(s)}(r) + O(\xi^2).$$

As a result, we arrive at the following relationship between the system with real repulsion and the reference model of interacting sites

$$y_{\alpha\beta}(r) = y_{\alpha\beta}^{(c)}(r) + y_{\alpha\beta(d)}^{(s)}(r) + O(\xi^2)$$

or in terms of the distribution functions

$$F_{\alpha\beta}(r) = e^{-\beta\varphi_{\alpha\beta}(r)} \left[y_{\alpha\beta}^{(c)}(r) + y_{\alpha\beta(d)}^{(s)}(r) + O(\xi^2) \right]. \quad (4.2.72)$$

Here, the sizes of the hard spheres are determined by (4.2.69).

Thus, the reference model of interacting sites plays a fundamental role in describing real molecular systems. Therefore, solving the Ornstein–Zernike equation, even in the approximation (4.2.68), remains an important task for this model. In the simplest case of homonuclear molecules consisting of two spheres of diameter d at a distance L , MacInnes and Farquahar [226] transformed the Chandler–Andersen equation in such a way that the functions $c_{\alpha\beta}(r)$ are expressed through the functions $h_{\alpha\beta}(r)$, which are defined only in the interval $(0, \sigma + L)$. However, an analytical solution has not yet been obtained.

In Fig. 16, taken from [227], the functions $F_{11}(r)$ are present, obtained by numerically solving the Chandler–Andersen equation for this simplest model at $L = 0.3\sigma$ and various density values. As expected, the function $F_{11}(r)$ exhibits a discontinuity at $r = \sigma$ and a cusp at $r = \sigma + L$. In the low-density region, initially $F_{11}(\sigma+) < F_{11}(\sigma + L)$, but with increasing density, the value

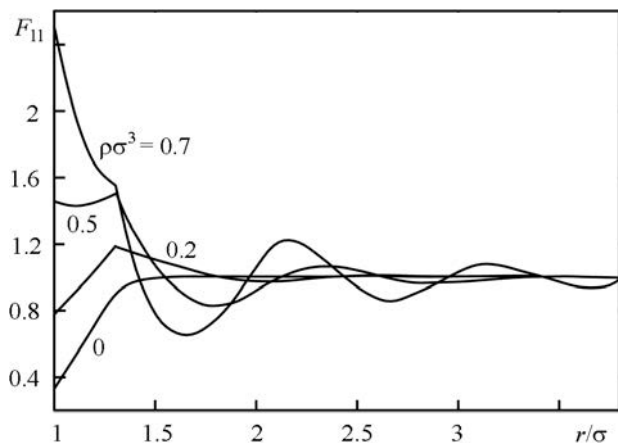


Fig. 16. Radial distribution function $F_{11}(r)$ obtained by numerically solving the Chandler–Andersen equation for a simple model with $L = 0.3\sigma$ at different densities

of $F_{11}(\sigma+)$ grows faster than $F_{11}(\sigma + L)$, indicating the orientational ordering of molecules due to their geometric shape. With increasing density, the function $F_{11}(r)$ acquires a more pronounced oscillatory character, associated with the emergence of short-range order in the system. Comparison of the distribution functions of diatomic systems (Fig. 16) with the corresponding curves for monoatomic systems (Fig. 3) indicates a significant difference in their structure. A study conducted in [223] comparing theoretical results with computer simulation data shows that the Chandler–Andersen approximation yields sufficiently accurate results. A slight deviation is observed only in the region of the first maximum of the pair distribution function.

In work [228], results obtained using the approximation (4.2.68) for RISM were applied to describe structure factors of various molecular liquids. If all interacting sites coincide with the molecular nuclei, the molecular structure factor, obtained from neutron scattering, is

$$\mathbf{m}_2(k) = \left(\sum_{\alpha=1}^X b_{\alpha}^2 \right)^{-1} \sum_{\alpha,\beta} b_{\alpha} b_{\beta} [S_{\alpha\beta}(k) + \rho h_{\alpha\beta}(k)], \quad (4.2.73)$$

where b_{α} is the amplitude of coherent neutron scattering on the nucleus α . In X -ray experiments, b_{α} is replaced by $f_{\alpha}(k)$, the average amplitude of X -ray scattering by the atom α . Quantities b_{α} and $f_{\alpha}(k)$ are tabulated in the relevant literature. Comparison of theoretical and experimental curves shows that for the considered liquids, the primary contribution to molecular structure factors comes from short-range interactions.

Up to this point, we have assumed that molecules are completely rigid. Of course, this requirement does not always correspond to reality. Nevertheless, as recently demonstrated by Chandler and Pratt [224], a molecular system

should be considered as an assembly of atoms, between which chemical bonds may form.

Consider, for example, a diatomic molecule AB. Its intramolecular function

$$\frac{1}{V}G_{AB}(r_{12}) = (1 - \delta_{AB})\langle\delta(\mathbf{r}_1 - \mathbf{r}_A)\delta(\mathbf{r}_2 - \mathbf{r}_B)\rangle,$$

where averaging is carried out over all configurations of the system. In this case

$$\frac{1}{V}\int G_{AB}(r)d\mathbf{r} = 1. \quad (4.2.74)$$

Since chemical reactions may occur in the system, resulting in the total number of particles not being conserved, its description should be carried out within the grand canonical ensemble. The general scheme for describing the grand canonical ensemble will be considered in the next chapter. Using relation (5.1.17), we represent the function $G_{AB}(r)$ in the form

$$G_{AB}(r) = \frac{\rho_A\rho_B}{\rho_{AB}}q_A^{AB}q_B^{AB}\frac{1}{\nu_{AB}}b_{AB}(r)y_{AB}(r), \quad (4.2.75)$$

where ρ_A , ρ_B , ρ_{AB} are the densities of atoms A, B and that of molecule AB, correspondingly; ν_{AB} is the symmetry index of a molecule; $b_{AB}(r) = \exp\{-\beta u_{AB}(r)\}$ is the Boltzmann factor, describing the chemical bond between atoms A and B in the molecule AB. The function $y_{AB}(r)$ represents the set of diagrams $G_{AB}(r)$ describing the indirect interaction of atoms A and B in the molecule AB via the other particles in the system. It is clear that if all particles are hard spheres $y_2(r) = F_2(r)e^{\beta\varphi_2(r)}$, where $\varphi_2(r)$ is the hard spheres potential; $F_2(r)$ is the corresponding pair distribution function. The quantities q_A^{AB} and q_B^{AB} take into account the fact that the forces of interatomic interaction generally depend on the type of molecule to which a given atom belongs. In the spatially inhomogeneous case, q_A^{AB} , for example, is determined by the ratio of the singlet distribution function of atom A in molecule AB to the unary function of a free atom A. For a system of hard spheres $q_A^{AB} = \exp[-\beta(W_A(AB) - W_A(A))]$, where $W_A(AB)$ is the free energy of cavity formation for an atom A of the molecule AB; $W_A(A)$ is the free energy of cavity formation for a free atom A. If their sizes are identical, then $q_A^{AB} = 1$.

From the normalisation conditions (4.2.74) and (4.2.75), we have

$$\frac{\rho_A\rho_B}{\rho_{AB}} = K = \frac{q_A^{AB}q_B^{AB}}{\nu_{AB}}\int d\mathbf{r}b_{AB}(r)y_{AB}(r). \quad (4.2.76)$$

The quantity K is the chemical equilibrium constant for the reaction $A + B \rightleftharpoons AB$. Substituting (4.2.76) into (4.2.75), we find

$$G_{AB}(r) = b_{AB}(r)y_{AB}(r)\left[\int d\mathbf{r}b_{AB}(r)y_{AB}(r)\right]^{-1}. \quad (4.2.77)$$

For rigid molecules, due to the continuity of $y_{AB}(r)$, expression (4.2.77) for $G_{AB}(r)$ coincides with (4.2.39).

The results (4.2.75)–(4.2.77) are easily generalized to the case of more complex molecules. It is important to note the significant role of intramolecular distribution functions in describing the changes in molecular structure under environmental influences. For example, using the formula $r_{AB} = \int G_{AB}(r)r d\mathbf{r}$ one can determine the average bond length of molecule AB, etc. A number of specific examples of the practical application of the obtained results were demonstrated in work [224].

4.3. Systems with electrostatic interactions

An important place among molecular systems is occupied by systems with electrostatic interactions. Of particular interest are polar molecules. The dipole-dipole nature of their interaction leads to long-range orientational correlations, which are closely related to the dielectric properties of the system.

4.3.1. Application of the collective variables method

The electrostatic interaction potential of two molecules, whose centres of mass are at a distance R_{12} , is given by

$$\Phi_{ab}(R_{12}, \Omega_1, \Omega_2) = \int \frac{\rho_a(l_1)\rho_b(l_2)}{|R_{12} + \mathbf{l}_1 - \mathbf{l}_2|} d\mathbf{l}_1 d\mathbf{l}_2, \quad (4.3.1)$$

where $\rho_a(l_1)$, $\rho_b(l_2)$ are the charge density of the spatial distribution of molecules of type a and b , respectively; l_1 and l_2 are their relative coordinates.

The charge density at an arbitrary point $\mathbf{R}$ is

$$\rho(\mathbf{R}) = \sum_{a=1}^M \sum_{j=1}^{N_a} \int \rho_a(l_j) \delta(\mathbf{R}_j + \mathbf{l}_j - \mathbf{R}) d\mathbf{l}_j = \sum_{a=1}^M \sum_{j=1}^{N_a} Q_a(\nabla) \delta(\mathbf{R} - \mathbf{R}_j), \quad (4.3.2)$$

where $Q_a(\nabla) = \int \rho_a(l) e^{i\mathbf{l}\cdot\nabla} d\mathbf{l}$ is the generalized charge of particles of type a .

Using generalized charges, the potential (4.3.1) can be represented as (see Section 1.2 in Chapter 1)

$$\Phi_{ab}(R, \Omega_1 \Omega_2) = Q_a(\nabla) Q_b(-\nabla) \frac{1}{R}. \quad (4.3.3)$$

Recall that the expansion of the exponent in $Q_a(\nabla)$ leads to a multipole expansion

$$Q_a(\nabla) = p_a^{(0)} - \mathbf{p}_a^{(1)} \cdot \nabla + \frac{1}{3} p_a^{(2)} : \widehat{\nabla \nabla} + \dots, \quad (4.3.4)$$

where the zeros moment $p_a^{(0)} = \int \rho_a(l) d\mathbf{l} = ez_a$ is the full ion charge and is equal to zero for molecules; other quantities $\mathbf{p}_a^{(n)} = \int \rho_a(l) l^n d\mathbf{l}$ are 2^n -pole moments. Expanding the Coulomb potential into a Fourier series, we obtain

$$\Phi_{ab}(R, \Omega_1 \Omega_2) = \sum_{\mathbf{k}} \frac{4\pi}{V} \frac{Q_a(\mathbf{k}) Q_b(-\mathbf{k})}{k^2} e^{i\mathbf{k}\mathbf{R}}, \quad (4.3.5)$$

where

$$Q_a(\mathbf{k}) = \int \rho_a(l) e^{i\mathbf{k}\mathbf{l}} d\mathbf{l} = \rho_a(\mathbf{k}) = p_a^{(0)} + i(\mathbf{p}_a^{(1)} \mathbf{k}) + \dots \quad (4.3.6)$$

are Fourier components of the generalized charge, which, as we can see, coincide with the Fourier transforms of the charge distribution of the molecule.

For the electrostatic part of the potential energy, according to (4.3.5), we have

$$\begin{aligned} v(R, \Omega) &= \sum_{a,b} \sum_{i < j} \Phi_{ab}(R_{ij} \Omega_i \Omega_j) = \frac{1}{2\beta} \sum_{\mathbf{k}} \alpha(k) (\hat{\rho}_{\mathbf{k}} \rho_{-\mathbf{k}} - 1) + \\ &+ \frac{1}{2} \sum_{a,b} \sum_{i \neq j} \frac{1}{V} \int d\mathbf{R}_{ij} \Phi_{ab}(R_{ij} \Omega_i \Omega_j), \end{aligned}$$

where

$$\begin{aligned} \hat{\rho}_{\mathbf{k}} &= \sum_{a,j} \lambda_a(k) e^{i\mathbf{k}\mathbf{R}_j} \quad (k \neq 0), \quad \lambda_a(k) = \frac{Q_a(k)}{(\sum_a N_a |Q_a(k)|^2)^{1/2}}, \\ \alpha(k) &= \frac{4\pi}{k^2} \beta \sum_a \frac{N_a}{V} |Q_a(k)|^2. \end{aligned} \quad (4.3.7)$$

At the same time

$$\begin{aligned} \alpha(k) &= \frac{4\pi}{k^2} \beta \sum_a \frac{N_a}{V} \int d\Omega_a |Q_a(k)|^2, \\ v(\mathbf{k} = 0) &= \frac{1}{2} \sum_{a,b} \sum_{i \neq j} \frac{1}{V} \int \Phi_{ab}(R_{ij}, \Omega_i \Omega_j) d\mathbf{R}_{ij} = \\ &= \sum_{a,b} \frac{N_a N_b}{2V} \int \Phi_{ab}(R, \Omega_1 \Omega_2) d\mathbf{R} d\Omega_1 d\Omega_2 \end{aligned} \quad (4.3.8)$$

due to the orientational invariance of the system. Using the transformation function to collective variables $J(\rho R) = \prod_{\mathbf{k}} \delta(\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}})$ we represent the electrostatic part of the configuration integral in the form

$$\begin{aligned} Q_N^{(\ell)} &= \frac{1}{V^N} \int (d\mathbf{R}) (d\Omega) e^{-\beta v(R, \Omega)} = \\ &= \int (d\rho) (d\Omega) \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}}' \alpha(k) [\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1] \right\} \exp \{ -\beta v(\mathbf{k} = 0) \} J(\rho), \end{aligned}$$

where the Jacobian

$$J(\rho) = \frac{1}{V^N} \int (d\mathbf{R}) J(\rho R) = \exp \left[\sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right] \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \ln \pi \right],$$

$$\hat{D}_n(\partial/\partial\rho) = \frac{(-1)^n}{n!} \sum_a N_a \sum_{\substack{\{\mathbf{k}_s\} \\ 1 \leq s \leq n}} \prod_{s=1}^n \lambda_a(\mathbf{k}_s) \frac{\partial^n}{\partial \rho_{\mathbf{k}_s}} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0}.$$

The calculation of $Q_N^{(\ell)}$ follows the same scheme as in the case of ionic systems (see Section 3.4 in Chapter 3) and leads to similar results, except that now each field vertex corresponds to the operation $\sum_a \frac{N_a}{V} \int d\mathbf{R} d\Omega$, and the screened potentials

$$g_{ab}(R, \Omega_1 \Omega_2) = - \sum_{\mathbf{k}} \lambda_a(\mathbf{k}) \lambda_b(-\mathbf{k}) \frac{\alpha(k)}{1 + \alpha(k)} e^{i\mathbf{k}\mathbf{R}} =$$

$$= -\beta Q_a(\nabla) Q_b(\nabla) \sum_{\mathbf{k}} \frac{4\pi}{V k^2} \left[1 + \beta \frac{4\pi}{k^2} \sum_a \frac{N_a}{V} \int |Q_a(\mathbf{k})|^2 d\Omega \right]^{-1} e^{i\mathbf{k}\mathbf{R}}. \quad (4.3.9)$$

Using the expansion (4.3.4) for generalized charges, we see that the screening of different interactions occurs differently. While ionic screening leads to the replacement of the Coulomb potential $1/R$ with the Debye potential $1/Re^{-\varkappa R}$, where $\varkappa$ is the inverse Debye length, dipole screening does not change the form of the potential, and only causes the appearance of a multiplicative factor

$$\varepsilon = 1 + 4\pi\beta \sum_a \frac{N_a}{V} \int \frac{1}{k^2} (\mathbf{p}_a^{(1)} \mathbf{k})^2 d\Omega = 1 + 3y \quad (4.3.10)$$

having the meaning of dielectric permittivity; $y = \frac{4}{3}\pi \sum_a \frac{N_a}{V} \chi_a$; $\chi_a = \frac{1}{3}\beta(p_a^{(1)})$ are the orientational polarisability of dipolar molecules.

The averaging in (4.3.10) is carried out over the ideal distribution, taking into account internal degrees of freedom

$$\chi_a = \beta \frac{1}{\text{Sp}[e^{-\beta E_a}]} \frac{1}{k^2} \text{Sp} \left[(\mathbf{p}_a^{(1)} \mathbf{k})^2 e^{-\beta E_a} \right], \quad (4.3.11)$$

where E_a is the energy of a molecule of type a . Thus, assuming that $|\mathbf{p}_a^{(1)}| = p_a^{(1)} + \left(\frac{\partial p_a^{(1)}}{\partial \xi} \right)_{\xi=0} \xi$, where $\mathbf{p}_a^{(1)}$ is the equilibrium value of the dipole moment, ξ is its displacement from the equilibrium value, in the harmonic oscillator

approximation with frequency ω_a for diatomic molecules, we obtain

$$\begin{aligned}\chi_a &= \frac{1}{k^2} \beta \frac{\int (\mathbf{p}_a^{(1)} \cdot \mathbf{k})^2 \exp \left\{ -\frac{1}{2} \beta \mu_a \omega_a^2 \xi^2 \right\} (r_a + \xi)^2 d\Omega d\xi}{\int \exp \left\{ -\frac{1}{2} \beta \mu_a \omega_a^2 \xi^2 \right\} (r_a + \xi)^2 d\Omega d\xi} = \\ &= \frac{1}{3} \beta (p_a^{(1)})^2 + \frac{2}{3} \frac{(p_a^{(1)})^2}{J_a \omega_a^2 + \beta^{-1}} + \left(\frac{\partial p_a^{(1)}}{\partial \xi} \right)_{\xi=0} (\mu_a \omega_a^2)^{-1},\end{aligned}\quad (4.3.12)$$

where μ_a is the reduced mass of the molecule; r_a is the equilibrium internuclear distance, and $J_a = \mu_a r_a^2$. The two additional terms present here correspond to the polarisability due to dipole moment oscillations and the polarisability of the molecule as an oscillator [229, 230].

Quadrupole screening leads to the formation of a quadrupole packet $\frac{1}{R}[1 - e^{-R/q}]$, whose radius is $q = \left[\frac{1}{45} 4\pi\beta \sum_a \frac{N_a}{V} (\mathbf{p}_a^{(2)} : \mathbf{p}_a^{(2)}) \right]^{1/2}$. Considering the entire multipole series (4.3.4) results in the emergence of a dielectric function

$$\varepsilon(k) = 1 + 4\pi\beta \frac{1}{k^2} \sum_a \frac{N_a}{V} \int Q_a(\mathbf{k}) Q_a(-\mathbf{k}) d\Omega, \quad (4.3.13)$$

which for $k = 0$ (large distances) coincides with expression (4.3.10), and for large k (small distances) equals unity.

However, it should be noted that the discussed results are mainly of a qualitative nature, since the molecular orientations were not accounted for strictly enough in obtaining the screened potential (4.3.9). Indeed, in (4.3.3), the molecular orientations are defined with respect to the axis $\mathbf{R}$. However, as noted at the beginning of the chapter, to accurately account for orientations, it is necessary to separate the orientation of molecules from the orientation of their axes. To this end, we pass from the expansion (4.3.3) to the equivalent expansion given in [35]

$$\Phi_{ab}(R, \Omega_1 \Omega_2) = \sum_{mn\mu} \frac{(-1)^{n+\mu} (m+n)! \mathbf{m}_a^{(m\mu)} \mathbf{m}_b^{*(n\mu)}}{\sqrt{(n-\mu)! (n+\mu)! (m-\mu)! (m+\mu)!}} \frac{1}{R^{m+n+1}}, \quad (4.3.14)$$

where $\mathbf{m}_a^{(m\mu)} = \int l^m \rho_a(l, \vartheta, \varphi) D_{0\mu}^m(\Omega') l^2 dl d\Omega'$, are the elements of the tensor of the $2m$ -pole moment $\mathbf{p}_a^{(m)}$, $\Omega' = (\vartheta, \varphi)$. In particular, the charge of the ion $p_a^{(0)} = ez_a = \mathbf{m}_a^{(0,0)}$, and the components of the dipole moment

$$\begin{aligned}\mathbf{p}_{a,z}^{(1)} &= \mathbf{m}_a^{(1,0)}, \quad \mathbf{p}_{a,x}^{(1)} = \frac{1}{2} \left[\mathbf{m}_a^{(1,1)} + \mathbf{m}_a^{(1,-1)} \right], \\ \mathbf{p}_{a,y}^{(1)} &= \frac{1}{2i} \left[\mathbf{m}_a^{(1,1)} - \mathbf{m}_a^{(1,-1)} \right] \text{ etc.}\end{aligned}$$

At small distances, the expansion (4.3.14) is invalid. Nevertheless, due to the presence of short-range interactions of a strongly repulsive nature, in the region $R < \sigma_{ab}$ we can assume $\Phi_{ab}(R, \Omega_1 \Omega_2) = 0$, where σ_{ab} are the effective sizes of the interacting particles.

The separation of orientations is carried out according to formula (4.1.14), leading to the components of the multipole moments $p_a^{(m,\mu)}(\Omega) = \int l^m \times \rho_a(l, \Omega) D_{\nu 0}^m(\Omega) l^2 dl d\Omega$, expressed relative to a fixed reference system for orientation. The molecular orientations are explicitly singled out using relation (4.1.28). By applying (4.1.35) and noting that

$$\frac{l! (-1)^n}{\sqrt{(n+\mu)! (n-\mu)! (m+\mu)! (m-\mu)!}} = \sqrt{\frac{(2l+1)!}{(2m)! (2n)!}} \begin{pmatrix} m & n & l \\ \mu & -\mu & 0 \end{pmatrix},$$

we represent expression (4.3.14) in an invariant form

$$\Phi_{ab}(R, \Omega_1, \Omega_2) = \sum_{\substack{mnl \\ \mu\nu}} \frac{1}{R^{l+1}} u_{\mu\nu,ab}^{mnl} \hat{\Psi}_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_R), \quad (4.3.15)$$

where

$$u_{\mu\nu,ab}^{mnl} = (-1)^m \sqrt{\frac{(2l+1)!}{(2m+1)! (2n+1)!}} p_a^{(m\nu)} p_b^{*(n\nu)} \delta_{m+n,l}, \quad (4.3.16)$$

$$\begin{aligned} \hat{\Psi}_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_R) &= \sqrt{(2m+1)(2n+1)} \sum_{\mu'\nu'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda \end{pmatrix} \times \\ &\times D_{\mu'\mu}^m(\Omega_1) D_{\nu'\nu}^n(\Omega_2) D_{\lambda 0}^l(\Omega_R). \end{aligned}$$

Now, to describe the system, we use the methodology developed at the beginning of this chapter. To simplify the derivations, we will further consider a one-component system. Expanding the electrostatic potential into a Fourier series, according to (4.1.34), we obtain

$$\Phi_2(R, \Omega_1 \Omega_2) = \sum_{\mathbf{k}} \sum_{\substack{mnl \\ \mu\nu}} \frac{1}{V} e^{i\mathbf{k}\mathbf{R}} \hat{\Phi}_{\mu\nu}^{mnl}(\mathbf{k}) \hat{\Psi}_{\mu\nu}^{mnl}(\Omega_1 \Omega_2 \Omega_{\mathbf{k}}), \quad (4.3.17)$$

where

$$\hat{\Phi}_{\mu\nu}^{mnl}(\mathbf{k}) = 4\pi i^l u_{\mu\nu}^{mnl} \int_{\sigma}^{\infty} j_l(kR) \frac{1}{R^{l+1}} R^2 dR = 4\pi i^l u_{\mu\nu}^{mnl} \frac{k^l}{k^2} \frac{j_{l-1}(k\sigma)}{(k\sigma)^{l-1}},$$

In the limit of point multipoles $\sigma \rightarrow 0$ and $\hat{\Phi}_{\mu\nu}^{mnl}(\mathbf{k}) = 4\pi i^l u_{\mu\nu}^{mnl} \frac{k^l}{k^2} \frac{1}{(2l-1)!!}$ for $l > 0$ and $\Phi_{00}^{000}(\mathbf{k}) = \frac{4\pi}{k^2} (p^{(0)})^2$ for the Coulomb potential.

Calculation of the electrostatic part of configuration integral is carried out using the methodology presented in Subsection 4 and leads to the cluster expansion (4.1.46), constructed based on the screened potential, which, according to (4.1.48) and (4.1.49), is given by [231]

$$g(R, \Omega_1 \Omega_2) = \sum_{mn\mu} g^{(mn\mu)}(R) \lambda^{(m\mu)} \lambda^{*(n\mu)}, \quad (4.3.18)$$

where

$$g^{(mn\mu)}(R) = \sum_l i^l (2l+1) \begin{pmatrix} m & n & l \\ \mu & -\mu & 0 \end{pmatrix} \sum_{\lambda} \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} \times \\ \times \frac{V}{2\pi^2} \int_0^\infty j_l(kR) k^2 dk \left[\frac{\partial \ln \det(\mathbf{1} + \tilde{\alpha}(k))}{\partial \tilde{\alpha}(k, m, n, \lambda)} - \delta_{m,n} \right], \quad (4.3.19)$$

the matrix $\tilde{\alpha}(k)$ consists of elements

$$\tilde{\alpha}(k, m, n, \lambda) = 4\pi\beta \frac{N}{V} (-1)^{n+\lambda} \frac{(ki)^{m+n}}{k^2} \frac{j_{m+n-1}(k\sigma)}{(k\sigma)^{m+n-1}} \times \\ \times \frac{(m+n)!}{\sqrt{(m-\lambda)! (m+\lambda)! (n-\lambda)! (n+\lambda)!}} \frac{\sqrt{(p^{(m)} [m] p^{(m)})}}{(2m+1)} \frac{\sqrt{(p^{(n)} [n] p^{(n)})}}{(2n+1)}, \\ \lambda^{(n\mu)} = p^{(n\mu)} \left[\sum_{i,\nu} p^{(n\nu)} p^{*(n\nu)} \right]^{-1/2} \text{ are the dimensionless components of the } 2^n\text{-} \\ \text{pole moment. By definition, } \sum_{\nu} p^{(n\nu)} p^{*(n\nu)} = \left(\mathbf{p}^{(n)} [n] \mathbf{p}^{(n)} \right), \text{ where } [n] \text{ is the} \\ \text{tensor convolution.}$$

For a system of point ions and dipoles ($\sigma \rightarrow 0$):

$$\alpha(k, 00\lambda) = \frac{\varkappa^2}{k^2}, \quad \alpha(k, 11\lambda) = \frac{(-1)^\lambda}{(1-\lambda)!(1+\lambda)!} 2y, \quad y = \frac{4}{9}\pi \frac{N}{V} \beta \left(p^{(1)} \right)^2, \\ \alpha(k, 10\lambda) = -\alpha(k, 01\lambda) = i\sqrt{\frac{3}{2}} \alpha(k, 00\lambda) \alpha(k, 11\lambda).$$

After substituting them into (4.3.18) and (4.3.19), we arrive at the following expressions for potentials screened only by dipoles:

$$g^{(0,0)}(R) = -\lambda_1^{(0,0)} \lambda_2^{(0,0)} \frac{V}{2\pi^2} \int_0^\infty j_0(kR) k^2 dk \times \\ \times \frac{\alpha(k, 000) + \alpha(k, 000)\alpha(k, 110) - \alpha(k, 100)\alpha(k, 010)}{1 + \alpha(k, 110)} = \\ = -\beta e^2 \frac{z_1 z_2}{\varepsilon R}. \quad (4.3.20)$$

for ion-ion interaction;

$$\begin{aligned}
 g^{(1,0)}(R) &= -i \sum_{\mu} \lambda_1^{(00)} \lambda_2^{*(1\mu)} \frac{V}{2\pi^2} \int_0^{\infty} j_1(kR) k^2 dk \frac{\alpha(k, 010)}{1 + \alpha(k, 110)} = \\
 &= \beta e z_1 (\mathbf{p}_{\text{ef}} \nabla) \frac{1}{\varepsilon R}.
 \end{aligned} \tag{4.3.21}$$

for ion-dipole interaction;

$$\begin{aligned}
 g^{(1,1)}(R) &= 3 \sum_{\mu} \lambda_1^{(1\mu)} \lambda_2^{*(1\mu)} \begin{pmatrix} 1 & 1 & 2 \\ \mu & -\mu & 0 \end{pmatrix} \sum_{\lambda} \begin{pmatrix} 1 & 1 & 2 \\ \lambda & -\lambda & 0 \end{pmatrix} \frac{V}{2\pi^2} \int_0^{\infty} j_2(kR) \times \\
 &\times k^2 dk \frac{\alpha(k, 11\lambda)}{1 + \alpha(k, 11\lambda)} = \beta (\mathbf{p}_{\text{ef}} \nabla) (\mathbf{p}_{\text{ef}} \nabla) \frac{1}{\varepsilon R}.
 \end{aligned} \tag{4.3.22}$$

for dipole-dipole interaction.

Thus, by precisely accounting for orientations, as before, dipole screening leads to the emergence of dielectric permittivity. For the latter, instead of (4.3.10), we have the expression:

$$\varepsilon = \frac{1 + 2y}{1 - y} \quad \text{or} \quad \frac{\varepsilon - 1}{\varepsilon + 2} = y, \tag{4.3.23}$$

which is exactly the same as the well-known Clausius—Mossotti formula [35, 232]. Moreover, as a result of screening, the dipole moment of the molecule is replaced by an effective value, equal to⁶

$$p_{\text{ef}} = \frac{\varepsilon - 1}{3y} p^{(1)} = \frac{p^{(1)}}{1 - y}. \tag{4.3.24}$$

The inclusion of higher multipole moments also does not alter the previously drawn conclusions about the nature of screening, although the values of the higher multipole moments are replaced by their effective values.

4.3.2. Screened potentials in the reference system approach to short-range interactions

For molecular systems, the non-electrostatic part of the potential, $\varphi_2(R, \Omega_1, \Omega_2)$, likewise $\Phi_2(R, \Omega_1, \Omega_2)$, also has a noncentral character. Nevertheless, for simplification of the description, we first consider a certain model system with a central short-range potential $\varphi_2(R)$ and an electrostatic potential $\Phi_2(R, \Omega_1, \Omega_2)$. In this case, finding the screened potentials that ensure

⁶The results (4.3.20)—(4.3.22) were also obtained by summing the chain diagrams in [201].

the best convergence of the cluster expansions (4.1.56) reduces to solving the Ornstein–Zernike equation (4.1.61) in the mean spherical approximation

$$\begin{aligned} c_2(R, \Omega_1 \Omega_2) &= -\beta \Phi_2(R, \Omega_1 \Omega_2), \quad R > \sigma; \\ F_2(R, \Omega_1 \Omega_2) &= 0, \quad R < \sigma. \end{aligned} \quad (4.3.25)$$

In the previously adopted notations (see Section 4.1), according to (4.3.15), $\hat{c}_{\mu\nu}^{mnl}(R) = -\beta u_{\mu\nu}^{mnl} \frac{1}{R^{l+1}}$, $R > \sigma$. Substituting this expression into (4.1.76) and using the function $\Theta_l(R, r)$ from the relation (4.1.81), we verify that the functions $C_{\mu\nu}^{mnl}(r)$ satisfy the boundary conditions [204]

$$C_{\mu\nu}^{mnl}(r) = -\beta u_{\mu\nu}^{mnl} \frac{1}{r^{l+1}} + \beta u_{\mu\nu}^{mnl} \int_r^\infty P_l' \left(\frac{r}{R} \right) \frac{dR}{R^{l+1}} = 0, \quad R > \sigma. \quad (4.3.26)$$

These conditions, of course, are also satisfied by the functions $S_{\mu\nu, \chi}^{mn, \pm}(r)$ defined according to (4.1.88).

The second set of conditions follows from the second relation (4.3.25). For $R < \sigma$, $h_{00}^{000}(R) = F_{00}^{000}(R) - 1 = -1$. Since $\Phi_2(R, \Omega_1 \Omega_2)$ does not contain an orientation-independent part, $c_{00}^{000}(R) = 0$ for $R > \sigma$. Thus, the function $F_{00}^{000}(R)$ is the solution to the Percus–Yevick equation for hard spheres. For non-zero (m, n) , $\hat{h}_{\mu\nu}^{mnl}(R) = 0$ for $R < \sigma$. Hence, using relations (4.1.76) and (4.1.81), we verify that $H_{\mu\nu}^{mnl}(r)$ (and thus $I_{\mu\nu, \chi}^{mn, \pm}$) in the region $r < \sigma$ are represented as polynomials of r . Using relations (4.1.95), Blum [205] showed that for $r < \sigma$, the functions $\mathbf{q}_\chi(r)$ are polynomials of r of order $2n_m$, where n_m is the highest multipole order in the potential $\Phi_2(R, \Omega_1 \Omega_2)$. Knowing the function $\mathbf{q}_\chi(r)$, using relations (4.1.94) and (4.1.95), one can determine $S_\chi^\pm(r)$ and $I_\chi^\pm(r)$.

For a model of hard spheres with a dipole moment $\mathbf{p} \cdot \mathbf{n} = m = 1$, $\mu = \nu = 0$, $l = 0; 2$, and from (4.1.76)

$$\begin{aligned} H^{110}(r) &= \hat{h}^{110}(r), \quad H^{112}(r) = \hat{h}^{112}(r) - 3 \int_r^\infty \frac{1}{R} \hat{h}^{112}(R) dR, \\ C^{110}(r) &= \hat{c}^{110}(r), \quad C^{112}(r) = \hat{c}^{112}(r) - 3 \int_r^\infty \frac{1}{R} \hat{c}^{112}(R) dR. \end{aligned} \quad (4.3.27)$$

In the region $r < \sigma$,

$$\hat{h}^{112}(r) = \hat{h}^{110}(r) = H^{110}(r) = 0, \quad H^{112}(r) = -\sqrt{30}K, \quad (4.3.28)$$

where $\frac{\sqrt{30}}{3}K = \int_\sigma^\infty \frac{1}{R} h^{112}(R) dR$. For $r > \sigma$,

$$\hat{c}^{110}(r) = C^{110}(r) = C^{112}(r) = 0, \quad \hat{c}^{112}(r) = \frac{\sqrt{30}}{3} \beta p^2 \frac{1}{r^3}. \quad (4.3.29)$$

According to the definition (4.1.86)

$$\begin{aligned}
 \bar{H}_0^{11}(r) &= \frac{2}{\sqrt{30}} H^{112}(r) - \frac{1}{\sqrt{3}} H^{110}(r), \\
 \bar{C}_0^{11}(r) &= \frac{2}{\sqrt{30}} C^{112}(r) - \frac{1}{\sqrt{3}} C^{110}(r), \\
 \bar{H}_{\pm 1}^{11}(r) &= \frac{1}{\sqrt{30}} H^{112}(r) + \frac{1}{\sqrt{3}} H^{110}(r), \\
 \bar{C}_{\pm 1}^{11}(r) &= \frac{1}{\sqrt{30}} C^{112}(r) + \frac{1}{\sqrt{3}} C^{110}(r).
 \end{aligned} \tag{4.3.30}$$

At the same time, according to (4.3.28):

$$\begin{aligned}
 \bar{H}_{\pm 1}^{11}(r) &= -K, \quad \bar{H}_1^{11}(r) = -2K, \quad r < \sigma, \\
 \bar{C}_{\pm 1}^{11}(r) &= \bar{C}_0^{11}(r) = 0, \quad r > \sigma.
 \end{aligned} \tag{4.3.31}$$

Since $\bar{H}_1^{11}(r) = \bar{H}_{-1}^{11}(r)$ and $\bar{C}_1^{11}(r) = \bar{C}_{-1}^{11}(r)$, there are only two pairs of unknown functions. Expressions for them can be written immediately, noting that the functions $\bar{H}_\chi^{11}(r)$ and $\bar{C}_\chi^{11}(r)$ are related by the Ornstein—Zernike equation system. Indeed, since for even l ,

$$H_\chi^{11}(k) = 4\pi \int_0^\infty r^2 dr j_0(kr) \bar{H}_\chi^{11}(r), \quad C_\chi^{11}(k) = 4\pi \int_0^\infty r^2 dr j_0(kr) \bar{C}_\chi^{11}(r),$$

then, according to (4.1.73),

$$\begin{aligned}
 \bar{H}_0^{11}(r) - \bar{C}_0^{11}(r) &= \frac{N}{V} \int \bar{H}_0^{11}(r') \bar{C}_0^{11}(|r - r'|) dr', \\
 \bar{H}_1^{11}(r) - \bar{C}_1^{11}(r) &= -\frac{N}{V} \int \bar{H}_1^{11}(r') \bar{C}_1^{11}(|r - r'|) dr'.
 \end{aligned} \tag{4.3.32}$$

The conditions (4.3.31), which the functions $\bar{H}_\chi^{11}(r)$ and $\bar{C}_\chi^{11}(r)$ satisfy, differ from the boundary conditions of the Percus—Yevick equation for hard spheres only in that, in the region $r < \sigma$, the pair correlation function is not equal to -1 , but rather to a different constant. The equation $H(r) - C(r) = \frac{N}{V} \int H(r') C(|r - r'|) dr'$ with the additional conditions $C(r) = 0$ for $r > \sigma$ and $\bar{H}(r) = -K$ for $r < \sigma$ is equivalent to the equation $h(r) - c(r) = K \frac{N}{V} \int h(r') c(|r - r'|) dr'$ with additional conditions $h(r) = -1$ for $r < \sigma$ and $c(r) = 0$ for $r > \sigma$. At the same time:

$$H\left(r, \frac{N}{V}\right) = K h\left(r, K \frac{N}{V}\right), \quad C(r) = K c\left(r, K \frac{N}{V}\right),$$

where $h(r)$ and $c(r)$ are the correlation functions of hard spheres with density $\frac{N}{V}K$. Thus,

$$\begin{aligned}\bar{H}_0^{11}(r) &= 2K h_2^{(\text{PY})}\left(r, 2K\frac{N}{V}\right), & \bar{C}_0^{11}(r) &= 2K c_2^{(\text{PY})}\left(r, 2K\frac{N}{V}\right), \\ \bar{H}_1^{11}(r) &= K h_2^{(\text{PY})}\left(r, -K\frac{N}{V}\right), & \bar{C}_1^{11}(r) &= K c_2^{(\text{PY})}\left(r, -K\frac{N}{V}\right).\end{aligned}\quad (4.3.33)$$

Here, $h_2^{(\text{PY})}(r)$ and $c_2^{(\text{PY})}(r)$ are the correlation functions of hard spheres, taken in the Percus–Yevick approximation.

Now, according to (4.3.30)

$$\begin{aligned}H^{112}(r) &= \frac{\sqrt{30}}{3} [\bar{H}_0^{11}(r) + \bar{H}_1^{11}(r)] = \\ &= \frac{\sqrt{30}}{3} K \left[h_2^{(\text{PY})}\left(r, 2K\frac{N}{V}\right) + h_2^{(\text{PY})}\left(r, -K\frac{N}{V}\right) \right], \\ H^{110}(r) &= \frac{\sqrt{3}}{3} [2\bar{H}_1^{11}(r) - \bar{H}_0^{11}(r)] = \\ &= \frac{2\sqrt{3}}{3} K \left[h_2^{(\text{PY})}\left(r, K\frac{N}{V}\right) - h_2^{(\text{PY})}\left(r, -K\frac{N}{V}\right) \right], \\ C^{112}(r) &= \frac{\sqrt{30}}{3} \left[K \left(c_2^{(\text{PY})}\left(r, 2K\frac{N}{V}\right) + c_2^{(\text{PY})}\left(r, -K\frac{N}{V}\right) \right) \right], \\ C^{110}(r) &= \frac{2\sqrt{3}}{3} K \left[c_2^{(\text{PY})}\left(r, K\frac{N}{V}\right) - c_2^{(\text{PY})}\left(r, -K\frac{N}{V}\right) \right].\end{aligned}\quad (4.3.34)$$

According to equation (4.1.79):

$$\begin{aligned}\hat{h}^{112}(R) &= H^{112}(R) - \frac{3}{R^3} \int_0^R H^{112}(r) r^2 dr, \\ \hat{c}^{112}(R) &= C^{112}(R) - \frac{3}{R^3} \int_0^R C^{112}(r) r^2 dr, \\ \hat{h}^{110}(R) &= H^{110}(R), \quad \hat{c}^{110}(R) = C^{110}(R).\end{aligned}\quad (4.3.35)$$

From the boundary conditions (4.3.29) for $R > \sigma$:

$$\hat{c}^{112}(R) = -\beta \frac{\sqrt{30}}{3} p^2 \frac{1}{R^3} = -\frac{3}{R^3} \int_0^\sigma C^{112}(r) r^2 dr.$$

Hence, we obtain an equation for K

$$y = \frac{1}{3} [q(2\zeta) - q(-\zeta)], \quad (4.3.36)$$

where $y = \frac{4}{9}\pi\beta p^2 \frac{N}{V}$; $\zeta = K\eta$; $\eta = \frac{1}{6}\pi \frac{N}{V}\sigma^3$,

$$q(\eta) = 1 - 4\pi \frac{N}{V} \int_0^\sigma c_2^{(\text{PY})} \left(r, \frac{N}{V}\right) r^2 dr = \frac{(1+2\eta)^2}{(1-\eta)^4} \quad (4.3.37)$$

is the expression for the hard-spheres compressibility in the Percus–Yevick approximation (see (3.1.62a)).

For all $0 < y < \infty$, $q(2\zeta) - q(-\zeta)$ is a monotonous function of ζ in the interval $0 < \zeta < 1/2$. In this case, the solution of the Percus–Yevick equation for $\eta \geq 0$, obtained in Chapter 3, remains valid even for $0 > \eta > -1/2$, which corresponds to the range of variation of ζ in $q(-\zeta)$.

Thus, for the screened potential, we have

$$\begin{aligned} g(R, \Omega_1, \Omega_2) &= \hat{h}^{110}(R) \hat{\Psi}^{110}(\Omega_1, \Omega_2 \Omega_{\mathbf{R}}) + \\ &\quad + \hat{h}^{112}(R) \hat{\Psi}^{112}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}), \\ \hat{h}^{110}(R) \hat{\Psi}^{110}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}) &= 2K[h_2^{(\text{PY})}(R, 2K\eta) - \\ &\quad - h_2^{(\text{PY})}(R, -K\eta)] \cos \vartheta_{12}, \\ \hat{h}^{112}(R), \hat{\Psi}^{112}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}) &= K\{2h_2^{(\text{PY})}(R, 2K\eta) + \\ &\quad + h_2^{(\text{PY})}(R, -K\eta) - \frac{3}{R^3} \int_0^R r^2 dr [2h_2^{(\text{PY})}(r, 2K\eta) + \\ &\quad + h_2^{(\text{PY})}(r, -K\eta)]\} (3 \cos \vartheta_1 \cos \vartheta_2 - \cos \vartheta_{12}), \end{aligned} \quad (4.3.38)$$

where the constant K is determined by equation (4.3.36); ϑ_{12} is an angle between dipole moments of two molecules; ϑ_1, ϑ_2 are the angles between dipole moments of molecules and the axis $\mathbf{R}$; $\hat{h}^{110}(R)$ is a short-range function. The long-range part of the screened potential is expressed via $\hat{h}^{112}(R)$ and is equal

to $\frac{3}{R^3} \int_0^\infty H^{112}(r) r^2 dr$, from which it follows

$$\lim_{R \rightarrow \infty} \frac{g(R, \Omega_1 \Omega_2)}{-\beta \Phi_2(R, \Omega_1 \Omega_2)} = [q(2K\eta)q(-K\eta)]^{-1} \quad (4.3.39)$$

and thus, it is a smooth function of $\zeta = K\eta$ (and, therefore, of y), changing from unity for $y = 0$ to zero for $y = \infty$. The expression (4.3.39) is independent of molecular sizes, thus at $\sigma \rightarrow 0$, the previously obtained result (4.3.22) for point dipoles does not follow from this. This seemingly paradoxical result is due to the specific nature of dipole interactions, and we address it when discussing dielectric properties.

Expression (4.3.38) was first obtained by Wertheim [233]. The results can be easily generalized to the case of a multicomponent system of dipolar molecules with identical sizes. In this case, as shown in [206], in the mean-spherical approximation, it is equivalent to a one-component system with an effective dipole moment $\hat{p} = \left(\frac{1}{M} \sum_{a=1}^M p_a^2 \right)^{1/2}$ and an effective density $\hat{\eta} = \frac{1}{\hat{p}^2} \sum_{a=1}^M \eta_a p_a^2$. Screened potentials for a mixture of dipolar molecules with different sizes were considered in [234].

4.3.3. Thermodynamic and structural properties of a system

As in the case of ionic systems, in accordance with the Bogolyubov–Gibbs inequality (2.3.95), we have the exact value of the upper bound of the free energy

$$F - F_0 \leq F_{\text{HTA}} = \frac{N^2}{2V} \int \Phi_2(R, \Omega_1 \Omega_2) F_2^0(R, \Omega_1 \Omega_2) d\mathbf{R} d\Omega_1 d\Omega_2. \quad (4.3.40)$$

For systems with a central short-range interaction $F_{\text{HTA}} = 0$, so that $F - F_0 \leq 0$. The lower bound of the free energy is related to the property of “saturation” of electrostatic forces and is determined by the Onsager inequality (3.4.4)

$$\frac{F - F_0}{N} \geq -u^{\text{el}}, \quad (4.3.41)$$

where u^{el} is the intrinsic electrostatic energy of the molecule. In particular, for hard spheres with a dipole moment $\mathbf{p}$ $u^{\text{el}} = 4p^2/\sigma^3$.

The set of inequalities (4.3.40), (4.3.41) establishes the existence of a thermodynamic limit for systems with arbitrary electrostatic interactions. From (4.3.41), it also follows that as the intensity of the electrostatic interaction increases, the free energy “saturates”, changing proportionally to the square of the multipole moment.

Let us now focus specifically on the model of hard spheres with dipole interactions, for which the screened potential was obtained in the previous section. Expanding the pair distribution function into a series

$$F_2(R, \Omega_1 \Omega_2) = F_2^{(s)}(R) + \hat{h}^{110}(R) \hat{\Psi}^{110}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}) + \hat{h}^{112}(R) \hat{\Psi}^{112}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}) + \dots, \quad (4.3.42)$$

according to (4.1.31), for this model we have

$$\frac{E - E_{\text{id}}}{N} \beta = -\sqrt{30} y \int_{\sigma}^{\infty} \hat{h}^{112}(R) \frac{1}{R} dR,$$

$$\begin{aligned}\frac{P}{\rho}\beta &= 1 + 4\eta F_2^{(s)}(\sigma+) + \frac{E - E_{\text{id}}}{N}\beta, \\ \frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right)_T &= 1 + \rho \int [F_2^{(s)}(R) - 1] d\mathbf{R},\end{aligned}\tag{4.3.43}$$

where $F_2^{(s)}(R) = F_{00}^{000}(R)$ is the radial function.

In the description, we proceed from the cluster expansion (4.1.56). As in the case of ionic systems, $F_{\text{HTA}} = 0$, and the contribution of electrostatic forces to the free energy begins with the term

$$F_{\text{ORPA}} = -\frac{N^2}{2V} \int_0^1 d\xi \int d\mathbf{R} d\Omega_1 d\Omega_2 \Phi_2(R, \Omega_1 \Omega_2) g(R, \Omega_1 \Omega_2 \xi). \tag{4.3.44}$$

In this approximation $F_2(R, \Omega_1 \Omega_2) = F_2^0(R) + g(R, \Omega_1 \Omega_2)$, so that $F_2^{(s)}(R) = F_2^0(R)$, and according to (4.3.38) and (4.3.43)

$$\begin{aligned}\frac{E - E_{\text{id}}}{N}\beta &= -3yK, & \frac{P - P_0}{\rho}\beta &= -3yK, \\ \frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right)_T &= \frac{1}{\beta} \left(\frac{\partial \rho}{\partial P_0} \right)_T,\end{aligned}\tag{4.3.45}$$

where P_0 is the pressure in the hard spheres model.

Let us substitute (4.3.38) into (4.3.44), to obtain

$$\frac{F_{\text{ORPA}}}{Nk_{\text{B}}T} = -3y \int_0^1 d\xi K(\xi),$$

where $K(\xi)$ is determined by equation (4.3.36) through changing y with $y(\xi) = \xi y$, and $\zeta(\xi) = K(\xi)\eta$. Integrating by parts, we find [235]

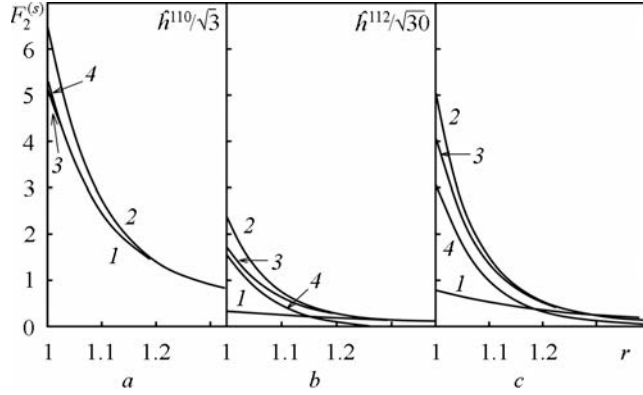
$$\frac{F_{\text{ORPA}}}{Nk_{\text{B}}T} = -8\eta K^2 \left[\frac{(1 + \eta K)^2}{(1 - 2K\eta)^4} + \frac{(2 - K\eta)^2}{8(1 + \eta K)^4} \right]. \tag{4.3.46}$$

It is important to note that at $y \rightarrow \infty$ $\zeta \rightarrow \frac{1}{2}$ and $\frac{F_{\text{ORPA}}}{Nk_{\text{B}}T} \rightarrow -\frac{3}{2}$, $\frac{y}{\eta} = -\beta \frac{4p^2}{\sigma^3}$, thus ensuring the fulfilment of inequality (4.3.41). Differentiating (4.3.46) with respect to V , we arrive at the equation of state

$$\frac{P - P_0}{\rho}\beta = -3yK - \frac{1}{N} F_{\text{ORPA}}\beta. \tag{4.3.47}$$

The discrepancy between (4.3.45) and (4.3.47) is related to the thermodynamic inconsistency of the ORPA approximation. Differentiating the internal

Fig. 17. First expansion coefficients of the pair distribution function $F_2^{(s)}(R)$ for a thermodynamic state characterized by $\beta p \sigma^3 / \rho = 1$ and $\rho^* = 0.9$. Curve 1: ORPA approximation; curve 2: second cluster coefficient approximation; curve 3: approximation from equation (4.3.49); curve 4: Monte Carlo results



energy (4.3.45) with respect to temperature, we obtain an expression for the heat capacity per unit volume [236]

$$C_V = \frac{3}{2} \rho k + 18k \frac{y^2}{\pi \sigma^3} \frac{\partial K}{\partial y}. \quad (4.3.48)$$

Since K is a monotonous function of y , $\partial K / \partial y > 0$ and thus $C_V > 0$ for all temperatures.

However, while comparing theoretical results with the results of the MC simulation [237, 238], it was found that the ORPA approximation is being taken into account unsatisfactory. The cluster coefficients of the expansion (4.1.56) does not improve the results as well. In particular, it turned out that the approximation of the second cluster coefficient for the pair distribution function $F_2(R, \Omega_1 \Omega_2) = F_2^0(R) \exp \{g(R, \Omega_1 \Omega_2)\}$ leads to considerably overestimated results, especially in the region $R \simeq \sigma$. As a solution, Verlet and Weis [238] proposed to use a linearized approximation

$$F_2(R, \Omega_1 \Omega_2) = F_2^0(R) [1 + g(R, \Omega_1 \Omega_2)]. \quad (4.3.49)$$

Although this approximation is inherently incorrect in the limit of low densities, it leads to fairly good results in the region of high densities. In Fig. 17, taken from [238], the first coefficients of the expansion (4.3.42) of the pair distribution function for the thermodynamic state $\beta p^2 / \sigma^3 = 1$, $\rho^* = N \sigma^3 / V = 0.9$ are presented. In this case, curve 1 represents the ORPA approximation, curve 2 corresponds to the approximation of the second cluster coefficient, and curve 3 represents the results of the MC simulation. As we can see, only approximation (4.3.49), corresponding to curve 4, satisfactorily agrees with computer simulation results. It should be noted that in this approximation, as well as in the mean-spherical approach $F_2^{(s)}(R) = F_2^0(R)$, meaning that for $F_2^{(s)}(R)$ curve 1 and curve 3 coincide. As shown by Stell and Weis [239], approximation (4.3.49) is the most accurate for the function $\hat{h}^{110}(R)$ (see Fig. 17, b).

The approximation

$$\begin{aligned}
 F_2(R, \Omega_1, \Omega_2) &= F_2^0(R)[1 + g(R, \Omega_1\Omega_2) + F_2^{(3L)}(R, \Omega_1\Omega_2)], \\
 F_2^{(3L)}(R_{12}, \Omega_1\Omega_2) &= \rho \int d\mathbf{R}_3 d\Omega_3 h_2^0(R_{13}) \times \\
 &\times g(R_{13}, \Omega_1, \Omega_3)[h_2^0(R_{32})g(R_{32}, \Omega_3, \Omega_2) + \\
 &+ 2(h_2^0(R_{32}) + g(R_{32}, \Omega_3, \Omega_2))],
 \end{aligned} \tag{4.3.50}$$

based on the consideration of the linearized third cluster coefficient, considerably improves the description of $\hat{h}^{112}(R)$ (see Fig. 17, *c*), although it leads to an overestimated value of the second maximum. However, for $\hat{h}^{110}(R)$, approximation (4.3.49) is better than (4.3.50). In both approximations, $F_2^{(s)}(R) = F_2^{(0)}(R)$, which, apart from the region of the first maximum, agrees quite well with computer simulation results.

In Table 11, also taken from [238], the electrostatic part of the free energy $\beta \frac{F - F_0}{N}$ obtained by various methods for $\rho^* = 0.9$ and different values of the dipole moment is presented. As we can see, considering the second and third cluster coefficients does not lead to a significant improvement in the ORPA approximation. Nevertheless, for sufficiently accurate results throughout the considered region of $\beta \frac{p^2}{\sigma^3}$, the approximation ORPA + LB_2 + LB_3 corresponding to expression (4.3.50) for the pair distribution function is used. This approximation is based on considering only the second cluster coefficient term $LB_2 = \frac{1}{2}\rho^2 \int \frac{1}{2}g^2(R, \Omega_1\Omega_2)h_2^0(R)d\mathbf{R}d\Omega_1d\Omega_2$ and the linearized third cluster coefficient LB_3 , obtained from B_3 by replacing $e^{g(R)} - 1$ with $g(R_1\Omega_1\Omega_2)$ which corresponds to the first diagrams previously included in the renormalised screened potential (see subsection 2.3.3 in Chapter 2).

For describing the thermodynamic properties of systems with electrostatic interactions, a series from the perturbation theory (2.3.90) can also be used. In

Table 11. **Electrostatic part of the free energy** $\frac{1}{N}\beta(F - F_0)$
for the hard-sphere model with dipole momentum at $\frac{N}{V}\sigma^3 = 0.9$

$\beta \frac{p^2}{\sigma^3}$	ORPA (4.3.46)	ORPA + + B_2 + B_3	ORPA + + LB_2 + LB_3	Padé F (4.3.51)	MC
0.50	-0.129	-0.214	-0.217	-0.224	-0.218
1.00	-0.436	-0.661	-0.702	-0.745	-0.708
2.00	-1.345	-1.495	-2.076	-2.229	-2.101
4.00	-3.804	—	-5.854	-5.934	-5.620

Table 12. Critical parameter values for the hard-sphere model with dipole momentum $\left(T^* = \eta \frac{1}{y}, P^* = \frac{\pi}{16} \frac{\sigma^6}{p^2} P\right)$

Approximation	T_c^*	η_c	y_c	ε_c	$P_c^* \times 10$
ORPA (4.3.46)	0.0844	0.0555	0.6581	4.232	1.382
Padé F (4.3.51)	0.1047	0.0833	0.7956	—	2.773
Onsager (4.3.88)	0.0457	0.0151	0.3297	2.210	0.1937

this case, for the model of hard spheres with dipole interactions, we arrive at the expansion of the free energy in powers of βp^2 :

$$\beta \frac{F - F_0}{N} = (\beta p^2)^2 F^2 + (\beta p^2)^3 F^{(3)} + \dots, \quad (4.3.51)$$

where

$$F^{(2)} = -\frac{1}{6} \rho \int \frac{1}{R^6} F_2^0(R) d\mathbf{R};$$

$$F^{(3)} = \frac{1}{54} \rho^2 \int u_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \times F_3^0(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) d\mathbf{R}_{12} d\mathbf{R}_{13};$$

and $F_2^0(R)$, $F_3^0(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ are the pair and three-particle distribution functions for hard spheres, respectively;

$$u_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = \frac{1 + 3 \cos \vartheta_1 \cos \vartheta_2 \cos \vartheta_3}{(R_{12} R_{13} R_{23})^3};$$

$\vartheta_1, \vartheta_2, \vartheta_3$ are the angles between the sides of the triangle formed by the vectors $\mathbf{R}_{12}, \mathbf{R}_{13}, \mathbf{R}_{23}$.

Noting the poor convergence of the series (4.3.51), Rushbrook, Stell, and Høye [235] approximated it using a Padé approximant

$$\beta \frac{F - F_0}{N} = (\beta p^2)^2 \frac{F^{(2)}}{1 - \beta p^2 F^{(3)} / F^{(2)}}. \quad (4.3.52)$$

According to this approximation, the first two terms of the series (4.3.51) are taken into account exactly, while the remaining terms are assumed to form a geometric progression. An important property of approximation (4.3.52) is that it ensures the correct behaviour of the free energy in two important limits $\beta p^2 \rightarrow 0$ and $\beta p^2 \rightarrow \infty$, which permits the expression (4.3.52) to be considered a very successful interpolation formula. The values of the free energy calculated using this formula are presented in Table 11. As we can see, they quite well agree with the results of the computer simulation.

An important property of the considered system is the presence of a critical point. The critical parameter values obtained in [236] are presented in Table 12⁷. It should be noted that the behaviour of the system in the considered

⁷For the hard-spheres pressure, the Carnahan—Starling expression was used.

approximations is classical. In particular, in the ORPA approximation, compressibility diverges as $(T - T_c)^{-1}$, while heat capacity, as noted earlier, remains finite. It is interesting to stress that the existence of a critical point for this model is due exclusively to dipole forces. The values of the dielectric permittivity at the critical point, presented in Table 12, obtained using expression (4.3.73) and (4.3.88), considerably differ from those of real liquids. This is undoubtedly due to the model nature of the considered system and indicates the necessity of accounting for dispersion and other interactions present in real systems.

The simplicity of expression (4.3.52) and, at the same time, the remarkable accuracy of the results obtained using it have attracted attention of many researchers. Using the condition of thermodynamic consistency and restricting themselves to the first three terms of the expansion (4.3.42), Høye and Stell [240] performed a parametrisation of the expression for the pair distribution function within this approximation. The obtained expression turned out to be particularly successful for $F_2^{(s)}(R)$, satisfactory for $\hat{h}^{112}(R)$, and less accurate for $\hat{h}^{110}(R)$ [239].

In [241], expression (4.3.52) was used to describe a system with the Stockmayer potential. An approximation similar to (4.3.52) was also proposed for the internal energy [237] and function $F_2^{(s)}(R)$ [242]. Patey and Valleau [243] utilized approximation (4.3.52) to describe mixtures of hard spheres with dipole and quadrupole interactions and also found a good agreement with computer simulation results. An interesting outcome of this work is that the contribution of quadrupole interactions to the thermodynamic and structural properties of the system turned out to be more significant than that of dipole interactions. Quadrupole interactions also considerably alter the values of critical parameters [188]. The consideration of quadrupole and higher multipole interactions is the focus of works [244, 245], which also discuss the need to account for the noncentral nature of short-range forces. A number of studies [246–248] employed the approximation (4.3.52) to describe molecular mixtures with dipole, quadrupole, octupole, and anisotropic short-range interactions. It was found that noncentral interactions play an important role and, in particular, can lead to mutual insolubility of different components.

In works [74, 75], the authors limited themselves to the first three terms of the expansion

$$\begin{aligned} c_2(R, \Omega_1 \Omega_2) = & c_2^{(s)}(R) + \hat{c}^{110}(R) \hat{\Psi}^{110}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}) + \\ & + \hat{c}^{112}(R) \hat{\Psi}^{112}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}) + \dots, \end{aligned}$$

within the framework of the generalized mean spherical approximation, the parametrisation of the functions $F_2^{(s)}(R)$, $\hat{h}^{110}(R)$ and $\hat{h}^{112}(R)$ was performed.

Since for $R < \sigma F_2^{(s)}(R) = \hat{h}^{110}(R) = \hat{h}^{112}(R) = 0$, it is assumed that for $R > \sigma$

$$\begin{aligned} c_2^{(s)}(R) &= K_s \frac{1}{R} e^{-\alpha_s R}, \quad \frac{\sqrt{3}}{3} \hat{c}^{110}(R) = \frac{1}{R} A_1 e^{-\lambda_1 R} + \frac{1}{R} A_2 e^{-\lambda_2 R}, \\ \frac{\sqrt{30}}{3} \hat{c}^{112}(R) &= \beta p^2 \frac{1}{R^3} + 2A_1 b_1(R) + A_2 b_2(R), \end{aligned} \quad (4.3.53)$$

where $b_j = \lambda_j e^{-\lambda_j R} \left[\frac{1}{\lambda_j R} + \frac{3}{\lambda_j^2 R^2} + \frac{3}{\lambda_j^3 R^3} \right]$, $j = 1, 2$.

The constants A_j , λ_j are determined by the internal energy according to (4.3.43), the dielectric permittivity according to (4.3.87), and by the contact values of functions $\hat{h}^{110}(R)$ and $\hat{h}^{112}(R)$. The constants K_s and α_s are determined by compressibility and pressure according to (4.3.43). The functions $F_2^{(s)}(R)$, $\hat{h}^{110}(R)$, and $\hat{h}^{112}(R)$ obtained in this way show an excellent agreement with the results of computer simulations [239].

Water occupies an important place among systems with electrostatic interactions. In each water molecule, two of the four outer orbitals form bonds with hydrogen nuclei, while the remaining two are lone electron pairs. Various electrostatic models are often used to describe the water molecule, among which the Bjerrum model appears to correspond most closely to reality. In this model, each water molecule is represented as a tetrahedron, with four point charges at its vertices – two positive and two negative. The positive charges correspond to hydrogen nuclei, while the negative ones correspond to lone electron pairs. At the centre of the tetrahedron there is the oxygen atom. The values of ez_α and the distances of the charges from the tetrahedron centre l_α are chosen based on experimental values of the dipole moment and quadrupole coefficient. For example, in the Bjerrum model, as modified by Ben-Naim and Stillinger, it is assumed [249]: $ez_\alpha = \pm 0.19e$, $l_\alpha = 1A$.

In this case, the electrostatic part of the intermolecular interaction between the point charges of one molecule and the point charges of another is given by

$$\Phi_2(R, \Omega_1 \Omega_2) = \sum_{\alpha, \beta} \frac{e^2 z_\alpha z_\beta}{|\mathbf{R} + \mathbf{l}_\alpha + \mathbf{l}_\beta|}.$$

The nonelectrostatic part of the interaction has the same form as in the case of nonpolar molecules and can be described by the Lennard-Jones potential. Molecular dynamics studies for this model, conducted by Rahman and Stillinger [249–252], presented the structure of water as a deformed network of random hydrogen bonds, gradually breaking down with temperature. Other models are also used. In particular, in works [253, 254], a model of three charged force centres with empirical site-site potentials was proposed to describe the interaction of water molecules.

In recent years, thanks to the intensive development of computers, extensive studies of water molecule interactions have been conducted using the Hartree–Fock approximation (ab initio methods) [255, 256]. Although, as noted in Chapter 1, this approximation does not account for correlation effects (in particular, dispersion interactions), the latter can be additionally considered [257]. The interaction potentials obtained in this way have been used to describe the thermodynamic and structural properties of water based on the MC simulation [257–259]. One of the important results obtained in the studies using the Hartree–Fock approximation is the conclusion about a significant role of the contribution of many-particle forces to intermolecular interactions [260].

When nonpolar particles are introduced into water or into another polar medium, specific so-called hydrophobic interactions arise between them, resulting in the aggregation of nonpolar molecules into separate groups [261, 262]. This effect appears to play a significant role in the stability of various protein structures [263].

4.3.4. Dielectric properties of a system

The specific features of systems with dipole interactions are related to the phenomenon of dielectric polarisation, which manifests as the orientational ordering of molecular dipole moments under the influence of an external electric field. As a result, a macroscopic dipole moment arises in the field direction, the specific value of which is called the polarisation vector $\mathbf{P}$ and serves as the main characteristic of this phenomenon. Consequently, the macroscopic Maxwell field $\mathbf{E}$ consists of the external field $\mathbf{E}_0$ and the field created by polarisation:

$$\mathbf{E}(\mathbf{R}) = \mathbf{E}_0(\mathbf{R}) + \int d\mathbf{R}' \mathbf{T}(\mathbf{R}, \mathbf{R}') \mathbf{P}(\mathbf{R}'), \quad (4.3.54)$$

where $\mathbf{T}(\mathbf{R}, \mathbf{R}') = -\widehat{\nabla \nabla} \frac{1}{|\mathbf{R} - \mathbf{R}'|}$ is the dipole-dipole interaction tensor, since the electrostatic potential $\Phi_2(\mathbf{R}) = -(\mathbf{p}_1 \nabla)(\mathbf{p}_2 \nabla) \frac{1}{R} = -(\widehat{\mathbf{p}_1 \mathbf{p}_2}) : \left(\widehat{\nabla \nabla} \frac{1}{R} \right)$; $\widehat{\mathbf{p}_1 \mathbf{p}_2}$ is a usual vector dyad.

The integral in (4.3.54) has a singularity at the point $\mathbf{R} = \mathbf{R}'$, and its value depends on the method of regularization. Extracting from the integration region a sphere of infinitely small radius centred at $\mathbf{R} = \mathbf{R}'$, we obtain:

$$\mathbf{E}(\mathbf{R}) = \mathbf{E}_0(\mathbf{R}) - \frac{4}{3}\pi \mathbf{P}(\mathbf{R}) + \lim_{\delta \rightarrow 0} \int d\mathbf{R}' \mathbf{T}_\delta(\mathbf{R}, \mathbf{R}') \mathbf{P}(\mathbf{R}'), \quad (4.3.55)$$

where

$$\mathbf{T}_\delta(\mathbf{R}, \mathbf{R}') = H(|\mathbf{R} - \mathbf{R}'| - \delta) \mathbf{T}(\mathbf{R}, \mathbf{R}'); \quad H(x) = \begin{cases} 0, & x < 0, \\ 1, & x > 0. \end{cases}$$

Equation (4.3.55) contains two unknown quantities, $E(R)$ and $P(R)$ and thus remains unclosed. An additional relation is usually postulated in the form [232]

$$\mathbf{P}(R) = \frac{\varepsilon - 1}{4\pi} \mathbf{E}(R). \quad (4.3.56)$$

The quantity ε appearing here is called the dielectric permittivity. If instead of $\mathbf{E}(R)$ we consider the field inside an infinitely small spherical cavity, given by $\mathbf{E}_L(R) = \mathbf{E}(R) + \frac{4}{3}\pi\mathbf{P}(R)$, then equation (4.3.56) can be rewritten as

$$\frac{4}{3}\pi\mathbf{P}(R) = \frac{\varepsilon - 1}{\varepsilon + 1} \mathbf{E}_L(R). \quad (4.3.57)$$

At the core of (4.3.56) and (4.3.57) there lies a fundamental assumption of the local relationship between $\mathbf{P}(R)$ and $\mathbf{E}(R)$ or $\mathbf{E}_L(R)$, meaning that neither (4.3.56) nor (4.3.57) can be considered as definitions of ε . However, it is clear that the validity of these relations also provides an answer to the question of the existence of ε .

Since the total dipole moment of the system at an arbitrary point $\mathbf{R}$ is given by $\sum_{i=1}^N \mathbf{p}_i \delta(\mathbf{R} - \mathbf{R}_i)$ then, by definition of the polarisation vector

$$\mathbf{P}(R) = \frac{1}{V} \frac{\int e^{-\beta U_N} \left[\sum_{i=1}^N \mathbf{p}_i \delta(\mathbf{R} - \mathbf{R}_i) \right] (d\mathbf{R})(d\Omega)}{\int e^{-\beta U_N} (d\mathbf{R})(d\Omega)}, \quad (4.3.58)$$

where $U_N = U_N(\mathbf{E}_0 = 0) + \sum_{i=1}^N (\mathbf{p}_i \mathbf{E}_0(R_i))$ is the system potential energy; $U_N(\mathbf{E}_0 = 0)$ is the energy of intermolecular interaction; $\sum_{i=1}^N (\mathbf{p}_i \mathbf{E}_0(R_i))$ is the energy of an external field. In the linear approximation with respect to the field [264]

$$\mathbf{P}(R) = \frac{1}{V} \int d\mathbf{R}' K(\mathbf{R}, \mathbf{R}') \mathbf{E}_0(\mathbf{R}'), \quad (4.3.59)$$

where

$$K(\mathbf{R}, \mathbf{R}') = \beta \rho \left[\frac{1}{3} p^2 \delta(\mathbf{R} - \mathbf{R}') + \rho \int d\Omega_1 d\Omega_2 \widehat{\mathbf{p}_1 \mathbf{p}_2} F_2(|\mathbf{R} - \mathbf{R}'|, \Omega_1 \Omega_2) \right]. \quad (4.3.60)$$

Here, $F_2(|\mathbf{R} - \mathbf{R}'|, \Omega_1, \Omega_2)$ is the pair distribution function of the system at the absence of the external field.

Equation (4.3.59) expresses the polarisation at point $\mathbf{R}$ as a linear superposition of the effects created by the external field $\mathbf{E}_0(R')$ at all points $\mathbf{R}'$ of the system, thus leading to a non-local relationship between $\mathbf{P}(R)$ and $\mathbf{E}_0(R')$. This nature of the relationship does not contradict (4.3.56) and is

solely due to the dipole-dipole interaction. It was previously noted that the screened potentials of a dipolar system at $R \rightarrow \infty$ exhibit the same asymptotics as the interaction potential itself. Clearly, the same asymptotic behaviour applies to the pair distribution function [265, 266]. This leads to the presence of long-range orientational correlations in the system. Indeed, the number of molecules with orientation Ω_2 that are correlated with a molecule of orientation Ω_1 , which is located at the centres of a sphere of radius R , is given

by $4\pi \frac{N}{V} \int_0^R R'^2 dR' [F_2(R', \Omega_1, \Omega_2) - 1] \sim \ln R \rightarrow \infty$ as $R \rightarrow \infty$. The effect

of such long-range correlations will differ from zero even at macroscopic distances, which, undoubtedly, significantly complicates the statistical description of the system.

To avoid these difficulties, one can, as is customary in the theory of dielectrics [232, 267], switch to the description of a finite-sized macroscopic sample. In this case, due to long-range correlations, the polarisability and consequently, the long-range part of the pair distribution function will depend on the geometry of the sample and on the medium in which it is located. In the theory of dielectrics, this effect is eliminated when considering the specific situation of a spherical sample placed in a medium of the same material. However, this introduces an equally complex problem related to accounting for the reaction field of the medium [267].

A formal expression for the dielectric permittivity was derived by Kirkwood and Yvon [232]. Considering a dielectric sphere placed in a vacuum within a constant field $\mathbf{E}_0$ under the assumptions of (4.3.57) and according to (4.3.59), we obtain

$$\frac{\varepsilon - 1}{\varepsilon + 2} = y \left[1 + 3\rho \int_V d\mathbf{R} d\Omega_1 d\Omega_2 \frac{(\mathbf{p}_1 \mathbf{E}_0)(\mathbf{p}_2 \mathbf{E}_0)}{\mathbf{p}^2 \mathbf{E}_0^2} F_2(R, \Omega_1 \Omega_2) \right], \quad (4.3.61)$$

where $y = \frac{4}{9} \pi \beta \rho p^2$. Hence, neglecting the contribution of intermolecular correlations, we arrive at the Clausius—Mossotti formula (4.3.23), which is exact in the limit of low densities $\rho = \frac{N}{V} \rightarrow 0$. It is clear that in this limit, the previously obtained expressions (4.3.10) and (4.3.23) are identical.

To account for intermolecular interactions, following [268], for the pair distribution function in (4.3.61), we use the cluster expansion (2.2.63) constructed on the screened potential (4.3.22). Since $\int d\Omega_1 d\Omega_2 g(R, \Omega_1 \Omega_2) \times (\mathbf{p}_1 \mathbf{E}_0)(\mathbf{p}_2 \mathbf{E}_0) = 0$, the first nonzero contribution in the power series in y is introduced by the term $\beta(\mathbf{p}_1 \mathbf{p}_2) \left[\frac{1}{4} R^3 - 3\sigma^2 R + 4\sigma^3 \right] \frac{y}{\sigma^6} (1 + 2y)^{-2} (1 - y)^{-2}$, $\sigma < R < 2\sigma$ from the third cluster coefficient. According to (4.3.61), this con-

tribution equals $\frac{17}{16}y^3$. However, as shown by Jepsen [269], for a dielectric sphere of radius $\mathcal{R}$ there is an additional term $-\beta(\mathbf{p}_1\mathbf{p}_2)\frac{1}{\mathcal{R}^3}2y(1+2y)^{-2}(1-y)^{-2}$, which leads to a contribution of $-2y^3$. Therefore,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = y + \frac{17}{16}y^3 - 2y^3 + \dots = y - \frac{15}{16}y^3 + O(y^4). \quad (4.3.62)$$

Thus, when calculating the dielectric permittivity using formula (4.3.61), it is necessary first to perform the integration and only then take the limit $V \rightarrow \infty$, which is always associated with considerable difficulties. It should also be noted that expression (4.3.61) does not prove the existence of ε , since it was obtained under the assumption of (4.3.56).

The issue of the microscopic justification of relation (4.3.56) was thoroughly investigated by Ramshaw [270, 271]. He demonstrated that expression (4.3.56) is related to the assumption of the long-range asymptotic behaviour of the direct correlation function $c_2(R, \Omega_1\Omega_2) \rightarrow -\beta\Phi_2(R, \Omega_1\Omega_2)$ as $R \rightarrow \infty$, according to which

$$c_2(R_{12}, \Omega_1\Omega_2) = -\beta(\widehat{\mathbf{p}_1\mathbf{p}_2} : \mathbf{T}_\delta(\mathbf{R}_1, \mathbf{R}_2)) + c_2^{(sh)}(R_{12}, \Omega_1\Omega_2), \quad (4.3.63)$$

where $c_2^{(sh)}(R_{12}, \Omega_1\Omega_2)$ is the short-range part of the direct correlation function. This asymptotic behaviour is explicitly or implicitly assumed in many works and, apparently, is correct [73, 266]. In this case, the direct correlation function does not depend on the geometry of the sample, but the convolution in the Ornstein–Zernike equation (4.1.61) leads to such a dependence for the pair distribution function.

By definition (4.3.58), the polarisation vector can be represented as

$$\mathbf{P}(\mathbf{R}) = \rho \int \mathbf{p}_1 [F_1(\mathbf{R}, \Omega) - 1] d\Omega, \quad (4.3.64)$$

where $F_1(\mathbf{R}, \Omega)$ is the one-particle function of the system in the external field $E_0(R)$. In the linear approximation with respect to the field

$$F_1(\mathbf{R}, \Omega) = 1 + \int \Phi_1(\mathbf{R}_2, \Omega_2) \left(\frac{\delta F_1(\mathbf{R}, \Omega)}{\delta \Phi_1(\mathbf{R}_2, \Omega_2)} \right)_{E_0=0} d\mathbf{R}_2 d\Omega_2 + \dots, \quad (4.3.65)$$

where $\Phi_1(\mathbf{R}, \Omega) = (\mathbf{p}_1 \mathbf{E}_0(R))$ is the energy of the molecule in the external field. Expression (4.3.65) corresponds to the inverse

$$\Phi_1(\mathbf{R}, \Omega) = \int \left(\frac{\delta \Phi_1(\mathbf{R}, \Omega)}{\delta F_1(\mathbf{R}_2, \Omega_2)} \right)_{E_0} [F_1(\mathbf{R}_2, \Omega_2) - 1] d\mathbf{R}_2 d\Omega_2 + \dots \quad (4.3.66)$$

By definition (see (5.1.21), (5.1.22))

$$\begin{aligned} \left(\frac{\delta F_1(\mathbf{R}_1, \Omega_1)}{\delta \Phi_1(\mathbf{R}_2, \Omega_2)} \right)_{\mathbf{E}_0} &= -\beta |\delta(R_{12})\delta(\Omega_1 - \Omega_2) + \rho h_2(R_{12}, \Omega_1\Omega_2)|, \\ -\beta \left(\frac{\delta \Phi_1(\mathbf{R}_1, \Omega_1)}{\delta F_1(\mathbf{R}_2, \Omega_2)} \right)_{\mathbf{E}_0} &= \delta(R_{12})\delta(\Omega_1 - \Omega_2) - \rho c_2(R_{12}, \Omega_1\Omega_2), \end{aligned}$$

where $h_2(R_{12}, \Omega_1\Omega_2)$ and $c_2(R_{12}, \Omega_1\Omega_2)$ are the corresponding correlation functions of the system in the absence of an external field.

Expression (4.3.66) can now be rewritten as

$$-\beta \Phi_1(R_1\Omega_1) = F_1(R_1\Omega_1) - 1 - \rho \int d\mathbf{R}_2 d\Omega_2 [F_1(R_2\Omega_2) - 1] c_2(R_{12}\Omega_1\Omega_2).$$

Multiplying the obtained equation by $\mathbf{P}_1$ and integrating over $d\Omega_1$, we obtain $3y\mathbf{E}_0(\mathbf{R}_1) = 4\pi\mathbf{P}(\mathbf{R}_1) - \rho^2 \int d\mathbf{R}_2 d\Omega_1 d\Omega_2 \mathbf{p}_1 [F_1(\mathbf{R}_2\Omega_2) - 1] c_2(\mathbf{R}_{12}\Omega_1\Omega_2)$, from which, under assumption (4.3.63), we obtain

$$3y\mathbf{E}_L(\mathbf{R}_1) = 4\pi\mathbf{P}(\mathbf{R}_1) - \rho^2 \int d\mathbf{R}_2 d\Omega_1 d\Omega_2 \mathbf{p}_1 [F(\mathbf{R}_2\Omega_2) - 1] c_2^{(sh)}(\mathbf{R}_{12}\Omega_1\Omega_2), \quad (4.3.67)$$

where $\mathbf{E}_L(\mathbf{R}_1) = \mathbf{E}_0(\mathbf{R}_1) + \int d\mathbf{R}_2 \mathbf{T}_\delta(\mathbf{R}_1, \mathbf{R}_2) \mathbf{P}(\mathbf{R}_2)$.

For a weak field inhomogeneity under the integral in (4.3.67), we can approximate $F_1(\mathbf{R}_2\Omega_2) \approx F_1(R_1\Omega_1)$. Then,

$$3y\mathbf{E}_L(\mathbf{R}) = 4\pi\alpha\mathbf{P}(\mathbf{R}), \quad (4.3.68)$$

where

$$1 - \alpha = \rho \int d\mathbf{R}_2 d\Omega_2 d\Omega_1 \cos \vartheta_{12} c_2^{(sh)}(R_{12}, \Omega_1\Omega_2). \quad (4.3.69)$$

Expression (4.3.68) coincides with (4.3.57), thereby proving (4.3.56). Comparing (4.3.57) and (4.3.68), for the dielectric permittivity, we arrive at Ramshaw's expression [270, 271]

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{\alpha} y. \quad (4.3.70)$$

Since $c_2^{(sh)}(R_{12}, \Omega_1\Omega_2)$ is a short-range function (decaying faster than $1/R^3$), the parameter α (and consequently ε) does not depend on the geometry of the sample and on its surroundings, being an intrinsic property of the system under consideration. Using the invariant expansion (4.1.63) for the direct correlation function, we obtain

$$\alpha = 1 - \frac{1}{\sqrt{3}} 4\pi\rho \int_0^\infty \hat{c}^{110}(R) R^2 dR. \quad (4.3.71)$$

In particular, substituting expression (4.3.34) for $\hat{c}^{110}(R)$, we obtain $\alpha = \frac{1}{3}[q(2K\eta) + 2q(-K\eta)]$. From this and (4.3.70), we arrive at Wertheim's formula [233] for the dielectric permittivity

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{3y}{q(2K\eta) + 2q(-K\eta)} \quad (4.3.72)$$

or according to (4.3.37)

$$\varepsilon = \frac{q(2K\eta)}{q(-K\eta)} = \frac{(1 + 4K\eta)^2(1 + K\eta)^4}{(1 - 2K\eta)^6}, \quad (4.3.73)$$

where $K\eta$ is determined by equation (4.3.36). It is important to note that expanding (4.3.72) in powers of y yields exact values for the first two coefficients of the series (4.3.62).

Høye and Stell [272] noted that relation (4.3.70) is valid only for molecules with axial symmetry. For molecules of arbitrary shape, they derived the expression

$$\frac{\varepsilon - 1}{\varepsilon + 2} = y \frac{\partial}{\partial \alpha_{00}} \ln \det \alpha, \quad (4.3.74)$$

where the matrix α consists of elements $\alpha_{\mu\nu} = \delta_{\mu\nu} - \frac{1}{\sqrt{3}}4\pi\rho \int_0^\infty \hat{c}_{\mu\nu}^{110}(R)R^2 dR$.

Certainly, the previously used definition of dielectric permittivity based on equation (4.3.56) is not the only possible one. Dielectric permittivity can be determined in various equivalent ways, for instance, as the ratio of the limiting potential of interaction between two ions in a vacuum to the effective potential of their interaction in the medium at $R \rightarrow \infty$. Earlier, we established that screening of the Coulomb potential by dipole interactions leads to the emergence of dielectric permittivity ε . However, this approach makes expressions (4.3.10) and (4.3.23) valid only in the limit $y \rightarrow 0$. Nevertheless, as shown earlier, the contribution of intermolecular interactions in formula (4.3.61) being taken into account results in the geometric effects of the sample that play a role. Since, in the calculation of screened potentials, they correspond to a term with $\mathbf{k} = 0$ in the original interaction potential, which was previously omitted, we first reproduce the results (4.3.20)–(4.3.22) taking this term into account. These screened potentials are determined by the Ornstein–Zernike equation, in which $c_2(R_1, \Omega_1\Omega_2) = -\beta\Phi_2(R, \Omega_1\Omega_2)$. Let us first focus on the screened potential of dipole-dipole interaction.

As in other systems, for hard spheres with dipole interactions, a finite function can be added to the dipole potential in the unphysical region $R < \sigma$ without altering the general properties of the system. Let

$$\Phi_2(R_1, \Omega_1\Omega_2) = \hat{\Phi}^{110}(R)\hat{\Psi}^{110}(\Omega_1\Omega_2\Omega_R) + \hat{\Phi}^{112}(R)\hat{\Psi}^{112}(\Omega_1\Omega_2\Omega_R),$$

where for $R > \sigma$ one has $\hat{\Phi}^{110}(R) = 0$; $\hat{\Phi}^{112}(R) = -\frac{\sqrt{30}}{3}p^2\frac{1}{R^3}$. Following Høye and Stell [272], we introduce a parameter θ

$$\frac{4}{3}\pi p^2\theta = \frac{\sqrt{3}}{3} \int \Phi^{110}(R) dR$$

and set

$$\frac{\sqrt{3}}{3}\hat{\Phi}^{110}(R) = \begin{cases} p^2\theta, & R < \sigma, \\ 0, & R > \sigma; \end{cases} \quad \frac{\sqrt{30}}{3}\hat{\Phi}^{112}(R) = \begin{cases} -p^2\frac{1}{R^3}, & R < \sigma, \\ 0, & R > \sigma. \end{cases}$$

In terms of the previously accepted notation, we have

$$\begin{aligned} h_2(R, \Omega_1\Omega_2) &= g^{(1,1)}(R, \Omega_1\Omega_2) = \\ &= \hat{h}^{112}(R)\hat{\Psi}^{112}(\Omega_1\Omega_2\Omega_R) + \hat{h}^{110}(R)\hat{\Psi}^{110}(\Omega_1\Omega_2\Omega_R), \\ c_2(R, \Omega_1\Omega_2) &= -\beta\Phi_2(R, \Omega_1\Omega_2) = \\ &= \hat{c}^{112}(R)\hat{\Psi}^{112}(\Omega_1\Omega_2\Omega_R) + \hat{c}^{110}(R)\hat{\Psi}^{110}(\Omega_1\Omega_2\Omega_R), \end{aligned}$$

where

$$\begin{aligned} \hat{c}^{112}(R) &= \begin{cases} \frac{\sqrt{30}}{3}\beta p^2\frac{1}{R^3}, & R > \sigma, \\ 0, & R < \sigma; \end{cases} \\ \hat{c}^{110}(R) &= \begin{cases} 0, & R > \sigma, \\ -\beta p^2\frac{1}{\sqrt{3}}\theta, & R < \sigma. \end{cases} \end{aligned}$$

For the Fourier-components, according to (4.1.65), we have

$$\begin{aligned} \hat{h}^{11l}(k) &= 4\pi i^l \int_0^\infty \hat{h}^{11l}(R) j_l(kR) R^2 dR, \\ \hat{c}^{110}(k) &= -\frac{\sqrt{3}}{3}4\pi\beta p^2\theta \frac{j_1(k\sigma)}{k\sigma}, \quad \hat{c}^{112}(k) = -\frac{\sqrt{30}}{3}4\pi\beta p^2 \frac{j_1(k\sigma)}{k\sigma}. \end{aligned}$$

According to (4.1.73), the functions

$$\begin{aligned} H_0^{11}(k) &= \frac{2}{\sqrt{30}}\hat{h}^{112}(k) - \frac{1}{\sqrt{3}}\hat{h}^{110}(k), \\ H_1^{11}(k) &= \frac{1}{\sqrt{30}}\hat{h}^{112}(k) + \frac{1}{\sqrt{3}}\hat{h}^{110}(k), \\ C_0^{11}(k) &= \frac{2}{\sqrt{30}}\hat{c}^{112}(k) - \frac{1}{\sqrt{3}}\hat{c}^{110}(k), \\ C_1^{11}(k) &= \frac{1}{\sqrt{30}}\hat{c}^{112}(k) + \frac{1}{\sqrt{3}}\hat{c}^{110}(k) \end{aligned} \tag{4.3.75}$$

satisfy the following set of equations

$$\begin{aligned} H_0^{11}(k) - C_0^{11}(k) &= \rho H_0^{11}(k) C_0^{11}(k), \\ H_1^{11}(k) - C_1^{11}(k) &= -\rho H_1^{11}(k) C_1^{11}(k). \end{aligned} \quad (4.3.76)$$

Hence, it follows

$$\begin{aligned} \hat{h}^{112}(k) &= \frac{\hat{c}^{112}(k)}{\left[1 + \rho \left(\frac{1}{\sqrt{30}} \hat{c}^{112}(k) + \frac{1}{\sqrt{3}} \hat{c}^{110}(k)\right)\right]} \times \\ &\times \left[1 - \rho \left(\frac{2}{\sqrt{30}} \hat{c}^{112}(k) - \frac{1}{\sqrt{3}} \hat{c}^{110}(k)\right)\right]^{-1}, \\ \hat{h}^{110}(k) &= \frac{1}{\sqrt{10}} \hat{h}^{112}(k) \left[\left(1 + \sqrt{10} \frac{\hat{c}^{110}(k)}{\hat{c}^{112}(k)}\right) \times \right. \\ &\times \left. \left(1 - \rho \left(\frac{2}{\sqrt{30}} \hat{c}^{112}(k) - \frac{1}{\sqrt{3}} \hat{c}^{110}(k)\right) - 1\right) \right]. \end{aligned} \quad (4.3.77)$$

In the limit of $R \rightarrow \infty$, which corresponds to $k \rightarrow 0$, we arrive at the following expression for the screened potential

$$\begin{aligned} g^{(1,1)}(R, \theta) &= \beta(\mathbf{p}_1^{\text{ef}} \nabla)(\mathbf{p}_2^{\text{ef}} \nabla) \frac{1}{\varepsilon R} + \beta[\theta - (1 - \theta)(2 + \theta)y] \times \\ &\times \frac{1}{\varepsilon} \frac{4}{3} \pi (\mathbf{p}_1^{\text{ef}} \mathbf{p}_2^{\text{ef}}) \delta(R), \end{aligned} \quad (4.3.78)$$

which differs in form from (4.3.22) only by the presence of a second short-range term.

For the screened potential of ion-dipole interaction, we have

$$\begin{aligned} h_2(R_{12}, \Omega_2) &= c_2(R_{12}, \Omega_2) + \\ &+ \rho \int c_2(R_{13}, \Omega_3) g^{(1,1)}(R_{32}, \Omega_3, \Omega_2) d\mathbf{R}_3 d\Omega_3, \end{aligned} \quad (4.3.79)$$

where

$$\begin{aligned} c_2(R_{12}, \Omega_2) &= \hat{c}^{011}(R_{12}) \hat{\Psi}^{011}(\Omega_2, \Omega_{\mathbf{R}_{12}}), \\ \hat{c}^{011}(R) &= \begin{cases} \beta e z_a p \frac{1}{R^2}, & R > \sigma, \\ 0, & R < \sigma; \end{cases} \\ h_2(R, \Omega_2) &= g^{(0,1)}(R, \Omega_2) = \hat{h}^{011}(R) \hat{\Psi}^{011}(\Omega_2, \Omega_{\mathbf{R}}). \end{aligned}$$

According to (4.1.65),

$$\hat{h}^{011}(k) = 4\pi i \int_0^\infty \hat{h}^{011}(R) j_1(kR) R^2 dR, \quad \hat{c}^{011}(k) = 4\pi i \frac{1}{k} \beta p e z_a j_0(k\sigma).$$

For the function $C_0^{01}(k) = \frac{1}{\sqrt{3}}\hat{c}^{011}(k)$, $H_0^{01}(k) = \frac{1}{\sqrt{3}}\hat{h}^{011}(k)$ based on (4.1.75), we have

$$H_0^{01}(k) = C_0^{01}(k)[1 + \rho H_0^{11}(k)].$$

Using the previously derived expression for $H_0^{11}(k)$, in the limit $k \rightarrow 0$, we obtain a result that matches the form of (4.3.21).

Finally, for ion-ion interaction

$$h_2(R) = g^{(0,0)}(R) = c_2(R) + \rho \int c_2(R_{13}, \Omega_3) g^{(1,0)}(R_{32}, \Omega_3) d\mathbf{R}_3 d\Omega_3$$

or according to (4.3.79)

$$\begin{aligned} g^{(0,0)}(R) = c_2(R) + \rho \int c_2(R_{13}, \Omega_3) c_2(R_{32}, \Omega_3) d\mathbf{R}_3 d\Omega_3 + \rho^2 \int c_2(R_{13}, \Omega_3) \times \\ \times g^{(1,1)}(R_{34}, \Omega_3 \Omega_4) c_2(R_{42}, \Omega_4) d\mathbf{R}_3 d\Omega_3 d\mathbf{R}_4 d\Omega_4, \end{aligned} \quad (4.3.80)$$

where

$$c_2(R) = \hat{c}^{000}(R) = \begin{cases} -\beta e^2 z_a z_b \frac{1}{R}, & R > \sigma, \\ 0, & R < \sigma, \end{cases} \quad g^{(0,0)}(R) = \hat{h}^{000}(R).$$

For the Fourier-components

$$\begin{aligned} \hat{c}^{000}(k) = C_0^{00}(k) = -4\pi\beta e^2 z_a z_b \frac{1}{k^2} \cos(k\sigma), \\ \hat{h}^{000}(k) = H_0^{00}(k) = 4\pi \int_0^\infty \hat{h}^{000}(k) j_0(kR) R^2 dR \end{aligned}$$

taking into account (4.3.80) and (4.1.73), we have

$$H_0^{00}(k) = C_0^{00}(k) + \rho C_0^{01}(k) C_0^{10}(k) + \rho^2 C_0^{01}(k) H_0^{11}(k) C_0^{10}(k). \quad (4.3.81)$$

Hence, in the limit $k \rightarrow 0$, we arrive at an expression that coincides in form with (4.3.20).

The dielectric permittivity and the effective value of the dipole moment obtained as a result of screening are determined by the expressions

$$\varepsilon = \frac{1 + (2 + \theta)y}{1 - (1 - \theta)y} \quad \text{or} \quad \frac{\varepsilon - 1}{(1 - \theta)\varepsilon + 2 + \theta} = y, \quad \mathbf{p}^{\text{ef}} = \frac{1}{1 - (1 - \theta)y} \mathbf{p}, \quad (4.3.82)$$

which coincide with (4.3.23) and (4.3.24) for $\theta = 0$.

It is clear that the exact value of ε should not depend on the method of interaction separation and, consequently, on θ . Since the obtained screened potentials determine the asymptotics of pair distribution functions in the random phase approximation, to accurately express the dielectric permittivity, it is necessary to determine the precise asymptotics of pair distribution functions.

Substituting into (4.3.80) the exact correlation function $h_2(R, \Omega_1 \Omega_2)$ instead of $g^{(1,1)}(R, \Omega_1 \Omega_2)$, we find that to determine ε , it is sufficient to consider the component $H_0^{11}(k)$, which we represent as the sum of long-range and short-range contributions in the form of terms $H_0^{11}(k) = H_0^{11(\ell)}(k) + H_0^{11(sh)}(k)$. In accordance with (4.3.63) $C_0^{11}(k) = C_0^{11(\ell)}(k) + C_0^{11(sh)}(k)$, where $C_0^{11(\ell)}(k) = -\frac{4}{3}\pi\beta p^2 \frac{j_1(k\sigma)}{k\sigma}(2+\theta) \rightarrow -\frac{y}{\rho}(2+\theta)$ as $k \rightarrow 0$. From (4.3.76), we have

$$H_0^{11(\ell)}(k) = \frac{M_0^{11}(k)C_0^{11(\ell)}(k)M_0^{11}(k)}{1 - \rho C_0^{11(\ell)}(k)M_0^{11}(k)}, \quad (4.3.83)$$

where $M_0^{11}(k) = 1 + \rho H_0^{11(sh)}(k)$

Substituting (4.3.83) into (4.3.81), we find

$$H_0^{00}(k) = C_0^{00}(k) + \rho C_0^{01}(k)M_0^{11}(k)C_0^{10}(k) + \rho^2 C_0^{01}(k)M_0^{11}(k) \times \\ \times C_0^{11(\ell)}(k)M_0^{11}(k)C_0^{10}(k) \left[1 - \rho C_0^{11(\ell)}(k)M_0^{11}(k)\right]^{-1}.$$

Thus, in the limit $k \rightarrow 0$ for the screened potential of ion-ion interaction, we again arrive at expression (4.3.20), in which, however, the dielectric permittivity is determined by the relation

$$\frac{\varepsilon - 1}{(1 - \theta)\varepsilon + 2 + \theta} = z = yM_0^{11}(k=0), \quad (4.3.84)$$

derived by Høye and Stell [272]. Since at $k = 0$, $j_l(kR) \neq 0$ only for $l = 0$, then, $H_0^{11(sh)}(k=0) = -\frac{1}{\sqrt{3}}\hat{h}^{110(sh)}(k=0)$ and, thus, only the term $\hat{h}^{110(sh)}$ contributes to ε . The quantity z can be represented in the form

$$z = \frac{4}{9}\pi\beta\rho(\mathbf{p}\mathbf{p}_{\text{HS}}), \quad (4.3.85)$$

where $\mathbf{p}_{\text{HS}}(\Omega_1, \theta) = \mathbf{p}_1(\Omega_1) + \rho \int h_2^{(sh)}(R, \Omega_1 \Omega_2) \mathbf{p}(\Omega_2) d\mathbf{R} d\Omega_2$ is the Høye—Stell expression for the effective dipole moment of a molecule.

According to the outlined scheme, the asymptotics of the ion-dipole and dipole-dipole distribution functions can also be determined. In particular, according to (4.3.83) and (4.3.84), we have

$$\rho H_0^{11}(k=0) = \rho H_0^{11(sh)}(k=0) + \frac{\rho M_0^{11}(k=0)C_0^{11(\ell)}(k=0)M_0^{11}(k=0)}{1 - \rho C_0^{11(\ell)}(k=0)M_0^{11}(k=0)} = \\ = \frac{z}{y} - 1 - \frac{z}{y} \frac{(2+\theta)z}{1 + (2+\theta)z}.$$

Similarly, for $H_1^{11}(k = 0)$. Assuming $H_1^{11}(k) = H_1^{11(\ell)}(k) + H_1^{11(sh)}(k)$, $C_1^{11}(k) = C_1^{11(\ell)}(k) + C_1^{11(sh)}(k)$, where $C_1^{11(\ell)}(k) = -\frac{4}{3}\pi\beta p^2 \frac{j_1(k\sigma)}{k\sigma}(1-\theta) \rightarrow -\frac{y}{\rho}(1-\theta)$ as $k \rightarrow 0$, and according to (4.3.76), we have

$$H_1^{11(\ell)}(k) = \frac{M_1^{11}(k)C_1^{11(\ell)}(k)M_1^{11}(k)}{1 + \rho C_1^{11(\ell)}(k)M_1^{11}(k)}, \quad M_1^{11}(k) = 1 - \rho H_1^{11(sh)}(k).$$

Since $H_1^{11(sh)}(k = 0) = \frac{1}{\sqrt{3}}\hat{h}^{110(sh)}(k = 0)$, then $M_1^{11}(k = 0) = M_0^{11}(k = 0) = \frac{z}{y}$. Thus $\rho H_1^{11(\ell)}(k = 0) = 1 - \frac{z}{y} - \frac{z}{y} \frac{z(1-\theta)}{1-z(1-\theta)}$ and according to (4.3.75)

$$\begin{aligned} \frac{3}{\sqrt{30}}\rho\hat{h}^{112}(k = 0) &= \rho [H_0^{11}(k = 0) + H_1^{11}(k = 0)] = \\ &= -\frac{3z^2}{y[1-z(1-\theta)][1+z(2+\theta)]}, \\ \frac{3}{\sqrt{3}}\rho\hat{h}^{110}(k = 0) &= \rho [2H_1^{11}(k = 0) - H_0^{11}(k = 0)] = \\ &= -3\left(\frac{z}{y} - 1\right) - \frac{3z^2[z(2+\theta)(1-\theta) - \theta]}{y[1-z(1-\theta)][1+z(2+\theta)]}. \end{aligned}$$

Excluding z according to (4.3.84), we obtain

$$\begin{aligned} \frac{3}{\sqrt{30}}\rho\hat{h}^{112}(k = 0) &= \frac{(\varepsilon - 1)^2}{3y\varepsilon}, \\ \frac{3}{\sqrt{3}}\rho\hat{h}^{110}(k = 0) &= 3\left[\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon y} - 1\right]. \end{aligned} \tag{4.3.86}$$

From the second relation for the dielectric permittivity, we arrive at the well-known Kirkwood formula [267]

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = yg_K, \tag{4.3.87}$$

where $g_K = 1 + \frac{1}{\sqrt{3}}\rho \int \hat{h}^{110}(R)d\mathbf{R}$ is the Kirkwood g -factor. Setting $\hat{h}^{110}(R) = 0$, we obtain $g_K = 1$, and according to (4.3.87), we arrive at the Onsager equation

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = y. \tag{4.3.88}$$

This formula is undoubtedly better than the Clausius–Mossotti relation (4.3.23), but unlike the Wertheim equation (4.3.73), it leads to an expansion

$\frac{\varepsilon - 1}{\varepsilon + 2} = y - 2y^3 + \dots$ that differs from (4.3.62). Determining ε from (4.3.88) and substituting it into the first formula (4.3.86), we obtain an expression for the pair distribution function

$$F_2(R, \Omega_1 \Omega_2) = H(R - \sigma) 3\beta \frac{\varepsilon - 1}{2\varepsilon + 1} (\mathbf{p}_1 \nabla)(\mathbf{p}_2 \nabla) \frac{1}{R},$$

using which one can obtain the free energy and other thermodynamic quantities [236]. In particular, Table 12 presents the values of critical parameters found in this way within the Onsager approximation.

The expressions for the dielectric permittivity (4.3.84) and (4.3.86) are exact. In particular, the first one generalizes a number of well-known relations in the literature. For instance, by setting $\theta = 0$ in (4.3.84), we arrive at the expression obtained by Høye and Stell in [273]:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = z(\theta = 0) = \frac{4}{9} \pi \beta \rho (\mathbf{p} \mathbf{p}_{\text{ef}}), \quad (4.3.89)$$

where

$$\mathbf{p}_{\text{ef}} = \mathbf{p}_{\text{HS}}(\theta = 0) = \mathbf{p}_1 + \rho \int h_2^{(sh)}(R, \Omega_1, \Omega_2, \theta = 0) \mathbf{p}_2 d\mathbf{R} d\Omega_2.$$

It is easy to verify the equivalence of this relation with the previously derived Ramshaw equation (4.3.70) (or, in the general case, (4.3.74)). For $\theta = 1$, from (4.3.84), we obtain the expression derived by Nienhuis and Deutch [266]:

$$\varepsilon = 1 + \frac{4}{3} \pi \beta \rho (\mathbf{p} \mathbf{p}_{\text{ND}}), \quad (4.3.90)$$

where $\mathbf{p}_{\text{ND}} = \mathbf{p}_{\text{HS}}(\theta = 1) = \mathbf{p}_1 + \rho \int h_2^{(sh)}(R, \Omega_1 \Omega_2, \theta = 1) \mathbf{p}_2 d\Omega_2 d\mathbf{R}$.

The expression coincides with (4.3.10) by form, differing only by the replacement of one of the dipole moments with its effective value $\mathbf{p}_{\text{ND}}$.

It should be noted that equations (4.3.89) and (4.3.90) are not mutually exclusive, as might initially appear. The difference between them is related to the ambiguity in the separation of interactions. Since the physical properties of the system should not depend on the method of this separation, the dielectric permittivity, like other physical quantities, should be invariant with respect to the choice of the parameter θ . At the same time, the results of approximate theories may considerably depend on θ . This is particularly characteristic of random phase approximation.

For systems of hard spheres with dipole interactions, this section has considered three different methods of interaction separation. Let us briefly discuss them. As noted, for this system, exact conditions hold

$$\hat{h}^{00}(R) = -1, \quad R < \sigma, \quad (4.3.91)$$

$$\hat{h}^{110}(R) = \hat{h}^{112}(R) = 0, \quad R < \sigma. \quad (4.3.92)$$

In the random phase approximation

$$\hat{c}^{110}(R) = 0, \quad \hat{c}^{112}(R) = \frac{\sqrt{30}}{3}\beta\frac{p^2}{R^3}, \quad R > \sigma. \quad (4.3.93)$$

The function $\hat{c}^{000}(R)$ for $R > \sigma$ is also considered given. To be specific, we set $\hat{c}^{000}(R) = 0$ for $R > \sigma$, which corresponds to the Percus—Yevick approximation for hard spheres. Assuming $\hat{c}^{110}(R) = \hat{c}^{112}(R) = 0$ for $R < \sigma$, we arrive at the Clausius—Mossotti equation (4.3.23) for the dielectric permittivity. However, this violates the exact relation (4.3.92).

In the second method of interaction separation, we assume $\hat{h}^{110}(R) = 0$ for all R . For the dielectric permittivity, this leads to the Onsager equation (4.3.88). Nevertheless, this still violates condition (4.3.92) for the function $\hat{h}^{112}(R)$. The best method of interaction separation is based on the exact condition (4.3.92) and for the dielectric permittivity leads to the Wertheim equation (4.3.73). Høye and Stell [272] showed that these three approximations can be considered as different variants of continuum models in the theory of dielectrics.

Ramshaw [274] provided a geometric interpretation for the parameter θ , showing that the apparent ambiguity in determining the dielectric permittivity is related to an actual indeterminacy while evaluating the integral in (4.3.54) and defining the local field $\mathbf{E}_L(R)$. By extracting from the integration region an ellipsoidal cavity of infinitely small volume centred at $\mathbf{R}' = \mathbf{R}$ and aligned along the polarisation vector, instead of (4.3.55), we obtain

$$\mathbf{E}(\mathbf{R}) = \mathbf{E}_0(\mathbf{R}) - \frac{4}{3}\pi(1 - \theta)\mathbf{P}(\mathbf{R}) + \lim_{\delta \rightarrow 0} \int d\mathbf{R}' T_\delta(\mathbf{R}, \mathbf{R}')\mathbf{P}(\mathbf{R}'), \quad (4.3.94)$$

where $\theta = 1 - 3D$; D is the depolarisation factor of the ellipsoid along its symmetry axes [232]. In particular, for a sphere, we have $D = 1/3$ and $\theta = 0$. The maximum value $\theta = 1$ corresponds to a needle-like cavity ($D = 0$), while the minimum value $\theta = -2$ corresponds to an infinitely thin disk ($D = 1$). If we now consider the field inside the ellipsoid $\mathbf{E}_L(R) = \mathbf{E}(R) + \frac{4}{3}\pi(1 - \theta)\mathbf{P}(R)$ (instead of the macroscopic field $\mathbf{E}(R)$), then instead of (4.3.57), we arrive at the relation

$$\frac{4}{3}\pi\mathbf{P}(R) = \frac{\varepsilon - 1}{(1 - \theta)\varepsilon + 2 + \theta}\mathbf{E}_L(R), \quad (4.3.95)$$

from which expressions (4.3.82) and (4.3.84) can be derived.

It should be noted that for a fixed θ , the previously obtained expression (4.3.78) for the screened potential may diverge. Substituting (4.3.82) into (4.3.84), we obtain

$$g^{(1,1)}(R) = \beta \frac{(\mathbf{p}_1 \nabla)(\mathbf{p}_2 \nabla) \frac{1}{R} + [\theta - (1 - \theta)(2 + \theta)y] \frac{4}{3}\pi(\mathbf{p}_1 \mathbf{p}_2)\delta(R)}{[1 + (2 + \theta)y][1 - (1 - \theta)y]}. \quad (4.3.96)$$

The divergence is associated with the denominator tending to zero and is possible in two cases. In the first case $1 - (1 - \theta)y = 0$, from which it follows that $y = \frac{1}{1 - \theta}$. According to (4.3.82), $\varepsilon = \infty$, which apparently corresponds to ferroelectric phase ordering, where the dipole moments of molecules align in one direction. In the second case, we arrive at the equation $1 + (2 + \theta)y = 0$, which has no solutions. Nevertheless, for $k \neq 0$, $3y \frac{j_1(k\sigma)}{k\sigma}$ should be substituted for y , leading to equation $1 + (2 + \theta)3y \frac{j_1(k\sigma)}{k\sigma} = 0$. According to (4.3.82) we have $y = \frac{\varepsilon - 1}{3\varepsilon} \left(1 - \frac{1}{3} \frac{k\sigma}{j_1(k\sigma)}\right)$. The minimum value of $3 \frac{j_1(k\sigma)}{k\sigma}$ corresponds to $k\sigma \approx 5.76$, which, apparently, should be considered as a point of a possible second phase transition in the system.

A common drawback of the expressions for the dielectric permittivity obtained in the random phase approximation is that they do not lead to an explicit dependence of ε on η . However, knowing the pair distribution function, the dielectric permittivity can be determined using one of the previously discussed formulas, for example, (4.3.87). In particular, in the approximation (4.3.49) for the g -factor, we obtain

$$g_K = g_{\text{ORPA}} + \frac{1}{\sqrt{3}} 4\pi\rho \int_0^\infty h_2^0(R) \hat{g}^{110}(R) R^2 dR, \quad (4.3.97)$$

where the approximation $g_K = g_{\text{ORPA}}$ corresponds to the Wertheim formula (4.3.73). The inclusion of the second term in (4.3.97) leads to an explicit dependence of the dielectric permittivity on two parameters, y and η . However, it is important to note the dielectric inconsistency of the approximation (4.3.49). The dielectric permittivity found using the first formula (4.3.86) coincides with Wertheim's expression (4.3.73).

In Table 13, compiled based on the work [239], the values of the dielectric permittivity obtained in various approximations using formula (4.3.87) for a system of hard spheres with dipole interactions at a density of $N/V\sigma^3 = 0.8$

Table 13. Dielectric permittivity of the hard sphere model with a dipole moment at density $\frac{N}{V}\sigma^3 = 0.8$

$\frac{\beta p^2}{\sigma^3}$	y	Onsager (4.3.88)	ORPA (4.3.73)	ORPA + LB_2 (4.3.49)	ORPA + LB_2 + + LB_3 (4.3.50)	MC
0.5	0.558	3.22	3.59	3.84	3.76	3.73 ± 0.1
1.0	1.116	5.62	7.80	9.27	9.66	9.0 ± 0.5
2.0	2.232	10.6	20.00	27.06	37.93	—
2.75	3.069	12.4	31.86	45.62	79.17	—
4.00	4.464	20.6	55.94	84.95	195.6	—

are presented. As seen from the table, Wertheim equation (4.3.73) is more accurate than Onsager expression (4.3.88). The most accurate results are given by approximations (4.3.49) and (4.3.50), but the latter, in the region of large values of $\beta p^2/\sigma^3$ apparently leads to considerably overestimated results.

However, the dipolar systems considered so far are, in many respects, purely model-based. Real molecules possess a non-spherical shape, a specific spatial charge distribution, and some intrinsic polarisability. The presence of the latter leads to a many-particle induction and dispersion interactions, which considerably contribute to the thermodynamic and dielectric properties of the system.

Using equation (4.3.86), Høye and Stell [275] derived an expression for the dielectric permittivity with the help of site-site distribution functions. For simplicity, we restrict our considerations to linear molecules in which the dipole moment direction coincides with the molecular symmetry axis. According to definition (4.2.37), for the Fourier transform of the site-site correlation function of force centres α and β in two rigid molecules, we have

$$h_{\alpha\beta}(k) = \int h_2(k, \Omega_1 \Omega_2) e^{i\mathbf{k}(\mathbf{l}_\alpha - \mathbf{l}_\beta)} d\Omega_1 \Omega_2,$$

where $\mathbf{l}_\alpha, \mathbf{l}_\beta$ are the relative coordinates of the force centres of the two molecules (see Fig. 15). Using the expression (4.1.33) for $e^{i\mathbf{k}\mathbf{l}_\alpha}$ and $e^{-i\mathbf{k}\mathbf{l}_\beta}$, and representing $h(k, \Omega_1 \Omega_2)$ in the form (4.1.23), after integration over orientations, we have

$$\begin{aligned} h_{\alpha\beta}(k) = & \sum_{lmn} \begin{pmatrix} m & n & l \\ 0 & 0 & 0 \end{pmatrix} i^{m+n} j_m(kl_\alpha) j_n(-kl_\beta) \hat{h}^{lmn}(k) = j_0(kl_\alpha) \times \\ & \times j_0(-kl_\beta) \hat{h}^{000}(k) - j_1(kl_\alpha) j_1(-kl_\beta) \left[\frac{2}{\sqrt{30}} \hat{h}^{112}(k) - \frac{1}{\sqrt{3}} \hat{h}^{110}(k) \right] + \dots, \end{aligned}$$

where $j_0(kl) = 1 - \frac{1}{6}k^2l^2 + \dots$, $j_1(kl) = \frac{1}{3}kl + \dots$ are the spherical Bessel functions.

Let a point charge ez_α be concentrated at each force centre. Then, according to (4.3.86), in the limit $k \rightarrow 0$

$$\rho \sum_{\alpha, \beta} h_{\alpha\beta}(k) e^2 z_\alpha z_\beta = \frac{1}{9} k^2 p^2 \left(\frac{\varepsilon - 1}{y\varepsilon} - 3 \right), \quad (4.3.98)$$

where $\mathbf{p} = \sum_{\alpha} ez_\alpha \mathbf{l}_\alpha$ is the value for the dipole moment of a molecule.

This is the final expression for the dielectric permittivity through site-site distribution functions. Hence, an important conclusion follows regarding the short-range nature of site-site correlation functions. According to

(4.3.98), as $r \rightarrow \infty$

$$h_{\alpha\beta}(r) \simeq h^{000}(r) + \frac{1}{9}l_{\alpha}l_{\beta}\frac{1}{r}\frac{\partial^2}{\partial r^2} [r(H^{112}(r) + H^{110}(r))] = O\left(\frac{1}{r^6}\right). \quad (4.3.99)$$

The results (4.3.98) and (4.3.99) are also generalized to the case of molecules of arbitrary shape [275].

Dielectric properties of polar systems, taking into account the intrinsic polarisability of molecules, were thoroughly studied by Wertheim [276–278]. An important result of these works is renormalisation of the dipole moment and polarisability values of molecules due to multi-particle induction interactions. Chandler [220] obtained an expression for the dielectric permittivity of non-rigid polarisable dipolar molecules using site-site distribution functions.

In conclusion, it should be noted that dielectric permittivity is not the only effect associated with molecular polarisation. Dipole interactions play an important role, for example, in the Kerr effect, characterized by a constant, which is determined by the quantity [279, 280]

$$G_2 = \rho \int P_2(\cos \vartheta_{12}) h_2(R, \Omega_1 \Omega_2) d\mathbf{R} d\Omega_1 d\Omega_2, \quad (4.3.100)$$

for which Høye and Stell [281] recently obtained an expression through site-site distribution functions.

4.4. Ion-molecular systems

The characteristic features of a mixed system of ions and polar molecules are associated with a mutual screening of electrostatic interactions. At the same time, as it has been established, dipole screening determines the dielectric properties of the molecular subsystem, while the ion screening leads to an exponentially decreasing electrostatic force. In nature, mixed ion-molecular systems are widely present in the form of electrolyte solutions, which play an important role in electrochemical and in many biological phenomena. The first attempts to construct theories of electrolyte solutions were based on an explicit consideration of only the ionic subsystem. This approach is associated with the osmotic method described above (see Subsection 3.3.3, which is based on excluding one of the subsystems (in this case, the molecular one) from explicit consideration. It is clear that the sequential execution of this operation is at least as complex as describing the entire system as a whole. Moreover, the phenomenological description of effective intermolecular interactions, usually adopted in such cases, is insufficiently accurate since it does not consider either the molecular structure of the solvent or its changes due to the influence of ions.

The construction of a microscopic theory applicable in a wide range of ionic concentrations should be based on a sequential consideration of all components

forming the solution and their mutual interactions. The foundation of such a theory was laid by the one of the authors in works [282–284], where they formulated a systematic microscopic study of mixed ion-dipole systems — the simplest model of electrolyte solutions.

4.4.1. Application of the collective variables method

We begin the description of the system with a generalization of the results presented at the beginning of the previous paragraph. Now, the generalized charge for ions of type a is understood as the charge of the ion ez_a , while for molecules of type s , their generalized charge is $Q_s(\nabla)$, with the series (4.3.4) for which starting from the dipole term⁸

$$Q_x(\nabla) = \begin{cases} ez_a, & x = a, \\ Q_s(\nabla), & \text{if } x = s. \end{cases}$$

Repeating the derivations presented in Chapter 2, for free energy and distribution functions, we arrive at cluster expansions, the construction of which is based on the screened potential (4.3.9). However, truncation of the multipole series for $Q_s(\nabla)$ leads to the difficulties primarily related to the divergence of the used Fourier expansion (4.3.5). In this regard, the Jacobian $J(\rho)$ can be transformed in such a way that it leads only to ionic screening. Decomposing $D_2(\omega)$ in expression (2.1.40) into ionic and molecular parts

$$D_2(\omega) = -\frac{\pi^2}{2} \sum_{\mathbf{k}} \left(\sum_a N_a \lambda_a(\mathbf{k}) \lambda_a(-\mathbf{k}) + \sum_s N_s \lambda_s(\mathbf{k}) \lambda_s(-\mathbf{k}) \right) \omega_{\mathbf{k}} \omega_{-\mathbf{k}},$$

where

$$\begin{aligned} \lambda_a(\mathbf{k}) &= ez_a \left[\sum_a N_a e^2 z_a^2 + \sum_s N_s Q_s(\mathbf{k}) Q_s(-\mathbf{k}) \right]^{-1/2}; \\ \lambda_s(\mathbf{k}) &= Q_s(\mathbf{k}) \left[\sum_a N_a e^2 z_a^2 + \sum_s N_s Q_s(\mathbf{k}) Q_s(-\mathbf{k}) \right]^{-1/2}. \end{aligned}$$

Performing in the molecular part a substitution $i\pi\omega_{\mathbf{k}} = \partial/\partial\rho_{\mathbf{k}}$, after integrating over $(d\omega)$, we obtain

$$J(\rho) = \exp \left\{ \hat{D}_2^{(s)}(\partial/\partial\rho) + \sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right\} J_G(\rho), \quad (4.4.1)$$

where

$$\hat{D}_2^{(s)}(\partial/\partial\rho) = \frac{1}{2} \sum_{\mathbf{k}} \sum_s N_s \lambda_s(\mathbf{k}) \lambda_s(-\mathbf{k}) \frac{\partial^2}{\partial\rho_{\mathbf{k}} \partial\rho_{-\mathbf{k}}};$$

⁸Further in this paragraph, the letters $a, b, c, \dots$ denote ion types, while $s, t, u, \dots$ denote the molecule types. The indexes $x, y, \dots$ refer to both ions and molecules.

$$J_G(\rho) = \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \left[\frac{1}{\gamma^2(\mathbf{k})} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \ln(\pi \gamma^2(\mathbf{k})) \right] \right\};$$

$$\gamma^2(\mathbf{k}) = \left(\sum_a N_a e^2 z_a^2 \right) \left[\sum_a N_a e^2 z_a^2 + \sum_s N_s Q_s(\mathbf{k}) Q_s(-\mathbf{k}) \right]^{-1}.$$

Now, while integrating over collective variables, each paired derivative $\partial^2 / \partial \rho_{\mathbf{k}} \partial \rho_{-\mathbf{k}}$ corresponds to the factor $\gamma^{-2}(\mathbf{k}) [\gamma^{-2}(\mathbf{k}) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1]$. As a result, we arrive at cluster expansions constructed on screened potentials

$$\begin{aligned} g_{xy}(R) &= - \sum_{\mathbf{k}} \lambda_x(\mathbf{k}) \lambda_y(-\mathbf{k}) \frac{\alpha(k)}{1 + \alpha(k) \gamma^2(k)} e^{i\mathbf{k}\mathbf{R}} = \\ &= -\beta Q_x(\nabla) Q_y(-\nabla) \frac{1}{R} e^{-\varkappa R}, \end{aligned} \quad (4.4.2)$$

where $\varkappa = \left[4\pi\beta \sum_a \frac{N_a}{V} e^2 z_a^2 \right]^{1/2}$ is the quantity inverse to the Debye length.

Thus, the ions screen not only the Coulomb potential but also other electrostatic interactions in the system. A novel aspect of the considered method is the action of the operator $\exp[\hat{D}_2^{(s)}(\partial/\partial\rho)]$, which generates the diagrams with the vertices from which only two light lines emerge. In particular, the action of the operator $\exp[\hat{D}_2^{(s)}(\partial/\partial\rho)]$ on $J_G(\rho)$ leads to the expression

$$\exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \sum_s N_s \lambda_s(\mathbf{k}) \lambda_s(-\mathbf{k}) \frac{\alpha(k)}{1 + \alpha(k) \gamma^2(k)} \right\}. \quad (4.4.3)$$

Accordingly, we represent $\exp \left\{ \frac{1}{2} \sum_{\mathbf{k}} \alpha(k) \right\}$, which appears in the expression for the configuration integral $Q_N^{(\ell)}$, in the form

$$\exp \left\{ \frac{1}{2} \sum_a \sum_{\mathbf{k}} N_a \lambda_a^2(k) \alpha(k) + \frac{1}{2} \sum_s \sum_{\mathbf{k}} N_s \lambda_s(\mathbf{k}) \lambda_s(-\mathbf{k}) \alpha(k) \right\}.$$

The first term, together with the factor $\prod'_{\mathbf{k}} [1 + \gamma^2(k) \alpha(k)]^{-1}$, arising as a result of integration over collective variables, leads to the Debye expression for the free energy of the ionic subsystem. Combining the second term with (4.4.3), we obtain an additional contribution to the second cluster coefficient

$$-\beta \sum_{a,s} \frac{N_a N_s}{2V} \int \Phi_{as}(R, \Omega) g_{as}(R, \Omega) d\mathbf{R} d\Omega.$$

Another contribution to the second cluster coefficient is also given by the pairing of operators $\frac{1}{2}\hat{D}_2^{(s)}(\partial/\partial\rho)\hat{D}_2^{(s)}(\partial/\partial\rho)$, and it is equal to $\sum_{s,t} \frac{N_s N_t}{2V} \int g_{st}^2(R\Omega_1\Omega_2) d\mathbf{R} d\Omega_1 d\Omega_2$.

The pairing of operators $\frac{1}{3!}\hat{D}_2^{(s)}\hat{D}_2^{(s)}\hat{D}_2^{(s)}$ and $\frac{1}{2}\hat{D}_2^{(s)}[\hat{D}_3\hat{D}_3 + \dots]$ contributes to the third cluster coefficient⁹

$$\frac{1}{2 \cdot 3} \left[\begin{array}{c} \text{s} \\ \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \\ \diagdown \quad \diagup \\ \text{s} \quad \text{s} \end{array} + 3 \begin{array}{c} \text{s} \\ \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \\ \diagdown \quad \diagup \\ \text{s} \quad \text{s} \end{array} \right] \text{ etc.}$$

The consideration of short-range interactions follows the scheme presented in Chapter 2. The difference lies only in the fact that the functional derivatives $\delta g_{xy}/\delta\Phi_{x'y'}$ will be different depending on which exactly potential the derivative is taken with respect to. According to (4.4.2), the derivatives with respect to the potentials of ion-molecular and intermolecular interactions are equal

$$\begin{aligned} \frac{\delta g_{xs}}{\delta\Phi_{yt}} &= \frac{1}{V^2} [\delta_{xy}\delta_{st}\delta(\mathbf{R}_{xy})\delta(\mathbf{R}_{st})\delta(\Omega_x - \Omega_y)\delta(\Omega_s - \Omega_t) + \\ &\quad + \delta_{xt}\delta_{ys}\delta(\mathbf{R}_{xt})\delta(\mathbf{R}_{ys})\delta(\Omega_x - \Omega_t)\delta(\Omega_y - \Omega_s)]. \end{aligned}$$

The derivatives with respect to ionic potentials are taken in accordance with (2.2.43). As before, accounting for short-range interactions leads to the replacement of the exponent $e^{g_{ab}(R)}$ with $\exp\{g_{ab}(R) - \beta\varphi_{ab}(R)\}$. By functionally differentiating the free energy with respect to the interaction potentials, we arrive at expressions for pair distribution functions

$$F_{ab}(R) = \exp[g_{ab}(R) - \beta\varphi_{ab}(R)] \left[1 + \begin{array}{c} \bullet \\ \diagup \quad \diagdown \\ \circ \quad \circ \end{array} - \begin{array}{c} i \\ \diagup \quad \diagdown \\ \circ \quad \circ \end{array} + \dots \right],$$

where i denotes that the corresponding vertex is solely ionic.

The adopted modification of the Jacobian $J(\rho)$ eliminates the molecular screening and is not mandatory. For example, one may formally retain the complete expression for $Q_s(\nabla)$ and truncate the multipole series (4.3.4) only in the final results. In this case, the screened potential is determined by expression (4.3.9). In particular, for a mixed system of ions and dipolar molecules

$$g_{xy}(R) = -\beta Q_x(\nabla)Q_y(-\nabla)\frac{1}{\varepsilon R}e^{-\frac{\kappa}{\sqrt{\varepsilon}}R}, \quad (4.4.4)$$

⁹The letter s indicates that the vertex to which it refers is molecular.

where for ions $Q_x(\nabla) = ez_a$, for dipoles $Q_x(\nabla) = Q_s(\nabla) = (\mathbf{p}_s^{(1)} \nabla)$, and $\varepsilon = 1 + 3y$ is the part of the dielectric permittivity associated with screening and coinciding with (4.3.10).

Taking into account the entire multipole series, molecular screening leads to the emergence of a dielectric function defined by expression (4.3.13). The latter coincides with (4.3.10) only in the limit $k \rightarrow 0$, while for $k \rightarrow \infty$ it decreases according to the Coulomb law and approaches unity. Considering these two limits, it can be approximated by the expression $\varepsilon(k) = 1 + \frac{\varepsilon(0) - 1}{1 + q^2 k^2}$, where $\varepsilon(0) = 1 + 3y$, and q is a certain approximation parameter. Then, for the screened potentials, we have [285]

$$g_{xy}(R) = -\beta Q_x(\nabla) Q_y(-\nabla) \frac{1}{R} \frac{(1 - \alpha_-^2 q^2) e^{-\alpha_- R} - (1 - \alpha_+^2 q^2) e^{-\alpha_+ R}}{\sqrt{[\varepsilon(0) + \kappa^2 q^2]^2 - 4q^2 \kappa^2}}, \quad (4.4.5)$$

where

$$\alpha_{\pm} = \frac{1}{\sqrt{2}q} \left[\varepsilon(0) + \kappa^2 q^2 \pm \sqrt{[\varepsilon(0) + \kappa^2 q^2]^2 - 4q^2 \kappa^2} \right]^{1/2}.$$

or low ionic concentrations, when $q\kappa \ll 1$, we have $\alpha_- \simeq \frac{\kappa}{\sqrt{\varepsilon(0)}}$, $\alpha_+ \simeq \left[\frac{q}{\sqrt{\varepsilon(0)}} \right]^{-1}$ and the screened potentials take the well-known Debye form

$$g_{xy}(R) = -\beta Q_x(\nabla) Q_y(-\nabla) \frac{1}{\varepsilon(0)R} \left[e^{-\frac{\kappa}{\sqrt{\varepsilon(0)}} R} - (1 - \varepsilon(0)) e^{-R \frac{q}{\sqrt{\varepsilon(0)}}} \right].$$

As expected, at small distances

$$g_{xy}(R) = -\beta Q_x(\nabla) Q_y(-\nabla) \frac{1}{R} = -\beta \Phi_{xy}(R).$$

With increasing concentration, under the condition $q\kappa \gg 1$, one finds $\alpha_- \simeq 1/q$, $\alpha_+ \simeq \kappa$, and the screened potentials again assume the Debye form, but this time without molecular screening

$$g_{xy}(R) = -\beta Q_x(\nabla) Q_y(-\nabla) \frac{1}{R} e^{-\kappa R}.$$

However, at such high concentrations, the particles cannot any longer be treated as point-like, which necessitates accounting for short-range interactions at the basic (reference) level.

When orientations are accurately taken into consideration, the screened potentials are determined by equations (4.3.18) and (4.3.19). In particular, for an ion-dipole system, the screened potential of the ion-ion interaction once

again takes on the Debye form [231]

$$\begin{aligned}
 g_{ab}^{(0,0)}(R) &= -\lambda_a^{(0,0)}\lambda_b^{(0,0)}\frac{V}{2\pi^2}\int_0^\infty j_0(kR)k^2dk \times \\
 &\times \frac{\alpha(k,000) + \alpha(k,000)\alpha(k,110) - \alpha(k,100)\alpha(k,010)}{1 + \alpha(k,000) + \alpha(k,110) + \alpha(k,000)\alpha(k,110) - \alpha(k,100)\alpha(k,010)} = \\
 &= -\beta e^2 z_a z_b \frac{1}{\varepsilon R} \exp\left\{-\frac{\varkappa}{\sqrt{\varepsilon}}R\right\}
 \end{aligned} \tag{4.4.6}$$

but now, emerging due to dipole screening, the dielectric permittivity is determined by expression (4.3.24). The screened potential of the ion-dipole interaction

$$\begin{aligned}
 g_{as}^{(10)}(R, \Omega) &= \lambda_a^{(0,0)}\lambda_s^{*(1,0)}i\frac{V}{2\pi^2}\int_0^\infty j_1(kR)k^2dk\alpha(k,010) \times \\
 &\times [1 + \alpha(k,000) + \alpha(k,110) + \alpha(k,000)\alpha(k,110) - \\
 &- \alpha(k,100)\alpha(k,010)]^{-1} = \beta e z_a (\mathbf{p}_s^{\text{ef}} \nabla) \frac{1}{\varepsilon R} \exp\left\{-\frac{\varkappa}{\sqrt{\varepsilon}}R\right\},
 \end{aligned} \tag{4.4.7}$$

where $\mathbf{p}_s^{\text{ef}}$ is determined by (4.3.24).

To account for the specificity of the dipole interaction in calculating the dipole-dipole screened potential, we make use of the following equation

$$\begin{aligned}
 g_{ss}^{(1,1)}(R_{12}, \Omega_1 \Omega_2) &= -\beta \Phi_{ss}(R_{12}, \Omega_1 \Omega_2) - \beta \frac{N_s}{V} \int \Phi_{ss}(R_{13}, \Omega_1 \Omega_3) \times \\
 &\times g_{ss}^{(11)}(R_{32}, \Omega_3 \Omega_2) d\mathbf{R}_3 d\Omega_3 - \beta \sum_a \frac{N_a}{V} \int \Phi_{sa}(R_{13}, \Omega_1) \times \\
 &\times g_{as}^{(10)}(R_{32}, \Omega_2) d\mathbf{R}_3.
 \end{aligned} \tag{4.4.8}$$

Let us represent all the functions appearing here in an invariant form

$$\begin{aligned}
 -\beta \Phi_{ss}(R, \Omega_1 \Omega_2) &= \hat{c}^{112}(R) \hat{\Psi}^{112}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}), \\
 -\beta \Phi_{sa}(R, \Omega_1) &= \hat{c}^{101}(R) \hat{\Psi}^{101}(\Omega_1, 0, \Omega_{\mathbf{R}}), \\
 g_{ss}^{(1,1)}(R, \Omega_1 \Omega_2) &= \hat{g}^{112}(R) \hat{\Psi}^{112}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}) + \hat{g}^{110}(R) \hat{\Psi}^{110}(\Omega_1 \Omega_2 \Omega_{\mathbf{R}}), \\
 g_{as}^{(01)}(R, \Omega_2) &= \hat{g}^{011}(R) \hat{\Psi}^{010}(0, \Omega_2 \Omega_{\mathbf{R}}),
 \end{aligned} \tag{4.4.9}$$

where

$$\begin{aligned}
 \hat{c}^{112}(R) &= \frac{\sqrt{30}}{3} \beta p_s^2 \frac{1}{R^3}; \quad \hat{c}^{101}(R) = \beta e z_a p_s \frac{1}{R^2}; \\
 \hat{g}^{011}(R) &= \beta e z_a p_s^{\text{ef}} \frac{1}{\varepsilon R^2} \left[1 + \frac{\varkappa}{\sqrt{\varepsilon}} R \right] \exp\left\{-\frac{\varkappa}{\sqrt{\varepsilon}} R\right\}.
 \end{aligned}$$

According to (4.1.73), equation (4.4.8) is represented by a set of equations

$$\begin{aligned} H_0^{11}(k) - C_0^{11}(k) &= \frac{N_s}{V} H_0^{11}(k) C_0^{11}(k) + \sum_a \frac{N_a}{V} H_{0,a}^{10}(k) C_{0,a}^{01}(k), \\ H_1^{11}(k) - C_1^{11}(k) &= -\frac{N_s}{V} H_1^{11}(k) C_1^{11}(k), \end{aligned} \quad (4.4.10)$$

where

$$\begin{aligned} \frac{N_s}{V} C_0^{11}(k) &= -2y; \quad \frac{N_s}{V} C_1^{11}(k) = -y; \\ C_{0,a}^{01}(k) &= -\frac{1}{\sqrt{3}} 4\pi \beta i e z_a p_s, \\ H_{0,a}^{10}(k) &= \frac{4\pi i}{\sqrt{3}} \frac{1}{k} \beta e z_a p_s \left[\frac{\kappa^2}{k^2} (1-y) + (1+2y) \right]^{-1}. \end{aligned}$$

Hence, it follows

$$\begin{aligned} \frac{N_s}{V} H_1^{11}(k) &= -\frac{y}{1-y}, \\ \frac{N_s}{V} H_0^{11}(k) &= -\frac{3y}{1+2y} \left[\frac{2}{3} - \frac{\kappa^2}{k^2(1+2y)} \left(\frac{\kappa^2}{k^2} \frac{(1-y)}{1+2y} + 1 \right)^{-1} \right] \end{aligned}$$

or, according to (4.3.75)

$$\begin{aligned} \frac{3}{\sqrt{30}} \frac{N_s}{V} \hat{g}^{112}(k) &= -\frac{3y}{(1+2y)(1-y)} \left[1 + \frac{\kappa^2}{k^2} \frac{(1-y)}{(1+2y)} \right]^{-1}, \\ \frac{3}{\sqrt{3}} \frac{N_s}{V} \hat{g}^{110}(k) &= -\frac{3y}{(1+2y)(1-y)} \left[2y - \frac{\kappa^2}{k^2} \frac{(1-y)}{(1+2y)} \left(1 + \frac{\kappa^2}{k^2} \frac{(1-y)}{(1+2y)} \right)^{-1} \right]. \end{aligned}$$

With the help of the inverse Fourier transform, we find

$$\begin{aligned} \frac{3}{\sqrt{30}} \hat{g}^{112}(R) &= -\frac{1}{2\pi^2} \int_0^\infty \frac{3}{\sqrt{30}} \hat{g}^{112}(k) j_2(kR) k^2 dk = \\ &= -\frac{1}{2\pi^2} \int_0^\infty \frac{3}{\sqrt{30}} \hat{g}^{112}(k) R \frac{\partial}{\partial R} \left[\frac{1}{R} \frac{\partial}{\partial R} j_0(kR) \right] dk = \\ &= \frac{\beta p_s^2}{(1+2y)(1-y)} \frac{1}{R^3} \left[1 + \frac{\kappa}{\sqrt{\varepsilon}} R + \frac{1}{3} \frac{\kappa^2}{\varepsilon} R^2 \right] e^{-\frac{\kappa R}{\sqrt{\varepsilon}}}, \\ \frac{3}{\sqrt{3}} \hat{g}^{110}(R) &= \frac{1}{2\pi^2} \int_0^\infty \frac{3}{\sqrt{3}} \hat{g}^{110}(k) j_0(kR) k^2 dk = \\ &= \frac{1}{3} \frac{\beta p_s^2}{(1+2y)(1-y)} \left[\frac{\kappa^2}{\varepsilon R} e^{-\frac{\kappa R}{\sqrt{\varepsilon}}} + 8\pi y \delta(\mathbf{R}) \right] \end{aligned}$$

thus,

$$g_{ss}^{(1,1)}(R, \Omega_1 \Omega_2) = \beta \frac{1}{\varepsilon} \left\{ (\mathbf{p}_s^{\text{ef}} \nabla) (\mathbf{p}_s^{\text{ef}} \nabla) \frac{1}{R} e^{\frac{\chi}{\sqrt{\varepsilon}} R} + \frac{8}{3} \pi y (\mathbf{p}_s^{\text{ef}} \mathbf{p}_s^{\text{ef}}) \delta(\mathbf{R}) \right\}. \quad (4.4.11)$$

As expected, a precise accounting of orientations only modifies the effects of dipole screening.

When the multipole series for $Q_s(\nabla)$ is truncated, the self-consistent part of the free energy

$$\beta F_{\text{RPA}} = -\frac{1}{2} \sum_{\mathbf{k}} [\alpha(k) - \ln(1 + \alpha(k))] \quad (4.4.12)$$

diverges. However, as shown in [284], it can be represented as a series in terms of group integrals¹⁰

$$-\beta F_{\text{RPA}} = \frac{1}{2} \text{---} \text{---} - \frac{2}{3} \triangle + \frac{3}{4} \square - \dots \quad (4.4.13)$$

This representation permits the exclusion of diagrams with molecular vertices from F_{RPA} and their transformation into the cluster coefficients, where they are compensated by corresponding terms. In (4.4.13), only diagrams with ionic vertices remain. Their summing leads to the expression

$$-\beta F_{\text{RPA}}^{(i)} = \frac{1}{2} \sum_{\mathbf{k}} \left[\frac{\chi^2}{k^2 \varepsilon(k)} - \ln \left(1 + \frac{\chi^2}{k^2 \varepsilon(k)} \right) \right] \quad (4.4.14)$$

which, in the case of an ion-dipole system, coincides with the expression for the Debye part of the free energy of ions with a dielectric permittivity of $\varepsilon = 1 + 3y$ or, when accounting precisely for orientations, as determined by formula (4.3.23). Finally, after incorporation of short-range interactions, the free energy takes the form

$$F = F_{\text{id}} + F_{\text{RPA}}^{(i)} - \frac{1}{\beta} (B_2 + B_3 + \dots), \quad (4.4.15)$$

where

$$\begin{aligned} B_2 = & \sum_{a,b} \frac{N_a N_b}{2V} \int \left[e^{g_{ab}(R) - \beta \varphi_{ab}(R)} - 1 - g_{ab}(R) - \frac{1}{2} g_{ab}^2(R) \right] d\mathbf{R} + \\ & + \sum_a \frac{N_a N_s}{V} \int \left[e^{g_{as}(R, \Omega) - \beta \varphi_{as}(R)} - 1 \right] d\mathbf{R} d\Omega + \\ & + \frac{N_s^2}{2V} \int \left[e^{g_{ss}(R, \Omega_1 \Omega_2) - \beta \varphi_{ss}(R)} - 1 \right] d\mathbf{R} d\Omega_1 d\Omega_2 \end{aligned}$$

is the second cluster coefficient, B_3 is the third one, and so on.

¹⁰The equivalence of (4.4.12) and (4.4.13) is easily verified by simply summing the series (4.4.13).

4.4.2. Pair distribution functions of mixed ion-dipole systems. Study of cluster expansions

The specific features of mixed ion-molecular systems are primarily due to the presence of electrostatic interactions. To clarify their role, it would first be necessary to study the properties of the system without electrostatic forces and then introduce them. This goal is achieved by cluster expansions obtained within the basic treatment of short-range interactions. At the same time, for a more complete understanding of the role of electrostatics, it is important to go beyond the limits of the second cluster coefficient, which has so far been the primary constraint. However, given the complexity of the required calculations, we first focus on a simpler version of cluster expansions based on the short-range interaction method of functional differentiation.

As the object of study, we consider a system of three types of particles: two oppositely charged types of ions (cations and anions) and dipolar molecules. To simplify calculations, we use the screened potentials (4.4.4), obtained without precise consideration of orientations. After differentiation, we obtain

$$\begin{aligned}
 g_{ab}(R) &= -\beta \frac{e^2 z_a z_b}{\varepsilon R} \exp\left(-\frac{\varkappa}{\sqrt{\varepsilon}} R\right), \\
 g_{as}(R, \Omega_s) &= \beta e z_a p_s \frac{1}{\varepsilon R} \left(\frac{1}{R} + \frac{\varkappa}{\sqrt{\varepsilon}}\right) \exp\left\{-\frac{\varkappa}{\sqrt{\varepsilon}} R\right\} \cos \vartheta_s, \\
 g_{st}(R, \Omega_s, \Omega_t) &= \beta p_s p_t \frac{1}{\varepsilon R} \left\{ \left[\frac{2}{R^2} + \frac{2\varkappa}{\sqrt{\varepsilon} R} + \frac{\varkappa^2}{\varepsilon} \right] \cos \vartheta_s \cos \vartheta_t - \right. \\
 &\quad \left. - \frac{1}{R} \left[\frac{1}{R} + \frac{\varkappa}{\sqrt{\varepsilon}} \right] \sin \vartheta_s \sin \vartheta_t \cos(\varphi_s - \varphi_t) \right\} \exp\left(-\frac{\varkappa}{\sqrt{\varepsilon}} R\right), \quad (4.4.16)
 \end{aligned}$$

where $\Omega_s = (\vartheta_s, \varphi_s)$ are the polar angles describing the orientation of the s -th dipole relative to the axis connecting the centres of mass of the interacting particles, and $\varepsilon = 1 + 3y$.

In this study, we proceed from the pair distribution functions, for which there are two forms of cluster expansions, (2.2.63) and (2.2.65). The absence of a short-range potential in diagrams with light lines leads to divergences of dipolar molecules associated with an incorrect extrapolation of the dipole potential to small distances. In this regard, we assume that the screened potentials in the region of short-range interactions are zero, which, as is known, corresponds to the optimal separation of interactions. Of course, this results in a certain modification of the screened potentials, which we ignore for now.

To simplify the calculations, we also employ an approximate treatment of orientations in the computation of the cluster coefficients. In this case, the integration over orientations in the third cluster coefficient is carried out ana-

lytically [286], and after transforming to a bipolar coordinate system, we obtain

$$\begin{aligned}
 F_{xy}^{(3)}(r) = & \frac{2\pi}{r} \sum_c \rho_c^* \int_0^\infty u du \int_{|r-u|}^{r+u} v dv [\Psi_{xc}(u) \Psi_{cy}(v) - g_{xc}(u) g_{cy}(v)] + \\
 & + \frac{2\pi}{r} \rho_s^* \int_0^\infty u du \int_{|r-u|}^{r+u} v dv [\Phi_{xy}(u, v) - \chi_{xy}(u, v)], \quad (4.4.17)
 \end{aligned}$$

where the sum over c pertains only to ions, and the unit of length is taken as σ_{as} — the distance of closest approach between the centres of mass of an ion of type a and a molecule; $\rho_c^* = N_c/V\sigma_{as}^3$; $\rho_s^* = N_s/V\sigma_{as}^3$; $r = R/\sigma_{as}$,

$$\begin{aligned}
 \Psi_{xc}(u) &= \exp \{-\beta \varphi_{xc}(u) + g_{xc}(u)\} - 1, \\
 \Phi_{xy}(u, v) &= \exp \{-\beta [\varphi_{xs}(u) + \varphi_{sy}(v)]\} \frac{\sinh G_{xy}(u, v)}{G_{xy}(u, v)} - \\
 &- e^{-\beta \varphi_{xs}(u)} \frac{\sinh G_x(u)}{G_x(u)} - e^{-\beta \varphi_{sy}(v)} \frac{\sinh G_y(v)}{G_y(v)} + 1. \quad (4.4.18)
 \end{aligned}$$

For two ions of types a and b

$$\begin{aligned}
 G_{ab}(u, v) &= G_a(u) + G_b(v), \quad \chi_{ab}(u, v) = \frac{1}{3} G_a(u) G_b(v), \\
 G_a(u) &= \begin{cases} q_{as} \frac{1}{u} e^{-\tilde{\kappa} u} \left(\tilde{\kappa} + \frac{1}{u} \right), & u > 1, \\ 0, & r < 1; \end{cases} \quad (4.4.19) \\
 g_{ab}(r) &= \begin{cases} -\beta_{ab}^* \frac{1}{r} e^{-\tilde{\kappa} r}, & r > \tilde{\sigma}_{ab}, \\ 0, & r < \tilde{\sigma}_{ab}, \end{cases}
 \end{aligned}$$

where

$$q_{as} = \beta \frac{e z_a p_s}{\varepsilon \sigma_{as}^2}, \quad \tilde{\kappa} = \frac{\kappa}{\sqrt{\varepsilon}} \sigma_{as}, \quad \tilde{\sigma}_{ab} = \frac{\sigma_{ab}}{\sigma_{as}}, \quad \beta_{ab}^* = \frac{e^2 z_a z_b}{\varepsilon \sigma_{as}}.$$

For an ion of type a and a dipole molecule

$$\begin{aligned}
 G_{as}(u, v) &= [G_a^2(u) + G_s^2(v) + 3! \chi_{as}(u, v)]^{1/2}, \\
 \chi_{as}(u, v) &= \frac{1}{3} G_a(u) g^c(v) \cos \vartheta_s, \quad g_{as}(r) = G_a(r) \cos \vartheta_s, \\
 G_s(v) &= [(g^c(v) \cos \vartheta_s)^2 + (g^s(v) \sin \vartheta_s)^2]^{1/2},
 \end{aligned}$$

$$\begin{aligned}
g^c(v) &= \begin{cases} \omega_{ss} \left(\tilde{\kappa}^2 + \frac{2}{v} \tilde{\kappa} + \frac{2}{v^2} \right) \frac{1}{v} e^{-\tilde{\kappa}v}, & v > \tilde{\sigma}_{ss}, \\ 0, & v < \tilde{\sigma}_{ss}; \end{cases} \\
g^s(v) &= \begin{cases} \omega_{ss} \left(\tilde{\kappa} + \frac{1}{v} \right) \frac{1}{v^2} e^{-\tilde{\kappa}v}, & v > \tilde{\sigma}_{ss}, \\ 0, & v < \tilde{\sigma}_{ss}, \end{cases}
\end{aligned} \tag{4.4.20}$$

where

$$\tilde{\sigma}_{ss} = \frac{\sigma_{ss}}{\sigma_{as}}; \quad \omega_{ss} = \beta \frac{p_s^2}{\varepsilon \sigma_{as}^3}.$$

For two dipole molecules

$$\begin{aligned}
G_{st}(u, v) &= [G_s^2(u) + G_t^2(v) + 3! \chi_{st}(u, v)]^{1/2}, \\
\chi_{st}(u, v) &= \frac{1}{3} \{ g^c(u) g^c(v) \cos \vartheta_s \cos \vartheta_t + \\
&\quad + g^s(u) g^s(v) \sin \vartheta_s \sin \vartheta_t \cos(\varphi_s - \varphi_t) \}, \\
g_{st}(r, \Omega_s, \Omega_t) &= g^c(r) \cos \vartheta_s \cos \vartheta_t - g^s(r) \sin \vartheta_s \sin \vartheta_t \cos(\varphi_s - \varphi_t).
\end{aligned} \tag{4.4.21}$$

A comprehensive study of the third cluster coefficient conducted in the works of Vysochansky and other authors [287–290] (see also the review [291]). In this context, the Lennard-Jones potential is used as the short-range potential $\varphi_{xy}(R) = 4\epsilon_{xy} \left[\left(\frac{\sigma_{xy}}{R} \right)^{12} - \left(\frac{\sigma_{xy}}{R} \right)^6 \right]$, where ϵ_{xy} characterizes the depth of the potential well.

In the considered case, there are six different pair distribution functions $F_{++}(r)$, $F_{+-}(r)$, $F_{--}(r)$, $F_{+s}(r, \vartheta_s)$, $F_{-s}(r, \vartheta_s)$, $F_{st}(r, \Omega_s \Omega_t)$. Their properties and behaviour are determined by the following parameters: the reduced temperature $T^* = (\beta \epsilon_{as})^{-1}$, the densities of molecules ρ_s^* and ions $\rho_i^* = \frac{N_a}{V} \sigma_{as}^3$, the dipole moment p_s , the valencies z_a, z_b , and the parameters of short-range potentials $\tilde{\sigma}_{xy} = \frac{\sigma_{xy}}{\sigma_{as}}, \tilde{\epsilon}_{xy} = \frac{\epsilon_{xy}}{\epsilon_{as}}$. Considering real solutions of electrolytes, we assume that throughout the entire considered concentration range $\rho_s^* \gg \rho_i^*$.

A particular interest lies in understanding the influence of electrostatic interactions as a function of the ion concentration ρ_i^* . It is clear that as the ion concentration increases, the role of electrostatic forces diminishes due to ionic screening. Fig. 18 presents the pair distribution function $F_{+-}(r)$ for $z_+ = -z_- = 1, \rho_s^* = 0.5, p_s = 2D, \rho_i^* = 5$ mol/L. The short-range interactions for all particles are assumed to be identical $\tilde{\sigma}_{xy} = 1, \tilde{\epsilon}_{xy} = 1, \sigma_{as} = 2 \text{ \AA}, T^* = 1.5$. In the second cluster coefficient approximation, the pair distribution function has only one maximum, corresponding to the minimum of the potential (curve 1). The remaining curves correspond to the approximation of the third cluster coefficient. As can be seen, accounting for the dipolar subsystem solely

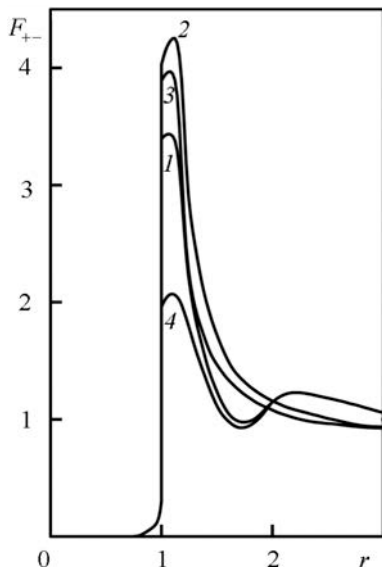


Fig. 18. Pair distribution function $F_{+-}(r)$ for a two-component system of charged particles with equal size and short-range repulsion, at $T^* = 1.5$. Curve 1: second cluster coefficient approximation. Curve 2: third cluster coefficient approximation with dielectric permittivity correction. Curve 3: third cluster coefficient approximation with explicit dipolar subsystem, showing a second peak associated with short-range structuring. Curve 4: reference system without electrostatic interactions

through the dielectric permittivity ε does not lead to considerable changes (curve 2). Only when the dipolar subsystem is explicitly taken into account does a second maximum appear on the curve, associated with the presence of short-range order in the system (curve 3). Comparing curve 3 with the pair distribution function of a system without electrostatic forces (curve 4), we see that in the considered concentration range, under the previously adopted approximations, the contribution of electrostatic forces is mainly reflected in the first maximum of the distribution function.

A similar pattern is observed for the other distribution functions. Since $z_+ = -z_-$, $\tilde{\sigma}_{xy} = \tilde{\epsilon}_{xy} = 1$, $F_{++}(r) = F_{--}(r)$, $F_{+s}(r, \vartheta_s) = F_{-s}(r, \pi - \vartheta_s)$. The corresponding curves, within the third cluster coefficient approximation and for the same parameter values as in Fig. 18, are shown in Fig. 19 [290] for different ionic concentrations (mol/L): 5 (1); 2.5 (2); 1 (3); 0.1 (4); 0 (5). As the ion concentration decreases, the ionic screening radius increases, enhancing the contribution of electrostatic forces. At a fixed molecular density ρ_s^* , this leads to an increasing role of higher-order cluster coefficients, primarily due to dipolar terms¹¹. Numerical calculations showed that as ρ_i^* decreases, the third cluster coefficient becomes negative and, starting from a certain concentration, its absolute value exceeds unity. Clearly, using the form (2.2.63) for cluster expansions is incorrect in this case since it results in a negative distribution function. Physically correct results are obtained when using the exponential

¹¹In the ionic terms, each field vertex corresponds to a factor of ρ_i^* , consequently, as $\rho_i^* \rightarrow 0$, the ionic contribution vanishes.

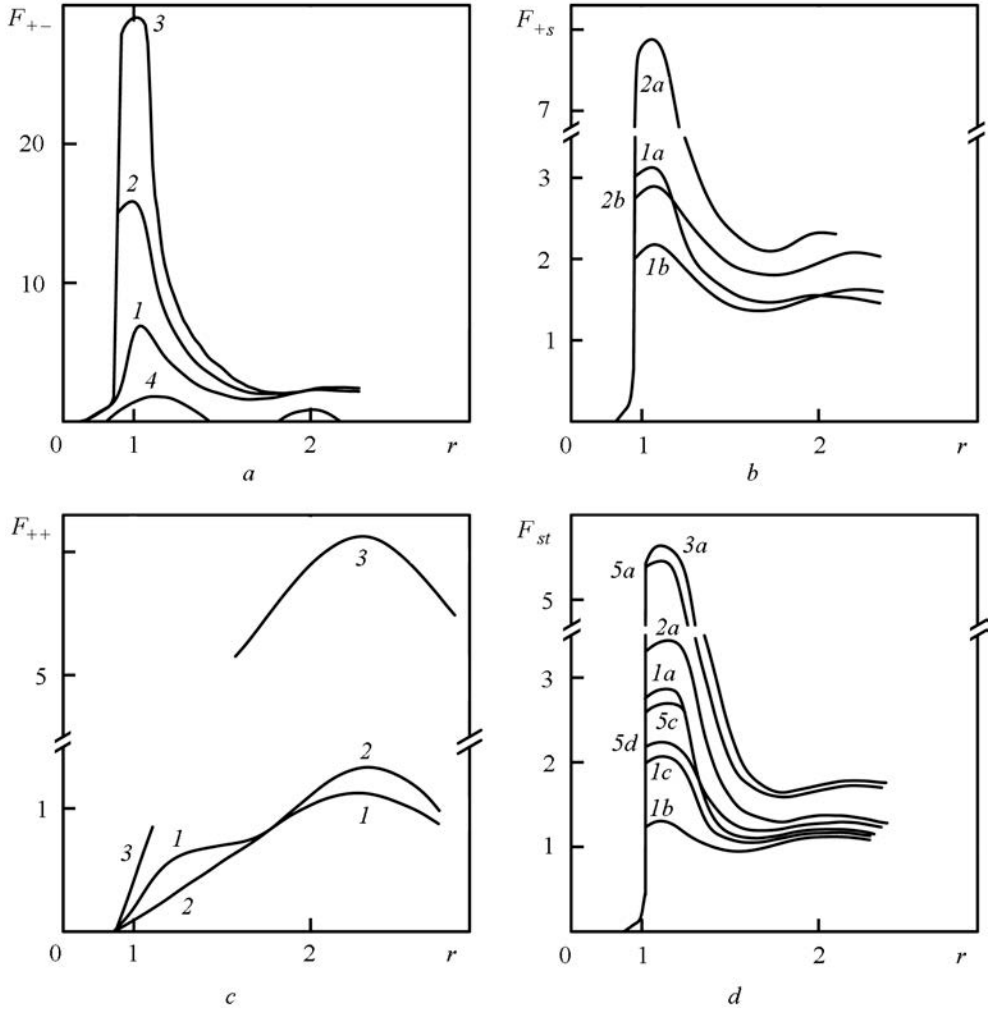


Fig. 19. Pair distribution functions $F_{+-}(r)$, $F_{++}(r)$, $F_{+s}(r, \vartheta_s)$, and $F_{st}(r, \Omega_s, \Omega_t)$ for a model of charged particles at various ion concentrations and dipolar orientations. The first peak in $F_{+-}(r)$ considerably grows as ion concentration decreases, indicating the formation of correlated complexes. The function $F_{++}(r)$ shows a second peak at lower concentrations, attributed to dipolar interactions. Orientation-resolved functions reveal a preferred alignment along $\vartheta_s = 0$ for the first peak and $\vartheta_s = \pi/2$ for the second

form of cluster expansions (2.2.65). In the region of high ion concentrations, due to the small magnitude of the third cluster coefficient, the results for both expansion forms are practically identical. However, while using (2.2.63) at low concentrations leads to a “catastrophe”, the results obtained based on the exponential form remain physically valid across the entire concentration range.

As seen in Fig. 19, *a*, when the ion concentration decreases from 5 to 1 mol/L, the height of the first maximum of the pair distribution function

$F_{+-}(r)$ rapidly increases, primarily due to the second cluster coefficient. This shape of the curves indicates the formation of complexes of oppositely charged ions — contact “ion pairs”. With a further decrease in ion concentration and an increasing role of the third cluster coefficient, the height of the first maximum decreases, and at a concentration of 0.1 mol/L in the region $r < 3$, $F_{+-}(r) < 1$. Only at larger distances between the ions does $F_{+-}(r) \rightarrow 1$. This form of the pair distribution function indicates the absence of “ion pairs” in this concentration range. With a further decrease in concentration, the first maximum increases again, but such behaviour of the pair distribution function is physically unjustified, and for an accurate description, it is necessary to take into account the fourth cluster coefficient.

The pair distribution function of two cations $F_{++}(r)$ (Fig. 19, *b*) at high ion concentrations exhibits a small first maximum due to short-range ion attraction and a higher second maximum, whose appearance is associated with explicit dipole effects. As the ion concentration decreases from 5 to 1 mol/L, the first maximum disappears while the second maximum height increases, which corresponds to the formation of complexes of like-charged ions. The ions in these pairs are located at a distance of $r \simeq 2$, and their binding occurs via a dipolar molecule. With a further decrease in concentration, these pairs, like those of oppositely charged ions, dissociate. Instead, a picture of solvated ions emerges, which can only be described after accounting for the fourth cluster coefficient.

Next, we consider the distribution functions $F_{+s}(r, \vartheta_s)$ and $F_{st}(r, \Omega_s, \Omega_t)$ for fixed orientations. As seen in Fig. 19, *c*, the first maximum of $F_{+s}(r, \vartheta_s)$ is larger when $\vartheta_s = 0$, whereas the second maximum is more pronounced for orientations $\vartheta_s = \frac{\pi}{2}$. Thus, as a dipolar molecule approaches an ion, it rotates. However, with decreasing ion concentration, the orientational motion of the dipole weakens, and at 2.5 mol/L, the orientation $\vartheta_s = 0$ dominates in both the first and second maximum regions.

For the distribution function $F_{st}(r, \Omega_s, \Omega_t)$ (Fig. 19, *d*), the orientation $\vartheta_s = \vartheta_t = 0$, $\varphi_s = \varphi_t$ dominates at all concentrations and distances. As the ion concentration decreases, the screening radius increases, enhancing the contribution of electrostatic forces into the height of the first maximum. The pair distribution function $F_{st}(r, \Omega_s, \Omega_t)$ in the absence of an ion was also considered in [292]. Under the parameters used in this study, it was found that in the region of the first maximum, the most probable orientation is $\vartheta_s = \vartheta_t = 0$, $\varphi_s = \varphi_t$, while in the second maximum region, it is $-\vartheta_s = \frac{\pi}{2}$, $\vartheta_t = \frac{3}{2}\pi$, $\varphi_s = \varphi_t$. Hence, it was concluded that dipoles rotate when moving away from each other. Fig. 19, *d* shows that in the absence of ions, the orientation $\vartheta_s = \vartheta_t = 0$, $\varphi_s = \varphi_t$ is the most probable at all distances. However, curves 5*c* and 5*d* indicate the presence of ionic oscillations (the first maximum of curve 5*c* is higher than that of curve 5*d*, while the second maximum behaves

oppositely). With increasing ion concentration, these oscillations weaken, and a different type of motion emerges, similar to what was previously observed in the function $F_{+s}(r, \vartheta_s)$.

The obtained results for the third cluster coefficient can be used in the calculation of most diagrams of the fourth cluster coefficient [293]. Using the following notations

$$\begin{aligned} \circ \cdots \circ &= F_{xy}^{(3)}(r)[1 + \psi_{xy}(r)], & \text{wavy line} &= \text{triangle diagram}, \\ \circ \cdots \circ &= F_{xy}^{(3)}(r)\psi_{xy}(r) - \text{wavy line}, & \text{line with square} &= g_{xy}(r), \\ \text{line with square} &= \psi_{xy}(r) = \exp\{g_{xy}(r) - \beta\varphi_{xy}(r)\} - 1, \end{aligned}$$

the fourth cluster coefficient in expression (2.2.64) for the pair distribution function can be presented in the form

$$F_{xy}^{(4)}(r) = \text{triangle diagram} + \text{triangle diagram} + \text{triangle diagram} + \frac{1}{2} \text{square diagram} + \frac{1}{2} (F_{xy}^{(3)}(r))^2. \quad (4.4.22)$$

Due to the weak orientational dependence of the third cluster coefficient, the dipole orientations in $F_{xy}^{(3)}(r)$ can be replaced with a certain average values. For example, setting $\vartheta_s = \vartheta_t = 55^\circ 44'$, $\varphi_s = \varphi_t$, which corresponds to replacing $\cos^2\vartheta$ with its average value of $1/3$. Then, integration over orientations and the transformation to a bipolar coordinate system in the first three diagrams of (4.4.22) are carried out similarly to the case of the third cluster coefficient. The last diagram (4.4.22) is subsequently neglected, which corresponds to the hypernetted-chain approximation in the theory of neutral particle systems.

In the region of high ionic concentrations, accounting for the fourth cluster coefficient leads to the emergence of a third maximum on the curves, while also refining the two previous maxima. Thus, at high ion concentrations, the following clear pattern emerges: each cluster coefficient contributes to the appearance of its own maximum on the distribution function curves [293].

Of particular interest is the consideration of the fourth cluster coefficient in the region of low ionic concentrations. As noted earlier in the discussion of the function $F_{+-}(r)$, this is necessary for physically correct results. However, the calculation of $F_{xy}^{(4)}(r)$ at low concentrations is a more complex task, since as the concentration decreases, $F_{xy}^{(3)}(r)$ becomes more sensitive to molecular orientations. Apparently, the role of the elementary diagram also increases. For estimation purposes, we limit ourselves to the approximations adopted for high concentrations.

In Fig. 20, the distribution function $F_{+-}(r)$ obtained in this way is presented in the approximation of the fourth cluster coefficient at the limit of

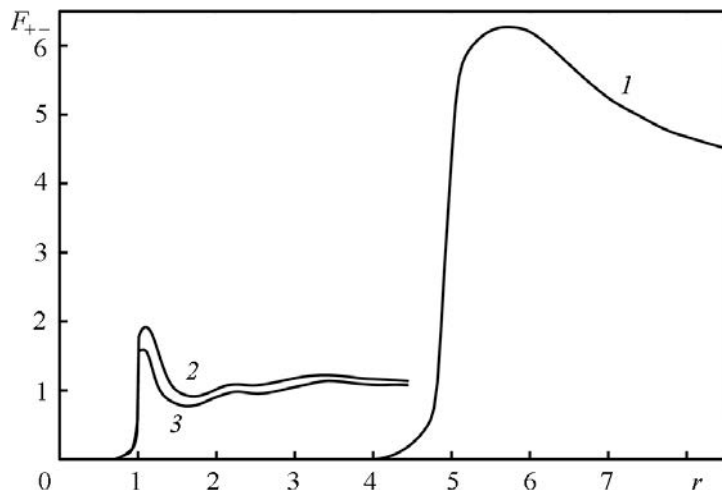


Fig. 20. Pair distribution function $F_{+-}(r)$ calculated in the fourth cluster coefficient approximation at infinite dilution of ions ($\rho_i^* = 0$): 1 — distribution of ions at infinite dilution, showing a single maximum at a distance of about five particle diameters; 2 — distribution function for two nonpolar molecules interacting via Lennard-Jones potential; 3 — distribution function for polar molecules. The difference between curves 2 and 3 is attributed to the contribution of the fourth cluster coefficient

infinite ionic dilution $\rho_i^* = 0$ (curve 1). It exhibits a single maximum of natural magnitude, located at distances of the order of several particle diameters. Thus, while high concentrations are characterized by the formation of “ion pairs,” in the low-concentration region, each ion is surrounded only by dipolar molecules. This structural transformation of the system is consistent with X-ray studies of electrolyte solutions, as well as with the concepts introduced by Mishchenko and Sukhotin regarding the boundary of complete solvation [294]. For comparison, Fig. 20 presents the distribution function of two nonpolar molecules interacting via the Lennard-Jones potential and present in a system of such nonpolar molecules (curve 2), as well as in a system of polar molecules (curve 3). It should be noted that the curves differ only when the fourth cluster coefficient is considered, as $\tilde{\alpha} = 0$, $q_{as} = 0$, $\rho_i^* = 0$, $\beta_i^* = 0$. Curve 3 exhibits only one maximum before approaching unity. This behaviour of the distribution function of nonpolar particles in a dipolar medium aligns with the concept of solvophobic interactions discussed in the previous paragraph.

Let us briefly discuss the contribution of other parameters. We begin with high concentrations [289]. Since the emergence of short-range order is clearly associated with the explicit consideration of the dipole subsystem, it is evident that an increase in dipole density contributes to the ordering of the entire system. An increase in molecular polarity leads to a rise in ϵ , as well as an increased contribution of electrostatic interactions involving molecules. As in the

case of a system of neutral particles, an increase in temperature promotes disorder in the system. A decrease in particle size enhances the role of electrostatic interactions due to the contribution from short-range effects. The influence of various parameters in the region of low ion concentrations is discussed in the next section.

4.4.3. Effective interionic interactions.

Application to the description of electrolyte solutions

The most traditional approach to describing electrolyte solutions is based on the osmotic formalism, in which the study of the solution is reduced to an explicit consideration of the ionic subsystem only. At the same time, however, it is necessary to take into account the solvation energy $w_a(i)$ and the effective interaction potentials $w_{ab}(ij)$, $w_{abc}(ijl)$, ... of ions of types $a, b, c, \dots$ at infinite dilution. Expressions for these quantities are conveniently given by the set of diagrams (3.3.16), in which each fixed vertex represents an ion, and each field vertex corresponds to a molecule. In the case of an ion-dipole system, the potential of ion-molecular interaction is $u_{as}(R, \Omega_s) = \Phi_{as}(R, \Omega_s) + \varphi_{as}(R)$, where $\Phi_{as}(R, \Omega_s) = -ez_a(p_s \nabla) \frac{1}{R}$ is the electrostatic part of the potential, and $\varphi_{as}(R)$ is the short-range interaction part. Expanding in (3.3.16) all Mayer functions into a series in powers of the charge

$$f_{as}(R, \Omega_s) = e^{-\beta\varphi_{as}(R)} - 1 + e^{-\beta\varphi_{as}(R)} \sum_{n>0} \frac{1}{n!} (-\beta\Phi_{as}(R, \Omega_s))^n,$$

in the case of spherically symmetric potentials $\varphi_{as}(R)$, we arrive at the expansions [142]

$$\begin{aligned} w_a(i) &= \sum_{n \geq 0} (ez_a)^{2n} w_a^{(2n)}(i), \\ w_{ab}(ij) &= \sum_{n \geq 0} \sum_{m=0}^{2n} e^{2n} z_a^m z_b^{2n-m} w_{ab}^{(n, 2n-m)}(ij), \\ w_{abc}(ijl) &= \sum_{n \geq 0} \sum_{m=0}^{2n} \sum_{p=0}^{2n-2m} e^{2n} z_a^p z_b^m z_c^{2n-m-p} w_{abc}^{(p, m, 2n-m-p)}(ijl), \dots, \end{aligned} \quad (4.4.23)$$

since all odd terms in e vanish as a result of integration over dipole orientations.

The first terms $w_a^{(0)}(i)$, $w_{ab}^{(0,0)}(ij)$, ... represent the contribution of short-range forces and describe, respectively, the solvation energy and the effective interaction potentials of nonpolar particles in a dipolar medium. Quadratic terms describe electrostatic contributions. Assuming for the short-range forces $\varphi_{as}(R)$ a model of hard spheres with size σ_{as} , in the asymptotic limit $R \rightarrow \infty$,

we obtain

$$\begin{aligned} e^2 z_a^2 w_a^{(2)}(i) &= -\frac{e^2 z_a^2}{2\sigma_{as}} \frac{\varepsilon_s - 1}{\varepsilon_s}, \quad e^2 z_a z_b w_{ab}^{(1,1)}(ij) = \frac{e^2 z_a z_b}{\varepsilon_s R_{ij}}, \\ e^2 z_a^2 w_{ab}^{(2,0)}(ij) &= e^2 z_a^2 \frac{\sigma_{bs}^3}{2R_{ij}^4} \gamma_s \frac{\varepsilon_s - 1}{\varepsilon_s}, \end{aligned} \quad (4.4.24)$$

where $\varepsilon_s^{-1} = 1 - 3y \left[1 + \rho_s \int \cos \vartheta_{12} h_2(R, \Omega_1, \Omega_2) d\mathbf{R} d\Omega_1 d\Omega_2 \right]$ is the expression for the dielectric permittivity of the dipole subsystem¹².

The first relation (4.4.24) represents the well-known Born expression for the solvation energy of an ion, the second — the Coulomb potential of ion interactions in a dipolar medium. The third term describes interionic interaction caused by the polarisation of the cavity of one of the ions by the electric field of the dipolar medium:

$$\begin{aligned} 3\gamma_s &= 1 + \left[\rho_s \int \cos^2 \vartheta_1 h_2(R, \Omega_1 \Omega_2) d\mathbf{R} d\Omega_1 d\Omega_2 + \right. \\ &+ \rho_s^2 \int \cos \vartheta_{12} h_3(R_{12}, R_{13}, \Omega_1 \Omega_2 \Omega_3) d\mathbf{R}_{12} d\mathbf{R}_{13} d\Omega_1 d\Omega_2 d\Omega_3 \left. \right] \times \\ &\times \left[1 + \rho_s \int \cos \vartheta_{12} h_2(R, \Omega_1 \Omega_2) d\mathbf{R} d\Omega_1 d\Omega_2 \right]^{-1}. \end{aligned}$$

In the macroscopic calculation [295] $\gamma_s^{-1} = 2\varepsilon_s + 1$. The obtained expression for $e^2 z_a^2 w_{ab}^{(2,0)}(ij)$ has a repulsive nature, independent of the ion's charge sign. Nevertheless, like the second relation in (4.4.24), it is only the first term in the expansion of these quantities in a series of powers of $1/R$.

The higher-order terms in the expansion (4.4.23) apparently play an important role at small and intermediate distances. As noted in the previous section, at low concentrations, solvated ions are separated by solvent molecules. Since the concentration dependence of the thermodynamic properties of the solute is entirely determined by the potentials of effective interionic interactions, in the low-concentration region one can approximate the interaction using a pair potential. Accordingly, in agreement with (4.4.24), we assume

$$w_{ab}(R) = \Phi_{ab}(R) + \varphi_{ab}(R), \quad (4.4.25)$$

where $\Phi_{ab}(R) = \frac{e^2 z_a z_b}{\varepsilon_s R}$ is the Coulomb part of the potential, and $\varphi_{ab}(R)$ is the remaining part.

The simplest model is obtained by considering solvated ions as uniformly charged hard spheres. The sizes of these spheres are typically treated as fitting parameters. However, thermodynamic property calculations for aqueous

¹²Excluding the long-range part from $h_2(R, \Omega_1, \Omega_2)$, one can verify the equivalence of this expression with the relations for ε_s discussed in the previous paragraph.

solutions of alkali metal halides, performed by Rasaiah [180] within the hyperchain approximation, clearly indicate the inappropriateness of the charged hard sphere model for real electrolyte solutions. While for one thermodynamic quantity an agreement with experimental data can be achieved by selecting different ion sizes, using these parameters in calculations of other thermodynamic properties does not result in any clear correlation with theoretical and experimental data. More realistic results are obtained by using a square-well potential model for short-range interactions

$$\varphi_{ab}(R) = \begin{cases} \infty, & R < \sigma_{ab}, \\ \epsilon_{ab}, & \sigma_{ab} < R < \sigma_{ab}\mu_{ab}, \\ 0, & R > \sigma_{ab}\mu_{ab}. \end{cases} \quad (4.4.26)$$

By selecting the crystallographic sizes of ions and assuming that the well width equals the diameter of a water molecule, Rasaiah demonstrated that an agreement with experiment can be achieved through the independent selection of two parameters — the well depth ϵ_{ab} and its temperature coefficient $(\partial\epsilon_{ab}/\partial T)_P$.

Ramanathan and Friedman [296] represented the short-range potential as the sum of three terms

$$\varphi_{ab}(R) = \varphi_{ab}^{(\text{cor})}(R) + \varphi_{ab}^{(\text{cav})}(R) + \varphi_{ab}^{(\text{Gurn})}(R). \quad (4.4.27)$$

The first term describes the short-range repulsion of ions, determined by the sum of their crystallographic radii σ_{ab} . It is assumed that the medium has an insignificant effect on this potential. The second term describes the effect of cavity polarisation of ions by the field of the medium, and in accordance with (4.4.24), it is given by $\varphi_{ab}^{(\text{cav})}(R) = \frac{1}{2\epsilon_s R^4} \frac{\epsilon_s - 1}{2\epsilon_s + 1} (e^2 z_a^2 \sigma_{bs}^3 + e^2 z_b^2 \sigma_{as}^3)$.

According to the concept of Gurney [297] and Frank [298], molecules in the solvation shell differ in their properties from the rest of the molecules. When solvation shells of ions overlap, some of these molecules return to their normal state. This process is accompanied by certain structural changes, which are accounted for by the terms $\varphi_{ab}^{(\text{Gurn})}(R)$. In the work [296], it is assumed that $\varphi_{ab}^{(\text{Gurn})}(R) = \frac{1}{V_s} A_{ab} V_{ab}(R)$, where A_{ab} is the free energy associated with the aforementioned structural changes, and V_s is the molecular volume of the normal solvent. The volume function

$$\begin{aligned} V_{ab}(R) = \pi \left\{ -\frac{1}{4R} \left[\left(\frac{1}{2}\sigma_{aa} + \sigma_{ss} \right)^2 - \left(\frac{1}{2}\sigma_{bb} + \sigma_{ss} \right)^2 \right]^2 + \right. \\ \left. + \frac{2}{3} \left[\left(\frac{1}{2}\sigma_{aa} + \sigma_{ss} \right)^3 + \left(\frac{1}{2}\sigma_{bb} + \sigma_{ss} \right)^3 \right] - \frac{1}{2}R \left[\left(\frac{1}{2}\sigma_{aa} + \sigma_{ss} \right)^2 + \right. \right. \\ \left. \left. + \left(\frac{1}{2}\sigma_{bb} + \sigma_{ss} \right)^2 \right] + \frac{1}{12}R^3 \right\}, \quad R \leq \sigma_{ab} + \sigma_{ss} \end{aligned}$$

is determined geometrically by considering the overlap region of two solvation spheres and, in its form, coincides with the expression for the third cluster coefficient of the pair distribution function of a mixture of hard spheres. As shown by the calculations in [296], the thermodynamic properties of the system are highly sensitive to the choice of parameters $A_{ab}(T, P)$.

The considered models, although they clarify some general features of interionic interactions, do not fully reveal their true nature. They almost completely neglect the structure of the solvent, considering it only through the dielectric permittivity ε_s and the fitting parameters of the short-range potential. The true interaction potential of ions in a liquid polar medium considerably differs from their interaction potential in a vacuum, and its specific form is determined both by the possibility of forming various ionic associates and by the capability of the electrolyte to dissociate.

Stell [299], analysing the conditions under which the previously discussed models can be applied, demonstrated that the solvent can be considered to be a continuous dielectric medium only for ions of macroscopic size. Instead of the limit of large ions ($\sigma_{ab} \rightarrow \infty$), one can consider the limit of point molecules ($\sigma_{ss} \rightarrow 0$). If according to the condition of additivity of hard spheres $\sigma_{as} = \frac{1}{2}(\sigma_{aa} + \sigma_{ss})$ one sets $\sigma_{as} = \frac{1}{2}\sigma_{aa}$, we arrive at the charged hard-sphere model, since in addition to the Coulomb interaction, there is also an interaction of the type $e^2 z_a^2 \omega_{ab}^{(2,0)}(R)$. To obtain a model of charged hard spheres, it is necessary to set $\sigma_{as} \rightarrow 0$ which means that the additivity condition of hard spheres for the short-range potential $\varphi_{as}(R)$ is violated and allows solvent molecules to penetrate inside the ionic spheres, resulting in the dielectric permittivity of the ions being the same as that of the solvent.

Stell noted an important role of ion-dipole interactions in the formation of effective interionic potentials. In particular, the presence of an ion-dipole term is the key factor ensuring the emergence of the dielectric permittivity ε_s in the Coulomb potential. If a situation could arise that ion-molecular interactions coincide with intermolecular interactions, then the interionic interaction potential would be equal to

$$w_{ab}(R) = u_{ab}(R) - u_{ss}(R) - \frac{1}{\beta} \ln F_{ss}(R),$$

where $F_{ss}(R)$ is the distribution function of the pure solvent.

Such a potential would have an oscillatory character at short distances, determined by the behaviour of $F_{ss}(R)$. According to the Stell's considerations, the actual picture lies between the model of charged hard spheres and a model in which the long-range part of the ion-dipole potential is absent. The first model is more realistic at large distances, while the second one is more applicable at short distances.

The formation of ionic potentials is associated with the influence of solvent molecules, which occurs through two mechanisms: directly via ion-molecular interactions and indirectly through the structure of the solvent, which is determined by intermolecular interactions. The pure contribution of ion-molecular interactions is determined by the first diagrams of the expansions (3.3.16). The remaining diagrams characterize the contribution of intermolecular interactions. Stell [299] analysed the contribution of ion-molecular interactions to various terms in the expansion (4.4.27). However, the resulting expression for the dielectric permittivity $\varepsilon_s = [1 - 3y]^{-1}$ leads to unrealistic results for the electrostatic terms in (4.4.24).

In this regard, cluster expansions obtained using the method of collective variables have a significant advantage over (3.3.16) since they screen ion-dipole interaction potentials and incorporate, albeit incompletely, the dielectric permittivity of the solvent. According to (2.2.65), for the effective interaction potentials of two ions of types a and b , we have

$$-\beta w_{ab}(R) = \beta \varphi_{ab}(R) + g_{ab}(R) + \sum_{n \geq 1} \tilde{F}_{ab}^{(n+2)}(R), \quad (4.4.28)$$

where $\varphi_{ab}(R)$ is the short-range interaction potential of ions in vacuum; $g_{ab}(R) = -\beta e^2 z_a z_b \frac{1}{\varepsilon_s R}$; $\varepsilon_s = 1 + 3y$; $\tilde{F}_{ab}^{(n+2)}(R)$ are the cluster coefficients at infinite dilution.

Among all the cluster coefficients, only $\tilde{F}_{ab}^{(3)}(R)$ does not depend on the nature of intermolecular interactions. Therefore, by limiting ourselves in (4.4.28) to the third cluster coefficient, we arrive at an idealized picture of the solution, where intermolecular interactions are expressed solely through the self-consistent part of the dielectric permittivity $\varepsilon_s = 1 + 3y$. The inclusion of the fourth and higher-order cluster coefficients corresponds to accounting for the real structure of the solvent.

Following the methodology outlined in the previous section, detailed studies of interionic potentials in the approximation of the third and fourth cluster coefficients were conducted in works [300–304]. These results for two monovalent oppositely and like-charged ions are presented in Fig. 21. In these studies, Lennard-Jones potentials were used as short-range potentials, with parameters corresponding to an aqueous solution of LiCl [305]. All other parameters are the same as those in Figs. 18–20. The curves are labeled with numbers, where the first corresponds to the short-range interaction potential between a cation and a solvent molecule, the second to the anion and a solvent molecule¹³, and the third to two solvent molecules. Notably, all curves, regardless of the approximation and the potentials chosen, exhibit the same asymp-

¹³For like-charged ions, the first and second numbers coincide, corresponding to the short-range ion-molecular interaction potential.

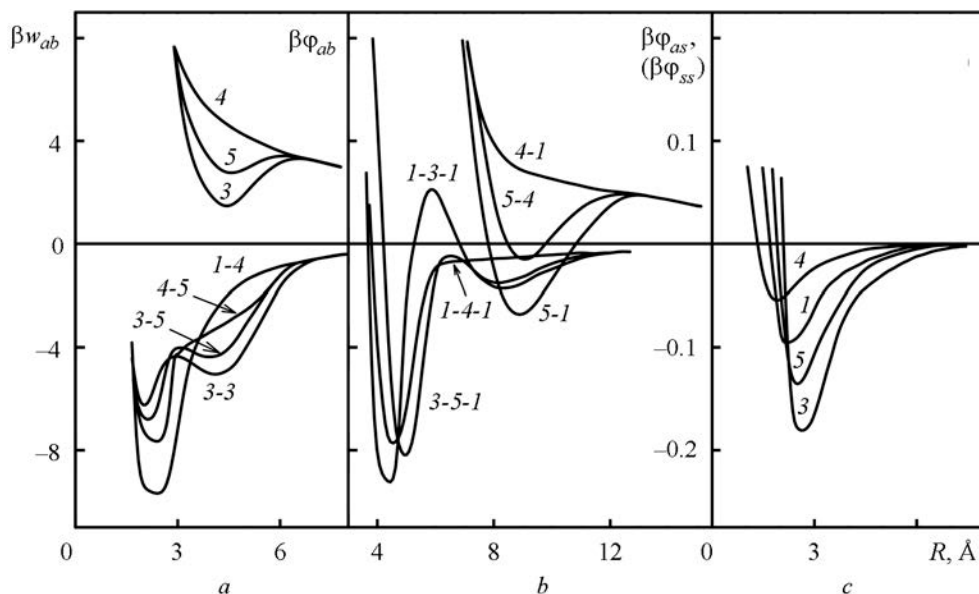


Fig. 21. Effective interaction potentials $\beta w_{ab}(R)$ for two like-charged ions calculated under different approximations. Third cluster coefficient approximation, showing the emergence of a minimum associated with the ion pair formation (a). Fourth cluster coefficient approximation, where the minima become deeper and correspond to ion pairs separated by solvent molecules (b). Corrections to the effective inter-ionic interactions by including solvent-solvent interactions (c). The results use Lennard-Jones potentials with parameters corresponding to an aqueous LiCl solution

otics, which coincide with the Coulomb potential but with a dielectric permittivity considerably greater than $1 + 3y$. In the third cluster coefficient approximation, $\epsilon_s \simeq 14$.

In the region of short distances, within the approximation of the third cluster coefficient (Fig. 21, a), the curves for oppositely charged ions exhibit a rather deep minimum, indicating that they predominantly exist as bound contact ion pairs. Nevertheless, some curves show a distinct tendency toward the formation of a second minimum. In particular, for curve 3-3, one can speak of partial solvation of ions by one solvent molecule. In this case, some ions are in the form of contact ion pairs, while others exist as solvent-separated ion pairs. For like-charged ions, all curves generally exhibit a repulsive nature. However, in the distance range $R \simeq 5 \text{ \AA}$ a distinct trend toward the formation of a minimum is observed, corresponding to the solvent-separated ion pairs of like-charged ions.

In the approximation of the fourth cluster coefficient (Fig. 21, b), all curves for oppositely charged ions exhibit a second minimum, corresponding to an ion pair separated by two solvent molecules. At the same time, the first minimum is located at distances that exclude the possibility of forming undissociated ion

pairs. As seen from the figure, with a fixed intermolecular potential, increasing the depth of the first minimum is accompanied by an increase in the depth of the second minimum. At a certain value of the short-range ion-molecular potential, the two minima merge (curve *3-5-1*), corresponding to the formation of an ion pair separated by two solvent molecules but not aligned along a same line with the ions. For like-charged ions, some curves exhibit a minimum, indicating the formation of like-charged ion pairs separated by two or three solvent molecules. Our studies of the interionic potential for modified Lennard-Jones solutions show that the behaviour of these potentials at short and intermediate distances considerably depends on the form of the short-range interaction potential. Specifically, with a certain increase in the depth of the potential well of the short-range ion-molecular interaction, we arrive at the complete solvation of ions even within the third cluster coefficient approximation [302]. Nevertheless, in all cases, the interaction between ions retains its Coulombic character at large distances.

Studies of the potentials of oppositely charged ions, depending on the magnitude of the dipole moment and the density of solvent molecules, have shown that ion solvation occurs only beyond a certain value of the dipole moment and the corresponding density of dipole molecules. These factors effectively regulate the ratio between solvent-separated and contact ion pairs [300, 302]. In Fig. 22, *a*, the interionic potentials obtained in the approximation of the fourth cluster coefficient for different dipole molecule densities are presented. The potential *1jD2* was chosen as the short-range intermolecular interaction potential, which has a deeper well compared to potential 1 (Fig. 22, *b*). As seen, increasing density leads to a gradual transformation from contact ion pairs to solvated ions. Initially, at low densities, only contact pairs exist, and then ion pairs separated by a single molecule begin to form. With a further increase in density, a second minimum appears, corresponding to the formation of ion pairs separated by two molecules. At a density $\rho_s^* = 0.5$, ion pairs separated by a single molecule become unstable.

Until now, in describing the potentials of interionic interaction (as well as the distribution functions of a mixed ion-dipole system) in the approximation of the fourth cluster coefficient, we have neglected the contribution of the



the inclusion of which is associated with the computation of complex and multiple integrals. The calculations performed in [304] show that taking into account the elementary diagram does not change the overall qualitative picture; however, it is essential for describing the detailed behaviour of interionic potentials. In Fig. 23, *a*, the potentials of interaction between a cation and an anion, obtained in the approximation of the fourth cluster coefficient, are presented with (curve 1) and without (curve 2) consideration of the elementary diagram. For comparison, the result of the third clus-

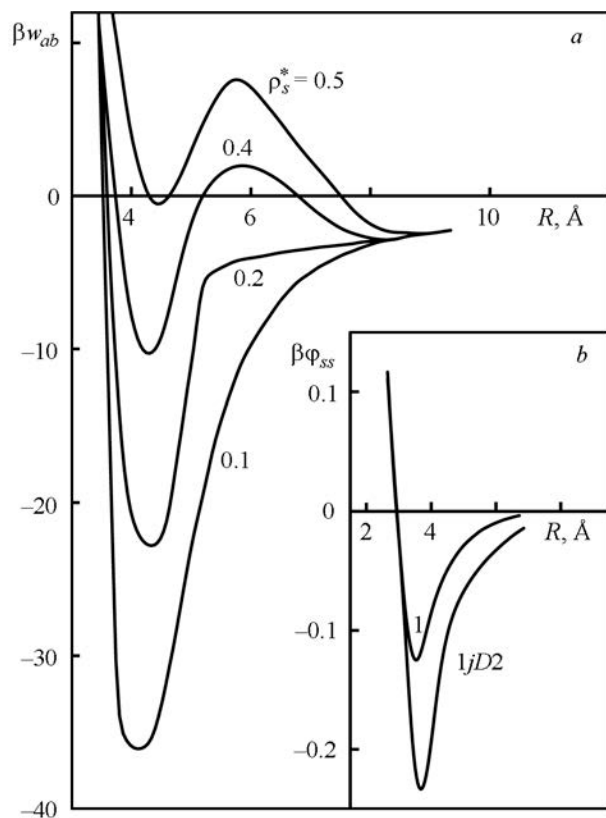


Fig. 22. Effective pair interaction potentials calculated within the fourth cluster coefficient approximation for different densities of dipolar molecules. Effective potential $\beta w_{ab}(R)$ between ions for various reduced solvent densities $\rho_s^* = 0.1, 0.2, 0.4, 0.5$ (a). Effective potential $\beta \varphi_{ss}(R)$ between solvent molecules at the corresponding conditions (b)

ter coefficient approximation is also provided (curve 3). Potentials 4 and 5 are taken as model molecular interaction potentials, while for molecular interactions, potential $1jD1$, is used, which has a deeper well compared to potential 1 (Fig. 23, b). As seen from the figure, the inclusion of the elementary diagram shifts the interionic potential downward, resulting in the appearance of an additional stable minimum corresponding to ion pairs separated by one and two molecules. At the same time, without taking into account the elementary diagram, the first minimum corresponds to an unstable configuration. A comparison of these results with computer simulations [306, 307] and with potentials obtained based on the expansion (4.4.28) shows that the latter correctly reproduce the behaviour, although the approximation of the fourth cluster coefficient apparently considerably overestimates the role of intermolecular interactions.

With an increase in ion concentration, the need arises to account for many-particle interionic interactions. In this case, it is advisable to proceed from cluster expansions that explicitly consider the molecular subsystem. The studies conducted in this direction are primarily based on expression (4.4.15) for the free energy of mixed ion-dipole systems. Typically, this approach is limited to the second cluster coefficient approximation, but instead of the

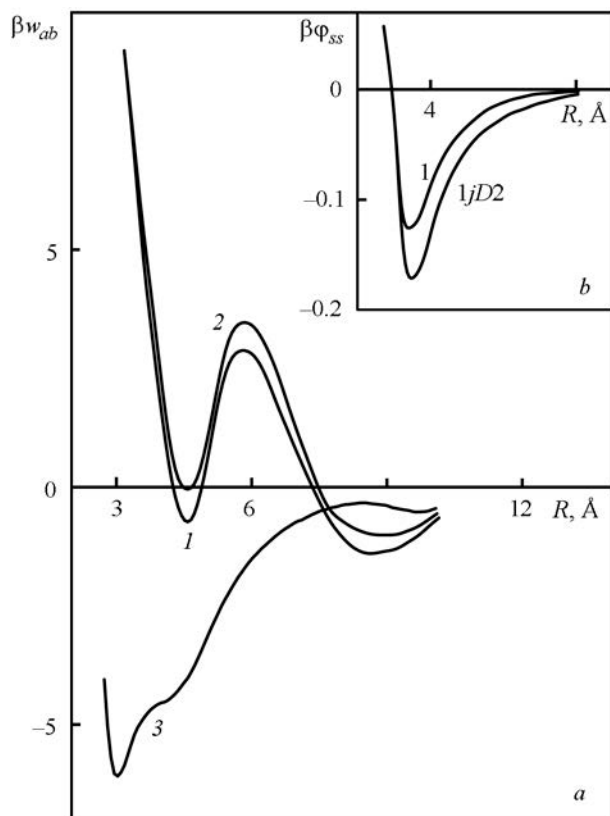


Fig. 23. The potential of cation-anion interaction obtained in the approximation of the fourth cluster coefficient with considering (curve 1) and without considering (curve 2) the elementary diagram. For comparison, curve 3 shows the result of the third cluster coefficient approximation. Potentials 4 and 5 were used for molecular interactions, and the potential $1jD2$ with a deeper well was chosen for ion-molecular interactions

expressions $\varepsilon_s = 1 + 3y$ for the dielectric permittivity, a macroscopic value is used. Assuming hard sphere models for short-range interaction forces and considering ion sizes as adjustable parameters, Roshchina and Sverdun [308–310] demonstrated that the agreement between theoretical and experimental data is achieved when ion radii are much larger than crystallographic values, approximately equal to the diameter of solvent molecules. The obtained agreement between theoretical and experimental data extends to the concentration dependences of the osmotic coefficient and activity coefficients in aqueous solutions of electrolytes of different valencies. The results obtained were also used to describe the concentration dependence of the isotropic part of light scattering in electrolyte solutions. In work [311], the second cluster coefficient approximation was also used in the calculation of the degree of dissociation of electrolyte solutions.

However, despite good agreement with experiment, the results obtained within the second cluster coefficient approximation are apparently not free from the drawback previously noted for purely ionic systems, i.e. exact results for the ion-dipole model may deviate considerably from those of the second cluster

coefficient approximation. More reliable results within this approximation can be obtained by employing cluster expansions, which fundamentally account for short-range interactions.

4.4.4. Reference system approach to short-range interactions

The description of mixed ion-molecular systems naturally leads to a generalization of the results previously obtained for ionic systems and molecular systems with electrostatic interactions (see Section 3.4 in Chapter 3 and Section 4.3 of the current Chapter). Apparently, the simplest way to describe ion-molecular systems over a wide range of temperatures and densities is to generalize the Padé expressions (3.4.26) and (4.3.52). The first leads to a cluster expansion (3.3.51) obtained in the collective variables method with a fundamental consideration of short-range interactions, while the second results in the usual thermodynamic perturbation theory (2.3.90), when generalizing the relations (3.4.26) and (4.3.52) to ion-molecular systems. Thus, one should proceed with cluster expansions that account solely for ionic screening.

In this regard, as in the beginning of this paragraph, we transform the Jacobian in such a way that it does not lead to molecular screening.

For simplicity, let us assume that the short-range interactions are identical for all particles of the system under consideration. Then, for the Jacobian of the transformation $J(\rho)$, we arrive at expression (4.4.1), in which $\hat{D}_2^{(s)}(\partial/\partial\rho)$ and $\gamma^2(k)$ coincide with the corresponding quantities used earlier, while the operators $\hat{D}_n(\partial/\partial\rho)$ for $n \geq 3$ contain n -particle structure factors of short-range interactions.

Assuming that long-range interactions have an electrostatic nature at all distances, after integration over collective variables, we arrive at the cluster expansion (4.1.56) for the free energy, constructed within the framework of the electroneutrality condition (3.4.1) and a disordered distribution of molecules in screened potentials (4.4.2). In this case, as for ionic systems, $F_{\text{HTA}} = 0$, $F_{\text{RPA}} = -V/4\pi\beta\kappa^3/3$. Expanding the operator part of $J(\rho)$, we obtain expressions for the cluster coefficients. In particular, for the second cluster coefficient, we have

$$\begin{aligned} B_2 = & \sum_{a,b} \frac{N_a N_b}{2V} \int \left\{ F_2^0(R) \left[e^{g_{ab}(R)} - 1 - g_{ab}(R) \right] - \frac{1}{2} g_{ab}^2(R) \right\} d\mathbf{R} + \\ & + \sum_{a,s} \frac{N_a N_s}{V} \int \left\{ F_2^0(R) \left[e^{g_{as}(R\Omega)} - 1 - g_{as}(R\Omega) \right] - \right. \\ & \quad \left. - \frac{1}{2} g_{as}(R\Omega) [g_{as}(R\Omega) + \beta\Phi_{as}(R\Omega)] \right\} d\mathbf{R} d\Omega + \\ & + \sum_{s,t} \frac{N_s N_t}{2V} \int F_2^0(R) \left[e^{g_{st}(R, \Omega_s \Omega_t)} - 1 - g_{st}(R, \Omega_s \Omega_t) \right] d\mathbf{R} d\Omega_s d\Omega_t, \end{aligned} \quad (4.4.29)$$

where $F_2^0(R)$ is the pair distribution function of the system with short-range interaction.

Let us consider in more detail the simplest model: a three-component system of hard spheres of equal size, where one of the components has a dipole moment p_s , while the other two are monovalent oppositely charged ions. Using the cluster expansion obtained above, we represent the free energy of the system under consideration as a double series in the parameters $x = \kappa\sigma$ and $\gamma = \beta p_s^2 N_s / V$:

$$-\beta \frac{F - F_0}{V} \sigma^3 = \frac{x^3}{12\pi} + F^{(1)}(x, \gamma) + F^{(2)}(x, \gamma) + F^{(3)}(x, \gamma) + \dots, \quad (4.4.30)$$

where

$$\begin{aligned} F^{(1)}(x, \gamma) &= \frac{A_1}{12\pi} x^4 + A_4 x^2 \gamma + A_6 \gamma^2, \\ F^{(2)}(x, \gamma) &= \frac{A_2}{12\pi} x^5 - \frac{1}{6} x^3 \gamma, \\ F^{(3)}(x, \gamma) &= \frac{A_3}{12\pi} x^6 + A_5 x^4 \gamma + A_7 x^2 \gamma^2 + A_8 \gamma^3, \end{aligned} \quad (4.4.31)$$

and the values of the coefficients A_1, A_2, A_3 are the same as in (3.4.25). For other coefficients we have

$$\begin{aligned} A_4 &= \frac{1}{6} \int_0^\infty F_2^0(r) \frac{1}{r^2} dr, \quad A_6 = \frac{2}{3} \pi \int_0^\infty F_2^0(r) \frac{1}{r^4} dr, \\ A_5 &= -\frac{1}{6} \int_0^\infty [F_2^0(r) - 1] dr - \frac{1}{6} \frac{1}{(4\pi)^2} \int u_1(r_{12}, r_{13}, r_{32}) \times \\ &\quad \times [h_3^0(r_{12}, r_{13}, r_{32}) - h_2^0(r_{12})] d\mathbf{r}_{12} d\mathbf{r}_{13}, \\ A_7 &= -\frac{2\pi}{9} \int_0^\infty \frac{1}{r^2} F_2^0(r) dr - \\ &\quad - \frac{1}{9} \frac{1}{4\pi} \int u_2(r_{12}, r_{13}, r_{32}) [F_3^0(r_{12}, r_{13}, r_{32}) - F_2^0(r_{13})] d\mathbf{r}_{12} d\mathbf{r}_{13}, \\ A_8 &= -\frac{1}{54} \int u_3(r_{12}, r_{13}, r_{32}) F_3^0(r_{12}, r_{13}, r_{32}) d\mathbf{r}_{12} d\mathbf{r}_{13}, \end{aligned} \quad (4.4.32)$$

where $r = R/\sigma$, $F_2^0(r)$ and $F_3^0(r_{12}, r_{13}, r_{32})$ are pair and three-particle distribution functions for hard spheres, respectively,

$$\begin{aligned} u_1(r_{12}, r_{13}, r_{32}) &= \frac{\cos \vartheta_3}{r_{12} r_{13}^2 r_{32}^2}; \quad u_2(r_{12}, r_{13}, r_{32}) = \frac{\cos \vartheta_1 \cos \vartheta_3 + \cos(\vartheta_1 - \vartheta_3)}{r_{12}^2 r_{13}^3 r_{32}^2}; \\ u_3(r_{12}, r_{13}, r_{32}) &= \frac{1 + 3 \cos \vartheta_1 \cos \vartheta_2 \cos \vartheta_3}{r_{12}^3 r_{13}^3 r_{32}^2}; \end{aligned}$$

$\vartheta_1, \vartheta_2, \vartheta_3$ are the angles between the sides of a triangle built by the vectors $\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{32}$.

Although the expansion (4.4.30) is valid only in the region of small values of x and γ , a Padé approximant can be constructed based on it

$$-\beta \frac{F - F_0}{V} \sigma^3 = \frac{\frac{x^3}{12\pi} + a_1(x, \gamma)}{1 + a_2(x, \gamma) + a_3(x, \gamma)}, \quad (4.4.33)$$

where

$$\begin{aligned} a_1(x, \gamma) &= \frac{[F^{(1)}(x, \gamma)]^3 - 2F^{(1)}(x, \gamma)F^{(2)}(x, \gamma) + \frac{x^6}{(12\pi)^2}F^{(3)}(x, \gamma)}{[F^{(1)}(x, \gamma)]^2 - \frac{x^3}{12\pi}F^{(2)}(x, \gamma)}, \\ a_2(x, \gamma) &= \frac{\frac{x^3}{12\pi}F^{(3)}(x, \gamma) - F^{(1)}(x, \gamma)F^{(2)}(x, \gamma)}{[F^{(1)}(x, \gamma)]^2 - \frac{x^3}{12\pi}F^{(2)}(x, \gamma)}, \\ a_3(x, \gamma) &= \frac{[F^{(2)}(x, \gamma)]^2 - F^{(1)}(x, \gamma)F^{(3)}(x, \gamma)}{[F^{(1)}(x, \gamma)]^2 - \frac{x^3}{12\pi}F^{(2)}(x, \gamma)}. \end{aligned}$$

Expression (4.4.33) for purely ionic systems ($\gamma = 0$) coincides with equation (3.4.26), while for purely dipolar systems ($x = 0$) it coincides with (4.3.52). Therefore, it can be considered as an interpolation formula valid for both large and small values of x and γ .

Another approach to describing mixed ion-molecular systems may be based on the use of screened potentials, which ensure an optimal convergence of cluster expansions. In this case, as for other previously considered systems, the determination of screened potentials reduces to solving the Ornstein–Zernike equations in the mean spherical approximation:

$$\begin{aligned} h_{xy}(R) &= F_{xy}(R) - 1 = -1, \quad R < \sigma_{xy}; \\ c_{ab}(R) &= -\beta \frac{e^2 z_a z_b}{R}, \quad c_{as}(R, \Omega) = -\beta e z_a Q_s(-\nabla) \frac{1}{R}, \\ c_{st}(R, \Omega_1 \Omega_2) &= -\beta Q_s(\nabla) Q_t(-\nabla) \frac{1}{R}, \quad R > \sigma_{xy}, \end{aligned} \quad (4.4.34)$$

where σ_{xy} characterizes the sizes of interacting particles, while indices (x, y) take the values corresponding to both types of ions with charges ez_a, ez_b , and dipolar molecules with generalized charges $Q_s(\nabla), Q_t(\nabla)$. In this case, the pair distribution functions $F_{xy}(R) = F_{xy}^0(R) + g_{xy}(R)$, where $F_{xy}^0(R)$ are the pair distribution functions of hard spheres found in the Percus–Yevick approximation, and $g_{xy}(R)$ are the screened potentials.

The solution of the Ornstein–Zernike equation in the approximation (4.4.34) for the three-component ion-dipole model considered above was ob-

tained by Blum [50, 312], Adelman, and Deutch [313]. According to the previously adopted invariant notation for this model, we have

$$\begin{aligned}
g_{++}(R) &= -g_{+-}(R) = -g_{-+}(R) = g_{--}(R) = \hat{h}^{000}(R), \\
c_{++}(R) - c_2^0(R) &= -[c_{+-}(R) - c_2^0(R)] = \\
&= -[c_{-+}(R) - c_2^0(R)] = c_{--}(R) - c_2^0(R) = \hat{C}^{000}(R), \\
g_{+s}(R, \Omega_s) &= -g_{-s}(R, \Omega_s) = \hat{h}^{011}(R) \hat{\Psi}^{011}(0, \Omega_s \Omega_R), \\
g_{s+}(R, \Omega_s) &= -g_{s-}(R, \Omega_s) = \hat{h}^{101}(R) \hat{\Psi}^{101}(\Omega_s, 0 \Omega_R), \\
c_{+s}(R, \Omega_s) - c_2^0(R) &= -[c_{-s}(R, \Omega_s) - c_2^0(R)] = \hat{c}^{011}(R) \hat{\Psi}^{011}(\Omega_s, 0 \Omega_R), \\
c_{s+}(R, \Omega_s) - c_2^0(R) &= -[c_{s-}(R, \Omega_s) - c_2^0(R)] = \hat{c}^{101}(R) \hat{\Psi}^{101}(\Omega_s, 0 \Omega_R), \\
g_{st}(R, \Omega_s \Omega_t) &= \hat{h}^{110}(R) \hat{\Psi}^{110}(\Omega_s \Omega_t \Omega_R) + \hat{h}^{112}(R) \hat{\Psi}^{112}(\Omega_s \Omega_t \Omega_R), \\
c_{st}(R, \Omega_s \Omega_t) &= c_2^0(R) + \hat{c}^{110}(R) \hat{\Psi}^{110}(\Omega_s \Omega_t \Omega_R) + \hat{c}^{112}(R) \hat{\Psi}^{112}(\Omega_s \Omega_t \Omega_R),
\end{aligned} \tag{4.4.35}$$

here $\hat{h}^{101}(R) = -\hat{h}^{011}(R)$, $\hat{c}^{101}(R) = -\hat{c}^{011}(R)$.

From (4.4.34) it follows that

$$\begin{aligned}
h_2^0(R) &= -1, \quad \hat{h}^{000}(R) = \hat{h}^{011}(R) = \hat{h}^{110}(R) = \hat{h}^{112}(R) = 0, \quad R < \sigma; \\
c_2^0(R) &= 0, \quad \hat{c}^{000}(R) = -\beta \frac{e^2}{R}, \quad \hat{c}^{011} = \beta e p_s \frac{1}{R^2}, \\
\hat{c}^{110}(R) &= 0, \quad \hat{c}^{112}(R) = \frac{\sqrt{30}}{3} \beta p_s^2 \frac{1}{R^3}, \quad R > \sigma.
\end{aligned} \tag{4.4.36}$$

According to (4.1.73), in the case under consideration, the Ornstein—Zernike equation decomposes into a set of equations

$$\begin{aligned}
h_2^0(k) - c_2^0(k) &= \frac{N}{V} h_2^0(k) c_2^0(k), \\
H_1^{11}(k) - C_1^{11}(k) &= -\frac{N_s}{V} H_1^{11}(k) C_1^{11}(k), \\
H_0^{11}(k) - C_0^{11}(k) &= \frac{N_0}{V} C_0^{10}(k) H_0^{01}(k) + \frac{N_s}{V} C_0^{11}(k) H_0^{11}(k), \\
H_0^{01}(k) - C_0^{01}(k) &= \frac{N_0}{V} C_0^{00}(k) H_0^{01}(k) + \frac{N_s}{V} C_0^{01}(k) H_0^{11}(k), \\
H_0^{10}(k) - C_0^{10}(k) &= \frac{N_0}{V} C_0^{10}(k) H_0^{00}(k) + \frac{N_s}{V} C_0^{11}(k) H_0^{10}(k), \\
H_0^{00}(k) - C_0^{00}(k) &= \frac{N_0}{V} C_0^{00}(k) H_0^{00}(k) + \frac{N_s}{V} C_0^{01}(k) H_0^{10}(k).
\end{aligned} \tag{4.4.37}$$

The first equation determines the correlation functions of the reference system and, according to the conditions (4.4.36), coincides with the Percus—Yevick equation for a system of hard spheres with size σ and the density $\eta = \frac{1}{6} \pi \frac{N}{V} \sigma^3$, where $N = N_+ + N_- + N_s$ is the total number of particles in the system, and according to the condition of overall electroneutrality of the system (3.4.1) $N_+ = N_- = \frac{1}{2} N_0$. The functions H_χ^{11} and $C_\chi^{11}(k)$ appearing in (4.4.37) are given by the relations (4.3.75). In agreement with (4.1.71), $H_0^{00}(k) = \hat{h}^{000}(k)$, $C_0^{00}(k) = \hat{c}^{000}(k)$, $H_0^{01}(k) = \frac{1}{\sqrt{3}} \hat{h}^{011}(k)$, $C_0^{01}(k) = \frac{1}{\sqrt{3}} \hat{c}^{011}(k)$, where $\hat{h}^{mnl}(k)$ and $\hat{c}^{mnl}(k)$ are defined via (4.1.65). In accordance with (4.1.76), we associate $\hat{c}^{mnl}(R)$ and $\hat{h}^{mnl}(R)$ with the functions

$$\begin{aligned} H^{000}(r) &= \hat{h}^{000}(r), & H^{101}(r) &= \hat{h}^{101}(r) - \frac{1}{r} \int_r^\infty \hat{h}^{101}(R) dR, \\ H^{110}(r) &= \hat{h}^{110}(r), & H^{112}(r) &= \hat{h}^{112}(r) - 3 \int_r^\infty \hat{h}^{112}(R) \frac{1}{R} dR, \\ C^{000}(r) &= \hat{c}^{000}(r), & C^{101}(r) &= \hat{c}^{101}(r) - \frac{1}{r} \int_r^\infty \hat{c}^{101}(R) dR, \\ C^{110}(r) &= \hat{c}^{110}(r), & C^{112}(r) &= \hat{c}^{112}(r) - 3 \int_r^\infty \hat{c}^{112}(R) \frac{1}{R} dR. \end{aligned} \tag{4.4.38}$$

Or, according to (4.1.79),

$$\begin{aligned} \hat{h}^{101}(R) &= H^{101}(R) - \frac{1}{R^2} \int_0^R H^{101}(r) r dr, \\ \hat{h}^{112}(R) &= H^{112}(R) - \frac{3}{R^3} \int_0^R H^{112}(r) r^2 dr, \\ \hat{c}^{101}(R) &= C^{101}(R) - \frac{1}{R^2} \int_0^R C^{101}(r) r dr, \\ \hat{c}^{112}(R) &= C^{112}(R) - \frac{3}{R^3} \int_0^R C^{112}(r) r^2 dr. \end{aligned} \tag{4.4.39}$$

By analogy, in accordance with (4.1.86), $H_\chi^{mn}(k)$ and $C_\chi^{mn}(k)$ we associate with the functions

$$\begin{aligned}\bar{H}_0^{00}(r) &= H^{000}(r), & \bar{C}_0^{00}(r) &= C^{000}(r), \\ \bar{H}_0^{01}(r) &= -\frac{1}{\sqrt{3}} H^{011}(r), & \bar{C}_0^{01}(r) &= -\frac{1}{\sqrt{3}} C^{011}(r)\end{aligned}\quad (4.4.40)$$

and functions $\bar{H}_\chi^{11}(r)$ and $\bar{C}_\chi^{11}(r)$ defined via (4.3.30).

The introduced functions, according to (4.4.36) and (4.4.38), satisfy the boundary conditions

$$\begin{aligned}\bar{H}_0^{00}(r) &= 0, & \bar{H}_0^{01}(r) &= -K_1 \frac{\sigma}{r}, & \bar{H}_0^{11}(r) &= -2K_2, \\ \bar{H}_1^{11}(r) &= -K_2, & r &< \sigma; \\ \bar{C}_0^{00}(r) &= -\beta \frac{e^2}{r}, & \bar{C}_0^{01}(r) &= \bar{C}_0^{11}(r) = \bar{C}_1^{11}(r) = 0, & r &> \sigma,\end{aligned}\quad (4.4.41)$$

where

$$\begin{aligned}K_1 &= \frac{1}{\sqrt{3}} \frac{1}{\sigma} \int_{\sigma}^{\infty} \hat{h}^{101}(R) dR; \\ K_2 &= \frac{3}{\sqrt{30}} \int_{\sigma}^{\infty} \hat{h}^{112}(R) \frac{1}{R} dR.\end{aligned}\quad (4.4.42)$$

The second equation (4.4.37) together with the above derived boundary condition (4.4.41), represent the Percus—Yevick equation for the hard spheres with an effective density $-K_2 \frac{N_s}{V}$, so that

$$\begin{aligned}\bar{H}_1^{11}(r) &= K_2 h_2^{(\text{PY})} \left(r, -K_2 \frac{N_s}{V} \right), \\ \bar{C}_1^{11}(r) &= K_2 c_2^{(\text{PY})} \left(r, -K_2 \frac{N_s}{V} \right).\end{aligned}\quad (4.4.43)$$

We rewrite the set of the four remaining equations (4.4.37) in the form

$$[\mathbf{1} + \mathbf{H}(k)][\mathbf{1} - \mathbf{C}(k)] = 1, \quad (4.4.44)$$

where matrices $\mathbf{C}(k)$ and $\mathbf{H}(k)$ consist of elements

$$\begin{aligned}H^{mn}(k) &= \sqrt{\rho_m \rho_n} H_0^{mn}(k), \\ C^{mn}(k) &= \sqrt{\rho_m \rho_n} C_0^{mn}(k)\end{aligned}\quad (4.4.45)$$

whilst $\rho_0 = N_0/V$, $\rho_1 = N_s/V$. Similarly as in the case of ion systems, for correctness of calculations it is required that $C_0^{00}(R) = c_0(R) + \beta \frac{e^2}{R} e^{-\alpha R}$, where $\alpha \rightarrow 0+$.

Repeating the steps presented in the derivation of the relations (3.3.74) and (4.1.92), we obtain

$$\mathbf{1} - \mathbf{C}(k) = \mathbf{Q}(k)\mathbf{Q}^T(-k), \quad (4.4.46)$$

where $\mathbf{Q}^T(k)$ denotes the transpose of the matrix $\mathbf{Q}(k)$. According to the Wiener–Hopf method, the matrix $\mathbf{Q}(k)$ is equated to the matrix $\mathbf{q}(R)$, which is given by $-\mathbf{A}e^{-\alpha R}$ for $R > \sigma$, while for $0 < R < \sigma$ it is defined by the relation

$$\mathbf{Q}(k) = \mathbf{1} - \int_0^\sigma \mathbf{q}(R) e^{ikR} dR + \mathbf{A} \int_\sigma^\infty e^{-\alpha R} e^{ikR} dR, \quad (4.4.47)$$

where, in accordance with boundary conditions (4.4.41), $\mathbf{A} = \begin{pmatrix} a_1 & a_2 \\ 0 & 0 \end{pmatrix}$. As a result, the initial system splits into equations

$$\mathbf{I}(R) = \mathbf{q}(R) + \int_0^R \mathbf{I}(R-t)\mathbf{q}(t)dt + \int_R^\infty \mathbf{I}^T(t-R)\mathbf{q}(t)dt, \quad (4.4.48)$$

$$\mathbf{S}(R) = \mathbf{q}(R) - \int_0^\infty \mathbf{q}(t+R)\mathbf{q}(t)dt, \quad (4.4.49)$$

where the matrix elements $\mathbf{I}(R)$ and $\mathbf{S}(R)$ are defined via (4.1.88) and contain an additional factor $\sqrt{\rho_m \rho_n}$. Taking into account the boundary conditions (4.4.41) in the region $R < \sigma$

$$\begin{aligned} \mathbf{I}(R) = 2\pi\sigma^2 \left[\rho_0 \begin{pmatrix} K_0 & 0 \\ 0 & K'_0 \end{pmatrix} + \sqrt{\rho_0 \rho_1} \begin{pmatrix} 0 & K_1 \\ -K_1 & 0 \end{pmatrix} \frac{R}{\sigma} + \right. \\ \left. + \rho_0 \begin{pmatrix} 0 & 0 \\ 0 & K_2 \end{pmatrix} \frac{R^2}{\sigma^2} \right], \end{aligned} \quad (4.4.50)$$

where $K_0 = \frac{1}{\sigma^2} \int_\sigma^\infty \hat{h}^{000}(R)RdR$; K_1 and K_2 are defined according to (4.4.42);

$$K'_0 = -\frac{1}{\sqrt{3}} \frac{1}{\sigma^2} \int_\sigma^\infty \hat{h}^{110}(R)RdR - \frac{1}{\sqrt{30}} \frac{1}{\sigma} \int_\sigma^\infty \hat{h}^{112}(R)dR.$$

Using the condition of local electroneutrality (3.4.12), which can be expressed as

$$\int_0^\infty \mathbf{I}(R)\mathbf{A}dR = -\frac{1}{2}\mathbf{A}, \quad (4.4.51)$$

from equation (4.4.48), following [50, 312], we exclude the function $\mathbf{I}(R)$ for $R > \sigma$. As a result, we obtain

$$\begin{aligned} \mathbf{I}(R) = & \mathbf{q}(R) + \int_0^R dt \mathbf{I}(R-t) \mathbf{q}(t) + \int_R^\sigma dt \mathbf{I}^\mathrm{T}(t-R) \mathbf{q}(t) + \\ & + \frac{1}{2} \begin{pmatrix} a_1 & 0 \\ 0 & 0 \end{pmatrix} + \int_0^{\sigma-R} dt \mathbf{I}^\mathrm{T}(t) \mathbf{A}. \end{aligned} \quad (4.4.52)$$

Hence, it follows that in the region $R < \sigma$, $\mathbf{q}(R)$ there exists a polynomial of the form

$$\mathbf{q}(R) = \mathbf{q}_0 + \mathbf{q}_1 R + \mathbf{q}_2 R^2, \quad (4.4.53)$$

while, due to the continuity of the functions $q(R)$

$$\mathbf{q}(\sigma-) = -\mathbf{A}. \quad (4.4.54)$$

From the boundary conditions (4.4.36) and the relations (4.4.39), (4.4.43), (4.4.46), for $\alpha \rightarrow 0$, we find

$$a_1^2 + a_2^2 = 4\pi\beta e^2 \rho_0 = \varkappa^2, \quad (4.4.55)$$

$$a_1 L_{10} + a_2 (1 - L_{11}) = \varkappa \sqrt{3y}, \quad (4.4.56)$$

$$L_{10}^2 + (1 - L_{11})^2 = 3y + q(1 - \eta_1 K_2), \quad (4.4.57)$$

where

$$\begin{aligned} y = \frac{4}{9} \pi \beta \rho_1 p_s^2, \quad \eta_1 = \frac{1}{6} \pi \rho_1 \sigma^3, \quad q(\eta) = \frac{(1 + 2\eta)^2}{(1 - \eta)^4}, \\ L_{mn} = \frac{1}{\sigma^2} \int_0^\sigma q^{mn}(R) dR. \end{aligned} \quad (4.4.58)$$

From the equations (4.4.55), (4.4.56) we find

$$a_1 = \frac{\varkappa}{3y + q(-\eta_1 K_2)} \left[L_{10} \sqrt{3y} + (1 - L_{11}) \sqrt{q(-\eta_1 K_2)} \right], \quad (4.4.59)$$

$$a_2 = \frac{\varkappa}{3y + q(-\eta_1 K_2)} \left[(1 - L_{11}) \sqrt{3y} + L_{10} \sqrt{q(-\eta_1 K_2)} \right]. \quad (4.4.60)$$

Further, from the relations (4.4.50), (4.4.52) we obtain

$$a_1 \sigma = \frac{12}{b_2} \left[\zeta_0 (1 - 2\zeta_2)^2 - 4\zeta_1^2 \left(1 - \frac{1}{2} \zeta_2 \right) \right], \quad (4.4.61)$$

$$a_2 \sigma = \frac{12\zeta_1}{b_2 - \frac{1}{2}b_1} \left[1 + \zeta_2 + 6\zeta_0 (1 + 4\zeta_2) + 12\zeta_1^2 \right], \quad (4.4.62)$$

$$\begin{aligned} L_{10} &= -\frac{6\zeta_1}{b_1} \left\{ 1 + 2a_1\sigma \left[3\zeta_0 + \frac{1}{3} \left(1 - \frac{1}{2} \zeta_2 \right) \right] \right\}, \\ 1 - L_{11} &= \frac{1}{b_1} \left\{ 1 + 4\zeta_2 - 12\zeta_1 a_2\sigma \left[3\zeta_0 + \frac{1}{3} \left(1 - \frac{1}{2} \zeta_2 \right) \right] \right\}, \end{aligned} \quad (4.4.63)$$

where

$$\begin{aligned} b_1 &= (1 - 2\zeta_2)^2 + 36\zeta_1^2, \\ b_2 &= -\frac{1}{2} [(1 + 12\zeta_0)(1 - 2\zeta_2) - 12\zeta_1^2], \\ \zeta_0 &= \eta_0 K_0, \quad \zeta_1 = \sqrt{\eta_0 \eta_1} K_1, \quad \zeta_2 = \eta_1 K_2, \quad \eta_0 = \frac{1}{6} \pi \rho_0 \sigma^3. \end{aligned} \quad (4.4.64)$$

Substituting these expressions into (4.4.57), (4.4.59), and (4.4.60), we arrive at a system of three nonlinear algebraic equations for K_0 , K_1 and K_2 . From these, equation (4.4.59) is solved analytically for K_0 , leading to a set of two nonlinear equations defining K_1 and K_2 as functions of κ and y .

Hence, in the limiting case $\rho_1 = 0$, we have $a_2 = 0$, $a_1\sigma = \kappa\sigma = \frac{12\zeta_0}{1 + 6\zeta_0}$, which completely coincides with the results found in the previous chapter for purely ionic systems, where $6\zeta_0 = B$ (see (3.4.46)). Similarly, in the limiting case $\rho_0 = 0$, we arrive at the results previously obtained for purely dipolar systems. In this case, $K_2 = K$, which is determined by equation (4.3.36).

Knowing the coefficients K_0 , K_1 , K_2 , from the equation (4.4.52) we find the functions $q(R)$. With these functions, equations (4.4.48) and (4.4.49) allow us to determine the direct correlation functions $\mathbf{C}(R)$ and the screened potentials $\mathbf{H}(R)$. In particular, for $R < \sigma$ from (4.4.49), we have

$$RC(R) = \mathbf{C}_0 + \mathbf{C}_1 R + \mathbf{C}_2 R^2 + \mathbf{C}_3 R^3 + \mathbf{C}_4 R^4, \quad (4.4.65)$$

where $\mathbf{C}_0$, $\mathbf{C}_1$, $\mathbf{C}_2$, $\mathbf{C}_3$, $\mathbf{C}_4$ are determined through K_0 , K_1 , K_2 [313].

According to formula (4.1.31), we arrive at the expression for the internal energy

$$\beta \frac{E - E_{\text{id}}}{V} = \frac{1}{2} \rho_0 \kappa^2 \sigma^2 K_0 - 3\kappa\sigma \sqrt{\rho_0 \rho_1 y} K_1 - 3y\rho_1 K_2, \quad (4.4.66)$$

from which, for the first non-zero contribution of electrostatic forces to the free energy, we obtain

$$\begin{aligned} \beta \frac{F_{\text{ORPA}}}{V} &= \frac{1}{2} \rho_0 \kappa^2 \sigma^2 \int_0^1 K_0(\xi) d\xi - 3\kappa\sigma \sqrt{\rho_0 \rho_1 y} \int_0^1 K_1(\xi) d\xi - \\ &\quad - 3y\rho_1 \int_0^1 K_2(\xi) d\xi. \end{aligned} \quad (4.4.67)$$

Although this expression is quite suitable for the ionic subsystem, as noted in the previous section, it is not adequate for the dipolar particles.

When considering cluster expansions, it becomes necessary to account for the different truncation characteristics of the cluster series for the ionic and dipolar subsystems.

For example, in the second cluster coefficient approximation for ions, the full expression (3.3.52) should be used, whereas for dipoles, it is more appropriate to use its linearized value, corresponding to the expression for the pair distribution function (4.3.49).

Among other approaches to describing mixed ion-dipole systems, the development of the generalized mean spherical approximation methodology is also of interest. It is clear that the resulting expressions should reduce to the results of (4.3.53) for purely dipolar systems and, in the absence of dipoles, should coincide with (3.4.63) for purely ionic systems.

When describing real ion-molecule systems, it is necessary to account for multiparticle induction and dispersion interactions, as well as the non-central character of short-range interactions involving polar molecules. In this regard, the phenomenological approach proposed by Dogonadze and colleagues [314] deserves attention, in which they describe the solvation energy of ions and the effective interionic interactions using the dielectric formalism. The dielectric function $\varepsilon(\mathbf{k}, \omega)$, employed by them, can also be calculated microscopically.

A special place among real ion-molecular systems is occupied by ion-water systems. Various electrostatic models can be used to describe both intra- and intermolecular interactions in ion-molecular systems. In particular, the Bjerrum model, discussed in the previous section, is such an approach. However, as noted by Kruglyak [315] in his review, electrostatic models can only be considered as the first step toward understanding the true nature of ion-molecular interactions. To date, extensive studies of ion interactions with water molecules have been conducted using the Hartree–Fock approximation (*ab initio*) and quantum chemistry techniques [316–318]. First of all, it has been found that the nature of interactions differs for cations and anions. Unlike ion-dipole interactions, whose orientational dependence is determined by the cosine of the angle between the dipole moment and the axis passing through centres of mass of interacting particles, the orientational dependence of the interaction potential for ions with water molecules is more complex. For instance, in the orientation dependence of the interaction potential of a molecule with an anion, two rotation barriers are observed, which gradually disappear as the distance increases. For anions, there are two stable minima corresponding to the ion approaching two protons of the molecule. It should be noted that a similar orientational dependence is also observed for certain electrostatic models [285].

An important result of the studies conducted within the Hartree–Fock approximation is the explanation of the experimentally observed transfer of electron density from the solvent molecule to the ion. In ion-molecular interactions, unlike intermolecular interactions, correlation effects are less significant. The ion-molecular and intermolecular interaction potentials obtained in this way have been used in the study of the thermodynamic and structural properties of ion-water complexes based on the Monte Carlo simulation, as well as in the calculation of solvation energies of certain biological molecules [258, 319, 320].

To date, Hartree–Fock approximation studies have also been conducted on the interaction potentials of ions with other polar molecules [265].

The difference in spatial heterogeneity leads to significant changes in the behaviour of distribution functions. In particular, the singlet distribution function is no longer a constant, but depends on the coordinates of a fixed particle. Similarly, a pair distribution function depends not only on the relative distance between two fixed particles, but also on their absolute coordinates.

The origin of spatial inhomogeneity can be very different. For example, we have already discussed it in the description of crystalline ordering in a system of hard spheres. The spatial inhomogeneity can be induced by the presence of an external field. It also plays an important role in a description of the peculiarities appearing in condensed systems at interfaces.

5.1. System of interacting particles in an external field

5.1.1. General relations

Let us start with a description of a system of interacting particles in an external field by generalizing the main results of Chapter 1. For simplicity, we restrict ourselves to considering a one-component system of monatomic particles with a pair interaction. In the presence of an external field, the potential energy of the system:

$$U_N = \sum_{i=1}^N u_1(R_i) + \sum_{i<j} u_2(R_{ij}), \quad (5.1.1)$$

where $u_1(R)$ is an interaction potential of particles with an external field; $u_2(R)$ is a potential of interparticle interaction.

The statistical description of the system will be carried out in the grand canonical ensemble, in which the independent variables are the temperature T and the chemical potential μ . The problem is reduced to the calculation of grand partition function, which according to (1.1.22) and (1.1.17) is equal to:

$$\Xi = \sum_{N \geq 0} \frac{1}{N!} \zeta^N \int e^{-\beta U_N} (d\mathbf{R}), \quad (5.1.2)$$

where $\zeta = z\lambda^{-3}$; $z = e^{\beta\mu}$ — absolute activity; λ — the de Broglie wavelength.

As in the usual canonical ensemble, for the considered system one can introduce n -particle distribution functions [87, 95]

$$\rho_n(\mathbf{R}_1, \dots, \mathbf{R}_n) = \frac{1}{\Xi} \sum_{N \geq n} \frac{\zeta^N}{(N-n)!} \int e^{-\beta U_N} d\mathbf{R}_{n+1} \dots d\mathbf{R}_N \quad (5.1.3)$$

related to the distribution functions $F_n(\mathbf{R}_1, \dots, \mathbf{R}_n)$, which were discussed earlier, by the expression

$$\rho_n(\mathbf{R}_1, \dots, \mathbf{R}_n) = \frac{1}{V^n} \langle N(N-1) \dots [N-(n-1)] \rangle F_n(\mathbf{R}_1, \dots, \mathbf{R}_n)$$

or in the thermodynamic limit $V \rightarrow \infty$

$$\rho_n(\mathbf{R}_1, \dots, \mathbf{R}_n) = \rho^n F_n(\mathbf{R}_1, \dots, \mathbf{R}_n), \quad (5.1.4)$$

where $\rho^n = \frac{\langle N^n \rangle}{V^n}$, $\langle \dots \rangle$ is the average value of the corresponding quantity.

For systems with potential energy (5.1.1), the singlet and pair correlation functions play the most important role, which are used to determine all thermodynamic properties. In particular, according to (1.1.23), the average density of the system

$$\rho = \frac{1}{V} \int \rho_1(\mathbf{R}) d\mathbf{R}. \quad (5.1.5)$$

For the internal energy, one has

$$E = \frac{3}{2} \frac{1}{\beta} \rho V + \int d\mathbf{R} \rho_1(\mathbf{R}) u_1(\mathbf{R}) + \frac{1}{2} \int d\mathbf{R}_1 d\mathbf{R}_2 \rho_2(\mathbf{R}_1, \mathbf{R}_2) u_2(\mathbf{R}_{12}). \quad (5.1.6)$$

From the fluctuation relationships, an expression for the isothermal compressibility is as follows:

$$\frac{1}{\beta} \rho \chi_T = \frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right)_T = 1 + \frac{1}{V \rho} \int d\mathbf{R}_1 d\mathbf{R}_2 [\rho_2(\mathbf{R}_1, \mathbf{R}_2) - \rho_1(\mathbf{R}_1) \rho_1(\mathbf{R}_2)]. \quad (5.1.7)$$

The expression for the free energy is obtained using relation (1.1.24):

$$\beta \frac{F}{V} = \beta \rho \mu - \beta P = \rho \ln z - \frac{1}{V} \ln \Xi. \quad (5.1.8)$$

The distribution functions can also be found by functional differentiation. Following [321], we represent the partition function in the form

$$\Xi = \sum_{N \geq 0} \frac{1}{N!} \int (d\mathbf{R}) \prod_{i=1}^N z(R_i) \exp \left\{ -\beta \sum_{i < j} u_2(R_{ij}) \right\},$$

where $z(R) = \zeta \exp(-\beta u_1(R))$. Then, according to (5.1.3)

$$\rho_n(\mathbf{R}_1, \dots, \mathbf{R}_n) = \frac{1}{\Xi} \frac{\delta^n \Xi}{\delta \ln z(R_1) \dots \delta \ln z(R_n)}. \quad (5.1.9)$$

In particular,

$$\rho_1(\mathbf{R}) = \frac{\delta \ln \Xi}{\delta \ln z(R)}. \quad (5.1.10)$$

For higher derivatives of $\ln \Xi$, we arrive at functions

$$\mathbf{m}_n(\mathbf{R}_1, \dots, \mathbf{R}_n) = \frac{\delta^n \ln \Xi}{\delta \ln z(R_1) \dots \delta \ln z(R_n)}, \quad (5.1.11)$$

whose Fourier transforms are the known cumulants or n -body structure factors (2.3.11).

The distribution functions can also be found through the functional differentiation over an interaction potential, specifically as

$$\rho_2(\mathbf{R}_1, \mathbf{R}_2) = -\frac{2}{\beta} \frac{\delta \ln \Xi}{\delta u_2(R_{12})}. \quad (5.1.12)$$

To construct Mayer cluster expansions, we represent the partition function in the form of

$$\Xi = \sum_{N \geq 0} \frac{1}{N!} \int (\mathrm{d}\mathbf{R}) \prod_{i=1}^N z(R_i) \prod_{i < j} [1 + f(R_{ij})], \quad (5.1.13)$$

where $f(R) = e^{-\beta u_2(R)} - 1$ is the Mayer function. Using the notations

$$\bullet = \int z(R) \mathrm{d}\mathbf{R}, \quad \text{---} = f(R), \quad (5.1.14)$$

similar to the spatially homogeneous case, we expand the product of Mayer functions into a series and arrive at a cluster expansion, which can be represented as diagrams in the form¹:

$$\Xi = 1 + \text{sum of all diagrams built using the notations (5.1.14)}.$$

By excluding disconnected diagrams, the partition function can be represented in exponential form:

$$\ln \Xi = \bullet + \text{sum of all connected diagrams built using the notations (5.1.14)}.$$

¹Here, the unity corresponds to $N = 0$.

By functional differentiation according to (5.1.10), we arrive at the expression for the singlet function:

$$\rho_1(R) = z(R)[1 + \text{sum of all connected diagrams with one fixed vertex, for which integration in (5.1.14) is not performed}].$$

By excluding the diagrams with parallel connections, one can obtain

$$\ln \rho_1(R) = \ln z(R) + \text{sum of all irreducible diagrams with one fixed vertex.}$$

By replacing each field vertex with a field vertex indexed by ρ , corresponding to the operation $\int \rho_1(R) d\mathbf{R}$, the singlet function can be represented by a set of essentially irreducible diagrams, with at least two independent lines emerging from each vertex:

$$\begin{aligned} \ln \rho_1(R) &= \ln z(R) + \text{the sum of all essentially irreducible diagrams} \\ &\text{built on the bonds } \text{---} = f(R), \quad \bullet^\rho = \int \rho_1(R) d\mathbf{R} \\ &\text{and having one fixed vertex.} \end{aligned} \quad (5.1.15)$$

According to (5.1.10)

$$\begin{aligned} \delta \ln \Xi &= \int d\mathbf{R} \rho_1(R) \delta \ln z(R) = \delta \int d\mathbf{R} \rho_1(R) \ln z(R) - \\ &\quad - \int d\mathbf{R} \ln z(R) \delta \rho_1(R). \end{aligned}$$

Using (5.1.15), we find

$$\begin{aligned} \ln \Xi &= \int d\mathbf{R} \rho_1(R) \ln z(R) - \int d\mathbf{R} \rho_1(R) [\ln \rho_1(R) - 1] + \\ &\quad + \text{sum of all essentially irreducible diagrams,} \\ &\text{built with connections } \text{---} = f(R) \text{ and } \bullet^\rho = \int \rho_1(R) d\mathbf{R}. \end{aligned} \quad (5.1.16)$$

The first two terms correspond to the partition function of a system of independent particles placed in an external field, while the remaining terms describe the contribution of intermolecular interactions.

By performing functional differentiation with respect to the interaction potential in accordance with (5.1.12), we obtain an expression for the pair distribution function:

$$\rho_2(\mathbf{R}_1, \mathbf{R}_2) = \rho_1(\mathbf{R}_1) \rho_1(\mathbf{R}_2) \exp \{-\beta u_2(R_{12})\} (1 + \text{sum of all connected diagrams formed with connections } \text{---} = f(R), \bullet^\rho \text{ and containing two fixed vertices, that are not directly connected to each other}).$$

Let us present the pair distribution function in the form

$$\rho_2(\mathbf{R}_1, \mathbf{R}_2) = \rho_1(\mathbf{R}_1)\rho_1(\mathbf{R}_2) [1 + h_2(\mathbf{R}_1, \mathbf{R}_2)], \quad (5.1.17)$$

where $h_2(\mathbf{R}_1, \mathbf{R}_2)$ equals the sum of all connected diagrams built with connections $\text{---} = f(R)$ and $\bullet^\rho$ and containing two fixed vertices that are not directly connected.

As in the spatially homogeneous case, the entire set of $h_2(\mathbf{R}_1, \mathbf{R}_2)$ can be divided into two groups:

$$h_2(\mathbf{R}_1, \mathbf{R}_2) = N_2(\mathbf{R}_1, \mathbf{R}_2) + c_2(\mathbf{R}_1, \mathbf{R}_2), \quad (5.1.18)$$

where $N_2(\mathbf{R}_1, \mathbf{R}_1)$ is the set of diagrams with nodal vertices, and $c_2(\mathbf{R}_1, \mathbf{R}_1)$ is without nodal vertices.

Collecting diagrams by the number of nodal vertices, we arrive at the equation

$$h_2(\mathbf{R}_1, \mathbf{R}_2) = c_2(\mathbf{R}_1, \mathbf{R}_2) + \int \rho_1(\mathbf{R}_3) h_2(\mathbf{R}_1, \mathbf{R}_3) c_2(\mathbf{R}_3, \mathbf{R}_2) d\mathbf{R}_3, \quad (5.1.19)$$

which generalizes the Ornstein–Zernike equation to the spatially inhomogeneous case.

It can also be considered as the definition of the direct correlation function $c_2(\mathbf{R}_1, \mathbf{R}_2)$. The latter, using functional differentiation, can be represented as

$$\frac{\delta \ln z(\mathbf{R}_1)}{\delta \rho_1(\mathbf{R}_2)} = \frac{\delta(\mathbf{R}_1 - \mathbf{R}_2)}{\rho_1(\mathbf{R}_1)} - c_2(\mathbf{R}_1, \mathbf{R}_2). \quad (5.1.20)$$

Since, according to (5.1.9)–(5.1.11)

$$\frac{\delta \rho_1(\mathbf{R}_1)}{\delta \ln z(\mathbf{R}_2)} = \rho_1(\mathbf{R}_1) \delta(\mathbf{R}_1 - \mathbf{R}_2) + \rho_1(\mathbf{R}_1) \rho_1(\mathbf{R}_2) h_2(\mathbf{R}_1, \mathbf{R}_2), \quad (5.1.21)$$

equation (5.1.19) represents the usual relationship between the direct and inverse derivatives

$$\int d\mathbf{R}_3 \frac{\delta \rho_1(\mathbf{R}_1)}{\delta \ln z(\mathbf{R}_3)} \frac{\delta \ln z(\mathbf{R}_3)}{\delta \rho_1(\mathbf{R}_2)} = \delta(\mathbf{R}_1 - \mathbf{R}_2). \quad (5.1.22)$$

The configurational part of the free energy, according to (5.1.8) and (5.1.16) equal to:

$$-\beta F^{(\text{int})} = \ln \Xi + \int d\mathbf{R} \rho_1(R) \left[\ln \frac{\rho_1(R)}{z(R)} - 1 \right], \quad (5.1.23)$$

can be considered as the generating functional for the set of direct correlation functions [322]. Defining the singlet direct correlation function by the relation

$$c_1(R) = \beta \frac{\delta F^{(\text{int})}}{\delta \rho_1(R)}, \quad (5.1.24)$$

the singlet distribution function can be represented as

$$\rho_1(R) = z(R)e^{c_1(R)}. \quad (5.1.25)$$

Higher-order direct correlation functions are introduced by functional differentiation

$$c_n(\mathbf{R}_1, \dots, \mathbf{R}_n) = \frac{\delta^{n-1} c_1(R_1)}{\delta \rho_1(R_2) \dots \delta \rho_1(R_n)} = \frac{\delta^n (\beta F^{(\text{int})})}{\delta \rho_1(R_1) \dots \delta \rho_1(R_n)}. \quad (5.1.26)$$

As in the spatially homogeneous case, the function $1 + h_2(\mathbf{R}_1, \mathbf{R}_2)$ can be represented in an exponential form:

$$\begin{aligned} 1 + h_2(\mathbf{R}_1, \mathbf{R}_2) &= \exp \{ -\beta u_2(R_{12}) + w_2(\mathbf{R}_1, \mathbf{R}_2) \}, \\ w_2(\mathbf{R}_1, \mathbf{R}_2) &= N_2(\mathbf{R}_1, \mathbf{R}_2) + E_2(\mathbf{R}_1, \mathbf{R}_2), \end{aligned} \quad (5.1.27)$$

where $E_2(\mathbf{R}_1, \mathbf{R}_2)$ is the set of elementary diagrams, which reduces to the sum of basic diagrams constructed on bonds $\sim\sim\sim = h_2(\mathbf{R}_1, \mathbf{R}_2)$, $\bullet^\rho$. According to (5.1.18),

$$\begin{aligned} \ln [1 + h_2(\mathbf{R}_1, \mathbf{R}_2)] &= \ln [1 + f_2(R_{12})] + h_2(\mathbf{R}_1, \mathbf{R}_2) + \\ &+ E_2(\mathbf{R}_1, \mathbf{R}_2) - c_2(\mathbf{R}_1, \mathbf{R}_2). \end{aligned}$$

Eliminating the function $c_2(\mathbf{R}_1, \mathbf{R}_2)$ using (5.1.19), we obtain

$$\begin{aligned} \ln [1 + h_2(\mathbf{R}_1, \mathbf{R}_2)] &= \ln [1 + f_2(R_{12})] + \text{diagram with two wavy lines and a } \bullet^\rho \text{ vertex} - \\ &- \text{diagram with two wavy lines and two } \bullet^\rho \text{ vertices} + \dots + E_2(\mathbf{R}_1, \mathbf{R}_2). \end{aligned} \quad (5.1.28)$$

Now, the expression for the partition function can be presented in a more compact form. According to (5.1.12)

$$\begin{aligned} \delta \ln \Xi &= -\frac{1}{2\beta} \int d\mathbf{R}_1 d\mathbf{R}_2 \rho_2(\mathbf{R}_1, \mathbf{R}_2) \delta u_2(R_{12}) = \\ &= -\frac{1}{2\beta} \delta \int d\mathbf{R}_1 d\mathbf{R}_2 \rho_2(\mathbf{R}_1, \mathbf{R}_2) u_2(R_{12}) + \\ &+ \frac{1}{2\beta} \int d\mathbf{R}_1 d\mathbf{R}_2 u_2(R_{12}) \delta \rho_2(\mathbf{R}_1, \mathbf{R}_2). \end{aligned}$$

Hence, using (5.1.28), (5.1.16), and (5.1.17), we find

$$\begin{aligned} \ln \Xi &= \int d\mathbf{R} \rho_1(R) \ln z(R) - \int d\mathbf{R} \rho_1(R) [\ln \rho_1(R) - 1] - \\ &- \frac{1}{2\beta} \int d\mathbf{R}_1 d\mathbf{R}_2 u_2(R_{12}) \rho_2(\mathbf{R}_1, \mathbf{R}_2) - \end{aligned}$$

$$\begin{aligned}
 & -\frac{1}{2} \int d\mathbf{R}_1 d\mathbf{R}_2 [\rho_2(\mathbf{R}_1 \mathbf{R}_2) \ln(1 + h_2(\mathbf{R}_1 \mathbf{R}_2)) - \rho_1(\mathbf{R}_1) \rho_1(\mathbf{R}_2) h_2(\mathbf{R}_1 \mathbf{R}_2)] + \\
 & + \text{diagram with two vertices and two wavy lines} - \text{diagram with two vertices and two wavy lines} + \dots + \text{sum of elementary diagrams.} \quad (5.1.29)
 \end{aligned}$$

Hence, according to (5.1.10), we also arrive at a more compact expression for the singlet function

$$\begin{aligned}
 \ln \rho_1(\mathbf{R}_1) = & \ln z(\mathbf{R}_1) - \beta \int d\mathbf{R}_2 \rho_1(\mathbf{R}_2) u_2(R_{12}) [1 + h_2(\mathbf{R}_1 \mathbf{R}_2)] - \\
 & - \int d\mathbf{R}_2 \rho_1(\mathbf{R}_2) \{ [1 + h_2(\mathbf{R}_1 \mathbf{R}_2)] \ln(1 + h_2(\mathbf{R}_1 \mathbf{R}_2)) - \\
 & - h_2(\mathbf{R}_1 \mathbf{R}_2) \} + \text{diagram with two vertices and two wavy lines} - \text{diagram with two vertices and two wavy lines} + \\
 & + \dots + \text{sum of elementary diagrams with one fixed vertex.} \quad (5.1.30)
 \end{aligned}$$

Equations (5.1.28) and (5.1.30) establish a relation between the singlet and pair distribution functions and the interaction potentials. However, they contain infinite series and, therefore, are not closed. Various assumptions regarding the sum of elementary diagrams lead to closed equations, generalizing the equations considered in Chapter 1 for the spatially inhomogeneous case.

The obtained results are easily generalized for multicomponent systems and systems with non-central interactions. In this case, only the meaning of the field vertex changes. Thus, for multicomponent systems $\bullet^\rho = \sum_a \int \rho_a(R) d\mathbf{R}$, where $\rho_a(R)$ is the singlet distribution function for particles^a of type a . For systems with non-central interactions $\bullet^\rho = \int \rho_1(R, \Omega) d\mathbf{R} d\Omega$, where Ω is the particle orientation.

5.1.2. Extension of the collective variables method

Let us assume that the interaction potentials can be represented as the sum of two terms:

$$u_1(R) = \Phi_1(R) + \varphi_1(R), \quad u_2(R_{12}) = \Phi_2(R_{12}) + \varphi_2(R_{12}), \quad (5.1.31)$$

where the first terms, $\Phi_1(R)$ and $\Phi_2(R_{12})$, describe the long-range part of the interaction, while the second ones, $\varphi_1(R)$ and $\varphi_2(R_{12})$, correspond to the short-range part.

By expanding the long-range part of the potential energy into a Fourier series

$$v(R) = \sum_{i=1}^N \Phi_1(R_i) + \sum_{i < j} \Phi_2(R_{ij}) = \sum_i \sum_k \frac{1}{V} \mu(k) e^{ikR_j} + \sum_{i < j} \sum_k \frac{1}{V} \nu(k) e^{ikR_{ij}},$$

it can be written in the following form

$$\begin{aligned} \beta v(R) = & \frac{1}{2} \sum_{\mathbf{k}}' \alpha(k) (\hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}} - 1) + \sum_{\mathbf{k}} \gamma(k) \hat{\rho}_{\mathbf{k}} + \\ & + \frac{N}{2} \alpha(k=0) + \sqrt{N} \gamma(k=0), \end{aligned} \quad (5.1.32)$$

where

$$\begin{aligned} \alpha(k) = \beta \frac{N}{V} \nu(k); \quad \gamma(k) = \beta \frac{\sqrt{N}}{V} \mu(k); \quad \nu(k) = \int d\mathbf{R} e^{i\mathbf{k}\mathbf{R}} \Phi_2(R); \\ \mu(k) = \int d\mathbf{R} e^{i\mathbf{k}\mathbf{R}} \Phi_1(R); \quad \hat{\rho}_{\mathbf{k}} = \frac{1}{\sqrt{N}} \sum_{i=1}^N e^{i\mathbf{k}\mathbf{R}_i}, \quad k \neq 0. \end{aligned}$$

Although the description of spatially inhomogeneous systems is more appropriate to perform in the grand canonical ensemble, let us first consider the configuration integral of the usual canonical ensemble [323]. Using the representation of collective variables, the configuration integral of the system under consideration can be rewritten in the form:

$$Q_N = \frac{1}{V^N} \int (d\mathbf{R}) e^{-\beta U_N} = \frac{1}{V^N} \int (d\mathbf{R}) (d\rho) J(\rho R) e^{-\beta v(\rho)} e^{-\beta U_0(R)}, \quad (5.1.33)$$

where

$$\beta v(\rho) = \frac{1}{2} \sum_{\mathbf{k}}' \alpha(k) (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 1) + \sum_{\mathbf{k}} \gamma(k) \rho_{\mathbf{k}} + \frac{N}{2} \alpha(k=0) + \sqrt{N} \gamma(k=0)$$

is the representation of collective variables for the function $\beta v(\mathbf{R})$; $J(\rho R) = \prod_{\mathbf{k}}' \delta(\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}})$ is the Jacobian of the transformation to collective variables; $U_0 = \sum_{i=1}^N \varphi_1(R_i) + \sum_{i<j} \varphi_2(R_{ij})$ is the short-range contribution to the potential energy.

As in the spatially homogeneous case, let us first consider the configuration integral of a system without short-range interactions.

$$Q_N^{(\ell)} = \int (d\rho) J(\rho) e^{-\beta v(\rho)}, \quad (5.1.34)$$

where $J(\rho) = \frac{1}{V^N} \int (d\mathbf{R}) J(\rho R)$ is the Jacobian, for which there exists the expression (2.1.43) or, after decomposition of the operator part, the expression (2.2.10).

Unlike the spatially homogeneous case, the presence of the factor $\sum_{\mathbf{k}} \gamma(k) \rho_{\mathbf{k}}$ in the expression for $\beta v(\rho)$ leads to the contribution of unpaired

derivatives to $Q_N^{(\ell)}$ in (2.2.10). According to the notations adopted in Chapter 2, all paired operators correspond to the derivatives $\partial^2/\partial\rho_{\mathbf{k}}\partial\rho_{-\mathbf{k}}$, or to the result of its action on $J_G(\rho)$ — the factor $(\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - 1)$. The latter in (5.1.34) after integration is replaced by the derivative $-\partial/\partial\alpha(k)$. All unpaired operators correspond to the derivatives $\partial/\partial\rho_{\mathbf{k}}$, which is applied to $J_G(\rho)$ and produces the factor $\rho_{\mathbf{k}}$. The latter is replaced by the derivative $-\partial/\partial\gamma_{\mathbf{k}}$ in (5.1.34). Integration with respect to collective variables in the remaining part of (5.1.34) leads to the random phase approximation for the long-range part of the configuration integral

$$Q_G^{(\ell)} = \exp \left\{ -\frac{1}{2} \sum'_{\mathbf{k}} [\alpha(k)(\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - 1) + 2\gamma(k)\rho_{\mathbf{k}}] - \frac{N}{2}\alpha(k=0) - \sqrt{N}\gamma(k=0) \right\} J_G(\rho)(d\rho) = Q_{\text{HTA}}^{(\ell)} Q_{\text{RPA}}^{(\ell)}, \quad (5.1.35)$$

where

$$\begin{aligned} Q_{\text{HTA}}^{(\ell)} &= \exp \left\{ -\frac{N}{2}\alpha(k=0) - \sqrt{N}\gamma(k=0) \right\} = \\ &= \exp \left\{ -\frac{1}{2}\beta\frac{N^2}{V} \int d\mathbf{R}\Phi_2(R) - \beta\frac{N}{V} \int d\mathbf{R}\Phi_1(R) \right\} \end{aligned} \quad (5.1.36)$$

is the high-temperature part of the configuration integral $Q_N^{(\ell)}$;

$$Q_{\text{RPA}}^{(\ell)} = \prod'_{\mathbf{k}} \frac{1}{1 + \alpha(k)} \exp \left\{ \frac{1}{2} \sum'_{\mathbf{k}} \left[\alpha(k) + \frac{\gamma(k)\gamma(-k)}{1 + \alpha(k)} \right] \right\} \quad (5.1.37)$$

is the random phase approximation for $Q_N^{(\ell)}$. Both $Q_{\text{RPA}}^{(\ell)}$ and $Q_{\text{HTA}}^{(\ell)}$ consist of two parts. The first part coincides with the expression for the spatially uniform case, while the second part is related to the presence of an external field.

Next, let us examine the action of the operator part of the Jacobian $J(\rho)$ in (5.1.34). The derivative $-\partial/\partial\alpha(k)$, acting on $Q_G^{(\ell)}$, leads to the appearance of the factor $-\frac{\alpha(k)}{1 + \alpha(k)}$, while the derivative $-\partial/\partial\gamma(k)$ produces the factor $-\frac{\gamma(k)}{1 + \alpha(k)}$. As before, from the inverse Fourier transform of each diagrammatic edge, we find that each paired derivative corresponds to the screened potential of interparticle interaction

$$g_2(R) = -\frac{1}{N} \sum_{\mathbf{k}} \frac{\alpha(k)}{1 + \alpha(k)} e^{i\mathbf{k}\mathbf{R}} = -\frac{1}{V}\beta \sum_{\mathbf{k}} \frac{\nu(k)e^{i\mathbf{k}\mathbf{R}}}{1 + \beta\frac{N}{V}\nu(k)}, \quad (5.1.38)$$

and each unpaired derivative corresponds to the screened potential of interaction with the external field.

$$g_1(R) = -\frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \frac{\nu(k)}{1 + \alpha(k)} e^{i\mathbf{k}\mathbf{R}} = -\frac{1}{V}\beta \sum_{\mathbf{k}} \frac{\mu(k)e^{i\mathbf{k}\mathbf{R}}}{1 + \beta\frac{N}{V}\nu(k)}. \quad (5.1.39)$$

As a result, for $Q_{(N)}^{(\ell)}$, we arrive at the following expression:

$$Q_N^{(\ell)} = \exp [B'_1 + B'_2 + B'_3 + \dots] Q_G^{(\ell)}, \quad (5.1.40)$$

where in B'_n all the connected diagrams with n vertices are collected. As usual, each vertex corresponds to the operation $\frac{N}{V} \int d\mathbf{R}$. In particular, the sum of the operators $\hat{D}_n$ leads to the expression for the first cluster coefficient:

$$B'_1 = \text{diagram with 1 vertex and 1 line} + \text{diagram with 1 vertex and 2 lines} + \dots = \frac{N}{V} \int d\mathbf{R} \left[e^{g_1(R)} - 1 - g_1(R) - \frac{1}{2} g_1^2(R) \right]. \quad (5.1.41)$$

The expression for the second cluster coefficient B'_2 is obtained from the diagrams



by completing those parts where two or more paired or unpaired lines exit from the vertices. As a result, after summation we have

$$\begin{aligned} B'_2 = \frac{1}{2} \frac{N^2}{V^2} \int \left\{ \left[e^{g_2(R_{12})} - 1 - g_2(R_{12}) \right] \left[e^{g_1(R_1)} - 1 \right] \left[e^{g_1(R_2)} - 1 \right] + \right. \\ + g_2(R_{12}) \left[e^{g_1(R_1)} - 1 - g_1(R_1) \right] \left[e^{g_1(R_2)} - 1 - g_1(R_2) \right] - \\ - g_1(R_1) g_1(R_2) \left[e^{g_2(R_{12})} - 1 - g_2(R_{12}) \right] + e^{g_2(R_{12})} - \\ \left. - 1 - g_2(R_{12}) - \frac{1}{2} g_2^2(R_{12}) \right\} d\mathbf{R}_1 d\mathbf{R}_2, \end{aligned} \quad (5.1.42)$$

where $R_{12} = |\mathbf{R}_1 - \mathbf{R}_2|$.

Higher cluster coefficients are determined in a similar manner. Substituting expression (5.1.40) to (1.1.6), we obtain a cluster expansion for the long-range part of the free energy:

$$F^{(\ell)} = F_{\text{id}} + F_{\text{HTA}} + F_{\text{RPA}} - \frac{1}{\beta} (B'_1 + B'_2 + B'_3 + \dots), \quad (5.1.43)$$

where F_{id} is the ideal part of the free energy; $F_{\text{HTA}} = \frac{1}{2} \frac{N_2}{V} \int \Phi_2(R) d\mathbf{R} + \frac{N}{V} \int \Phi_1(R) d\mathbf{R}$ is the average energy of the system, averaged over the ideal distribution; $\beta F_{\text{RPA}} = -\frac{1}{2} \sum_{\mathbf{k}} \left[\alpha(k) - \ln(1 + \alpha(k)) + \frac{\gamma(\mathbf{k}) \gamma(-\mathbf{k})}{1 + \alpha(k)} \right]$ is the en-

ergy of screening; B'_1, B'_2 are the cluster coefficients. Since any particle introduced into the system can be the source of the external field, the cluster expansion (5.1.43) coincides with the analogous expression (2.2.22), generalized to a system of N particles plus one additional particle.

Let us return to the full configuration integral (5.1.33). Using the Mayer functions of short-range forces $f_1(R) = e^{-\beta\varphi_1(R)} - 1$, $f_2(R) = e^{-\beta\varphi_2(R)} - 1$, the free energy of the system can be represented as a series

$$\begin{aligned}
 F - F_{\text{id}} = & -\frac{1}{\beta} \ln Q_N = (F)_{f=0} + \sum_{i=1}^N \int \left(\frac{\delta F}{\delta f_1(R_i)} \right)_{f=0} f_1(R_i) d\mathbf{R}_i + \\
 & + \sum_{i \neq j} \int \left[\left(\frac{\delta^2 F}{\delta f_1(R_i) \delta f_1(R_j)} \right)_{f=0} f_1(R_i) f_1(R_j) + \left(\frac{\delta F}{\delta f_2(R_{ij})} \right)_{f=0} f_2(R_{ij}) \right] d\mathbf{R}_i d\mathbf{R}_j + \\
 & + \sum_{i \neq j \neq l} \int \left[\left(\frac{\delta^3 F}{\delta f_1(R_i) \delta f_1(R_j) \delta f_1(R_l)} \right)_{f=0} f_1(R_i) f_1(R_j) f_1(R_l) + \right. \\
 & \left. + \left(\frac{\delta^2 F}{\delta f_1(R_i) \delta f_2(R_{jl})} \right)_{f=0} f_1(R_i) f_2(R_{jl}) \right] d\mathbf{R}_i d\mathbf{R}_j d\mathbf{R}_l + \dots \quad (5.1.44)
 \end{aligned}$$

The derivatives appearing here can be replaced by the derivatives of the long-range part of the free energy with respect to the long-range potentials. In particular,

$$\left(\frac{\delta F}{\delta f_1(R)} \right)_{f=0} = -\frac{1}{\beta} \frac{\delta F^{(\ell)}}{\delta \Phi_1(R)}, \quad \left(\frac{\delta F}{\delta f_2(R)} \right)_{f=0} = -\frac{1}{\beta} \frac{\delta F^{(\ell)}}{\delta \Phi_2(R)}, \text{ and so on.}$$

To find these derivatives, one needs to know the derivative $\frac{\delta g_1(R')}{\delta \Phi_1(R)}$. According to (5.1.39), $g_1(R)$ satisfies the equation

$$g_1(R_1) + \beta \frac{N}{V} \int \Phi_2(R_{12}) g_1(R_2) d\mathbf{R}_2 = -\beta \Phi_1(R_1),$$

from which we obtain the equation for $\delta g_1(R)$:

$$\begin{aligned}
 \delta g_1(R_1) + \beta \frac{N}{V} \int \Phi_2(R_{12}) \delta g_1(R_2) d\mathbf{R}_2 = & -\beta \delta \Phi_1(R_2) + \\
 & + \beta \frac{N}{V} \int \delta \Phi_2(R_{12}) g_1(R_2) d\mathbf{R}_2.
 \end{aligned}$$

The solution is given by the expression

$$\begin{aligned}
 \delta g_1(R_1) = & -\beta \delta \Phi_1(R_1) - \beta \frac{N}{V} \int [\delta \Phi_2(R_{12}) g_1(R_2) + \\
 & + g_2(R_{12}) \delta \Phi_1(R_2)] d\mathbf{R}_2 - \beta \frac{N_2}{V^2} \int g_2(R_{13}) \delta \Phi_2(R_{32}) g_1(R_2) d\mathbf{R}_2 d\mathbf{R}_3. \quad (5.1.45)
 \end{aligned}$$

Hence, we have

$$\begin{aligned} \frac{\delta g_1(R_1)}{\delta \Phi_1(R_2)} &= - \left[\delta(R_1 - R_2) + \frac{1}{V} g_2(R_{12}) \right], \\ \frac{\delta g_1(R_1)}{\delta \Phi_2(R_{23})} &= - \frac{1}{V} [\delta(R_1 - R_2) g_1(R_3) + \delta(R_1 - R_3) g_1(R_2)] - \\ &\quad - \frac{1}{V^2} [g_2(R_{12}) g_1(R_3) + g_2(R_{13}) g_1(R_2)]. \end{aligned} \quad (5.1.46)$$

For the derivative $\delta g_2(R_{12})/\delta \Phi_2(R_{34})$, the Equation (2.2.43) is in place. In addition, we have the relation $\delta g_2(R_{12})/\delta \Phi_1(R_3) = 0$.

The derivatives of the terms in Equation (5.1.43) are as follows

$$\begin{aligned} \frac{\delta F_{\text{HTA}}}{\delta \Phi_1(R)} &= \frac{1}{V}, \quad \frac{\delta F_{\text{RPA}}}{\delta \Phi_1(R)} = -\frac{1}{V} g_1(R), \\ \frac{\delta F_{\text{RPA}}}{\delta \Phi_2(R_{12})} &= \frac{1}{V^2} [g_2(R_{12}) - g_1(R_1) g_1(R_2)], \\ -\beta \frac{\delta(B'_1 + B'_2 + \dots)}{\delta \Phi_1(R)} &= -\beta \sum_{i=1}^N \int \frac{\delta(B'_1 + B'_2 + \dots)}{\delta g_1(R_i)} \frac{\delta g_1(R_i)}{\delta \Phi_1(R)} d\mathbf{R}_i, \text{ etc.} \end{aligned} \quad (5.1.47)$$

The first derivative with respect to the external field is, therefore,

$$\begin{aligned} V \frac{\delta F^{(\ell)}}{\delta \Phi_1(R_1)} &= e^{g_1(R_1)} \left[1 + \frac{N}{V} \int \left\{ [e^{g_1(R_2)} - 1] [e^{g_2(R_{12})} - 1] - \right. \right. \\ &\quad \left. \left. - g_2(R_{12}) g_1(R_2) \right\} d\mathbf{R}_2 + \dots \right]. \end{aligned} \quad (5.1.48)$$

In a similar way, we find the derivative

$$V^2 \frac{\delta F^{(\ell)}}{\delta \Phi_2(R_{12})} = e^{g_2(R_{12})} \left[1 + \left(e^{g_1(R_1)-1} \right) \left(e^{g_1(R_2)-1} \right) + \dots \right] \quad (5.1.49)$$

and other derivatives. Substituting their values into (5.1.44), we arrive at a cluster expansion for the free energy

$$F = F_{\text{id}} + F_{\text{HTA}} + F_{\text{RPA}} - \frac{1}{\beta} (B_1 + B_2 + \dots), \quad (5.1.50)$$

where

$$B_1 = \frac{N}{V} \int d\mathbf{R} \left[\exp \{ -\beta \varphi_1(R) + g_1(R) \} - 1 - g_1(R) - \frac{1}{2} g_1^2(R) \right]$$

is the first cluster coefficient; B_2 is the second cluster coefficient, and so on.

As in the spatially homogeneous case, the structure of the series for the free energy is determined by the free energy without the short-range forces. The cluster coefficients B_n and B'_n differ from each other only by replacing the

factors $e^{g_1(R)}$ and $e^{g_2(R)}$ with $\exp[g_1(R) - \beta\varphi_1(R)]$ and $\exp[g_2(R) - \beta\varphi_2(R)]$, respectively.

By functional differentiation of the free energy with respect to the interaction potentials, we obtain a sequence of distribution functions. In particular, for the singlet function, we have the expression:

$$F_1(R_1) = V \frac{\delta F}{\delta \varphi_1(R_1)} = \exp[-\beta\varphi_1(R_1) + g_1(R_1)] \times \\ \times \left\{ 1 + \frac{N}{V} \int ([\exp\{-\beta\varphi_1(R_2) + g_1(R_2)\} - 1] [\exp\{-\beta\varphi_2(R_{12}) + g_2(R_{12})\} - 1] - g_1(R_1)g_2(R_{12})) d\mathbf{R}_2 + \dots \right\}, \quad (5.1.51)$$

which coincides with the corresponding expression (2.2.63) for the pair distribution function of a spatially homogeneous system.

The pair distribution function, in the presence of an external field, can be found in two ways. By functionally differentiating (5.1.51) with respect to the external field, we find

$$\frac{1}{V^2} F_2(\mathbf{R}_1, \mathbf{R}_2) = -\frac{\delta^2 F}{\beta \delta \varphi_1(R_1) \delta \varphi_1(R_2)} + \frac{\delta F}{\delta \varphi_1(R_1)} \frac{\delta R}{\delta \varphi_1(R_2)} = \\ = \frac{1}{V^2} \exp\{-\beta\varphi_1(R_1) + g_1(R_1)\} \exp\{-\beta\varphi_2(R_{12}) + g_2(R_{12})\} \exp\{-\beta\varphi_1(R_2) + g_1(R_2)\} \{1 + \dots\}, \quad (5.1.52)$$

which completely coincides with the expression (2.2.47) for the ternary function of a spatially homogeneous system.

However, direct differentiation with respect to the intermolecular interaction potential leads to the expression

$$\frac{1}{V^2} F_2(\mathbf{R}_1, \mathbf{R}_2) = \frac{\delta F}{\delta \varphi_2(R_{12})} = \frac{1}{V^2} \exp\{-\beta\varphi_2(R_{12}) + g_2(R_{12})\} \times \\ \times \{1 + [\exp\{-\beta\varphi_1(R_1) + g_1(R_1)\} - 1] [\exp\{-\beta\varphi_1(R_2) + g_1(R_2)\} - 1] + \dots\}. \quad (5.1.53)$$

Of the two formulas for the pair distribution function, the expression in (5.1.52) is preferred. However, the difference between (5.1.52) and (5.1.53) points to difficulties that arise when describing spatially inhomogeneous systems in the canonical ensemble, where the external parameters are the temperature β^{-1} and the particle number density $\rho = N/V$. However, since the latter, according to (5.1.5), is determined by the single-particle function, another quantity should be taken as the external parameter. Therefore, it is more appropriate to describe spatially inhomogeneous systems in the grand canonical ensemble.

5.1.3. Application of the collective variables method to the description of a system in the grand canonical ensemble

When starting the calculation of the partition function in the grand canonical ensemble, we rewrite the expression for the long-range part of the potential energy as:

$$\beta v(R) = \frac{1}{2} \sum_{\mathbf{k}} \alpha(k) (\hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}} - 1) + \sum_{\mathbf{k}} \gamma(k) \hat{\rho}_{\mathbf{k}}, \quad (5.1.54)$$

where $\alpha(k) = \beta \frac{1}{V} \nu(k)$; $\gamma(k) = \frac{1}{V} \beta \mu(k)$; $\hat{\rho}_{\mathbf{k}} = \sum_{j=1}^N e^{i\mathbf{k} \cdot \mathbf{R}_j}$. In contrast to (5.1.32), the sum over k in (5.1.54) includes $\mathbf{k} = 0$.

In accordance with the method of collective variables, the grand partition function in equation (5.1.2) is presented as

$$\Xi = \sum_{N \geq 0} \frac{\zeta^N}{N!} \int (d\rho) (d\mathbf{R}) J(\rho R) e^{-\beta v(\rho)} e^{-\beta U_0(R)}, \quad (5.1.55)$$

where $J(\rho R) = \prod_{\mathbf{k}}' \delta(\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}})$ is the Jacobian of the transformation to collective variables; $\beta v(\rho) = \frac{1}{2} \sum_{\mathbf{k}} \alpha(k) (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - N) + \sum_{\mathbf{k}} \gamma(k) \rho_{\mathbf{k}}$ represents the function $\beta v(\rho)$ in terms of collective variables;

$$U_0(R) = \sum_i \varphi_1(R_i) + \sum_{i < j} \varphi_2(R_{ij}).$$

Let us first calculate the partition function of the system without short-range interactions

$$\Xi^{(\ell)} = \sum_{N \geq 0} \frac{\zeta^N}{N!} \int (d\rho) (d\mathbf{R}) J(\rho R) e^{-\beta v(\rho)}. \quad (5.1.56)$$

Using the integral representation of the δ -functions, after summing over N in (5.1.56), we obtain [324]

$$\Xi^{(\ell)} = \int (d\rho) \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} [\alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + 2\gamma(k) \rho_{\mathbf{k}}] \right\} J(\rho, \zeta), \quad (5.1.57)$$

where

$$J(\rho, \zeta) = \int (d\omega) \exp \left\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \zeta e^{\frac{1}{2} \sum_{\mathbf{k}} \alpha(k)} \int d\mathbf{R} \exp \left\{ -i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}} \right\} \right\}. \quad (5.1.58)$$

In accordance with (2.1.36), let us set

$$\int d\mathbf{R} \exp \left\{ -i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}} \right\} = V \exp \left\{ \sum_{n \geq 1} D_n(\omega) \right\}, \quad (5.1.59)$$

where

$$D_n(\omega) = \frac{(-i\pi)^n}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0}. \quad (5.1.60)$$

The Kronecker symbol here, as in (2.1.39), means that the sum of the vectors $\mathbf{k}_1 + \dots + \mathbf{k}_n$ is closed and irreducible. Substituting (5.1.59) into (5.1.58), we obtain

$$J(\rho, \zeta) = \int (d\omega) \exp \left\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \zeta V \exp \left[\frac{1}{2} \sum_{\mathbf{k}} \alpha(k) + \sum_{n \geq 1} D_n(\omega) \right] \right\}. \quad (5.1.61)$$

Next, we expand the upper exponential into a series:

$$\exp \left[\frac{1}{2} \sum_{\mathbf{k}} \alpha(k) + \sum_{n \geq 1} D_n(\omega) \right] = 1 + \frac{1}{2} \sum_{\mathbf{k}} \alpha(k) + \sum_{n \geq 1} D_n(\omega) + \dots \quad (5.1.62)$$

We then substitute the resulting expression for the Jacobian $J(\rho, \zeta)$ into the equation for the partition function in (5.1.57). Considering only the linear terms in the expansion of (5.1.62) for the Jacobian, we arrive at the approximation

$$\begin{aligned} J_1(\rho, \zeta) &= \exp \left\{ \zeta V + \frac{1}{2} \sum_{\mathbf{k}} \zeta V_{\alpha}(k) \right\} \int (d\omega) \exp \left\{ i\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \right. \\ &+ \left. \zeta V \sum_{n \geq 1} D_n(\omega) \right\} = \exp \left\{ \zeta V + \frac{1}{2} \zeta V \sum_{\mathbf{k}} \alpha(k) + \sum_{n \geq 3} \zeta V \hat{D}_n(\partial/\partial \rho) \right\} \times \\ &\times J_G(\rho, \zeta) \delta(\rho_0 - \zeta V), \end{aligned} \quad (5.1.63)$$

where

$$\begin{aligned} \hat{D}_n(\partial/\partial \rho) &= \frac{(-1)^n}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \frac{\partial^n}{\partial \rho_{\mathbf{k}_1} \dots \partial \rho_{\mathbf{k}_n}} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n, 0}, \\ J_G(\rho, \zeta) &= \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k} \neq 0} \left[\frac{1}{\zeta V} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \ln(\pi \zeta V) \right] \right\}. \end{aligned} \quad (5.1.64)$$

The partition function with the Jacobian $J_1(\rho, \zeta)$ is calculated using the method outlined in the previous section, and leads to the result

$$\Xi_1^{(\ell)} = \exp \{ \zeta V + b_1(\zeta) + b_2(\zeta) + \dots \} \Xi_{\text{HTA}}^{(\ell)} \Xi_{\text{RPA}}^{(\ell)}, \quad (5.1.65)$$

where

$$\begin{aligned}\Xi_{\text{HTA}}^{(\ell)} &= \exp \left\{ -\frac{1}{2} \zeta^2 V^2 \alpha(k=0) - \zeta V \gamma(k=0) \right\}, \\ \Xi_{\text{RPA}}^{(\ell)} &= \exp \left\{ \frac{1}{2} \sum_{\mathbf{k}} \left[\zeta V \alpha(k) - \ln(1 + \zeta V \alpha(k)) + \right. \right. \\ &\quad \left. \left. + \zeta^2 V^2 \frac{\gamma(k) \gamma(-k)}{1 + \alpha(k) \zeta V} \right] \right\},\end{aligned}\quad (5.1.66)$$

which differ from (5.1.36) and (5.1.37) only in N/V having been replaced by ζ . The expressions for the screened potentials are determined similarly to the equations (5.1.39) and (5.1.40). The cluster coefficients $b_1(\zeta)$, $b_2(\zeta)$ follow the relations (5.1.41), (5.1.42), ... with the replacement of N/V by ζ . Using (5.1.10), we arrive at the expression for the singlet function (see (5.1.51))

$$\begin{aligned}\rho_1(R_1) &= \zeta e^{g_1(R_1)} \left\{ 1 + \zeta \int \left[\left(e^{g_1(R_2)} - 1 \right) \left(e^{g_2(R_{12})} - 1 \right) - \right. \right. \\ &\quad \left. \left. - g_2(R_{12}) g_1(R_2) \right] d\mathbf{R}_2 + \dots \right\}.\end{aligned}\quad (5.1.67)$$

For the pair distribution function, using equation (5.1.9), we arrive at an expression that differs from (5.1.52) only in N/V replaced by ζ . Similarly, using equation (5.1.12), we arrive at an expression of the type (5.1.53).

The remaining part of the Jacobian $J(\rho, \zeta)$ being taken into account leads to a set of reducible diagrams which are connected to the terms in (5.1.65). When calculating the pair distribution function using (5.1.12), the reducible diagrams contribute the term $\exp\{-\beta\varphi_2(R_{12}) + g_2(R_{12})\} \times \{\exp(-\beta\varphi_1(R_1) + g_1(R_1)) - 1\} + [\exp(-\beta\varphi_1(R_2) + g_1(R_2)) - 1] + \dots$, which cancels out with the corresponding terms in (5.1.53). As a result, just as with equation (5.1.9), we arrive at the expression (5.1.52) for the pair distribution function. Thus, accounting for the reducible diagrams eliminates the difficulties that arise when describing the system in the canonical ensemble.

By assembling ζV , the second terms in $\Xi_{\text{HTA}}^{(\ell)}$, $\Xi_{\text{RPA}}^{(\ell)}$, the first cluster coefficient, and the associated reducible diagrams, we arrive at a well-known expression from Section 5.1 of this Chapter: $-\int \rho_1(R) \left[\ln \frac{1}{\zeta} \rho_1(R) + \beta \Phi_1(R) - 1 \right] d\mathbf{R}$.

The part of the reducible diagrams associated with the first term in $\Xi_{\text{HTA}}^{(\ell)}$ leads to the expression: $-\beta F_{\text{HTA}} = \frac{1}{2} \beta \int \rho_1(R_1) \Phi_2(R_{12}) \rho_1(R_2) d\mathbf{R}_1 d\mathbf{R}_2$, while the

part associated with the first term in $\Xi_{\text{RPA}}^{(\ell)}$ pertains to screening. Their inclusion leads to the expression for the screened potential, which corresponds to (5.1.19). In this equation we set $c_2(\mathbf{R}_1, \mathbf{R}_2) = -\beta \Phi_2(R_{12})$, $h_2(\mathbf{R}_1, \mathbf{R}_2) = g_2(\mathbf{R}_1, \mathbf{R}_2)$. The remaining reducible diagrams lead to renormalisation of the

vertices of the cluster coefficients. As a result, for the configurational part of the free energy defined according to (5.1.23), we arrive at a cluster expansion:

$$-\beta F^{(\text{int})} = -\beta F_{\text{HTA}} - \beta F_{\text{RPA}} + B_2 + B_3 + \dots, \quad (5.1.68)$$

This series coincides structurally with the expression (2.2.56), differing only in N/V having been replaced by $\rho_1(R)$ in the last term.

Using the outlined method, we can also take into account short-range interactions when calculating the full partition function in (5.1.55). In this case, for the configurational part of the free energy, we arrive at cluster expansions in equation (2.3.59), where N/V is replaced everywhere by $\rho_1(R)$. As we can see, when describing spatially inhomogeneous systems, it is necessary to calculate the singlet function and the screened potential in parallel with accounting for the cluster expansions.

5.1.4. Relation to the classical density field theory

With suitable modifications, the above calculations establish a connection between the collective variables approach and the classical density field theory [325–327]. To this end, following [328–330], we introduce collective variables using the particle density operator

$$\hat{n}(\mathbf{R}) = \sum_{i=1}^N \delta(\mathbf{R} - \mathbf{R}_i). \quad (5.1.69)$$

As usual in the collective variables approach, in order to design a continuous field theory, an auxiliary field $\omega(\mathbf{R})$ can be introduced through the identity

$$\int D\omega(\mathbf{R}) \int Dn(\mathbf{R}) \exp \left[i \int d\mathbf{R} \omega(\mathbf{R}) [n(\mathbf{R}) - \hat{n}(\mathbf{R})] \right] = 1. \quad (5.1.70)$$

After substitution of (5.1.70) into (5.1.2) and summation over N , the grand partition function for the system without short-range interactions can be presented in the form

$$\begin{aligned} \Xi^{(\ell)} = & \int D\omega(\mathbf{R}) \int Dn(\mathbf{R}) \exp \left[-\frac{\beta}{2} \int d\mathbf{R} \int d\mathbf{R}' \Phi_2(\mathbf{R} - \mathbf{R}') \times \right. \\ & \times [n(\mathbf{R})n(\mathbf{R}') - n(\mathbf{R})\delta(\mathbf{R} - \mathbf{R}')] - \beta \int d\mathbf{R} \Phi_1(\mathbf{R})n(\mathbf{R}) + \\ & \left. + i \int d\mathbf{R} \omega(\mathbf{R})n(\mathbf{R}) + \xi \int d\mathbf{R} \exp(-i\omega(\mathbf{R})) \right], \end{aligned} \quad (5.1.71)$$

where $\xi = e^{\beta\mu}/\lambda^3$ is the fugacity defined in terms of the chemical potential μ and the de Broglie thermal wavelength λ .

The integration in (5.1.71) over the field $\omega(\mathbf{R})$ can be performed by the saddle point approximation, and as a result, the long-range part of the grand

partition function can be presented in the form [328, 329]

$$\Xi^{(\ell)} = \int Dn(\mathbf{R}) \exp[-\beta H_{\text{sad}}(n(\mathbf{R}))], \quad (5.1.72)$$

where

$$\begin{aligned} H_{\text{sad}}(n(\mathbf{R})) = & \frac{1}{2} \int d\mathbf{R} \int d\mathbf{R}' \Phi_2(\mathbf{R} - \mathbf{R}') \left[n(\mathbf{R})n(\mathbf{R}') - \right. \\ & \left. - n(\mathbf{R})\delta(\mathbf{R} - \mathbf{R}') \right] - \beta\mu \int d\mathbf{R} n(\mathbf{R}) + \int d\mathbf{R} n(\mathbf{R})\beta\Phi_1(\mathbf{R}) + \\ & + \int d\mathbf{R} n(\mathbf{R}) [\ln(n(\mathbf{R})\lambda^3) - 1]. \end{aligned} \quad (5.1.73)$$

The last term describes the ideal entropic contribution to the Hamiltonian $H_{\text{sad}}(n(\mathbf{R}))$ in the field theoretical approach and is connected with the Jacobian of transformation to collective variables $n(\mathbf{R})$. The remaining part of the Hamiltonian (5) is connected with long-range interactions. The Hamiltonian of this form has been used to describe ionic systems [325, 326] and systems with the Yukawa potential at a hard wall [331–333]. Accounting for short-range interactions within field theory is more complex and leads to the appearance in the entropic term of an infinite number of cumulants described by n -particle connected correlation functions of the reference system [330].

5.1.5. Application of the obtained results to the description of the microfield distributions

As an example of applications of the obtained results, let us consider the problem of describing the distribution of fluctuating microfields in systems with electrostatic interactions [334, 335].

It is well known that the electric field generated at an arbitrary point $\mathbf{R}$ can be presented as a linear superposition of the fields of all the particles in the system

$$\mathbf{E}(\mathbf{R}) = \sum_{i=1}^N \mathbf{E}(\mathbf{R} - \mathbf{R}_i), \quad (5.1.74)$$

where $\mathbf{E}(\mathbf{R} - \mathbf{R}_i) = \nabla_{\psi}(|\mathbf{R} - \mathbf{R}_i|)$ is the field induced by particle i , $\psi(|\mathbf{R} - \mathbf{R}_i|)$ is the corresponding electrostatic potential.

By definition (see, for example, [336]), the probability distribution function of the electric field generated by the system at the observed point $\mathbf{R}$ is given by

$$W(\mathbf{E}) = \frac{1}{Q_N} \int \exp\{-\beta U_{N+1}\} \delta(\mathbf{E} - \mathbf{E}(\mathbf{R})) (d\mathbf{R}), \quad (5.1.75)$$

where

$$U_{N+1} = \sum_{1 \leq i < j \leq N} [\Phi_2(R_{ij}) + \varphi_2(R_{ij})] + \sum_{i=1}^N [\Phi_1(R_i) + \varphi_1(R_i)]$$

is the potential energy of the entire system including the test particle; $Q_N = \int \exp\{-\beta U_{N+1}\} (d\mathbf{R})$ is the unnormalised configuration integral of the system ($d\mathbf{R} = d\mathbf{R}_1, \dots, d\mathbf{R}_N$).

Using the integral representation of the δ -function, the expression for the micro-field distribution density $P(E) = 4\pi E^2 W(E)$ can be written as:

$$P(E) = 8\pi E \int_0^\infty T(l) \sin(2\pi El) l dl, \quad (5.1.76)$$

where

$$\begin{aligned} T(l) &= \frac{1}{Q_N} \int \exp \left\{ -\beta U_{N+1} - 2\pi i \sum_{j=1}^N (\mathbf{l} \mathbf{E}(\mathbf{R} - \mathbf{R}_j)) \right\} (d\mathbf{R}) = \\ &= \exp \{ -\beta [F(l) - F(0)] \} \end{aligned} \quad (5.1.77)$$

is the Fourier spectral function of the microfield distribution.

Thus, the problem reduces to calculating the quantity

$$F(l) = -\frac{1}{\beta} \ln \left[\int (d\mathbf{R}) \exp \left\{ -\beta \left[U_{N+1} + \frac{1}{\beta} 2\pi i \sum_{j=1}^N (\mathbf{l} \mathbf{E}(\mathbf{R} - \mathbf{R}_j)) \right] \right\} \right], \quad (5.1.78)$$

which can be interpreted as the free energy of the system in an external field with the potential interaction $\Phi_1(R) + \varphi_1(R) + \frac{1}{\beta} 2\pi i (\mathbf{l} \mathbf{E}(R))$; $F(0) = F(l = 0) = -\frac{1}{\beta} \ln Q_N$ is the free energy of the system in the external field of a test particle. It is clear that for the calculation of (5.1.78), we can directly use the results from subsection 5.1.2. Considering short-range interactions using the method of functional differentiation, for $F(0)$ there is the cluster expansion (5.1.50) and an analogous expansion for $F(l)$, with the only change being the replacement of $\mu(k)$ by $\mu(k) - 2\pi \frac{1}{\beta} (\mathbf{l} \mathbf{k}) \psi(k)$. Here, $\mu(k)$ and $\psi(k)$ are the Fourier components of the interaction potential $\Phi_1(R)$ and the field interaction $\Psi(R)$. According to (5.1.77),

$$T(l) = \exp \{ -\beta \mathcal{F}_{\text{RPA}}(l) + \mathcal{B}_1(l) + \mathcal{B}_2(l) + \dots \}, \quad (5.1.79)$$

where

$$\beta \mathcal{F}_{\text{RPA}}(l) = \frac{1}{2} \frac{N}{V} \sum_{\mathbf{k}} \frac{[2\pi (\mathbf{l} \mathbf{k}) \psi(k)]^2}{1 + \beta \frac{N}{V} \nu(k)} \quad (5.1.80)$$

is the contribution from the random phase approximation to the spectral function, $\mathcal{B}_1(l) = B_1(l) - B_1(0)$; $\mathcal{B}_2(l) = B_2(l) - B_2(0)$ are the contributions from the cluster coefficients; $B_1(l), B_2(l), \dots, B_1(0), B_2(0), \dots$ are the corresponding cluster coefficients for $F(l)$ and $F(0)$.

The construction of the cluster coefficients is carried out based on the screened potentials, where $g_2(R)$ is defined in (5.1.38), and $g_1(0, R)$ is defined according to (5.1.39):

$$g_1(l, R) = g_1(0, R) + G(l, R), \quad (5.1.81)$$

where $G(l, R) = -2\pi i(\mathbf{l} \mathbf{e}(R))$; $\mathbf{e}(R) = -\nabla \Psi(R)$ is the screened field:

$$\Psi(R) = \sum_{\mathbf{k}} \frac{1}{V} \frac{\psi(\mathbf{k})}{1 + \beta \frac{N}{V} \nu(\mathbf{k})} e^{i\mathbf{k} \cdot \mathbf{R}} \quad (5.1.82)$$

is the screened field potential.

An important feature of the cluster expansions in (5.1.79) is that they are built on screened potentials and screened fields. The obtained results are easily generalized to multicomponent systems or systems with non-central interactions. In particular, for a mixed ion-dipole system, when accounting for orientations approximately,

$$\begin{aligned} g_{ab}(R) &= -\beta Q_a(\nabla) Q_b(-\nabla) \frac{1}{\varepsilon R} \exp \left\{ -\frac{\varkappa}{\sqrt{\varepsilon}} R \right\}, \\ g_a(0, R) &= -\beta Q_a(\nabla) Q(-\nabla) \frac{1}{\varepsilon R} \exp \left\{ -\frac{\varkappa}{\sqrt{\varepsilon}} R \right\}, \\ \Psi_a(R) &= Q_a(\nabla) \frac{1}{\varepsilon R} \exp \left\{ -\frac{\varkappa}{\sqrt{\varepsilon}} R \right\}, \end{aligned} \quad (5.1.83)$$

where $\varkappa^2 = 4\pi\beta \sum_a \frac{N_a}{V} e^2 z_a^2$, $Q_a(\nabla) = e z_a + (\mathbf{p}_a \nabla)$; $e z_a$, $\mathbf{p}_a$ are the charge and the dipole moment of a particle of component a ; $\varepsilon = 1 + 4\pi \frac{1}{3} \beta \sum_a \frac{N_a}{V} p_a^2$ is the self-consistent part of the dielectric permittivity, and $Q(\nabla)$ is the generalized charge of the test particle.

However, in the case of point particles, the expression (5.1.80) diverges. Nevertheless, as in the previous chapter when describing ion-molecular systems, $\mathcal{F}_{\text{RPA}}(l)$ can be represented as an infinite series of cluster integrals

$$\begin{aligned} -\beta \mathcal{F}_{\text{RPA}}(l) &= \frac{1}{2} \frac{N}{V} \int G^2(l, R) d\mathbf{R} + \frac{1}{2} \frac{N^2}{V^2} \int G(l, R_1) g_2(R_{12}) \times \\ &\quad \times G(l, R_2) d\mathbf{R}_1 d\mathbf{R}_2 + \dots, \end{aligned} \quad (5.1.84)$$

which cancel out with the corresponding terms from the cluster series. As a result, instead of (5.1.79), we have

$$T(l) = \exp \{ \mathcal{B}_1(l) + \mathcal{B}_2(l) + \dots \}, \quad (5.1.85)$$

where

$$\mathcal{B}_1(l) = \frac{N}{V} \int \exp \{g_1(0, R) - \beta \varphi_1(R)\} [e^{G(l, R)} - 1] d\mathbf{R} \quad (5.1.86)$$

is the contribution from the first cluster coefficient.

The contribution from the second cluster coefficient includes the second term in the series (5.1.84), and so on.

In the limit of high temperatures or low densities, in (5.1.85) we can keep only the contribution from the first cluster coefficient. In particular, for charged point particles,

$$\begin{aligned} \mathcal{B}_1(l) &\rightarrow 4\pi \sum_a \frac{N_a}{V} \int_0^\infty \left[\frac{\sin(2\pi l \frac{ez_a}{\varepsilon R^2})}{2\pi l \frac{ez_a}{\varepsilon R^2}} - 1 \right] R^2 dR = \\ &= -\frac{2}{5} \sqrt{2\pi} L^{3/2} \simeq L^{3/2}, \end{aligned} \quad (5.1.87)$$

where $L = 2\pi l E_0$, $E_0 = \left[\sum_a E_a^{3/2} \right]^{2/3}$, $E_a = \frac{ez_a}{\varepsilon r_a^2}$, r_a is the average distance between particles of component a defined by the relation $\frac{4}{3}\pi \frac{N}{V} r_a^3 = 1$.

Equation (5.1.87) leads to the well-known result of Holtsmark for the microfield distribution density [337]

$$P(x) = \frac{2}{\pi x} \int_0^\infty L \sin L \exp \left\{ -\left(\frac{L}{x} \right)^{3/2} \right\} dL \quad (5.1.88)$$

with asymptotic boundaries $P(x) \rightarrow \frac{4}{3\pi} x^2$, $x \rightarrow 0$, $P(x) \rightarrow \frac{3}{2} x^{-5/2}$, $x \rightarrow \infty$, where $x = \frac{E}{E_0}$.

For a system of point dipole molecules

$$\mathcal{B}_1(l) = 4\pi \frac{N}{V} \int_0^l d(\cos \vartheta) \int_0^\infty R^2 dR \left[\frac{\sin \left(\frac{2\pi l p}{\varepsilon R^3} \sqrt{1 + 3 \cos^2 \vartheta} \right)}{\frac{2\pi l p}{\varepsilon R^3} \sqrt{1 + 3 \cos^2 \vartheta}} - 1 \right] = -\gamma L, \quad (5.1.89)$$

where $\gamma = \frac{\pi}{4} \left[1 + \frac{\sqrt{3}}{6} \ln(2 + \sqrt{3}) \right] \simeq 1.082$; $L = 2\pi l E_0$, $E_0 = \frac{p}{\varepsilon r_0^3}$; p is the dipole moment of the molecule; r_0 is the average distance from the relation $\frac{4}{3}\pi \frac{N}{V} r_0^3 = 1$.

Using (5.1.89), we arrive at the following expression for the microfield distribution function

$$P(x) = \frac{2}{\pi x} \int_0^\infty L \sin L \exp \left\{ -\gamma \frac{L}{x} \right\} dL = \frac{4\gamma}{\pi} \frac{x^2}{(\gamma^2 + x^2)^2}. \quad (5.1.90)$$

The microfield distribution functions play an important role in describing the electrical properties of the system. In particular, they are instrumental in determining the shape of the spectral lines emitted or absorbed by the system. Assuming that the only reason for the broadening of the spectral lines is the interaction of the emitted particle with the medium, we arrive at the following expression for the shape of the spectral line [338] (see also [334, 335]):

$$I(\omega) = \int_0^{\infty} I(\omega, E) P(E) dE,$$

where $I(\omega, E)$ is the shape of the spectral line emitted by an isolated particle in an external electric field of intensity E ; ω is the radiation frequency.

5.2. Interfacial properties of condensed systems

A special case of spatial inhomogeneity is realized at the interface between two bulk phases. Due to intermolecular interactions, a transition layer arises whose structure and properties, such as the separation of the system into two phases, are determined by the absolute minimum of its free energy. Depending on the specific nature of the coexisting phases, two types of surfaces are realized in the one-component case: the interface between two isotropic phases, liquid and its saturated vapor, or the interface between an anisotropic crystalline phase and an isotropic phase, liquid or vapour. For multicomponent systems, other types of surfaces are also possible, such as the interface between two immiscible liquids.

5.2.1. Liquid-vapour interface

A liquid and its saturated vapour can exist in phase equilibrium within the temperature range between the triple and critical points. Near the triple point, when the density difference between the two phases is maximal, the thickness of the transition layer is minimal. As the temperature increases, the densities of both phases gradually equalize, and the thickness of the transition layer grows. The density distribution in the interfacial region is described by a singlet function $\rho_1(R)$, also known as the density profile. For simplicity, we limit our discussion to the case of a flat interface, which is typically formed under the influence of a weak gravitational field.

By a special choice of the dividing surface, the entire system can be conventionally divided into three parts: two bulk phases and a surface of zero thickness. The latter is also called the Gibbs surface, and its position z_0 is determined by the condition [17, 35]:

$$\int_{-\infty}^{z_0} (\rho_L - \rho_1(z)) dz = \int_{z_0}^{\infty} (\rho_1(z) - \rho_G) dz, \quad (5.2.1)$$

according to which the real system and a hypothetical system, in which the particle density at the Gibbs surface changes abruptly from its value in the liquid phase ρ_L to its value in the vapour phase ρ_G , contain the same number of particles. If the origin of coordinates is placed on the Gibbs surface, then $z_0 = 0$, and z is the distance normal to the surface. In this case, any extensive quantity can be presented as the sum of three terms, two of which belong to the bulk phases and the third to the surface. Thus, we introduce surface quantities such as energy, entropy, etc., which will subsequently be denoted by the index s .

In the presence of a surface, the fundamental thermodynamic equation (1.1.1), as well as the differentials of other characteristic functions, acquire an additional term $\gamma d\xi$, where $d\xi$ is the element of the interfacial area. The intensive quantity γ is called the surface tension and essentially represents the work performed by the system when increasing the surface area by one unit. Choosing the free energy as the characteristic function, we have:

$$\gamma = - \left(\frac{\partial F}{\partial \xi} \right)_{T,V}. \quad (5.2.2)$$

From a mechanical point of view, the surface can be characterized by the excess stress caused by the presence of the interfacial boundary (see, for example, [17, 339]):

$$\gamma_t = \int_{-\infty}^{\infty} [P_t(z) - P_n(z)] dz, \quad (5.2.3)$$

where $P_t(z)$ and $P_n(z)$ are the tangential and normal components of the pressure tensor, respectively.

For spatially homogeneous phases, $P_t(z)$ coincides with the usual bulk phase pressure. In this case, the quantities γ and γ_t are equal. For systems with pair interactions, both formulas lead to the expression [15, 340]:

$$\gamma = -\frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int d\mathbf{R}_{12} \left[z_{12} \frac{\partial u_2(R_{12})}{\partial z_{12}} - x_{12} \frac{\partial u_2(R_{12})}{\partial x_{12}} \right] \rho_2(z_1, R_{12}), \quad (5.2.4)$$

where $z_{12} = z_1 - z_2$, $x_{12} = x_1 - x_2$ are the perpendicular and the parallel Cartesian coordinates of the vector $\mathbf{R}_{12}$, respectively.

For central interactions:

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int d\mathbf{R}_{12} \frac{x_{12}^2 - z_{12}^2}{R_{12}} \frac{\partial u_2(R_{12})}{\partial R_{12}} \rho_1(z_1) \rho_1(z_2) [1 + h_2(R_{12}, z_1, z_2)], \quad (5.2.5)$$

where the pair distribution function $\rho_2(z_1, R_{12})$ is replaced with its expression (5.1.17).

If the structure of the transition layer can be neglected, then for a very low vapour density, we can assume:

$$\rho_1(z) = \begin{cases} 0, & z > 0, \\ \rho_L, & z < 0, \end{cases} \quad h_2(R, z_1, z_2) = h_2(\rho_L, R), \quad (5.2.6)$$

where $h_2(\rho_L, R)$ is the pair correlation function of the liquid phase. Substituting (5.2.6) into (5.2.5), we arrive at Fowler's well-known expression for surface tension [15, 339]:

$$\begin{aligned} \gamma &= \frac{\pi}{2} \int_0^\infty dR \frac{\partial u_2(R)}{\partial R} [1 + h_2(R, \rho_L)] \times \\ &\times \left[- \int_{-R}^R z dz (R^2 - z^2) \int_{-\infty}^\infty dz_1 \frac{\partial \rho_1(z_1)}{\partial z_1} \rho_1(z + z_1) \right] - \\ &= \frac{\pi}{8} \rho_L^2 \int_0^\infty [1 + h_2(R, \rho_L)] \frac{\partial u_2(R)}{\partial R} R^4 dR. \end{aligned} \quad (5.2.7)$$

However, this simple formula is poorly suited to describe the temperature dependence of surface tension. Clearly, to improve the results, a more consistent consideration of the structure of the transition region is needed. The singlet and pair distribution functions are related by the first equation of the Bogolyubov—Born—Green—Kirkwood—Yvon (BBGKY) hierarchy (1.1.28), which in this case can be written as:

$$\frac{\partial \ln \rho_1(z_1)}{\partial z_1} = \beta \int \rho_1(z_2) [1 + h_2(R_{12}, z_1, z_2)] \frac{z_{12}}{R_{12}} \frac{\partial u_2(R_{12})}{\partial R_{12}} d\mathbf{R}_{12}, \quad (5.2.8)$$

Neglecting the influence of spatial inhomogeneity of the transition layer, to close the equation, we can assume [341]:

$$h_2(R_{12}, z_1, z_2) = \begin{cases} h_2(R_{12}, \rho_L), & z_1 + z_2 < 0, \\ h_2(R_{12}, \rho_G), & z_1 + z_2 > 0, \end{cases} \quad (5.2.9)$$

where $h_2(R_{12}, \rho_G)$ is the correlation function of the vapour phase. The singlet distribution function obtained in this way coincides at large distances with the density of the corresponding bulk phase but has oscillations in the interfacial region. These oscillations were considered as an indication of the layered nature of the transition region [15, 17]. However, such behaviour of the single distribution function was not ultimately confirmed in computer simulations

[342]. The actual density profile is monotonous, which makes the assumption in (5.2.9) insufficiently accurate.

Studies described in [343] indicate a strong sensitivity of the singlet function to the form of the approximation for $h_2(R_{12}, z_1, z_2)$. Toxvaerd [344] used the approximation:

$$\begin{aligned} & (\rho_L - \rho_G) [h_2(R_{12}, z_1, z_2) + 1] = \\ & = (\tilde{\rho} - \rho_G) [h_2(R_{12}, \rho_L) + 1] - (\tilde{\rho} - \rho_L) [h_2(R_{12}, \rho_G) + 1], \\ & \tilde{\rho} = \alpha \rho_1(z_1) + (1 - \alpha) \rho_1(z_2), \end{aligned} \quad (5.2.10)$$

where α is the variational parameter. As a result, he arrived at a monotonous profile that is satisfactorily reproduced by a function of the type:

$$\rho_1(z) = \frac{\rho_L \exp[a(b - z)] + \rho_G}{\exp[a(b - z)] + 1}, \quad (5.2.11)$$

where a and b are fitting parameters.

Due to the smooth nature of the singlet function, the local density approximation is quite justified, especially near the critical point:

$$h_2(R_{12}, z_1, z_2) = h_2\left(R_{12}, \rho_1\left(\frac{z_1 + z_2}{2}\right)\right), \quad (5.2.12)$$

according to which $h_2(R_{12}, z_1, z_2)$ coincides with the correlation function of the bulk phase taken at the density $\rho_1\left(\frac{z_1 + z_2}{2}\right)$. Equation (5.2.12) being substituted into (5.2.8) leads to a very complicated equation; therefore, in this approximation, it is more expedient to start from the free energy.

Following the work of Bongiorno and Davis [345], we limit ourselves to the high-temperature approximation for the free energy $F = F_0 + F_{\text{HTA}}$ and, in the local density approximation, we assume

$$\begin{aligned} F_0 &= \int f_0(\rho_1(R)) d\mathbf{R}, \\ F_{\text{HTA}} &= \frac{1}{2} \int \rho_1(R_1) \rho_1(R_2) F_2^0 \times \\ &\times \left(R_{12}, \rho_1\left(\frac{R_1 + R_2}{2}\right)\right) \Phi_2(R_{12}) d\mathbf{R}_1 d\mathbf{R}_2, \end{aligned} \quad (5.2.13)$$

where $f_0(\rho_1(R))$ and $F_2^0\left(R_{12}, \rho_1\left(\frac{R_1 + R_2}{2}\right)\right)$ are the local free energy and the pair distribution function of the reference system, respectively. These coincide with the corresponding expressions for a spatially homogeneous system but are taken with the density equal to the singlet function; $\Phi_2(R)$ is the long-range part of the interaction potential.

From a thermodynamic point of view, the chemical potential and the normal pressure must be constant at every point of an equilibrium system. The requirement of constancy of the chemical potential leads to the integral equation

$$\begin{aligned} \mu = & \int \left[\rho_1(\mathbf{r} + \mathbf{R}) F_2^0 \left(R, \rho_1 \left(\mathbf{r} + \frac{1}{2} \mathbf{R} \right) \right) + \right. \\ & \left. + \frac{1}{2} \rho_1 \left(\mathbf{r} + \frac{1}{2} \mathbf{R} \right) \rho_1 \left(\mathbf{r} - \frac{1}{2} \mathbf{R} \right) \frac{\partial F_2^0(R, \rho_1(r))}{\partial \rho_1(r)} \right] \times \\ & \times \Phi_2(R) d\mathbf{R} + \frac{\partial f_0(\rho_1(r))}{\partial \rho_1(r)}. \end{aligned} \quad (5.2.14)$$

where the transformation to relative coordinates has been made: $\mathbf{R} = \mathbf{R}_{12}$, $\mathbf{r} = \frac{1}{2}(\mathbf{R}_1 + \mathbf{R}_2)$, and μ is the chemical potential.

For sufficiently smooth changes in the singlet function:

$$\begin{aligned} & \int \rho_1(\mathbf{r} + \mathbf{R}) F_2^0 \left(R, \rho_1 \left(\mathbf{r} + \frac{1}{2} \mathbf{R} \right) \right) \Phi_2(R) d\mathbf{R} = -\rho_1(r) w_0(\rho_1(r)) - \\ & - [\nabla^2 \rho_1(r)] \left[\frac{1}{2} w_2(\rho_1(r)) + \frac{1}{8} \rho_1(r) \frac{\partial w_2(\rho_1(r))}{\partial \rho_1(r)} \right] - \\ & - [\nabla \rho_1(r)]^2 \left[\frac{1}{2} \frac{\partial w_2(\rho_1(r))}{\partial \rho_1(r)} + \frac{1}{8} \rho_1(r) \frac{\partial^2 w_2(\rho_1(r))}{\partial (\rho_1(r))^2} \right] + O[(\nabla \rho_1(r))^4], \\ & \int \rho_1 \left(\mathbf{r} + \frac{1}{2} \mathbf{R} \right) \rho_1 \left(\mathbf{r} - \frac{1}{2} \mathbf{R} \right) \frac{\partial F_2^0(R, \rho_1(r))}{\partial \rho_1(r)} \Phi_2(R) d\mathbf{R} = \\ & = -\frac{\partial w_0}{\partial \rho_1(r)} \rho_1^2(r) - \frac{1}{4} \frac{\partial w_2}{\partial \rho_1(r)} \left[\rho_1(r) \nabla^2 \rho_1(r) - (\nabla \rho_1(r))^2 \right] + O[(\nabla \rho_1(r))^4], \end{aligned} \quad (5.2.15)$$

where

$$w_0 = - \int \Phi_2(R) F_2^0(R, \rho_1(r)) d\mathbf{R}, \quad w_2 = -\frac{1}{3} \int R^2 \Phi_2(R) F_2^0(R, \rho_1(r)) d\mathbf{R}.$$

Neglecting fourth-order terms in the density gradient, we arrive at the differential equation:

$$\begin{aligned} & \frac{1}{4\rho_1(r)} \frac{\partial}{\partial \rho_1(r)} [\rho_1^2(r) w_2] \nabla^2 \rho_1(r) + \frac{1}{8\rho_1^2(r)} \frac{\partial}{\partial \rho_1(r)} \left[\rho_1^3(r) \frac{\partial w_2}{\partial \rho_1(r)} \right] \times \\ & \times [\nabla \rho_1(r)]^2 = -\frac{\partial}{\partial \rho_1(r)} P(\rho_1(r)), \end{aligned} \quad (5.2.16)$$

where

$$P(\rho_1(r)) = -f_0(\rho_1(r)) + \frac{1}{2} \rho_1^2(r) w_0 + \mu \rho_1(r), \quad (5.2.17)$$

is the pressure in a homogeneous system with density $\rho_1(r)$.

For a flat interface, we arrive at the equation:

$$\frac{d}{dz} \left[\frac{1}{2} \chi(\rho_1(z)) \left(\frac{d\rho_1(z)}{dz} \right)^2 \right] = - \frac{dP(\rho_1(z))}{dz}, \quad (5.2.18)$$

where

$$\chi(\rho_1(z)) = \frac{1}{4\rho_1(z)} \frac{\partial}{\partial z} [\rho_1^2(z) w_2]. \quad (5.2.19)$$

Far from the interfacial region, the singlet function coincides with the bulk phase densities such that:

$$\rho_1(z) = \begin{cases} \rho_L, & z \rightarrow -\infty, \\ \rho_G, & z \rightarrow \infty, \end{cases} \quad \frac{d\rho_1(z)}{dz} = 0 \text{ as } z \rightarrow \pm\infty. \quad (5.2.20)$$

The quantities ρ_L, ρ_G , and μ are determined from the conditions of pressure equality and constancy in the bulk phases:

$$P(\rho_L) = P(\rho_G), \quad \left(\frac{\partial P}{\partial \rho} \right)_{\rho=\rho_L} = \left(\frac{\partial P}{\partial \rho} \right)_{\rho=\rho_G} = 0. \quad (5.2.21)$$

Integrating equation (5.2.18), we get:

$$\frac{1}{2} \chi(\rho) \left[\frac{d\rho_1(z)}{dz} \right]^2 = P(\rho_L) - P(\rho),$$

or:

$$\frac{d}{dz} \rho_1(z) = -\sqrt{2} \left[\frac{P(\rho_L) - P(\rho)}{\chi(\rho)} \right]^{1/2}.$$

For the density profile, we then have:

$$z - z_0 = -\frac{1}{\sqrt{2}} \int_{\rho_1(z_0)}^{\rho_1(z)} \sqrt{\frac{\chi(\rho)}{P(\rho_L) - P(\rho)}} d\rho. \quad (5.2.22)$$

From the free energy using (5.2.2), the authors of [345] derived a simple expression for the surface tension coefficient:

$$\gamma = \int_{-\infty}^{\infty} \chi(\rho) \left[\frac{d\rho}{dz} \right]^2 dz = -\sqrt{2} \int_{\rho_G}^{\rho_L} \sqrt{\chi(\rho) [P(\rho_L) - P(\rho)]} d\rho. \quad (5.2.23)$$

Equations (5.2.22) and (5.2.23) were subsequently used to describe the surface properties of a system with Lennard-Jones interactions. To separation the

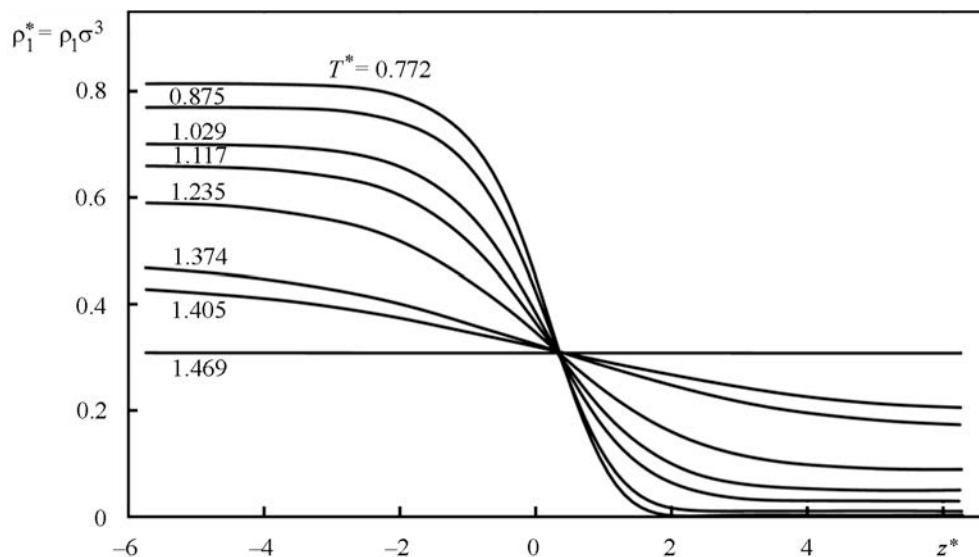


Fig. 24. Density profile $\rho_1^* = \rho_1 \sigma^3$ as a function of the reduced coordinate z^* at different reduced temperatures T^* . The data are obtained using the methodology of Weeks—Chandler—Andersen. The origin is chosen at the Gibbs dividing surface. The curves correspond to various temperatures as indicated. All curves intersect at a common point corresponding to the critical density

interactions and describe the reference system, the methodology of Weeks—Chandler—Andersen, outlined in Section 3.2 of Chapter 3, was used. The results obtained for the density profile in dimensionless variables $\rho^* = \rho \sigma^3$, $T^* = k_B T / \epsilon$, $z^* = z / \sigma$ are shown in Fig. 24. The Gibbs surface, defined by (5.2.1), is chosen as the origin. According to the law of corresponding states, the density profile is a universal function of T^* and z^* . As the temperature T^* increases, the width of the transition region increases, as expected. Interestingly, all curves, regardless of temperature, intersect at one point, with a density corresponding to the critical point. It is also worth to note the satisfactory agreement of the obtained density profile shape with the results of computer simulations.

The use of local free energy to describe the transition layer was first proposed by van der Waals. However, justification for this approach was achieved only relatively recently [103, 346]. According to (5.1.23), the free energy of a spatially inhomogeneous system can be expressed as:

$$\beta F = \int d\mathbf{R} [\beta u_1(R) + \ln(\lambda^3 \rho_1(R)) - 1] \rho_1(R) + \beta F^{(\text{int})}, \quad (5.2.24)$$

where $u_1(R)$ is the external field potential, and λ is the de Broglie thermal wavelength. In accordance with (5.1.24)–(5.1.26), the configurational part of

the free energy can be written as:

$$\begin{aligned}\beta F^{(\text{int})} &= \beta \int d\mathbf{R}_1 \int_0^{\rho_1(\mathbf{R}_1)} \frac{\delta F^{(\text{int})}}{\delta \rho_1(\mathbf{R}_1)} d\rho_1(\mathbf{R}_1) = \int d\mathbf{R}_1 \rho_1(\mathbf{R}_1) \int_0^1 c_1(\mathbf{R}_1, \xi \rho) d\xi = \\ &= \int d\mathbf{R}_1 d\mathbf{R}_2 \rho_1(\mathbf{R}_1) \rho_1(\mathbf{R}_2) \int_0^1 d\xi \int_0^\xi d\xi' c_2(\mathbf{R}_1, \mathbf{R}_2, \xi' \rho). \quad (5.2.25)\end{aligned}$$

since at $\rho_1(R) = 0$, we have that $\beta F^{(\text{int})} = 0$, and $c_1(R) = 0$.

Replacing (5.2.25) into (5.2.24), we can rewrite the free energy as

$$\begin{aligned}F &= \int f_1(\mathbf{R}) d\mathbf{R}, \\ \beta f_1(\mathbf{R}_1) &= \rho_1(\mathbf{R}_1) \left[\beta u_1(\mathbf{R}_1) + \ln(\lambda^3 \rho_1(\mathbf{R}_1)) - 1 - \right. \\ &\quad \left. - \int \rho_1(\mathbf{R}_2) \int_0^1 d\xi \int_0^\xi d\xi' c_2(\mathbf{R}_1, \mathbf{R}_2, \xi' \rho) d\mathbf{R}_2 \right]. \quad (5.2.26)\end{aligned}$$

The direct correlation function $c_2(\mathbf{R}_1, \mathbf{R}_2)$ is expanded in a Taylor series around the local density $\rho_1(\mathbf{R}_1)$:

$$\begin{aligned}c_2(\mathbf{R}_1, \mathbf{R}_2) &= c_2(R_{12}, \rho_1(\mathbf{R}_1)) + \int d\mathbf{R}_3 c_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \rho_1(\mathbf{R}_1)) \left[\rho_1(\mathbf{R}_3) - \right. \\ &\quad \left. - \rho_1(\mathbf{R}_1) \right] + \frac{1}{2} \int d\mathbf{R}_3 d\mathbf{R}_4 c_4(\mathbf{R}_1, \dots, \mathbf{R}_4, \rho_1(\mathbf{R}_1)) \left[\rho_1(\mathbf{R}_3) - \right. \\ &\quad \left. - \rho_1(\mathbf{R}_1) \right] \left[\rho_1(\mathbf{R}_4) - \rho_1(\mathbf{R}_3) \right] + \dots, \quad (5.2.27)\end{aligned}$$

where $c_2(R_{12}, \rho_1(\mathbf{R}_1))$, $c_3(R_1, R_2, R_3, \rho_1(R_1))$, ... are the correlation functions of a spatially homogeneous system with local density $\rho_1(\mathbf{R}_1)$.

Substituting (5.2.27) into (5.2.26) and using translational invariance of the spatially homogeneous system in the absence of an external field, we have:

$$\begin{aligned}\beta f(\mathbf{R}) &= \rho_1(\mathbf{R}) \left[\ln(\lambda^3 \rho_1(\mathbf{R})) - 1 - \int d\mathbf{R}_2 \tilde{c}_2(\mathbf{R}_2, \rho_1(\mathbf{R})) \rho_1(\mathbf{R} + \mathbf{R}_2) - \right. \\ &\quad \left. - \int d\mathbf{R}_2 d\mathbf{R}_3 \tilde{c}_3(\mathbf{R}_2, \mathbf{R}_3, \rho_1(\mathbf{R})) \rho_1(\mathbf{R} + \mathbf{R}_2) \left[\rho_1(\mathbf{R} + \mathbf{R}_3) - \rho_1(\mathbf{R}) \right] - \right. \\ &\quad \left. - \frac{1}{2} \int d\mathbf{R}_2 d\mathbf{R}_3 d\mathbf{R}_4 \tilde{c}_4(\mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4, \rho_1(\mathbf{R})) \rho_1(\mathbf{R} + \mathbf{R}_2) \left[\rho_1(\mathbf{R} + \mathbf{R}_3) - \right. \right. \\ &\quad \left. \left. - \rho_1(\mathbf{R}) \right] \left[\rho_1(\mathbf{R} + \mathbf{R}_4) - \rho_1(\mathbf{R}) \right] - \dots \right]. \quad (5.2.28)\end{aligned}$$

Here,

$$\tilde{c}_n(\mathbf{R}_2, \dots, \mathbf{R}_n, \rho_1(\mathbf{R})) = \int_0^1 d\xi \int_0^\xi d\xi' c_n(\mathbf{R}_2, \dots, \mathbf{R}_n, \xi' \rho_1(\mathbf{R})).$$

Expanding the singlet functions $\rho_1(\mathbf{R} + \mathbf{R}_2)$ around the point $\mathbf{R}$ in a Taylor series:

$$\rho_1(\mathbf{R} + \mathbf{R}_2) = \rho_1(\mathbf{R}) + (\mathbf{R}_2 \nabla) \rho_1(\mathbf{R}) + \frac{1}{2} (\mathbf{R}_2 \nabla)^2 \rho_1(\mathbf{R}) + \dots,$$

and keeping only the terms up to quadratic order, we get:

$$f(\mathbf{R}) = f_0(\rho_1(\mathbf{R})) - f_1(\rho_1(\mathbf{R})) \nabla^2 \rho_1(\mathbf{R}) - f_2(\rho_1(\mathbf{R})) [\nabla \rho_1(\mathbf{R})]^2, \quad (5.2.29)$$

where $\beta f_0(\rho) = \rho \left[\ln(\lambda^3 \rho) - 1 - \rho \int d\mathbf{R}_2 \tilde{c}_2(\mathbf{R}_2, \rho) \right]$ is the free energy of the spatially homogeneous system with density $\rho = \rho_1(\mathbf{R})$,

$$\begin{aligned} \beta f_1(\rho) &= \frac{1}{6} \rho \int d\mathbf{R}_2 R_2^2 \left\{ \tilde{c}_2(\mathbf{R}_2, \rho) + \rho \int d\mathbf{R}_3 \tilde{c}_3(\mathbf{R}_2, \mathbf{R}_3, \rho) \right\}, \\ \beta f_2(\rho) &= \frac{1}{3} \rho \int d\mathbf{R}_2 d\mathbf{R}_3 (\mathbf{R}_2 \mathbf{R}_3) \times \\ &\quad \times \left\{ \tilde{c}_3(\mathbf{R}_2, \mathbf{R}_3, \rho) + \frac{1}{2} \rho \int d\mathbf{R}_4 \tilde{c}_4(\mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4, \rho) \right\} = \\ &= \frac{1}{3} \rho \int d\mathbf{R}_2 R_2^2 \left[\int d\mathbf{R}_3 \tilde{c}_3(\mathbf{R}_2 \mathbf{R}_3, \rho) + \frac{1}{2} \rho \int d\mathbf{R}_3 d\mathbf{R}_4 \tilde{c}_4(\mathbf{R}_2 \mathbf{R}_3 \mathbf{R}_4, \rho) \right]. \end{aligned}$$

Now, rewriting equation (5.2.29) as:

$$\begin{aligned} f(\mathbf{R}) &= f_0(\rho_1(\mathbf{R})) + \frac{1}{2} A(\rho_1(\mathbf{R})) [\nabla \rho_1(\mathbf{R})]^2 - \\ &\quad - \nabla \left[f_1(\rho_1(\mathbf{R})) \nabla \rho_1(\mathbf{R}) \right], \end{aligned} \quad (5.2.30)$$

where $\frac{1}{2} A(\rho) = \frac{\partial f_1(\rho)}{\partial \rho} - f_2(\rho)$.

The last term in (5.2.30) can be omitted since it vanishes when substituted into (5.2.26). As a result, for the local energy, we arrive at the following expression:

$$f(\mathbf{R}) = f_0(\rho_1(\mathbf{R})) + \frac{1}{2} A(\rho_1(\mathbf{R})) [\nabla \rho_1(\mathbf{R})]^2, \quad (5.2.31)$$

which was first proposed by van der Waals. Using Baxter's relations (1.3.29), the expression for the coefficient $A(\rho)$ can be written as:

$$A(\rho) = \frac{1}{6} \int R_2^2 d\mathbf{R}_2 c_2(R_2, \rho) = \frac{2}{3} \pi \int_0^\infty R^4 dR c_2(R, \rho). \quad (5.2.32)$$

The singlet function $\rho_1(R)$, appearing in (5.2.31), is determined by minimizing the expression for the free energy.

The separation of the system into two phases usually occurs in the presence of a weak gravitational field, under the influence of which the denser liquid phase is located at the bottom, and the less dense vapour phase is at the top. Density fluctuations in the transition region lead to collective oscillations manifested in the propagation of capillary waves. Fluctuation theory allows to relate the surface tension to the direct correlation function, thus obtaining a relation that, unlike (5.2.5), is valid without assuming pair interactions. Following the work of Triezenberg and Zwanzig [251], consider the density fluctuation in the interfacial region, which results in the singlet function changing by:

$$\Delta\rho_1(r, z) = \rho_1(r, z) - \rho_1(z), \quad (5.2.33)$$

where $r = \sqrt{x^2 + y^2}$ is the magnitude of the two-dimensional radius vector.

According to (5.2.1), this leads to a shift in the Gibbs surface position by:

$$z_0(r) = \int dz \frac{\Delta\rho_1(r, z)}{\rho_L - \rho_G}, \quad (5.2.34)$$

resulting in a change in the surface area:

$$\Delta\xi = \xi - \xi_0 = \frac{1}{2} \int d\mathbf{r} |\nabla_r z_0(r)|^2. \quad (5.2.35)$$

Expanding (5.2.33) and (5.2.34) in a two-dimensional Fourier series:

$$z_0(r) = \sum_{\mathbf{q}} z_0(q) e^{i\mathbf{q}\mathbf{r}}, \quad \Delta\rho_1(r, z) = \sum_{\mathbf{q}} \Delta\rho_1(q, z) e^{i\mathbf{q}\mathbf{r}}, \quad (5.2.36)$$

we find:

$$\Delta\xi = \frac{1}{2} \xi_0 \sum_{\mathbf{q}} q^2 |z_0(q)|^2, \quad (5.2.37)$$

where $\mathbf{q}$ and $\mathbf{r}$ are corresponding two-dimensional vectors in the xy -plane, and $z_0(q) = \int dz \frac{\Delta\rho_1(q, z)}{\rho_L - \rho_G}$. As a result of the fluctuation (5.2.33), the free energy changes by:

$$\beta\Delta F = \beta\gamma\Delta\xi = \frac{1}{2} \int d\mathbf{R}_1 d\mathbf{R}_2 \Delta\rho_1(\mathbf{r}_1, z_1) K(\mathbf{R}_1, \mathbf{R}_2) \Delta\rho_1(z_2, \mathbf{r}_2), \quad (5.2.38)$$

where, according to (5.1.20),

$$K(\mathbf{R}_1, \mathbf{R}_2) = \frac{1}{\rho_1(\mathbf{R}_1)} \delta(\mathbf{R}_1 - \mathbf{R}_2) - c_2(\mathbf{R}_1, \mathbf{R}_2).$$

Using the two-dimensional Fourier transform, (5.2.38) can be rewritten as:

$$\beta\Delta F = \frac{1}{2} \xi_0 \int dz_1 dz_2 \sum_{\mathbf{q}} [\Delta\rho_1(\mathbf{q}, z_1)]^* K(\mathbf{q}, z_1 z_2) \Delta\rho_1(\mathbf{q}, z_2), \quad (5.2.39)$$

where

$$K(\mathbf{q}, z_1 z_2) = \frac{1}{\rho_1(z_1)} \delta(z_1 - z_2) - c_2(\mathbf{q}, z_1, z_2),$$

$$c_2(\mathbf{q}, z_1 z_2) = \int d\mathbf{r} c_2(z_1, z_2, \mathbf{r}) e^{i\mathbf{q}\mathbf{r}}.$$

For long-wavelength fluctuations, we can assume:

$$\Delta\rho_1(\mathbf{q}, z) = -z_0(q) \frac{\partial\rho_1(z)}{\partial z} + \dots, \quad K(\mathbf{q}, z_1 z_2) = K_0(z_1, z_2) + q^2 K_2(z_1 z_2) + \dots \quad (5.2.40)$$

where

$$K_2(z_1 z_2) = \frac{1}{4} \int dz_1 dz_2 \int r^2 d\mathbf{r} c_2(z_1 z_2, \mathbf{r}).$$

Substituting (5.2.40) into (5.2.39) according to (5.2.38), we obtain:

$$\beta\gamma = \frac{1}{4} \int_{-\infty}^{\infty} dz_1 \int d\mathbf{R}_{12} \frac{\partial\rho_1(z_1)}{\partial z_1} c_2(z_1, R_{12}) \frac{\partial\rho_1(z_2)}{\partial z_2} r_{12}^2. \quad (5.2.41)$$

Another way to derive this expression was presented in [347].

Considering an explicit gravitational field, Wertheim [348] discovered the existence of long-range correlations in the plane parallel to the interfacial surface. In his work, he started with two equations. The first equation can be obtained by differentiating the relation (5.1.25) with respect to the particle coordinate, noting that $\nabla_1 c_1(R_1) = \int c_2(R_1 R_2) \nabla_2 \rho_1(R_2) d\mathbf{R}_2$. As a result:

$$\nabla \ln \rho_1(\mathbf{R}_1) - \int c_2(\mathbf{R}_1, \mathbf{R}_2) \nabla_2 \rho_1(\mathbf{R}_2) d\mathbf{R}_2 = -\beta \nabla_1 u_1(\mathbf{R}_1). \quad (5.2.42)$$

Using relation (5.1.19), the second equation becomes:

$$\nabla_1 \rho_1(\mathbf{R}_1) = -\beta \rho_1(\mathbf{R}_1) \nabla_1 u_1(\mathbf{R}_1) - \beta \int G_2(\mathbf{R}_1 \mathbf{R}_2) \nabla_2 u_1(\mathbf{R}_2) d\mathbf{R}_2, \quad (5.2.43)$$

where

$$G_2(\mathbf{R}_1 \mathbf{R}_2) = \rho_2(\mathbf{R}_1 \mathbf{R}_2) - \rho_1(\mathbf{R}_1) \rho_1(\mathbf{R}_2) = \rho_1(\mathbf{R}_1) \rho_1(\mathbf{R}_2) h_2(\mathbf{R}_1 \mathbf{R}_2).$$

Here, $u_1(\mathbf{R})$ is the potential of the external field.

For a gravitational field, $\beta u_1(R) = \beta m g z = K z$, and $\rho_1(R) = \rho_1(z)$, which leads to the following functions:

$$C(z_1, z_2) = \frac{1}{\rho_1(z_1)} \delta(z_1 - z_2) - 2\pi \int_0^{\infty} c_2(z_1 z_2, r) r dr,$$

$$G(z_1, z_2) = \rho_1(z_1) \delta(z_1 - z_2) + 2\pi \int_0^{\infty} G_2(z_1 z_2, r) r dr, \quad (5.2.44)$$

where $r = \sqrt{x_{12}^2 + y_{12}^2}$.

Using these functions, equations (5.2.46) and (5.2.47) can be expressed as:

$$\int_{-\infty}^{\infty} C(z_1, z_2) \rho'_1(z_2) dz_2 = -K, \quad (5.2.45)$$

$$\rho'_1(z_1) = -K \int_{-\infty}^{\infty} G(z_1 z_2) dz_2, \quad (5.2.46)$$

where $\rho'_1(z) = \partial \rho_1(z) / \partial z$.

In the limit $K \rightarrow 0$, equations (5.2.45) and (5.2.46) may have two solutions. The first, $\rho'_1(z) = 0$, corresponds to the one-phase region where the system is above the critical point. In the second solution, below the critical point, the system separates into two phases $\rho'_1(z) \neq 0$, which implies that the integral

$\int_{-\infty}^{\infty} G(z_1 z_2) dz_2$ diverges as $K \rightarrow 0$. This indicates that in the interfacial region,

in the plane parallel to the interface, there exist long-range correlations of a macroscopic nature. Such behaviour of the pair distribution function may be a strong argument against using interpolation formulas like (5.2.9) or (5.2.10). Weeks [349], by dividing the system into a set of very narrow columns, showed that fluctuations in the positions of their Gibbs surfaces lead to a dependence of the thickness of the entire system's interfacial region on the intensity of the external field. This provides the explanation for the fluctuations predicted within Wertheim's perturbation theory.

Recently, efforts have been made to generalise the presented results to molecular systems with non-central interactions. The generalisation of, for example, equation (5.2.4) is trivial. This requires only replacing $\int d\mathbf{R}_{12}$ by $\int d\mathbf{R}_{12} d\Omega_1 d\Omega_2$ and accounting for the orientational dependence of the interaction potential and distribution functions [340]. Calculations conducted so far are primarily based on approximation (5.2.6). In particular, in [340, 350], using asymptotic results (4.3.86), the contribution of dipole forces to the surface tension is given by the expression:

$$\gamma = \frac{3}{64\pi\sigma^2} \frac{(2\varepsilon + 1)(\varepsilon - 1)}{(\varepsilon + 1)}. \quad (5.2.47)$$

Here, σ denotes the size of the dipole molecule.

In [351, 352], to describe the surface tension of systems with electrostatic interactions, Padé approximation was used, similar to the case of spatially homogeneous systems (Section 4.3 of Chapter 4).

5.2.2. Solid-liquid and solid-vapour interfaces

The description of the interfacial region at the boundary of a solid is complicated by additional spatial inhomogeneity due to its crystalline structure. This results in anisotropy of surface properties, which causes the values of γ and γ_i , defined by expressions (5.2.2) and (5.2.3), to differ and have distinct meanings. The first represents the actual surface tension coefficient, while the second corresponds to the surface stress tensor [353].

When solid and liquid (or vapour) phases come into contact, mutual dissolution of matter occurs, with the equilibrium state determined by the equality of the chemical potentials in both phases. The dissolution of the solid phase is of greatest interest. Neglecting its structure, the solid is considered as an ideal impermeable wall. Under this approach, the problem reduces to describing a mixture of particles, one of whose components is at extreme dilution and has infinitely large dimensions. As a result, the results obtained previously for multicomponent systems can be used to describe the surface properties.

In the simplest case of a binary mixture at the extreme dilution of one component, for example, of type s , according to (3.3.17):

$$h_{as}(R) = c_{as}(R) + \frac{N_a}{V} \int h_{aa}(R') c_{as}(|\mathbf{R} - \mathbf{R}'|) d\mathbf{R}', \quad (5.2.48)$$

where $h_{aa}(R) = h_2(R)$ is the pair correlation function of the bulk phase, $\rho = N_a/V$ is its density, and $h_{as}(R)$ and $c_{as}(R)$ are the corresponding correlation functions for a particle of the system and the wall. In the limit where the radius of curvature of the surface tends to infinity, after transforming to a bipolar coordinate system, we have:

$$h_{as}(z) = c_{as}(z) + 2\pi\rho \int_0^\infty u du h_2(u) \int_{z-u}^{z+u} c_{as}(v) dv, \quad (5.2.49)$$

where z is the distance between the walls and the fixed particle.

In this case, the singlet function describing the density profile is $\rho_1(z) = \rho[1 + h_{as}(z)]$. Due to the special nature of the interaction potential of the particles with the wall, $u_1(z) = \begin{cases} 0, & z > 0, \\ \infty, & z < 0, \end{cases}$ a series of exact relations can be derived for the singlet function. First, since the density of molecules at the wall equals $\rho_1(z = 0+)$, we have [15]:

$$\rho_1(z = 0+) = \beta P, \quad (5.2.50)$$

where P is the pressure in the system.

The second relation is obtained from (5.2.43). Since $d/dz[e^{-\beta u_1(z)}] = \delta(z)$, we have [354]:

$$\left[\frac{\partial}{\partial z_1} \rho_1(z_1) \right]_{z_1=0+} = \rho_1^2(z_1 = 0+) \int d\mathbf{r} h_2(z_1 = z_2 = 0, r), \quad (5.2.51)$$

where $h_2(z_1, z_2, r)$ is the pair correlation function of the system, defined according to (5.1.17), and $\mathbf{r}$ is a two-dimensional vector in the surface plane.

To determine the pair distribution function $\rho_2(z_1 z_2 R_{12})$, it is necessary to start from the Ornstein—Zernike equation for the spatially inhomogeneous case. However, as a simple approximation, the superposition approximation can be used, assuming:

$$\rho_2(z_1 z_2 R_{12}) = \rho_1(z_1) \rho_1(z_2) [1 + h_2(R_{12})], \quad (5.2.52)$$

In [355, 356], a solution to equation (5.2.49) was found for a system of hard spheres with diameter σ in the Percus—Yevick approximation for the functions $c_{as}(z)$ and $h_2(R)$. Since in the Percus—Yevick approximation $c_{as}^{(PY)}(z) = 0$, $z > 0$, equation (5.2.49) can be rewritten as:

$$h_{as}^{(PY)}(z) = c_{as}^{(PY)}(z) + 12\eta \int_z^\infty u h_2^{(PY)}(u) du \int_{z-u}^0 c_{as}(v) dv, \quad (5.2.53)$$

where $\eta = \frac{1}{6}\pi \frac{N}{V} \sigma^3$ is the packing fraction.

According to (3.3.86), in the limit $d \frac{N_s}{V} \rightarrow 0$, $\sigma_{ss} \rightarrow \infty$, we have:

$$c_{as}^{(PY)}(z) = \begin{cases} -\lambda_2^2, & z < -1, \\ -\lambda_2^2 - 3c_1(z+1)^2 - 4c_2(z+1)^3, & -1 < z < 0, \\ 0, & z > 0, \end{cases} \quad (5.2.54)$$

where $\lambda_2 = \frac{1+2\eta}{(1-\eta)^2}$, $c_1 = -2\eta \frac{1+\frac{1}{2}\eta}{(1-\eta)^2} \lambda_2$, $c_2 = \frac{1}{2}\eta \lambda_2^2$.

For the pair distribution function of hard spheres $F_2^{(PY)}(R) = 1 + h_2^{(PY)}(R)$ in the Percus—Yevick approximation, we have an analytical expression (3.1.73). Substituting (5.2.54) into (5.2.53) for $z > 0$, we obtain:

$$\begin{aligned} h_{as}^{(PY)}(z) = & -12\eta \int_z^\infty u [\lambda_2^2(u-z) + c_1 + c_2] h_2^{(PY)}(u) du + \\ & + 12\eta \int_z^{z+1} u(z+1-u)^3 [c_1 + c_2(z+1-u)] h_2^{(PY)}(u) du. \end{aligned} \quad (5.2.55)$$

Using relations (3.1.38) and (3.2.18), this expression can be rewritten in a form more convenient for integration

$$\begin{aligned} \frac{1}{\rho} \rho_1^{(PY)}(z) = & \lambda_2 - \frac{3}{5} \eta \frac{10 - 2\eta + \eta^2}{1 + 2\eta} \lambda_2^2 z + \frac{1}{5} \eta (3c_1 + 2c_2) + \\ & + 12\eta \int_0^z u [\lambda_2^2(u-z) + c_1 + c_2] h_2^{(PY)}(u) du + \end{aligned}$$

$$+ 12\eta \int_z^{z+1} u(z+1-u)^3 [c_1 + c_2(z-1+u)] h_2^{(\text{PY})}(u) du. \quad (5.2.56)$$

The singlet function $\frac{1}{\rho} \rho_1^{(\text{PY})}(z)$, determined by this formula at density $\frac{N}{V} \sigma^3 = 0.8$, is shown in Fig. 25, taken from [355]. For the same density, the pair distribution function of the bulk phase $F_2^{(\text{PY})}(R) = 1 + h_2^{(\text{PY})}(R)$ is also presented. As seen, the singlet function differs from $F_2^{(\text{PY})}(R)$ only by having more pronounced oscillations. The density profile found agrees well with the results of computer simulations, except for the region of small distances and high densities [356]. In particular, for the contact value of the singlet function, from (5.2.56) we have:

$$\frac{1}{\rho} \rho_1^{(\text{PY})}(z = 0+) = \lambda_2 = \frac{1 + 2\eta}{(1 - \eta)^2}. \quad (5.2.57)$$

Meanwhile, using the Carnahan–Starling expression for the pressure of hard spheres (3.1.52), we find from (5.2.50):

$$\frac{1}{\rho} \rho_1^{(\text{CS})}(z = 0+) = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (5.2.58)$$

Thus, as the density increases, the Percus–Yevick approximation underestimates the value of $\frac{1}{\rho} \rho_1(z = 0+)$. Similarly, for the pair distribution function,

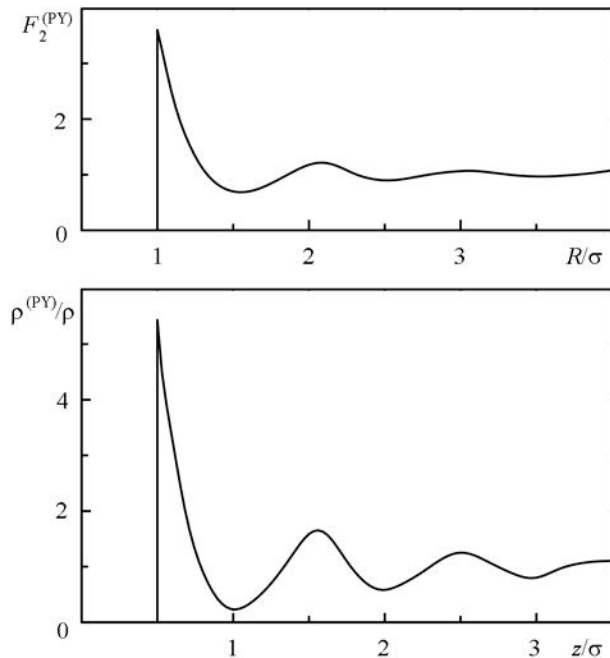


Fig. 25. The pair distribution function $F_2^{(\text{PY})}(R)$ (top panel) and the singlet density profile $\rho_1^{(\text{PY})}(z)/\rho$ (bottom panel) at the reduced density $N/V \sigma^3 = 0.8$. The functions are obtained within the Percus–Yevick (PY) approximation

increasing the density leads to a negative value of the first minimum of the function $\rho_1(z)$. However, due to more pronounced oscillations, this effect arises earlier, at densities $\frac{N}{V}\sigma^3 \gtrsim 0.85^2$.

To address this shortcoming, a variant of the generalized mean spherical approximation was developed in [357]. In particular, a solution to equation (5.2.49) was obtained under the assumption that for $z > 0$, $c_{as}(z) = Be^{-\alpha z}$. This solution can be expressed as:

$$c_{as}(z) = c_{as}^{(PY)}(z) + \Delta c_{as}(z), \quad (5.2.59)$$

$$\Delta c_{as}(z) = \begin{cases} 0, & z < -1, \\ 12\eta A \left\{ -\frac{(1+2\eta)(z-1)^2}{2\alpha} + \right. \\ \left. + \left[1 + 2\eta + \alpha \left(1 + \frac{1}{2}\eta \right) \right] \times \right. \\ \left. \times \left[z - 1 + \frac{1}{\alpha}(e^{-\alpha(z-1)} - 1) \right] \frac{1}{\alpha^2} \right\}, & -1 < z < 0, \\ Be^{-\alpha z}, & z > 0, \end{cases}$$

where $A = Be^\alpha f(\alpha, \eta)$, and $f(\alpha, \eta) = \alpha^3 [L(\alpha) + S(\alpha)e^\alpha]^{-1}$. The functions $L(\alpha)$ and $S(\alpha)$ are defined by expressions (3.1.70).

Hence, for the contact value of the singlet function, we have:

$$\frac{1}{\rho}\rho_1(z=0+) = \frac{1}{\rho}\rho_1^{(PY)}(z=0+) + A(1-\eta)^2, \quad (5.2.60)$$

Comparing this expression with (5.2.58), we obtain:

$$A = \eta^2 \frac{3-\eta}{(1-\eta)^2}. \quad (5.2.61)$$

The second equation:

$$\alpha^{-1} = \frac{(1+2\eta)(1-\eta)}{\eta^2(3-\eta)} \left[\frac{9\eta(1+2\eta) + \eta^2(4-\eta)(1-4\eta)}{6[(1+2\eta)^2 - \eta^3(4-\eta)]} - \frac{3\eta}{2(1+2\eta)} \right], \quad (5.2.62)$$

follows from the requirement of thermodynamic self-consistency of pressure, derived using the compressibility formula (3.3.10) and according to (5.2.50).

The considered model of hard spheres with a hard wall can serve as the reference system for describing systems with more realistic interactions.

²Recall that $F_2^{(PY)}(R)$ becomes negative at densities $\frac{N}{V}\sigma^3 \gtrsim 1.2$

5.2.3. Electric double layer

For many electrochemistry problems, it is essential to describing the behaviour of ions at the boundary with a solid surface, most often an electrode. The spatial redistribution of ions in the interfacial region leads to the formation of a specific transition region, known as the electric double layer, and the emergence of an electric potential difference between the phases. For simplicity, let us consider a planar interface separating a perfectly hard slab with dielectric permittivity ε_0 and an ionic solution in a structureless medium with dielectric permittivity ε . Let the ionic system occupy the upper half-space ($z \geq 0$). The electrostatic part of ionic interaction is described by the equations of electrostatics, which in this case lead to the well-known method of electrostatic images [358]. As a result, the potential of interaction of ions of type a with the surface can be expressed as the sum of three terms:

$$u_a(z) = \varphi_a(z) + \Phi_a(z) + \Psi_a(z), \quad (5.2.63)$$

where the first term describes the short-range interaction; the second term,

$$\Phi_a(z) = \frac{e^2 z_a^2}{2\varepsilon} \frac{\varepsilon - \varepsilon_0}{\varepsilon + \varepsilon_0} \frac{1}{2z}$$

is the interaction of the ion with its image, and the third term,

$$\Psi_a(z) = -\frac{1}{\varepsilon} e z_a E_0 z,$$

is the interaction of the ion with the surface charge, creating a uniform electric field with intensity E_0 .

Similarly, the potential of interionic interaction in the presence of a surface can be expressed as:

$$u_{ab}(R_{12}, z_1, z_2) = \Phi_{ab}(R_{12}, z_1 z_2) + \varphi_{ab}(R_{12}, z_1 z_2), \quad (5.2.64)$$

where $\varphi_{ab}(R_{12}, z_1 z_2)$ is the short-range part of the potential, and $\Phi_{ab}(R_{12}, z_1 z_2)$ is the electrostatic part. The latter includes the usual Coulomb interaction and the interaction of ions with their images

$$\Phi_{ab}(R_{12}, z_1 z_2) = \frac{e^2 z_a z_b}{\varepsilon R_{12}} + \frac{e^2 z_a z_b}{\varepsilon R_{12}^{(\text{im})}} \frac{\varepsilon - \varepsilon_0}{\varepsilon + \varepsilon_0}, \quad (5.2.65)$$

where $R_{12}^{(\text{im})} = \sqrt{R_{12}^2 + 4z_1 z_2}$ is the distance between one ion and the mirror image of the second ion.

A more consistent description of ionic interactions (or other particles) in the presence of a surface can be based on the osmotic formalism presented in Section 3.3 of Chapter 3 [142]. For simplicity, let us assume that the system consists of two subsystems: particles of type s , forming the surface and located in the lower half-space ($z \leq 0$), and particles of type a , occupying the space

above the surface ($z \geq 0$). The presence of the surface can be accounted for by introducing an external field [15]:

$$u_a(z) = \begin{cases} 0, & z \geq 0, \\ \infty, & z < 0, \end{cases} \quad u_s(z) = \begin{cases} \infty, & z > 0, \\ 0, & z \leq 0, \end{cases} \quad (5.2.66)$$

which prevents the particles of type s from locating in the upper half-space and particles of type a from locating in the lower half-space.

Averaging the Gibbs distribution function over the configuration space of particles of type s eliminates the surface from explicit consideration. However, according to (3.3.13), the potential energy of these particles is replaced by the free energy of their interaction in the presence of the surface. The latter decomposes into a set of terms (3.3.15), leading to cluster expansions (3.4.16), with the distinction that the correlation functions corresponding to ovals exhibit spatial inhomogeneity, and each field vertex corresponds to a factor $\int \rho_s(z) d\mathbf{R}$, where $\rho_s(z)$ is the singlet function for particles of type s . In this case, the singlet terms of the series (3.4.15) describe the interaction of particles with the surface, the pair terms describe interparticle interactions in the presence of the surface, and so on.

The difference between these potentials and conventional interactions is evident in the first diagram for $w(i)$. Assuming $\rho_s(z) = \begin{cases} 0, & z > 0, \\ \rho_s, & z < 0, \end{cases}$ and considering the van der Waals nature of the interaction, we obtain the asymptotic behaviour:

$$w(z) \sim -2\pi \int_z^\infty dz_1 \int_0^\infty \frac{r dr}{(r^2 + z_1^2)^3} = -\frac{\pi}{6} \frac{1}{z^3}.$$

In the case of ions, for the electrostatic part of the interaction, we naturally arrive at the results previously obtained using the method of electrostatic images [142]. For an ionic system, as in the spatially homogeneous case, the conditions of overall and local electroneutrality must be satisfied. To achieve this, as shown by Martynov [166], in expressions (3.4.1) and (3.4.12), the densities N_a/V should be replaced by the singlet distribution functions $\rho_a(R)$, and the electrode charge should be included in the overall electroneutrality condition (3.4.1).

The application of the method of collective variables to describe confined ionic systems is detailed in [358, 359]. Following these works, let us expand the electrostatic part of the potential energy in a Fourier series. The expansion is expressed separately in terms of planar momenta $\mathbf{q}$ and momenta p along the z -axis. Assuming the surface is uncharged, we have:

$$\begin{aligned} v(R) &= \sum_{a,b} \sum_{i < j} \Phi_{ab}(R_{ij}, z_i z_j) + \sum_{a,i} \Phi_a(z_i) = \\ &= \frac{1}{2\beta} \sum'_{p,q} \alpha(p, \mathbf{q}) [\hat{\rho}(p, \mathbf{q}) \hat{\rho}^*(p, \mathbf{q}) - 1] + v(p = q = 0), \end{aligned} \quad (5.2.67)$$

where

$$\begin{aligned}\hat{\rho}(p, \mathbf{q}) &= \sum_{a=1}^M \lambda_a \sum_{i=1}^{N_a} \sqrt{\frac{2}{\varepsilon + \varepsilon_0}} [\sqrt{\varepsilon} \cos(pz_j) + \sqrt{\varepsilon_0} \sin(pz_j)] e^{i\mathbf{q} \cdot \mathbf{r}_j} = \\ &= \sum_{a=1}^M \lambda_a \sum_{j=1}^{N_a} [v e^{ipz_j} + \mu e^{-ipz_j}] e^{i\mathbf{q} \cdot \mathbf{r}_j}, \quad (p, \mathbf{q}) \neq 0.\end{aligned}$$

Here: $v = \frac{\sqrt{2}}{2} \frac{\sqrt{\varepsilon} + \sqrt{\varepsilon_0}}{\sqrt{\varepsilon + \varepsilon_0}}$, $\mu = \frac{\sqrt{2}}{2} \frac{\sqrt{\varepsilon} - \sqrt{\varepsilon_0}}{\sqrt{\varepsilon + \varepsilon_0}}$, $\hat{\rho}^*(p, \mathbf{q}) = \hat{\rho}(-p, -\mathbf{q})$, $\lambda_a = e z_a \left[\sum_a N_a e^2 z_a^2 \right]^{-1/2}$ is the dimensionless charge of the ion, $\alpha(p, q) = \frac{\kappa^2}{p^2 + q^2}$, $\kappa^2 = 4\pi\beta \frac{1}{\varepsilon} \sum_a \frac{N_a}{V} e^2 z_a^2$ is the square of the quantity inversely proportional to the Debye length, $v(p = q = 0) = \frac{1}{2\beta} \sum_{a,b} N_a N_b \lambda_a \lambda_b \alpha(p = q = 0) = 0$ as a consequence of the overall electroneutrality condition of the system.

Using the transformation function $J(\rho, R) = \prod_{p, \mathbf{q}}' \delta(\rho(p, \mathbf{q}) - \hat{\rho}(p, \mathbf{q}))$, the electrostatic part of the configuration integral can be presented as an analytical functional:

$$Q^{(\ell)} = \frac{1}{(V/2)^N} \int_{(z \geq 0)} (d\mathbf{R}) \int (d\rho) e^{-\beta v(\rho)} J(\rho R) = \int (d\rho) e^{-\beta v(\rho)} J(\rho), \quad (5.2.68)$$

where $v(\rho) = \frac{1}{2\beta} \sum_{p, \mathbf{q}}' \alpha(p, q) (\rho(p, \mathbf{q}) \rho^*(p, \mathbf{q}) - 1)$ is the collective variable representation for the electrostatic part of the potential energy, and $J(\rho) = \left(\frac{V}{2}\right)^{-N} \times$

$\times \int_{(z \geq 0)} (d\mathbf{R}) J(\rho R)$ is the Jacobian of the transformation to collective variables.

Using the integral representation of the δ -functions and performing integration in Cartesian coordinate space, we obtain:

$$J(\rho) = \int (d\omega) \exp \left[i\pi \sum_{p, \mathbf{q}} \omega(p, \mathbf{q}) \rho(p, \mathbf{q}) + \sum_{n \geq 2} D_n(\omega) \right], \quad (5.2.69)$$

where

$$D_n(\omega) = \frac{(-i\pi)^n}{n!} \sum_a \lambda_a^n N_a \sum_{\substack{\{p_s, \mathbf{q}_s\} \\ (1 \leq s \leq n)}} \prod_{s=1}^n \omega(p_s, \mathbf{q}_s) [v \delta_-(p_s) + \mu \delta_+(p_s)] \delta_{\mathbf{q}_1 + \dots + \mathbf{q}_n, 0}.$$

The functions

$$\delta_+(p) = \frac{1}{2\pi} \int_0^\infty e^{ipz} dz, \quad \delta_-(p) = \frac{1}{2\pi} \int_{-\infty}^0 e^{ipz} dz = \frac{1}{2\pi} \int_0^\infty e^{-ipz} dz$$

arise from the condition $z \geq 0$ during integration over $(d\mathbf{R})$.

Far from the critical point, the Jacobian of the transformation can be expressed in the standard Gaussian form:

$$J(\rho) = \exp \left\{ \sum_{n \geq 3} \hat{D}_n(\partial/\partial\rho) \right\} J_G(\rho), \quad (5.2.70)$$

where

$$\begin{aligned} \hat{D}_n(\partial/\partial\rho) &= \frac{(-1)^n}{n!} \sum_a N_a \lambda_a^n \sum_{\substack{\{p_s, q_s\} \\ (1 \leq s \leq n)}} \prod_{s=1}^n [v\delta_-(p_s) + \mu\delta_+(p_s)] \times \\ &\quad \times \frac{\partial^n}{\partial \rho(p_s q_s)} \delta_{\mathbf{q}_1 + \dots + \mathbf{q}_n, 0}, \\ J_G(\rho) &= \exp \left\{ -\frac{1}{2} \sum'_{p, q} [\rho(p, q) \rho^*(p, q) + \ln \pi] \right\}. \end{aligned}$$

Further integration over the collective variables and accounting for short-range interactions are performed using the standard methodology outlined in this book, leading to cluster expansions (4.1.50). In this case, the screened potential of interparticle interaction consists of two terms:

$$g_{ab}(\mathbf{R}_1, \mathbf{R}_2) = g_{ab}(R_{12}) + g_{ab}^{(\text{im})}(R_{12}, z_1 z_2), \quad (5.2.71)$$

where

$$\begin{aligned} g_{ab}(R_{12}) &= - (v^2 + \mu^2) \sum_{p, q} \lambda_a \lambda_b \frac{\alpha(p, q)}{1 + \alpha(p, q)} e^{i\mathbf{q} \cdot \mathbf{r}_{12}} e^{ip(z_1 - z_2)} = \\ &= -\beta \frac{e^2 z_a z_b}{\varepsilon R_{12}} e^{-\kappa R_{12}}. \end{aligned}$$

is the screened Coulomb potential of ions. The screened potential of ion interaction with its image is:

$$\begin{aligned} g_{ab}^{(\text{im})}(R_{12}, z_1 z_2) &= -2\nu\mu \sum_{p, q} \lambda_a \lambda_b \frac{\alpha(p, q)}{1 + \alpha(p, q)} e^{i\mathbf{q} \cdot \mathbf{r}_{12}} e^{ip(z_1 + z_2)} = \\ &= -\beta \frac{\varepsilon - \varepsilon_0}{\varepsilon - \varepsilon_0} \frac{e^2 z_a z_b}{\varepsilon R_{12}^{(\text{im})}} e^{-\kappa R_{12}^{(\text{im})}}. \end{aligned}$$

The screened potential of interaction between an ion and an external field equals the screened potential of interaction between the ion and its image.

$$g_a(z) = -\frac{e^2 z_a z_b}{2\varepsilon} \beta \frac{\varepsilon - \varepsilon_0}{\varepsilon + \varepsilon_0} \frac{1}{2z} e^{-2\kappa z}. \quad (5.2.72)$$

According to (5.1.51), for the singlet function we obtain:

$$\rho_a(z) = \rho_a \exp \{ -\beta \varphi_a(z) + g_a(z) \} [1 + \dots]. \quad (5.2.73)$$

As we can see, depending on the dielectric properties of the contacting media, the screened potential (5.2.72) can lead to ion repulsion from the surface (for $\varepsilon > \varepsilon_0$) or ion attraction (for $\varepsilon < \varepsilon_0$).

In [360], the results obtained were generalized to describe electrolyte films confined by heterogeneous media with dielectric permittivities ε_1 and ε_2 . The solution to the electrostatic problem leads to the following expression for the potential energy of the system:

$$v(R) = \frac{1}{2\beta} \sum'_{p,q} \alpha(p, q) \left\{ \gamma_1(q) \hat{\rho}_c(p, \mathbf{q}) \hat{\rho}_c^*(p, \mathbf{q}) + \gamma_2(p, q) \hat{\rho}_s(p, \mathbf{q}) \times \right. \\ \left. \times \hat{\rho}_s^*(p, \mathbf{q}) + 2\gamma_3(q) \hat{\rho}_c(p, \mathbf{q}) \hat{\rho}_s^*(p, \mathbf{q}) - \frac{1}{2} [\gamma_1(q) + \gamma_3(q)] \right\}. \quad (5.2.74)$$

where

$$\hat{\rho}_c(p, \mathbf{q}) = \sum_{a=1}^M \lambda_a \sum_{j=1}^{N_a} \cos(pz_j) e^{-i\mathbf{q}\mathbf{r}_j}, \\ \hat{\rho}_s(p, \mathbf{q}) = \sum_{a=1}^M \lambda_a \sum_{j=1}^{N_a} \sin(pz_j) e^{-i\mathbf{q}\mathbf{r}_j}, \quad (p, \mathbf{q}) \neq 0, \\ \alpha(p, q) = \left[1 - e^{-2qh} \right] \left[1 - \frac{\varepsilon - \varepsilon_1}{\varepsilon + \varepsilon_1} \frac{\varepsilon - \varepsilon_2}{\varepsilon + \varepsilon_2} e^{-2qh} \frac{\varkappa^2}{p^2 + q^2} \right]^{-1}, \quad (5.2.75) \\ \gamma_1(q) = 2 \left[1 + \frac{\varepsilon - \varepsilon_1}{\varepsilon + \varepsilon_1} \frac{\varepsilon - \varepsilon_2}{\varepsilon + \varepsilon_2} e^{-qh} \right] \left[1 + e^{-qh} \right]^{-1} + \frac{\varepsilon - \varepsilon_1}{\varepsilon + \varepsilon_1} + \frac{\varepsilon - \varepsilon_2}{\varepsilon + \varepsilon_2}, \\ \gamma_3(q) = 2 \left[1 + \frac{\varepsilon - \varepsilon_1}{\varepsilon + \varepsilon_1} \frac{\varepsilon - \varepsilon_2}{\varepsilon + \varepsilon_2} e^{-qh} \right] \left[1 + e^{-qh} \right]^{-1} - \frac{\varepsilon - \varepsilon_1}{\varepsilon + \varepsilon_1} - \frac{\varepsilon - \varepsilon_2}{\varepsilon + \varepsilon_2}, \\ \gamma_2(q, p) = \frac{p}{q} \left[\frac{\varepsilon - \varepsilon_1}{\varepsilon + \varepsilon_1} - \frac{\varepsilon - \varepsilon_2}{\varepsilon + \varepsilon_2} \right],$$

h is the thickness of the film.

Repeating the derivations performed earlier, we again arrive at the cluster expansions (5.1.50). However, the screened potentials now have a more complex form. In particular, the screened potential for the interaction of an ion with its image for sufficiently thick films ($\varkappa h \gg 1$) is given by:

$$g_a(z) = -\frac{e^2 z_a^2}{\varepsilon h} \beta \int_0^\infty q^* dq^* L(q^*) \times \\ \times \left\{ \frac{\text{ch} \left[\sqrt{q^{*2} + \gamma_1(q^*)} \varkappa^2 h^2 \left(1 - \frac{2z}{h} \right) \right]}{\sqrt{q^{*2} + \gamma_1(q^*)} \varkappa^2 h^2 \text{sh} \sqrt{q^{*2} + \gamma_1(q^*)} \varkappa^2 h^2} + \frac{2}{\gamma_1(q^*) - \gamma_3(q^*)} \right\} \times$$

$$\begin{aligned}
& \times \left[\frac{\text{sh} \left[\sqrt{q^{*2} + \gamma_1 (q^*) \kappa^2 h^2} \left(1 - \frac{2z}{h} \right) \right]}{\sqrt{q^{*2} + \gamma_1 (q^*) \kappa^2 h^2} \text{sh} \sqrt{q^{*2} + \gamma_1 (q^*) \kappa^2 h^2}} - \right. \\
& - \frac{\text{sh} \left[\sqrt{q^{*2} + \gamma_3 (q^*) \kappa^2 h^2} \left(1 - 2\frac{z}{h} \right) \right]}{\sqrt{q^{*2} + \gamma_3 (q^*) \kappa^2 h^2} \text{sh} \sqrt{q^{*2} + \gamma_3 (q^*) \kappa^2 h^2}} \left. \right] - \\
& - \frac{\text{ch} \left[\sqrt{q^{*2} + \gamma_3 (q^*) \kappa^2 h^2} \left(1 - 2\frac{z}{h} \right) \right]}{\sqrt{q^{*2} + \gamma_3 (q^*) \kappa^2 h^2} \text{sh} \sqrt{q^{*2} + \gamma_3 (q^*) \kappa^2 h^2}} \left. \right\}, \quad (5.2.76)
\end{aligned}$$

where

$$L(q^*) = \left(1 - e^{-2q^*} \right) \left(1 - \frac{\varepsilon - \varepsilon_1}{\varepsilon + \varepsilon_1} \frac{\varepsilon - \varepsilon_2}{\varepsilon + \varepsilon_2} e^{-2q^*} \right)^{-1}, \quad q^* = qh.$$

Even more complex forms are observed for the screened potentials of interparticle interactions.

In Fig. 26, taken from [360], the profiles are presented of the singlet function obtained in the exponential approximation (5.2.73) without accounting for short-range forces. The case shown in Fig. 26, *a* corresponds to a film bounded

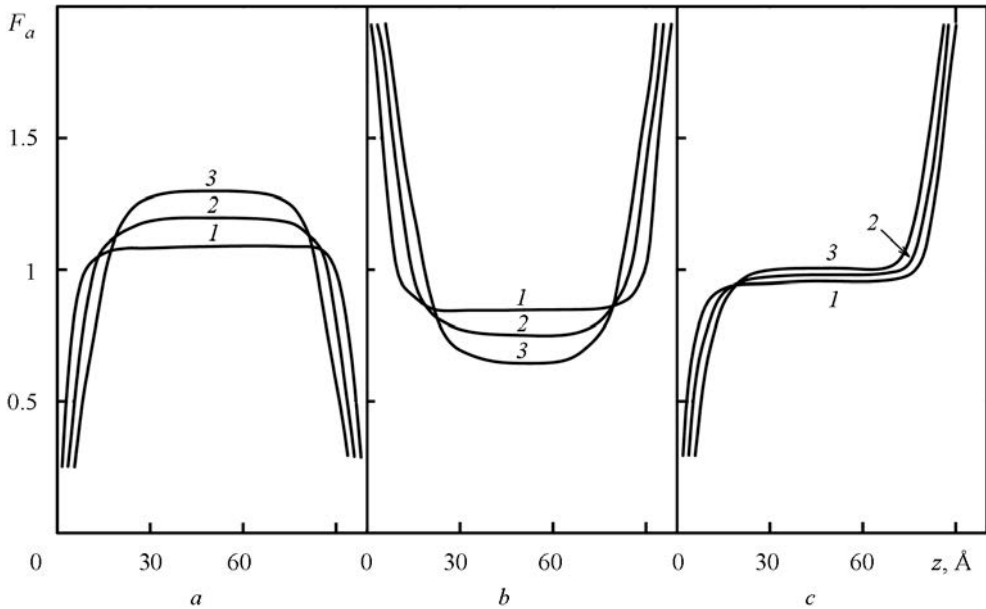


Fig. 26. Profiles of the singlet function obtained in the exponential approximation (5.2.73) without considering short-range interaction. Panel (*a*) corresponds to a film bounded by air on both sides ($\varepsilon_1 = \varepsilon_2 = 1$); panel (*b*) to a film bounded by metallic media ($\varepsilon_1 = \varepsilon_2 = \infty$); panel (*c*) to a film bounded by a metallic surface on one side ($\varepsilon_1 = \infty$) and air on the other ($\varepsilon_2 = 1$). Curves are shown for different ion concentrations: 0.1 mol/L (1), 0.01 mol/L (2), 0.001 mol/L (3)

on both sides by air ($\varepsilon_1 = \varepsilon_2 = 1$); Fig. 26, b corresponds to a film bounded by metallic media ($\varepsilon_1 = \varepsilon_2 = \infty$); Fig. 26, c corresponds to a film bounded on one side by a metallic surface and on the other by air ($\varepsilon_1 = \infty, \varepsilon_2 = 1$). The curves are presented for an aqueous solution with different ion concentrations: 0.1 (1), 0.01 (2), and 0.001 mol/L (3). As expected, near the metallic surface, there is a positive adsorption, while at the boundary with air, there is negative adsorption. The former corresponds to an excess of ions at the surface, and the latter to their deficit. As the ion concentration increases, the role of electrostatic forces diminishes considerably.

In regions of high concentrations, there arises a need to fundamentally account for short-range interactions. For the screened potentials of ion-surface interactions, we arrive at a set of equations analogous to (5.2.49):

$$h_{as}(z) = c_{as}(z) + 2\pi \sum_b \frac{N_b}{V} \int_0^\infty u du c_{ab}(u) \int_{z-u}^{z+} h_{bs}(v) dv, \quad (5.2.77)$$

where

$$h_{as}(z) = h_{as}^0(z) + g_a(z), \quad c_{as}(z) = c_{as}^0(z) - \beta [\Phi_a(z) + \Psi_a(z)],$$

$h_{as}^0(z)$ and $c_{as}^0(z)$ are the corresponding correlation functions of the reference system; $\Phi_a(z) + \Psi_a(z)$ is the long-range part of the ion-wall interaction defined according to (5.2.63); $g_a(z)$ are the screened potentials; and $c_{ab}(R)$ are the direct correlation functions of the bulk phase.

As the reference system, it is appropriate to use the hard-sphere model with a hard wall considered earlier. In the Percus—Yevick approximation for the reference system and optimal separation of interactions, we arrive at the mean spherical approximation:

$$c_{as}(z) = \begin{cases} c_{as}^0(z), & z < \frac{1}{2}\sigma_{aa}, \\ -\beta [\Phi_a(z) + \Psi_a(z)], & z > \frac{1}{2}\sigma_{aa}, \end{cases} \quad (5.2.78)$$

$$h_{as}(z) = h_{as}^0(z) = -1, \quad z < \frac{1}{2}\sigma_{aa},$$

where σ_{aa} is the diameter of an ion of type a .

Using Fourier transform, the system in (5.2.77) can be presented as:

$$\mathbf{h}_s(k)[1 - \rho \mathbf{c}(k)] = \mathbf{c}_s(k). \quad (5.2.79)$$

where the vectors $\mathbf{h}_s(k)$, $\mathbf{c}_s(k)$, ρ consist of the elements:

$$h_{as}(k) = \int_{-\infty}^{\infty} h_{as}(z) e^{ikz} dz, \quad c_{as}(k) = \int_{-\infty}^{\infty} c_{as}(z) e^{ikz} dz, \quad \rho_a = \frac{N_a}{V}.$$

The matrix $\mathbf{c}(k)$ consists of elements

$$c_{ab}(k) = \frac{4\pi}{k} \int_0^{\infty} R \sin(kR) c_{ab}(R) dR.$$

According to (5.2.78),

$$\begin{aligned} c_{as}(k) &= \int_{-\infty}^{\frac{1}{2}\sigma_{aa}} c_{as}^0(z) e^{ikz} dz - \beta \int_{\frac{1}{2}\sigma_{aa}}^{\infty} [\Psi_a(z) + \Phi_a(z)] e^{ikz} dz = \\ &= c_{as}^0(k) - \beta [\Psi_a(k) + \Phi_a(k)]. \end{aligned} \quad (5.2.80)$$

As in solving the Ornstein–Zernike equation for the bulk phase, following [361], we use the Wiener–Hopf method, according to which we assume:

$$1 - \rho \mathbf{c}(k) = \mathbf{Q}(k) \mathbf{Q}^T(-k), \quad (5.2.81)$$

where $\mathbf{Q}(k)$ is an analytical matrix in the upper half-plane, and $\mathbf{Q}^T(-k)$ in the lower half-plane. Each element $\mathbf{Q}_{ab}(k)$ corresponds to a function $q_{ab}(R)$ such that:

$$\mathbf{Q}_{ab}(k) = \delta_{ab} - \rho_b \int_{\lambda_{ba}}^{\infty} e^{ikR} q_{ab}(R) dR, \quad (5.2.82)$$

where

$$\lambda_{ab} = \frac{1}{2} |\sigma_{aa} - \sigma_{bb}|.$$

Substituting (5.2.81) into (5.2.79), we obtain:

$$\mathbf{h}_s(k) \mathbf{Q}(k) = [\mathbf{c}_s^0(k) - \beta \Phi(k) - \beta \Psi(k)] [\mathbf{Q}^T(-k)]^{-1}. \quad (5.2.83)$$

Multiplying both sides of (5.2.83) by e^{-ikz} and performing the inverse Fourier transform on $z > \frac{1}{2}\sigma_{aa}$, we note that the functions $\mathbf{c}_s^0(k)$ and $\mathbf{Q}^T(-k)$ are analytic and have no singularities in the lower half-plane. By closing the contour of integration in this region, we arrive at the result obtained by Blum and Stell [362]

$$\begin{aligned} h_{as}(z) - \sum_b \frac{N_b}{V} \int_{\lambda_{ab}}^{\infty} h_{bs}(z - R) q_{ba}(R) dR &= L_a(z) \\ &= -\beta \sum_b \int_{\frac{1}{2}\sigma_{bb}}^{\infty} [\Phi_b(y) + \Psi_b(y)] P_{ba}(y - z) dy, \end{aligned} \quad (5.2.84)$$

where

$$P_{ab}(R) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikR} \left[\mathbf{Q}^{\top}(-k) \right]_{ab}^{-1} dk. \quad (5.2.85)$$

Hence, for the Laplace transforms of the singlet functions of the reference system, according to (3.3.84), we have:

$$\begin{aligned} \mathcal{T}_{as}^0(s) &= \int_{\frac{1}{2}\sigma_{aa}}^{\infty} F_{as}(z) e^{-sz} dz = \\ &= \sum_b \frac{e^{-\frac{1}{2}s\sigma_{bb}}}{s(1-\eta)^2} \left[1 - \eta + \frac{1}{4}\rho s_m \sigma_{bb} \right] [\mathbf{Q}(\text{is})]_{ba}^{-1}, \end{aligned} \quad (5.2.86)$$

which is a generalization of (5.2.55) to the multicomponent case. In particular, for $z = \frac{1}{2}\sigma_{aa}$, from (5.2.84), we obtain:

$$F_{as}^0\left(z = \frac{1}{2}\sigma_{aa} +\right) = \frac{1}{1-\eta} + \frac{1}{4}\rho s_m \sigma_{aa} (1-\eta)^{-2}. \quad (5.2.87)$$

For the screened potentials from (5.2.84), we have:

$$\begin{aligned} g_a(z) &= -\beta \sum_{b,c} \int_{\frac{1}{2}\sigma_{aa}}^z dy \int_{\lambda_{bc}}^{\infty} [\Phi_c(y+R) + \Psi_c(y+R)] P_{cb}(R) P_{ba}^{\top}(z-y) dR, \\ \mathcal{L}_a(s) &= \int_{\frac{1}{2}\sigma_{aa}}^{\infty} e^{-sz} g_a(z) dz = \sum_b \mathcal{L}_b(s) [\mathbf{Q}(\text{is})]_{ab}^{-1}, \\ \mathcal{L}_a(s) &= \int_{\frac{1}{2}\sigma_{aa}}^{\infty} L_a(z) e^{-sz} dz. \end{aligned} \quad (5.2.88)$$

At the boundary:

$$g_a\left(z = \frac{1}{2}\sigma_{aa}^+\right) = -L_a\left(\frac{1}{2}\sigma_{aa}\right). \quad (5.2.89)$$

According to (5.2.84), $L_a(z)$ can be decomposed into two terms:

$$\begin{aligned} L_a(z) &= L_a^{\psi}(z) + L_a^{\Phi}(z) = \beta \frac{1}{\varepsilon} e E_0 \sum_b z_b \int_{\lambda_{ab}}^{\infty} (z+y) P_{ba}(y) dy + \\ &+ \beta \frac{e^2}{2\varepsilon} \frac{\varepsilon - \varepsilon_0}{\varepsilon + \varepsilon_0} \sum_b z_b^2 \int_{\lambda_{ab}}^{\infty} P_{ba}(y) [z+y]^{-1} dy. \end{aligned} \quad (5.2.90)$$

Blum [361] showed that for a system of ions with equal sizes:

$$L_a^\psi(z) = \lim_{s \rightarrow 0} \frac{\beta e E_0}{\varepsilon} \sum_b z_b \left(z - \frac{\partial}{\partial s} \right) \mathcal{P}_{ba}(s) = \beta \frac{e z_a E_0}{\varepsilon \kappa}, \quad (5.2.91)$$

where

$$\mathcal{P}_{ba}(s) = \int_{\lambda_{ab}}^{\infty} e^{-sz} P_{ba}(z) dz; \quad \kappa = \left[4\pi\beta \frac{1}{\varepsilon} \sum_a \frac{N_a}{V} e^2 z_a^2 \right]^{1/2}.$$

Substituting (5.2.90) into (5.2.88), we get:

$$g_a(z) = g_a^\psi(z) + g_a^\Phi(z), \quad (5.2.92)$$

where

$$\begin{aligned} g_a^\psi(z) &= -\beta \frac{e E_0}{\varepsilon \kappa} \sum_b z_b \int_{\frac{1}{2}\sigma_{bb}}^z P_{ba}^\mathrm{T}(z-y) dy, \\ g_a^\Phi(z) &= -\sum_b \int_{\frac{1}{2}\sigma_{bb}}^z P_{ba}^\mathrm{T}(z-y) L_b^\Phi(y) dy. \end{aligned} \quad (5.2.93)$$

If the ions have the same size, then according to the results of Chapter 3:

$$\mathcal{P}_{ab}(s) = \delta_{ab} + \frac{1}{\rho} \rho_b \mathcal{P}^0(s) + \frac{z_a z_b}{\sum_c \rho_c z_c^2} \rho_b \mathcal{P}^\pm(s), \quad (5.2.94)$$

where $\rho = \sum_a \rho_a$, and

$$1 + \mathcal{P}^0(s) = [1 - \rho Q_0(s)]^{-1} = \frac{s^3(1-\eta)^2}{S(s) + L(s)e^{-s\sigma}},$$

which represents the short-range interaction part. The functions $L(s)$ and $S(s)$ are defined according to (3.1.70). For the electrostatic part, in accordance with (3.4.49):

$$1 + \mathcal{P}^\pm(s) = \frac{s^2}{s^2 + 2\Gamma s + 2\Gamma^2(1 - e^{-s\sigma})}.$$

Using the inverse Laplace transform, the functions $P_{ab}(z)$ are determined, and then, according to (5.2.90) and (5.2.93), the screened potentials are calculated, which define the singlet functions:

$$\rho_a(z) = \rho_a F_{as}^0(z) \exp \{ g_a^\Psi(z) + g_a^\Phi(z) \} [1 + \dots]. \quad (5.2.95)$$

To describe thermodynamic properties of the double layer, the surface tension γ must be found. The derivative of the surface tension coefficient with respect to the electrostatic potential determines the surface charge density

q_s , and the second derivative with respect to the potential determines the differential capacitance of the double layer c_D :

$$\frac{\partial \gamma}{\partial \Psi} = -q_s, \quad \frac{\partial q_s}{\partial \Psi} = c_D. \quad (5.2.96)$$

These relationships are known in electrochemistry [363] as the first and second Lippmann equations. To determine the surface tension, according to (5.2.5) or (5.2.41), in addition to the singlet function, it is also necessary to know the pair correlation functions. However, as shown by Blum [361], for electric capacitance it is sufficient to know only the singlet function. Since the electric charge density at a distance z from the surface is given by

$$q(z) = \sum_a \rho_a(z) e z_a, \quad (5.2.97)$$

then, according to the condition of overall electroneutrality, the total charge per unit area of the electrode, in absolute magnitude, equals the surface charge density:

$$q_s = - \int_0^\infty q(z) dz. \quad (5.2.98)$$

The distribution $q(z)$ corresponds to the electrostatic potential:

$$\Psi(z) = \int d\mathbf{R}_1 \frac{q(z_1)}{\varepsilon |\mathbf{R} - \mathbf{R}_1|} = \frac{4\pi}{\varepsilon} \int_z^\infty q(z_1)(z - z_1) dz_1,$$

so that the electrode potential is:

$$\Psi = - \frac{4\pi}{\varepsilon} \int_0^\infty z q(z) dz. \quad (5.2.99)$$

Now, in accordance with (5.2.96)–(5.2.99):

$$C_D = \frac{(\partial q_s / \partial E_0)}{(\partial \Psi / \partial E_0)} = \frac{\varepsilon \int_0^\infty dz (\partial q(z) / \partial E_0)}{4\pi \int_0^\infty dz z (\partial q(z) / \partial E_0)} = - \frac{\varepsilon}{4\pi} \frac{\partial \tilde{q}(s=0)}{\partial \tilde{q}'(s=0)}, \quad (5.2.100)$$

where $\tilde{q}(s) = \int_0^\infty e^{-sz} q(z) dz$; $-\tilde{q}'(s) = \int_0^\infty e^{-sz} q(z) z dz$.

Similarly, the electrostatic part of the surface energy is given by

$$\Delta E = \int_0^\infty dz q(z) \Psi(z) = \frac{2\pi}{\varepsilon} \int_0^\infty \int_0^\infty dz_1 dz_2 q(z_1) q(z_2) |z_1 - z_2|, \quad (5.2.101)$$

from which the free energy and other thermodynamic characteristics can be determined.

In the presented framework, as described in Blum's work [361], an attempt was made to account for pairwise electrostatic interactions. This effectively introduces a new long-range term, which, however, involves the pair distribution function of the system. Consequently, its consideration poses significant challenges.

So far, we have assumed that the interaction of ions in the presence of a surface, apart from repulsion at short distances, is primarily electrostatic. In reality, it has a more complex nature and, as in the bulk case, depends considerably on the structure of the solvent and the surface. This necessitates the explicit consideration of solvent molecules and surface particles. An attempt to solve such a problem was made in [364]. In this study, the system was considered where the lower part contains molecules of type s possessing a dipole moment p_s . They form a surface for a mixed system of ions of types $a, b, c, \dots$ and dipoles of type t located in the upper part of the space. It is assumed that the interactions between particles are similar to those in the bulk case (see Section 4.4 of Chapter 4. The surface is accounted for by imposing an external field of the type given in (5.2.66). Next, we consider a more general case where ions are also present in the upper part of the space, but with a concentration different from that in the lower part [365].

The application of the collective variable method leads to cluster expansions based on screened potentials. These potentials are determined by integral equations of the type:

$$g_{x_1 x_2}(R_1, R_2) = -\beta \Phi_{x_1 x_2}(R_{12}) - \beta \sum_{x_3} \int dR_3 d\Omega_3 \Phi_{x_1 x_3}(R_{13}, \Omega_3) \rho_{x_3}(R_3) g_{x_3 x_2}(R_3, R_2, \Omega_3), \quad (5.2.102)$$

where $x = \{a, s, t\}$.

The solution to equation (5.2.102), under the assumption:

$$\rho_s(z) = \begin{cases} 0, & z > 0, \\ \rho_s, & z \leq 0, \end{cases} \quad \rho_x(z) = \begin{cases} 0, & z < 0, \\ \rho_x, & z \geq 0, \end{cases} \quad \text{for } x = (a, t),$$

leads to the following screened potentials [365–367]:

$$g_{xy}(R_{12}, z_1, z_2) = -\beta Q_x(\nabla_1) Q_y(\nabla_2) \left\{ \frac{\exp(-\kappa_+ R_{12}/\sqrt{\varepsilon_+})}{\varepsilon_+ R_{12}} + \int_0^\infty p dp J_0(p s_{12}) \times \right. \\ \left. \times \frac{1}{\varepsilon_+ \alpha_+(p)} \left(\frac{\varepsilon_+ \alpha_+(p) - \varepsilon_- \alpha_-(p)}{\varepsilon_+ \alpha_+(p) + \varepsilon_- \alpha_-(p)} \right) \exp(-\alpha_+(p)(z_1 + z_2)) \right\} \quad (5.2.103)$$

for $z_1 > 0, z_2 > 0$,

$$g_{xy}(R_{12}, z_1, z_2) = -\beta Q_x(\nabla_1) Q_y(\nabla_2) \int_0^\infty p dp J_0(ps_{12}) \times \\ \times \frac{2}{[\varepsilon_+ \alpha_+(p) + \varepsilon_- \alpha_-(p)]} \exp(-\alpha_+(p)z_1 + \alpha_-(p)z_2) \quad (5.2.104)$$

for $z_1 > 0, z_2 < 0$, where

$$s_{12} = [R_{12}^2 - (z_1 - z_2)^2]^{1/2}, \quad \alpha_\pm(p) = \left[\frac{\varkappa_\pm^2}{\varepsilon_\pm} + p^2 \right]^{1/2},$$

$\varkappa_\pm$ are the inverse Debye lengths corresponding to the upper ($\varkappa_+$) and lower ($\varkappa_-$) half-spaces, respectively; $\varepsilon_\pm$ similarly denote the dielectric susceptibilities of the upper and lower half-spaces; p is the planar wave vector; $J_0(ps_{12})$ is the Bessel function; and $Q_x(\nabla)$ are generalized multipole charges: for ions, these coincide with the ordinary ionic charges eZ_a , while for molecules they are operator-valued. In particular, for dipolar molecules, $Q_s(\nabla) = (p_s \nabla)$, where p_s is the dipole moment of the molecule.

The expression for the singlet screened potentials has the form

$$g_x(z) = -\frac{1}{2} \beta Q_x^2(\nabla) \int_0^\infty \frac{p dp}{\varepsilon_+ \alpha_+(p)} \left(\frac{\varepsilon_+ \alpha_+(p) - \varepsilon_- \alpha_-(p)}{\varepsilon_+ \alpha_+(p) + \varepsilon_- \alpha_-(p)} \right) \exp(-2\alpha_+(p)z), \quad z > 0. \quad (5.2.105)$$

As expected, these formulas for the ionic screened potentials coincide with the corresponding expressions obtained by various authors [368, 369] for a system of point ions near the interface between two dielectric media. A significant feature of expressions (5.2.103) and (5.2.104), when $\varkappa_- = 0$, is the presence of long-range asymptotics in the plane parallel to the interface.

However, the obtained screened potentials do not include contributions from the short-range interactions since we neglected them in the calculation of the Jacobian. Therefore, at present, one of the pressing problems in the theory of spatially inhomogeneous ion-molecular systems is the inclusion of short-range interactions in the reference system simultaneously with the reference system treatment of external fields that induce spatial inhomogeneity.

In this final chapter, we present a brief overview of new methods for constructing cluster expansions and integral equations for the free energy and pair distribution functions of classical equilibrium systems of interacting particles, developed since the first edition of this book. These methods, as those in the previous chapters, are based on the idea of splitting the interaction potential into short- and long-range components and employing different techniques to describe their respective contributions. The starting point is the set of relations obtained from the classification and summation of Mayer cluster expansions for the pair distribution function, as outlined in Section 1.3.

Both approaches to accounting for short-range interactions are considered: one that leads to a generalization of Mayer cluster expansions for systems with both long-range and short-range interactions, and another employing a reference treatment of short-range interactions. The corresponding results were obtained in works [365, 370–372] and are presented in the first section of this chapter. Complete agreement is demonstrated between these results and those derived earlier in the book using the method of collective variables.

The subsequent section examines the so-called multi-density formalism [372–375], in the framework of which the original interaction potentials are separated into three parts. In addition to setting apart short-range and long-range interactions, strongly attractive interactions, responsible for the formation of various types of clusters, are also treated separately. The description in this case is based on a combination of standard Mayer expansions in density (for short- and long-range interactions) with an expansion in the powers of activity to describe strongly attractive interactions at intermediate distances.

6.1. Cluster expansions for systems with short- and long-range interactions

Similar as in Chapter 2, the intermolecular pair potential in classical many-particle systems may be described as a sum of two parts

$$u(12) = \varphi(12) + \Phi(12), \quad (6.1.1)$$

where $\varphi(12)$ is the short-range part and $\Phi(12)$ is the long-range part of the interaction. The argument (12) indicates that both contributions can also contain anisotropic parts, e.g. depend on the mutual orientation of both molecules.

Short-range interactions have a strongly repulsive character, and a fast decay over a few interparticle diameters. They describe the mutual nonpenetrability of classical particles, the result of which leads to a decrease of the free volume available to the system. The long-range interactions are primarily electrostatic, i.e. Coulombic in the case of ions, dipolar for polar molecules, and of van der Waals type for nonpolar molecules. They change more slowly in comparison with the short-range interactions, therefore they are able to act between a greater number of particles. This leads to collective effects such as screening or renormalisation of the interactions for greater separations. Both types of interaction have different effects on the properties of the system. Therefore, they demand different approaches in approximate treatments.

In this book this idea was realized in the framework of collective variable approach in which the description of the system is given in an extended phase space, consisting of the individual coordinates of the particles and of waves of oscillation of number density of particles, so-called collective variables. The individual variables are used to describe the short-range interactions, while the collective variables are applied to the long-range parts. In this case, one first calculates the free energy of the subsystem with long-range forces. The transformation to collective coordinates is realized by a transition Jacobian, represented by an infinite operator series that acts on the separated Gaussian part of Jacobian. The separate calculation of the Gaussian part assures the screening, and consideration of the operator part leads to cluster expansions based on screened potentials. For calculation of the short-range contribution the free energy of the system is represented by a functional series of Mayer functions of the short-range interactions. The coefficients of this series are the distribution functions of the subsystem with only long-range forces, producing a functional which is the free energy of this subsystem.

Another approach to different descriptions of the contributions of the short- and long-range parts of the interactions has also been developed. It is based on the separation of the contributions from short-range interactions which usually contribute in an important way to the structural properties of dense systems. The cluster expansions, derived in this way, describe only long-range contributions, whereas earlier, cluster expansions were based on renor-

malised potentials derived from screening long-range potentials. In contrast to the earlier cases, screening is now accomplished not by point particles, but by consideration of short-range interactions. The choice in the separation of short- and long-range interactions, as noted by Andersen and Chandler [26], and the method of optimal separation proposed by them, leads to the problem of finding the screened potentials in the mean spherical approximation (MSA), in which analytical expressions are derived for simple ionic [149, 193], dipolar [233], ion-dipolar [312, 313, 376–378], and other models. In this way, the MSA assures the correct consideration of the influence of the diameter of the particles on the screening. The procedure of optimal separation of the interaction itself, while not assuring absolute convergence of the cluster expansions, leads to improved convergence. Therefore the approach, based on the use of cluster expansions with optimized separation of the interactions, was given the name optimized cluster theory (OCT).

Based on the well-know results of the diagrammatic analysis of the Mayer cluster expansions presented in Section 1.3, we propose here a very simple alternative way of constructing cluster expansions. This approach contains screened potentials for the pair distribution functions instead of long-range potentials for both types of description of the short-range interactions.

6.1.1. Extension of Mayer cluster expansions to systems with short- and long-range interactions

We start from the well-known expressions discussed in Section 1.3. The pair distribution function of the system with pair particle interactions $u(12)$ can be represented as

$$F_2(12) = \exp [-\beta u(12) + h(12) - c(12) + E(12)], \quad (6.1.2)$$

where $h(12)$ and $c(12)$ are the pair and direct correlation functions respectively, connected by the Ornstein–Zernike (OZ) equation

$$h_2(12) = c(12) + \rho \int c(13)h(32)d3, \quad (6.1.3)$$

where $\int d3$ means integration over angular and translational coordinates of the third particles, $\rho = \frac{N}{V}$ is the number density. The relation (6.1.3) is actually the definition of the direct correlation function on the terms of $h(12) = F_2(12) - 1$. $E(12)$ is the sum of so-called elementary diagrams constructed on $h(12)$ bonds.

As discussed in the previous chapters, for many cases the direct correlation function is proportional to the long-range part of the potential for larger interparticle distances and for a wide variety of thermodynamic states

$$c(12) = -\beta\Phi(12) \quad (6.1.4)$$

and

$$h(12) = g(12) \quad (6.1.5)$$

leads together with OZ equation (6.1.3) to the well-known renormalisation of the long-range potential of point particles, that is, without the consideration of short-range interaction

$$g(12) = -\beta\Phi(12) - \beta\rho \int \Phi(13)g(32)d3. \quad (6.1.6)$$

Now we represent the correlation functions $h(12)$ and $c(12)$ in the form

$$h(12) = g(12) + \delta h(12), \quad c(12) = -\beta\Phi(12) + \delta c(12). \quad (6.1.7)$$

After subtracting (6.1.6) from (6.1.3) we arrive at

$$\begin{aligned} \delta h(12) - \delta c(12) &= \rho \int [\delta c(13)h(32) + g(13)\delta c(32)] d3 + \\ &+ \rho^2 \int g(13)\delta c(34)h(42)d3d4 \end{aligned} \quad (6.1.8)$$

or in diagrammatical form

$$\delta h(12) - \delta c(12) = \text{diagram 1} + \text{diagram 2} + \text{diagram 3}, \quad (6.1.9)$$

where

$$\text{---}+ = \delta c(12), \quad \sim = h(12), \quad \text{---} = g(12), \quad \bullet = \rho \int d3. \quad (6.1.10)$$

Substituting the expressions (6.1.7) for the correlation functions into equation (6.1.2)

$$F_2(12) = \exp [-\beta\varphi(12) + g(12) + \delta h(12) - \delta c(12) + E(12)] \quad (6.1.11)$$

or using (6.1.9)

$$F_2(12) = \exp \left[-\beta\varphi(12) + g(12) + \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + E(12) \right]. \quad (6.1.12)$$

The relation (6.1.9) and (6.1.11) are the integral equation for the estimation of the pair distribution function, where the closure relation is given by the approximation for the function $E(12)$.

Now we will show how an iterative procedure of solving this equation automatically leads to cluster expansions for the pair distribution functions constructed on the basis of screened potentials $g(12)$. From (6.1.11) we define the function $\delta c(12)$

$$\delta c(12) = h(12) + E(12) - \beta\varphi(12) - \ln F_2(12). \quad (6.1.13)$$

As a zeroth approximation to the iteration procedure we use

$$F_2(12) = \exp [-\beta\varphi(12) + g(12)], \quad (6.1.14)$$

which corresponds to the approximation for a first iteration

$$\begin{aligned}\delta c(12) &= \exp[-\beta\varphi(12) + g(12)] - 1 - g(12) = \\ &= \Psi(12) - g(12) = \text{---}\text{---}\text{---}, \\ h(12) &= \Psi(12) = \text{---}\text{---}\text{---}, \quad E(12) = 0.\end{aligned}\tag{6.1.15}$$

Collecting in (6.1.11) all diagrams with one field point we get the expression for the pair distribution function up to the third cluster coefficient

$$F_2(12) = \exp[-\beta\varphi(12) + g(12) + F_2^{(3)}(12)],\tag{6.1.16}$$

where

$$F_2^{(3)}(12) = \text{---}\text{---}\text{---} + \text{---}\text{---}\text{---} + \text{---}\text{---}\text{---} - \text{---}\text{---}\text{---}.\tag{6.1.17}$$

To derive the next cluster coefficient $F_2^{(4)}(12)$ which contains all diagrams with two field points, one proceeds in the following way. There is a contribution from the elementary graphs. The first diagram is $\frac{1}{2}$ . One obtains other contributions from the analysis of higher order terms in (6.1.9). One linearizes the derived approximation (see (6.1.16)) for $h(12)$ with respect to the graphs with one field point

$$\begin{aligned}h(12) &= \exp[-\beta\varphi(12) + g(12)](1 + F_2^{(3)}(12)) - 1 = \\ &= \Psi(12) + (1 + \Psi(12)) F_2^{(3)}(12).\end{aligned}\tag{6.1.18}$$

From equation (6.1.16) we see that in this iteration step

$$\delta h(12) - \delta c(12) = \varphi(12) - g(12) - \delta c(12) = F_2^{(3)}(12)\tag{6.1.19}$$

leading to a new approximation for $\delta c(12)$

$$\delta c(12) = \Psi(12) [1 + F_2^{(3)}(12)] - g(12).\tag{6.1.20}$$

The expressions (6.1.12) and (6.1.20) are now used in the right side of equation (6.1.9), and the terms arising are classified by the number of field points. Then one obtains for the pair distribution function the approximation up to the fourth cluster coefficient

$$F_2(12) = \exp[-\beta\varphi(12) + g(12) + F_2^{(3)}(12) + F_2^{(4)}(12)]\tag{6.1.21}$$

with

$$\begin{aligned}F_2^{(4)}(12) &= \text{---}\text{---}\text{---} - \text{---}\text{---}\text{---} - \text{---}\text{---}\text{---} + \text{---}\text{---}\text{---} + \\ &+ \text{---}\text{---}\text{---} - \text{---}\text{---}\text{---} + \text{---}\text{---}\text{---} - \text{---}\text{---}\text{---} + \frac{1}{2} \text{---}\text{---}\text{---}.\end{aligned}\tag{6.1.22}$$

The third iteration leads to the approximation of the fifth cluster coefficient and so on. The cluster coefficients derived in this way agree fully with the expressions obtained in Chapter 2. Neglecting in equation (6.1.11) the elementary diagrams $E(12)$, we arrive at the hypernetted chain approximation (HNC)

$$F_2^{(\text{HNC})}(12) = \exp[-\beta\varphi(12) + g(12) + \delta h(12) - \delta c(12)] \quad (6.1.23)$$

derived in [378, 379] by partial summation of corresponding cluster expansion. Linearizing the expression (6.1.11) and neglecting the nonlinear terms of $\delta h(12) - \delta c(12)$ and all terms in $E(12)$, we get in analogy to [378, 379] the Percus—Yevick—Allnatt approximation (PYA)

$$F_2^{(\text{PYA})}(12) = \exp[-\beta\varphi(12) + g(12)](1 + \delta h(12) - \delta c(12)). \quad (6.1.24)$$

6.1.2. Generalized cluster expansions with the reference system approach to short-range interactions

Here we consider a second type of cluster expansions for the description of the systems with short- and long-range interactions. We start again from the relations (6.1.2) and (6.1.3). But in contrast to the previous approach we separate here the subsystem with short-range interaction which we will consider as the reference system with known properties. The reference system is given by a set of equations analogous to (6.1.2) and (6.1.3)

$$F_2^0(12) = \exp[-\beta\varphi(12) + h_0(12) - c_0(12) + E_0(12)], \quad (6.1.25)$$

$$h^0(12) = c^0(12) + \rho \int c^0(13)h^0(32)d3. \quad (6.1.26)$$

Since in accordance with (6.1.4) the direct correlation function $c(12)$ at large interparticle distance has asymptotic of long-range potential $\Phi(12)$, we can put

$$c(12) = c^0(12) - \beta\Phi(12) + \delta c(12) = C(12) + \delta c(12), \quad (6.1.27)$$

$$h(12) = h^0(12) + G(12) + \delta h(12) = H(12) + \delta h(12), \quad (6.1.28)$$

where $c^0(12)$ and $h^0(12)$ are corresponding correlation functions of the subsystem with the short-range interactions.

Substituting (6.1.27)—(6.1.28) into (6.1.2) yields the following form for the pair distribution function

$$F_2(12) = F_2^0(12) \exp[G(12) + \delta h(12) - \delta c(12) + \delta E(12)], \quad (6.1.29)$$

where $\delta E(12) = E(12) - E_0(12)$. The functions $G(12)$ play the role of screened potential and are determined through the functions $H(12)$ and $C(12)$ introduced according to (6.1.27) and (6.1.28) which are related by the Ornstein—Zernike equation

$$H(12) = C(12) + \rho \int C(13)H(32)d3, \quad (6.1.30)$$

which provides the contribution of the short-range interactions into the screened potentials. Another contributor of the short-range interactions into the screened potentials appears when using the condition of optimal separation of interaction [26] motivated by the strongly repulsive character of the interaction at short distances. In the case of the model of hard spheres with a long-range interaction it reduces to the exact condition

$$F_2^0(12) + G(12) = 0 \quad \text{for } r < \sigma, \quad (6.1.31)$$

where σ are the sizes of hard spheres.

When describing the hard spheres in the Percus—Yevick (PY) approximation, which writes as $C^0(12) = 0$ for $r > \sigma$, we get

$$C(12) = -\beta\Phi(12) \quad \text{for } r > \sigma, \quad (6.1.32)$$

which is peculiar to the mean spherical approximation (MSA). Such an approach gives a possibility to describe correctly the screening effects for non-point particles.

The cluster expansions and integral equations derived from it correspond to the optimized cluster theory (OCT). To build them up, subtract equation (6.1.30) from (6.1.3), which gives the equation

$$\begin{aligned} \delta h(12) - \delta c(12) = \rho \int [\delta c(13)h(32) + H(13)\delta c(32)] d3 + \\ + \rho^2 \int H(13)\delta c(34)h(42)d3d4, \end{aligned} \quad (6.1.33)$$

which is similar to (6.1.8) or (6.1.9) in diagrammatic form with only change $g(13)$ to $H(13)$. According to (6.1.29),

$$\delta c(12) = F_2(12) - F_2^0(12) - \ln \frac{F_2(12)}{F_2^0(12)} + \delta E(12). \quad (6.1.34)$$

It is significant that the function $\delta c(12)$ has generally a short-range character, which in line with (6.1.27) and (6.1.28) ensures the asymptotic (6.1.4) of the direct correlation function $c(12)$ to be corrected and the related peculiarities of the systems with an interaction to be covered.

The relation (6.1.29) and (6.1.33) is in fact the integral equation for the pair distribution function whose closure is allied to the manner of definition of the function $\delta E(12)$. In particular, specifying $\delta E(12) = 0$ fields the reference hypernetted chain approximation (RHNC). Making use of the iteration procedure leads to cluster expansions built up on the screened potential $G(12)$. In the process, taking

$$F_2(12) = F_2^0(12) \exp(G(12)) \quad (6.1.35)$$

as the first exponential approximation (EXP2) and collecting in (6.1.29) the diagrams with one field point, we arrive at the third cluster coefficient approximation (EXP3)

$$F_2(12) = F_2^0(12) \exp \left[G(12) + F_2^{(3)}(12) \right], \quad (6.1.36)$$

where $F_2^{(3)}(12)$ has the same diagrammatic structure as (6.1.17) with only change notations

$$\begin{aligned} \circ \text{---} \text{---} \text{---} \circ &= F_2^0(12) [\exp(G(12)) - 1] - G(12) = S(12), \\ \circ \text{---} \text{---} \text{---} \circ &= H(12) = h^0(12) + G(12). \end{aligned} \quad (6.1.37)$$

Using for the second interaction the expression

$$F_2(12) = F_2^0(12) \exp(G(12)) \left[1 + F_2^{(3)}(12) \right] \quad (6.1.38)$$

which corresponds to the approximations

$$\begin{aligned} \delta c(12) &= F_2^0(12) [\exp(G(12)) - 1] + \\ &+ \left[F_2^0(12)(e^{G(12)} - 1) + H(12) \right] F_2^{(3)}(12), \end{aligned} \quad (6.1.39)$$

$$\begin{aligned} h(12) &= F_2^0(12) [\exp(G(12)) - 1] + H(12) + \\ &+ \left[1 + F_2^0(12) [\exp(G(12)) - 1] + H(12) \right] F_2^{(3)}(12), \end{aligned} \quad (6.1.40)$$

$$\delta E = \frac{1}{2} \left[\text{Diagram 1} - \text{Diagram 2} \right], \quad (6.1.41)$$

where $\circ \text{---} \text{---} \text{---} \circ = h_2^0(12)$.

Again collecting all diagrams with two field points, we come to the approximation for the fourth cluster coefficient

$$F_2(12) = F_2^0(12) \exp \left[G(12) + F_2^3(12) + F_2^{(4)}(12) \right] \quad (6.1.42)$$

with

$$\begin{aligned} F_2^{(4)}(12) = F_2^{(4)}(R) &= \text{Diagram 1} + \text{Diagram 2} - \text{Diagram 3} + \text{Diagram 4} + \\ &+ \text{Diagram 5} - \text{Diagram 6} - \text{Diagram 7} + \frac{1}{2} \left(\text{Diagram 8} - \text{Diagram 9} \right) \end{aligned} \quad (6.1.43)$$

corresponding in the diagrammatic form to (6.1.22) but with new notation (6.1.37). Because of the extraction of the reference system a corresponding term of the elementary graphs is also subtracted. From this scheme one can obtain corresponding expressions for the fifth and higher order cluster coefficients.

The obtained cluster expansions describe the many-particle contributions of long-range interactions or more generally perturbation interactions. They are fundamental for the description of equilibrium properties of dense classical systems, the main contribution to which are given by the reference interactions. In the case of stronger perturbations the role of the many-particle correlations arises and one has to calculate all higher cluster coefficients. In that case one has to consider (6.1.33) and (6.1.34) as an integral equations for the function

$\delta h(12)$. If we put as a closure relation $\delta E = 0$ we get the reference hypernetted chain equation (RHNC)

$$F_2^{(\text{RHNC})} = F_2^0(12) \exp [G(12) + \delta h(12) - \delta c(12)]. \quad (6.1.44)$$

But this equation is now, in contrast, for example, to [379] based on screened potentials with correct consideration of reference structure factors in them. Therefore, it is possible that in numerical solution procedures very few interactions will be required. By analogy to equation (6.1.24) it is also possible to obtain the reference Percus—Yevick—Allnatt-like closure (RPYA) with inclusion of the influence of the reference system

$$F_2^{(\text{RPYA})}(12) = F_2^0(12) \exp(G(12)) [1 + \delta h(12) - \delta c(12)]. \quad (6.1.45)$$

From the obtained cluster expansions for the pair distribution function we can derive the perturbation contribution to the free energy by a coupling parameter integration if the free energy of the reference systems is known. We take the linear “charging” scheme

$$\Phi(12, \xi) = \xi \Phi(12), \quad (6.1.46)$$

where $0 \leq \xi \leq 1$, and the pair distribution function in the form

$$\begin{aligned} F_2(12, \xi) &= F_2^0(12) \exp \left[G(12, \xi) + F_2^{(3)}(12, \xi) + \dots \right] = \\ &= F_2^0(12) F_2^{\text{ex}}(12, \xi). \end{aligned} \quad (6.1.47)$$

Then, the excess Helmholtz free energy can be written as

$$F - F_0 = F^{\text{ex}} = \frac{1}{2} \frac{N^2}{V^2} \int F_2^0(12) \frac{\partial(\Phi(12, \xi))}{\partial \xi} F_2^{\text{ex}}(12, \xi) d1 d2 d\xi \quad (6.1.48)$$

and it leads to a cluster series

$$F^{\text{ex}} = F^{\text{HTA}} + F^{\text{ORPA}} + \delta B_2 + \delta B_3 + \delta B_4 + \dots \quad (6.1.49)$$

The first few terms in (6.1.49) are the high-temperature approximation (HTA)

$$F^{\text{HTA}} = \frac{1}{2} \frac{N^2}{V^2} \int F_2^0(12) \Phi(12) d1 d2, \quad (6.1.50)$$

the optimized random phase approximation (ORPA)

$$F^{\text{ORPA}} = \frac{1}{2} \frac{N^2}{V^2} \int d1 d2 \int_0^1 d\xi \Phi(12) G(12, \xi), \quad (6.1.51)$$

and the second cluster coefficient

$$\begin{aligned} \delta B_2 &= \frac{1}{2} \rho^2 \int \int \left[F_2^0(12) \left(e^{G(12, \xi)} - 1 - G(12, \xi) - \frac{1}{2} G^2(12, \xi) \right) + \right. \\ &\quad \left. + \frac{1}{2} G^2(12, \xi) (F_2^0(12) - 1) \right] d1 d2. \end{aligned} \quad (6.1.52)$$

Using the screening potential $G(12, \xi)$ we can perform all ξ -integration in order to obtain the higher cluster coefficients. From $F_2^{(3)}(12)$ we get δB_3

$$\delta B_3 = \frac{1}{6} \rho^3 \int \int \int [S(12)S(13)S(23) + H(12)S(13)S(23)] d1d2d3 \quad (6.1.53)$$

to calculate δB_4 we use for $F_2^{(4)}(12)$. After integration about ξ we will have

$$\delta B_4 = \frac{1}{8} \left(\begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \end{array} + 2 \left(\begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \end{array} + 2 \begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \end{array} \right) + \right. \\ \left. + 2 \begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \end{array} + 4 \left(\begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \end{array} + 2 \begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \end{array} + 2 \begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \end{array} \right) + \frac{1}{3} \left(\begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \end{array} - \begin{array}{c} \text{---} \text{---} \text{---} \\ | \quad | \quad | \\ \text{---} \text{---} \end{array} \right) \right). \quad (6.1.54)$$

6.2. Separation of an interparticle potential into three parts: short-range, long-range and intermediate strong attractive interactions

For many real classical many-particle systems, the interparticle interactions include, besides short-range repulsive and long-range interactions at intermediate distances, also the short-range strongly attractive interactions giving rise to various complexes and associates. For example, in electrolyte solutions of intermolecular interactions, these are specific orientationally directed short-range ones resulting in hydrogen bonds and other formations common for aqueous and other solutions. The strongly attractive part of interionic interactions between cations and anions is responsible for familiar ionic associates and that of ion-molecular interactions leads to formation of solvated ionic structures being peculiar to electrolyte solutions. Due to this, in many cases it is appropriate to separate the interparticle potentials into three parts instead of (6.1.1)

$$u(12) = \varphi(12) + \psi(12) + \Phi(12), \quad (6.2.1)$$

where $\varphi(12)$ is the short-range repulsive part, $\psi(12)$ is the short-range strongly attractive one, which we will term associative below, $\Phi(12)$ is the long-range part.

The specific feature of associative interactions is that the increase of the strong interparticle attraction leads to the clustering of particles into pairs or larger groups such as chains, networks, self-assembling aggregates etc. Due to clustering, the δ -like interparticle distribution function appears in the total distribution function, which can be separated into the intra and interparticle parts

$$F_2(r) = F_2^{\text{intra}}(r) + F_2^{\text{inter}}(r). \quad (6.2.2)$$

For clarity, we can use the function of the corresponding running integration numbers

$$n(R) = 4\pi\rho \int_0^R r^2 dr F_2(r), \quad (6.2.3)$$

which gives the average number of particles within a sphere of radius R around a particle placed at the center of the sphere. Resulting from clusterization, $n(R)$ splits into bonded (intra) and non-bonded (inter) parts

$$n(R) = n_{\text{intra}}(R) + n_{\text{inter}}(R). \quad (6.2.4)$$

The distinctive feature of associative interaction $\psi(12)$ is that the bonds arising due to it are saturated. Due to saturation of bonding

$$n_{\text{intra}}(R) \leq n_{\text{bond}}, \quad (6.2.5)$$

where the number of bounds n_{bond} is fixed. Specifically, for pairs (dimers) $n_{\text{bond}} = 1$, for chains $n_{\text{bond}} = 2$, for branched chains $n_{\text{bond}} = 3$, for networks $n_{\text{bond}} = 4$, etc.

6.2.1. Activity and density expansions

The background of the traditional description of equilibrium properties in the framework of cluster expansions or integral equations techniques can be connected with the diagram analysis of the Mayer density expansions of the pair distribution function which are not adapted correctly for the description of the clusterization phenomena. The clusterization is caused by the attractive part of interparticle interaction and to describe their contribution it is more convenient to use the activity expansions. In particular, in order to reproduce the correct low-density limit for the fluids with strong clusterization, an infinite number of terms in the density expansion must be included, while only a few terms of the activity expansion are sufficient for this purpose [374, 380]. Consider, for example, the series in the activity z for the pressure P and density ρ terminated at second order terms

$$\beta P = \frac{1}{V} \ln \Xi(z, T, V) = z + b_2 z^2, \quad (6.2.6)$$

$$\rho = \frac{1}{V} z \frac{\partial}{\partial z} \ln \Xi(z, T, V) = z + 2b_2 z^2, \quad (6.2.7)$$

where b_2 is the attractive part of the second cluster coefficient, and $\beta = 1/(k_B T)$.

Elimination of z from equation (6.2.7) yields

$$\frac{\beta P}{\rho} = \frac{1}{2} + \frac{\sqrt{1 + 8b_2\rho} - 1}{8b_2\rho}. \quad (6.2.8)$$

The more familiar corresponding virial equation of state is obtained from (6.2.8) by expanding in the power series of ρ

$$\frac{\beta P}{\rho} = 1 - b_2\rho + 4b_2^2\rho^2 - 20b_2^3\rho^3 + \dots \quad (6.2.9)$$

For systems with weak attraction $b_2 \rightarrow 0$ and both expressions (6.2.8) and (6.2.9) reproduce the ideal gas equation of state $\beta P/\rho = 1$. However, in the limit of strong attraction between pairs, $b_2 \rightarrow \infty$ and the correct equation of state for an ideal gas of pairs $\beta P/\rho = 1/2$ follows directly from equation (6.2.8). In order to obtain this result from equation (6.2.9), the infinite number of terms should be included.

In a more general case

$$\begin{aligned}\beta P &= z + b_2 z^2 + \dots + b_n z^n + \dots, \\ \rho &= z + 2b_2 z^2 + \dots + n b_n z^n + \dots,\end{aligned}\tag{6.2.10}$$

where b_n is the attractive part of the n -th cluster coefficient. Hence, the strong interparticle attraction $z \leq 1$ and in the limits $z \rightarrow 0$, $b_n \rightarrow \infty$

$$b_n z^n = \frac{1}{n} \rho - \frac{z}{n} - \frac{2}{n} b_2 z^2 - \dots - \frac{n-1}{n} b_{n-1} z^{n-1} \rightarrow \frac{1}{n} \rho.\tag{6.2.11}$$

After elimination of z from equations (6.2.10), we obtain the equation of state that will be changed from the ideal gas equation $\beta P/\rho = 1$ to the equation of the ideal gas of pairs $\beta P/\rho = 1/2$, the ideal gas of trimers $\beta P/\rho = 1/3, \dots$, and in general the ideal gas of n -mers $\beta P/\rho = 1/n$. Moreover, the summation of the infinite series in (6.2.10) leads to the possibility of self-assembling in the system. In the approximation $b_n \approx b_2^{n-1}$, the expansions (6.2.10) reduce to the following form

$$\beta P = \frac{z}{1 - b_2 z}, \quad \rho = \frac{z}{(1 - b_2 z)^2},\tag{6.2.12}$$

which is well known in the thermodynamic theory of micellization [381]. For this reason $z = \rho_0$ can be identified with the monomer density of amphiphilic molecules and the divergence point $z_c = \rho_c = 1/b_2$ has the sense of the critical micelle concentration (CMC).

From these considerations it might be expected that a theory which combines the activity and density expansions would be advantageous. The second and higher terms in the expansions (6.2.10) can be interpreted as the dimers density $\rho_1 = b_2 z^2$, the trimers density $\rho_2 = b_3 z^3, \dots$, and the n -mers density $\rho_{n-1} = b_n z^n$ correspondingly. Such an interpretation suggests the possibility of the description of clusterization by introducing the multi-density formalism for this purpose.

The distinctive feature of associative interactions is that the resulting bonds are saturable. In some models this condition can be satisfied exactly. Examples include hard-sphere fluids with a fixed number of off-centre square-well bonding sites embedded within the hard core region [11–14]. In such systems, the type of clusters formed depends on the number of bonding sites: with one site only dimers are possible; with two sites, linear chain clusters

appear; and with three or more sites, branched chains and network structures can form. Another class of models where saturation is strictly enforced are hard-sphere fluids with a shielded, sticky attractive shell. Here the key parameter is the distance L between the attractive shells of two spheres. For $L < \sigma/2$ only dimerisation occurs, whereas for $L > \sigma/2$ more complex clusters re-emerge. This model was originally introduced by Boltzmann [382] in his theory of chemical association, and later studied in detail by Stell and co-workers [383]. For more realistic models, the principle of bond saturation can only be treated approximately, and the corresponding theoretical predictions must be tested against computer simulations.

During the topological analysis of the diagrams arising for the singlet and pair correlation functions, we arrive at a generalized form of the Ornstein—Zernike equation. In the presence of associative interactions, the particle density splits into a sum of partial densities, each corresponding to a complex formed in the system as a result of association. The corresponding technique of describing molecular systems in the framework of the multi-density formalism was proposed by Wertheim [11–14]. In this approach, descriptions in terms of the activity and density expansions are combined. The theory has been applied to describe clusterization of various types in fluids modelled by hard spheres with a number of off-centre square-well bonding sites embedded into the hard-core region. The multi-density formalism was reformulated in order to treat the effects of clusterization in fluids with spherically symmetric attraction [384] and was applied to ionic systems [374, 385–390]. The multi-density integral equation approach was used to describe the chain [391–393] and network [394] forming fluids, molecular and macromolecular liquids [395], fluids with the multi-arm star polymerization [396] etc.

In the following we will start from the simplest approximation that considers only dimers formation.

6.2.2. Two-density approaches: application to ionic systems

The general idea of the multi-density formalism is connected with the separation of the pair interaction potential $u(12)$ into the bonding and non-bonding parts

$$u(12) = u_{\text{bond}}(12) + u_{\text{nonb}}(12), \quad (6.2.13)$$

where $u_{\text{bond}}(12)$ is the attractive part of the short-range interaction which includes at least some part of the minimum potential energy of $u(12)$ and plays the role of associative interaction. The non-bonding part $u_{\text{nonb}}(12)$ includes the short-range repulsive part and the long-range tail of $u(12)$. As a result, the Mayer function can be presented as the sum

$$f(12) = e^{-\beta u(12)} - 1 = f_{\text{nonas}}(12) + e^{-\beta U_{\text{nonb}}(12)} f_{\text{as}}(12)$$

of non-associative and associative Mayer functions

$$\begin{aligned} f_{\text{nonas}}(12) &= e^{-\beta U_{\text{nonb}}(12)} - 1, \\ f_{\text{as}}(12) &= e^{-\beta U_{\text{bond}}(12)} - 1. \end{aligned}$$

The diagrams appearing in the activity expansions of the singlet distribution function $\rho(1)$ can be presented as the sum

$$\rho(1) = \rho_0(1) + \rho_1(1), \quad (6.2.14)$$

where $\rho_0(1)$ and $\rho_1(1)$ are normalized to the densities of non-bonded particles (monomers), ρ_0 , and bonded particles, ρ_1 , respectively. The transition from activity expansions proceeds in the usual manner: disconnected diagrams are excluded, and each field vertex involves the replacement $\int z(R)d\mathbf{R} \rightarrow \int \rho(R)d\mathbf{R}$, as discussed in Subsection 5.1.1. In the case of a vertex connected by an associative line, the corresponding replacement is $\int \rho_0(R)d\mathbf{R}$.

Similarly, the pair distribution function will split into four terms

$$\begin{aligned} \rho(12) &= \rho(1)g(12)\rho(2) = \\ &= \rho(1)g_{00}(12)\rho(2) + \rho(1)g_{01}(12)\rho_0(2) + \\ &\quad + \rho_0(1)g_{10}(12)\rho(2) + \rho_0(1)g_{11}(12)\rho_0(2) \end{aligned} \quad (6.2.15)$$

or

$$g(r) = g_{00}(R) + xg_{10}(R) + xg_{01}(R) + x^2g_{11}(R), \quad (6.2.16)$$

where $x = \rho_0/\rho$ is the fraction of non-bonded particles.

Each vertex in the diagram expansion may carry many non-associative bonds $f_{\text{nonas}}(12)$, but due to bond saturation it can either carry no associative bonds $f_{\text{as}}(12)$ or exactly one such bond. The first class of diagrams contributing to $\rho(1)$ corresponds to $\rho_0(1)$, while the second class corresponds to $\rho_1(1)$. Because of bond saturation, the restriction to pair formation leads to a self-consistent relation for x

$$1 = x + 4\pi x^2 \rho \int_0^\infty g_{00}(R)f_{\text{as}}(R)R^2 dR, \quad (6.2.17)$$

where $f_{\text{as}}(R)$ is the orientationally averaged function $f_{\text{as}}(12)$:

$$f_{\text{as}}(R) = \frac{1}{(4\pi)^2} \int f_{\text{as}}(12) d\Omega_1 d\Omega_2. \quad (6.2.18)$$

In the sticky limit $f_{\text{as}}(R) = B\delta(R - \sigma)$ and equation (6.2.17) can be rewritten in the form

$$\frac{1-x}{x^2} = 4\pi\rho B\sigma^2 g_{00}(\sigma), \quad (6.2.19)$$

where $g_{00}(\sigma)$ is the contact value at $R = \sigma$ of the pair distribution function $g_{00}(R)$, $B = \int f_{as}(R)R^2 dR$.

The equation (6.2.19) is a special representation of the so-called mass action law (MAL) written usually in the form [397]

$$\frac{1-x}{x^2} = \rho K_A \frac{(y')^2}{y'_0}, \quad (6.2.20)$$

where K_A is the equilibrium constant of pairing, y' is the activity coefficient of free particles, y'_0 is that of the bonded particles.

From comparison of equations (6.2.19) and (6.2.20) we have

$$K_A = 4\pi B \sigma^2 \exp(-\beta u_{\text{bond}}(R = \sigma)), \quad (6.2.21)$$

$$\frac{(y')^2}{y'_0} = \exp(\beta u_{\text{bond}}(R = \sigma)) g_{00}(R = \sigma). \quad (6.2.22)$$

The classification and topological reduction of the diagrams for the pair correlation function leads to a generalized version of the OZ equation

$$\mathbf{h}(R_{12}) = \mathbf{c}(R_{12}) + \int d\bar{R}_{13} \mathbf{c}(R_{13}) \boldsymbol{\rho} \mathbf{h}(R_{32}), \quad (6.2.23)$$

where the corresponding matrices have the following form:

$$\mathbf{h} = \begin{pmatrix} h_{00} & h_{01} \\ h_{10} & h_{11} \end{pmatrix}, \quad \mathbf{c} = \begin{pmatrix} c_{00} & c_{01} \\ c_{10} & c_{11} \end{pmatrix}, \quad \boldsymbol{\rho} = \begin{pmatrix} \rho & \rho_0 \\ \rho_0 & 0 \end{pmatrix}, \quad (6.2.24)$$

$$h_{00} = g_{00} - 1, \quad h_{01} = g_{01}, \quad h_{10} = g_{10}, \quad h_{11} = g_{11}.$$

The diagram analysis of the Mayer cluster expansions enables the partial distribution functions to be presented as

$$g^{00}(12) = \exp[-\beta\varphi(12) - \beta\Phi(12) + \tau^{00}(12)], \quad (6.2.25)$$

$$g^{01}(12) = g^{00}(12)\tau^{01}(12), \quad g^{10}(12) = g^{00}(12)\tau^{10}(12),$$

$$g^{11}(12) = g^{00}(12) [\tau^{11}(12) + \tau^{10}(12)\tau^{01}(12) + f^{as}(12)], \quad (6.2.26)$$

where

$$\tau^{\alpha\beta}(12) = h^{\alpha\beta}(12) - c^{\alpha\beta}(12) + E^{\alpha\beta}(12), \quad (6.2.27)$$

$\alpha = 0$ or 1 .

As usual, the OZ-like equation (6.2.19) should be supplemented by closure relations. Among them we distinguish the associative hypernetted-chain (AHNC) closure

$$g_{00}(12) = \exp[-\beta u_{\text{nonb}}(12) + t_{00}(12)],$$

$$g_{01}(12) = g_{00}(12)t_{01}(12), \quad g_{10}(12) = g_{00}(12)t_{10}(12), \quad (6.2.28)$$

$$g_{11}(12) = g_{00}(12) [t_{10}(12)t_{01}(12) + t_{11}(12) + f_{as}(12)],$$

where $t_{\alpha\beta}(12) = h_{\alpha\beta}(12) - c_{\alpha\beta}(12)$.

The associative Percus—Yevick (APY) closure

$$\begin{aligned}
 g_{00}(12) &= \exp[-\beta u_{\text{nonb}}(12)] y_{00}(12), \\
 g_{01}(12) &= \exp[-\beta u_{\text{nonb}}(12)] y_{01}(12), \\
 g_{10}(12) &= \exp[-\beta u_{\text{nonb}}(12)] y_{10}(12), \\
 g_{11}(12) &= \exp[-\beta u_{\text{nonb}}(12)] [y_{11}(12) + f_{\text{as}}(12) y_{00}(12)],
 \end{aligned} \tag{6.2.29}$$

where $y_{\alpha\beta}(12) = g_{\alpha\beta}(12) - c_{\alpha\beta}(12)$.

The associative mean spherical approximation (AMSA) closure

$$\begin{aligned}
 h_{00}(12) &= -1, \quad h_{01}(12) = h_{10}(12) = h_{11}(12) = 0 \quad \text{for } R \leq \sigma \\
 g_{10}(12) &= \exp[-\beta u_{\text{nonb}}(12)] y_{10}(12), \quad c_{00}(12) = -\beta \Phi(12), \\
 c_{01}(12) &= c_{10}(12) = 0, \quad c_{11}(12) = g_{00}(12) f_{\text{as}}(12) \quad \text{for } R > \sigma.
 \end{aligned} \tag{6.2.30}$$

The analytical solution of OZ-like equation for the dimerizing hard spheres in APY approximation was done in [398, 399]. The different versions of analytical solution AMSA for ionic systems are considered in [385–387, 399, 400]. In [401] in the framework of AMSA to calculate the fraction of non-bonded ions x in the equation (6.2.17) an exponential approximation was introduced for

$$g_{00}(R) = g_{\text{nonb}}(R) \exp(G_{00}(R)), \tag{6.2.31}$$

where $g_{\text{nonb}}(R)$ is the pair distribution function of the reference system with the interparticle interaction $u_{\text{nonb}}(R)$,

$$G_{00}(R) = g_{00}^{\text{AMSA}}(R) - g^{\text{nonb}}(R). \tag{6.2.32}$$

The approximation (6.2.31) for very dilute ionic solutions is consistent with the intuitive idea of Bjerum [402] to introduce the concept of ionic pair to improve the Debye—Hückel [164] treatment of ionic systems when interionic interaction increases. It was shown [401] that the electrostatic part of the excess thermodynamic properties has the same form as in the ordinary MSA, but the screening parameter Γ should be changed to a new one Γ_{B} defined by equation

$$4(\Gamma_{\text{B}}\sigma)^2(1 + \Gamma_{\text{B}}\sigma)^2 = (\varkappa\sigma)^2 \frac{x + \Gamma_{\text{B}}\sigma}{1 + \Gamma_{\text{B}}\sigma}, \tag{6.2.33}$$

where $\varkappa^2 = 4\pi\beta \frac{1}{\varepsilon} e^2 \sum_a \rho_a z_a^2$ is the Debye—Hückel parameter. The exponential approximation (6.2.31) was also used [403] for the extension of the Høye—Stell scheme [88] of the calculation of thermodynamic properties in the framework of the two-density formalism for the fluids with arbitrary interparticle long-range interactions. It was proposed in equation (6.2.17) for the calculation of

the fraction of non-bonded particles x together with the approximation for $g_{00}(R)$ (6.2.28) for $f_{as}(R)$ to put [404]

$$f_{as}(R) = \exp(-\beta\Phi(R)) - 1 + \beta\Phi(R) - \frac{1}{2}\beta^2\Phi^2(R), \quad (6.2.34)$$

where instead of the separation (6.2.13) we split the total potential into the repulsive and attractive parts

$$u(R) = \varphi(R) + \Phi(R). \quad (6.2.35)$$

The choice of $f_{as}(R)$ in the form (6.2.34), according to the Ebeling idea [405], fixes the second cluster coefficient of the system and gives the correct description of thermodynamic properties at least for the small concentrations. Such a scheme has been used to describe the thermodynamic properties of non-aqueous electrolyte solutions [404].

In AMSA for symmetrical electrolyte solutions

$$\ln y' = \frac{-b\Gamma_B\sigma}{1 + \Gamma_B\sigma}, \quad \ln y_0 = -\frac{b(\Gamma_B\sigma)^2}{(1 + \Gamma_B\sigma)^2}, \quad (6.2.36)$$

$b = \frac{\beta e^2}{\varepsilon\sigma}$ is the Bjerrum parameter characterizing the Coulomb interactions between ions at the contact distance.

As in the previous Section 6.1, we can present the partial correlation functions

$$\begin{aligned} h^{\alpha\beta}(12) &= h^{(0)\alpha\beta} + G^{\alpha\beta}(12) + \delta h^{\alpha\beta}(12) = \\ &= H^{\alpha\beta}(12) + \delta h^{\alpha\beta}(12), \\ c^{\alpha\beta}(12) &= c^{(0)\alpha\beta}(12) - \beta\Phi(12)\delta_{0\alpha}\delta_{0\beta} + \delta c^{\alpha\beta}(12) = \\ &= C^{\alpha\beta}(12) + \delta c^{\alpha\beta}(12), \end{aligned} \quad (6.2.37)$$

where $h^{(0)\alpha\beta}(12)$ and $c^{(0)\alpha\beta}(12)$ are the corresponding partial correlation functions in the absence of the long-range interactions $\Phi(12)$. $G^{\alpha\beta}(12)$ are the screened potentials defined by the associative OZ equations taking to (6.2.20) with the associative mean spherical approximation-like (AMSA) closure

$$\begin{aligned} H^{\alpha\beta}(12) &= -\delta_{\alpha 0}\delta_{\beta 0} \quad \text{for } R < \sigma, \\ C^{\alpha\beta}(12) &= -\beta\Phi(12)\delta_{\alpha 0}\delta_{\beta 0} + g^{00}(12)f_{as}(12)\delta_{\alpha 1}\delta_{\beta 1} \quad \text{for } R \geq \sigma. \end{aligned} \quad (6.2.38)$$

Substituting (6.2.22) to (6.2.21) gives

$$\begin{aligned} g^{00}(12) &= g^{(0)00}(12) \exp [G^{00}(12) + \delta\tau^{00}(12)], \\ g^{01}(12) &= \exp [G^{00}(12) + \delta\tau^{00}(12)] [g^{(0)01}(12)G^{01}(12) + \delta\tau^{01}(12)], \\ g^{11}(12) &= \exp [G^{00}(12) + \delta\tau^{00}(12)] [g^{(0)01}(12)G^{01}(12) + \delta\tau^{01}(12)] + \\ &+ g^{(0)01}(12) [G^{10}(12) + \delta\tau^{10}(12)] + g^{(0)00}(12) [[G^{10}(12) + \delta\tau^{10}(12)] \times \\ &\times [G^{01}(12) + \delta\tau^{01}(12)] + [G^{11}(12) + \delta\tau^{11}(12)]], \end{aligned} \quad (6.2.39)$$

where

$$\delta\tau^{\alpha\beta}(12) = \delta h^{\alpha\beta}(12) - \delta c^{\alpha\beta}(12) + \delta E^{\alpha\beta}(12).$$

Setting $\delta E^{\alpha\beta}(12) = 0$ for closure, we arrive at the associative reference hypernetted chain approximation (ARHNC). Putting $\delta\tau^{\alpha\beta}(12) = 0$ we set the exponential approximation (EXP2)

$$\begin{aligned} g^{00}(12) &= g^{(0)00}(12) \exp(G_{00}(12)), \\ g^{01}(12) &= [g^{(0)01}(12) + g^{(0)00}(12)G^{(0)01}(12)] \exp(G^{00}(12)), \\ g^{11}(12) &= [g^{(0)11}(12) + g^{(0)01}(12)G^{(0)01}(12) + g^{(0)10}(12)G^{10}(12) + \\ &\quad + g^{(0)00}(12) [G^{10}(12)G^{01}(12) + G^{11}(12)]] \exp(G^{00}(12)), \end{aligned} \quad (6.2.40)$$

which can serve as a zeroth iteration when building up optimized cluster expansions.

It should be pointed out that different approximations yield distinct forms of the functions $g_{00}(12)$ by (6.2.31), resulting in distinct values of the fractions on non-associated particles as well. Therefore even the reference system is dependent on the long-range contribution into $g_{00}(12)$.

Similar as in previous paragraph the optimized cluster expansions with including the association phenomena can be generalized also for the free energy

$$\frac{\beta(F - F_0)}{N} = \frac{\beta F^{\text{MAL}}}{N} + \frac{\beta F^{\text{HTA}}}{N} + \frac{\beta F^{\text{ORPA}}}{N} + \delta B_2 + \delta B_3 + \dots, \quad (6.2.41)$$

where

$$\frac{\beta F^{\text{MAL}}}{N} = \left[\ln x + \frac{1}{2}(1 - x) \right] \quad (6.2.42)$$

is associative contribution, x is the fraction of free non-associated particles, described by the MAL (6.2.31), βF^{ORPA} is optimized random phase contribution corresponding to AMSA approximation, $\delta B_2, \delta B_3$ — corresponds to generalization of the second, third and higher cluster contributions.

6.2.3. Multi-density approach

Finally we add a few words about a multi-density approach. For the particles having more than one bonding site, the formation of chains, rings, networks and more complex aggregates is possible. Such aggregates can be viewed as a collection of monomers (segments) bonded at asymmetric attraction sites. The multi-density formalism is needed for the description of such fluids. In general, for the particles with M bonding sites the density is split into 2^M densities of different bonding states. The diagram analysis leads to the generalized version of the OZ equation which has a form similar to (6.2.16)

where h , c , ρ are $2^M \times 2^M$ matrices. In general, $2M$ self-consistent relations are needed instead of the relation (6.2.16) for the pairing case since the total number density of the system is split into 2^M densities of bonding states. Some simplification can be connected with the approximation that the bond creation between two molecules is independent of the existence of other bonds. As a result, the fraction of molecules that have $n < M$ bonded neighbours can be given by the binomial distribution

$$x_M^n = \binom{M}{n} p^n (1-p)^{M-n}, \quad (6.2.43)$$

where $p = 1 - \alpha$ is the fraction of particles non-bonded by one fixed site.

For the molecules with two attractive sites A and B (one is donor, the other is acceptor) the assumption (6.2.43) leads to the ideal chain approximation (ICA) [391] and $\alpha = 1/m$, where m can be considered the mean chain length. For this case the matrices $\mathbf{h}$, $\mathbf{c}$ and ρ have the following forms

$$\mathbf{h} = \begin{pmatrix} h_{00} & h_{0A} & h_{0B} & h_{0\Gamma} \\ h_{A0} & h_{AA} & h_{AB} & h_{A\Gamma} \\ h_{B0} & h_{BA} & h_{BB} & h_{B\Gamma} \\ h_{\Gamma 0} & h_{\Gamma A} & h_{\Gamma B} & h_{\Gamma\Gamma} \end{pmatrix}, \quad \mathbf{c} = \begin{pmatrix} c_{00} & c_{0A} & c_{0B} & c_{0\Gamma} \\ c_{A0} & c_{AA} & c_{AB} & c_{A\Gamma} \\ c_{B0} & c_{BA} & c_{BB} & c_{B\Gamma} \\ c_{\Gamma 0} & c_{\Gamma A} & c_{\Gamma B} & c_{\Gamma\Gamma} \end{pmatrix}, \quad (6.2.44)$$

$$\rho = \rho \begin{pmatrix} 1 & 1/m & 1/m & 1/m^2 \\ 1/m & 0 & 1/m^2 & 0 \\ 1/m & 1/m^2 & 0 & 0 \\ 1/m^2 & 0 & 0 & 0 \end{pmatrix},$$

where the lower indices X denote the unbonded ($X = 0$), singly bonded ($X = G$) and doubly bonded ($X = \Gamma$) states of the corresponding particles.

Similar to [390] the pair distribution function

$$g(r) = g_{00}(r) + \frac{2}{m} (g_{0A}(r) + g_{0B}(r)) + \frac{2}{m^2} (g_{AA}(r) + g_{AB}(r)), \quad (6.2.45)$$

where in ICA approximation $g_{0\Gamma}(r) = g_{A\Gamma}(r) = g_{B\Gamma}(r) = g_{\Gamma\Gamma}(r) = 0$.

The analytical solution of the OZ-like equation in the polymer PY (PPY) approximation for the chain forming fluids in the ICA approximation was obtained and discussed in [391, 393, 406]. In the ICA approximation the formation of the ring polymers is neglected. This approximation can be used to describe a system of chain polymers, polydisperse in length, that is characterized by a prescribed mean chain length. Some other approach in the framework of PPY approximation is used in [392, 407, 408]. These studies are focused on the investigation of the polymer fluids represented by the system of monomers that have completely associated into polymers of a fixed size, usually into linear freely-joined chain polymers of a fixed length. Such an approach makes it possible to consider the system at all the degrees of polymerization, including the

limits of completely dissociated and completely associated systems. The latter limit enables us to describe molecular and macromolecular liquids in the multi-density approach [395]. In [409, 410] the multi-density formalism was applied for the polyelectrolytes, with the flexible linear polyion chains. It was shown again that the electrostatic part of the excess thermodynamic properties has the same form, as the ordinary MSA, but screening parameter Γ should be changed to the parameter Γ_B for the chain polyelectrolytes.

For the molecules with four attractive sites A, B, C and D (two are donors and two are acceptors) the assumption (6.2.43) leads to the ideal network approximation (INA) [394]. The matrices $\mathbf{h}$, $\mathbf{c}$ and $\boldsymbol{\rho}$ can be written in the form similar to (6.2.44) with the difference that every matrix element is a submatrice. For example

$$h_{0A} = \begin{pmatrix} h_{0A}^{00} & h_{0A}^{0C} & h_{0A}^{0D} & h_{0A}^{0\Gamma} \\ h_{0A}^{C0} & h_{0A}^{CC} & h_{0A}^{CD} & h_{0A}^{C\Gamma} \\ h_{0A}^{D0} & h_{0A}^{DC} & h_{0A}^{DD} & h_{0A}^{D\Gamma} \\ h_{0A}^{\Gamma 0} & h_{0A}^{\Gamma C} & h_{0A}^{\Gamma D} & h_{0A}^{\Gamma \Gamma} \end{pmatrix}. \quad (6.2.46)$$

The analytical solution of the OZ-like equation for the network forming fluids in the network Percus—Yevick (NPY) and INA approximations was done in [394, 411]. It was shown in [393, 394] that the calculated structure factors for chain and network systems exhibit a peculiarity — a so-called pre-peak at small wave numbers connected with the formation of relatively large molecular aggregates. It was shown that such a peculiarity plays an important role in describing the structure factor of liquid sulphur [411]. The possibility of the existence of a pre-peak in the structure factor of water is discussed based on the combination of computer simulations and the integral equation theory [412]. Recently, such a peculiarity has been observed in many polymer and glassy substances, as well as in ionic liquids [414], where correlations between relatively large clusters can lead to mesoscopic-scale ordering.

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Монографія, перше видання якої побачило світ у видавництві «Наукова думка» 1980 року, дає систематичний виклад статистичної теорії класичних рівноважних систем. Це одна з перших монографій у світовій літературі, присвячена мікроскопічній теорії рідкого стану, яка фактично стала підручником. З єдиної точки зору розглянуто широкий клас систем, що описують реальні гази, рідини та розчини. Опис систем взаємодіючих частинок здійснено у розширеному фазовому просторі, що складається з індивідуальних координат частинок й простору колективних змінних, які описують флуктуаційні хвилі густини для відповідної характеристики. Індивідуальні та колективні змінні описують, відповідно, ефекти, зумовлені короткосяжними і далекосяжними взаємодіями. Розвинуто іонно-молекулярний підхід у теорії розчинів електролітів, де рівноправно враховуються всі взаємодії між іонами електроліту та молекулами розчинника. Показано, що характер екранування електростатичних взаємодій іонами і молекулами розчинника є принципово різним. Розглянуто також просторово-неоднорідні системи.

Наукове видання

НАЦІОНАЛЬНА АКАДЕМІЯ НАУК УКРАЇНИ
ІНСТИТУТ ФІЗИКИ КОНДЕНСОВАНИХ СИСТЕМ
імені І.Р. ЮХНОВСЬКОГО НАН УКРАЇНИ

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СТАТИСТИЧНА ТЕОРІЯ КЛАСИЧНИХ РІВНОВАЖНИХ СИСТЕМ

Англійською мовою

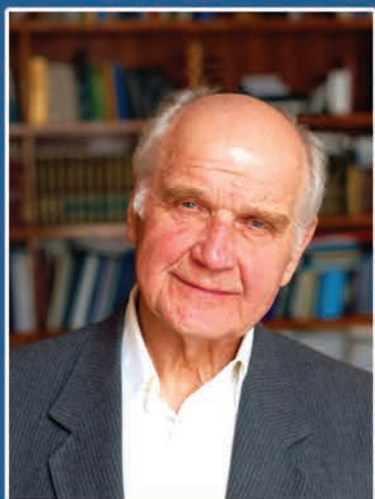
В авторській редакції

Художнє оформлення *Є.І. Ільницького*
Технічний редактор *Т.М. Шендерович*
Комп'ютерна верстка *Л.І. Шмагайло*

Підп. до друку 20.11.2025. Формат 70×100/16.
Гарн. Computer Modern. Ум. друк. арк. 36,24. Обл.-вид. арк. 35,88.
Тираж 100 прим. Зам. 7861

Видавець і виготовлювач Видавничий дім “Академперіодика” НАН України
01024, Київ, вул. Терещенківська, 4

Свідцтво суб'єкта видавничої справи ДК № 544 від 27.07.2001



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