

ON TAKING ACCOUNT OF INTERACTIONS IN THE STATISTICAL THEORY OF ELECTROLYTE SOLUTIONS

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The problems of taking account of interactions in the statistical theory of ion-molecular systems are considered. The procedure proposed is based on dividing the interparticle potential into three parts: a short-range repulsion, a strong intermediate-range attraction, and long-range electrostatic interactions. Optimized cluster expansions of the correlation functions are proposed. Various types of models describing an ion-molecular system are studied: multipole models, site-site ones, associative ones, realistic models that using computer simulation of the reference system. The problems of description of spatially inhomogeneous ion-molecular systems are discussed.

1. Introduction

The problem of a microscopic theory of electrolyte solutions entails an explicit consideration of the solute ions and the solvent polar molecules as well as proper taking into account all the various interactions between the solution particles. Over many years, in the theory of electrolytes the primary attention was paid to allow for the Coulomb interactions between ions, the long-range character of which results in strong interparticle correlations. The Debye-Hückel theory [1] was the first of such theories that gave a quantitative description of the idea of screening the Coulomb interactions. However it appears to be valid only in the region of infinitely diluted solutions since that theory does not consider solvent molecules as well as the effect of short-range non-Coulomb interactions.

M. M. Bogolubov originally obtained Debye-Hückel's results proceeding from the statistical-mechanical method [2]. He not only pointed out the way to improve the theory, but also demonstrated rigorously that the short- and long-range interactions are characterized with different small parameters and this is why in approximate calculations they require different methods to be treated. One way to solve this problem properly is the method of collective variables evolved by I. R. Yukhnovsky [3-6]. In its framework the system is described in the extended space comprising fluctuative oscillation modes of density waves of the electric charge of collective variables as well as individual coordinates of particles. Therewith the individual coordinates of particles are used to describe short-range parts of the interactions, and the collective variables for long-range ones.

Two variants of construction of cluster expansions are developed according to the technique of taking into account short-range interactions. In the

former case, expansions of the electrostatic part of the free energy are built up in the framework of the method of collective variables [3,4]. The short-range interactions are allowed for by the functional differentiation. This way to calculate the thermodynamic and structural properties leads to generalization of Mayer expansions to systems with an electrostatic interaction. In the process the long-range interaction is so renormalized that the cluster expansions are set up basing on screened and short-range potentials. This eliminates the divergence of the expressions for the thermodynamic and structure functions at large interparticle distances. In the latter case, first the contribution of short-range interactions is separated out, and thereafter long-range interactions in the system are allowed for [5-9]. This way to take short-range interactions into account is most acceptable to describe dense systems, among them liquids and solutions.

The method of collective variables generalized by I. R. Yukhnovsky first to ion-dipole systems [10-12] and next to systems with an arbitrary electrostatic interaction [13] initiated development of the ion-molecular approach in the theory of electrolytes. The explicit consideration of a molecular solvent opened up crucially new opportunities for construction of a microscopic theory of electrolyte solutions. In particular, it has been made feasible to quantitatively describe ionic solvation and study its changes in dependence on the ionic concentration and the solvent properties. Taking into account the specific features of ion-molecular and intermolecular interactions along with interionic ones forms a basis for the ion-molecular approach.

However the division of interparticle potentials into the short- and long-range parts appeared inadequate. The strongly attractive part of interparticle potentials gives rise to various complexes which must be allowed for in a microscopic theory of electrolyte solutions. Therefore proper taking the interactions into account requires to divide the potentials into three parts: a short-range repulsion at small distances, a strong short-range attraction at middle distances, and long-range electrostatic interactions at large interparticle distances. It is clear that correct consideration of these interaction parts calls for different approximate methods of description of their contributions. Such a theory is based on the procedures which are worked out in the theory of associative liquids [14-16] and was first used to describe ionic systems in [17-19].

When describing surface phenomena in electrolyte solutions, in addition to the above-listed problems there appear the issues of correct consideration of external field potentials responsible for an interface structure. The microscopic approach to description of surface phenomena in electrolyte solutions developed in the framework of the method of collective variables provides a tool of consistent allowing for particles of the confining surface as well as ions and molecules of the electrolyte solution.

In this work we will dwell on the analysis of these aspects of taking account of interactions when constructing the microscopic theory of electrolyte solutions.

2. Cluster expansions of the free energy and correlation functions

We begin to take account of interactions in the statistical theory of electrolytes from considering cluster expansions for the free energy and correlation functions of systems in which the interaction can be presented as a sum of two parts,

$$U_{ab}(12) = \varphi_{ab}(12) + \Phi_{ab}(12), \quad (2.1)$$

where $\varphi_{ab}(12)$ and $\Phi_{ab}(12)$ are the short- and long-range parts of the interaction potential, respectively; a, b, \dots denote species of particles; $1, 2, \dots$ mean the set of particle coordinates which, in general, can include coordinates of orientational and internal degrees of freedom besides Cartesian ones.

The cluster expansions of the free energy and binary distribution functions obtained in the method of collective variables have gained wide acceptance in the description of ionic and ion-molecular systems. Following [20-22], in this work we will consider a somewhat different way to build up cluster expansions, which next will be extended to site-site correlation functions and to the case of the presence of associative interactions. The approach under consideration is based on the results of a diagram analysis of Mayer cluster expansions [23-24], whereby the binary distribution functions of systems with the pair interaction potentials (2.1) can be presented as

$$g_{ab}(12) = \exp[-\beta U_{ab}(12) + h_{ab}(12) - c_{ab}(12) + E_{ab}(12)], \quad (2.2)$$

where $h_{ab}(12) = g_{ab}(12) - 1$ and $c_{ab}(12)$ are respectively the pair and direct correlation functions related to each other by the set of Ornstein-Zernike (OZ) equations

$$h_{ab}(12) = c_{ab}(12) + \sum_c \rho_c \int d3 c_{ac}(13) h_{cb}(32), \quad (2.3)$$

ρ_c is the density of particles of sort c , $E_{ab}(12)$ is the collection of elementary diagrams, $\beta = 1/kT$ inverse temperature.

In accordance with (2.2), the direct correlation function

$$c_{ab}(12) = h_{ab}(12) - \ln g_{ab}(12) - \beta U_{ab}(12) + E_{ab}(12) \quad (2.4)$$

has the asymptotics identical to that of the potential $U_{ab}(12)$. Therefore it is sensible to write the correlation functions as

$$\begin{aligned} c_{ab}(12) &= c_{ab}^0(12) - \beta \Phi_{ab}(12) + \delta c_{ab}(12) = C_{ab}(12) + \delta c_{ab}(12), \\ h_{ab}(12) &= h_{ab}^0(12) - G_{ab}(12) + \delta h_{ab}(12) = H_{ab}(12) + \delta h_{ab}(12), \end{aligned} \quad (2.5)$$

where $h_{ab}^0(12)$ and $c_{ab}^0(12)$ are the corresponding correlation functions of the subsystem with the short-range interaction.

Substituting (2.5) into (2.2) yields the following form of the binary functions:

$$g_{ab}(12) = g_{ab}^0(12) \exp[G_{ab}(12) + \delta h_{ab}(12) - \delta c_{ab}(12) + \delta E_{ab}(12)], \quad (2.6)$$

where $\delta E_{ab}(12) = E_{ab}(12) - E_{ab}^0(12)$. The functions $G_{ab}(12)$ play the role of screened potentials and are determined through the functions $H_{ab}(12)$ and $C_{ab}(12)$ introduced according to (2.5) which are related by the Ornstein-Zernike equations

$$H_{ab}(12) = C_{ab}(12) + \sum_c \rho_c \int d3 C_{ac}(13) H_{cb}(32) \quad (2.7)$$

which provide 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

division of interactions [25] which is 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

$$g_{ab}^0(12) + G_{ab}(12) = 0, \quad r < \sigma_{ab}, \quad (2.8)$$

where σ_{ab} are the sizes of the hard spheres. When describing the hard spheres in the Percus-Yevick (PY) approximation which writes as $c_{ab}^0(12) = 0$ for $r > \sigma_{ab}$, we get

$$C_{ab}(12) = -\beta\Phi_{ab}(12) \quad \text{for } r > \sigma_{ab}, \quad (2.9)$$

which is peculiar to the mean spherical approximation.

The cluster expansions and the integral equations derived from it correspond to the optimized cluster theory. To build them up, subtract equations (2.7) from (2.3), which gives the set of equations

$$\delta h_{ab}(12) - \delta c_{ab}(12) = \delta c \wedge h + H \wedge \delta c + H \downarrow h \quad (2.10)$$

According to (2.6),

$$\delta c_{ab}(12) = g_{ab}(12) - g_{ab}^0(12) - \ln \frac{g_{ab}(12)}{g_{ab}^0(12)} + \delta E_{ab}(12). \quad (2.11)$$

It is significant that the functions $\delta c_{ab}(12)$ have generally a short-range character, which in line with (2.5) ensures the asymptotics of the direct correlation functions $c_{ab}(12)$ to be correct and the related peculiarities of systems with an electrostatic interaction to be covered [5].

The relations (2.6) and (2.10) are in fact the set of integral equations for the binary distribution functions, whose closure is allied to the manner of definition of the functions $\delta E_{ab}(12)$. In particular, specifying $\delta E_{ab} = 0$ yields the reference hypernetted chain approximation (RHNC). Making use of the iteration procedure leads to cluster expansions built up on the screened potentials $G_{ab}(12)$ [20-22]. In the process, taking

$$g_{ab}(12) = g_{ab}^0(12) \exp(G_{ab}(12)) \quad (2.12)$$

as the first exponential approximation (EXP2), and collecting in (2.6) the diagrams with one field point in (2.6), we arrive at the third-cluster-coefficient approximation (EXP3),

$$g_{ab}(12) = g_{ab}^0(12) \exp(G_{ab}(12) + g_{ab}^{(3)}(12)), \quad (2.13)$$

where

$$g_{ab}^{(3)}(12) = \mathcal{A} - \mathcal{A}_0, \quad (2.14)$$

$$\mathcal{A}_0 = g_{ab}^0(12) \exp(G_{ab}(12) - 1), \quad (2.15)$$

$$\mathcal{A} = H_{ab}(12).$$

The next iteration gives the fourth-cluster-coefficient approximation and so on.

Having the binary distribution functions, from the known relations we get the cluster expansions for the free energy [22]

$$F = F_0 + F_{HTA} + F_{RPA} - kT(B_2 + B_3 + \dots), \quad (2.16)$$

where F_0 is the free energy of the subsystem with the short-range interaction,

$$F_{HTA} = \frac{1}{2} \sum_{a,b} \rho_a \rho_b \int d1d2 \Phi_{ab}(12) g_{ab}^0(12) \quad (2.17)$$

is the high-temperature approximation,

$$F_{RPA} = \frac{1}{2} \sum_{a,b} \rho_a \rho_b \int d1d2 \int_0^1 d\xi G_{ab}(12, \xi) \quad (2.18)$$

is the random-phase approximation, B_2, B_3, \dots are the corresponding cluster coefficients. In so doing the structure of the cluster expansions of both the free energy and the binary distribution functions remains the same as was obtained in the method of collective variables when allowing for short-range forces by the functional differentiation method; only the diagram notation is changed in accordance with (2.15).

3. Ion-molecular models

The ion-molecular models employed in constructing the theory of electrolyte solutions differ in the way of description of ion-molecular and intermolecular interactions. Among them one distinguishes models involving multipole expansions to describe long-range interactions with the participation of molecules. Another means of description consists in mimicing molecules with a set of sites and using site-site distribution functions to describe them. More complicated ion-molecular models are employed in modern computer simulations.

In this section we consider the application of the cluster expansions obtained above to describe and analyze these three types of ion-molecular models.

3.1. Ion-dipole models

The simplest among the ion-multipole models is the ion-dipole one, in which the molecule is characterized with dipole moment p_s ¹. As a consequence, the long-range parts of interion, ion-molecular, and intermolecular potentials have the Coulomb, ion-dipole, and dipole-dipole character, respectively,

$$\Phi_{ab}(r) = \frac{e^2 Z_a Z_b}{r}, \quad \Phi_{as}(r, v_2) = -e Z_a p_s \frac{1}{r^2} \cos v_2, \quad (3.1)$$

$$\Phi_{ss}(r, v_1, v_2, \varphi) = -p_s^2 \frac{1}{r^3} (2 \cos v_1 \cos v_2 - \sin v_1 \sin v_2 \cos \varphi),$$

where r is the interparticle distance; (v, φ) are the polar angles between the dipole-moment vector and the axis \mathbf{r} ; Z_a, Z_b the corresponding ion valences.

The early studies were carried out in the framework of cluster expansions obtained when allowing for short-range interactions by the functional-differentiation technique [3-6]. The numerical calculations of the binary

¹From here on, we denote molecules with the letter s keeping the notations a, b, \dots for particle sorts.

distribution functions performed in doing so made it possible to reveal a fundamental role of a solvent in describing ionic solvation, the specifics of a short-range order, and the peculiarities of effective interionic interactions in solutions [26-29].

Treating short-range interactions as a reference system and separating out long-range ones optimally make it feasible to describe some of these effects analytically making the calculations in the lowest approximations. In this strategy, screened potentials have first to be obtained, which amounts to solving the Ornstein-Zernike equations in the mean spherical approximation (MSA), i.e. the set (2.7) complemented with the conditions (2.8) and (2.9), where the long-range potentials $\Phi_{ab}(12)$ for an ion-dipole system are specified by (3.1).

The trait of solution of the MSA in this case stems, first of all, from the necessity to allow for orientational dependencies correctly, which brings on the ion-molecular and intermolecular correlation functions to be presented in the orientationally-invariant form [5, 30, 31]

$$h_{ab}(12) = \sum_{mnl} h_{ab}^{mnl}(r) \psi^{mnl}(\Omega_1, \Omega_2, \Omega_{\mathbf{r}}), \quad (3.2)$$

where Ω_1 are the Euler angles that specify the molecule orientation, $\Omega_{\mathbf{r}}$ sets the orientation of vector \mathbf{r} ,

$$\begin{aligned} \psi^{mnl}(\Omega_1, \Omega_2, \Omega_{bf\mathbf{r}}) &= \sqrt{(2m+1)(2n+1)} \sum_{\mu\nu\lambda} \begin{pmatrix} mnl \\ \mu\nu\lambda \end{pmatrix} \times \\ &\times D_{0\mu}^m(\Omega_1) D_{0\nu}^n(\Omega_2) D_{0\lambda}^l(\Omega_{\mathbf{r}}), \end{aligned} \quad (3.3)$$

where Wigner's 3j-symbols and the generalized spherical harmonics are denoted with the standard quantum-mechanical notations [32].

On integrating over the orientations of the third particle and changing to the orientations Ω_1 and Ω_2 measured with respect to the axis \mathbf{r}_{12} , the Ornstein-Zernike equation reduces to the set of equations for the coefficients of the orientationally invariant expansion. In the Fourier space it writes as

$$H_{\lambda,ab}^{mn}(k) = C_{\lambda,ab}^{mn}(k) + \sum_c \sum_l (-1)^\lambda \rho_c H_{\lambda,ac}^{ml}(k) C_{\lambda,cb}^{ln}, \quad (3.4)$$

where

$$\begin{aligned} H_{\lambda,ab}^{mn}(k) &= \int_0^\infty dr \left(e^{ikr} J_{\lambda,ab}^{mn}(r) + e^{-ikr} J_{\lambda,ab}^{nm}(r) \right), \\ J_{\lambda,ab}^{mn}(k) &= 2\pi (-1)^\lambda \sum_l \begin{pmatrix} mnl \\ -\lambda\lambda 0 \end{pmatrix} \int_{\mathbf{r}} dR R P_l\left(\frac{r}{R}\right) h_{ab}^{mnl}(R), \end{aligned} \quad (3.5)$$

$C_{\lambda,ab}^{mn}(k)$ are similar to (3.5), $P_l(r/R)$ are the Legendre polynomials.

The set (3.4) breaks up into two independent subsystems for $\lambda = 0$ and $\lambda = 1$, respectively. The equation for $\lambda = 1$ is in fact similar to the case

of a pure dipole system which, as is known, reduces to the Percus-Yevick equation for hard spheres with the effective density $b_2/12$, where

$$b_2 = \frac{1}{\sqrt{30}} 6\pi\rho_s\sigma_s^3 \int_0^\infty \frac{1}{r} dr h_{ss}^{112}(r). \quad (3.6)$$

Solving the set (3.4) at $\lambda = 0$ employs the Winer-Hopf factorization technique. The Wertheim-Baxter correlation functions [33-34] introduced in the process have the form

$$Q_{ab}^{mn}(r) = \begin{cases} 0, & r < \lambda_{ba} = \frac{1}{2}(\sigma_b - \sigma_a) \\ q_{ab}^{mn}(r) - Z_a a_b^n, & \lambda_{ba} \leq r \leq \sigma_{ab} \\ -Z_a a_b^n, & r > \sigma_{ab} = \frac{1}{2}(\sigma_a + \sigma_b) \end{cases} \quad (3.7)$$

where the functions $q_{ab}^{mn}(r)$ are polynomials such that $q_{ab}^{mn}(r = \sigma_{ab}) = 0$.

The relationship between the coefficients of the factorizing functions $Q_{ab}^{mn}(r)$ and the corresponding parameters of the system was found first for the simplified model with all the sort of particles equal in size [35-36] and then more generally in [37-40]. The expressions for the screened potentials in case of equal sizes were obtained independently in [41] and [42], and in a more general case in [39-40].

Consider thoroughly the properties of the somewhat simplified three-sort model comprising molecules with size σ_s and dipole moment p_s , and ions with equal sizes $\sigma_+ = \sigma_- = \sigma$ and valences $Z_+ = -Z_- = Z_i$. In this case the behavior of the screened potentials is determined by the three parameters $x = \kappa\sigma$, $y = \frac{4}{9}\pi\rho_s\beta p_s^2$, and $\alpha = \sigma_i/\sigma_s$, where the parameters x and y characterize intensity of the ionic and dipole interactions, respectively, and κ is the inverse Debye radius. For small values of the parameters x and y , the screened potentials display a monotonic behavior. However when increasing x , y , they become oscillating which is representative of ordering in the system [6, 43]. As this takes place, the increase in the parameter y characterizes the influence of solvation effects on screening. With rise in the parameter x , there appear specific features of screening bound up with the occurrence of short-range ordering peculiar to ionic melts [44]. Figure 1 displays the ionic screened potentials for three characteristic region in the case of $\sigma_i = \sigma_s$ and various $\beta_i^* = \beta e^2 Z_i^2 / \sigma$.

As it must, in the region of small ionic concentrations the screened potentials have the Debye asymptotics at large distances,

$$G_{ab}(12) = -\beta Q_a(\nabla) Q_b(-\nabla) \frac{1}{\epsilon r} \exp\left(-\frac{\kappa}{\sqrt{\epsilon}} r\right), \quad (3.8)$$

where $Q_a(\nabla)$ is the generalized charge which coincides with the charge eZ_a in the case of ions, and is $Q_s(\nabla) = (p_s \nabla)$ for molecules. The effect of dipoles appears as the rise of the dielectric permittivity

$$\epsilon = 1 + 3y\beta_{12}^4 / \beta_6^2 \quad (3.9)$$

which decreases with increasing the ion concentration, and for the infinite dilution coincides with the corresponding Wertheim's expression [45]. The

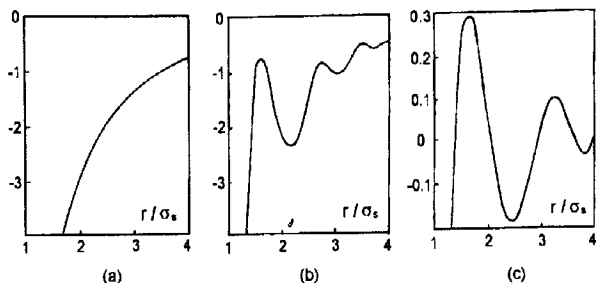


Figure 1. The ionic screened potentials: (a) the Debye-Hückel region ($x = 0.3$, $y = 0.5$, $\beta_i^* = 50$); (b) the solvation region ($x = 1.33$, $y = 9.85$, $\beta_i^* = 185$); (c) the high-ionic-concentration region ($x = 16.1$, $y = 0.16$, $\beta_i^* = 30$).

values $\beta_{3,2^n} = 1 + (-1)^n b_2 / (3 \cdot 2^n)$ are represented by the parameter b_2 defined from (3.6).

Having screened potentials, one can proceed to a study of the thermodynamic, structure, and other properties of electrolyte solutions. In contrast to the traditional ionic approaches, the explicit consideration of solvent molecules enables to describe the concentration dependencies as well as the temperature and pressure ones, and to calculate the properties of infinitely dilute solutions known as standard states.

The three-sort model considered above was used in [46-48] to describe the thermodynamic properties of aqueous electrolyte solutions. This gives the expressions for the thermodynamic functions comprising four terms; for instance, the ionic chemical potentials are

$$\mu_i = \mu_i^0 + \mu_i^{nel} + \mu_i^{el} + \mu_i^{sn}, \quad (3.10)$$

where μ_i^0 are the chemical potential values in the hard-spheres model which can be described using the Mansoori-Carnahan-Starling-Leland approximation [49], μ_i^{nel} is the contribution coming from non-electrostatic interactions (inductive and dispersive forces) which can be allowed for in the framework of the high-temperature approximation (HTA), μ_i^{el} the contribution from electrostatic interactions which can be done in the framework of the optimized random-phase approximation (ORPA), μ_i^{sn} the term related to the change in the standard-solution density.

The chemical potentials are usually presented as a sum:

$$\mu_i = \mu_i^\Phi + \frac{1}{\beta} \ln \gamma_i, \quad (3.11)$$

where μ_i^Φ is the standard value of the chemical potential which corresponds to the infinite dilution of ions, γ_i are the ionic activity coefficients.

Figure 2 exhibits the temperature dependencies of the standard enthalpy values $h_i^\Phi = \mu_i^\Phi - T(\frac{\partial \mu_i^\Phi}{\partial T})_p$, the partial molar volume $V_i^\Phi = T(\frac{\partial \mu_i^\Phi}{\partial p})_T$, and the hydration specific heat $C_{ip}^\Phi = -T(\frac{\partial^2 \mu_i^\Phi}{\partial T^2})_p$ calculated in this way for the NaCl aqueous solution. A comparison between the theoretical curves and the corresponding experimental data shows a satisfactory quantitative description, in particular, for high temperature and pressure.

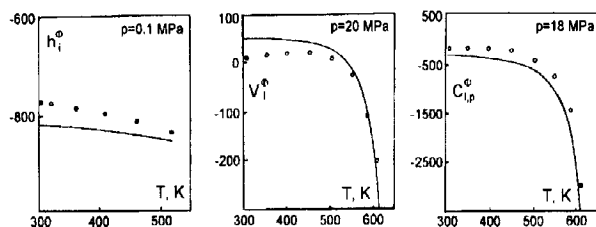


Figure 2. Theoretical values of the standard properties of NaCl aqueous electrolyte solution at various temperature T and pressure p as compared to experimental data. h_i^Φ is the hydration enthalpy, V_i^Φ is the hydration volume, $c_{p,i}^\Phi$ is the hydration specific heat.

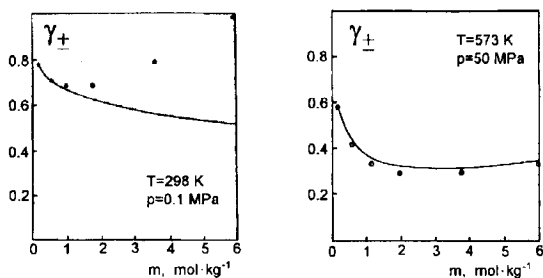


Figure 3. Calculated and experimental concentration dependencies of mean ionic activity coefficients γ_{\pm} for NaCl aqueous electrolyte solution.

Figure 3 depicts the concentration dependencies of the ionic activity coefficients for the NaCl aqueous solution calculated according to (3.10) - (3.11). As seen from the picture, at the normal conditions the calculated values of the coefficients γ_i fit the experimental ones for the concentration up to 1 mol/kg. At the same time, in the region of high temperature and pressure the calculated and experimental results agree in the whole range of the concentrations considered.

As is evident, the ion-dipole model can be used successfully to treat experimental data and to describe semiquantitatively the thermodynamic properties of salt-aqueous solutions in a wide range of the thermodynamic parameters. However, to represent the thermodynamic derivatives with respect to temperature and pressure requires the ion-dipole model to be improved essentially (especially for normal conditions).

The general expressions for screened potentials obtained in [39-40] have been employed in [50-51] to make a microscopic analysis of a nature of hydration forces. There have been obtained a number of important corrections to the classical Derjaguin-Landau-Verwey-Overbeek theory [52], among which is the effect of dipole alignment near macroions.

The inclusion of a compensating background appeared to be another important application of the results got in [40]. Such a two-sort model was employed in [53-54] as basic to describe the structure properties of metal-ammonia solutions. Figure 4 shows the binary distribution functions of the kalium-ammonia solution calculated for this model in the approximation (2.12). The calculations intimate that the ammonia structure has a density-controlled-ordering character and depends only slightly on the ion

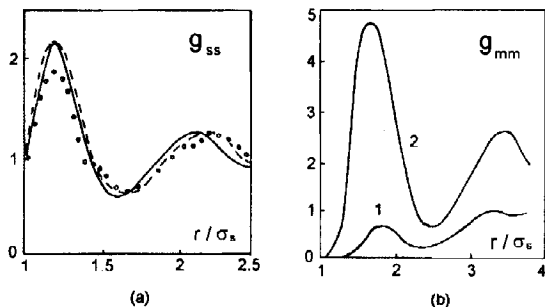


Figure 4. The distribution functions for Na-NH₄ solution: (a) N-N pair distribution function $g_{ss}(r)$ at Na concentration $x = 0.001$, (—) theory, (---) MD, (····) experiment; (b) Na-Na distribution function $g_{mm}(r)$ at (1) $x = 0.05$, (2) $x = 0.1$.

concentration. The comparison drawn in Figure 4 for the radial function $g_{ss}(r)$ exhibits satisfactory agreement between the curve obtained and the experimental data as well as the computer simulation data. At the same time the ion functions vary from the form typical for the solvation region with the Debye asymptotics at small concentrations to that inherent in density-controlled ordering for the metallic region.

3.2. Ion-site-site models

The necessity of more realistic modelling interactions that involve molecules, in particular, correct allowing for electrostatic interactions without resorting to multipole expansions caused the description of ion-molecular systems to be performed with the site-site approach [5, 55]. Here each molecule is represented as a set of sites, with the result that the ion-molecular and intermolecular potentials write as a sum of ion-site and site-site potentials:

$$U_{ss}(12) = \sum_{\alpha\beta} U_{ss}^{\alpha\beta}(r_{\alpha\beta}), \quad U_{as}(12) = \sum_{\alpha} U_{as}(r_{a\alpha}), \quad (3.12)$$

where $r_{a\alpha}$ and $r_{\alpha\beta}$ are the corresponding distances between the interacting sites.

In the process the system can be described with the site-site, ion-site, and ion-ion binary distribution functions giving the probability density of distribution of two sites that appear in the different particles. The site-site binary distribution functions $g_{ab}^{\alpha\beta}(r)$ are related to the intermolecular ones $g_{ab}(12)$ by

$$g_{ab}^{\alpha\beta}(r_{\alpha\beta}) = \int d\mathbf{l}_1 d\mathbf{l}_2 g_{ab}(12) \delta(\mathbf{r}_\alpha - \mathbf{r}_1 - \mathbf{l}_1^\alpha) \delta(\mathbf{r}_\beta - \mathbf{r}_2 - \mathbf{l}_2^\beta), \quad (3.13)$$

where \mathbf{r}_1 and \mathbf{r}_2 are the molecule center-of-mass coordinates, \mathbf{l}_1^α and \mathbf{l}_2^β the relative site coordinates.

Besides the functions $g_{ab}^{\alpha\beta}(r)$, of great importance in the site-site approach are also the intramolecular distribution functions $w_a^{\alpha\beta}(r)$ which have a δ -like shape. The presence of these functions modifies the Ornstein-Zernike equation which assumes the following matrix form in the site-site case:

$$\mathbf{h}(k) = \mathbf{S}(k)\mathbf{c}(k)\mathbf{S}(k) + \mathbf{S}(k)\mathbf{c}(k)\boldsymbol{\rho}\mathbf{h}(k), \quad (3.14)$$

where $h_{ab}^{\alpha\beta}(k)$ and $c_{ab}^{\alpha\beta}(k)$ are the Fourier-transforms of the corresponding pair and direct site-site correlation functions, ρ is the diagonal matrix comprising the elements $\rho_a \delta_{ab} \delta_{\alpha\beta}$. For rigid molecules, the elements of the matrix $\mathbf{S}(k)$ write as

$$S_{ab}^{\alpha\beta}(k) = \delta_{ab} \left(\delta_{\alpha\beta} + (1 - \delta_{\alpha\beta}) \frac{\sin kl_a^{\alpha\beta}}{kl_a^{\alpha\beta}} \right), \quad (3.15)$$

where $l_a^{\alpha\beta}$ is the distance between two sites of the same particle of sort a .

Following [56], first generalize the cluster expansions presented in the previous section to the site-site case. To do this, we divide the site-site potentials into the short- and long-range parts similarly to (2.1),

$$U_{ab}^{\alpha\beta}(r) = \varphi_{ab}^{\alpha\beta}(r) + \Phi_{ab}^{\alpha\beta}(r). \quad (3.16)$$

In the same way to (2.5), we present the site-site correlation functions in the form

$$\begin{aligned} c_{ab}^{\alpha\beta}(r) &= c_{ab}^{(0)\alpha\beta}(r) - \beta \Phi_{ab}^{\alpha\beta}(r) + \delta c_{ab}^{\alpha\beta}(r) = C_{ab}^{\alpha\beta}(r) + \delta c_{ab}^{\alpha\beta}(r), \\ h_{ab}^{\alpha\beta}(r) &= h_{ab}^{(0)\alpha\beta}(r) + G_{ab}^{\alpha\beta}(r) + \delta h_{ab}^{\alpha\beta}(r) = H_{ab}^{\alpha\beta}(r) + \delta h_{ab}^{\alpha\beta}(r), \end{aligned} \quad (3.17)$$

where the functions $H_{ab}^{\alpha\beta}(r)$ and $C_{ab}^{\alpha\beta}(r)$ are related by the site-site Ornstein-Zernike equations analogous to (3.14), which are closed by the MSA-like conditions

$$\begin{aligned} G_{ab}^{\alpha\beta}(r) + g_{ab}^{(0)\alpha\beta} &= 0 \quad \text{for } r < \sigma_{ab}^{\alpha\beta}, \\ C_{ab}^{\alpha\beta}(r) &= -\beta \Phi_{ab}^{\alpha\beta}(r) \quad \text{for } r > \sigma_{ab}^{\alpha\beta}, \end{aligned} \quad (3.18)$$

where $\sigma_{ab}^{\alpha\beta} = \frac{1}{2}(\sigma_a^\alpha + \sigma_b^\beta)$ are the sizes of the corresponding sites.

Assuming the site-site binary functions can be presented in the form similar to (2.2), the substitution (3.17) yields the expression

$$g_{ab}^{\alpha\beta}(r) = g_{ab}^{(0)\alpha\beta}(r) \exp \left(G_{ab}^{\alpha\beta}(r) + \delta h_{ab}^{\alpha\beta}(r) - \delta c_{ab}^{\alpha\beta}(r) + \delta E_{ab}^{\alpha\beta}(r) \right), \quad (3.19)$$

where $\delta h_{ab}^{\alpha\beta}(r)$ and $\delta c_{ab}^{\alpha\beta}(r)$ are related by the set of equations akin to (3.14) with $\mathbf{S}(k)$ replaced by $\mathbf{S}(k) + \rho \mathbf{H}(k)$, $\delta E_{ab}^{\alpha\beta}(r) = E_{ab}^{\alpha\beta}(r) - E_{ab}^{(0)\alpha\beta}(r)$.

As is evident, an exponential approximation similar to (2.12) can be chosen to be the zeroth approximation to the site-site binary functions:

$$g_{ab}^{\alpha\beta}(r) = g_{ab}^{(0)\alpha\beta}(r) \exp(G_{ab}^{\alpha\beta}(r)). \quad (3.20)$$

By way of illustration, we will enlarge on the simplified three-sort model consisting of positively and negatively charged ions of valences $Z_+ = -Z_- = Z_i$ and symmetric molecules with n_s sites, half of which have charge eZ_s , and the other $-eZ_s$. Figure 5 sketches three of such models. For simplicity sake all the ions and sites will be considered to be of the same size σ . In this case the set of site-site Ornstein-Zernike equations in the mean spherical approximation breaks up into two subsets

$$\begin{aligned} h^{(0)}(k) &= \mathbf{w}(k) \mathbf{c}^{(0)}(k) \mathbf{w}(k) + \mathbf{w}(k) \mathbf{c}^{(0)}(k) \rho \mathbf{h}^{(0)}(k), \\ \mathbf{G}(k) &= \mathbf{W}(k) \mathbf{C}^{(i)}(k) \mathbf{W}(k) + \mathbf{W}(k) \mathbf{C}^{(i)}(k) \rho \mathbf{G}(k), \end{aligned} \quad (3.21)$$

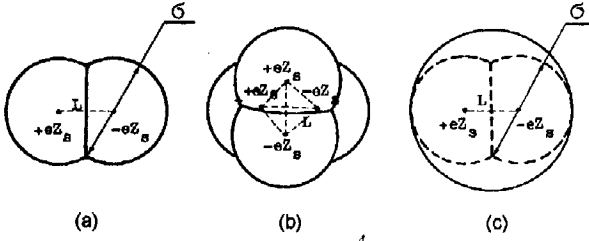


Figure 5. The models of molecules with (a) two and (b) four charged sites, and with (c) two auxiliary charged sites.

which are closed respectively by the conditions

$$\begin{aligned} \mathbf{h}^{(0)}(k) &= -1, \quad r < \sigma & \mathbf{G}(r) &= 0, \quad r < \sigma \\ & \text{and} & & & & \\ \mathbf{c}^{(0)}(r) &= 0, \quad r > \sigma & \mathbf{C}^{(i)}(r) &= -\beta \frac{e^2 Z_i^2}{r}, \quad r > \sigma \end{aligned} \quad (3.22)$$

where we introduced the two-dimensional matrices

$$\mathbf{G}(k) = \begin{pmatrix} G_{ii}(k) & G_{is}(k) \\ G_{si}(k) & G_{ss}(k) \end{pmatrix}$$

and $\mathbf{h}^{(0)}(k)$, $\mathbf{c}^{(0)}(k)$, $\mathbf{C}^{(i)}(k)$ along similar lines,

$$\begin{aligned} \mathbf{w}(k) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 + (n_s - 1)S(k) \end{pmatrix}, & \mathbf{W}(k) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 - S(k) \end{pmatrix}, \\ \boldsymbol{\rho} &= \begin{pmatrix} \rho_i & 0 \\ 0 & n_s \rho_s \end{pmatrix}, & \mathbf{Z}^2 &= \begin{pmatrix} Z_i^2 & Z_i Z_s \\ Z_s Z_i & Z_s^2 \end{pmatrix}, \end{aligned}$$

where $S(k) = \frac{\sin k l_s}{k l_s}$, l_s is the equilibrium distance between the sites in the molecule.

The former equation of (3.21) describes the basic model and was solved in [57]. The latter governs the screened potentials and its solution was considered in [58]. Solving these equations rests on employing the Winer-Hopf factorization technique. A peculiarity of its use in this case is due to the presence of the matrices $\mathbf{w}(k)$ and $\mathbf{W}(k)$. In particular, the Baxter factorizing functions for the screened potentials are

$$Q^{lm}(r) = q_{lm}(r) - Z_{lm} - \sum_{n \neq 0} \chi_{lm}^n \exp(-i \delta_n r), \quad (3.23)$$

where δ_n are the non-zero roots of the equation

$$1 - \frac{\sin(\delta_n L)}{\delta_n L} = 0, \quad L = l_s / \sigma.$$

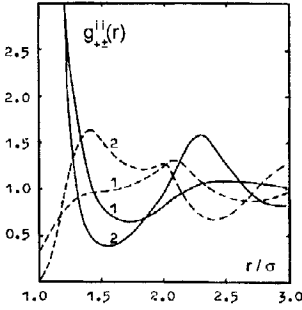


Figure 6. The ion-ion radial distribution functions for the ion-molecular system with polar hard dumb-bells at $\eta_s = 0.12$; $\kappa_{ss} = 2.18$, $L = 0.5$. Curves (1): $\eta_i = 0.25$, $\kappa_{ii} = 10.0$; (2): $\eta_i = 0.3$, $\kappa_{ii} = 13.8$; (—) $g_{+-}^{ii}(r)$; (---) $g_{++}^{ii}(r)$.

Although the short-range part of the Baxter function $q_{lm}(r) = 0$ for $r > \sigma$, the presence of $\mathbf{w}(k)$ brings about a discontinuity of the function $q_{ss}(r)$, determined by the condition

$$q_{ss}(l_s + 0) - q_{ss}(l_s - 0) = \frac{1}{24\eta_s L}, \quad (3.24)$$

where $\eta_s = \frac{1}{6}\pi\rho_s\sigma^3 n_s$. On the contrary to the ion-dipole case, the functions $q_{lm}(r)$ are more complicated and are not polynomials. The particular form of $q_{lm}(r)$ essentially depends on L . For densities η_s corresponding to a liquid solute, the last term in (3.23) can be neglected. This so-called zero-pole approximation (ZPA) is frequently used in analytical calculations.

The factorizing functions have a similar form when obtaining the distribution functions of the reference system as well, however with the long-range term Z_{lm} missing. The properties of the ion-molecular system under examination are governed by the set of six parameters, namely, the reduced ionic and molecular densities $\eta_i = \frac{1}{6}\pi\rho_i\sigma^3$ and η_s determining the reference-system properties, the reduced ionic and molecular parameters $\kappa_{ii}^2 = 24\eta_i e^2 Z_i^2 \beta \sigma^{-1}$ and $\kappa_{ss}^2 = 24\eta_s e^2 Z_s^2 \beta \sigma^{-1}$ responsible for the features of the screened-potentials, and also the parameters L and n_s specifying the structure of the molecule. Based on the EXP-like approximation (3.20), the studies of the site-site binary distribution functions make it apparent that, as for the ion-dipole system, three characteristic regions can be clearly distinguished depending on ratio between the parameters just listed: the regions of density-controlled ordering, solvation, and ion-controlled ordering. The distinctive behavior of the distribution functions for the last-named region is illustrated in Figure 6.

There has been made an investigation of the effect of the molecule shape and the molecule charge distribution on the characteristic features of the short-range order in the system, holding the ionic parameters η_i and κ_{ii}^2 as well as the reduced molecule dipole moment μ_s and the the packing factor η_s^0 constant ($\mu_s^2 = \frac{1}{2}\beta e^2 Z_s^2 L^2 n_s \sigma^{-1}$, $\eta_s^0 = \rho_s V_s$, V_s is the volume of the molecule). The behavior of the ion-ion distribution function is demonstrated not to be uniquely determined by the above-listed parameters but to be dependent on the molecule shape as well, which is enhanced with increasing μ_s^2 . This shape sensitivity of the ion-ion functions is pictured in Figure 7.

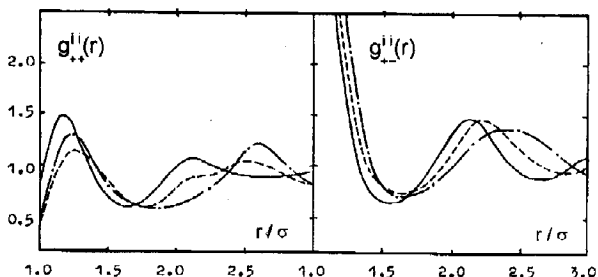


Figure 7. The ion-ion radial distribution functions for the ion-molecular systems with polar hard dumb-bells (—), polar hard tetraatomics (- - - -), and hard spheres with two charged auxiliary sites (- · - · -) at $L = 0.5$, $\eta_i = 0.03$, $\kappa_{ii} = 1.56$, $\eta_s^0 = 0.5$, $\mu_s = 7.95$.

3.3. Application of the computer simulation methods to describe the reference system

Correct description of the properties of electrolyte solutions requires using more realistic ion-molecular models. First of all, the short-range interactions should be described with smooth repulsive potentials instead of the hard-sphere model employed above. In [44] the Weeks-Chandler-Andersen (WCA) formalism [59] on taking account of softness of a short-range repulsion was extended to ionic systems, which gave good agreement between the calculated radial distribution functions of alkaline-haloid melts and experimental data.

However, in the majority of electrolyte solutions the short-range interaction is more complicated. Besides a repulsion, it comprises strongly attractive short-range interactions which can be strictly directed. In the case of water, for instance, it gives rise to a network of hydrogen bonds.

Such a reference system can be described by computer simulation methods, allowing for the long-range interactions by the cluster expansions considered in the previous section. This idea lies at the basis of the technique of description of aqueous electrolyte solutions combining the computer simulation methods with the analytical ones [60]. In line with the cluster expansions developed above, the proposed procedure implies dividing the starting potential into long- and short-range parts according to (2.1). In doing so, one has to match the conditions of computer simulation, $\varphi_{ab}(r) = 0$ and $\frac{\partial \varphi_{ab}}{\partial r} = 0$ for $r < r_c$, where $r_c < L/2$, and L is the simulation-box size. Clearly the cutoff parameter r_c has to be sufficiently large to include the potential well into $\varphi_{ab}(r)$ giving rise to hydrogen bonds and other association effects. A computer simulation is performed with the use of the short-range part $\varphi_{ab}(r)$, which yields the binary functions $g_{ab}^{cs}(r)$ for $r < L/2$. Next the Ornstein-Zernike equation

$$h_{ab}^{(0)}(r_{12}) - c_{ab}^{(0)}(r_{12}) = \sum_c \rho_c \int d\mathbf{r}_3 h_{ac}^{(0)}(r_{13}) c_{cb}^{(0)}(r_{32}) \quad (3.25)$$

with the closure

$$\begin{aligned} h_{ab}^{(0)}(r) &= h_{ab}^{cs} & \text{for } r < r_s \leq L/2, \\ c_{ab}^{(0)}(r) &= 0 & \text{for } r > r_s, \end{aligned} \quad (3.26)$$

is solved numerically to give the correlation functions of the reference system $h_{ab}^{(0)}(r)$ for $r > r_s$ and $c_{ab}^{(0)}(r)$ for $r < r_s$.

Then, to calculate the screened potentials, a set of equations like to (2.7) is solved with the closure (2.8)-(2.9) replaced by

$$\begin{aligned} H_{ab}(r) &= h_{ab}^{cs}(r) & \text{for } r \leq d_{ab}, \\ c_{ab}(r) &= c_{ab}^{(0)}(r) - \beta \Phi_{ab}(r) & \text{for } r > d_{ab}, \end{aligned} \quad (3.27)$$

where the parameters d_{ab} specify the optimization region. Besides the area where $g_{ab}(r) = 0$, there is good reason to include into it intramolecular parts of $g_{ab}(r)$ as well.

The gained solution gives the screened potentials $G_{ab}(r)$ by (2.5) to yield the binary distribution functions with the known relations. The technique worked out makes it possible not only to correctly allow for the contribution of long-range interactions, but also to extend the correlation functions to the distances much larger than a computer-simulation box, which is important in calculation of the corresponding integral characteristics.

In [60-62] the devised approach has been employed to examine water in the framework of the Bopp-Jancso-Heinzinger (BJH) model [63]. The binary distribution functions calculated already in the simplest approximation

$$g_{ab}(r) = g_{ab}^{(0)}(r) + G_{ab}(r) \quad (3.28)$$

for the distances $r < L/2$ actually coincide with the computer-simulation data using the Ewald method. At the same time the knowledge of $g_{ab}(r)$ for $r > L/2$ is found to be essential for calculation of the thermodynamic and structure properties of water as well as the behavior of its structure factors in the region of a small wave vector k . The results for the intermolecular part of the internal energy U , the pressure P , the isothermal compressibility κ_T , and the dielectric constant ϵ obtained in this way are tabulated in Table 1. As is seen from the table, proper allowing for the electrostatic part of the interaction improves agreement with experimental data greatly. The extension of $g_{ab}(r)$ to larger distances appeared to be essential also for calculation of the structure factors in the small-wave-vector region. In particular, the calculations revealed the presence of a pre-peak in the structure factor of water at 0.6 \AA^{-1} , which is an indication of the existence of spatial correlations between the tetrahedral-like water configurations at the distances about 10 \AA .

4. Taking account of associative interactions

As we noted above, for real electrolyte solutions, the short-range potential needs to include besides repulsions also strongly-attractive interactions giving rise to various complexes and associates. Of intermolecular interactions, these are the specific orientationally-directed short-range ones resulting in hydrogen bonds and other formations common to aqueous and other solutions. The strongly-attractive part of interionic interactions is responsible for familiar ionic associates and that of ion-molecular interactions for solvative ionic structures being peculiar to electrolyte solutions. Thus, in the case of electrolyte solutions it is appropriate to divide the interparticle potentials into three parts instead of (2.1),

$$U_{ab}(12) = \varphi_{ab}(12) + \Psi_{ab}(12) + \Phi_{ab}(12), \quad (4.1)$$

Table 1. Thermodynamic and dielectric properties of water for the central-force model

	MD with Ewald summ.	MD with switching function	shifted-force potential model	BJH model	expt.
U, kJ/mol	-39.70 ¹⁾	-41.25 ⁴⁾	-34.40 ⁵⁾	-40.63 ⁵⁾	-41.42
$Z = \beta P/\rho$	2.7 ²⁾	2.36 ± 0.06 ⁴⁾	2.7 ⁵⁾	1.3 ⁵⁾	0.07
$\kappa_T, \text{Pa}^{-1} \cdot 10^{-11}$	33.00 ³⁾	-	-	41.36 ⁵⁾	45.25
ϵ	77 ± 14 ²⁾	-	-	79.29 ⁶⁾	80

- 1) F. H. Stillinger, A. Rahman J.Chem.Phys., 1978, 68, 666
- 2) D. E. Smith, A. D. J. Haymet J.Chem.Phys., 1992, 96, 8450
- 3) I. Ruff, D. J. Diestler, J.Chem.Phys., 1990, 93, 2032
- 4) T. A. Andrea, W. C. Swope, H. C. Andersen, Mol.Phys., 1983, 79, 4576
- 5) from [63]
- 6) from [61].

where $\varphi_{ab}(12)$ is the short-range repulsion part of the potential, $\Psi_{ab}(12)$ the short-range strongly-attractive one which will be termed associative below, $\Phi_{ab}(12)$ the long-range one.

The distinctive feature of associative interactions is that the bonds arising due to them are saturated. Since they can be allowed for correctly by expansion in terms of activity [18, 64-65], the problem of description of liquids and solutions with associative interactions requires combining the traditional methods to take into account short- and long-range interactions with activity expansions to do associative ones. In the process the topological reduction of the diagrams results in the corresponding generalization of the Ornstein-Zernike equations, in which due to the presence of associative interactions the particle densities break up into a sum of densities, each being a density of complexes existing in the system. The corresponding technique of description of molecular systems in the framework of the multidensity formalism was proposed by Wertheim [14-15] and in [16] was extended to central-force-like spherically-symmetric models. Below we will enlarge on the simplest approximation that considers only dimers, although generalization to the case of more complicated formations, among them polymer chains, a network of bonds, etc., presents no fundamental problems.

In the dimer approximation the particle density breaks up into two ones,

$$\rho_a = \rho_a^0 + \rho_a^1, \quad (4.2)$$

where ρ_a^0 and ρ_a^1 are respectively the densities of non-associated and associated particles of sort a . Accordingly the pair correlation functions

$$h_{ab}(12) = h_{ab}^{00}(12) + x_a h_{ab}^{00}(10) + x_b h_{ab}^{00}(01) + x_a x_b h_{ab}^{00}(11), \quad (4.3)$$

where $x_a = \rho_a^0/\rho_a$, and $h_{ab}^{\alpha\beta}(12)$ are the partial pair correlation functions, are related to the corresponding direct correlation functions $c_{ab}^{\alpha\beta}(12)$ by the

associative Ornstein-Zernike equations which in the two-density formalism write in the matrix form as

$$\mathbf{h}_{ab}(12) = \mathbf{c}_{ab}(12) + \sum_c \int d3\mathbf{c}_{ac}(13)\rho_c \mathbf{h}_{cb}(32), \quad (4.4)$$

where the two-dimensional matrices are

$$\mathbf{h}_{ab} = \begin{pmatrix} h_{ab}^{00} & h_{ab}^{01} \\ h_{ab}^{10} & h_{ab}^{11} \end{pmatrix}, \quad \mathbf{c}_{ab} = \begin{pmatrix} c_{ab}^{00} & c_{ab}^{01} \\ c_{ab}^{10} & c_{ab}^{11} \end{pmatrix}, \quad \boldsymbol{\rho}_a = \begin{pmatrix} \rho_a & \rho_a^0 \\ \rho_a^0 & 0 \end{pmatrix}, \quad (4.5)$$

and the upper indices denote non-associated or associated particles.

The densities ρ_a and ρ_a^0 are related by the self-consistent equation

$$\rho_a = \rho_a^0 + \rho_a^0 \sum_b \rho_b^0 \int d2g_{ab}^{00}(12)f_{ab}^{as}(12), \quad (4.6)$$

where $g_{ab}^{00}(12) = 1 + h_{ab}^{00}(12)$, and $f_{ab}^{as}(12) = \exp(-\beta\Psi_{ab}(12)) - 1$.

The diagram analysis of the Mayer cluster expansions enables the partial distribution functions to be presented as

$$\begin{aligned} g_{ab}^{00}(12) &= \exp(-\beta\varphi_{ab}(12) - \beta\Phi_{ab}(12) + \tau_{ab}^{00}(12)), \\ g_{ab}^{01}(12) &= g_{ab}^{00}(12)\tau_{ab}^{01}(12), \\ g_{ab}^{10}(12) &= g_{ab}^{00}(12)\tau_{ab}^{10}(12), \\ g_{ab}^{11}(12) &= g_{ab}^{00}(12)(\tau_{ab}^{11}(12) + \tau_{ab}^{10}(12)\tau_{ab}^{01}(12) + f_{ab}^{as}(12)), \end{aligned} \quad (4.7)$$

$$\text{where} \quad \tau_{ab}^{\alpha\beta}(12) = h_{ab}^{\alpha\beta}(12) - C_{ab}^{\alpha\beta}(12) + E_{ab}^{\alpha\beta}(12). \quad (4.8)$$

As before, present the partial correlation functions in the form

$$\begin{aligned} h_{ab}^{\alpha\beta}(12) &= h_{ab}^{(0)\alpha\beta}(12) + G_{ab}^{\alpha\beta}(12) + \delta h_{ab}^{\alpha\beta}(12) = \\ &= H_{ab}^{\alpha\beta}(12) + \delta h_{ab}^{\alpha\beta}(12), \\ c_{ab}^{\alpha\beta}(12) &= c_{ab}^{(0)\alpha\beta}(12) - \beta\Phi_{ab}(12)\delta_{\alpha 0}\delta_{\beta 0} + \delta c_{ab}^{\alpha\beta}(12) = \\ &= C_{ab}^{\alpha\beta}(12) + \delta c_{ab}^{\alpha\beta}(12), \end{aligned} \quad (4.9)$$

where $h_{ab}^{(0)\alpha\beta}(12)$ and $c_{ab}^{(0)\alpha\beta}(12)$ are the corresponding partial correlation functions in the absence of the long-range interactions $\Phi_{ab}(12)$, $G_{ab}^{\alpha\beta}(12)$ are the screened potentials defined through the functions $H_{ab}^{\alpha\beta}(12)$ and $C_{ab}^{\alpha\beta}(12)$ related by the associative Ornstein-Zernike equations akin to (4.4) with the associative mean-spherical-approximation-like (AMSA) closure

$$\begin{aligned} H_{ab}^{\alpha\beta}(12) &= -\delta_{\alpha 0}\delta_{\beta 0} \\ &\quad \text{for } r < \sigma_{ab}, \\ C_{ab}^{\alpha\beta}(12) &= -\beta\Phi_{ab}(12)\delta_{\alpha 0}\delta_{\beta 0} + g_{ab}^{00}(12)f_{ab}^{(as)}(12)\delta_{\alpha 1}\delta_{\beta 1} \\ &\quad \text{for } r > \sigma_{ab}. \end{aligned} \quad (4.10)$$

Substituting (4.9) into (4.7) gives

$$\begin{aligned}
g_{ab}^{00}(12) &= g_{ab}^{(0)00}(12) \exp \left(G_{ab}^{00}(12) + \delta\tau_{ab}^{00}(12) \right), \\
g_{ab}^{01}(12) &= \exp \left(G_{ab}^{00}(12) + \delta\tau_{ab}^{00}(12) \right) \times \\
&\quad \times \left(g_{ab}^{(0)01}(12) + g_{ab}^{(0)00}(12)(G_{ab}^{01}(12) + \delta\tau_{ab}^{01}(12)) \right), \\
g_{ab}^{11}(12) &= \exp \left(G_{ab}^{00}(12) + \delta\tau_{ab}^{00}(12) \right) (g_{ab}^{(0)11}(12) + \\
&\quad + g_{ab}^{(0)10}(12)(G_{ab}^{01}(12) + \delta\tau_{ab}^{01}(12)) + \\
&\quad + g_{ab}^{(0)01}(12)(G_{ab}^{10}(12) + \delta\tau_{ab}^{10}(12)) + \\
&\quad + g_{ab}^{(0)00}(12)((G_{ab}^{10}(12) + \delta\tau_{ab}^{10}(12))(G_{ab}^{01}(12) + \delta\tau_{ab}^{01}(12)) + \\
&\quad + G_{ab}^{11}(12) + \delta\tau_{ab}^{11}(12))), \tag{4.11}
\end{aligned}$$

where $\delta\tau_{ab}^{\alpha\beta}(12) = \delta h_{ab}^{\alpha\beta}(12) - \delta c_{ab}^{\alpha\beta}(12) - \delta E_{ab}^{\alpha\beta}(12)$.

Setting $\delta E_{ab}^{\alpha\beta}(12) = 0$ for closure, we arrive at the associative reference hypernetted chain (ARHNC) approximation.

Putting $\delta\tau_{ab}^{\alpha\beta}(12) = 0$, we get the exponential approximation (EXP2),

$$\begin{aligned}
g_{ab}^{00}(12) &= g_{ab}^{(0)00}(12) \exp(G_{ab}^{00}(12)), \\
g_{ab}^{01}(12) &= \left(g_{ab}^{(0)01}(12) + g_{ab}^{(0)00}(12)G_{ab}^{01}(12) \right) \exp(G_{ab}^{00}(12)), \\
g_{ab}^{11}(12) &= \left(g_{ab}^{(0)11}(12) + g_{ab}^{(0)01}(12)G_{ab}^{01}(12) + \right. \\
&\quad + g_{ab}^{(0)01}(12)G_{ab}^{10}(12) + g_{ab}^{(0)00}(12)(G_{ab}^{10}(12)G_{ab}^{01}(12) + \\
&\quad \left. + G_{ab}^{11}(12)) \exp(G_{ab}^{00}(12)), \tag{4.12}
\end{aligned}$$

which can serve as a zeroth iteration when building up cluster expansions.

It should be pointed out that unlike the approaches discussed in the previous section, different approximations yield distinct forms of the functions $g_{ab}^{00}(12)$, by (4.6) resulting in distinct values of the concentration of non-associated particles as well. Therefore even the reference system is dependent on the long-range contribution into $g_{ab}^{00}(12)$.

Solving the associative version of the MSA and obtaining the screened potentials employ the scheme of orientationally-invariant expansions and the Winer-Hopf factorization technique. In this case the Wertheim-Baxter factorizing functions are similar to (3.7) but with the difference that they have a discontinuity at the point $r = l_s = \sigma$ due to the presence of associative interactions as in the site-site case.

An analytical solution for dimerizing hard spheres in the Percus-Yevick approximation is found in [67] and then generalized to the multicomponent mixture of dimerizing hard spheres [68]. The case of $l_s < \sigma$ is studied in [69-70], and in [71-72] the results are extended to polymerizing hard spheres. The most general case has been considered in the recent work [73].

At present, much efforts are underway to apply the devised technique to describe various ionic and ion-molecular systems. The AMSA solution for dimerizing ionic systems with equal sizes has been found in [17] and extended to the multicomponent case with different sizes in [74-75].

Notice that associative effects can be brought about by electrostatic interactions as well. Recently this has been used to treat the model of charged hard spheres [18-19]. The associative potential is presented by a sum of the Yukawa-like potentials separated out from the pure Coulomb interaction. The thermodynamic and structure properties of ionic systems calculated in this way are in good agreement with computer-simulation data.

A peculiar associative version of the integral equations arises for polyelectrolytes. Due to the strong asymmetry in sizes and charges we can treat each counterion as singly bondable, while each polyion can bind to an arbitrary number of counterions. This investigation was carried out in the framework of the hypernetted chain approximation [76-77]. Recently analytical solutions have been found first for the corresponding reference system [78] and thereafter in the mean spherical approximation as well [79].

5. Spatially inhomogeneous ion-molecular systems

The presence of a spatial inhomogeneity modifies strongly the results discussed above. With an interface present, the unary distribution function depends on the distance of the particle from the interface, and the binary one does on the distance of the two particles from the surface as well as on their separation. In particular, the Ornstein-Zernike equation for spatially inhomogeneous systems assumes the form

$$h_{ab}(12) = c_{ab}(12) + \sum_c \int d3 \rho_c(3) c_{ac}(13) h_{cb}(32) \quad (5.1)$$

which has to be complemented, besides a usual closure, with a relation between the unary functions $\rho_a(1)$ and the pair correlation functions. Such a relation can be chosen to be, for instance, the first of the Bogolubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy [2, 5] or the Wertheim-Lovett-Mou-Buff (WLMB) relation [5, 80]. Therefore the spatial inhomogeneity causes modification of the above-discussed cluster expansions of the free energy and the distribution functions. The corresponding cluster expansions for spatially confined ion-molecular systems by means of the method of collective variables were obtained in [81-84].

As before, the first step to use cluster expansions is calculation of screened potentials. Commonly such a problem is quite complicated for analytical description when taking account of short-range interactions in a reference system, and considering the unary and binary distribution functions self-consistently. Therefore we will restrict the discussion to the case of point particles. In [85] the equation (5.1) is solved for the system of point ions, approximating their distribution by the function

$$\rho_a(1) = \frac{\rho_a^{(+)} \exp(az_1) + \rho_a^{(-)} \exp(-az_1)}{\exp(az_1) + \exp(-az_1)}, \quad (5.2)$$

where $\rho_a^{(+)}$ and $\rho_a^{(-)}$ are the bulk densities of ion of sort a above and below the interface, respectively; the smoothness parameter a has to be determined from the relation between $\rho_a(1)$ and the binary distribution functions.

In the case of point ions we have

$$\begin{aligned} c_{ab}(12) &= -\beta\Phi_{ab}(12), \\ h_{ab}(12) &= G_{ab}(12). \end{aligned}$$

Then the Fourier transformation turns equation (5.1) into

$$P_+(k_1)\tilde{g}(k_1 - ia) + P_-(k_1)\tilde{g}(k_1 + ia) = -\frac{8\pi^2\beta}{\epsilon}\delta(k_1 + k_2), \quad (5.3)$$

where

$$\begin{aligned} P_{\pm}(k_1) &= k_1^2 + \alpha_{\pm}^2(k_s), \\ \alpha_{\pm}^2(k_s) &= k_s^2 + \kappa_{\pm}^2, \end{aligned} \quad (5.4)$$

k_1 is the projection of the vector \mathbf{k}_1 on the axis oz , k_s is the projection of the vector $\mathbf{k}_1 - \mathbf{k}_2$ on the interface plane, κ_{\pm} are the bulk values of the inverse Debye radius in the upper (+) and lower (-) half-planes, $\tilde{g}(k)$ the Fourier transform of the auxiliary function related to the screened potential by

$$g(12) = \frac{1}{e^2 Z_a Z_b} \frac{G_{ab}}{\exp(az_1) + \exp(az_2)}, \quad (5.5)$$

ϵ is the dielectric constant of the medium. Because the ions are point, factorization of the equation with an argument shift (5.3) is possible in the Fourier space. It consists in presenting the ratio of the binomials $P_+(k_1)$ and $P_-(k_1)$ as

$$\frac{P_-(k_1)}{P_+(k_1)} = \frac{\tilde{Q}(k_1 + ia)}{\tilde{Q}(k_1 - ia)}. \quad (5.6)$$

Here the function $\tilde{Q}(q)$ has a meaning of the Wertheim-Baxter factorizing function similarly to (3.7), and from (5.5) is equal to

$$Q(k_1) = \frac{\Gamma((a + \alpha_+(k_s) + ik_1)/2a)\Gamma((a + \alpha_-(k_s) - ik_1)/2a)}{\Gamma((a + \alpha_+(k_s) - ik_1)/2a)\Gamma((a + \alpha_-(k_s) + ik_1)/2a)}, \quad (5.7)$$

where $\Gamma(z)$ is the Gamma-function.

Factorizing equation (5.3) and simple rearranging give the screened potential as

$$\begin{aligned} G_{ab}(12) &= -\frac{1}{2\pi a\epsilon}\beta e^2 Z_a Z_b \cosh(az_1) \int_0^{\infty} k_s dk_s J_0(k_s s_{12}) \times \\ &\times \int_{-\infty}^{\infty} dk_1 \frac{1}{Q(k_1)} \exp(-ik_1 z_1) \times \\ &\times \int_{-\infty}^{\infty} dk_2 \frac{Q(-k_2 - ia)}{P_+(k_2)} \frac{\exp(-ik_2 z_2)}{\cosh(\frac{\pi}{2a}(k_1 + k_2))}. \end{aligned} \quad (5.8)$$

In the case of an infinitely thin interface region between two electrolyte solutions being in contact ($a \rightarrow \infty$), equation (5.3) goes over into the familiar Riemann problem [86]

$$P_+(k_1)\tilde{G}_+(k_1) - P_-(k_1)\tilde{G}_-(k_1) = -\frac{8\pi^2\beta}{\epsilon}\delta(k_1 + k_2), \quad (5.9)$$

where $\tilde{G}_+(k_1)$ and $\tilde{G}_-(k_1)$ are analytical in respectively the upper and lower parts of the function complex plane, and satisfy (5.9) on the real axis. The Fourier transform of the screened potential is defined by the relation

$$\tilde{G}(k_1) = \tilde{G}_+(k_1) - \tilde{G}_-(k_1). \quad (5.10)$$

The problem (5.9) permits extending to an ion-molecular two-phase system of point particles. In [87-88] there have been obtained the expressions for the screened potentials of a spatially inhomogeneous two-phase system with a planar interface specified by

$$\rho_a(1) = \begin{cases} n_a^{(+)} & \text{for } z_1 > 0 \\ n_a^{(-)} & \text{for } z_1 < 0 \end{cases} \quad (5.11)$$

in the case of molecules possessing quadrupole as well as dipole moments.

For the sake of simplicity, restrict the discussion to a two-phase ion-dipole system. In this case the Riemann problem writes as

$$\epsilon_+ P_+(k_1)\tilde{G}_+(k_1) - \epsilon_- P_-(k_1)\tilde{G}_-(k_1) = H(k_1), \quad (5.12)$$

where

$$\begin{aligned} P_{\pm}(k_1) &= k_1^2 + \alpha_{\pm}^2(k_s), \\ \alpha_{\pm}^2(k_s) &= k_1^2 + \kappa_{\pm}^2/\epsilon_{\pm}, \end{aligned} \quad (5.13)$$

ϵ_{\pm} is the bulk value of the self-consistent part of the dielectric permittivity respectively in the upper and lower half-spaces. Unlike (5.9), the constant term of the Riemann problem is

$$H(k_1) = -4\pi\beta\delta(k_1 + k_2) - (\epsilon_+ - \epsilon_-)G_0k_1, \quad (5.14)$$

where G_0 is determined from the condition

$$k_1\tilde{G}_{\pm}(k_1) \rightarrow 0 \quad \text{as } k \rightarrow \pm\infty. \quad (5.15)$$

Factorizing equation (5.12) consists in presenting the ratio $P_-(k_1)/P_+(k_1)$ as that of the functions $Q_+(k_1)/Q_-(k_1)$ analytical respectively in the upper and lower half-planes of the complex plane. The Wertheim-Baxter functions in this case are

$$Q_+(k_1) = \frac{k_1 + i\alpha_-(k_s)}{k_1 + i\alpha_+(k_s)}, \quad Q_-(k_1) = \frac{k_1 - i\alpha_+(k_s)}{k_1 - i\alpha_-(k_s)}. \quad (5.16)$$

Dividing both the sides of equation (5.12) by $P_+(k_1)Q_+(k_1)$ and presenting the constant term as the difference of functions analytical in the upper and

lower half-planes of the complex plane yields a solution of the Riemann problem. Making use of the condition (5.15) gives the screened potentials of a two-phase ion-dipole system of point particles with a planar interface [87]

$$\begin{aligned}
 G_{ab}(12) &= -\hat{Q}_a(\vec{\nabla}_1)\hat{Q}_b(\vec{\nabla}_2)\beta\frac{1}{\epsilon_+}\int_0^\infty k_s dk_s J_0(k_s, s_{12}) \times \\
 &\times \left(\frac{1}{\alpha_+(k_s)} \exp(-\alpha_+(k_s)|z_1 - z_2|) + \right. \\
 &+ \frac{1}{\alpha_+(k_s)} \frac{\epsilon_+ \alpha_+(k_s) - \epsilon_- \alpha_-(k_s)}{\epsilon_+ \alpha_+(k_s) + \epsilon_- \alpha_-(k_s)} \times \\
 &\times \exp(-\alpha_+(k_s)(z_1 - z_2)) \quad \text{for } z_1, z_2 > 0;
 \end{aligned} \tag{5.17a}$$

$$\begin{aligned}
 G_{ab}(12) &= -\hat{Q}_a(\vec{\nabla}_1)\hat{Q}_b(\vec{\nabla}_2)\beta\int_0^\infty k_s = dk_s J_0(k_s, s_{12}) \times \\
 &\times \frac{2}{\epsilon_+ \alpha_+(k_s) + \epsilon_- \alpha_-(k_s)} \times \\
 &\times \exp(-\alpha_+(k_s)z_1 + \alpha_-(k_s)z_2) \quad \text{for } z_1 > 0, z_2 < 0;
 \end{aligned} \tag{5.18b}$$

$$\begin{aligned}
 G_{ab}(12) &= -\hat{Q}_a(\vec{\nabla}_1)\hat{Q}_b(\vec{\nabla}_2)\beta\frac{1}{\epsilon_-}\int_0^\infty k_s dk_s J_0(k_s, s_{12}) \times \\
 &\times \left(\frac{1}{\alpha_-(k_s)} \exp(-\alpha_+(k_s)|z_1 - z_2|) - \right. \\
 &- \frac{\epsilon_+ \alpha_+(k_s) - \epsilon_- \alpha_-(k_s)}{\epsilon_+ \alpha_+(k_s) + \epsilon_- \alpha_-(k_s)} \times \\
 &\times \exp(\alpha_-(k_s)(z_1 + z_2))) \quad \text{for } z_1, z_2 < 0.
 \end{aligned} \tag{5.19c}$$

The screened potentials gained are in complete agreement with those obtained by other means in [89-90]. It should be noted that they go over into the corresponding bulk expressions as the particles are away from the interface because the image forces fall off rapidly with distance from the surface. In the absence of an ion subsystem in one of the two half-spaces the two-particle correlations along the interface have a dipole-like decay character, no matter what half-space the particles are located in.

The expressions (5.17) allow to get one-particle screened potentials defined as a screened interaction of the particle with its own electrostatic image:

$$\begin{aligned}
G_a(1) &= -\hat{Q}_a(\vec{\nabla}_1)\hat{Q}_a(\vec{\nabla}_1)\frac{1}{\epsilon_+}\beta\int_0^\infty k_s dk_s J_0(k_s s_{12})\times \\
&\times \frac{1}{\alpha_+(k_s)}\frac{\epsilon_+\alpha_+(k_s) - \epsilon_-\alpha_-(k_s)}{\epsilon_+\alpha_+(k_s) + \epsilon_-\alpha_-(k_s)}\times \\
&\times \exp(-2\alpha_+(k_s)z_1) \qquad \text{for } z_1 > 0.
\end{aligned} \tag{5.20}$$

A similar relation holds in the case of $z_1 < 0$.

The one- as well as two-particle screened potentials made it possible to examine the distribution of ions and dipole molecules near an interface within the framework of the two-phase ion-molecular model of point particles. Enrichment or depletion of the upper half-space in ions have been demonstrated to occur depending on the dielectric constants ratio, $\epsilon_+ < \epsilon_-$ or $\epsilon_+ > \epsilon_-$, respectively. Therewith the thickness of the adsorption layer for ions is proportional to the Debye radius in the given half-space, whereas that for dipoles amounts to several molecular layers. A tendency for ionic ordering of the interface layer arises with increase in the electrolyte concentration.

Another way of description of spatially confined ion-molecular systems is based on the Henderson-Abraham-Barker (HAB) approach [91] which regards the unary distribution function as the wall-particle binary one. This permits the bulk results to be drawn on for description of the surface properties by making the size of one sort of particles tend to infinity and their concentration do to zero. Although this approach offers means of taking account of short-range interactions with relative ease, studying the effect of images on the interface structure requires the corresponding diagrams in the cluster expansions to be calculated and resumed [92-93]. The calculations carried out in [94-96] make it possible to inquire into the character of ion and dipole ordering in dependence on the surface charge and the ionic concentration. Within the framework of the HAB model, recent attempts are made to allow for the influence of association effects in ionic systems [97-98] as well as a surface crystalline structure [99-101] on the near-surface properties.

A vital issue in description of an interface is investigation of changes in the quantum properties of particles near the surface. We considered such a problem within the model of a hydrogen-like atom near a hard wall [102-106]. This approach can be used for description of shallow donors and excitons located near a semiconductor-electrolyte interface. The results obtained revealed that the surface causes a significant decrease in the ionization energy of a donor as well as exciton [102], and yet little affects the binding energy of a donor-exciton complex [103-104]. Further studies involve more realistic models allowing for finiteness of a surface potential barrier [105], a surface structure, and a self-consistent action of adsorbed particles on the adsorbate.

References

- [1] Debye P., Hückel E. On Theory of Electrolyte. // Phys. Z., 1923, vol. 24, No 9, p. 185-206.
- [2] Bogolubov N.N. The problems of dynamic theory in statistical physics. // Gostehizdat, Moscow, 1946, p. 119, (in Russian).

- [3] Yukhnovsky I.R. Application of collective variables and taking account of short-range forces in a system of charged particles. // *Sov. Phys-JETP*, 1958, vol. 34, No 2, p. 379-389, (in Russian).
- [4] Yukhnovsky I.R. On the statistical theory of ionic systems. // *Ukr. Fiz. Zhurn.*, 1959, vol. 4, No 2, p. 167-176, (in Ukrainian)
- [5] Yukhnovsky I.R., Holovko M.F. The statistical theory of the classical equilibrium systems. *Naukova Dumka*, Kyiv, 1980, p. 372, (in Ukrainian)
- [6] Golovko M.F., Yukhnovsky I.R. Approaches to the many-body theory of dense ion-dipole plasma. Application to ionic solvation. In: *Chemical Physics of Solvation*, Elsevier, Amsterdam, 1985, vol. A, p. 207-262.
- [7] Yukhnovsky I.R. Separating out a reference system in the method of collective variables, Preprint Inst. Theor. Phys., Acad. Sci. Ukr. SSR: ITP-74-149R, Kiev, 1974, p. 35, (in Russian)
- [8] Holovko M.F., Pizio O.O. Reference-system taking account of short-range interactions in the theory of ionic systems. // *Ukr. Fiz. Zhurn.*, 1976, vol. 21, No 4, p. 653-662, (in Russian).
- [9] Yukhnovsky I.R. On the statistical theory of condensed systems comprising long- and short-range interactions, Preprint Inst. Theor. Phys., Acad. Sci. Ukr. SSR: ITP-79-133R, Kiev, 1979, p. 35, (in Russian).
- [10] Yukhnovsky I.R. On the statistical theory of mixed ion-dipole systems of interacting particles. // *Dokl. AN USSR*, 1961, vol. 138, No 6, p. 1317-1320, (in Ukrainian).
- [11] Yukhnovsky I.R. Spatially distributed particles in the method of collective variables. // *Ukr. Fiz. Zhurn.*, 1962, vol. 7, No 3, p. 267-277, (in Ukrainian).
- [12] Yukhnovsky I.R., Nekrot A.O. The free energy and the binary distribution functions of an ion-dipole system. // *Ukr. Fiz. Zhurn.*, 1963, vol. 8, No 6, p. 635-644, (in Ukrainian).
- [13] Yukhnovsky I.R., Holovko M.F. The statistical theory of equilibrium systems of particles of a complex electrostatic structure. // *Ukr. Fiz. Zhurn.*, 1969, vol. 14, No 5, p. 705-719, (in Ukrainian).
- [14] Wertheim M.S. Fluids with highly directional attractive forces. I, II // *J. Stat. Phys.*, 1984, vol. 35, No 1/2, p. 19-34; 35-47.
- [15] Wertheim M.S. Fluids with highly directional attractive forces. III, IV // *J. Stat. Phys.*, 1986, vol. 42, No 3/4, p. 459-476; 477-492.
- [16] Kalyuzhnyi Yu.V., Stell G. On the effects of association in fluids with spherically symmetric interactions. // *Mol. Phys.*, 1993, vol. 78, No 5, p. 1247-1258; Kalyuzhnyi Yu.V., Holovko M.F. The statistical theory of the effects of association in fluids with spherically symmetric interactions. // *Phys. Liq. State*, (in Ukrainian, to be published).
- [17] Holovko M.F., Kalyuzhnyi Yu.V. On the effects of association in the statistical theory of ionic systems. // *Mol. Phys.*, 1991, vol. 73, No 6, p. 1145-1157.
- [18] Kalyuzhnyi Yu.V., Holovko M.F., Haymet A.D.J. Integral equation theory for associating liquids; Weakly associated 2-2 electrolytes. // *J. Chem. Phys.*, 1991, vol. 95, No 12, p. 9151-9164.
- [19] Kalyuzhnyi Yu.V., Holovko M.F. An analytical study of the effects of association in the 2-2 electrolyte solution. // *Mol. Phys.*, 1993, vol. 80, No 5, p. 1165-1176.
- [20] Holovko M.F. Cluster expansions and integral equations in the op-

- timized cluster theory, Preprint Inst. Theor. Phys., Acad. Sci. Ukr. SSR: ITP-84-187R, Kiev, 1985, p. 22, (in Russian).
- [21] Holovko M.F. Cluster expansions and integral equations for the binary distribution functions with short-range interactions allowed for in a reference system, Modern problems of statistical physics, vol. 1 (Naukova Dumka, Kiev, 1989), p. 54-58, (in Russian).
- [22] Golovko M.F., Krienke H. Generalized virial expansions. // Mol. Phys., 1989, vol. 68, No 4, p. 967-977.
- [23] Morita T., Hiroike K. A new approach to the theory of classical fluids. // Progr. Theoret. Phys., 1960, vol. 23, No 6, p. 1003-1027.
- [24] Stell G. Cluster expansions for classical systems in equilibrium. In: The equilibrium theory of classical fluids, ed. H. Frisch, J. Lebowitz, Benjamin, New York, 1964, p. 171-267.
- [25] Andersen H.C., Chandler D. Optimized cluster expansions for classical fluids. // J. Chem. Phys., 1972, vol. 57, No 5, p. 1918-1929.
- [26] Yukhnovsky I.R., Holovko M.F., Vysochansky V.S. The binary distribution functions of mixed ion-molecular systems. // Phys. Liquid State, 1978, No 6, p. 101-104, (in Russian).
- [27] Yukhnovsky I.R., Grouba V.D., Golovko M. F., Kessler Yu.M. The role of the ion-molecule and molecule-molecule interactions in the formation of the two ion average force interaction potential, Preprint Inst. Theor. Phys., Acad. Sci. Ukr. SSR: ITP-83-84E, Kiev, 1983, p. 44.
- [28] Yukhnovsky I.R., Popov A.V., Holovko M.F. The binary distribution functions of ion-dipole systems in the third-cluster-coefficient approximation. // Ukr. Fiz. Zhurn., 1986, vol. 31, No 4, p. 618-625, (in Russian).
- [29] Yukhnovsky I.R., Holovko M.F., Popov A.V. The binary distribution functions of ion-dipole systems in the fourth-cluster-coefficient approximation. // Ukr. Fiz. Zhurn., 1986, vol. 31, No 5, p.789-794, (in Russian).
- [30] Blum L., Torruella A.J. Invariant expansion for two-body correlations: thermodynamic functions, scattering, and the Ornstein-Zernike equations. // J. Chem. Phys., 1972, vol. 56, No 1, p. 303-310.
- [31] Blum L. Invariant expansion. // J. Chem. Phys., 1972, vol. 57, No 5, p. 1862-1869.
- [32] Davydov A.S. Quantum Mechanics. Nauka, Moscow, 1973, p. 703, (in Russian).
- [33] Wertheim M.S. Solution of the Percus-Yevick integral equation. // J. Math. Phys., 1964, vol. 5, No 3, p. 643-654.
- [34] Baxter R.J. Ornstein-Zernike relation for a disordered fluid. // Austral. J. Phys., 1968, vol. 21, No 5, p. 563-569.
- [35] Blum L. Solution of a model for the solvent-electrolyte interactions in the mean spherical approximation. // J. Chem. Phys., 1974, vol. 61, No 5, p. 2129-2133.
- [36] Adelman S.A., Deutch J.M. Exact solution of the mean spherical approximation for the strong electrolytes in polar solvents. // J. Chem. Phys., 1974, vol 60, No 10, p. 3935-3949.
- [37] Blum L., Wei D.Q. Analytic solution of the mean spherical approximation for an arbitrary mixture of ions in a dipolar solvent. // J. Chem. Phys., 1987, vol. 87, No 1, p. 555-565.
- [38] Wei D.Q., Blum L. The mean spherical approximation for an arbitrary mixture of ions in a dipolar solvent: Approximate solution, pair

- correlation functions, and thermodynamics. // *J. Chem. Phys.*, 1987, vol. 87, No 5, p. 2999-3007.
- [39] Golovko M.F., Protsykevich I.A. Pair correlation functions for the asymmetric ion-dipole model in the mean spherical approximation. // *Chem. Phys. Lett.*, 1987, vol. 142, No 6, p. 463-468.
- [40] Golovko M.F., Protsykevich I.A. Analytical solution of the mean spherical approximation for ion-dipole model in a neutralizing background. // *J. Stat. Phys.*, 1989, vol. 54, No 3/4, p. 707-733.
- [41] Holovko M.F. The statistical theory of mixed ion-molecular systems, Doctoral Thesis, Institute for Theoretical Physics, Kiev, 1979, p. 360.
- [42] Vericat F., Blum L. Mean spherical model for hard ions and dipoles. // *J. Stat. Phys.*, 1980, vol. 32, No 5, p. 593-604.
- [43] Pizio O.O., Holovko M.F., Trokhimchuk A.D. The pair correlation functions and thermodynamical properties of the ion-dipole model of electrolyte solutions. // *Acta. Chemica Hungarica*, 1988, vol. 125, p. 385-402.
- [44] Holovko M.F., Pizio O.O., Trokhimchuk A.D. The investigations of the binary distribution functions of ionic melts. // *Ukr. Fiz. Zhurn.*, 1985, vol. 30, No 5, p. 734-740, (in Russian).
- [45] Wertheim M.S. Exact solution of the mean spherical model for fluids of hard spheres with permanent electric dipole moments. // *J. Chem. Phys.*, 1971, vol. 54, No 10, p. 4291-4298.
- [46] Lvov S.N., Holovko M.F. The theoretical calculations of standard thermodynamic properties of aqueous solutions under high temperatures and pressures, *Termodinamika i structura rastvorov*. Ivanovo, 1986, p. 46-51, (in Russian).
- [47] Lvov S.N., Umniashkin V.A., Sharygin A., Holovko M.F. The molecular statistical theory of infinite dilute solutions based on the ion-dipole model with Lennard-Jones interactions. // *Fluid Phase Equilibria*, 1990, vol. 58, No 3, p. 283-305.
- [48] Lvov S.N., Dolbunov W.N., Trokhimchuk A.D., Protsykevich I.A., Holovko M.F. Thermodynamical Properties of the electrolyte solutions, Preprint Inst. Theor. Phys., Acad. Sci. Ukr. SSR: ITP-88-150R, Kiev, 1988, p. 32, (in Russian).
- [49] Mansoori G.A., Carnahan N.F., Starling K.E., Leland T.W. Equilibrium thermodynamic properties of the mixture of hard spheres. // *J. Chem. Phys.*, 1971, vol. 54, No 4, p. 1523-1525.
- [50] Holovko M.F., Trokhymchuk A.D., Protsykevich I.A., Henderson D.J. The Laplace transform of the MSA pair distribution functions between macroions in a ion-dipole fluid. // *J. Stat. Phys.*, 1993, vol. 72, No 5/6, p. 1391-1399.
- [51] Trokhymchuk A.D., Holovko M.F., Henderson D.J. The contribution of dipole alignment to the force between macroions in an ion-dipole fluid. // *Mol. Phys.*, 1993, vol. 80, No 4, p. 1009-1020.
- [52] Verwey E.Y.W., Overbeek J.T. Theory of Stability of Lyophobic Colloids (Elsevier, Amsterdam, 1948), p. 240.
- [53] Golovko M.F., Protsykevich I.A. Solutions of Sodium in liquid ammonia as described by a hard sphere charge-dipole model in the neutralizing background. // *Z. Naturforsch.*, 1991, vol. 46a, p. 19-26.
- [54] Holovko M.F., Protsykevich I.A. Ion-molecular models in the neutralizing background as a reference system for a metal-polar liquid solutions. // *J. de physique IV*, 1991, vol. 1, C5, p. 51-57.
- [55] Chandler D. Equilibrium theory of polyatomic fluids. In: *The liquid state of matter: fluids simple and complex*. Ed. by E. W. Montoll and

- J. L. Lebowitz, North-Holland, Amsterdam, 1982, p. 275-340.
- [56] Holovko M.F., Kalyuzhnyi Yu.V. On the application of the EXP-like approximation for the description of the site-site ion-molecular model. // *Mol. Phys.*, 1989, vol. 68, No 6, p. 1239-1253.
- [57] Holovko M.F., Kalyuzhnyi Yu.V. Analytic solution of the reference interaction site model equation for a mixture of hard spheres and symmetric rigid molecules. // *J. Phys.: Condens. Matter*, 1989, vol. 1, No 12, p. 2891-2909.
- [58] Holovko M.F., Kalyuzhnyi Yu.V. Screened potentials of the site-site ion-molecular model. The mean spherical approximation. // *Mol. Phys.*, 1989, vol. 66, No 2, p. 375-396.
- [59] Weeks J.D., Chandler D., Andersen H.C. Role of repulsive forces in determining the equilibrium structure of simple liquids. // *J. Chem. Phys.*, 1971, vol. 54, No 12, p. 5237-5246.
- [60] Trokhymchuk A.D., Holovko M.F., Spohr E., Heinzinger K. Combination of computer simulation methods and optimized cluster theory in determining equilibrium properties of electrolyte solutions. // *Mol. Phys.*, 1992, vol. 77, No 4, p. 903-920.
- [61] Trokhymchuk A.D., Holovko M.F., Heinzinger K. Static dielectric properties of the flexible model of water. // *J. Chem. Phys.*, 1993, vol. 99, No 4, p. 2964-2970.
- [62] Trokhymchuk A.D., Holovko M.F., Heinzinger K. On the structure factor for water at small wavenumbers. // *Z. Naturforsch.*, 1995, vol. 50, No 1, p. 18-20.
- [63] Bopp p., Jancso G., Heinzinger K. An improved potential for non-rigid water molecules on the liquid phase. // *Chem. Phys. Lett.*, 1983, vol. 98, No 3, p. 129-133.
- [64] Hill T. *Statistical mechanics*. Hill, New York, 1956, p. 486.
- [65] Ebeling W., Kraeft W.D., Kremp D. *Theory of bound states and ionization equilibrium in plasmas and solids*. Akademie-Verlag, Berlin, 1976, p. 262.
- [66] Holovko M.F., Kalyuzhnyi Yu.V. Third Liblice conference *Statistical mechanics of liquids*. Bechine, Czechoslovakia, 1990 (unpublished).
- [67] Wertheim M.S. Fluids of dimerizing hard spheres, and fluid mixtures of hard spheres and dispheres. // *J. Chem. Phys.*, 1986, vol. 85, No 5, p. 2929-2936.
- [68] Kalyuzhnyi Yu.V., Protsykevich I.A., Holovko M.F. Solution of the associative Percus-Yevick approximation for the n-component mixture of dimerizing hard spheres. // *Chem. Phys. Lett.*, 1993, vol. 215, No 1, p. 1-4.
- [69] Kalyuzhnyi Yu.V., Duda Yu.Ya. Analytic solution of the Wertheim's PY approximation for the shielded sticky-point model of associating liquid. // *Condensed Matter Physics*, 1993, No 2, p. 20-31.
- [70] Kalyuzhnyi Yu.V., Stell G., Llano-Restrepo M.L., Chapman V.G., Holovko M.F. Primitive models of chemical association. // *J. Chem. Phys.*, 1994, vol. 101, No 9, p. 7039-7052.
- [71] Kalyuzhnyi Yu.V., Stell G., Holovko M.F. Analytical solution of the multidensity OZ equation for polymerizing fluid. // *Chem. Phys. Lett.*, 1995, vol. 235, No 6, p. 335-364.
- [72] Chang J., Sandler S.I. The correlation functions of hard-sphere chain fluids. // *J. Chem. Phys.*, 1995, vol. 102, No 1, p. 437-449.
- [73] Holovko M.F., Protsykevich I.A. Solution of the Percus-Yevick approximation for n-component mixture of associating hard spheres in multidensity formalism. // *Mol. Phys.*, 1995, (in press).

- [74] Blum L., Bernard O. The general solution of the binding mean spherical approximation for pairing ions. // *J. Stat. Phys.*, 1995, vol. 79, No 3/4, p. 569-582.
- [75] Protsykevich I.A., Holovko M.F. The mean spherical approximation for multicomponent mixture of dimerizing charged hard spheres. // *Ukr. Fiz. Zhurn.*, (in press).
- [76] Kalyuzhnyi Yu.V., Vlachy V. Integral equation theory for highly asymmetric electrolyte solutions. // *Chem. Phys. Let.*, 1993, vol. 215, No 5, p. 518-522.
- [77] Kalyuzhnyi Yu.V., Vlachy V., Holovko M.F., Stell G. Multidensity integral equation theory for highly asymmetric electrolyte solutions. // *J. Chem. Phys.*, 1995, vol. 102, No 14, p. 5770-5780.
- [78] Protsykevych I.A., Holovko M.F. The reference system of highly asymmetric electrolyte solutions: The analytical treatment. // *Chem. Phys. Let.*, 1995, (in press).
- [79] Protsykevych I.A., Holovko M.F. The mean associative spherical approximation for highly asymmetric electrolyte solutions, (in preparation).
- [80] Rowlinson J.S., Widom B. *Molecular theory of capillarity*. Clarendon press, Oxford, 1982, p. 375.
- [81] Yukhnovsky I.R., Holovko M.F., Kuryliak I.J. The screened potential of a spatially confined ion-dipole system. // *Ukr. Fiz. Zhurn.*, 1978 vol. 23, No 6, p. 927-937, (in Russian).
- [82] Yukhnovsky I.R., Holovko M.F., Kuryliak I.J., Sovyak E.N. The method of collective variables in the statistical theory of confined ion-molecular systems. // *Physics of Molecules*. Naukova Dumka, Kiev, 1981, No 10, p. 26-43, (in Russian).
- [83] Kuryliak I.J., Yukhnovsky I.R. The method of collective variables in the equilibrium statistical theory of confined systems of charged particles. // *Theor. Math. Phys.*, 1982, vol. 52, No 1, p. 114-126, (in Russian).
- [84] Yukhnovsky I.R., Sovyak E.N. The free energy and the distribution functions of a spatially confined ion-molecular system. // *Manyparticle System Physics*. Naukova Dumka, Kiev, 1983, No 3, p. 13-18, (in Russian).
- [85] Sovyak E.M. The screened potentials of two-phase systems with the influence of the interface region taken into account. // *Ukr. Fiz. Zhurn.*, 1990, vol. 35, No 2, p. 300-305, (in Ukrainian).
- [86] Gakhov F.D., Cherskij Yu.I. *Convolution-like equations*. Nauka, Moscow, 1978, p. 295, (in Russian).
- [87] Yukhnovsky I.R., Holovko M.F., Sovyak E.N. The screened potentials of a spatially confined ion-molecular system. The general technique of solution, Preprint Inst. Theor. Phys., Acad. Sci. Ukr. SSR: ITP-82-159R, Kiev, 1982, p. 18, (in Russian).
- [88] Sovyak E.M. Taking account of multipole moments of particles in the screened potentials of spatially inhomogeneous ion-molecular systems. // *Condensed Matter Physics*, 1993, No 2, p. 84-94, (in Ukrainian).
- [89] Jancovici B. Classical Coulomb systems near a plane wall. // *J. Stat. Phys.*, 1982, vol. 28, No 1, p. 43-65.
- [90] Klimontovich Yu.L., Vilhelmsson H., Yakymenko I.p., Zagorodny A.G. *Statistical theory of plasma-molecular systems*. Moscow University, Moscow, 1990, p. 223, (in Russian).

- [91] Henderson D., Abraham F.F., Barker J.A. The Ornstein-Zernike equation for a fluid in contact with a surface. // *Mol. Phys.*, 1976, vol. 31, No 4, p. 1291-1295.; Errata // *Mol. Phys.*, 1976, vol. 32, No 6, p. 1976.
- [92] Badiali J.P. Structure of a polar fluid near a wall. // *J. Chem. Phys.*, 1989, vol. 90, No 8, p. 4401-4412.
- [93] Badiali J.P., Russier V., Holovko M.F. Analysis of the Henderson-Abraham-Barker equation in the case of a polar liquid near a neutral hard wall. // *J. Chem. Phys.*, 1993, vol. 99, No 10, p. 8051-8055.
- [94] Golovko M.F., Blotsky S.N., Pizio O.A. On the application of optimized cluster series for the description of the electrolyte model near a charged hard wall. // *Electrochimica Acta*, 1989, vol. 34, p. 63-66.
- [95] Holovko M.F., Blotsky S.N., Pizio O.O. The structure properties of the ion-dipole model of electrolyte solutions near a charged and non-charged surface. The approach of an optimized third cluster coefficient. // *Ukr. Fiz. Zhurn.*, 1990, vol. 35, No 4, p. 585-590, (in Ukrainian).
- [96] Holovko M.F., Pizio O.O., Halytch Z.B. On the probability density of solvent molecule orientation for the ion-dipole model of the electrical double layer. // *Electrochimica Acta*, 1991, vol. 36, p. 1715-1717.
- [97] Holovko M.F., Vakarin E.V. Adsorption of the associative fluid onto the lattice of sticky sites. // *Chem. Phys. Lett.*, 1994, vol. 230, No 12, p. 507-509.
- [98] Holovko M.F., Vakarin E.V. An associative version of the Henderson-Abraham-Barker equation. // *Mol. Phys.*, 1995, (in press).
- [99] Holovko M.F., Vakarin E.V. The role of association effects in theory of an electrified interface. // *Mol. Phys.*, 1995, (in press).
- [100] Badiali J.p., Blum L., Rosinberg M.L. On the adsorption of a dense fluid onto a lattice of sticky sites. // *Chem. Phys. Letters*, 1986, vol. 129, No 1, p. 149-154.
- [101] Hukkaby D.A., Blum L. Exact results for the adsorption of a dense fluid onto a triangular lattice of sticky sites. // *J. Chem. Phys.*, 1990, vol. 92, No 4, p. 2646-2649.
- [102] Kovalenko A.F., Sovyak E.N., Golovko M.F. Electronic states of hydrogen atom near a hard wall. // *Phys. Stat. Sol. (b)*, 1989, vol. 155, p. 549-558.
- [103] Kovalenko A.F., Sovyak E.N., Holovko M.F. Quantum properties of a hydrogen-like particle near a hard wall. // *Electrochimica Acta*, 1991, vol. 36, p. 1711-1713.
- [104] Kovalenko A.F., Sovyak E.N., Holovko M.F. On the quantum properties of adsorbed particles within the model of a hydrogen atom near a hard wall. // *Intern. J. Quant. Chem.*, 1992, vol. 42, p. 321-337.
- [105] Kovalenko A.F., Holovko M.F. A hydrogen-like atom near a potential barrier. // *J. Phys. B*, 1992, vol. 25, p. L233-L236.
- [106] Kovalenko A.F. Coulomb Scattering in a Semi-Infinite Space. // *J. Phys. B*, 1993, vol. 26, p. L287-L290.

ПРО ВРАХУВАННЯ ВЗАЄМОДІЙ В СТАТИСТИЧНІЙ ТЕОРІЇ РОЗЧИНІВ ЕЛЕКТРОЛІТІВ

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Розглядаються проблеми врахування взаємодій в статистичній теорії іонно-молекулярних систем. Пропонована методика базується на виділенні в потенціалах міжчастинкової взаємодії короткосяжної відштовхувальної частини на малих відстанях, короткосяжного притягання на проміжних відстанях і далекосяжних електростатичних взаємодій на великих відстанях. Для кореляційних функцій запропоновано оптимізовані групові розвинення. Розглядаються різні способи моделювання іонно-молекулярних систем: іонно-мультипольні моделі; атом-атомні моделі; асоціативні моделі; реалістичні моделі, в яких при описі базисної підсистеми використовуються результати комп'ютерного моделювання. Обговорюються проблеми опису просторово обмежених іонно-молекулярних систем.