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Analytic Solution of the Mean Spherical Approximation for Ion–Dipole Model in a Neutralizing Background

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The analytic solution of the mean spherical approximation (MSA) for a multicomponent mixture of hard ions and hard dipoles with arbitrary valences and sizes of particles in a uniform neutralizing background is found. Expressions for the pair correlation functions and thermodynamics in the MSA are obtained.

KEY WORDS: Mean spherical approximation; asymmetric ion–dipole model in a neutralizing background; total and direct correlation functions.

1. INTRODUCTION

The development of the statistical theory of ion–molecular systems is stimulated by the necessity to develop the microscopic theory of electrolyte solutions, which has to be grounded on the explicit consideration of ion–molecular and intermolecular interactions besides the ion–ion ones. An explicit allowance for the molecular solvent results in new possibilities to describe and interpret on a quantitative level the solvation and other effects appearing due to the liquid polar solvent influence.[1–3]

The simplest model for the electrolyte solution within the ion–molecular approach is the ion–dipole model, consisting of charged hard spheres (ions) and hard spheres possessing dipole moments (molecules). It has been investigated recently within the hypernetted chain approximation,[4,5] the modified Poisson–Boltzmann equation,[6,7] and the mean spherical approximation (MSA).[8–16]

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The MSA introduced by Lebowitz and Percus[17] reduces to the solution of the Ornstein–Zernike (OZ) integral equations

$$h_{ij}(X_1, X_2) = c_{ij}(X_1, X_2) + \sum_{i_1=1}^{M} \rho_{i_1} \int dX_3\, h_{ii_1}(X_1, X_3)\, c_{i_1 j}(X_3, X_2) \quad (1)$$

supplemented by the closure for the total correlation functions (TCF) $h_{ij}(X_1, X_2) = g_{ij}(X_1, X_2) - 1$ and the direct correlation functions (DCF) $c_{ij}(X_1, X_2)$, where

$$h_{ij}(X_1, X_2) = -1, \qquad r_{12} < \sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \quad (2)$$

$$c_{ij}(X_1, X_2) = -\beta U_{ij}(X_1, X_2), \qquad r_{12} > \sigma_{ij} \quad (3)$$

where $g_{ij}(X_1, X_2)$ are the pair distribution functions (PDF); $U_{ij}(X_1, X_2)$ are the electrostatic interaction pair potentials; $\beta = 1/k_B T$ is the Boltzmann thermal factor; $\rho_i = N_i/V$ is the number density of species i ($i = 1,..., M$); M is the number of species in the mixture; $X_1 = (r_1, \Omega_1)$ denotes the set of coordinates of particle 1; Ω_1 is the set of Euler angles necessary to define the orientation of the molecule; r_{12} is the interparticle distance; and σ_i denotes the size of a particle of species i.

If one considers the hard sphere model with long-range interactions $U_{ij}(X_1, X_2)$, then the relation (2) is exact, and Eq. (3), being approximate, provides the correct asymptotics of the DCF at $r_{12} \to \infty$.

The MSA can be solved analytically for several models and leads to relatively simple and qualitatively correct results if compared with the more accurate approximations and the computer simulation. Moreover, the MSA results can be improved either within an optimized cluster expansion[1,18] or by introduction of the short-range terms into the DCF within the generalized mean spherical approximation.[2,19,20]

The analytical solution of the MSA for charged hard spheres of equal sizes has been obtained by Waisman and Lebowitz[21] and for multicomponent ionic systems with arbitrary charge and size of ions by Blum and Høye.[22,23] In the case of dipole hard spheres the MSA solution was given by Wertheim.[24]

The simplest ion–dipole model is the mixture of particles of equal sizes, which has been solved analytically in the MSA by Blum[8] and independently by Adelman and Deutch.[9] The analytical expressions for the TCF and thermodynamics for this model were given in refs. 10–12. For the more general case of multicomponent ion–dipole system with arbitrary sizes of particles and arbitrary valences of ions the MSA solution has been considered in refs. 13–16. For the solution a Baxter factorized version[27] of the OZ equations and the technique of Blum and co-workers[25,26] was used. In refs. 15 and 16 the general expressions for the Baxter–Wertheim (BW) factor correlation functions were obtained and a method for the calculation of the TCF was proposed.

Here we aim to generalize the results of refs. 13–16 for an ion–dipole system in a uniform neutralizing background. This model was proposed as a reference system to describe the structural properties of metal–polar liquid solutions.[29] These are the metal–ammonia solutions[30] in particular. In the model, screening and aggregation due to the metallic electrons are neglected. The considered solution is the generalization of the MSA solution for charged hard spheres in a neutralizing background,[31–33] which has been used to describe the structural and thermodynamic properties of liquid metals[34,35] and metal–salt solutions.[36,37]

2. GENERAL METHOD OF SOLUTION

The considered model consists of hard spheres with charges eZ_i, densities ρ_i, and diameters σ_i of sort i $(1 \leqslant i \leqslant M-1)$ and one sort of hard sphere with point dipole p_s, density ρ_s, and diameter σ_s. Unlike in refs. 13–16, the M-component ion–dipole system is embedded in a uniform neutralizing background of density

$$\rho_\varphi = \sum_{i=1}^{M} \rho_i Z_i \tag{4}$$

similar to the model considered already in ref. 29. Here $Z_s = 0$.

The method for solving the MSA problem is similar to the case of the electroneutral ion–dipole model.[13–16]

The TCF and DCF are presented in the orientation-invariant form[25,26]

$$\begin{aligned} h_{ij}(X_1, X_2) &= \sum_{m,n,l} h_{ij}^{mnl}(r_{12})\, \varphi_{00}^{mnl}(\Omega_1, \Omega_2, \Omega_{r_{12}}) \\ c_{ij}(X_1, X_2) &= \sum_{m,n,l} c_{ij}^{mnl}(r_{12})\, \varphi_{00}^{mnl}(\Omega_1, \Omega_2, \Omega_{r_{12}}) \end{aligned} \tag{5}$$

where the linear symmetry of the dipoles has been taken into account; Ω_1, Ω_2, and $\Omega_{r_{12}}$ are, respectively, the Euler angles specifying the orientation with respect to an arbitrary set of axes of molecules 1 and 2 and of the vector r_{12} joining their centers of mass and

$$\begin{aligned} \varphi_{00}^{mnl}(\Omega_1, \Omega_2, \Omega_r) = {} & [(2m+1)(2n+1)]^{1/2} \sum_{\mu,\nu,\lambda} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} \\ & \times D_{0\mu}^{m}(\Omega_1)\, D_{0\nu}^{n}(\Omega_2)\, D_{0\lambda}^{l}(\Omega_r) \end{aligned}$$

The standard notations for the Wigner $3-j$ symbols and generalized spherical harmonics have been applied.

After integration by orientations and transition to the orientation frame, respectively, to the axis connecting the centers of masses of the particles, Eqs. (1) reduce to the equations in Fourier space

$$\tilde{H}^{mn}_{\lambda,ij}(k) - \tilde{C}^{mn}_{\lambda,ij}(k) = \sum_{i_1=1}^{M} \sum_{n_1=0}^{1} (-1)^{\lambda} \rho_{i_1} \tilde{H}^{mn_1}_{\lambda,ii_1}(k)\, \tilde{C}^{n_1 n}_{\lambda,i_1 j}(k) \tag{6}$$

where

$$\begin{aligned} \tilde{H}^{mn}_{\lambda,ij}(k) &= \int_0^\infty dr\, [e^{ikr} J^{mn}_{\lambda,ij}(r) + e^{-ikr} J^{nm}_{\lambda,ji}(r)] \\ \tilde{C}^{mn}_{\lambda,ij}(k) &= \int_0^\infty dr\, [e^{ikr} S^{mn}_{\lambda,ij}(r) + e^{-ikr} S^{nm}_{\lambda,ji}(r)] \end{aligned} \tag{7}$$

Here the functions $J^{mn}_{\lambda,ij}(r)$ and $S^{mn}_{\lambda,ij}(r)$ can be represented through the coefficients in Eqs. (5),

$$\begin{aligned} J^{mn}_{\lambda,ij}(r) &= 2\pi(-1)^{\lambda} \sum_l \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} \int_r^\infty dt\, t P_l\left(\frac{r}{t}\right) h^{mnl}_{ij}(t) \\ S^{mn}_{\lambda,ij}(r) &= 2\pi(-1)^{\lambda} \sum_l \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} \int_r^\infty dt\, t P_l\left(\frac{r}{t}\right) c^{mnl}_{ij}(t) \end{aligned} \tag{8}$$

where the $P_l(r/t)$ are the Legendre polynomials. The derivatives of the functions (8) are

$$\begin{aligned} \frac{-d}{dr} J^{mn}_{\lambda,ij}(r) &= (-1)^{\lambda}\, 2\pi r H^{mn}_{\lambda,ij}(r) = (-1)^{\lambda}\, 2\pi r \sum_l \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} H^{mnl}_{ij}(r) \\ \frac{-d}{dr} S^{mn}_{\lambda,ij}(r) &= (-1)^{\lambda}\, 2\pi r C^{mn}_{\lambda,ij}(r) = (-1)^{\lambda}\, 2\pi r \sum_l \begin{pmatrix} m & n & l \\ \lambda & -\lambda & 0 \end{pmatrix} C^{mnl}_{ij}(r) \end{aligned} \tag{9}$$

where the new functions $H^{mnl}_{ij}(r)$ and $C^{mnl}_{ij}(r)$ relate to the initial ones $h^{mnl}_{ij}(r)$ and $c^{mnl}_{ij}(r)$ through the transformation[2,13]

$$\begin{aligned} H^{mnl}_{ij}(r) &= h^{mnl}_{ij}(r) - \frac{1}{r} \int_r^\infty dt\, P'_l\left(\frac{r}{t}\right) h^{mnl}_{ij}(t) \\ C^{mnl}_{ij}(r) &= c^{mnl}_{ij}(r) - \frac{1}{r} \int_r^\infty dt\, P'_l\left(\frac{r}{t}\right) c^{mnl}_{ij}(t) \end{aligned} \tag{10}$$

and vice versa

$$
\begin{aligned}
h_{ij}^{mnl}(r) &= H_{ij}^{mnl}(r) - \frac{1}{r^2}\int_0^r dt\, tP_l'\left(\frac{t}{r}\right) H_{ij}^{mnl}(t) \\
c_{ij}^{mnl}(r) &= C_{ij}^{mnl}(r) - \frac{1}{r^2}\int_0^r dt\, tP_l'\left(\frac{t}{r}\right) C_{ij}^{mnl}(t)
\end{aligned} \tag{11}
$$

In accordance with the MSA closure (2), (3):

$$h_{ij}^{000}(r) = -1, \qquad h_{ij}^{mnl}(r) = 0 \qquad \text{if} \quad m \text{ or } n \neq 0, \qquad r < \sigma_{ij} \tag{12}$$

$$c_{ij}^{mnl}(r) = -\beta u_{ij}^{mnl} \frac{1}{r^{l+1}}, \qquad r > \sigma_{ij} \tag{13}$$

where

$$u_{ij}^{mnl} = (-1)^m \delta_{m+n,l} \left[\frac{(2l+1)!}{(2m+1)!\,(2n+1)!}\right]^{1/2} p_i^m p_j^n \tag{14}$$

and p_i^m is the linear multipole moment of order m.

In the ion–dipole case considered, the indices m and n equal zero or unity and the set of equations (6) decouples into two independent equations for $\lambda = 0$ and $\lambda = 1$, respectively,

$$[\mathbf{I} + \sqrt{\boldsymbol{\rho}} * \tilde{\mathbf{H}}_0(k) * \sqrt{\boldsymbol{\rho}}] * [\mathbf{I} - \sqrt{\boldsymbol{\rho}} * \tilde{\mathbf{C}}_0(k) * \sqrt{\boldsymbol{\rho}}] = \mathbf{I} \tag{15}$$

$$[1 + \rho_s \tilde{H}_{1,ss}^{11}(k)][1 - \rho_s \tilde{C}_{1,ss}^{11}(k)] = 1 \tag{16}$$

where $\mathbf{I}$ is the unit matrix; $\boldsymbol{\rho}$ is the $(M+1)$-order diagonal matrix of the number densities of the ions and the solvent $(\rho_{M+1} = \rho_s)$; $\tilde{\mathbf{H}}_0(k)$ and $\tilde{\mathbf{C}}_0(k)$ are the square matrices of order $M+1$; and the asterisk denotes the multiplication of two matrices.

Equation (16) has a form similar to the one-component dipole system and reduces to the Percus–Yevick (PY) equation for hard spheres with effective density $\eta = -b_2/12$, where

$$b_2 = \rho_s \sigma_s^3 J_{ss}^{11} = \rho_s \sigma_s^3 \frac{6\pi}{\sqrt{30}} \int_0^\infty dr\, \frac{h_{ss}^{112}(r)}{r} \tag{17}$$

Thus,[24]

$$
\begin{aligned}
H_{1,ss}^{11}(r) &= \frac{b_2}{2\pi\rho_s\sigma_s} h_2^{(\mathrm{PY})}\left(r, -\frac{b_2}{12}\right) \\
C_{1,ss}^{11}(r) &= \frac{b_2}{2\pi\rho_s\sigma_s^3} c_2^{(\mathrm{PY})}\left(r, -\frac{b_2}{12}\right)
\end{aligned} \tag{18}
$$

where $h_2^{(\mathrm{PY})}(r)$ and $c_2^{(\mathrm{PY})}(r)$ are the correlation functions of the one-component hard sphere model in the PY approximation. In order to solve Eqs. (15), one can apply the BW method,[27,28] which leads to the representation

$$\mathbf{I} - \sqrt{\boldsymbol{\rho}} * \tilde{\mathbf{C}}(k) * \sqrt{\boldsymbol{\rho}} = \tilde{\mathbf{Q}}(k) * \tilde{\mathbf{Q}}^T(-k) \tag{19}$$

$$[\mathbf{I} + \sqrt{\boldsymbol{\rho}} * \tilde{\mathbf{H}}(k) * \sqrt{\boldsymbol{\rho}}] * \tilde{\mathbf{Q}}(k) = \tilde{\mathbf{Q}}^T(-k)^{-1} \tag{20}$$

where for simplicity the indices zero in the functions $H_{0,ij}^{mn}(k)$ and $C_{0,ij}^{mn}(k)$, which both correspond to the case $\lambda = 0$, are omitted; T indicates matrix transpose.

The closure condition on the functions (8) can be written in matrix form as

$$\begin{aligned}
\mathbf{J}(r) &= \begin{bmatrix} (J_{ij}^{00} + \pi r^2)_{M,M} & (J_{is}^{01} r)_{M,1} \\ (J_{sj}^{10} r)_{1,M} & (I_{ss}^{11} + J_{ss}^{11} r^2)_{1,1} \end{bmatrix}, \qquad r < \sigma_{ij} \\
\mathbf{S}(r) &= \begin{bmatrix} \left(4\pi\beta e^2 Z_i Z_j \dfrac{\exp(-\mu r)}{2\mu}\right)_{M,M} & \left(\dfrac{4}{\sqrt{3}} \beta e Z_i p_s\right)_{M,1} \\ \left(\dfrac{-4\pi}{\sqrt{3}} \beta e Z_j p_s\right)_{1,M} & (0)_{1,1} \end{bmatrix}, \qquad r > \sigma_{ij}
\end{aligned} \tag{21}$$

where $\mathbf{J}(r)$ and $\mathbf{S}(r)$ are $(M+1)$-order matrices. The first index in the matrix element denotes the number of rows and the second denotes the number of columns of the corresponding submatrix. To provide the correctness of calculations one assumes that the Coulomb potential has been replaced by the potential $[\exp(-\mu r)]/r$ with the limit $\mu \to 0$ in the final results. We have introduced the following notations:

$$\begin{aligned}
J_{ij}^{00} &= 2\pi \int_0^\infty dr\, r h_{ij}^{000}(r), \qquad J_{is}^{01} = -J_{si}^{10} = 2\frac{\pi}{\sqrt{3}} \int_0^\infty dr\, h_{si}^{101}(r) \\
I_{ss}^{11} &= -\frac{2\pi}{\sqrt{3}} \left[\int_0^\infty dr\, r h_{ss}^{110}(r) + \frac{1}{\sqrt{10}} \int_0^\infty dr\, r h_{ss}^{112}(r) \right]
\end{aligned} \tag{22}$$

By analyzing Eq. (19) taking account of the closure for $S(r)$, one represents the functions $Q_{ij}^{mn}(k)$ as[13]

$$\tilde{Q}_{ij}^{mn}(k) = \delta_{ij}^{mn} - (\rho_i \rho_j)^{1/2} \left[\int_{\lambda_{ji}}^{\sigma_{ij}} dr\, q_{ij}^{mn}(r)\, e^{ikr} - A_{ij}^{mn} \int_{\lambda_{ji}}^{\infty} dr\, e^{(ik-\mu)r} \right] \tag{23}$$

where $q_{ij}^{mn}(r) = 0$ at $r > \sigma_{ij}$; $\lambda_{ji} = (\sigma_j - \sigma_i)/2$; $\delta_{ij}^{mn} = \delta_{ij}\delta_{mn}$; δ_{ij} is the Kronecker delta function.

Performing the inverse Fourier transform of Eqs. (19) and (20), we obtain

$$S_{ij}^{mn}(r) = -Q_{ij}^{mn}(r)\,\theta(r-\lambda_{ji}) - Q_{ji}^{nm}(-r)\,\theta(-r-\lambda_{ij}) + \sum_{i_1=1}^{M}\sum_{n_1=0}^{1}\rho_{i_1}$$

$$\times\left\{A_{ii_1}^{mn_1}A_{ji_1}^{nn_1}\frac{\exp(-\mu r)}{2\mu} + \int_{[\lambda_{i_1 i},\lambda_{i_1 j}+r]}^{[\sigma_{ii_1},\sigma_{ji_1}+r]} dt\, q_{ii_1}^{mn_1}(t)\,q_{ji_1}^{nn_1}(t-r)\right.$$

$$\left. - A_{ji_1}^{nn_1}\int_{[\lambda_{i_1 i},\lambda_{i_1 j}+r]}^{\sigma_{ii_1}} dt\, q_{ii_1}^{mn_1}(t) - A_{ii_1}^{mn_1}\int_{[\lambda_{i_1 j},\lambda_{i_1 i}-r]}^{\sigma_{i_1 j}} dt\, q_{ji_1}^{nn_1}(t)\right\} \tag{24}$$

$$J_{ij}^{mn}(r) = \sum_{i_1=1}^{M}\sum_{n_1=0}^{1}\rho_{i_1}\left\{\int_{\lambda_{ji_1}}^{r} dt\, J_{ii_1}^{mn_1}(r-t)\,Q_{i_1 j}^{n_1 n}(t)\right.$$

$$\left. + \int_{r}^{\infty} dt\, J_{i_1 i}^{n_1 m}(t-r)\,Q_{i_1 j}^{n_1 n}(t)\right\} + Q_{ij}^{mn}(r) \tag{25}$$

where in the lower ranges of integration the maximum number has to be chosen and in the upper ranges the minimum; $\theta(r)$ is the Heaviside function.

We get from Eqs. (24) relations obtained previously in ref. 13:

$$\begin{aligned} 4\pi\beta e^2 Z_i Z_j &= \sum_{i_1=1}^{M}\sum_{n_1=0}^{1}\rho_{i_1}A_{ii_1}^{mn_1}A_{ji_1}^{nn_1} \\ \frac{4\pi}{\sqrt{3}}\beta e Z_i p_s &= A_{is}^{01} - \sum_{i_1=1}^{M}\sum_{n_1=0}^{1}\rho_{i_1}A_{ii_1}^{0n_1}K_{si_1}^{1n_1} \end{aligned} \tag{26}$$

where

$$K_{ij}^{mn} = \int_{\lambda_{ji}}^{\sigma_{ij}} dr\, q_{ij}^{mn}(r) \tag{27}$$

The first of Eqs. (26) provides that

$$A_{ij}^{mn} = Z_i a_j^n \tag{28}$$

From Eqs. (25), taking account of the closure (21), it follows that $q_{ij}^{mn}(r)$ must be a polynomial of the third degree and can be represented in a form providing the continuity of the BW functions at $r=\sigma_{ij}$,

$$q_{ij}^{mn}(r) = (r-\sigma_{ij})\,q_{ij}'^{mn} + \tfrac{1}{2}(r-\sigma_{ij})^2\,q_{ij}''^{mn} + \tfrac{1}{6}(r-\sigma_{ij})^3\,q_{ij}'''^{mn} \tag{29}$$

The coefficients of $q_{ij}^{mn}(r)$ can be found by a method given in ref. 13:

$$q_{ij}'^{mn}=\begin{bmatrix} \left(\dfrac{2\pi}{\Delta}\sigma_{ij}+\dfrac{\pi^2}{2\Delta^2}\xi_2\sigma_i\sigma_j\right)_{M,M} & (0)_{M,1} \\ (0)_{1,M} & (0)_{1,1} \end{bmatrix}$$
$$+\frac{D_\Omega}{2}\begin{bmatrix}(-a_i^0)_{M,M+1}\\ (a_s^1)_{1,M+1}\end{bmatrix}*\mathbf{a}$$
$$+\begin{bmatrix} \left(-\dfrac{\sigma_s^2}{2D}\rho_s\eta_i\eta_j\right)_{M,M} & \left(-\dfrac{1}{D}y_0\eta_i\right)_{M,1} \\ \left(\dfrac{1}{D}y_0\eta_j\right)_{1,M} & \left[\dfrac{2}{\rho_s\sigma_s^2}\left(\dfrac{1}{D}y_0^2-1\right)\right]_{1,1} \end{bmatrix} \tag{30}$$

$$q_{ij}''^{mn}=\begin{bmatrix} \left(\dfrac{2\pi}{\Delta}+\dfrac{\pi^2}{\Delta^2}\xi_2\sigma_j\right)_{M,M} & (0)_{M,1} \\ (0)_{1,M} & (0)_{1,1} \end{bmatrix}$$
$$+\begin{bmatrix} \left(-\dfrac{\pi}{2\Delta}\dfrac{\sigma_s^2}{D}\rho_s P_v\eta_j\right)_{M,ML} & \left(-\dfrac{\pi}{\Delta}\dfrac{y_0}{D}P_v\right)_{M,1} \\ \left(\dfrac{b_2}{\sigma_s\beta_6 D}\eta_j\right)_{1,M} & \left(\dfrac{2b_2}{\rho_s\sigma_s^3\beta_6}\dfrac{y_0}{D}\right)_{1,1} \end{bmatrix}$$
$$+\begin{bmatrix} \left(\dfrac{\pi}{\Delta}P_M+\pi\rho_\varphi\sigma_i\right)_{M,M+1} \\ \left(\sum_{i=1}^{M}\rho_i Z_i^* v_i+\dfrac{b_2}{2\sigma_s\beta_6}\sum_{i=1}^{M}\rho_i\sigma_i v_i\mathcal{M}_i\right)_{1,M+1} \end{bmatrix}*\mathbf{a} \tag{31}$$

$$q_{ij}'''^{mn}=\begin{bmatrix}(2\pi\rho_\varphi)_{M,M+1}\\ (0)_{1,M+1}\end{bmatrix}*\mathbf{a} \tag{32}$$

where

$$\xi_m=\sum_{i=1}^{M}\rho_i(\sigma_i)^m;\qquad \beta_{3\times 2^m}=1+\frac{b_2}{3\times(-2)^m};\qquad y_0=\frac{\beta_3}{\beta_6}$$

$$D_\Omega=\sum_{i=1}^{M}\rho_i\mathcal{M}_i^2+\frac{\sigma_s^2}{4}\rho_s\left(\sum_{i=1}^{M}\rho_i\sigma_i v_i\mathcal{M}_i\right)^2$$

$$D = 1 + \frac{\sigma_s^2}{4} \rho_s \sum_{i=1}^{M} \rho_i \sigma_i^2 \nu_i^2$$

$$P_M = \sum_{i=1}^{M} \rho_i \sigma_i \mathcal{M}_i; \qquad P_\nu = \sum_{i=1}^{M} \rho_i \sigma_i^2 \nu_i \tag{33}$$

$$\eta_j = \nu_j + \frac{\pi}{2\Delta} P_\nu \sigma_j; \qquad Z_j^* = Z_j - \frac{\pi}{6} \rho_\varphi \sigma_j^3 \tag{34}$$

The first terms in Eqs. (30) and (31) correspond to the coefficients of the BW functions for the model of hard spheres with arbitrary sizes. The elements of the matrix **a** are given by $a_i^m \delta_{ij}^{mn}$. The a_i^m can be found from the derivative of Eqs. (24) at $r = 0$,[14]

$$a_i^0 = \frac{2}{D_\Omega \sigma_i} \left(Z_i^* - \mathcal{M}_i - \frac{\pi}{2\Delta} P_M \sigma_i^2 \right) \tag{35}$$

$$a_s^1 = \frac{\sigma_s}{D_\Omega} \sum_{j=1}^{M} \rho_j Z_j^* \nu_j + \frac{y_0}{D_\Omega} \sum_{j=1}^{M} \rho_j \sigma_j \nu_j \mathcal{M}_j \tag{36}$$

From the condition which comes from Eqs. (8) and (24) and symmetry of $C_{0,ij}^{mn}(r)$

$$q_{ij}^{mn}(\lambda_{ji}) - A_{ij}^{mn} = q_{ji}^{nm}(\lambda_{ij}) - A_{ji}^{nm} \tag{37}$$

one obtains the set of nonlinear equations for the parameters $\mathcal{M}_i$ and ν_i

$$D_\Omega a_i^0 = 2\Gamma \mathcal{M}_i + \frac{\sigma_s^2}{2} \rho_s (\eta_i + \Gamma \sigma_i \nu_i) \sum_{j=1}^{M} \rho_j \sigma_j \nu_j \mathcal{M}_j - \frac{\sigma_s^2}{2\beta_6} \rho_s \sigma_i \nu_i B^{10}$$

$$\mathcal{M}_i a_s^1 D = y_0 \sigma_i \nu_i + \sigma_s \eta_i + \frac{\sigma_s}{2} D a_i^0 \sum_{j=1}^{M} \rho_j \sigma_j \nu_j \mathcal{M}_j \tag{38}$$

where the screening parameter Γ and ion–dipole interaction parameter B^{10} are introduced. Equations (38) are similar to the ones given in ref. 14 if $Z_j \to Z_j^*$. The set of equations (38), as in refs. 13–16, has to be supplemented by three equations which couple Γ, B^{10}, and b_2 with the parameters of ion–ion, ion–dipole, and dipole–dipole interactions,

$$\alpha_0^2 = 4\pi\beta e^2, \qquad \alpha_1^2 = \alpha_0 \alpha_2, \qquad \alpha_2^2 = (4\pi/3)\, \beta p_s^2 \tag{39}$$

Two of them are Eqs. (26) supplemented by Eqs. (28) and the third is defined by the closure (13) for the $c_{ss}^{112}(r)$ and has the form

$$\frac{\beta_6^2}{\beta_{12}^4} + \rho_s \alpha_2^2 = (1 - \rho_s K_{ss}^{11})^2 + \rho_s \sum_{i=1}^{M} \rho_i (K_{si}^{10})^2 \tag{40}$$

Defining the constants K_{ij}^{mn} by Eqs. (27), taking account of Eqs. (29), the necessary set of equations has the form

$$\alpha_0^2 = \sum_{i=1}^{M} \sum_{m=0}^{1} \rho_i (a_i^m)^2$$

$$\alpha_0(\alpha_2 - \alpha_0 \Lambda^{10}) \beta_6 D = \frac{\sigma_s^2}{2} \sum_{i=1}^{M} \rho_i a_i^0 \eta_i + a_s^1 y_0 \qquad (41)$$

$$\left(D \frac{\beta_6^2}{\beta_{12}^2}\right)^2 + \rho_s [(\alpha_2 - \alpha_0 \Lambda^{10}) \beta_6 D]^2 = \frac{\sigma_s^2}{4} \rho_s \sum_{i=1}^{M} \rho_i \eta_i^2 + y_0^2$$

where

$$\Lambda^{10} = \frac{\sigma_s^3}{12} \sum_{i=1}^{M} \rho_i Z_i^* v_i + \frac{\sigma_s^2}{4\beta_6} \sum_{i=1}^{M} \rho_i \sigma_i v_i \mathscr{M}_i$$

Therefore, similarly to the case of an ionic system in a neutralizing background,[32,33] the equations for the parameters Γ, B^{10}, and b_2 coincide with the corresponding set of equations for the electroneutral ion–dipole model.[12–16] The presence of a neutralizing background leads to the renormalization of the valences according to Eqs. (34) and the value of the dipole moment does not change. The presence of the neutralizing background results in the appearance of a cubic term in the polynomials $q_{ij}^{mn}(r)$ and the additional term $\pi \rho_\varphi \sigma_i a_j^n$ in the coefficients q_{ij}^{mn} for the BW factor correlation functions.

In the absence of a neutralizing background the obtained expressions are reduced to the previous results for the electroneutral ion–dipole model[10–16] as well as in the absence of dipoles ($\rho_s = 0$) to the results for an ionic system in a neutralizing background.[31–33] In the latter case, assuming that $b_2 = 0$, $B^{10} = 0$, and $v_j = 0$, we find from Eqs. (38)

$$P_M = \sum_{i=1}^{M} \rho_i \sigma_i \mathscr{M}_i = \sum_{i=1}^{M} \frac{\rho_i Z_i^* \sigma_i}{1 + \Gamma \sigma_i} \Bigg/ \left(1 + \frac{\pi}{2\Delta} \sum_{j=1}^{M} \frac{\rho_j \sigma_j^3}{1 + \Gamma \sigma_j}\right)$$

and then in accordance with Eqs. (36) and (41) obtain the equation for the definition of the screening parameter

$$4\Gamma^2 = \alpha_0^2 \sum_{i=1}^{M} \rho_i \left[\frac{Z_i^* - (\pi/2\Delta) P_M \sigma_i^2}{1 + \Gamma \sigma_i}\right]^2 \qquad (42)$$

which coincides with a similar equation given in ref. 32.

3. THE TOTAL AND DIRECT PAIR CORRELATION FUNCTIONS

The functions $H_{ij}^{mn}(r)$ in accordance with Eqs. (12) obey the closure, which can be rewritten as

$$\mathbf{H}(r)=\begin{bmatrix} (-1)_{M,M} & \left[\frac{\beta_6}{2\pi r}\left(v_i-\frac{\pi}{6}\sum_{j=1}^{M}\rho_j\sigma_j^3 v_j\right)\right]_{M,1} \\ \left[\frac{-\beta_6}{2\pi r}\left(v_j-\frac{\pi}{6}\sum_{i=1}^{M}\rho_i\sigma_i^3 v_i\right)\right]_{1,M} & \left(\frac{-b_2}{\pi\rho_s\sigma_s^3}\right)_{1,1}\end{bmatrix}, \qquad r<\sigma_{ij} \tag{43}$$

Let us introduce the functions

$$G_{ij}^{mn}(r)=H_{ij}^{mn}(r)-E_{ij}^{mn}(r) \tag{44}$$

where $E_{ij}^{mn}(r)$ are functions equal to $H_{ij}^{mn}(r)$ in the hard core region. By the differentiation of Eqs. (25), similarly to refs. 10 and 14, we arrive at the following equations for $G_{ij}^{mn}(r)$:

$$\begin{aligned} 2\pi r[G_{ij}^{mn}(r)+E_{ij}^{mn}(r)]+\frac{d}{dr}q_{ij}^{mn}(r) &= \sum_{i_1=1}^{M}\sum_{n_1=0}^{1}\rho_{i_1}J_{ii_1}^{mn_1}(0)\,Z_{i_1}a_j^n \\ &\quad +2\pi\sum_{i_1=1}^{M}\sum_{n_1=0}^{1}\rho_{i_1}\left\{Z_{i_1}a_j^n\int_0^{r-\lambda_{ji_1}}dt\,t[G_{ii_1}^{mn_1}(t)+E_{ii_1}^{mn_1}(t)]\right. \\ &\quad \left.+\int_{\lambda_{ji_1}}^{\sigma_{ji_1}}dt\,(r-t)[G_{ii_1}^{mn_1}(|r-t|)+E_{ii_1}^{mn_1}(|r-t|)]\,q_{i_1j}^{n_1n}(t)\right\} \end{aligned} \tag{45}$$

With the account of the closure for $G_{ij}^{mn}(r)$,

$$G_{ij}^{mn}(r)=0, \qquad r<\sigma_{ij} \tag{46}$$

the set of convolution integral equations can be obtained

$$\begin{aligned} rG_{ij}^{mn}(r)-\sum_{i_1=1}^{M}\sum_{n_1=0}^{1}\rho_{i_1}\int_{\lambda_{ji_1}}^{r}dt\,(r-t)\,G_{ii_1}^{mn_1}(r-t)\,Q_{i_1j}^{n_1n}(t) \\ =\frac{1}{2\pi}\left[q_{ij}^{\prime mn}+(r-\sigma_{ij})\,q_{ij}^{\prime\prime mn}+\frac{1}{2}(r-\sigma_{ij})^2\,q_{ij}^{\prime\prime\prime mn}\right] \end{aligned} \tag{47}$$

By a Laplace transformation, we arrive at the linear algebraic equations for $\hat{G}_{ij}^{mn}(s)$:

$$\sum_{i_1=1}^{M} \sum_{n_1=0}^{1} \hat{G}_{ii_1}^{mn_1}(s)[\delta_{ji_1}^{nn_1} - \rho_{i_1} \hat{Q}_{i_1 j}^{n_1 n}(s)] = \frac{\exp(-s\sigma_{ij})}{2\pi s^3} (q_{ij}^{'''mn} + s q_{ij}^{''mn} + s^2 q_{ij}^{'mn}) \tag{48}$$

where $\hat{Q}_{ij}^{mn}(s)$ are the Laplace transforms of the BW functions:

$$\hat{Q}_{ij}^{mn}(s) = e^{s\lambda_{ij}} \left[\varphi_1(\sigma_i)\, q_{ij}^{'mn} + \varphi_2(\sigma_i)\, q_{ij}^{''mn} + \varphi_3(\sigma_i)\, q_{ij}^{'''mn} - \frac{Z_i}{s} a_j^n \right]$$

$$\varphi_m(\sigma) = s^{-m-1} \left[\sum_{k=0}^{m} \frac{(-s\sigma)^k}{k!} - \exp(-s\sigma) \right], \qquad m = 0, 1, 2, 3 \tag{49}$$

$$\hat{G}_{ij}^{mn}(s) = \int_0^\infty dr\, r G_{ij}^{mn}(r) \exp(-sr)$$

The solution of Eqs. (48) reduces in the general case to the evaluation of the inverse matrix $\mathbf{W}^{-1}$, where the matrix $\mathbf{W}$ consists of the elements

$$W_{ij}^{mn} = \delta_{ij}^{mn} - \rho_i \hat{Q}_{ij}^{mn}(s) \tag{50}$$

In order to do this, we mention that the coefficients of $q_{ij}^{mn}(r)$ given by Eqs. (30)–(32) can be rewritten as

$$\begin{aligned} q_{ij}^{'mn} &= \frac{\pi}{\Delta} \left(\check{b}_i^m \check{d}_j^n + \check{d}_i^m \check{b}_j^n + \frac{\pi}{2\Delta} \xi_2 \check{d}_i^m \check{d}_j^n \right) - \frac{2}{\rho_s \sigma_s^2} \check{v}_i^m \check{v}_j^n \\ &\quad + \left(D_\Omega \check{f}_i^m \check{f}_j^n - \frac{\sigma_s^2}{D} \rho_s \check{y}_i^m \check{y}_j^n \right) \left(\check{v}_i^m - \frac{1}{2} \right) \\ q_{ij}^{''mn} &= \frac{2\pi}{\Delta} \check{b}_i^m \check{b}_j^n + \frac{\pi^2}{\Delta^2} \xi_2 \check{b}_i^m \check{d}_j^n + \frac{b_2}{\sigma_s \beta_6 D} \check{v}_i^m \check{y}_j^n \\ &\quad - \frac{\pi}{2\Delta} \frac{\sigma_s^2}{D} \rho_s P_v \check{b}_i^m \check{y}_j^n + \check{u}_i^m \check{f}_j^n \\ q_{ij}^{'''mn} &= 2\pi \rho_\varphi \check{b}_i^m \check{f}_j^n \end{aligned} \tag{51}$$

where we used the inverted caret to denote an $(M+1)$-component vector. The components of the vectors are given by

$$\begin{aligned} &\check{b}_i^m = 1 - \check{v}_i^m, \qquad \check{v}_i^m = \delta_{si}^{1m}, \qquad \check{d}_i^m = \sigma_i \check{b}_i^m, \qquad \check{f}_i^m = a_i^m \\ &\check{y}_i^m = \eta_i \check{b}_i^m + \frac{2y_0}{\rho_s \sigma_s^2} \check{v}_i^m \\ &\check{u}_i^m = \left(\frac{\pi}{\Delta} P_M + \pi \rho_\varphi \sigma_i \right) \check{b}_i^m + \sum_{j=1}^{M} \rho_j v_j \left(Z_j^* - \frac{b_2 \sigma_j}{2\sigma_s \beta_6} \mathscr{M}_j \right) \check{v}_i^m \end{aligned} \tag{52}$$

Then the matrix **W** can be represented as the Jacobi matrix

$$W_{ij}^{mn} = \delta_{ij}^{mn} - \check{a}_i^m \check{b}_j^n - \check{c}_i^m \check{d}_j^n - \check{e}_i^m \check{f}_j^n - \check{z}_i^m \check{y}_j^n - \check{w}_i^m \check{v}_j^n \tag{53}$$

with the following components of the vectors:

$$\begin{aligned}
\check{a}_i^m &= \frac{2\pi}{s\Delta}\rho_i\left[\frac{\sigma_i}{2}\varphi_0(\sigma_i)+\varphi_1(\sigma_i)\right]\check{b}_i^m\\
\check{e}_i^m &= \rho_i\left[\check{u}_i^m\varphi_2(\sigma_i)+D_\Omega\varphi_1(\sigma_i)\check{f}_i^m\left(\check{v}_i^m-\frac{1}{2}\right)-\frac{Z_i^*}{s}\check{b}_i^m\right]+\frac{\Delta}{s}\rho_\varphi\check{a}_i^m\\
\check{z}_i^m &= \frac{\rho_s}{D}\left[\varphi_2(\sigma_i)\left(\frac{b_2}{\sigma_s\beta_6}\check{v}_i^m-\frac{\pi}{2\Delta}\sigma_s^2\rho_s P_v\check{b}_i^m\right)-\frac{\sigma_s^2}{2}\rho_i\varphi_1(\sigma_i)\check{y}_i^m\right]\\
\check{c}_i^m &= \frac{\pi}{\Delta}\left[\rho_i\varphi_1(\sigma_i)\check{b}_i^m+\frac{1}{2}\xi_2\check{a}_i^m\right]\\
\check{w}_i^m &= -\frac{2}{\sigma_s^2}\varphi_1(\sigma_s)\check{v}_i^m
\end{aligned} \tag{54}$$

The following procedure to calculate $\mathbf{W}^{-1}$ is given in the Appendix. Multiplying the set (48) by the inverse matrix $\mathbf{W}^{-1}$, we obtain the following expression:

$$\begin{aligned}
\hat{G}_{ij}^{mn}(s) = \frac{\exp(-s\sigma_{ij})}{2\pi s^2}\Bigg\{&\left(\frac{2\pi}{\Delta}\check{b}_i^m+\frac{\pi s}{\Delta}\check{d}_i^m\right)\left[\frac{1-\check{c}\check{d}}{D_0(s)}(\check{b}_j^n+\mathscr{E}_{\check{b}}\check{h}_j^n+\mathscr{Z}_{\check{b}}\check{p}_j^n)\right.\\
&\left.+\frac{(\check{c}\check{b})}{D_0(s)}(\check{d}_j^n+\mathscr{E}_{\check{d}}\check{h}_j^n+\mathscr{Z}_{\check{d}}\check{p}_j^n)\right]\\
&+\left(\frac{\pi^2}{\Delta^2}\xi_2\check{b}_i^m+\frac{\pi}{\Delta}s\check{b}_i^m+\frac{\pi^2 s}{2\Delta^2}\xi_2\check{d}_i^m\right)\\
&\times\left[\frac{(\check{a}\check{d})}{D_0(s)}(\check{b}_j^n+\mathscr{E}_{\check{b}}\check{h}_j^n+\mathscr{Z}_{\check{b}}\check{p}_j^n)\right.\\
&\left.+\frac{1-(\check{a}\check{b})}{D_0(s)}(\check{d}_j^n+\mathscr{E}_{\check{d}}\check{h}_j^n+\mathscr{Z}_{\check{d}}\check{p}_j^n)\right]+\left(\frac{1-(\check{e}\check{h})}{D_T(s)}\check{p}_j^n+\mathscr{E}_{\check{p}}\check{h}_j^n\right)\\
&\times\left[\frac{b_2}{\sigma_s\beta_6 D}\check{v}_i^m-\frac{\pi}{2\Delta}\frac{\sigma_s^2}{D}\rho_s P_v\check{b}_i^m+s\frac{\sigma_s^2}{D}\rho_s\check{y}_i^m\left(\check{v}_i^m-\frac{1}{2}\right)\right]\\
&+\left(\frac{1-(\check{z}\check{p})}{D_T(s)}\check{h}_j^n+\frac{(\check{z}\check{h})}{D_T(s)}\check{p}_j^n\right)\\
&\times\left[\check{u}_i^m+sD_\Omega\left(\check{v}_i^m-\frac{1}{2}\right)\check{f}_i^m+\frac{2\pi}{s}\rho_\varphi\check{b}_i^m\right]\\
&-\frac{2s}{\rho_s\sigma_s^2}\frac{\check{v}_i^m}{1-(\check{w}\check{v})}(\check{v}_j^n+\mathscr{E}_{\check{v}}\check{h}_j^n+\mathscr{Z}_{\check{v}}\check{p}_j^n)\Bigg\}
\end{aligned} \tag{55}$$

where

$$\mathscr{E}_{\check{x}} = \frac{1}{D_T(s)} [(1 - \check{z}\check{p})(\check{e}\check{x}) + (\check{e}\check{p})(\check{z}\check{x})] \tag{56}$$

$$\mathscr{Z}_{\check{x}} = \frac{1}{D_T(s)} [(1 - \check{e}\check{h})(\check{z}\check{x}) + (\check{z}\check{h})(\check{e}\check{x})] \tag{57}$$

In Eqs. (55) we have used the following definitions, which are introduced in the Appendix:

$$\check{h}_i^m = \check{f}_i^m + [(1 - \check{c}\check{d})(\check{a}\check{f}) + (\check{a}\check{d})(\check{c}\check{f})] \frac{\check{b}_i^m}{D_0(s)}$$
$$+ [(1 - \check{a}\check{b})(\check{c}\check{f}) + (\check{c}\check{b})(\check{a}\check{f})] \frac{\check{d}_i^m}{D_0(s)} + \frac{(\check{w}\check{f})}{1 - \check{w}\check{v}} \check{v}_i^m$$

$$\check{p}_i^m = \check{y}_i^m + [(1 - \check{c}\check{d})(\check{a}\check{y}) + (\check{a}\check{d})(\check{c}\check{y})] \frac{1}{D_0(s)} \check{b}_i^m$$
$$+ [(1 - \check{a}\check{b})(\check{c}\check{y}) + (\check{c}\check{b})(\check{a}\check{y})] \frac{1}{D_0(s)} \check{d}_i^m + \frac{(\check{w}\check{v})}{1 - \check{w}\check{v}} \check{v}_i^m$$

$$D_0(s) = (1 - \check{a}\check{b})(1 - \check{c}\check{d}) - (\check{a}\check{d})(\check{b}\check{c})$$

$$D_T(s) = (1 - \check{e}\check{h})(1 - \check{z}\check{p}) - (\check{e}\check{p})(\check{z}\check{h})$$

$(\check{a}\check{b})$ is the product

$$(\check{a}\check{b}) = \sum_{i=1}^{M} \sum_{m=0}^{1} \check{a}_i^m \check{b}_i^m \tag{58}$$

Applying the symmetry condition of the invariant expansion coefficients of the TCF $h_{ij}^{mnl}(r)$, which leads to

$$\hat{G}_{ij}^{mn}(s) = (-1)^{m+n} \hat{G}_{ji}^{nm}(s) \tag{59}$$

one can rewrite Eqs. (55) in a more compact form,[16,29]

$$\hat{G}_{ij}^{mn}(s) = \hat{G}_{ij}^{\mathrm{HS}}(s) \check{b}_i^m \check{b}_j^n + \frac{\exp(-s\sigma_{ij})}{2\pi s} \left\{ \frac{\check{v}_i^m - 1/2}{D_T(s)} \left[\frac{\sigma_s^2}{D} \rho_s (1 - \check{e}\check{h}) \check{p}_i^m \check{p}_j^n \right.\right.$$
$$\left. + D_\Omega (1 - \check{z}\check{p}) \check{h}_i^m \check{h}_j^n + D_\Omega (\check{z}\check{h})(\check{h}_i^m \check{p}_j^n + \check{p}_i^m \check{h}_j^n) \right]$$
$$\left. - \frac{2}{\rho_s \sigma_s^2} \frac{\check{v}_i^m \check{v}_j^n}{1 - \check{w}\check{v}} \right\} \tag{60}$$

where $\hat{G}_{ij}^{\mathrm{HS}}(s)$ are the Laplace transforms of the PDF of the hard spheres with different sizes in the PY approximation.

The explicit dependence of $\hat{G}_{ij}^{mn}(s)$ on the background density is involved in the vector $\check{e}_i^m$ only,

$$\check{e}_i^0 = (\check{e}_i^0)^* + \frac{\Delta}{s}\rho_\varphi \check{a}_i^0 + \pi\rho_\varphi \sigma_i \varphi_2(\sigma_i)$$

where $(\check{e}_i^0)^*$ is the vector corresponding to the same vector for the electroneutral ion–dipole system[15,16] with the substitution of Z_j by Z_j^*.

It is shown in ref. 29 that

$$(\check{e}\check{h}) = (\check{e}^*\check{h}), \qquad (\check{e}\check{p}) = (\check{e}^*\check{p}) \tag{61}$$

Therefore, the presence of a background does not change the analytical expression for $\hat{G}_{ij}^{mn}(s)$ which was obtained in refs. 15 and 16. However, it is necessary to replace the valence Z_j by Z_j^* everywhere in the calculation of all the coefficients. This effective value Z_j^* defines the change of the PDF in the presence of a neutralizing background.

The obtained results generalize the ones given previously for the following limiting cases: (1) the electroneutral ion–dipole system, i.e., $\rho_\varphi = 0$; (2) the mixture of charged hard spheres in a neutralizing background.

In the former, assuming $\rho_\varphi = 0$, one obtains $Z_j^* = Z_j$, and then Eq. (60) is reduced to the corresponding result given in refs. 15 and 16.

In the second case one has to assume $p_s = 0$. Then the $(M+1)$th element of all vectors equals zero. It follows then that $\check{w}_i^m = \check{z}_i^m = \check{y}_i^m = 0$ and

$$D_T(s) = 1 - (\check{e}\check{h}) = 1 - (\check{e}\check{f}) - \frac{\Delta D_T(s)}{D_0(s)} \tag{62}$$

where

$$\Delta D_T(s) = (1 - \check{a}\check{b})(\check{e}\check{d})(\check{c}\check{f}) + (1 - \check{c}\check{d})(\check{a}\check{f})(\check{e}\check{b})$$
$$+ (\check{a}\check{f})(\check{c}\check{b})(\check{e}\check{d}) + (\check{a}\check{d})(\check{c}\check{f})(\check{e}\check{b})$$

The expression for the Laplace transform of the ion–ion PDF can be written as

$$\hat{G}_{ij}^{00}(s) = \hat{G}_{ij}^{\mathrm{HS}}(s) - \frac{\exp(-s\sigma_{ij})}{4\pi s}\frac{D_\Omega}{D_T(s)}\check{h}_i^0 \check{h}_j^0 \tag{63}$$

If we introduce the notations

$$\check{t}_j = D_0(s)\,\check{f}_j^0 + \frac{\pi}{\Delta}\,(\delta_1 P_{\varphi_1} + \delta_3 P_{\varphi_0})\,\sigma_j + \frac{\pi}{s\Delta}\,(\delta_1 P_{\varphi_0} + 2\delta_2 P_{\varphi_1})$$

$$\begin{aligned}
P_{\varphi_0} &= \sum_{i=1}^{M} \rho_i \sigma_i \check{f}_i^0 \varphi_0(\sigma_i) \\
P_{\varphi_1} &= \sum_{i=1}^{M} \rho_i \check{f}_i^0 \varphi_1(\sigma_i) \\
\delta_1 &= 1 - \frac{\pi}{\Delta} \sum_{i=1}^{M} \rho_i \sigma_i \varphi_1(\sigma_i) \\
\delta_2 &= 1 + \frac{\pi}{2\Delta} \sum_{i=1}^{M} \rho_i \sigma_i^2 \varphi_0(\sigma_i) \\
\delta_3 &= \frac{\pi}{\Delta} \sum_{i=1}^{M} \rho_i \varphi_2(\sigma_i) \\
D_T^*(s) &= D_T(s)\,D_0(s)
\end{aligned} \tag{64}$$

the expression (63) can be rewritten in the form

$$\hat{G}_{ij}^{00}(s) = \hat{G}_{ij}^{\mathrm{HS}}(s) - \frac{\exp(-s\sigma_{ij})}{\pi s}\left(\frac{\Gamma}{\alpha_0}\right)^2 \frac{\check{t}_i \check{t}_j}{D_T^*(s)} \tag{65}$$

which coincides with the result obtained in ref. 33 for the pure ionic case, and in the absence of the background ($\rho_\varphi = 0$) reduces to the case of a multicomponent electroneutral ionic system.[23]

Replacing in (60) the Laplace transform by the Fourier transform yields

$$\tilde{D}_{ij}^{mn}(k) = \lim_{s \to ik} \left\{\frac{2\pi}{s}\,[\hat{G}_{ij}^{mn}(-s) - \hat{G}_{ij}^{mn}(s)]\right\} \tag{66}$$

Inverting Eqs. (66) to r space, the functions $D_{ij}^{mn}(r)$ are

$$\begin{aligned}
D_{ij}^{mn}(r) &= H_{ij}^{mn}(r), \qquad m = n \\
&= G_{ij}^{mn}(r), \qquad m \neq n
\end{aligned} \tag{67}$$

Having in mind Eqs. (5) and (11), the TCFs of the asymmetric ion–dipole model in the neutralizing background in the MSA are given by

$$h_{ij}(X_1, X_2) = D_{ij}^{00}(r_{12}), \qquad 1 \leqslant i, j \leqslant M-1$$

$$h_{is}(X_1, X_2) = D_{is}^{00}(r_{12}) + \left\{ D_{is}^{01}(r_{12}) - \frac{1}{(r_{12})^2} \int_0^{r_{12}} dt\, t D_{is}^{01}(t) \right\} \cos \vartheta_2$$

$$\begin{aligned} h_{ss}(X_1, X_2) = {} & D_{ss}^{00}(r_{12}) + \{ D_{ss}^{11}(r_{12}) - 2H_{1,ss}^{11}(r_{12}) \} \cos \vartheta_{12} \\ & + \left\{ D_{ss}^{11}(r_{12}) + H_{1,ss}^{11}(r_{12}) \right. \\ & \left. - \frac{3}{(r_{12})^3} \int_0^{r_{12}} dt\, t^2 [D_{ss}^{11}(t) + H_{1,ss}^{11}(t)] \right\} \\ & \times (3 \cos \vartheta_1 \cos \vartheta_2 - \cos \vartheta_{12}) \end{aligned} \tag{68}$$

where ϑ_1 denotes the orientation of the dipole moment of molecule 1 and ϑ_{12} is the angle between dipole moments of molecules 1 and 2.

Finally, we shall present expressions for the coefficients of the DCF $C_{ij}^{mn}(r)$ given in Eqs. (9). To find them, it is necessary to differentiate Eqs. (24). We choose $\sigma_j > \sigma_i$ for concreteness. When $0 \leqslant r \leqslant \lambda_{ji}$, one obtains

$$\begin{aligned} -2\pi r C_{ij}^{mn}(r) = {} & q_{ji}'^{nm} - (r + \sigma_{ij})\, q_{ji}''^{nm} + \frac{1}{2} (r + \sigma_{ij})^2\, q_{ji}'''^{nm} - \frac{\alpha_0^2}{2} Z_i Z_j \\ & - \sum_{i_1=1}^{M} \sum_{n_1=0}^{1} \rho_{i_1} \left\{ \int_{\lambda_{i_1 i}}^{\sigma_{ii_1}} dt\, q_{ii_1}^{mn_1}(t) \frac{d}{d(t-r)}\, q_{ji_1}^{nn_1}(t-r) \right. \\ & \left. + A_{ii_1}^{mn_1} q_{ji_1}^{nn_1}(\lambda_{i_1 i} - r) \right\} \end{aligned} \tag{69}$$

and after substitution of Eqs. (29) for $q_{ij}^{mn}(r)$ into Eqs. (69),

$$\begin{aligned} -2\pi r C_{ij}^{mn}(r) = {} & q_{ji}'^{nm} - (r + \sigma_{ij})\, q_{ji}''^{nm} + \frac{1}{2} (r + \sigma_{ij})^2\, q_{ji}'''^{nm} - \frac{\alpha_0^2}{2} Z_i Z_j \\ & - \sum_{i_1=1}^{M} \sum_{n_1=0}^{1} \rho_{i_1} \left\{ (r + \sigma_{ij})\, A_{ii_1}^{mn_1} q_{ji_1}'^{nn_1} \right. \\ & - \frac{1}{2} (r + \sigma_{ij})^2\, A_{ii_1}^{mn_1} q_{ji_1}''^{nn_1} + \frac{1}{6} (r + \sigma_{ij})^3\, A_{ii_1}^{mn_1} q_{ji_1}'''^{nn_1} \\ & - \frac{1}{2} \sigma_i^2 q_{ii_1}'^{mn_1} q_{ji_1}'^{nn_1} - \left[\frac{\sigma_i^3}{3} + \frac{\sigma_i^2}{2} (r + \lambda_{ji}) \right] q_{ii_1}'^{mn_1} q_{ji_1}''^{nn_1} \\ & - \frac{\sigma_i^3}{6}\, q_{ii_1}''^{mn_1} q_{ji_1}'^{nn_1} \end{aligned}$$

$$+\left[\frac{\sigma_i^4}{8}+\frac{\sigma_i^3}{3}(r+\lambda_{ji})+\frac{\sigma_i^2}{4}(r+\lambda_{ji})^2\right]q_{ii_1}^{\prime mn_1}q_{ji_1}^{\prime\prime\prime nn_1}$$

$$+\frac{\sigma_i^4}{24}q_{ii_1}^{\prime\prime\prime mn_1}q_{ji_1}^{\prime nn_1}+\left[\frac{\sigma_i^4}{8}+\frac{\sigma_i^3}{6}(r+\lambda_{ji})\right]q_{ii_1}^{\prime\prime mn_1}q_{ji_1}^{\prime\prime nn_1}$$

$$-\left[\frac{\sigma_i^5}{20}+\frac{\sigma_i^4}{8}(r+\lambda_{ji})+\frac{\sigma_i^3}{12}(r+\lambda_{ji})^2\right]q_{ii_1}^{\prime\prime mn_1}q_{ji_1}^{\prime\prime\prime nn_1}$$

$$-\left[\frac{\sigma_i^5}{30}+\frac{\sigma_i^4}{24}(r+\lambda_{ji})\right]q_{ii_1}^{\prime\prime\prime mn_1}q_{ji_1}^{\prime\prime nn_1}$$

$$+\left[\frac{\sigma_i^6}{72}+\frac{\sigma_i^5}{30}(r+\lambda_{ji})+\frac{\sigma_i^4}{48}(r+\lambda_{ji})^2\right]q_{ii_1}^{\prime\prime\prime mn_1}q_{ji_1}^{\prime\prime\prime nn_1}\Bigg\} \tag{70}$$

When $\lambda_{ji}\leqslant r\leqslant\sigma_{ij}$, after differentiation of Eqs. (24), one obtains

$$-2\pi rC_{ij}^{mn}(r)=-\frac{d}{dr}q_{ij}^{mn}(r)+\sum_{i_1=1}^{M}\sum_{n_1=0}^{1}\rho_{i_1}\Bigg\{-q_{ii_1}^{mn_1}(\lambda_{i_1j}+r)\,q_{ji_1}^{nn_1}(\lambda_{i_1j})$$

$$+\int_{r-\lambda_{ji_1}}^{\sigma_{ii_1}}dt\,q_{ii_1}^{mn_1}(t)\frac{d}{d(t-r)}q_{ji_1}^{nn_1}(t-r)$$

$$+A_{ji_1}^{nn_1}q_{ii_1}^{mn_1}(\lambda_{i_1j}+r)-\frac{1}{2}A_{ii_1}^{mn_1}A_{ji_1}^{nn_1}\Bigg\}$$

and after substitution of Eqs. (29),

$$-2\pi rC_{ij}^{mn}(r)=-q_{ij}^{\prime mn}-(r-\sigma_{ij})\,q_{ij}^{\prime\prime mn}-\frac{1}{2}(r-\sigma_{ij})^2\,q_{ij}^{\prime\prime\prime mn}-\frac{\alpha_0^2}{2}Z_iZ_j$$

$$+\sum_{i_1=1}^{M}\sum_{n_1=0}^{1}\rho_{i_1}\Bigg\{(r-\sigma_{ij})\,q_{ii_1}^{\prime mn_1}A_{ji_1}^{nn_1}$$

$$+\frac{1}{2}(r-\sigma_{ij})^2\,q_{ii_1}^{\prime\prime mn_1}A_{ji_1}^{nn_1}+\frac{1}{6}(r-\sigma_{ij})^3\,q_{ii_1}^{\prime\prime\prime mn_1}A_{ji_1}^{nn_1}$$

$$+\left[\sigma_j(r-\sigma_{ij})+\frac{1}{2}(r-\sigma_{ij})^2\right]q_{ii_1}^{\prime mn_1}q_{ji_1}^{\prime nn_1}$$

$$+\left[\frac{1}{3}(r-\sigma_{ij})^3-\frac{1}{2}(r-\sigma_{ij})^2(r+\lambda_{ji})\right.$$

$$\left.-\frac{1}{2}\sigma_j^2(r-\sigma_{ij})\right]q_{ii_1}^{\prime mn_1}q_{ji_1}^{\prime\prime nn_1}$$

$$
\begin{aligned}
&+\left[\frac{1}{6}(r-\sigma_{ij})^3+\frac{\sigma_j}{2}(r-\sigma_{ij})^2\right] q_{ii_1}^{\prime\prime mn_1} q_{ji_1}^{\prime mn_1}\\
&+\left[\frac{1}{24}(r-\sigma_{ij})^4+\frac{\sigma_j}{6}(r-\sigma_{ij})^3\right] q_{ii_1}^{\prime\prime\prime mn_1} q_{ji_1}^{\prime nn_1}\\
&+\left[\frac{1}{8}(r-\sigma_{ij})^4-\frac{1}{3}(r-\sigma_{ij})^3(r+\lambda_{ji})\right.\\
&\left.+\frac{1}{4}(r-\sigma_{ij})^2(r+\lambda_{ji})^2+\frac{\sigma_j^3}{6}(r-\sigma_{ij})\right] q_{ii_1}^{\prime mn_1} q_{ji_1}^{\prime\prime\prime nn_1}\\
&+\left[\frac{1}{8}(r-\sigma_{ij})^4-\frac{1}{6}(r-\sigma_{ij})^3(r+\lambda_{ji})\right.\\
&\left.-\frac{\sigma_j^2}{4}(r-\sigma_{ij})\right] q_{ii_1}^{\prime\prime mn_1} q_{ji_1}^{\prime\prime nn_1}\\
&+\left[\frac{1}{20}(r-\sigma_{ij})^5-\frac{1}{8}(r-\sigma_{ij})^4(r+\lambda_{ji})\right.\\
&\left.+\frac{1}{12}(r-\sigma_{ij})^3(r+\lambda_{ji})^2+\frac{\sigma_j^3}{12}(r-\sigma_{ij})^2\right] q_{ii_1}^{\prime\prime mn_1} q_{ji_1}^{\prime\prime\prime nn_1}\\
&+\left[\frac{1}{30}(r-\sigma_{ij})^5-\frac{1}{24}(r-\sigma_{ij})^4(r+\lambda_{ji})\right.\\
&\left.-\frac{\sigma_j^2}{12}(r-\sigma_{ij})^3\right] q_{ii_1}^{\prime\prime\prime mn_1} q_{ji_1}^{\prime\prime nn_1}\\
&+\left[\frac{1}{72}(r-\sigma_{ij})^6-\frac{1}{30}(r-\sigma_{ij})^5(r+\lambda_{ji})\right.\\
&\left.\left.+\frac{1}{48}(r-\sigma_{ij})^4(r+\lambda_{ji})^2+\frac{\sigma_j^3}{36}(r-\sigma_{ij})^3\right] q_{ii_1}^{\prime\prime\prime mn_1} q_{ji_1}^{\prime\prime\prime nn_1}\right\} \qquad (71)
\end{aligned}
$$

So, the functions $C_{ij}^{mn}(r)$ are given for $0 \leqslant r \leqslant \lambda_{ji}$ by Eqs. (70), for $\lambda_{ji} \leqslant r \leqslant \sigma_{ij}$ by Eqs. (71), and for $r > \sigma_{ij}$ in accordance with (21).

Then the DCF $c_{ij}(X_1, X_2)$ as well as the TCF are given by expressions (5) and (11).

4. THERMODYNAMIC PROPERTIES AND DIELECTRIC CONSTANT

The thermodynamic properties can be calculated by three independent methods starting from the internal energy, from the virial equation of state, or from the compressibility equation.[1,2] However, due to the thermodynamic non-self-consistancy of the MSA all three lead to different results. The best are the results based on the internal energy calculations. Høye and Stell[38] have developed a general method making it possible to obtain the excess Helmholtz free energy, the excess chemical potentials, the excess free enthalpy (or Gibbs free energy), and the equation of state in terms of interaction parameters. This scheme has been applied for the electroneutral ion–dipole model by Blum and Wei.[13,14]

We present an analytic formulation for the excess thermodynamic properties which is based on the analytic solution of the MSA for the asymmetric ion–dipole model in a neutralizing background.

By definition,[1,2] the electrostatic part of the internal energy for the ith component is given by

$$\beta \frac{E_i^{\mathrm{el}}}{V} = 2\pi\beta\rho_i \sum_{j=1}^{M} \rho_j \sum_{m,n,l} \frac{(-1)^l}{2l+1} \int_0^\infty dr\, r^2 g_{ij}^{mnl}(r)\, U_{ij}^{mnl}(r) \tag{72}$$

Taking account of Eqs. (22), the excess internal energy can be written

$$\beta \frac{E_i^{\mathrm{el}}}{N_i} = \frac{\alpha_0^2}{4\pi} Z_i B_i - \frac{\alpha_1^2}{4\pi} \rho_s Z_i \beta_6 \left(v_i - \frac{\pi}{6} \sum_{j=1}^{M} \rho_j \sigma_j^3 v_j \right), \qquad i = 1,\ldots, M-1 \tag{73}$$

$$\beta \frac{E_s^{\mathrm{el}}}{N_s} = -\frac{\alpha_1^2}{4\pi} B^{10} - \frac{\alpha_2^2}{4\pi} \frac{b_2}{\sigma_s^3} \tag{74}$$

Then the excess internal energy of the system is given by

$$\beta \frac{E^{\mathrm{el}}}{V} = \frac{\alpha_0^2}{4\pi} \sum_{i=1}^{M} \rho_i Z_i B_i - \frac{\alpha_1^2}{2\pi} \rho_s B^{10} - \frac{\alpha_2^2}{2\pi} \frac{\rho_s}{\sigma_s^3} b_2 \tag{75}$$

We have applied the following notations in Eqs. (73)–(75):

$$B_i = \mathcal{N}_i - \frac{\pi}{6} \sum_{j=1}^{M} \rho_j \sigma_j^3 \mathcal{N}_j - \frac{\pi}{4} \chi_2 - \frac{\pi}{12} \rho_\varphi \sigma_i^2 + \frac{\pi^2}{180} \rho_\varphi \xi_5 \tag{76}$$

$$\mathcal{N}_i = \frac{1}{\sigma_i} (\mathcal{M}_i - Z_i^*) + \frac{\sigma_s^2}{4} \rho_s v_i \left(\frac{\sigma_s}{3} B^{10} + \sum_{j=1}^{M} \rho_j \sigma_j v_j \mathcal{M}_j \right) \tag{77}$$

where $\chi_m = \sum_{i=1}^{M} \rho_i Z_i \sigma_i^m$.

In the limiting case $p_s = 0$, one obtains

$$\mathcal{N}_i = -\Gamma \mathcal{M}_i - \frac{\pi}{6} \rho_\varphi \sigma_i^2 - \frac{\pi}{6\Delta} P_M \sigma_i \tag{78}$$

and the expression (75) reduces to the result given by Parinello and Tosi[32] for a multicomponent ionic system in a neutralizing background:

$$\beta \frac{E^{\text{el}}}{V} = \frac{\alpha_0^2}{4\pi} \left\{ -\Gamma \sum_{i=1}^{M} \rho_i \frac{(Z_i^*)^2}{1+\Gamma\sigma_i} - \frac{\pi}{2\Delta} P_M \sum_{i=1}^{M} \frac{\rho_i Z_i^* \sigma_i}{1+\Gamma\sigma_i} \right.$$
$$\left. - \frac{\pi}{2} \rho_\varphi \chi_2 + \frac{\pi^2}{30} \rho_\varphi^2 \xi_5 \right\} \tag{79}$$

The excess Helmholtz free energy can be given as[38]

$$\beta \frac{F^{\text{el}}}{V} = \beta \frac{E^{\text{el}}}{V} - J - J' - J'' \tag{80}$$

where

$$J = -\frac{2\pi}{3} \beta \sum_{i=1}^{M} \sum_{j=1}^{M} \rho_i \rho_j \sum_{m,n,l} \frac{(-1)^l}{2l+1} \int_0^\infty dr\, r^{1-l} g_{ij}^{mnl}(r) \frac{dU_{ij}^{mnl}(r)}{dr}$$
$$= \frac{1}{12\pi} \left(\alpha_0^2 \sum_{i=1}^{M} \rho_i Z_i B_i - 4\alpha_1^2 \rho_s B^{10} - 6\alpha_2^2 \rho_s \frac{b_2}{\sigma_s^3} \right) \tag{81}$$

$$J' = \frac{\pi}{3} \sum_{i=1}^{M} \sum_{j=1}^{M} \rho_i \rho_j \sigma_{ij}^3 \left\{ \sum_{m,n,l} \frac{(-1)^l}{2l+1} [g_{ij}^{mnl}(\sigma_{ij})]^2 - [g_{ij}^{\text{HS}}(\sigma_{ij})]^2 \right\} \tag{82}$$

$$J'' = \frac{1}{2} \sum_{i=1}^{M} \sum_{j=1}^{M} \rho_i \rho_j \, \{ \tilde{c}_{ij}^{R,000}(k=0) - \tilde{c}_{ij}^{\text{HS}}(k=0) \} \tag{83}$$

The contact values of the coefficients of the invariant expansion of the PDF $g_{ij}^{mnl}(\sigma_{ij})$ are obtained from Eqs. (9), (11), (30), and (45):

$$g_{ij}^{000}(\sigma_{ij}) = \frac{1}{2\pi\sigma_{ij}} \left(\frac{2\pi\sigma_{ij}}{\Delta} + \frac{\pi^2}{2\Delta^2} \xi_2 \sigma_i \sigma_j \right.$$
$$\left. - \frac{D_\Omega}{2} a_i^0 a_j^0 - \frac{\sigma_s^2}{2D} \rho_s \eta_i \eta_j \right) \tag{84}$$

$$g_{si}^{101}(\sigma_{is}) = -g_{is}^{011}(\sigma_{is}) = \frac{-\sqrt{3}}{2\pi\sigma_{is}} \left(\frac{y_0}{D} \eta_i + \frac{1}{2} D_\Omega a_s^1 a_i^0 \right) \tag{85}$$

$$g_{ss}^{110}(\sigma_s) = \frac{1}{2\sqrt{3}\,\pi\sigma_s} \left[\frac{2}{\rho_s \sigma_s^2} \left(1 + \frac{\beta_{24}}{(\beta_{12})^2} b_2 - \frac{1}{D} y_0^2 \right) \right.$$
$$\left. + \frac{1}{2} D_\Omega (a_s^1)^2 \right] \tag{86}$$

$$g_{ss}^{112}(\sigma_s)=\frac{\sqrt{10}}{2\sqrt{3}\,\pi\sigma_s}\left[\frac{2}{\rho_s\sigma_s^2}\left(b_2-1+\frac{1}{D}\,y_0^2+\frac{\beta_{24}}{2(\beta_{12})^2}\,b_2\right)\right.$$
$$\left.+\frac{1}{2}\,D_\Omega(a_s^1)^2\right] \tag{87}$$

The Fourier transforms of the coefficients of the invariant expansion of the DCF $\tilde{c}_{ij}^{mnl}(k)$ at $k=0$ are given in accordance with Eqs. (69)–(71) as follows:

$$\tilde{c}_{ij}^{R,000}(k=0)=\tilde{C}_{0,ij}^{R,00}(k=0) \tag{88}$$

where $\tilde{C}_{0,ij}^{R,00}(k=0)$ denotes the regular part of the functions $\tilde{C}_{0,ij}^{00}(k=0)$, i.e.

$$\tilde{C}_{0,ij}^{R,00}(k=0)=\lim_{k\to 0}\left(\frac{4\pi}{k}\int_0^\infty dr\,r\sin(kr)\,\tilde{C}_{0,ij}^{00}(r)+\frac{\alpha_0^2}{k^2}\,Z_iZ_j\right) \tag{89}$$

For the hard-sphere model in the PY approximation the contact values of the PDF and the Fourier transforms of the DCF at $k=0$ are given by

$$g_{ij}^{\mathrm{HS}}(\sigma_{ij})=\frac{1}{\Delta}+\frac{\pi}{4\Delta^2\sigma_{ij}}\,\xi_2\sigma_i\sigma_j \tag{90}$$

$$\tilde{c}_{ij}^{\mathrm{HS}}(k=0)=K_{ij}^{\mathrm{HS}}+K_{ji}^{\mathrm{HS}}-\sum_{i_1=1}^{M}\rho_{i_1}K_{ii_1}^{\mathrm{HS}}K_{ji_1}^{\mathrm{HS}} \tag{91}$$

where

$$K_{ij}^{\mathrm{HS}}=\int_{\lambda_{ji}}^{\sigma_{ij}}dr\,q_{ij}^{\mathrm{HS}}(r)=-\frac{\pi}{6\Delta}\,\sigma_i^3-\frac{\pi}{2\Delta}\,\sigma_i^2\sigma_j-\frac{\pi^2}{12\Delta^2}\,\xi_2\sigma_i^3\sigma_j$$

The expression (83) for J'' can be expressed through isothermal compressibilities as follows

$$J''=\frac{1}{2}\,\xi_0\left(\frac{1}{\chi^{\mathrm{HS}}}-\frac{1}{\chi}\right) \tag{92}$$

where

$$\frac{1}{\chi}=1-\frac{1}{\xi_0}\sum_{i=1}^{M}\sum_{j=1}^{M}\rho_i\rho_j\tilde{c}_{ij}^{R,000}(k=0) \tag{93}$$

$$\frac{1}{\chi^{\mathrm{HS}}}=\frac{1}{\Delta^2}+\frac{\pi}{\Delta^3\xi_0}\,\xi_1\xi_2+\frac{\pi^2}{4\Delta^4\xi_0}\,(\xi_2)^3 \tag{94}$$

The electrostatic part of the chemical potentials is given by[38] for ions,

$$\beta\mu_i^{\mathrm{el}} = \beta\frac{E_i^{\mathrm{el}}}{N_i} - \frac{1}{2}\sum_{j=1}^{M}\rho_j[\tilde{c}_{ij}^{R,000}(k=0) - \tilde{c}_{ij}^{\mathrm{HS}}(k=0)] \tag{95}$$

for dipoles,

$$\beta\mu_s^{\mathrm{el}} = \beta\frac{E_s^{\mathrm{el}}}{N_s} - \frac{1}{2}\sum_{j=1}^{M}\rho_j[\tilde{c}_{sj}^{000}(k=0) - \tilde{c}_{sj}^{\mathrm{HS}}(k=0)] \tag{96}$$

In the low ionic density region ($\rho_0 = \sum_{i=1}^{M-1}\rho_i Z_i^2 \to 0$) the interaction parameters can be written in the form (one has to neglect the terms linear and higher order in ρ_0)

$$b_2 \to b_2^{(0)} \tag{97}$$

$$\mathscr{M}_i \to Z_i\left(1 - \frac{\alpha_0}{2\sqrt{\mathscr{E}_{\mathrm{W}}}}\sigma_i\sqrt{\rho_0}\right) \tag{98}$$

$$\nu_i \to Z_i\frac{\alpha_1^2}{\sqrt{\mathscr{E}_{\mathrm{W}}}}\frac{\beta_{12}^2}{\sigma_s\beta_6 + \sigma_i\beta_3} \tag{99}$$

$$B_i \to \mathscr{N}_i \to -\frac{\alpha_0}{2\sqrt{\mathscr{E}_{\mathrm{W}}}}Z_i\sqrt{\rho_0} \tag{100}$$

where $\mathscr{E}_{\mathrm{W}} = (\beta_{12}^2\beta_3/\beta_6^3)^2$ is the Wertheim dielectric constant.[24] Then the expression for the excess chemical potential of ions is

$$\beta\mu_i^{\mathrm{el}} \to \frac{\alpha_0^2}{4\pi\sigma_i}Z_i^2\left(\frac{1}{\mathscr{E}_{\mathrm{W}}} - 1\right)\bigg/\left(1 + \frac{\sigma_s\beta_6}{\sigma_i\beta_3}\right) - \frac{\alpha_0^3}{8\pi}\frac{Z_i^2}{\sqrt{\mathscr{E}_{\mathrm{W}}}}\sqrt{\rho_0} \tag{101}$$

where the first term corresponds to the Born expression and the second is the Debye one.

When $\rho_0 = 0$, we get the ionic solvation energy W_i^{el}

$$\beta W_i^{\mathrm{el}} = \frac{\alpha_0^2}{4\pi\sigma_i}Z_i^2\left(\frac{1}{\mathscr{E}_{\mathrm{W}}} - 1\right)\bigg/\left(1 + \frac{\sigma_s\beta_6}{\sigma_i\beta_3}\right) \tag{102}$$

which coincides with ref. 39. The remaining part of the chemical potentials defines the electrostatic part of the activity coefficients

$$\ln\gamma_i^{\mathrm{el}} = \beta\mu_i^{\mathrm{el}} - \beta W_i^{\mathrm{el}} \tag{103}$$

In the low-dipole-density region, $b_2 \to 0$, and Γ reduces to the corresponding value for ionic system in the neutralizing background ($\rho_s = 0$).[32] The parameters v_j are

$$v_j = \frac{\alpha_0 \alpha_2}{1 + \Gamma^2 \sigma_s^2} \sum_{i=1}^{M} \frac{\mathscr{M}_i}{\sigma_s + \sigma_i} L_{ij} \tag{104}$$

where

$$L_{ij} = \delta_{ij} + \frac{1}{D_L} [(1 - \check{c}\check{d})\, \check{a}_i \check{b}_j + (\check{c}\check{b})\, \check{a}_i \check{d}_j + (\check{a}\check{d})\, \check{c}_i \check{b}_j + (1 - \check{a}\check{b})\, \check{c}_i \check{d}_j]$$

$$D_L = (1 - \check{a}\check{b})(1 - \check{c}\check{d}) - (\check{a}\check{d})(\check{b}\check{c})$$

$$\check{a}_i = \frac{\pi}{2\Delta} \frac{1}{\sigma_s + \sigma_i} \left(\sigma_s \sigma_i + \frac{\Gamma \sigma_s^2}{1 + \Gamma^2 \sigma_s^2} \frac{1}{D_\Omega} P_M \mathscr{M}_i \right)$$

$$\check{b}_j = -\rho_j \sigma_j^2$$

$$\check{c}_i = \frac{\Gamma \sigma_s}{\sigma_s + \sigma_i} \frac{1}{D_\Omega} \mathscr{M}_i$$

$$\check{d}_j = \frac{2}{3} \frac{\Gamma \sigma_s}{1 + \Gamma^2 \sigma_s^2} \rho_j Z_j^* - \frac{\sigma_s + \sigma_j + \Gamma^2 \sigma_s^2 \sigma_j}{1 + \Gamma^2 \sigma_s^2} \rho_j \mathscr{M}_j$$

For the equal-ionic-size case the formula (104) is of much simpler form:

$$v_j = \frac{\alpha_0 \alpha_2}{1 + \Gamma \sigma_j} Z_j \frac{3}{\sigma_j (\Gamma \sigma_s)^3 + (3\sigma_j + \sigma_s)(\Gamma \sigma_s)^2 + 3(\sigma_j + \sigma_s)(1 + \Gamma \sigma_s)} \tag{105}$$

The excess chemical potentials are, for ions,

$$\beta \mu_i^{\text{el}} \to \frac{\alpha_0^2}{4\pi} Z_i \left(\frac{\mathscr{M}_i - Z_i^*}{\sigma_i} - \frac{\pi}{6} \sum_{j=1}^{M} \rho_j \sigma_j^2 \mathscr{M}_j - \frac{\pi}{12} (\chi_2 + \rho_\varphi \sigma_i^2) - \frac{\pi^2}{45} \rho_\varphi \xi_5 \right) \tag{106}$$

and for dipoles

$$\beta \mu_s^{\text{el}} \to \beta W_s^{\text{el}} = -\frac{\alpha_0 \alpha_2}{4\pi \beta_6} B^{10} \tag{107}$$

where W_s^{el} is the solvation energy of the dipole molecules in an ionic solvent.

The excess Gibbs free energy is given by

$$\beta \frac{G^{\text{el}}}{V} = \beta \sum_{i=1}^{M} \rho_i \mu_i^{\text{el}} = \beta \frac{E^{\text{el}}}{V} - J'' \tag{108}$$

For the excess pressure we have from ref. 38

$$\beta P^{\text{el}} = J + J' \tag{109}$$

Adelman's dielectric constant can be written as

$$\mathscr{E} = 1 + \rho_s \alpha_2^2 (\beta_{12}^4 / \beta_6^2) \tag{110}$$

Finally, we note that the set of interaction parameters $\mathscr{M}_j$, v_j, Γ, B^{10}, and b_2 defining the MSA analytical solution is calculated by numerical methods (a standard multidimensional Newton-Raphson technique, for example). The choice of the set of initial values is important here. Depending on the thermodynamic state, either the equal-ionic-size case or the limit of low ionic or dipole concentration is taken as a starting point to iterate the interaction parameters.

The numerical investigation of the considered model will be given elsewhere.

APPENDIX. THE INVERSE MATRIX CALCULATION

In the inverse matrix calculation procedure for simplification we write (53) in the form

$$W_{ij}^{mn} = M_{ij}^{mn} - \check{e}_i^m \check{f}_j^n - \check{z}_i^m \check{y}_j^n \tag{A1}$$

where

$$M_{ij}^{mn} = \delta_{ij}^{mn} - \check{a}_i^m \check{b}_j^n - \check{c}_i^m \check{d}_j^n - \check{w}_i^m \check{v}_j^n \tag{A2}$$

Then for the matrix inverse to M_{ij}^{mn} one obtains

$$(\mathbf{M}^{-1})_{ij}^{mn} = \delta_{ij}^{mn} + \frac{1}{D_0(s)} [(1 - \check{c}\check{d})\, \check{a}_i^m \check{b}_j^n + (\check{c}\check{b})\, \check{a}_i^m \check{d}_j^n + (\check{a}\check{d})\, \check{c}_i^m \check{b}_j^n + (1 - \check{a}\check{b})\, \check{c}_i^m \check{d}_j^n] + \frac{\check{w}_i^m \check{v}_j^n}{1 - \check{w}\check{v}} \tag{A3}$$

where

$$D_0(s) = (1 - \check{a}\check{b})(1 - \check{c}\check{d}) - (\check{a}\check{d})(\check{b}\check{c}) \tag{A4}$$

$$(\check{a}\check{b}) = \sum_{i=1}^{M} \sum_{m=0}^{1} \check{a}_i^m \check{b}_i^m, \ldots \tag{A5}$$

Multiplying W_{ij}^{mn} by $(\mathbf{M}^{-1})_{ij}^{mn}$, we get the expression

$$L_{ij}^{mn} = (\mathbf{W} * \mathbf{M}^{-1})_{ij}^{mn} = \delta_{ij}^{mn} - \check{e}_i^m \check{h}_j^n - \check{z}_i^m \check{p}_j^n \tag{A6}$$

$$\begin{aligned} \check{h}_j^m = \check{f}_j^m &+ [(1 - \check{c}\check{d})(\check{a}\check{f}) + (\check{a}\check{d})(\check{c}\check{f})]\, \check{b}_j^m \frac{1}{D_0(s)} \\ &+ [(1 - \check{a}\check{b})(\check{c}\check{f}) + (\check{c}\check{b})(\check{a}\check{f})]\, \check{d}_j^m \frac{1}{D_0(s)} + \frac{(\check{w}\check{f})}{1 - \check{w}\check{v}} \check{v}_j^m \end{aligned} \tag{A7}$$

$$\begin{aligned} \check{p}_j^m = \check{y}_j^m &+ [(1 - \check{c}\check{d})(\check{a}\check{y}) + (\check{a}\check{d})(\check{c}\check{y})]\, \check{b}_j^m \frac{1}{D_0(s)} \\ &+ [(1 - \check{a}\check{b})(\check{c}\check{y}) + (\check{c}\check{b})(\check{a}\check{y})]\, \check{d}_j^m \frac{1}{D_0(s)} + \frac{(\check{w}\check{y})}{1 - \check{w}\check{v}} \check{v}_j^m \end{aligned} \tag{A8}$$

and, correspondingly, for the inverse matrix

$$\begin{aligned} (\mathbf{L}^{-1})_{ij}^{mn} = \delta_{ij}^{mn} &+ \frac{1}{D_T(s)} [(1 - \check{z}\check{p})\, \check{e}_i^m \check{h}_j^n + (\check{z}\check{h})\, \check{e}_i^m \check{p}_j^n \\ &+ (1 - \check{e}\check{h})\, \check{z}_i^m \check{p}_j^n + (\check{e}\check{p})\, \check{z}_i^m \check{h}_j^n] \end{aligned} \tag{A9}$$

where

$$D_T(s) = (1 - \check{e}\check{h})(1 - \check{z}\check{p}) - (\check{e}\check{p})(\check{z}\check{h}) \tag{A10}$$

One then can find the inverse matrix by applying (A3) and (A9):

$$(\mathbf{W}^{-1})_{ij}^{mn} = (\mathbf{M}^{-1} * \mathbf{L}^{-1})_{ij}^{mn} \tag{A11}$$

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