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A Solution of the Multiple-Binding Mean Spherical Approximation for Ionic Mixtures

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The mean spherical approximation (MSA) for an arbitrary mixture of charged hard spheres with saturating bonds is solved in the Wertheim formalism. Any number of bonds is allowed. It is shown that the general solution is given in terms of a screening MSA-like parameter Γ^T, a cross-interaction parameter η^B that will depend on the binding association equations, the set of binding association fractions, and an additional algebraic equation. The equation for Γ^T is given for the general case. The equation for η^B, however, depends strongly on the particular closure that is used to compute the contact pair correlation function. The full solution requires, as in the dimer case recently solved by Blum and Bernard, solving $m+2$ equations and additionally the inversion of a matrix of size $[(\nu-1)m]$ for a system with m components and ν bonds. We recall that when $\nu=1$, only dimers are allowed; for $\nu=2$, only linear chains are formed; and when $\nu \geqslant 3$, branching of the polymers occurs. It can be shown that the excess entropy for the polymer case is as before, $\Delta S^{\mathrm{MSA}} = (\Gamma^T)^3/3\pi +$ sticky terms, where the sticky terms depend on the model and will be given in future work.

KEY WORDS: Ionic mixtures; mean spherical approximation; polymerizing ions; multiple binding.

1. INTRODUCTION

The mean spherical approximation $(\mathrm{MSA})^{(1-3)}$ is an analytical theory for the primitive model of ionic solutions as well as for models with molecular solvents.$^{(4-11)}$ Some of the remarkable properties of the MSA are the fact that for electrolytes the mathematical solution is expressed in terms of a single screening parameter Γ, which plays a role similar to the well-known

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Debye–Hückel (DH) screening parameter κ_D. The MSA is asymptotically correct in the limit of high screening parameter (Debye length going to zero, which implies either infinite charge or zero temperature for dense systems),(12,13) where it satisfies the Onsager bounds(14) for the Helmholtz free energy and the internal energy of the system. Notice that the requirement for the free energy means that the ratio of the entropy to the internal energy must go to zero in this limit, which is true for the MSA. These limits are of course satisfied by the hypernetted chain theory (HNC)(15) and its improved versions. The internal energy of the MSA is an exact lower bound(12,13) and is as accurate as the HNC and its modifications for extreme high densities and charges.

A statistical mechanical approach to pairing is that of Stell and coworkers,(16–18) in which the association is represented by Baxter's sticky potential inside the hard core. The general ionic mixture with arbitrary surface sticky interactions has been solved in the MSA(19,20) and it has been shown that the excess functions due to the charges are *all*(19,21) given in terms of the scaling parameter Γ^B, which now depends on the degree of association determined by the sticky potential.

The proper Ornstein–Zernike (OZ) equation which accounts for saturation effects was constructed by Wertheim.(22,23) This formalism can accommodate both mechanisms in one single association parameter. The association causes saturation effects in which only one bond is allowed between the ions and the formalism has to be changed at the level of the Ornstein–Zernike equation in a special way. The treatment now includes the fraction of sites that are bonded, and that fraction is obtained by imposing chemical equilibrium-type mass action laws. The Wertheim formalism is the proper way of incorporating the mass action law into the statistical mechanical treatment of ionic mixtures.

This formalism was shown to be very successful for ionic systems, as was the HNC approximation.(24–26) More recently the Wertheim formalism was used to study numerically the binding effect for the restricted MSA(27) applied to a symmetric 2–2 equal-size electrolyte, with excellent results for the thermodynamic functions. A solution of the restricted linear polymer MSA has been given by Kalyuzhnyi and Stell.(28)

In this paper we extend the solution of the binding MSA for dimers (BIMSA) of our previous work(29) to the case of an arbitrary mixture of polymerizing ions with any number of bonds ν.(30) As in our previous work, the solution is given in terms of a scaling parameter(4,19) Γ^T and a number of coupling parameters that depends on the number of binding association equations, plus the binding association equations themselves. The theory and the analytical solution are presented in Section 2. In this case the results will depend on the specific closures taken for the binding association equations. We will discuss one case in this work and leave other interesting cases for future publications. The excess thermodynamic properties, computed by charging up the "bound" system, keeps the form as functions of the new screening parameter Γ^T.

2. THEORY

The Wertheim theory was initially formulated for sticky adsorption points. The extension to isotropic bonding with saturation effects was carried out by Kalyuzhnyi and Stell.(31) We consider a system with an arbitrary number of components $0 < i \leqslant m$, with number density ρ_i, charge ez_i (e is the elementary charge), and hard-core diameter σ_i. The solvent is a continuum with dielectric constant ε_0.

The temperature of the system is T, Boltzmann's constant is k_B, and we use $\beta = 1/k_B T$ throughout. Our system is neutral:

$$\sum_k \rho_k z_k = 0 \tag{1}$$

We define the matrices $\mathbf{h}_{ij}$ and $\mathbf{c}_{ij}$, which correspond to the pair indirect and direct correlation functions

$$\mathbf{h}_{ij} = \begin{bmatrix} h_{ij}^{(00)} & \mathbf{h}_{ij}^{(0b)} \\ \mathbf{h}_{ij}^{(a0)} & \mathbf{h}_{ij}^{(ab)} \end{bmatrix}, \qquad a, b \neq 0 \tag{2}$$

$$\mathbf{c}_{ij} = \begin{bmatrix} c_{ij}^{(00)} & \mathbf{c}_{ij}^{(0b)} \\ \mathbf{c}_{ij}^{(a0)} & \mathbf{c}_{ij}^{(ab)} \end{bmatrix}, \qquad a, b \neq 0 \tag{3}$$

where the indices a, b indicate the degree of association.

The density parameters in the Wertheim–Ornstein–Zernike equation (WOZ) are defined as

$$\boldsymbol{\sigma}_i = \begin{bmatrix} \sigma_i^{(0)} & \boldsymbol{\sigma}_i^{(a)} \\ \boldsymbol{\sigma}_i^{(b)} & \boldsymbol{\sigma}_i^{(a,b)} \theta^{\mathrm{H}}(\nu - a - b) \end{bmatrix} \tag{4}$$

where $\nu \geqslant a$ is the largest number of bonds per particle and the matrix $\boldsymbol{\sigma}^{(a,b)}$ has nonzero elements when the Heaviside function is satisfied. We have

$$\boldsymbol{\sigma}_i^{(a)} = \sum_{b=0}^{a} \rho_i^{(b)} \tag{5}$$

so, for example,

$$\sigma_i^{(2)} = \rho_i^{(0)} \tag{6}$$

$$\sigma_i^{(1)} = \rho_i^{(0)} + \rho_i^{(1)} \tag{7}$$

$$\sigma_i^{(0)} = \rho_i^{(0)} + \rho_i^{(1)} + \rho_i^{(2)} \tag{8}$$

and so on.

In Wertheim's theory the density of i is split into "bonded" $\rho_i^{(a)}$ and "not-bonded" $\rho_i^{(0)}$ parts, which correspond to the (a) associated and non-associated ions, respectively. We have the relation for the total or initial density of species i

$$\rho_i = \sigma_i^{(0)} \tag{9}$$

To avoid confusion in the notation with the symbol σ, it will be convenient to use instead the degree of dissociation

$$\alpha_i^{(a)} = \frac{\sigma_i^{(a)}}{\rho_i} \tag{10}$$

Then, since $\alpha_i^{(0)} = 1$,

$$\boldsymbol{\sigma}_i = \rho_i [\alpha_i^{(a)}] = \rho_i \boldsymbol{\alpha}_i \tag{11}$$

For example, for $\nu = 2$

$$\boldsymbol{\alpha}_i = \begin{bmatrix} 1 & \alpha_i^{(1)} & \alpha_i^{(2)} \\ \alpha_i^{(1)} & \alpha_i^{(2)} & 0 \\ \alpha_i^{(2)} & 0 & 0 \end{bmatrix} \tag{12}$$

which defines the matrix $\boldsymbol{\alpha}_i$. The "normal" pair correlation function therefore is

$$h_{ij}(r) = h_{ij}^{(00)}(r) + \sum_a \alpha_i^{(a)} h_{ij}^{(a0)}(r) + \sum_b \alpha_j^{(b)} h_{ij}^{(0b)}(r) + \sum_{a,b} \alpha_i^{(a)} \alpha_j^{(b)} h_{ij}^{(ab)}(r) \tag{13}$$

The WOZ is

$$\mathbf{h}_{ij}(r) = \mathbf{c}_{ij}(r) - \sum_k \rho_k \int d\mathbf{r}_1\, \mathbf{c}_{ik}(|\mathbf{r}_1 - \mathbf{r}|)\, \boldsymbol{\alpha}_k \mathbf{h}_{kj}(\mathbf{r}_1) \tag{14}$$

where $\mathbf{r}$ is the position, and the superscripts a, b run from 0 to ν.

The BIMSA boundary conditions are taken as(1,25)

$$\mathbf{c}_{ij}^{(00)}(r) = -\frac{\beta e^2}{\varepsilon_0}\frac{z_j z_i}{r}\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \qquad r > \sigma_{ij} \tag{15}$$

where $\sigma_{ij} = (1/2)(\sigma_i + \sigma_j)$ is now (and in the rest of this paper) the distance of closest approach of the ions i and j.

Consider the sticky interactions $u_{ij}^{\mathrm{st}}(r)$ for the pair ij,

$$\exp[-\beta u_{ij}^{\mathrm{st}}(r)] = \mathscr{B}_{ij}^{(ab)} \delta(r - \sigma_{ij}^{-}) \tag{16}$$

where $\mathscr{B}_{ij}$ is the matrix of the sticky interactions, which are given. Then, the Mayer function

$$f_{ij} = \exp[-\beta u_{ij}^{\mathrm{st}}(r)] = -1 + \mathscr{B}_{ij}^{(ab)} \delta(r - \sigma_{ij}^{-}) \tag{17}$$

and the fraction of nonbound ions i, α_i,(22,23,27) is given by a set of equations that depends on the closure used. Our discussion is relevant to any closure of the WOZ of the form

$$\alpha_i^{(b)} = \mathrm{Functional}_1[\mathbf{g}_{ij}(\sigma_{ij})\, \mathscr{B}_{ij}^{(ab)}] \tag{18}$$

Specific closures for linear polymers, for example, have been discussed by several authors.(31,32)

The feature of our solution is that the electrostatic charging process can be computed in the MSA irrespective of the kind of closure. This happens also when the normal Ornstein–Zernike equation is used.(19,21,33)

To make contact with earlier work(19,21) we will use the parameter t_{ij},

$$t_{ij}^{(ab)} = \mathrm{Functional}_2[\mathbf{g}_{ij}(\sigma_{ij})\, \mathscr{B}_{ij}^{(ab)}] \tag{19}$$

The model should provide the relation of this parameter to the α parameters of Eq. (18).

For the pair correlation function matrix the boundary condition is, in this notation,

$$\mathbf{h}_{ij}(r) = \begin{bmatrix} -1 & 0 \\ 0 & t_{ij}^{(ab)}/(2\pi\sigma_{ij})\, \delta(r - \sigma_{ij}^{-}) \end{bmatrix}, \qquad r \leqslant \sigma_{ij} \tag{20}$$

where $t_{ij}^{(ab)}$ is the sticky parameter for the association of the ions i and j defined by Eq. (19). The observation already made in previous work(19,21) is that there is an explicit general solution of the MSA for the class of closures defined by Eq. (20).

We use now the extension of the Baxter–Wertheim(34,35) factorization method to charged systems.(4) We define the projections $\mathbf{J}_{ij}$ and $\mathbf{S}_{ij}$,

$$\mathbf{J}_{ij}(r) = 2\pi \int_r^{\infty} ds\, s\mathbf{h}_{ij}(s) \tag{21}$$

$$\mathbf{S}_{ij}(r) = 2\pi \int_r^{\infty} ds\, s\mathbf{c}_{ij}(s) \tag{22}$$

From the boundary conditions (15) and (20) we get

$$\mathbf{J}_{ij}(r) = \begin{bmatrix} \pi r^2 + J_{ij}^{(00)} & J_{ij}^{(0b)} \\ J_{ij}^{(a0)} & J_{ij}^{(ab)} \end{bmatrix}, \qquad r \leqslant \sigma_{ij} \tag{23}$$

$$\mathbf{S}_{ij}(r) = -\frac{\beta e^2}{\varepsilon_0} \frac{z_j z_i e^{-\mu |r|}}{\mu} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \qquad r > \sigma_{ij} \tag{24}$$

where the limit $\mu = 0$ needs to be taken at the end of the calculation.

We solve the set of coupled equations, as in previous work,

$$\mathbf{S}_{ij}(r) = \mathcal{Q}_{ij}(r) - \sum_k \rho_k \int dr_1\, \mathcal{Q}_{ik}(r_1)\, \boldsymbol{\alpha}_k \mathcal{Q}_{jk}^T(r_1 - r) \tag{25}$$

$$\mathbf{J}_{ij}(r) = \mathcal{Q}_{ij}(r) + \sum_k \rho_k \int dr_1\, \mathbf{J}_{ik}(|r_1 - r|)\, \boldsymbol{\alpha}_k \mathcal{Q}_{kj}(r_1) \tag{26}$$

The factor correlation functions $\mathcal{Q}_{ij}(r)$ are unknown.

From the analysis of the singularities of the problem(4,19) we see that this function must be of the form

$$\mathcal{Q}_{ij}(r) \Rightarrow [\mathbf{Q}_{ij}(r) + \mathbf{t}_{ij}]\, \theta(\sigma_{ij} - r) - z_i \mathbf{a}_j e^{-\mu r}, \qquad \lambda_{ji} < r \tag{27}$$

where we used the definition

$$\lambda_{ji} = \tfrac{1}{2}(\sigma_j - \sigma_i) \tag{28}$$

Performing the integrals in Eq. (25), we see that in the limit $\mu = 0$ both sides have a simple pole. The residues of this pole must be equal, and therefore

$$4\pi \frac{\beta e^2}{\varepsilon_0} = \sum_k \rho_k [\mathbf{a}_k \boldsymbol{\alpha}_k \mathbf{a}_k^T]^{(00)} \tag{29}$$

where

$$\mathbf{a}_j = \begin{bmatrix} a_j^{(0)} & a_j^{(a)} \\ \mathbf{0} & \mathbf{0} \end{bmatrix} \tag{30}$$

Similarly, from the discontinuity at $r=\sigma_{ij}$ in Eq. (25) we need

$$\mathbf{t}_{ij}=\begin{bmatrix} 0 & \mathbf{0} \\ \mathbf{0} & [\mathbf{t}]_{ij}^{(ab)} \end{bmatrix} \tag{31}$$

It is also clear that from Eq. (21, 26) $\mathbf{Q}_{ij}(r)$ must be a polynomial of second degree, which is zero for $r=\sigma_{ij}$. For convenience we write

$$\mathbf{Q}_{ij}(r)=(1/2)\,\mathbf{A}_{ij}(r-\sigma_{ij})(r-\lambda_{ji})+\boldsymbol{\beta}_{ij}(r-\sigma_{ij}) \tag{32}$$

where the coefficients are matrices

$$\mathbf{A}_{ij}=\begin{bmatrix} A_{ij}^{(00)} & A_{ij}^{(0b)} \\ A_{ij}^{(a0)} & A_{ij}^{(ab)} \end{bmatrix} \tag{33}$$

and

$$\boldsymbol{\beta}_{ij}=\begin{bmatrix} \beta_{ij}^{(00)} & \beta_{ij}^{(0b)} \\ \beta_{ij}^{(a0)} & \beta_{ij}^{(ab)} \end{bmatrix} \tag{34}$$

We remark some of the properties of this function:

$$\mathbf{Q}_{ij}(\sigma_{ij})=0 \tag{35}$$

$$\mathbf{Q}'_{ij}(\sigma_{ij})=(1/2)\,\sigma_j\mathbf{A}_{ij}+\boldsymbol{\beta}_{ij} \tag{36}$$

This last quantity yields the contact probability needed to calculate the closure of the Wertheim theory (19). In fact, from Eq. (26) we get the relation

$$2\pi\sigma_{ij}\mathbf{g}_{ij}(\sigma_{ij})=\tfrac{1}{2}\sigma_i\mathbf{A}_j+\boldsymbol{\beta}_{ij}+\sum_k \rho_k\mathbf{t}_{ik}\hat{\alpha}_k[-\sigma_k\boldsymbol{\beta}_{kj}-z_k\mathbf{a}_j+\mathbf{t}_{kj}] \tag{37}$$

The solution of these equations leads to

$$\beta_{ij}^{(00)}=\frac{\pi\sigma_j}{\Delta}+M_i^{(0)}a_j^{(0)}, \qquad \beta_{ij}^{(0b)}=M_i^{(0)}a_j^{(b)}, \qquad b=0,1,\ldots,\nu \tag{38}$$

$$\beta_{ij}^{(ab)}=B_i^{(a)}a_j^{(b)}, \qquad a\geqslant 1, \quad b=0,1,\ldots,\nu \tag{39}$$

and

$$A_j^{(ab)}=0, \qquad a\geqslant 1, \quad b=0,1,\ldots,\nu \tag{40}$$

$$A_j^{(00)}=\frac{2\pi}{\Delta}\left[1+\zeta_2\sigma_j\frac{\pi}{2\Delta}\right]+2a_j^{(0)}\eta^B, \qquad A_j^{(0b)}=-\frac{2\pi}{\Delta}\tau_j^{(b)}+2a_j^{(b)}\eta^B \tag{41}$$

We have used the following notation(4,19):

$$\zeta_n = \sum_k \rho_k \sigma_k^n \tag{42}$$

$$\Delta = 1 - \pi\zeta_3/6 \tag{43}$$

$$\chi_2 = \sum_k \rho_k z_k \sigma_k^2 \tag{44}$$

$$B_j^{(b)} = \sum_k \rho_k z_k \alpha_k^{(a)} J_{kj}^{(ab)} \tag{45}$$

Furthermore,

$$B_j^T = \sum_b B_j^{(b)} \alpha_j^{(b)} \tag{46}$$

corresponds to the total electrostatic interaction parameter B_j of previous work.(4,19) It will be convenient to introduce

$$N_j^T = B_j^T + \frac{\pi}{6\Delta} \sum_k \rho_k \sigma_k^3 B_k^T + \frac{\pi}{4\Delta} \chi_2 \tag{47}$$

We have also

$$N_j^{(a)} = B_j^{(a)} + \frac{\pi}{6\Delta} \sum_k \rho_k \sigma_k^3 B_k^{(a)} + \frac{\pi}{4\Delta} \chi_2, \qquad a \geqslant 0 \tag{48}$$

$$M_j^{(0)} = N_j^{(0)} + \frac{\pi}{6\Delta} \sum_k \rho_k \sigma_k^3 \sum_{a \geqslant 1} \alpha_k^{(a)} B_k^{(a)} \tag{49}$$

and

$$\eta^B = \frac{\pi}{2\Delta} \sum_k \rho_k \sigma_k [\sigma_k N_k^T + z_k] \tag{50}$$

We use the notation

$$\mathscr{X}_i^{(0)} = X_i^{(0)} = \sigma_i M_i^{(0)} + z_i; \qquad \mathscr{X}_i^{(b)} = \sigma_i B_i^{(b)}, \quad b \geqslant 1 \tag{51}$$

and we will use this symbol in vector form,

$$\mathscr{X}_i = \begin{bmatrix} \mathscr{X}_i^{(0)} \\ \mathscr{X}_i^{(1)} \\ \mathscr{X}_i^{(2)} \\ \vdots \end{bmatrix} \tag{52}$$

We turn to the calculation of the coefficients $\mathbf{a}_j$. From Eq. (25), taking the first derivative, and since the direct correlation function must be finite at the origin, we get(4, 19)

$$-2\mathbf{Q}'_{ii}(0) = \sum_k \rho_k [\mathbf{Q}_{ik}(\lambda_{ki}) - z_i \mathbf{a}_k + \mathbf{t}_{ik}]\, \hat{\alpha}_k [\mathbf{Q}^T_{ik}(\lambda_{ki}) - z_i \mathbf{a}^T_k + \mathbf{t}^T_{ik}] \tag{53}$$

Using Eq. (32) together with the above results, we find after some long but straightforward algebra

$$a_i^{(0)} = \frac{1}{\mathscr{D}} [-2M_i^{(0)} - 2\sigma_i \eta^B] \tag{54}$$

$$a_i^{(a)} = \frac{1}{\mathscr{D}} \left[-2B_i^{(a)} + \sum_k \{[\mathbf{t}]_{ik}\, \rho_k \boldsymbol{\alpha}_k \mathscr{X}_k\}^{(a)} \right] \tag{55}$$

where $\mathscr{D}$ is defined by

$$\mathscr{D} = \sum_k \rho_k \mathscr{X}_k \boldsymbol{\alpha}_k [\mathscr{X}_k]^T \tag{56}$$

Here N^T_k is defined by Eq. (47) and η^B is given by Eq. (50).

We examine again Eq. (25). From the symmetry requirement

$$c_{ij}^{(ab)} = c_{ji}^{(ba)} \tag{57}$$

we get

$$\mathscr{Q}_{ij}(\lambda_{ji}) = \mathscr{Q}^T_{ji}(\lambda_{ij}) \tag{58}$$

Using Eqs. (27) and (32), we obtain

$$\beta_{ij}^{(00)} \sigma_i + z_i a_j^{(0)} = \beta_{ji}^{(00)} \sigma_j + z_j a_i^{(0)} \tag{59}$$

$$\beta_{ij}^{(0b)} \sigma_i + z_i a_j^{(b)} = \beta_{ji}^{(b0)} \sigma_j \tag{60}$$

$$\beta_{ij}^{(ab)} \sigma_i = \beta_{ji}^{(ba)} \sigma_j \tag{61}$$

and from Eq. (38)

$$[X_i^{(0)}]\, a_j^{(0)} = [X_j^{(0)}]\, a_i^{(0)} \tag{62}$$

$$[X_i^{(0)}]\, a_j^{(b)} = \sigma_j B_j^{(b)} a_i^{(0)} \tag{63}$$

$$\sigma_i B_i^{(a)} a_j^{(b)} = \sigma_j B_j^{(b)} a_i^{(a)} \tag{64}$$

Then

$$a_i^{(a)} = \frac{2\Gamma^T}{\mathscr{D}} \mathscr{X}_i^{(a)}, \qquad a \geqslant 0 \tag{65}$$

where Γ^T is the MSA scaling parameter. In matrix form,

$$[\boldsymbol{\alpha}_k] = \frac{2\Gamma^T}{\mathscr{D}} [\mathscr{X}_k] \tag{66}$$

Here $\mathscr{D}$ is given by Eq. (56), N_k^T is defined by Eq. (47), and η^B is given by Eq. (50):

$$\eta^B = \frac{\pi}{2\Delta} \left[\sum_k \rho_k \sigma_k \sum_a \mathscr{X}_k^{(a)} \alpha_k^{(a)} \right] \tag{67}$$

The full solution of the problem is obtained by solving the linear system (59)–(67):

$$\sum_k [\mathscr{M}_{ik}][\mathscr{X}_k] = [\mathbf{z}_i] \tag{68}$$

where $[\boldsymbol{\alpha}]_k$ is defined by Eq. (11) and

$$[\mathscr{M}_{ik}] = (1 + \Gamma^T \sigma_k)\, \delta_{ik} \mathbf{I} + \sigma_i \begin{bmatrix} (\pi/2\Delta)\, \sigma_k \sigma_i & \mathbf{0} \\ \mathbf{0} & -[\mathbf{t}]_{ik} \end{bmatrix} \rho_k \boldsymbol{\alpha}_k \tag{69}$$

$$[\mathbf{z}_i] = \begin{bmatrix} z_i \\ 0 \\ 0 \\ \vdots \end{bmatrix} \tag{70}$$

The formal solution of Eq. (68) is

$$[\mathscr{X}]_i = \sum_k [\mathscr{M}_{ik}]^{-1} [\mathbf{z}_k] \tag{71}$$

Explicit forms of this matrix for various models for the linear chain and the colloidal mixture will be given in future work. Using this result in Eq. (29), we get the closure equation for the parameter Γ^T,

$$[\Gamma^T]^2 = \pi \frac{\beta e^2}{\varepsilon_0} \sum_k \rho_k [\mathscr{X}_k][\boldsymbol{\alpha}_k][\mathscr{X}_k]^T \tag{72}$$

There is a second nonlinear equation for the parameter η^B, which depends strongly on the closure approximation for the single density matrix. This equation changes with the model and the approximations, but requires the contact probability. We observe that from Eqs. (36), (38), and (41) we get for the contact probability in the MSA,

$$\begin{aligned} 2\pi\sigma_{ij} g_{ij}^{ab}(\sigma_{ij}) &= 2\pi\sigma_{ij} g_{ij}^{\mathrm{HardSphere}}(\sigma_{ij})\, \delta_{a0}\delta_{b0} - 2\pi \frac{\beta e^2}{\varepsilon_0} \mathscr{X}_i^{a}\mathscr{X}_j^{b} \\ &\quad + \mathscr{T}_{ij}^{(ab)}[\delta_{a0} - 1][\delta_{b0} - 1] + \frac{\pi\sigma_i}{\Delta} \tau_j^{(b)} \delta_{a0}[\delta_{b0} - 1] \\ &\quad + \frac{\pi\sigma_j}{\Delta} \tau_i^{(a)} \delta_{b0}[\delta_{a0} - 1], \qquad a, b \geqslant 0 \end{aligned} \tag{73}$$

We have used

$$\tau_j^{(b)} = \sum_k \rho_k \sigma_k \sum_a \alpha_k^{(a)} t_{kj}^{(ab)} \tag{74}$$

and

$$\mathscr{T}_{ij} = \sum_k \rho_k \mathbf{t}_{ik} \boldsymbol{\alpha}_k \mathbf{t}_{kj} \tag{75}$$

We will need in the next section

$$\left[\frac{\partial\, \Delta E^{\mathrm{MSA}}}{\partial \Gamma^T}\right]_{\alpha} = \sum_i \left[\rho_i \frac{z_i}{\sigma_i} \frac{\partial X^T}{\partial \Gamma^T}\right]_{\hat{\alpha}, \mathbf{t}} \tag{76}$$

From the above equations we get by direct differentiation an expression of the derivative of the right-hand side term:

$$\left[\frac{\partial [\mathscr{X}_i]}{\partial \Gamma^T}\right]_{\hat{\alpha}, \mathbf{t}} = \sum_k \sigma_k [\mathscr{M}_{ik}]^{-1} [\mathscr{X}_i] \tag{77}$$

Using the closure relation (72), we get the simple and useful relation

$$\left[\beta \frac{\partial\, \Delta E^{\mathrm{MSA}}}{\partial \Gamma^{T}}\right]_{\alpha, t} = \frac{[\Gamma^{T}]^{2}}{\pi} \tag{78}$$

which will be used below.

2.1. Thermodynamic Properties

The standard expression for the excess energy per unit volume is(4)

$$\Delta E^{\mathrm{MSA}} = \tfrac{1}{2} \sum_{ij} \rho_i \rho_j \int_0^{\infty} dr\, u_{ij}(r)\, g_{ij}(r)\, 4\pi r^2 \tag{79}$$

where $u_{ij}(r)$ is the electrostatic interaction potential and $g_{ij}(r) = h_{ij}(r) + 1$ is the total radial distribution function. After some calculations(4,29,36) we get

$$\beta\, \Delta E^{\mathrm{MSA}} = \frac{e^2}{\varepsilon} \sum_i \rho_i z_i N_i^T = \frac{e^2}{\varepsilon} \sum_i \rho_i \frac{z_i}{\sigma_i} [X_i^T - z_i] \tag{80}$$

We calculate the excess free energy by charging up the system of the polymerizing discharged ions. We use the thermodynamic relation

$$\frac{\partial}{\partial \beta} (\beta\, \Delta A^{\mathrm{MSA}}) = \Delta E^{\mathrm{MSA}} \tag{81}$$

where ΔA^{MSA} is the excess free energy. Integrating by parts this equation, we have(19,36)

$$\beta\, \Delta A^{\mathrm{MSA}} = \Delta E^{\mathrm{MSA}} - \int_0^{\Gamma^T} d\Gamma'\, \beta' \frac{\partial}{\partial \Gamma'} \Delta E^{\mathrm{MSA}} \tag{82}$$

We need to compute

$$\beta \frac{\partial\, \Delta E^{\mathrm{MSA}}}{\partial \Gamma^T} = \left[\beta \frac{\partial\, \Delta E^{\mathrm{MSA}}}{\partial \Gamma^T}\right]_{\hat{\alpha}} + \sum_{i,a} \left[\beta \frac{\partial\, \Delta E^{\mathrm{MSA}}}{\partial \alpha_{i,a}}\right]_{\Gamma^B} \frac{\partial \alpha_{i,a}}{\partial \Gamma^T} \tag{83}$$

Using Eq. (78), we get the following expression of the Helmholtz free energy:

$$\beta\, \Delta A^{\mathrm{MSA}} = \beta\, \Delta E^{\mathrm{MSA}} + \frac{[\Gamma^T]^3}{3\pi} - \beta\, \Delta S^{\mathrm{sticky}} \tag{84}$$

where

$$\Delta S^{\text{sticky}} = k_{\text{B}} \int_0^{\Gamma^T} d\Gamma' \, \beta' \sum_{i,a}^{m,\nu} \left[\left[\frac{\partial \, \Delta E^{\text{MSA}}}{\partial \alpha_i^{(a)}} \right]_{\Gamma^B, \mathbf{t}} \frac{\partial \alpha_i^{(a)}}{\partial \Gamma^T} \right.$$
$$\left. + \sum_{j,b} \left[\frac{\partial \, \Delta E^{\text{MSA}}}{\partial t_{i,j}^{(a,b)}} \right]_{\Gamma^B, \hat{\alpha}} \frac{\partial t_{i,j}^{(a,b)}}{\partial \Gamma^T} \right] \tag{85}$$

We need to calculate $\partial \alpha_i^{(a)} / \partial \Gamma^T$ and $\partial t_{i,j}^{(a,b)} / \partial \Gamma^T$, which are obtained from the closure relations of the association problem. An explicit general solution of this system is complex, but some simpler cases of interest can be solved explicitly. This is left for the future.

The excess osmotic coefficient φ^{MSA} is obtained as before from the thermodynamic relation$^{(19)}$

$$\varphi^{\text{MSA}} = \zeta_0 \frac{\partial}{\partial \zeta_0} \left[\frac{\Delta A^{\text{MSA}}}{\zeta_0} \right]_{\Gamma^T = \text{const}}$$
$$= \zeta_0 \frac{\partial}{\partial \zeta_0} \left[\frac{\Delta E^{\text{MSA}}}{\zeta_0} \right]_{\Gamma^T = \text{const}} - \frac{[\Gamma^B]^3}{3\pi \zeta_0} - \left(\frac{1}{k_{\text{B}}} \right) \zeta_0 \frac{\partial}{\partial \zeta_0} \left[\frac{\Delta S^{\text{sticky}}}{\zeta_0} \right]_{\Gamma^T = \text{const}} \tag{86}$$

where ζ_0 is given by Eq. (42). Finally, we get the activity coefficient from the thermodynamic formula

$$\Delta \ln \gamma_{\mp} = \beta \frac{\Delta A^{\text{MSA}}}{\zeta_0} + \Delta \varphi^{\text{MSA}} \tag{87}$$

which yields

$$\Delta \ln \gamma_{\mp} = \beta \left[\frac{\partial \, \Delta E^{\text{MSA}}}{\partial \zeta_0} \right]_{\Gamma^T = \text{const}} - \left(\frac{1}{k_{\text{B}}} \right) \beta \left[\frac{\partial \, \Delta S^{\text{sticky}}}{\partial \zeta_0} \right]_{\Gamma^T = \text{const}} \tag{88}$$

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