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The General Solution of the Binding Mean Spherical Approximation for Pairing Ions

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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. Only pairs are allowed. It is shown that the general solution is given in terms of two scaling parameters and the set of binding fractions. One of the scales is the screening parameter, and the other is a coupling parameter analogous to that of the simple MSA, but that now is found solving a cubic equation. Therefore the full solution requires solving $m+2$ nonlinear algebraic equations for a system with m components. A brief discussion of the thermodynamics is given.

KEY WORDS: Ionic mixtures; mean spherical approximation; dimerizing ions.

1. INTRODUCTION

The mean spherical approximation (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 Debye–Hückel (DH) screening parameter κ_D. However, as has been recently shown, the MSA is *asymptotically correct* in the limit of high density and infinite charge,$^{(12,13)}$ where, unlike the DH theory, it satisfies the exact Onsager bounds$^{(14)}$ for the Helmholtz free energy and the internal energy of the system. These limits are of course satisfied by the hypernetted chain theory (HNC)$^{(15)}$ and its improved versions. The internal energy of

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the MSA is an axact lower bound for extreme high densities and charges, and is as accurate as the HNC and its modifications in these limits. This has been shown explicitly by Rosenfeld^(16,17) for extremely dense one-component plasmas, where the MSA agrees with much more costly HNC calculations.

The MSA is inaccurate for dilute systems in the region near the repulsive core of the ions, such as the high-charge dilute ionic solutions. To remedy this problem, an approximation that works remarkably well is to use a closure (the "soft"-MSA, SMSA^(18)) that interpolates between the MSA closure for large distances and the Percus–Yevick (PY) closure for the small distances. Analytical schemes such as the "generalized" MSA use a nonzero direct correlation function outside of the core given by an exponential form, with free parameters that are determined by some consistency criteria^(19,20) or by a variational form such as the SMSA mentioned above.

One simple and very popular way to correct these problems was proposed by Bjerrum,^(21) who developed the theory of ionic association in conjunction with the DH theory. The ionic association in electrolytes occurs in two different ways:

1. By "electrostatic" association, in which the clustering process is due to strong Coulomb interactions.
2. By the "chemical" association mechanism, in which there is a true chemical bond formed.

In the hypernetted chain equation the nonlinear effects produce very high contact probabilities for oppositely charged ion pairs. Therefore one expects that the HNC will account for the electrostatic association mechanism (1). But, as it has been recently shown, it does not do a very good job here, and alternative schemes have to be used.^(22–24)

In the MSA this has been done combining the concept of ionic association with the calculation of thermodynamic properties in various ways: By simply correcting the ionic concentration, that is, using the effective ionic concentrations obtained from the law of mass action,^(25,26) excellent fitting to the properties of real ionic solutions is obtained. In ref. 25 only the electrostatic association is discussed, while in ref. 26, the association parameter includes both electrostatic and chemical association. This method, however, does not give structural correlation functions. A better approach is that of the physical clusters.^(27–29)

A statistical mechanical approach to pairing is that of Stell and coworkers,^(30–32) 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,(33,34) and it has been shown that the excess functions due to the charges are *all*(33,35) given in terms of the scaling parameter Γ^T, 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.(36,37) 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 in the HNC approximation.(22–24) More recently the Wertheim formalism was used to study numerically the binding effect for the restricted MSA(38) applied to a symmetric 2–2 equal-size electrolyte, with excellent results for the thermodynamic functions.

In this paper we obtain the full and general solution of the binding MSA (BIMSA) for the arbitrary mixture of pairing ions. It is given in terms of a scaling parameter Γ^B, just as in the solution of the general MSA(4) for charged hard spheres. For sticky hard spheres the MSA solution still depends on Γ^T,(33) a single (but different) parameter. The remarkable simplicity of the MSA thermodynamics persists for the sticky case, even though no explicit solutions are obtained until the matrix of the sticky interactions is set.

The situation in the BIMSA is not quite the same: In a way it is simpler than the sticky MSA since an explicit solution can be obtained for the general mixture with an arbitrary matrix of the sticky interactions. This solution is given in terms of the screening parameter Γ^B, and the cross scaling parameter η^B, which was discussed in previous work(39) on the scaling properties of the MSA. In the hard-core MSA, η is obtained simply from Γ. In the present case, η^B has to be calculated by solving a cubic equation, with coefficients that depend on Γ^B and the degrees of association, which are given by m (= the number of components) quadratic equations. In other words, for a mixture with m species, we need to solve a system of $m+2$ nonlinear algebraic equations. The theory and the analytical solution are presented in Section 2.

Expressions for the excess thermodynamics are given in Section 3.

2. THEORY

The Wertheim theory was initially formulated for sticky adsorption points. The extension to isotropic bonding with saturation effects was carried out by Yakub[40] and by Kalyuzhnyi and Stell.[41] We consider a system with an arbitrary number of components $0 \leqslant i \leqslant m$, 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 electroneutral

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

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

$$\mathbf{h}_{ij} = \begin{bmatrix} h_{ij}^{(00)} & h_{ij}^{(01)} \\ h_{ij}^{(10)} & h_{ij}^{(11)} \end{bmatrix} \tag{2}$$

$$\mathbf{c}_{ij} = \begin{bmatrix} c_{ij}^{(00)} & c_{ij}^{(01)} \\ c_{ij}^{(10)} & c_{ij}^{(11)} \end{bmatrix} \tag{3}$$

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

$$\boldsymbol{\rho}_i = \begin{bmatrix} \rho_i & \rho_i^{(0)} \\ \rho_i^{(0)} & 0 \end{bmatrix} \tag{4}$$

In Wertheim's theory the density of i is split into "bonded," $\rho_i^{(1)}$, and "not-bonded," $\rho_i^{(0)}$, parts, which correspond to the associated and nonassociated ions. We have the relation for the total or initial density of species i

$$\rho_i = \rho_i^{(0)} + \rho_i^{(1)} \tag{5}$$

It will be convenient to use also the degree of dissociation

$$\alpha_i = \frac{\rho_i^{(0)}}{\rho_i} \tag{6}$$

Then

$$\boldsymbol{\rho}_i = \rho_i \begin{bmatrix} 1 & \alpha_i \\ \alpha_i & 0 \end{bmatrix} = \rho_i \hat{\boldsymbol{\alpha}}_i \tag{7}$$

The "normal" pair correlation function therefore is

$$h_{ij}(r) = h_{ij}^{(00)}(r) + \alpha_i h_{ij}^{(10)}(r) + \alpha_j h_{ij}^{(01)}(r) + \alpha_i \alpha_j h_{ij}^{(11)}(r) \tag{8}$$

The WOZ is

$$\mathbf{h}_{ij}(r) = \mathbf{c}_{ij}(r) - \sum_k \rho_k \int d\mathbf{r}_1 \, \mathbf{c}_{ik}(|\mathbf{r}_1 - \mathbf{r}|) \, \hat{\alpha}_k \mathbf{h}_{kj}(\mathbf{r}_1) \tag{9}$$

where **r** is the position.

If we restrict ourselves to only the pairing case, then the BIMSA boundary conditions are

$$\mathbf{c}_{ij}(r) = -\frac{\beta e^2}{\varepsilon_0} \frac{z_j z_i}{r} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \qquad r > \sigma_{ij} \tag{10}$$

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

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

$$\exp[-\beta u_{ij}^{\mathrm{st}}(r)] = \mathscr{B}_{ij} \delta(r - \sigma_{ij}^-) \tag{11}$$

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

$$f_{ij} = \exp[-\beta u_{ij}^{\mathrm{st}}(r)] = -1 + \mathscr{B}_{ij} \delta(r - \sigma_{ij}^-) \tag{12}$$

and the fraction of nonbound ions i, α_i,(36–38) is

$$1 = \alpha_i \left[1 + \sum_j \rho_j \alpha_j 4\pi\sigma_{ij}^2 g_{ij}^{00}(\sigma_{ij}) \, \mathscr{B}_{ij} \right] \tag{13}$$

In our solution, and to make contact with earlier work,(33,35) we will use the parameter t_{ij},

$$t_{ij} = 2\pi\sigma_{ij} g_{ij}^{00}(\sigma_{ij}) \, \mathscr{B}_{ij} \tag{14}$$

With this parameter Eq. (13) reads

$$1 = \alpha_i \left[1 + \sum_j \rho_j \alpha_j 2\sigma_{ij} t_{ij} \right] \tag{15}$$

For the pair correlation function matrix we get the boundary condition in this notation

$$\mathbf{h}_{ij}(r) = \begin{bmatrix} -1 & 0 \\ 0 & (t_{ij}/2\pi\sigma_{ij}) \, \delta(r - \sigma_{ij}^-) \end{bmatrix}, \qquad r \leqslant \sigma_{ij} \tag{16}$$

where t_{ij} is the sticky parameter for the association of the ions i and j defined by Eq. (14).

We use now the extension of the Baxter–Wertheim(42,43) factorization method to charged systems.(4) We define the projections $\mathbf{J}_{ij}$ and $\mathbf{S}_{ij}$

$$\mathbf{J}_{ij}(r) = 2\pi \int_r^\infty ds\, s\mathbf{h}_{ij}(s) \tag{17}$$

$$\mathbf{S}_{ij}(r) = 2\pi \int_r^\infty ds\, s\mathbf{c}_{ij}(s) \tag{18}$$

From the boundary conditions (10), (16) we get

$$\mathbf{J}_{ij}(r) = \begin{bmatrix} \pi r^2 + J_{ij}^{00} & J_{ij}^{(01)} \\ J_{ij}^{(10)} & J_{ij}^{(11)} \end{bmatrix}, \qquad r \leqslant \sigma_{ij} \tag{19}$$

$$\mathbf{S}_{ij}(r) = -\frac{\beta e^2}{\varepsilon_0} \lim_{\mu=0} \frac{z_j z_i e^{-\mu|r|}}{\mu} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \qquad r > \sigma_{ij} \tag{20}$$

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

$$\mathbf{S}_{ij}(r) = \mathcal{Q}_{ij}(r) - \sum_k \rho_k \int dr_1\, \mathcal{Q}_{ik}(r_1)\, \hat{\alpha}_k \mathcal{Q}_{jk}^T(r_1 - r) \tag{21}$$

$$\mathbf{J}_{ij}(r) = \mathcal{Q}_{ij}(r) - \sum_k \rho_k \int dr_1\, \mathbf{J}_{ik}(|r_1 - r|)\, \hat{\alpha}_k \mathcal{Q}_{kj}(r_1) \tag{22}$$

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

From the analysis of the singularities of the problem(4,33) we see that this function must be of the form

$$\mathcal{Q}_{ij}(r) \Rightarrow [\mathbf{Q}_{ij}(r) + \mathbf{t}_{ij}]\, \theta(\sigma_{ij} - r) - z_i \mathbf{a}_j e^{-\mu r}, \qquad \lambda_{ji} < r \tag{23}$$

where we used the definition

$$\lambda_{ji} = \tfrac{1}{2}(\sigma_j - \sigma_i) \tag{24}$$

Performing the integrals in Eq. (21), we see that in the limit $\mu = 0$ both sides have a simple pole. The residues of this pole must be equal, and therefore

$$4\pi \frac{\beta e^2}{\varepsilon_0} z_j z_i \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} = z_j z_i \sum_k \rho_k \mathbf{a}_k \hat{\alpha}_k \mathbf{a}_k^T \tag{25}$$

From here we see that the only form compatible with this is

$$\mathbf{a}_j = \begin{bmatrix} a_j^0 & a_j^1 \\ 0 & 0 \end{bmatrix} \tag{26}$$

and we require

$$4\pi \frac{\beta e^2}{\varepsilon_0} = \sum_{k=1}^{m} \rho_k [(a_k^0)^2 + 2a_k^0 \alpha_k a_k^1] \tag{27}$$

This is one of the important boundary conditions.

Similarly, from the discontinuity at $r = \sigma_{ij}$ in Eq. (21) we need

$$\mathbf{t}_{ij} = \begin{bmatrix} 0 & 0 \\ 0 & t_{ij} \end{bmatrix} \tag{28}$$

It is also clear from Eq. (17) and (22) that $\mathbf{Q}_{ij}(r)$ must be a polynomial of second degree, which is zero for $r = \sigma_{ij}$. For convenience we write

$$\mathbf{Q}_{ij}(r) = (1/2)\, \mathbf{A}_{ij}(r - \sigma_{ij})(r - \lambda_{ji}) + \boldsymbol{\beta}_{ij}(r - \sigma_{ij}) \tag{29}$$

where the coefficients are matrices

$$\mathbf{A}_{ij} = \begin{bmatrix} A_{ij}^{(00)} & A_{ij}^{(01)} \\ A_{ij}^{(10)} & A_{ij}^{(11)} \end{bmatrix} \tag{30}$$

and

$$\boldsymbol{\beta}_{ij} = \begin{bmatrix} \beta_{ij}^{(00)} & \beta_{ij}^{(01)} \\ \beta_{ij}^{(10)} & \beta_{ij}^{(11)} \end{bmatrix} \tag{31}$$

We remark some of the properties of this function:

$$\mathbf{Q}_{ij}(\sigma_{ij}) = 0 \tag{32}$$

$$\mathbf{Q}'_{ij}(\sigma_{ij}) = (1/2)\, \sigma_j \mathbf{A}_{ij} + \boldsymbol{\beta}_{ij} \tag{33}$$

This quantity yields the contact probability, needed to calculate the closure of the Wertheim theory, Eq. (14). In fact, from Eq. (22) we get the important relation

$$2\pi\sigma_{ij} \mathbf{g}_{ij}(\sigma_{ij}) = (1/2)\, \sigma_i \mathbf{A}_j + \boldsymbol{\beta}_{ij} + \sum_k \rho_k \alpha_k t_{ik} [-\sigma_k \boldsymbol{\beta}_{kj} - z_k \mathbf{a}_j + t_{kj}] \tag{34}$$

Furthermore, we need

$$\mathbf{Q}'_{ij}(\sigma_j/2)=\hat{\beta}_{ij} \tag{35}$$

$$\mathbf{Q}'_{ii}(0)=-(1/2)\,\sigma_i\mathbf{A}_{ii}+\hat{\beta}_{ii} \tag{36}$$

$$\mathbf{Q}''_{ij}(\sigma_{ij})=\mathbf{A}_{ij} \tag{37}$$

We also need the moments of $\mathbf{Q}_{ij}(r)$ defined by

$$\mathbf{K}^{n}_{kj}=\int_0^{\sigma_k} dr_1\, r_1^n Q_{kj}(r_1+\lambda_{jk}) \tag{38}$$

We get, using Eq. (29),

$$\mathbf{K}^0_{kj}=-(1/12)\,\sigma_k^3\mathbf{A}_{kj}-(1/2)\,\sigma_k^2\hat{\beta}_{kj} \tag{39}$$

A useful relation is

$$\mathbf{K}^1_{kj}-(\sigma_k/2)\,\mathbf{K}^0_{kj}=(1/12)\,\hat{\beta}_{kj}\sigma_k^3 \tag{40}$$

We take now the first derivative of Eq. (22) at $r=\sigma_j/2$:

$$\begin{bmatrix}\pi\sigma_j & 0\\ 0 & 0\end{bmatrix}=\hat{\beta}_{ij}-\frac{\pi}{6}\sum_k \rho_k\sigma_k^3\hat{\alpha}_k\hat{\beta}_{kj}+\sum_k \rho_k z_k\mathbf{J}_{ik}\hat{\alpha}_k\mathbf{a}_j \tag{41}$$

From the second derivative of Eq. (22) we get

$$\begin{aligned}\begin{bmatrix}2\pi & 0\\ 0 & 0\end{bmatrix}=\mathbf{A}_{ij}-\pi\sum_k \rho_k\hat{\alpha}_k](\sigma_k^3/6)\,\mathbf{A}_{kj}+\sigma_k^2\hat{\beta}_{kj}]\\ +2\pi\sum_k \rho_k\hat{\alpha}_k\mathbf{t}_{kj}-2\pi\sum_k \rho_k z_k\sigma_k\mathbf{a}_j\end{aligned} \tag{42}$$

The solution of Eq. (41) yields

$$\beta^{10}_{ij}=B^1_i a^0_j,\qquad \beta^{11}_{ij}=B^1_i a^1_j \tag{43}$$

$$\beta^{00}_{ij}=\frac{\pi\sigma_j}{\Delta}+M^{01}_i a^0_j,\qquad \beta^{01}_{ij}=M^{01}_i a^1_j \tag{44}$$

With these results we obtain from Eq. (42)

$$A^{10}_j=0,\qquad A^{11}_j=0 \tag{45}$$

$$A^{00}_j=\frac{2\pi}{\Delta}\left[1+\zeta_2\sigma_j\frac{\pi}{\Delta}\right]+2a^0_j\eta^B,\qquad A^{01}_j=-\frac{2\pi}{\Delta}\tau^{11}_j+a^1_j\eta^B \tag{46}$$

Here we have used the following notation[4,33]:

$$\zeta_n = \sum_k \rho_k \sigma_k^n \tag{47}$$

$$\Delta = 1 - \pi\zeta_3/6 \tag{48}$$

$$\chi_2 = \sum_k \rho_k z_k \sigma_k^2 \tag{49}$$

$$B_j^\alpha = \sum_k \rho_k z_k [J_{jk}^{\alpha 0} + \alpha_k J_{jk}^{\alpha 1}], \qquad \alpha = 0, 1 \tag{50}$$

Here

$$B_j^T = B_j^0 + \alpha_j B_j^1 \tag{51}$$

corresponds to the total electrostatic interaction parameter B_J of previous work.[4,33] Furthermore, we have used

$$N_j^T = B_j^T + \frac{\pi}{6\Delta} \sum_k \rho_k \sigma_k^3 B_k^T + \frac{\pi}{4\Delta} \chi_2 \tag{52}$$

We have also

$$N_j^\alpha = B_j^\alpha + \frac{\pi}{6\Delta} \sum_k \rho_k \sigma_k^3 B_k^\alpha + \frac{\pi}{4\Delta} \chi_2, \qquad \alpha = 0, 1 \tag{53}$$

$$M_j^{01} = N_j^0 + \frac{\pi}{6\Delta} \sum_k \rho_k \alpha_k \sigma_k^3 B_k^1 \tag{54}$$

$$\tau_j^{11} = \sum_k \rho_k \sigma_k \alpha_k t_{jk}^{11} \tag{55}$$

and

$$\eta^B = \frac{\pi}{2\Delta} \sum_k \rho_k \sigma_k [\sigma_k (M_k^{01} + \alpha_k B_k^1) + z_k] = \frac{\pi}{2\Delta} \sum_k \rho_k \sigma_k [\sigma_k N_k^T + z_k] \tag{56}$$

We remark that

$$M_j^{01} = N_j^T - \alpha_j B_j^1 \tag{57}$$

Before turning to the calculation of the coefficients $\mathbf{a}_j$, we examine again Eq. (21). From the symmetry requirement

$$c_{ij}^{01} = c_{ij}^{10} \tag{58}$$

we get

$$\mathcal{Q}_{ij}(\lambda_{ji}) = \mathcal{Q}_{ji}^T(\lambda_{ij}) \tag{59}$$

Using Eqs. (23) and (29), we obtain

$$\beta_{ij}^{00}\sigma_i + z_i a_j^0 = \beta_{ji}^{00}\sigma_j + z_j a_i^0 \tag{60}$$

$$\beta_{ij}^{01}\sigma_i + z_i a_j^1 = \beta_{ji}^{10}\sigma_j \tag{61}$$

$$\beta_{ij}^{11}\sigma_i = \beta_{ji}^{11}\sigma_j \tag{62}$$

and from Eq. (44) we have

$$[X_i^{01}]\, a_j^0 = [X_j^{01}]\, a_i^0 \tag{63}$$

$$[X_i^{01}]\, a_j^1 = \sigma_j B_j^1 a_i^0 \tag{64}$$

$$\sigma_i B_i^1 a_j^1 = \sigma_j B_j^1 a_i^1 \tag{65}$$

where we have used the notation

$$X_i^{01} = \sigma_i M_i^{01} + z_i \tag{66}$$

These three relations are simultaneously satisfied by a *single* scaling parameter Γ^B, which gives

$$a_i^0 = \frac{2\Gamma^B}{D_a}[X_i^{01}] \tag{67}$$

$$a_i^1 = \frac{2\Gamma^B}{D_a}\sigma_i B_i^1 \tag{68}$$

where D_a is just a constant for the time being, which will be defined below Eq. (72).

We turn now again to Eq. (21). Taking the first derivative, and since the direct correlation function must be finite at the origin, we get(4,33)

$$-2\mathbf{Q}'_{ii}(0) = \sum_k \rho_k[\mathbf{Q}_{ik}(\lambda_{ki}) - z_i\mathbf{a}_k + \mathbf{t}_{ik}]\,\hat{\alpha}_k[\mathbf{Q}_{ik}^T(\lambda_{ki}) - z_i\mathbf{a}_k^T + \mathbf{t}_{ik}] \tag{69}$$

Using Eq. (29) and (36), together with the above results, we find, after some long but straightforward algebra,

$$a_i^0 = \frac{1}{D_a}[-2M_i^{01} - 2\sigma_i\eta^B] \tag{70}$$

$$a_i^1 = \frac{1}{D_a}\left[-2B_i^1 + 2\sum_k \rho_k\alpha_k X_k^{01} t_{ki}\right] \tag{71}$$

where now

$$D_a=\sum_k \rho_k(\sigma_k N_k^T+z_k)^2-\sum_k \rho_k[\alpha_k\sigma_k B_k^1]^2 \tag{72}$$

and N_k^T is defined by Eq. (52).

Consider now Eqs. (70) and (67): We get the system of equations

$$\Gamma^B X_i^{01}=-M_i^{01}-\sigma_i\eta^B \tag{73}$$

As in our previous work,(4,33) this system has the solution

$$X_i^{01}=\frac{z_i-\eta^B\sigma_i^2}{1+\Gamma^B\sigma_i} \tag{74}$$

and

$$M_i^{01}=-\frac{\Gamma^B z_i+\eta^B\sigma_i}{1+\Gamma^B\sigma_i} \tag{75}$$

where η^B is given by Eq. (56),

$$\eta^B=\frac{\pi}{2\Delta}\left[\sum_k \rho_k\sigma_k X_k^{01}+\sum_k \rho_k\sigma_k\alpha_k B_k^1\right] \tag{76}$$

Direct substitution into Eq. (68) will lead to B_i^1,

$$B_i^1=\frac{\sum_k \rho_k\alpha_k X_k^{01} t_{ki}}{1+\Gamma^B\sigma_i} \tag{77}$$

With these results and using the boundary condition (27) and the scaling relations, Eqs. (67) and (68) lead to

$$[\Gamma^B]^2=\frac{\beta e^2}{\varepsilon_0}\sum_k \rho_k[(X_k^{01})^2+2X_k^{01}\sigma_k\alpha_k B_k^1] \tag{78}$$

which now becomes

$$[\Gamma^B]^2=\frac{\beta e^2}{\varepsilon_0}\sum_k \rho_k\frac{z_k-\eta^B\sigma_k^2}{(1+\Gamma^B\sigma_k)^2}\times\left[(z_k-\eta^B\sigma_k^2)+2\sigma_k\alpha_k\sum_l\frac{\rho_l\alpha_l(z_l-\eta^B\sigma_l^2)\,t_{lk}}{1+\Gamma^B\sigma_l}\right] \tag{79}$$

We observe also that from Eqs. (34), (44), and (46) we get the contact probability

$$2\pi\sigma_{ij}g_{ij}^{00}(\sigma_{ij}) = 2\pi\sigma_{ij}g_{ij}^{\text{HardSphere}}(\sigma_{ij}) - 2\pi\frac{\beta e^2}{\varepsilon_0}X_i^{01}X_j^{01} \tag{80}$$

The final step in the solution is to obtain an equation for η^B. Let us now turn to Eq. (14): Using the above equation, we get

$$t_{ij} = t_{ij}^{\text{HS}} - 2\pi\frac{\beta e^2}{\varepsilon_0}X_i^{01}X_j^{01}\mathscr{B}_{ij} \tag{81}$$

where

$$t_{ij}^{\text{HS}} = \mathscr{B}_{ij}\frac{2\pi}{\Delta}\left[\sigma_{ij} + \zeta_2\sigma_i\sigma_j\frac{\pi}{\Delta}\right] \tag{82}$$

Now from Eqs. (76) and (77) we get

$$\eta^B = \frac{\pi}{2\Delta}\left\{\sum_k \rho_k\sigma_k X_k^{01} + \sum_k \frac{\rho_k\sigma_k\alpha_k}{1+\Gamma^B\sigma_k}\sum_l \rho_l\alpha_l X_l^{01}\left[t_{lk}^{\text{HS}} - 2\pi\frac{\beta e^2}{\varepsilon_0}X_k^{01}X_l^{01}\mathscr{B}_{kl}\right]\right\} \tag{83}$$

We now substitute the expression for X_k^{01}, Eq. (74). We get after some lengthy algebra the cubic equation

$$(\eta^B)^3 A_B + (\eta^B)^2 B_B + \eta^B C_B + D_B = 0 \tag{84}$$

where

$$A_B = -2\pi\frac{\beta e^2}{\varepsilon_0}T(\sigma_k^4, \sigma_l^4), \qquad B_B = 6\pi\frac{\beta e^2}{\varepsilon_0}T(\sigma_k^4, \sigma_l^2 z_l)$$

$$C_B = 1 + \Omega_n + S_{\sigma,\sigma}^{\text{HS}} - 2\pi\frac{\beta e^2}{\varepsilon_0}[3T(\sigma_k^2 z_k, \sigma_l^2 z_l) + 2T(\sigma_k^4, z_l^2)] \tag{85}$$

$$D_B = -P_n + S_{\sigma,z}^{\text{HS}} - 2\pi\frac{\beta e^2}{\varepsilon_0}T(\sigma_k^2 z_k, z_l^2)$$

where we define the sums

$$P_n = \frac{\pi}{2\Delta}\sum_k \frac{\rho_k\sigma_k z_k}{1+\Gamma\sigma_k} \tag{86}$$

$$\Omega_n = \frac{\pi}{2\Delta}\sum_k \frac{\rho_k\sigma_k^3}{1+\Gamma\sigma_k} \tag{87}$$

$$S_{a_k,b_l}^{\text{HS}} = \frac{\pi}{2\Delta}\sum_{kl}\frac{\rho_k\alpha_k a_k}{1+\Gamma\sigma_k}\frac{\rho_l\alpha_l b_l}{1+\Gamma\sigma_l}t_{k,l}^{\text{HS}}, \qquad a_k, b_k = \sigma_k^2, z_k \tag{88}$$

and

$$T(a_k, b_l) = \frac{\pi}{2\Delta} \sum_{kl} \frac{\rho_k \alpha_k a_k}{(1 + \Gamma\sigma_k)^2} \frac{\rho_l \alpha_l b_l}{(1 + \Gamma\sigma_l)^2} \mathscr{B}_{kl} \tag{89}$$

This completes the analytical solution of the WOZ for the binding mean spherical approximation. For an m-component system we need to solve the system of equations formed by Eq. (15) from which we get the parameters α_k. With these parameters we will compute η_B and Γ^B solving the two equations (79) and (84). Our equations agree with the previous solution of Holovko and Kalyuzhnyi(38) for the restricted case up to the point where they obtained explicit results.

Thermodynamic Properties

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

$$\Delta E^{\mathrm{MSA}} = (1/2) \sum_{ij} \rho_i \rho_j \int_0^\infty dr\, u_{ij}(r)\, g_{ij}(r)\, 4\pi r^2 \tag{90}$$

where $u_{ij}(r)$ is the electrostatic interaction potential and $g_{ij}(r)$ is the total radial distribution function. After some calculations(4,44) we get

$$\beta\, \Delta E^{\mathrm{MSA}} = \frac{e^2}{\varepsilon} \sum_i \rho_i z_i N_i^T = \frac{e^2}{\varepsilon} \sum_i \rho_i z_i [M_i^{01} + \alpha_i B_i^1] \tag{91}$$

Using Eqs. (75) and (77) of the last section, we get

$$\beta\, \Delta E^{\mathrm{MSA}} = -\frac{e^2}{\varepsilon} \sum_i \rho_i \left[\frac{\rho_i z_i^2 \Gamma^B}{1 + \Gamma^B \sigma_i} + \eta^B \frac{2\Delta}{\pi} [P_n - S(\sigma_k^2, z_l)] + \frac{2\Delta}{\pi} S(z_k, z_l) \right] \tag{92}$$

where

$$S(a_k, b_l) = \frac{\pi}{2\Delta} \sum_{kl} \frac{\rho_k \alpha_k a_k}{1 + \Gamma\sigma_k} \frac{\rho_l \alpha_l b_l}{1 + \Gamma\sigma_l} t_{k,l} \tag{93}$$

To evaluate the excess free energy, we take the thermodynamic relation(33)

$$\frac{\partial}{\partial\beta} (\beta\, \Delta A^{\mathrm{MSA}}) = \Delta E^{\mathrm{MSA}} \tag{94}$$

where ΔA^{MSA} is the excess free energy. Integrating by parts this equation, we have(44,33)

$$\beta\, \Delta A^{\mathrm{MSA}} = \Delta E^{\mathrm{MSA}} - \int_0^{\Gamma^B} d\Gamma'\, \beta' \frac{\partial}{\partial \Gamma'} \Delta E^{\mathrm{MSA}} \tag{95}$$

Unfortunately, the simplifying relation

$$\pi\beta \frac{\partial}{\partial \Gamma^B} \Delta E^{\mathrm{MSA}} = [\Gamma^B]^2 \tag{96}$$

is not satisfied here, and therefore the entropy is of the form

$$\Delta S^{\mathrm{MSA}} = -k \frac{[\Gamma^B]^3}{3\pi} + \text{sticky term} \tag{97}$$

We hope to come back to this point in the future.

The excess osmotic coefficient φ^{MSA} is obtained as before from the thermodynamic relation(33)

$$\varphi^{\mathrm{MSA}} = \zeta_0 \frac{\partial}{\partial \zeta_0} \left[\frac{\Delta A^{\mathrm{MSA}}}{\zeta_0} \right]_{\Gamma^B = \mathrm{const}} \tag{98}$$

where ζ_0 is given by Eq. (47). Finally, we get the activity coefficient from the thermodynamic formula

$$\Delta \ln \gamma_{\mp} = \beta \frac{\Delta A^{\mathrm{MSA}}}{\zeta_0} + \Delta \varphi^{\mathrm{MSA}} \tag{99}$$

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