Exact solution of the mean spherical model for strong electrolytes in polar solvents*

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The mean spherical model (MSM) for dense fluids is solved for an arbitrary mixture of equal radii charged hard spheres with permanent embedded dipole moments. The model provides a treatment of ionic solutions that includes the feature of a molecular solvent. Thus, it gives a basis for investigating deviations from the familiar continuum dielectric model in ionic solution theory. The arbitrary polar–ionic mixture is first reduced to an effective two component problem. One component is an effective charged species while the other is an effective polar species. This two component problem is solved in terms of three parameters closely related to the thermodynamic functions of the fluid. Nonlinear algebraic equations for these parameters are obtained. Although these equations appear to be analytically intractable for arbitrary ionic and dipolar strengths, explicit results are obtained for low ionic strength. In this limit, the ion–ion contribution to the Helmholtz free energy is given by the classical Debye–Hückel result. The dielectric constant in the Debye–Hückel formula is that of the MSM polar fluid mixture that results if the ionic components of the polar–ion solution are discharged. The self-energy of charging, however, differs from the classical result. The model also exhibits Debye shielding of the solvent–solvent and solvent–solute interactions as well as the more familiar solute–solute shielding.

I. INTRODUCTION

We present an exact solution of the *mean spherical model* (MSM) for an arbitrary mixture of charged equal radii hard spheres with permanent dipole moments. Our motivation for addressing this problem is to investigate, for the first time, a nontrivial model for concentrated ionic solutions that includes the feature of a molecular polar solvent. The model provides a basis for examining deviations from the usual continuum dielectric approximation widely employed in ionic solution theory.

The MSM was introduced by Lebowitz and Percus[1] as a generalization to fluid systems with hard sphere interactions of the spherical model for Ising spin systems. The MSM which is specified in Sec. II, is based on reasonable though somewhat drastic approximations. It invites study because it has the virtue of yielding analytic results for systems of physical interest.

Our method of solution is a generalization of the invariant expansion technique for the solution of the MSM for neutral hard spheres with multipolar interactions developed by Blum.[2] These techniques derive from the fundamental work of Wertheim[3] on the pure MSM polar fluid. In the limit of vanishing charge, our model reduces to MSM for polar mixtures[4] and in the limit of vanishing dipole moment, our model reduces to MSM for equal radii charged hard sphere mixtures solved by Waisman and Lebowitz.[5]

The reader will find that despite efforts to present only the essential features of the solution to the model, the analysis presented is quite involved. Accordingly, we summarize here our main results and indicate where these results may be found in the body of the paper.

(1) The arbitrary mixture of charged hard spheres with permanent dipole moments is reduced to an effective two component fluid where one species bears an effective charge $\hat{e}$ Eq. (III. 62) at an effective density $\hat{\eta}_0$ Eq. (III. 64) and one species bears an effective dipole moment $\hat{\mu}$ Eq. (III. 63) at an effective density $\hat{\eta}_1$, Eq. (III. 65).

(2) The solution to the MSM is formally obtained in terms of the direct correlation function $w\mathbf{c}^{(0)}(w)$ of the effective two component fluid as a polynomial of fourth order in $w = (r/d)$ Eq. (III. 98). Here d is the hard sphere diameter. Explicit results for the coefficients of the polynomial require numerical solution of a coupled set of nonlinear algebraic equations, Eqs. (III. 122), (III. 123), (III. 124).

(3) The model displays the interesting feature that the asymptotic potentials of mean force between the solvent dipoles exhibit Debye shielding due to the presence of the ions. There also is Debye shielding between the solute ions and the solvent dipoles as well as between the solute ions. See Eqs. (III. 82), (III. 80), and Appendix C.

(4) The thermodynamics of the model derived from the internal energy, is obtained in terms of the properties of the effective two component fluid Eq. (V. 2). The Helmholtz free energy is determined by three different charging processes, Eqs. (V. 4), (V. 5), (V. 7).

(5) Explicit results for the model are obtained in Sec. IV in the limit of low ionic strength. See Eqs. (IV. 28)–(IV. 37) in conjunction with Eqs. (III. 109)–(III. 112).

(6) In Sec. V the low ionic strength results are used to obtain an explicit expression for the excess Helmholtz free energy ΔA.

$$\beta V^{-1}\Delta A = \beta V^{-1}\Delta A(W) - (12\pi)^{-1}\kappa_w^3 + \hat{\rho}_0 S \,. \tag{I. 1}$$

The first term is the excess free energy of the MSM hard sphere dipolar mixture in the absence of charges.[4] The second term is the classical Debye–Hückel result where κ_w denotes the inverse Debye screening length *in a fluid of dielectric constant* ϵ_w. Here ϵ_w is the Wertheim dielectric constant[3] obtained for the MSM hard sphere dipolar mixture.[4] The final term $\hat{\rho}_0 S$ is propor-

tional to the density of the charges and accordingly corresponds to a self-energy of charging. In contrast to the ionic interaction term at low ionic strength, this self-energy term does not reduce to its classical electrostatic value.

We wish to emphasize that our solution to this MSM model gives the first calculation of the Debye–Hückel limiting expression for the free energy with the dielectric solvent treated on a molecular basis.

Our future efforts on this model will be directed toward obtaining explicit results at higher ionic strength. These results may be employed in combination with a variety of thermodynamic perturbation theory procedures to investigate solvent effects in concentrated ionic solutions from a molecular viewpoint.

II. SPECIFICATION OF THE MODEL

Consider an m-component fluid mixture of charged hard spheres with permanent embedded dipole moments. The ith component of the mixture is characterized by a hard sphere diameter d_i, a dipole moment μ_i, a charge e_i, and a number density ρ_i. For reasons of mathematical simplicity, we assume all the d_i are equal to a common value d. The dipole moments, however, can have any nonnegative value including zero. The charges can have any value including zero but must satisfy the total electroneutrality condition.

$$\sum_{i=1}^{m}\rho_i e_i = 0 \ . \tag{II. 1}$$

The ionic solution is of course an important special case of the system described above as is the polar fluid mixture.

It will prove convenient to represent the collections of dipole moments, charges, and densities as diagonal matrices μ, $\mathbf{e}$, and ρ, respectively; i.e.,

$$\mu = \begin{pmatrix} \mu_1 & 0 & \cdots & 0 \\ 0 & \mu_2 & \cdots & 0 \\ \vdots & & & \vdots \\ 0 & 0 & \cdots & \mu_m \end{pmatrix} \tag{II. 2}$$

with corresponding definitions for $\mathbf{e}$ and ρ.

In this notation the total electroneutrality condition Eq. (II. 1) becomes

$$\mathrm{tr}\rho\mathbf{e} = 0 \ . \tag{II. 3}$$

The Ornstein–Zernike equation for our mixture is

$$H_{ij}(X_1X_2) - C_{ij}(X_1X_2) = (4\pi)^{-1}\sum_{k=1}^{m}\rho_k\int C_{ik}(X_1X_3)H_{kj}(X_3X_2)dX_3 \ . \tag{II. 4a}$$

In Eq. (II. 4), $X_i = (\mathbf{r}_i, \Omega_i)$ denotes the position $\mathbf{r}_i$, of molecule i and the orientation Ω_i of its dipole moment. The functions $H_{ij}(X_1X_2)$, $C_{ij}(X_1X_2)$ are, respectively, the direct and indirect correlation functions for species i and j. We rewrite Eq. (II. 4a) in matrix notation as

$$\mathbf{H}(X_1X_2) - \mathbf{C}(X_1X_2) = (4\pi)^{-1}\int \mathbf{C}(X_1X_3)\rho\mathbf{H}(X_3X_2)dX_3 \ . \tag{II. 4b}$$

The Mean Spherical Model[1] is defined by the above equations along with the closure conditions

$$\mathbf{V}(X_1X_2) = \infty \ \text{ or } \ \mathbf{H}(X_1X_2) = -\mathbf{I}, \ \text{for } \ |\mathbf{r}_2 - \mathbf{r}_1| \equiv r_{12} < d \tag{II. 5}$$

$$\mathbf{C}(X_1X_2) = -\beta\mathbf{V}(X_1X_2), \ \text{for } r_{12} > d \ . \tag{II. 6}$$

In Eqs. (II. 5) and (II. 6), $\mathbf{V}(X_1X_2)$ is the potential energy matrix which for our model includes hard sphere, charge–charge, charge–dipole, and dipole–dipole interactions. The quantity β is the inverse of Boltzmann's constant times the temperature while $\mathbf{I}$ is a matrix with *all* elements equal to unity.

III. FORMAL SOLUTION OF THE MODEL

In this section we obtain a formal solution of the model described above. We express the direct correlation function matrix $\mathbf{C}(X_1X_2)$ in terms of certain auxiliary quantities which are solutions to a set of coupled nonlinear algebraic equations.

In Sec. IV, we obtain explicit expressions for these quantities (which are closely related to the thermodynamic functions of the system) in the limit of low ionic strength.

We begin by expanding the correlation functions[6] ($\mathbf{F} = \mathbf{H}$ or $\mathbf{C}$) in a complete set of rotational invariants[7]; i.e., we expand

$$\mathbf{F}(X_1X_2) = (4\pi)^{3/2}\sum_{l_1l_2l_3}\mathbf{f}(l_1l_2l_3; r_{12})\phi_{l_1l_2l_3}(\Omega_1\Omega_2\Omega_{12}) \ , \tag{III. 1}$$

where the invariants $\phi_{l_1l_2l_3}(\Omega_1\Omega_2\Omega_{12})$ are given by[8]

$$\phi_{l_1l_2l_3}(\Omega_1\Omega_2\Omega_{12}) = \sum_{m_1m_2m_3}(-)^{m_2}\begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix} Y^*_{l_1m_1}(\Omega_1)Y_{l_2m_2}(\Omega_2)Y_{l_3m_3}(\Omega_{12}) \ . \tag{III. 2}$$

The solid angles Ω_1 and Ω_2 describe, respectively, the orientation of the dipoles on molecules one and two while the solid angle Ω_{12} specifies the orientation of the internuclear vector $\mathbf{r}_{12} = (r_{12}, \Omega_{12}) \equiv \mathbf{r}_2 - \mathbf{r}_1$.

From the relation

$$\mathbf{F}(X_2X_1) = \mathbf{F}^T(X_1X_2)$$

we obtain from Eqs. (III. 1) and (III. 2) the important symmetry condition

$$\mathbf{f}(l_1l_2l_3; r) = (-)^{l_1+l_2}\mathbf{f}^T(l_2l_1l_3; r) \ . \tag{III. 3}$$

Inserting Eqs. (III. 1) and (III. 2) into Eq. (II. 4) gives the following set of coupled equations for the Fourier transforms of $f(l_1l_2l_3; r)$[7]

$$\mathbf{h}(l_1L_2\lambda_3; k) - \mathbf{c}(l_1L_2\lambda_3; k) = (2\pi)^{3/2}\sum_{l_2l_3L_3}(-)^{l_2+\lambda_3}[(2\lambda_3+1)(2l_3+1)(2L_3+1)]^{1/2} \times \begin{Bmatrix} l_3 & L_3 & \lambda_3 \\ L_2 & l_1 & l_2 \end{Bmatrix}\begin{pmatrix} l_3 & L_3 & \lambda_3 \\ 0 & 0 & 0 \end{pmatrix}\mathbf{c}(l_1l_2l_3; k)\rho\mathbf{h}(l_2L_2L_3; k) \ , \tag{III. 4}$$

where

$$\mathbf{f}(l_1l_2l_3; k)$$

$$= \left(\frac{1}{2\pi}\right)^{3/2} \int e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{f}(l_1 l_2 l_3; r) d\mathbf{r}$$

$$= \frac{4\pi i^{l_3}}{(2\pi)^{3/2}} \int_0^\infty r^2 j_{l_3}(kr) \mathbf{f}(l_1 l_2 l_3; r) dr \,. \quad \text{(III. 5)}$$

The quantity $j_{l_3}(kr)$ is the spherical Bessel function of order l_3. Since $j_l(-x) = (-)^l j_l(x)$, we see that

$$\mathbf{f}(l_1 l_2 l_3; -k) = (-)^{l_3} \mathbf{f}(l_1 l_2 l_3; k) \,. \quad \text{(III. 6)}$$

We can write Eq. (III. 4) more compactly as[7]

$$\mathbf{h}^{(m)}(l_1 L_2; k) - \mathbf{c}^{(m)}(l_1 L_2; k)$$

$$= (-)^m (2\pi)^{3/2} \sum_{l_2} \mathbf{c}^{(m)}(l_1 l_2; k) \rho \mathbf{h}^{(m)}(l_2 L_2; k) \,, \quad \text{(III. 7)}$$

where

$$\mathbf{f}^{(m)}(l_1 l_2; k) = \sum_{l_3} (2l_3 + 1)^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ m & -m & 0 \end{pmatrix} \mathbf{f}(l_1 l_2 l_3; k) \,. \quad \text{(III. 8)}$$

So far our development has been free of approximations. We now specialize to the MSM. We also restrict ourselves to the model of the last section; that is we assume that the quadrupole and higher moments vanish. This last assumption leads to substantial simplification of the analysis but is not essential.

With the restriction to MSM ionic-polar mixtures, we find that only the functions $\mathbf{f}^{(0)}(00; k)$, $\mathbf{f}^{(0)}(01; k)$, $\mathbf{f}^{(0)}(10; k)$, $\mathbf{f}^{(0)}(11; k)$, and $\mathbf{f}^{(1)}(11; k)$ are nonvanishing. We note that these functions all have definite parity, because of Eqs. (III. 6) and (III. 8), and we will make use of this below. In fact $\mathbf{f}^{(0)}(01; k)$ and $\mathbf{f}^{(0)}(10; k)$ are odd functions of k while the others are even in k.

For our model, Eq. (III. 7) reduces to

$$\mathbf{h}^{(1)}(11; k) - \mathbf{c}^{(1)}(11; k) = -(2\pi)^{3/2} \mathbf{c}^{(1)}(11; k) \rho \mathbf{h}^{(1)}(11; k) \quad \text{(III. 9)}$$

for $m = \pm 1$. For $m = 0$, we obtain the set of four coupled equations

$$\begin{pmatrix} \mathbf{h}^{(0)}(00; k) & \mathbf{h}^{(0)}(01; k) \\ \mathbf{h}^{(0)}(10; k) & \mathbf{h}^{(0)}(11; k) \end{pmatrix} - \begin{pmatrix} \mathbf{c}^{(0)}(00; k) & \mathbf{c}^{(0)}(01; k) \\ \mathbf{c}^{(0)}(10; k) & \mathbf{c}^{(0)}(11; k) \end{pmatrix} = (2\pi)^{3/2} \begin{pmatrix} \mathbf{c}^{(0)}(00; k) & \mathbf{c}^{(0)}(01; k) \\ \mathbf{c}^{(0)}(10; k) & \mathbf{c}^{(0)}(11; k) \end{pmatrix} \rho \begin{pmatrix} \mathbf{h}^{(0)}(00; k) & \mathbf{h}^{(0)}(01; k) \\ \mathbf{h}^{(0)}(10; k) & \mathbf{h}^{(0)}(11; k) \end{pmatrix} . \quad \text{(III. 10)}$$

We will solve Eqs. (III. 9) and (III. 10) by Fourier transforming them back to r space and then applying a generalization of Wertheim's[9] method for the hard sphere Percus–Yevick problem. We thus define the Fourier transforms

$$\bar{\mathbf{f}}(l_1 l_2 l_3; r) = \frac{4\pi r^{-1}}{(2\pi)^{3/2}} \int_0^\infty k \sin kr \, \mathbf{f}(l_1 l_2 l_3; k) dk$$

$$\text{(for } l_3 \text{ even)} \,, \quad \text{(III. 11a)}$$

$$\bar{\mathbf{f}}(l_1 l_2 l_3; r) = \frac{4\pi i r^{-1}}{(2\pi)^{3/2}} \int_0^\infty k \cos kr \, \mathbf{f}(l_1 l_2 l_3; k) dk$$

$$\text{(for } l_3 \text{ odd)} \,. \quad \text{(III. 11b)}$$

The inverse relations are

$$\mathbf{f}(l_1 l_2 l_3; k) = \frac{4\pi k^{-1}}{(2\pi)^{3/2}} \int_0^\infty r \sin kr \, \bar{\mathbf{f}}(l_1 l_2 l_3; r) dr$$

$$\text{(for } l_3 \text{ even)} \,, \quad \text{(III. 12a)}$$

$$\mathbf{f}(l_1 l_2 l_3; k) = -\frac{4\pi i k^{-1}}{(2\pi)^{3/2}} \int_0^\infty r \cos kr \, \bar{\mathbf{f}}(l_1 l_2 l_3; r) dr$$

$$\text{(for } l_3 \text{ odd)} \,. \quad \text{(III. 12b)}$$

Note that Eqs. (III. 12) are consistent with the parity relation Eq. (III. 6). This is the motivation for defining the Fourier transforms differently for even and odd l_3. Had we used, for example, the sine transform for odd l_3 we would have created an inconsistency.

We also define the quantities [cf. Eq. (III. 8)]

$$\mathbf{f}^{(m)}(l_1 l_2; r) = \sum_{l_3} (2l_3 + 1)^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ m & -m & 0 \end{pmatrix} \bar{\mathbf{f}}(l_1 l_2 l_3; r) \,. \quad \text{(III. 13)}$$

For our model we only require

$$\mathbf{f}^{(0)}(00; r) = \bar{\mathbf{f}}(000; r) \,, \quad \text{(III. 14)}$$

$$\mathbf{f}^{(0)}(10; r) = -\bar{\mathbf{f}}(101; r) \,, \quad \text{(III. 15)}$$

$$\mathbf{f}^{(0)}(01; r) = -\bar{\mathbf{f}}(011; r) \,, \quad \text{(III. 16)}$$

$$\mathbf{f}^{(0)}(11; r) = (\tfrac{1}{3})^{1/2} \{\sqrt{2}\, \bar{\mathbf{f}}(112; r) - \bar{\mathbf{f}}(110; r)\} \,, \quad \text{(III. 17)}$$

$$\mathbf{f}^{(1)}(11; r) = (\tfrac{1}{3})^{1/2} \{\tfrac{1}{2}\sqrt{2}\, \bar{\mathbf{f}}(112; r) + \bar{\mathbf{f}}(110; r)\} \,. \quad \text{(III. 18)}$$

The above r-space functions are related to the corresponding $\mathbf{f}^{(m)}(l_1 l_2; k)$ by simple sine and cosine transforms like those in Eqs. (III. 11), (III. 12). This is because the relevant $\mathbf{f}^{(m)}(l_1 l_2; k)$ have definite parity. Combining Eqs. (III. 8), (III. 11), and (III. 13) then gives

$$\mathbf{f}^{(0)}(00; r) = \frac{4\pi r^{-1}}{(2\pi)^{3/2}} \int_0^\infty k \sin kr \, \mathbf{f}^{(0)}(00; k) dk \,, \quad \text{(III. 19)}$$

$$\mathbf{f}^{(0)}(01; r) = \frac{4\pi i r^{-1}}{(2\pi)^{3/2}} \int_0^\infty k \cos kr \, \mathbf{f}^{(0)}(01; k) dk \,, \quad \text{(III. 20)}$$

$$\mathbf{f}^{(0)}(10; r) = \frac{4\pi i r^{-1}}{(2\pi)^{3/2}} \int_0^\infty k \cos kr \, \mathbf{f}^{(0)}(10; k) dk \,, \quad \text{(III. 21)}$$

$$\mathbf{f}^{(m)}(11; r) = \frac{4\pi r^{-1}}{(2\pi)^{3/2}} \int_0^\infty k \sin kr \, \mathbf{f}^{(m)}(11; k) dk$$

$$\text{(for } m = 0, 1) \,. \quad \text{(III. 22)}$$

We can now Fourier transform Eqs. (III. 9)–(III. 10) to obtain a set of r-space integral equations for the functions $\mathbf{f}^{(m)}(l_1, l_2; r)$. One slight complication arises. Equation (III. 10) in addition to containing the usual binary products of even k-space functions contains products of two odd k-space functions and also mixed products of even and odd functions. The usual three dimen-

sional Fourier convolution theorem for spherically symmetric functions applies only to transforms of products of even k-space functions. In Appendix A we work out the convolution theorems for odd k-space products and for mixed k-space products. All three convolution theorems take a similar form.

Using Eqs. (A9)–(A11) we find for the transforms of Eqs. (III. 9)–(III. 10),

$$\mathbf{h}^{(1)}(11;r)-\mathbf{c}^{(1)}(11;r) = -2\pi r^{-1}\int_0^\infty u\,du\int_{1u-r1}^{u+r} v\,\mathbf{c}^{(1)}(11;u)\rho\mathbf{h}^{(1)}(11;v)\,dv, \quad \text{(III. 23)}$$

$$\mathbf{h}^{(0)}(00;r)-\mathbf{c}^{(0)}(00;r) = 2\pi r^{-1}\int_0^\infty u\,du\int_{1u-r1}^{u+r} v\,\mathbf{c}^{(0)}(00;u)\rho\mathbf{h}^{(0)}(00;v)\,dv - 2\pi r^{-1}\int_0^\infty u\,du\int_{u-r}^{u+r} v\,\mathbf{c}^{(0)}(01;u)\rho\mathbf{h}^{(0)}(10;v)\,dv, \quad \text{(III. 24a)}$$

$$\mathbf{h}^{(0)}(01;r)-\mathbf{c}^{(0)}(01;r) = 2\pi r^{-1}\int_0^\infty u\,du\int_{r-u}^{u+r} v\,\mathbf{c}^{(0)}(00;u)\rho\mathbf{h}^{(0)}(01;v)\,dv + 2\pi r^{-1}\int_0^\infty u\,du\int_{r-u}^{u+r} v\,\mathbf{c}^{(0)}(01;v)\rho\mathbf{h}^{(0)}(11;u)\,dv, \quad \text{(III. 24b)}$$

$$\mathbf{h}^{(0)}(10;r)-\mathbf{c}^{(0)}(10;r) = 2\pi r^{-1}\int_0^\infty u\,du\int_{r-u}^{u+r} v\,\mathbf{c}^{(0)}(10;v)\rho\mathbf{h}^{(0)}(00;u)\,dv + 2\pi r^{-1}\int_0^\infty u\,du\int_{r-u}^{u+r} v\,\mathbf{c}^{(0)}(11;u)\rho\mathbf{h}^{(0)}(10;v)\,dv, \quad \text{(III. 24c)}$$

$$\mathbf{h}^{(0)}(11;r)-\mathbf{c}^{(0)}(11;r) = -2\pi r^{-1}\int_0^\infty u\,du\int_{u-r}^{u+r} v\,\mathbf{c}^{(0)}(10;u)\rho\mathbf{h}^{(0)}(01;v)\,dv + 2\pi r^{-1}\int_0^\infty u\,du\int_{1u-r1}^{u+r} v\,\mathbf{c}^{(0)}(11;u)\rho\mathbf{h}^{(0)}(11;v)\,dv. \quad \text{(III. 24d)}$$

We now relate the solutions of the above integral equations to the coefficients $\mathbf{f}(l_1l_2l_3;r)$ in Eq. (III. 1). Actually we only have to relate the coefficients $\mathbf{f}(l_1l_2l_3;r)$ to the transforms $\bar{\mathbf{f}}(l_1l_2l_3;r)$ defined by Eq. (III. 11) since these latter functions are related to the solutions $\mathbf{f}^{(m)}(l_1l_2;r)$ by Eqs. (III. 13)–(III. 18).

The relationship between $\mathbf{f}(l_1l_2l_3;r)$ and $\bar{\mathbf{f}}(l_1l_2l_3;r)$ is obtained by using the second form of Eq. (III. 5) in Eq. (III. 11). We find

$$\bar{\mathbf{f}}(l_1l_2l_3;r) = (2/\pi)\int_0^\infty r'^2\mathbf{f}(l_1l_2l_3;r')Q_{l_3}(r',r)\,dr', \quad \text{(III. 25)}$$

where

$$Q_{l_3}(r',r) = i^{l_3}r^{-1}\int_0^\infty k\sin kr\,j_{l_3}(kr')\,dk \quad \text{for } l_3 \text{ even}$$
$$= i^{l_3+1}r^{-1}\int_0^\infty k\cos kr\,j_{l_3}(kr')\,dk \quad \text{for } l_3 \text{ odd}. \quad \text{(III. 26)}$$

For l_3 even, $Q_{l_3}(r',r)$ was evaluated in a previous paper.[4] The same method can be applied for l_3 odd and, in fact, the result is identical for both cases. We find

$$Q_{l_3}(r',r) = \frac{\pi}{2rr'}\left[\delta(r'-r) - \frac{1}{r'}\,\theta(r'-r)P'_{l_3}\left(\frac{r}{r'}\right)\right], \quad \text{(III. 27)}$$

where $\theta(x)$ is the unit step function and $P'_l(x)$ is the derivative of the lth Legendre polynomial. Combining Eqs. (III. 25) and (III. 27) then gives[10]

$$\bar{\mathbf{f}}(l_1l_2l_3;r) = \mathbf{f}(l_1l_2l_3;r) - r^{-1}\int_r^\infty P'_{l_3}(r/r')\mathbf{f}(l_1l_2l_3;r')\,dr'. \quad \text{(III. 28)}$$

The inverse relation can be similarly obtained. We find

$$\mathbf{f}(l_1l_2l_3;r) = \bar{\mathbf{f}}(l_1l_2l_3;r) - r^{-2}\int_0^r r'P'_{l_3}(r'/r)\bar{\mathbf{f}}(l_1l_2l_3;r')\,dr'. \quad \text{(III. 29)}$$

We now obtain closure conditions for the integral Eqs. (III. 23) and (III. 24).

We make an invariant angular expansion of the potential energy [cf. Eq. (III. 1)]

$$\mathbf{V}(X_1X_2) = (4\pi)^{3/2}\sum_{l_1l_2l_3}\mathbf{v}(l_1l_2l_3;r)\phi_{l_1l_2l_3}(\Omega_1\Omega_2\Omega_{12}). \quad \text{(III. 30)}$$

For our model only the following radial coefficients $\mathbf{v}(l_1l_2l_3;r)$ are nonvanishing

$$\mathbf{v}(000;r) = v_{\rm HS}(r)\mathbf{I} + \mathbf{ele}r^{-1}, \quad \text{(III. 31)}$$
$$\mathbf{v}(101;r) = -(\tfrac{1}{3})^{1/2}\mu\mathbf{le}r^{-2}, \quad \text{(III. 32)}$$
$$\mathbf{v}(011;r) = (\tfrac{1}{3})^{1/2}\mathbf{el}\mu r^{-2}, \quad \text{(III. 33)}$$
$$\mathbf{v}(112;r) = -(\tfrac{2}{3})^{1/2}\mu\mathbf{I}\mu r^{-3}. \quad \text{(III. 34)}$$

The quantity $v_{\rm HS}(r)$ is the potential for hard spheres of diameter d while the other terms are the multipole interactions. The MSM closure conditions Eqs. (II. 5), (II. 6) thus become

$$\mathbf{h}(000;r) = -\mathbf{I} \qquad r<d \qquad \text{(III. 35a)}$$
$$\mathbf{c}(000;r) = -\beta\mathbf{ele}r^{-1} \qquad r>d \qquad \text{(III. 35b)}$$
$$\mathbf{h}(101;r) = 0 \qquad r<d \qquad \text{(III. 36a)}$$
$$\mathbf{c}(101;r) = (\tfrac{1}{3})^{1/2}\beta\mu\mathbf{le}r^{-2} \qquad r>d \qquad \text{(III. 36b)}$$
$$\mathbf{h}(011;r) = 0 \qquad r<d \qquad \text{(III. 37a)}$$
$$\mathbf{c}(011;r) = -(\tfrac{1}{3})^{1/2}\beta\mathbf{el}\mu r^{-2} \qquad r>d \qquad \text{(III. 37b)}$$
$$\mathbf{h}(110;r) = 0 \qquad r<d \qquad \text{(III. 38a)}$$
$$\mathbf{c}(110;r) = 0 \qquad r>d \qquad \text{(III. 38b)}$$
$$\mathbf{h}(112;r) = 0 \qquad r<d \qquad \text{(III. 39a)}$$
$$\mathbf{c}(112;r) = (\tfrac{2}{3})^{1/2}\beta\mu\mathbf{I}\mu r^{-3} \qquad r>d \qquad \text{(III. 39b)}$$

In addition to satisfying the above closure conditions, the correlation functions must satisfy the local electroneutrality constraint

$$(1/4\pi)\int dX_2\sum_{j=1}^{m}[H_{ij}(X_1X_2)+1]\rho_j e_j = -e_i. \quad \text{(III. 40)}$$

This states that the total charge in a large sphere centered on a molecule of species i vanishes; that is the charge on the "ionic atmosphere" surrounding the molecule exactly cancels its charge.

Equation (III. 40) can be simplified by using Eq. (II. 1), changing to matrix notation, introducing Eq. (III. 1) into the resulting relation, and then integrating over angles. We finally obtain

$$4\pi\int_0^\infty dr\, r^2 \mathbf{h}(000;r)\rho\mathbf{el} = -\mathbf{el}\ . \qquad \text{(III. 40')}$$

We will now obtain closure conditions for Eqs. (III. 23)–(III. 24). We write out the transforms (III. 28) and (III. 29) explicitly for the correlation functions we require. These are

$$\bar{\mathbf{f}}(000;r) = \mathbf{f}(000;r) \qquad \text{(III. 41)}$$

$$\bar{\mathbf{f}}(110;r) = \mathbf{f}(110;r) \qquad \text{(III. 42)}$$

$$\bar{\mathbf{f}}(101;r) = \mathbf{f}(101;r) - r^{-1}\int_r^\infty \mathbf{f}(101;r')dr' \qquad \text{(III. 43)}$$

$$\mathbf{f}(101;r) = \bar{\mathbf{f}}(101;r) - r^{-2}\int_0^r r'\bar{\mathbf{f}}(101;r')dr' \qquad \text{(III. 44)}$$

$$\bar{\mathbf{f}}(112;r) = \mathbf{f}(112;r) - 3\int_r^\infty (1/r')\mathbf{f}(112;r')dr' \qquad \text{(III. 45)}$$

$$\mathbf{f}(112;r) = \bar{\mathbf{f}}(112;r) - 3r^{-3}\int_0^r r'^2\bar{\mathbf{f}}(112;r')dr'\ . \qquad \text{(III. 46)}$$

The relations between $\mathbf{f}(011;r)$ and $\bar{\mathbf{f}}(011;r)$ are by Eq. (III. 3) identical in form to Eqs. (III. 43) and (III. 44). We now define the dimensionless quantities

$$w = r/d \qquad \text{(III. 47)}$$

$$\eta = (\pi d^3/6)\rho \qquad \text{(III. 48)}$$

and introduce the simpler notation

$$\mathbf{f}_{l_1l_2}(w) = \mathbf{f}^{(0)}(l_1l_2;r)$$
$$\mathbf{f}_{11}^{(1)}(w) = \mathbf{f}^{(1)}(11;r)\ . \qquad \text{(III. 49)}$$

Combining Eqs. (III. 14)–(III. 18), (III. 35)–(III. 39), and (III. 41)–(III. 49) then gives the closure relations

$$\mathbf{h}_{00}(w) = -\mathbf{I} \qquad w<1 \qquad \text{(III. 50a)}$$

$$\mathbf{c}_{00}(w) = -\beta\mathbf{ele}(wd)^{-1} \qquad w>1 \qquad \text{(III. 50b)}$$

$$\mathbf{h}_{10}(w) = -\mathbf{n}_{10}w^{-1} \qquad w<1 \qquad \text{(III. 51a)}$$

$$\mathbf{c}_{10}(w) = 0 \qquad w>1 \qquad \text{(III. 51b)}$$

$$\mathbf{h}_{11}(w) = -2\mathbf{n}_{11} \qquad w<1 \qquad \text{(III. 52a)}$$

$$\mathbf{c}_{11}(w) = 0 \qquad w>1 \qquad \text{(III. 52b)}$$

$$\mathbf{h}_{11}^{(1)}(w) = -\mathbf{n}_{11} \qquad w<1 \qquad \text{(III. 53a)}$$

$$\mathbf{c}_{11}^{(1)}(w) = 0 \qquad w>1\ . \qquad \text{(III. 53b)}$$

The quantities $\mathbf{n}_{10}$ and $\mathbf{n}_{11}$ are given by

$$\mathbf{n}_{10} = -d^{-1}\int_d^\infty \mathbf{h}(101;r')dr' \qquad \text{(III. 54)}$$

$$\mathbf{n}_{11} = \left(\frac{3}{2}\right)^{1/2}\int_d^\infty \frac{1}{r'}\mathbf{h}(112;r')dr'\ . \qquad \text{(III. 55)}$$

Because of Eqs. (III. 3), (III. 13), (III. 25), and (III. 49)

$$\mathbf{f}_{01}(w) = -\mathbf{f}_{10}^T(w) \qquad \text{(III. 56)}$$

and this is why we have not given the closure relations for $\mathbf{f}_{01}(w)$.

It is important to notice that $\mathbf{c}_{10}(w)$, $\mathbf{c}_{11}(w)$, and $\mathbf{c}_{11}^{(1)}(w)$ vanish outside the hard core, i.e., for $w>1$. The untransformed functions $\mathbf{c}(l_1l_2l_3;r)$ are nonvanishing outside the hard core [cf. Eqs. (III. 35)–(III. 39)]. The transformation (III. 28) thus has the important property of truncating the long-range multipole tails for all the $\mathbf{c}(l_1l_2l_3;r)$ except $\mathbf{c}(000;r)$ which remains Coulombic outside the hard core. Because of this truncation, our problem can be treated by a suitable adaptation of Wertheim's technique[9] for the hard sphere Percus–Yevick (PY) problem.

In fact, for the MSM polar fluid mixture[4] problem where $\mathbf{f}_{00}(w) = \mathbf{f}_{10}(w) = 0$, the solution can be expressed solely in terms of PY hard sphere correlation functions. The functions $\mathbf{f}_{11}^{(1)}(w)$ in our problem will also be expressed in terms of PY hard sphere solutions but the quantities $\mathbf{f}_{l_1l_2}(w)$ are of more complicated form.

We now reduce our multicomponent problem to a much simpler form.[11] Eq. (III. 23) will simplify to a one-component PY hard sphere problem. The set of Eqs. (III. 24) will reduce to two uncoupled problems. One is the PY hard sphere problem for the (one-component) reference fluid with $\mathbf{e} = \mu = 0$. The other is a set of equations for an effective two-component problem which we will solve below.

To accomplish this reduction we assume that the solutions of Eqs. (III. 23)–(III. 24) have the form

$$\mathbf{f}_{00}(w) = f_{\mathrm{HS}}(w)\mathbf{I} + \hat{e}^{-2}\mathbf{ele}f_{00}(w)\ , \qquad \text{(III. 57)}$$

$$\mathbf{f}_{10}(w) = (\hat{\mu}\hat{e})^{-1}\boldsymbol{\mu}\mathbf{le}f_{10}(w)\ , \qquad \text{(III. 58)}$$

$$\mathbf{f}_{01}(w) = (\hat{e}\hat{\mu})^{-1}\mathbf{el}\boldsymbol{\mu}f_{01}(w)\ , \qquad \text{(III. 59)}$$

$$\mathbf{f}_{11}(w) = \hat{\mu}^{-2}\boldsymbol{\mu}\mathbf{I}\boldsymbol{\mu}f_{11}(w)\ , \qquad \text{(III. 60)}$$

$$\mathbf{f}_{11}^{(1)}(w) = \hat{\mu}^{-2}\boldsymbol{\mu}\mathbf{I}\boldsymbol{\mu}f_{11}^{(1)}(w)\ . \qquad \text{(III. 61)}$$

In the above equations $\hat{e}$ is an effective charge given by

$$\hat{e}^2 = m^{-1}\sum_{i=1}^m e_i^2 \qquad \text{(III. 62)}$$

and $\hat{\mu}$ is an effective dipole moment defined analogously as

$$\hat{\mu}^2 = m^{-1}\sum_{i=1}^m \mu_i^2\ . \qquad \text{(III. 63)}$$

We also require the effective reduced densities

$$\hat{\eta}_0 = \hat{e}^{-2}\mathrm{tr}\boldsymbol{\eta}\mathbf{e}^2\ , \qquad \text{(III. 64)}$$

$$\hat{\eta}_1 = \hat{\mu}^{-2}\mathrm{tr}\boldsymbol{\eta}\boldsymbol{\mu}^2\ , \qquad \text{(III. 65)}$$

and the true total reduced density

$$\eta = \mathrm{tr}\,\boldsymbol{\eta}\ . \qquad \text{(III. 66)}$$

We first reduce Eq. (III. 23) to one-component form. Combining Eqs. (III. 23), (III. 47)–(III. 49), (III. 61), and using the definitions (III. 63) and (III. 65), and also using the identity

$$\mathbf{I}\lambda\mathbf{I} = \mathbf{I}\mathrm{tr}\lambda \qquad \text{(III. 67)}$$

valid for diagonal λ we find the equation

$$h_{11}^{(1)}(w) - c_{11}^{(1)}(w)$$
$$= -12\hat{\eta}_1 w^{-1}\int_0^\infty uc_{11}^{(1)}(u)du\int_{|u-w|}^{u+w} vh_{11}^{(1)}(v)dv\ . \qquad \text{(III. 68)}$$

The closure Eq. (III. 53) becomes

$$h_{11}^{(1)}(w) = -n_{11} \qquad w<1 \qquad \text{(III. 69a)}$$

$$c_{11}^{(1)}(w) = 0 \qquad w>1 \qquad \text{(III. 69b)}$$

where n_{11} is defined by the equation

$$\mathbf{n}_{11} = n_{11}\hat{\mu}^{-2}\boldsymbol{\mu}\mathbf{I}\boldsymbol{\mu} \ . \tag{III. 70}$$

Equations (III. 68)–(III. 69) define a PY hard sphere problem for a reduced density of $-[\hat{n}_1 n_{11}]$. Thus we have reduced Eq. (III. 23) to a PY hard sphere problem, the solution of which is well known. [12]

Equation (III. 24), as mentioned above, cannot be reduced to a hard-sphere PY problem. Instead using Eqs. (III. 47)–(III. 49), (III. 57)–(III. 66), the total electroneutrality condition Eq. (II. 3), and the identity Eq. (III. 67) gives us two equations. The first equation

$$h_{\mathrm{HS}}(w) - c_{\mathrm{HS}}(w) = 12\eta w^{-1}\int_0^\infty u c_{\mathrm{HS}}(u)du \int_{1w-u1}^{w+u} v h_{\mathrm{HS}}(v)dv \tag{III. 71}$$

along with the closure relations,

$$h_{\mathrm{HS}}(w) = -1 \qquad w < 1 \tag{III. 72a}$$

$$c_{\mathrm{HS}}(w) = 0 \qquad w > 1 \tag{III. 72b}$$

describe the reference PY hard sphere fluid.

The second equation is a matrix set of equations which describe an effective two-component system. These are

$$h_{00}(w) - c_{00}(w) = 12\hat{\eta}_0 w^{-1}\int_0^\infty u c_{00}(u)du \int_{1u-w1}^{u+w} v h_{00}(v)dv - 12\hat{\eta}_1 w^{-1}\int_0^\infty u c_{01}(u)du \int_{u-w}^{u+w} v h_{10}(v)dv \ , \tag{III. 73a}$$

$$h_{01}(w) - c_{01}(w) = 12\hat{\eta}_0 w^{-1}\int_0^\infty u c_{00}(u)du \int_{w-u}^{u+w} v h_{01}(v)dv + 12\hat{\eta}_1 w^{-1}\int_0^\infty u h_{11}(u)du \int_{w-u}^{u+w} v c_{01}(v)dv \ , \tag{III. 73b}$$

$$h_{10}(w) - c_{10}(w) = +12\hat{\eta}_0 w^{-1}\int_0^\infty u h_{00}(u)du \int_{w-u}^{w+u} v c_{10}(v)dv + 12\hat{\eta}_1 w^{-1}\int_0^\infty u c_{11}(u)du \int_{w-u}^{w+u} v h_{10}(v)dv \ , \tag{III. 73c}$$

$$h_{11}(w) - c_{11}(w) = -12\hat{\eta}_0 w^{-1}\int_0^\infty u c_{10}(u)du \int_{u-w}^{u+w} v h_{01}(v)dv + 12\hat{\eta}_1 w^{-1}\int_0^\infty u c_{11}(u)du \int_{1u-w1}^{u+w} v h_{11}(v)dv \ . \tag{III. 73d}$$

Defining n_{10} by

$$\mathbf{n}_{10} = n_{10}(\hat{\mu}\hat{e})^{-1}\boldsymbol{\mu}\mathbf{I}\mathbf{e} \tag{III. 74}$$

we can write the closure conditions for Eq. (III. 73) as

$$h_{00}(w) = 0 \qquad w < 1 \tag{III. 75a}$$

$$c_{00}(w) = -\beta\hat{e}^2(wd)^{-1} \qquad w > 1 \tag{III. 75b}$$

$$h_{10}(w) = -n_{10}w^{-1} \qquad w < 1 \tag{III. 76a}$$

$$c_{10}(w) = 0 \qquad w > 1 \tag{III. 76b}$$

$$h_{11}(w) = -2n_{11} \qquad w < 1 \tag{III. 77a}$$

$$c_{11}(w) = 0 \qquad w > 1 \ . \tag{III. 77b}$$

Notice that because of the total electroneutrality condition Eq. (II. 3) we have been able to completely decouple the reference fluid problem. This provides a substantial simplification.

The symmetry relation Eq. (III. 56) and the local electroneutrality condition Eq. (III. 40a) provide additional constraints on the correlation functions. These constraints can be written in terms of our new functions as

$$f_{01}(w) = -f_{10}(w) \tag{III. 78}$$

$$1 + 24\hat{\eta}_0\int_0^\infty w^2 h_{00}(w)dw = 0 \ . \tag{III. 79}$$

Finally from Eq. (III. 75b) one can verify that the first double integral in Eq. (III. 73b) is divergent unless

$$\int_0^\infty w h_{01}(w)dw = 0 \ . \tag{III. 80}$$

The above condition implies that

$$\lim_{r\to\infty}\int_0^r r'\bar{\mathbf{h}}(101;r')dr' = 0 \ . \tag{III. 81}$$

The physical interpretation of this result is one of the interesting consequences of our model. Comparing Eq. (III. 81) with Eq. (III. 44) shows that $\mathbf{h}(101;r)$ falls off faster than r^{-2} for large r [since $\bar{\mathbf{h}}(101;r)$ is of short range]. Thus the charge–dipole component of the asymptotic potential of mean force decays more rapidly than r^{-2}. Debye screening of the charge–dipole interaction in the fluid[13] is responsible for this rapid decay.

We also expect Debye screening of the dipole–dipole component of the potential of mean force. [13] From Eq. (III. 46) this implies

$$\int_0^\infty r'^2\bar{\mathbf{f}}(112;r')dr' = 0 \ . \tag{III. 82}$$

In terms of our new functions this condition may be written as [see Eqs. (III. 17)–(III. 18)]

$$\int_0^\infty w^2 h_{11}(w)dw = -\int_0^\infty w^2 h_{11}^{(1)}(w)dw \ . \tag{III. 83}$$

Now we must solve the coupled system Eq. (III. 73). To do this we introduce the following quantities.

$$b_{00}(w) = h_{00}(w) \ , \tag{III. 84a}$$

$$b_{10}(w) = -b_{01}(w) = h_{10}(w) + n_{10}w^{-1} \ , \tag{III. 84b}$$

$$b_{11}(w) = h_{11}(w) + 2n_{11} \ , \tag{III. 84c}$$

$$c_{00}^{(0)}(w) = c_{00}(w) + \beta\hat{e}^2(dw)^{-1} \equiv c_{00}(w) + \gamma w^{-1} \ . \tag{III. 85}$$

Note that

$$b_{ij}(w) = 0 \qquad w < 1 \tag{III. 86a}$$

$$c_{ij}^{(0)}(w) = 0 \qquad w > 1 \tag{III. 86b}$$

where

$$c_{ij}^{(0)}(w) \equiv c_{00}^{(0)}(w) \qquad ij = 00 \qquad \equiv c_{ij}(w) \qquad ij \neq 00 \ . \tag{III. 87}$$

Also define the following Laplace transforms

$$H_{ij}(S) = \int_0^\infty e^{-Sw} w h_{ij}(w) dw \ , \tag{III. 88}$$

$$B_{ij}(S) = \int_1^\infty e^{-Sw} w b_{ij}(w) dw \ , \tag{III. 89}$$

$$C_{ij}(S) = \int_0^1 e^{-Sw} w c_{ij}^{(0)}(w) dw \ . \tag{III. 90}$$

In terms of these Laplace transforms, the local electroneutrality condition and the charge–dipole Debye screening condition, respectively, become

$$B'_{00}(0) = (24\hat{\eta}_0)^{-1} \tag{III. 91}$$

$$H_{01}(0) = H_{10}(0) = 0 \ . \tag{III. 92}$$

We can now Laplace transform Eq. (III. 73). Since Laplace transformation of some of the convolution integrals in Eq. (III. 73) is quite involved, we work out one of the integrals explicitly in Appendix B to illustrate the general procedure. We find using the relation $C_{10}(S) = -C_{01}(S)$ that we can write the Laplace transform of Eq. (III. 73) in matrix notation as

$$\mathbf{B}(S) - \mathbf{C}(S) = \mathbf{R}(S) + 12\gamma S^{-2}\mathbf{M}\hat{\eta}\mathbf{B}(S) - 12S^{-1}[\mathbf{C}(S) - \mathbf{C}^T(-S)]\hat{\eta}\mathbf{B}(S) \ . \tag{III. 93}$$

In Eq. (III. 93)

$$\hat{\eta} = \begin{pmatrix} \hat{\eta}_0 & 0 \\ 0 & \hat{\eta}_1 \end{pmatrix} \tag{III. 94}$$

$$\mathbf{M} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \tag{III. 95}$$

and γ is as defined in Eq. (III. 85). Some of the elements of $\mathbf{R}(S)$ are quite complicated. Rather than list them explicitly, we give the following prescription for obtaining them. Expand all quantities but $\mathbf{R}(S)$ in Eq. (III. 93) in a Laurent series about $S = 0$ using the fact that $\mathbf{C}(S)$ and $\mathbf{H}(S)$ are analytic at $S = 0$. Then $\mathbf{R}(S)$ is the quantity required to make the singular parts of both sides of Eq. (III. 93) agree. For example,

$$R_{00}(S) = -\gamma S^{-1} - 24\{\hat{\eta}_0\gamma B_{00}(0) + \hat{\eta}_1 n_{10} C_{10}(0)\}S^{-2} \ . \tag{III. 96}$$

We wish to obtain $w\mathbf{c}_{00}^{(0)}(w) = \mathcal{L}^{-1}\mathbf{C}(S)$, where $\mathcal{L}^{-1}$ denotes an inverse Laplace transform. For $w < 1$, the range for which $\mathbf{c}^{(0)}(w)$ is nonvanishing, we find from Eq. (III. 93)

$$-w\mathbf{c}^{(0)}(w) = \mathcal{L}^{-1}\mathbf{R}(S) + 12\mathcal{L}^{-1}[S^{-1}\mathbf{C}^T(-S)\hat{\eta}\mathbf{B}(S)] \ . \tag{III. 97}$$

The above equation follows from Eq. (III. 86a) and the Laplace convolution theorem. $\mathcal{L}^{-1}\mathbf{R}(S)$ is easy to obtain [see Eq. (III. 96)]. The second inverse transform in Eq. (III. 97), however, cannot be performed in a straightforward manner. Wertheim,[9] however, by means of an ingenious application of complex variable theory, has shown how to overcome this difficulty. Since his method has been described elsewhere in connection with several different problems[5,9,14,15] and since the calculation is quite lengthy for our case we omit the details here.

We find for $\mathbf{c}^{(0)}(w)$

$$-w\mathbf{c}^{(0)}(w) = \mathbf{V} + \mathbf{W}w + \mathbf{X}w^2 + \mathbf{Y}w^3 + \mathbf{Z}w^4 \ , \tag{III. 98}$$

where $\mathbf{V}$, $\mathbf{W}$, $\mathbf{X}$, $\mathbf{Y}$, and $\mathbf{Z}$ are (2×2) matrices which are independent of w. Explicit results for these quantities are presented below in terms of a briefer notation which we now introduce.

We define the dimensionless strength parameters

$$\delta_{00}^2 = 24\hat{\eta}_0\beta\hat{e}^2 d^{-1} \ , \tag{III. 99a}$$

$$\delta_{11}^2 = (\tfrac{1}{3})24\hat{\eta}_1\beta\hat{\mu}^2 d^{-3} \ , \tag{III. 99b}$$

$$\delta_{10}^2 = \delta_{00}\delta_{11} = (\tfrac{1}{3})^{1/2}24\bar{\eta}\beta\hat{\mu}\hat{e}d^{-2} \ , \tag{III. 99c}$$

where

$$\bar{\eta} = (\hat{\eta}_0\hat{\eta}_1)^{1/2} \ . \tag{III. 100}$$

Note that

$$\delta_{00} = \kappa_0 d \ , \tag{III. 101}$$

where

$$\kappa_0 = (4\pi\hat{\rho}_0\hat{e}^2\beta)^{1/2} \tag{III. 102}$$

is the Debye inverse shielding length for an electrolyte in a solvent with unit dielectric constant. The quantities $\hat{\rho}_0, \hat{\rho}_1$ are the effective densities associated with the reduced densities $\hat{\eta}_0, \hat{\eta}_1$.

We also require the relation

$$C_{10}(0) = \int_0^1 w c_{10}(w) dw = \delta_{10}^2/24\bar{\eta} \tag{III. 103}$$

which follows from Eqs. (III. 15), (III. 36b), (III. 44), and (III. 51b) written in terms of the effective two component fluid. A similar calculation gives another important relationship

$$q^+ - q^- = \delta_{11}^2 \ , \tag{III. 104}$$

where

$$q^+ = 1 - 24\hat{\eta}_1 \int_0^1 w^2 c_{11}(w) dw \tag{III. 105a}$$

$$q^- = 1 + 24\hat{\eta}_1 \int_0^1 w^2 c_{11}^{(1)}(w) dw \ . \tag{III. 105b}$$

As mentioned earlier $c_{11}^{(1)}(w)$ is the PY hard sphere direct correlation function for reduced density $-[\hat{\eta}_1 n_{11}]$. Thus q^- is simply related to

$$q(\eta) = (1 + 2\eta)^2/(1 - \eta)^4 \ , \tag{III. 106}$$

where $q(\eta)$ is the PY hard sphere inverse compressibility.[12] In fact

$$q^- = q(-\hat{\eta}_1 n_{11}) \ . \tag{III. 107}$$

We further define

$$x = \hat{\eta}_0 B_{00}(0) \ , \tag{III. 108a}$$

$$y = \bar{\eta} n_{10} \ , \tag{III. 108b}$$

$$z = 2\hat{\eta}_1 n_{11} \ . \tag{III. 108c}$$

We now can compactly present the explicit forms of the matrices appearing in Eq. (III. 98). These are

$$\hat{\eta}_0 V_{00} = -\tfrac{1}{24}\delta_{00}^2 \ , \tag{III. 109a}$$

$$\hat{\eta}_0 W_{00} = -(x\delta_{00}^2 + y\delta_{10}^2) \ , \tag{III. 109b}$$

$$\hat{\eta}_0 X_{00} = -6(x^2\delta_{00}^2 + 2xy\delta_{10}^2 + y^2 q^+) \ , \tag{III. 109c}$$

$$\bar{\eta} V_{10} = x\delta_{10}^2 + yq^+ \ , \tag{III. 110a}$$

$$\bar{\eta} X_{10} = -\tfrac{1}{4}(y\delta_{00}^2 - z\delta_{10}^2) \ , \tag{III. 110b}$$

$$\bar{\eta} Y_{10} = -2(xy\delta_{00}^2 + y^2\delta_{10}^2 - xz\delta_{10}^2 - yzq^+) \ , \tag{III. 110c}$$

$$\bar{\eta}V_{01} = -y - 24[\hat{\eta}_0 C'_{00}(0)y + \bar{\eta}H'_{01}(0)\delta^2_{00} + \hat{\eta}_1 H_{11}(0)\delta^2_{10} + 12\bar{\eta}C'_{10}(0)z] , \quad \text{(III. 111a)}$$

$$\bar{\eta}X_{01} = -\bar{\eta}X_{10} , \quad \text{(III. 111b)}$$

$$\bar{\eta}Y_{01} = -\bar{\eta}Y_{10} , \quad \text{(III. 111c)}$$

$$\hat{\eta}_1 W_{11} = -y\delta^2_{10} + zq^+ , \quad \text{(III. 112a)}$$

$$\hat{\eta}_1 X_{11} = 6[\hat{\eta}_1 H_{11}(0)(zq^+ - y\delta^2_{10}) - \bar{\eta}H'_{01}(0)(y\delta^2_{00} - z\delta^2_{10}) - y(x\delta^2_{10} + yq^+) + \hat{\eta}_1 C_{11}(0)z] , \quad \text{(III. 112b)}$$

$$\hat{\eta}_1 Z_{11} = \tfrac{1}{2}z^2 q^+ + \tfrac{1}{2}y^2\delta^2_{00} - yz\delta^2_{10} . \quad \text{(III. 112c)}$$

Several comments are necessary. First elements of **V**, **W**, **X**, **Y**, and **Z** which vanish are not listed in Eqs. (III. 109)–(III. 112). Also because of Eq. (III. 78), the quantities V_{01}, X_{01}, and Y_{01} are, respectively, the negatives of V_{10}, X_{10}, and Y_{10}. For X_{01} and Y_{01} this symmetry is obvious from the explicit forms yielded by the calculation. This provides a useful check of the calculation. The explicit forms we have obtained for $-V_{01}$ and V_{10} are not obviously equal. The requirement that $V_{10} = -V_{01}$, in fact, leads us to a relation which will prove useful below.

Finally to obtain Eqs. (III. 109)–(III. 112) we have repeatedly used the local electroneutrality condition Eq. (III. 91) and the charge–dipole Debye shielding condition Eq. (III. 92). Since we arrived at these relationships, as well as Eq. (III. 83), by physical arguments and since they are essential to our method of solution it is worthwhile to derive them from our model. This is done in Appendix C.

One problem remains. Eq. (III. 112b) is in an inconvenient form since it contains the quantities $H_{11}(0)$ and $H'_{01}(0)$. We thus require two relationships involving these quantities in order to eliminate them from Eq. (III. 112b). The first relation follows from the requirement $V_{01} = -V_{10}$. The second is obtained by expanding the (1, 1) element of Eq. (III. 93) in a Laurent series about $S = 0$ and equating terms of order S^0. We eventually obtain

$$\hat{\eta}_1 X_{11} = 6\{2z\hat{\eta}_1 C_{11}(0) - 4z^2\hat{\eta}_1 C^{(3)}_{11}(0) + yz[24\bar{\eta}C^{(2)}_{10}(0)] + y^2[1 + 24\hat{\eta}_0 C'_{00}(0)] - 2y(x\delta^2_{10} + yq^+)\} . \quad \text{(III. 112b′)}$$

Equations (III. 109)–(III. 112) now contain two types of unknown quantities. First we have quantities $\mathbf{C}^{(n)}(0)$, the Laplace transform $\mathbf{C}(S)$ and its derivatives evaluated at $S = 0$. These can be readily eliminated from our equations as we will describe below. Second we have the parameters x, y, and z. After we have eliminated the $\mathbf{C}^{(n)}(0)$, we will obtain a set of three coupled nonlinear algebraic equations for x, y, and z. The model is completely solved when we have obtained the physical roots of this set of equations.

The $\mathbf{C}^{(n)}(0)$ are eliminated in the following way. Consider, for example,

$$q^+ = 1 + 24\hat{\eta}_1 C'_{11}(0) = 1 + 24\hat{\eta}_1(\tfrac{1}{3}W_{11} + \tfrac{1}{4}X_{11} + \tfrac{1}{6}Z_{11}) . \quad \text{(III. 113)}$$

Using analogous expressions for $C_{11}(0)$ and $C^{(3)}_{11}(0)$, we eliminate these quantities from all terms in Eq. (III. 112) which are nonvanishing in the polar fluid limit; i.e., when $\delta_{00} = 0$. This leads to a set of coupled linear equations for X_{11}, Y_{11}, and Z_{11}. Solving these gives

$$\hat{\eta}_1 W_{11} = \frac{z(1+2z)^2}{(1-z)^4} + D_W , \quad \text{(III. 114a)}$$

$$\hat{\eta}_1 X_{11} = -6\frac{z^2(1+\frac{1}{2}z)^2}{(1-z)^4} + D_X , \quad \text{(III. 114b)}$$

$$\hat{\eta}_1 Z_{11} = \tfrac{1}{2}z\hat{\eta}_1 W_{11} + \tfrac{1}{48}\Delta_Z , \quad \text{(III. 114c)}$$

where

$$24D_W = (1-z)^{-4}\det\begin{pmatrix} (1+2z)^2 & \Delta_X - (\frac{6}{5} + \frac{3}{2}z)z\Delta_Z \\ -6z & 2z\Delta_Z + \Delta_W \end{pmatrix} \quad \text{(III. 115)}$$

$$24D_X = (1-z)^{-4}\det\begin{pmatrix} \Delta_x - (\frac{6}{5} + \frac{3}{2}z)z\Delta_Z & 6z(1+\frac{1}{2}z)^2 \\ 2z\Delta_Z + \Delta_W & 1 - 8z - 2z^2 \end{pmatrix} , \quad \text{(III. 116)}$$

with

$$\Delta_W = -24y\delta^2_{10} , \quad \text{(III. 117)}$$

$$\Delta_X = 144\{yz[24\bar{\eta}C^{(2)}_{10}(0)] - 2y(x\delta^2_{10} + yq^+) + y^2[1 + 24\hat{\eta}_0 C'_{00}(0)]\} , \quad \text{(III. 118)}$$

$$\Delta_Z = 24y(y\delta^2_{00} - z\delta^2_{10}) . \quad \text{(III. 119)}$$

Since $C'_{10}(0)$ and $C'_{00}(0)$ can be expressed in terms of x, y, z, and q^+, we only need these latter quantities in order to obtain W_{11}, X_{11}, and Z_{11}. There appears to be one problem. By Eq. (III. 113) q^+ depends on W_{11}, X_{11}, and Z_{11}. But, as we have just mentioned, W_{11}, X_{11}, and Z_{11} depend on q^+. Thus our solution for W_{11}, X_{11}, and Z_{11} is apparently implicit. This is not actually the case, however, since q^+ can be eliminated in favor of q^- using Eq. (III. 104) and, because of Eqs. (III. 106)–(III. 108),

$$q^- = (1-z)^2/(1+\tfrac{1}{2}z)^4 \quad \text{(III. 120)}$$

is a function only of z. Thus if we know x, y, and z we can compute W_{11}, X_{11}, and Z_{11}. In fact we can determine all of the elements of **V**, **W**, **X**, **Y**, and **Z** in terms of x, y, and z. Thus to completely solve our model we now only require the values of x, y, and z.

We now determine three equations for x, y, and z. Combining

$$C_{10}(0) = -(V_{10} + \tfrac{1}{3}X_{10} + \tfrac{1}{4}Y_{10}) \quad \text{(III. 121)}$$

with Eqs. (III. 103) and (III. 110) we obtain the first equation. It is

$$24[(x\delta^2_{10} + yq^+)(1 + \tfrac{1}{2}z) - \tfrac{1}{12}(y\delta^2_{00} - z\delta^2_{10}) - \tfrac{1}{2}(xy\delta^2_{00} + y^2\delta^2_{10})] = -\delta^2_{10} . \quad \text{(III. 122)}$$

A second equation relating the unknowns follows from the continuity of $h_{00}(w) - c_{00}(w)$ at $w = 1$. [16]

$$\hat{\eta}_0 X_{00} + 6[\hat{\eta}_0 C^{(0)}_{00}(1)]^2 + 6[\bar{\eta}C_{10}(1)]^2 = 0 . \quad \text{(III. 123)}$$

Using Eqs. (III. 109)–(III. 10) in Eq. (III. 123) gives the explicit relationship.

A third relation follows from Eqs. (III. 104), (III. 112a),

Eq. (III. 114) and Eq. (III. 120). It is

$$\delta_{11}^2 = \left[\frac{(1+2z)^2}{(1-z)^4} - \frac{(1-z)^2}{(1+\frac{1}{2}z)^4}\right] + z^{-1}[D_W + y\delta_{10}^2] \,. \qquad \text{(III. 124)}$$

Again, as in the case of Eq. (III. 123), Eq. (III. 124) can be rewritten as an explicit but complicated relation between x, y, z, and q^+.

Equations (III. 122)–(III. 124) along with Eqs. (III. 104) and (III. 120), which allow us to express q^+ in terms of z, provide a closed but very complicated system of equations for x, y, and z. For arbitrary values of δ_{00} and δ_{11}, these equations must be solved numerically. For small δ_{00} they can be treated analytically by perturbation theory.

IV. PERTURBATION SOLUTION FOR LOW IONIC STRENGTH

We now solve the coupled system, Eqs. (III. 122), (III. 124) for small δ_{00}, that is for the limit of small ionic strength. Show that to low order in δ_{00} the model gives results similar to those obtained in the usual continuum dielectric theories of ionic solutions.

The important unknown parameters of our model are x, y, z, and q^+. We assume these have the following expansions in δ_{00}

$$x = x_1\delta_{00} + x_2\delta_{00}^2 + x_3\delta_{00}^3 + \cdots \qquad \text{(IV. 1)}$$

$$y = y_1\delta_{00} + y_2\delta_{00}^2 + y_3\delta_{00}^3 + \cdots \qquad \text{(IV. 2)}$$

$$z = z_0 + z_2\delta_{00}^2 + z_3\delta_{00}^3 \qquad \text{(IV. 3)}$$

$$q^+ = q_0^+ + q_2^+\delta_{00}^2 + q_3^+\delta_{00}^3 \,. \qquad \text{(IV. 4)}$$

We will also require the expansion of q^- which we assume to be

$$q^- = q_0^- + q_2^-\delta_{00}^2 + q_3^-\delta_{00}^3 \,. \qquad \text{(IV. 5)}$$

Note that z_0, q_0^+, and q_0^- refer to the polar fluid solvent characterized by an effective density ρ_1 and an effective dipole moment μ_1. We know from previous work[3,4] or from equations presented here that

$$q_0^+ = (1+2z_0)^2/(1-z_0)^4 \qquad \text{(IV. 6)}$$

$$q_0^- = (1-z_0)^2/(1+\tfrac{1}{2}z_0)^4 \qquad \text{(IV. 7)}$$

with z_0 determined from the relation [cf. Eq. (III. 104)]

$$\delta_{11}^2 = q_0^+ - q_0^- \,. \qquad \text{(IV. 8)}$$

Also note that we have assumed in Eqs. (IV. 3)–(IV. 5) that z_1, q_1^+, $q_1^- = 0$. This follows from the fact that D_w and $y\delta_{10}^2$ are of order δ_{00}^2 for small ionic strength. Thus from Eqs. (III. 112a) and (III. 114a) we see

$$q^+ = \frac{[1+2(z_0+z_1\delta_{00})]^2}{[1-(z_0+z_1\delta_{00})]^4} + O(\delta_{00}^2)$$

or

$$q_1^+ = 8q_0^+\frac{(1+\frac{1}{2}z_0)}{(1-z_0)(1+2z_0)}z_1 \,. \qquad \text{(IV. 9)}$$

Similarily from Eq. (III. 120) we see

$$q_1^- = -4q_0^-\frac{(1-\frac{1}{4}z_0)}{(1-z_0)(1+\frac{1}{2}z_0)}z_1 \,. \qquad \text{(IV. 10)}$$

Finally because of Eq. (III. 104) we

$$q_n^- = q_n^+ \quad \text{for } n \geq 1 \,. \qquad \text{(IV. 11)}$$

Comparing Eqs. (IV. 9)–(IV. 11) shows that $q_1^+ = z_1 = q_1^- = 0$.

The second order terms in Eqs. (IV. 3)–(IV. 5) do not vanish. Instead we find [cf. Eq. (IV. 10)]

$$q_2^+ = q_2^- = -\frac{4q_0^-(1-\frac{1}{4}z_0)}{(1-z_0)(1+\frac{1}{2}z_0)}z_2 \,. \qquad \text{(IV. 12)}$$

This relation will prove useful below.

We now turn to the problem of computing the low order contributions to x and y. Inserting our expansions Eqs. (IV. 1)–(IV. 4) into Eq. (III. 122), using $\delta_{10}^2 = \delta_{10}\delta_{00}$, and equating like powers of δ_{00} on both sides of the resulting relation, gives the following three equations:

$$y_1 = -\frac{1}{24}\frac{\delta_{11}}{q_0^+}\frac{1+2z_0}{1+\frac{1}{2}z_0} \,, \qquad \text{(IV. 13)}$$

$$x_1\delta_{11} + y_2q_0^+ = 0 \,, \qquad \text{(IV. 14)}$$

$$x_2\delta_{11} + y_3q_0^+ = -\tfrac{1}{24}(1+\tfrac{1}{2}z_0)^{-1}[24y_1q_2^+(1+\tfrac{1}{2}z_0) + 12y_1z_2q_0^+ - 12y_1^2\delta_{11} + 2z_2\delta_{11} - 2y_1] \,. \qquad \text{(IV. 15)}$$

We similarily combine Eqs. (III. 109)–(III. 110) and (III. 123) with the expansions (IV. 1)–(IV. 4). We equate like orders in δ_{00} on both sides of the resulting relation and consider the three lowest order equations which arise.

The first two equations reproduce Eqs. (IV. 13)–(IV. 14). This provides a valuable check. The third equation gives new information. It involves the unknown quantities x_1, x_2, y_1, y_2, y_3, z_2, and q_2^+. Fortunately, the higher order quantities x_2 and y_3 occur in the combination $x_2\delta_{11} + y_3q_0^+$ and therefore can be eliminated using Eq. (IV. 15). The quantities y_1 and y_2 are then eliminated using Eqs. (IV. 13) and (IV. 14). This leaves us with an equation involving only x_1, z_2, and q_2^+. After a very lengthy simplification this equation finally becomes

$$\frac{q_0^-}{q_0^+}(24x_1)^2 = 1 - 2\frac{\delta_{11}^2}{q_0^+} + \frac{\delta_{11}^4}{[q_0^+]^2} + T \,, \qquad \text{(IV. 16)}$$

where

$$T = \left[\frac{\delta_{11}^2}{q_0^+}\right]^2\left[-1 + \frac{9}{16}\frac{(1+2z_0)^2}{(1+\frac{1}{2}z_0)^4} + \frac{1}{6}\frac{(1-z_0)^2}{(1+\frac{1}{2}z_0)^2}(1+2z_0) + \frac{\delta_{11}^2}{[q_0^+]^2}\frac{(1+2z_0)^2}{(1+\frac{1}{2}z_0)^2}q_2^+ - 8\frac{\delta_{11}^2}{q_0^+}\frac{(1+2z_0)}{(1-z_0)(1+\frac{1}{2}z_0)}z_2\right] \,. \qquad \text{(IV. 17)}$$

Fortunately, as we will show below by explicit calculation of z_2 and q_2^+, the quantity T vanishes. Thus

$$\frac{q_0^-}{q_0^+}(24x_1)^2 = \left(1 - \frac{\delta_{11}^2}{q_0^+}\right)^2$$

or using Eq. (IV. 8)

$$24x_1 = \pm(1/\epsilon_W)^{1/2}, \tag{IV. 18}$$

where

$$\epsilon_W = q_0^+/q_0^- \tag{IV. 19}$$

is Wertheim's formula for the dielectric constant of the effective polar fluid solvent. The sign ambiguity in Eq. (IV. 18) is settled by examining the small ionic strength limit of Waisman and Lebowitz's[5] solution of the MSM primitive electrolyte problem. We find

$$24x_1 = -(1/\epsilon_W)^{1/2}. \tag{IV. 20}$$

The simplicity of Eq. (IV. 20) may appear remarkable in view of the complexity of the proceeding calculation. Actually, x_1 must be of the form of Eq. (IV. 20) in order that the model give results in agreement with the continuum dielectric picture for low ionic strength.

To see this we recall the definition of x, Eq. (III. 108a), and of $B_{00}(0)$, Eq. (III. 89). Then using Eq. (III. 101) gives Eq. (IV. 20) in the form

$$24\hat{\eta}_0 \lim_{\delta_{00}\to 0} \int_1^\infty w h_{00}(w)dw = -\kappa_W d, \tag{IV. 21}$$

where

$$\kappa_W = \kappa_0/\sqrt{\epsilon_W} \tag{IV. 22}$$

is the Debye inverse length in a medium with dielectric constant ϵ_W.

We rewrite Eq. (IV. 21) in terms of the unreduced radial distance $r = wd$ as

$$4\pi\hat{\rho}_0 \lim_{\delta_{00}\to 0} \int_d^\infty r h_{00}(r/d)dr = -\kappa_W. \tag{IV. 23}$$

Now we take the limit $d \to 0$ in Eq. (IV. 23). [Note that the right hand side of Eq. (IV. 23) is independent of d.] If our model is consistent with the continuum dielectric picture, then we should have

$$\lim_{\substack{\delta_{00}\to 0 \\ d\to 0}} h_{00}\left(\frac{r}{d}\right) = -\frac{\kappa_W^2}{4\pi\hat{\rho}_0}\frac{e^{-\kappa_W r}}{r}$$

the Debye–Hückel result. We can easily verify that Eq. (IV. 23) is consistent with the continuum dielectric approximation.

The above argument is essentially a calculation of the dielectric constant by the test charge method.[17] It is interesting that we obtained Wertheim's result. He used a fluctuation formula and it is well known that in an approximate theory like the MSM, different routes to observables may give different results.

We now show that T defined in Eq. (IV. 17) vanishes. To do this we must determine explicit forms for q_2^+ and z_2. We already have one relation between these quantities, Eq. (IV. 12) and we will use Eq. (III. 112a) in the form [see Eq. (III. 114a)]

$$q^+ = \frac{(1+2z)^2}{(1-z)^4} + z^{-1}[D_W' + y\delta_{10}^2] \tag{IV. 24}$$

to obtain a second relation.

Expanding Eq. (IV. 24) to order δ_{00}^2 gives after a lengthy calculation

$$q_2^+ = \frac{8q_0^+}{(1-z_0)}\frac{(1+\frac{1}{2}z_0)}{(1+2z_0)}z_2 + \frac{\delta_{11}^2}{48}\frac{(1-z_0)^3}{(1+\frac{1}{2}z_0)^2} \times (13+19z_0+4z_0^2)(1+2z_0)^{-2}. \tag{IV. 25}$$

Using Eq. (IV. 12) to eliminate z_2 gives

$$q_2^+ = \frac{\delta_{11}^2}{48}\frac{(1-z_0)^3}{(1+\frac{1}{2}z_0)^2}\frac{13+19z_0+4z_0^2}{(1+2z_0)^2}D, \tag{IV. 26}$$

where

$$D = \left[1 + 2\frac{q_0^+}{q_0^-}\frac{(1+\frac{1}{2}z_0)^2}{(1-\frac{1}{4}z_0)(1+2z_0)}\right]^{-1}. \tag{IV. 27}$$

Finally we use Eqs. (IV. 12) and (IV. 26) to eliminate q_2^+ and z_2 from Eq. (IV. 17). After rearrangement we establish that $T = 0$.

In order to solve our model to order δ_{00}^3, we also require q_3^+ and z_3. These can be obtained by a calculation similar to that sketched above for q_2^+ and z_2. The results are given in Eqs. (IV. 36) and (IV. 37).

The following equations summarize the results of this section

$$q_0^+ = (1+2z_0)^2/(1-z_0)^4 \tag{IV. 28}$$

$$q_0^- = (1-z_0)^2/(1+\tfrac{1}{2}z_0)^4 \tag{IV. 29}$$

with z_0 determined from

$$\delta_{11}^2 = q_0^+ - q_0^-. \tag{IV. 30}$$

Also

$$x_1 = -\tfrac{1}{24}(1/\epsilon_W)^{1/2}, \tag{IV. 31}$$

$$y_1 = -\frac{1}{24}\frac{\delta_{11}}{q_0^+}\frac{1+2z_0}{1+\frac{1}{2}z_0}, \tag{IV. 32}$$

$$q_2^+ = q_2^- = \frac{1}{48}\frac{\delta_{11}^2}{q_0^+}\frac{13+19z_0+4z_0^2}{(1-z_0)(1+\frac{1}{2}z_0)^2}D, \tag{IV. 33}$$

$$y_2 = -(\delta_{11}/q_0^+)x_1, \tag{IV. 34}$$

$$z_2 = -\frac{1}{192}\frac{\delta_{11}^2}{q_0^+q_0^-}\frac{13+19z_0+4z_0^2}{(1-\frac{1}{4}z_0)(1+\frac{1}{2}z_0)}D, \tag{IV. 35}$$

$$q_3^+ = q_3^- = \frac{8x_1\delta_{11}^2}{q_0^+}\frac{1+\frac{1}{2}z_0}{(1+2z_0)(1-\frac{1}{4}z_0)}D, \tag{IV. 36}$$

$$z_3 = -\frac{2x_1\delta_{11}^2}{q_0^+q_0^-}\frac{(1+\frac{1}{2}z_0)^2}{(1+2z_0)(1-\frac{1}{4}z_0)}D. \tag{IV. 37}$$

From the above equations we can compute the low ionic strength limits of the direct correlation function $\mathbf{C}(X_1, X_2)$ [Eq. (II. 4)], the pair correlation function $\mathbf{H}(X_1, X_2)$ [Eq. (II. 4)] and the thermodynamic properties of our model. The direct correlation function is of little interest so we omit the detailed formulas here. The pair correlation function is of considerable interest.[18] From it we can, for example, obtain the potential of mean force at infinite dilution, a key quantity in the MacMil-

lan–Mayer theory of solutions. Unfortunately calculation of this quantity requires substantial additional labor. We will examine it in a subsequent paper.

The thermodynamic properties of our model, however, can be easily obtained from the results given in this paper. We consider these properties in the next section.

V. THERMODYNAMICS

The excess thermodynamic properties of this model can be expressed in terms of x, y, z, δ_{00}^2, and δ_{11}^2; the parameters of the effective two component fluid.

We begin with the expression for the excess internal energy per unit volume which is

$$V^{-1}\Delta E = [2V(4\pi)^2]^{-1}\sum_{ij=1}^{m}\rho_i\rho_j\int V_{ij}(X_1X_2)G_{ij}(X_1X_2)dX_1dX_2\ . \tag{V.1}$$

Here $G_{ij}=(H_{ij}+1)$ is the pair distribution function for species i and j, and the sum is over all m components of the true mixture. After a straightforward calculation, [17] Eq. (V.1) can be reduced to the following simple form

$$V^{-1}\Delta E = [3/\beta\pi d^3]\,[x\delta_{00}^2 + 2y\delta_{00}\delta_{11} - z\delta_{11}^2]\ . \tag{V.2}$$

This expression has a very simple interpretation. Recall that we have reduced the solution of our model to the problem of solving an effective binary fluid mixture problem [see Eq. (III.73)]. This mixture contains an effective charged component with charge $\hat{e}$ and density $\hat{\rho}_0$ and an effective polar component with dipole moment $\hat{\mu}$ and density $\hat{\rho}_1$. The effective mixture, of course, does not correspond to any physical ionic solution; for example it contains charges of only one sign. It is simply a convenient mathematical device for solving the MSM and for discussing the thermodynamic properties of the true mixture. For example in Eq. (V.2) the term $[x\delta_{00}^2]$ can be attributed to the mutual interaction of charges $\hat{e}$ in the effective mixture while $[y\delta_{00}\delta_{11}]$ describes the interaction of the effective charges with the effective dipoles. Similarly the term $[-z\delta_{11}^2]$ is the effective dipolar interaction term.

The Helmholtz free energy of the mixture may be obtained by application of conventional thermodynamic perturbation theory of which the Gibbs–Helmholtz equation is a special case. In this approach a portion of the pair potential energy of interaction, for simplicity denoted u_{ij}, is scaled by a parameter λ so that $u_{ij}\to\lambda u_{ij}$. The excess free energy $\Delta A(\lambda=1)$ in the system of interest when the potential u_{ij} is completely "turned on," i.e., $\lambda=1$ is related to the excess free energy $\Delta A(\lambda=0)$ in a reference system when the potential u_{ij} is completely absent i.e., $\lambda=0$ by

$$\Delta A(\lambda=1)-\Delta A(\lambda=0) = [2(4\pi)^2\beta]^{-1}\sum_{ij}{}'\rho_i\rho_j\int_0^1 d\lambda\int u_{ij}(X_1X_2)G_{ij}(X_1X_2;\lambda)dX_1dX_2\ , \tag{V.3}$$

where the prime superscript on the sum denotes that the sum runs over the species (i,j) for which the potential u_{ij} has been scaled. In Eq. (V.3) $G_{ij}(X_1, X_2;\lambda)$ is the two particle distribution function in the system of interest when the potential u_{ij} is replaced by λu_{ij}.

This procedure can be applied to the model we are studying in a number of interesting ways according to what part of the potential we select to scale. First we may choose to scale every charge and every dipole in the true mixture by $e_i\to\lambda^{1/2}e_i$ and $\mu_j\to\lambda^{1/2}\mu_j$. This choice corresponds to turning on dipole and charge interactions from a reference hard sphere fluid. In terms of the effective two component system we find for our model the result

$$\Delta A(\lambda=1)-\Delta A(\mathrm{hs}) = V[3/\beta\pi d^3]\int_0^1 d\lambda[x(\lambda)\delta_{00}^2 + 2y(\lambda)\delta_{00}\delta_{11} - z(\lambda)\delta_{11}^2], \tag{V.4}$$

where $\Delta A(\mathrm{hs})$ is the configurational free energy of the reference PY hard sphere fluid. In Eq. (V.4) the explicit dependence of the parameters (x, y, z) on λ has been denoted, e.g., since in the system of interest $x=x(\delta_{00},\delta_{11})$, we have written $x(\lambda)=x(\lambda^{1/2}\delta_{00},\lambda^{1/2}\delta_{11})$.

Second we may choose to scale every dipole in the true mixture by $\mu_i\to\lambda_d^{1/2}\mu_i$ and maintain every charge in the system at its physical value. This choice corresponds to "turning on" dipole–dipole and charge–dipole interaction in a MSM ionic system. Here the reference system consists of the MSM charged-hard sphere fluid studied by Waisman and Lebowitz. [5] For this scaling one finds the result

$$\Delta A(\lambda_d=1)-\Delta A(L,W) = V[3/\beta\pi d^3]\int_0^1 d\lambda_d[\lambda_d^{-1/2}y(\lambda_d)\delta_{00}\delta_{11} - z(\lambda_d)\delta_{11}^2]\ , \tag{V.5}$$

where $\Delta A(L, W)$ denotes exactly the excess free energy for a charged hard sphere mixture in the MSM approximation as determined by Waisman and Lebowitz. [5] In Eq. (V.5)

$$\begin{aligned} y(\lambda_d) &= y(\delta_{00},\lambda_d^{1/2}\delta_{11})\\ z(\lambda_d) &= z(\delta_{00},\lambda_d^{1/2}\delta_{11})\ . \end{aligned} \tag{V.6}$$

Finally we may choose to scale every charge in the true mixture by $e_i\to\lambda_c^{1/2}e_i$ and maintain every dipole in the system at its physical value. This choice corresponds to "turning on" charge–charge and charge–dipole interactions in a MSM dipolar system. Here the reference system consists of the MSM dipolar mixture. For this scaling one finds the result

$$\Delta A(\lambda_c=1)-\Delta A(W) = V(3/\beta\pi d^3)\int_0^1 d\lambda_c[x(\lambda_c)\delta_{00}^2 + \lambda_c^{-1/2}y(\lambda_c)\delta_{00}\delta_{11}]\ , \tag{V.7}$$

where $\Delta A(W)$ denotes exactly the excess free energy for a dipolar hard sphere mixture in the MSM approximation as determined by us[4] from Wertheim's[3] elegant solution of the one component dipolar hard sphere system. In Eq. (V.7)

$$\begin{aligned} x(\lambda_c) &= x(\lambda_c^{1/2}\delta_{00},\delta_{11})\\ y(\lambda_c) &= y(\lambda_c^{1/2}\delta_{00},\delta_{11})\ . \end{aligned} \tag{V.8}$$

We note that, of course, a second scaling may be used to relate either $\Delta A(L, W)$ or $\Delta A(W)$ to $\Delta A(\mathrm{hs})$. For example in the case of the pure MSM dipolar hard sphere system, Nienhuis and Deutch[19] explicitly show how

$\Delta A(W)$ is related to ΔA(hs). We also remark that the reference system free energies ΔA(hs), $\Delta A(L, W)$ and $\Delta A(W)$ depend upon the densities (and compositions) of the charged species although they bear no charge in the reference system. Accordingly these reference free energies are not at 'infinite dilution.'

In an exact treatment of an ionic–dipole mixture the true excess free energy ΔA could be obtained by any one of these three scaling procedures and one could conclude

$$\Delta A = \Delta A(\lambda = 1) = \Delta A(\lambda_d = 1) = \Delta A(\lambda_c = 1) \ . \tag{V.9}$$

Accordingly one can infer nontrivial relations between the exact formal expressions for $\Delta A(\lambda)$, $\Delta A(\lambda_d)$, and $\Delta A(\lambda_c)$ which might be employed as convenient starting points for practical thermodynamic perturbation theory calculations. We investigate this matter further in a forthcoming publication.

The MSM, however, is an approximation to the true mixture and accordingly the relation displayed in Eq. (V.9) may not hold for the model under investigation here. The point is that the MSM is an approximate theory which need not preserve thermodynamic identities. For example the compressibility obtained from Eqs. (V.4), (V.5), or (V.7) will not agree with that obtained from the compressibility theorem. The failure of two procedures to lead to equivalent results is a frequent failing of approximate models of the liquid state.

While we have not proven the relation displayed in Eq. (V.9) for the MSM ionic–dipolar mixture we conjecture that it holds in general for this model. If this is true Eqs. (V.4), (V.5), and (V.7) may be used advantageously to compute coefficients in the expansions of x, y, z in parameters δ_{00} and δ_{11}.

Since explicit results for x, y, and z for arbitrary value of δ_{00} and δ_{11} cannot be obtained without numerical solution of the coupled system of Eqs. (III.122), (III.123), and (III.124) we cannot explicitly evaluate the integrals appearing in Eqs. (V.4), (V.5), and (V.7). However we can obtain explicit results in the limit of low ionic strength, i.e., δ_{00} small, employing the results of Sec. IV. This is a most important step since it permits comparison with Debye–Hückel theory. The MSM model investigated here is the first model which attributes a molecular character to the solvent in an ionic system and it is most important to verify agreement with conventional Debye–Hückel treatment where the solvent is treated completely as a dielectric continuum.

For low ionic strength clearly Eq. (V.7) is the convenient choice for computing ΔA. The evaluation of ΔA is accomplished by employing the expansions obtained from Eqs. (IV.1), (IV.2):

$$\begin{aligned} x(\lambda_c) &= x_1\lambda_c^{1/2}\delta_{00} + O(\delta_{00}^2) \\ y(\lambda_c) &= y_1\lambda_c^{1/2}\delta_{00} + y_2\lambda_c\delta_{00}^2 \ . \end{aligned} \tag{V.10}$$

When these expansions are substituted into Eq. (V.7) we obtain the result for the excess free energy:

$$\begin{aligned} &V^{-1}\beta[\Delta A - \Delta A(W)] \\ &\quad = [2/\pi d^3]\{(x_1 + y_2\delta_{11})\delta_{00}^3 + y_1\delta_{00}^2\delta_{11}\} \ . \end{aligned} \tag{V.11}$$

The terms on the right hand side of this equation can be given a physical interpretation in terms of Debye–Hückel theory. Employing Eqs. (IV.19), (IV.30), (IV.31), and (IV.34) we may express the factor $[x_1 + y_2\delta_{11}]$ in first term as

$$x_1 + y_2\delta_{11} = [x_1/\epsilon_w] = -\tfrac{1}{24}(\epsilon_w)^{-3/2} \ . \tag{V.12}$$

Notice what has happened. The quantity $(x_1\delta_{00}^3)$ is (within factors) the *vacuum* Coulomb potential energy averaged over the *medium* charge–charge pair distribution function and accordingly varies as $\epsilon_w^{-1/2}$. Addition of the charge–dipole term $[y_2\delta_{11}\delta_{00}^3]$ has the effect of dividing the vacuum Coulomb potential energy by ϵ_w; that is the charge–dipole interaction, in this low order, has the effect of "renormalizing" the vacuum Coulomb potential to a Coulomb potential appropriate in a dielectric medium with dielectric constant ϵ_w. If we substitute Eq. (V.12) into the first term on the rhs of Eq. (V.11) and employ Eq. (III.101) we obtain for this contribution

$$V^{-1}\beta\Delta A(\mathrm{DH}) = -(1/12\pi)[\kappa_0/\epsilon_w^{1/2}]^3 \ , \tag{V.13}$$

where $\kappa_0 = (4\pi\hat{\rho}_0\hat{e}^2\beta)^{1/2}$. We have denoted this contribution as ΔA(DH) because it is exactly the classical Debye–Hückel theory result with an inverse Debye shielding length $\kappa_w = (\kappa_0/\epsilon_w^{1/2})$ appropriate for a medium with dielectric constant ϵ_w.

The second term on the rhs of Eq. (V.11) depends upon δ_{00}^2 and accordingly is *linear* in the density of the effective charges $\hat{\rho}_0$. Clearly this term cannot be associated with charge–charge interactions. This term can be interpreted as the contribution to the free energy of the self charging of $\hat{\rho}_0$ effective charges per unit volume in a medium with dielectric constant ϵ_w. The classical result for this quantity $\hat{\rho}_0 S_c$ is simply

$$\hat{\rho}_0 S_c = (\hat{\rho}_0\hat{e}^2/2d)[\epsilon_w^{-1} - 1] \ . \tag{V.14}$$

A calculation of the entire contribution of this second term, denoted $\hat{\rho}_0 S$ on the rhs of Eq. (V.11) employing Eqs. (IV.19), (IV.30), and (IV.32) yields the result

$$\hat{\rho}_0 S = \hat{\rho}_0 S_c\left[1 + \frac{\frac{3}{2}z_0}{1 + (\frac{1}{2})z_0}\right], \tag{V.15}$$

where z_0 is the leading term in Eq. (IV.3). Thus we find that the self-energy term S, unlike the Debye–Hückel term, does not reduce to the classical electrostatic value. The deviation of S from S_c may be considerable. On a molecular level it is not surprising that a deviation between S and S_c exists since the local arrangement of the solvent dipoles near a charge may differ greatly from their arrangement in bulk solvent. Furthermore the fact that the self-charging energy contribution, S, is a single charged particle quantity should lead us to suspect the MSM prediction Eq. (V.15). The deviation of S from S_c must arise from dipoles in the close vicinity of a single charge. But it is precisely at these close separations that approximations inherent in the MSM may lead to unphysical results. We note that the term $\rho_0 S$ in the free energy will not contribute to the activity coefficient of the ionic species in the solution because the term is linear in ρ_0 and S may be absorbed into the definition of the reference chemical potential of the ions.

Note added in proof. A different treatment of this model has been presented by Professor L. Blum.

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APPENDIX A

We wish to convert the following k-space products to r-space convolutions.

$$N_{++}(k) = (2\pi)^{3/2} m_+(k) n_+(k) , \tag{A1}$$

$$N_{--}(k) = (2\pi)^{3/2} m_-(k) n_-(k) , \tag{A2}$$

$$N_{+-}(k) = (2\pi)^{3/2} m_+(k) n_-(k) . \tag{A3}$$

In the above equations, $m_+(k)$ and $n_+(k)$ are even functions of k while $m_-(k)$ and $n_-(k)$ are odd in k. Thus, $N_{++}(k)$ and $N_{--}(k)$ are even functions while $N_{+-}(k)$ is odd.

For an even function, $E(k)$, the appropriate Fourier transform is [cf. Eq. (III. 11)]

$$\hat{E}(r) = \frac{4\pi r^{-1}}{(2\pi)^{3/2}} \int_0^\infty k \sin kr\, E(k) dk \tag{A4}$$

while for $O(k)$, an odd function, we use

$$\hat{O}(r) = \frac{4\pi i r^{-1}}{(2\pi)^{3/2}} \int_0^\infty k \cos kr\, O(k) dk . \tag{A5}$$

Using Eqs. (A4)–(A5) and their inverses we can express $\hat{N}_{+-}(r)$ (for example), the transform of $\hat{N}_{+-}(k)$, in terms of the transforms $\hat{m}_+(r)$ and $\hat{n}_-(r)$. We find

$$N_{+-}(r) = 8r^{-1} \int_0^\infty u m_+(u) du \int_0^\infty v \hat{n}_-(v) dv I(r, u, v) ; \tag{A6}$$

where

$$I(r, u, v) = \int_0^\infty k^{-1} \cos kr \sin ku \cos kv dk . \tag{A7}$$

Expanding the integrand in Eq. (A7) as a sum of terms of the form $\sin k(r \pm u \pm v)$ and using the following representation of the unit step function

$$\theta(x) = \tfrac{1}{2} + \pi^{-1} \int_0^\infty k^{-1} \sin kx dk$$

we rewrite Eq. (A7) as

$$I(r, u, v) = (\pi/4)[\theta(r+u+v) + \theta(r+u-v) - \theta(r-u+v) - \theta(r-u-v)] . \tag{A8}$$

We consider two cases:

(a) $u > r$.

For this case

$$I(r, u, v) = (\pi/4)[1 + \theta(r+u-v) - \theta(r-u+v)] . \tag{A8'}$$

Inserting Eq. (A9) in Eq. (A6) and using the fact that $\hat{n}_-(-v) = -\hat{n}_-(v)$, which follows from Eq. (A5), we can show

$$\hat{N}_{+-}(r) = 2\pi r^{-1} \int_0^\infty u \hat{m}_+(u) du \int_{r-u}^{u+r} v \hat{n}_-(v) dv . \tag{A9}$$

(b) $u < r$.

For this case

$$I(r, u, v) = (\pi/4)[\theta(r+u-v) - \theta(r-u-v)]$$

and we find that $N_{+-}(r)$ takes the same form as in Eq. (A9). Thus, for all r

$$\hat{N}_{+-}(r) = 2\pi r^{-1} \int_0^\infty u \hat{m}_+(u) du \int_{r-u}^{u+r} v \hat{n}_-(v) dv . \tag{A9}$$

We can similarly establish

$$\hat{N}_{++}(r) = 2\pi r^{-1} \int_0^\infty u \hat{m}_+(u) du \int_{|u-r|}^{u+r} v \hat{n}_+(v) dv \tag{A10}$$

$$\hat{N}_{--}(r) = -2\pi r^{-1} \int_0^\infty u \hat{m}_-(u) du \int_{u-r}^{u+r} v n_-(v) dv . \tag{A11}$$

Note that Eq. (A10) is the usual three-dimensional Fourier convolution theorem expressed in bipolar coordinates.

APPENDIX B

Consider the Laplace transforms

$$P(S) = \int_0^\infty e^{-Sw} p(w) dw , \tag{B1}$$

where

$$p(w) = \int_0^\infty u c_{00}(u) du \int_{w-u}^{u+w} v h_{01}(v) dv . \tag{B2}$$

Note $p(w)$ is the first of the two convolution integrals in Eq. (III. 73b).

We break $p(w)$ into two terms

$$p(w) = q(w) + r(w) , \tag{B3}$$

where

$$q(w) = \int_0^\infty u c_{00}(u) du \int_{w-u}^{u-w} v h_{01}(v) dv \theta(u-w) \tag{B4}$$

and

$$r(w) = \int_0^\infty u c_{00}(u) du \int_{|u-w|}^{u+w} v h_{01}(v) dv . \tag{B5}$$

We use the fact that $h_{01}(v) = -h_{01}(-v)$ [see Eq. (III. 20)] to write $Q(S)$, the Laplace transform of $q(w)$ as

$$Q(S) = -2S^{-1}[I(S) - I(0)] , \tag{B6}$$

where

$$I(S) = \int_0^\infty e^{-Su} u c_{00}(u) du \int_0^u e^{Sv} v h_{01}(v) dv . \tag{B7}$$

Using Eqs. (III. 84b) and (III. 85) we rewrite this as ($n_{10} = -n_{01}$)

$$I(S) = -n_{01} \int_0^\infty e^{-Su} u c_{00}^{(0)}(u) du \int_0^u e^{Sv} dv + \int_0^\infty e^{-Su} u c_{00}^{(0)}(u) du \int_0^u e^{Sv} v b_{01}(v) dv - \gamma \int_0^\infty e^{-Su} du \int_0^u e^{Sv} v h_{01}(v) dv .$$

The second double integral vanishes because of the closure conditions (III. 86).

The third double integral also vanishes. This can be seen by interchanging the integration order, explicitly evaluating the inner integral, and then using the charge–dipole Debye shielding condition Eq. (III. 80). Thus we find

$$I(S) = S^{-1} n_{01}[C_{00}(S) - C_{00}(0)] \ . \tag{B8}$$

To determine $I(0)$, it would appear sufficient to expand $I(S)$ about $S=0$. This gives

$$I(0) = n_{01} C'_{00}(0) \ .$$

Interestingly, this result is incorrect; certain of the integration interchanges used to obtain Eq. (B8) are invalid for $S=0$. Instead we find, working directly with the $S=0$ limit of Eq. (B7),

$$I(0) = n_{01} C'_{00}(0) - \gamma H'_{01}(0) \ . \tag{B9}$$

Combining Eqs. (B6), (B8)–(B9) we obtain

$$Q(S) = 2n_{01} S^{-2}[C_{00}(0) - C_{00}(S)] + 2n_{01} C'_{00}(0) S^{-1} - 2\gamma H'_{01}(0) S^{-1} \ . \tag{B10}$$

Now consider $R(s)$, the Laplace transform of $r(w)$. To calculate it, we rewrite $r(w)$ as

$$r(w) = -n_{01} \int_0^\infty u c_{00}^{(0)} du \int_{1u-w1}^{u+w} dv - \gamma \int_0^\infty v h_{01}(v) dv \int_{1v-w1}^{v+w} du + \int_0^\infty v b_{01}(v) dv \int_{1u-w1}^{u+w} u c_{00}^{(0)}(u) du \ . \tag{B11}$$

We rewrite the first double integral in Eq. (B11) as

$$r_1(w) = -n_{10} \int_0^w u c_{00}^{(0)}(u) du \int_{w-u}^{w+u} dv + \int_w^\infty u c_{00}^{(0)}(u) du \int_{u-w}^{u+w} dv$$

or

$$r_1(w) = 2n_{01} w C_{00}(0) + \int_0^w u^2 c_{00}^{(0)}(u) du - w \int_0^w u c_{00}^{(0)}(u) du \ .$$

The Laplace transform of $r_1(w)$ can now be determined. After a brief calculation we find

$$R_1(S) = 2n_{01} S^{-2}[C_{00}(S) - C_{00}(0)] \ . \tag{B12}$$

An analogous calculation gives for the Laplace transform of the second double integral in Eq. (B11)

$$R_2(S) = 2\gamma S^{-2} H_{01}(S) \tag{B13}$$

where we have used Eq. (III. 92).

The third double integral is of the type which appears in the PY hard sphere problem. Its transform is easily found to be

$$R_3(S) = -S^{-1} B_{01}(S)[C_{00}(S) - C_{00}(-S)] \ . \tag{B14}$$

Combining Eqs. (B10) and (B12)–(B14) finally gives

$$P(S) = 2\gamma n_{10} S^{-3} - 2n_{10} C'_{00}(0) S^{-1} - 2\gamma H'_{01}(0) S^{-1} + 2\gamma S^{-2} B_{01}(S) - S^{-1} B_{01}(S)[C_{00}(S) - C_{00}(-S)] \ . \tag{B15}$$

APPENDIX C

We show in this appendix that the local electroneutrality constraint Eq. (III. 79) and the charge–dipole and dipole–dipole shielding conditions Eqs. (III. 80) and (III. 83) follow from our model, that is, they do not have to be separately imposed as was done in Sec. III.

Since all three conditions are closely related, we only discuss the dipole–dipole shielding condition in detail.

We begin with the relationship

$$q^- = [1 - 24\hat{\eta}_1 \int_0^\infty w^2 h_{11}^{(1)}(w) dw]^{-1} \ . \tag{C1}$$

This follows from the definition of q^-, Eq. (III. 105), in the standard manner, that is by evaluating the Fourier transform of Eq. (III. 68) at zero wave vector.

We can apply the matrix analogue of this procedure to the Fourier transform of Eq. (III. 73). This gives four relationships, one for each element of $\mathbf{h}_{l\lambda}(w)$. From the relationship for $\mathbf{h}_{11}(w)$ we find

$$q^+ - \delta_{11}^2 = [1 + 24\hat{\eta}_1 \int_0^\infty w^2 h_{11}(w) dw]^{-1} \ . \tag{C2}$$

To obtain Eq. (C2) we have used the fact that the Fourier transform of the Coulomb potential has a double pole at zero wave vector. Then combining Eqs. (C1)–(C2) with Eq. (III. 104) gives the dipole–dipole screening condition Eq. (III. 83).

Using the relationships for $h_{00}(w)$ and $h_{10}(w)$ analogous to Eq. (C2), we can similarly prove the local electroneutrality constraint and the charge–dipole screening equation.

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