A model of solvent structure around ions

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The nature of solvent structure around ions is considered using a model of hard spheres with embedded point charges in a solvent of hard spheres with embedded point dipoles. The statistical mechanics of this model is treated in the mean spherical approximation which is a natural extension of the Debye–Hückel theory of electrolytes to include discrete charges and dipoles of finite size. Our results include (i) a modified expression for the Born energy which had been used empirically to fit solubility data, (ii) explicit forms for the polarization density about an ion from which we can deduce the orientation order of the dipolar solvents and the validity or otherwise of the concept of a "local" dielectric constant near charged bodies, and (iii) the form of the interaction free energy (potential of mean force) between ions at separations comparable to the solvent size. In presenting these results which are given in detail in Section IV only a familiarity with the general description of this model given in Section II is assumed; it will not be necessary to refer to the mathematical detail in Section III.

I. INTRODUCTION

A survey of the recent literature will reveal a continuing interest in the role of solvents in determining the interaction between solute molecules. The nature of indirect solvent mediated or structural interactions in nonionic model systems has been considered in a number of recent papers. These included mean field theories,[1] asymptotic analysis of corrections to the continuum theory of dispersion interactions due to solvent structure,[2,3] the use of the integral equation approach (Percus Yevick and Hypernetted Chain) to elucidate the role of intermolecular potentials[4–7] and size effects,[8] exact analysis using one-dimensional models,[9,10] as well as studies using machine simulation.[11] For ionic or electrolyte systems, there are also attempts to go beyond the "primitive" model in which the solvent is treated only as a continuum of given dielectric constant. One approach was to retain the continuum nature of the solvent but to parameterise unknown effects due to the molecular structure of the solvent upon the ion–ion interaction potential by the addition of the so called "cavity" term and a "Gurney" potential.[12] Another approach is to treat both the ions and solvents on a equal, molecular basis, albeit using model potentials. These model systems have been solved under certain approximations[13–15] and analyzed in the asymptotic regime[16,17] to give expressions for the large separation behavior of ion–ion, ion–solvent, and solvent–solvent interactions. The contribution of solvent structure to the short range interaction between ions has been considered only by Monte Carlo simulations.[18,19]

In this paper we consider a model electrolyte solution comprised of a mixture of ions of equal size, modeled as hard spheres plus embedded point charges, in a dipolar solvent, modeled as hard spheres (of different size to those of the ions) plus embedded point dipoles. Our interest is to study, in the limit of vanishing ionic concentration, the structure of solvent molecules about an ion and its effect on the interaction or potential of mean force between two ions. We treat ion–dipole and dipole–dipole interactions in the Mean Spherical Approximation (MSA) while the ion–ion interaction is obtained using a nonlinear MSA. This approximation is analogous to the Debye–Hückel theory for electrolytes extended to handle discrete molecular size and the ion–dipole and dipole–dipole potential (see Sec. II for details).

We have three major results. Firstly, we derive an expression for the electrostatic contribution to the ionic solvation energy (Born energy) which differs from that given by the continuum picture or the primitive model. It has the same form which had been found empirically to fit solvation energies in aqueous and nonaqueous electrolytes. The second result is the polarization density of solvent molecules near an ion. Apart from giving a measure of the orientation structure of dipolar solvents about an ion, the results cast doubt on the validity of assigning a lower dielectric constant or using a spatially varying dielectric constant to account for so called dielectric saturation effects near charged particles or charged surfaces. The third results, the potential of mean force between ions, gives an indication of solvent effects on ion pairing. A comparison is made with available Monte Carlo results.

In the next section we give a physical description of the nature of the approximations used in this calculation and to relate this to the more familiar Debye–Hückel and Poisson–Boltzmann approximation. It is aimed to provide a physically perspicuous picture of the approximations used here for the readers not already *au fait* with the rather difficult liquid state literature. The formal details of the solution of this model as well as asymptotic forms of the distribution functions are given in Sec. III. The main results, given in Sec. IV can be assimilated without reference to the details in Sec. III. The paper closes with a discussion on the failure of the MSA to give a physical description of the properties of electrolytes beyond the Debye–Hückel limiting law.

II. DESCRIPTION OF THE MODEL

Here we give a description of the model ionic solution and the physical interpretations behind the approximations which we make. The ionic solutes are treated as

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hard spheres of *diameter* R_1, number densities ρ_1, $\rho_2, \ldots$ valencies $z_1, z_2, \ldots$ which satisfy the electroneutrality condition

$$\sum_i \rho_i z_i = 0 \ . \tag{2.1}$$

The solvent is modeled as a fluid of hard spheres of number density ρ_d, *diameter* R_2 with embedded point dipoles of dipole moment μ. The intermolecular potentials have the form:

ion–ion

$$\begin{aligned} u_{ij}(r) &= \infty \ , & r < R_1 \\ &= \frac{z_i z_j e^2}{r}, & r > R_1 \ , \end{aligned} \tag{2.2}$$

ion–dipole

$$\begin{aligned} u_{id}(\mathbf{r}, \omega) &= \infty \ , & r < R_{12} \equiv \tfrac{1}{2}(R_1 + R_2) \\ &= \frac{-z_i e \mu(\omega) \cdot \hat{r}}{r^2}, & r > R_{12} \ , \end{aligned} \tag{2.3}$$

dipole–dipole

$$\begin{aligned} u_{dd}(\omega_1, \mathbf{r}, \omega_2) &= \infty \ , & r < R_2 \\ &= -\frac{\mu^2 D_{12}}{r^3} \ , & r > R_2 \ , \end{aligned} \tag{2.4}$$

and

$$D_{12} \equiv \hat{\mu}(\omega_1) \cdot (3\hat{r}\hat{r} - \mathbf{I}) \cdot \hat{\mu}(\omega_2) \ , \tag{2.5}$$

where e is the protonic charge and $\mathbf{I}$ the 3×3 unit tensor. $\hat{\mu}(\omega)$ is a unit vector in the direction of the angle variable $\omega = (\theta, \phi)$ with $\int d\omega = 4\pi$. The subscripts $i, j, k, \ldots$ will hereafter be reserved for ionic quantities and the subscript d for dipoles. The vector $\mathbf{r}$ specifies the relative position of the centers of the molecules and is directed from the first molecule towards the second, e.g., in $u_{id}(\mathbf{r})$, $\mathbf{r} \equiv \mathbf{r}_d - \mathbf{r}_i$.

In a microscopic description of a fluid the quantity which embodies the important features of molecular structure is the probability of finding two particles in a given configuration or equivalently the *pair distribution function* $g = 1 + h$, where h is the *total correlation function*. The *potential of mean force* W which describes the interaction between two particles averaged over the configurations of the rest of the particles in the system is given by ($\beta = 1/kT$)

$$\beta W \equiv -\ln g = -\ln(1 + h) \ . \tag{2.6}$$

Our aim, therefore, is to calculate one of the quantities W, g, or h, whichever is most convenient.

We give a pedagogical derivation of the Mean Spherical Approximation (MSA) by reformulating the Debye–Hückel and Poisson–Boltzmann theory in term distribution functions. Then it will become clear that the MSA is a logical extension of Debye–Hückel theory to include finite in size. Consider an assembly of overall neutral point charges in a medium of unit dielectric constant. The electrostatic potential at a distance r from an ion having valence z_i is

$$\psi_i(r) = \frac{z_i e}{r} + \int d\mathbf{r}' \sum_k \frac{\rho_k z_k e h_{ik}(r')}{|\mathbf{r} - \mathbf{r}'|} \ . \tag{2.7}$$

The first term on the rhs is the direct Coulomb potential. Contributions to $\psi_i(r)$ from the adsorption excess of other ions about the ith ion are contained in the second term. To be exact, the pair distribution function g_{ik} should appear in place of the total correlation function $h_{ik} = g_{ik} - 1$. However, the constant term vanishes because of the charge neutrality condition [Eq. (2.1)]. The mean electrostatic energy between two ions i and j is $z_j e \psi_i(r)$. The Debye–Hückel or Poisson–Boltzmann theory approximates the potential of mean force by the mean electrostatic potential, that is, we write

$$\beta W_{ij}(r) = -\ln(1 + h_{ij}(r)) \approx \beta z_j e \psi_i(r) \ . \tag{2.8}$$

Combining Eqs. (2.7) and (2.8) gives a closed set of equations for the total correlation functions, $h_{ij}(r)$, which is equivalent to the Poisson–Boltzmann equation. However, for *point* ions, this leads to nonintegrable divergences in $h_{ij}(r)$ as $r \to 0$. If $h_{ij}(r) < 1$ we can expand the logarithm in Eq. (2.8). Keeping only the linear term and write

$$h_{ij}(r) \approx -\beta z_j e \psi_i(r) \tag{2.9}$$

gives the Debye–Hückel theory. This can be readily verified by combining Eqs. (2.7) and (2.9) and noting that the $h_{ij}(r)$ or $\psi_i(r)$ is of the form $\sim e^{-\kappa r}/r$.

If the ions have finite size, a hard sphere diameter, R_1 say, the centers of any two ions must be separated by at least one diameter. Thus we have the exact condition on the pair distribution function

$$g_{ij}(r) = 1 + h_{ij}(r) = 0 \ . \tag{2.10}$$

Now we can write the result of combining Eqs. (2.7) and (2.8) as

$$\ln(1 + h_{ij}(r)) = c_{ij}(r) + \sum_k \rho_k \int d\mathbf{r}' \, h_{ik}(r') c_{kj}(|\mathbf{r} - \mathbf{r}'|) \ . \tag{2.11}$$

The direct correlation function $c_{ij}(r)$ is given by

$$c_{ij}(r) = -\frac{\beta z_i z_j e^2}{r} \equiv -\beta u_{ij}(r) \ , \quad r > R_1 \ . \tag{2.12}$$

This form for $c_{ij}(r)$ is only valid for $r > R_1$ because for $r < R_1$, $h_{ij}(r)$ is given exactly by Eq. (2.10) so we must use Eq. (2.11) to determine $c_{ij}(r)$ for $r < R_1$. Equations (2.10)–(2.12) constitute the nonlinear MSA or EXP-MSA. It can be regarded as a natural extension of the Poisson–Boltzmann equation to include finite ion size. The MSA further replaces $\ln(1 + h_{ij}(r))$ by $h_{ij}(r)$ in Eq. (2.11). This last approximation gives a Debye–Hückel type approximation with finite size and has the added advantage that the resulting linear equations for $h_{ij}(r)$ have analytic solutions.

For the ion/dipole mixture, the physics is similar and additional equations like (2.11) are required to describe ion–dipole and dipole–dipole correlations. It is important to note that with a dipolar solvent, it is not possible to consider point dipoles as with the case for ions. As $r \to 0$, the r^{-3} divergence in the dipole–dipole potential renders the concept of a point dipole unphysical.[20] In the limit in which the ions and dipoles are completely discharged, the MSA reduces to a hard sphere fluid to be solved in the Percus–Yevick approxi-

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TABLE I. Multiplication table for the angular convolution $1/4\pi \int A(\omega_1, \omega_3)B(\omega_3, \omega_2)d\omega_3$.

$A(\omega_1, \omega_3)$ \ $B(\omega_3, \omega_2)$	1	Δ_{32}	D_{32}	E_3	E_2
1	1	0	0	0	E_2
Δ_{13}	0	$\frac{1}{3}\Delta_{12}$	$\frac{1}{3}D_{12}$	$\frac{1}{3}E_1$	0
D_{13}	0	$\frac{1}{3}D_{12}$	$\frac{1}{3}(D_{12}+2\Delta_{12})$	$\frac{2}{3}E_1$	0
E_3	0	$\frac{1}{3}E_2$	$\frac{2}{3}E_2$	$\frac{1}{3}$	0
E_1	E_1	0	0	0	$\frac{1}{3}(D_{12}+\Delta_{12})$

mation which is known to give a good description for such systems.

In the next section, we give the solution of the linearized version of Eq. (2.11) for a system of hard sphere ion and dipoles. However, in interpreting the results for the ion–ion potential of mean force in the limit of zero ionic concentration we shall retain the nonlinear equation for the ion–ion correlation function.

III. THE MSA: METHOD OF SOLUTION

Adelman and Deutch[13] and Blum[14] have solved the statistical mechanics of an equal size hard sphere ion/dipole mixture in the MSA. Their method of solution requires considerable dexterity in the manipulation of rotational invariants. Our solution for the case of unequal size ion/dipole mixture is along the lines of Wertheim's solution of the MSA dipolar fluid,[20] and where possible we retain his notation. Explicit answers are obtained by the Baxter–Wiener–Hopf factorization method.[21]

The MSA for the hard sphere ion/dipole mixture can be cast as the solution of the Ornstein–Zernike (OZ) equations for the ion–ion correlation function

$$h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k \int d\mathbf{s}\, c_{ik}(|\mathbf{r}-\mathbf{s}|)h_{kj}(s) + \frac{\rho_d}{4\pi}\int d\omega_3\, d\mathbf{s}\, c_{id}(\mathbf{r}-\mathbf{s}, \omega_3)h_{dj}(\omega_3, \mathbf{s}) , \quad (3.1a)$$

the ion–dipole correlation function

$$h_{id}(\mathbf{r}, \omega_2) = c_{id}(\mathbf{r}, \omega_2) + \sum_k \rho_k \int d\mathbf{s}\, c_{ik}(|\mathbf{r}-\mathbf{s}|)h_{kd}(\mathbf{s}, \omega_2) + \frac{\rho_d}{4\pi}\int d\omega_3\, d\mathbf{s}\, c_{id}(\mathbf{r}-\mathbf{s}, \omega_3)h_{dd}(\omega_3, \mathbf{s}, \omega_2) , \quad (3.1b)$$

the dipole–ion correlation function

$$h_{di}(\omega_1, \mathbf{r}) = c_{di}(\omega_1, \mathbf{r}) + \sum_k \rho_k \int d\mathbf{s}\, c_{dk}(\omega_1, \mathbf{r}-\mathbf{s})h_{ki}(s) + \frac{\rho_d}{4\pi}\int d\omega_3\, d\mathbf{s}\, c_{dd}(\omega_1, \mathbf{r}-\mathbf{s}, \omega_3)h_{di}(\omega_3, \mathbf{s}) , \quad (3.1c)$$

and the dipole–dipole correlation function

$$h_{dd}(\omega_1, \mathbf{r}, \omega_2) = c_{dd}(\omega_1, \mathbf{r}, \omega_2) + \sum_k \rho_k \int d\mathbf{s}\, c_{dk}(\omega_1, \mathbf{r}-\mathbf{s})h_{kd}(\mathbf{s}, \omega_2) + \frac{\rho_d}{4\pi}\int d\omega_3\, d\mathbf{s}\, c_{dd}(\omega_1, \mathbf{r}-\mathbf{s}, \omega_3)h_{dd}(\omega_3, \mathbf{s}, \omega_2) , \quad (3.1d)$$

where the summation is over all ionic species. The MSA closure conditions for the OZ equation are

$$c_{ij}(r) = -\frac{z_i z_j \beta e^2}{r} , \quad r > R_1 \quad (3.2a)$$

$$c_{id}(\mathbf{r}, \omega_2) = \frac{z_i \beta e \mu}{r^2} E_2 , \quad r > R_{12} \quad (3.2b)$$

$$c_{di}(\omega_1, \mathbf{r}) = -\frac{z_i \beta e \mu}{r^2} E_1 , \quad r > R_{12} \quad (3.2c)$$

$$c_{dd}(\omega_1, \mathbf{r}, \omega_2) = \frac{\beta \mu^2}{r^3} D_{12} , \quad r > R_2 , \quad (3.2d)$$

where D_{12} was defined in Eq. (2.5) and

$$E_\alpha \equiv \hat{\mu}(\omega_\alpha) \cdot \hat{r} , \quad \alpha = 1, 2 . \quad (3.3)$$

We recall our convention that the vector $\mathbf{r}$ in Eqs. (3.2b) and (3.2c) is directed from the first particle towards the second, and the subscripts $i, j, k, \ldots$ denote ions and d, dipoles. In addition to Eq. (3.2) we also have the exact hard core conditions

$$h_{ij}(r) = -1 , \quad r < R_1 \quad (3.4a)$$

$$h_{id}(\mathbf{r}, \omega_2) = h_{di}(\omega_1, \mathbf{r}) = -1 , \quad r < R_{12} \quad (3.4b)$$

$$h_{dd}(\omega_1, \mathbf{r}, \omega_2) = -1 , \quad r < R_2 . \quad (3.4c)$$

We can proceed to examine the decomposition of the correlation functions into various angular components. If we introduce the angular function

$$\Delta_{12} = \hat{\mu}(\omega_1) \cdot \hat{\mu}(\omega_2) \quad (3.5)$$

we find that the function 1, E, Δ, and D form a closed set under the angular convolution $1/4\pi \int A(\omega_1, \omega_3)B(\omega_3, \omega_2)d\omega_3$. The multiplication table for these quantities is set out in Table I. This can be derived using the identities

$$\frac{1}{4\pi}\int d\omega\, \hat{\mu}(\omega) = 0 \quad (3.6)$$

$$\frac{1}{4\pi}\int d\omega\, \hat{\mu}(\omega)\hat{\mu}(\omega) = \tfrac{1}{3}\mathbf{I} \quad (3.7)$$

and noting that for $\mathbf{T} = 3\hat{r}\hat{r} - \mathbf{I}$ we have the matrix multiplication

$$\mathbf{T}\mathbf{T} = \mathbf{T} + 2\mathbf{I} . \quad (3.8)$$

The existence of a closed set of angular functions together with the fact that all ions have the same hard

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sphere diameter strongly suggest an *ansatz* of the form

$$f_{ij}(r) \equiv f_{11}^{\rm HS}(r) + z_i z_j f^C(r) \tag{3.9a}$$

$$f_{id}(\mathbf{r}, \omega_2) \equiv f_{12}^{\rm HS}(r) + z_i f^E(r) E_2 \tag{3.9b}$$

$$f_{di}(\omega_1, \mathbf{r}) \equiv f_{21}^{\rm HS}(r) - z_i f^E(r) E_1 \tag{3.9c}$$

$$f_{dd}(\omega_1, \mathbf{r}, \omega_2) \equiv f_{22}^{\rm HS}(r) + f^\Delta(r)\Delta_{12} + f^D(r) D_{12}\,, \tag{3.9d}$$

where f stands for h or c and by symmetry $f_{12}^{\rm HS} = f_{21}^{\rm HS}$. The functions $f_{\alpha\beta}^{\rm HS}$ ($\alpha, \beta = 1$ or 2) will later turn out to be the Percus–Yevick hard sphere correlation function which describes density–density correlations. This unsatisfactory feature of the MSA is due to its failure to take into account the angle averaged potential which affects density–density correlations. Charge–charge correlations are given by f^C, charge–dipole by f^E, and dipole–dipole by f^Δ and f^D. Note that all these functions only depend on $r = |\mathbf{r}|$. This form of the decomposition, in particular, the simple explicit dependence on valence follows from the fact that all ions have identical size. Otherwise the hard sphere correlation functions will also depend on the valence and furthermore terms in E_1 and E_2 will have to be added to the dipole–dipole correlation functions, Eq. (3.9d).

The problem is now reduced to solving for the seven functions introduced in Eq. (3.9). We use this decomposition in the OZ equation (3.1) and effect the Fourier transform over $\mathbf{r}$ space using the convolution theorem. However, because of the dependence upon $\hat{\mathbf{r}}$ in the angular functions E and D, functions associated with these quantities transform in a slightly different way. Adopting the notation

$$\tilde{f}(\mathbf{k}) = \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}) \tag{3.10}$$

the Fourier transform of Eq. (3.1) becomes

$$\tilde{h}_{ij}(k) = \tilde{c}_{ij}(k) + \sum_k \rho_k \tilde{c}_{ik}(k)\tilde{h}_{kj}(k) + \frac{\rho_d}{4\pi}\int d\omega_3\, \tilde{c}_{id}(\mathbf{k}, \omega_3)\tilde{h}_{dj}(\omega_3, \mathbf{k}) \tag{3.11a}$$

$$\tilde{h}_{id}(\mathbf{k}, \omega_2) = \tilde{c}_{id}(\mathbf{k}, \omega_2) + \sum_k \rho_k \tilde{c}_{ik}(k)\tilde{h}_{kd}(\mathbf{k}, \omega) + \frac{\rho_d}{4\pi}\int d\omega_3\, \tilde{c}_{id}(\mathbf{k}, \omega_3)\tilde{h}_{dd}(\omega_3, \mathbf{k}, \omega_2) \tag{3.11b}$$

$$\tilde{h}_{di}(\omega_1, \mathbf{k}) = \tilde{c}_{di}(\omega_1, \mathbf{k}) + \sum_k \rho_k \tilde{c}_{dk}(\omega_1, \mathbf{k})\tilde{h}_{ki}(k) + \frac{\rho_d}{4\pi}\int d\omega_3\, \tilde{c}_{dd}(\omega_1, \mathbf{k}, \omega_3)\tilde{h}_{di}(\omega_3, \mathbf{k}) \tag{3.11c}$$

$$\tilde{h}_{dd}(\omega_1, \mathbf{k}, \omega_2) = \tilde{c}_{dd}(\omega_1, \mathbf{k}, \omega_2) + \sum_k \rho_k \tilde{c}_{dk}(\omega_1, \mathbf{k})\tilde{h}_{kd}(\mathbf{k}, \omega_2) + \frac{\rho_d}{4\pi}\int d\omega_3\, \tilde{c}_{dd}(\omega_1, \mathbf{k}, \omega_3)\tilde{h}_{dd}(\omega_3, \mathbf{k}, \omega_2)\,, \tag{3.11d}$$

where [$\tilde{f} = \tilde{h}$ or $\tilde{c}$, cf., Eqs. (3.9)]

$$\tilde{f}_{ij}(k) = \tilde{f}_{11}^{\rm HS}(k) + z_i z_j \tilde{f}^C(k) \tag{3.12a}$$

$$\tilde{f}_{id}(\mathbf{k}, \omega_2) = \tilde{f}_{12}^{\rm HS}(k) + z_i \tilde{f}^E(k)\tilde{E}_2 \tag{3.12b}$$

$$\tilde{f}_{di}(\omega_1, \mathbf{k}) = \tilde{f}_{21}^{\rm HS}(k) - z_i \tilde{f}^E(k)\tilde{E}_1 \tag{3.12c}$$

$$\tilde{f}_{dd}(\omega_1, \mathbf{k}, \omega_2) = \tilde{f}_{22}^{\rm HS}(k) + \tilde{f}^\Delta(k)\Delta_{12} + \tilde{f}^D(k)\tilde{D}_{12} \tag{3.12d}$$

with

$$\tilde{E}_\alpha = \hat{\mu}(\omega_\alpha)\cdot\hat{k}\,, \qquad \alpha = 1, 2 \tag{3.13}$$

$$\tilde{D}_{12} = \hat{\mu}(\omega_1)\cdot(3\hat{k}\hat{k} - \mathbf{I})\cdot\hat{\mu}(\omega_2) \tag{3.14}$$

and

$$\tilde{f}^D(k) = -4\pi\int_0^\infty dr\, r^2 j_2(kr) f^D(r) \tag{3.15a}$$

$$\tilde{f}^E(k) = -4\pi i\int_0^\infty dr\, r^2 j_1(kr) f^E(r) \tag{3.15b}$$

$$\tilde{f}(k) = 4\pi\int_0^\infty dr\, r^2 j_0(kr) f(r) \tag{3.15c}$$

$\tilde{f}$ being $\tilde{f}_{\alpha\beta}^{\rm HS}$ ($\alpha, \beta = 1, 2$), $\tilde{f}^\Delta$ or $\tilde{f}^C$ and $j_n(x)$ is the spherical Bessel function.[22]

We must now combine Eqs. (3.11) and (3.12) to see how the various angular components are coupled by the angular convolution. Before doing so it is convenient to construct two *orthogonal* angular functions out of Δ and $\tilde{D}$. These are

$$J^+ \equiv \Delta + 2\tilde{D} \tag{3.16a}$$

$$J^- \equiv \Delta - \tilde{D} \tag{3.16b}$$

with corresponding coefficients ($f = h$ or c)

$$\tilde{f}^+ \equiv \tilde{f}^\Delta + 2\tilde{f}^D \tag{3.17a}$$

$$\tilde{f}^- \equiv \tilde{f}^\Delta - \tilde{f}^D\,. \tag{3.17b}$$

With the aid of Table I we can summarise the result of combining Eqs. (3.11), (3.12), (3.16), and (3.17) as

$$\tilde{h}_{\alpha\beta}(\omega_1, \omega_2) = \tilde{c}_{\alpha\beta}(\omega_1, \omega_2) + \frac{1}{4\pi}\sum_\gamma \rho_\gamma \int d\omega_3\, \tilde{c}_{\alpha\gamma}(\omega_1, \omega_3)\tilde{h}_{\gamma\beta}(\omega_3, \omega_2) \tag{3.18}$$

when the angular components are represented as vectors, Eq. (3.18) has the form

$$\begin{bmatrix} 1 \\ \tilde{E}_1 \\ \tilde{E}_2 \\ J^+ \\ J^- \end{bmatrix}_{\alpha\beta} = \begin{bmatrix} 1 \\ \tilde{E}_1 \\ \tilde{E}_2 \\ J^+ \\ J^- \end{bmatrix}_{\alpha\beta} + \rho_\gamma \begin{bmatrix} 1 & \frac{1}{3}\tilde{E}_2 & 0 & 0 & 0 \\ \tilde{E}_1 & \frac{1}{3}J^+ & 0 & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{3}\tilde{E}_2 & 0 \\ 0 & 0 & \tilde{E}_1 & \frac{1}{3}J^+ & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{3}J^- \end{bmatrix}_{\alpha\gamma} \begin{bmatrix} 1 \\ \tilde{E}_1 \\ \tilde{E}_2 \\ J^+ \\ J^- \end{bmatrix}_{\gamma\beta} \tag{3.19}$$

It is now a straightforward matter to use Eq. (3.19) to write out explicitly the various coupled equations generated by the angular convolution. In all there are seven distinct equations which decouple into three separate groups. We list first the scalar (angle independent) functions:

$$\text{I:}\quad \tilde{h}_{11}^{\rm HS}(k) = \tilde{c}_{11}^{\rm HS}(k) + \left(\sum_i \rho_i\right)\tilde{c}_{11}^{\rm HS}(k)\tilde{h}_{11}^{\rm HS}(k) + \rho_d \tilde{c}_{12}^{\rm HS}(k)\tilde{h}_{21}^{\rm HS}(k) \tag{3.20}$$

$$\begin{aligned}\text{II:}\quad \tilde{h}_{12}^{\rm HS}(k) &= \tilde{c}_{12}^{\rm HS}(k) + \left(\sum_i \rho_i\right)\tilde{c}_{11}^{\rm HS}(k)\tilde{h}_{12}^{\rm HS}(k) + \rho_d \tilde{c}_{12}^{\rm HS}(k)\tilde{h}_{22}^{\rm HS}(k) \\ &= \tilde{c}_{21}^{\rm HS}(k) + \left(\sum_i \rho_i\right)\tilde{c}_{21}^{\rm HS}(k)\tilde{h}_{11}^{\rm HS}(k) + \rho_d \tilde{c}_{22}^{\rm HS}(k)\tilde{h}_{21}^{\rm HS}(k) \\ &= \tilde{h}_{21}^{\rm HS}(k)\end{aligned} \tag{3.21}$$

$$\text{III:}\quad \tilde{h}_{22}^{\rm HS}(k) = \tilde{c}_{22}^{\rm HS}(k) + \left(\sum_i \rho_i\right)\tilde{c}_{21}^{\rm HS}(k)\tilde{h}_{12}^{\rm HS}(k) + \rho_d \tilde{c}_{22}^{\rm HS}(k)\tilde{h}_{22}^{\rm HS}(k) \tag{3.22}$$

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From the closure relations, Eqs. (3.2) and (3.4), we can see that these three equations are just the OZ equations with the Percus–Yevick closure for a mixture of hard spheres of diameter R_1 at density $(\sum_i \rho_i)$ and diameter R_2 at density ρ_d. The solution to these equations are known.[21] The remaining scalar equation, which can be decoupled from the hard sphere equations by the electroneutrality condition [Eq. (2.1)], together with the E and J^+ functions form the next group of coupled equations

$$\text{IV:}\quad \tilde{h}^C(k) = \tilde{c}^C(k) + \rho_c \tilde{c}^C(k)\tilde{h}^C(k) - \tfrac{1}{3}\rho_d \tilde{c}^E(k)\tilde{h}^E(k) \tag{3.23}$$

$$\begin{aligned}\text{V:}\quad \tilde{h}^E(k) &= \tilde{c}^E(k) + \rho_c \tilde{c}^E(k)\tilde{h}^C(k) + \tfrac{1}{3}\rho_d \tilde{c}^+(k)\tilde{h}^E(k)\\ &= \tilde{c}^E(k) + \rho_c \tilde{c}^C(k)\tilde{h}^E(k) + \tfrac{1}{3}\rho_d \tilde{c}^E(k)\tilde{h}^+(k)\end{aligned} \tag{3.24}$$

$$\text{VI:}\quad \tilde{h}^+(k) = \tilde{c}^+(k) - \rho_c \tilde{c}^E(k)\tilde{h}^E(k) + \tfrac{1}{3}\rho_d \tilde{c}^+(k)\tilde{h}^+(k)\ , \tag{3.25}$$

where

$$\rho_c \equiv \sum_i \rho_i z_i^2\ . \tag{3.26}$$

Again it follows from the closure conditions (3.2) that this group of functions C, E, and J^+ describe correlations due to electrostatic interactions. Finally the J^- function is decoupled from the rest:

$$\text{VII:}\quad \tilde{h}^-(k) = \tilde{c}^-(k) + \tfrac{1}{3}\rho_d \tilde{c}^-(k)\tilde{h}^-(k)\ . \tag{3.27}$$

The J^+ and J^- functions also occur in the MSA solution for the pure hard sphere dipole fluid.[20] Here we see that the J^- function is *not* affected by the addition of ions and therefore remains the same as that for the pure dipolar fluid.

The decoupling of the J^- function has a simple physical interpretation. Consider a dipolar system in an external electric field, $\mathbf{E}^{\text{ext}}$ which couples with the system by an additional term in the Hamiltonian of the form $-\boldsymbol{\mu}\cdot\mathbf{E}^{\text{ext}}$. From linear response theory the induced dipole moment in k space is[16]:

$$\begin{aligned}\langle\mu\rangle &= \beta\langle\mu\mu\rangle\cdot\tilde{\mathbf{E}}^{\text{ext}}(k)\\ &= \left\{\beta/(4\pi)^2\int d\omega_1 d\omega_2 \mu(\omega_1)\tilde{h}_{dd}(\omega_1,\mathbf{k},\omega_2)\mu(\omega_2)\right\}\cdot\tilde{\mathbf{E}}^{\text{ext}}(k)\\ &= (\beta/9)\tilde{h}^+(k)[\hat{k}\cdot\mathbf{E}^{\text{ext}}(k)] + (\beta/9)\tilde{h}^-(k)[\hat{k}\times\mathbf{E}^{\text{ext}}(k)]\ .\end{aligned} \tag{3.28}$$

Now it is obvious that h^+ and h^- are, respectively, the longitudinal and transverse (relative to $\hat{k}$) response functions of a dipolar system. The electrostatic Coulomb potential is a longitudinal field and therefore only couples with J^+ functions while the transverse response of a dipolar system is unaffected by the addition of ions.

In fact it is possible to give a definition of the longitudinal dielectric constant of an ion/dipole mixture in the MSA via the Stillinger–Lovett condition.[23] We sketch the derivation briefly only as details may be found in Ref. 16. We begin with Eqs. (3.23) and (3.24) and let the various functions have expansions of the general form as $k\to 0$[16]:

$$\begin{aligned}\tilde{h}^C(k) &= \tilde{h}^C(0) + k^2\tilde{h}_2^C + \cdots\\ \tilde{h}^E(k) &= k\,\tilde{h}_1^E + \cdots\\ \tilde{c}^C(k) &= -\frac{4\pi\beta e^2}{k^2} + \tilde{c}_0^C + \cdots\\ \tilde{c}^E(k) &= -\frac{4\pi i\beta e\mu}{k} + k\,\tilde{c}_1^E + \cdots\\ \tilde{c}^+(k) &= \tilde{c}^+(0) + \cdots\ ,\end{aligned} \tag{3.29}$$

where $\tilde{h}_2^C$, $\tilde{h}_1^E$, $\tilde{c}_0^C$, and $\tilde{c}_1^E$ are constants.

Combining Eqs. (3.23), (3.24), and (3.29) we can equate coefficients of powers of k. The electroneutrality condition follows from equating the coefficients of k^{-2}

$$\rho_c\tilde{h}^C(0) = -1\ . \tag{3.30}$$

The coefficients of k^0 gives the Stillinger–Lovett condition:

$$4\pi\beta e^2\rho_c^2\tilde{h}_2^C\left\{1 - \frac{4\pi\beta\rho_d\mu^2/3}{1-\frac{1}{3}\rho_d\tilde{c}^+(0)}\right\} = 1 \tag{3.31}$$

from which we can identify the longitudinal dielectric constant of the ion dipole mixture, ϵ_L

$$\frac{1}{\epsilon_L} = 1 - \frac{4\pi\beta\rho_d\mu^2/3}{1-\frac{1}{3}\rho_d\tilde{c}^+(0)}\ . \tag{3.32}$$

This quantity measures the longitudinal response of the dipoles which takes into account the presence of the ions, but the direct response of the ions, namely the conductivity, has been substracted out. Experimentally one would measure ϵ_L at a frequency too high for the ions to respond (above the plasma frequency, say) and yet low enough so that the dipoles still see an essentially static field.

Before we proceed to extract asymptotic forms for the distribution functions in the limit of low ionic concentration let us briefly recapitulate the known MSA results for a pure dipolar fluid.[20] It can be shown that $h^\pm$ and $c^\pm$ satisfy the Percus–Yevick equation for hard spheres at renormalized reduced densities. In particular

$$1 - \tfrac{1}{3}\rho_d\tilde{c}^+(0) = q(2\xi) \equiv q_+ \tag{3.33a}$$

$$1 - \tfrac{1}{3}\rho_d\tilde{c}^-(0) = q(-\xi) \equiv q_-\ , \tag{3.33b}$$

where $q(\eta)$ is the Percus–Yevick hard sphere inverse compressibility at reduced density η

$$q(\eta) = \frac{(1+2\eta)^2}{(1-\eta)^4} \tag{3.34}$$

and the constant ξ is the solution of the equation

$$q_+ - q_- \equiv \frac{(1+4\xi)^2}{(1-2\xi)^4} - \frac{(1-2\xi)^2}{(1+\xi)^4} = \frac{4\pi}{9}\beta\rho_d\mu^2\ . \tag{3.35}$$

The dielectric constant of the pure dipolar fluid is given by

$$\epsilon = q_+/q_-\ . \tag{3.36}$$

It is *independent* of the hard sphere diameter of the dipoles and is only a function of the dipole moment and number density of the fluid through the dimensionless constant

$$y \equiv \frac{4\pi\beta\rho_d\mu^2}{9}\ . \tag{3.37}$$

A. Asymptotic forms of distribution functions

At low ionic densities ($\rho_c\to 0$), the large distance behavior of the distribution functions can be obtained di-

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rectly from Eqs. (3.23)–(3.25) at $k\sim 0$. From Eqs. (3.2), (3.12), and (3.15) we have as $k\to 0$

$$\tilde{c}^C(k)\to -\frac{4\pi\beta e^2}{k^2} \tag{3.38a}$$

$$\tilde{c}^E(k)\to -4\pi i\frac{\beta e\mu}{k}\,. \tag{3.38b}$$

Combining Eqs. (3.23) and (3.24) we get

$$\tilde{h}^C(k)=\frac{\tilde{c}^C-\frac{1}{3}\rho_d(\tilde{c}^C\tilde{c}^+ + \tilde{c}^E\tilde{c}^E)}{(1-\rho_c\tilde{c}^C)(1-\frac{1}{3}\rho_d\tilde{c}^+)+\frac{1}{3}\rho_c\rho_d\tilde{c}^E\tilde{c}^E} \tag{3.39}$$

$$\to -\frac{4\pi\beta e^2}{\epsilon}\frac{1}{k^2+\kappa_D^2}\,,\quad k\to 0 \tag{3.40}$$

with the aid of Eqs. (3.29), (3.33), and 3.36). Here

$$\kappa_D^2=\frac{4\pi\beta\rho_c e^2}{\epsilon} \tag{3.41}$$

is the classical Debye screening parameter. Fourier inversion of Eq. (3.40) gives the asymptotic form ($r\to\infty$)

$$h_{ij}(r)\to\frac{-z_iz_j\beta e^2}{r}e^{-\kappa_D r}\,. \tag{3.42}$$

From Eqs. (3.24) and 3.39) we can obtain the asymptotic form of the ion–dipole distribution function

$$\tilde{h}^E(k)=\frac{\tilde{c}^E(1+\rho_d\tilde{h}^C)}{(1-\frac{1}{3}\rho_d\tilde{c}^+)} \tag{3.43}$$

$$\to -\frac{4\pi i\beta e(\mu/q_-)}{\epsilon}\frac{k}{k^2+\kappa_D^2}\,,\quad k\to 0 \tag{3.44}$$

or in r space

$$h_{id}(\mathbf{r},\omega)\to\frac{z_i\beta e(\mu/q_-)}{\epsilon r^2}e^{-\kappa_D r}(\hat{\mu}(\omega)\cdot\hat{r})\,,\quad r\to\infty\,. \tag{3.45}$$

Similarly from Eq. (3.25) we get

$$\tilde{h}^+(k)=\frac{\tilde{c}^+-\rho_c(\tilde{c}^+\tilde{c}^C+\tilde{c}^E\tilde{c}^E)}{(1-\rho_c\tilde{c}^C)(1-\frac{1}{3}\rho_d\tilde{c}^+)+\frac{1}{3}\rho_c\rho_d\tilde{c}^E\tilde{c}^E} \tag{3.46}$$

$$\to\frac{3}{\rho_d}\left\{\frac{1}{q_+}\cdot\frac{k^2+\epsilon\kappa_D^2}{k^2+\kappa_D^2}-1\right\}\,,\quad k\to 0 \tag{3.47}$$

whence from Eqs. (3.17), (3.27), and (3.29)

$$\tilde{h}^D(k)\to -\frac{4\pi\beta}{3\epsilon}(\mu/q_-)^2\frac{k^2}{k^2+\kappa_D^2}\,,\quad k\to 0 \tag{3.48}$$

or in r space the asymptotic form of the dipole–dipole correlation function is

$$h_{dd}(\omega_1,\mathbf{r},\omega_2)\to\frac{\beta(\mu/q_-)^2}{\epsilon r^3}e^{-\kappa_D r}D_{12}\,,\quad r\to\infty\,. \tag{3.49}$$

We note the appearance of the expected exponential screening in all the correlation functions where at low ionic concentrations the decay length is the classical Debye value. The effective dipole moment in Eqs. (3.45) and (3.49) coincides with the earlier result[17]

$$\mu^{eff}\equiv\mu/q_-=\left(\frac{\epsilon-1}{3y}\right)\mu$$

$$=\frac{\mu}{1-\frac{1}{3}\rho_d\tilde{c}^-(0)}$$

$$=\mu(1+\tfrac{1}{3}\rho_d\tilde{h}^-(0))=\mu(1+\tfrac{1}{3}\rho_d(\tilde{h}^\Delta(0)-\tilde{h}^D(0)) \tag{3.50}$$

and has the interpretation that the intrinsic dipole is replaced by the dipole plus its surrounding polarization density.

B. The Born energy

The Born energy, that is, the change in free energy due to electrostatic interactions for the transfer of one ion from vacuum into solution at infinite dilution, can be obtained from the coupled equations (3.23)–(3.25), with $\rho_c=0$. Since the functions $\tilde{f}^C$, $\tilde{f}^E$, and $\tilde{f}^+$ ($f=h$ or c), which describe electrostatic interactions, depend only upon $k=|\mathbf{k}|$, they can be transformed back into r space by a *one-dimensional* Fourier inversion

$$F(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dk\,e^{-ikx}\tilde{f}(k)\,. \tag{3.51}$$

The relation between these "one-dimensional" functions (upper case) and their "three-dimensional" counterparts (lower case) follows from Eqs. (3.15) and (3.51): ($f=h$ or c)

$$F^{C,\Delta}(x)=2\pi\int_x^\infty dr\,P_0(x/r)rf^{C,\Delta}(r)$$

$$F^E(x)=2\pi\int_x^\infty dr\,P_1(x/r)rf^E(r) \tag{3.52}$$

$$F^D(x)=2\pi\int_x^\infty dr\,P_2(x/r)rf^D(r)\,,$$

where $P_0(x)=1$, $P_1(x)=x$, $P_2(x)=\frac{1}{2}(3x^2-1)$ are Legendre polynomials; or equivalently

$$2\pi rf^{C,\Delta}(r)=-\frac{d}{dr}F^{C,\Delta}(r)$$

$$2\pi rf^E(r)=\left(\frac{1}{r}-\frac{d}{dr}\right)F^E(r) \tag{3.53}$$

$$\pi^2f^D(r)=-r^2\left(\frac{1}{r}\frac{d}{dr}\right)^2\frac{1}{r}\int_0^r F^D(x)dx\,.$$

Baxter's method[21] provides uncoupled one dimensional integral equations for $H(x)$ and $C(x)$.

By definition, the interaction energy of a single ion with charge (ze) with a dipolar fluid is

$$E_{\text{Born}}=\frac{\rho_d}{4\pi}\iint dr\,d\omega\,u_{id}(\mathbf{r},\omega)g_{id}(\mathbf{r},\omega) \tag{3.54a}$$

$$=-\frac{4\pi}{3}\rho_d\mu z^2e\int_{R_{12}}^\infty dr\,h^E(r)\,, \tag{3.54b}$$

where the second equality follows from Eqs. (2.3), (3.4), (3.9), and Table I. From Eq. (3.52) we see that since $h^E(r)=0$ for $r<R_{12}\equiv\frac{1}{2}(R_1+R_2)$, $H^E(x)$ is a linear function of x in the same range and is continuous at $x=R_{12}$; that is,

$$H^E(x)=2\pi x\int_{R_{12}}^\infty dr\,h^E(r)\equiv xH_1^E\,,\quad x\leq R_{12} \tag{3.55}$$

and the constant H_1^E is required in the expression for the interaction energy

$$E_{\text{Born}}=-\tfrac{2}{3}\rho_d\mu z^2eH_1^E\,. \tag{3.56}$$

We find H_1^E from Eq. (3.24) at $\rho_c=0$

$$\tilde{h}^E(k)=\tilde{c}^E(k)+\tfrac{1}{3}\rho_d\tilde{c}^+(k)\tilde{h}^E(k)\,, \tag{3.57}$$

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where $\tilde{c}^*(k)$ is that for a *pure* dipolar fluid and is known.[20] Baxter's factorization[21] gives for $x > S_{21} \equiv \frac{1}{2}(R_2 - R_1)$

$$H^E(x) = -Q_{21}^E(x) + \tfrac{1}{3}\rho_d \int_0^{R_2} Q^*(y) H^E(x-y)\,dy \tag{3.58}$$

or using Eq. (3.55) when $S_{21} < x \leq R_{12}$

$$xH_1^E = -Q_{21}^E(x) + \tfrac{1}{3}\rho_d H_1^E \int_0^{R_d} (x-y) Q^*(y)\,dy\ , \tag{3.59}$$

where[20]

$$\tfrac{1}{3}\rho_d R_d Q^*(x) = 24\xi[\tfrac{1}{2}a((x/R_2)^2 - 1) + b((x/R_2) - 1)]\ , \quad 0 < x < R_2 \tag{3.60}$$
$$= 0 \text{ otherwise}$$

$$a = \frac{1+4\xi}{(1-2\xi)^2} \equiv q_+^{1/2}\ ; \quad b = -\frac{3\xi}{(1-2\xi)^2} \tag{3.61}$$

and ξ is the solution of Eq. (3.35). Baxter's method also provides another equation for $C(x)$

$$-C^E(x) = Q_{21}^E(x) - \tfrac{1}{3}\rho_d \int_0^{R_2} Q^*(y) Q_{21}^E(x+y)\,dy\ , \quad x > S_{21}\ . \tag{3.62}$$

From Eqs. (3.2), (3.9), and (3.52)

$$C^E(x) = 2\pi \int_x^\infty dr (x/r) r (\beta e\mu/r^2)$$
$$= 2\pi\beta e\mu\ , \quad x \geq R_{12} \tag{3.63}$$

whence from Eq. (3.62)

$$Q_{21}^E(x) = -2\pi\beta e/q_+^{1/2}\ , \quad x \geq R_{12} \tag{3.64}$$

using this result in Eq. (3.59) at $x = R_{12}$ gives

$$H_1^E = \frac{2\pi\beta e\mu/q^*}{\left\{R_{12} + \frac{\rho_d}{3q_+^{1/2}} \int_0^{R_d} dy\, y Q^*(y)\right\}} \tag{3.65}$$

and the final expression for the Born energy can be obtained from a coupling constant integration and using Eq. (3.60)

$$F_{\text{Born}} = \int_0^e (E_{\text{Born}}/e)\,de \tag{3.66a}$$

$$= -\frac{\frac{1}{2}(ze)^2\left(1 - \frac{1}{\epsilon}\right)}{\left\{R_{12} - \frac{3\xi R_2}{(1+4\xi)}\right\}}\ . \tag{3.66b}$$

A discussion on the interpretation of this result is given in Sec. IV.

C. The polarization density about an ion

In this section we derive an expression for the polarization density about a single ion of charge (ze) at infinite dilution, $\rho_c = 0$. By definition the polarization density $\mathbf{P}(r) = P(r)\hat{r}$ is

$$P(r) = \frac{\rho_d}{4\pi} \int d\omega\, g_{id}(\mathbf{r}, \omega)(\mu(\omega)\cdot\hat{r})$$
$$= \tfrac{1}{3}\rho_d \mu h^E(r)\ . \tag{3.67}$$

In the limit $r \to \infty$ this has the form expected from macroscopic electrostatics

$$P(r) \to P_{\text{mac}}(r) \equiv \left(\frac{\epsilon - 1}{4\pi}\right)\frac{ze}{\epsilon r^2}\ , \tag{3.68}$$

where we have used Eq. (3.45) with $\kappa_D = 0$. From Eq. (3.53) we see that

$$h^E(r) = \frac{1}{2\pi r}\left\{\frac{1}{r}H^E(r) - \frac{d}{dr}H^E(r)\right\}\ , \tag{3.69}$$

where $H^E(r)$ is given by Eq. (3.58), and has the asymptotic form, cf. Eq. (3.45),

$$H^E(r) \to \frac{2\pi\beta e\mu}{q_+}\ , \quad r \to \infty\ . \tag{3.70}$$

If we introduce a dimensionless function $F(r)$ by

$$H^E(r) \equiv \frac{2\pi\beta e\mu}{q_+}(F(r) + 1) \tag{3.71}$$

then it follows from Eqs. (3.55), (3.58), and (3.65) that,

$$F(r) = \int_0^{R_2} [\tfrac{1}{3}\rho_d Q^*(s)] F(r-s)\,ds\ , \quad r > R_{12}$$
$$= \frac{r}{R_{12} - \frac{3\xi R_2}{(1+4\xi)}} - 1\ , \quad r < R_{12}\ . \tag{3.72}$$

Since the integral equation for $F(r)$ only relies on earlier values and the kernel is known [Eq. (3.60)] $F(r)$ can be generated by a simple trapezoidal rule. The polarization density can then be written as

$$\frac{P(r)}{P_{\text{mac}}(r)} = 1 - r\frac{dF(r)}{dr} + F(r)\ . \tag{3.73}$$

Numerical values of $P(r)/P_{\text{mac}}(r)$ will be presented in Sec. IV together with a discussion of the implications of the results.

D. The potential of mean force between ions

We derive the potential of mean force between two ions of charge $(z_i e)$ and $(z_j e)$ in a dipolar fluid in the limit of zero ion density $(\rho_c = 0)$ and equal size ions and dipoles, $R_1 = R_2 = R$. Ion–dipole and dipole–dipole distribution functions are calculated in the MSA. However, a nonlinear or EXP–MSA scheme is used to interpret the result for the potential of mean force between the ions. That is, for the ion–ion correlation function, h_{ij} or the potential of mean force, W_{ij} we use

$$g_{ij} = 1 + h_{ij} = \exp[h_{ij}^{\text{MSA}}] \tag{3.74}$$

or equivalently

$$\beta W_{ij} = -h_{ij}^{\text{MSA}}\ , \tag{3.75}$$

where h_{ij}^{MSA} is the ion–ion total correlation function calculated in the MSA. It can be readily shown that when this nonlinear MSA is used to calculate the interaction between charged surfaces across a Debye–Hückel electrolyte ("primitive" model with point ions) the result is equivalent to the so-called superposition or overlap approximation in electrical double layer theory.[24]

We require the MSA ion–ion correlation function which can be obtained from the appropriate factorized equation of Baxter with $\rho_c = 0$.[21] This gives

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$$H^C(r) = Q^C(r) - \tfrac{1}{3}\rho_d \int_0^\infty Q_{12}^E(s) H^E(r-s)ds \ , \quad r \geq R$$
$$\equiv 2\pi \int_r^\infty ds\, s h^C(s) \ . \tag{3.76}$$

We have already seen how to calculate $H^E(r)$ in the preceding section. Differentiation of Eq. (3.76) followed by an integration by parts gives

$$-2\pi r h^C(r) = \frac{dQ^C(r)}{dr} + \tfrac{1}{3}\rho_d [Q_{12}^E(s) H^E(r-s)]_0^\infty - \frac{1}{3}\int_0^R \left[\frac{dQ_{12}^E(s)}{ds}\right] H^E(r-s)ds \ , \quad r \geq R \ . \tag{3.77}$$

The unknowns to be determined are $Q^C(r)$, $Q_{12}^E(r)$, and $H^E(-\infty)$.

The properties of $Q_{12}^E(r)$ for $r > R$ can be obtained from the Baxter equation[21]

$$C^E(r) = Q_{12}^E(r) - \tfrac{1}{3}\rho_d \int_0^{R-r} Q_{21}^E(s) Q^+(r+s)ds \ , \quad r > 0 \ . \tag{3.78}$$

Now since $Q^+(r) = 0$ for $r \geq R$ [cf. Eq. (3.60)] and for $r > R$

$$C^E(r) = 2\pi r \int_r^\infty ds \frac{\beta e \mu}{s^2}$$
$$= 2\pi \beta e \mu \ , \quad r \geq R \tag{3.79}$$

we get

$$Q_{12}^E(r) = 2\pi\beta e\mu \ , \quad r \geq R \ . \tag{3.80}$$

The properties of $Q_{12}^E(r)$ for $r < R$ follows from the factorized equation[21]

$$H^E(r) = Q_{12}^E(r) + \tfrac{1}{3}\rho_d \int_0^R Q_{12}^E(s) H^+(r-s)ds \ , \quad r > 0 \ . \tag{3.81}$$

Here $H^+(r)$ is that for a *pure* dipolar fluid and is known to be a quadratic function for $r < R$[20]

$$H^+(r) = H^+(0) + \left(\frac{36\xi}{\rho_d R^3}\right) r^2 \ , \quad r < R \ . \tag{3.82}$$

From Eqs. (3.55), (3.81), and (3.82) we see that $Q_{12}^E(r)$ must be also a quadratic function for $r < R$ and since $Q_{12}^E(r)$ is continuous at $r = R$ it must be of the form

$$Q_{12}^E(r) = a(r^2 - R^2) + bR(r-R) + 2\pi\beta e\mu \ , \tag{3.83}$$

where the constants a and b can be determined by substitution into Eq. (3.81). This gives

$$a = \frac{(2\pi\beta e\mu/R^2)}{(1+12\xi-4\xi^2)} \times \left\{12\xi(1+4\xi) - 6\xi\left[12\xi + \frac{(1-2\xi)^4}{(1+4\xi)(1+\xi)}\right]\right\} \tag{3.84}$$

$$b = \frac{(2\pi\beta e\mu/R^2)}{(1+12\xi-4\xi^2)} \times \left\{(1+8\xi)\left[12\xi + \frac{(1-2\xi)^4}{(1+4\xi)(1+\xi)}\right] - 72\xi^2\right\} \ . \tag{3.85}$$

The constant $H^E(-\infty)$, required in Eq. (3.77), can be determined by observing that $H^E(r)$ is an odd function of r and therefore

$$H^E(-\infty) = -H^E(\infty)$$
$$= -2\pi \lim_{r\to\infty} r \int_r^\infty ds\, h^E(s)$$
$$= -2\pi r \int_r^\infty ds \left(\frac{\beta e\mu}{q_+ s^2}\right)$$
$$= -\frac{2\pi\beta e\mu}{q_+} \ . \tag{3.86}$$

Finally the function $Q^C(r)$ required in Eq. (3.77) can be obtained from the Baxter equation[21]

$$C^C(r) = Q^C(r) - \tfrac{1}{3}\rho_d \int_0^\infty Q_{21}^E(s) Q_{21}^E(r+s)ds \ , \quad r > 0 \ . \tag{3.87}$$

Now for $r > R$, $Q_{21}^E(r)$ is a constant [Eq. (3.64)]. Thus differentiating Eq. (3.87) with respect to r and using the fact that

$$\frac{d}{dr} C^C(r) = -2\pi r c^C(r)$$
$$= 2\pi\beta e^2 \ , \quad r > R \tag{3.88}$$

we get

$$\frac{dQ^C(r)}{dr} = 2\pi\beta e^2 \ , \quad r > R \ . \tag{3.89}$$

Having determined $Q^C(r)$, $Q_{12}^E(r)$, and $H^E(-\infty)$ we can now calculate the electrostatic part of the MSA ion–ion total correlation h^C using Eq. (3.77). This can be done most efficiently by making the substitution

$$h^C(r) \equiv -\frac{\beta e^2}{\epsilon r}[1 + G(r)] \ , \tag{3.90}$$

where the dimensionless function $G(r)$ is given by

$$G(r) = \tfrac{1}{2}(\epsilon - 1)\left\{\int_0^R ds[2A(s/R) + B]F(r-s) - (A+B-1)F(r)\right\} \ , \tag{3.91}$$

where $F(r)$ is the solution of Eq. (3.72) and the constants A, B are related to a, b of Eqs. (3.84) and (3.85) by

$$\begin{Bmatrix} a \\ b \end{Bmatrix} = (2\pi\beta e\mu/R^2) \begin{Bmatrix} A \\ B \end{Bmatrix} \ . \tag{3.92}$$

Following Eq. (3.75) we relate the MSA correlation functions to the potential of mean force between two ions of charge $(z_i e)$ and $(z_j e)$ by [cf. Eq. (3.9a)]

$$\beta W_{ij}(r) = -(h^{HS}(r) + z_i z_j h^C(r)) \ , \tag{3.93}$$

where $h^{HS}(r)$ is the hard sphere total correlation function in the Percus–Yevick approximation.

IV. RESULTS AND DISCUSSION

We present numerical results for the Born energy, the polarization density about an ion, and the ion–ion potential of mean force for an ion/dipole mixture in the MSA in the limit of zero ionic density. Implications of these results on real electrolyte systems as well as constraints in developing more realistic model systems will be discussed.

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A. The Born energy

The Born energy is the electrostatic contribution to the interaction free energy between an ion of charge ze and a solvent in which the ionic density is zero. For an ion/dipole system the statistical mechanical expression for the Born energy F_{Born} is given by Eqs. (3.66a) and 3.54a). For our mean field theory of a hard sphere ion/dipole mixture F_{Born} can be written as [cf. Eq. (3.66b)]

$$F_{\text{Born}} = -\frac{(ze)^2}{2(\frac{1}{2}R_1 + R_s)}\left(1 - \frac{1}{\epsilon}\right), \tag{4.1}$$

where R_1 is the ionic hard sphere *diameter* and

$$R_s \equiv \left(\frac{1}{2} - \frac{3\xi}{1+4\xi}\right)R_2 . \tag{4.2}$$

Here R_2 is the dipole hard sphere *diameter* and the constant ξ $(0<\xi<\frac{1}{2})$ is related to the dipole number density, dipole moment, and the dielectric constant, ϵ of the pure dipolar fluid [see Eqs. (3.35)–(3.37)]. Consequently R_s is a length which depends only on the properties of the dipolar fluid. In the limit of a large ion $(R_1/R_2 \to \infty)$ Eq. (4.1) reduces to the classical expression for the Born energy.

It is interesting to note that an empirical formula of the form identical to Eq. (4.1) has been used for some time to fit experimental solvation energies of ions and free energies of transferring ions between different solvents.[25] For aqueous electrolytes, the literature values of R_s for cations lies in the range 0.64–0.84 Å, and for anions 0.1–0.42 Å. In the MSA, with dielectric constant $\epsilon = 80$ $(\xi = 0.178)$ Eq. (4.2) gives $R_s = 0.56$ Å for $R_2 = 3$ Å.

The interpretation of Eq. (4.1) in terms of a continuum picture of the solvent ion lead to two differing views of the arrangement of solvent molecules in the vicinity of the ion. If one adopts the view that in a continuum picture, the solvent should have the bulk value of the dielectric constant up to the surface of the bare ion then the appearance of the factor $(\frac{1}{2}R_1 + R_s)$ instead of $\frac{1}{2}R_1$, in the expression for the Born energy would be interpreted as "dielectric saturation." That is, "irrotationally bound" dipoles in the vicinity of the ion produce a low value for the dielectric constant and this is parameterized by having a shell around the ion of thickness R_s with unit dielectric constant. However, if one recognizes that the solvent molecules have a finite diameter R_2 then the centers of any solvent molecule and the ion cannot be separated by a distance less than $\frac{1}{2}(R_1 + R_2)$. If beyond this distance the solvent can be characterized by the bulk dielectric constant and then one would expect $\frac{1}{2}R_2$ to appear in place of R_s in the expression for the Born energy. Now since $0<\xi<\frac{1}{2}$, R_s is always *less* than $\frac{1}{2}R_2$, therefore, the solvent appears to have bulk dielectric properties at distances from the ion which are *smaller* than the separation of closest approach between an ion and a dipole. Thus the local dielectric constant appears higher due to the adsorption of dipoles or excess polarization around the ion. The situation becomes clearer when we examine the polarization density about an ion when it can be demonstrated that the concept of a local dielectric constant becomes extremely tenuous.

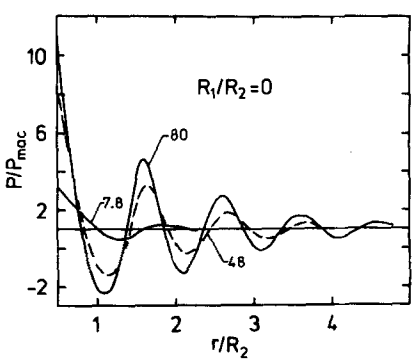

FIG. 1. The normalized polarization density, P/P_{mac} [cf. Eqs. (4.3) and (4.4)] about a point ion, $R_1/R_2 = 0$, as a function of the distance, r from the center of the ion. Curves are labeled with the dielectric constants of the dipolar solvent.

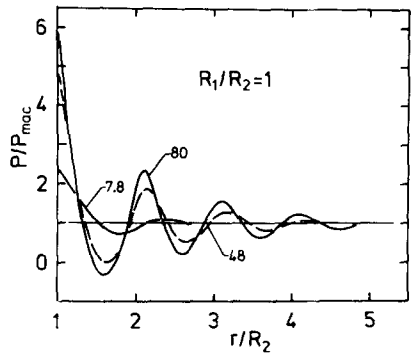

FIG. 2. The normalized polarization density, P/P_{mac} about an ion of the same size as the dipoles, $R_1/R_2 = 1$, as a function of the distance, r from the center of the ion. Curves are labeled with the dielectric constants of the dipolar solvent.

B. The polarization density

The orientation order of dipolar solvent molecules near an ion is contained implicitly in the polarization density or the induced dipole moment per unit volume in the vicinity of the ion. We present results for the polarization density $\mathbf{P}(\mathbf{r}) \equiv P(r)\hat{r}$ about a single ion in the MSA in the limit of zero ionic concentration. The statistical mechanical definition of $P(r)$ is

$$P(r) = \frac{\rho_d}{4\pi}\int d\omega\, g_{id}(\mathbf{r}, \omega)(\mu(\omega)\cdot\hat{r}) . \tag{4.3}$$

In the limit $r \to \infty$ this has the form expected from macroscopic electrostatics

$$P(r) \to P_{\text{mac}}(r) \equiv \left(\frac{\epsilon - 1}{4\pi}\right)\frac{ze}{\epsilon r^2} . \tag{4.4}$$

Our results are given in terms of the ratio $P(r)/P_{\text{mac}}(r)$. The dipolar fluid is chosen to have bulk dielectric constant ϵ equal to 80 $(\xi = 0.1785)$, 48 $(\xi = 0.159)$, and 7.8 $(\xi = 0.086)$. According to the MSA a hard sphere dipolar fluid with the density and intrinsic dipole moment of water $(\mu = 1.8$ D) has a dielectric constant of 48 at room temperatures. A dipole moment of 2.62 D is needed to give a dielectric constant of 80 under the same conditions. The value 7.8 is chosen to facilitate comparison with available Monte Carlo results on ion/dipole mixtures. In Figs. 1 and 2 we plot the ratio $P(r)/P_{\text{mac}}(r)$

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for ion/dipole size ratio $R_1/R_2=0,1$. The polarization density near the ion oscillates about the macroscopic value, in contrast to that predicted by a recent mean field theory.[26] The effects of increasing the ion/dipole size ratio, R_1/R_2 or lowering the bulk dielectric constant is similar; namely, the peaks in $P(r)/P_{mac}(r)$ become lower, broader, and occurs at larger distances from the ion. In one case ($\epsilon=80$) the polarization density has an opposite sign to the macroscopic value within the first shell. This indicates that due to the strong alignment of dipoles immediately adjacent to the ion, solvent molecules which are just away from contact with the ion will in fact prefer to orientate in the opposite direction. Although this phenomenon cannot be excluded from physical considerations, there is still a possibility that it is an artifact of the MSA.

The magnitude of the oscillations in $P(r)/P_{mac}(r)$ is of particular relevance to the concept of a "local" dielectric constant near an ion due to "dielectric saturation." In electrostatic theory the displacement vector D, the macroscopic electric field E_{mac}, and macroscopic polarization density P_{mac} are related by

$$D=E_{mac}+4\pi P_{mac}=\epsilon E_{mac}\ , \tag{4.5}$$

where ϵ is the bulk dielectric constant. In a region where macroscopic theory does not apply, we can still write

$$D=E+4\pi P \tag{4.6}$$

and then to attempt as usual to define a "local" dielectric constant by

$$D\equiv\epsilon_{loc}E\ . \tag{4.7}$$

Specifically for an ion of charge (ze) in a dielectric we have $D=ze/r^2$, $E_{mac}=ze/\epsilon r^2$, and P_{mac} is given by Eq. (4.4). Now combining Eqs. (4.5)–(4.7) we find the general result

$$\frac{E}{E_{mac}}=\frac{\epsilon}{\epsilon_{loc}}=1-(\epsilon-1)\left(\frac{P-P_{mac}}{P_{mac}}\right)\ . \tag{4.8}$$

From the results in Figs. 1 and 2 the large value of ϵ (compared to unity) and oscillations $P(r)/P_{mac}(r)$ imply that the "local" dielectric constant as defined in Eq. (4.7) is an oscillatory function of distance which can even become negative. This is quite different from the normal assumption that ϵ_{loc} is either a step function

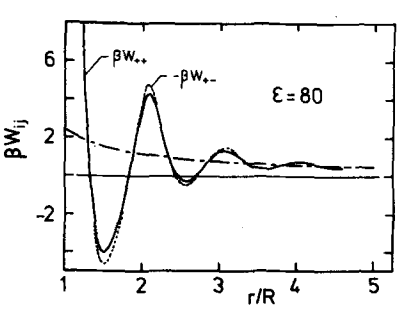

FIG. 3. The potential of mean force between two univalent ions of the same size as the dipoles, $R_1=R_2=R$; for ions have the same signs (——), opposite signs (- - - - -). The function $\beta e^2/\epsilon r$ is shown as (— — —) and the dielectric constant of the dipolar solvent is 80.

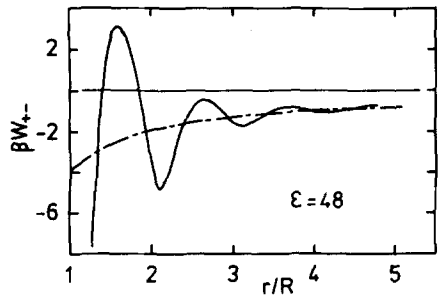

FIG. 4. The potential of the mean force between two univalent ions of the opposite signs and having the same size as the dipoles, $R_1=R_2=R$, (——). The function $-\beta e^2/\epsilon r$ is shown as (— - —) and the dielectric constant of the dipolar solvent is 48.

(representing bound solvent molecules) or some smoothly varying (positive) function of distance. While such models were able to give good fit to experimental results, they may be painting an erroneous picture of the physical situation and as such should be treated with caution.

C. The potential of mean force between ions

We calculate the potential of mean force, W_{ij} between two ions of charge (z_ie) and (z_je) from the MSA correlation function by using a nonlinear or EXP–MSA interpretation in the final step,

$$\left.\begin{aligned}\beta W_{ij}(r)&=-h_{ij}^{MSA}(r)\\&=-(h^{HS}(r)+z_iz_jh^C(r))\end{aligned}\right\}\ . \tag{4.9}$$

It can be shown that when this scheme is used to calculate the interaction between charged surfaces across a Debye–Hückel electrolyte ("primitive" model with point ions) the result is equivalent to the superposition or overlap approximation in electrical double layer theory.[24] The decomposition in Eq. (4.9) is peculiar to the MSA when all the ions have the same size. The term $h^{HS}(r)$ accounts for the solvent mediated interaction between ions due solely to the hard sphere part of their potentials (purely size effects). This is calculated in the Percus–Yevick approximation which is known to give a good description of hard sphere fluids. Electrostatic interactions (charge–charge, charge–dipole, and dipole–dipole) are contained in the term $h^C(r)$. We give results for W_{ij} for the case of equal size ions and dipoles ($R_1=R_2=R$) at zero ionic concentration, and z_i, $z_j=\pm1$.

The potential of mean force between univalent ions are shown in Figs. 3–5. The dielectric constants of the solvent are 80, 48, and 7.8, respectively, obtained by varying the dipole moment. The reduced density of the solvent is held constant at $\rho R^3=0.8$. The continuum theory result in Figs. 3–5 correspond to $T=300$ K and $R=3$ Å. The hard sphere contribution to the potential of mean force is less than 5% in all cases, cf. Fig. 3. The deep minimum in the potential of mean force between ions of *opposite* signs W_{+-} at $r=2R$ suggest the possibility of a relatively stable ion-pairing configuration where the ions are separated by one dipolar solvent molecule (Figs. 3 and 4). It is also interesting to note

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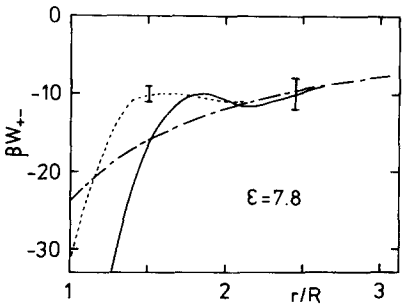

FIG. 5. The potential of mean force between two univalent ions of opposite signs and having the same size as the dipoles, $R_1 = R_2 = R$, (——), The function $-\beta e^2/\epsilon r$ is shown as (— - —) and the dielectric constant of the dipolar solvent is 7.8. Monte Carlo results (Ref. 18) are shown as (· · ·) with the error bar indicated by (I).

the minimum at $r = \frac{3}{2}R$ in the potential of mean force between ions of *like* sign (Fig. 3). Here, when the dielectric constant of the fluid is high, two like ions in close proximity are behaving like a doubly charged ion and the negative change in Born energy (relative to two ions at infinite separation) can be comparable to the positive direct unscreened Coulomb repulsion. In Fig. 5 we compare our results with available Monte Carlo data.[18] It is clear that the large interaction at small separation, mitigated by the small dielectric constant, cannot be described properly by the MSA, which after all is only a linear theory. Nonetheless the MSA should at least contain the correct trends.

V. THE MSA AT FINITE IONIC CONCENTRATIONS

A natural progression from the work of the previous section is to consider the case of finite ionic concentrations. Here the thermodynamic quantity of interest is the mean activity coefficients for the ions from which we can check, for example, the validity of the extended Debye–Hückel theory. Blum[14] had expressed the thermodynamic properties of an equal size ion/dipole mixture in the MSA in terms of the solution of seven simultaneous algebraic equation. Two of those equations appeared with typographical errors in his paper. Denoting equations in Blum's paper[14] by the prefix B, Eq. (B2.24) should read (in Blum's notation)

$$a_2 = (b_1/D_1)[1 + b_2/12 + \tfrac{1}{2}b_0(b + b_2/3) + b_1^2/12] \qquad (5.1)$$

and Eq. (B2.25) should read

$$K_{10} = (b_2/2\Delta)\{1 + a_1[\tfrac{1}{2}b_0 + \tfrac{2}{3}(1 - b_2/24)]\} . \qquad (5.2)$$

Blum gave an explicit expression for the mean ionic activity coefficient in the limit of low ionic concentrations. This expression was obtained via the energy equation. As he had omitted to account for the ionic concentration dependence of the ion–dipole and dipole–dipole interaction energy, his expression for the activity coefficient differed from the Debye–Hückel limiting law by a factor of the dielectric constant [Eq. (B5.6)].

We derive an expression for the activity coefficient for an equal size ion/dipole mixture by a direct charging process instead of via the energy equation. Consider the addition of an extraneous charge of magnitude q to an ion/dipole mixture. The change in electrostatic free energy for this process is

$$\begin{aligned} kT\ln\gamma &= \int_0^q dq \left\{ \sum_i \rho_i \int d\mathbf{r}\, h_{qi}(r) u_{qi}(r) \right. \\ &\quad \left. + \frac{\rho_d}{4\pi} \int d\mathbf{r}\, d\omega\, h_{qd}(\mathbf{r},\omega) u_{qd}(\mathbf{r},\omega) \right\} \qquad (5.3) \\ &= \frac{q^2}{R} b_0 + \frac{q\mu}{R}\left(\frac{\rho_d}{3\rho_c}\right)^{1/2} b_1 . \end{aligned}$$

Here h_{qi} and h_{qd} describe the distribution of ions and dipole about the charge q. The constants b_0 and b_1 which represent contributions to $\ln\gamma$ from ion–ion and ion–dipole interactions are implicit functions of ionic concentration and can be obtained from Blum's seven simultaneous equations.

We have computed $\ln\gamma$ using Eq. (5.3) as well as Blum's expression Eq. (B5.5). The results are not equal since the MSA only gives approximate pair distribution functions. However in both cases $\ln\gamma$ as a function of ionic concentration failed to exhibit the characteristic turning point. The MSA predicted that $\ln\gamma$ is a monotonic function of ionic concentration but follows the Debye–Hückel limiting law as the ionic concentration tends to zero. The failure of the MSA can be traced to its inability to handle the large unscreened ion–ion interaction at small separations where it gave large negative values for the pair distribution functions between ions of opposite signs.

VI. CONCLUSION

In this paper, we have tried to gain some insight into the behavior of solvent molecules in the neighborhood of ions and their role in determining the short range part of the ion–ion potential of mean force. We have chosen as our model hard sphere ions in a solvent of hard sphere dipoles. Solutions are obtained in the MSA. This is because of its analytical tractability and close lineage with more familiar mean field theories. We have been able to recover a familiar empirical correction to the Born energy, indicate the pitfalls in assuming empirical functional forms to describe dielectric saturation and to demonstrate deviations from the continuum description of ion–ion interaction at close separations where because of the discrete nature of the solvent, the solvent molecules can no longer screen the Coulomb potential properly. Due to its inherent inability to handle nonlinearities, the fluctuation potential and image effects the MSA cannot be relied upon to give accurate quantitative description of ion–dipole systems.

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