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Mixtures of hard ions and dipoles against a charged wall: The Ornstein–Zernike equation, some exact results, and the mean spherical approximation

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The Ornstein–Zernike equation for a mixture of ions and dipoles near a hard charged wall is obtained. It is shown that the same exact contact and monotonicity theorems, previously derived for the primitive (continuum dielectric) case, also are valid for this model. Rather simple expressions for the contact density, potential difference, capacitance, and distribution functions are obtained in the mean spherical approximation (MSA). These expressions reduce to previously known results in the limits of low and high concentrations of ions. It is found that cooperative alignment of the dipoles near the wall results in an increased potential difference and reduced capacitance of the double layer compared to that calculated when the solvent is represented by a continuum dielectric.

I. INTRODUCTION

The subject of solvent structure at electrode interfaces has been investigated by many workers¹ in the field of electrochemistry. All of the proposed models^{2–15} treat the solvent in the diffuse layer as a continuum, and consider the structure of the solvent only in the monolayer which is adjacent to the electrode (the so-called inner Helmholtz layer). Even there, the simplistic view of only a few possible orientations for the solvent molecules is considered, as, for example, in the recent work of Fawcett¹⁵ in which three dipole orientations (two normal and one parallel to the surface) are taken into consideration. Inasmuch as Fawcett has been able to predict correctly a wide variety of phenomena, this would appear to be a justifiable assumption. Nevertheless, it is necessary, in an *ab initio* statistical theory, to treat the solvent as a fully orientable molecular system, to take into account the long ranged nature of the electrostatic interaction, and to consider fully the solvent molecules not adjacent to the electrode.

The purpose of this note is to present some results of a simplified model in which the solvent interactions can be treated without restricting the analysis to the inner Helmholtz layer. This model consists of a collection of hard spheres near a charged wall. For simplicity in the formulation, all of the spheres are of equal diameter. The ions are represented by hard spheres with a charge and the solvent is represented by hard spheres with a permanent point dipole at the center of each dipolar hard sphere. Clearly, a collection of hard spheres with a permanent point dipole is not water (although it might be a reasonable model for an organic solvent). However, it is a first step in the direction of modeling water.

The ion–dipole mixture has been studied in the bulk using the mean spherical approximation (MSA),^{16–18} a rather ingenious mean field theory,¹⁹ which we call the

extended Onsager approximation (EOA), the linear hypernetted chain approximation,²⁰ and the modified Poisson Boltzmann equation.²¹ The most reliable information, however, comes from computer simulations.²²

It is clear that using the ideas introduced by Henderson, Abraham, and Barker²³ and Percus²⁴ of allowing one of the particles to grow without limit in size while letting its density go to zero, a linear response theory of the ion–dipole mixture with the electrode wall can be formulated. This problem has been considered recently by Carnie and Chan,²⁵ also.

In Sec. II we find the appropriate form of the Ornstein–Zernike equation²⁶ for the case of ions in “dipolium” (our model solvent). In Sec. III we present extensions of our contact value²⁷ and potential monotonicity²⁸ theorems to this model. In Sec. IV we apply the MSA to this model and in Sec. V we evaluate the MSA results in the limit of low and high concentrations of ions.

II. THE ORNSTEIN–ZERNIKE (OZ) EQUATION

Consider first a system of a more general nature than the dipolium model: We have a mixture of hard ions of different diameter and a solvent which consists of hard spheres with arbitrary (multipolar) interactions. Then, in Fourier space, the Ornstein–Zernike equation is^{29–31}

$$[I + (-)^{\chi} \rho \tilde{H}_{\chi}(k)] [I - (-)^{\chi} \rho \tilde{C}_{\chi}(k)] = I, \quad (1)$$

where I is the unit matrix, χ is the helicity, ρ is the diagonal matrix of the number densities of the ions and the solvent, the element of the Fourier transform of the pair correlation function $\tilde{H}_{\chi}(k)$ are given by

$$\begin{aligned} \tilde{H}_{\alpha\beta}^{mn}(k) = & (-)^{\chi} \sum_{l=m-n}^{m+n} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} 4\pi i^l \\ & \times \int_0^{\infty} dr r^2 j_l(kr) h_{\alpha\beta}^{mn}(r), \end{aligned} \quad (2)$$

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where m, n are indices for the multipolar interaction (see Ref. 29), and the function $j_l(\chi)$ is the spherical Bessel function of order l . We have used the standard notation for the $3j$ symbols. The functions $h_{\alpha\beta}^{mn}(\mathbf{r})$ are the coefficients of the invariant expansion of the pair correlation function between atom of species α, β :

$$h_{\alpha\beta}(\mathbf{X}_\alpha, \mathbf{X}_\beta) = \sum_{mnl} h_{\alpha\beta}^{mnl}(\mathbf{r}_{\alpha\beta}) \Phi^{mnl}(\Omega_\alpha, \Omega_\beta, \hat{\mathbf{R}}_{\alpha\beta}), \quad (3)$$

with

$$\begin{aligned} \Phi^{mnl}(\Omega_\alpha, \Omega_\beta, \hat{\mathbf{R}}_{\alpha\beta}) &= [(2m+1)(2n+1)]^{1/2} \\ &\times \sum_{\mu'\nu'\lambda'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} \\ &\times D_{\mu\nu}^m(\Omega_1) D_{\mu'\nu'}^n(\Omega_2) D_{0\lambda}^l(\hat{\mathbf{R}}_{12}), \end{aligned} \quad (4)$$

where we have used the standard notation for Wigner's generalized spherical harmonics $D_{\mu\nu}^m(\Omega)$. Using the representation of the spherical Bessel function

$$j_l(kr) = \frac{1}{2i^l} \int_0^1 dt P_l(t) [e^{ikrt} + (-)^l e^{-ikrt}], \quad (5)$$

where the $P_l(t)$ are the Legendre polynomials, we can write

$$\tilde{\mathbf{H}}_\chi(k) = \int_0^\infty dr [e^{ikr} \mathbf{J}_\chi(r) + e^{-ikr} \mathbf{J}_\chi^T(r)], \quad (6)$$

with

$$\begin{aligned} J_{\alpha\beta, \chi}^{mn}(r) &\equiv (-)^n 2\pi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \\ &\times \int_r^\infty dr_1 r_1 P_l(r/r_1) h_{\alpha\beta}^{mnl}(r_1). \end{aligned} \quad (7)$$

We introduce similar definitions for the Fourier-Bessel transforms of the direct correlation function $c_{\alpha\beta}^{mnl}$:

$$\tilde{\mathbf{C}}_\chi(k) = \int_0^\infty dr [e^{ikr} \mathbf{S}(r) + e^{-ikr} \mathbf{S}^T(r)]. \quad (8)$$

Combining Eqs. (1), (6), and (8), and performing the inverse Fourier transform, we get the very simple matrix expression

$$\mathbf{J}_\chi(r) - \mathbf{S}_\chi(r) = \int_{-\infty}^\infty dr_1 \mathbf{J}_\chi(r-r_1) \rho \mathbf{S}_\chi(r_1). \quad (9)$$

Let us define the functions

$$(-)^n 2\pi r \mathcal{J}_{\alpha\beta, \chi}^{mn}(r) = -\frac{\partial}{\partial r} J_{\alpha\beta, \chi}^{mn}(r), \quad (10)$$

$$(-)^n 2\pi r \mathcal{C}_{\alpha\beta, \chi}^{mn}(r) = -\frac{\partial}{\partial r} S_{\alpha\beta, \chi}^{mn}(r). \quad (11)$$

Differentiating Eq. (9), we get after some rather straightforward calculations

$$\mathcal{J}_\chi(r) - \mathcal{C}_\chi(r) = (-)^n \frac{2\pi}{r} \int_0^\infty dt t \left[- \int_{t-r}^\infty ds \mathcal{J}_\chi^T(t) \rho \mathbf{S}_\chi(s) \right.$$

$$\left. + \int_{t-r}^\infty ds \mathcal{J}_\chi(t) \rho \mathbf{S}_\chi^T(s) \right], \quad (12)$$

where we have also used the symmetry conditions³¹

$$\mathbf{J}_\chi(r) = \mathbf{J}_\chi^T(-r), \quad \mathbf{S}_\chi(r) = \mathbf{S}_\chi^T(-r). \quad (13)$$

Consider now the matrix $\mathbf{S}_0(r)$. This matrix¹⁶ has long ranged parts which correspond to the ion-ion and ion-dipole interactions. We recall that

$$\mathbf{S}_{\alpha\beta}^{mn}(r) = \hat{\mathbf{S}}_{\alpha\beta}^{mn}(r) + D_{\alpha\beta}^{mn} \varphi^{mn}(r), \quad (14)$$

where $\hat{\mathbf{S}}_{\alpha\beta}^{mn}(r)$ is the short ranged part of the transformed direct correlation function, and that¹⁶

$$\text{ion-ion: } D_{\alpha\beta}^{00} = \alpha_0^2 z_\alpha z_\beta, \quad \varphi^{00}(r) = \lim_{z \rightarrow 0} \frac{e^{-z|r|}}{2z}; \quad (15)$$

$$\text{ion-dipole: } D_{\alpha n}^{01} = \alpha_1 z_\alpha, \quad \varphi^{01}(r) = \lim_{z \rightarrow 0} e^{-zr} \theta(r); \quad (16)$$

$$\text{dipole-ion: } D_{n\beta}^{10} = \alpha_1 z_\beta, \quad \varphi^{10}(r) = \lim_{z \rightarrow 0} e^{zr} \theta(-r), \quad (17)$$

$$\alpha_0^2 = 4\pi\beta e^2, \quad \alpha_1 = \frac{4\pi}{\sqrt{3}} \beta e \mu, \quad (18)$$

where z_α is the valence of an ion of species α , μ is the dipole moment, and $\theta(r)$ is the Heaviside function.

Using Eq. (11) we get

$$\mathcal{C}_{\alpha\beta}^{00}(r) = \hat{\mathcal{C}}_{\alpha\beta}^{00}(r) - \frac{\alpha_0^2}{4\pi r} [\theta(r) - \theta(-r)] z_\alpha z_\beta, \quad (19)$$

$$\mathcal{C}_{\alpha n}^{01}(r) = \hat{\mathcal{C}}_{\alpha n}^{01}(r) - \frac{\alpha_1}{2\pi r} \delta(r) z_\alpha, \quad (20)$$

and

$$\mathcal{C}_{n\beta}^{10}(r) = \hat{\mathcal{C}}_{n\beta}^{10}(r) + \frac{\alpha_1}{2\pi r} \delta(r) z_\beta, \quad (21)$$

where $\hat{\mathcal{C}}_{\alpha\beta}^{mn}(r)$ is the short ranged part of the direct correlation function.

Consider now the limit in which one of the ionic species w becomes the electrode: The density $\rho_w \rightarrow 0$, while the charge z_w and the radius R_w go to infinity. We have, in this limit,

$$\begin{aligned} \rho_w R_w^3, \quad z_w, \quad R_w &\rightarrow \infty, \\ ez_w/4\pi R_w^2 &= q_s, \end{aligned} \quad (22)$$

where q_s is the surface charge density on the electrode. Replacing these expressions for the direct correlation function (19)–(21) into the OZ equation (12), we get an expression from which the limiting form (22) can be calculated. This is best performed defining the new variables

$$\begin{aligned} x &= r - R_w, \\ t' &= t - R_w. \end{aligned} \quad (23)$$

Details of the procedure can be found in Refs. 23, 26, [Eq. (17) ff], and 30. We find the set of coupled equations

$$h_{\alpha}^w(x) - c_{\alpha}^w(x) = 2\pi \sum_{\beta} \rho_{\beta} \int_{-\infty}^{\infty} dt \int_{|x-t|}^{\infty} h_{\beta}^w(t) s \hat{c}_{\beta\alpha}^{00}(s) \\ + 2\pi \rho_d \int_{-\infty}^{\infty} dt \int_{|t-x|}^{\infty} ds h_d^w(t) s \hat{c}_{\alpha d}^{01}(s) + \frac{1}{2} \alpha_0^2 z_{\alpha} \sum_{\beta} z_{\beta} \rho_{\beta} \int_0^{\infty} dt h_{\beta}^w(t) (t+x+|x-t|) - \alpha_1 \rho_d z_{\alpha} \int_0^x dt h_d^w(t) \quad (24)$$

and

$$h_d^w(x) - c_d^w(x) = 2\pi \sum_{\beta} \rho_{\beta} \int_{-\infty}^{\infty} dt \int_{|t-x|}^{\infty} ds h_{\beta}^w(t) s \hat{c}_{d\beta}^{10}(s) + 2\pi \rho_d \int_{-\infty}^{\infty} dt \int_{|t-x|}^{\infty} ds h_d^w(t) s \hat{c}_{dd}^{11}(s) \\ - \alpha_1 \sum_{\beta} \rho_{\beta} z_{\beta} \int_0^x dt h_{\beta}^w(t), \quad (25)$$

where we have adopted the index "w" for the wall particle and have defined

$$h_{\alpha}^w(x) = \lim_{R \rightarrow \infty} \mathcal{H}_{w\alpha}^{00}(r), \quad (26)$$

$$c_{\alpha}^w(x) = \lim_{R \rightarrow \infty} c_{w\alpha}^{00}(r), \quad (27)$$

$$h_d^w(x) = \lim_{R \rightarrow \infty} \mathcal{H}_{wd}^{01}(r), \quad (28)$$

and

$$c_d^w(x) = \lim_{R \rightarrow \infty} c_{wd}^{01}(r). \quad (29)$$

The indices α and β run over *all* of the species (ions and dipoles). Of course, for the dipoles $z_{\alpha} = 0$. Thus, $h_{\alpha}^w(x)$ gives the probability of finding centers of hard spheres of species α at a distance x from the wall. The function $h_d^w(x)$ is the coefficient of $\cos\theta$ in the expansion of the pair distribution function of the dipolar hard spheres. Also, ρ_{α} is the number density of hard spheres of species α . In particular, ρ_d is the number density of dipolar hard spheres. The OZ equations (24) and (25) were derived using restrictive assumptions. A more general derivation will be presented later.

III. SOME EXACT RESULTS

For the case of an arbitrary mixture of hard ions and dipoles near a charged wall, the particle wall interaction is for all the particles

$$U_E = -eE \sum_{\alpha} z_{\alpha} x_{\alpha} - \mathbf{E} \cdot \sum_{\alpha} \mu_{\alpha}, \quad (30)$$

where \mathbf{E} is the bare (unscreened) electric field. In other words, the surface charge density on the wall is

$$q_s = E/4\pi. \quad (31)$$

The potential difference across the interface is

$$\Delta\psi = -\left(\frac{\partial A_s}{\partial q_s}\right)_T = -4\pi \left(\frac{\partial A_s}{\partial E}\right)_T, \quad (32)$$

where A_s is the surface free energy per unit area. Hence,

$$\Delta\psi = 4\pi \left[e \sum_{\alpha} z_{\alpha} \rho_{\alpha} \int_0^{\infty} dx x h_{\alpha}^w(x) + \rho_d \frac{\mu}{\sqrt{3}} \int_0^{\infty} dx h_d^w(x) \right], \quad (33)$$

where $\mu = |\mu|$. The factor $1/\sqrt{3}$ is a normalization

constant arising from the definition of the projection $h_d^w(x)$.

We could write Eq. (33) as

$$\left(\frac{\partial A_s}{\partial E}\right)_T = -\frac{\Delta\psi}{4\pi} = \langle U \rangle, \quad (34)$$

where $U = U_E/E$. Differentiating once more gives

$$\left(\frac{\partial^2 A_s}{\partial E^2}\right)_T = -\frac{1}{4\pi} \left(\frac{\partial \Delta\psi}{\partial E}\right)_T \\ = -\beta [\langle U^2 \rangle - \langle U \rangle^2] \leq 0. \quad (35)$$

Hence,

$$\left(\frac{\partial \Delta\psi}{\partial E}\right)_T \geq 0, \quad (36)$$

so that $\Delta\psi$ is a monotonic function²⁷ of the charge density on the wall.

Finally, we consider the force balance equation²⁸

$$P = \sum_{\alpha} \left[kT \rho_{\alpha} (\sigma_{\alpha}/2) - \int_0^{\infty} dx \rho_{\alpha}(x) \frac{\partial W_{\alpha}(x)}{\partial x} \right], \quad (37)$$

where p is the bulk pressure, $\rho_{\alpha}(x) = \rho_{\alpha} [h_{\alpha}^w(x) + 1]$ is the density profile, σ_{α} is the hard core diameter of species α , and $\partial W_{\alpha}/\partial x$ is the force between species α and the wall. Thus,

$$\frac{\partial W_{\alpha}(x)}{\partial x} = z_{\alpha} e E/2 \quad (\text{ion-wall}), \quad (38)$$

$$\frac{\partial W_{\alpha}(x)}{\partial x} = 0 \quad (\text{dipole-wall}), \quad (39)$$

since the wall exerts a torque (not a force) on a dipole. In Eq. (38), E is the bare (unscreened) electric field. In other words the charge density on the wall is $q_s = E/4\pi$. If we think of the wall as a particle, $W_{\alpha}(x)$ is the pair potential between the wall and the particle of species α .

Hence, Eq. (37) becomes

$$p = kT \sum_{\alpha} \rho_{\alpha} (\sigma_{\alpha}/2) + \frac{eE}{2} \sum_{\alpha} z_{\alpha} \int_0^{\infty} dx \rho_{\alpha}(x). \quad (40)$$

Using the charge neutrality condition

$$e \sum_{\alpha} z_{\alpha} \int_0^{\infty} dx \rho_{\alpha}(x) = E/4\pi, \quad (41)$$

Eq. (40) becomes

$$p + \frac{E^2}{8\pi} = kT \sum_{\alpha} \rho_{\alpha} (\sigma_{\alpha}/2) \\ = kT \sum_i \rho_i (\sigma_i/2) + kT \sum_d \rho_d (\sigma_d/2). \quad (42)$$

The index i denotes ions and the index d dipoles. The same result could be obtained from an analysis of the Maxwell stress tensor.

IV. THE MEAN SPHERICAL APPROXIMATION

The mean spherical approximation (MSA) was introduced by Lebowitz and Percus³² as an extension of a model used for the study of phase transitions in lattice systems. It has remarkable analytical simplicity, and, in many cases, yields reasonably accurate thermodynamic and structure functions for ionic systems.

For the primitive electrode interface^{33,34} the MSA yields an extension of the linearized Gouy–Chapman equation, or the zero charge values of the thermodynamic and structural parameters. In this paper we report the results of this approximation for our model molecular solvent.

Consider the mixture of *equal* size hard ions and dipoles against a hard wall. We know³³ that the Laplace transform of the charge produced by the charge on the distribution function is

$$\Delta \tilde{g}_{\alpha}(s) = -e^{-s\sigma/2} \sum_{\beta, \gamma} \left\{ \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \frac{e^{-ik\sigma/2}}{s+ik} \right. \\ \left. \times \tilde{\phi}_{\beta}(k) \sqrt{\frac{\rho_{\beta}}{\rho_{\gamma}}} [\tilde{Q}^T(-k)]_{\beta\gamma}^{-1} [\tilde{Q}(is)]_{\gamma\alpha}^{-1} \sqrt{\frac{\rho_{\alpha}}{\rho_{\gamma}}} \right\}, \quad (43)$$

where the indices α, β, γ are either i (ions) or d (dipoles). The Baxter functions $Q(r)$ and its Laplace transform $\tilde{Q}(s)$ are 2×2 matrices, and are defined and discussed in Appendix A.^{16,17} The factors $\sqrt{\rho_{\alpha}/\rho_{\beta}}$ arise from the different definitions of Q in Refs. 16 and 33.

We also have used

$$\Delta \tilde{g}_{\alpha}(s) = \int_0^{\infty} dx e^{-sx} \Delta g_{\alpha}(x) \quad (44)$$

and

$$\tilde{\phi}_{\gamma}(k) = \int_0^{\infty} dx e^{ikx} U_{\gamma}(x)/kT, \quad (45)$$

where x is the distance to the hard wall, $\Delta g_{\alpha}(x)$ is the change in the wall- α distribution function due to the charge on the wall, and $U_{\gamma}(x)$ is the coefficient in the irreducible expansion²⁹ ($x=0$) of the bare wall- γ interaction:

$$U_i(x) = \frac{eEx}{kT} \quad (\text{ion-wall}), \quad (46)$$

$$U_d(x) = \frac{E\mu}{\sqrt{3}kT} \quad (\text{dipole-wall}), \quad (47)$$

where E is the bare electric field, $\pm e$ the ionic charge, and μ the magnitude of the dipole moment. For simplicity and without loss of generality we have assumed in this section that the ions are monovalent. The

Fourier transforms (45) are

$$\tilde{\phi}_i(k) = - \left[\frac{\partial}{\partial z} \left(\frac{Ee}{kT} \right) \frac{e^{(-s+ik)\sigma/2}}{z-ik} \right] \Big|_{z=0}, \quad (48)$$

$$\tilde{\phi}_d(k) = \left(\frac{\mu E}{\sqrt{3}kT} \right) \frac{e^{ik\sigma/2}}{z-ik} \Big|_{z=0}. \quad (49)$$

Now we write Eq. (43) in a more compact form

$$\Delta \tilde{g}_{\alpha}(s) = -e^{-s\sigma/2} \sum_{\gamma} \hat{F}_{\gamma}(s) \sqrt{\frac{\rho_{\alpha}}{\rho_{\gamma}}} [\tilde{Q}(is)]_{\gamma\alpha}^{-1}, \quad (50)$$

with

$$\hat{F}_{\gamma}(s) = \frac{1}{2\pi} \sum_{\beta} \int_{-\infty}^{\infty} dk \frac{e^{-ik\sigma/2}}{s+ik} \tilde{\phi}_{\beta}(k) \sqrt{\frac{\rho_{\beta}}{\rho_{\gamma}}} [\tilde{Q}^T(-k)]_{\beta\gamma}^{-1}. \quad (51)$$

The explicit calculation of $\hat{F}_{\gamma}(s)$ is carried out in Appendix B. We get

$$\Delta \hat{g}_i(s) = -\frac{e^{-s\sigma/2}}{sD_q(s)} \left(\frac{\beta E e}{d_0^2} \right) [a_1 \tilde{Q}_{dd}(is) + a_2 \tilde{Q}_{di}(is)], \quad (52)$$

$$\Delta \hat{g}_d(s) = \frac{e^{-s\sigma/2}}{sD_q(s)} \left(\frac{\beta E \mu}{\sqrt{3} d_0 d_2} \right) [a_1 \tilde{Q}_{id}(is) + a_2 \tilde{Q}_{ii}(is)], \quad (53)$$

where $\beta = 1/kT$, we have used Eqs. (B6) and (B7), and $D_q(s)$ is defined by Eq. (A32).

Using Eq. (29) of Ref. 33, we get very simple expressions for the contact values of the distribution functions

$$\Delta g_i(\sigma/2) = -s \hat{F}_i(s) = \frac{\beta E e}{d_0^2} a_1, \quad (54)$$

$$\Delta g_d(\sigma/2) = -s \hat{F}_d(s) = \frac{\beta E \mu}{d_0 d_2} \left(\frac{\mu}{\sqrt{3}} \right) a_2. \quad (55)$$

Using Eqs. (B8) and (B9), we obtain the alternative expressions

$$\Delta g_i(\sigma/2) = \frac{\beta E e \Delta}{d_0} \left(\frac{\beta_3 y_1 + y_3 b_1/2}{\beta_3^2 + b_1^2/4} \right), \quad (56)$$

$$\Delta g_d(\sigma/2) = \frac{\beta E \mu \Delta}{\sqrt{3} d_2} \left(\frac{-\beta_3 y_3 + y_1 b_1/2}{\beta_3^2 + b_1^2/4} \right). \quad (57)$$

Another set of interesting relations is obtained from Eqs. (52) and (53) by taking the $s \rightarrow 0$ limit. This is done explicitly in Appendix C. For the ionic distribution function we get

$$\int_0^{\infty} dx \Delta g_i(x) = \Delta \tilde{g}_i(0) \\ = -\frac{\beta E e}{d_0^2} \left[\frac{a_1(1 - K_{dd}^0) + a_2 K_{di}^0}{d_0 y_1} \right] = -\frac{\beta E e}{d_0^2}, \quad (58)$$

which is the electroneutrality relation

$$e \rho_i \int_0^{\infty} dx \Delta g_i(x) = -\frac{E}{4\pi}, \quad (59)$$

where ρ_i is the number density of the ions. Furthermore, from Eq. (C8)

$$\int_0^{\infty} dx \Delta g_d(x) = \frac{E}{4\pi e \sqrt{\rho_i \rho_d}} \left(\frac{b_1 \beta_{12}}{b_0 \beta_3 + b_1^2/6} \right). \quad (60)$$

From Eq. (60) we get the polarization produced by the electrode

$$P = \frac{\rho_d \mu}{\sqrt{3}} \int_0^\infty dx \Delta g_d(x) = \sqrt{\frac{\rho_d}{3\rho_i}} \left(\frac{\mu E}{4\pi e} \right) \frac{b_1 \beta_{12}}{b_0 \beta_3 + b_1^2/6} \quad (61)$$

The potential difference across the interface can be calculated from Eq. (33), which can be expressed in terms of the Laplace transform (44) as

$$\begin{aligned} \Delta\psi &= 4\pi \left[-\rho_0 e \Delta \tilde{g}'_i(0) + \rho_d \frac{\mu}{\sqrt{3}} \Delta \tilde{g}_d(0) \right] \\ &= 4\pi (\rho_0 e \langle x \rangle_i + \rho_d (\mu/\sqrt{3}) \langle 1 \rangle_d), \end{aligned} \quad (62)$$

where $\langle x_i \rangle = \Delta \tilde{g}'_i(0)$ and $\langle 1 \rangle_d = \Delta \tilde{g}_d(0)$. Using Eqs. (C6) and (C8), we get

$$\Delta\psi = \frac{E}{2d_0^2 D_F} (a_1 \beta_6 - b_1 a_2/2), \quad (63)$$

while the capacitance (and also the differential capacitance) is

$$C = C_D = \frac{1}{4\pi} \frac{2d_0^2 D_F}{a_1 \beta_6 - b_1 a_2/2}. \quad (64)$$

The parameters in this equation are defined in Appendix A.

V. LOW AND HIGH CONCENTRATIONS

It is of interest to examine these results in the limits of low and high concentrations of ions. First, we consider low concentrations. To order $\kappa = d_0/\sqrt{\epsilon} = (4\pi\beta e^2 \rho_0/\epsilon)^{1/2}$, the dielectric properties of the mixture are unchanged from those of the pure solvent. Thus,

$$b_2 = 12\xi, \quad (65)$$

where ξ is Wertheim's parameter³⁵ for the dipolar solvent; b_2 (or ξ) is defined by

$$d_2^2 = \frac{\beta_3^2}{\beta_6} - \frac{\beta_6^2}{\beta_{12}^2} = y_3^2. \quad (66)$$

In addition

$$\epsilon = \beta_{12}^4 \beta_3^2 / \beta_6^6, \quad (67)$$

so that

$$d_2^2 = (\epsilon - 1)(\beta_6^2 / \beta_{12}^4). \quad (68)$$

Also,

$$y_1 = \beta_6 / \beta_{12}^2 \quad (69)$$

and

$$\Delta = \beta_6^2. \quad (70)$$

Expanding in powers of κ ,

$$b_0 = -(\kappa\sigma/2), \quad (71)$$

$$b_1 = \kappa\sigma d_2 \beta_6 \beta_{12}/2, \quad (72)$$

$$D_F = \frac{1}{2} \beta_6 \left(1 - \frac{\kappa\sigma}{2} \right), \quad (73)$$

$$\frac{a_1}{d_0} = \frac{1}{\sqrt{\epsilon}} \left[1 + \frac{\kappa\sigma(\epsilon-1)\beta_6^2}{4\beta_3\beta_{12}} \right], \quad (74)$$

and

$$\frac{a_2}{d_0} = -\sqrt{\frac{\epsilon-1}{\epsilon}} \left(1 - \frac{\kappa\sigma\beta_6^2}{4\beta_3\beta_{12}} \right). \quad (75)$$

Substitution of these results in Eqs. (63), (64), (54), and (55) gives

$$\Delta\psi = \frac{E}{\epsilon\kappa} \left\{ 1 + \frac{\kappa\sigma}{2} \left[1 + \frac{(\epsilon-1)\beta_6}{\beta_3} \right] \right\}, \quad (76)$$

$$C_D = \left(\frac{\epsilon}{4\pi} \right) \frac{\kappa}{1 + \frac{\kappa\sigma}{2} \left[1 + \frac{(\epsilon-1)\beta_6}{\beta_3} \right]}, \quad (77)$$

$$\Delta g_i(\sigma/2) = \frac{\beta E e}{\epsilon\kappa} \left[1 + \frac{\kappa\sigma(\epsilon-1)\beta_6^2}{4\beta_3\beta_{12}} \right], \quad (78)$$

and

$$\Delta g_d(\sigma/2) = -\frac{\beta E \mu \beta_6^2}{\sqrt{3}\beta_3} \left(1 - \frac{\kappa\sigma\beta_6^2}{4\beta_3\beta_{12}} \right). \quad (79)$$

Equation (76) has already been obtained by Carnie and Chan.²⁵

In the primitive model,

$$C_D = \frac{\epsilon}{4\pi} 2\Gamma \approx \left(\frac{\epsilon}{4\pi} \right) \frac{\kappa}{1 + \frac{\kappa\sigma}{2}}. \quad (80)$$

The capacitance calculated from Eq. (80) is much greater than that observed experimentally. As observed from Eqs. (76) and (77), the lowering is due to cooperative alignment of the dipoles near (but not necessarily next to) the surface which is a consequence of the theory and not a result of any *ad hoc* assumptions.

Finally, as we saw in Eq. (61), the polarization produced by the electrode is $\rho_d \mu/\sqrt{3}$ times the integral of $\Delta g_d(x)$. Using Eq. (C8) and expanding,

$$P = \left(\frac{\epsilon-1}{\epsilon} \right) \frac{E}{4\pi\kappa} \left[1 + \frac{\kappa\sigma}{2} \left(1 - \frac{\beta_6}{\beta_3} \right) \right]. \quad (81)$$

The first term is the polarization of the dielectric continuum. The second (positive) term results from the cooperative alignment of the dipoles.

In the limit of high concentrations $d_2 = 0$,

$$\epsilon = 1, \quad (82)$$

$$b_1 = b_2 = 0, \quad (83)$$

$$y_1 = 1, \quad (84)$$

and

$$b_0 = -\frac{\Gamma\sigma}{1+\Gamma\sigma}, \quad (85)$$

where

$$\kappa = 2\Gamma(1+\Gamma\sigma). \quad (86)$$

Thus,

$$D_F = \frac{1}{2} (1+b_0) = \frac{1}{2(1+\Gamma\sigma)}, \quad (87)$$

$$\Delta = 1, \quad (88)$$

$$a_1 = \kappa = d_0, \quad (89)$$

and

$$a_2 = 0. \quad (90)$$

Therefore,

$$\Delta\psi = E/2\Gamma, \quad (91)$$

$$C_D = 2\Gamma/4\pi, \quad (92)$$

$$\Delta g_i(\sigma/2) = \beta E e / \kappa, \quad (93)$$

and

$$\Delta g_d(\sigma/2) = 0, \quad (94)$$

in agreement with the results of Blum.³⁴

VI. REMARKS

We have obtained results, using the MSA, for the potential difference and other related properties of an electrolyte solution consisting of charged hard sphere in a solvent of discrete dipolar hard spheres. We give results for the particular case where the dipolar and charged hard spheres have the same diameter. These results complement those of Carnie and Chan.²⁵

We give explicit results only for the limit of low concentrations of the charged hard spheres. An exhaustive numerical study for all concentrations would be an extensive task in itself. Such a study would be of doubtful value because of the limitations of the MSA. It is probable that these MSA results are mainly of qualitative interest.

The main qualitative conclusion reported here is that cooperative alignment of the dipoles near the wall results in an increased potential difference across the double layer which in turn results in a reduced differential capacitance. These cooperative effects persist for several layers into the fluid. They are *not* confined to a single Stern-like layer next to the wall. Also, at higher concentrations, the dominant term in the capacitance is the second term in the denominator of Eq. (77) which results from hard core and solvent effects. These effects are in general agreement with experiment and are consequences of the model itself and not of any *ad hoc* assumptions involving, for example, a reduced dielectric constant near the wall.

A fundamental study of the dipole alignment as a function of the charge density on the wall is of great interest and is one of the goals of our future work.

Note added in proof: Dr. J. R. Macdonald has kindly brought to our attention that he and Barlow have made calculations using fully orientable dipoles. Details may be found in J. Chem. Phys. 36, 3062 (1962).

APPENDIX A: BULK BAXTER FUNCTIONS

The matrix Baxter function for the ion-dipole mixture in the MSA has been discussed in previous work.^{16,17} For the restricted, equal size case we may write

$$\tilde{Q}(is) = I - \int_0^\infty dr e^{-sr} Q(r), \quad (A1)$$

$$Q(r) = Q^0(r) - A\theta(r-1), \quad (A2)$$

and

$$Q^0(r) = \theta(1-r) \left[(r-1) \hat{P} + \frac{1}{2} Q'(r-1)r - rA \right], \quad (A3)$$

where \hat{P} is a symmetric matrix with elements

$$\hat{P}_{ii} = -2 + \frac{\beta_6}{D_F}, \quad (A4)$$

$$\hat{P}_{id} = -\frac{b_1}{2D_F}, \quad (A5)$$

and

$$\hat{P}_{dd} = -6 + \frac{3(1+b_0)}{D_F}. \quad (A6)$$

We have used¹⁷

$$b_0 = 2\pi\rho_i \int_0^\infty dr r h_{ii}^{000}(r), \quad (A7)$$

$$b_1 = 2\pi \left(\frac{\rho_i \rho_d}{3} \right)^{1/2} \int_0^\infty dr h_{id}^{101}(r), \quad (A8)$$

$$b_2 = 3\pi \left(\frac{2}{15} \right)^{1/2} \rho_d \int_1^\infty dr h_{dd}^{112}(r), \quad (A9)$$

$$\beta_{3,2}^n = 1 + (-)^n b_2 / (3 \cdot 2^n), \quad (A10)$$

and

$$D_F = \frac{1}{2} [\beta_6(1+b_0) - b_1^2/12]. \quad (A11)$$

Furthermore,

$$A = \begin{bmatrix} a_1 & a_2 \\ 0 & 0 \end{bmatrix}, \quad (A12)$$

and

$$a_1 = \frac{1}{2D_F^2} (-b_0\beta_6^2 + b_1^2\beta_{24}/3), \quad (A13)$$

$$a_2 = -\frac{b_1}{2D_F^2} [\beta_{12} + \frac{1}{2}(b_0\beta_3 + b_1^2/6)]. \quad (A14)$$

For our calculations we will need $\tilde{Q}(is)$ and its derivatives at $s=0$. After some algebra we get, from Eqs. (2.10) and (2.36)–(2.38) of Ref. 17,

$$\tilde{Q}_{ii}(0) = -\frac{a_1}{2} + \frac{\beta_6}{2D_F}, \quad (A15)$$

$$\tilde{Q}_{id}(0) = \frac{a_2}{2} + \frac{b_1}{4D_F}, \quad (A16)$$

$$\tilde{Q}_{di}(0) = \frac{1}{b_1} \left(2 - \frac{\beta_6}{D_F} \right) + \frac{1+b_0}{b_1} a_1, \quad (A17)$$

$$\tilde{Q}_{dd}(0) = -\frac{1}{2D_F} - \frac{1+b_0}{b_1} a_2, \quad (A18)$$

and the first derivatives

$$\tilde{Q}'_{ii}(0) = -\frac{1}{3} [1 - \tilde{Q}_{ii}(0)], \quad (A19)$$

$$\tilde{Q}'_{id}(0) = -\frac{1}{3} \tilde{Q}_{id}(0), \quad (A20)$$

$$\tilde{Q}'_{di}(0) = -\frac{1}{2} \tilde{Q}_{di}(0) + \frac{1}{12} P_{di}, \quad (A21)$$

$$\tilde{Q}'_{dd}(0) = -\frac{1}{2} [1 - \tilde{Q}_{dd}(0)] + \frac{1}{12} P_{dd}. \quad (A22)$$

We also get the matrices $\tilde{Q}(is)$ as

$$\tilde{Q}(is) = \begin{bmatrix} \tilde{Q}_{is}(is) & \tilde{Q}_{id}(is) \\ \tilde{Q}_{di}(is) & \tilde{Q}_{dd}(is) \end{bmatrix}, \quad (A23)$$

where

$$\tilde{Q}_{\alpha\beta}(is) = \delta_{\alpha\beta} - \varphi_1(s) \hat{P}_{\alpha\beta} - \varphi_3(s) Q''_{\alpha\beta} - A_{\alpha\beta} \varphi_0/s, \quad (\text{A24})$$

with

$$\varphi_0(s) = \frac{1}{s} (1 - e^{-s}), \quad (\text{A25})$$

$$\varphi_1(s) = \frac{1}{s^2} (1 - s - e^{-s}), \quad (\text{A26})$$

$$\varphi_3(s) = \frac{1}{s^3} \left[1 - \frac{s}{2} - e^{-s} \left(1 + \frac{s}{2} \right) \right], \quad (\text{A27})$$

and

$$Q''_{\alpha\beta} = 3 [\tilde{Q}_{\alpha\beta}(0) - \delta_{\alpha\beta} - \frac{1}{2} \hat{P}_{\alpha\beta} + \frac{1}{2} A_{\alpha\beta}], \quad (\text{A28})$$

$$A_{\alpha\beta} = \begin{bmatrix} a_1 & a_2 \\ 0 & 0 \end{bmatrix}. \quad (\text{A29})$$

Furthermore,

$$\tilde{Q}^{-1}(is) = \frac{1}{D_q} \begin{bmatrix} \tilde{Q}_{dd}(is) & -\tilde{Q}_{id}(is) \\ -\tilde{Q}_{di}(is) & \tilde{Q}_{ii}(is) \end{bmatrix}, \quad (\text{A30})$$

$$[\tilde{Q}^T(is)]^{-1} = \frac{1}{D_q} \begin{bmatrix} \tilde{Q}_{dd}(is) & -\tilde{Q}_{di}(is) \\ -\tilde{Q}_{id}(is) & \tilde{Q}_{ii}(is) \end{bmatrix}, \quad (\text{A31})$$

where

$$D_q(s) = \tilde{Q}_{dd}(is) \tilde{Q}_{ii}(is) - \tilde{Q}_{di}(is). \quad (\text{A32})$$

For small values of s we see from Eqs. (A24) and (A29) that $D_q(s)$ has a simple pole for $s \rightarrow 0$. Therefore, the expansion of $D_q(s)$ for small s reads

$$D_q(s) = \frac{\alpha_1}{s} + \alpha_0 + s\alpha_1 + \dots. \quad (\text{A33})$$

A lengthy but straightforward calculation¹⁷ yields

$$\begin{aligned} D_q(s) = & \frac{d_0 y_1}{s} + \frac{1}{3} a_1 + \tilde{Q}_{dd}(0) + d_0 y_1 \left(\frac{1}{2} b_0 - \frac{1}{3} \beta_{12} \right) \\ & + \frac{s}{6} \left\{ \frac{\beta_6}{D_F} + \frac{b_1 a_2}{12} - 2\beta_{12} \tilde{Q}_{dd}(0) \right. \\ & \left. - d_0 y_1 \left[b_0(1 + \beta_{12}) + 1 + \frac{2b_2}{15} \right] \right\} + \dots, \end{aligned} \quad (\text{A34})$$

where

$$d_0^2 = 4\pi\beta e^2 \rho_0, \quad (\text{A35})$$

$$y_1 = \beta_6 / \beta_{12}^2, \quad (\text{A36})$$

and the remaining symbols are explained above.

For small s , we obtain for Eqs. (A30) and (A31)

$$[\tilde{Q}(is)]^{-1} = \frac{1}{D_q} \begin{bmatrix} 1 - K_{dd}^0 + sK'_{dd} & -a_2/s + K_{id}^0 - sK'_{id} \\ K_{di}^0 - sK'_{di} & a_1/s + 1 - K_{ii}^0 + sK'_{ii} \end{bmatrix}, \quad (\text{A37})$$

$$[\tilde{Q}^T(is)]^{-1} = \begin{bmatrix} 1 - K_{dd}^0 + sK'_{dd} & K_{di}^0 - sK'_{di} \\ -a_2/s + K_{id}^0 - sK'_{id} & a_1/s + 1 - K_{ii}^0 + sK'_{ii} \end{bmatrix}, \quad (\text{A38})$$

where

$$1 - K_{dd}^0 = \frac{1}{d_0} (y_1 a_1 - a_2 d_2) = -\frac{1}{2D_F} - \left(\frac{1+b_0}{b_1} \right) a_2, \quad (\text{A39})$$

$$K_{di}^0 = \frac{1}{d_0} (y_1 a_2 + a_1 d_2) = \frac{1}{b_1} \left(2 - \frac{\beta_6}{D_F} \right) + \left(\frac{1+b_0}{b_1} \right) a_1, \quad (\text{A40})$$

$$1 - K_{ii}^0 = -\frac{a_1}{2} + \frac{\beta_6}{2D_F}, \quad (\text{A41})$$

$$K_{id}^0 = \frac{b_1}{4D_F} + \frac{a_2}{2}, \quad (\text{A42})$$

and

$$d_2^2 = \frac{4\pi}{3} \rho_d \beta \mu^2.$$

From Eq. (A37) we get

$$\lim_{s \rightarrow 0} \frac{\partial}{\partial z} [\tilde{Q}^T(iz)]_{ii}^{-1} = \frac{1 - K_{dd}^0}{d_0 y_1}, \quad (\text{A43})$$

$$\lim_{s \rightarrow 0} \frac{\partial}{\partial z} [\tilde{Q}^T(iz)]_{id}^{-1} = \frac{K_{di}^0}{d_0 y_1}, \quad (\text{A44})$$

$$\lim_{s \rightarrow 0} [\tilde{Q}^T(iz)]_{di}^{-1} = -\frac{a_2}{d_0 y_1}, \quad (\text{A45})$$

and

$$\lim_{s \rightarrow 0} [\tilde{Q}^T(iz)]_{dd}^{-1} = \frac{a_1}{d_0 y_1}. \quad (\text{A46})$$

Furthermore, we observe that¹⁷

$$a_1(1 - K_{dd}^0) + a_2 K_{di}^0 = d_0 y_1, \quad (\text{A47})$$

$$a_1 K'_{dd} - a_2 K'_{di} = \frac{1}{3} (a_1 - \beta_{12} d_0 y_1), \quad (\text{A48})$$

$$a_1 K_{id}^0 + a_2 (1 - K_{ii}^0) = a_2 - \frac{1}{2} d_0 y_1 b_1 = -\frac{b_1 \beta_{12}}{2D_F^2}, \quad (\text{A49})$$

and from

$$a_1^2 + a_2^2 = d_0^2, \quad (\text{A50})$$

$$a_1 \beta_3 + \frac{a_2 b_1}{2} = d_0 y_1 \Delta, \quad (\text{A51})$$

we get, in matrix form,

$$\begin{bmatrix} a_1 & a_2 \\ \beta_3 & \frac{b_1}{2} \end{bmatrix} \begin{bmatrix} a_1 & \beta_3 \\ a_2 & \frac{b_1}{2} \end{bmatrix} = \begin{bmatrix} d_0^2 & d_0 y_1 \Delta \\ d_0 y_1 \Delta & \beta_3^2 + \frac{b_1^2}{4} \end{bmatrix}, \quad (\text{A52})$$

and from the determinants

$$\frac{a_1 b_1}{2} - a_2 \beta_3 = d_0 y_3 \Delta, \quad (\text{A53})$$

$$y_3^2 = \frac{\beta_3^2 + \frac{b_1^2}{4}}{\left(\beta_6^2 + \frac{b_1^2}{4} \right)^2} - \left(\frac{\beta_6}{\beta_{12}^2} \right)^2, \quad (\text{A54})$$

so that from Eqs. (A51) and (A53),

$$a_1 = \frac{d_0 \Delta}{\beta_3^2 + b_1^2/4} (\beta_3 y_1 + y_3 b_1/2), \quad (\text{A55})$$

$$a_2 = \frac{d_0 \Delta}{\beta_3^2 + b_1^2/4} (y_1 b_1/2 - \beta_3 y_3). \quad (\text{A56})$$

Substituting Eqs. (A13) and (A14) into Eq. (A51) yields the interesting relation

$$b_0 \beta_3 + \frac{b_1^2}{6} = -2d_0 y_1 D_F^2. \quad (\text{A57})$$

Squaring and using Eq. (A50) gives

$$\left(b_0 \beta_3 + \frac{b_1^2}{6}\right)^2 = y_1^2 \left\{ (b_0 \beta_3 - b_1^2 \beta_{24}/3)^2 + b_1^2 [\beta_{12} + \frac{1}{2}(b_0 \beta_3 + b_1^2/6)]^2 \right\}. \quad (\text{A58})$$

For dilute solutions ($b_0 \rightarrow 0$) this leads to

$$b_1^2 \approx \frac{\beta_3^4 (\epsilon - 1) b_0^2}{\beta_{12}^2}. \quad (\text{A59})$$

Furthermore, from Eqs. (A13) and (A57),

$$a_1 = \frac{d_0}{\sqrt{\epsilon_\omega}} \left[1 - \frac{b_1^2 \beta_{12}}{2\beta_3^2 (b_0 \beta_3 + b_1^2/6)} \right], \quad (\text{A60})$$

where $\sqrt{\epsilon_\omega} = \beta_3 \beta_{12}^2 / \beta_0^3$. Similarly,

$$a_2 = \frac{d_0 y_1 b_1}{2} \left(1 + \frac{2\beta_{12}}{b_0 \beta_3 + b_1^2/6} \right). \quad (\text{A61})$$

APPENDIX B

To compute Eq. (51),

$$\hat{F}_\gamma(s) = \frac{1}{2\pi} \sum_\beta \int_{-\infty}^{\infty} dk \frac{e^{-ik\sigma/2}}{s+ik} \tilde{\phi}_\beta(k) [\tilde{Q}^T(-k)]_{\beta\gamma}^{-1} \sqrt{\frac{\rho_\beta}{\rho_\gamma}}. \quad (\text{B1})$$

We close a circuit around the lower half complex k plane, where $\tilde{Q}^T(-k)$ is analytic and nonsingular. We obtain

$$\begin{aligned} \hat{F}_\gamma(s) = & \frac{1}{2\pi \sqrt{\rho_\gamma}} \int_{-\infty}^{\infty} dk \frac{e^{-ik\sigma/2}}{s+ik} \\ & \times \{ \sqrt{\rho_i} \tilde{\phi}_i(k) [\tilde{Q}^T(-k)]_{i\gamma}^{-1} + \sqrt{\rho_d} \tilde{\phi}_d(k) [\tilde{Q}^T(-k)]_{d\gamma}^{-1} \}. \end{aligned} \quad (\text{B2})$$

Using (48), (49), and the fact that the only pole is at $k = -iz$, we get

$$\begin{aligned} \tilde{F}_\gamma(s) = & \frac{\beta E}{\sqrt{\rho_\gamma} s} \lim_{\sigma \rightarrow 0} \left\{ -e \sqrt{\rho_i} \frac{\partial}{\partial z} [\tilde{Q}^T(iz)]_{i\gamma}^{-1} \right. \\ & \left. + \mu \sqrt{\frac{\rho_d}{3}} [\tilde{Q}^T(iz)]_{d\gamma}^{-1} \right\}. \end{aligned} \quad (\text{B3})$$

Using Eqs. (A43)–(A46) we find

$$\tilde{F}_i(s) = - \frac{\beta E}{s \sqrt{\rho_i} d_0 y_1} \left[e \sqrt{\rho_i} (1 - K_{dd}^0) + \mu \sqrt{\frac{\rho_d}{3}} a_2 \right] \quad (\text{B4})$$

and

$$\tilde{F}_d(s) = \frac{\beta E}{s \sqrt{\rho_d} d_0 y_1} \left(-e \sqrt{\rho_i} K_{di}^0 + \mu \sqrt{\frac{\rho_d}{3}} a_1 \right), \quad (\text{B5})$$

where d_0 and y_1 are given by Eqs. (A35) and (A36).

Using these and Eqs. (A41) and (A42), we get

$$\tilde{F}_i(s) = - \frac{\beta E e}{s d_0^2 y_1} [d_0 (1 - K_{dd}^0) + d_2 a_2] = - \frac{\beta E e}{s d_0^2} a_1, \quad (\text{B6})$$

$$\tilde{F}_d(s) = \frac{\beta E \mu}{\sqrt{3} d_0 d_2 s y_1} (-d_0 K_{di}^0 + d_2 a_1) = - \frac{\beta E \mu}{\sqrt{3} s d_0 d_2} a_2. \quad (\text{B7})$$

Using the relations (A55) and (A56),

$$a_1 = \frac{\Delta d_0}{\beta_3^2 + b_1^2/4} (\beta_3 y_1 + y_3 b_1/2), \quad (\text{B8})$$

$$a_2 = \frac{\Delta d_0}{\beta_3^2 + b_1^2/4} (-\beta_3 y_3 + y_1 b_1/2), \quad (\text{B9})$$

where

$$y_3^2 = \frac{\beta_3^2 + b_1^2/4}{\Delta^2} - y_1^2. \quad (\text{B10})$$

We get

$$\tilde{F}_i(s) = - \frac{\beta E e \Delta}{s d_0} \left(\frac{\beta_3 y_1 + y_3 b_1/2}{\beta_3^2 + b_1^2/4} \right), \quad (\text{B11})$$

$$\tilde{F}_d(s) = - \frac{\beta E \mu \Delta}{\sqrt{3} s d_2} \left(\frac{-\beta_3 y_3 + y_1 b_1/2}{\beta_3^2 + b_1^2/4} \right). \quad (\text{B12})$$

In the limit of $\rho_i \rightarrow 0$, the first expression is

$$\tilde{F}_i(s) = - \frac{\beta E e}{s d_0} \left(\frac{\beta_3^2 y_1}{\beta_3} \right). \quad (\text{B13})$$

However, the dielectric constant of the pure solvent is

$$\sqrt{\epsilon} = \beta_3 \frac{\beta_{12}^2}{\beta_0^3} = \frac{\beta_3}{\beta_0^2 y_1}. \quad (\text{B14})$$

Thus,

$$F_i(s) = - \frac{\beta E e}{s d_0 \sqrt{\epsilon}}, \quad (\text{B15})$$

which is in full agreement with the result of the primitive case [Eq. (2.42)] of Ref. 34:

$$F_i = - \frac{\beta e E}{\epsilon \kappa}, \quad (\text{B16})$$

where κ is the Debye–Hückel length

$$\kappa^2 = 4\pi \beta e^2 \rho_0 / \epsilon. \quad (\text{B17})$$

APPENDIX C: MOMENTS OF THE DISTRIBUTION FUNCTION

We derive here the moments of the MSA distribution function that are needed for the computation of the potential difference in Sec. IV. We need

$$\langle x \rangle_i = \int_0^\infty dx x \Delta g_i(s) = - \frac{\partial}{\partial s} \Delta \tilde{g}_i(s) = - \Delta \tilde{g}_i'(0). \quad (\text{C1})$$

Using Eqs. (52), (A33), and (A37)ff, we get

$$\begin{aligned} \langle x \rangle_i = & - \frac{\partial}{\partial s} \left\{ \frac{e^{-s\sigma/2}}{s D_i(s)} \left(\frac{\beta E e}{d_0^2} \right) [a_1 \tilde{Q}_{dd}(is) + a_2 \tilde{Q}_{di}(is)] \right\} \Big|_{s=0}, \\ = & - \frac{\partial}{\partial s} \left(\frac{\beta E e}{d_0^2} \right) \frac{(1 - s\sigma/2 + \dots)}{d_0 y_1 + s a_0} \end{aligned} \quad (\text{C2})$$

$$\times \{ [a_1 (1 - K_{dd}^0) + a_2 K_{di}^0 + s (a_1 K'_{dd} - a_2 K'_{di})] \}. \quad (\text{C3})$$

From Eqs. (A47) and (A48),

$$= - \left(\frac{\beta E e}{d_0^2} \right) \frac{\partial}{\partial s} \left\{ \frac{(1 - s\sigma/2 + \dots)}{d_0 y_1 + s\alpha_0} \times \left[d_0 y_1 + \frac{s}{3} (a_1 \beta_{12} d_0 y_1) + \dots \right] \right\}. \quad (C4)$$

Here α_0 is given by Eq. (A34):

$$\alpha_0 = \frac{1}{3} a_1 + 1 - K_{dd}^0 + d_0 y_1 \left(\frac{1}{2} b_0 - \frac{1}{3} \beta_{12} \right). \quad (C5)$$

We get

$$\begin{aligned} \langle x \rangle_i &= - \frac{\beta E e}{d_0^2} \left[\frac{1}{2} (1 + b_0) + \frac{1 - K_{dd}^0}{d_0 y_1} \right] \\ &= - \frac{\beta E e}{d_0^3 y_1} \frac{\beta_3 (1 + b_0) + b_1^2/2}{4D_F^2}. \end{aligned} \quad (C6)$$

We also require the zeroth moment of g_d as

$$\langle 1 \rangle_d = \int_0^\infty dx \Delta g_d(x) = \Delta \tilde{g}_d(0). \quad (C7)$$

We have, from Eqs. (53) and (A49),

$$\begin{aligned} \langle 1 \rangle_d &= \frac{\beta E \mu}{\sqrt{3} d_0^2 d_2 y_1} [a_1 K_{id}^0 + a_2 (1 - K_{ii}^0)] \\ &= \frac{\beta E \mu}{\sqrt{3} d_0^2 d_2 y_1} (a_2 - d_0 y_1 b_1/2) \\ &= - \frac{\beta E \mu b_1 \beta_{12}}{2 \sqrt{3} d_0^2 d_2 y_1 D_F^2} \\ &= \frac{\beta E \mu}{\sqrt{3} d_0 d_2} \left(\frac{b_1 \beta_{12}}{b_0 \beta_3 + b_1^2/6} \right). \end{aligned} \quad (C8)$$

¹For a recent review, see R. W. Fawcett, Israel J. Chem. **18**, 3 (1979).

²R. J. Watts-Tobin, Philos. Mag. **6**, 133 (1961).

³N. F. Mott and R. J. Watts-Tobin, Electrochim. Acta **4**, 79 (1961).

⁴J. O'M. Bockris, M. A. V. Devanathan, and K. Muller, Proc. R. Soc. London Ser. A **274**, 55 (1963).

⁵B. B. Damaskin, Elektrokhimiya **1**, 1258 (1965); **2**, 828 (1966).

⁶J. O'M. Bockris, E. Gileadi, and K. Muller, Electrochim.

Acta **12**, 1301 (1967).

⁷S. Levine, G. M. Bell, and A. L. Smith, J. Phys. Chem. **73**, 3534 (1969).

⁸B. B. Damaskin and A. N. Frumkin, Electrochim. Acta **19**, 173 (1974).

⁹R. Parsons, J. Electroanal. Chem. **59**, 229 (1975).

¹⁰I. L. Cooper and J. A. Harrison, J. Electroanal. Chem. **66**, 85 (1975).

¹¹J. O'M. Bockris and M. A. Habib, J. Electroanal. Chem. **65**, 473 (1975).

¹²J. O'M. Bockris and M. A. Habib, Electrochim. Acta **22**, 41 (1977).

¹³R. Parsons, Electrochim. Acta **21**, 681 (1976).

¹⁴B. B. Damaskin, J. Electroanal. Chem. **75**, 359 (1977).

¹⁵W. R. Fawcett, J. Phys. Chem. **82**, 1385 (1978).

¹⁶L. Blum, Chem. Phys. Lett. **26**, 200 (1974); J. Chem. Phys. **61**, 3263 (1974); J. Stat. Phys. **18**, 451 (1978).

¹⁷E. Vericat and L. Blum, J. Stat. Phys. **22**, 593 (1980).

¹⁸S. A. Adelman and J. M. Deutch, J. Chem. Phys. **60**, 3935 (1974).

¹⁹S. A. Adelman and S. Chen, J. Chem. Phys. **70**, 4291 (1979).

²⁰D. Levesque, J. J. Weis, and G. N. Patey, Chem. Phys. Lett. **A66**, 115 (1978); J. Chem. Phys. **72**, 1887 (1980).

²¹C. W. Outhwaite, Mol. Phys. **31**, 1345 (1976); **33**, 1229 (1977).

²²G. N. Patey and J. P. Valleau, J. Chem. Phys. **63**, 2334 (1975).

²³D. Henderson, F. F. Abraham, and J. A. Barker, Mol. Phys. **31**, 1291 (1976).

²⁴J. K. Percus, J. Stat. Phys. **15**, 423 (1976).

²⁵S. L. Carnie and D. Y. C. Chan, J. Chem. Phys. **73**, 2949 (1980).

²⁶D. Henderson and L. Blum, J. Chem. Phys. **69**, 5441 (1978).

²⁷L. Blum, J. Lebowitz, and D. Henderson, J. Chem. Phys. **72**, 4249 (1980).

²⁸D. Henderson, L. Blum, and J. L. Lebowitz, J. Electroanal. Chem. **102**, 315 (1979).

²⁹L. Blum and A. J. Torruella, J. Chem. Phys. **56**, 303 (1972).

³⁰L. Blum, J. Chem. Phys. **57**, 1862 (1972).

³¹L. Blum, J. Chem. Phys. **58**, 3295 (1973).

³²J. L. Lebowitz and J. K. Percus, Phys. Rev. **144**, 251 (1966).

³³L. Blum and G. Stell, J. Stat. Phys. **15**, 439 (1976).

³⁴L. Blum, J. Phys. Chem. **81**, 136 (1977).

³⁵M. S. Wertheim, J. Chem. Phys. **55**, 4291 (1971).