Numerical Method and General Discussion of Integral Equations for the Primitive Model of the Electric Interface

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We describe an efficient numerical algorithm for solving integral equations commonly used in the theory of the primitive electrode. The method is applied to an approximation obtained from the first Born–Green–Yvon (BGY) equation using a modified Croxton–McQuarrie local neutrality ansatz, with accurate bulk correlations. For 1 M solutions of 1–1 electrolytes, and 0.5 M solutions of 2–2, 2–1, and 1–2 electrolytes, the agreement with computer experiments is good. To apply the method to other integral equations we formulate them as approximation schemes for the closure of the first member of the BGY hierarchy. Many of them are then seen to satisfy the local electroneutrality condition. We also suggest a new approximation which might be accurate even at very high couplings.

I. Introduction

There has been a revival of interest in the theory of the electric double layer. This research is centered primarily on the charge and potential distribution near the electrode walls where most of the interesting phenomena occur. For historic reasons it is customary to separate the electric double layer in the vicinity of the electrode into the inner Helmholtz–Stern[1] layer and the outer or diffuse layer. The theory of the outer layer, which is the one that we shall be concerned with here, was first developed by Gouy and Chapman[2] (GC). The GC theory neglects all correlations between the ions and much work has been devoted to improve this theory by including these interactions. The list of papers is rather long and we refer the reader to other recent work.[3-5] We only note here that, in spite of its oversimplification, the GC theory gives charge density profiles that satisfy the electroneutrality condition

$$\int_0^\infty dz \sum_i e_i \rho_i(z) = -\epsilon E_0/4\pi \qquad (1\text{-}1)$$

where z is the distance from the wall, e_i the charge and $\rho_i(z)$ the number density of ions of species i at point z, ϵ is the dielectric constant, and E_0 is the "bare" external field. The GC theory also satisfies, asymptotically for high electric fields E_0, the contact theorem[6]

$$kT\sum_i \rho_i(0) = P_B + \epsilon E_0^2/8\pi \qquad (1\text{-}2)$$

where kT is the Boltzmann thermal factor, and P_B is the bulk osmotic pressure. In the Gouy–Chapman theory $P_B = kT\sum_i \rho_i$ (ρ_i is the bulk number density of ions i) which is the ideal gas pressure. For even moderate charge densities, however, the pressure term is relatively small and can, therefore, be neglected.

The GC theory thus contains much of the essential features of the system and has in practice been used essentially without modification for the treatment of the diffuse layer. It might be thought in fact that, since the GC density profiles curves have the correct "area" and are correct at contact, nothing very drastic can happen when correlations are included in the theory. This is not so: The GC theory predicts a monotone decay of the potential $\phi(z)$ with distance, while this investigation as well as other recent theoretical work[5,7,8] and computer simulations[9] clearly indicate that for high valence and surface charge the potential oscillates, i.e., that there are layers of alternating charge near a flat electrode.

It is the purpose of this work to analyze further and solve some of the integral equations attempting to improve the GC theory.

In section II the basic integral equations are cast in a form reminiscent of the Poisson–Boltzmann theory

$$\rho_i(z) = \rho_i \exp[-e_i\psi(z) + J_i(z)] \qquad (1\text{-}3)$$

where $\rho_i(z)$ is the density, $\psi(z)$ is an electrostatic potential that satisfies Poisson's equation, and $J_i(z)$ is a correction term that depends on the particular approximation used. (The full notation is explained below.) This form of the equations lends itself to an efficient iteration algorithm based on the solution of the Poisson equation. This algorithm is illustrated by a numerical solution of the first BGY equation[10] with a simple closure.

(1) J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry", Plenum Press, New York, 1970.

(2) G. Gouy, *J. Phys.*, **9**, 457 (1910).

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

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

(5) C. W. Outhwaite, L. B. Bhuiyan, and S. Levine, *J. Chem. Soc., Faraday Trans. 2*, **76**, 1388 (1980).

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

(7) L. B. Bhuiyan, C. W. Outhwaite, and S. Levine, *Mol. Phys.*, **42**, 1271 (1981).

(8) L. Blum, L. B. Bhuiyan, and D. Henderson, presented at the 161st Meeting of the Electrochemical Society, Montreal, 1982.

(9) G. M. Torrie and J. P. Valleau, *Chem. Phys. Lett.*, **65**, 343 (1979); *J. Chem. Phys.*, **73**, 5807 (1980); *J. Phys. Chem.*, **86**, 3251 (1982).

In sections III and IV we discuss approximations based on closures for the pair correlation and direct pair correlation function. In particular, we discuss how well these approximations satisfy various sum rules, and try to formulate better approximations. The relation of the BGY-based theories to the modified Poisson–Boltzmann (MPB) theory of Loeb, Levine, and Outhwaite is clarified and we outline the solution of the MPB theory.

The relation of the Wertheim, Lovett, Mou, and Buff[11,12] (WLMB) theory to the hypernetted chain (HNC) equation is also discussed, and, in particular it is shown that the pair correlations of this theory satisfy the local electroneutrality theorem. A slightly different version of the HNC is derived from WLMB, but all of these approximations fail to satisfy eq 1-2 at low charges—while this is not very important for the primitive model, it is crucial in the case of molecular models, where the solvent is not a continuum dielectric.

II. Basic Equations

The primitive model of the electrode–electrolyte interface makes the following simplifications; the ions are hard spheres of diameter σ_i, electrical charge e_i, and bulk density ρ_i, $\sum \rho_i e_i = 0$. The solvent is a continuum of dielectric constant ϵ and the electrode is made of material with the same dielectric constant, ϵ. Thus, we ignore image forces.

The n-particle distribution functions of the electrolyte are denoted by

$$\rho_{i,j,...,k}(1,2,...,n) = \rho_{i,j,...,k}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_n) \quad (2\text{-}1)$$

where $i, j, ..., k$ denote the ionic species of particles located at positions $\vec{r}_1, \vec{r}_2, ..., \vec{r}_n$. We define the correlation function $g_{i,j,...,k}(1,2,...,n)$ by

$$\rho_i(1) = \rho_i g_i(1) \quad (2\text{-}2)$$

$$\rho_{ij}(1,2) = \rho_i(1) \, \rho_j(2) \, g_{ij}(1,2) \quad (2\text{-}3)$$

$$\rho_{ijk}(1,2,3) = \rho(1) \, \rho_j(2) \, \rho_k(3) \, g_{ijk}(1,2,3) \quad (2\text{-}4)$$

The truncated correlation functions $j_{i,j,...,k}(1,2,...,n)$ are also used:

$$h_i(1) = g_i(1) - 1 \quad (2\text{-}5)$$

$$h_{im}(1,2) = g_{ij}(1,2) - 1, \text{ etc.} \quad (2\text{-}6)$$

We start with the first Born–Green–Yvon equation[10] which has the form

$$-kT\vec{\nabla}_1 \ln \rho_1(1) =$$
$$\vec{\nabla}_1 U_1(1) + \int d\vec{r}_2 \sum_j \{\rho_j(2) \, g_{ij}(1,2)\vec{\nabla}_1 U_{ij}(1,2)\} \quad (2\text{-}7)$$

where $U_i(1)$ and $U_{ij}(1,2)$ are the one- and two-body potentials. These can be written as

$$U_i(1) = U_i^0(1) + e_i\psi^0(1) \quad (2\text{-}8)$$

$$U_{ij}(1,2) = U_{ij}^0(1,2) + e_i e_j/\epsilon r_{12} \quad (2\text{-}9)$$

$$r_{12} = |r_1 - r_2|$$

where $U_i^0(1)$ is the short-ranged part of the ion–wall interaction and $U_{ij}^0(1,2)$ the short-range ion–ion interaction. $\psi^0(1)$ is the bare electrostatic potential at $\vec{r}_1$. For semiinfinite system bounded by a flat electrode located at $z = 0$

$$\psi^0(1) = -E_0 z_1 \quad (2\text{-}10)$$

with E_0 the electric field in the positive z direction: This is the only direction in which there will be any spatial variation.

We now introduce the effective local electrostatic potential

$$\phi(1) = \psi^0(1) + \int d\vec{r}_2 \sum_j e_j\rho_j(2)/r_{12} \quad (2\text{-}11)$$

Since the charges shield the bare electrostatic potential, we expect that $\phi(z) \to 0$ as $z \to \infty$, so that $\phi(z)$ will be short-ranged. Equation 2-7 may now be rewritten as

$$kT\vec{\nabla}_1 \ln \rho_i(1) + \vec{\nabla}_1 U_1^0(1) + e_i\vec{\nabla}_1\phi(1) = \vec{I}_i^F(1) + e_i\vec{E}_i^F(1) \quad (2\text{-}12)$$

where

$$\vec{I}_i^F(1) = -\int d\vec{r}_2 \{\sum_j \rho_j(2) \, g_{ij}(1,2)\vec{\nabla}_1 U_{ij}^0(1,2)\} \quad (2\text{-}13)$$

$$\vec{E}_i^F = -\int d\vec{r}_2 \{\sum_j e_j\rho_j(2) \, h_{ij}(1,2)\}\vec{r}_{12}/|r_{12}|^3 \quad (2\text{-}14)$$

Equation 2-12 is a force balance equation: the singlet contributions on the left-hand side must balance the doublet contributions on the right-hand side. $\vec{I}_i^F(1)$ represents the contribution of the short-ranged (in our case, hard-core) pair forces, while $e_i\vec{E}_i^F(1)$ is the electrostatic contribution. The field $\vec{E}_i^F(1)$ is referred to in the modified Poisson–Boltzmann literature as the fluctuation field.[13-15]

Since the only spatial variation in our system is assumed to be in the z direction, we may write

$$\vec{I}_i^F(1) = -\vec{\nabla}_1 J_i^F(1) \quad (2\text{-}15)$$

$$\vec{E}_i^F(1) = -\vec{\nabla}_1\psi_i^F(1) \quad (2\text{-}16)$$

where $J_i^F(1)$ and $\psi_i^F(1)$ are, in the language of the MPB, the fluctuation potentials. Making use of eq 2-15 and 2-16 we can integrate the BGY equation 2-12 to yield

$$kT \ln [\rho(1)/\rho_i] + e_i\phi(1) = J_i^F(1) + e_i\psi_i^F(1) \quad (2\text{-}17)$$

where we have used the boundary conditions at infinity

$$\lim_{z \to \infty} J_i^F(1) = J_i^F(\infty) = \psi_i^F(\infty) = \phi(\infty) = 0 \quad (2\text{-}18)$$

$$\lim_{z \to \infty} \rho_i(1) = \rho_i \quad (2\text{-}19)$$

Equation 2-17 is exact as it stands. It is, however, not closed unless the inhomogeneous position-dependent $g_{ij}(1,2)$ is known. There are at least two methods by which we may proceed: (i) make an ansatz for the inhomogeneous $g_{ij}(1,2)$ in terms of the homogeneous $g_{ij}(r_{12})$ and the position-dependent densities $\rho_i(z)$; (ii) express the right-hand side of eq 2-17 in terms of the inhomogeneous direct correlation function $c_{ij}(1,2)$, and then make the corresponding ansatz for it.

The numerical scheme proposed here applies to both cases. This is an iteration scheme which starts by setting the right-hand side of eq 2-12 equal to zero. The resulting equation together with Poisson's equation, obtained from eq 2-11, gives the modified Gouy–Chapman equation.

$$\nabla_1^2\phi_0(1) = -(4\pi/\epsilon)\sum_i e_i\rho_i \exp[-e_i\phi_0(1)/kT] \quad (2\text{-}20)$$

Solving eq 2-20 for $\phi_0(1)$ and substituting it into eq 2-17 with the right-hand side set equal to zero yields the den-

(10) M. Born and H. S. Green, *Proc. R. Soc. London*, **188**, 10 (1946), J. Yvon, "La Theorie Statistique des Fuides", Hermann, Paris, 1935.
(11) M. S. Wertheim, *J. Chem. Phys.*, **65**, 2377 (1976).
(12) R. Lovett, C. Y. Mou, and F. P. Buff, *J. Chem. Phys.*, **65**, 570 (1976).

(13) A. L. Loeb, *J. Colloid Sci.*, **6**, 75 (1951).
(14) S. Levine and C. W. Outhwaite, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1670 (1978).
(15) C. W. Outhwaite, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1214 (1978).

sities $\rho_i^{MGC}(z)$. We now use these densities to compute the inhomogeneous $g_{ij}(1,2)$ or $c_{ij}(1,2)$. From this we get both the fluctuation terms $J_i^F(1|\rho^{MGC})$ and $\psi_i^F(1|\rho^{MGC})$. With the aid of Poisson's equation we now get a new equation for the first iterate $\phi_1(1)$

$$\nabla^2\phi_1(1) = \frac{-4\pi}{\epsilon}\sum_i e_i\rho_i \exp\left\{\frac{1}{kT}[-e_i\phi(1) + J_i^F(1|\rho^{MGC}) + \right.$$
$$\left. e_i\psi_i^F(1|\rho^{MGC})]\right\} \quad (2\text{-}21)$$

This equation is solved numerically by using the highly efficient predictor–corrector algorithm, with the boundary conditions

$$-\nabla\phi(1) = E_0 \qquad (z_1 = 0) \qquad (2\text{-}22)$$

$$\phi(1) = 0 \qquad (z_1 \to \infty) \qquad (2\text{-}23)$$

Once $\phi_1(1)$ is obtained, a new density profile $\rho_i^1(1)$ is calculated via eq 2-17, from which new fluctuation terms $J_i^F(1|\rho^1)$, $\psi_i^F(1|\rho^1)$ are calculated, and so on. The procedure is illustrated in Appendix A where it is used with a closure based on the local electroneutrality condition,[16] modified to make $g_{ij}(r) = 0$ for $r < \sigma_{ij}$.

We close this section by showing explicitly that the $c_{ij}(1,2)$-based approximation can be written in the form of eq 2-17. These are the WLMB[11,12] equation and the HNC equation.[17-20] The WLMB equation was originally derived for finite-range forces. A rigorous derivation[21-23] was recently given for the case of Coulombic interactions. (This derivation is based on the first and second member of the BGY hierarchy and, of course, the Ornstein–Zernike (OZ) equations which define the inhomogeneous direct correlation function $c_{ij}(1,2)$.) We write it in the form

$$kT\vec{\nabla}_1 \ln \rho_i(1) + \vec{\nabla}_1 U_i^0(1) + e_i\vec{\nabla}_1\phi(1) =$$
$$-kT\sum_j \int d\vec{r}_2 \, \rho_j(2)\vec{\nabla}_2 c_{ij}^s(1,2) \quad (2\text{-}24)$$

where we have introduced c_{ij}^s, the (hopefully) short-ranged part of c_{ij} by the definition

$$c_{ij}^s(1,2) \boxminus c_{ij}(1,2) + \frac{1}{\epsilon kT}\frac{e_i e_j}{r_{12}} \quad (2\text{-}25)$$

Clearly

$$J_i^{WLMB}(1) = -kT\int_{z_1}^{\infty} dz_2 \sum_j \int d\vec{r}_3 \, \rho_j(3)\vec{\nabla}_3 c_{ij}^s(2,3) \quad (2\text{-}26)$$

This is an exact expression, which is not closed however until $c_{ij}^s(2,3)$ is approximated. The corresponding expression for the HNC approximation is

$$J_i^{HNC}(1) = kT\sum_j \int d\vec{r}_2 \, c_{ij}^B(r_{12})[\rho_j(2) - \rho_j] \quad (2\text{-}27)$$

where $c_{ij}^B(r_{12})$ is the (in principle) known bulk direct pair correlation function. The relationship between these two equations will be discussed in section IV.

(16) T. L. Croxton and D. A. McQuarrie, *Mol. Phys.*, **42**, 141 (1981).
(17) L. Blum and G. Stell, *J. Stat. Phys.*, **15**, 439 (1976).
(18) D. E. Sullivan and G. Stell, *J. Chem. Phys.*, **67**, 2567 (1977).
(19) D. Henderson, L. Blum, and W. R. Smith, *Chem. Phys. Lett.*, **63**, 381 (1979).
(20) S. L. Carnie, D. Y. C. Chan, D. J. Mitchell, and B. W. Ninham, *J. Chem. Phys.*, **74**, 1472 (1981).
(21) A. R. Altenberger, *J. Chem. Phys.*, **76**, 1473 (1982).
(22) A. R. Altenberger and H. L. Friedmann, *J. Chem. Phys.*, in press.
(23) L. Blum, Ch. Gruber, D. Henderson, J. L. Lebowitz, and P. A. Martin, *J. Chem. Phys.*, **78**, 3195 (1982).
(24) C. Gruber, J. L. Lebowitz, and P. A. Martin, *J. Chem. Phys.*, 994 (1981).

III. Approximations Based on the Pair Distribution Function

We start with the second member of the BGY hierarchy,[10] which relates $g_{ij}(1,2)$ to the triplet correlation function

$$-kT\vec{\nabla}_1 \ln \rho_{ij}(1,2) = \vec{\nabla}_1[U_i(1) + U_{ij}(1,2)] +$$
$$\sum_k \int d\vec{r}_3 \, [\rho_{ijk}(1,2,3)/\rho_{ij}(1,2)]\vec{\nabla}_1 U_{ik}(1,3) \quad (3\text{-}1)$$

where the potentials are given by eq 2-8 and 2-9. As it stands eq 3-1 has both long-ranged and short-ranged terms. For our discussion it will be convenient to convert all the manifestly long-ranged terms to short-ranged ones. Substracting eq 2-7 from eq 3-1 yields

$$\vec{\nabla}_1[kT \ln g_{ij}(1,2) + U_{ij}(1,2)] =$$
$$-\sum_k \int d\vec{r}_3 \, [\rho_{ijk}(1,2,3)/\rho_{ij}(1,2) - \rho_{ik}(1,3)/\rho_i(1)]\vec{\nabla}_1 U_{ik}(1,3) \quad (3\text{-}2)$$

We now introduce the "conditional potential", i.e., the potential at r_1 given that there is a particle of species j at r_2

$$\phi_j^c(1/2) = e_j/\epsilon r_{12} + \sum_k e_k \int d\vec{r}_3 \, \rho_k(3) \, h_{jk}(2,3)/\epsilon r_{13} \quad (3\text{-}3)$$

This permits us to rewrite eq 3-2 in a form which no longer contains the unscreened Coulomb potential

$$\vec{\nabla}_1[kT \ln g_{ij}(1,2) + U_{ij}^0(1,2) + e_j\phi_j^c(1|2)] =$$
$$\vec{I}_{ij}^{F2}(1|2) + e_i\vec{E}_{ij}^{F2}(1|2) \quad (3\text{-}4)$$

where

$$\vec{I}_{ij}^{F2}(1|2) =$$
$$\sum_k \int d\vec{r}_3 \, [g_{ijk}(1,2,3)/g_{ij}(1,2) - g_{ik}(1,3)]\rho_k(3)\vec{\nabla}_1 U_{ik}^0(1,3) \quad (3\text{-}5)$$

is the hard-core contribution to the two-body fluctuation force, and

$$\vec{E}_{ij}^{F2}(1/2) = (1/\epsilon)\sum_k e_k \int d\vec{r}_3 \, [g_{ijk}(1,2,3)/g_{ij}(1,2) - g_{ik}(1,3) - h_{jk}(2,3)]\rho_k(3)z_{13}/r_{13}^3 \quad (3\text{-}6)$$

The conditional potential ϕ_j^c satisfies the Poisson equation, as can be seen from eq 3-3 and the fact that

$$\nabla_1^2 1/|r_{1i}| = -4\pi\delta(\vec{r}_1 - \vec{r}_i) \quad (3\text{-}7)$$

$$\nabla_1^2\phi_j^c(1|2) = -(4\pi/\epsilon)[e_j\delta(\vec{r}_{12}) + \sum_k e_k\rho_k(1) \, h_{jk}(2,1)] \quad (3\text{-}8)$$

Any charge distribution that satisfies eq 3-8 with the proper boundary conditions will also satisfy the electroneutrality condition

$$\int d\vec{r}_2 \sum_k e_k\rho_k(2) \, h_{ik}(1,2) = -e_i \quad (3\text{-}9)$$

We are now ready to consider some approximation schemes.

Convolution Approximation. The truncated triplet correlation function is defined as The Totsuji–Ichimaru[25]

$$h_{ijk}(1,2,3) = g_{ijk}(1,2,3) - g_{ij}(1,2) - g_{ik}(1,3) - g_{jk}(2,3) + 2 \quad (3\text{-}10)$$

convolution approximation consists of setting

$$h_{ijk}(1,2,3) = h_{ij}(1,2) \, h_{jk}(2,3) + h_{ik}(1,3)h_{kj}(3,2) +$$
$$h_{ki}(3,1) \, h_{ij}(1,2) + \sum \int d\vec{r}_4 \, \rho_l(4) \, h_{il}(1,4) \, h_{jl}(2,4) \, h_{kl}(3,4) \quad (3\text{-}11)$$

(25) H. Totsuji and S. Ichimaru, *Prog. Theor. Phys.*, **50**, 753 (1973).

The convolution approximation has the desirable property that, if the pair distributions satisfy the electroneutrality condition 3-9, then the triplet function will automatically satisfy "its" electroneutrality condition; i.e., using eq 3-11 and 3-9 gives

$$\sum_k e_k \int d\vec{r}_3 \, \rho_k(3) \, h_{ijk}(1,2,3) =$$

$$h_{ij}(1,2) \sum_k e_k \int d\vec{r}_3 \, \rho_k(3)[h_{jk}(2,3) + h_{ik}(1,3)] +$$

$$\sum_k e_k \int d\vec{r}_3 \, \rho_k(3) \, h_{ik}(1,3) \, h_{kj}(3,2) +$$

$$\sum_{k,l} e_k \int d\vec{r}_3 \, d\vec{r}_4 \, \rho_k(3) \, \rho_l(4) \, h_{il}(1,4) \, h_{jl}(2,4) \, h_{kl}(3,4)$$

$$= -(e_i + e_j) h_{ij}(1,2) \quad (3\text{-}12)$$

The equality between the left and right sides of eq 3-12 can be proven to hold[26] whenever correlations decay faster than r^{-3}. It also holds[23,27] for a flat interface, the case being considered here, when the correlations parallel to the wall are expected to decay precisely as r^{-3}. We note however that for flat interfaces the long-ranged correlations produce nonzero dipole moments in the pair and higher distributions.[27] These satisfy the relations

$$kT \, (\partial \ln \rho_i(1)/\partial E) = \sum_j e_j \int d\vec{r}_2 \, (z_2 - z_1)\rho_j(2) \, h_{ij}(1,2)$$

$$(3\text{-}13)$$

$$kT \frac{\partial \ln \rho_{ij}(1,2)}{\partial E} = -\tfrac{1}{2}(e_i - e_j)(z_1 - z_2) +$$

$$\sum_k e_k \int d\vec{r}_3 \, [\rho_{ijk}(1,2,3)/\rho_{ij}(1,2) - \rho_k(3)]\left(\frac{z_1 + z_2}{2} - z_3\right)$$

$$(3\text{-}14)$$

The convolution approximation fails to satisfy these relations.

Finally, because it satisfies the first two members of the Born–Green–Yvon hierarchy and the electroneutrality sum rule, it is clear that the convolution approximation will also satisfy the derivative sum rule[23]

$$-\vec{\nabla}_1 \rho_i(1) = \sum_j \int d\vec{r}_2 \, \vec{\nabla}_2[\rho_i(1) \, \rho_j(2) \, h_{ij}(1,2)] \quad (3\text{-}15)$$

The convolution approximation thus satisfies "almost all" the known exact relations and for this (or other unknown) reason it gives good results for the pair correlation in the uniform one-component plasma. We expect therefore that it will be reasonably accurate theory also for charged interfaces. We hope to have numerical results for the convolution approximation equations in the near future. These are explicitly eq 2-17 and the set

$$\vec{\nabla}_1[kT \ln g_{ij}(1,2) + U_{ij}^0(1,2) + e_i\phi_j(1|2)] =$$
$$\vec{I}_{ij}^{F2}(1|2) + e_i\vec{E}_{ij}^{F2}(1|2) \quad (3\text{-}16)$$

with

$$\vec{I}_{ij}^{F2}(1|2) =$$
$$-\sum_k \int d\vec{r}_3 \, [g_{ijk}(1,2,3)/g_{ij}(1,2) - g_{ik}(1,3)]\rho_k(3)\vec{\nabla}_1 U_{ik}^0(1,3)$$

$$(3\text{-}17)$$

$$\vec{E}_{ij}^{F2}(1|2) =$$
$$\sum_k e_k \int d\vec{r}_3 \, [\rho_k(3)/g_{ij}(1,2)][z_{13}/\epsilon r_{13}^3]\Big[h_{ik}(1,3) \, h_{kj}(3,2) +$$
$$\sum_l \int d\vec{r}_4 \, \rho_l(4) \, h_{il}(1,4) \, h_{jl}(2,4) \, h_{kl}(3,4)\Big] \quad (3\text{-}18)$$

(26) L. Blum, C. Gruber, J. L. Lebowitz, and P. A. Martin, *Phys. Rev. Lett.*, **48**, 1769 (1982).
(27) L. Blum, D. Henderson, J. L. Lebowitz, C. Gruber, and P. A. Martin, *J. Chem. Phys.*, **75**, 5974 (1981).

Modified Poisson–Boltzman Theory. Although the modified Poisson–Boltzmann theory can be derived from the BGY equation, it was originally formulated in a more intuitive manner.[12,14,15] For the purpose of our discussion we will follow (loosely) Outhwaite's work.[15] The basic assumption is to set the right side of eq 3-4 equal to zero yielding

$$\vec{\nabla}_1[kT \ln g_{ij}(1,2) + U_{ij}^0 + e_i\phi_j^c(1|2)] = 0 \quad (3\text{-}19)$$

or equivalently, letting θ be the step function

$$g_{ij}(1,2) = \theta(|r_{12}| - \sigma_{ij}) \, \exp[-e_i\phi_j^c(1|2)/kT] \quad (3\text{-}20)$$

This is then substituted into eq 3-9 to give

$$\nabla_1^2\phi_j(1|2) = -(4\pi/\epsilon)[e_j\delta(\vec{r}_1 - \vec{r}_2)] +$$
$$\sum_k e_k\rho_k(1)[\theta(|r_{12}| - \sigma_{ij}) \, \exp\{-e_k\phi_j^c(1|2)\} - 1] \quad (3\text{-}21)$$

Linearizing eq 3-19 we get a Debye–Hückel-like equation in the form

$$\nabla_1^2\phi_j(1|2) = \phi_j^c(1|2) \, q^2(1) - 4\pi e_j \, \delta(\vec{r}_1 - \vec{r}_2) \quad (3\text{-}22)$$

where

$$q^2(1) = \frac{4\pi}{\epsilon kT}\sum_i \rho_i(1)e_i^2 \quad (3\text{-}23)$$

This equation has to be solved with the boundary conditions appropriate for our geometry. The solution for the plane electrode case is discussed in Appendix B.

It is clear that, in this version, the MPB will satisfy the electroneutrality for both the singlet and pair distribution functions, and, in an approximate form, the contact theorem. But the pair distribution function, which here is given by either the Poisson–Boltzmann theory or the Debye–Hückel theory will be far off the exact known values. Clearly also, the MPB does not satisfy the dipole sum rule (eq 3-13), although in the version proposed here it will have a nonzero dipole moment.

Croxton–McQuarrie Approximation. In its modified version[26] the Croxton–McQuarrie closure of the BGY has the form

$$h_{ij}(1,2) = f_i(1) \, f_j(2) \, h_{ij}(r_{12}) \quad (r > \sigma_{ij})$$

$$= -1 \quad (r \le \sigma_{ij}) \quad (3\text{-}24)$$

where the functions $f_i(1)$ are found from the solution of the electroneutrality relation

$$-e_i = \sum_j \int d\vec{r}_2 \, \rho_j(2) \, h_{ij}(1,2) \quad (3\text{-}25)$$

This approximation is discussed in Appendix A. It satisfies the electroneutrality and contact theorems but violates the first moment rule, eq 3-13, which implies long-ranged correlations along the electrode wall.

Modified Convolution Approximation. An alternative closure at this level, which will also satisfy the local electroneutrality theorem for the pair distribution function, is obtained from the Totsuji–Ichimaru convolution approximation for three 3 ions in a homogeneous system by blowing up one of them to make it the wall. We get

$$\rho_{ij}^T(1,2) = \rho_{ij}(1,2) - \rho_i(1) \, \rho_j(2)$$
$$= h_{ij}^B(r_{12})[\rho_j\rho_i(1) + \rho_j(2)\rho_i - \rho_i\rho_j] +$$
$$\rho_i\rho_j\sum_l \int d\vec{r}_4 \, h_{il}^B(r_{14}) \, h_{jl}^B(r_{24})[\rho_l(4) - \rho_l] \quad (3\text{-}26)$$

IV. Approximations Based on the Direct Correlation Function

It was shown at the end of section II that the replacement of $h_{ij}(1,2)$ by the direct correlation function $c_{ij}(1,2)$,

defined through the Ornstein–Zernike relation, yields an exact equation which contains the potential ϕ and the short-ranged part $c_{ij}(1,2)$. In the HNC theory and related approximations $c_{ij}^s(1,2)$ is replaced by the short-range part of bulk direct correlation function $c_{ij}^B(1,2)$. We will now show that, while this fails to satisfy the contact relation exactly, it will do so approximately for high fields because it satisfies the Poisson equation. We will also show that, although these equations do not involve h_{ij} explicitly, the h_{ij} which is computed via the inhomogeneous OZ equation will always satisfy the electroneutrality condition.

Integrating eq 2-24 over z_1 and summing over i, we get

$$kT[\textstyle\sum_i \rho_i - \sum_i \rho_i(0)] + \epsilon E_0^2/8\pi =$$
$$-kT \sum_{i,j} \int_0^z dz_1 \int d\vec{r}_2 \, [\rho_i(1) \, \rho_j(2)\vec{\nabla}_2 c_{ij}^s(1,2)] \quad (4\text{-}1)$$

By a slight rearrangement eq 4-1 can be written in a form similar to the contact theorem

$$kT\textstyle\sum_i \rho_i(0) - \epsilon E_0^2/8\pi =$$
$$kT\sum_i \left\{\rho_i - \sum_j \int_0^z dz_1 \int d\vec{r}_2 \, \rho_i(1) \, \rho_j(2)\vec{\nabla}_2 c_{ij}^s(1,2)\right\} \quad (4\text{-}2)$$

$$kT\textstyle\sum_i \rho_i(0) = (\epsilon E_0^2/8\pi) - P_B \quad (4\text{-}3)$$

where P_B is the bulk pressure.

Now, the direct correlation function can be written as the sum of the bulk direct correlation function and a correction term

$$c_{ij}^s(1,2) = c_{ij}^B(r_{12}) + c_{ij}^\Delta(1,2) \quad (4\text{-}4)$$

If we neglect the correction term $c_{ij}^\Delta(1,2)$, then the right-hand side of eq 4-2 is

$$-kT \sum_{i,j} \int_0^z dz_1 \int d\vec{r}_2 \, \rho_i(1) \, \rho_j(2)\vec{\nabla}_2 c_{ij}^B(1,2) =$$
$$-kT \, 2\pi \sum_{i,j} \left\{\int_0^z dz_1 \int_0^\infty dq_{12}\rho_i(1) \, \rho_j(2)\vec{\nabla}_2 c_{ij}^B(r_{12}) + \right.$$
$$\left. \int_0^z dz_1 \int_z^\infty dz_2 \, \rho_i(1) \, \rho_j(2) \int_0^\infty d\vec{r}_{12} \, q_{12}\frac{\partial}{\partial z_2}c_{ij}^B(r_{12})\right\}$$
$$= kT \sum_{i,j} \rho_i\rho_j \int d\vec{r}_{12} \, c_{ij}^B(r_{12}) \quad (4\text{-}5)$$

where we have set $q_{12} = (r_{12}^2 - z_{12}^2)^{1/2}$ and used the symmetry properties (translational symmetry in this case) of the bulk direct correlation function. The WLMB equation in this approximation is

$$kT \ln\,[\rho_i(1)/\rho_i] + e_i\phi(1) =$$
$$-kT\sum_i\left\{\int d\vec{r}_2 \, \rho_j(2)c_{ij}^B(r_{12}) - \rho_j \int dr_2 \, c_{ij}^B(r_{12})|_{r_1=\infty}\right\} \quad (4\text{-}6)$$

which leads to the relation

$$kT\textstyle\sum_i \rho_i(0) - \frac{\epsilon E_0^2}{8\pi} = kT \sum_{i,j} \rho_j\left[\delta_{ij} - \rho_j \int d\vec{r}_2 \, c_{ij}^B(r_{12})\right]$$
$$= \textstyle\sum \rho_i(\partial P_B/\partial \rho_i) \quad (4\text{-}7)$$

The right-hand side of eq 4-7 is not equal to P_B, as it ought to be according to eq 1-2. We note however that for low concentrations the error introduced is small: indeed, both the inverse compresibility and the pressure are equal for ideal gases. We also remark that the hypernetted chain approximation, and, in fact, any equation derived from eq 2.27, yields for the contact densities the relation

$$kT\textstyle\sum_i \rho_i(0) - \epsilon E_0^2/8\pi =$$
$$\textstyle\sum_i \rho_i(\partial P_B/\partial \rho_i)_i + kT\sum_{ij}\rho_i(0) \int d\vec{r}_2 \, \rho_j(2) \, c_{ij}^B(r_{12})|_{z_1=0} \quad (4\text{-}8)$$

For low fields this is an error by roughly the square root of the isothermal compressibility. This is the most serious problem of the HNC equation.

Sum Rules. There is the question of how well approximations based on the direct correlation function satisfy the exact sum rules for the inhomogeneous distribution functions.[24] We will assume that, although not explicitly given or used in those theories, the pair correlation functions are defined by the inhomogeneous Ornstein–Zernike equation

$$h_{ij}(1,2) = c_{ij}(1,2) + \sum_k \int d\vec{r}_3 \, h_{ik}(1,3) \, \rho_k(3) \, c_{kj}(3,2) \quad (4\text{-}9)$$

and define the charge correlations and local screening parameter

$$S(1,2) = \sum_{i,j} e_i e_j \rho_{ij}^T(1,2) \quad (4\text{-}10)$$

$$\hat{S}(1,2) = \sum_{i,j} e_i e_j \hat{\rho}_{ij}^T(1,2) \quad (4\text{-}11)$$

where

$$\rho_{ij}^T(1,2) = \rho_i(1) \, \rho_j(2) \, h_{ij}(1,2) \quad (4\text{-}12)$$

$$\hat{\rho}_{ij}^T(1,2) = \rho_{ij}^T(1,2) + \rho_i(1) \, \rho_j(2) \, \delta(\vec{r}_1 - \vec{r}_2)\delta_{ij} \quad (4\text{-}13)$$

Using eq 4-9 and the definition 2-25 gives the relation

$$S(1,2) = I(1,2) - \frac{q^2(1)}{4\pi} \int dr_3 \, \frac{1}{r_{13}}\hat{S}(3,2) \quad (4\text{-}14)$$

with

$$q^2(1) = (4\pi\beta/\epsilon)\textstyle\sum_i e_i^2\rho_i(1) \quad (4\text{-}15)$$

$$I(1,2) = \sum_{i,j,k} e_i e_j\rho_i(1) \int d\vec{r}_3 \, c_{ik}^s(1,3) \, \hat{\rho}_{kj}^T(3,2) \quad (4\text{-}16)$$

In the presence of the flat wall the system has cylindrical symmetry. Consider, therefore, the two-dimensional Fourier transform

$$\tilde{S}(k;z_1z_2) = \int dx_{12} \, dy_{12} \, e^{ik_1q_{12}}S(1,2) \quad (4\text{-}17)$$

Then, since

$$\int dx_{12} \, dy_{12} \, (e^{ikq_{12}}/r_{12}) = e^{-K|z_{12}|}/K \quad (4\text{-}18)$$

we arrive at

$$\tilde{S}(K;z_1z_2) = \tilde{I}(K;z_1z_2) - \frac{q^2(1)}{4\pi K} \int dz_3 \, e^{-K|z_{13}|}\hat{S}(K;z_1) \quad (4\text{-}19)$$

If one assumes now that $\tilde{S}(K;z_1z_2)$ and $\tilde{I}(K;z_1z_2)$ are the transforms of finite-ranged nonsingular functions, they will have the form

$$\tilde{S}(K;z_1z_2) = S^3(z_1z_2) + KS^1(z_1z_2) + \dots \quad (4\text{-}20)$$

$$\tilde{I}(K;z_1z_2) = I^3(z_1z_2) + KI^1(z_1z_2) + \dots \quad (4\text{-}21)$$

Therefore, the coefficient of $1/K$ in eq 4-19 must be zero

$$\int_0^\infty dz_3 \, \hat{S}(0;z_3z_2) = 0 \quad (4\text{-}22)$$

TABLE I: Comparison of the Different Theories to the Computer Simulations of Torrie and Valleau

charge								no. of
σ covl/M^2	b^a	M Carlo	MGC	MPB4	HNC/MSA	BGY	1st iterate	iterations
1-1 Electrolyte, 1 M								
0.0996	1.505	1.09	1.390	1.00	0.985	1.033	1.06	7
0.2501	3.78	2.13	2.787	2.04	1.954	2.082	2.15	8
0.4249	6.422	3.08	3.766		2.444	$(3.18)^b$	(3.27)	9
2-2 Electrolyte, 0.5 M								
0.1704	3.65	0.60	1.362		0.500	0.593	0.69	9
2-1 Electrolyte, 0.5 M								
0.0989	2.12	1.04	1.310	0.953	1.004	0.959	0.946	5
0.20	4.28	1.94	2.366	1.797	1.898	1.859	1.871	8
1-2 Electrolyte, 0.5 M								
0.05	1.07	0.40	0.547	0.18	0.336	0.365	0.344	6
0.10	2.14	0.50	0.9597	0.22	0.471	0.499	0.467	5
0.170	3.65	0.45	1.380	0.20	0.487	0.541	0.515	11
0.240	5.14	0.35	1.684	0.176	0.354	0.498	0.478	12

^{a} The adimensional parameter b is defined in ref 28 and 29. ^{b} In this case the electroneutrality relation yielded a small region with negative correlations. We suppressed this unphysical region by setting the correlations to zero in this region, which was of about 0.1 A wide near the electrode.
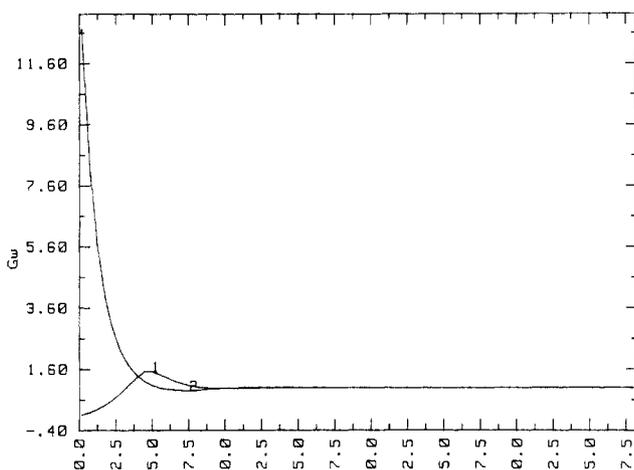

Figure 1. Profile of $G_w = \rho_i(2)/\rho_i$ for a 2-2 (0.5 M) electrolyte near a charged wall. Surface charge density is 0.174 C/m^2 ($b = 3.65$).
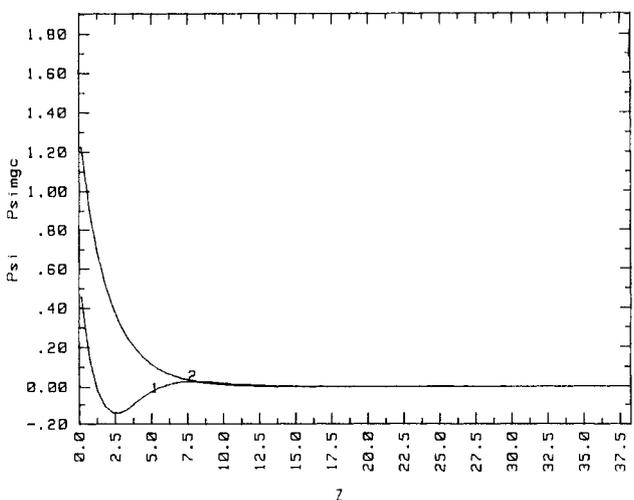

Figure 2. Voltage profile for a 2-2 (0.5 M) electrolyte near a charged wall. Curve 2 is the Modified Gouy–Chapman voltage.

which in turn implies the electroneutrality condition 3-27.

It follows then that the HNC in any of its versions, where c^s is replaced by the short-range part of the bulk HNC or bulk MSA, gives direct correlation function with pair distribution functions that satisfy the local electro-

neutrality theorem.

Appendix A

Numerical Solution of the *BGY + EN Equation.* The numerical solution of the BGY + EN equation for 1-1 electrolytes was found by Croxton and McQuarrie[16] using Picards iteration. This algorithm needs a large number of iterations, typically 10^3, to reach convergence. For high couplings (2-2, 1-2 electrolytes) we were not able to get convergence with a reasonable number of iterations.

Consider, the Poisson equation 2.21

$$\nabla^2 \phi(1) = -(4\pi/\epsilon)\sum_i e_i\rho_i \exp\{\beta[e_i(-\phi(1)) + \psi_i^F(1|\rho(1)) + J_i^F(1|\rho(1))]\}$$

$$(A\text{-}1)$$

This is a nonlinear integrodifferential equation. The worst nonlinearity, which creates the instability and convergence problems, is connected to the singlet potential $\phi(1)$. In general, the field terms ψ_i^F, J^F (called fluctuation potentials in the MPB literature[13-15]) are small at reasonably low couplings. We may, therefore, ignore them in the first iteration, which will then give us the GC equation. From eq 2.13 and 2.14 we have explicit expressions.

$$J_i^F(z) = 2\pi kT \sum_j \int_z^\infty dz_1 \int_{[0,z_1-\sigma_{ij}]}^{z_1+\sigma_{ij}} dz_2\, z_{12}\rho_j(z_2) \times$$
$$[f_i(z_1)\, f_j(z_2)\, h_{ij}^B(\sigma_{ij}) + 1] \quad (A\text{-}2)$$

where σ_{ij} is the distance of closest approach

$$\psi_i^F(z) = \frac{2\pi}{\epsilon}\sum_j e_j \int_z^\infty dz_1 \int_0^\infty dz_2\, \rho_j(z_{12}) \times$$
$$|z_2|f_i(z_1)\, f_j(z_2) \left[\int_{[\sigma_{ij},|z_{12}|]}^\infty dr_{12}\, h_{ij}^B(r_{12})/r_{12}^2\right] \quad (A\text{-}3)$$

The functions $f_i(z)$ are obtained by solving by iteration the electroneutrality relation

$$e_i = \pi \sum_j e_j \int_{[0,z_1-\sigma_{ij}]}^{z_1+\sigma_{ij}} dz_2 \ (\sigma_{ij}{}^2 - z_{12}{}^2)\rho_j(z_2) -$$

$$2\pi f_i(z_1) \sum_j e_j \int_0^\infty dz_2 \ \rho_j(z_2) \ f_j(z_2) \int_{[\sigma_{ij},|z_{12}|]}^\infty dr_{12} \ r_{12} h_{ij}{}^B(r_{12})$$

$$(A\text{-}4)$$

In all of the above formulas we have used the Croxton–McQuarrie ansatz for the pair distribution function.[16] In their work, however, the pair correlation function is not −1 inside the exclusion volume. The ansatz must be corrected to

$$h_{ij}(1,2) = f_i(z_1) \ f_j(z_2) \ h^B(r_{12}) \quad (r_{12} > \sigma_{ij})$$

$$= -1 \qquad (r_{12} \le \sigma_{ij}) \qquad (A\text{-}5)$$

Once the functions $f_i(z)$ and $\rho_i(z)$ are computed, we calculate $J_i{}^F(z)$ and $\psi_i{}^F(z)$. These results are plugged into eq A-1. This equation is then solved numerically by a predictor–corrector algorithm: This requires the knowledge of both the potential and field at $z = 0$. Since only the field is known, we just guess the potential and solve until $\psi_\infty = \lim_{z \to \infty} \psi(z)$ blows up. A new $\psi(0)$ is then tried until $\psi_\infty <$ tolerance. We remark that this is quite fast because it involves only a one-dimensional integral.

The convergence of the overall procedure is excellent. Usually the first iteration will produce an acceptable answer (within 5% of the final one). (See Table I.)

The results for (1 M) 1–1 salts are in good agreement with both the HNC/MSA theories and not in drastic disagreement with the GC theory. However, the results for 0.496 M 2–2 salts and 2–1 salts were in sharp disagreement with the MGC results. The results are given in Table I and Figures 1 and 2.

The overall agreement with the computer experiments of Torrie and Valleau is excellent for the few cases that have been computed. We must remark that our calculations are based on HNC bulk pair distribution functions, which are rather accurate.

The agreement is not so good only at the highest coupling, namely, the case of the 2:1 electrolyte.

Appendix B

Modified Poisson–Boltzmann Approximation. We give here an explicit solution of the linearized Debye-Huckel-like equation 3-24, when the ions are assumed to be pointlike particles. Our solution does take into account the symmetry explicitly and therefore is closely related to the recent work of Jancovici.[31] The correlations obtained in this way will satisfy local electroneutrality and also will have long-ranged correlations along the electrode surface.

Consider now eq 3-24

$$-\nabla_i{}^2 \phi_j(1|2) = q^2(1) \ \phi_j(1|2) - (4\pi/\epsilon)e_j\delta(\vec{r}_1 - \vec{r}_2) \qquad (B\text{-}1)$$

The two-dimensional Fourier transform (along the electrode surface) is

$$\tilde{\phi}_j(K;z_1 z_2) = \int dx_{12} \ dy_{12} \ e^{i\vec{K}_1\vec{q}_{12}}\phi_j(1|2) \qquad (B\text{-}2)$$

Then eq B-1 becomes

$$\left[\frac{\partial^2}{\partial z_1{}^2} - K^2 - q^2(1)\right]\tilde{\phi}_j(K;z_1 z_2) = \frac{-4\pi}{\epsilon}e_j\delta(|z_{12}|)$$

$$z_1 > 0 \qquad (B\text{-}3)$$

$$\left[\frac{\partial^2}{\partial z_1{}^2} - K^2\right]\tilde{\phi}_j(K;z_1 z_2) = 0$$

$$z_1 < 0 \qquad (B\text{-}4)$$

Equation B-3 has no analytical solution for arbitrary $q^2(1)$. However, if we can approximate $q^2(1)$ by a sum of exponentials

$$q^2(1) = \sum_{n=1}^\infty \theta_n e^{-nz_1 q^\infty} + q_\infty{}^2 \qquad (B\text{-}5)$$

Then eq B-3 is Hill's equation[32] and has closed-form solution.

Let us first comment on the expansion B-5. This expansion is accurate for low applied fields E_0 and high ionic concentration.

For the case of 1–1 electrolyte, the Gouy–Chapman result is

$$\theta_{2n} = 8nq_\infty{}^2 \tanh \ [\beta e\phi_0/4] \qquad \theta_{2n+1} = 0 \qquad (B\text{-}6)$$

where ϕ_0 is the potential drop across the diffuse layer. To simplify the notation, let us write ϕ_j for $\phi_j(K;z_1 z_2)$. The solution of eq B-3 and B-4 will consist of three pieces:

$$\tilde{\phi}_j{}^L = A_j{}^L(z_2)e^{kz_1} \qquad z_1 < 0 \qquad (B\text{-}7)$$

$$\tilde{\phi}_j{}^I = A_j{}^I(z_2) \ \eta_+(z_1) + B_j{}^I(z_2) \ \eta_-(z_1) \qquad 0 < z_1 < z_2 \quad (B\text{-}8)$$

$$\tilde{\phi}_j{}^{II} = B_j{}^{II}(z_2) \ \eta_-(z_1) \qquad z_1 < z_2 < \infty \qquad (B\text{-}9)$$

These solutions must satisfy the following boundary conditions:

$$\tilde{\phi}_j{}^L \to 0 \qquad \text{for } z_1 \to -\infty \qquad (B\text{-}10)$$

$$\tilde{\phi}^{II} \to 0 \qquad \text{for } z_1 \to \infty \qquad (B\text{-}11)$$

$$\tilde{\phi}_j{}^L = \tilde{\phi}_j{}^L \qquad \text{at } z_1 = 0 \qquad (B\text{-}12)$$

$$\tilde{\phi}_j{}^I = \tilde{\phi}_j{}^{II} \qquad \text{at } z_1 = z_2 \qquad (B\text{-}13)$$

$$\frac{\partial}{\partial z_1}[\tilde{\phi}_j{}^L] = \frac{\partial}{\partial z_1}[\tilde{\phi}_j{}^I] \qquad \text{at } z_1 = 0 \qquad (B\text{-}14)$$

$$\frac{\partial}{\partial z_1}[\tilde{\phi}_j{}^I] - \frac{\partial}{\partial z_1}[\tilde{\phi}_j{}^{II}] = \frac{4\pi}{\epsilon}e_j \qquad \text{at } z_1 = 0 \quad (B\text{-}15)$$

The functions $\eta_+(z_1)$ and $\eta_-(z_1)$ are the solutions of the homogeneous Hill equation

$$\left\{\frac{\partial^2}{\partial z_1{}^2} - K^2 - q_\infty{}^2 - \sum_{n=1}^\infty \theta_n e^{-nz_1 q^\infty}\right\}\tilde{\phi} = 0 \quad (B\text{-}16)$$

Clearly

$$\eta_+(z_1) = e^{+z_1(K^2+q\infty^2)^{1/2}}[1 + \sum_{n=1}^\infty c_n{}^+ e^{-nq\infty z_1}] \quad (B\text{-}17)$$

$$\eta_-(z) = e^{-z_1(K^2+q\infty^2)^{1/2}}[1 + \sum_{n=1}^\infty c_n{}^- e^{-nq\infty z_1}] \quad (B\text{-}18)$$

Direct substitution of eq B-17 and B-18 into eq B-16 yields explicit expression for the coefficients $c_n{}^\pm$. We get

$$\mathbf{c}^\pm \mathbf{M}^\pm = \theta \qquad (B\text{-}19)$$

(28) D. Henderson, L. Blum, and L. B. Bhuiyan, *Mol. Phys.*, **43**, 1185 (1981).

(29) M. Lozada-Cassou and D. Henderson, *J. Chem. Phys.*, **77**, 5150 (1982).

(30) M. Lozada-Cassou and D. Henderson, *J. Chem. Phys.*, in press.

(31) B. Jancovici, *J. Stat. Phys.*, **28**, 43 (1982).

(32) E. T. Whittaker and G. N. Watson, "A Course of Modern Analysis", Cambridge University Press, New York, 1958.

with

$$c = \begin{vmatrix} c_1^{\pm} \\ c_2^{\pm} \\ c_3^{\pm} \\ \cdot \\ \cdot \\ \cdot \end{vmatrix} \qquad \text{(B-20)}$$

$$M^{\pm} = \begin{vmatrix} \Lambda_1^{\pm} & 0 & 0 & 0 & \cdots \\ -\theta_1 & \Lambda_2^{\pm} & 0 & 0 & \cdots \\ & & & 0 & \\ -\theta_2 & -\theta_1 & \Lambda_3^{\pm} & 0 & \cdots \\ -\theta_3 & -\theta_2 & -\theta_1 & \Lambda_4^{\pm} & \cdots \end{vmatrix} \qquad \text{(B-21)}$$

where

$$-\Lambda_n^{\pm} = \mp 2nq_{\infty}(K^2 + q_{\infty}^2)^{1/2} + n^2 q_{\infty}^2 \qquad \text{(B-22)}$$

$$\theta = \begin{vmatrix} \theta_1 \\ \theta_2 \\ \theta_3 \\ \cdot \\ \cdot \\ \cdot \end{vmatrix} \qquad \text{(B-23)}$$

clearly

$$c^{\pm} = [M^{\pm}]^{-1}\theta \qquad \text{(B-24)}$$

$$[M^{\pm}]^{-1} = \begin{vmatrix} (\Lambda_1^{\pm})^{-1} & 0 & 0 & \cdots \\ \theta_1/\Lambda_1^{\pm}\Lambda_2^{\pm} & (\Lambda_2^{\pm})^{-1} & 0 & \cdots \\ \dfrac{(\theta_2\Lambda_2^{\pm} + \theta_1{}^2)}{\Lambda_1^{\pm}\Lambda_2^{\pm}\Lambda_3^{\pm}} & \theta_1/\Lambda_2^{\pm}\Lambda_3^{\pm} & 1/\Lambda_3^{\pm} & \cdots \end{vmatrix} \qquad \text{(B-25)}$$

If the density $\rho_j(1)$ is given by the Gouy–Chapman theory (eq B-6), then the inverse of **M** is a somewhat simpler expression

$$[M^{\pm}]^{-1} = \begin{vmatrix} 1/\Lambda_1^{\pm} & 0 & 0 & \cdots \\ 0 & 1/\Lambda_2^{\pm} & 0 & \cdots \\ \theta_2/\Lambda_1^{\pm}\Lambda_3^{\pm} & 0 & 1/\Lambda_3^{\pm} & \cdots \end{vmatrix} \qquad \text{(B-26)}$$

The solution of the boundary conditions B-12 and B-1 yields then

$$\tilde{\phi}_j^L(K;z_1z_2) = \frac{-4\pi e_j}{\epsilon} \frac{W_{12}(0)}{W_{12}(z_2)} \frac{\eta_-(2)e^{K_1 z}}{\eta_i(0) - K\eta_-(0)} \qquad \text{(B-27)}$$

where we have also introduced the Wronskian

$$\Delta_{12}(z) = \eta_-'(z)\,\eta_+(z) - \eta_-'(z)\,\eta_-(z)$$

$$\eta'(z) = \partial[\eta(z)]/\partial z \qquad \text{(B-28)}$$

Furthermore

$$\tilde{\phi}_j^I(K;z_1z_2) = \frac{4\pi e_j}{\epsilon} \frac{\eta_i(2)}{W_{12}(z_2)}[-\eta_+(z_1) + \alpha(k)\,\eta_-(z_1)]$$

$$z_2 > z_1 \qquad \text{(B-29)}$$

$$\tilde{\phi}_j^{II}(K;z_1z_2) = \frac{4\pi e_j}{\epsilon} \frac{\eta_-(1)}{W_{12}(z_2)}[-\eta_+(z_2) + \alpha(k)\,\eta_-(z_2)]$$

$$z_1 > z_2 \qquad \text{(B-30)}$$

with

$$\alpha(k) = \frac{\eta_+'(0) - k\eta_+(0)}{\eta_-'(0) - k\eta_-(0)} \qquad \text{(B-31)}$$

The fluctuation potential is then from eq B-2

$$\phi_j(1|2) =$$

$$\frac{2e_j}{\epsilon} \frac{1}{W_{12}(z_2)} \int_0^{\infty} dk\ k J_0(kq_{12}) \{\alpha(k)\,\eta_-(z_1)\,\eta_-(z_2) -$$

$$[\eta_-(z_2)\,\eta_+(z_1)\,\theta(z_2 - z_1) + \eta_-(z_1)\,\eta_+(z_2)\,\theta(z_1 - z_2)]\} \qquad \text{(B-32)}$$

This is the Debye-Hückel-like solution for the electric double layer with the correct boundary conditions. We hope to discuss the MPB in this context in future work.