Beyond Poisson–Boltzmann: Images and correlations in the electric double layer. I. Counterions only

Phil Attard, D. John Mitchell, and Barry W. Ninham
Department of Applied Mathematics, Research School of Physical Sciences, Australian National University, Canberra, ACT 2601, Australia

(Received 29 September 1987; accepted 21 December 1987)

The general solution to the zero size mean spherical model is found for an inhomogeneous electrolyte (with specified profile) between charged planar surfaces. The analysis includes the effects of images and correlations. It provides the primary correction to the classical mean field theory of the double layer and allows the error in that theory to be easily estimated over experimental regimes. The relationship between Lifshitz theory and primitive model theories of electrolytes is made explicit. Results obtained for the one component double layer are accurate for systems with low coupling.

I. INTRODUCTION

The Gouy–Chapman theory of double layer interactions lies at the heart of colloid and surface science. As a mean field theory, it ignores ion–ion correlations and electrostatic image interactions. A key improvement was the method of Kjellander and Marčelja\(^1\) who obtained an accurate solution to the problem in the anisotropic permutated chain approximation. Complementary to this is work on one component electrolytes between charged walls studied via Monte Carlo simulations.\(^2\) Both approaches agree in their predictions, which can be very different to those of the classical theory. Indeed, for realistic conditions, ion–ion correlations can actually conspire to give “double layer” forces which at some distance regimes are even attractive.\(^2\)\(^,\)\(^3\) Both methods involve heavy computation for each and every problem of interest. The present paper is concerned with the derivation and illustration of a new formalism that gives analytic expression for these double layer forces which can be computed easily. It complements the other approaches since the results obtained are valid in precisely the large distance regime not easily accessible to those.

Just how good or bad the theory of double layer forces based on the Poisson–Boltzmann equation is in a given experimental situation is an old problem. Any improvement brings in the issue of the van der Waals forces. In the DLVO theory of particle interactions, van der Waals and double layer forces are treated separately. That approximation must be reasonable for those correlation contributions to the Lifshitz theory of attractive forces which arise from fluctuations in the infrared or ultraviolet.\(^4\) However, for the temperature dependent contributions from permanent dipole correlations it is not. These classical (zero frequency) terms dominate the van der Waals forces in surfactant or oil/water systems.\(^5\) And in the absence of surface charge the zero frequency terms are screened by electrolyte.\(^6\) Generally then, van der Waals and double layer forces are intimately related, and a primitive model theory that includes ion correlations and images should include the dipole–dipole correlations on the same footing. Otherwise they give anomalous (erroneous) long range repulsions.\(^6\) Our approach does treat double layer and van der Waals forces consistently. The theory provides a rigorous justification for earlier attempts to extend double layer theory\(^4\)\(^,\)\(^7\) based on the Van Kampen modal approach.\(^8\) The modified Poisson–Boltzmann theory,\(^9\) a numerical scheme which has been used to study the ionic profiles of isolated double layers, also includes images and correlations, and is roughly equivalent to the analytic approach taken here. Ionic correlations per se have previously\(^10\) been studied for the electric double layer (isolated, but in a variety of geometries) in an approximate fashion, similar to the manner by which they are here included in the free energy for the interacting double layers.

The paper comprises general theory and particular analysis. Section II sets out a general formalism for inhomogeneous fluids. From this emerges the mean field Poisson–Boltzmann (PB) analysis and the next order approximation, which includes both images and correlations. That section concludes with an explicit general solution for the zero size mean spherical model (Debye–Hückel theory) for an arbitrary inhomogeneous electrolyte profile. Section III illustrates the application of the theory for a particular limiting case: the one component double layer. Numerical comparisons are made between the present theory and “exact” HNC calculations for parameters of experimental interest. Those results allow a demarcation of regimes in which the theory provides an adequate description of the primitive model, and estimates of the error in Gouy–Chapman theory.

II. THEORETICAL ANALYSIS

A. Formalism

In standard notation the grand partition function for a multicomponent classical fluid\(^10\) in an external field is

\[
\Xi = \sum_{\{\varepsilon_a\}} \prod_a \left( \frac{\lambda_a^{3N_a}}{N_a!} \right)^{\frac{1}{2}} \int \cdots \int \{dr_{ai}\} \times \exp\left( -\beta \left[ H - \sum_a \mu_a N_a \right] \right),
\]

where \(\alpha\) labels each molecular species, \(\lambda_a\) is the thermal wavelength, and \(\mu_a\) the chemical potential. The configurational Hamiltonian is

\[ H = H_0 + \sum_{\alpha} \Phi_{\alpha}(r_{\alpha}) + \frac{1}{2} \sum_{(\alpha,i) \neq (\gamma,j)} \sum_{r_{\alpha i}} u_{\alpha\gamma}(r_{\alpha i}, r_{\gamma j}), \]  
(2.2)

where \( H_0 \) is the effective Hamiltonian in the absence of the solute species \( \{\alpha\} \), \( \Phi_{\alpha}(r) \) is the external potential, and \( u_{\alpha\gamma}(r, s) \) is pair potential. This form ignores bulk self-energy terms like the Born energy of an ion, or the dispersion self-energy.\(^4\) These are constant and therefore irrelevant. However, when dielectric discontinuities are present self-image terms arise which will be incorporated into the external potential. The intrinsic chemical potential \( \mu_{\alpha}(r) \equiv \mu_{\alpha} - \Phi_{\alpha}(r) \) ultimately determines the density profile\(^10\) and in terms of this entity we can write

\[ H - \sum_{\alpha} \mu_{\alpha} N_{\alpha} = H_0 - \sum_{\alpha} \int \rho_{\alpha}(r) \mu_{\alpha}(r) \, dr + \frac{1}{2} \sum_{\alpha, \gamma} \int \rho_{(\alpha)}^{(2)}(r, s) u_{\alpha\gamma}(r, s) \, ds, \]

(2.3)

with the density and pair correlation operators defined as

\[ \rho_{\alpha}(r) = \sum_{\gamma} \delta(r - r_{\alpha \gamma}), \]

\[ \rho_{(\alpha)}^{(2)}(r, s) = \rho_{\alpha}(r) \rho_{\gamma}(s) - \rho_{\alpha}(r) \delta_{\alpha\gamma} \delta(r - s). \]

(2.4)

Ensemble averages of these two operators are the equilibrium density profile \( \rho_{\alpha}(r) \), and the pair distribution function \( \rho_{(\alpha)(\gamma)}^{(2)}(r, s) = \rho_{\alpha}(r) \rho_{\gamma}(s) \{h_{\alpha\gamma}(r, s) + 1\} \), \( h_{\alpha\gamma}(r, s) \) being the usual indirect correlation function.

The thermodynamic potential \( \Omega = -k_B^T \ln \Xi \) is more easily obtained from \( \rho^{(2)} \) rather than directly from the partition function. One approach is to express \( \Omega \) in terms of \( \rho^{(2)} \) by considering its change due to a shift in the Hamiltonian, viz.,

\[ \delta \Omega = \langle \delta H \rangle = -\sum_{\alpha} \int \rho_{\alpha}(r) \delta \mu_{\alpha}(r) \, dr + \frac{1}{2} \sum_{\alpha, \gamma} \int \rho_{(\alpha)}^{(2)}(r, s) \delta u_{\alpha\gamma}(r, s) \, ds, \]

(2.5)

where in principle \( \Omega \) follows from a coupling constant integration that switches on the pair potential. This route to thermodynamics is also difficult, because \( \rho^{(2)} \) is a functional of the profile. As shown by Evans,\(^10\) it is more convenient to express the system as a functional of the density profile. The idea is that since the external potential prescribes the profile uniquely, an alternate description is through the density profile rather than through the external field. To see this, define a free energy \( \mathcal{F} \), where

\[ \mathcal{F} = \Omega + \sum_{\alpha} \int \rho_{\alpha}(r) \mu_{\alpha}(r) \, dr - H_0, \]

\[ \equiv F - \sum_{\alpha} \int \rho_{\alpha}(r) \Phi_{\alpha}(r) \, dr - H_0. \]

(2.6)

The functional \( \mathcal{F} \) is the internal part of the Helmholtz free energy \( F \), since the second term represents the mean contribution from the external potential. From Eq. (2.5),

\[ \delta \mathcal{F} = \sum_{\alpha} \int \mu_{\alpha}(r) \delta \rho_{\alpha}(r) \, dr + \frac{1}{2} \sum_{\alpha, \gamma} \int \rho_{(\alpha)}^{(2)}(r, s) \delta u_{\alpha\gamma}(r, s) \, ds, \]

(2.7)

in which form it is evident that \( \mathcal{F} = \mathcal{F}[\rho] \) is a functional of the profile. If the profile is known \( \mathcal{F}[\rho] \) can be obtained by calculating the correlation functions at fixed \( \rho_{\alpha}(r) \) as the pair potential coupling constant is turned on. Inversion of Eq. (2.6) now defines a thermodynamic potential functional

\[ \Omega[\rho] = \mathcal{F}[\rho] - \sum_{\alpha} \int \rho_{\alpha}(r) \mu_{\alpha}(r) \, dr + H_0, \]

(2.8)

with the property that \( \Omega[\rho] = \Omega \) at the equilibrium density profile. The profile is given by Eq. (2.7), or explicitly as

\[ \frac{\delta \mathcal{F}[\rho]}{\delta \rho_{\alpha}(r)} = \mu_{\alpha}(r). \]

(2.9)

Hence by taking the functional derivative of Eq. (2.8), it is clear that \( \Omega[\rho] \) is optimized at the equilibrium profile. An advantage of this variational formulation is that the thermodynamic potential functional is relatively insensitive to the approximations to the density profile. This fact will be exploited later. To proceed further we require the Ornstein–Zernike equation which relates the direct \( (c) \) and indirect \( (h) \) correlation functions:

\[ h_{\alpha\gamma}(r, s) = c_{\alpha\gamma}(r, s) + \sum_{\delta} \int c_{\delta\alpha}(r, t) \rho_{\delta}(t) h_{\delta\gamma}(t, s) \, dt. \]

(2.10)

Also required is the density–density correlation function which gives the linear response of the density to the external field (intrinsic chemical potential):

\[ \delta \rho_{\alpha}(r) = \beta \sum_{\gamma} \left[ \rho_{\alpha}(r) \delta_{\alpha\gamma}(r - s) \right] + \left[ \rho_{\alpha}(r) \rho_{\gamma}(s) h_{\alpha\gamma}(r, s) \right] \delta \rho_{\gamma}(s). \]

(2.11)

Using Eq. (2.10), this can be inverted to give

\[ \delta \rho_{\alpha}(r) = k_B T \sum_{\gamma} \left[ \delta \rho_{\alpha}(r) \delta(r - s) \right] \times \delta \rho_{\gamma}(s). \]

(2.12)

where follows the compact form for the direct correlation function

\[ c_{\alpha\gamma}(r, s) = -\beta S_{\alpha\gamma}^F(\mathcal{F} - \mathcal{F}^{id}) \delta \rho_{\alpha}(r) \delta \rho_{\gamma}(s). \]

(2.13)

Here \( \mathcal{F}^{id} \) is the ideal gas \( \mathcal{F} \):

\[ \mathcal{F}^{id} = k_B T \sum_{\alpha} \int \rho_{\alpha}(r) \ln \left[ \lambda^a \rho_{\alpha}(r) \right] - 1 \, dr. \]

(2.14)

This completes the required formalism. We now proceed to successive approximations that describe the electric double layer.
B. Mean field approximation

In lowest order approximation correlations are ignored so that \( \rho_{\alpha \gamma}^{(2)}(r,s) = \rho_{\alpha}(r) \rho_{\gamma}(s) \). Then with the ideal gas as a reference system \([u_{\alpha \gamma}(r,s) = 0]\) integration of Eq. (2.7) yields the mean field result

\[
\mathcal{F}^{mf} = \mathcal{F}^{id} + \frac{1}{2} \sum_{\alpha \gamma} \int \rho_{\alpha}(r) \rho_{\gamma}(s) u_{\alpha \gamma}(r,s) dr ds,
\]

(2.15)

with the equilibrium profile determined from Eq. (2.9) as

\[
\mu_{\alpha}(r) = \mu_{\alpha} - \Phi_{\alpha}(r) = k_{B} T \ln \left( \lambda_{\alpha}^{2} \rho_{\alpha}(r) \right) + \psi_{\alpha}(r),
\]

(2.16)

\[
\psi_{\alpha}(r) = \sum_{\gamma} \int \rho_{\gamma}(s) u_{\alpha \gamma}(r,s) ds.
\]

(2.17)

In this mean field theory the pair potential contributes to the profile only through the mean potential \( \psi_{\alpha}(r) \). Rearranging gives the Boltzmann equation

\[
\rho_{\alpha}(r) = z_{\alpha} \exp \left( - \beta \left( \psi_{\alpha}(r) + \Phi_{\alpha}(r) \right) \right).
\]

(2.18)

In the absence of any mean or external potentials, the fugacity \( z_{\alpha} = \lambda_{\alpha}^{-1} \exp(\beta \mu_{\alpha}) \) reduces to the density of species \( \alpha \) in a uniform bulk fluid.

The Poisson–Boltzmann (PB) description of the double layer follows if all short range interactions and image potentials due to dielectric discontinuities are ignored. Note that the self-image interaction (part of the external field) should remain in any rigorous mean field analysis. However, since in reality this is screened, including it while ignoring correlations gives strange results at large separations. Hence no image charge effects are considered in lowest approximation and the pair potential is taken to be the Coulomb interaction in an infinite medium with uniform dielectric constant \( \epsilon_{1} \),

\[
u_{\alpha \gamma}(r,s) = \frac{q_{\alpha} q_{\gamma}}{\epsilon_{1} |r-s|},
\]

(2.19)

where \( q_{\alpha} \) is the charge of the species \( \alpha \). Taking the total mean electrostatic potential as \( \psi(r) = [\psi_{\alpha}(r) + \Phi_{\alpha}(r)] / q_{\alpha} \) the nonlinear PB equation emerges as

\[
\nabla^{2} \psi(r) = - \frac{4 \pi}{\epsilon_{1}} \sum_{\alpha} q_{\alpha} z_{\alpha} \exp \left( - \beta q_{\alpha} \psi(r) \right).
\]

(2.20)

We now give the PB result for the thermodynamic potential. To do this, substitute \( \mathcal{F}^{mf} \) Eq. (2.15) into Eq. (2.8), and take \( H_{0} \) to be the external, configuration independent, electrostatic free energy only. Then the thermodynamic potential consists of an ideal term (less the chemical potential part) and mean electrostatic terms; i.e., with the ionic charge density \( Q(r) \equiv \sum q_{\alpha} \rho_{\alpha}(r) \), and an external charge density \( \sigma(r) \), we have

\[
\Omega_{PB}^{\alpha} = \mathcal{F}^{id} - \sum_{\alpha} \mu_{\alpha} \int \rho_{\alpha}(r) dr + \frac{1}{2} \int Q(r) \psi(r) dr + \frac{1}{2} \int \sigma(r) \psi(r) dr.
\]

(2.21)

Use of the optimized profile (2.16) gives

\[
\Omega_{PB}^{\alpha} = - k_{B} T \sum_{\alpha} \int \rho_{\alpha}(r) dr - \frac{1}{2} \int Q(r) \psi(r) dr
\]

\[
+ \frac{1}{2} \int \sigma(r) \psi(r) dr
\]

\[
= - k_{B} T \sum_{\alpha} \int \rho_{\alpha}(r) dr - \frac{1}{8 \pi} \int \epsilon(r) \left( \nabla \psi(r) \right)^{2} dr
\]

\[
+ \int \sigma(r) \psi(r) dr.
\]

(2.22)

In obtaining the final line we have used the known result which identifies the middle term as the mean electrostatic energy. The PB pressure is obtained by differentiation with respect to separation.

The term \( H_{0} \) we have used above does not include the Lifshitz interaction. The reason is that the Coulomb potential (2.19) is that for an infinite uniform dielectric medium. Since the image interactions have been excluded in the PB analysis, it is not appropriate to add here the Lifshitz interaction which also arises from dielectric discontinuities. It is also inconsistent to include dipolar fluctuations while ignoring those due to ions. In next approximation both image charge effects and correlations in the electrolyte will be included. It is then essential to include the Lifshitz contribution in \( H_{0} \). Otherwise, as will be made explicit, when dielectric discontinuities are present the primitive model gives a spurious long range repulsion which is canceled identically by the zero frequency Lifshitz term.

C. Images and correlations

The mean field approximation above includes no correlations. Both the direct and indirect correlation functions were taken to be zero. A better approximation follows from Eq. (2.13) if we take the second functional derivative of the nonideal part of the mean field free energy (2.16). This gives

\[
c_{\alpha \gamma}(r,s) = - \beta u_{\alpha \gamma}(r,s).
\]

(2.23)

Note that this closure is a Debye–Hückel approximation which is equivalent to the mean spherical model with no hard core radius. In fact, this is the correct asymptotic form for the direct correlation function, which is to be expected since the mean field superposition approximation for the pair correlation function is also exact for large particle separations. Use of this closure provides an improved description of the double layer. For bulk electrolytes Debye–Hückel theory fails at high concentrations because short range effects become important. However, the thermodynamics is given correctly in the low dilution limit, since there the system is dominated by the tail of the Coulomb potential. This provides some motivation for persisting with this approximation. However, the real justification will come a posteriori, when we compare the results with more sophisticated calculations.

We proceed by substituting Eq. (2.23) into the Ornstein–Zernike equation and obtain an expression for the indirect correlation function. The pair potential coupling constant integral can then be formally evaluated to give the next approximation for \( \mathcal{F} \).

To turn on the pair potential, invoke a coupling con-
stant, i.e., $u_{av}(r,s;\lambda) = \lambda u_{av}(r,s)$. Then if $F = F^{mf} + F^{corr}$, with the mean field free energy given by Eq. (2.15), we have

$$F^{corr} = \frac{1}{2} \sum_{\alpha,\gamma} \int_0^1 d\lambda \int \rho_\alpha(r) \rho_\gamma(s) \times h_{av}(r,s;\lambda) u_{av}(r,s) dr ds.$$  
(2.24)

The required partially coupled indirect correlation function $h_{av}(r,s;\lambda)$ follows from the Ornstein–Zernike equation with $c_{av}(r,s;\lambda) = -\beta \lambda u_{av}(r,s)$ as

$$h_{av}(r,s;\lambda) = -\beta \lambda u_{av}(r,s) \times -\beta \lambda \sum_{\gamma} \int \rho_\gamma(t) h_{av}(t,s;\lambda) dt.$$  
(2.25)

Integration of this equation, substitution into Eq. (2.24), followed by the coupling constant integration, then gives for the correlation free energy

$$F^{corr} = \frac{\beta}{4} \sum_{\alpha,\gamma} \int \rho_\alpha(r) \rho_\gamma(s) u_{av}(r,s) u_{av}(s,r) dr ds + \frac{\beta^2}{6} \sum_{\alpha,\gamma,\delta} \int \rho_\alpha(r) \rho_\gamma(s) \rho_\delta(t) u_{av}(r,s) \times u_{av}(s,t) u_{av}(t,r) dr ds dt \cdots.$$  
(2.26)

By discretizing this expression (replace the integrals by Riemann sums), it becomes clear that it represents a sum of traces of powers of a matrix. The expression can be resummed if we determine the eigenvalues $\Lambda$ of the integral equation

$$-\beta \sum_{\gamma} \int \rho_\alpha(s) u_{av}(r,s) f_\gamma(s) ds = \Lambda f_\alpha(r).$$  
(2.27)

Then the correlation free energy may be rewritten as sums of powers of the eigenvalues

$$F^{corr} = -\frac{k_B T}{2} \sum_{n=1}^\infty \frac{1}{n} \sum_{\gamma=1}^\infty \Lambda_\gamma^n = \frac{k_B T}{2} \sum_{\gamma=1}^\infty \ln(1 - \Lambda_\gamma) + \Lambda_\gamma.$$  
(2.28)

Note that the term in $\Lambda_1$ represents the self-interaction which cancels the first term in the expansion of the logarithm. Since we will later add the self-image interaction via the external field, it is actually only the (infinite) direct Coulombic self-interaction which is excluded from the free energy.

Further progress requires determination of the eigenvalues. For notational convenience first write the pair potential as $u_{av}(r,s) = q_\alpha q_\gamma u(r,s)$ and define the local inverse Debye length by

$$\kappa^2(r) = \frac{4\pi \beta}{\epsilon_1} I(r) = \int \frac{4\pi \beta}{\epsilon_1} \rho_\alpha(r),$$  
(2.29)

where $I(r)$ is the ionic strength. Then the eigenvalue equation (2.27) for the eigenfunction $f_\alpha(r) = q_\alpha f(r)$ may be rewritten

$$-\beta \int I(s) u(r,s) f(s) ds = \Lambda f(r).$$  
(2.30)

Note that the profile remains unspecified in the present analysis.

We now particularize to planar geometry. The electrolyte is confined to a region of dielectric constant $\epsilon_1$ of width $d = h + 2w$ separating two half-spaces of dielectric constant $\epsilon_2$ (Fig. 1) with the distance of closest approach of the ions to each surface being $w$ (the zeroth-order Stern layer). As the area $A$ of the planar surfaces becomes infinite, the spectrum of the eigenvalues becomes continuous in the $(x,y)$ direction parallel to the interfaces. Then in Fourier space the sum over wave vectors $k$ is replaced by a two-dimensional integral with a density of modes $A/(2\pi)^2$. The correlation free energy can then be written (with $d k = 2\pi dk$)

$$F^{corr} = \frac{k_B T A}{2\pi^2} \sum_{n=1}^\infty \left\{ \ln[1 - \Lambda_1(k)] + \Lambda_1(k) \right\} dk,$$  
(2.31)

and the eigenvalue equation becomes

$$-\beta \int \hat{u}(k,z_1,1) I_1(z_1) f_1(z_1) dz_1 = \Lambda(k) f_1(z_1).$$  
(2.32)

The circumflex denotes the two-dimensional Fourier transform of the cylindrically symmetric potential, and the eigenfunction is an implicit function of $k$.

Because $u(r,s)$ is the potential at $r$ due to a charge in the electrolyte at $s$, it satisfies $\nabla^2 u = 0, \left| z \right| > h/2$ and $\nabla^2 u = -(4\pi/\epsilon_1) \delta(r-s) \left| z \right| < h/2$. In Fourier space these equations can be written

$$\hat{u}^\ast(k,z_1,1) - k^2 \hat{u}(k,z_1,1) = -\frac{4\pi}{\epsilon_1} \delta(z - z_1),$$  
(2.33)

and the boundary condition can be shown to be

$$k \epsilon_2 \hat{u}(k,d/2,z_1) + \epsilon_1 \hat{u}(k,d/2,z_1) = 0.$$  
(2.34)

Using these results the eigenvalue equation (2.32) can be rewritten as

$$f^\ast(z) - [k^2 + \lambda(\epsilon_2)(z)] f(z) = 0,$$  
(2.35)

where $\lambda = 1/\Lambda$, and the same boundary condition holds.

Now define $C_1(z)$ and $S_1(z)$ as the (even and odd) solutions which satisfy the initial conditions at the midpoint:

$$C_1(0) = 1, \quad S_1(0) = 0.$$  
(2.36a)

![FIG. 1. In planar geometry, the width of the electrolyte is $h$ and that of each Stern layer (from which the ions are excluded) is $w$. The separation of the surfaces is $d = h + 2w$, which is also the width of the intervening uniform dielectric $\epsilon_1$. This region separates two half-spaces with dielectric constant $\epsilon_2$.](image-url)
\[ S_\lambda(0) = 0, \quad S'_\lambda(0) = 1. \]  

(2.36b)

These functions are defined between the surfaces, and their \( k \) dependence has not been shown explicitly. The initial conditions, together with the differential equation (2.35), completely determine the \( C_\lambda(z) \) and the \( S_\lambda(z) \). The eigenvalues are those values of \( \lambda \) for which the solutions satisfy the boundary condition (2.34), and this requirement yields the secular determinant

\[ \mathcal{D}_\lambda(k) = \{ ke_l C_\lambda(d/2) + \epsilon_l C'_\lambda(d/2) \} \times \{ ke_l S_\lambda(d/2) + \epsilon_l S'_\lambda(d/2) \}. \]  

(2.37)

It is desirable to have the functions evaluated at the boundary of the Stern layer rather than at the surface. Since \( \kappa(z) = 0 \) within the Stern layer, each of \( C_\lambda(z) \) and \( S_\lambda(z) \) are here a sum of exponentials. Then from their continuity (and that of their first derivative), we can express Eq. (2.37) in terms of functions evaluated at \( h/2 \). This gives for the secular determinant

\[ \mathcal{D}_\lambda(k) = Y C_\lambda(h/2) + k C_\lambda(h/2) + \Delta_{12} \left[ C_\lambda(h/2) - k C_\lambda(h/2) \right] e^{-2kW} \times \{ S_\lambda(h/2) + k S_\lambda(h/2) + \Delta_{12} \left[ S_\lambda(h/2) - k S_\lambda(h/2) \right] e^{-2kW} \}. \]  

(2.38)

Here \( Y = k^2(\epsilon_\lambda + \epsilon_\nu)2^{-2kW/4} \) is independent of \( \lambda \). Since secular determinants are determined up to an arbitrary constant, it is only their ratio that will prove physically meaningful. We have also defined \( \Delta_{12} = (\epsilon_\nu - \epsilon_\lambda)/(\epsilon_1 + \epsilon_\nu) \).

The allowed eigenvalues are then the zeros \( \mathcal{D}_\lambda(k) = 0 \). Using this, the sum over the possible modes Eq. (2.31) can be expressed as a contour integral in the complex \( \lambda \) plane (Fig. 2). By the Cauchy residue theorem we have

\[ \sum \ln \left[ 1 - 1/\lambda_i(k) \right] = \frac{1}{2\pi i} \int \mathcal{D}_\lambda(k) \ln \left[ 1 - 1/\lambda \right] d\lambda, \]  

(2.39)

where the dot denotes differentiation with respect to \( \lambda \). Spurious zeros of the secular determinant have been excluded by fixing the initial conditions, and this precludes trivial solutions. It remains to show that there are no unwanted residues by showing that \( \mathcal{D}_\lambda(k) \) has no poles. If in addition the integral around the arc vanishes (as its radius is taken to infinity), then what is left is an integral around the branch cut between 0 and 1, and the problem of evaluating \( \mathcal{F}_{\text{corr}} \) reduces to a tractable form.

To do this we make the following argument. From the form of the secular determinant (2.38) it is sufficient to show that each of the functions \( C_\lambda(k), C'_\lambda(k), S_\lambda(k), \) and \( S'_\lambda(k) \) is entire. As solutions of a differential equation, these functions must be finite, continuous, and single valued [from the initial conditions (2.36)] for any finite value of \( \lambda \). To show that they are analytic it must be shown that their derivatives with respect to \( \lambda \) exist. Accordingly differentiate Eq. (2.35) to obtain

\[ \frac{df(z)}{dz} = \frac{d}{dz} \left[ \frac{[k^2 + \kappa^2(z)] f(z)}{k^2} \right] = \kappa^2(z) f(z). \]  

(2.40)

Now with \( f(z) \) equal to \( C_\lambda(z) \) or \( S_\lambda(z) \), we have already shown that the right-hand side is finite, continuous, and single valued. Hence the solutions to the equation, which must be \( C_\lambda(z) \) and \( S_\lambda(z) \), respectively, are also finite and continuous functions of \( \lambda \). The conclusion also holds for their \( z \) derivatives. That they are single valued follows by taking the derivative with respect to \( \lambda \) of the initial conditions (2.36). Finally, since a function is analytic if its derivative exists, we conclude that the four functions which comprise the secular determinant (2.38) are entire, and that the contour integral (2.39) contains no spurious contributions from poles.

Next consider the behavior of the secular determinant for large \( \lambda \). We analyze the differential equation (2.35) using a WKB approximation. Let \( f(z) = \exp(w(z)) \). Then [since \( \kappa(z) \) is nonzero within the electrolyte]

\[ \frac{f''(z)}{f(z)} = w''(z) + \left[ w'(z)^2 \right] \approx \lambda^2 \kappa^2(z). \]  

(2.41)

It follows that \( w' \ll (w')^2 \), and that \( w \sim \lambda^{1/2} \). Thus \( C_\lambda(h/2) \) and \( S_\lambda(h/2) \) behave as \( \exp \{ \alpha \lambda^{1/2} \} [\alpha \approx \kappa^{-1/2}(z) dz] \). Then \( \mathcal{D}_\lambda(k) \sim \exp(2\alpha \lambda^{1/2}) \), and the vanishing of the integral (2.39) around the outer contour as \( \lambda \to \infty \) is assured.

There remains the integral around the branch cut between 0 and 1 (Fig. 2) which gives the final result for the correlation free energy:

\[ \mathcal{F}_{\text{corr}} = \frac{AkT}{8\pi^2} \int \ln \left[ \mathcal{D}_\lambda(k) \right] d\mathbf{k} - \mathcal{F}_{\text{self}}. \]  

(2.42)

Here the sum over the eigenvalues themselves gives the self-interaction term, which, from Eq. (2.26) may be written

\[ \mathcal{F}_{\text{self}} = \frac{1}{2} \sum_a \int \rho_a(r) u_{aa}(r,r) dr \]

\[ = \frac{A}{8\pi^2} \int \int I(z) \hat{u}(k,z,z) d\mathbf{k} dz. \]  

(2.43)

Note that when we add the external term, \( \mathcal{F}_{\text{self}} \) will be partially canceled by the self-image interaction. This will leave only the divergent Coulombic self-energy term in which \( \hat{u} \) is replaced in the above by \( \hat{S}_{\text{corr}}(k,z,z) = 2\pi \epsilon_\nu k \). The free energy contains bulk and surface as well as separation depen-
dent contributions. Our concern is with the pressure between the surfaces, and we are therefore interested only in the interaction part of \( \mathcal{F}^\text{corr} \) above.

Consider then the structure of Eq. (2.42). It involves \( \mathcal{D}_0(k) \), the secular determinant evaluated at \( \lambda = 0 \), which case is equivalent to one of no electrolyte between the surfaces. The expression for \( \mathcal{F}^\text{corr} \) Eq. (2.42) includes a repulsive contribution \( -\Omega^\text{aff} \) where

\[
\Omega^\text{aff} = \frac{4k_BT}{8\pi^2} \int \ln(\mathcal{D}_0(k)/(Ykab^2)) d^2k,
\]

\[
= \frac{4k_BT}{8\pi^2} \int \ln(1 - \Delta^2 e^{-2k^2/\sigma}) d^2k,
\]

and we have used \( C_0(z) = \cosh(kz), S_0(z) = \sinh(kz)/k \). These are the solutions of Eq. (2.35) with \( \lambda = 0 \), or in the absence of electrolyte [i.e., \( \kappa(z) = 0 \)]. The factor \( Y \) is canceled by the numerator, and the factor \( k^2ab^2 \) must be incorporated with \( \mathcal{D}_0(k)/Y \) in the final expression. Now \( \Omega^\text{aff} \) is the usual Lifshitz interaction, at zero frequency, between two dielectric half-spaces. The free energy (2.42) therefore contains a spurious power law repulsion and for consistency one must add the Lifshitz term back on via \( H_0 \). The permanent dipole fluctuations of the dielectric media in the absence of ions (not included in the above) has been made earlier and is a missing and misleading feature of previous primitive model analyses. In the present analysis in which the Lifshitz term appears explicitly, it is quite clear that it must be canceled. Clearly too the Lifshitz theory and the double layer theory are now treated at the same level of approximation. This can also be seen from the representation (2.26), which is equivalent to a generalized ring diagram approach. It can be shown that Lifshitz theory can also be derived by that method, and both approximate theories are at the same level, at least for the classical zero frequency term. The high frequency Lifshitz (quantum mechanical) terms (which are approximately independent of the electrolyte), remain in the \( H_0 \) and must be added when describing real physical data. We are not concerned with these higher frequency terms in this paper. But we do add in the zero frequency Lifshitz contribution and so eliminate the artificial repulsion in Eq. (2.42).

III. ONE COMPONENT DOUBLE LAYER

We now illustrate the application of this theory to a specific system: two identical charged planar surfaces interacting across an aqueous phase which includes only the dissociated counterions. The analysis is here more transparent than for the general double layer problem since the elliptic functions which arise there reduce now to trigonometric functions. The principal qualitative features detailed below are also present in the more general problem.

To calculate the correlation interaction free energy, it is necessary to choose a profile, i.e., specify \( \kappa(z) \). We choose the mean field profile given by the Boltzmann form (2.18). In principle, one could take the higher order approximation that uses the free energy \( \mathcal{F}^\text{int} + \mathcal{F}^\text{corr} \) (rather than \( \mathcal{F}^\text{int} \) alone), and determine the profile from Eq. (2.9). However, the accuracy so gained is more than offset by analytic obscurity. Since the formalism is variational, use of the mean field approximation for the profile should be adequate. Hereafter we refer to the results so obtained as the extended Poisson–Boltzmann (EPB) approximation.

A. Poisson–Boltzmann theory

For a single species of counterions of charge \( q \), the PB profile which satisfies Eq. (2.20) is given by

\[
\kappa^2(z) = 2\alpha^2 \sec^2(\alpha z),
\]

(3.1)

where \( \kappa^2(z) = 4\pi\beta q^2 \rho(z)/\epsilon_1 \). The separation dependent parameter \( \alpha \) satisfies the transcendental equation

\[
\alpha \tan(\alpha h/2) = -\frac{2\beta q\sigma}{\epsilon_1} \equiv \frac{s}{2},
\]

(3.2)

where \( \sigma \) is the surface charge density (\( \sigma < 0 \)) and \( h \) is defined as in Fig. 1.

The perpendicular component of the pressure is uniform throughout the system and is given by

\[
P^\text{PB} = k_BT P(0) - \frac{\epsilon_1}{8\pi} \left[ \frac{d\kappa^2}{dz} \right]^2.
\]

(3.3)

Since the electric field vanishes at the midplane (from the symmetry of this system), the mean field pressure can also be written as

\[
P^\text{PB} = k_BT P(0) - \frac{\epsilon_1}{2\pi} \left[ \frac{k_BT}{q} \right]^2 \alpha^2.
\]

(3.4)

The corresponding free energy can be obtained from Eq. (2.22) which in the case of the symmetric planar geometry can be rewritten

\[
\Omega^\text{PB}/A = hP^\text{PB} - k_BT \sum_\alpha \Gamma_\alpha + 2\sigma\psi(h/2),
\]

(3.5)

where \( \Gamma_\alpha \) is the total number of ions per unit area of species \( \alpha \). In the limit of counterions only the thermodynamic potential diverges, so we choose instead to work with \( F \) rather than \( \Omega \). Taking \( \Gamma = -2\alpha q/\sigma \) to be the total number of counterions per unit area and using the profile expression (2.16) to eliminate the chemical potential, it follows that

\[
F^\text{PB}/A = hP^\text{PB} - 2\Gamma k_BT + \Gamma k_BT \ln[\lambda^2 \rho(h/2)].
\]

(3.6)

We require only the interaction (separation dependent) part of the free energy. The surface charge and \( \Gamma \) are here constant. Equation (3.6) can be rearranged using the equations for the profile Eqs. (3.1), (3.2), and (3.4) to obtain

\[
F^\text{PB}/A = \frac{\epsilon_1}{2\pi} \left[ \frac{k_BT}{q} \right]^2 \left[ \alpha^2 h + s \ln \left( 1 + \frac{4\alpha^2}{\alpha^2} \right) \right].
\]

(3.7)

This is the interaction free energy per unit area. Differentiation of this with respect to separation followed by some manipulation, yields the pressure Eq. (3.4). It is of interest to explore the asymptotic behavior for large separation. Iterative solution of Eq. (3.2) yields the form

\[
\alpha \sim \frac{\pi h}{\delta} \left[ 1 - \frac{2}{\delta h} + \frac{8}{(\delta h)^2} + O((\delta h)^{-3}) \right].
\]

(3.8)

Note that this is also the expansion for large surface charge.
although the PB theory is not expected to be valid there. Using this expansion, we find for the interaction free energy

$$F_{int}/A \sim \frac{\varepsilon_1}{2\pi} \left[ \frac{k_B T}{q} \right]^2 \left[ \frac{\pi^2}{h} \left( 1 + \frac{4}{(sh)^2} + O(sh)^{-3} \right) \right].$$

(3.9)

Asymptotically, the PB interaction free energy behaves as a power law, decaying inversely with separation. What is particularly interesting is that, to leading order, this expression (and hence the pressure) is independent of surface charge. The power law of the one component double layer contrasts with the exponential decay of the pressure for the full double layer.

### B. Extended Poisson–Boltzmann (EPB) theory

The correlation free energy depends on the secular determinant evaluated at $\lambda = 1$. Accordingly, choosing the PB profile Eq. (3.1), we must solve the differential equation (2.35). With $\lambda = 1$ this is

$$f''(z) - \{ k^2 + 2a^2 \sec^2(az) \} f(z) = 0.$$  

(3.10)

The even and odd solutions that satisfy the initial conditions (2.36) can be shown to be

$$C_1(z) = \frac{\alpha}{k} \sinh(kz) \tan(\alpha z) + \cosh(kz),$$

(3.11a)

$$S_1(z) = \frac{k}{k^2 + \alpha^2} \sinh(kz) + \frac{\alpha}{k^2 + \alpha^2} \cosh(kz) \tan(\alpha z).$$

(3.11b)

The algebra required to evaluate the secular determinant (2.38) is tedious but straightforward. The result, for the interaction part, is

$$\mathcal{D}_{int}(k) = \left[ 1 + \frac{\alpha^2}{2kX} \left( 1 + \frac{s^2}{8k} \right) \right]$$

$$- \left[ \frac{\alpha^2}{2k} + \frac{s^2}{8k} \right] (1 + \Delta_{12} e^{-2k \mu})$$

$$- \left( \frac{s}{2} - k \right) \Delta_{12} e^{-2k \mu} \frac{e^{-2k \beta}}{X^2},$$

(3.12)

where $X \equiv k + s/2 + (1 + \Delta_{12} e^{-2k \mu}) s^2/8k$. In deriving this result we have discarded a surface term $X^2/k^2$, and canceled the term $Y k e^{\alpha \beta}$ with the corresponding factor in $\mathcal{D}_d(k)$. The formal expression for $\mathcal{F}_{int}$ has the self-interaction term canceling a divergent contribution in the logarithm of $\mathcal{D}_1(k)$ in Eq. (2.42). This self-interaction term splits into the direct Coulomb self-interaction and a self-image term. Now for the counterion only case, the number of ions $\Gamma$ is constant (independent of the separation), and hence the direct Coulomb self-potential does not contribute to the interaction free energy. The self-image term is separation dependent. But in converting from $\mathcal{F}$ to the Helmholtz free energy $F$, this same self-image term must be added via the contribution of the external potential [cf. Eq. (2.6)]. It then cancels identically and does not appear explicitly in $F$ [cf. Eq. (2.43)]. Again, the artificial repulsion represented by $\mathcal{D}_d(k)$ [Eq. (2.44)] is canceled identically by the zero frequency Lifshitz contribution in the effective Hamiltonian $H_0$. This leaves us with the net expression for the interaction free energy per unit area in the one component double layer,

$$F_{int}/A = F_{int}^{\text{PB}}/A + \frac{k_B T}{8\pi^2} \int \ln \left[ \mathcal{D}_1^{\text{int}}(k) \right] d k.$$  

(3.13)

The EPB result includes the effects of correlations (of both the ions and the dielectric media) and all effects due to images.

In general, asymptotic expansions for the correlation contribution are complicated, and are not instructive. However, for the case without images ($\Delta_{12} = 0$) the asymptotic form is tractable. It is

$$F_{int}/A \sim F_{int}^{\text{PB}}/A + \frac{k_B T}{4\pi} \left\{ \frac{\xi(3)}{4\pi^2} \right\} - \alpha^2 \left( \frac{\pi}{4} + \frac{1}{2} \right) \frac{\xi(3)}{4\pi^2} + O(h^{-3}).$$

(3.14)

Here $\xi(3) = 1.202...$ is a Riemann zeta function. (This term is precisely the classical Lifshitz interaction between conducting surfaces.) Since $\alpha$ decays as $h^{-1}$ [Eq. (3.8)], we see that the correlation contribution decays more rapidly than the PB expression (3.9) and the usual Poisson–Boltzmann form eventually dominates. If one uses the correct $\alpha$ given by Eq. (3.2) (rather than the asymptotic expansion), the above form is surprisingly accurate. For example, for monovalent counterions it already agrees to within 1% of the complete integral of Eq. (3.12) at 10 Å separation (at 100 Å$^2$ per surface charge). The dependence on surface charge is here also rather weak, at least to this order. Images still contribute to the asymptotics to the same order as the image free case above. Their inclusion requires evaluation of the full integral of $\mathcal{D}_1^{\text{int}}(k)$.

### C. Numerical results

We now present the results of explicit numerical calculations for the counterion-only case using parameters relevant to experimental data. In order to assess the validity of the EPB approximation, we compare the results with accurate numerical calculations for the same primitive model. We then elucidate the effects of image charges on the predicted pressures. Finally, we remark the regimes in which this analysis, and primitive model analyses generally, may be applied to experiments.

Figure 3 compares the pressure between flat charged surfaces (71.4 Å$^2$ per unit surface charge, or $\sigma = 0.224$ C m$^{-2}$) for the one component double layer. As there are no dielectric discontinuities ($\varepsilon_2 = \varepsilon_1 = 80$), in this special case there are no image charge effects. The benchmark for comparison is the numerical solution to the hypernetted chain (HNC) equation$^{12}$ for point ions, since there is good agreement between that method$^1$ and Monte Carlo (MC) simulations.$^2$ Within the HNC, one can evaluate the pressure directly (as has been done for the results presented here) or via the free energy.$^3$ The discrepancy between the two methods (a useful check on the consistency of the
HNC) is less than that between the HNC and EPB, and we take the former to be exact. We see that the PB theory ($3.4$) overestimates the repulsion, being too large by some 30% at 50 Å separation. Ionic correlations substantially lower the repulsion, and this means that fitting the PB theory to measured force data underestimates the surface charge (i.e., predicts more ion binding than occurs in reality). The EPB pressure, obtained by numerical differentiation of the total interaction free energy ($3.13$), is 16% below the HNC result at $h = 50$ Å. This qualitative behavior appears to be generally true: accurate solutions of the primitive model (with zero hard core radius) lie between the PB prediction and the EPB result which does include correlations. Indeed, the discrepancy between the latter two may be taken as a guide to the accuracy of the Gouy–Chapman theory. That is a useful result without recourse to involved calculations. Previously there was no easy way of assessing the validity of the PB theory. However, since our theory is trivial to implement, it is now possible to estimate the error of the PB theory in any experimental regime.

For large separations, both approximate theories (PB and EPB) become more accurate. At 100 Å, the repulsive pressure predicted by EPB is too small by 7%, and by 4% at 200 Å. Compare this with the PB theory which is too large by 20% and by 12%, respectively. It appears that our EPB approximation predicts the pressure accurately in precisely those large separation regions where HNC (or MC) calculations become difficult.

The EPB results can be expected to be valid in the low surface charge regime where the counterion density is low and the interaction free energy is therefore dominated by the long range tail of the Coulomb potential (cf. the Debye–Hückel limiting law for bulk electrolyte). This is illustrated in Fig. 4, for an area per surface charge of $200 \text{ Å}^2$. It can be seen that at 50 Å separation, the predictions are 8% lower than the HNC result (cf. Gouy–Chapman which is too large by 20% here).

In the opposite limit of high coupling, short range effects become important and calculated EPB pressures are not quite so accurate. As an example, because the correlations are overestimated attractive pressures are predicted at lower couplings than found by HNC or by MC calculations. (Clearly these attractions also occur for monovalents at close separations and large surface charges.) Similarly in denser systems the effect of hard cores (e.g., monovalent ions with radius 2.3 Å, for $\sigma = 0.224 \text{ C m}^{-2}$ below about 50 Å) conspire to make the pressure more repulsive. These short-range effects become less important at larger separations.

Figure 5 shows the predicted pressures in the presence of dielectric discontinuities. The low dielectric region is
placed behind the charged surfaces, as commonly occurs experimentally. Comparing those with Fig. 4, we see that the repulsion has now increased, a characteristic of image effects. A consequence of this is that the HNC pressure will lie closer to the PB prediction (which ignores both images and correlations). However, this is coincidental and for larger separations the EPB approximation does better. Note that the zero frequency Lifshitz attraction has been added to the HNC primitive model results. Figure 6 shows the effects of varying the dielectric parameters, and gives an indication of the sensitivity of experimental systems to image charge effects. The curves at the lower surface charge density indicate that as the images are turned off ($\Delta_{12}=0$) or as the Stern layer thickness increases, the predicted pressure decreases as it approaches the case without images. The effects of images are obviously relatively more important at low surface charges and close separations. Indeed, at 1000 Å² per surface charge ($\sigma=0.0160$ C m⁻²), we see that EPB predicts a larger repulsion than the PB theory. In an attractive regime, although the present theory is not then quantitatively accurate, the images can enhance the correlations, as has been found by HNC calculations.³

The PB theory will be valid in experimental systems which are not too highly coupled. To be more precise, we note that, for point ions in the one component double layer without images, one can characterize the system by the dimensionless parameters¹¹

$$\chi = \frac{4\pi q^2}{k_B T \varepsilon_1}, \quad \xi = \frac{16\pi q^3}{(k_B T \varepsilon_1)^2} \sigma.$$  (3.15)

Apart from a trivial factor, the partition function is completely specified by a coordinate in the $\chi$-$\xi$ plane. Higher values of these parameters correspond to increased coupling in the system and it is here that one expects the PB and EPB approximations to break down. This is borne out by Fig. 7 where we have compared the accuracy of the EPB expressions with HNC calculations. Points lying beyond the outer hyperbola are accurate to better than 10%. The inner curve indicates the limit within which the EPB results are less than half those calculated by the HNC method. Note that for high surface charges there is always a separation beyond which EPB is a good approximation. Similarly, one can find separations and surface charges where our theory will describe the divergent ion situation quite accurately.

For given parameters which specify an experiment, Fig. 7 allows a quantitative estimate of the accuracy of the theory one fits to the data. Depending on the error one is willing to tolerate, the conclusions drawn from the fitted theory (e.g., the degree of ion binding or dissociation) may now be treated with a known confidence. The error predictions that result by considering the discrepancy between PB and EPB may be useful more generally. In a practical situation one often wishes to establish the acceptability of the simple PB theory. To do so via the HNC or MC methods requires inordinate lengthy computation for each and every case. By contrast the EPB results are easy to obtain. Since they overestimate deviations from PB due to correlation effects, EPB provides immediate strong bounds on the error.

**IV. CONCLUSIONS**

In this paper we have solved the zero size mean spherical model for inhomogeneous planar Coulomb systems. The analytic result is in terms of the solutions of a second order differential equation and depends on the profile. Since the free energy functional is optimal, we chose the lowest order approximation, the PB profile. This choice for the profile allows explicit solution of the differential equation and the free energy reduces to a one-dimensional integral. An advantage of the analytic approach is that the relationship between

---

**Fig. 6**. The effects of images on the pressure predicted by EPB. The upper curves are for an area per charge of 100 Å², with $\varepsilon_1=80$, $\varepsilon_2=2$, and $w=1$ Å (---) showing the largest image charge effects. Turning down the images ($\varepsilon_1=80$, $\varepsilon_2=20$, $w=1$ Å; - - -) or making the Stern layer larger ($\varepsilon_1=80$, $\varepsilon_2=2$, $w=3$ Å; - - -) causes the curves to approach for that the system without images ($\varepsilon_1=\varepsilon_2=80$; - - -). At a lower surface charge density (1000 Å²), images become relatively more important ($\varepsilon_1=80$, $\varepsilon_2=2$, $w=1$ Å; - - -), and the predicted repulsion is now larger than the mean field Poisson–Boltzmann (---).

**Fig. 7**. The region of validity of EPB approximation as a description of the primitive model for the one component double layer without images. The major axes are the reciprocal of the two dimensionless parameters $\chi=8\pi q^2/(k_B T \varepsilon_1)$ and $\xi=-16\pi q^3/(k_B T \varepsilon_1)^2$ which characterize the system. Lower values of these parameters correspond to lower coupling and this is where EPB is valid. Beyond the outer hyperbola the theory is accurate to better than 10%. The inner hyperbola delimits the region within which predicted pressure is less than half the actual pressure in the primitive model. The minor axes (included only for convenience) show the equivalent separation and area per surface charge for monovalent counterions at $T=300$ K and $\varepsilon_1=80$.
Lifshitz theory and the primitive model is transparent. In particular if ionic correlations are allowed by a theory, one would predict a spurious repulsion unless the effects of fluctuations in the polar media (the Lifshitz zero frequency term) were also added.6,14

The EPB method has been implemented explicitly for the special case of the one component double layer. The solution of the full double layer problem is also readily accessible and this will be examined in a subsequent paper. The theory gives the primary departure from the PB approximation, and allows the EPB to be used to easily assess the accuracy of the PB theory in general. The accuracy of the extended Poisson–Boltzmann scheme itself was also shown to be satisfactory in the large separation and/or low surface charge regime of experimental interest. It can be inferred that the theory provides an acceptable approximation to the primitive model of the double layer, a model which might be expected to be a valid description of reality asymptotically, as indeed is Lifshitz theory. Finally we remark that that distinction so often made between van der Waals and double layer forces is illusory.

ACKNOWLEDGMENTS

We thank Roland Kjellander and Stjepan Marčelja for many helpful discussions and for allowing us to use their

HNC computer for supplementary calculations.