

The structure of electrolytes at charged surfaces: Ion-dipole mixtures

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The detailed structure of the double layer is investigated using a model fluid consisting of hard spheres with embedded point charges in a solvent of hard spheres with embedded point dipoles against a hard wall with smeared-out surface charge. Such a model treats solute and solvent particles on an equal basis, unlike the primitive model of electrolytes. The statistical mechanics is solved using the mean spherical approximation for all interactions. This limits the validity of any results to the regime of low ionic concentrations, where, in this approximation, the model fluid has the correct limiting behavior for bulk thermodynamic quantities. In this regime, simple analytic results for the surface properties are given, which are correct to order (κR) . In particular, the surface potential has the classical Stern layer form, with solvent structuring responsible for the inner layer capacitance. This result is the first derivation, as opposed to postulation, of Stern layer behavior. In addition, the polarization density oscillates about the continuum theory result for 3–4 molecular diameters away from the surface. Such behavior shows the difficulty in defining a local dielectric constant close to the surface.

I. INTRODUCTION

Theoretical studies of the electrical double layer began some seventy years ago when Gouy¹ and Chapman² constructed their mean field theory based on the Poisson-Boltzmann equation. The Gouy-Chapman theory, which is based on the "primitive" model electrolyte, has served as an extremely useful conceptual framework. In many instances, it provided good quantitative descriptions of the behavior of colloidal systems that are due to electrostatic interactions. However, in the "primitive" model, the solvent is only regarded as a dielectric continuum, consequently it has been necessary in some instances to modify the Gouy-Chapman picture to include solvent structure effects. The earliest and perhaps the most significant modification is due to Stern³ who suggested that there should be a thin region adjacent to the charged surface, possibly with different dielectric properties from the bulk solution, from which all ions are excluded. Thus in one phenomenological model Stern was able to subsume effects due to ion and solvent size as well as solvent structure into one parameter—the inner layer capacitance (per unit area) $\epsilon_s/4\pi d$, where ϵ_s is the dielectric constant of this Stern layer and d is its thickness. Subsequent modifications to the Stern picture include a position dependent and electric field dependent (dielectric saturation) dielectric constant for the inner region of the double layer. While such attempts were able to account for experimental (thermodynamic) observations with not unphysical choices of parameters in the models, nevertheless, they still rely on the "primitive" model and consequently we cannot be certain that these models actually give an accurate description of the detailed structure of the double layer.

The only unambiguous method of investigating the structure of ions and solvents near charged surfaces is to employ a "civilized" model in which both the ions and the solvent are treated on an equal basis—as discrete particles.⁴ Thus any structuring of the solvent that gives rise to distance-dependent dielectric constants or dielectric saturation effects should emerge

as a natural consequence of calculations based on such models. Due to the inherent complexities of the "civilized" model, we can only deal with model solvents and ions that are still some way from the ultimate problem of interest—aqueous electrolytes. One approach that enjoyed some success in fitting experimental data is to treat only the monolayer of solvent adjacent to the electrode as discrete molecules. The electrolyte located beyond this first layer is modelled as a continuum according to the Gouy-Chapman theory. For a recent review of the various models based on this approach see Ref. 5.

In this paper we consider a model electrolyte solution comprised of a mixture of ions of equal size, modeled as hard spheres plus embedded point charges in a dipolar solvent, modeled as hard spheres (of different size to those of the ions) plus embedded permanent point dipoles. We study the structure of this model electrolyte at a uniformly charged planar surface in the mean spherical approximation (MSA). This approximation is a *linear* theory, analogous to the Debye-Hückel theory, extended to handle finite molecular size in a consistent fashion. A pedagogical but heuristic discussion of this approximation for the non liquid state specialists is given in an earlier paper.⁶ In this model the concept of an inner layer region emerges as a natural consequence of the perturbation of the electrolyte structure by the charged surface and the thermodynamic properties can be easily interpreted in terms of the classical Stern picture. Furthermore, it is not difficult to demonstrate that a machine simulation of this relatively simple problem will at least for the time being require an exorbitant amount of computer time; consequently any approximate analytic solution will be useful.

In view of the complicated nature of the solution, which relies heavily on earlier work, the layout of this paper will be slightly unorthodox. In Sec. II, we give a detailed description of the model and the limitations of our approximation. The results of our calculations will be given in Sec. III, where a comparison with the clas-

sical Stern model will be made. While this is the most important section of this paper, it will stand independent of the detailed workings in Sec. IV or any prior knowledge of the MSA for ion-dipole mixtures. The paper closes with a short conclusion.

II. THE MODEL

The electrolyte is modeled as a mixture of ions and dipolar molecules. The dielectric constant is determined by specifying the molecular properties of the dipolar solvent.

The ionic solutes are taken to be hard spheres of equal diameter R_1 , number densities ρ_1, ρ_2, \dots , valencies z_1, z_2, \dots which satisfy the bulk electroneutrality condition

$$\sum_i \rho_i z_i = 0. \quad (2.1)$$

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

ion-ion,

$$u_{ij}(r) = \infty, \quad r < R_1 \\ = \frac{z_i z_j e^2}{r}, \quad r > R_1, \quad (2.2)$$

ion-dipole,

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

dipole-dipole,

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

and

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

where e is the protonic charge and \mathbf{I} the 3×3 unit tensor. $\hat{\mu}(\omega)$ is a unit vector in the direction of the dipole moment whose orientation is specified by the angular variable $\omega = (\theta, \phi)$ with $\int d\omega = 4\pi$. The subscripts i, j, k, \dots will hereafter be reserved for ionic quantities and the subscript d for dipoles.

It is obvious that this model electrolyte system is still rather unsophisticated. Effects such as polarization of the ions and solvents have been omitted altogether. However, we believe we have the basic ingredients to take the first step away from the "primitive" model electrolyte.

The structure of this ion-dipole mixture at a uniformly charged planar surface is obtained by first considering the structure about a *single* spherical colloidal particle of diameter $R_0 (\gg R_1)$ and valence z_0 . The structure at a planar surface is then recovered by taking the limit $R_0 \rightarrow \infty, z_0 \rightarrow \infty$, but at constant surface charge density $\sigma = z_0 e / \pi R_0^2$. This limit is only taken when it is "safe" to do so without causing any divergences. The interaction potentials between the surface and the ions and dipoles are:

surface-ion,

$$u_{id}(\mathbf{r}, \omega) = \infty, \quad r < R_{10} \equiv \frac{1}{2}(R_1 + R_0) \\ = \frac{z_i z_0 e^2}{r}, \quad r > R_{10}, \quad (2.6)$$

surface-dipole,

$$u_{od}(\mathbf{r}, \omega) = \infty, \quad r < R_{20} \equiv \frac{1}{2}(R_2 + R_0) \\ = \frac{-z_0 e \mu(\omega) \cdot \hat{\mathbf{r}}}{r^2}, \quad r > R_{20}, \quad (2.7)$$

with the subscript o referring to quantities associated with the surface. Note that for potentials of the form given by Eqs. (2.6) and (2.7), the surface or wall is assumed to have unit dielectric constant. Since the use of the MSA closure for $c_{io}(r)$ and $c_{do}(r)$ precludes the treatment of image interactions,⁷ this choice of the value of the wall dielectric constant is consistent with the capabilities of the MSA.

The main statistical mechanical problem is to evaluate the density distribution of ionic species $\rho_{oi}(r) \equiv \rho_{oi}[1 + h_{oi}(r)]$ and dipolar species $\rho_{od}(\mathbf{r}, \omega) \equiv \rho_d[1 + h_{od}(\mathbf{r}, \omega)]$ around the colloidal particle. Here $h_{oi}(r)$ is the surface (or colloidal particle)—ion indirect correlation function at a distance r from the center of the colloidal particle and $h_{od}(\mathbf{r}, \omega)$ is the indirect correlation function between the surface and a dipole at position \mathbf{r} and orientation ω . All thermodynamic quantities associated with the surface can be written in terms of $h_{oi}(r)$ and $h_{od}(\mathbf{r}, \omega)$.

III. RESULTS

As stated in Sec. I, the MSA treatment of an ion-dipole mixture at a charged surface is only a *linear* theory. Even so, the final results, though analytic, are still intractable. For example, in the general expression for the surface potential, Eq. (4.36), which is valid for all ionic concentrations and ion/dipole size ratios, the physical content is not immediately apparent. However, for the interesting limit of a dilute electrolyte, that is, when $\kappa R_1 \ll 1$ where κ^{-1} is the Debye screening length, simple and physically perspicuous results can be extracted. Before we present results in this regime, it is useful to briefly recapitulate the classical Debye-Hückel result for the purpose of comparison with and interpretation of our new results.

A. Debye-Hückel theory with Stern correction

Consider the classical Stern picture in Fig. 1 where a Stern layer of thickness d and dielectric constant ϵ_s has been set up adjacent to a planar surface with uniform surface charge density σ and surface potential ψ_0 . The ionic solution is confined in the region $x > 0$, where the dielectric constant is ϵ . In the Debye-Hückel theory, the relation between the surface charge σ and surface potential ψ_0 is

$$\psi_0 = \frac{4\pi\sigma}{\epsilon\kappa} \left(1 + \frac{\epsilon}{\epsilon_s} \kappa d \right). \quad (3.1)$$

The adjustable parameter in this model is the capacitance (per unit area) C_s of the Stern layer given by

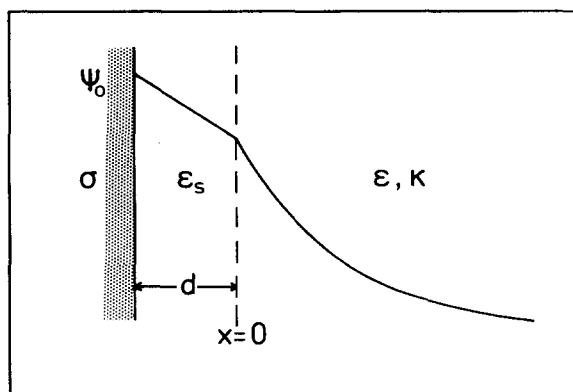


FIG. 1. Classical Stern model of the double layer.

$$C_s = \epsilon_s / 4\pi d. \quad (3.2)$$

The capacitance of the diffuse part of the double layer is

$$C_{dl} = \frac{\epsilon \kappa}{4\pi}. \quad (3.3)$$

Another macroscopic quantity that contains information about the structure of solvents in the double layer is the polarization density or dipole moment per unit volume $P(x)$. This is a measure of the degree of polarization or orientation of the solvent molecules due to the presence of the charged surface. In the macroscopic continuum theory $P_{\text{mac}}(x)$ is given by

$$\begin{aligned} P_{\text{mac}}(x) &= \left(\frac{\epsilon - 1}{4\pi} \right) E(x) = \left(\frac{\epsilon - 1}{4\pi} \right) \left(-\frac{\partial \psi}{\partial x} \right) \\ &= \left(\frac{\epsilon - 1}{\epsilon} \right) \sigma e^{-\kappa x}, \quad x \geq 0 \end{aligned} \quad (3.4)$$

since the potential profile is given by

$$\psi(x) = \frac{4\pi\sigma}{\epsilon\kappa} e^{-\kappa x}, \quad x \geq 0. \quad (3.5)$$

Having stated these familiar results, we can examine the corresponding quantities for the ion-dipole mixture at a charged surface.

B. MSA results for ion-dipole mixtures

The analytic results given in this section are derived in Sec. IV. Their validity is limited to low electrolyte concentrations i.e., $\kappa R_1 \ll 1$. All expressions are correct to order (κR_1) and terms proportional to $(\kappa R_1)^2$ or higher powers have been neglected.

For the bulk ion-dipole mixture, the dielectric constant will in general be a function of the properties of the dipoles and also of the ionic concentration. It turns out however, that to order κR_1 , the dielectric constant is the same as that of the pure dipolar fluid^{6,8,9} and its value is given by

$$\epsilon = q(2\xi)/q(-\xi), \quad (3.6)$$

where

$$q(x) \equiv \frac{(1+2x)^2}{(1-x)^4} \quad (3.7)$$

and the parameter ξ ($0 \leq \xi < \frac{1}{2}$) is the solution of the equation

$$q(2\xi) - q(-\xi) \equiv \frac{(1+4\xi)^2}{(1-2\xi)^4} - \frac{(1-2\xi)^2}{(1+\xi)^4} = \frac{4\pi\rho_d\mu^2}{3kT}. \quad (3.8)$$

Consequently the Debye screening parameter retains its normal definition

$$\kappa^2 = 4\pi e^2 \sum_i \rho_i z_i^2 / \epsilon kT. \quad (3.9)$$

1. Surface charge vs surface potential

An important quantity in electrical double layer problems is the relationship between the surface charge and surface potential. The statistical mechanical definition of the surface potential of a spherical colloidal particle of diameter R_0 is

$$\begin{aligned} \psi_0 &= \frac{z_0 e}{(R_0/2)} + \int d\mathbf{r}' \frac{\sum_i \rho_i z_i e h_{oi}(\mathbf{r}')}{|\mathbf{r}' - \frac{1}{2}R_0\hat{\mathbf{r}}|} \\ &+ \frac{\rho_d \mu}{4\pi} \int d\mathbf{r}' \int d\omega \frac{h_{od}(\mathbf{r}', \omega) \hat{\mu}(\omega) \cdot \hat{\mathbf{r}}'}{|\mathbf{r}' - \frac{1}{2}R_0\hat{\mathbf{r}}|^2}, \end{aligned} \quad (3.10)$$

where we have chosen the origin of the coordinate system to be at the center of the colloidal particle. The significance of the three terms in Eq. (3.10) is as follows. The first term is the direct Coulomb potential due to the colloidal particle. The second term accounts for the potential due to the charge distribution about the colloidal particle. The expression for the charge density $\sum_i \rho_i z_i e h_{oi}(\mathbf{r})$ follows from the definition of the local ionic concentration, viz. $\rho_i [1 + h_{oi}(\mathbf{r})]$ and the bulk electroneutrality condition Eq. (2.1). Contributions to the surface potential from the dipolar species is given by the third term on the right-hand side of Eq. (3.10). Although the number density of dipoles at position \mathbf{r} with orientation ω is $\rho_d [1 + h_{od}(\mathbf{r}, \omega)]$, the constant term vanishes because of the angular integration.

We have evaluated the necessary integrals and then passed to the limit $R_0 \rightarrow \infty$ to obtain the surface potential ψ_0 at a flat surface. The result, correct to order κR_1 and κR_2 , is

$$\psi_0 = \frac{4\pi\sigma}{\epsilon\kappa} \left[1 + \frac{1}{2}\kappa R_1 \left(1 + \frac{\epsilon - 1}{\lambda} \frac{R_2}{R_1} \right) \right]. \quad (3.11)$$

The dimensionless constant λ is only a function of the properties of the pure dipolar fluid and its value is given by

$$\lambda = \left(\frac{1+4\xi}{1-2\xi} \right) \geq 1 \quad (3.12)$$

or, more simply, in terms of the dielectric constant ϵ

$$\lambda^2(1+\lambda)^4 = 16\epsilon \quad (3.13)$$

[cf. Eqs. (3.6)–(3.8)]. This constant is related to the scale length R_s encountered earlier in the MSA expression for the Born energy of an ion in a dipolar solvent⁶:

$$2R_s \equiv R_2 / \lambda \leq R_2. \quad (3.14)$$

To begin our discussion of the physical significance of Eq. (3.11) and its relation to classical theory we note that in the limit of point ions and dipoles ($R_1, R_2 \rightarrow 0$) we recover the Debye-Hückel result without the Stern correction [cf. Eq. (3.1) with $d=0$]. We can also recover the "primitive" model result by letting $R_2 \rightarrow 0$ to get

$$\psi_0 = \frac{4\pi\sigma}{\epsilon\kappa} \left(1 + \frac{1}{2}\kappa R_1\right) \quad (3.15)$$

(cf. Eq. (3.1) with $\epsilon_s = \epsilon$). We recognize that this is the Debye-Hückel result with a modification to exclude ionic centers from a layer one ionic radius ($\frac{1}{2}R_1$) thick adjacent to the surface. To lowest order in κR_1 , this is the correction to the Debye-Hückel result due to finite ion size. To the same order in ionic concentration this result also coincides with the MSA expression for a "primitive" model electrolyte at a charged surface.¹⁰ However, for an ion-dipole mixture of finite particle sizes Eq. (3.11) indicates that in addition to the capacitance due to the diffuse part of the electrical double layer, Eq. (3.3), there are separate contributions to the total double layer capacitance from the ions:

$$C_{\text{ion}} = \epsilon/2\pi R_1 \quad (3.16)$$

and from the dipolar solvent:

$$C_{\text{solv}} = (\epsilon/\epsilon - 1)(\lambda/2\pi R_2) \quad (3.17)$$

The contribution corresponding to C_{solv} will give an additional term to the entropy of the double layer due to solvent structuring. However, for small values of κR_2 this is not a very large effect.

We now attempt to relate our surface charge-surface potential relationship derived for an ion-dipole mixture at a charged surface to the Stern result.

For simplicity we consider the special case of equal size ions and dipoles and so set $R_1 = R_2 = R$ in Eq. (3.11). On comparing this with the Stern result in Eq. (3.1), we can make the formal identification

$$\frac{d}{\epsilon_s} = \frac{R}{2\epsilon} \left(1 + \frac{\epsilon - 1}{\lambda}\right) \quad (3.18)$$

Now, we have two possible ways of identifying the thickness d and dielectric constant ϵ_s of the effective Stern layer of the ion-dipole mixture.

(a) If we choose the thickness d of the Stern layer to be a molecular radius (see Fig. 2) i.e., $d = \frac{1}{2}R$, then we would expect $\epsilon_s = 1$, since the centers of all molecules (ions and dipoles) are excluded from the region with $\frac{1}{2}R$ of the surface. However, Eq. (3.18) gives, for $d = \frac{1}{2}R$, a dielectric constant

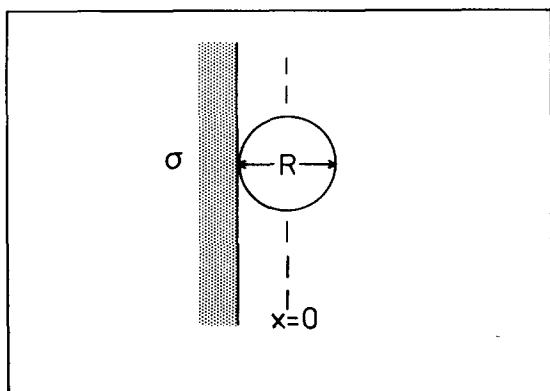


FIG. 2. Ion-dipole model of the surface.

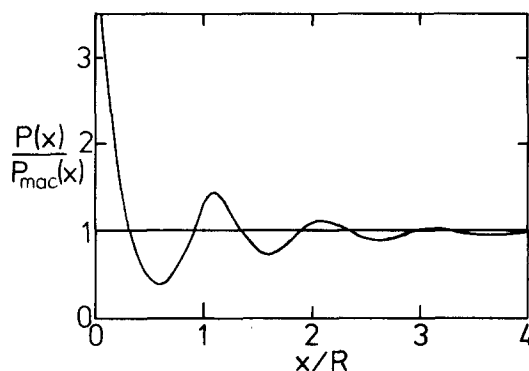


FIG. 3. Polarization density at the surface. $R_1 = R_2 = 3 \text{ \AA}$; $\rho_d R^3 = 0.8$; $T = 298 \text{ K}$; $\epsilon = 80$. Electrolyte concentration = $0.01M$.

$$\epsilon_s = \frac{\epsilon}{1 + (\epsilon - 1)/\lambda} \quad (3.19)$$

For $\epsilon = 80$, Eqs. (2.13) and (3.19) give $\epsilon_s = 2.6$. Thus, in this interpretation, the effect of solvent structure in the region $x \geq 0$ is to *increase* the dielectric constant of the Stern layer above unity.

(b) If, on the other hand, we choose to fix the dielectric constant of the Stern layer to be unity, then Eq. (3.18) gives the thickness of the Stern layer to be

$$d = \frac{R}{2\epsilon} \left(1 + \frac{\epsilon - 1}{\lambda}\right) \leq \frac{R}{2} \quad (3.20)$$

where the last inequality follows from Eqs. (3.12) and (3.13). In other words, as a result of solvent structure the region of unit dielectric constant from which all ions and dipoles are excluded appears *thinner* than the molecular radius.

As we shall see in the next section, both interpretations arise from the attempt to model the complex dielectric response of a structured region of ions and solvent molecules adjacent to the surface by an equivalent system consisting of regions of *uniform* dielectric constant. (In this respect, the Stern picture is analogous to the Gibbs dividing surface construction in adsorption problems.) In particular, a region of *high* local dielectric constant near $x = 0$ could give rise to interpretations (a) and (b). To examine more closely the structure at the interface, we now investigate the polarization density.

2. Polarization density

The polarization density or dipole moment per unit volume is a measure of the local dielectric response or orientational order of the dipolar solvent in an applied field. The statistical mechanical definition of the polarization density around the spherical colloidal particle $P(r) = P(r)\hat{r}$ is

$$P(r) = \frac{\rho_d}{4\pi} \int d\omega h_{od}(r, \omega)(\mu(\omega) \cdot \hat{r}) \quad (3.21)$$

The polarization density $P(x)$ at a planar charged surface is obtained by taking the limit of an infinitely large colloidal particle, $R_0 \rightarrow \infty$. In Fig. 3 we plot the ratio $P(x)/P_{\text{mac}}(x)$ [see Eq. (3.4)] as a function of the distance

x from the charged surface. Here $P(x)$ is calculated to lowest order in κR . Within 3–4 molecular diameters from the surface there are significant deviations in $P(x)$ from the macroscopic result. Although the magnitude of the oscillations may be overestimated due to the linear nature of the MSA, the oscillatory nature of $P(x)/P_{\text{mac}}(x)$ indicates the strong cooperative alignment of dipolar molecules that are located near the surface. This oscillatory form of $P(x)/P_{\text{mac}}(x)$, which can only come from a discrete (rather than continuum) treatment of the solvent, is similar to the polarization density around a single ion in a dipolar solvent.⁶ In the regime $\kappa R \ll 1$, the form of $P(x)$ is insensitive to the electrolyte concentration, since it is determined mainly by the properties of the dipolar fluid. Effects of the electrolyte can only be important at distances $\sim \kappa^{-1}$ from the surface (i.e., for low concentrations, at distances much greater than R).

For the result in Fig. 3, the total polarization $\int_0^\infty P(x) dx$ is in excess of that given by macroscopic theory. That is, a discrete treatment of the solvent allows for the possibility of a *larger* depolarizing field due to the dipoles. Consequently, if we were to use some sort of “local” dielectric constant to characterize the dielectric response of the solvent near the surface, this local dielectric constant would be *larger* than the bulk value.

The result in Fig. 3 also shows the difficulties in justifying the use of a position-dependent local dielectric constant. Since our model, which has no such local dielectric constant, still reproduces the Stern layer form for the $\psi_0 - \sigma$ relationship, the ability to mimic thermodynamic properties of the surface is, by itself, no justification for a particular choice of the form of a local dielectric constant.

Finally we note that to order κR the asymptotic form of $P(x)$ far from the surface, $\kappa x \gg 1$, is the same as the macroscopic value $P_{\text{mac}}(x)$, cf. Eq. (3.4). This is consistent with the observation that to order κR the dielectric constant of the ion–dipole mixture is the same as that for the pure dipolar fluid.

3. Charge density

In the MSA the number density of ions of species i (valence z_i) near the charged surface has the form

$$\rho_i(x) = \rho^{\text{hs}}(x) + z_i \rho^{\text{C}}(x). \quad (3.22)$$

The linear decomposition into a hard sphere part (hs) and charge part (C) proportional to the valence is a direct consequence of the linearity of the MSA. The hard sphere contribution $\rho^{\text{hs}}(x)$ is the Percus–Yevick density profile of a hard sphere solute of diameter R_1 , density $(\sum_i \rho_i)$ in a hard sphere solvent of diameter R_2 , density ρ_2 , against a hard wall. At typical liquid solvent densities ($\rho_2 R_2^3 \sim 0.8$), $\rho^{\text{hs}}(x)$ will exhibit the characteristic oscillatory behavior. However, the local charge density $\sum_i z_i e \rho_i(x)$ is *independent* of $\rho^{\text{hs}}(x)$ in the MSA because of the bulk electroneutrality condition, Eq. (2.1), and the linear form of Eq. (3.22). In fact, for low electrolyte concentrations, $\kappa R_1 \ll 1$, the local charge density [pro-

portional to $\rho^{\text{C}}(x)$] is very similar to the Debye–Hückel result.

IV. METHOD OF SOLUTION

In this section, we give details of the solutions of an ion–dipole mixture against a charged wall in the MSA. The method of solution is an adaptation of Wertheim’s solution for the MSA dipolar fluid¹¹ and the Baxter factorization method of the Ornstein–Zernike (OZ) equation which had been applied previously to the bulk ion–dipole mixture.⁶ As the present work draws heavily on the bulk ion–dipole problem, the reader will be assumed to have a fair degree of familiarity with the content and notation in Ref. 6 (hereafter referred to as I).

The bulk ion–dipole problem begins with the OZ equation

$$h_{\alpha\beta}(1, 2) = c_{\alpha\beta}(1, 2) + \sum_\gamma \frac{\rho_\gamma}{4\pi} \int c_{\alpha\gamma}(1, 3) h_{\gamma\beta}(3, 2) d\mathbf{3}, \quad (4.1)$$

where $\alpha, \beta, \gamma, \dots$ denote both ionic (i, j, k, \dots) and dipolar species (d) and the variables $1, 2, 3, \dots$ denote both spatial and angular coordinates. In the MSA, Eq. (4.1) is supplemented by the closure conditions [see Eqs. (2.2)–(2.5)]

$$h_{\alpha\beta}(1, 2) = -1, \quad |\mathbf{r}_1 - \mathbf{r}_2| < R_{\alpha\beta} \equiv \frac{1}{2}(R_\alpha + R_\beta) \quad (4.2)$$

$$c_{\alpha\beta}(1, 2) = -u_{\alpha\beta}(1, 2)/kT, \quad |\mathbf{r}_1 - \mathbf{r}_2| > R_{\alpha\beta}. \quad (4.3)$$

The major step in Wertheim’s method as applied to this problem is to recognize that Eqs. (4.1)–(4.3) have solutions for h and c that can be written as linear combinations of the angular functions $1, E_i = \hat{\mu}(\omega_i) \cdot \hat{\mathbf{r}}, \Delta_{12} = \hat{\mu}(\omega_1) \cdot \hat{\mu}(\omega_2)$ and $D_{12} = \hat{\mu}(\omega_1) \cdot (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \hat{\mu}(\omega_2)$ with coefficients that are only functions of $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. This decomposition enables Eq. (4.1) to be written as a set of OZ-like equations whose correlation functions only depend on the distance between the centers of the molecules and not their orientations. The Baxter method can then be used on this latter set of equations (see I for details).

Turning now to the problem of an ion–dipole mixture at a charged wall, the quantities we want are the ion–wall, $h_{i0}(r)$, and dipole–wall, $h_{d0}(\omega, \mathbf{r})$, indirect correlation functions. The OZ equations for these two correlation functions can be written in the general form

$$h_{\alpha o}(1, 2) = c_{\alpha o}(1, 2) + \sum_\beta \frac{\rho_\beta}{4\pi} \int c_{\alpha\beta}(1, 3) h_{\beta o}(3, 2) d\mathbf{3}, \quad (4.4)$$

where summation is over all ionic and dipolar species in the fluid mixture. The MSA closure on $h_{\alpha o}$ and $c_{\alpha o}$ is [see Eqs. (2.6) and (2.7)]

$$h_{\alpha o}(1, 2) = -1, \quad |\mathbf{r}_1 - \mathbf{r}_2| < R_{\alpha o} \quad (4.5)$$

$$c_{\alpha o}(1, 2) = -u_{\alpha o}(1, 2)/kT, \quad |\mathbf{r}_1 - \mathbf{r}_2| > R_{\alpha o}. \quad (4.6)$$

The bulk direct correlation functions $c_{\alpha\beta}$ are assumed to be known from the bulk problem. We proceed, as in the bulk problem, with the decomposition [see Eq. (I 3.9), equations from Ref. 6 are prefixed by I] ($f = h$ or c)

$$f_{i0}(\mathbf{r}) = f_{i0}^{hs}(\mathbf{r}) + z_i z_0 f_{i0}^c(\mathbf{r}), \quad (4.7)$$

$$f_{d0}(\omega, \mathbf{r}) = f_{d0}^{hs}(\mathbf{r}) - z_0 f_{d0}^E(\mathbf{r}) E_1. \quad (4.8)$$

As before, the functions $f_{i0}^{hs}(\mathbf{r})$ and $f_{d0}^{hs}(\mathbf{r})$ are the Percus-Yevick hard sphere correlation functions of a two component hard sphere fluid of densities ($\sum_i \rho_i$) and ρ_d and diameters R_1 and R_2 at a hard wall. In the MSA these functions describe the density profile at the surface. This unsatisfactory feature of the MSA is due to its failure to properly account for the angle averaged potential and image effects, which also affect the density profiles. The electrostatic properties of the interface are determined solely by f_{i0}^c and f_{d0}^E which we shall study in detail.

We can now take the Fourier transform of Eq. (4.4). Using the bulk electroneutrality condition, we can uncouple the "electrostatic" members of the correlation functions. These are

$$\bar{h}_{10}^c(k) = \bar{c}_{10}^c(k) + \rho_1 \bar{c}^c(k) \bar{h}_{10}^c(k) - \rho_2 \bar{c}_{12}^E(k) \bar{h}_{20}^E(k), \quad (4.9)$$

$$\bar{h}_{20}^E(k) = \bar{c}_{20}^E(k) + \rho_1 \bar{c}_{21}^E(k) \bar{h}_{10}^c(k) + \rho_2 \bar{c}^*(k) \bar{h}_{20}^E(k), \quad (4.10)$$

where

$$\rho_1 \equiv \sum_i \rho_i z_i^2, \quad (4.11)$$

$$\rho_2 \equiv \frac{1}{3} \rho_d, \quad (4.12)$$

$$\bar{c}_{12}^E = \bar{c}_{21}^E = \bar{c}^E, \quad (4.13)$$

and \bar{c}^c , \bar{c}^E and \bar{c}^* are known direct correlation functions from the bulk problem.⁶ The Fourier transforms of the functions in Eqs. (4.9) and (4.10) are defined in Eqs. (I 3.15)–(I 3.17). If we make the following definitions,

$$\begin{aligned} \bar{c}_{11} &\equiv \bar{c}^c \\ \bar{c}_{12} &\equiv \bar{c}_{12}^E \\ \bar{c}_{21} &\equiv -\bar{c}_{21}^E \\ \bar{c}_{22} &\equiv \bar{c}^* \\ \bar{f}_{10} &\equiv \bar{f}_{10}^c \quad (f = h \text{ or } c) \\ \bar{f}_{20} &\equiv -\bar{f}_{20}^E \end{aligned} \quad (4.14)$$

Eqs. (4.9) and (4.10) can be written in the standard form

$$\begin{aligned} Q_{12}(r) &= 0, \quad r > R_{12} \\ &= -\frac{1}{2} \left(\rho_1 A_{21} H_{21} + \frac{24\xi}{R_2^3} M_{12}^{(0)} \right) (r^2 - R_{12}^2) + \left[-H_{21}(a_1 - \rho_1 A_{11} R_1) + \frac{24\xi}{R_2^3} (R_{12} M_{12}^{(0)} - M_{12}^{(1)}) \right] (r - R_{12}), \quad S_{12} < r_1 < R_{12} \end{aligned} \quad (4.19c)$$

$$\begin{aligned} Q_{22}(r) &= 0, \quad r > R_2 \\ &= \frac{1}{2} \left[\frac{24\xi}{\rho_2 R_2^3} a_2 - \rho_1 A_{21} H_{21} \right] (r^2 - R_2^2) + \left[\rho_1 H_{21} M_{21}^{(0)} + \rho_1 A_{21} H_{21} R_{12} - \frac{24\xi}{\rho_2 R_2^3} (R_2 a_2 - s) \right] (r - R_2) \quad 0 < r < R_2 \end{aligned} \quad (4.19d)$$

where ρ_1 and ρ_2 are given by Eqs. (4.11) and (4.12),

$$H_{11} \equiv 2\pi \int_0^\infty dr r h_{11}(r) \quad (4.20)$$

$$\bar{h}_{\alpha\alpha}(k) = \bar{c}_{\alpha\alpha}(k) + \sum_{\beta=1}^2 \rho_\beta \bar{c}_{\alpha\beta}(k) \bar{h}_{\beta\alpha}(k) \quad (\alpha = 1, 2) \quad (4.15)$$

which is suitable for the Baxter factorization method. Baxter's method involves finding the auxiliary functions $\bar{q}_{\alpha\alpha}(k)$ that satisfy

$$\bar{c}_{\alpha\alpha}(k) = \bar{q}_{\alpha\alpha}(k) + \bar{q}_{\alpha\alpha}(-k) - \sum_{\beta=1}^2 \rho_\beta \bar{q}_{\beta\alpha}(-k) \bar{q}_{\beta\alpha}(k) \quad (4.16)$$

with the appropriate analytic properties.¹² The functions $\bar{q}_{\beta\alpha}$ are known from the bulk problem. The solutions to Eq. (4.15) can then be written as

$$H_{\alpha\alpha}(r) = Q_{\alpha\alpha}(r) + \sum_{\beta=1}^2 \rho_\beta \int_{S_{\alpha\beta}}^\infty ds Q_{\alpha\beta}(s) H_{\beta\alpha}(r-s), \quad (4.17)$$

where

$$\begin{aligned} Q_{\alpha\alpha}(r) &= \frac{1}{2\pi} \int_{-\infty}^\infty e^{-ikr} \bar{q}_{\alpha\alpha}(k) dk \\ S_{\alpha\beta} &= \frac{1}{2} (R_\alpha - R_\beta). \end{aligned} \quad (4.18)$$

The functions $H_{\alpha\alpha}(r)$ are one-dimensional Fourier inversions of $\bar{h}_{\alpha\alpha}(k)$ and are related to their three-dimensional counterparts $h_{\alpha\alpha}(r)$ by Eq. (I 3.52). The functions $Q_{\alpha\beta}$ are known from the bulk problem.

This completes the formal solution to the problem of an ion-dipole mixture at a charged surface. However, in order to derive the results given in Sec. III we require solutions to the bulk ion-dipole problem to order κR_1 .

A. Bulk ion-dipole mixture

For completeness, we shall briefly recapitulate the results for the bulk ion-dipole mixture.^{6,9}

The auxiliary functions $Q_{\alpha\beta}$ have the following form:

$$\begin{aligned} Q_{11}(r) &= -A_{11}, \quad r > R_1 \\ &= (\rho_1 A_{11} H_{11} - \rho_2 H_{21} M_{12}^{(0)}) (r - R_1) - A_{11}, \quad 0 < r < R_1 \end{aligned} \quad (4.19a)$$

$$\begin{aligned} Q_{21}(r) &= -A_{21} \\ &= (\rho_1 A_{21} H_{11} + H_{21} a_2) (r - R_{12}) - A_{21}, \quad S_{21} < r < R_{21} \end{aligned} \quad (4.19b)$$

$$H_{21} \equiv 2\pi \int_0^\infty dr r h_{21}(r), \quad (4.21)$$

the moments $M_{\alpha\beta}^{(n)}$ are defined by

$$M_{\alpha\beta}^{(n)} \equiv \int_{S_{\alpha\beta}}^{R_{\alpha\beta}} (R_{\alpha\beta} - r)^n Q_{\alpha\beta}(r) dr \quad (4.22)$$

and

$$a_1 = 1 - \rho_1 M_{11}^{(0)}, \quad (4.23)$$

$$a_2 = 1 - \rho_2 M_{22}^{(0)}, \quad (4.24)$$

$$s = R_2 - \rho_2 M_{22}^{(1)}. \quad (4.25)$$

All the constants in Eq. (4.19) (A_{11} , A_{21} , a_1 , a_2 , H_{11} , H_{21} , s , ξ , $M_{12}^{(0)}$, $M_{21}^{(0)}$, and $M_{12}^{(1)}$) can be found by solving the following eleven simultaneous algebraic equations:

$$4\pi\beta e^2 = \rho_1 A_{11}^2 + \rho_2 A_{21}^2, \quad (4.26a)$$

$$4\pi\beta e\mu = A_{21} a_2 - \rho_1 A_{11} M_{12}^{(0)}, \quad (4.26b)$$

$$4\pi\beta\rho_2\mu^2 = a_2^2 + \rho_1\rho_2 M_{12}^{(0)2} - q(-\xi), \quad (4.26c)$$

$$1 - a_1 = -\rho_1 A_{11} R_1 + \frac{1}{2}\rho_1 R_1^2 [\rho_2 H_{21} M_{12}^{(0)} - \rho_1 A_{11} H_{11}], \quad (4.26d)$$

$$H_{21} [s + S_{12} a_2] = -\frac{1}{2} A_{21} + \rho_1 H_{11} M_{21}^{(0)}, \quad (4.26e)$$

$$M_{21}^{(0)} = -A_{21} R_1 - \frac{1}{2} R_1^2 (\rho_1 A_{21} H_{11} + H_{21} a_2), \quad (4.26f)$$

$$H_{11} a_1 = -\frac{1}{2} A_{11} + \rho_2 H_{21} (M_{12}^{(1)} + S_{12} M_{12}^{(0)}), \quad (4.26g)$$

$$M_{12}^{(0)} = \frac{\frac{1}{2} R_2^2 H_{21}}{(1-2\xi)^2} \left\{ a_1 - \rho_1 A_{11} \left[R_2 \left(\frac{1+\xi}{3} \right) + S_{12} \right] \right\}, \quad (4.26h)$$

$$M_{12}^{(1)} = \frac{-\frac{1}{2} R_2^3 H_{21}}{(1-2\xi)^2} \left\{ \frac{1}{3} a_1 (\xi - 2) + \rho_1 A_{11} \left[\frac{1}{3} R_2 + \frac{1}{3} S_{12} (\xi - 2) \right] \right\}, \quad (4.26i)$$

$$a_2 = [q(2\xi)]^{1/2} + \frac{\frac{1}{2} \rho_1 \rho_2 R_2^2 H_{21}}{(1-2\xi)^2} \times \left\{ M_{21}^{(0)} + A_{21} \left[R_2 \left(\frac{1+\xi}{3} \right) + S_{12} \right] \right\}, \quad (4.26j)$$

$$\frac{s}{R_2} = \frac{1+\xi}{(1-2\xi)^2} + \frac{\frac{1}{2} \rho_1 \rho_2 R_2^2 H_{21}}{(1-2\xi)^2} \times \left[\left(\frac{2-\xi}{2} \right) M_{21}^{(0)} + A_{21} \left(\frac{1}{4} R_2 + \frac{2-\xi}{2} S_{12} \right) \right]. \quad (4.26k)$$

To order (κR_1) or equivalently to order $\rho_1^{1/2}$ we have the following solutions:

$$a_2 = q_+^{1/2}, \quad (4.27a)$$

$$\rho_1 A_{11} = \kappa \left[1 + \frac{\gamma(\epsilon - 1)\kappa R_2}{4q_+^{1/2}} \right], \quad (4.27b)$$

$$a_1 = 1 + \kappa R_1, \quad (4.27c)$$

$$A_{21} = \frac{4\pi\beta e\mu}{q_+^{1/2}} \left(1 - \frac{\gamma\kappa R_2}{4q_+^{1/2}} \right), \quad (4.27d)$$

$$M_{12}^{(0)} = \frac{-\pi\beta e\mu\gamma R_2}{q_+^{1/2}}, \quad (4.27e)$$

$$M_{21}^{(0)} = \frac{-4\pi\beta e\mu R_1}{q_+^{1/2}} \left(1 - \frac{\gamma(1+4\xi)R_1}{4R_2} \right), \quad (4.27f)$$

where

$$\gamma \equiv \frac{R_2}{R_2(1+\xi) + S_{12}(1+4\xi)}, \quad (4.28)$$

$$q_+ \equiv q(2\xi), \quad (4.29)$$

and ξ is the solution of Eq. (3.8).

With these results from the bulk fluid, we can return to the problem of an ion-dipole mixture at a charged surface.

B. Surface potential

Using the definition given by Eq. (3.10), the surface potential ψ_0 can be written as

$$\psi_0 = 2z_0 e \left(\frac{1}{R_0} + \rho_1 H_{10} + \rho_2 \frac{\mu}{e} H_{20} \right), \quad (4.30)$$

where

$$H_{10} \equiv 2\pi \int_0^\infty dr r h_{10}(r), \quad (4.31)$$

$$H_{20} \equiv 2\pi \int_0^\infty dr h_{20}(r). \quad (4.32)$$

From the behavior of Eq. (4.16) around $k=0$ and from Eq. (4.17), we deduce that

$$Q_{10}(r) = -A_{10}, \quad r > R_{10} \\ = [\rho_1 A_{11} H_{10} - \rho_2 H_{20} M_{12}^{(0)}] (r - R_{10}) - A_{10}, \quad S_{10} < r < R_{10} \quad (4.33a)$$

$$Q_{20}(r) = -A_{20}, \quad r > R_{20} \\ = [H_{20}(1 - \rho_2 M_{22}^{(0)}) + \rho_1 A_{21} H_{10}] (r - R_{10}) - A_{20}, \quad S_{20} < r < R_{20} \quad (4.33b)$$

with

$$A_{10} = A_{11} \quad (4.34a)$$

$$A_{20} = A_{21} \quad (4.34b)$$

and the constants H_{10} and H_{20} are the solutions of

$$-H_{10}(1 - \rho_1 A_{11} S_{10} - \rho_1 M_{11}^{(0)}) + H_{20} \rho_2 (M_{12}^{(1)} - S_{20} M_{12}^{(0)}) = \frac{1}{2} A_{11}, \quad (4.35a)$$

$$H_{10} \rho_1 (M_{21}^{(0)} + S_{10} A_{21}) + H_{20} [R_{20} - \rho_2 (M_{22}^{(1)} - S_{20} M_{22}^{(0)})] = \frac{1}{2} A_{21}. \quad (4.35b)$$

In the planar limit $R_0 \rightarrow \infty$, $z_0 \rightarrow \infty$, $\sigma = z_0 e / \pi R_0^2$, we find

$$\psi_0 = \left(\frac{4\pi\sigma}{e} \right) \left\{ e [a_2 (a_1 - \frac{1}{2} \rho_1 A_{11} R_1) - \rho_1 \rho_2 M_{12}^{(0)} (M_{21}^{(0)} + \frac{1}{2} R_1 A_{21})] - \mu \rho_2 (\rho_1 A_{11} M_{21}^{(0)} + A_{21} a_1) \right\} \left\{ \rho_1 A_{11} a_2 + \rho_1 \rho_2 A_{21} M_{12}^{(0)-1} \right\}^{-1} \quad (4.36)$$

which is the general expression for the surface potential, valid for all ionic concentrations and ion/dipole size ratios.

Using the solution given by Eq. (4.27) we obtain the expression for the surface potential ψ_0 , correct to $O(\kappa R_1)$, which is given by Eq. (3.11).

C. Polarization and charge density

In terms of the distribution functions defined in Eq. (4.14) the charge density can be expressed as

$$\rho^C(r) = \sum_i \rho_i z_i e h_{i0}(r) = \rho_1 e z_0 h_{10}(r) \quad (4.37)$$

while the polarization density becomes [cf. Eq. (3.21)]

$$P(r) = \frac{\rho_d}{4\pi} \int d\omega h_{od}(r, \omega) [\mu(\omega) \cdot \hat{r}]$$

$$= -\rho_2 \mu z_0 h_{20}(r) . \quad (4.38)$$

The functions $h_{10}(r) = h_{10}^E(r)$ and $h_{20}(r) = h_{20}^E(r)$ can be obtained by differentiating Eq. (4.17) [cf. Eq. (I 3.52)]. If we define

$$H_1(x') \equiv z_0 h_{10}(R_{10} + x') , \quad (4.39)$$

$$H_2(x) \equiv z_0 h_{20}(R_{20} + x) , \quad (4.40)$$

where

$$r = R_{10} + x' = R_{20} + x \quad (4.41)$$

so that

$$x' = x + S_{21} , \quad (4.42)$$

we can take the planar limit $R_0 \rightarrow \infty$, $z_0 \rightarrow \infty$, with $\sigma \equiv z_0 e / \pi R_0^2$ constant to get

$$H_1(x') = -A_{11} \left(\frac{\sigma}{e} \right) - \rho_1 A_{11} \int_0^{x'} H_1(y) dy + \rho_2 \int_{S_{12}}^{R_{12}} Q_{12}^0(y) H_2(x-y) dy + \rho_1 \int_0^{R_1} Q_{11}^0(y) H_1(x'-y) dy \quad (4.43)$$

$$H_2(x) = -A_{21} \left(\frac{\sigma}{e} \right) - \rho_1 A_{21} \int_0^{x'} H_1(y) dy + \rho_2 \int_0^{R_2} Q_{22}^0(y) H_2(x-y) dy + \rho_1 \int_{S_{21}}^{R_{21}} Q_{21}^0(y) H_1(x'-y) dy \quad (4.44)$$

where

$$\left. \begin{aligned} Q_{ij}^0(r) &= Q_{ij}(r) + A_{ij} , & S_{ij} < r < R_{ij} \\ &= 0 , & r > R_{ij} . \end{aligned} \right\} \quad (4.45)$$

At this stage, we take $R_1 = R_2 = R$ for simplicity. Careful analysis shows that, to lowest order in κR , Eqs. (4.43) and (4.44) then become

$$H_1(x) = -A_{11} \frac{\sigma}{e} - \rho_1 A_{11} \int_0^x H_1(y) dy \quad (4.46)$$

and

$$H_2(x) = -A_{21} \frac{\sigma}{e} - \rho_1 A_{21} \int_0^x H_1(y) dy + \rho_2 \int_0^R Q_{22}^0(y) H_2(x-y) dy . \quad (4.47)$$

The solution of Eq. (4.46) is

$$H_1(x) = \frac{-\kappa\sigma}{\rho_1 e} e^{-\kappa x} , \quad (4.48)$$

i. e., the Debye-Hückel result [using Eqs. (4.37) and (4.39)]. This leads to

$$H_2(x) = -A_{21} \frac{\sigma}{e} e^{-\kappa x} + \rho_2 \int_0^R Q_{22}^0(y) H_2(x-y) dy , \quad (4.49)$$

where the only terms to be retained to this order in $Q_{22}^0(y)$ are

$$Q_{22}^0(r) = \frac{12\xi a_2}{\rho_2 R^3} (r^2 - R^2) - \frac{24\xi}{\rho_2 R^3} (Ra_2 - s)(r - R) . \quad (4.50)$$

Equation (4.49) can be solved numerically by Perram's method¹³ to give Fig. 3, or it can be solved analytically by Laplace transform methods. Such analytic investigation shows that the inverse decay length of the charge density from the surface has the form $\kappa [1 + \alpha(\kappa R)^2]$ just as is the case for the MSA bulk primitive model electrolyte. Similarly, corrections to the asymptotic forms of the charge and polarization densities have no terms of order κR .

V. CONCLUSION

This paper is the first attempt to *derive* an expression for the Stern layer capacitance and other surface

properties of the electrical double layer from a well-defined model fluid that treats the ions and solvents as discrete entities throughout the entire double layer. Only for low ionic concentrations can simple analytic expressions be found. For higher concentrations, the complex sets of equations given in Sec. IV need to be solved numerically. However, as a function of ionic concentration this model does *not* exhibit the characteristic turning point in the ionic activity coefficients,⁶ and so is suitable for use only at low concentrations, where it gives the correct limiting-law behavior.

The other major limitation of our calculation is the use of the MSA for the dipolar fluid. Simulations¹⁴ have shown this to be not very accurate even for relatively low dielectric constant polar fluids. More complex closures¹⁵⁻¹⁷ analogous to the Poisson-Boltzmann theory can be used for this problem, but an analytic solution will no longer be possible so we feel the results of Sec. III are still of value.

The present model (hard sphere ion-dipole mixture) is still too simple to mimic a real electrolyte; short range interactions (e.g., dispersion forces, image forces, quadrupolar effects, hydrogen bonding, and molecular polarizability) have not been included. Such effects, parametrized in terms of specific ionic adsorption and dipolar adsorption/orientation at the surface, can be added to the present model. These refinements will be the subject of a later publication.

The most important conclusion is that even though the Stern layer model of double layer capacitance is undoubtedly successful, it can be produced in a model solely from solvent structure rather than from dielectric saturation or hydrogen-bonding effects. Also, the idea of a position-dependent local dielectric constant is a tenuous one and the ability of such theories to model surface thermodynamic properties does not give validity to the microscopic picture envisaged in these theories. The Stern layer model is a useful parametrization of the surface properties of the double layer, but is actually an attempt to model a complex double layer structure by discrete regions of uniform dielectric constant.

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