AN ITERATED THREE-LAYER MODEL OF THE DOUBLE LAYER WITH PERMANENT DIPOLES

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There does not exist a theory of the ionic double layer at a completely blocking metal electrode in liquid electrolytes which is adequate in the charge/potential region where ions and solvent molecules begin to approach saturated conditions. Under these conditions, a continuum theory, such as that of Gouy and Chapman (GC), becomes entirely inadequate. Here the problem is attacked in a semi-discrete way by first partitioning the space charge region into layers parallel to the planar blocking electrode. Each layer is part of a cubic lattice with lattice-site spacing determined by the pure solvent concentration. Lattice sites may be occupied by ions of either sign or by solvent molecules, taken as spheres having a permanent dipole moment. The solvent molecule finite-length dipoles are then approximated by slabs of constant point-dipole polarization. Thus each of the planes parallel to the electrode is a locus of ion centers, and the polarization is accounted for by equal and opposite charge layers equidistant on either side of an ionic charge layer. The mean polarization and ionic concentration in each three-layer region are determined self-consistently by free energy minimization, and electrostatic equations are employed to couple the electrical conditions in one layer to those adjacent. This ion-dipole model (IDM) is solved self-consistently for arbitrary molarity in two regimes: the weak-field situation where the electrode charge approaches zero, and the arbitrary field-strength regime. In the first case, an exact, closed-form solution is obtained which reduces to that of GC in the appropriate limit, but numerical analysis is required in the second situation. The present treatment provides a more realistic account of the electrical effects of discrete solvent dipoles than do those treatments, such as the GC model, which represent them entirely by a background, non-saturable, or even saturable, bulk dielectric constant. Here polarization saturation enters naturally in a fully self-consistent way. Thus although dipoles line up with the field in high-field regions, they tend to be displaced by ions of a given sign in the layers immediately adjacent to the blocking electrode, reducing the net polarization. A simpler model, more directly appropriate for single crystals than for liquids, the layered lattice gas model (LLM), retains layering but represents the permanent dipolar polarization by a non-saturable continuum bulk dielectric constant; it is thus intermediate between the IDM and the GCM. Predictions of the three models are compared with Grahame's experimental differential capacitance results for NaF in the low-field region. The IDM is found to be much

superior to either the LMM or the GCM. Many results are presented for the three models in the arbitrary field region. One of the most striking is that the IDM alone yields a strong oscillation in potential versus distance away from the blocking electrode, as first predicted by Kirkwood and Poirier for layered ionic structures.

1. Introduction

There is no fully adequate theory of the electrical double layer in solids and liquids, although much recent effort has been devoted to the problem [1–18]. The classical approach was that of Gouy [19] and Chapman [20], based on a model in which point-charge ions move in a background of homogeneous dielectric characterized by a dielectric constant. This theory takes no account of ion size and thus is unable to model the approach to charge saturation in the neighborhood of a blocking electrode. When applied to aqueous solutions, the dielectric constant is taken as that of bulk water, $\epsilon_B \approx 80$. Because of ionic hydration and the resulting dielectric saturation, this must be a poor approximation in the immediate neighborhood of an ion. The same difficulty exists near an electrode where the local electric field may be very high.

Most modern statistical treatments of the double layer have used the homogeneous dielectric model with finite-size ions [1-6]. These works make use of sophisticated mathematical tools such as the modified Poisson-Boltzmann equation, the hypernetted chain approximation, or the Ornstein-Zernike equation. The formulation is invariably very complicated, involving the solution of nonlinear integral equations. On the other hand, these approaches do not appear to be of practical value for medium or high ionic concentrations and/or for potential differences across the double layer much beyond the thermal voltage $V_T \equiv kT/e$. Neither the nonlinear theories nor the simpler linearized mean spherical approximation [1,2,4,6,9,15] yield a valid description of charge saturation.

Predictions of the statistical theories have been compared with results of Monte Carlo calculations [17,22,23]. This numerical procedure can be applied in the physically important range where charge saturation effects begin to appear. Nevertheless, the assumption of a homogeneous dielectric medium makes the results of the calculations unreliable for aqueous electrolytes.

An alternative way to simulate the finite size of ions is to require them to occupy points on a three-dimensional lattice. The ion-ion interaction can be treated in the mean field approximation, and it has been found that a single mean field parameter allows an excellent fit to the Monte Carlo results over a wide range of double layer potential and ion concentration, including the beginning of the charge saturation region [11,12].

As mentioned earlier, water as a solvent is poorly represented by a homogeneous dielectric. Several statistical treatments of a fluid of ions and solvent molecules, both approximated as hard spheres of the same size, have appeared recently [9,13,15,16]. The solvent molecules possess an effective dipole moment, and the induced polarizabilities of both ions and solvent molecules are neglected. These treatments are naturally more complex than those that assume a homogeneous dielectric, and their linearized forms are again limited to the small concentration and low potential region.

Because of the limitations of the existing theories, it seemed worthwhile to us to develop a statistical theory of the double layer which would trade off exactness for simplicity. After all, what is most needed is a theory which can be compared with experiments that measure average quantities such as electrode charge and differential capacitance. In the following lattice-gas approach we make approximations which preclude the exact calculation of local quantities; we include solvent dipoles; we take some of the discreteness of the double layer problem into account; and we find a straightforward solution for ion concentrations up to saturation and over the entire range of double layer potential of interest in experiments on aqueous electrolytes. This ion-dipole model (IDM), defined in detail in section 2, requires both ions and solvent dipoles to occupy positions on a lattice. Its equations are also derived in section 2. Section 3 deals with the analytic solution of the model equations in the weak elecrode-potential limit. Finally, in section 4 numerical results for high electrode potential and ion concentration regions are discussed.

2. The ion-dipole model

The model we use is a more refined version of a lattice model for the double layer proposed by Liu [8,14] and is also a generalization of a layered lattice gas model (LLM) investigated by Macdonald and co-workers [12]. A simple cubic lattice is erected with one cubic face parallel to the electrode. The lattice sites are populated by either spherical ions or solvent molecules. Both ion species are assumed to be monovalent, and the solvent molecules are treated as permanent dipoles. The probability that a lattice point is occupied by an ion or a dipole is determined by the respective Boltzmann factors, with ions interacting with the local electric potential and dipoles interacting with the local electric field. The field variables are determined self-consistently from the charge and polarization densities through electrostatic equations.

In the early version of the IDM [8,14], the dielectric properties of the interstitial region were not specified. Macdonald [18] showed that this led to inconsistencies in setting up the electrostatic field equations. To make the model both more general and internally consistent, he proposed the iterated layer model depicted in fig. 1. Here, each layer of molecules (ions and/or solvent) is assumed to occupy a slab of width d. The ions are taken as point charges residing on lattice points of a planar square lattice at the center plane



Fig. 1. An iterated layer model of the electrical double layer, showing distance, charge, potential, and field quantities for several values of the layer marker, *i*. For i > 0, regions of constant permanent dipole polarization are shown cross-hatched.

of the slab, and the solvent molecules, also residing on lattice points, have a diameter equal to the width of the slab. The net polarization of the slab, assumed to be uniform for simplicity, is represented by equal and opposite surface charges at the faces of the slab. Thus each basic slab involves three charge layers. The neighboring slabs are separated by a distance b. There is a blocking electrode at x = 0 and an ohmic or indifferent electrode at $x = \infty$. Between these electrodes is a periodic array of an infinite number of slabs. The effective separation between the blocking electrode and the first slab is determined by charge overlapping effects [24], so that this distance, denoted by b_0 , is to be determined experimentally. To model the polarizabilities of the molecular species, the entire right half space is filled with a dielectric with $\epsilon_a = 6$ [18,25,26]. Inside a slab the effective dielectric constant is thus ϵ_a plus the contribution from permanent dipoles, which is a function of the local electric field. In this particular respect the model goes beyond the LLM investigated by Macdonald and coworkers [12], who approximated the dielectric properties of the solvent molecules by a bulk dielectric constant. Note that in the present IDM, as well as in the LLM, one takes all quantities as averaged over the plane to which they apply. No such specifically planar averaging occurs in earlier continuum lattice gas models [7,11] or in the continuum ideal gas Gouy-Chapman model [19,20] (GCM).

The rest of the model parameters are defined as follows. The lattice parameter a is $(N_v)^{-1/3}$, where $N_v \cong 3.3456 \times 10^{22}$ cm⁻³ is the number of water molecules per cubic centimeter. The concentration of ions is given in terms of the bulk molarity M_0 so that the number of ions of each charge in a

unit volume is $c_0 \approx 6.022 \times 10^{20} M_0$ cm⁻³. We label the slabs by *i* (*i* = 1, 2, 3,...), with *i* = 1 being the slab closest to the blocking electrode.

As was pointed out in the earlier work [8,12,18], the layered model becomes mathematically tractable when one assumes all field and density variables to be functions of only one spatial variable, i.e. the distance from the electrode. Accordingly, for the *i*th slab the potentials at the left surface, center plane, and right surfaces are denoted by ψ_{id} , ψ_i , and ψ_{di} respectively, and the charge densities of these surfaces are σ_{id} , σ_i , and σ_{di} respectively. The electrode at infinity has zero potential and zero charge, while the metal blocking electrode has potential ψ_m and charge density σ_m . The electric fields within and between the slabs are related to the potential by

$$\psi_{d,i-1} - \psi_{id} = bE_{i-1,i},\tag{1}$$

$$\psi_{id} - \psi_i = (d/2) E_{id}, \tag{2}$$

$$\psi_i - \psi_{di} = (d/2) E_{di}, \tag{3}$$

$$\psi_{di} - \psi_{i+1,d} = bE_{i,i+1}.$$
(4)

Across each charge layer the change in electric field is related to the surface charge density by

$$E_{i-1,i} - E_{id} = -\left(4\pi/\epsilon_a\right)\sigma_{id},\tag{5}$$

$$E_{id} - E_{di} = -\left(4\pi/\epsilon_{a}\right)\sigma_{i},\tag{6}$$

$$E_{di} - E_{i,i+1} = -\left(4\pi/\epsilon_a\right)\sigma_{di}.$$
(7)

The polarization charges are functions of the polarization density P_i of the slab:

$$\sigma_{\rm di} = -\sigma_{\rm id} = P_{\rm i},\tag{8}$$

and overall charge neutrality requires that

$$\sigma_{\rm m} = -\sum_{i=1}^{\infty} \sigma_i. \tag{9}$$

The electric field E_i at the center plane of the slab is defined by

$$E_i = \frac{1}{2} (E_{id} + E_{di}). \tag{10}$$

In addition we relate P_i and σ_i to the local potential ψ_i and electric field E_i by statistical mechanics [8,18]

$$\sigma_i = -2eaN_v\delta\sinh(\phi_i)/Z_i,\tag{11}$$

$$P_i = N_v (1 - 2\delta) p \left[y_i \cosh(y_i) - \sinh(y_i) \right] / y_i^2 Z_i,$$
(12)

$$Z_i = 2\delta \cosh(\phi_i) + (1 - 2\delta) \sinh(y_i) / y_i.$$
(13)

In the above equations $\delta \equiv c_0/N_v$, $\phi_i \equiv e\psi_i/kT$, $y_i \equiv \bar{p}E_i/kT$, p is the effective dipole moment of the solvent molecule, \bar{p} is the enhanced dipole moment due

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to short range dipole-dipole correlation caused by hydrogen bonds [8], k is the Boltzmann constant, and T is the absolute temperature. Finally, the potential at the blocking electrode is given by

$$\psi_{\rm m} = \psi_{\rm 1d} + b_0 E_{01},\tag{14}$$

and the total double layer differential capacitance is simply

$$C_{\rm D} \equiv \mathrm{d}\sigma_{\rm m}/\mathrm{d}\psi_{\rm m},\tag{15}$$

while that for the diffuse space charge region alone is

$$C_{\rm d} \equiv {\rm d}\sigma_{\rm m}/{\rm d}\psi_{\rm 1d}.$$
 (16)

The equations are made simpler and the task of numerical analysis easier if all variables are measured in natural units so that they are dimensionless. A natural length scale in the problem is the Debye length

$$L_{\mathrm{Da}} \equiv \left(\epsilon_{\mathrm{a}} kT / 8\pi e^2 c_0\right)^{1/2},$$

and a natural potential scale is the thermal voltage $V_T \equiv kT/e$. The relevant lengths in the model are reduced to $\theta \equiv d/L_{Da}$, $\xi \equiv b/L_{Da}$, and $\Delta_a \equiv a/L_{Da} = \theta + \xi \equiv \Delta$. The reduced electric potential and field are $\phi \equiv \psi/V_T$, and $\mathcal{E} \equiv E/E_n \equiv E/(V_T/L_{Da})$; the reduced charge density is $Q \equiv \sigma/\sigma_n$; and the polarization density is $\mathfrak{P} \equiv P/E_n$. The unit of electric field is $E_n \equiv (kT/eL_{Da})$, and the unit of charge density is $\sigma_n \equiv 2ec_0L_{Da} \equiv C_{da}V_T$, where $C_{da} \equiv \epsilon_a/4\pi L_{Da}$ is the unit of double layer capacitance/unit area; this is the Gouy-Chapman low field limiting double layer capacitance/unit area of an electrolyte with ion density c_0 and dielectric constant ϵ_a . We may also define C_{dB} , where ϵ_a is everywhere replaced by ϵ_B , the bulk dielectric constant. In the above units the model equations reduce to

$$\phi_{\mathbf{d},i-1} - \phi_{i\mathbf{d}} = \xi \mathcal{E}_{i-1,i},\tag{1'}$$

$$\phi_{id} - \phi_i = (\theta/2) \mathcal{E}_{id}, \qquad (2')$$

$$\phi_i - \phi_{d_i} = (\theta/2) \mathcal{E}_{d_i}, \tag{3'}$$

$$\phi_{\mathrm{d}i} - \phi_{i+1,\mathrm{d}} = \xi \mathcal{E}_{i,i+1},\tag{4'}$$

$$\mathcal{E}_{i-1,i} - \mathcal{E}_{id} = Q_{di},\tag{5'}$$

$$\mathcal{E}_{id} - \mathcal{E}_{di} = -Q_i, \tag{6'}$$

$$\mathcal{E}_{di} - \mathcal{E}_{i,i+1} = -Q_{di},\tag{7}$$

$$Q_{di} = (4\pi/\epsilon_a) \mathcal{G}_i, \tag{8'}$$

$$Q_{\rm m} = -\sum_{i=1}^{N} Q_i, \tag{9'}$$

$$\mathcal{E}_i = 0.5(\mathcal{E}_{d_i} + \mathcal{E}_{id}). \tag{10'}$$

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The statistical relations take the forms

$$Q_i = -\Delta \sinh(\phi_i) / Z_i, \tag{11'}$$

$$Q_{di} = 3\mathcal{E}_i(1-2\delta)(\epsilon_{x0}/\epsilon_a-1)\left(\left[y_i\cosh(y_i)-\sinh(y_i)\right]/y_i^3Z_i\right), \quad (12')$$

where $y_i \equiv s \mathcal{E}_i$; $p' \equiv p/eL_{Da}$; $s = \bar{p}/eL_{Da}$; and Z_i is given by eq. (13). Here $s \equiv s_1 M_0^{1/2}$ is a normalized dielectric saturation parameter. In order to simplify later comparison with GC predictions, we have defined the new dielectric constant ϵ_{x0} in (12') through the relation

$$\epsilon_{x0}/\epsilon_a - 1 \equiv sp'/6\delta \equiv 4\pi N_v p\bar{p}/3\epsilon_a kT.$$
⁽¹⁷⁾

The electrode potential is

$$\phi_{\rm m} = \phi_{1\rm d} + \xi_0 \hat{s}_{01}, \tag{14'}$$

where $\xi_0 \equiv b_0 / L_{Da}$, and the total double layer capacitance is

$$C_{\rm D} = C_{\rm da} \, \mathrm{d}Q_{\rm m}/\mathrm{d}\phi_{\rm m} \equiv C_{\rm da}C_{\rm DN},\tag{15'}$$

where $C_{\rm DN}$ is the normalized capacitance. We may also define the effective dielectric constant of the polarization layer for any values of ϵ_i and M_0 as

$$\epsilon_{\rm x} \equiv \epsilon_{\rm a} + 4\pi P_i / E_i = \epsilon_{\rm a} (1 + Q_{\rm d} / \tilde{\mathcal{E}}_i). \tag{18}$$

In the next two sections we will discuss the solutions of these equations in the linear, weak-potential region and the nonlinear, strong-potential region.

3. Analytic solution in weak field limit

In the limit of $|\phi_i| \ll 1$ and $|\mathcal{E}_i| \ll 1$ for all *i*, the model equations can be linearized and solved analytically. For this purpose it is convenient to manipulate eqs. (1') to (10') and derive the following recurrence relations

$$\phi_i + \left(\frac{1}{2}\theta + \xi\right) \left(\mathfrak{S}_i - \frac{1}{2}Q_i\right) + \xi Q_{di} = \phi_{i-1} - \frac{1}{2}\theta \left(\mathfrak{S}_{i-1} + \frac{1}{2}Q_{i-1}\right), \tag{19}$$

$$\mathcal{E}_{i} + Q_{di} - \frac{1}{2}Q_{i} = \mathcal{E}_{i-1} + Q_{d,i-1} + \frac{1}{2}Q_{i-1}.$$
(20)

The equations for Q_i and Q_{di} simplify to

$$Q_i = -\Delta \phi_i, \tag{21}$$

$$Q_{di} = (1 - 2\delta)(p's/6\delta)\mathcal{E}_i \equiv (1 - 2\delta)(4\delta p\bar{p}N_v/3\epsilon_a)\mathcal{E}_i \equiv (\epsilon_x/\epsilon_a - 1)\mathcal{E}_i, \quad (22)$$

where ϵ_x , defined above, becomes in the present weak field limit,

$$\epsilon_{x} \equiv \epsilon_{a} + 4\pi N_{v} (1 - 2\delta) p\bar{p}/3kT = \epsilon_{a} + (1 - 2\delta)(\epsilon_{x0} - \epsilon_{a}).$$
⁽²³⁾

Its value for $\delta = 0$ (pure solvent) is of course ϵ_{x0} . For comparison, the Gouy-Chapman approach uses a homogeneous dielectric constant, which, in the presence of ions, may be written analogously as

$$\epsilon_{\rm B} = \epsilon_{\rm a} + (1 - 2\delta)(\epsilon_{\rm B0} - \epsilon_{\rm a}). \tag{24}$$

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Substituting eqs. (21) and (22) into eqs. (19) and (20), we obtain

$$(1 + \frac{1}{4}\theta\Delta)(\phi_{i-1} - \phi_i) + \frac{1}{2}\xi\Delta\phi_i = \frac{1}{2}\theta(\mathcal{E}_{i-1} + \mathcal{E}_i) + (\xi/R_x)\mathcal{E}_i,$$
(19')

$$\mathcal{E}_{i-1} - \mathcal{E}_{i} = 0.5R_{x}\Delta(\phi_{i} + \phi_{i-1}), \tag{20'}$$

where $R_x \equiv \epsilon_a/\epsilon_x$. This set of linear difference equations can be solved by the substitutions $\phi_i = \phi_{i-1}\gamma$ and $\mathcal{E}_i = \mathcal{E}_{i-1}\gamma$, where γ is a decay constant which satisfies $\gamma \leq 1$. The conditions that eqs. (17') and (18') have nonzero solutions for ϕ_i and \mathcal{E}_i determines γ , with the result

$$\gamma = \Lambda - (\Lambda^2 - 1)^{1/2},$$
(25)

where

$$\Lambda = \left[1 + \frac{1}{4}\theta\Delta(1 - R_{x}) + \frac{1}{2}\xi\Delta\right] / \left[1 + \frac{1}{4}\theta\Delta(1 - R_{x})\right].$$
(26)

Note that when $\Delta \to 0$, $\gamma \to 1$. The relation between \mathcal{E}_i and ϕ_i is

$$\mathcal{E}_i/\phi_i = \frac{1}{2}R_x \Delta [(1+\gamma)/(1-\gamma)]. \tag{27}$$

The charge on the blocking electrode is just

$$Q_{\rm m} = \Delta \sum_{i=1}^{\infty} \phi_i = \Delta \phi_i / (1 - \gamma).$$
⁽²⁸⁾

The potential of the blocking electrode is found to be

$$\phi_{\rm m} = \phi_1 (1 + \xi_0 \Delta \gamma / (1 - \gamma) + \frac{1}{4} \theta \Delta [1 + R_{\rm x} [(1 + \gamma) / (1 - \gamma)]]).$$
(29)

Thus the total double layer capacitance, here equal to $C_{da}Q_m/\phi_m$, is given by $C_D = C_{da}\Delta/[(1 + \frac{1}{4}\theta\Delta)(1 - \gamma) + \frac{1}{4}\theta\Delta R_x(1 + \gamma) + \xi_0\Delta],$ (30)

and C_d is obtained by just setting $\xi_0 = 0$. At first glance, this IDM expression for C_D may seem to contain a considerable number of adjustable parameters such as Δ , θ , and R_x . But as we shall show shortly, a subtle relation is required between two of these parameters, greatly reducing the range of their independent variation.

Our results become particularly simple if we make the gaps between the slabs infinitesimal, i.e. we let b and $b_0 \rightarrow 0$. We then find

$$\gamma = (1 - \lambda)/(1 + \lambda), \tag{31}$$

where

$$\lambda = \Delta \left[R_{\star} / (4 + \Delta^2) \right]^{1/2}, \tag{32}$$

$$C_{\rm D} = C_{\rm d} = C_{\rm da} / \left\{ R_{\rm x} \left[1 + (\Delta/2)^2 \right] \right\}^{1/2} = C_{\rm dB} / \left\{ \left(R_{\rm x} / R_{\rm B} \right) \left[1 + (\Delta/2)^2 \right] \right\}^{1/2}.$$
(33)

The quantity $C_{dB} \equiv \epsilon_B/4\pi L_{DB} \equiv C_{da}/(R_B)^{1/2} = (\epsilon_B e^2 c_0/8\pi kT)^{1/2}$ is the low field Gouy-Chapman result for the double layer capacitance of a material of uniform dielectric constant ϵ_B . Here $R_B \equiv \epsilon_a/\epsilon_B$. It is clear from eq. (33) that

when $\Delta \to 0$ and $\epsilon_{x0} = \epsilon_{B0}$, we find $C_d = C_{dB}$, showing agreement between the IDM and the GCM in this limit. Such agreement is important since the difficulties with the GCM mentioned earlier disappear as $M_0 \to 0$. But as eq. (33) shows the IDM predicts a lower capacitance for $\Delta > 0$ than the GCM, which comes about because of the dielectric screening of the slabs. As $\Delta \to 0$, on the other hand, the ion density becomes so low that the Debye length in the dielectric becomes very large compared with the interatomic distance and the capacitance approaches the classical limit for the choice $\epsilon_{x0} = \epsilon_{B0}$.

Another interesting prediction of the model is that the potential in the dielectric has large oscillations. We can see this more easily in the case $b \rightarrow 0$, so that $\psi_{id} = \psi_{d,i-1}$ is the potential at the boundary between the i-1 and the *i*th slabs. A simple calculation gives

$$\psi_{id}/\psi_{i} = \left[1 + (\Delta/2)^{2}\right]^{1/2} \left\{ \left[1 + (\Delta/2)^{2}\right]^{1/2} + \sqrt{R_{\rm B}}\Delta/2 \right\}.$$
(34)

The ratio is greater than one. Similarly,

$$\psi_{id}/\psi_{i-1} = \left[1 + (\Delta/2)^2\right]^{1/2} \left\{ \left[1 + (\Delta/2)^2\right]^{1/2} - \sqrt{R_{\rm B}} \Delta/2 \right\},\tag{35}$$

which is also greater than one in most electrolytes. Thus, the spatial dependence of the potential has the form of an exponentially damped periodic oscillation, as shown in fig. 2. Here, where the choice $b_0 = 0$ has been made, the distance from one layer center to the next is a = d = 3.1 Å.

The origin of the potential oscillation shown in fig. 2 can be traced to the discreteness of the charge distribution in the electrolyte. In the IDM the ions



Fig. 2. Normalized potential versus layer index i for $M_0 = 1$ and $b_0 = 0$ in the low field region.

form charged planes at the center of the slabs, so the electric field undergoes a discontinuous change across each charged plane. As a result the electric field oscillates alternatively above and below the average value, and this causes the electric potential to vary rapidly. When the layered structure of the electrolyte is ignored, as in the GCM, the potential and field oscillations disappear. The connection between the layered structure of the charges and the oscillation of the electric potential was discovered by Kirkwood and Poirier [27].

Carnie and Chan [15] have discussed another source of oscillatory behavior which arises from the microscopic structure of the solvent. In their theory the solvent is assumed to be a collection of dipole spheres. When these spheres are stacked up in layers, the density of the dielectric medium varies periodically in space and gives rise to over-screened and under-screened regions. A spatial variation of the potential can result from the inhomogeneneity in the screening strength of the medium. In the IDM the inhomogeneous dipole screening effect can be seen as electric field variations at the boundaries between a dielectric slab and the spaces on either side of the slab. The discontinuities disappear when we take b = 0.

As a consequence of the potential oscillation near the electrode, the electric field strength near the electrode is higher than that predicted by the classical theory. We may define an electric field enhancement factor by

$$\mathcal{E}_{id}/\mathcal{E}_{i} = 1 + R_{\rm B}^{-1}(1-\gamma)/(1+\gamma).$$
 (36)

For a 1M aqueous electrolyte we estimate that $\gamma \approx 0.607$ and $R_{\rm B} \approx 0.0716$, so that the enhancement factor is 4.17. The factor is smaller for more dilute electrolytes. It is difficult to assess the accuracy of this prediction except in qualitative terms. In treating the ions as point charges, the IDM overestimates the potential variation arising from the inhomogeneous charge distribution. On the other hand, in assuming uniform dielectric slabs, the model underestimates the effect due to the inhomogeneous dipole distribution. Since the two effects cause errors in opposite directions, one may hope that the prediction is not far from reality. The only experimental evidence indicates that this is the case [28]. In this work a Ag(100) surface is immersed in an aqueous electrolyte and the reflectivity of the surface is measured as a function of the bias potential relative to the bulk of the electrolyte. Two absorption features, attributable to excitations into two unoccupied surface states, are seen to shift in energy very rapidly when the bias potential is varied. The authors estimated that the electric field seen by the surface states is about three times as high as that calculated from the classical theory, in reasonable agreement with the present predictions.

Now let us examine $C_{\rm DN} \equiv C_{\rm D}/C_{\rm da}$ in more detail. First define $r \equiv d/a$, the fractional filling factor, which may be held constant as M_0 and Δ go to zero. Then $\theta \equiv r\Delta$ and eq. (30) may be expressed in normalized form as three

capacitances in series, .

$$C_{\rm DN}^{-1} \equiv C_{\rm dN}^{-1} + C_{\rm ILN}^{-1}, \tag{37}$$

where

$$C_{\rm dN}^{-1} \equiv C_{\rm DIN}^{-1} + C_{\rm ION}^{-1}, \tag{38}$$

and the normalized inner layer capacitance C_{IL}/C_{da} is just

$$C_{\rm ILN} \equiv \xi_0^{-1}.$$

The dipole contribution to the diffuse layer capacitance, C_{DIN} , is

$$C_{\rm DIN} \equiv \Delta / (1 - \gamma), \tag{39}$$

and the ionic contribution is

$$C_{\rm ION} \equiv \{ (r\Delta/4) [1 - \gamma + R_x (1 + \gamma)] \}^{-1}.$$
(40)

We have made these identifications on the following basis. Consider the $\Delta \rightarrow 0$ limit in which there should be no ionic contribution to $C_{\rm DN}$ remaining. One can readily show from eqs. (25) and (26) that in this limit to first order in Δ ,

$$1 - \gamma \rightarrow [rR_x + (1 - r)]^{1/2} \Delta.$$

Then it is clear that as $\Delta \rightarrow 0$, $C_{\text{ION}}^{-1} \rightarrow 0$, and

$$C_{\text{DIN}} \to (rR_x + 1 - r)^{1/2},$$
 (41)

a constant value. Further, if it were possible for M_0 to go to infinity, one would find that both C_{ION} and C_{DIN} would become infinite and thus make no contribution to C_{DN} . But $\delta \equiv c_0/N_v \cong 0.018M_0$ and cannot exceed 0.5. Thus the largest possible value of M_0 in the present model is $M_{0max} = (2 \times 0.018)^{-1}$ $= 27.\overline{7}$. The corresponding value of Δ with a = 3.1 Å is about 19.43.

Now from eq. (41) we may express C_{D1} with C_{dB} normalization, $C_{D1BN} \equiv C_{D1}/C_{dB} = C_{D1N}\sqrt{R_B}$, as

$$C_{\rm DIBN} = \left[R_{\rm B} / (rR_{\rm x} + 1 - r) \right]^{1/2}$$
(42)

in the $\Delta \to 0$ limit. Clearly when r = 1 and $R_x = R_B$, it yields $C_{DI} = C_{dB}$, in agreement with eq. (30) in this limit. But it is of interest to explore under what conditions $C_{DI} = C_{dB}$ for $\Delta \to 0$ and $r \le 1$. Eq. (42) immediately yields the relation

$$R_{\rm x} = r^{-1}(R_{\rm B} + r - 1), \tag{43}$$

which only allows a positive R_x solution for $1 - R_B < r \le 1$. For $R_B = 6/80.4 \approx 0.075$, appropriate for water when $\delta \to 0$, one finds $0.925 \le r \le 1$, showing that there is only a limited range of r values for which the present model can agree exactly with GCM predictions in the $\Delta \to 0$ limit. Put another way, b/a must equal or exceed R_B , and thus the b gap cannot be greater than about

eight percent of the water molecule diameter. Note that eq. (43) is equivalent to $d/\epsilon_x + b/\epsilon_a = a/\epsilon_B$, which is just the condition that the layered model exhibits the bulk dielectric constant $\epsilon_B = \epsilon_{B0}$ for any possible r and ϵ_x value when $M_0 \rightarrow 0$. When r < 1, ϵ_x must be greater than ϵ_B in order to compensate for the effects of the low dielectric constant b > 0 regions where $\epsilon = \epsilon_a$.

In the $r \rightarrow 0$ limit, the IDM should degenerate to the LLM and no R_x effects should remain since no region of permanent dipole polarization is then present. One finds

$$\gamma = 1 + (\Delta/2)^2 - \Delta \left[1 + (\Delta/2)^2 \right]^{1/2},$$
(44)

$$C_{\rm dN} = \left\{ \left[1 + (\Delta/2)^2 \right]^{1/2} - \Delta/2 \right\}^{-1}.$$
 (45)

Thus we have found a general closed form expression for C_{dN} in the LLM case as well. If we take $\epsilon_a \rightarrow \epsilon_B$ for this model and let $\Delta \rightarrow 0$, we obtain $C_{dN} \rightarrow C_{dBN}$ = 1, again in agreement with GCM predictions.

For most of the rest of this work, we shall compare results for the LLM, the GCM, and the IDM with r = 1. Let us first examine the dependence of C_d on M_0 in the present $\phi_{1d} \rightarrow 0$ case. Fig. 3 shows such results up to M_{0max} . The LLM curve has been calculated using eq. (45) and $\epsilon_a \rightarrow \epsilon_B$ with ϵ_B given by eq. (24) and $\epsilon_{B0} = 80.4$. The GCM curve is just that for $C_{dB} \equiv \epsilon_B/4\pi L_{DB}$, and the IDM C_d curve follows from eq. (30) with r = 1. Note especially the maximum



Fig. 3. Comparison of differential capacitance, C_d , dependence on molarity, M_0 , for several models in the limit of zero electrode charge.

in the IDM C_d near $M_0 = 3$. Since hydration effects are not included in the present model, the IDM curve is not likely to be very significant for M_0 greater than 2 or 3.

Now although we have thus far distinguished between ϕ_m and ϕ_{1d} (see fig. 1) because b_0 may not be zero, it should be noted that even when $b_0 = 0$ the present theory is not just a theory of the diffuse double layer alone but a theory of the full double layer. The charge Q_{1d} is not a true charge but a pseudo charge used to calculate polarization effects in the *d* region most readily. Thus, even when $b_0 = 0$ there is still a charge-free region of thickness d/2 between the electrode at x = 0 and the first real charge layer at x = d/2. It is not therefore surprising that when we take $b_0 = 0$ so that $\phi_m = \phi_{1d}$ and $C_D = C_d$ is the differential capacitance of the full double layer, inner layer effects should become apparent. As long as r > 0, charge-free polarized regions will be present, explaining the general dependence of the C_d curve for the IDM in fig. 3.

Table 1 shows some results for the LLM, GCM, and IDM situations. To emphasize the $\phi_{1d} \rightarrow 0$ situation, we have written C_d and C_D as C_{d0} and C_{D0} here. The first two models deal with ions in an ϵ_B background, while the IDM involves ions and permanent dipoles in an $\epsilon_a = 6$ background. In addition to the r = 1 IDM results, some for $r \approx 0.93$ have also been included. The value of r used requires $\epsilon_x \approx 970$, much greater than ϵ_{B0} . But this is about the value which follows directly from free energy minimization if one takes an effective dipole moment of $\vec{p}_e = 17.2$ D (see later discussion); such moments have been augmented by the presence of surrounding water dipoles and are thus much larger than that of an isolated dipole [8,18]. This value of \vec{p}_e is found through interpreting experimental dielectric saturation measurements on pure water. The combination of layers of polarization involving $\epsilon_x - \epsilon_a \approx 964$ of thickness

Table I

Molar- ity M ₀	No series capacitor				Series capacitor: $C_{1L} = 31$ $\mu F/cm^2$			Experi-
	LLM r = 0 C_{d0}	GCM С _{dB}	$IDM r = 1 C_{d0}$	$IDM r = 0.93 C_{d0}$	GCM C _{D0}	$IDM r = 1 C_{D0}$	$IDM r = 0.93 C_{D0}$	NaF [29] C _{D0}
10-3	7.3	7.2	7.2	7.3	5.8	5.8	5.9	6
10^{-2}	24.0	22.8	22.5	23.5	13.1	13.0	13.4	13.1
10-1	84.7	72.1	62.3	71.5	21.7	20.7	21.6	20.7
1	.369.3	224.5	107.1	138.9	27.2	24.0	25.4	26

Differential capacitance (μ F/cm²) of aqueous electrolyte for $\phi_{1d} \rightarrow 0$, several concentrations, $T = 25^{\circ}$ C, $\epsilon_{B0} = 78.4$, $\epsilon_a = 6$, a = 3.1 Å, and different situations

 $d = \sim 0.93a$ and surrounding layers of $\epsilon_a = 6$ of thickness $a - d \approx 0.07a$ yields $\epsilon_{B0} = 77.72$ in the $M_0 \rightarrow 0$ limit. Thus this layer model of the water dielectric constant works properly although it may seem a bit strange.

Also shown in table 1 are Grahame's NaF results for the total differential capacitance at the electrocapillary maximum ($\phi_{1d} = 0$), C_D . Although the two sets of IDM results agree better with experiment than does that for the GCM, they clearly are far from entirely explaining the experimental results. It appears that inner layer effects in the present IDM involve too large an effective inner-layer capacitance to allow agreement with experiment. It seems probable that later work using finite dipoles directly and including hydration effects will yield appreciably better agreement. For the present, we have shown the effect on the GC and ID models of including a conventional [24] direct inner layer capacitance of $C_{IL} = 31 \,\mu \text{F/cm}^2$. The r = 1 IDM then exhibits especially good agreement with Grahame's results. This C_{IL} value corresponds to a thickness of about 0.29 Å if its effective dielectric constant is taken as unity. This is too small a value to be entirely explained by field penetration into the metal electrode, which generally leads to a value of about 0.5 Å. On the other hand, it seems quite explicable on the basis of non-local electron overlap effects [24].

It should be mentioned, however, that Henderson [13] has obtained low-field values of C_D less than the experimental ones using the Mean Spherical Approximation results of Carnie and Chan [15] and Blum and Henderson [9]. This treatment does not include an explicit separate charge-free inner layer, but there is some question whether it applies well up to concentrations as large as $M_0 = 1$. Henderson ascribes the lowering of his C_D values to orientation of dipoles near the electrode. In our treatment such orientation can be increased if needed by including a mean field polarization interaction [14].

4. Numerical results for large applied potentials

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Although the equations of the problem may be solved exactly in the $\phi_{1d} \rightarrow 0$ situation, as was illustrated in the last section, numerical solution techniques are required when $|\phi_{1d}| > 0$. Consider first a typical layer denoted by the index *i*. On combining several of eqs. (1') through (7') one obtains

$$\phi_i = \phi_{id} - (\theta/2) (\mathcal{E}_{i-1,i} - Q_{di}), \tag{46}$$

$$\mathcal{E}_{i} = \mathcal{E}_{i-1,i} + Q_{i}/2 - Q_{di}, \tag{47}$$

where for forward incrementation, ϕ_{id} and $\mathcal{E}_{i-1,i}$ will be known (for i = 1 and $b_0 = 0$, their values are $\phi_m = \phi_{Id}$ and $\mathcal{E}_{01} = Q_m$). Now Q_i and Q_{di} , given by eqs. (11'), (12') and (13), are functions of both ϕ_i and \mathcal{E}_i . Thus eqs. (46) and (47) form a coupled self-consistency set which can only be solved for ϕ_i and \mathcal{E}_i by iteration when $|\phi_i|$ is not infinitesimal. Such solution must be carried out for each value of *i*.

Now we wish to find a completely blocking solution, one where ϕ_i and \mathcal{E}_i approach zero as $i \to \infty$ under the constraint (9'). For a given choice of ϕ_{1d} , there is only one, initially unknown, value of Q_m which leads to such a blocking solution. In the present work we have elected to use forward incrementation [12], to fix ϕ_{1d} , and find the corresponding blocking-electrode Q_m value by iteration. Alternatively, Q_m could have been fixed and the corresponding ϕ_{1d} found. Some checks of the present results using reverse incrementation [8] show excellent agreement and thus verify the applicability of both methods [18].

As mentioned earlier, even the present $b_0 = 0$ choice does not lead to just diffuse double layer conditions in the IDM. But for agreement with experimental data it will generally be necessary nevertheless to take $b_0 \neq 0$ and thus add an extra inner layer capacitance C_{1L} explicitly. Rather than include it in the analysis in this section, it has been omitted for simplicity but can be incorporated to change C_d to C_D very simply when desired. Our present model assumes constant polarization in each individual layer, thereby replacing the finite-length dipoles actually residing in each layer by a layer of finite thickness made up of infinitesimal dipoles all similarly aligned. In future work on unadsorbed systems, all permanent dipoles effects will be represented by finite-length permanent dipoles, with the main inner layer populated only by such dipoles and with succeeding layers containing ions as well.

Once the set (46) and (47) has been solved for given *i*, one needs equations which will allow progression to i + 1. Simple manipulation of the earlier equations leads to the required results,

$$\phi_{i+1} = \phi_{id} - \Delta \mathcal{E}_{i-1,i} + \theta Q_{di} - (\Delta - \theta/2) Q_i, \tag{48}$$

$$\mathcal{E}_{i,i+1} = \mathcal{E}_{i-1,i} + Q_i. \tag{49}$$

Our solution procedure may now be summarized as follows. First, a value of ϕ_{1d} is selected. Next an initial choice for the corresponding Q_m is made, based on any earlier information available. Then eqs. (46) and (47) are solved for i = 1; eqs. (48) and (49) are used to progress to i = 2; eqs. (46) and (47) are then solved for i = 2; and so on. Such incrementation is continued until ϕ_{id} or $\phi_{id} - \phi_{i+1,d}$ changes sign or until $\phi_{id}/\phi_{1d} \leq 10^{-6}$. When the latter condition is satisfied, we accept the result as a good solution, i.e. a sufficiently good approximation to $\phi_{id}/\phi_{1d} \rightarrow 0$ as $i \rightarrow \infty$. Of course, such a solution will not be found immediately with the initial approximate choice for Q_m , and the above procedure is automatically repeated until a value of Q_m has been found which does satisfy the final criterion above. This consistent value must generally be determined to 10 to 12 decimal places in order to achieve a good solution. Further, the number of layers required for a good solution varies with the magnitude of Δ and ranges from around 30 for the largest Δ values of the present work to about 130 for the smallest. Incidentally, the solution procedure above for the IDM is also used for the LLM, but there one has only a single consistency relation replacing eqs. (46) and (47) since Q_{di} is identically zero for this model.

We shall next consider reasonable numerical values of the various parameters which enter the theory. We shall pick $T = 20^{\circ}$ C for the work of this section since this value was Liu's original choice [8] and is the temperature at which the most recent dielectric saturation measurements on water have been made [30]. For simplicity, we shall also take r = 1 throughout the rest of this work. Now $\delta \cong 0.018M_0$. Further, following the results of the last section, we take $\epsilon_x \equiv \epsilon_B = 80.4 - 2.6784M_0$. Now we have already chosen a = 3.1 Å and $\epsilon_a = 6$. We find $L_{Da} \cong 0.83395M_0^{-1/2}$ Å and $\Delta \equiv \Delta_a \equiv \Delta_1 \sqrt{M_0}$, where $\Delta_1 \cong 3.7172$. At $M_0 = 1$, $R_B \cong 0.0772$. Further, $C_{da} = 63.702\sqrt{M_0}$ µF/cm², $E_n \cong 3.0293 \times 10^6 \sqrt{M_0}$ V/cm, and $\sigma_n \cong 1.6093 \sqrt{M_0}$ µC/cm².

It now remains to decide what values of p and \bar{p} to use. The dipole moment of an isolated water molecule is about $p_0 = 1.85$ D, but Liu has used 2.35 and 9.54 D for p and \bar{p} , respectively, since the Booth-Onsager-Kirkwood theory of dielectric saturation requires effective dipole moments augmented by various dipole-dipole interactions. Now from eq. (23) we have

$4\pi N_{\rm v} p\bar{p}/3kT = \epsilon_{\rm B0} - \epsilon_{\rm a} = 74.4.$

This low-field limiting relation leads to $p\bar{p} \approx 21.488 \text{ D}^2$, in reasonable agreement with 2.35 × 9.54 = 22.42. Part of the difference arises because Liu set $\epsilon_a = 1$. Now as already discussed [18], there is a problem when one attempts to estimate values of p and \bar{p} from experiment using the above value for $p\bar{p}$ and experimental dielectric saturation results. For the present theory, expansion of $\epsilon_x = \epsilon_B$ to first order in E^2 using eq. (18) leads to

$$(\epsilon_{\rm B0}-\epsilon_{\rm B})/E^2=4\pi N_{\rm v}p\bar{p}^3/45(kT)^3.$$

Recent saturation measurements on water at 20°C up to fields of 10⁵ V/cm suggest that $(\epsilon_{B0} - \epsilon_B)/E^2$ is about 10^{-11} (cm/V)² in the E^2 dependence region [30]. This yields $p\bar{p}^3 = 6.378 \times 10^3 \text{ D}^4$. Now on dividing out p, one finds $\bar{p} \approx 17.229$ D, a very large value. The corresponding p obtained from the $p\bar{p}$ product is only 1.247 D, a very small value [18].

These values are not very plausible, and there is even doubt about the applicability of the Booth theory at high fields. We can avoid some of the uncertainty by using the experimental $\epsilon_{B0} - \epsilon_a$ value in the formulas. Then the only remaining parameter needed is \bar{p} , which then only plays the role of a saturation constant. It will be convenient to use s_1 , the $M_0 = 1$ value of $s \equiv \bar{p}/eL_{Da}$ to set the strength of saturation. If \bar{p} is measured in debyes, it turns out for the present situation that $s_1 \cong 0.25\bar{p}$. Thus when \bar{p} is 17.23 D, $s_1 \cong 4.30$. But this value will lead to very rapid dielectric saturation, and although we shall investigate its effects, we shall carry out most of our calculations for a smaller intermediate value, $s_1 = 1.175$, corresponding to $\bar{p} \cong 4.705$ D, essen-

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tially equal to the square root of the geometric means of the two $p\bar{p}$ values given above. This is a plausible value when p and \bar{p} are replaced by a single value. Free energy minimization for a region containing ions and non-interacting infinitesimal dipoles leads, in fact, to equations of the form of (11) to (13) but ones which involve a single dipole moment, unless rather ad hoc modifications are made. Dipole-dipole interactions can be taken into account approximately in the present average-field treatment by simply taking $p = \bar{p}$ larger than p_0 , as we have done above. At a somewhat increased level of sophistication, one could add mean-field dipole-dipole interactions into the theory with bare dipole moments of $p = p_0$. The effects of such interactions, which will be investigated in a later paper, would make the effective dipole moment dependent on field, however, and would thus change the character of the dielectric saturation to at least some degree.



Fig. 4. Electrode charge, σ_m , versus normalized applied PD, ϕ_{1d} , for three double layer models and a range of molarities. No inner layer has been added to any one of the models.

Fig. 4 shows comparisons for a range of molarities of the total electrode charge versus total applied PD for the three different models already discussed. Note how the IDM leads to nearly linear dependence in this range, quite unlike the essentially exponential dependences of the other two models. In making this comparison we have not included an inner layer in any of the three models. The predictions of IDM are clearly more realistic because in treating water as a collection of dipoles some properties of the inner layer are contained in the model. What is absent in the model are microscopic interactions between the metal electrode and the molecules in the electrolyte. There is hope that when these interactions are understood and added to IDM, both the inner layer and the diffuse layer can be described by one consistent model. The values of C_{dB} in the box of this figure are in $\mu F/cm^2$. Now, differential capacitance is an even more sensitive indicator of differences between models. Fig. 5 compares C_d versus ϕ_{1d} results for the three models in the relatively low ϕ_{1d} range. The $M_0 = 1$ GCM and LLM C_d results are too large to appear on this graph. It is particularly interesting to note the single cross-over point of the IDM curves at $\phi_{1d} \cong 10$. Although, as already mentioned in the last section, the present results with $b_0 = 0$ still represent the full electrical double layer, not just the diffuse double layer, they clearly lead to much larger values of C_d , both as $\phi_{1d} \rightarrow 0$ and for larger values of ϕ_{1d} , than found experimentally [29]. Some kind of an additional inner layer is still required for better agreement with experiment.

Fig. 6 is similar to fig. 5 but shows results for the IDM alone; it includes a



Fig. 5. Differential capacitance, C_d , versus normalized applied PD, ϕ_{1d} , for the three double layer models and a range of molarities.

wider range of ϕ_{1d} , extending up to about the maximum experimental applied PD; and it demonstrates how C_d curves depend on different values of the saturation strength parameter s_1 . The value of $s_1 = 10^{-5}$ used here is sufficiently small that the polarization does not change from its $\phi_{1d} \rightarrow 0$ value over the entire ϕ_{1d} range. Note that we are using an expression for Q_{di} that depends on $\epsilon_{B0} - \epsilon_a$ as in eq. (12'), rather than one that involves separate p and \bar{p} values, which would both decrease as one changed p_0 . Here, $\epsilon_{B0} - \epsilon_a$ is kept equal to the experimental value for water as \bar{p} (and s_1) is changed. If it were not held constant, the limit $s_1 \rightarrow 0$ would change the IDM into the LLM. As it is, the $s_1 \approx 0$ curve here represents an IDM situation involving non-saturable ideal permanent dipoles. The slow decrease of the $s_1 = 10^{-5}$ curve does not arise from changes in orientation of the permanent dipoles but is associated with shielding of the field as one progresses layer by layer away from the electrode. The $s_1 = 4.3$ curves included here exhibit such a rapid decay as ϕ_{1d}



Fig. 6. Differential capacitance, C_d , versus ϕ_{1d} for the IDM alone for several saturation-strength parameter, s_1 , values.

increases that they soon reach a value of C_d smaller than Grahame's minimum value of about 16 μ F/cm² found experimentally for the entire double layer in NaF. Thus, the IDM with this large a value of s_1 is unacceptable. It is possible that later work using finite rather than infinitesimal permanent dipoles will yield more satisfactory results. Incidentally, the $s_1 = 4.3$ curves have not been extended to higher ϕ_{1d} values here because it becomes quite difficult (and requires much computer time) to find the proper Q_m consistent with a given value of ϕ_{1d} when \mathfrak{P}_i is near saturation. In the present case for $s_1 = 4.3$, $M_0 = 1$, and $\phi_{1d} = 10$, one finds, in fact, that the ratio of \mathfrak{P}_i to its fully saturated value is about 0.81, 0.58, and 0.36 for i = 1, 2, and 3, respectively, appreciably larger values than those for $s_1 = 1.175$ even at a ϕ_{1d} as large as 30.

Fig. 7 shows how the potential varies as *i* increases for a large value of ϕ_{1d} . Note the non-exponential decay for large values of the local potential near the



Fig. 7. Normalized potential versus layer index *i* for $M_0 = 1$, $b_0 = 0$, and a normalized electrode potential of 30. Note that each separate polarization layer extends from i - 0.5 to i + 0.5 (solid circles), and the layer centers are at the various values of *i* itself (open circles).



Fig. 8. Normalized potential versus layer index i with the mean exponential response of the potential removed, yielding pure oscillatory response.

electrode (here at i = 0.5). In this r = 1 situation, ϕ_{di} and $\phi_{i+1,d}$ are the same; they appear at i + 0.5 positions and ϕ_i is plotted at the center of each layer. Although the potential will actually change linearly between solid and open dot positions, such linear dependence does not lead to straight lines on a semi-log plot [12]: the straight line joining the dots in the present graph are included to guide the eye. These results should be compared with those of fig. 2: here the large value of ϕ_{1d} makes the initial dependence of ϕ_i or ϕ_{id} on *i* non-exponential while the $\phi_{1d} \ll 1$ results of fig. 2 show overall exponential response for all values of *i*. In fig. 8 the average mean exponential response, determined from the large *i* region, has been removed from the values of fig. 7, leaving only the oscillatory response, ϕ_{osc} , discussed in the last section, remaining. The non-exponential behavior for i < 3 thus shows up clearly. In the present linear plot, the straight-line response shown is meaningful.

In fig. 9, ϕ_{id} values are plotted directly, omitting ϕ_i ones in order to show exponential and non-exponential response more clearly. The curves indicate that the initial non-exponential response increases as both s_1 and ϕ_{1d} increase. The $\phi_{1d} = 4$, $s_1 = 10^{-5}$ curve has been omitted: it lies so close above the $s_1 = 1.175$ curve that it would not be well resolved on this graph. It is interesting that even as large a ϕ_{1d} value as 4 still leads to essentially perfect exponential decay here. Fig. 10 is similar to fig. 9 but involves ϕ_i rather than ϕ_{id} , and we show IDM results for only a single s_1 value and compare them with LLM response. In order that the IDM and LLM curves begin with the same i = 1 value, the LLM ones have been calculated with the IDM i = 1 ϕ_i value



Fig. 9. Dependence of ϕ_{id} alone on *i* for $M_0 = 1$, $\phi_{1d} = 30$ and 4, and widely different values of s_1 .

taken as the total applied PD. These values, for $\phi_{1d} = 30$ and 4, are shown on the graph. As one might expect, these results show that decay is much more rapid for the LLM than for the IDM because of the absence of permanent dipole shielding and that the IDM leads to appreciably greater non-exponential behavior for small *i* than does the LLM. Fig. 11 is similar to 10 but involves $M_0 = 0.01$. In this case a good IDM solution requires $i_{max} \sim 130$; here we have plotted the first 40 values of ϕ_i versus 1 without showing separate dots for each value. For this value of M_0 the difference in decay rates for the LLM and IDM is extreme. Note that the IDM nonlinearity is greatly increased as s_1 increases from 10^{-5} to 1.175.

Finally, fig. 12 shows some high- ϕ_{1d} layer-by-layer results for Q_i^* , \mathfrak{P}_{iN} , and ϵ_i . Here $Q_1^* \equiv Q_i/Q_1$, $\mathfrak{P}_{iN} \equiv \mathfrak{P}_i/\mathfrak{P}_{imax}$, and ϵ_i is given by eq. (18) with $\epsilon_i = \epsilon_x$. Further, from eqs. (11'), (12'), (8'), and (13) it is readily shown that the Q_{1max} and \mathfrak{P}_{imax} are $-\Delta/2\delta$ and $(3/4\pi)(\epsilon_{B0} - \epsilon_a)/s$, respectively. This expression



Fig. 10. Dependence of ϕ_i alone on *i* for $M_0 = 1$, showing LLM and IDM differences.

for $\mathcal{P}_{i\max}$ corresponds, as it should to $P_{i\max} = N_v p$. In the present case, $Q_{i\max} \approx -103$ and $\mathcal{P}_{i\max} \approx 15.1$. Although \mathcal{P}_{1N} is about 0.7 here, it is not as large as that mentioned earlier for $s_1 = 4.3$, $\phi_{1d} = 10$, and $M_0 = 1$, By chance the particular \mathcal{P}_{iN} and Q_i^* curves plotted here happen to have nearly the same values for the large *i* region.

Although the LLM curve (with a straight line drawn between the first two points) shows that Q_1 and even Q_2 are beginning to approach their saturated values at this high ϕ_{1d} value, this is not true for the IDM. One finds that Q_1 and Q_2 are about -28.7 and -20.9 for the LLM but are only -3.27 and -2.47 for the IDM. These differences of course arise from the strong permanent dipole polarization, represented here by \mathfrak{P}_{iN} . It also leads to the strong reduction in ϵ_i for i = 1 and 2 from its $i \to \infty$ value of ϵ_B .



Fig. 11. Dependence of ϕ_i alone on *i* for $M_0 = 0.01$, showing LLM and IDM differences and the effect of different s_1 values.

The foregoing results show the great differences that arise between the LLM, which uses a homogeneous $\epsilon_{\rm B}$ that implicitly includes permanent dipole effects, and the IDM, where the effects of the permanent dipoles are taken into account explicitly through using a consistent average permanent dipole moment for each individual layer. Although the results found for the IDM are far closer to those found experimentally than those predicted by the GC and LL models, they ar still not in good agreement with the data. As already discussed, agreement can be greatly improved by taking $b_0 \neq 0$ and thus including more of a Stern inner layer than that already implicit in the IDM. But the present IDM results are still based on the approximation of replacing a region containing a single finite-length permanent dipole by a region of the same maximum extent containing a uniform polarization associated with infinitesimal permanent dipoles. In future work on the double layer problem, the entire treatment will involve finite dipoles from the beginning, including an initial inner layer of finite dipoles but no charge, if necessary to achieve best agreement with experiment. Eventually, it should also be possible to take into account hydration effects around ions [18] in an averaged model of the present type and to include dipole-dipole interactions in a plane by mean-field type corrections [11,12,14]. Much still remains to be done.

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Fig. 12. Comparison of LLM and IDM predictions versus *i* for the layer charge (normalized to unity at i = 1), the IDM relative polarization, \mathcal{P}_{iN} , and the effective dielectric constant, ϵ_i .

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References

[2] D. Henderson and L. Blum, J. Chem. Phys. 69 (1978) 5441.

^[1] L. Blum, J. Phys. Chem. 81 (1977) 136.

- [3] S. Levine and C.W. Outhwaite, J. Chem. Soc. Faraday Trans. II, 74 (1978) 1670.
- [4] D. Henderson, L. Blum and W.R. Smith, Chem. Phys. Letters 63 (1979) 381.
- [5] C.W. Outhwaite, L.B. Bhuiyan and S. Levine, J. Chem. Soc. Faraday Trans. II, 76 (1980) 1388.
- [6] D. Henderson and L. Blum, Surface Sci. 101 (1980) 189.
- [7] J.R. Macdonald, D.R. Franceschetti and A.P. Lehnen, J. Chem. Phys. 73 (1980) 5272.
- [8] S.H. Liu, Surface Sci. 101 (1980) 49.
- [9] L. Blum and D. Henderson, J. Chem. Phys. 74 (1981) 1902.
- [10] T.L. Croxton and D.A. McQuarrie, Mol. Phys. 42 (1981) 141.
- [11] J.R. Macdonald, J. Chem. Phys. 75 (1981) 3155.
- [12] J.R. Macdonald, D.R. Franceschetti and A.P. Lehnen, Solid State Ionics 5 (1981) 105; J.R. Macdonald, D.R. Franceschetti and A.P. Lehnen, in: Fast Ionic Transport in Solids, Proc. Intern. Conf. on Fast Ionic Transport in Solids, Gatlinburg, TN, 1981, Eds. J.B. Bates and G.C. Farrington (North-Holland, Amsterdam, 1981).
- [13] D. Henderson, Kinam 3 (1981) 87.
- [14] S.H. Liu, Surface Sci. 105 (1981) 429.
- [15] S.L. Carnie and D.Y.C. Chan, J. Chem. Phys. 73 (1980) 2949.
- [16] C. Outhwaite, Can. J. Chem. 59 (1981) 1854.
- [17] T. Croxton, D.A. McQuarrie, G.N. Patey, G.M. Torrie and J.P. Valleau, Can. J. Chem. 59 (1981) 1998.
- [18] J.R. Macdonald, Surface Sci. 116 (1982) 135.
- [19] G. Gouy, J. Physique Radium 9 (1910) 457.
- [20] D.L. Chapman, Phil. Mag. 25 (1913) 475.
- [21] T.B. Grimley, Proc. Roy Soc. (London) A201 (1950) 40.
- [22] G.M. Torrie and J.P. Valleau, Chem. Phys. Letters 65 (1979) 343; J. Chem. Phys. 73 (1980) 5807.
- [23] I. Snook and W. van Megen, J. Chem. Phys. 75 (1981) 4104.
- [24] A.A. Kornyshev and M.A. Vorotyntsev, Surface Sci. 101 (1980) 23; Can. J. Chem. 59 (1981) 2031.
- See also A.A. Kornyshev and M.A. Vorotyntsev, Electrochim. Acta 26 (1981) 1.
- [25] J.R. Macdonald and C.A. Barlow, Jr., J. Chem. Phys. 36 (1962) 3062.
- [26] C.A. Barlow, Jr. and J.R. Macdonald, Advan. Electrochem. Electrochem. Eng. 6 (1967) 1.
- [27] J.G. Kirkwood and J.C. Poirier, J. Chem. Phys. 58 (1954) 591.
- [28] D.M. Kolb, W. Boeck, K.M. Ho and S.H. Liu, Phys. Rev. Letters 47 (1981) 1921.
- [29] D.C. Grahame, J. Am. Chem. Soc. 76 (1954) 4819.
- [30] H.A. Kolodziej and G.P. Jones, J. Chem. Soc. Faraday Trans. II, 71 (1975) 269.