

## LAYERED LATTICE GAS MODEL FOR THE METAL–ELECTROLYTE INTERFACE

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Several models of the diffuse double layer in liquid electrolytes are discussed. These models all involve partitioning the space charge region into a number of planar layers parallel to the metal electrode, with ionic liquid lattice gas, as opposed to idea gas, response in each layer. Each layer may contain both ions and solvent molecules. Several difficulties implicit in the earlier work of Liu on such a model are pointed out. These problems seem to have caused the appearance of an initial charge-free region in Liu's results. A layer model involving Liu's original assumptions of point ionic charges and point dipoles is discussed in detail and is shown to be electrostatically inconsistent. It is replaced by a layer model in which ionic charge resides on each basic layer, with each such layer surrounded symmetrically by charge layers representing the effect of finite-extent permanent dipoles. This model leads, as it should, to Gouy–Chapman behavior in the continuum limit. Finally, a method of including ion hydration effects explicitly in such a model is proposed.

### 1. Introduction

The electrical double layer (EDL) plays a very important role in the electrical behavior of solid and liquid electrochemical systems, colloids, and living cells. But the conventional Gouy–Chapman (GC) [1,2] theory of the diffuse part of the double layer breaks down for concentrations well below 1 molar [3–5], and there is no wholly satisfactory theory of the inner or Stern part of the double layer [3,6,7], a charge-free region in the absence of specific adsorption. Various approaches have been suggested in order to obtain an improved theory of the EDL in unadsorbed electrolytes. Recently it has been found [8] that a continuum liquid lattice gas model of the diffuse double layer (DDL) region yields excellent agreement with Monte Carlo results for a simple aqueous electrolyte model when mean field corrections are included in order to take some account of ion–ion interactions beyond those implicit in the Poisson equation and thus to attempt to compensate for the difference between the local (or inner) electrostatic potential and the potential of mean force. The imposition of a three-dimensional lattice, even in liquid situations where it is clearly an approximation, implicitly takes some account of the finite size of charge carriers and limits the maximum space charge possible in any region, an

effect not present in GC theory where point ions are assumed.

The first application of lattice gas theory to the present area seems to have been that of Grimley [9], and a lattice gas approach has been applied recently to the electrical behavior of both single crystals [10–16], where it should be completely appropriate, and to liquid electrolytes [8,10,11,13,17]. The work of refs. [8,10,11,13–15] includes *mean field corrections*. All of the work cited above except that of Liu [17] assumes that the dielectric constant of the underlying lattice material, or that of the solvent in the liquid case, is independent of local field strength. It was, however, pointed out in [8] that dielectric saturation effects can be readily included in these treatments using the approach of [6]; this has been done in unpublished work of the author. But the introduction of a dielectric constant at all, even a field-dependent differential dielectric constant, in microscopic regions near an electrode is itself a serious approximation and clearly should be replaced by a discrete treatment involving induced and (when present) permanent polarization effects [18]. The recent work of Liu [17] is extremely valuable in showing how a reasonable start may be made in doing so.

There are two elements of Liu's work which are important in the present context. First is his use of statistical mechanics to include in a lattice gas treatment dielectric saturation effects arising from field-induced changes in the orientation of solvent–molecule permanent dipole moments. But further work, currently in train, should add the effects of induced polarization of both ions and solvent molecules as well and should consider the appropriate form of a *Lorentz-cavity type of correction and mean polarization effects* [19] to yield a more accurate expression for the field that produces the polarization at a given layer. When the solvent permanent dipole moment is taken zero in Liu's results, the expression for the space charge  $\rho$  reduces, as it should, to the ordinary liquid lattice gas result without mean field interactions [8–12]. Also in the absence of ions his results reduce to ordinary Langevin behavior.

The second interesting element of Liu's approach is his approximation of the three-dimensional charge and polarization distributions by means of two-dimensional layers parallel to the electrode. These layers contain the ions and solvent molecules, taken electrically as point charges and point dipoles. He elects to consider the layers as part of a three-dimensional lattice gas structure. For the last several years the present author and his associates have been investigating, particularly for single crystals, a nearly equivalent approach in which each layer may be considered a two-dimensional lattice gas, with or without mean field ion–ion interactions [10,13]. In the absence of such interactions, this approach is still slightly more general in one way than Liu's because the interplanar separation need not necessarily be the same as the lattice length parameter. The approach, which is quasi-discrete, as compared to a pure continuum model, is particularly appropriate in single crystals when the Debye length is of the order of the lattice spacing or less. Although Liu characterizes his method as involving a mean field approximation, this is not

the same as the mean field interaction mentioned above, which leads to the necessity of solving a self-consistency equation for the local charge density [8,10,11,13,14]. Instead, the Liu mean field approximation, also used in our work, assumes that each layer has a given mean local potential, mean charge density, and mean dielectric displacement.

A particularly surprising feature of Liu's discrete-layer numerical results [17] not found in the absence of permanent dipoles, [10,13] is the appearance next to the electrode of a virtually charge-free layer, analogous to the inner or Stern solvent–molecule layer found in aqueous electrolytes in the absence of specific adsorption. Beyond this first layer, ionic charge effects dominate permanent dipole polarization effects, as expected in the ordinary DDL. Since the Liu treatment included no explicit treatment of hydration, it seemed important to investigate whether the apparent inner-layer effect arose from approximations in the model or numerical calculation method or was an intrinsic feature of any model including permanent dipoles.

In the rest of this work, certain problems in Liu's analysis and calculations will be discussed, and equations describing a more self-consistent model which includes permanent dipoles will be discussed and compared to those of Liu. Although mean field corrections (Bragg–Williams) [8,10,11,13–16] can be readily added to this model, since they are not included in that of Liu, they will be omitted herein.

## 2. The Liu model

The equations which define the Liu model will be presented in normalized form for simplicity and generality. Then a layer diagram following from these equations will be presented and discussed and an alternate self-consistent model developed. Let  $\epsilon_B$  be the bulk dielectric constant of the solvent in the absence of solute ions. It is about 80.4 for water at 20°C. If  $c_0$  is the concentration of ions of either sign in the bulk for a molarity  $M_0$ , then  $c_0 = 6.022045 \times 10^{20} M_0$  per  $\text{cm}^3$ . At an absolute temperature  $T$ , the bulk Debye length  $L_D$  is then  $(\epsilon_B kT/8\pi e^2 c_0)^{1/2}$ , where  $k$  is Boltzmann's constant,  $e$  is the protonic charge, and a uni-univalent situation has been assumed. Normalized quantities of interest are potential,  $\phi \equiv \psi/(kT/e)$ ; field,  $\mathcal{E} \equiv E/(kT/eL_D)$ ; dielectric displacement,  $\mathcal{D} \equiv D/(kT/eL_D)$ ; polarization,  $\mathcal{P} \equiv P/(kT/eL_D)$ ; and mean charge density (two-dimensional) in a layer,  $Q \equiv \sigma/\sigma_n$ . Here the normalizing charge density  $\sigma_n$  is  $2ec_0 L_D \equiv C_{d0} V_T$ , and  $C_{d0} \equiv \epsilon_B/4\pi L_D$  is the diffuse-layer differential capacitance/unit area for an applied PD across the DDL of  $\psi_d \ll V_T \equiv kT/e$ . The quantity  $P$  is the polarization density per unit volume, and  $Pa$  will be the surface density arising from ideal permanent dipoles in a layer plane for layers separated by a distance  $a$ . For simplicity, in his actual calculations Liu neglects the direct contribution of the induced polarizability of solute ions and solvent molecules to the dielectric

constant in a layer,  $\epsilon$ , and takes  $\epsilon_\infty$ , the value of  $\epsilon$  when the permanent dipole contributions have been saturated out, as unity. It is usually considered to be about 6 for water. This value is larger than the square of the index of refraction because it includes water-molecule vibration and libration contributions [6,18].

If the solvent is water, as assumed by Liu, the concentration of water molecules in a region without ions is  $N \equiv N_A/18 \approx 3.3456 \times 10^{22} \text{ cm}^{-3}$ , where  $N_A$  is Avogadro's constant. The concentration  $N$  is taken as the density of lattice points for the lattice gas treatment. The above value is close to that used by Liu (private communication) of  $3.33 \times 10^{22} \text{ cm}^{-3}$ . It is convenient [8,10–14] to define the fractional or relative bulk concentration of ions as  $\delta \equiv c_0/N$ . Then  $\delta \approx 0.0180M_0$  for water. In Liu's work he defines  $c$  as the concentration of ions in the bulk, but it is clear that his  $c$  is actually the present  $\delta$ . In the general case, we need one more quantity,  $\Delta \equiv a/L_D$ , where  $a$  is taken as  $3.1 \text{ \AA}$  by Liu. For this value of  $a$  and  $\epsilon_B = 80.4$ ,  $\Delta \approx 1.015M_0^{1/2}$ .

We shall defer until later a discussion of the constitutive equations following from free energy minimization. They give  $P$  and the charge density  $\rho \equiv \sigma/a$  at a given point in terms of the local potential and field acting at that point. In normalized form, the pertinent Liu equations are

$$\mathfrak{D}_i = \epsilon_i \mathfrak{E}_i \equiv \mathfrak{E}_i + 4\pi \mathfrak{P}_i, \quad (1)$$

$$\mathfrak{D}_{i+1} = \mathfrak{D}_i + \epsilon_B Q_{i+1}, \quad (2)$$

$$\phi_{i+1} = \phi_i - \Delta \cdot \mathfrak{E}_{i+1}. \quad (3)$$

Here  $Q_i$  is the net normalized charge density on a layer  $i$  and  $\mathfrak{E}_{i+1}$  is the normalized field between layers  $i$  and  $i+1$ . The factor of  $\epsilon_B$  in (2) arises from the normalization. The model used by Liu is shown explicitly for the first few layers in fig. 1a. Normalized quantities are shown; explicit reference to normalization will be omitted hereafter. The charge on the completely blocking metal electrode is  $Q_m \equiv Q_0$  and the total PD from this electrode to an ohmic electrode at infinity is  $\phi_m = \phi_0$ . In normalized terms  $\mathfrak{D}_0 = \epsilon_B Q_0$ .

Although Liu assumed infinitesimal ideal dipoles, he elected to spread out the polarization arising from them through the space between layers, as shown in the figure. As shown by eq. (1),  $\mathfrak{D}_i = \mathfrak{D}_i(\mathfrak{E}_i)$ , but the polarization contributing to  $\mathfrak{D}_i$  actually should be associated with the plane  $i$ , that where the charge  $Q_i$  resides. This is necessary because the free energy calculation leading to  $\mathfrak{P}_i(\phi_i, \mathfrak{E}_i)$  and  $Q_i(\phi_i, \mathfrak{E}_i)$  requires that  $P_i$  and  $\rho_i \equiv \sigma_i/a$  be defined at the same point. Thus, the spreading out of the polarization is an inconsistency in the ideal-dipole Liu model. It could be removed by considering (actual) non-ideal finite-extent dipoles in a much more complicated treatment. If one does require the ideal dipole polarization  $\mathfrak{P}_i$  to be localized on the  $i$ th plane, it is clear that the normal field acting to orient the dipoles is the average of  $\mathfrak{E}_i$  and  $\mathfrak{E}_{i+1}$ , not  $\mathfrak{E}_i$ . Thus the use of  $\mathfrak{E}_i$  rather than  $\mathfrak{E}_{AV}$  overestimates polarization effects since  $|\mathfrak{E}_i|$  will be larger than  $|\mathfrak{E}_{AV}|$ .

There is one further serious problem in the Liu model. Eq. (2) is inconsistent

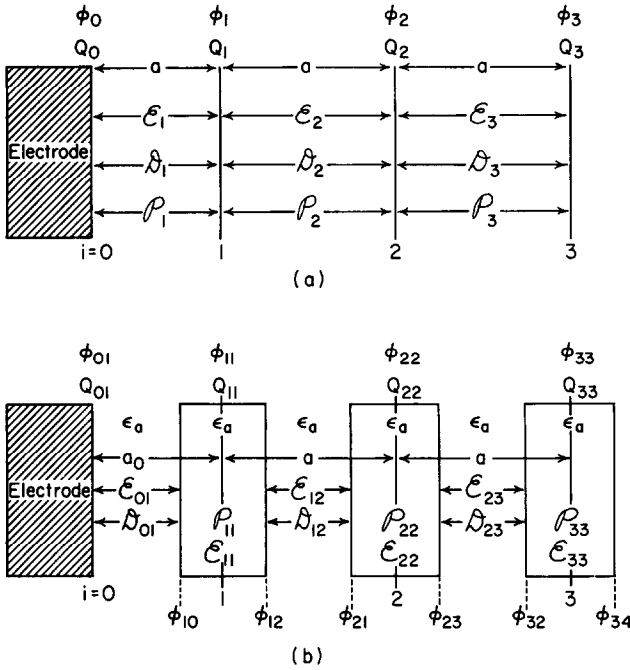


Fig. 1. (a) The Liu layered model. The separation between each charged plane is  $a$ . (b) A model involving infinitesimal dipoles.

with the boundary condition on the normal component of the displacement. The consistent equation involves the charge between  $\mathcal{D}_{i-1}$  and  $\mathcal{D}_i$ , but eq. (2) involves that between  $\mathcal{D}_i$  and  $\mathcal{D}_{i+1}$ . Thus eq. (2) should be replaced by

$$\mathcal{D}_{i+1} = \mathcal{D}_i + \epsilon_B Q_i. \tag{4}$$

It is very likely that the use of (2) rather than (4) in Liu's numerical work is the main reason for the appearance of virtually zero charge ( $Q_1 \cong 0$ ) on the plane  $i = 1$ , the first plane of the DDL.

Liu elected to obtain his  $\phi_i$ 's,  $Q_i$ 's and  $\mathcal{D}_i$ 's by starting at large  $i$ , say  $i = i_0$ , and progressing towards the electrode at the left. This is a valid procedure, although in our earlier work [10,13] we chose to start at  $i = 0$  and progress to the right. But Liu replaced the material for  $i \geq i_0$  by the continuum Gouy-Chapman model. While this is appropriate in that fields and potentials will be small for large  $i$ , one should not expect that a continuum model, based on the assumption that a single Debye length spans many molecules and ions - i.e. that these are of zero size in the continuum limit, will yield exactly the same spatial dependencies as a layer model where, for  $M_0 = 1$ , one of Liu's choices,  $\Delta \sim 1$  and there is only about one molecule per Debye length. In fact, earlier work on the  $P = 0$  case shows that the final slope in the exponential decay of  $\phi_i$

and  $Q_i$  is somewhat less for  $\Delta \sim 1$  than for  $\Delta \lesssim 0.01$ , a range which yields a good approximation to the continuum solution. One might guess that this initial difference at the  $i = i_0$  joining point could lead to growing errors as  $i$  progressed from  $i_0$  back towards zero. Fortunately this is not the case. Recent numerical work of Liu (private communication) shows that the slightly incorrect GC slope makes no difference after one progresses several layers into the discrete region, and the proper discrete slope is quickly established.

### 3. A self-consistent model

The first problem is what to do about the induced polarization contribution to the dielectric constant. Although non-zero induced polarizabilities for the solvent molecules and solute ions may be introduced into the free energy minimization calculation, the results are quite complex and their discussion will be deferred to a later paper. Here it seems reasonable to pick a middle way between the above choice (where an effective  $\epsilon_\infty$  will come out of the calculations) and that of taking  $\epsilon_\infty = 1$ . Thus, following the earlier work [10–14], which was particularly appropriate for solids, I shall here introduce an induced polarization contribution to the dielectric constant throughout the material of  $\epsilon_a$ , independent of position and field strength. It will usually be appropriate to take  $\epsilon_a = \epsilon_\infty$ .

First, a model consistent with Liu's original assumptions of infinitesimal charges and dipoles will be considered. But this model will be shown to be electrostatically inconsistent. Next, an outline will be presented of a model which allows dipole effects to be included explicitly and is electrostatically consistent. The actual working out of this model and discussion of its predictions will be deferred to a joint paper with S. Liu.

In order to describe the first model explicitly, it will initially be useful to use double subscripts. Further, since there is a potential drop across even an infinitesimal-thickness ideal dipole sheet, it will be convenient to show the dipole layer as of finite size in order to distinguish various quantities. The first model, in which the induced polarizability effects are spread out as in a continuum but the permanent dipole polarization is restricted to planes, is shown in fig. 1b. An explicit distinction has been made in fig. 1b between the distance  $a_0$  between the equipotential plane of the electrode and the charge centroids of the first layer of charge and  $a$ , the distance between the rest of the charge layers. A recent paper [7] suggests that because of nonlocal effects  $a_0$  may be as small as or smaller than the distance of field penetration into the metal,  $0(0.5 \text{ \AA})$ . This will be of no consequence for calculations of the DDL alone, since one can start the calculation at  $i = 1$  with  $\phi_{10} \equiv \phi_d$ , the total PD across the DDL, and treat the calculation of the PD ( $\phi_{01} - \phi_{10}$ ) separately whenever the total applied PD,  $\phi_m \equiv \phi_{01}$ , is required.

Note that the  $\phi$ 's in fig. 1b are not conceptually equivalent to those in fig.

1a. They do not include permanent dipole effects, and one can write

$$\mathfrak{D}_{i,i+1} = \epsilon_a \mathfrak{E}_{i,i+1} \equiv \mathfrak{E}_{i,i+1} + 4\pi \mathfrak{P}_{\text{ind}; i,i+1}, \quad (5)$$

Where  $\mathfrak{P}_{\text{ind}}$  is the induced polarization. The connection between sequential  $\mathfrak{D}$ 's may be written (for forward progression) as

$$\mathfrak{D}_{i,i+1} = \mathfrak{D}_{i-1,i} + \epsilon_B Q_{ii}, \quad (6)$$

leading to

$$\mathfrak{E}_{i,i+1} = \mathfrak{E}_{i-1,i} + (\epsilon_B / \epsilon_a) Q_{ii}. \quad (7)$$

Note that there is no overt contribution to eq. (6) from the dipole layer because its net charge is zero. But one should, of course, expect a stepfunction increase in potential to occur when passing from the negative to the positive side of a sheet of smeared-out ideal dipoles. In the present non-linear polarization situation, it is not clear exactly how to express this PD for the ideal dipole sheet. For illustrative purposes only, we shall use  $4\pi a P_{ii} / \epsilon_B$  and its normalized equivalent,  $4\pi \Delta \mathfrak{P}_{ii} / \epsilon_B$ , in the following equations. As we shall see, the use of ideal dipole sheets is itself inappropriate anyway in the present context, so the present choice is not critical. The normalized equation for the PD across the ideal dipole layer is

$$\phi_{i,i+1} = \phi_{i,i-1} + (4\pi \Delta / \epsilon_B) \mathfrak{P}_{ii}. \quad (8)$$

But the potential and field which produce  $Q_{ii}$  and  $\mathfrak{P}_{ii}$  are just the average values  $\phi_{ii}$  and  $\mathfrak{E}_{ii}$  shown on the diagram and given by

$$\phi_{ii} = 0.5(\phi_{i,i-1} + \phi_{i,i+1}), \quad (9)$$

$$\mathfrak{E}_{ii} = 0.5(\mathfrak{E}_{i-1,i} + \mathfrak{E}_{i,i+1}). \quad (10)$$

Now in forward progression we will always know such quantities as  $\phi_{i,i-1}$  and  $\mathfrak{E}_{i-1,i}$  and will need to calculate the successive equivalent values  $\phi_{i+1,i}$  and  $\mathfrak{E}_{i,i+1}$ . To do so, we need the relation which follows from the definition of  $\mathfrak{E}$ ,

$$\phi_{i,i+1} - \phi_{i+1,i} = \Delta \cdot \mathfrak{E}_{i,i+1}, \quad (11)$$

equivalent to eq. (3). Combination of eqs. (7) through (11) now yields the basic relations

$$\phi_{ii} = \phi_{i,i-1} + (2\pi \Delta / \epsilon_B) \mathfrak{P}_{ii} = \phi_{i-1,i} - \Delta \cdot \mathfrak{E}_{i-1,i} + (2\pi \Delta / \epsilon_B) \mathfrak{P}_{ii}, \quad (12)$$

$$\mathfrak{E}_{ii} = \mathfrak{E}_{i-1,i} + Q_{ii} / 2. \quad (13)$$

On combining eqs. (8) and (11) and eliminating  $\mathfrak{E}_{i,i+1}$  with eq. (7), one finds

$$\phi_{i+1,i} = \phi_{i,i-1} - \Delta \cdot \mathfrak{E}_{i-1,i} + (4\pi \Delta / \epsilon_B) \mathfrak{P}_{ii} - \Delta \cdot Q_{ii}, \quad (14)$$

allowing one to progress from the known prior values,  $\phi_{i,i-1}$  and  $\mathfrak{E}_{i-1,i}$  to the new value  $\phi_{i+1,i}$ , provided  $Q_{ii}$  and  $\mathfrak{P}_{ii}$  are known. Since these quantities both depend on  $\phi_{ii}$  and  $\mathfrak{E}_{ii}$ , the set of coupled equations (9) and (10) must first be solved self consistently before eqs. (7) and (14) may be used to progress from

one layer to the next. For forward progression, the calculation of the DDL response alone can begin with  $i=1$  and  $\phi_{10} \equiv \phi_d$  and  $\mathcal{E}_{01} = \mathcal{D}_{01}/\epsilon_a = (\epsilon_B/\epsilon_a) Q_{01} \equiv (\epsilon_B/\epsilon_a) Q_m$ .

It is possible to define as follows a dipole-layer dielectric constant  $\epsilon_{ii}$ , which will represent the response perpendicular to the layer:

$$\mathcal{D}_{ii} = \epsilon_{ii} \mathcal{E}_{ii} = \mathcal{E}_{ii} + 4\pi[\mathcal{P}_{\text{ind};ii} + \mathcal{P}_{ii}], \quad (15)$$

where  $\mathcal{P}_{\text{ind}}$  is again the response associated with  $(\epsilon_a - 1)$  and  $\mathcal{P}_{ii}$  arises from the permanent dipoles. Then

$$\epsilon_{ii} = \epsilon_a + 4\pi[\mathcal{P}_{ii}/\mathcal{E}_{ii}]. \quad (16)$$

In the  $\phi_{ii} \rightarrow 0$  and  $\mathcal{E}_{ii} \rightarrow 0$  limit,  $\epsilon_{ii}$  should equal  $\epsilon_B$ . Finally, for a completely blocking electrode at the left, overall electroneutrality requires that

$$Q_m + Q_d = 0, \quad (17)$$

where

$$Q_d \equiv \sum_{i=1}^{\infty} Q_{ii}, \quad (18)$$

$Q_m \equiv Q_{01}$ , and  $Q_d$  is the total charge in the DDL.

When  $\mathcal{P} = 0$ , eqs. (7) and (14) yield

$$\phi_{i+1,i} = \phi_{i,i-1} - \Delta \cdot \mathcal{E}_{i,i+1}, \quad (19)$$

equivalent to that used in earlier work [10,13] for this case. When  $\mathcal{P} \neq 0$ , however, it turns out that GC behavior is not obtained in the continuum limit. The difficulty is that the presence of a finite  $\mathcal{P}$  arising from dipole charge sheets infinitesimally separated from each other requires, in the limit, infinite dipole-sheet surface charge densities. But such charge densities are inconsistent with the dielectric coefficient discontinuity from  $\epsilon_a = 6$  to  $\epsilon_{ii}$  (which may be as large as 80 but is not infinite) and from  $\epsilon_{ii}$  to  $\epsilon_a$ . Thus this model must be scrapped.

A more consistent model is found if one replaces the finite-extent water dipoles by regions of uniform ideal-dipole polarization. Use a Debye length for normalization involving  $\epsilon_a$  instead of  $\epsilon_B$  and let the finite-dipole charge separation be  $d$  ( $\leq a$ ). Now represent the effect of the permanent dipoles by dipole sheets of normalized surface charge  $Q_d$  and  $-Q_d$ , separated by  $d$ . Then let  $Q_d \equiv \mathcal{P} \cdot (4\pi/\epsilon_a)$ , where the field and potential leading to  $\mathcal{P}(\phi, \mathcal{E})$  are just those at the center plane of the double layer. Although the effect of each permanent dipole has been spread out spatially through the introduction of the  $\pm Q_d$  charge sheets, the actual strength of the effective dipole moments is determined by the potential and field at the center plane, necessary for consistency. Finally, consistent with the mean field approach and the statistical mechanical treatment of  $\mathcal{P}$  and of  $Q$ , the ionic charge, place  $Q$  also on the center plane between the two dipole sheets. Then anywhere in the system except at actual charge centroids one will have  $\mathcal{D} = \epsilon_a \mathcal{E}$ , and it will be



unnecessary to deal explicitly with an  $\epsilon$  arising from  $\mathcal{P}$  directly. All such effects will have been included through the  $+Q_d$  and  $-Q_d$  sheets. If we let  $r \equiv d/a$ , the continuum limit will be obtained as  $d \rightarrow 0$  and  $a \rightarrow 0$ , keeping the value of  $r$  constant. Note that with  $r = 1$  the dipoles fill the material, and with  $d = 0$ , so  $r = 0$ , there are no dipoles and only charge layers remain. This model yields ordinary GC behavior (with  $\epsilon_B \gg \epsilon_a$ ) when  $p_0 \neq 0$  in the continuum limit ( $\Delta \rightarrow 0$ ) when  $\phi_d \rightarrow 0$  and  $r = 1$ . Results for different values of  $\Delta$ ,  $r$ , and  $\phi_d$  will be discussed in a later paper and may be expected to differ considerably from GC predictions when  $\phi_d$  and  $\Delta$  are appreciable, even for  $r = 1$ .

#### 4. Constitutive relations

The constitutive relations,  $Q_{ii}(\phi_{ii}, \mathcal{E}_{ii})$  and  $\mathcal{P}_{ii}(\phi_{ii}, \mathcal{E}_{ii})$ , are the essential element in Liu's important generalization of the layer model without permanent dipoles to a model including polarization from such dipoles. Some inconsistencies in his results, together with improved relations, will be discussed here. For simplicity, in this section we shall suppress the subscripts and take  $\psi_{ii} = \psi$ ,  $\phi_{ii} = \phi$ ,  $E_{ii} = E$ ,  $\mathcal{P}_{ii} = \mathcal{P}$ , etc.

Liu [17] found the following unnormalized expressions by means of a free energy minimization approach:

$$\rho = -2eN\delta \sinh(e\psi/kT)/Z, \tag{20}$$

and

$$P = N(1 - 2\delta) p [y \cosh(y) - \sinh(y)]/y^2 Z, \tag{21}$$

where  $y \equiv \bar{p}E/kT$  and the partition function  $Z$  is

$$Z \equiv 2\delta \cosh(e\psi/kT) + (1 - 2\delta) \sinh(y)/y. \tag{22}$$

Here  $p$  and  $\bar{p}$  are augmented dipole moments which take account of the effects of surrounding solvent molecules. If  $p_0$  is the permanent dipole moment of solvent molecules in isolation ( $p_0 \equiv 1.84$  Debye for water), then  $p_0 < p < \bar{p}$ . Eq. (20) leads to a result for  $\sigma \equiv a\rho$  in agreement with that found earlier [8–14] when  $p = 0$  and there are no dipoles present. Further, eq. (21) reduces as it should to just the Langevin expression when  $\delta \rightarrow 0$  and there are no ions present.

The high field limiting value of  $P$  is, from eq. (21),  $Np(1 - 2\delta)$ , which becomes just  $Np$  for pure solvent, consistent with Onsager's treatment of  $\epsilon_B$  for water. But for the high-field limit, where all dipoles point in the field direction, dipole polarization effects may be quite different than those assumed in the low-field Onsager theory. It seems at least plausible to assume that the maximum polarization, that when all dipole motion is saturated out, is just  $Np_0$ , a smaller value than  $Np$ . Further, in this limit (which may be approximated by conditions in the first layer next to the blocking electrode at

appreciable applied potentials), the solvent molecules near the electrode will be in regions of high pressure arising, loosely speaking, from the attraction of neighboring ions to the electrode [6]. Then the effective  $p_0$ ,  $p_{0e}$ , may be even smaller than  $p_0$  because of solvent molecule compression. Liu has also pointed out (private communication), that eq. (21) is inconsistent with (22), since the usual derivative relation between the partition function and the polarization leads to  $\bar{p}$  rather than the  $p$  of eq. (21), making the saturation polarization even larger. It is clear that this anomaly arises because dipoles with effective moment  $\bar{p}$  were used in the free energy but no energy interaction terms involving the change from dipoles with dipole moment  $p_0$  to  $\bar{p}$  were included. To include all necessary terms of this kind would be very difficult, and we prefer at this stage to attack the problem in a more heuristic way, one closely coupled to experimental results.

There are three immediate conditions which  $P$  and the dielectric constant  $\epsilon$  involving  $P$  should satisfy. We consider first dielectric saturation in bulk solvent since ionic effects may be readily added later. First, as  $E \rightarrow \infty$ , one should have  $P \rightarrow NP_{0e}$ . Second, as  $E \rightarrow 0$ , one should find  $\epsilon = \epsilon_B = \epsilon_\infty + 4\pi[P/E]$ . Now eq. (21) leads to

$$\epsilon = \epsilon_\infty + (4\pi N/3)(p\bar{p}/kT). \quad (23)$$

With Liu's values of  $p$  and  $\bar{p}$  for water,  $N = 3.346 \times 10^{22} \text{ cm}^{-3}$ , and  $\epsilon_\infty = 1$ , one obtains  $\epsilon \cong 77.6$ , close to the value  $\epsilon_B \cong 80.4$  at  $20^\circ\text{C}$ . But if  $p$  is replaced by the smaller  $p_0$  or  $p_{0e}$  in order to satisfy condition (1), it is clear that  $\bar{p}$  must be increased to  $\bar{p}_e$  in order that  $\epsilon \cong \epsilon_B$ . Thus we require that  $p\bar{p} = p_{0e}\bar{p}_e$  be consistent with the experimental value of  $\epsilon_B$ . Such an increase in  $\bar{p}$  means that the permanent dipoles are more easily saturated than predicted by the Liu-Booth [17,20] result.

Luckily, recent dielectric saturation data on water [21] allows one to obtain a larger, experimentally derived estimate for  $\bar{p}_e$ , and our third necessary condition will be that the value of  $\bar{p}_e$  agree with this result. All these conditions assume that the form of the expression for  $P(E)$  is reasonably valid. In the absence of very high field dielectric saturation experimental results or more sophisticated saturation theory for the region of appreciable saturation, this assumption appears reasonable.

Now Kolodziej et al. [21] found for water at  $20^\circ\text{C}$  that  $\Delta\epsilon/E^2 \cong 10^{-15} (\text{m/V})^2$  up to their maximum applied field of  $10^7 \text{ V/m}$ . Expansion of eq. (21) to first order in  $E^2$  with  $\delta = 0$  yields

$$\Delta\epsilon/E^2 = 4\pi Np\bar{p}^3/45(kT)^3 = [(\epsilon_B - \epsilon_\infty)/15](\bar{p}/kT)^2. \quad (24)$$

This leads to  $\Delta\epsilon/E^2 \cong 3.2 \times 10^{-16} (\text{m/V})^2$ , a factor of about 3.1 smaller than the experimental value. If we replace  $p$  and  $\bar{p}$  in eqs. (23) and (24) by  $p_{0e}$  and  $\bar{p}_e$  and use  $\epsilon_\infty = 6$ , then the requirements of agreement with the experimental  $\epsilon_B$  and the experimental saturation constant lead to  $p_{0e} \cong 1.27 \text{ D}$  and  $\bar{p}_e \cong 16.9 \text{ D}$ . Note that indeed  $p_{0e}$  is appreciably less than  $p_0$ .

When the constitutive equations are expressed in normalized form, one has for  $Q_{ii}(\phi_{ii}, \mathcal{E}_{ii})$ , the normalized charge density on plane  $i$ ,

$$Q = \frac{-Q_s \sinh(\phi)}{\cosh(\phi) + C_R [\sinh(b_1 \mathcal{E}) / (b_1 \mathcal{E})]} \quad (25)$$

where subscripts have been suppressed, the maximum magnitude of normalized layer charge density is  $Q_s \equiv \Delta/2\delta$ , and  $C_R \equiv (1 - 2\delta)/2\delta$ . This Liu result reduces to that found earlier [10,13] when  $b_1 \mathcal{E} \rightarrow 0$  and there is thus no dielectric saturation effect. It does not include the mean field corrections present in the work of refs. [10] and [13]. In eq. (25), we have set  $(\bar{p}_e/kT)E \equiv b_1 \mathcal{E}$ , so  $b_1$ , a normalized saturation parameter, is  $p_e/eL_D$ . For Liu's value of  $\bar{p}$  and for 20°C and  $M_0 = 1$ ,  $b_1 \approx 0.66$ . For the value of  $\bar{p}_e$  discussed above,  $b_1 \approx 1.18$ .

There is, unfortunately, no assurance that the Booth–Langevin dielectric saturation formula is valid, even to first order in  $E^2$ , much less in the region where  $|b_1 \mathcal{E}| \gtrsim 1$ . The large value of  $\bar{p}_e$  and the small value of  $p_{0e}$  found above suggest, in fact, that it is not. In the absence of a more plausible choice, however, we shall use the Booth–Langevin result here, considering  $b_1$  as a parameter whose effect will be investigated numerically for a plausible range of values. As shown below, the expression for  $\mathcal{P}$  to be used will be written so that the bulk dielectric constant  $\epsilon_B$  is recovered in the low field limit as  $M_0 \rightarrow 0$ . With  $\epsilon_\infty = \epsilon_a$  rather than unity, a reasonable way of writing the Booth–Langevin expression for polarization in the presence of ions in normalized form is

$$\mathcal{P} = \left( \frac{3C_R}{4\pi} \right) (\epsilon_B - \epsilon_a) \mathcal{E} \cdot F(b_1 \mathcal{E}), \quad (26)$$

where  $\epsilon_B$  is again the unsaturated bulk dielectric constant given by eq. (23) with  $p_{0e}$  and  $\bar{p}_e$ , and

$$F(b_1 \mathcal{E}) = (b_1 \mathcal{E})^{-3} \left[ \frac{(b_1 \mathcal{E}) \cosh(b_1 \mathcal{E}) - \sinh(b_1 \mathcal{E})}{\cosh(\phi) + C_R [\sinh(b_1 \mathcal{E}) / (b_1 \mathcal{E})]} \right]. \quad (27)$$

Note that when  $\phi$  and  $\mathcal{E}$  go to zero  $F(b_1 \mathcal{E}) \rightarrow 2\delta/3$ . Thus in the limit,  $[\mathcal{P}/\mathcal{E}] \rightarrow (1 - 2\delta)(\epsilon_B - \epsilon_a)/4\pi$ . The  $(1 - 2\delta)$  factor accounts for the reduced concentration of solvent dipoles in the bulk when ions are also present. The normalized dielectric displacement is given by eq. (15) and leads to the  $\epsilon$  of eq. (16).

Now hydration effects [22] cause the bulk dielectric constant of a water ion mixture to decrease appreciably as  $M_0$  increases. Thus for a NaF solute,  $\epsilon_B$  has decreased by about 15% from its  $M_0 \rightarrow 0$  value by  $M_0 = 1$ . The  $(1 - 2\delta)$  factor only reduces  $\epsilon_B$  by about 4% at  $M_0 = 1$ , however. This suggests that hydration effects could be much better accounted for in the present model if one applied the conventional approximation of dividing the water molecules in a given layer into three classes:  $h_+$  saturated water dipoles around each cation,  $h_-$

saturated water dipoles around each anion [22], and the remaining dipoles as completely unsaturated. Liu has assumed that all dipoles present in a layer are free to rotate under the influence of an external field and thermal perturbations. The present suggestion takes the hydration numbers  $h_+$  and  $h_-$  (which range from 1 to about 6), into account and assumes that the  $h_{\pm}$  dipoles around a given ion (its primary hydration sheath) are influenced by the above effects together with the strong Coulomb field of the ion (involving a saturated dielectric constant of about 6) at the position of its nearest-neighbor dipoles (one lattice spacing away from the centroid of charge of the ion). Only for a strong external field,  $\mathcal{E}$ , will these  $h_{\pm}$  dipoles have an appreciable component of dipole moment in the direction of  $\mathcal{E}$  and thus contribute to the effective  $\epsilon$  of the layer. At a layer where the local potential is  $\phi$ , if one sets  $Z=1$  for simplicity, there will be  $N_s \delta e^{\phi}$  anions and  $N_s \delta e^{-\phi}$  cations present, where  $N_s \equiv aN$ . Thus there will be  $h_- N_s \delta e^{\phi}$  dipoles in the primary hydration sheath around these anions,  $h_+ N_s \delta e^{-\phi}$  around the cations, and  $N_s [1 - \delta(h_- e^{\phi} + h_+ e^{-\phi})]$  free-to-rotate remaining dipoles. Although this division of the dipoles into three distinct classes is clearly an appreciable approximation, it should be considerably superior to no division at all and will be further pursued in a later paper. One of the immediate advantages of this approach is that if  $h_+ \neq h_-$ , the  $Q_m$  versus  $\phi_d$  curve obtained from the model will be asymmetric between its  $\phi_d > 0$  and  $\phi_d < 0$  regions, as is found experimentally.

There have been many theoretical treatments of the DDL in recent years (see, e.g., references in ref. [8]) which do not use the lattice gas approach and include permanent dipole effects only through the introduction of a background  $\epsilon_B (> \epsilon_{\infty})$ . These treatments are generally very complex, and become more so when discrete dipoles are included [23–25]; they are usually limited to low bulk ionic concentration and/or small values of  $\phi_d$ . The present approach does not suffer from these limitations but may be expected to yield less microscopic detail for the ionic and dipolar behavior because of mean field type averaging. There seems to be important roles for both kinds of models to play. Detailed comparisons between their predictions will be carried out in later papers.

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