A lattice model for the electric double layer

Andrew Steele Peterson

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A LATTICE MODEL FOR THE ELECTRIC DOUBLE LAYER

Iowa State University

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A lattice model for the electric double layer

by

Andrew Steele Peterson

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I. INTRODUCTION

A. The Metal-Electrolyte Interface

There are many important processes that occur within the transition region between a metal and a liquid electrolyte. Many metals corrode due to reactions between the metal surface and a thin layer of water on it. Other reactions that occur in this interfacial region have been exploited to produce and store electricity using solar cells, fuel cells, and simple storage batteries. Catalytic reactions at metal surfaces are important in the production of several useful materials. To better understand these and other important processes, it is necessary to understand in detail the equilibrium structure of the interfacial region.

One important property of the metal-electrolyte interface is that in general it is charged. A net charge may form on the metal side of the interface with a compensating charge in the electrolyte. This charge may occur due to chemical reactions in the interfacial region or it may be supplied by an external potential source. Since this charging occurs naturally and many of the reactions that occur within the interfacial region depend upon the size of this charge, it is important to understand how the structure of the interface depends upon the net charge on it. But, since the charge can be changed and controlled externally, this property may be used to understand the structure of the interfacial region.
In some ways the metal-electrolyte interface may be regarded as a capacitor, but there are some major differences. It is not possible to measure the potential difference across a single metal-electrolyte interface. Therefore, the capacitance of the interface is not directly measurable. It is possible, over a limited range of applied potentials, to determine the charge on the metal surface and the derivative of this charge with respect to the potential difference across the interface. Measurements of this differential capacitance as a function of the charge on the metal have been used to infer much about the structure of the metal-electrolyte interface.

If the interface behaved as a simple capacitor, the differential capacitance would be independent of the charge on the metal surface. The experimental results show large variations in the differential capacitance as the charge on the metal surface is changed. This indicates that the structure of the interface changes as the charge is varied. These differential capacitance measurements do not directly show the microscopic arrangement of the molecules in the interfacial region. Instead, it is necessary to propose a model for the structure of the interface and to compare the predictions based upon this model with the experimental results.
B. The Stern Model

The structure of the interfacial region and its connection to the differential capacitance is thought to be adequately described by the Stern model (1). The metal surface is treated as an infinite ideally smooth plane, so that variations in only one dimension need to be considered. The charge on the metal is assumed to form a two dimensional surface layer that does not contribute to the differential capacitance. Calculations have been done that indicate that this may not be a valid approximation (2, 3).

Adjacent to the metal surface is a thin inner region. This is the most difficult part of the interfacial region to treat properly. Most of the potential drop across the interface occurs in this region and the electric fields can become very large. It also may be necessary to consider short range interactions between the molecules of the electrolyte and those of the metal surface to properly describe the inner layer. This region will be considered in detail later.

Extending from the inner layer into the bulk of the solution is the diffuse region. Long range electrostatic interactions between the charge on the metal and the molecules in the electrolyte determine the structure of this region to a large degree. The solvent molecules are not greatly affected by the charge on the metal. The most important effect is that the distribution of the ions in the electrolyte changes
as the charge on the metal surface changes. Theories for this region can be more general than those for the inner layer. For dilute solutions the diffuse region is well described by the Gouy-Chapman theory (4, 5).

C. Gouy-Chapman Theory

The major assumptions of the Gouy-Chapman theory are that the ions may be treated as noninteracting and that the solvent behaves as a structureless dielectric. The charge density within the electrolyte obeys Poisson's equation,

\[ \frac{d^2 V}{dz^2} = \frac{-4\pi \rho}{\varepsilon} . \] (1.1)

Since the metal surface is regarded as an infinite plane, only variations in one dimension are considered. The potential, \( V \), goes to zero at large distances from the metal surface and \( z \) is the distance into the diffuse layer (not the distance from the metal surface). The concentration of each type of ion is assumed to be given by a simple Boltzmann factor,

\[ n_i = n_i(0) \exp(-z_i e V / kT) . \] (1.2)

The valence of the ion is \( z_i \), its concentration in the bulk electrolyte is \( n_i(0) \), \( e \) is the proton charge, \( T \) is the temperature, and \( k \) is Boltzmann's constant. The combination, \( kT \), will occur in many other equations used in this work.
The charge density in the electrolyte may be found by summing the contributions due to each kind of ion using Equation 1.2. This result may then be combined with Equation 1.1 to obtain the Poisson-Boltzmann equation,

\[ \frac{d^2V}{dz^2} = - \frac{4\pi}{\varepsilon} \sum_i n_i(0)z_i \exp(-z_i eV/kT). \] (1.3)

This equation can be solved to give the potential, electric field, and the charge density within the diffuse region. To compare the predictions of the Gouy-Chapman theory to experimental differential capacitance measurements, only the relationship between the total charge in the diffuse region and the potential difference across it is needed. For simplicity, an electrolyte that contains equal numbers of only two types of ions one with valence +1 and the other with valence -1 is considered. For this 1:1 electrolyte the result is

\[ Q_D = -2 \left( \frac{\varepsilon n(0) kT}{2 \pi} \right)^{1/2} \sinh \left( \frac{eV_I}{2kT} \right). \] (1.4)

The charge is for a unit area of metal surface (1 cm²), \( V_I \) is the potential at the inner edge of the diffuse region, and \( n(0) \) is the ionic concentration.

The predictions of the Gouy-Chapman theory regarding the structure of the diffuse region are most easily seen in the linearized version of the theory. If the potential is small,
the exponentials in Equation 1.3 may be expanded and only the first order terms need to be retained. For a 1:1 electrolyte, the resulting linearized Poisson-Boltzmann equation is

\[
\frac{d^2V}{dz^2} = \kappa^2 V. \tag{1.5}
\]

where \( \kappa^2 = \frac{8\pi n(0)e^2}{\epsilon kT} \). This equation can easily be solved to find the potential, electric field, and charge density within the diffuse region.

\[
V = V_i \exp(-\kappa z) \tag{1.6}
\]

\[
E = \kappa V_i \exp(-\kappa z) \tag{1.7}
\]

\[
\rho = \frac{-2n(0)e^2V_i}{kT} \exp(-\kappa z) \tag{1.8}
\]

Equations 1.6, 1.7, and 1.8 show that the changes in the electrolyte due to the charged metal surface decrease exponentially with distance into the diffuse region. The predictions of the nonlinear theory are qualitatively similar, but the equations that describe them are not as transparent. The thickness of the diffuse region is determined by \( \kappa^{-1} \), the Debye screening length. For aqueous solutions at room temperature, typical values of \( \kappa^{-1} \) are 10 Å for a 0.1 M solution and 3000 Å for a 10^{-6} M solution.
There are several deficiencies in the Gouy-Chapman theory. Since the ions are treated as point charges, the predicted charge density may reach unphysically large values. Interactions between the ions are not included in the theory. Since the solvent molecules are not explicitly treated, changes in the dielectric constant of the electrolyte are not included. For large charge densities on the metal, the electric field near the metal surface can become very large, and many of the solvent molecules align with the field. This dielectric saturation reduces the dielectric constant of the electrolyte near the metal surface. The large concentration of ions near the metal surface also alters the dielectric constant of the electrolyte.

There have been attempts to treat some of these additional effects (6-12). The primary difficulty of these theories is that the resulting equations can not be analytically solved. This causes problems in comparing the theory to experimental results. In most cases, the simple Gouy-Chapman theory is adequate.

D. The Inner Layer

The least well-understood part of the metal-electrolyte interfacial region is the inner layer. There is no generally accepted theory, such as the Gouy-Chapman theory, that explains the properties of the inner layer. This is because
the structure of the inner layer can be very different for different solvents, solutes, and metal surfaces.

In the mid-forties, Grahame (13) found a system where the properties of the inner layer may be simpler than might be expected. He split the differential capacitance of aqueous NaF solutions and mercury electrodes into two contributions, one due to the diffuse region and the other due to the inner layer. He used the Gouy-Chapman theory to describe the diffuse layer contribution. He found that for solute concentrations ranging from 0.916 M to 0.001 M the contribution due to the inner layer did not depend upon the concentration. Later measurements (14) have confirmed this finding for even more dilute solutions.

The independence of the inner layer capacitance on the ionic concentration indicates that there are no ions in the inner layer for this system. There have been other systems found that also show this behavior. For mercury electrodes, it is generally assumed that the aqueous electrolyte inner layer is void of most cation species. A charge free inner layer has also been found for other solvents (15, 16) and other metal electrodes (16, 17). The results for these other systems are not as complete as the measurements for the water inner layer next to mercury surfaces.

If the inner layer consists of only one kind of molecule, it should be an easier system to model. Even if there are
ions in the inner layer, most of the molecules are still solvent molecules. Thus, an understanding of the inner layer of pure solvent also leads to a better understanding of the inner layer that contains ions. For this reason, I will concentrate on this potentially easier system.

If there are no ions in the inner layer, it is possible to subtract the contribution of the diffuse layer from the experimental results to obtain a differential capacitance due solely to the inner layer. This is done in the following fashion. The potential difference, \( V \), across the interface can be considered as two potential drops, one across the inner layer and the other across the diffuse region,

\[
V = (V_m - V_I) + (V_I - V_b).
\]  

(1.9)

\( V_m \) is the potential at the metal surface, \( V_I \) is the potential at the juncture of the inner layer and the diffuse region, and \( V_b \) is the potential in the bulk solution (\( V_b = 0 \)). Taking the derivative of Equation 1.9 with respect to the charge density of the metal surface gives

\[
dV/dQ = d(V_m - V_I)/dQ + d(V_I - V_b)/dQ.
\]  

(1.10)

dV/dQ is the inverse of the differential capacity (in per area units). The system can be regarded as two capacitors connected in series.
The term $d(V_I - V_b)/dQ$ may be evaluated using the Gouy-Chapman theory. Since there are no ions in the inner layer, the charge on the metal is opposite to and equal to the charge contained in the diffuse region. This result can be used in Equation 1.4, and the equation can be solved to give the potential drop across the diffuse region,

$$V_I - V_b = \frac{2kT}{e} \left[ \left( \frac{\pi}{2\varepsilon \varepsilon_0 kT} \right)^{1/2} Q + \left( \frac{\pi Q^2}{2\varepsilon \varepsilon_0 kT} + 1 \right)^{1/2} \right]. \tag{1.11}$$

The derivative of Equation 1.11 with respect to $Q$ gives the inverse of the differential capacitance of the diffuse region,

$$\frac{1}{C_D} = \frac{2kT}{e} \left[ \left( \frac{\pi}{2\varepsilon \varepsilon_0 kT} \right)^{1/2} + \frac{Q}{2\varepsilon \varepsilon_0 kT \left( 1 + \frac{\pi Q^2}{2\varepsilon \varepsilon_0 kT} \right)^{1/2}} \right]. \tag{1.12}$$

This result may be subtracted from the inverse of the measured differential capacitance to obtain the differential capacitance of the inner layer.
E. Choice of Parameters to Describe the Inner Layer

To compare the predictions of a model with the measured inner layer differential capacitance curves, it is first necessary to find relationships among the measured quantities, the charge on the metal and the differential capacitance, and the appropriate variables for the inner layer, the electric field and the polarization. Two slightly different methods have been used to get these results. Both methods give final expressions for the differential capacitance of the inner layer as functions of the charge on the metal surface.

These methods have been used in several different models for the inner layer. Although some parts of these methods have been criticized, the general approach of attempting to write the differential capacitance as a function of the charge on the metal has not. I believe that this approach introduces problems with any model for the inner layer, and believe that a different method should be used.

In the standard methods, the inner layer is assumed to be uniform. Since there are no ions in the layer, the potential difference across it may be written as

\[ V_{m} - V_{I} = aE = a(D - 4\pi P). \]  \hspace{1cm} (1.13)
E (the electric field), D (the electric displacement), and P (the polarization) are constant throughout the inner region and a is the inner layer thickness. The charge density on the metal surface is related to the electrostatic properties of the inner region through

\[ Q = \frac{D}{4\pi}. \]  

(1.14)

Equation 1.14 can be used in Equation 1.13 to give

\[ V_{in} = 4\pi a (Q - P). \]  

(1.15)

The derivative of Equation 1.15 with respect to Q gives the inverse of the inner layer capacitance,

\[ \frac{1}{C_{in}} = 4\pi a (1 - \frac{dP}{dQ}). \]  

(1.16)

The capacitance is for a unit area and the thickness of the inner layer is assumed to be constant.

To complete the theory, it is necessary to propose a model of the inner layer that expresses the polarization of the molecules in the layer as a function of the charge on the metal surface. Generally, the polarization is considered as a
response of the molecules to the electric field in the material. It is not possible to express the electric field in the inner layer directly in terms of the charge on the metal.

In one of the standard methods, the water molecules are treated as polarizable point dipoles that occupy a two dimensional lattice. The lattice is assumed to lie in vacuum between the metal surface and the rest of the electrolyte. The water molecules are assumed to respond to the external field, $4\pi Q$.

There is a serious numerical problem with this approach. To fit the experimental differential capacitance curves, $dP/dQ$ must be nearly equal to one. Slight changes in $dP/dQ$ can result in much larger changes in $C_{\text{in}}$. As an example, for mercury electrodes the differential capacitance of the water inner layer has a minimum value of $18 \ \mu F/cm^2$. If the inner layer is assumed to be one monolayer thick ($a = 3 \ \text{Å}$), then $dP/dQ$ must equal 0.836 to match this value. Changing $dP/dQ$ by $\pm 10\%$ from this value produces changes of $+100\%$ to $-34\%$ in the resulting differential capacitance. At larger values of the differential capacitance this magnification becomes more pronounced.

This approach has been used by Fawcett et al. (18). The latest version of their theory can adequately reproduce the differential curves for the water inner layer at mercury electrodes. However, their theory requires eight parameters.
that are varied to fit the experimental results. They note that their theory is very sensitive to small changes in some of the adjustable parameters. This sensitivity is due primarily to the formalism they use to find the relationship to the experimental results (Equations 1.13-1.16) rather than the specific model they assume for the structure of the inner layer.

The numerical instability of this method is partially corrected in other models by the introduction of an "effective dielectric constant." In these models, the water molecules are treated as nonpolarizable, but they are considered to exist in a region that has a dielectric constant other than one due to the polarizability of the molecules. With this assumption, the expression for the inner layer capacitance is

$$\frac{1}{C_{in}} = \frac{4\pi \alpha}{\varepsilon_{ef}} \left( 1 - \frac{d\bar{P}}{dQ} \right).$$

(1.17)

$\bar{P}$ is due only to the permanent dipole moments of the molecules and $\varepsilon_{ef}$ is due to the nonorientational part of the polarization. The permanent dipoles are assumed to react to an effective field, $E_{ef} = 4\pi Q/\varepsilon_{ef}$.

Due to the presence of $\varepsilon_{ef}$ in Equation 1.17, $d\bar{P}/dQ$ need not be as nearly equal to one to reproduce the experimental results. For this reason, these theories are not as subject to numerical instabilities as those that use the first method.
The value for the "effective dielectric constant" is assumed to be about six.

The introduction of an "effective dielectric constant" has been criticized (19). The form of Equation 1.17 is not obvious from the development leading to Equations 1.13-1.16. A detailed derivation of Equation 1.17 shows an inconsistency in the "effective dielectric constant" theories.

For a uniform material, the dielectric constant may be written as

\[ \varepsilon = 1 + 4\pi \frac{P}{E}. \quad (1.18) \]

There are two contributions to the polarization. Part of it, \( P \), is due to the orientation of the permanent dipole moments. The rest, \( P_{\text{ind}} \), is due to induced dipole moments. \( P_{\text{ind}} \) is assumed to be proportional to the electric field. Its contribution to the dielectric constant can be replaced by an "effective dielectric constant,"

\[ \varepsilon_{\text{ef}} = 1 + 4\pi \frac{P_{\text{ind}}}{E}, \quad (1.19) \]

which would be the dielectric constant of the material if there were no contributions from the permanent dipole moments. With this substitution the entire dielectric constant may be written as

\[ \varepsilon = \varepsilon_{\text{ef}} + 4\pi \frac{P}{E}. \quad (1.20) \]
To apply this result to the theory of the inner layer, we write the electric field as

\[ E = \frac{D}{\varepsilon} = \frac{D}{(\varepsilon_{ef} + 4 \pi \bar{P}/E)} \]  

(1.21)

or

\[ E = \frac{(D - 4 \pi \bar{P})/\varepsilon_{ef}}{\varepsilon_{ef}}. \]  

(1.22)

For the inner layer, \( D = 4 \pi Q \) and \( V = a E \) (Equations 1.13 and 1.14). With these substitutions, the potential drop across the inner layer may be found from Equation 1.22,

\[ V = 4 \pi a \frac{(Q - \bar{P})/\varepsilon_{ef}}{\varepsilon_{ef}}. \]  

(1.23)

This equation may be differentiated with respect to \( Q \) to obtain the inverse of the inner layer capacitance, Equation 1.17.

These "effective dielectric constant" theories are inconsistent because the polarization of the inner layer depends upon two different fields. The permanent dipoles are assumed to respond to an effective electric field, \( \varepsilon_{ef} = 4 \pi Q/\varepsilon_{ef} \). But, to obtain an expression for the differential capacitance, the induced dipoles have to respond to the actual electric field within the layer.

I will use a method different from either of the two standard ones. For a uniform inner layer the potential difference across it may be written,
The charge density is related to the electrostatic properties of the inner layer by

\[ Q = \frac{D}{4\pi} = \frac{E}{4\pi} + P. \quad (1.25) \]

The inner layer thickness is assumed to be a constant and the differential capacity is given by

\[ C_{in} = \frac{dQ}{dV} = \frac{1}{a} \frac{dQ}{dE} = (\frac{1}{4\pi} + \frac{dP}{dE})/a. \quad (1.26) \]

Equations 1.25 and 1.26 express the differential capacitance of the inner layer and the charge density on the metal surface in terms of the electric field within the inner layer. The polarization of the molecules in the inner layer can then be treated as a response to the electric field in the layer. Since \( dP/dE \) is positive there is no need for subtraction of nearly equal quantities, so the theory contains no inherent instabilities.

It is not possible to write an expression for the differential capacitance as a function of the charge on the metal surface. This is not a serious problem. The equations that will be given to characterize the inner layer are complicated. It is necessary to use the numerical results of these equations to understand the predicted inner layer capacitance.
II. IMPORTANCE OF LOCAL ORDER IN THE INNER LAYER

A. Models for the Structure of the Inner Layer

The least precise part of the theory of the metal-electrolyte interface is modeling the structure of the molecules in the inner layer. There are no experiments that directly determine the microscopic arrangement of the molecules. Instead, a possible structure for the inner region must be assumed and the predictions based upon this assumed model must be compared with the experimental measurements. Since the conditions in the inner layer are different from those in the rest of the electrolyte, the structure of the inner layer may be very different from the bulk solution.

There have been many models proposed for the structure of an inner layer of pure solvent molecules (8, 18-27). These models have been reviewed in several articles (16, 23-30). Most of the proposed models have been used to analyze the inner layer of water at a mercury surface. The experimental results are more complete for this system than for any other metal or solvent, so I will also concentrate on this system.

Many of the assumptions made about the arrangement of the water molecules in the inner layer are common to each of the models. The assumed structure differs from that of the bulk solution. Hydrogen bonding between the water molecules in the bulk plays an important role. This leads to a tetrahedral
arrangement of the nearest neighbor water molecules. In response to an applied field, the molecules orient largely as clusters of molecules. These clusters span several layers of molecules and their existence is thought to be responsible for the large static dielectric constant of bulk water.

The inner region has been assumed to be a single monolayer thick. The water molecules are assumed to occupy a two dimensional lattice located between the metal surface and the rest of the electrolyte. When a geometry for this underlying lattice has been specified, it has been assumed to be triangular. Only effects due to the orientation of the molecules have been assumed to be important. Any contributions due to the motion of the water molecules have been neglected.

Interactions between the molecules in the inner layer and those in the rest of the electrolyte have been completely neglected. Interactions between molecules within the inner region have been assumed to be important, but these effects have only been included using mean-field approximations.

Usually only a limited number of possible orientations has been considered for a molecule in the inner layer. The simplest possible assumption is that the dipole moment of the water molecule points either directly into or away from the metal surface. Other possibilities have also been suggested, such as orientations where the dipole moment of the molecule is not directed normal to the metal surface (19) or more than
two possible orientations for the molecule (8, 26).

The simple two-state approximation with a mean-field treatment of the interactions is capable of reproducing several features of the inner layer capacitance curve, measured for water on mercury electrodes. It has been inferred from these capacitance measurements that the dielectric constant of the water in the inner region is much smaller than the bulk value. With a proper choice for the interaction strength, this result can be obtained with the simple two-state model. Another feature in the experimental results is the presence of a maximum in the \( \frac{dQ}{dV} \) versus \( Q \) curve near \( Q = 0 \). The decrease in \( \frac{dQ}{dV} \) away from this maximum has been attributed to dielectric saturation as most of the molecules become aligned with the applied field. The simple two-state model also shows this behavior.

There has been no consensus regarding the strength of the interactions between the molecules in the inner layer. The extreme cases of treating the molecules as noninteracting (22) and of assuming that some of the molecules interact so strongly that they form small stable clusters (18,22,24,25) have been considered. The interaction strength has also been assumed to be given by electrostatic dipole-dipole interactions between the molecules (8,18,19,25,26). In some models the interaction strength has been adjusted to fit the experimental inner layer capacitance (23, 27).
The success or failure of models of the inner layer has been largely based upon their ability to fit experimental inner layer capacitance curves. The newer models have generally contained more parameters that are varied to fit the experimental measurements. Consequently, these theories are better able to reproduce the experimental results than the older theories. Most of the assumptions about the structure of the inner layer that were made in the earliest theories have been retained in the newest models. It is possible to test some of these assumptions by considering a simple model of the inner layer.

If interactions between molecules in the inner layer with those in the rest of the electrolyte can be neglected, then the important interaction in the inner layer is a direct interaction between nearest neighbors. The strength of this interaction is about the same as the classical electric dipole-dipole interaction for two water molecules. This is a strong interaction. It has been speculated that the inner layer may order anti-ferroelectrically if the interactions are sufficiently strong (23). This possibility and its effect upon the differential capacitance have not been thoroughly explored.

It does not take long range order to change the behavior of the differential capacitance. Guidelli (27) has recently shown that if the effects of local order are included in the calculation, the differential capacitance calculated can be
very different than if only mean-field effects are considered. The effects due to local order depend greatly upon the strength of the interactions. The geometry of the assumed lattice structure of the inner layer also plays an important role if local order becomes important. This was apparently not realized by Guidelli, since he used an approximation that was incorrect for the inner layer geometry that he assumed.

I have considered some of these effects using a simple two-state approximation for the water molecules in the inner layer. To show the effects due to the geometry assumed, I have considered two cases. I have treated the case where the molecules lie on a triangular lattice, the geometry assumed in most of the other models, and have contrasted the behavior for this case with that of an underlying square lattice. To show the importance of local order, I have treated these two possible geometries using approximations that consider more than mean-field effects and have contrasted this behavior with that predicted by simple mean-field theory. To show the dependence of the interaction strength upon local order, I have used several different possible interaction strengths.

B. Simple Two-State Model

The major assumptions of this model are: the water molecules occupy a two dimensional lattice; only their orientation (not their motion) is important; the molecules can be
in only one of two possible orientations; and only nearest neighbor interactions are important. This model is equivalent to the Ising model in magnetism, but there are some slight differences.

The dipoles in the simple Ising model are assumed to orient either parallel or antiparallel to the applied field. The water molecules in the inner layer may orient such that their dipole moments form an oblique angle to the electric field within the layer. This may occur if the water molecule bonds to the metal surface through one of the hydrogen atoms or through one of the lone pair orbitals on the oxygen atom. The components of the polarization parallel to the metal surface are assumed to cancel, but the normal component of the dipole moment may be different for the two different orientations.

The interaction between the water molecule and the metal surface is more complicated than that for a point dipole in an external field. Due to the proximity of the metal surface image forces may also be important. If these are different for the two orientations they will play an important role.

Since the two state approximation for the inner layer is equivalent to the Ising model, it is possible to use some of the many approximations developed for the Ising model to include the effects of local order in the inner layer model.
To include some of the differences between the inner layer and the simple Ising model, it is necessary to redevelop the approximations and use more than the final results.

C. The Triangular Lattice

Treating the effects of local order properly when the water molecules are assumed to occupy a triangular lattice requires some care. Mean-field theory considers an average interaction between a molecule and its nearest neighbors based upon the average orientation of the molecules. The simplest approximation that includes local order is the Bethe (31) or quasi-chemical (32) approximation. Interactions between a molecule and its nearest neighbors are exactly treated, but interactions between molecules in the nearest neighbor shell are ignored. This approximation does not treat the triangular lattice correctly since there are nearest neighbor pairs within the nearest neighbor shell of any molecule. To treat the triangular lattice properly it is important to consider nearest trios of molecules, since each is a nearest neighbor of the others.

Kikuchi (33) proposed a simple closed form approximation to treat the Ising model, which can be used to include the effects of local order in the two state approximation for the inner layer. This approximation was originally given to treat a disordered or ferromagnetically ordered system of magnetic
dipoles in an external field. Burley (34) extended the approximation to treat antiferromagnetic ordering. I will only use the simple result for a disordered system, but will generalize some of the equations to treat aspects needed for the inner layer.

The triangular lattice is treated in the Kikuchi method by considering the probability of how single sites, nearest neighbor pairs of sites, and nearest trios of sites (triangles) are occupied by the water molecules. A single site can be occupied by a molecule with its normal dipole moment directed either away from the metal, an up orientation, or into the metal, a down orientation. The probability that the site is occupied by a molecule in one of these orientations is denoted by $x_u$ or $x_d$. Since each site must be occupied $x_u + x_d = 1$. There are three possibilities for a pair of sites. Two, one, or zero sites of the pair are occupied by a molecule in the up orientation. These probabilities are denoted by $y_{uu}$, $y_{ud}$, and $y_{dd}$ respectively. There are four possibilities for a nearest neighbor trio of sites. Three, two, one or zero of the sites are occupied by a molecule in the up orientation. These probabilities are given by $z_{uuu}$, $z_{uud}$, $z_{udd}$, and $z_{ddd}$. These probabilities are not independent. All of the probabilities may be expressed in terms of the probabilities on the nearest neighbor triangles. These relationships are summarized in Table 1.
Table 1. Relationships between the probabilities for the triangular lattice

<table>
<thead>
<tr>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>zuuu + zuud = yuu</td>
</tr>
<tr>
<td>zuud + zudd = yud</td>
</tr>
<tr>
<td>zudd + zddd = ydd</td>
</tr>
<tr>
<td>yuu + yud = xu</td>
</tr>
<tr>
<td>yud + ydd = xd</td>
</tr>
<tr>
<td>xu + xd = 1</td>
</tr>
<tr>
<td>yuu + 2yud + ydd = 1</td>
</tr>
<tr>
<td>zuuu + 3zuud + 3zudd + zddd = 1</td>
</tr>
</tbody>
</table>

The free energy can be expressed using these probabilities and the state of the system can be determined by minimizing the free energy with respect to the configuration. The internal energy of the system can be written exactly in terms of these probabilities as

\[ U = N(xu \ V_u + xd \ V_d + 3yu \ V_{uu} + 6yu \ V_{ud} + 3ydd \ V_{dd}). \] (2.1)

\( N \) is the total number of sites; \( V_u \) and \( V_d \) are the interaction energies of the molecule with the metal surface; and \( V_{uu} \), \( V_{ud} \), and \( V_{dd} \) are the interaction energies for nearest neighbor pairs. Since only nearest neighbor interactions are included, the probabilities on the triangles do not enter the expression.

The probabilities on the triangles are used in the expression for the entropy. It is not possible to write an exact expression for the entropy. The configurational part of the entropy is approximated by
\[ S_c = kN \left[ 3yuu \ln(yuu) + 6yud \ln(yud) + 3ydd \ln(ydd) \\
-2zuuu \ln(zuuu) - 6zuud \ln(zuud) - 6zudd \ln(zudd) \\
-2zddd \ln(zddd) - xu \ln(xu) - xd \ln(xd) \right], \] (2.2)

where \( k \) is Boltzmann's constant.

In the simple Ising model, this is the only contribution to the entropy. It may not be adequate to only include the configurational entropy in a model for the inner layer. In bulk water, the motion of the molecules contributes significantly to the entropy. Effects due to the motion of the molecules have also been included in calculations of the entropy of the inner layer \((35, 36)\). These effects have not been included in calculations of the inner layer capacitance. If these kinetic contributions to the entropy do not depend upon the orientation of the molecule, they do not influence the configuration of the system. This will be assumed here and only the configurational entropy will be treated.

The free energy, \( F = U - TS \), can be found from Equations 2.1 and 2.2. This result can be written in terms of the probabilities on the triangles as
The probabilities zuuu, zuud, zudd, and zddd are not independent. The constraint, zuuu + 3 zuud + 3 zudd + zddd = 1, may be used to eliminate one further variable. The configuration of the system at equilibrium can then be found by minimizing this expression with respect to the remaining three variables. This procedure eventually leads to the following equations which determine the properties of the system.

\[
X = t^3 \frac{((1 + r)/(t^2 + r))^3 (t^3 + 2 t r + r)/(t r + 2 r + 1)}{2} \quad (2.4)
\]

\[
r = \frac{1}{2} [(t^2 + 1)^2 - 4(t^2 - t(1 + t)^2 z^2)] \quad (2.5)
\]

\[
X = \exp((V_d - V_u + 3 (V_d - V_u))/kT) \quad (2.6)
\]

\[
z = \exp((V_u + V_d - 2V_u)/kT) \quad (2.7)
\]

The variables t and r are defined by \( t = zuud/zudd \) and \( r = zudd/zddd \). Using these definitions, the constraint condition \( zuuu + 3 zuud + 3 zudd + zddd = 1 \), and the relationship \( zuuu = (zuud/zudd)^3 \) (this result is derived during the
minimization of the free energy) it is possible to express
the probabilities on the triangles in terms of $t$ and $r$.

\begin{align}
\text{zuuu} &= t^3 \text{zddd} \\
\text{zuud} &= t \ r \ \text{zddd} \\
\text{zudd} &= \ r \ \text{zddd} \\
\text{zddd} &= (t^3 + 3 \ t \ r + 3 \ r + 1)^{-1}
\end{align}

Equations 2.4 through 2.11 determine the configuration of
the inner layer. To use these equations, it is necessary to
assume specific values for the potentials $V_u$, $V_d$, $V_{uu}$, $V_{ud}$,
and $V_{dd}$. Then $z^2$ is a constant determined by the form of
the pair interaction potentials. It is easiest to choose a
value for $t$ and solve for the other quantities. Since $t$ is
defined as $t = \text{zuud}/\text{zudd}$, the ratio of two probabilities, $t$
may take on values from zero to infinity. For a given $t$,
Equations 2.4 - 2.6 may be used to obtain the potentials $V_d$ $V_u$.

These potentials will depend upon the electric field
within the layer in an as yet unspecified fashion. Equations
2.5 and 2.8 through 2.11 determine the orientation of the
molecules in the layer. The relationships in Table 1 can be
used to get the probabilities for pairs of sites and single
sites. To compare with capacitance measurements the most
important of these quantities is the contribution of the
permanent dipoles to the polarization of the inner layer. This is given by

\[ P = N (xu pu - xd pd), \]
\[ = N \frac{pu (t^3+2 t r+r)-pd (t r+2 r+l)}{(t^3+3 t r+3 r+1)}; \]

(2.12)

where \( pu \) and \( pd \) are the components of the dipole moment normal to the metal surface for molecules in the up and down orientations.

To most clearly see how the effects of local order and the geometry of the underlying lattice affect the differential capacitance of the inner layer, it is best to consider the simplest possible system. This simplification will be considered after the general results for the square lattice and the mean-field cases are developed.

D. The Square Lattice

If the water molecules in the inner layer are assumed to occupy a square lattice, the effects of local order may be included using the Bethe (31) or quasi-chemical (32) approximation. The Kikuchi (33) method is equivalent to these methods if only the probabilities for single sites and pairs of sites are included.

The calculation of the configuration of the molecules in the inner layer is similar to that used to treat the triangular lattice. The internal energy of the system can be written as
\[ U = N \left( x_u V_u + x_d V_d + 2 y_{uu} V_{uu} + 4 y_{ud} V_{ud} + 2 y_{dd} V_{dd} \right). \] (2.13)

The probabilities and potentials have the same meaning as in the preceding section. The expression for the internal energy differs from that when the molecules occupy a triangular lattice (Equation 2.1) due to the different number of nearest neighbors for the two different lattices.

The configurational entropy is approximated by

\[ S_C = 4 \left( x_u \ln(x_u) + x_d \ln(x_d) \right) - 2 y_{uu} \ln(y_{uu}) - 4 y_{ud} \ln(y_{ud}) - 2 y_{dd} \ln(y_{dd}). \] (2.14)

This result may be combined with Equation 2.13 to obtain an expression for the free energy of the system. The relationship between the probabilities on the single sites and on the pairs of sites is the same as in the triangular lattice case. The relationships of Table 1 may be used to write the free energy in terms of the probabilities for the nearest neighbor pairs as

\[ F = N \left[ \left( y_{uu} + y_{ud} \right) V_u + \left( y_{ud} + y_{dd} \right) V_d + 2 y_{uu} V_{uu} + 4 y_{ud} V_{ud} + 2 y_{dd} V_{dd} \right. \]

\[ + 2 kT \left( y_{uu} \ln(y_{uu}) + 2 y_{ud} \ln(y_{ud}) + y_{dd} \ln(y_{dd}) \right) \]

\[ - 3 kT \left( \left( y_{uu} + y_{ud} \right) \ln(y_{uu} + y_{ud}) + \left( y_{ud} + y_{dd} \right) \ln(y_{ud} + y_{dd}) \right) \]. \] (2.15)

The constraint, \( y_{uu} + 2 y_{ud} + y_{dd} = 1 \), may be used to eliminate one more variable. Minimization of the resulting
expression for the free energy with respect to the remaining
two variables determines the configuration of the system at
equilibrium. This procedure eventually leads to

$$X = t \left( \frac{(1 + t z)}{(t + z)} \right)^3,$$  \hspace{1cm} (2.16)

$$X = \exp\left(\frac{(V_u - V_d + 2 (V_{uu} - V_{dd})}{kt}\right),$$  \hspace{1cm} (2.17)

$$z = \exp\left(\frac{(V_{uu} + V_{dd} - 2V_{ud})}{kT}\right).$$  \hspace{1cm} (2.18)

The variable $t$ is defined as $t = \frac{y_{ud}}{(y_{uu} z)}$. Using this
definition, the constraint $y_{uu} + 2 y_{ud} + y_{dd} = 1$, and the
relationship $z^2 = \frac{y_{ud}^2}{(y_{uu} y_{dd})}$ the probabilities for the
pairs may be written in terms of $t$ as

$$y_{uu} = \left(1 + 2 t z + t^2\right)^{-1},$$  \hspace{1cm} (2.19)

$$y_{ud} = t z y_{uu},$$  \hspace{1cm} (2.20)

$$y_{dd} = t^2 y_{uu}.$$  \hspace{1cm} (2.21)

The expression $z^2 = \frac{y_{ud}^2}{(y_{uu} y_{dd})}$ is found during the
minimization of the free energy and is recognizable as the
approximation used in the quasi-chemical method. The part of
the polarization due to the permanent dipoles may be found
with the help of the relationships of Table 1 as

$$P = N \left( \frac{p_u (1 + t z) - p_d (t z + t^2)}{(1 + 2 t z + t^2)} \right).$$  \hspace{1cm} (2.22)
As in the case of the triangular lattice, it is easiest to choose a value for $t$ and then solve for the other quantities.

E. Mean-Field Theory

Mean-field theory is insensitive to the geometry of the assumed underlying lattice. Only the product of the interaction strength and the number of nearest neighbors enters the calculation. In using the Kikuchi method, only the effects due to the probabilities on single sites and only the interaction of a molecule with the average orientation of its neighbors are considered. The internal energy is approximated by

$$U = N(x_u V_u + x_d V_d + \frac{s x_u}{2} (x_u V_{uu} + x_d V_{ud}) + \frac{s x_d}{2} (x_u V_{ud} + x_d V_{dd}) .$$  \hfill (2.23)

The number of nearest neighbors is given by $s$ (6 for the triangular lattice and 4 for the square lattice). The configurational entropy is approximated by

$$S_c = -N k (x_u \ln(x_u) + x_d \ln(x_d)) .$$  \hfill (2.24)

Since $x_u + x_d = 1$, it is possible to eliminate one of these variables from Equations 2.23 and 2.24. Agreement with the usual form of the mean-field theory can be obtained by replacing $x_u$ and $x_d$ with the combination $p = x_u - x_d$. In the simple Ising model, $p$ is proportional to the polarization.
Substituting $p$ into Equations 2.23 and 2.24 and combining them to obtain the free energy gives

$$F = N \left[ \frac{(1+p)}{2}V_u + \frac{(1-p)}{2}V_d + s\frac{(1+p)}{8}((1+p)V_{uu} + (1-p)V_{ud}) + s\frac{(1-p)}{2}((1+p)V_{ud} + (1-p)V_{dd}) \right. \\
+ \left. \frac{kT}{2}[(1+p)\ln\frac{(1+p)}{2} + (1-p)\ln\frac{(1-p)}{2}] \right]. \quad (2.25)$$

The configuration of the system may be found by minimizing Equation 2.25 with respect to $p$. This procedure gives

$$V_u - V_d + \frac{s}{2}(V_{uu} - V_{dd}) + \frac{sp}{2}(V_{uu} + V_{dd} - 2V_{ud}) + kT \ln\left[\frac{1+p}{1-p}\right] = 0. \quad (2.26)$$

The potentials are most easily found by choosing values of $p$ ($p$ ranges from $-1$ to $+1$). The contribution of the permanent dipoles to the polarization of the inner layer is given by

$$P = \frac{N}{2}(pu(1+p) - pd(1-p)). \quad (2.27)$$

F. Simplifications to Obtain Capacitance Curves

To compare the capacitance curves for the inner layer, it is necessary to choose specific forms for the potentials $V_u$, $V_d$, $V_{uu}$, $V_{ud}$, and $V_{dd}$ and to specify the orientation of the water molecule in its two assumed states. To show clearly the effects due to the inclusion of local order and due to the
geometry of the underlying lattice, it is wise to make the model as simple as possible.

I will make the following assumptions:

1. The molecule orients such that its dipole moment is normal to the metal surface.

2. Interactions between the water molecules, except for the electrostatic interaction with the charge on the metal surface, will be assumed to be the same for both orientations of the molecule.

3. The interactions between a pair of molecules in the up orientation is the same as for a pair of molecules in the down orientation ($V_{uu} = V_{dd}$).

4. The molecules are nonpolarizable.

Assumption no. 4 may seem drastic and this assumption would not be made if the model calculations were being compared to experimental results. Effects due to the polarizability of the molecules do not change the basic shape of the differential curve. This is evident from inspection of the equations that give the differential capacitance and the charge density on the metal surface.

\[ C = \left( \frac{1}{4\pi} + \frac{dP}{dE} \right) / a \]  \hspace{1cm} (1.26)

\[ Q = E/4\pi + P \]  \hspace{1cm} (1.25)

The polarization due to the distortion of the molecules may be assumed to be proportional to the electric field in the
inner layer. Including this effect would simply add a constant term to the differential capacitance and a term proportional to E to the charge density.

The potential for the molecule can be taken as

\[ V_d = -V_u = \bar{p} E \]  \hspace{1cm} (2.28)

This result is a consequence of assumptions no. 1 and 2. E is the average electric field in the inner layer and \( \bar{p} = 1.85 \times 10^{-18} \) esu is the dipole moment of the water molecule.

When the interaction between parallel molecules is assumed to be the same \( (V_{uu} = V_{dd}) \), the interaction between neighbors appears only in the form \( 2V_{ud} - (V_{uu} + V_{dd}) \). The capacitance results will be shown for several different values of this expression to show the effects of different interaction strengths. In the mean-field theory, this expression is multiplied by the number of nearest neighbors. Since this is the only place where the number of nearest neighbors occurs in the mean-field calculation, the results for this case may be used for either the triangular or the square lattice.

Expressions for the electric field, E, the polarization, P, and the derivative of the polarization with respect to the electric field, dP/dE, are needed to find the inner layer capacitance. This may be done for each of the cases that has been considered.
The mean-field results are easy to obtain. Equation 2.26 can be used to find the electric field in the inner region. With the assumptions made here, this becomes

\[
E = \frac{1}{z \rho} \left( \frac{kT}{\rho} \ln \left( \frac{1+p}{1-p} \right) - 2s \rho J \right). \tag{2.29}
\]

\(J\) is defined as

\[J = \frac{(2V_{ud} - (V_{uu} + V_{dd}))}{4}. \tag{2.30}\]

The polarization of the molecules in the inner layer becomes

\[P = N \rho \rho. \tag{2.31}\]

The term \(dP/dE\) can be found by differentiating Equation 2.29. The result is

\[
\frac{dP}{dE} = \frac{N \rho^2 (1-p^2)}{kT - sJ(1-p)^2}. \tag{2.32}
\]

Equations 2.29 through 2.32 give the electric field, polarization, and the derivative of the polarization with respect to the electric field written as functions of the parameter \(p\). This is the most convenient form of these equations for obtaining the differential capacitance curve. Equation 2.29 can also be rearranged to give the form generally seen in the mean-field theory

\[p = \tanh \left( \frac{\rho E}{kT} + \frac{psJ}{kT} \right). \tag{2.33}\]
The relationships needed to include local order on the square lattice are slightly more complicated. Equation 2.16 can be solved to give the electric field in the inner region,

\[ E = \frac{kT}{2p} \ln \left[ \frac{1}{t + \frac{z}{1 + tz}} \right]^3, \]  

(2.34)

where

\[ z = \exp(-2J/kT). \]  

(2.35)

Equation 2.35 is obtained from Equation 2.18 and the definition of \( J \) used in the mean-field calculation, Equation 2.30. The polarization given in Equation 2.22 simplifies to

\[ P = N\bar{p}(1 - t^2)/(1 + 2tz + t^2). \]  

(2.36)

d\( P/dE \) can be gotten by differentiating Equations 2.34 and 2.36 with respect to \( E \). This gives

\[ \frac{dP}{dE} = -2N \bar{p} \frac{(2t + z + zt^2)}{(t^2 + 2tz + 1)} \frac{dt}{dE}, \]  

(2.37)

where

\[ \frac{dt}{dE} = \frac{2\bar{p}}{kT} \left[ \frac{2t - z}{t(t + z)} - \frac{3z}{1 + tz} \right]^{-1}. \]  

(2.38)

Equations 2.34 through 2.38 express all of the quantities needed to find the capacitance curves as functions of \( t \).
It is possible to obtain the necessary relationships for the triangular lattice case also. The electric field in the inner layer can be gotten from Equation 2.4.

\[ E = \frac{kT}{2p} \ln \frac{t^3(1+r)^3(t^3+2tr+r)}{(t^2+r)^3(tr+2r+1)} \]  (2.39)

Equation 2.5 can still be used to find \( r \) with \( z = \exp(-2J/kT) \). Equation 2.12 simplifies to

\[ p = Np \frac{t^{3+tr-r-1}}{t^3+3tr+3r+1} \]  (2.40)

The term \( \frac{dP}{dE} \) can be gotten by differentiating Equations 2.5, 2.39, and 2.40 with respect to \( E \) and solving the resulting equations for \( \frac{dP}{dE} \). The final expression for \( \frac{dP}{dE} \) is complicated and it will not be given here. Instead, this expression will be given in Table 2 which is a summary of all the equations needed to find the differential capacitance curves.

Table 2. Equations used to obtain the capacitance curves

<table>
<thead>
<tr>
<th>General results</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C = (1/4\pi + \frac{dP}{dE})a ) \hspace{1cm} (1.26)</td>
</tr>
<tr>
<td>( Q = E/4\pi + P ) \hspace{1cm} (1.25)</td>
</tr>
<tr>
<td>( J = (2Vud - (Vuu + Vdd))/4 ) \hspace{1cm} (2.30)</td>
</tr>
<tr>
<td>( z = \exp(-2J/kT) ) \hspace{1cm} (2.35)</td>
</tr>
</tbody>
</table>
Table 2 (Continued)

Mean-field theory

\[ E = \frac{1}{2p} \left[ kT \ln \left( \frac{1+p}{1-p} \right) - 2spJ \right] \] (2.29)

\[ P = Npp \] (2.31)

\[ \frac{dP}{dE} = \frac{N \bar{p}^2 (1-p^2)}{kT - sJ (1-p^2)} \] (2.32)

The number of nearest neighbors is given by \( s \). These equations can be used to obtain the differential capacitance curve by choosing a set of values for \( p \), where \(-1 \leq p \leq +1\).

Square lattice (with local order included)

\[ E = \frac{kT}{2p} \ln \left[ \frac{(z+t)^3}{t(1+tz)} \right] \] (2.34)

\[ P = \bar{N} \frac{1-t^2}{1+2tz+t^2} \] (2.36)

\[ \frac{dP}{dE} = -2N \bar{p} \left( \frac{2t + z + zt^2}{t^2 + 2tz + 1} \right) \frac{dt}{dE} \] (2.37)

\[ \frac{dt}{dE} = \frac{2p}{kT} \left[ \frac{2t - z}{t(t+z)} - \frac{3z}{1+tz} \right]^{-1} \] (2.38)
These equations can be used to find the differential capacitance curve by choosing a set of values for \( t \), where \( 0 \leq t < \infty \).

**Triangular lattice (with local order included)**

\[
E = \frac{kT}{2p} \ln \left[ \frac{t^3(1+r)^3(t^3+2tr+r)}{(t^2+r)^3(tr+2r+1)} \right] \tag{2.39}
\]

\[
P = N\overline{p} \frac{t^3+3r-r-1}{t^3+3tr+3r+1} \tag{2.40}
\]

\[
r = \frac{1}{2} \left[ ((t^2+1)^2 - 4(t^2 - t(1+t)^2 z^2))^{1/2} - 1 - t^2 \right] \tag{2.5}
\]

\[
\frac{dP}{dE} = \frac{(N\overline{p}-P)3t^2 + (N\overline{p}-3P)r}{t^3+3tr+3r+1} \frac{dt}{dE}
\]

\[
+ \frac{(N\overline{p}-3P)t - (N\overline{p}+3P)}{t^3+3tr+3r+1} \frac{dr}{dE} \tag{2.41}
\]

\[
\frac{dr}{dE} = \frac{(3t^2+4t+1)z^2 - 2t(1+r)}{t^2+2r+1} \frac{dt}{dE} \tag{2.42}
\]

\[
\frac{dt}{dE} = \frac{2p}{kT} \left[ \frac{3}{t} - \frac{6t}{t^2+r} + \frac{3t^2+2r}{t^3+2tr+r} - \frac{r}{tr+2r+1} \right.
\]

\[
\left. + \left\{ \frac{3}{1+r} - \frac{3}{t^2+r} + \frac{2t+1}{t^3+2tr+r} - \frac{t+2}{tr+2r+1} \right\} \left[ \frac{(3t^2+4t+1)z^2 - 2t(1+r)}{t^2+2r+1} \right]^{-1} \right] \tag{2.43}
\]
The differential capacitance can be determined from these equations by choosing a set of values for $t$, where $0 \leq t < \infty$.

G. Capacitance Results and Discussion

The calculated inner layer differential capacitance with only mean-field effects included is shown in Figure 1. Due to the simplicity of the model, the differential capacitance curve is symmetric about zero charge on the metal. Several different values of the interaction strength are considered. For comparison, simple electric dipole-dipole interactions would give an interaction strength of $J/kT = -2.8$, for a 3.1 Å separation of the molecules at room temperature.

The capacitance is largest for $Q = 0$ and remains relatively constant until the charge on the metal becomes large. Then saturation occurs and the differential capacitance decreases drastically. Increasing the interaction strength does not qualitatively alter these results. The stronger interactions make it more difficult to polarize the inner layer and the differential capacitance decreases.

The rapid decrease in the capacitance due to dielectric saturation occurs at about the same value of the charge density
Figure 1. The inner layer capacitance curve calculated using mean-field theory. The inner layer thickness is 3 Å and $N = 10^{15}$ cm$^{-2}$. The interaction strengths are $sJ = -0.6$ kT (curve A), $sJ = -1.8$ kT (curve B), and $sJ = -4.2$ kT (curve C).
on the metal surface for any value of the interaction strength. This happens because the polarization of the inner layer is the dominant term in the expression for the charge on the metal surface,

\[ Q = \frac{E}{4\pi} + P. \]  

(1.25)

Saturation effects depend only upon the contribution of the permanent dipoles to the polarization. If the induced polarization of the inner layer were also included in the calculation, the charge density at which saturation becomes important would change more as the interaction strength is changed.

Figure 2 shows the differential capacitance that results if the water molecules are assumed to occupy a square lattice and local order is included in the calculation. For small values of the interaction strength the capacitance curve is nearly identical to that calculated using mean-field theory. For no interactions the two methods become identical. Important differences occur for larger values of the interaction strength. Instead of being maximum for \( Q = 0 \), the differential capacitance shows a local minimum at this value. The depth of this minimum increases as the interaction strength becomes larger. The differential capacitance grows for larger charge densities on the metal surface and then decreases at still higher charge densities due to saturation effects.

The minimum in the differential capacitance at \( Q = 0 \) is caused by a stable arrangement of the molecules that can not
Figure 2. The inner layer capacitance curve for the square lattice with local order included using the Kikuchi method. The thickness and the density are the same as in Figure 1. The interaction strengths are $J = -0.15 \text{ kT}$ (curve A), $J = -0.45 \text{ kT}$ (curve B), and $J = -1.05 \text{ kT}$ (curve C)
be obtained by simple mean-field methods. At zero polarization it is possible to arrange the molecules such that each one is antiparallel to its nearest neighbors. This arrangement is shown in Figure 3. Since the mean-field approximation assumes that only the average orientation of the molecules is important, effects due to an arrangement such as this are not accounted for. This could be considered using mean-field methods by dividing the lattice into two sub-lattices.

The method used to treat the square lattice also does not assume the presence of long range order as shown in Figure 3. But the inclusion of local order in the calculation allows for configurations of the molecules such that each is preferentially surrounded by neighbors with the opposite orientation. The Kikuchi method nicely shows how the number of these favorably interacting pairs depends upon the strength of the interactions. The probability that a pair of molecules are in opposite orientations is given by 2 yud. At zero net orientation of the molecules this probability becomes

\[ 2 \text{yud} = \frac{2 z}{1 + 2 z}, \quad (2.41) \]

where z is given by Equation 2.35. The behavior of this probability is shown in Figure 4. At zero interaction strength two-thirds of the pairs are in opposite orientations. This is the result predicted for the simple mean-field theory regardless of the interaction strength. As the interaction strength
Figure 3. The arrangement of the molecules on the square lattice that gives the maximum number of favorably orientated pairs. The open circles represent molecules orientated in one direction, while the filled circles represent molecules oriented in the opposite direction.
Figure 4. The probability that a pair of molecules is anti-parallel at zero net polarization of the inner layer.
is increased, the value for this probability approaches one, indicating that nearly all of the molecules assume favorable orientations with their neighbors. To polarize the inner layer it is necessary to break up these stable pairs. As the interaction strength is increased there are more of these pairs and they become more tightly bound. Thus, it becomes much harder to polarize the system and the differential capacitance shows a minimum.

It might be expected that including local order would change the capacitance results predicted for the triangular lattice in about the same manner as the capacitance for the square lattice was changed. Figure 5 shows the predicted inner layer differential capacitance when the water molecules are assumed to occupy a triangular lattice. For small interaction strengths, the results are nearly equal to the two other cases considered. For larger interaction strengths, the predicted capacitance differs qualitatively from both the square lattice result and the mean-field theory prediction.

The reasons for these differences are the local arrangement of the molecules and the geometry of the underlying lattice. It is not possible for each molecule on a triangular lattice to orient in the direction opposite to that of its nearest neighbors. The best that can occur is for four of the nearest neighbors to be favorably oriented (anti-parallel). This is best illustrated by considering a
Figure 5. The inner layer capacitance curve for the triangular lattice with local order included using the Kikuchi method. The thickness and the density are the same as in Figure 1. The interaction strengths are $J = -0.3 \, kT$ (curve A), $J = -0.6 \, kT$ (curve B), and $J = -1.0 \, kT$ (curve C).
configuration of the molecules that shows long range order. In Figure 6, only the orientations of two-thirds of the molecules are specified. This configuration shows the maximum net number of favorable bonds. The orientations of the molecules on the other sites do not change this number. So at zero polarization the orientations of the molecules on these sites will be random. As the charge on the metal is increased the molecules on these sites are free to align with the field. But as the system approaches one-third of maximum polarization, nearly all of these molecules will be aligned with the field and partial saturation occurs. To polarize the inner layer further, it becomes necessary to reduce the number of favorably oriented pairs. This explains why the differential capacitance shows a maximum at zero charge, a minimum for larger charges (which occurs at about one-third polarization) followed by another increase and a further decrease due to saturation as the inner layer becomes totally polarized. The calculation done for the triangular lattice does not consider long range order, but effects due simply to local order are sufficient to produce this behavior.

The results shown in this section indicate that including local order in the calculation of the inner layer differential capacitance can produce large changes. These effects could not be reproduced in a mean-field calculation by simply changing some of the parameters. The effects of local order
Figure 6. The arrangement of the molecules on the triangular lattice that gives the maximum number of favorably oriented pairs. The open circles represent molecules oriented in one direction, while the filled circles represent molecules oriented in the opposite direction. The orientations of the molecules on the remaining sites do not change the number of favorably orientated pairs.
become significant for small values of the interaction strength. Thus, any theory that assumes only mean-field theory but uses strong interactions, such as dipole-dipole interactions, is suspect. It is also evident that unless the interactions are weak, the geometry of the assumed lattice is important.
III. FIT TO EXPERIMENTAL CAPACITANCE

A. The Thickness of the Inner Layer

In order to use the two state model of water molecules occupying a triangular lattice presented in section II to analyze the inner layer capacitance for mercury electrodes, it is necessary to introduce one more assumption in the model. The simple model of section II predicts a differential capacitance curve that is symmetric about zero charge. The experimentally inferred inner layer capacitance is much larger for positive charges on the metal than for negative charges. This effect can be obtained using the inner layer model if the thickness of the inner layer is allowed to vary as the charge on the metal surface is changed.

Changes of the inner layer thickness have been considered in other models (8, 20). These thickness changes have been treated as compression of the water molecules due to the large electric fields in the inner region. Since water is nearly incompressible, these electrostriction effects become important only for large charge densities on the metal surface. The predicted compression does not depend upon the sign of the charge on the metal. A different form of thickness change is required to fit the experimental inner layer capacitance.

The thickness of the inner layer has usually been assumed to equal the diameter of a water molecule. This quantity is
determined by the density of bulk water. The inner layer thickness should be regarded as the distance between the metal surface and the closest ions in the electrolyte. This quantity may be slightly different from a water molecule's diameter and may depend upon the orientation of the water molecules in the inner region.

The interaction of a single water molecule and a metal surface has been theoretically studied. The calculations done for a mercury surface have been totally classical (37, 38). Some simple quantum mechanical calculations (LCMO) have been done to study the interaction between a water molecule and a platinum surface (39, 40). These calculations indicate that both the interaction strength and the equilibrium separation of the metal surface and the water molecule depend upon the orientation of the water molecule. Unequal separations between the water molecule and the metal due to the orientation of the water molecule can produce changes in the inner layer thickness that are different from simple compression.

The thickness of the inner region also depends upon the arrangement of the water molecules in the inner layer and the ions adjacent to the layer. Figure 7 shows a possible geometry where the thickness of the inner layer appears to be larger for cations adjacent to it than for anions. If these arrangements are favored by the ions, then the inner layer thickness changes as the charge on the metal is varied. These arguments
Figure 7. An arrangement where the thickness of the inner layer is less for anions nearest to the metal surface than for cations.
indicate that the effective thickness of the inner layer may depend upon the net orientation of the water molecules. The simplest possible dependence is that the change in the inner layer thickness is proportional to the net orientation of the water molecules in the inner layer. If this assumption is included in the model, it becomes possible to obtain good agreement between the calculated differential capacitance and the experimentally inferred result.

B. The Inner Layer Model

The basic assumptions about the model used to fit the measured inner layer capacitance have been given in the preceding sections. These will be repeated here for clarity. Some minor changes will be made in some of these assumptions.

The inner layer is assumed to be a single close packed layer of water molecules. The water molecules are assumed to orient such that the dipole moments point either into or away from the metal surface. The interactions between nearest neighbors are treated using the Kikuchi approximation.

The potential difference across the inner layer is given by

$$V = \alpha E.$$  \hfill (1.24)

The thickness of the inner layer is assumed to vary as

$$a = a_0 + a_1 (x_u - x_d).$$ \hfill (3.1)
The parameters $a_0$ and $a_1$ will be chosen to fit the experimental inner layer capacitance curve. The probabilities $x_u$ and $x_d$ were defined earlier, so $x_u - x_d$ gives the net orientation of the water molecules.

The relationship between the charge density of the metal and the electrostatic parameters of the inner layer is

$$Q = \frac{E}{4\pi} + P. \quad (1.25)$$

There are two contributions to the polarization of the inner region. The contribution due to the induced dipoles, which was ignored in section II will be included here. Calculations of the dielectric response of a bulk polar fluids show that the local field is enhanced by a factor $3\varepsilon/(2\varepsilon + 1)$. It is difficult to properly calculate the local field in the inner layer, so the bulk cavity field enhancement will be used instead. Since the dielectric constant in the inner layer is about 10, the $3\varepsilon/(2\varepsilon + 1)$ factor can be approximated by $3/2$. The polarization due to the induced dipoles is written as

$$P_{\text{ind}} = \frac{3}{2} N \alpha E, \quad (3.2)$$

where $\alpha = 1.44 \times 10^{-24}$ cm$^3$ is the polarizability of a water molecule.

The part of the polarization due to the orientation of the permanent dipoles is treated using the Kikuchi approximation for the triangular lattice. The interaction between
parallel molecules is assumed to be independent of the orientation of the pair. Then, interactions between the molecules only occurs in the term

\[ J = 2 \left( V_{ud} - (V_{uu} + V_{dd}) \right). \] (2.29a)

This term will be adjusted to fit the measured inner layer capacitance. The cavity field enhancement also affects the energy of the single molecules interacting with the metal surface. Therefore, the potentials \( V_u \) and \( V_d \) are written as

\[ V_d = -V_u = \frac{3}{2} p_o E, \] (3.3)

where \( p_o = 1.85 \times 10^{-18} \) esu is the dipole moment of the free water molecule. The expression used to find the electric field in the inner layer is slightly changed by the inclusion of the cavity field enhancement. The equation used to find the electric field becomes

\[ E = \frac{kT}{3p_o} \ln \left[ \frac{t^3(1+r)^3(t^3+2tr+r)}{(t^2+r)^3(tr+2r+1)} \right], \] (3.4)

where

\[ r = \frac{1}{4} \left( \left( t^2 + 1 \right)^2 - 4(2 - t(1 + t)^2 \ z^2) \right)^{1/2} - 1 - t^2 \] (2.5)

and

\[ z = \exp(-2J/kT). \] (2.33)
Calculations of the dielectric constant for bulk water indicate that the molecules behave as if they possess an enhanced dipole moment due to the interactions with the other molecules (41). This effect will be assumed here and the polarization due to the orientation of the permanent dipoles is written as

\[ \bar{P} = N \bar{p} \frac{(t^3 + t r-r-1)}{(t^3 + 3 t r+3 r+1)}, \]  
(2.38)

where \( \bar{p} = 2.35 \times 10^{-18} \) esu.

The differential capacitance curve may be calculated using these equations. It is necessary to assume values for the parameters \( a_0, a_1, \) and \( J \). All of the equations depend upon the parameter, \( t \). For a range of this parameter the charge density and the potential drop across the inner layer can be found. The differential capacitance is found by numerically differentiating the expression for the charge with respect to the potential difference.

The density of molecules in the inner layer depends upon how the thickness of the inner layer changes. If the thickness of the inner layer changes due to a difference in the anion and cation bonding to the water molecules as shown in Figure 7, the density should be considered a constant. But if the inner layer thickness changes due to differences in the bonding of the water molecules to the metal surface, the density of the molecules depends upon the orientation of the molecules and
should be found from

\[ N = N_1/a, \]  

(3.5)

where \( N_1 \) is the number of molecules for a unit area and \( a \) is the thickness of the inner region. It is possible to obtain fits to the measured inner layer capacitance using either of these choices. The fit assuming the second choice shows smaller changes in the inner layer thickness and this choice will be used.

C. Low Temperature Results

Figure 8 shows the calculated inner layer capacitance at 0°C and the experimental results for water on mercury electrodes. The adjustable parameters were chosen using reasonable initial guesses and simple trial and error. The parameters used to obtain Figure 8 are \( a_0 = 3.3 \ \text{Å}, a_1 = -0.6 \ \text{Å}, \) and \( J = 0.925 \ \text{kJ}. \) These parameters are not a best fit to the experimental results but only a possible result. It is very possible that the fit to the experimental measurements could be improved by using a more sophisticated method for choosing the parameters or by more extensive trial and error.

This simple method of choosing the adjustable parameters is possible because the differential capacitance curve changes in reasonable and distinguishable ways as the various parameters are changed. The effect of changing the interaction
Figure 8. The inner layer capacitance curve at 0°C. The experimental values are from the work of Grahame (42). The parameters used in the theory are $a_0 = 3.3 \, \text{Å}$, $a_1 = -0.6 \, \text{Å}$, and $J = -0.925 \, kT$. 
strength was partially shown in Figure 5. Figure 9 shows how the fit to the experimental inner layer capacitance is changed if the interaction strength is varied.

Changing the constant term \( a_0 \) in the inner layer thickness produces only minor changes in the shape of the differential curve. However, this term does play an important role in determining the overall magnitude of the calculated result. The term \( a_1 \) does affect the shape of the differential capacitance curve. Figure 10 shows the dependence of the capacitance curve upon this parameter. The extremes of the inner layer thickness are included in Figure 10.

D. Higher Temperature Results

The inner layer capacitance for water on mercury electrodes has been measured over a wide temperature range. The model presented for the inner layer predicts the changes in the capacitance due to temperature variations at least qualitatively. The predicted inner layer capacitance at 45°C is shown in Figure 11. The results of the model calculation deviate slightly from the experimental capacitance if the parameters used to fit the 0°C are retained.

Thermal expansion should cause an increase in the inner layer thickness. It is also possible that thermal expansion could alter the interaction strength and the rate at which the inner layer thickness changes. An improved fit to the
Figure 9. The effect of changing the interaction strength on the capacitance curve. The parameters used are $a_0 = 3.3 \text{ Å}$, $a_1 = -0.6 \text{ Å}$, $J = -0.8 \text{ kT}$ (curve A), $J = -0.9 \text{ kT}$ (curve B), and $J = -1.0 \text{ kT}$ (curve C).
Figure 10. The effect of $a_1$ on the capacitance curve. The parameters used are $a_0 = 3.3 \, \text{Å}$, $J = -0.925 \, \text{kT}$, $a_1 = -1 \, \text{Å}$ (curve A), $a_1 = -0.4 \, \text{Å}$ (curve B) and $a_1 = 0 \, \text{Å}$ (curve C). The extremes of the inner layer thickness are indicated in the figure (in angstroms).
Figure 11. The inner layer capacitance curve at 45°C. The experimental values are from the work of Grahame (42). In curve A, the parameters are those that were used to fit the 0°C curve. The parameters in curve B are $a_0 = 3.33 \text{ Å}, a_1 = -0.8 \text{ Å},$ and $J = -0.875 kT$. 
experimental capacitance may be obtained by changing the adjustable parameters slightly. Figure 11 also shows an improved fit to the experimental capacitance obtained using \( a_o = 3.33 \text{ Å}, a_\perp = -0.8 \text{ Å}, \) and \( J = -0.875 \text{ kT} \).

The comparison between the experimental inner layer capacitance at 85°C and the model calculations is shown in Figure 12. The discrepancy between the experimental result and the calculation using the parameters chosen to fit the 0°C capacitance is greater than it was for the 45°C results. A better fit to the experimental capacitance may be obtained with the parameters \( a_o = 3.45 \text{ Å}, a_\perp = -1.0 \text{ Å}, \) and \( J = -0.825 \text{ kT} \). Even when the parameters are varied, the fit to the experimental results is not as good as the results at 0° and 45°C were.

E. Discussion

The simple model proposed here for the inner layer agrees with the experimentally inferred inner layer capacitance over most of the measured temperature range. The fit to the experimental results is not as good at 85°C as it is for lower temperatures. The best fits to the experimental capacitance are obtained by allowing the adjustable parameters of the model to change with temperature. An understanding of the sizes of the parameters needed to fit the experimental results and their temperature dependences requires a better understanding of the
Figure 12. The inner layer capacitance curve at 85°C. The experimental values are from the work of Grahame (42). In curve A, the parameters are those that were used to fit the 0°C curve. The parameters used in curve B are $a_0 = 3.45 \text{ Å}$, $a_1 = -1 \text{ Å}$, and $J = -0.825 \text{ kT}$.
interactions that occur in the inner layer.

The interaction strength used to fit the experimental capacitance is about one-third as large as would be predicted by electrostatic dipole-dipole interactions between the water molecules. This may indicate that interactions between the molecules in the inner layer and those adjacent to the inner layer may be important. A proper treatment of these interactions requires consideration of more than one layer of molecules.

The inner layer thicknesses needed to fit the experimental capacitance curves are similar to the diameter of a water molecule, but there are significant thickness changes as the charge on the metal varies. These thickness changes are similar to those shown by the contribution of the water molecules to the excess surface volume, $V^*$, calculated by Reeves (43) from the measurements of Hills and Payne (44). This comparison is shown in Figure 13. The excess surface volume is a thermodynamic quantity, which refers to the entire interface (not just the inner layer). The maximum in $V^*$ at $Q = -10 \ \mu\text{C/cm}^2$, may indicate that it is necessary to include thickness changes due to electrostriction in the model of the inner layer.
Figure 13. The inner layer thickness and $V^*$ as functions of the charge on the metal. Curve A is the inner layer thickness used to fit the $85^\circ$C capacitance curve. Curve B is the $0^\circ$C inner layer thickness. Curve C is the $V^*$ calculation at $25^\circ$C (shifted to match the $0^\circ$C inner layer thickness at $Q = 0$).
F. Comparison with Other Models

There have been several other semi-microscopic models (18, 22, 24) proposed for the inner layer, which also are able to reproduce (at least qualitatively) the water-mercury inner layer differential capacitance. The assumptions behind these models are quite different from those of the model that has been presented here.

These models all assume that the water molecules exist in the inner layer in two different ways. Some of the molecules are assumed to bind together to form small stable clusters. The rest of the molecules are treated individually. The clusters are assumed to have a smaller dipole moment than the individual water molecules. This is very different from the effect produced by clusters in bulk water. In bulk water, the clustering of the water molecules due to hydrogen bonding increases the dielectric constant of the liquid. The clustering in the inner layer reduces the dielectric constant of the inner layer.

The inner layer consists of individual water molecules and small clusters of molecules. The clusters are assumed to bind to the metal surface by a nonelectrostatic interaction. For small charges on the electrode most of the inner layer consists of the clusters. As the charge density on the metal surface is increased these clusters align with the field and saturation occurs. This causes the minimum in the differential
capacitance. As the charge density is increased the electric field becomes greater and it becomes favorable for the individual water molecules to replace the clusters in the inner layer. This occurs because the single molecules are assumed to have a larger dipole moment than the clusters. This switching from clusters to individual water molecules creates the increase in the differential capacitance at large charges on the metal surface.

There are several adjustable parameters in these theories. The most important of these are the dipole moment of the clusters and the additional interaction energy of the clusters with the metal surface.

The assumptions made in these "cluster" models are different but no better justified than some of the assumptions made in the model presented here. Since the experimental results may be reproduced using either kind of model, it is apparent that the ability of a model to fit the measured inner layer capacitance is not a sufficient test of its validity for describing the inner layer.

There are techniques being developed that may supplement the knowledge gained through differential capacitance measurements. Several spectroscopic methods may eventually be used to determine the microscopic arrangement of the molecules in the inner layer. It appears that it may be possible to remove the metal from the electrolyte without disturbing the part of
the solution adjacent to it (45, 46). This would make it possible to use vacuum surface techniques to analyze the structure of the inner layer.

Studies of the adsorption of small amounts of water on metal surfaces will also clarify some of the assumptions used in models of the inner layer. Recent studies of the vibrational spectrum of water adsorbed on platinum (47, 48) have been interpreted as showing that even for very low coverages the water molecules arrange into clusters that resemble the structure of bulk water. This indicates that the structure of the inner layer might more closely resemble the structure of bulk water than any of the structures assumed in models of the inner layer.

A more complete understanding of the metal-electrolyte interface will require incorporating what is learned from these techniques into the models of the interface and especially the inner layer.
IV. REFERENCES


