COMPARISON OF TWO RECENT APPROACHES TOWARDS A UNIFIED THEORY OF THE ELECTRICAL DOUBLE LAYER

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Abstract—A theory of the electrical double layer recently proposed by Cooper and Harrison is compared to earlier, mainly lattice gas results. Detailed comparison of the Cooper–Harrison and lattice gas approaches reveals striking similarities as well as important differences. In both cases the charge density in the inner layer is derived from an effective potential. This potential is determined self-consistently as a function of the applied potential and the charge density itself. Close examination shows that the self-consistency equations are nearly identical. The main differences between the two approaches are the somewhat doubtful expression employed by Cooper and Harrison for the "cut-off" radius for ion–ion interactions, and the much greater generality of the earlier theory.

INTRODUCTION

In a paper, "The Role of Ion–Ion Interactions in the Electrical Double Layer: Symmetrical Electrolytes Containing Equal Size Ions", recently published in this journal, Cooper and Harrison (CH) have proposed a model of the electrolyte double layer which attempts to unify inner and diffuse layer treatments[1]. As CH state, a series of papers which also involve a unified approach to the same equilibrium double layer problem[2–7] were available at the time their work was carried out. Since then, two more in this series have appeared[8, 9]. These papers involve a lattice gas approximation for double layer ions and solvent molecules. Cooper and Harrison elected not to discuss this earlier work or compare it with theirs on the basis that they planned to do so in a later paper.

One of the authors of the present work (JRM) was a reviewer for another journal of an earlier (nearly identical) version of the CH paper and provided a long review and comparison of the two approaches in the summer of 1983. Rather than wait for the comparison promised by CH, we feel it useful to provide one based on our own points of view, drawing heavily on the review mentioned above.

Before giving a detailed comparison of some of the differences between the two approaches, we should mention some very important common features. Both theories assume that the ionic charge distribution can be described in terms of a single particle model with an effective potential which accounts for the ion–ion interactions. In view of the complexity of the situation it is difficult to avoid this assumption, but it remains a very considerable simplification. Both approaches also concentrate on the variation in charge density and potential perpendicular to the electrode and implicitly or explicitly average over variation parallel to the electrode. Finally, both theories attempt to provide a direct comparison with experiment by calculating quantities such as the differential capacitance of the system.

THE LATTICE GAS APPROACH

The main apparent difference between the approaches is the lattice gas approximation used in the earlier work. Since the actual system is usually a liquid, it is worth briefly discussing the rationale of this assumption. It requires that the double layer half space be divided into a regular lattice of points (simple cubic for simplicity) with separation usually based on h.c.p. or f.c.c. packing of spheres of the diameter of the solvent molecules. Every lattice point is taken to be occupied by either a solvent molecule (water usually assumed) or a positive or negative ion. Thus the double layer region may be dissected into layers parallel to the electrode interface. Such layering is a feature of both the CH and the earlier treatments. The primary function of the lattice gas approach is to ensure that particles cannot come nearer to one another than the sum of their hard-sphere radii. Thus, the lattice gas model ensures that there is a distance of closest approach and a corresponding realistic upper limit for the ionic concentration in any layer, a feature missing in the classical Gouy–Chapman diffuse double layer theory[10, 11].

Cooper and Harrison make a somewhat different assumption (to be discussed later) to try to ensure a limiting maximum ionic concentration. Although CH suggest that the lattice gas approach involves the introduction of extra parameters for which there is no direct experimental evidence available, this is not in fact the case. No more parameters enter the theory than there are in the CH approach, and CH must make additional, not necessarily physically reasonable, assumptions in their work which are obviated by the lattice treatment. Further, even though a lattice assumption is clearly an approximation for a liquid, particularly in regard to long range order, lattice gas treatments of the liquid state have led to quite reasonable results and should be particularly applicable for equilibrium conditions. Finally, it should be stressed that in the lattice gas treatments of the

earlier work the lattice structure does not enter appreciably for conditions *within* a planar layer perpendicular to the electrode except in ensuring a finite, maximum charge concentration in the layer. Both the earlier work and that of CH are one-dimensional treatments with the dimension of interest perpendicular to the electrode. Conditions within a layer are averaged and only the average charge of a layer enters the actual calculations.

THE COOPER–HARRISON APPROACH

Although the CH work is entitled, "The Role of Ion–Ion Interactions in the Electrical Double Layer", these authors do not actually consider this topic in depth. Only a fully microscopic many body theory can properly treat such interactions. By contrast, CH make such stringent approximations that they end up assuming that only ion–ion interactions within a certain cutoff radius of a given ion are important. Furthermore, their final Coulomb interaction expression effectively assumes that there are no other ions within this radius, so that the effective interaction potential is that arising from the difference between a uniform sheet of charge and a uniform sheet of charge with a circular hole in it. They state that they make this assumption "in the absence of more detailed information concerning the effective ion–ion interaction within the layer". Surely, however, in the absence of this information one should be cautious in formulating a theory about the role of such interactions!

The use of a sheet of charge with a circular hole in it in treating ionic double layer models was introduced by Grahame[12], and it, and generalizations of it, are considered in great detail in[13]. In Grahame's case the hole radius R_0 is given by $\pi R_0^2 N_s = 1$, a radius derived directly form the average area available for a single charge. Here N_s is the average two-dimensional number density of charge in a given layer, and the Grahame cut-off approach was introduced to account approximately for single imaging effects[13].

Cooper and Harrison use an order of magnitude argument based on energy to derive an expression for the hole radius

$$R_0 = e^2/4\pi\varepsilon_0\varepsilon_r^* kT, \tag{1}$$

where ε_r^* is an effective transverse dielectric constant mediating ion–ion interactions within a given layer. They consider various specific values for ε_r^* varying from 20 to 78, the approximate value for bulk water at room temperature. Equation (1) leads to $R_0 \simeq 570/\varepsilon_r^*$ A at 20°C. Thus for $\varepsilon_r^* = 78$, $R_0 \simeq 7.3$ A, not greatly larger than the diameter of a water molecule. It seems exceedingly unrealistic to use a value of $\varepsilon_r^* = 78$ here since clearly not enough water molecules can surround a given ion at reasonable ionic concentrations to lead to bulk water effects in its immediate neighbourhood. In addition, the water molecules which form the hydration sheath of a given ion in the first layer next to the electrode are in extremely high electric fields. If a dielectric constant different from unity is to be used at all in the Coulomb interaction formula. rather than a treatment which considers permanent and induced dipoles discretely[8, 9], it is more plausible to use a completely

saturated value of 5 or 6 for ε_r^* (with water solvent), especially at high molarities and/or high applied potentials[8, 9, 13]. Notice, however, that the CH R_0 does not depend on N_s and molarity at all. Further, this R_0 does not include the effects of steric interactions at all, and Equation (1) could possibly lead to an R_0 value smaller than the hard-core limitation for high-dielectric-constant materials at high temperatures.

The influence of laterally surrounding ions is accounted for in the CH treatment by adding to the bare potential of the layer next to the electrode a term

$$\psi_{CH} = \sigma_1 R_0/2\varepsilon_0\varepsilon_r^*, \tag{2}$$

where σ_1 is the mean ionic charge density of the layer, a quantity taken to depend self-consistently on the total effective (average) potential at the layer. It is this term which CH designate as a mean field correction. But a rather similar term occurs in the earlier work, again determined self-consistently. For example, in[4] and[7] the added mean field term is (in the rationalized units employed by CH)

$$\psi_M = \sigma_1 d/4\varepsilon_0\varepsilon_a, \tag{3}$$

where d is the diameter of a solvent molecule (setting the basic lattice spacing) and ε_a is the effective dielectric constant. If one sets $\psi_{CH} = \psi_M$ one obtains

$$R_0 = (d/2)(\varepsilon_r^*/\varepsilon_a), \tag{4}$$

leading to R_0 equal to the solvent radius if $\varepsilon_a = \varepsilon_r^*$. Thus the mean field term of the earlier work may also be interpreted, if desired, in terms of a R_0, albeit as we shall see, a somewhat more plausible one than that of CH.

There is a curious difference between Equation (3) and Equation (2) with Equation (1) used for R_0. In the latter case

$$\psi_{CH} = \sigma_1 e^2/[(8\pi kT)(\varepsilon_0\varepsilon_r^*)^2], \tag{5}$$

and we see that the CH mean field term involves $(\varepsilon_0\varepsilon_r^*)^{-2}$ rather than the more plausible and usual $(\varepsilon_0\varepsilon_r^*)^{-1}$ dependence such as that of Equation (3). It is difficult indeed to see how the effective lateral dielectric constant could act physically to reduce the feedback potential correction by more than a single factor of ε_r^*. A brief simplistic but discrete treatment of lateral "dielectric constant" effects appears in[13].

The only new feature of the CH work of significance is their expression for the cut-off radius, Equation (1). But as we have seen above, it leads to rather implausible results which certainly would require more detailed justification before acceptance. Further, CH make the rather dubious assumption of a possibly different effective dielectric constant for lateral and for transverse directions. In the double layer situation, where most processes of interest occur within a few tens of Angstroms of the electrode, it is far better not to introduce a dielectric constant at all, even a saturated one, as in some of the earlier work, but to employ as discrete a treatment as possible. In [8] and [9], we have analysed a unified double layer model which goes further than before toward this goal and replaces the approximate treatment of solvent molecule dipoles of finite size of[7] by a more accurate approach which also includes some attention to solvent ion polarizability as well. This treatment applies not just for the first layer next to the electrode but for all the layers of

the material. It is thus doubly self consistent. First, the added mean field term is required to be self consistent and, in addition one must determine the potential difference across the layer by iteration to make it consistent with the assumed electrode charge (or *vice versa*).

Some of the differences and the similarities of the various approaches are summarized in Table 1. Incidentally, the specific added mean field term of Equation (3) is required by simple electrostatics but does not appear in the CH treatment and is replaced by the alternate expression of Equation (5). Because the mean field terms appear in self-consistency equations ("negative feedback") for the effective potential their effects are more similar, however, than would otherwise be the case. In fact, the CH graphical and numerical differential capacitance results are not greatly different from those in the earlier work, excluding those of[8] and[9]. But the differences in how the effective dielectric constant appears (see above) and in its assumed values and the direct temperature dependence of Equation (5) not present in Equation (3) certainly lead to somewhat different behaviour, behaviour possibly worth trying to distinguish experimentally. However, much of the differences will be swamped by the need to include at least a narrow charge-free region thicker than a single ionic radius between the effective electrical surface of the electrode and the double layer[7–9]. The physical basis for this extra thickness may be the quantum mechanical "spillover" of the electron wave functions in the metal, a non-local field effect[14]. This inner layer is required with any current theory in order to achieve adequate agreement with experiment.

EXTENSIONS OF THE LATTICE GAS APPROACH

The domination of the total differential capacitance by that of the inner layer, which has been explicitly included in the older theories, emphasizes the great importance of the detailed structure of the solvent in this region. Fawcett[15] has represented the solvent by multi-state permanent dipoles. Recently this idea has been combined with a jellium model for the metal electrode to include non-local field effects in work by Schmickler and Henderson[16].

Much of the microscopic modelling can be incorporated in the lattice gas approach, thereby providing a more unified theory of the electrical double layer. For example, the more realistic treatments of[8] and[9] indicate that when the length of the dipole associated with the permanent dipole moment of the solvent molecule is taken finite rather than infinitesimal, as in the past, very little dielectric saturation (as measured by saturation of the average dipole moment) appears.

One weakness of our latest work is that while it attempts to treat the double layer problem in terms of discrete particles and processes, it nevertheless involves averages over each individual layer, blurring the effects of intra-layer ion–ion, ion–dipole, and dipole–dipole lateral interactions. We attempted to account for the effects of some of these lateral interactions by introducing two adjustable parameters where pertinent in the equations. It is our hope that future work will

Table 1. Comparison of various models

Feature	Ref.[1]	Refs[2–7]	Refs[8–9]
Mean field effects	Inner layer only	All layers	All layers
Interactions treated implicitly (mean field)	Ion–ion repulsion + steric interaction	Ion–ion repulsion	Ion–ion repulsion
Representation of solvent	Dielectric background	Semi-discrete	Semi-discrete
Model for solvent molecule	—	Permanent dipole moment	Permanent dipole moment (infinitesimal or finite-length); induced moment
Effect of the solvent	Screening only	Screening, dielectric saturation	Screening, dielectric saturation, statistical competition between ions and solvent molecules

elucidate the proper magnitudes and dependencies of these parameters on such variables as temperature and molarity. As a small start toward such elucidation we are currently carrying out (work in progress) a Monte Carlo study of a planar array of multi-state infinitesimal and finite-length permanent dipoles, including all Coulomb interactions exactly and not using the incorrect $\varepsilon_a = 78$ value which reduces these interactions far too much.

SUMMARY

The differences between the two approaches can now be summarized. The lattice gas theory begins by simplifying the physics so that more exact results for an idealized model can be obtained. Its assumptions are reasonable, clear, and above all, explicit. Within this simplified framework it is possible to include such important effects as ion–ion steric interactions, Coulomb repulsion, solvent molecule size, dielectric saturation, etc.

Cooper and Harrison begin with a slightly more exact statistical mechanical superstructure involving effective potential and ion–ion correlation functions. At various points in the theory they are forced to make severe and almost certainly unjustified assumptions, the effects of which are difficult to estimate. The final equations for the first layer are formally identical to those of the earlier theories, with the exception of the expression for the cut-off radius. But this expression is one of the most approximate results in the CH theory.

The dependence of the radius on the assumed dielectric constant is very questionable, and in any case a cut-out circle does not represent the "hole" truth!

The world still awaits a detailed theory of the role of ion–ion interactions in the electrical double layer. It is not evident that the CH line of attack is particularly promising.

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