

Monte Carlo, density functional theory, and Poisson–Boltzmann theory study of the structure of an electrolyte near an electrode

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(Received 28 December 2001; accepted 5 February 2002)

Monte Carlo (MC) and density functional theory (DFT) results are reported for an electrolyte, consisting of charged hard spheres of diameter 3 Å with the solvent modeled as a dielectric continuum, near a charged flat uniformly charged electrode. These results are more interesting than the earlier MC results of Torrie and Valleau [J. Chem. Phys. **73**, 5807 (1980); J. Phys. Chem. **86**, 3251 (1982)] for 4.25 Å spheres because the popular Gouy–Chapman (GC) theory is less successful for this system. The DFT results are in good agreement with the MC results. Both the MC and DFT results show particularly interesting features when the counterions are divalent. For such divalent counterions, the diffuse layer potential passes through a maximum magnitude, then declines, and ultimately has a sign that is opposite to that of the electrode charge. The consequences of this behavior are discussed. In contrast, the well-known GC theory consistently overestimates the magnitude of the diffuse layer potential, does not have any unusual behavior, and is in poor agreement with the simulation results. © 2002 American Institute of Physics.

[DOI: 10.1063/1.1464826]

INTRODUCTION

Few theories have enjoyed the longevity of the Poisson–Boltzmann (PB) theory that is now approaching its centennial. However, its popularity may be due as much to the ingenuity of its users in fitting parameters as to its accuracy. This theory is based on the assumption that the solvent in an electrolyte may be replaced by a dielectric continuum whose dielectric constant, ϵ , is equal to that of the solvent, together with the combination of Poisson's equation,

$$\nabla^2 \phi(r) = -\frac{4\pi e}{\epsilon} \sum_{i=1}^m z_i \rho_i g_i(r), \quad (1)$$

and the Boltzmann relation,

$$g_i(r) = \exp[-\beta z_i e \phi(r)]. \quad (2)$$

The PB theory is employed in electrochemistry, where it is known as the Gouy–Chapman (GC) theory,^{1,2} in solution chemistry, where it is known as the Debye–Hückel (DH) theory,³ in colloidal chemistry, where it is known as the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory,^{4,5} and in biophysics,^{6,7} where it is known simply as the PB

theory. The emphasis here is on the electrochemical application. However, we expect that our conclusions will have broader implications.

In Eqs. (1) and (2), m is the number of species of ions in the electrolyte, $\phi(r)$ is the electrostatic potential at a distance r from a central ion, e is the magnitude of the electronic charge, z_i and $\rho_i = N_i/V$ are the valence, including sign, and number density of an ion of species i , and $\beta = 1/kT$, k , being the Boltzmann constant. The function $g_i(r)$ is the normalized local density of an ion of species i at a distance r from a central ion. The quantities, V , T , and N_i are the volume, temperature, and number of ions of species i , respectively. Gaussian (cgs) units are employed. The difference in the formulas if rationalized MKS units are used is slight.

This study is devoted to the study of the accuracy of the PB theory for a system of ions in a model dielectric continuum. This model is called the primitive model (PM), a name that is well chosen. The question of whether it is reasonable to consider a solvent as a dielectric continuum is considered briefly at the end of this article.

One can hardly question Eq. (1), as it is equivalent to Coulomb's law. However, as is seen from the arguments of Henderson and Blum,^{8,9} Eq. (2) makes sense only for point ions. In reality, ions have a nonzero size. In this work, we assume that all the ions have the same diameter, d . This simplified PM with ions of equal size is called the restricted primitive model (RPM). Point ions are not just a simplifica-

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tion; they are a potential disaster because the Coulomb interaction will diverge at $r=0$. This disaster is averted in part by giving the central ion (the electrode in electrochemistry) a finite size. However, it is at best illogical to give a size to one ion and ignore the size of all other ions; at worst, quite incorrect results might be obtained. Clearly, a self-consistent theory is preferable.

The PB/GC theory predicts a layer of counterions near the electrode. This layer and the layer of charge in the electrode form what is called a double layer. By itself, the PB/GC theory gives poor results. The PB/GC theory is made useful by postulating what is variously called a Stern layer, or Helmholtz layer, or compact layer, or inner layer. The idea is that the center of charge of the ions cannot come right to the electrode but are prevented from doing so not only by their own radius, $d/2$, but also by a solvation layer of solvent, usually water, molecules. In electrochemical applications, the properties of this layer are expressed in terms of parameters, some of dubious physical significance, whose values are adjusted to fit the experiment. The idea is that the PB/GC theory is accurate for the region beyond the Stern layer, that is called the diffuse layer.

This means that, because of the use of adjustable parameters, the accuracy of the PB/GC theory cannot be determined by comparison with experiment. The first unambiguous test of the PB/GC theory was made by Torrie and Valleau (TV)^{10,11} almost 20 years ago in an important series of Monte Carlo (MC) simulations, that apart from statistical uncertainties are exact, for monovalent and divalent ions of diameter $d=4.25$ Å. Even with this rather large diameter, their results showed more disagreement with the PB/GC theory than they commented upon. Following their work, studies (at least simulation studies) were discontinued for a rather lengthy period. Recently, we have returned to such simulation studies. We have considered solvent effects,¹² molten salt double layers,¹³ and double layers at low (effective or dimensionless) temperatures¹⁴ and have found that the PB/GC theory has problems in describing the behavior of these systems. Also, we have applied density functional theory (DFT) to the PM double layer in molten salts and aqueous electrolytes at low effective temperatures¹⁵ and to a related membrane problem.^{16,17}

Density functional theory is a type of integral equation theory for an inhomogeneous fluid, based on a second-order density functional expansion in the difference, $\Delta\rho_i(\mathbf{r}) = \rho_i(\mathbf{r}) - \rho_i$, of the inhomogeneous density from the uniform reference density, yielding, after minimization of the free energy, an integral equation that is somewhat similar in form to less successful integral equations, such as the hypernetted chain (HNC) approximation equation. As is common with integral equations for inhomogeneous fluids, the DFT equation requires as input the direct correlation function (dcf) of the uniform fluid. Because DFT is quite standard, we refer to the paper of Rosenfeld¹⁸ for details. Why DFT should be more accurate than say the HNC theory even when the density inhomogeneities are very large as is the case here, is far from clear. Certainly, the use of a nonlocal density is crucial. Anyway, one cannot argue with success.

The value $d=4.25$ Å that was used by TV is somewhat

large. Presumably, this value was chosen to be representative of a solvated ion. Here, we examine the GC theory for $d=3$ Å. In addition, we consider DFT for ions with this smaller diameter. We do not use a compact layer with adjustable parameters. The ions, including those treated by the PB/GC theory, can approach to a distance $d/2$ from the electrode. The dielectric constant within this inner layer is equal to that in the diffuse layer.

THEORETICAL CONSIDERATIONS

The electrochemical interface is examined at room temperature with the dielectric constant of water, and $d=3$ Å. Specifically, for an i,j pair, we use the dimensionless or reduced coupling constant, $\beta z_i z_j e^2 / \epsilon d = 2.3811 z_i z_j$, or, equivalently, the dimensionless temperature, $T^* = \epsilon d k T / e^2 = 0.41995$. Our earlier studies have shown that the smaller the value of T^* , or the larger the value of the coupling constant, the greater the errors in the PB/GC theory. Since a large coupling constant can be achieved by reducing the temperature, the dielectric constant, or value of d , the value that is used here for d is likely to yield more interesting results than that used by TV. If the reader prefers rationalized MKS units, the definition of the dimensionless coupling constant is $\beta z_i z_j e^2 / 4\pi\epsilon_0 \epsilon d$ and the dimensionless temperature is $T^* = 4\pi\epsilon_0 \epsilon d k T / e^2$. The numerical values of these dimensionless quantities is the same in both systems of units.

There are three exact results that can be used to assess a theory. The first is electroneutrality,

$$e \sum_{i=1}^m z_i z_j \int_0^{\infty} g_i(t) dt = -\sigma, \quad (3)$$

where σ is the charge per unit area on the electrode surface. That is, the charge in the double layer must be the negative of that of the electrode. All acceptable theories, including PB/GC, satisfy this condition. As a result, we will not emphasize this test. The second is the contact value condition of Henderson *et al.*,¹⁹

$$kT \sum_{i=1}^m \rho_i(d/2) = p + \frac{2\pi\sigma^2}{\epsilon}, \quad (4)$$

where $\rho_i(t) = \rho_i g_i(t)$ and p is the pressure of the bulk electrolyte. This contact value condition is a force balance condition. The momentum transfer at the electrode must equal p plus the Maxwell stress. The corresponding PB/GC result is

$$kT \sum_{i=1}^m \rho_i(d/2) = kT \sum_{i=1}^m \rho_i + \frac{2\pi\sigma^2}{\epsilon}. \quad (5)$$

Because of the absence of an explicit solvent, the PM electrolyte is normally at a low-density system. Thus, at room temperatures and electrolyte concentrations, the pressure is close to that of an ideal gas and the PB/GC result for the charge profile at contact is nearly correct and becomes increasingly accurate as the charge of the electrode is increased and the second term on the right-hand side of Eqs. (4) and

(5) becomes dominant. The third is the set of MC results. As we have commented, apart from statistical uncertainties, these results are exact.

If the MSA bulk electrolyte dcf is used as input, is the corresponding DFT contact value condition is

$$kT \sum_{i=1}^m \rho_i(d/2) = a + \frac{2\pi\sigma^2}{\epsilon}. \quad (6)$$

The exact expression for a has not been determined but, numerically, it appears to be some function of the MSA compressibility. If an exact bulk electrolyte dcf is used as input, $a=p$ should follow and the DFT contact value should be exact. We have verified numerically that, if the generalized MSA (GMSA) dcf, which is not exact, is used, Eq. (6) is satisfied with a being some function of p , where p is the MSA pressure. In summary, the DFT satisfies the contact value condition in a manner that is related to the level of accuracy of the input MSA. The GMSA improvement will be discussed elsewhere; it is not an important issue for the system considered here since p , ρkT , and the inverse compressibility are nearly equal in the PM for the conditions considered here. Differences would be apparent when a molecular solvent is considered, at molten salt densities, or at low effective temperatures (or, equivalently, high coupling constants).

At this point, a few comments about the first two conditions are in order. Henderson has commented at the Southampton (1984) and Berlin (1986) electrochemistry meetings that since the PB/GC satisfies the first condition and nearly satisfies the second condition (in the PM at small coupling constants), the PB/GC charge profile starts with nearly the correct contact value and has the correct area (electroneutrality) and, therefore, cannot give terrible results for the profiles and potential. Stated this way, the observation is correct. However, this argument has been repeated frequently by others as an argument supporting the idea that the PB/GC is reliable, a conclusion that was never intended when the argument was stated and is frequently unjustified. Since we are on this subject, it is to be noted that whatever the merits of this observation, it is applicable only for the PM and has uncertain merit for real systems with a solvent.

We note that the choice of the variable that specifies the system is arbitrary. In simulations, it is convenient to specify the charge on the electrode. However, in many integral equation theories and in DFT calculations the electric potential of the electrode is a more convenient variable. Using the potential as the variable and assuming, for simplicity, that $m=2$ and the ions are monovalent, the PB/GC contact value condition is

$$g_i(d/2) = \exp[-\beta e \phi(d/2)] \quad (7)$$

or

$$kT \sum_{i=1}^2 \rho_i g_i(d/2) = \rho kT \cosh[\beta e \phi(d/2)], \quad (8)$$

where $\rho = \sum \rho_i$. Equation (8) is equivalent to Eq. (5) only if the relation between σ and $\phi(d/2)$ that is given by the PB/GC theory is accurate. If this relation is not accurate, we

TABLE I. The potential of the electrode, $\beta e \phi(0)$, for concentrations 0.1, 1, and 2 M, for various electrode charges, for 1:1 and 2:1 electrolytes using the ionic diameter $d=3 \text{ \AA}$.

		σ^*			
1:1					
c (M)		0.0562	0.1123	0.1685	0.2247
0.1		4.01	5.85	7.21	8.43
1.0		2.21	3.81	5.12	6.32
2.0		1.73	3.19	4.49	5.64
2:1		σ^*			
c (M)		0.0562	0.1123	0.1685	0.2247
0.1		3.53	5.36	6.76	7.95
1.0		1.73	3.34	4.65	5.88
2.0		1.24	2.64	3.90	5.09
2:1		σ^*			
c (M)		-0.0562	-0.1123	-0.1685	-0.2247
0.1		-1.99	-2.72	-3.32	-3.86
1.0		-1.35	-2.10	-2.67	-3.24
2.0		-1.20	-1.92	-2.48	-3.08

know from the contact value theorem and Eq. (5) that it is better to use charge rather than potential as the variable. However, from the point of view of logic there is no reason to make this choice. In fact, within the PB/GC theory, the potential seems more logical variable since it is the potential that appears in the formulation of the PB/GC theory, Eq. (2), and many of the results of this theory, especially for asymmetric electrolytes, are expressed more compactly if the potential is used as the variable. In this paper, the PB/GC theory and the DFT will be tested using both the charge and potential as the variable that specifies the system.

The MC simulations were performed using the method that is discussed in detail in our previous papers;^{12,13} this discussion is not repeated here. The MC calculations were performed on a SGI Power Challenge computer (R10000 chip).

The DFT calculations were based on the method of Rosenfeld¹⁹ that is outlined in our membrane study,^{16,17} assuming that the two walls of that study are far apart and the wall is so thick that the fluids on either side of the wall are independent of each other. We refer the reader to these two papers. The DFT calculations were performed with a Pentium III laptop.

RESULTS

The MC values of the charge and potential are listed in Tables I and II. An electrode surface charge density of 0.1 C/m^2 is equal to $\sigma^*=0.0562$. A concentration of 1 M is equal to a dimensionless density of $\rho^*=0.0162$, for the least abundant species. The PB/GC and DFT results for these quantities for a 1:1 electrolyte are compared with these MC results in Fig. 1 with parts (a) and (b) giving the potential of the electrode, $\phi(0)$, and the diffuse layer potential, $\phi(d/2)$, respectively, as functions of σ . The PB/GC potentials are uniformly too large. On the other hand, the DFT results are quite good. A comparison of the PB/GC and DFT profiles

TABLE II. The diffuse layer potential, $\beta e \phi(d/2)$, for concentrations 0.1, 1, and 2 M, for various electrode charges, for 1:1 and 2:1 electrolytes using the ionic diameter $d = 3 \text{ \AA}$.

1:1		σ^*			
$c \text{ (M)}$	0.0562	0.1123	0.1685	0.2247	
0.1	3.17	4.16	4.69	5.07	
1.0	1.37	2.13	2.60	2.96	
2.0	0.89	1.51	1.97	2.28	
2:1		σ^*			
$c \text{ (M)}$	0.0562	0.1123	0.1685	0.2247	
0.1	2.69	3.68	4.23	4.59	
1.0	0.89	1.66	2.13	2.52	
2.0	0.40	0.96	1.38	1.72	
2:1		σ^*			
$c \text{ (M)}$	-0.0562	-0.1123	-0.1685	-0.2247	
0.1	-1.15	-1.04	-0.80	-0.49	
1.0	-0.51	-0.42	-0.15	0.12	
2.0	-0.36	-0.24	0.05	0.28	

with the MC results for a 1:1 electrolyte is given in Fig. 2, with parts (a) and (b) making the comparison for the same electrode charge and the same diffuse layer potential, respectively. The PB/GC theory is somewhat better when the comparison is made at the same electrode charge, but even then the PB/GC results are still unsatisfactory. No matter what method is used for the comparison, the DFT theory is in quite good agreement with the MC results. These results are similar to those reported for 1:1 electrolytes for $d = 4.25 \text{ \AA}$ by TV, who made comparisons of the profiles only for equal electrode charge. In the TV simulations, the potential for a 1:1 electrolyte rises strongly at (unphysically) large electrode charge densities and crosses the PB/GC results, giving the illusion that the PB/GC theory is not so bad. However, the MC counterion profile contains a second layer.¹² This is seen in DFT,¹⁹ but not in the PB/GC theory. Presumably, a second layer would also be seen at large charge densities with the MC and DFT techniques for the system considered here. We do not pursue this question since unphysically large charges and potentials are involved.

A similar comparison is made in Figs. 3 and 4 for the 2:1 electrolyte. If the monovalent ions are the counterions, the results are much like those of the 1:1 case. However, the results for the case where the counterions are divalent is more interesting. As a result, profiles for the 2:1 electrolyte case are shown only for the case of divalent counterions. The PB/GC potentials lie above the MC results but by a greater degree than for the monovalent case. The DFT results are quite good. It is interesting to note that the MC and DFT diffuse layer potentials pass through a minimum and then increase, even to the extent that they change sign. The MC and DFT profiles for the divalent counterion case show charge inversion or charge oscillations. Farther from the electrode, the coion profile exceeds the counterion profile and the double layer has become a triple layer. The PB/GC results for the profiles are poor. They are particularly unsat-

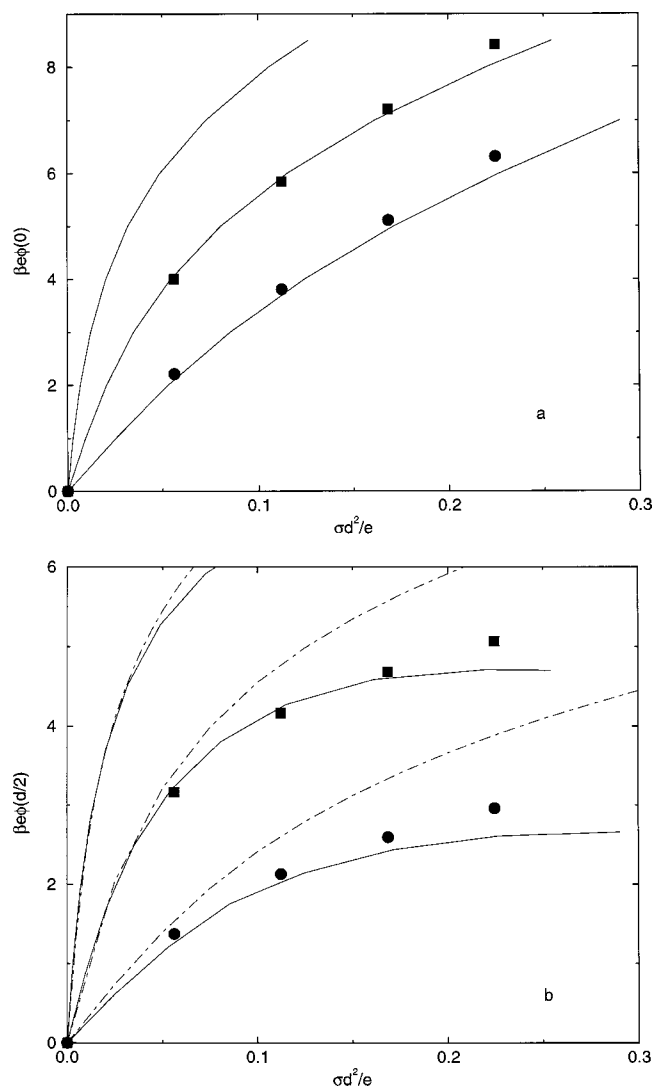


FIG. 1. Electric potential at contact [part (a)] and diffuse layer potential [part (b)] of a 1:1 electrolyte ($d = 3 \text{ \AA}$) as a function of the electrode charge density. The three sets of curves are, from top to bottom, for 0.01, 0.1, and 1 M. The points give the simulation results and the solid and dotted-dashed curves give the DFT and PB/GC results, respectively.

isfactory if the comparison is made at the same diffuse layer potential [Fig. 4(b)]. The DFT is insensitive to this issue.

These divalent counterion results are similar to but more extreme than the results reported by TV. In the TV study, the MC diffuse layer potential for divalent counterions levels off. There is a hint of a minimum and change of sign in the diffuse layer potential in the TV MC results, but its possible existence is obscured by statistical uncertainties.

DISCUSSION

Simulation results and the results of PB/GC theory and DFT for charged hard sphere ions in a dielectric medium (PM) are reported for spheres of diameter 3 \AA . This was expected to be a more severe test than the TV simulations that were performed for spheres of diameter 4.25 \AA . Simulations results are a 'gold standard' against which theory may be tested without any uncertainty regarding whether the PM is representative of experimental systems.

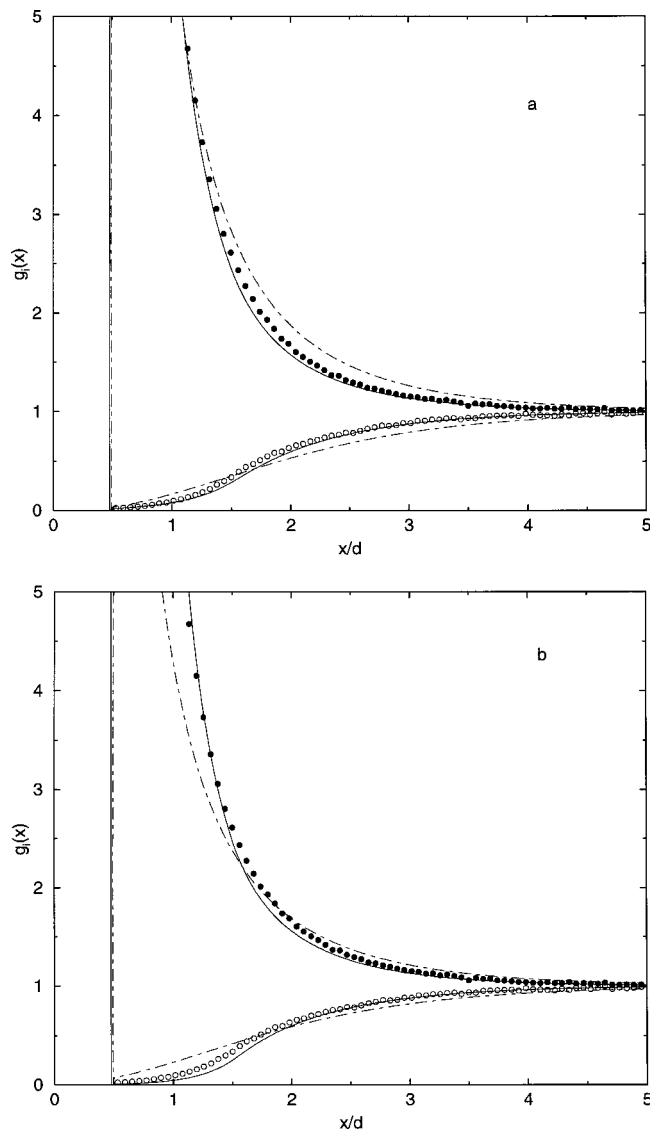


FIG. 2. Concentration profiles for a 1:1 electrolyte ($d = 3 \text{ \AA}$) at 1 M for the state with the MC value of $\sigma^* = 0.1685$ and $\beta e \phi(d/2) = 2.60$. The points give the simulation results and the solid and dotted-dashed curves give the DFT and PB/GC results, respectively. The comparison is made at the same electrode charge density [part (a)] and at the same diffuse layer potential [part (b)].

Density functional theory is quite accurate. In contrast, the PB/GC theory is not very successful. It consistently underestimates the magnitude of the electrostatic potential for a given charge density on the electrode. The errors in the PB/GC theory are even more apparent when divalent ions are present. When the divalent ions are the counterions, the MC and DFT diffuse layer potentials pass through a minimum and then increase and can even change sign. This means that the diffuse layer differential capacitance is infinite and then changes sign and becomes negative. Perhaps, the reader may be surprised by this result and may feel that it is unphysical. However, there is no law of nature that is violated. All that is assumed in the simulations is Poisson's equation and the Gibbs' expression for the probability distribution of a canonical ensemble. It is interesting to note that a negative contribution to the capacitance occurs in the study of the contribu-

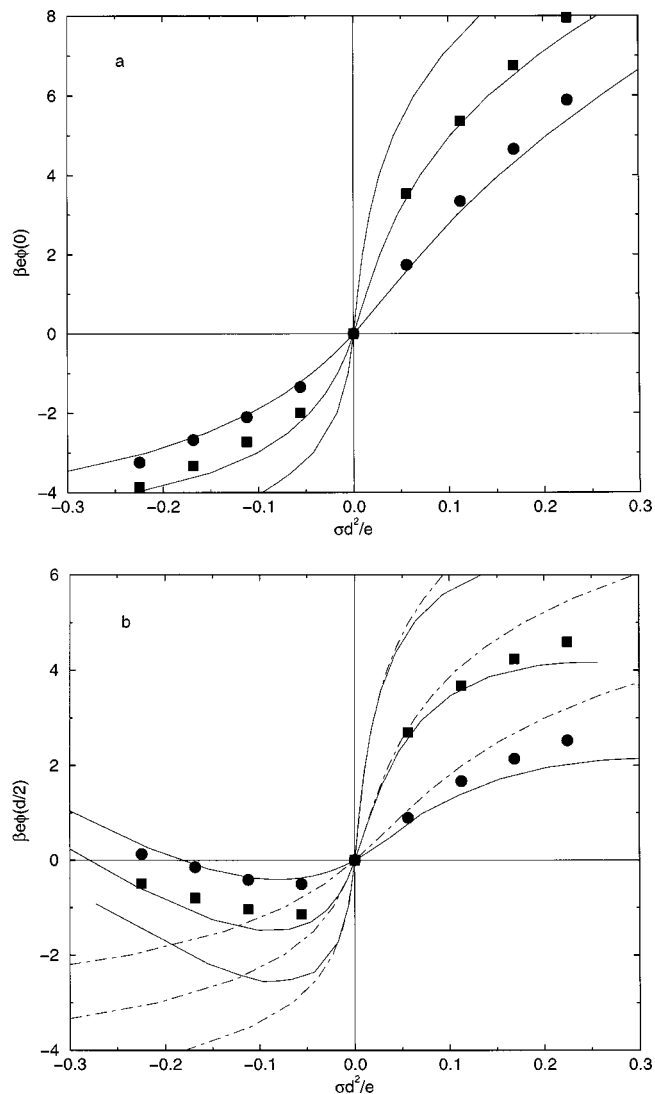


FIG. 3. Electric potential at contact [part (a)] and diffuse layer potential [part (b)] of a 2:1 electrolyte ($d = 3 \text{ \AA}$) as a function of the electrode charge density. The points and curves have the same meaning as in Fig. 1.

tion of the metal electrons to the capacitance;²⁰ a reversal of the potential has been seen in our previous work on membranes¹⁷ and in simulations of polyelectrolytes.²¹

A negative diffuse layer differential capacitance means that the exotic mechanisms that are invented²² to account for decreases in the differential capacitance at higher potentials may be unnecessary and may have the status of Ptolemy's epicycles. More importantly, electrochemical reactions take place at or near the distance of closest approach and requires an accurate result for the potential for that point. This means that theories of electrochemical reactions that employ the PB/GC theory are of uncertain accuracy. This is especially true for reactions involving a multivalent ion in a 1:1 electrolyte. For example, many experimental data involve studies of the kinetics of transition metal $3+/2+$ systems with a 1:1 supporting electrolyte. In the past, the presence of the foreign reactant in an otherwise simple 1:1 electrolyte has been treated in an overly simplified way. A proper analysis of such a system requires the application of more accurate approximations to a MIXED electrolyte system. To the best of our

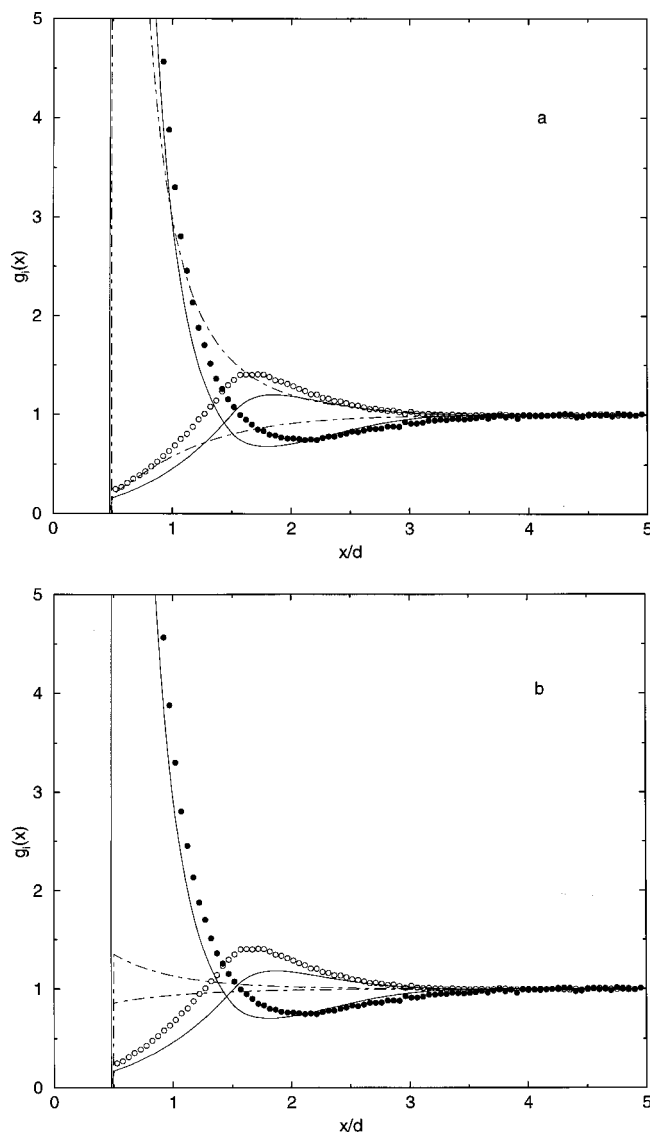


FIG. 4. Concentration profiles for a 2:1 electrolyte ($d = 3 \text{ \AA}$) at 1 M for the state with the MC value of $\sigma^* = -0.1685$ and $\beta e \phi(d/2) = -0.15$. The points and curves have the same meaning as in Fig. 2. The comparison is made at the same electrode charge density [part (a)] and at the same diffuse layer potential [part (b)].

knowledge, this type of calculation has not been undertaken yet.

The stronger the coupling or the lower the effective (dimensionless or reduced) temperature, the greater the errors in the PB/GC theory. It should be noted that the differences seen here between simulations and the PB/GC theory are but the beginnings of the large differences we have seen at low effective temperatures, where, among other things, the PB/GC theory predicts an incorrect negative sign for the temperature derivative of the capacitance.¹⁴ A positive temperature derivative for the capacitance has been seen in the experimental results of Hamelin *et al.*²³ for frozen electrolytes. Also, unexpected results, possibly due to large errors in the PB/GC theory, have been seen in the experimental results for 3:1 electrolytes of Andreu and Molero,²⁴ who have studied the differential capacity of dilute solutions of LaCl_3 at far negative electrode charge densities ($< -20 \mu\text{C}/\text{cm}^2$). How-

ever, the possibility that the double layer is not stable when cations of large charge are forced into the double layer cannot be discounted. In this connection, an extension of our simulations and DFT calculations to 3:1 electrolytes, where we expect even larger differences from the PB/GC theory, than those seen here, may be of value.

The MC and DFT are both good approaches. Regrettably, the PB/GC is unsatisfactory. The study here is based on the use of the PM (or RPM). Real electrolytes are dissolved in molecular solvents, not dielectric continua. Although under some circumstances a dielectric constant may give a reasonable description of the dielectric aspects of a solvent, the PM neglects the fact that solvent molecules occupy space. This causes the local density and potential profiles to oscillate with the result that the local environment in an electrolyte modeled using a reasonable model for the solvent is quite different from the PM, even if the PM is treated accurately (see Figs. 4 and 5 of the review of Schmickler and Henderson.²⁵ These effects are real and are seen in experiment.^{26,27} It is time to use a molecular solvent in electrochemical theory. To do this with a highly accurate model for (say) water would be difficult. However, the use of a hard sphere solvent with a dielectric background, the solvent primitive model, is no more difficult than the primitive model with a nonzero ionic diameter and captures much of this behavior.^{12,28-31} Electrochemists should adopt these concepts.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation (Grant No. CHE98-13729) and NATO (Grant No. HTECH CRG972915).

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