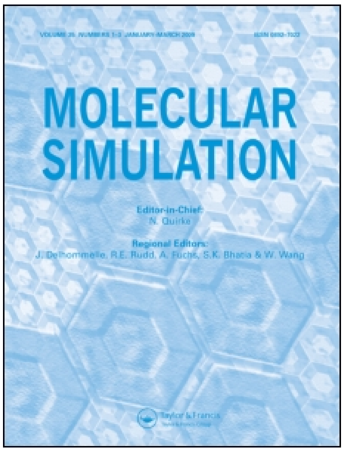

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Monte Carlo simulation of the double layer at an electrode including the effect of a dielectric boundary

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To cite this Article Alawneh, M. and Henderson, D.(2007) 'Monte Carlo simulation of the double layer at an electrode including the effect of a dielectric boundary', Molecular Simulation, 33: 6, 541 — 547

To link to this Article: DOI: 10.1080/08927020601054068

URL: http://dx.doi.org/10.1080/08927020601054068

Molecular Simulation, Vol. 33, No. 6, May 2007, 541–547

Monte Carlo simulation of the double layer at an electrode including the effect of a dielectric boundary

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(Received September 2006; in final form October 2006)

Monte Carlo values of the density profiles and related properties of the double layer formed by an electrolyte near a charged electrode are reported for the cases where the electrode has a dielectric coefficient greater, equal, and smaller than that of the electrolyte that causes a surface polarization that can be represented by electrostatic images. As expected, compared to the case where there is no dielectric boundary the ions near the electrode are attracted or repelled by the electrode if the dielectric coefficient is greater or smaller, respectively, than that of the electrolyte. This effect is most pronounced near the electrode and is stronger for 2:2 electrolytes than for 1:1 electrolytes. For both monovalent and divalent ions the effect of the dielectric boundary is stronger at low concentrations.

Keywords: Monte Carlo simulation; Dielectric boundary; Density profiles; Electrolyte; Double layer

1. Introduction

As is well known, the dielectric constant of an electrode differs from that of an electrolyte, resulting in an induced charge in the electrical double layer formed in an electrode/electrolyte interface. If the dielectric constant is not a constant but is different in the electrode and electrolyte it is perhaps better not to call this quantity a constant. In this work, we use the term dielectric coefficient. For a flat electrode and a single flat dielectric discontinuity at the electrode/electrolyte boundary, the charge induced by an ion can be represented by a fictitious image charge inside the electrode. Even a set of dielectric discontinuities can be represented by an infinite set of image charges.

Despite this simplification, the effect of a dielectric interface on the properties of a double layer is usually ignored in both theory and simulation. For example, the popular Gouy-Chapman-Stern (GC) theory [1–3], also known as the Poisson–Boltzmann (PB) theory, ignores the effect of a dielectric interface. The reason why this interface is usually ignored in theory and simulation is that if the induced charge is neglected, the density, charge, and potential profiles can be obtained by means of a singlet level treatment in which only the distance of an ion from the (assumed) flat electrode need be specified. In contrast, if the induced charge is considered, a pair level theory is needed. This can result in a considerable increase in the level of complexity of a theory. So far, only the modified Poisson–Boltzmann (MPB) theory [4] and the simple concept of a screened self image (SSI) of an ion [5–8] have been applied to study a dielectric interface. The SSI approximation keeps the theory at a singlet level. Second order theories [9–11] can be employed to treat dielectric boundaries but, in the case of the more sophisticated theories [9–10], at a cost in computation time. None-the-less, this has been done by Kjellander and Marcelja [9]. A computationally more simple second order theory is that of Carnie and Chan [11]. Finally, we mention that Vertenstein and Ronis [12] have applied cluster perturbation theory to this problem.

In the case of a simulation, the introduction of dielectric images does not result in an appreciable increase in the level of complexity of the computer code but does increase the computation time. This is not a fatal problem as the speed of computer processors has compensated for this increase since the original simulations of Torrie and Valleau [13] a quarter century ago. Even in 1982 Torrie *et al.* [7] were able to use a simulation to examine the effect of a dielectric discontinuity. Despite this, to our knowledge there have been only two simulations that

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Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020601054068

considered dielectric boundaries, the original Torrie *et al.* work and a recent publication of Henderson *et al.* [8].

Boda *et al.* [14] have developed a method, called the induced charge computation (ICC) method, that is convenient for a simulation and permits the study of interfaces for which simple image solutions are not available. This method was employed in Ref. [8]. The ICC method has been employed in a recent study of the selectivity of an ion channel [15] where no simple electrostatic solution is available.

In this paper, we consider the effect of the induced charge on an electrode surface due to the difference in the dielectric coefficients of the electrode and electrolyte. We approximate the electrode as an infinite flat uniformly hard charged surface whose surface is located at $z = 0$ and whose interior occupies the semi-infinite region $z < 0$. Thus, the ions are confined to the region $z > 0$. For such an interface, the image representation of the induced charge can be used. We could approximate the interfacial region of the electrolyte, the inner or Helmholtz layer, as a narrow region of low dielectric coefficient and have a system with three dielectric regions with two dielectric discontinuities. However, the study of Boda *et al.* [8] showed that because this region is narrow, its effect is negligible. Thus, there is no need to use the ICC method or the extended image solution, given in that paper, for this particular problem.

We consider the electrode to be uniform so that its dielectric coefficient is everywhere equal to ϵ_1 inside the electrode. The electrolyte is treated as a binary restricted primitive model electrolyte. That is, the solvent is considered to be a dielectric continuum with a dielectric coefficient equal to ϵ_2. The ions are regarded as a collection of charged hard spheres of diameter d. The charge of an ion of species i is $q_i e$, where q_i is the valence (including sign) and e is the magnitude of the electronic charge. We follow the usage of Torrie *et al.* The charge density on the electrode surface is σ. A charge Q that is located at (x,y,z) has an image whose charge, Q', given by

$$Q' = \frac{\epsilon_2 - \epsilon_1}{\varepsilon_2 + \varepsilon_1} Q = \alpha Q, \qquad (1)$$

is located at $(x, y, -z)$. Thus, the *total* surface charge density, σ, consists of the sum of two terms, the contribution of the image charges $-\alpha\sigma$, and what Torrie *et al.* call the *uniform* charge density, $(1 + \alpha)\sigma$. The excess charge density in the double layer is equal in magnitude but opposite in sign to σ. A positive value of α corresponds to a repulsive induced charge whereas a negative value corresponds to an attractive induced charge. In particular for a metallic electrode, the usual case, ϵ_1 is infinite and $\alpha = -1$.

It is convenient to use a dimensionless reduced density, $\rho^* = Nd^3/V$, where N is the total number of ions in the system and V is the volume of the system. It is also convenient to use a dimensionless reduced temperature. Using Gaussian units, the reduced temperature is given by $T^* = \epsilon_2 dkT/q^2e^2$, where q is the magnitude of the valence, k is the Boltzmann constant and T is the temperature. If SI units are preferred, the definition of T^* is modified slightly by placing $4\pi\epsilon_0$ in the numerator. Thus, a low value of T^* can be realized not merely by lowering the temperature but also by lowering the diameter, d, or electrolyte dielectric coefficient, ϵ_2, or by considering divalent or higher valence salts. Hence, a low value of T^* does not imply that unphysical temperatures are being employed.

Note that in contrast to a simple fluid, such as argon, the diameter, d, enters both in the definition of ρ^* and T^*. As a result, the GCS theory is not simply a zero diameter theory, as is often suggested, since simply putting $d = 0$ would produce $T^* = 0$. In contrast, for the simple fluid the diameter enters only in the definition of ρ^* and the ideal fluid limit is obtained by putting $d = 0$. In the context of the MPB theory, for the double layer problem one must consider not only the limit of small d but also neglect fluctuation terms to yield the GCS theory.

Distances are reduced by dividing by d. The dimensionless charge density is defined as $\sigma^* = \sigma d^2/e$. Potentials are reduced by dividing by kT/e.

2. Monte Carlo simulation

We use the same parameters as Torrie and Valleau, namely $\epsilon_2 = 78.5$ and $d = 4.25$ Å. Our intention was to use the same temperature as Torrie *et al.*, namely $T = 298$ K. However, through a miscommunication the simulations were actually performed for $T = 298.15$. The difference is negligible. Either temperature corresponds to $T^* = 0.595$ for a 1:1 electrolyte and $T^* = 0.149$ for a 2:2 electrolyte.

We consider 0.1 and 1.0 M q–q electrolytes ($\rho^* = 0.00925$ and 0.0925, respectively) consisting of monovalent and divalent ions near a positively charged electrode. The number of positive ions is $N_+ = 400$ and $N_- = 400 + \Delta N$ is the number of negative ions. Since the salts are symmetric, positive and negative charges can be reversed yielding the same results (with of, course, a change in the sign of σ and $\phi(x)$).

The simulation cell is rectangular and of size $XL \times YL \times ZL$. We use $YL = XL$. Since the electrode surface is located at $z = 0$, the cell extends from $-ZL/2$ to $ZL/2$. Thus, the charge of the electrode is ΔNqe. Periodic boundary conditions are applied in the x and y directions. Following Torrie and Valleau and Boda *et al.* a "sheets" method is used to account for the charges in the periodically replicated cells. This is satisfactory as long as XL is large. The bounding surfaces at $z = \pm ZL/2$ are hard and uncharged. The boundary at $z = -ZL/2$ is irrelevent since the ions are confined to the electrolyte region, $z > 0$. As long as ZL is large, the boundary at $ZL/2$ does not affect the results. Thus,

$$\Delta N = (XL/d)^2 \sigma^*/q. \qquad (2)$$

We use $XL/d = 40$ and 20 for 0.1 and 1.0 M, respectively.

Torrie *et al.* used a grand canonical ensemble and specified the bulk concentration by means of a determination of the chemical potential of the bulk fluid for this concentration that was obtained from earlier simulations. In contrast, we use the canonical ensemble. Thus, *ZL* determines the bulk concentration. Lamperski and Bhuiyan also used the canonical ensemble in their simulations [16]. Our computer code automatically optimizes *ZL* and gives a very accurate final concentration. Thus, repeated simulations to adjust the value of *ZL* are unnecessary. This canonical ensemble method is easier than using the grand canonical ensemble method and the resultant concentration should be as accurate as that of the chemical potential determined by the prior simulation that is required by a grand canonical simulation.

The simulation proceeds using the standard Metropolis algorithm with the interaction energy determined from equations (3)–(5) of Torrie *et al.* [7]. Typically, we use several thousand equilibration moves and then average over 10^6 moves. Because the value of ρ^* is small, the system equilibrates very quickly.

The density profiles, $g_i(z)$, are calculated and stored. The density profiles are normalized so that they are unity at large z. The potential profile is determined from

$$\phi(z) = \frac{4\pi e}{\epsilon_2}\sum_i q_i \rho_i \int_{d/2}^{\infty} (t-z) g_i(t)\mathrm{d}t. \tag{3}$$

The values $V = \phi(0)$ and $\phi(d/2)$ are the total (or electrode) and diffuse layer potential, respectively. They are related by:

$$V = \frac{2\pi\sigma d}{\epsilon_2} + \phi(d/2). \tag{4}$$

Of course, the charge profiles satisfy the charge neutrality condition,

$$\sigma = e\sum_i q_i \rho_i \int_{d/2}^{\infty} g_i(t)\mathrm{d}t. \tag{5}$$

The contact values, $g_+(d/2)$ and $g_-(d/2)$ can be determined by extrapolation of the $g_i(z)$ to $d/2$. This becomes less accurate for the counterions when σ becomes large because the profile of the counterions near $z = d/2$ increases rapidly as σ increases. For $\alpha = 0$, the contact values must satisfy the contact value condition of Henderson *et al.* [17],

$$\frac{1}{2}[g_+(d/2) + g_-(d/2)] = \frac{p}{\rho kT} + \frac{1}{2}b^2, \tag{6}$$

that is based on force balance considerations. In equation (6), p is the pressure of the bulk electrolyte and

$$b = \frac{4\pi\sigma\beta q e}{\epsilon_2 \kappa}, \tag{7}$$

where

$$\kappa^2 = \frac{4\pi\beta q^2 e^2 \rho}{\epsilon_2}. \tag{8}$$

is the Debye screening parameter.

There is no simple rigorous contact value condition for $\alpha \neq 0$. Carnie and Chan [18] have obtained a general expression for the contact value. However, in contrast to the $\alpha = 0$ case, the density profiles and, more seriously, the pair density functions must be known explicitly to employ their result. Regretably, this makes their result of marginal value. The results reported here should indicate a useful approximate contact value condition for $\alpha \neq 0$.

3. Results

We report results for the electrical double layer formed by a 1:1 and 2:2 0.1 and 1.0 M electrolyte for the cases $\epsilon_1 = 1$, 78.5 and ∞. The values, $\epsilon_1 = 1$ and ∞ are those for a vacuum and a metal, respectively. The corresponding values of α are 0.975, 0 and -1. These are the values used by Torrie *et al.* The results for a 1:1 0.1 M electrolyte were made mainly as a check on our results. Even though Torrie *et al.* have already reported results for this system, we report results for comparison with the results for the 1:1 1.0 M and 2:2 cases. We note that for the 1:1 0.1 M case, we agree with the Torrie *et al.* results. In this paper, we concentrate on nonzero values of σ^* since results for $\sigma^* = 0$ were reported in Ref. [8].

Results for the density profiles of a 1:1 electrolyte are shown in figure 1. The profiles for the three values of α differ mainly near $z = d/2$. As expected the ions near the electrode are attracted or repelled, relative to $\alpha = 0$, in the $\alpha = -1$ or $\alpha = 0.975$ cases. The differences between the three cases is most apparent at the lower concentration and for lower values of σ^*.

One interesting feature of the Torrie and Valleau simulation was the formation in a 1.0 M 1:1 electrolyte of a second peak in the counterion profile at $\sigma^* = 0.7$. We have examined $\sigma^* = 0.7$ and found that this peak is almost completely unaffected by the value of ϵ_1.

As there is no simple contact theorem for $\alpha \neq 0$, we have obtained values for the contact values of $g_{\mathrm{sum}}(z)$ for the three cases. Since the counterion profile is large and rapidly changing near contact and can be difficult to extrapolate to contact accurately at larger σ^*, we have extrapolated the difference of the counterion profiles from the $\alpha = 0$ case, where an exact result is known and compute the contact values of the individual counterion profiles from these results. Apart from statistical uncertainty, there is no difficulty in extrapolating the coion profiles to contact. Contact values of g_{sum} are plotted in figure 2. As mentioned there is no known exact simple contact theorem. However, the result

$$g_{\mathrm{sum}}(d/2; b) = g_{\mathrm{sum}}(d/2; b = 0) + \frac{1}{2}b^2, \tag{9}$$

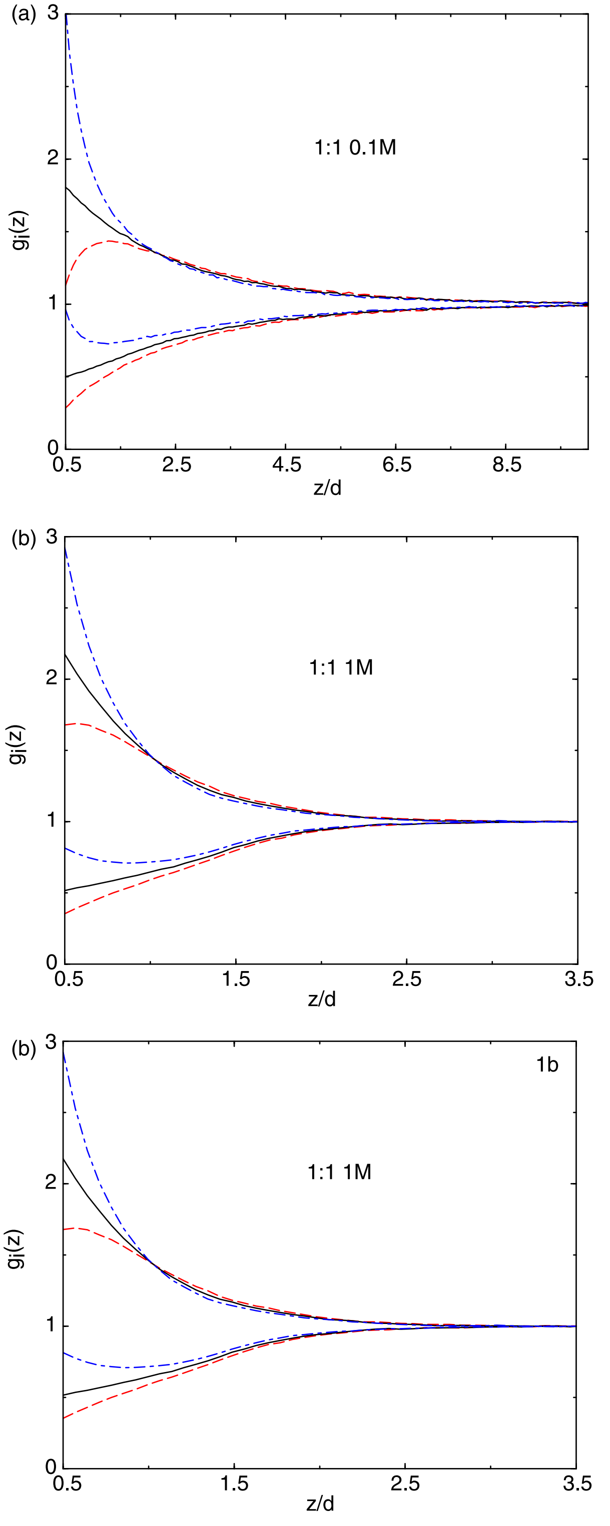

Figure 1. Density profiles for a 1:1 electrolyte whose dielectric coefficient is $\epsilon_2 = 78.5$ for 0.1 M with $\sigma^* = 0.014$ (part a) and for 1.0 M with $\sigma^* = 0.05$ (part b) and 0.10 (part c). The dot–dash, solid, and broken curves give the simulation results for $\epsilon_1 = \infty$ $(\alpha = -1)$, 78.5 $(\alpha = 0)$, and 1 $(\alpha = 0.975)$, respectively.

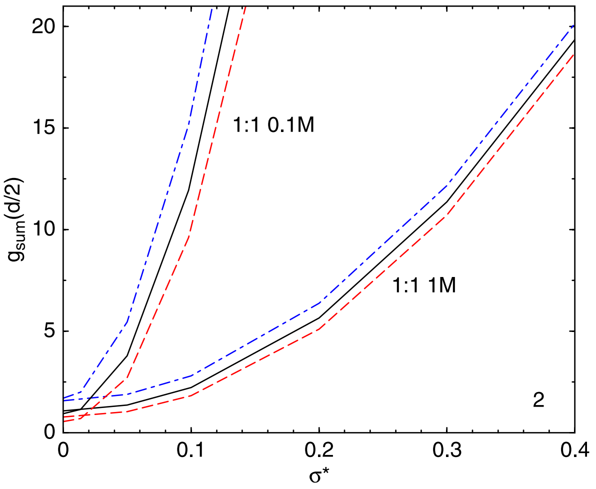

Figure 2. Contact values of $g_{\rm sum}(z)$ for a 1:1 electrolyte. The curves have the same meaning as in figure 1.

appears to be roughly satisfied and seems to be a useful guide. Clearly the dominant effect due to the charging of the electrode is given by the second term of equation (9), the Maxwell stress. However, in contrast to the case where there is no dielectric boundary, in agreement with Carnie and Chan, the contribution of the electrode charge is not given exclusively by this term.

In figure 3, values for the diffuse layer potential for the 1:1 electrolyte are plotted. The differences between the three cases is small because the potential is an average over the entire profile. Since the ions are repelled when $\epsilon_1 = 1$ $(\alpha = 0.975)$, the double layer is slightly wider and the diffuse layer potential is greater for this case than for $\epsilon_2 = 78.5$ $(\alpha = 0)$. The reverse is true for $\epsilon_1 = \infty$ $(\alpha = -1)$.

We now turn to the case of a 2:2 electrolyte. A small number of simulations of image effects for divalent ions have been made by Torrie *et al.* for a 0.05 M 2:2 electrolyte and 0.05 and 0.5 M 2:1 electrolytes. As a further test of our program we have made a few simulations for a 0.05 M 2:2 electrolyte and compared with the results of Torrie and Valleau with good agreement. Here we consider 0.1 and 1.0 M 2:2

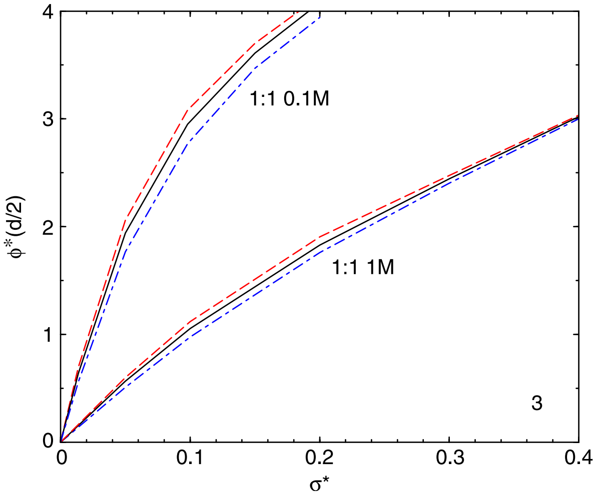

Figure 3. Diffuse layer potentials for a 1:1 electrolyte. The curves have the same meaning as in figure 1.

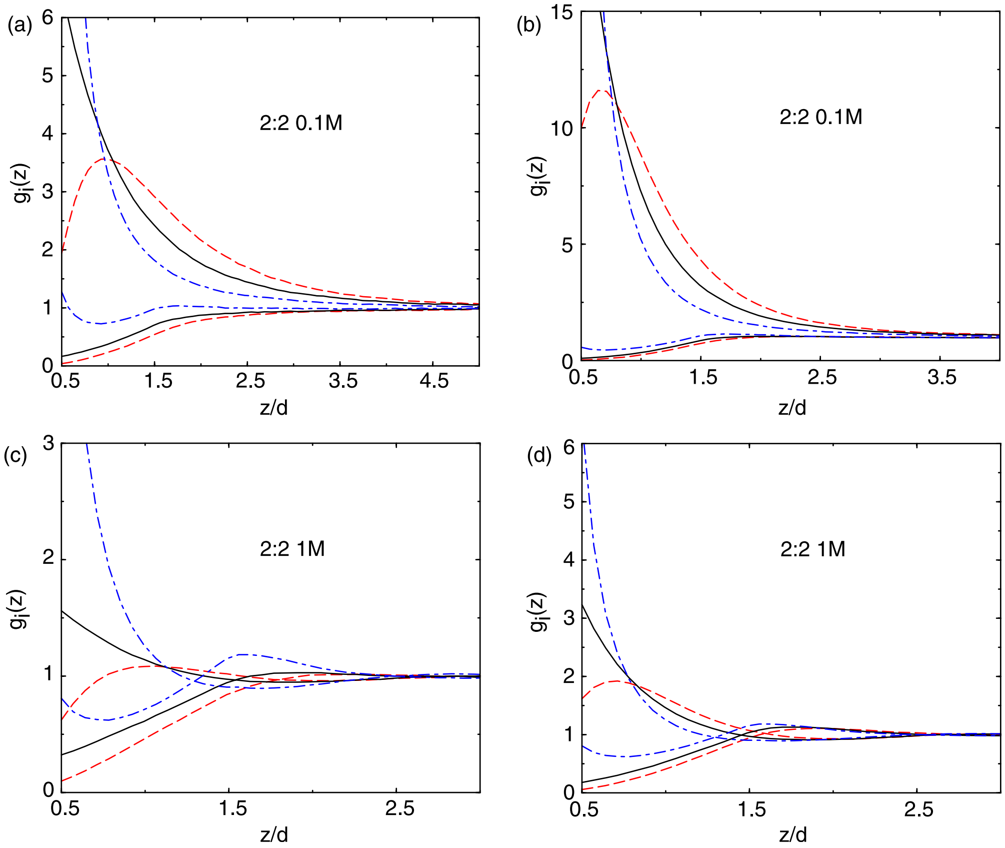

Figure 4. Density profiles for a 2:2 electrolyte. Results are shown for 0.1 M with $\sigma^* = 0.05$ (part a) and $\sigma^* = 0.10$ (part b) and for 1.0 M with $\sigma^* = 0.05$ (part c) and $\sigma^* = 0.10$ (part d). The curves have the same meaning as in figure 1.

electrolytes. Density profiles are plotted in figure 4. The charge inversion already seen in 2:2 density profiles when there is no dielectric boundary is also present when images are present. However, the location of this charge inversion is shifted slightly by the dielectric discontinuity. Again the effect of the dielectric boundary is more pronounced at lower concentrations and lower values of σ^*. Comparison of the 1:1 and 2:2 density profiles shows that the effect of the dielectric boundary is stronger for the 2:2 electrolyte than for the 1:1 electrolyte.

There is a general tendency, seen in both the 1−1 and 2−2 cases, for the counterion profile near the electrode to be larger or smaller in the $\alpha = -1$ or $\alpha = 0.975$ cases, respectively, compared with the $\alpha = 0$ case, but for this behaviour to be reversed further from the electrode. The coion profiles tend to be more uniformly larger ($\alpha = -1$) or smaller ($\alpha = 0.975$) compared with the $\alpha = 0$ case. The charge reversal already mentioned for 1.0 M is superimposed on this general behavior.

Values of $g_{\text{sum}}(d/2)$ for the 2:2 electrolyte are plotted in figure 5. Again equation (9) is roughly satisfied but the agreement of the simulation results with equation (9) is somewhat rougher than was the case in the 1:1 electrolyte.

The diffuse layer potential of the double layer formed from a 2:2 electrolyte is plotted in figure 6. For both concentrations, the diffuse layer potential, $\phi(d/2)$, at first increases with increasing electrode charge but then passes through a maximum and thereafter decreases with increasing electrode charge. For 1.0 M this decrease is strong enough to yield negative values of the diffuse layer potential. Torrie *et al.* and Boda *et al.* have drawn attention to this phenomenon. Negative values of the diffuse layer

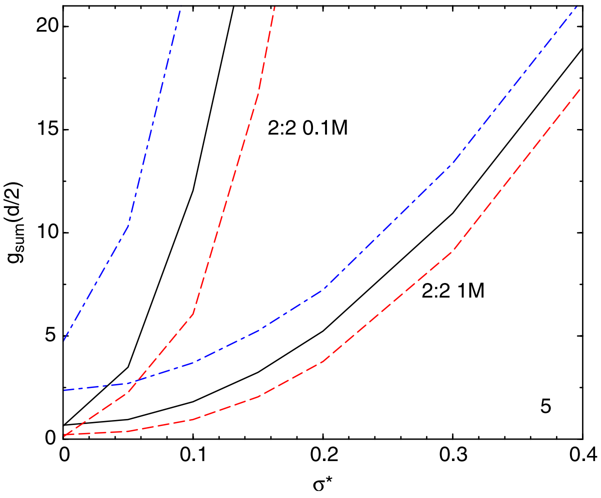

Figure 5. Contact values of $g_{\text{sum}}(z)$ for a 2:2 electrolyte. The curves have the same meaning as in figure 1.

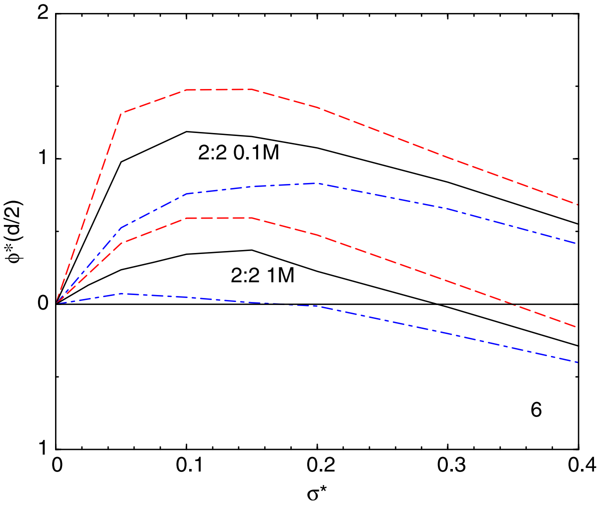

Figure 6. Diffuse layer potentials for a 2:2 electrolyte. The curves have the same meaning as in figure 1.

potential occur first in the $\alpha = -1$ case. The maximum and negative values of $\phi(d/2)$ are a result of the crossover of the $\alpha = -1$ and 0.975 counterion density profiles and the subsequent charge reversal of the counterion and coion profiles. The integral for the potential is weighted by the distance from the electrode and so reflects the behaviour of the profile away from the electrode.

Although we do not plot potential profiles here, we note that the potential profile is a monotonic function of z for the 1:1 case but is oscillatory and can change sign in the 2:2 case because of the charge inversion seen in the density profiles.

Finally, we mention that we examined the product $g_+(d/2)g_-(d/2)$ whose behavior we found to be interesting when there was no dielectric boundary [19]. The reason for our interest in this product was the fact that this product provided a direct test of the basis of the GCS theory as this product should be one in this theory. In the case of a dielectric boundary, the GCS theory is not expected to be valid and this product is not so useful. For this reason we do not plot this product here. However, we do comment that this product seems to exhibit the same behavior in the presence of images as was seen in our earlier work, namely, this product seems to tend to zero for large electrode charge. We cannot be more precise because the value of this product is large for the 1.0 M and $\alpha = -1$ case and the presumed small values would occur only for very large values of σ^*. At small electrode charge, the value of this product can rise first and pass through a maximum before decreasing to zero or tend monotonically to zero. In this regard, the $\alpha = -1$ and 0.975 cases seem to follow the behaviour of the $\alpha = 0$ case.

4. Summary

Computer simulation results are reported for the density profiles of 1:1 and 2:2 0.1 and 1.0 M restricted primitive model electrolytes near a polarizable uniform charged electrode whose dielectric coefficient may differ from that of the electrolyte. These results supplement those of Torrie and Valleau by examining different concentrations. Also the results reported here are useful since Torrie and Valleau did not report results for the ion profiles for 2:2 electrolytes with $\alpha \neq 0$. If the dielectric coefficient of the electrode is greater or smaller than that of the electrolyte, the ions are attracted or repelled, respectively. As a result, near the electrode the counterion and coion density profiles are greater or smaller if the electrode dielectric coefficient is greater or smaller than that of the electrolyte. The coion profile retains this behaviour away from the electrode but in the case of the counterion profile this behaviour is reversed away from the electrode. In the case of the 1:1 electrolyte the profiles are monotonic but are oscillatory for the 2:2 electrolyte. In addition, away from the electrode, the coion profile can exceed the counterion profile, resulting in a charge reversal. In the case of the 2:2 electrolyte, this causes the potential profile to oscillate and can result in a diffuse layer potential that can have the opposite sign to that of the charge on the electrode. Finally, contact values of the profile are considered with the goal of determining approximately the effect of a dielectric boundary on the contact value theorem. Further thoughts concerning this question and results for asymmetric electrolytes will be reported later.

Acknowledgements

The authors are grateful for the advice of David Busath and Dezso Boda and to Dezso Boda for kindly providing us with his Monte Carlo code. MA is grateful for the financial support of a Roland K. Robbins Graduate Research Fellowship. A generous allotment of computer time by the Ira and Marylou Fulton Supercomputing Center at BYU is acknowledged with thanks.

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