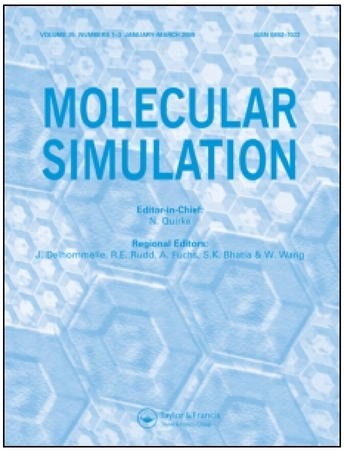

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Monte Carlo and Density Functional Theory Study of the Electrical Double Layer: The Dependence of the Charge/Voltage Relation on the Diameter of the Ions

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Monte Carlo and Density Functional Theory Study of the Electrical Double Layer: The Dependence of the Charge/Voltage Relation on the Diameter of the Ions

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According to the well known Gouy–Chapman theory (GCT) for ions modeled as charged hard spheres that are of equal diameter, the diffuse layer potential (DLP), the potential at the distance of closest approach, is independent of the ionic diameter. In this paper, the question of the dependence of the diffuse layer DLP on the ion diameter is examined by means of a Monte Carlo (MC) simulation for three values of the diameter, $d = 2$, 3 and 4.25 Å, for three ion concentrations, 0.1, 1 and 2 M, for the cases of 1:1 and 2:1 salts. For 1:1 salts at the lower concentrations, the dependence of the MC DLP on d is found to be rather weak. Thus, for these salts, the GCT is reasonably successful on this point even though the actual GCT values for the DLP are less satisfactory. For 1:1 salts, density functional theory (DFT), which is generally more accurate than the GCT, gives a dependence of the DLP on d that, at large electrode charge, is too great. The MC results for 2:1 salts show an appreciable dependence of the DLP on d at higher concentrations, especially when the divalent ions are the counterions. For these salts the GCT fails to describe both the actual values of the DLP and its d dependence; here DFT is more successful. Interestingly, at high concentrations, for 2:1 salts the MC and DFT (but not the GCT) values of the DLP can have the opposite sign to that of the electrode charge.

Keywords: Gouy–Chapman theory; Monte Carlo; Diffuse layer potential; Density functional theory

INTRODUCTION

Nearly a century ago, Gouy [1] and Chapman [2] formulated a theory of the electrical double layer (the space charge formed by ions near a charged electrode). This theory is widely used in describing such systems. The main advantage of the Gouy–Chapman theory (GCT) is the fact that it gives analytic expressions that are easily used. However, agreement with experiment requires empirical parameterization. This means that the GCT cannot be tested by comparison with experiment. In contrast, computer simulation provides an unambiguous test of the GCT as results are obtained that are accurate, aside from statistical uncertainties that can be determined and controlled, for exactly the model and thermodynamic state used by the theory.

The model used in the GCT and in this paper is the restricted primitive model (RPM), where the electrolyte is modeled as a system of charged hard spheres of equal diameter, d, (the ions) in a uniform dielectric medium (the solvent) whose dielectric constant is ϵ. Despite its simplicity, the RPM has proved to be useful in special cases such as channels

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and pores [3–5]. The first simulations of the electrical double layer (EDL) were those of Torrie and Valleau, who used the Monte Carlo (MC) method and studied the RPM with $d = 4.25\,\text{Å}$ at room temperature with ϵ equal to the dielectric constant of water. They found the GCT to be qualitatively reliable for 1:1 salts [6] but rather poor for 2:1 salts [7] when the divalent ion was the counterion.

More recently, Boda *et al.* have made MC simulations for double layers consisting of ions and dipoles [8], molten salts [9] and ions at lower concentrations [10]. Large differences between the GCT and MC results were seen in both these studies. This is because the dimensionless coupling constant, q^*_{ij}, defined by

$$q^{*2}_{ij} = \frac{\beta z_i z_j e^2}{\epsilon d},$$

where $\beta = 1/kT$ (T is the temperature and k is Boltzmann's constant), z_i is the valence of an ion of species i and e is the magnitude of the electron charge, was large. A large value of q^*_{ij} results from a small dielectric constant (as in molten salts), a small temperature (as in a frozen electrolyte), a small ion diameter, a large valence (or any combination thereof). The GCT and, indeed, almost all theories are useful only for small to moderate q^*_{ij}. Only theories that account for ion pairing [11,12] seem promising for large q^*_{ij}.

The GCT is a theory of point ions. The ion diameter does not appear in the GCT. In the GCT, the diffuse layer potential (DLP), the potential at the distance of closest approach, $d/2$, to the electrode, $\phi(d/2)$, is not a function of d. Of course, even in the GCT, the total potential, $\phi(0)$, will depend on d because the inner layer is of thickness $d/2$. Previously, we reported [8] a comparison with the Torrie–Valleau results for $d = 4.25\,\text{Å}$ and, recently, we reported results for $d = 3\,\text{Å}$ for double layers containing 1:1 and 2:1 salts. In this study, we report MC results for double layers containing 1:1 and 2:1 salts for $d = 4.25$, 3 and $2\,\text{Å}$ and examine the dependence of the DLP on d. In addition, we compare density functional theory (DFT) with our MC results. Presently, DFT is the best simple theory for the EDL.

RESULTS

Our MC method has been described earlier [8–10] and employs a modified version of the Torrie–Valleau charged sheets method [6] to account for the long range character of the coulomb interactions. Our DFT method, based on the version of DFT due to Rosenfeld [13], is described in our earlier publication [14]. An inconvenience is that in our MC method it is the charge density of the electrode, σ, that is specified whereas in our DFT method it is the electrode potential, $\phi(0)$, that is specified. As a result, if a comparison is desired for a specific state, one must iterate to find that value of the DFT $\phi(0)$ that gives the value of σ that was used in the MC simulation. Since the DFT calculation is fast, this inconvenience is minor. To be sure, we could modify the DFT program so that σ could be used as input. However, it was not thought to be worth the effort.

TABLE I The values of diffuse layer potential for a 1:1 electrolyte, at various concentrations, electrode charges and ionic diameters

1:1 Electrolyte

		d [Å]		
c [M]	*σ [C m^{-2}]*	*2.0*	*3.0*	*4.25*
0.1	− 0.1	− 3.199	− 3.167	− 3.174
	− 0.2	− 4.180	− 4.164	− 4.261
	− 0.3	− 4.665	− 4.685	− 5.009
	− 0.4	− 4.950	− 5.065	− 5.721
1.0	− 0.1	− 1.490	− 1.372	− 1.142
	− 0.2	− 2.313	− 2.127	− 2.024
	− 0.3	− 2.761	− 2.595	− 2.705
	− 0.4	− 2.976	− 2.958	− 3.400
2.0	− 0.1	− 1.111	− 0.890	− 0.621
	− 0.2	− 1.774	− 1.506	− 1.216
	− 0.3	− 2.158	− 1.972	− 1.814
	− 0.4	− 2.442	− 2.282	− 2.484

The results of our MC simulations are listed in Table I and the MC values for the DLP are plotted in Figs. 1 and 2. Note that we give the values of the charge density in experimental units (C m^{-2}) and not in the reduced (dimensionless) units that are common in theory. This is because the GCT DLP is independent of d at fixed charge density. The GCT DLP is not independent of d at fixed reduced charge density because d enters into the conversion between experimental and reduced charge density. The DFT and GCT results are plotted in Figs. 1 and 2 also.

One interesting result is that in the case of the 1:1 salts the dependence of the MC DLP is rather small at the smaller concentrations. The DFT shares this feature at small charge densities but exhibits too large a dependence at the large σ. The GCT is better in this regard. The practical consequences of this overestimate of the d dependence by DFT are minimal because values of σ greater than 0.2 Coul m^{-2} are difficult to achieve experimentally and because the contribution of the DLP to the total capacitance is small at large values of σ. A dependence of the DLP on d is more apparent for

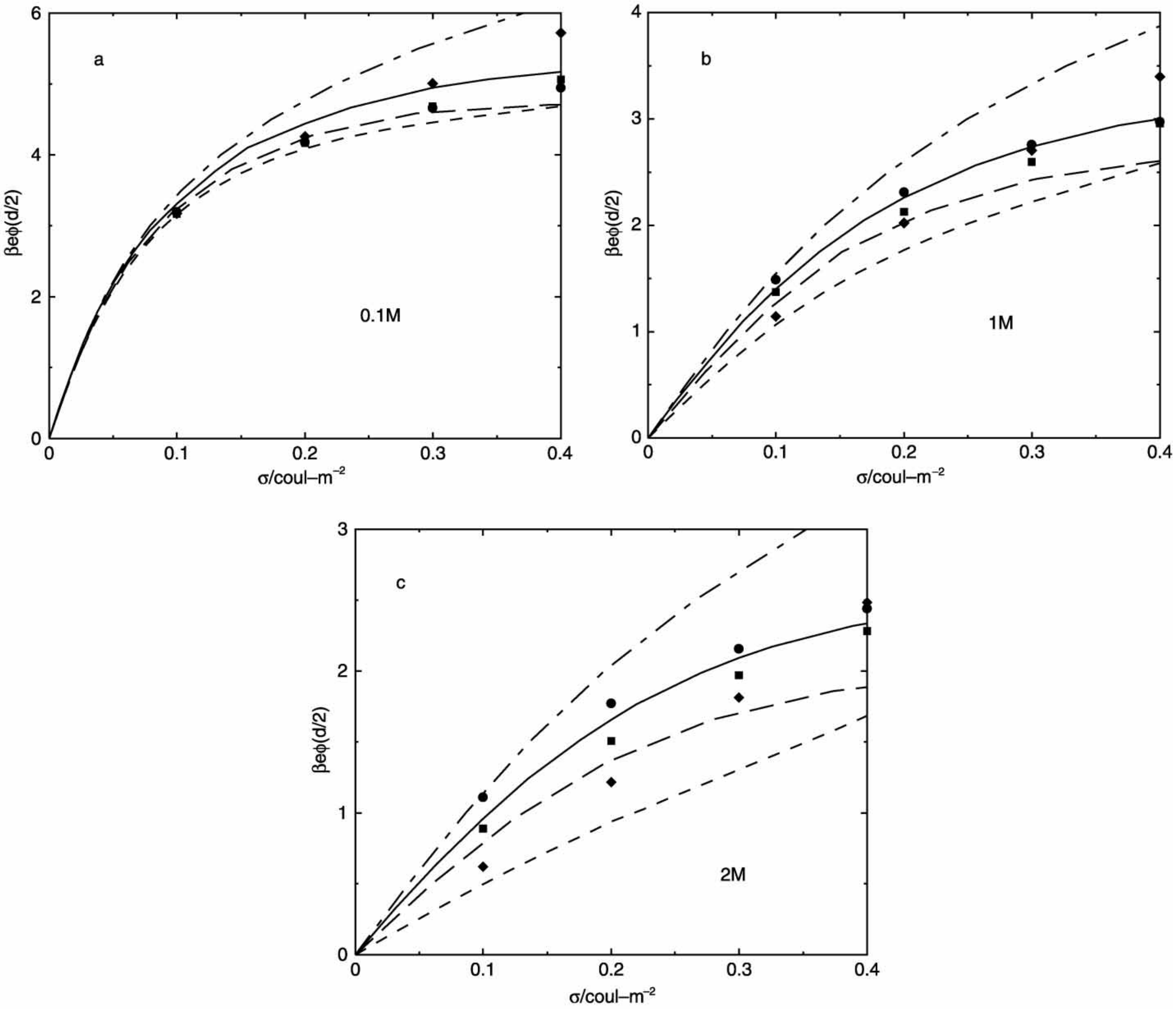

FIGURE 1 The DLP for a 1:1 electrolyte as a function of the electrode charge for various diameters. (a) $c = 0.1\,\mathrm{M}$, (b) $c = 1.0\,\mathrm{M}$, (c) $c = 2.0\,\mathrm{M}$. The circles, squares and diamonds give the MC results for $d = 2$, 3 and 4.25 Å, respectively. The solid, long dashed and short dashed curves give DFT results for $d = 2$, 3 and 4.25 Å, respectively. The dot dashed curve gives the GC results.

the 2:1 case when the divalent ions are the counterions. Again DFT overestimates this dependence but is in reasonable qualitative agreement with the MC results (Table II).

More positively, as was pointed out in our previous publications [14,15], DFT is able to account for some interesting features of the EDL. For example, as pointed out by Torrie and Valleau [6], for a 1:1 salt with $d = 4.25\,\mathrm{Å}$, a second layer of counterions is formed when $\sigma d^2/e \sim 0.7$. This is predicted by DFT but not by the GCT. This is of no practical consequence because this is such a large value of the charge density; nonetheless, it is an interesting phenomenon. Furthermore, when divalent ions are present, $\phi(d/2)$ can have the opposite sign to that of σ. This is because too much counter charge is drawn to the electrode and a subsequent layer of coions is formed. For a 2 M 2:1 salt with $d = 4.25\,\mathrm{Å}$, this effect is so strong that it occurs even at small values of σ; this effect can occur even when the monovalent ions are the counterions.

In a study that had escaped our memory and that we failed to cite in our previous paper [14], Torrie [16] noted that his MC results showed that the slope of $\phi(0)$ vs. σ changes sign in a double layer with a 0.05 M 2:1 salt, resulting in a negative total capacitance. This is another aspect of the behavior shown here and in our previous paper. We apologize to Professor Torrie for this unintentional oversight. Torrie's study resulted from the contribution of Attard *et al.* [17] who showed that, contrary to common belief, thermodynamics does not prohibit a negative total

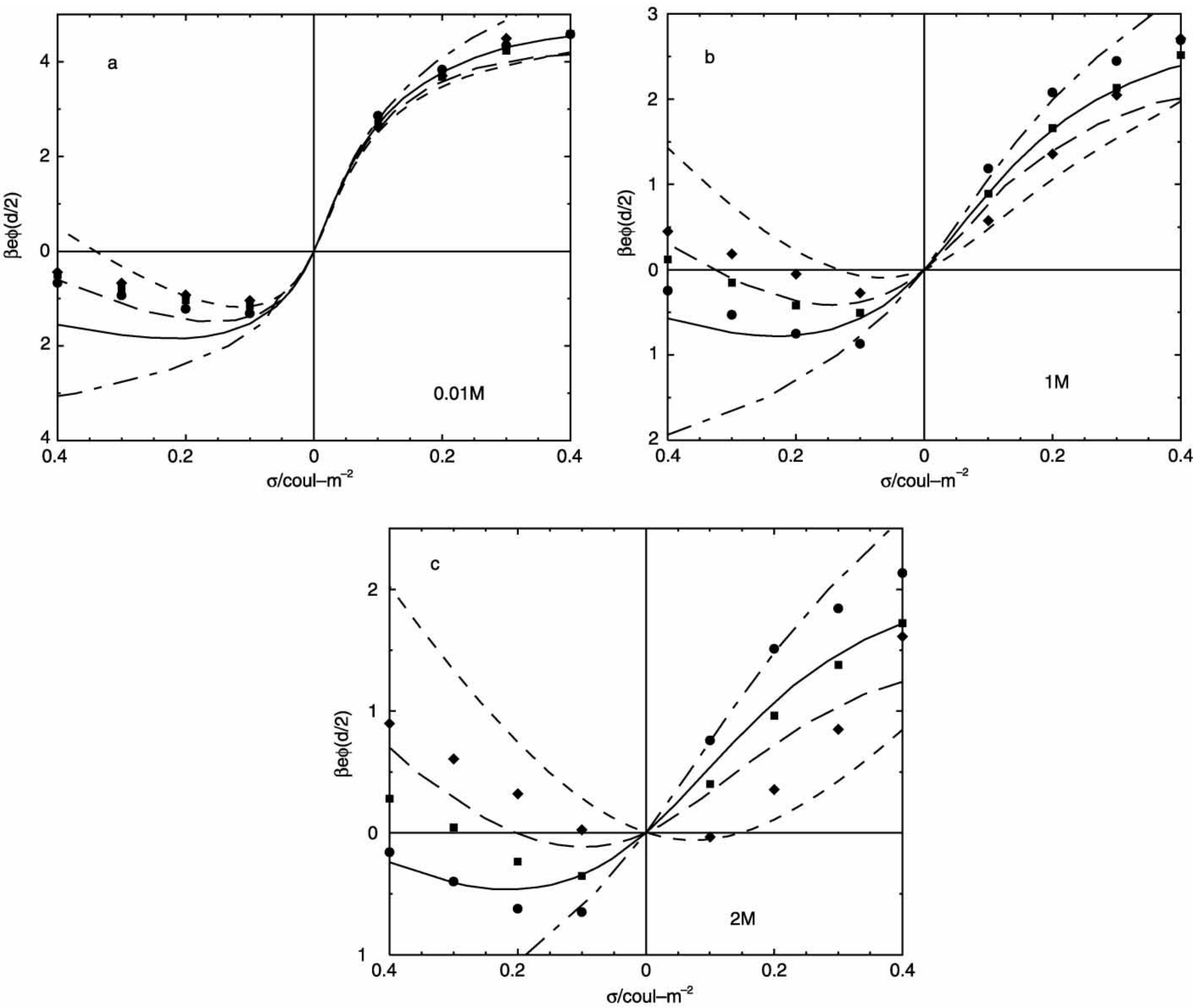

FIGURE 2 The DLP for a 2:1 electrolyte as a function of the electrode charge for various diameters. (a) $c = 0.1\,\mathrm{M}$, (b) $c = 1.0\,\mathrm{M}$, (c) $c = 2.0\,\mathrm{M}$. The points and curves have the same meaning as in Fig. 1.

capacitance. Recently, Partenskii and Jordan [18] have pointed out to us their contribution to this question.

SUMMARY

In the MC simulations, the DLP, $\phi(d/2)$, shows a slight dependence on d for double layers from 1:1 salts at lower concentrations. This dependence is considerably greater for 2:1 salts. DFT overestimates this dependence but does predict the effect. The Gouy Chapman theory predicts that there is no variation of $\phi(d/2)$ on d.

The tendency of $\phi(d/2)$ to have the opposite sign to the electrode charge density at higher concentrations that we observed earlier for 2:1 salts and $d = 3\,\text{Å}$ is even more striking for $d = 4.25\,\text{Å}$.

Curiously, the MC values at $-0.1\,\mathrm{Coul\,m^{-2}}$ for $d = 4.25\,\text{Å}$ salts at higher concentrations seem anomalously large in magnitude. Whether this numerical error in the MC results or indicates that the DFT has some difficulties with this state is uncertain. Further study of this region may be of value.

It is worth noting that for 2:1 salts with $d = 4.25\,\text{Å}$ and 2 M, the density functional DLP, and thus the total potential, need not be zero when the electrode charge is zero. In this work the effect is small and is conceivably the result of numerical uncertainties. However, we note that a potential at the point of zero charge is often taken as evidence for specific adsorption. A difference in ionic diameters, charge asymmetry, and layering in the density profiles may

TABLE II The values of diffuse layer potential for a 2:1 electrolyte, at various concentrations, electrode charges and ionic diameters

2:1 Electrolyte				
		d [Å]		
c [M]	σ [C m^{-2}]	*2.0*	*3.0*	*4.25*
0.1	− 0.4	− 0.667	− 0.494	− 0.440
	− 0.3	− 0.930	− 0.799	− 0.673
	− 0.2	− 1.216	− 1.038	− 0.926
	− 0.1	− 1.310	− 1.147	− 1.041
	0.1	2.861	2.692	2.616
	0.2	3.837	3.678	3.708
	0.3	4.346	4.234	4.492
	0.4	4.582	4.593	5.182
1.0	− 0.4	− 0.246	0.121	0.449
	− 0.3	− 0.528	− 0.151	0.184
	− 0.2	− 0.751	− 0.420	− 0.052
	− 0.1	− 0.869	− 0.507	− 0.274
	0.1	1.188	0.891	0.576
	0.2	2.079	1.662	1.355
	0.3	2.449	2.133	2.049
	0.4	2.694	2.519	2.712
2.0	− 0.4	− 0.157	0.282	0.897
	− 0.3	− 0.399	0.046	0.607
	− 0.2	− 0.622	− 0.235	0.321
	− 0.1	− 0.651	− 0.355	0.025
	0.1	0.760	0.402	− 0.033
	0.2	1.512	0.963	0.355
	0.3	1.845	1.380	0.851
	0.4	2.135	1.723	1.612

cause this effect even in the absence of specific adsorption.

Acknowledgements

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