A MEAN SPHERICAL APPROXIMATION STUDY OF THE CAPACITANCE OF AN ELECTRIC DOUBLE LAYER FORMED BY A HIGH DENSITY ELECTROLYTE

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Dedicated to Professor Ivo Nezbeda on the occasion of his 65th birthday.

In a recent grand canonical Monte Carlo simulation and modified Poisson–Boltzmann (MPB) theoretical study of the differential capacitance of a restricted primitive model double layer at high electrolyte densities, Lamperski, Outhwaite and Bhuiyan (*J. Phys. Chem. B* **2009**, *113*, 8925) have reported a maximum in the differential capacitance as a function of electrode charge, in contrast to that seen in double layers at lower ionic densities. The venerable Gouy–Chapman–Stern (GCS) theory always yields a minimum and gives values for the capacitance that tend to be too small at these higher densities. In contrast, the mean spherical approximation (MSA) leads to better agreement with the simulation results than does the GCS approximation at higher densities but the agreement is not quite as good as for the MPB approximation. Since the MSA is a linear response theory, it gives predictions only for small electrode charge. Nonetheless, the MSA is of value since it leads to analytic results. A simple extension of the MSA to higher electrode charges would be valuable.
Keywords: Electric double layer; Mean spherical approximation; Capacitance; Grand canonical Monte Carlo simulations; High density electrolytes; Electrochemistry.

An interfacial charged layer is formed in an electrolyte near a charged electrode. This layer is conventionally called a double layer but with the presence of divalent ions in the electrolyte and/or at high electrolyte con-

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centrations this layer may consist of alternating layers of charges of different sign. In planar geometry, that is, a planar electrode next to the electrolyte, the long standing Gouy–Chapman–Stern (GCS) theory[1–3] is the classical theory of double layer phenomenon, which is widely used. However, its popularity is due more to the fact that it is analytic and hence convenient to use rather than to its accuracy. A review of theoretical work on the double layer has been published recently[4].

The GCS theory is based on the assumption that the solvent can be replaced by a dielectric continuum whose relative permittivity, ε_r, is equal to that of the solvent and the ions are point ions with only an electrostatic interaction with the charged electrode, and which can approach the electrode not closer than a distance-of-closest-approach from the electrode. By ascribing an exclusion volume to the ions (spherical rigid ions), the underlying model that emerges is called the primitive model (PM) of the electrolyte. This is a simple, yet non-trivial model that has been enormously useful in our understanding of the properties of the electric double layer[4]. If the rigid ions are all of the same size, the model is called the restricted primitive model (RPM). Note that in the case of a high density system, such as an ionic liquid or a molten salt, there is no solvent and the neglect of a molecular solvent is not an approximation. For simplicity, let us restrict our attention to a symmetric salt (in both charge and diameter). One aspect of the GCS theory is that in this theory the differential capacitance has a minimum at small electrode charge and the capacitance rises to a constant that is independent of the concentration (called the inner layer capacitance) at large electrode charge. At a high enough ion density, the entire GCS capacitance becomes independent of electrode charge. However, under no circumstances is there a maximum in the GCS capacitance. This seems to be in qualitative agreement with experiment for low concentration aqueous electrolytes[5].

Lamperski and Kłos[6], and Lamperski, Outhwaite and Bhuiyan[7] have recently published a grand canonical Monte Carlo (GCMC) simulation and modified Poisson–Boltzmann (MPB) approximation study of the differential capacitance of the RPM planar double layer. They found that the nature of the differential capacitance (at and near zero electrode charge) changes from having a minimum at low electrolyte densities to having a maximum at sufficiently high electrolyte densities. This is true of both the simulation and MPB results. Such maxima have also been predicted by mean field lattice-gas type theories[8,9]. An interesting question seems to be whether the maximum at small electrode charge might exceed the inner layer capacitance at very large densities.

It is worth applying other theories to bear on this situation. After the GCS theory, the simplest theory of the double layer is the mean spherical approximation (MSA). This theory yields simple, closed form analytic results for the capacitance and explicit results for the potential, density and charge profiles. The MSA can be regarded as an extension of the linearized GCS theory with the ion diameters included in a self-consistent manner. As the MSA is a linear response theory, it is not possible to answer the question whether the capacitance is a minimum or maximum at a small electrode charge. However, the MSA values of the capacitance may be compared with the GCS, MPB and simulation results. This is the aim of the present paper. Since the MSA is restricted to small electrode charge where the potential is a linear function of electrode charge, there is no difference between differential and integral capacitances.

THEORY

In the GCS theory the differential capacitance for a symmetric valency electrolyte is

$$C = \varepsilon_0 \varepsilon_r \frac{\kappa \sqrt{1 + b^2 / 4}}{1 + \frac{1}{2} \kappa d \sqrt{1 + b^2 / 4}} \qquad (1)$$

where κ is the Debye screening parameter whose square is given by

$$\kappa^2 = \frac{\beta z^2 e^2 \rho}{\varepsilon_0 \varepsilon_r} \qquad (2)$$

$b = \beta z e \sigma / \kappa \varepsilon_0 \varepsilon_r$ is the dimensionless charge of the electrode, where σ is the charge/unit area in dimensional units, $d/2$ is the distance of closest approach of an ion to the electrode, ε_0 is the permittivity of vacuum, z is the magnitude of the ionic valency, and e the magnitude of the elementary charge. The parameter $\beta = 1/k_B T$, k_B being the Boltzmann constant, T is the absolute temperature, and ρ is the mean number density of all the ions.

Examination of Eq. (*1*) shows that the GCS capacitance has a minimum at $b = 0$. The GCS capacitance increases with increasing b and becomes a constant, $2\varepsilon_0 \varepsilon_r / d$ at large b. As mentioned earlier, at high ionic densities this is qualitatively different from the simulation results of Lamperski and co-workers[6,7].

Lamperski et al.[7] found that the MPB approximation gives a good description of the double layer differential capacitance, both qualitatively and

quantitatively. A detailed summary of the MPB approximation has been given in ref.[7]. It seems worthwhile to examine the consequences of the MSA theory applied to the problem. The MSA theory for the double layer[10] has the advantage of yielding a simple analytic expression for C. The disadvantage of the MSA is that it is a linear response theory yielding results only for small electrode charge. The MSA expression for C is

$$C = \varepsilon_0 \varepsilon_r 2\Gamma \tag{3}$$

where

$$2\Gamma d = \sqrt{1 + \kappa d} - 1 \tag{4}$$

is the MSA analogue of κ. Note that here d is the common ionic diameter. At low densities, $\Gamma = \kappa/2$ and the MSA expression for C reduces to the corresponding linearized GCS result. Furthermore, the MSA values for C can become very large; they do not have an upper limit as is the case for the GCS theory. However, the MSA C is independent of σ for a given concentration and so is unable to say whether there is a maximum at high densities or a minimum at low densities.

The details of the GCMC simulation method have been reported by Lamperski and co-workers[6,7] using the techniques described by Torrie and Valleau[11]. The mean activity coefficient needed in the simulations was calculated using the recently developed inverse grand canonical Monte Carlo technique[12] that allows an evaluation of the activity coefficient for a specified electrolyte concentration.

RESULTS AND DISCUSSION

To make contact with the results of ref.[7], we use the same state that was considered in that paper. Our simulations and theoretical results were obtained for d = 0.4 nm and $T^* = 4\pi k_B T \varepsilon_0 \varepsilon_r d/z^2 e^2 = 0.8$. The use of dimensionless T^* allows for a range of physical parameters to be studied. A range of values of $\rho^* = \rho d^3$ is considered. For the value of d = 0.4 nm, the values of $0.14 < \rho^* < 0.24$, the region of main interest here, encompasses the transition of C at $T^* = 0.8$ from a minimum to a maximum seen in the simulation and MPB study[7] and correspond to molar concentrations between 1.81 and 3.11 mol/dm^3.

Since the MSA is under study in this paper, we felt that it would be of value to examine the MSA prediction for the osmotic coefficient

$$a = \frac{pV}{Nk_B T} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} - \frac{\Gamma^3}{3\pi\rho} \tag{5}$$

where $\eta = \pi\rho d^3/6$. The MSA result for a has been found to be quite accurate for the low ionic densities, which are characteristic for aqueous electrolytes but as we believe that no previous simulation results at higher ionic densities have been reported to date, we have undertaken such a study here. Note that without the second term on the right hand side of Eq. (*5*), it reduces to the Carnahan–Starling (CS) expression[13] for the osmotic coefficient of a hard sphere fluid of the same size, which is well known in the literature as providing a very accurate description of the osmotic coefficient of hard sphere fluid systems. Plots of the MSA and simulation values of a within the range $0 < \rho^* < 0.6$ are shown in Fig. 1. The corresponding CS values of a are also plotted for comparison purposes. The MSA values of a are in better agreement with the simulation values overall than are the CS values. The two theoretical a's together with the simulation a tend to unity – the ideal gas limit, as $\rho^* \to 0$ as expected. In the GCS theory, one has the ideal gas value $a = 1$ for all states. The MSA values for a are close to the cor-

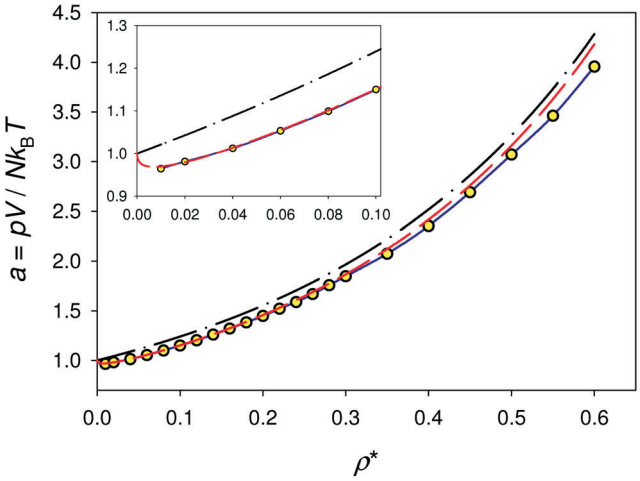

FIG. 1
The osmotic coefficient $a = pV/Nk_BT$ as a function of the reduced density ρ^* at the reduced temperature $T^* = 0.8$. The symbols are Monte Carlo data, while the dashed and the dash-dotted lines represent MSA and CS results, respectively. The line through the symbols is shown as a visual aid

responding simulation values for most of the density range studied, whereas the CS results lie consistently above those from the MSA and the simulations. As suggested by Eq. (*5*) and also borne out by the simulations, electrostatic interactions have the effect of lowering the osmotic pressure of the system.

At very low densities the MSA *a*'s lie below unity (as can be seen in the inset of Fig. 1) and agree well with the simulation results, while the CS *a*'s always exceed unity. Interestingly, the MSA estimate of the electrostatic contribution to *a* (the Γ^3 term on the right-hand side of Eq. (*5*)) does not depend strongly on the density. At very high densities the MSA *a*'s tend to be too large relative to the simulations. This would indicate that at such high densities either the hard core contribution to *a* is overestimated or the electrostatic contribution to *a* is underestimated in the MSA, or both. In contrast, the CS results for *a* are always too large. This is not surprising since the electrostatic contribution is missing in the CS formulation.

Although, the hard sphere term is the dominant contribution to *a* at high densities (see Fig. 1), one should not be misled into thinking that this is the case for all situations or properties. For example, at the values of T^* for divalent ions that are roughly four times smaller, the electrostatic contribu-

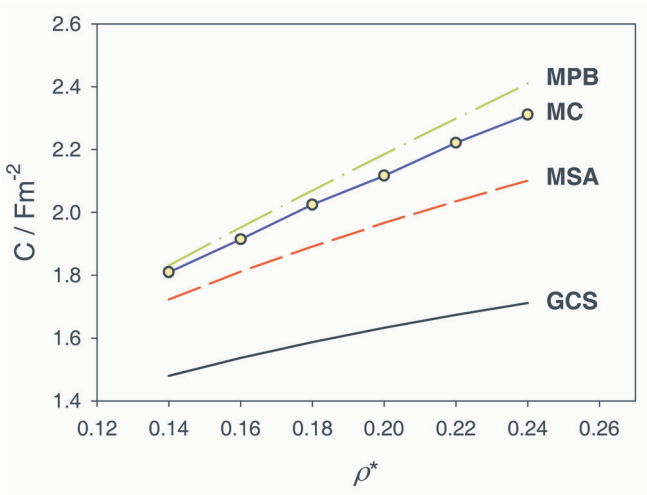

FIG. 2
The double layer capacitance *C* as a function of the reduced density ρ* at the reduced temperature $T^* = 0.8$. The symbols are Monte Carlo data, while the dashed, dash-dotted and solid lines represent MSA, MPB and GCS results, respectively. The line through the symbols is shown as a visual aid. The simulation, MPB and GCS capacitances are at zero surface charge

tion to *a* would be correspondingly larger. Furthermore, for some quantities, such as the excess energy, there is no hard sphere contribution. The point of Fig. 1 is that, except at the highest densities, the MSA expression *a* is quite accurate.

In Fig. 2, the MSA values for *C* are compared with the corresponding simulation, GCS and MPB results. Note that the latter three results have been evaluated at zero surface charge on the electrode. The GCS prediction is lower relative to the simulations. The MSA values are also lower but stay

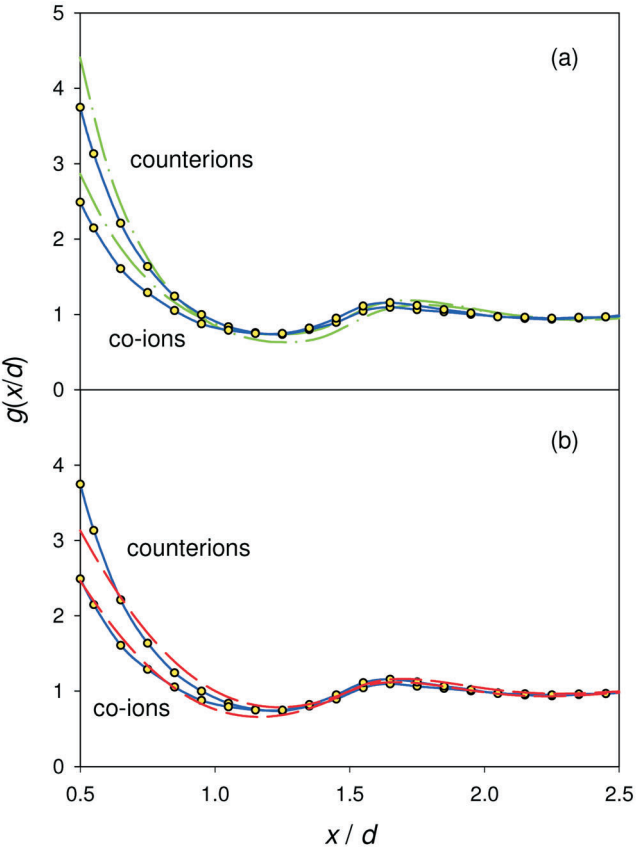

FIG. 3
The electrode-ion singlet distribution functions $g_i(x/d)$ at the reduced density $\rho^* = 0.5$, reduced temperature $T^* = 0.8$ and surface charge density $\sigma = 0.05$ C/m^2. The symbols are Monte Carlo data, while the dash-dotted and dashed lines represent MPB (a) and MSA (b) results, respectively. The line through the symbols is shown as a visual aid

much above the GCS values. The MPB values are a little high but are in good agreement with the simulation results.

In Fig. 3, the MSA and MPB electrode-ion singlet distributions along with the simulation results at a high salt concentration ($\rho^* = 0.5$) are shown for a low ($\sigma = 0.05$ C/m^2) surface charge density. For the sake of clarity we have chosen to present the MPB results in panel (a) and the MSA results in panel (b). At this charge, apart from the region around contact both the theories are qualitative corresponding to the simulation results.

In Fig. 4, the MPB singlet distribution functions along with those from the simulations are shown at a higher electrode charge of $\sigma = 0.3$ C/m^2 where the MPB profiles are seen to deviate somewhat more from the simulation values. As indicated earlier, the MSA is a linear theory valid only for small surface charge around $\sigma = 0$, and is thus not tenable here and hence not shown.

Since the conclusion of this work, it has come to our attention that Fawcett et al.[14] have made simulations for the RPM double layer at high electrolyte concentrations. They have reported estimates of some capacitance values and found that the mean field lattice-gas theories[8,9] were not in agreement with their simulation results.

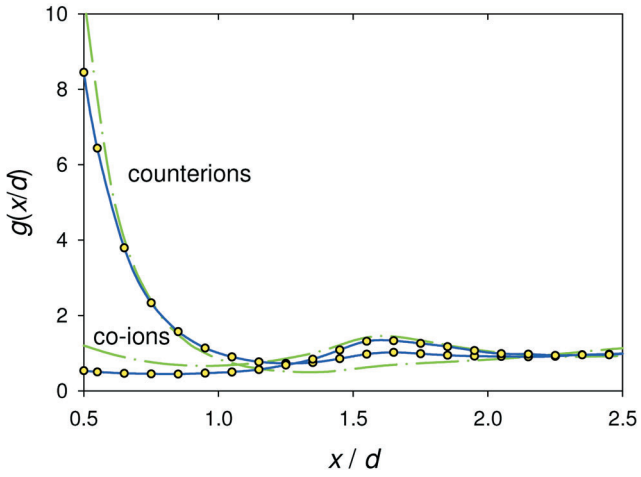

FIG. 4
The electrode-ion singlet distribution functions $g_i(x/d)$ at the reduced density $\rho^* = 0.5$, reduced temperature $T^* = 0.8$ and surface charge density $\sigma = 0.3$ C/m^2. The symbols are Monte Carlo data, while the dash-dotted lines represent MPB results. The line through the symbols is shown as a visual aid

CONCLUSIONS

The focus of this paper has been an in-depth examination of the MSA predictions for the capacitance of a RPM planar double layer. This is a topic of interest as some recent studies[6–8] in the literature have shown that the differential capacitance as a function of the electrode charge can reveal a maximum at sufficiently high salt concentrations. The traditional GCS theory does not capture this effect. In contrast, the MSA gives a good description of the capacitance for high ion densities and small electrode charge. The MSA has nothing to say about whether the capacitance has a maximum or a minimum. However, the MSA is identical to the linearized GCS theory at low densities. Thus, it is reasonable to say that the MSA is consistent with a minimum in the capacitance at low densities since its values for C at $\sigma = 0$ compare favorably to the GCS, MPB and simulation values that predict a mimimum at low densities. The reasonably good agreement of the MSA capacitance with the simulation and MPB results at a small electrode charge at high densities, which predict a maximum, suggest that the MSA results are consistent with a maximum. The MPB gives better results than does the MSA. However, the advantage of the MSA is that it yields analytic results, is easy to use, and hence is convenient when it comes to routine, everyday analysis of experimental data. Admittedly, a limitation is the fact that the MSA relation for capacitance is valid for small electrode charges around zero electrode charge. Thus an accurate extension, even semiempirical, of the MSA result for C to higher electrode charges would be valuable.

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