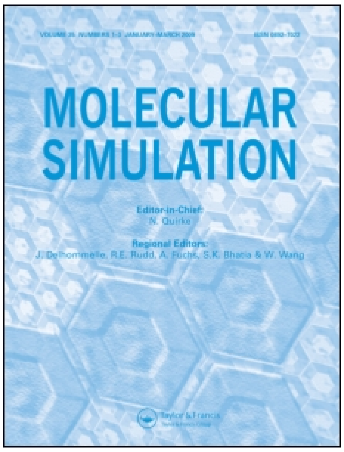

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The effect of dielectric polarization of the electrode on anomalous temperature effects in the electrical double layer

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The effect of dielectric polarization of the electrode on anomalous temperature effects in the electrical double layer

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Monte Carlo simulations and a modified Poisson–Boltzmann (MPB) theory are used to investigate the temperature dependence of the capacitance (around the potential of zero charge) of an electric double layer in the presence of surface polarization due to a dielectric boundary. Within the context of the *restricted primitive model planar double layer*, whose solvent dielectric constant is ϵ_2, the cases when the electrode is an insulator ($\epsilon_1 = 1$), when the electrode and the electrolyte have the same permittivity ($\epsilon_1 = \epsilon_2$, no polarization), and when the electrode is a conductor ($\epsilon_1 \rightarrow \infty$) are studied for the case where the electrolyte concentration is 0.1 M. The simulations reveal a capacitance anomaly, that is, a positive temperature dependence of the capacitance at low temperatures for the former two situations. The MPB theory also shows this effect for these two situations and is in qualitative or better agreement with the simulation data. In these two cases, both the simulations and theory show a dramatic increase of the diffuse layer potential in the temperature regime where capacitance anomaly occurs. However, in the latter situation, where the electrode is metallic, the capacitance always has a negative temperature derivative for the MPB theory and probably also for the simulation data.

Keywords: Monte Carlo simulation; electric double layer; dielectric boundary; capacitance; anomalous temperature effects; modified Poisson–Boltzmann

1. Introduction

Many of the recent advances in the theory of the electrochemical interface between an electrolyte and an electrode have been driven by simulations. The seminal simulations of Torrie et al. [1–3] showed that for divalent ions, where the electrical coupling, $\Gamma = z^2e^2/(\epsilon_2 dkT)$, is large, the conventional *Poisson–Boltzmann* theory of Gouy [4], Chapman [5] and Stern [6] GCS was unsatisfactory [3]. Even for monovalent ions, the GCS theory is reasonable only if the electrode charge, and not the electrode potential, is used as the independent variable. This point seems not to be appreciated. It is not trivial because the potential is the natural independent variable of the GCS theory. The parameters in the coupling constant are the ion valence, z, the magnitude of the electronic charge, e, the solvent dielectric coefficient, ϵ_2, the ion diameter, d, Boltzmann's constant, k, and the temperature, T. Neither theory nor simulations require that all the ions have the same diameter or valence. However, for simplicity, we restrict our attention to this case. In the GCS theory and in most simulations, the electrolyte is modelled by the *primitive model*, where the ions are treated as charged hard spheres (point ions in the case of the GCS theory) and the solvent is treated as a dielectric continuum. For the symmetric case, where the ions are presumed to have the same diameter, the model is called the *restricted primitive model* (RPM).

The most interesting phenomenon that has been observed in recent simulations is the anomalous temperature dependence of the capacitance C, when the coupling constant is very large and the temperature derivative of C reverses sign and becomes positive. This has been called the *anomalous capacitance effect* in the literature and seems to account for the sign of the temperature derivative of C, seen in experiments for frozen electrolytes and molten salts. In the low concentration electrolyte systems that are treated in this paper, this positive derivative and resulting small values for C at small ($T^* = 1/\Gamma$, the reciprocal of the coupling constant) are a result of the withdrawal of the ions from the electrode and resultant dramatic increase in the width of the double layer. This increase could be referred to as negative adsorption of the ions [7]. However, the effect is more than negative adsorption. Not only is there a depletion of ions near the electrode but there is also an increase in the width of the depleted interfacial region with decreasing T^*. This effect is akin to drying of the electrode by the ions. However, this is not a literal drying since the solvent is not depleted at the electrode. It is of relevance to note that high concentration systems such as

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molten salts also exhibit an increase of capacitance with T^*, but in this case, the mechanism is different. The broadening of the double layer is due to multilayer adsorption in a high density fluid [8].

The simulations that show the aforesaid effect and the GCS theory are both based on the assumption that the electrode is not polarized, which in turn means that the solvent and electrode are assumed to have the same dielectric coefficient. This is, of course, unlikely. Usually, the electrode is a metal whose dielectric coefficient, ϵ_1, is infinite. In this case, the resultant polarization charge on the electrode results in an additional attractive force on the ions. A reasonable question is whether this attractive force negates the anomalous temperature effect or merely delays it. We consider this question here. For completeness we also consider the case $\epsilon_1 = 1$, where the polarization results in a repulsion, and the case that we considered earlier, $\epsilon_1 = \epsilon_2$, where the electrode is not polarized.

2. Simulations and theory

We have discussed our simulation method before [7–9]. Briefly, we use the canonical (NVT) ensemble with a simulation cell whose dimensions are $XL \times YL \times ZL$ that contains $N = 400$ positive ions and and $N + \Delta N$ negative ions. Thus, in the absence of polarization effects, the electrode is presumed to be positively charged because of neutrality. The two walls at $\pm ZL$ are assumed to be hard and uncharged. The electrode is located at $z = 0$ and is hard and polarizable, while the boundaries in the x and y directions are periodic. Further, the ions are presumed to be monatomic, however, by changing the coupling constant, multivalent ions can be considered. The left half cell ($-ZL/2 < z < 0$) has a dielectric coefficient of ϵ_1. The ions are confined to the right half cell ($0 < z < ZL/2$), where the dielectric coefficient is $\epsilon_2 = 78.5$, which is appropriate for a water-like solvent, and the ion diameter is $d = 4.25$ Å. Typically, we made several thousand equilibration steps and averaged over a million configurations. Results are reported for a bulk concentration of $c = 0.1$ M. With the above value of d, this concentration corresponds to a reduced density $\rho d^3 = 0.00925$. The neutralizing charge density (charge/area), σ, on the electrode is $e\Delta N/(XL)^2$. Although, we mention specific values of d and ϵ_2, we report our results in dimensionless units. As a result, if the dimensionless density, rather than concentration, is used, our results are independent of these parameters. The value of $XL = YL$ is $170d$ with the value of ZL adjusted to give a bulk region with the desired bulk concentration. The effect of the polarization of the electrode is treated by means of fictitious image charges inside the electrode that mimic the polarization charge on the surface of the electrode. Each ion of charge q, located at (x,y,z) has an image whose charge is αq, located at $(x,y,-z)$. The parameter α is given by

$$\alpha = \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}. \tag{1}$$

Thus if the electrode is a metal, $\epsilon_1 = \infty$ and $\alpha = -1$. At the other extreme where the electrode is a dielectric with $\epsilon_1 = 1$ then $\alpha = 0.975$. The polarization force is attractive for a metallic electrode and repulsive for a dielectric electrode. If $\epsilon_1 = \epsilon_2 = 78.5$, $\alpha = 0$ and there is no polarization. Long-range electrostatic effects are taken into account by the charged sheets method of Torrie et al. [1], as improved by Boda et al. [7–8].

The anomalous temperature effect occurs only when the electrode charge is small. As soon as the charge of the electrode is significant, the attractive force of the electrode charge dominates and any depletion of ions ceases. To obtain C, we want to be in the linear regime, hence, ΔN should be small. However, since ΔN cannot be smaller than one, these places a limit on how small an electrode charge density we can simulate. Of course, we could achieve smaller electrode charge densities by using larger values for N and XL. However, this would make the simulation more lengthy and we decided not to do this and the value $\Delta N = 4$, corresponding to $\sigma^* = \sigma d^2/e = 0.0025$, was used. For completeness we made some simulations for larger values of σ^*.

The anomalous capacitance in the double layer was first seen in the simulations of Boda et al. [7,8]. More recently, it has been seen with density functional theory [10], the field theoretic approach of di Caprio et al. [11], and the modified Poisson–Boltzmann (MPB) theory [12,13]. However, the density functional theory and the field theoretic approach have not been applied to the case of the polarized electrode. Recently, Valiskó et al. [14] have reviewed the theoretical situation for an unpolarized electrode.

The MPB theory incorporates ion size and correlation effects that are missing in the GCS theory. It is the most easily used theory that predicts polarization effects accurately. There are though other theories that can be applied to treat polarization effects, *viz.*, those due to Kjellander and Marcelja [15], Plischke and Henderson [16], Carnie and Chan [17] and Vertenstein and Ronis [18]. Although, the Plischke–Henderson work does not include polarization, it is a pair theory that is capable of doing so. There have also been theories based on screened self-image ideas, by Onsager et al. [19] and Croxton et al. [20]. These are singlet level treatments and so are less sophisticated than the pair theories. Earlier, we summarized the MPB theory with emphasis on its applicability to dielectric polarization [21]. All the relevant equations related to polarization effects due to a dielectric discontinuity at the interface appear in this reference and will not be repeated here.

3. Results

First we report results for the case of no polarization ($\alpha = 0$). The MC results for the potential at contact, $\beta e\phi(d/2)$, or the diffuse layer potential, as a function of σ^* for various values of the reduced temperature T^* are displayed in Figure 1(b). In Figure 2(b) the corresponding MPB results are shown only at three values of T^* (0.1, 0.3 and 1) for clarity. The potential is nearly linear at the smallest values of σ^*. As stated earlier, we use the values of $\Delta N = 4$ or $\sigma^* = 0.0025$ to compute the capacitance. In addition to the linearity (or near linearity) of the curves in Figure 1 at small σ^*, it is interesting to note that the linear regime extends further for the higher T^* results. Our simulations [9] and MPB results [13,21] at larger values of σ^* also reveal that for $T^* = 0.15$, there is a maximum and a subsequent decrease in the diffuse layer potential as σ^* is increased beyond 0.01. This maximum is seen in Figure 3(a) for $T^* = 0.15$. The lower the value of T^*, the earlier the appearance of the maximum. This is evident in Ref. [9] and in some scattered simulation results for $\sigma^* = 0.04$, that we do not report here. As the temperature is increased above $T^* = 0.15$, it appears that the maximum gradually disappears as there is no evidence of a maximum for $T^* = 0.60$ even at very large values of σ^*. The maximum is a reflection of the fact that as the electrode is charged, the ion depletion that is the cause of the capacitance anomaly disappears.

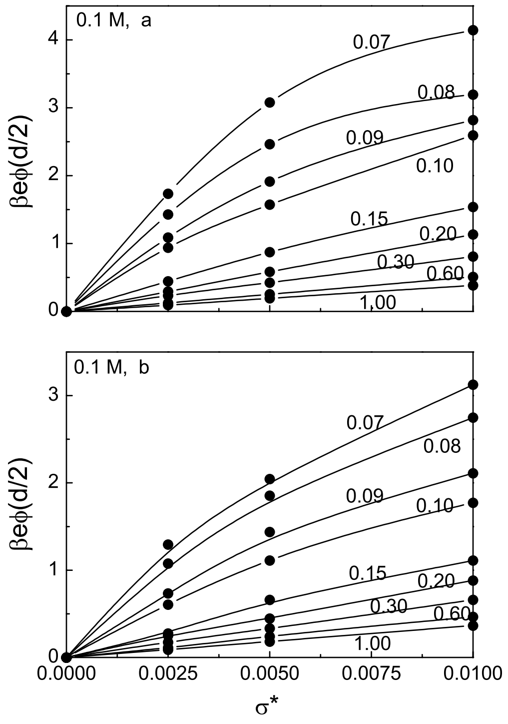

Figure 1. Monte Carlo reduced diffuse layer potential as a function of reduced electrode charge density at 0.1 M for (a) a dielectric electrode ($\alpha = 0.975$) and (b) unpolarised electrode ($\alpha = 0$). The curves are isotherms for several dimensionless temperatures. The solid circles give the simulation results and curves are a fit to these results.

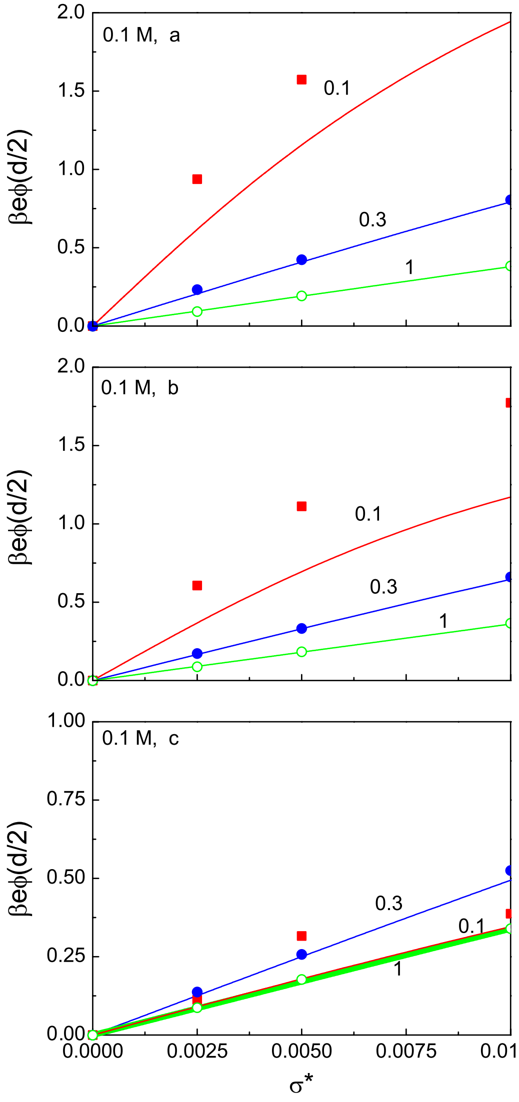

Figure 2. Monte Carlo and MPB reduced diffuse layer potential as a function of electrode charge density at 0.1 M at the reduced temperatures 0.1, 0.3 and 1 for (a) a dielectric electrode ($\alpha = 0.975$), (b) an unpolarized electrode ($\alpha = 0$) and (c) a metallic electrode ($\alpha = -1$). Symbols denote the MC results—solid rectangle $T^* = 0.1$, solid circle $T^* = 0.3$, and open circle $T^* = 1$, while the lines denote the MPB results.

In Figure 3 some of the values of $\beta e\phi(d/2)$ obtained in this simulation are compared to earlier results [9] for monovalent and divalent ions. The values for $T^* = 0.60$ correspond to the earlier $z_1 = z_2 = 1$ results and the $T^* = 0.15$ values correspond to the earlier $z_1 = z_2 = 2$ results (but with a factor of two due to the way in which the reduced potential was defined for divalent ions in Ref. [9]). The present results are those for small σ^* (≤ 0.01), while the previous results are those for large σ^* (≥ 0.05). The old and new results are in good agreement in the sense that they both fall on the same smooth curves.

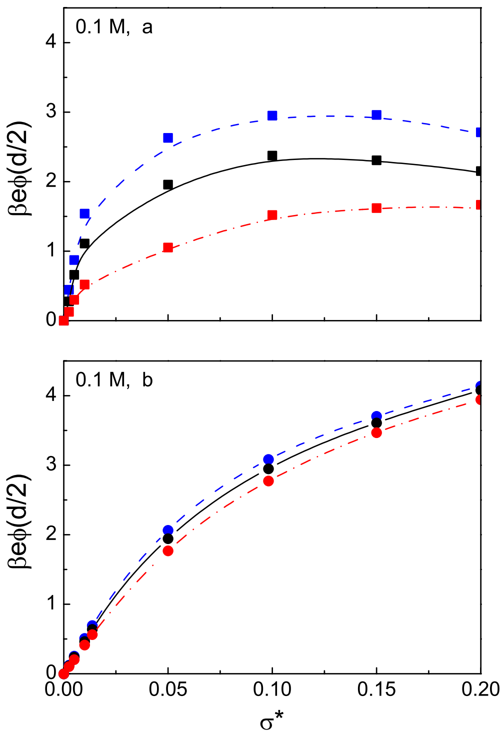

Figure 3. Monte Carlo reduced diffuse layer potential as a function of reduced electrode charge density at 0.1 M for (a) $T^* = 0.15$ and (b) $T^* = 0.60$. The curves are a fit of these results. The dashed, solid, and dot dashed curves give the results for a dielectric ($\alpha = 0.975$), unpolarized ($\alpha = 0$), and metallic ($\alpha = -1$) electrode, respectively.

The double layer capacitance C is determined from the electrode potential. Within the RPM, the inner layer capacitance is a constant and although the full capacitance and the diffuse layer capacitance differ in magnitude, the signs of their temperature derivatives are the same. Results for the reduced capacitance $C^*(=Cd)$ are given in Figure 4. The MC results for $\alpha = 0$ are similar to those reported earlier by Boda et al. [7]. The vertical lines indicate the values of T^* that correspond to monovalent (0.60) and divalent (0.15) ions at room temperature when the values $d = 4.25\,\text{Å}$ and $\epsilon_2 = 78.5$ are used. The temperature dependence of C reverses at the lowest values of T^*. This is the capacitance anomaly. Monovalent and divalent ions (barely) show the conventional temperature dependence. The MPB results also show this capacitance anomaly but tend to overestimate the capacitance at low T^*. This is reminiscent of earlier such comparative behaviour between MC and MPB capacitances seen in the studies by Bhuiyan et al. [12,13].

The effect of the ion depletion at low T^* is seen clearly and dramatically in Figure 5, where the reduced diffuse layer potential $\beta e\phi(d/2)$ at $\sigma^* = 0.0025$ is plotted as a function of T^*. The diffuse layer potential does not change significantly until small values of T^* are achieved. For $\alpha = 0$, near the value appropriate for divalent ions, the diffuse layer potential increases suddenly and very rapidly, reflecting the formation of an ever widening depletion or drying region. The MPB theory predicts similar trends and is in qualitative agreement overall with the MC results. Note that the MPB $\beta e\phi(d/2)$ is in almost quantitative agreement with the MC data for $T^* \geq 0.15$, although its rise for $T^* < 0.15$ is less than that in the MC. To our

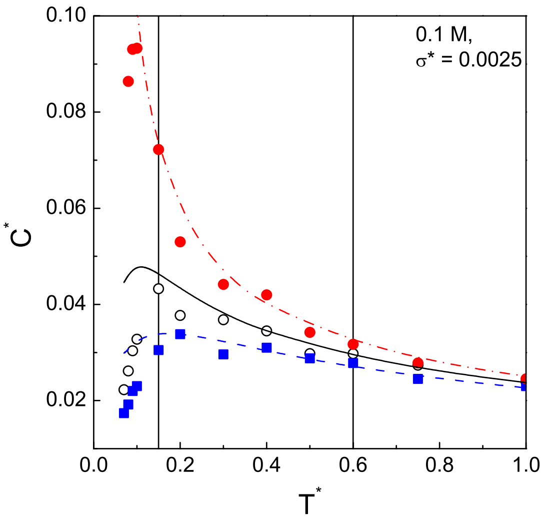

Figure 4. Reduced capacitance as a function of reduced temperature at 0.1 M bulk concentration and $\sigma^* = 0.0025$. The vertical lines at $T^* = 0.60$ and 0.15 show the location of a monovalent or divalent electrolyte for the parameters $d = 4.25\,\text{Å}$ and $\epsilon_2 = 78.5$, respectively. The symbols represent the MC results, while the solid, dashed, and dot-dashed curves give the MPB results for an unpolarized ($\alpha = 0$), a dielectric ($\alpha = 0.975$), and a metallic ($\alpha = -1$) electrode, respectively.

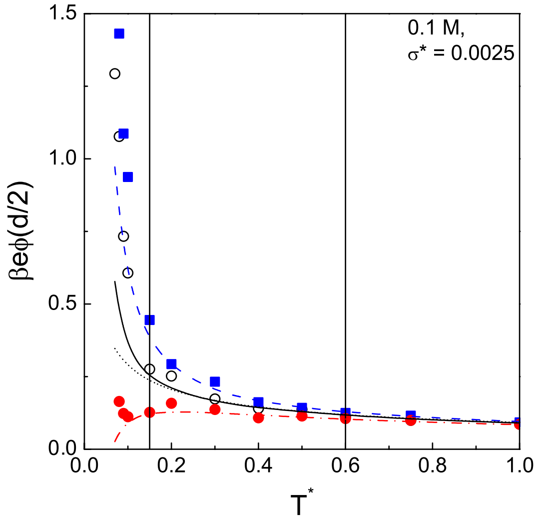

Figure 5. Reduced diffuse layer potential as a function of the reduced temperature at 0.1 M bulk concentration and $\sigma^* = 0.0025$. The dotted line gives the GCS result, which is applicable only to the case of no polarization. The symbols and all other curves have the same meaning as in Figure 4.

knowledge, the GCS values for the diffuse layer potential have not been plotted before as a function of T^*. For this reason, the GCS results are also included in Figure 5. The GCS curve rises with decreasing T^* but lacks the dramatic increase at the smallest T^*. The GCS theory can be applied only for $\alpha = 0$.

We now consider the effect of dielectric polarization. Simulation values and the MPB results for the diffuse layer potential and capacitance for a polarizable electrode are plotted in Figures 1–5. For the dielectric electrode ($\epsilon_1 = 1$ or $\alpha = 0.975$) the results are what may be expected. The repulsive forces of the polarization charge widen the depletion region and the onset of the capacitance anomaly occurs at somewhat larger values of T^* than for $\alpha = 0$. The MPB theory reproduces the MC data reasonably well except at very low T^* where it overestimates the MC capacitance.

The case of a metallic electrode ($\epsilon_1 \rightarrow \infty$ or $\alpha = -1$) is more interesting. We have not plotted the diffuse layer potentials for the metallic electrode with a small electrode charge in Figure 1 because they are small and nearly independent of T^*. Also noise in the simulation results is more of a factor for $\alpha = -1$ than for the other cases. We comment on this again later in the paper. Indeed the MC and MPB $\beta e\phi(d/2)$ for $\alpha = -1$ plotted in Figure 2 for a more widely spaced set of temperatures shows near independence of T^* and the MC noise in Figure 2(c). In Figure 4 there is seemingly no temperature anomaly in the capacitance at small T^*. There might be a small anomaly at the very lowest values of T^*, but we hesitate to make any claim on the basis of one point. In any case, it would occur at such a low temperature that it would be of limited interest. We could not obtain a meaningful simulation result at the lowest value of $T^* = 0.07$. The MPB prediction is less ambiguous, there being no capacitance anomaly for $\alpha = -1$. It is worth mentioning here that Outhwaite and Bhuiyan [22] have recently reported MPB calculations for capacitance of an electric double layer containing point ions. No capacitance anomaly was seen for a metallic electrode.

The diffuse layer potential at $\sigma^* = 0.0025$ is plotted as a function of T^* in Figure 5. As indicated earlier, the MC $\beta e\phi(d/2)$ for a metallic electrode is small with a weak dependence on temperature. The corresponding MPB results show a clear dip at very small T^* in contrast to the MC, otherwise, they are essentially in quantitative agreement with the MC results. For an insulating electrode the rise in the MC $\beta e\phi(d/2)$ at small T^* is higher than that for no polarization. Again the MPB follows this trend fairly well.

As mentioned in the Introduction, these effects have origins in the characteristics of the density profiles of the ions at and near the electrode, *viz.*, the drying of the electrode. To illustrate this point, a set of ionic density profiles are displayed in Figure 6(a), (b) for the case of 0.1 M, $T^* = 0.08$ and $\sigma^* = 0.0025$. The electrode–ion distribution function $g_i(x)$ is defined as $g_i(x) = \rho_i(x)/\rho_i(\infty)$, where $\rho_i(x)$ is the mean number density of ions of type i. There is a depletion of ions near the electrode in the case of the dielectric and unpolarized electrode but not in the case of the metallic electrode. As is seen in Figure 6(c) the potential profile is smaller and tends to zero much faster in the case of the metallic electrode than for the dielectric and unpolarized electrode.

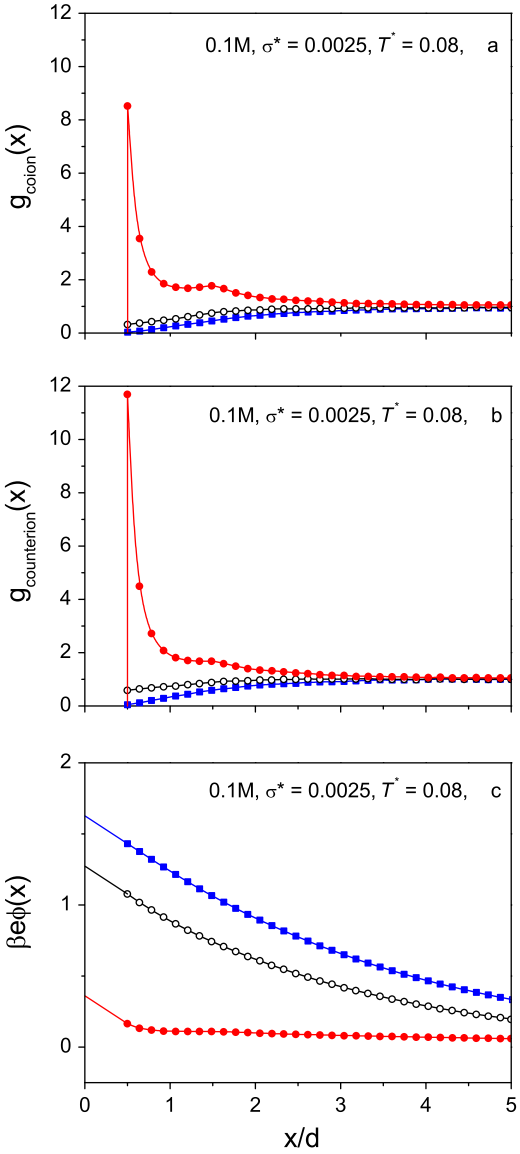

Figure 6. Reduced density profiles (parts a and b) and potential profile (part c) obtained from MC simulation at 0.1 M bulk concentration for $T^* = 0.08$ and $\sigma^* = 0.0025$. In parts a and b, the curves are (from top to bottom) for a metallic ($\alpha = -1$), unpolarised ($\alpha = 0$), and dielectric ($\alpha = 0.975$) electrode. In part c, the order is reversed with the dielectric electrode being the highest result and the metallic electrode being the smallest result.

4. Summary

Surface polarization forces radically influence the ion distribution and hence, the mean electrostatic potential, in the neighbourhood of an electrode. At a given surface charge the diffuse layer potential is increased for an insulating electrode and reduced for a metallic electrode when compared with the unpolarized case. As T^* is lowered the deviations become larger, while for small T^* the diffuse layer potential has a maximum as σ^* is increased. In the absence of any polarization the diffuse layer potential rises rapidly at small T^* and σ^* for decreasing T^*. This results from a depletion of ions near the electrode, in part due to ion pairing, and can lead to the anomalous capacitance effect. Introducing an insulating electrode increases the depletion of the ions, reduces the capacitance and causes the anomalous capacitance to occur over a larger T^* regime. Conversely, the metallic electrode reduces the ion depletion and for the parameters considered here, the MC simulations predict only a slight temperature dependence. Unfortunately the present MC simulations are somewhat unreliable at the lowest T^* value of 0.07 so that any possible capacitance anomaly is unresolved. The MPB diffuse layer potential is in good agreement with the simulations except at the lower values of T^*. For both the unpolarized and insulating cases, the anomalous capacitance effect is predicted although the capacitance is overestimated. In the metallic case, for all T^*, the MPB diffuse layer potential decreases as T^* decreases and hence no capacitance anomaly occurs.

The simulations, supported by the MPB theory, reveal that the dielectric electrode behaves qualitatively much like the unpolarized electrode. In contrast, the metallic electrode is quite different with the deviations in its behaviour from that of the unpolarized electrode being much larger; there appears to be no capacitance anomaly for the metallic electrode. In their MC simulations Alawneh and Henderson [9], observed that there was a general tendency for the counter ion profiles near the electrode to be greater for the metallic electrode and smaller for the dielectric electrode compared to those for the unpolarized electrode, but that this behaviour reverses further from the electrode. The earlier simulations of Torrie et al. [2] had suggested this, while the recent MPB calculations of Bhuiyan et al. [21] also testify to this result. In other words, the effective force in presence of polarization for a metallic electrode is attractive at short range but repulsive at longer range. The opposite is true for an insulating electrode but less strikingly so. This tendency becomes stronger as the coupling constant increases (or as T^* decreases) with the effect being particularly substantial for the metallic electrode. As a consequence, the contributions of the ionic profiles from near and further away from the electrode to the integrand that produces $\phi(x)$ tend to cancel each other being of opposite signs. This in turn leads to a $\beta e\phi(d/2)$ that is small in magnitude and relatively noisy as can be seen in Figures 2(c) and 5 for $\alpha = -1$.

The present MC simulations indicate the importance of considering surface polarization forces in determining the anomalous temperature effects in the electrical double layer. Further simulations, perhaps at different concentrations and very low T^*, are desirable to clarify whether or not a capacitance anomaly occurs for a metallic electrode. Other theories can predict the anomalous capacitance effect when there is no polarization, but to date only the MPB theory can also be used to study polarization effects easily. There are shortcomings in the MPB theory at low T^*, which we expect a more accurate treatment of the fluctuation potential problem to overcome.

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