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Local Semiempirical Formulas for the Contact Values of the Singlet Distribution Functions of a Double Layer[†]

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The electrochemical double layer is an important practical and theoretical problem. Generally speaking, experiment gives valuable information about quantities that involve integrals of density and charge profiles, such as potential differences, but does not provide direct information about the profiles themselves. Computer simulations have given numerical information about these profiles. However, explicit expressions are useful in understanding these data. For some years, an exact expression for the contact value of total density profile of the ions in the double layer has been known, but until recently, an expression for the contact value of the more important charge profile has been lacking. A few years ago, a semiempirical local result for the charge profile that is valid at low electrode charge was proposed, and very recently, it was extended to higher electrode charge. This expression contains a parameter; the effect of varying this parameter is explored in this paper, and the results are compared with a large set of simulation data for the contact values of various profiles that we have accumulated in the past few years. The agreement of the semiempirical expression with our simulation results is excellent. The best values for this parameter are fairly close to the value suggested by theory.

Introduction

Josef Barthel has made extensive contributions to theory and experiment for electrolytes, including the correlation and systematization of experimental data. We dedicate this paper to him and hope that our own modest efforts toward the systematization of data about the density and charge profiles of inhomogeneous electrolytes will be of interest to him and our colleagues.

As is well-known, the double layer is the interfacial region formed by an electrolyte near an electrode. The name *double layer* comes from the intuitive idea that the charge of the electrode is one charged layer and the charge of the interfacial electrolyte is a second layer that is equal in magnitude but opposite in sign to the electrode charge. Although the charge in the interfacial electrolyte is, in total, equal and opposite to the electrode charge (known in the double layer literature as *local electroneutrality*), the density and profile of the interfacial electrolyte can be nonmonotonic, and the charge profile of the interfacial electrolyte can even change sign. Actually, the charged layer in the electrode can also be nonmonotonic, but this is rarely considered. Even so, the name *double layer* persists.

An understanding of the double layer is helpful for studies of energy storage, corrosion, colloidal suspensions, and, if the "electrode" is a membrane or protein, physiology. Electrochemical experiments provide information about the voltage difference across the interfacial region as a function of the charge of the electrode but provide only limited information about the local distribution (the profiles) of charge within the double layer, whereas an understanding of corrosion, colloidal forces, and membrane function really requires such local information.

The "standard" theory of the double layer is the venerable classical theory due to Gouy, Chapman, and Stern[1−3] (GCS theory). It is based on what is usually called the *primitive model* (PM) of the electrolyte, in which the solvent is replaced by a dielectric continuum whose dielectric constant, ϵ_r, is equal to that of the solvent and the ions are mimicked by rigid spheres with charges at their centers. For simplicity, the electrode next to the electrolyte is assumed to be planar with all of the charge on the electrode confined at the surface (zero skin depth). If all of the ions have the same diameter, the PM is called the *restricted primitive model* (RPM), and the resultant double layer is called the RPM planar double layer. The GCS theory assumes that the ions are point ions, that their diameters may be neglected, and that an ion interacts with the electrode and the other ions only through a mean field generated by all of the ions. Thus, the theory neglects interionic correlations beyond this mean-field interaction. To avoid an electrostatic singularity, in the GCS theory the ions are given a distance of closest approach to the electrode. This is inconsistent but better than a singularity. The GCS theory provides information about both the local profiles and the nonlocal voltage difference across the double layer. This is exemplified by the GCS result for the density profiles at contact. If for further simplicity it is assumed that the ions are symmetric in charge and size, the GCS contact values are given by[4]

$$g_{\pm}^{\mathrm{GCS}}(d/2) = 1 + \frac{b^2}{2} \pm b\sqrt{1 + \frac{b^2}{4}} \tag{1}$$

where d is the common ion diameter and $d/2$ the distance of closest approach. The distance of closest approach need not be the ion

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radius, but this is the simplest choice and the one most consistent with the PM. The parameter $b = (\beta ze\sigma)/(\epsilon_0\epsilon_r\kappa)$, where z and e are the magnitudes of the common valence and the elementary charge, is a dimensionless measure of the electrode surface charge density, σ. The quantity β is equal to $1/k_BT$, where T is the absolute temperature and k_B is the Boltzmann constant. The parameter κ is the Debye inverse screening length, whose square is given by

$$\kappa^2 = \frac{\beta e^2}{\epsilon_0\epsilon_r}\sum_s z_s^{\,2}\rho_s = \frac{\beta e^2 z^2 \rho}{\epsilon_0\epsilon_r} \tag{2}$$

where $\rho = \sum\rho_s$ is the total ion density (counterions and co-ions). We can assume without loss of generality that the electrode is negatively charged, so the counterions have a positive sign while the co-ions have a negative sign. Thus, $g_{ctr}(d/2) = g_+(d/2)$ is the contact value of the counterions and $g_{co}(d/2) = g_-(d/2)$ is the contact value of the co-ions. The total density and charge profile results are proportional to the sum and difference of $g_{ctr}(x)$ and $g_{co}(x)$, respectively, where x is the perpendicular distance from the electrode surface into the electrolyte. Thus, $g_{sum}(x) = [g_{ctr}(x) + g_{co}(x)]/2$ and $g_{diff}(x) = [g_{ctr}(x) - g_{co}(x)]/2$. It should be noted that $g_{sum}^{GCS}(d/2)$ is equal to the first two terms in eq 1 and $g_{diff}^{GCS}(d/2)$ is equal to the last term in eq 1. Another profile of interest is the product profile, $g_{ctr}(x)g_{co}(x)$. It is seen from eq 1 that the GCS product profile at contact is equal to 1. Within the GCS theory, this is actually true for all x, that is, the GCS theory assumes that $g_{co}(x)$ is exactly the reciprocal of $g_{ctr}(x)$. There is no reason to suppose that this is true in general. Thus, the value of the product profile and its departure from unity is a useful test of the accuracy of the GCS theory.

Contact Value Theorems. The reason for our interest in the contact values is that they provide insight into the accuracy of a theory. Any decent theory must satisfy local electroneutrality, that is, it must have the correct value of the integral of the charge profile and thus the correct value of the integral of $g_{diff}(x)$. If a function has both the correct contact value and the correct integral, there is reason to hope that the function is fairly reliable.

Henderson and Blum[5] and Henderson et al.[6] have obtained an exact sum rule for the contact value of $g_{sum}(x)$. For a symmetric valence RPM double layer, their result is

$$g_{sum}(d/2) = a + \frac{b^2}{2} \tag{3}$$

where $a = p/\rho k_BT$ and p is the bulk (osmotic) pressure. Notably, the GCS expression satisfies eq 3 only if $a = 1$. This is a result of the neglect of ion diameters and ion−ion interactions, which leads to an ideal-gas approximation for a. If a is near unity, the GCS theory might be expected to be a fairly reasonable theory for $g_{sum}(x)$ but not necessarily for $g_{diff}(x)$. However, a is often not close to unity. Under such circumstances, the GCS theory is likely to fail even for $g_{sum}(x)$.

A contact value sum rule for $g_{diff}(d/2)$ would be of more value, since this quantity relates directly to the electrical properties of the double layer. Until recently, such a result was not available. However, two groups independently have recently proposed sum rules for $g_{diff}(d/2)$. The result of Holovko et al.[7−9] is exact and general but is nonlocal and difficult to use. Their expression is

$$g_{diff}(d/2) = -\beta ze\int_{d/2}^{\infty}\frac{\partial\phi(t)}{\partial t}g_{sum}(t)\,dt \tag{4}$$

The function $\phi(x)$ in eq 4 is the potential difference between x and ∞ and is obtained from

$$\phi(x) = -\frac{e}{\epsilon_0\epsilon_r}\sum_i z_i\rho_i\int_x^{\infty}(t - x)g_i(t)\,dt \tag{5}$$

which leads to

$$\frac{\partial\phi(x)}{\partial x} = -\frac{ez\rho}{\epsilon_0\epsilon_r}\int_x^{\infty}g_{diff}(t)\,dt \tag{6}$$

for a symmetric valence z:z electrolyte. Upon substitution of eq 6 in eq 4, it is seen that the latter now involves two integrations, is highly nonlocal, and is difficult to use. The result of Henderson and Boda[10] on the other hand,

$$g_{diff}(d/2) = ab + O(b^3) \tag{7}$$

is local and easy to use but valid only for small b. The quantity a can be determined from simulations of $g_{sum}(d/2)$ at small b or from the mean spherical approximation that we have found to be quite accurate.[11] Equation 7 is semiempirical and was obtained by inference from simulation results of Henderson and Boda.[10] If there is a method of obtaining eq 7 from eq 4, it is not obvious. The possibility that eq 7 might fail in some application beyond those covered by the Henderson−Boda simulations cannot be discounted but is not likely, as eq 7 has since been tested using a large set of simulations[12−16] covering a broad range of states. From eqs 3 and 7, a formula for the contact value of the product profile that is applicable for small b is

$$g_{ctr}(d/2)g_{co}(d/2) = a^2 + (a - a^2)b^2 + O(b^4) \tag{8}$$

This result correctly predicts the initial slope of $g_{ctr}(d/2)g_{co}(d/2)$ as a function of b.

The extension of eqs 7 and 8 to large b has been difficult. Because of the presence of the term containing $(a - a^2)$ on the right-hand side of eq 8, the possibility of unphysical negative values of the product $g_{ctr}(d/2)g_{co}(d/2)$ cannot be excluded. In a recent paper, henceforth to be denoted as I, Henderson and Bhuiyan[17] suggested an empirical relation for $g_{ctr}(d/2)g_{co}(d/2)$, namely,

$$g_{ctr}(d/2)g_{co}(d/2) = (a^2 + ab^2)\exp\left(-b^2\frac{1 + \rho^* b/2}{1 + \alpha b^2}\right) \tag{9}$$

where $\rho^* = \rho d^3$ and α is a parameter.

As in I, eq 9 may be combined with the exact contact condition (eq 3) to give eqs 10 to 12:

$$g_{diff}(d/2) = \left\{[g_{sum}(d/2)]^2 - g_{ctr}(d/2)g_{co}(d/2)\right\}^{1/2} \tag{10}$$

$$g_{ctr}(d/2) = a + \frac{b^2}{2} + g_{diff}(d/2) \tag{11}$$

$$g_{co}(d/2) = a + \frac{b^2}{2} - g_{diff}(d/2) \tag{12}$$

Equation 9 does not lead to negative values for the product of the contact values and was inspired by an expression of Lou and Lee,[18] who developed a theory that is applicable at large b. Henderson and Bhuiyan took their result at large b together with eq 8 at small b, with eq 9 as an interpolation between these two results. The parameter α does not appear explicitly in the theory of Lou and Lee. Their expression arises from what they call a modified Poisson−Boltzmann theory and is obtained from eq 9 in the limit of large b with a factor of $^1/_2$ in place of α. The physical significance of the parameter α may be seen by noting that α controls the rate at which the contact value of the product profile tends to zero at large b. The particular value $\alpha = {}^1/_2$ is well-founded in the Lou−Lee theory. This value was used in I and gave good results. However, the results were obtained at one temperature only. In this paper, we will explore eq 9 with α as a parameter for more states covering a broader

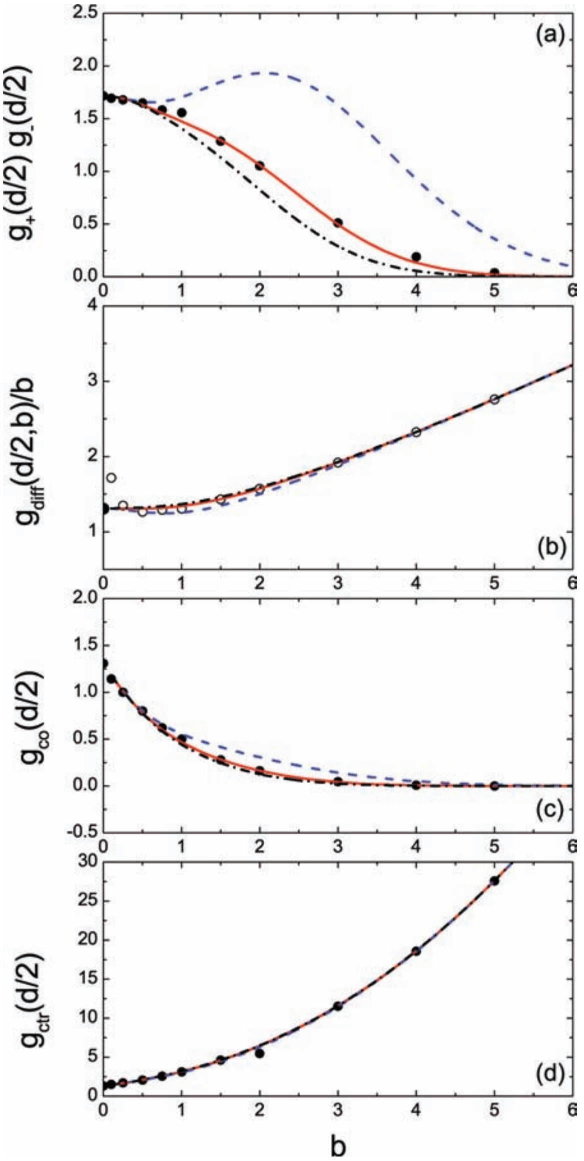

Figure 1. The product $g_+(d/2)g_-(d/2)$ and $g_{\mathrm{diff}}(d/2, b)$, $g_{\mathrm{co}}(d/2)$, and $g_{\mathrm{ctr}}(d/2)$ as functions of b in an RPM planar double layer at the reduced temperature $T^* = 0.15$ and reduced electrolyte density $\rho^* = 0.3$. The symbols are the MC simulation data, while the solid, dashed, and dash-dotted lines are the results from eq 9 with $\alpha = 0.6$, 1, and $^1/_2$, respectively.

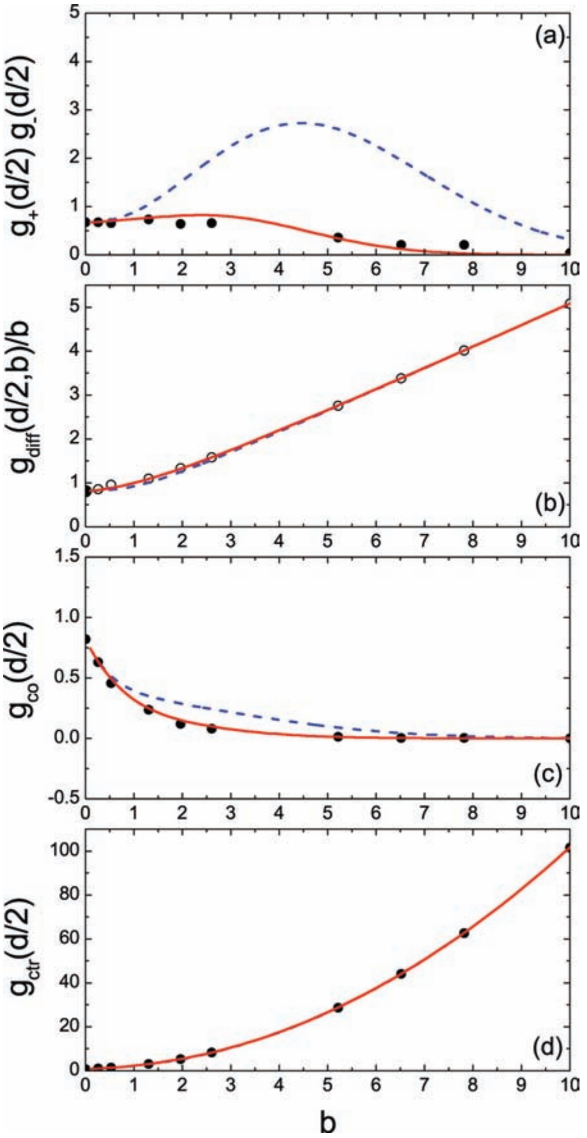

Figure 2. The product $g_+(d/2)g_-(d/2)$ and $g_{\mathrm{diff}}(d/2, b)$, $g_{\mathrm{co}}(d/2)$, and $g_{\mathrm{ctr}}(d/2)$ as functions of b in an RPM planar double layer at the reduced temperature $T^* = 0.20$ and reduced electrolyte density $\rho^* = 0.0925$. The symbols are the MC simulation data, while the solid and dashed lines are the results from eq 9 with $\alpha = 0.5$ and 1, respectively.

temperature range and will adjust α to give the best fit to the simulations.[13−17] A variable α is likely to offer insight into the asymptotic behavior of the product function $g_{\mathrm{ctr}}(d/2)g_{\mathrm{co}}(d/2)$ at large b under different physical conditions. We have also supplemented the simulation data by performing fresh simulations for more states. Although the "best" values of α differ from $^1/_2$, they are never far from $^1/_2$.

Monte Carlo Simulations. The Monte Carlo (MC) simulations were done in the canonical ensemble using the standard Metropolis algorithm. The central MC box was a rectangular parallelepiped with one face being the planar charged surface at $x = 0$ and the other face the uncharged surface at $x = l_x$. The parallel *charged sheets* method of Torrie and Valleau[19] was adopted to account for the long-range Coulomb interactions together with the usual minimum image plus periodic boundary conditions along the remaining y and z axes. This technique has been used in recent years by other groups.[20,21] Although Torrie and Valleau used the grand canonical ensemble, in the canonical ensemble the required bulk concentration can be achieved by adjusting the MC cell length l_x. The typical number of configurations was around 10^8 with the first 10^7 being employed for equilibration of the system. The uncertainty in reproducing the bulk concentration was never more than ± 2 %.

Results and Discussion

Results are presented in Figures 1 to 5 for a spectrum of states covering a range of electrolyte temperatures and densities. These are only a representative subset of 20 physical states that we examined. For the purposes of this discussion, it is convenient to use universal reduced (nondimensional) variables, namely, the reduced temperature $T^* = (4\pi\epsilon_0\epsilon_r k_B T d)/(z^2e^2)$ and the reduced density $\rho^* = \rho d^3$. It should be noted that $T^* = 1/\Gamma_p$, where Γ_p is the plasma coupling constant. The physical states studied ranged in T^* from 0.15 to 0.6 and encompassed both 1:1 and 2:2 valence electrolytes, while generally both low (0.00925) and high values (0.0925) of ρ^* were chosen to sample dilute and concentrated solutions. We have compared eq 9 to a large set of earlier simulation values[12−16] and new simulation values for $g_{\mathrm{ctr}}(d/2)$ and $g_{\mathrm{co}}(d/2)$.

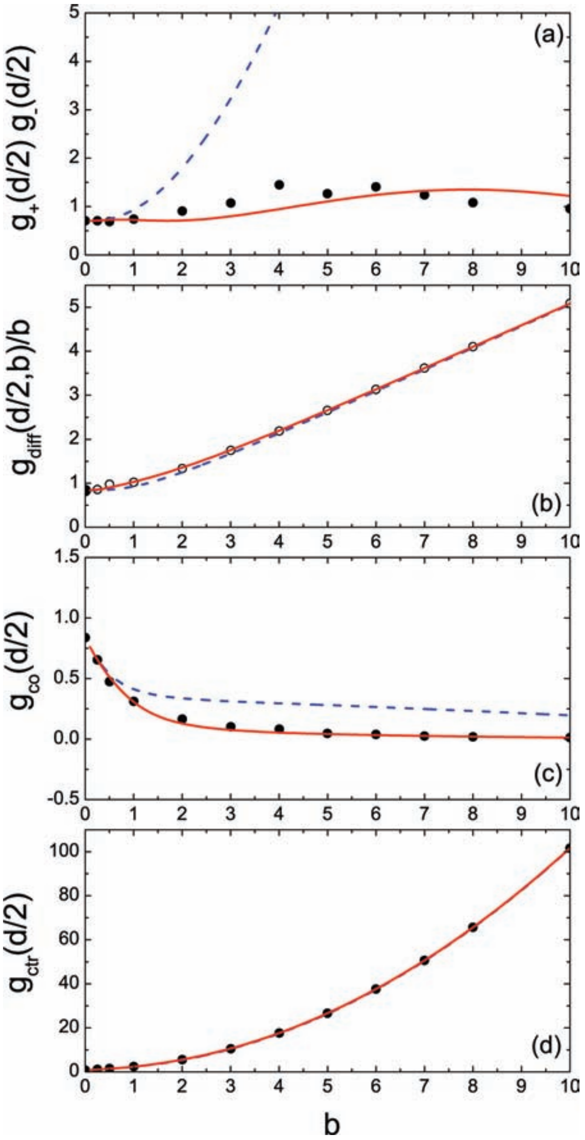

Figure 3. The same as Figure 2 but at the reduced temperature $T^* = 0.30$ and reduced electrolyte density $\rho^* = 0.00925$. The solid and dashed lines are the results from eq 9 with $\alpha = 0.335$ and 1, respectively.

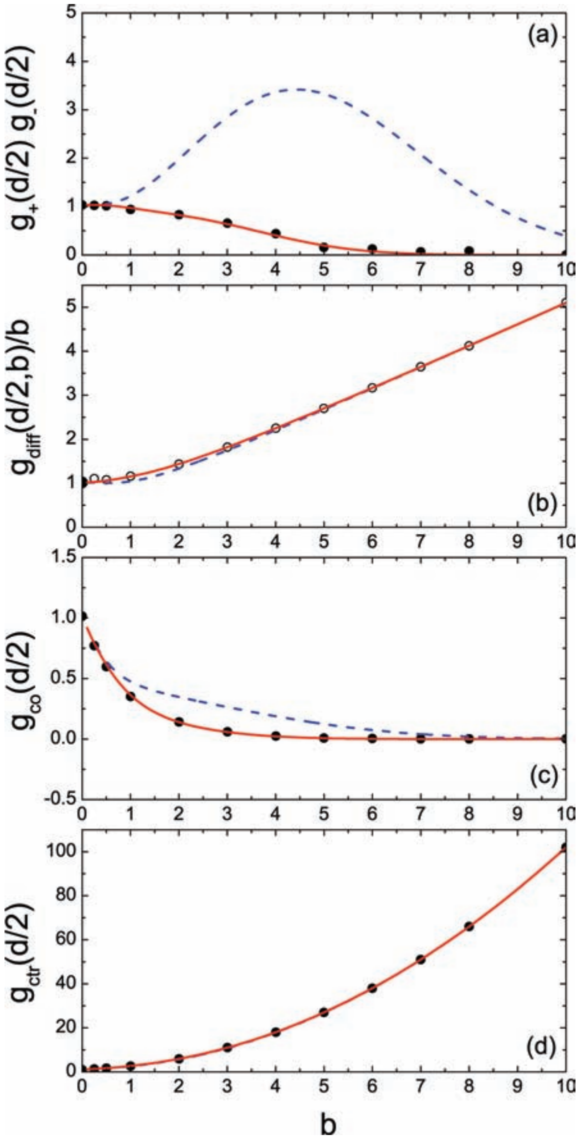

Figure 4. The same as Figure 2 but at the reduced temperature $T^* = 0.40$ and reduced electrolyte density $\rho^* = 0.0925$. The solid and dashed lines are the results from eq 9 with $\alpha = 0.4$ and 1, respectively.

For each physical state, we adjusted α by trial and error to optimize the fit of eq 9 to the corresponding simulation values of the product $g_{ctr}(d/2)g_{co}(d/2) = g_+(d/2)g_-(d/2)$. This optimum α was then used to evaluate $g_{diff}(d/2)$, $g_{ctr}(d/2)$, and $g_{co}(d/2)$ from eqs 10, 11, and 12, respectively. In the figures, results for $\alpha = 1$ are also given for comparison purposes. Additionally, in panel (a) of Figure 1, we included the result for $\alpha = {}^1/_2$ from I to make contact with the earlier work. It is clear from this figure that the optimum α value of 0.6 leads to a closer agreement of eq 9 with the simulations than does the earlier result with $\alpha = {}^1/_2$. Indeed, in the course of the current calculations we tested all of the situations presented in I, and in every case the results with a variable (optimum) α were superior to those with $\alpha = {}^1/_2$ vis-a-vis the simulations. These results are not shown here for reasons of clarity and brevity. A fuller set of our figures is provided in the Supporting Information.

The presence of the exponential factor on the right-hand side of eq 9 ensures that the product $g_{ctr}(d/2)g_{co}(d/2)$ goes to zero at large b. However, the manner in which this occurs is determined by the parameter α. For instance, because of the negative sign in the exponent, the exponential factor is relatively larger when α is large (≥ 1) than when α is small (< 1). It is evident from the figures that with an optimum α, eq 9 generally reproduces the simulation data very well. We note here that the optimum value of α in all cases is fairly close to the value of ${}^1/_2$ suggested by the Lou–Lee theory.[18] Values of α that differ substantially from ${}^1/_2$ can lead to quite different results. For example, the value of 1 for α can lead to very large values of $g_{ctr}(d/2)g_{co}(d/2)$ and a pronounced maximum. Such a maximum in this function was seen earlier in the MC simulation data of Bhuiyan et al.,[12] but that one was smaller and had a quite different origin. In the present case, it is apparent from eq 8 that when $a < 1$, the initial slope of this function is positive. Since eq 9 guarantees that this function tends to zero at large b, under these circumstances there must be a maximum in $g_{ctr}(d/2)g_{co}(d/2)$. However, since in the simulations this results from the initial slope of this function and the value of a, it is initially flat for $a \approx 1$ or sloping downward for $a > 1$.

Of the four functions that are presented in the figures, the product function $g_{ctr}(d/2)g_{co}(d/2)$ gives the best test of our contact value expression. The counterion contact value $g_{ctr}(d/2)$ is the least sensitive. This is not surprising since the co-ion contact value $g_{co}(d/2)$ is small at large b, so at large b, $g_{ctr}(d/2)$ resembles

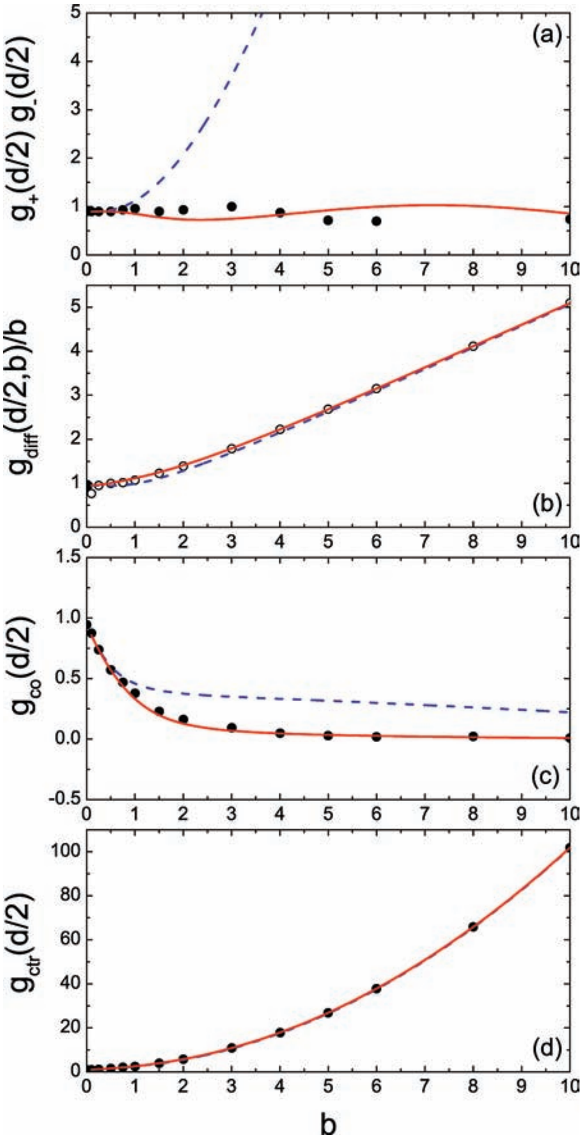

Figure 5. The same as Figure 2 but at the reduced temperature $T^* = 0.60$ and reduced electrolyte density $\rho^* = 0.00925$. The solid and dashed lines are the results from eq 9 with $\alpha = 0.3$ and 1, respectively.

$g_{sum}(d/2)$, which is given by eq 3. This demonstrates the utility of the product function and eq 9.

We are aware that a convincing, rigorous justification of eq 9 is lacking. Even though it is empirical, its accuracy in reproducing *exact* machine-simulated data, given an optimum α, is unmistakable. This result, coupled with the fact that the equations derived from it (i.e, eqs 10 to 12) are all accurate, further enhances arguments in favor of eq 9. From an experimental perspective, knowledge of the various contact properties can be useful, for example, in electrochemistry experiments that pertain to the electrode−electrolyte interface. It ought to be emphasized that obtaining an expression for the product function that goes to very small values at large b without passing through unphysical negative values has been a nontrivial exercise that has occupied our attention to varying degrees for several years. It is not correct to say that with an adjustable parameter one can fit any set of data points. The essential point of our paper is eq 9. The adjustment of the parameter α is secondary. With eq 9 we are able to fit a wide range of data with a single parameter that, as our results show, never varies appreciably from the value suggested by theory.[18] Indeed, as is seen in our study, a large variation of α from $^1/_2$ (e.g., $\alpha = 1$) gives markedly poorer results.

Supporting Information Available:

A fuller set of figures containing comparisons of the results of our simulations and fits for the double-layer correlations. This material is available free of charge via the Internet at http://pubs.acs.org.

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