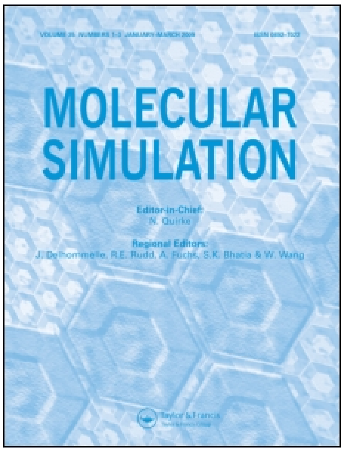

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Henderson, D. and Bhuiyan, L. B.(2007) 'Evidence for a second contact value formula for the electric double layer', Molecular Simulation, 33: 11, 953 — 957
To link to this Article: DOI: 10.1080/08927020701461247
URL: http://dx.doi.org/10.1080/08927020701461247

Molecular Simulation, Vol. 33, No. 11, September 2007, 953–957

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Evidence for a second contact value formula for the electric double layer

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(Received April 2007; in final form May 2007)

The results of some recent Monte Carlo simulations (Bhuiyan *et al. J. Electroanal. Chem.*, in press) for the electric double layer formed by rigid ions of equal diameter (the solute) in a continuum dielectric (the solvent), next to a uniformly charged planar hard wall are examined. A contact value formula for the sum of the density profiles of this system has long been known (Henderson *et al. J. Electroanal. Chem.* **102**, 315 (1979)). Here we propose a simple formula for the contact value of the charge profile in the limit of low electrode charge density. The evidence obtained from the aforementioned simulations supports this formula.

Keywords: Electric double layer; Contact value formula; Charge profile; Primitive model; Monte Carlo simulation

1. Introduction

Exact sum rules provide a standard against which theories can be tested. They are also useful for simulations as a test of their statistical accuracy. They are especially useful for charged systems, which are inherently more complex because of the long range nature of the Coulomb interaction.

One sum rule was established some years ago by Henderson *et al.* [1], who considered an electrical double layer formed by charged particles near a charged electrode. They considered a model system consisting of rigid spherical ions of diameter d_i, which represent the solute, in a continuum dielectric, which represents the solvent. This model electrolyte is called the primitive model (PM). The model electrode is flat, hard, uniformly charged and with the same dielectric constant as the electolyte. Henderson *et al.* sum rule for the density profiles at contact is

$$k_BT\sum_i \rho_i(d_i/2) = p + \frac{E^2}{8\pi\epsilon}, \qquad (1)$$

where k_B is the Boltzmann's constant, T is the temperature, p is the (osmotic) pressure of the ions, E is the electric field in the region near the electrode, which is related through Gauss' law to the charge density of the electrode, ϵ is the dielectric constant of the electrolyte (and the electrode -so that dielectric polarization does not occur), and $\rho_i(x)$ is the (number) density of ions of species i at a perpendicular distance x from the electrode. Equation (1) is a force balance statement and is intuitively appealing. The left hand side is the momentum transfer to the electrode and this is equal to the sum of the two terms on the right hand side, the pressure and the Maxwell stress.

For simplicity, we will focus on a binary symmetric system in which all the ions have the same diameter, d. This is the well known restricted primitive model (RPM) of an electrolyte in the literature. Further, the ions are assumed to have an equal charge, ze, z and e being the magnitudes of the valence and electronic charge, respectively. For this case, equation (1) becomes

$$g_s(d/2) = \frac{1}{2}[g_1(d/2)] + g_2(d/2)] = a + \frac{b^2}{2}, \qquad (2)$$

where

$$a = \frac{p}{pkT}$$

and $\rho = \rho_1 + \rho_2$. The densites ρ and ρ_i are the relevent bulk number densities so that $g_i(d/2) = \rho_i(d/2)/\rho_i$ are the density profiles normalized to unity at large distance from

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Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020701461247

the electrode. Finally, b, is a dimensionless electrode charge density defined by

$$b = \frac{\beta z^2 e^2 E}{\epsilon \kappa}, \tag{4}$$

where κ is the Debye screening parameter and is given by

$$\kappa^2 = \frac{4\pi\beta z^2 e^2 \rho}{\epsilon}. \tag{5}$$

with $\beta = 1/k_B T$.

Because the system is symmetric, it does not matter which subscript represents the counterion and which represents the coion. For definiteness, we assume that the electrode is negatively charged and species 1 and 2 have positive and negative charges, respectively. Thus, species 1 is the counterion and species 2 is the coion.

Equations (1) or (2) may be called the first contact value formula (CVF1). It has been quite useful. For example, it provides some insight into the accuracy of a theory. The classical, but not very accurate, theory of the planar double layer is that of Gouy [2], Chapman [3] and Stern [4] (GCS), which is based on the assumption that the diameter of the ions establishes a distance of closest approach of an ion to the electrode but otherwise may be neglected. The GCS version of the CVF1 is

$$g_s(d/2) = 1 + \frac{b^2}{2}. \tag{6}$$

That is, within the GCS theory, the osmotic pressure of the ions is given by the ideal gas formula, $p/\rho kT = 1$.

Additionally, CVF1 provides some indirect insight into what might be called the anomalous temperature behavior of the capacitance of the double layer when the coupling constant, $\beta z^2 e^2/\epsilon d$, is large. (low temperature, high valence, small dielectric constant, small diameter or any combination thereof). When the coupling constant is large, a becomes small. This can be seen from the mean spherical approximation (MSA) result [5], which is fairly accurate,

$$a = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{\Gamma^3}{3\pi\rho}, \tag{7}$$

where $\eta = \pi\rho d^3/6$ and Γ is a renormalized screening constant given by

$$\Gamma d = \frac{1}{2}\sqrt{1 + 2\kappa d} - \frac{1}{2}. \tag{8}$$

Thus, a consists of a positive (entropic) contribution due to the ion size and a negative (energetic) contribution due to the Coulombic interaction of the ions. Hence, increasing the density increases a whereas decreasing the temperature or dielectric constant decreases a.

At small coupling constant, a is given mainly by the first term, which is nearly one because ρ and η are small at (aqueous) electrolyte concentrations. However, at large coupling, the second term is significant and a can be small. When a is small, the ions withdraw from the electrode. In a non-primitive model with a molecular solvent, the solvent molecules, of course, do not withdraw. This ion withdrawal leads to a broadening of the double layer that, in turn, leads to an increased electrostatic potential and a lower capacitance. This behavior becomes more pronounced as the temperature is decreased and, as a result, the capacitance has a positive temperature derivative, in contrast to the more usual negative temperature derivative predicted by the GCS theory.

This anomalous temperature derivative of the capacitance is seen in frozen electrolytes [6] (low temperatures) and molten salts [7] (low dielectric constant) and probably can be found in other systems. Originally, the positive temperature derivative of the capacitance of the molten salt double layer was thought to be due to their high density (or concentration). However, it is a low temperature or low dielectric constant effect. All systems will exhibit this anomalous temperature effect at large coupling constant or small reduced temperature, $T^* = k_B T \epsilon d/z^2 e^2$, independently of concentration. This is confirmed by the simulations of Boda *et al.* [8,9].

The capacitance anomaly occurs only at low electrode charge. As soon as b becomes significant, the second term in equation (1) dominates and the question of whether a is small becomes irrelevant.

Low values of a are indicative of the capacitance anomaly but hardly a cause since the potential is determined by $g_d(x) = [g_1(x) - g_2(x)]/2$ rather than $g_s(x) = [g_1(x) + g_2(x)]/2$. Any information about the contact value of $g_d(x)$ would be particularly useful. A contribution towards this goal is given here.

2. Second contact value formula

The GCS result for $g_d(d/2)$ is

$$g_d(d/2) = b\sqrt{1 + \frac{b^2}{4}}. \tag{9}$$

If equation (6) is replaced by the correct result, CVF1, equation (9) should be modified since equations (6) and (9) would not yield a vanishing coion contact value, $g_2(d/2)$ at infinite b. With this is mind, Fawcett and Henderson [10] suggested

$$g_d(d/2) = b\sqrt{a + \frac{b^2}{4}}, \tag{10}$$

which does yield a vanishing $g_2(d/2)$ at infinite b. Regrettably, the withdrawal of charge suggested by equation (10) is not sufficient to cause the capacitance anomaly so an improvement is needed.

Boda and Henderson [11] suggested that

$$g_d(d/2) = ab \tag{11}$$

at small b. Boda and Henderson thought of equation (11) only as an approximation. However, as with a good marriage, love grows with time. We now believe that equation (11) is exact in the limit of small b. We refer to equation (11) as the second contact value formula (CVF2a). In this paper we present evidence supporting CVF2a from our recent simulation [12], together with some new simulation results, that we believe is convincing.

If equation (11) is correct a small b, thens

$$\lim_{b \to 0} g_d(d/2)/b = a \tag{12}$$

Our simulations present a fairly extensive set of Monte Carlo simulations at $T^* = 0.15$ for a range of densities where a is smaller than one, nearly equal to one, and greater than one. Specifically, these simulations are for reduced densities $\rho^* = \rho d^3$ equal to 0.02, 0.03, 0.05, 0.10, 0.20, 0.25 and 0.30, which, for $d = 4.25 \times 10^{-10}$ m, correspond to concentrations in the range 0.2 mol/dm^2–3 mol/dm^3. The reduced temperature, $T^* = 0.15$, corresponds to a 1:1 aqueous solution at 75 K or a 2:2 solution at 300 K. We obtain our value for a from $g_s(d/2)$ at $b = 0$ and not from an independent simulation of the pressure of a bulk electrolyte.

We have plotted $g_d(d/2)/b$ as a function of b in figures 1 and 2. There are no values for $g_d(d/2)/b$ at $b = 0$ since this is 0/0. However, $g_s(d/2)$ is plotted at $b = 0$ and it is clear that, apart from statistical noise due to fluctuations at small b, the values of $g_d(d/2)/b$ are tending to $g_s(d/2)$ as b tends to zero. Of course, we cannot be sure that equation (11) is exact. Conceivably, it might be only a good approximation. However, since a fairly wide range of states has been considered, we suggest that equation (11) is exact.

For $\rho^* = 0.3$, the value of $g_d(b/2)/b$ at the smallest value of b, where $g_d(d/2)/b$ seems to exceed a, requires some discussion. Taken in isolation this point might suggest a possible breakdown of equation (11) at high densities. For this reason, we made some new simulations for $\rho^* = 0.25$. As is seen in figure 3, these results do not indicate an onset of the seeming behavior seen at small b in the $\rho^* = 0.3$ curve. Fluctuations seem to play a significant role in the results for small b. This has origins in the fact that at small b numerical calculation of $g_d(d/2)$ involves a difference of two numbers, viz., $g_1(d/2)$ and $g_2(d/2)$, of comparable magnitudes. Thus $g_d(d/2)$ becomes rather sensitive to even the slightest variations in the contact g's. This, in turn, implies that there is likely to be statistical noise in the values of $g_d(d/2)/b$ at small b. This is amplified by the fact that the contact g's are obtained by extrapolation of the MC data.

Another point that should be kept in mind is that $g_d(d/2)$ and b are odd functions of b. Hence, their quotient must be an even function of b and the slope of this quotient must be zero at small b. This is plausible for the data in the curves for the lower values of b, but the data in the curve for $\rho^* = 0.3$ seems incompatible with this requirement.

This noise is seen in figure 4 where $g_d(d/2)/b$ for $b = 0.1$ and a are plotted as functions of ρ^*. The noise in the value at $\rho^* = 0.3$ seems especially large but we do not believe that a breakdown of equation (11) is indicated. Ideally, we would have liked to make a simulation at $\rho^* = 0.35$ but the computer requirements increase rapidly with increasing ρ^* so that this was not deemed necessary.

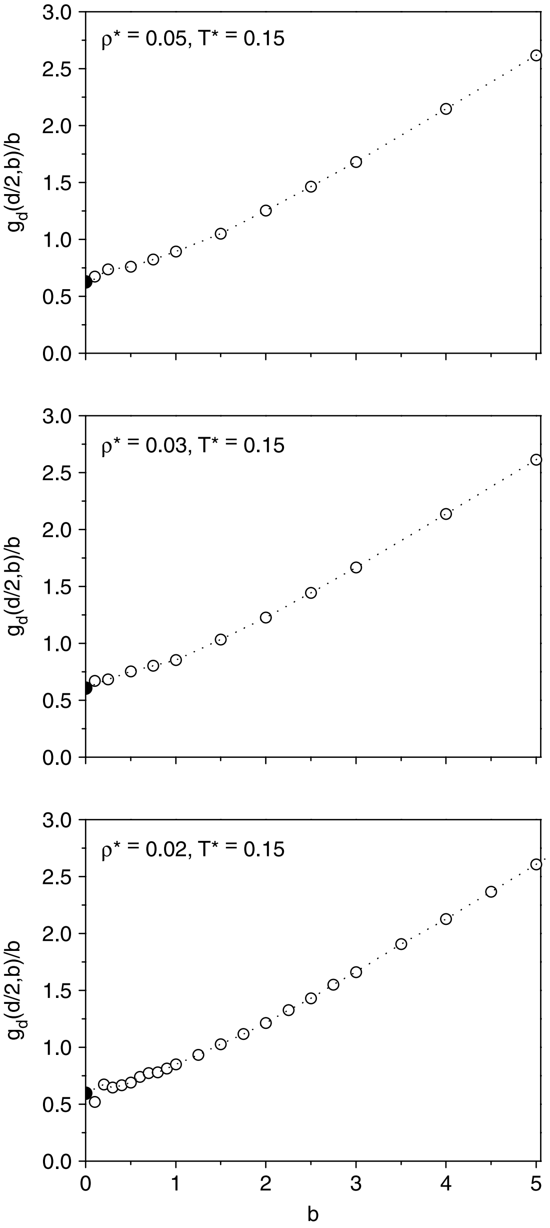

Figure 1. The Monte Carlo simulation results for $g_d(d/2, b)/b$ vs. b at the reduced temperature $T^* = 0.15$ and reduced densities $\rho^* = 0.02$ (bottom panel), 0.03 (middle panel), and 0.05 (top panel). The dotted line joining the MC points is given simply to act as a visual aid. MC data from reference [12]. The open circles give the values of $g_d(d/2)/b$ and the solid circle gives the value of a.

3. Summary

A second contact formula (CVF2a) has been suggested for the contact value of the charge profile, $g_d(x)$. This supplements the CVF1 for the contact value of the density profile. Our evidence for CVF2a is semi-empirical.

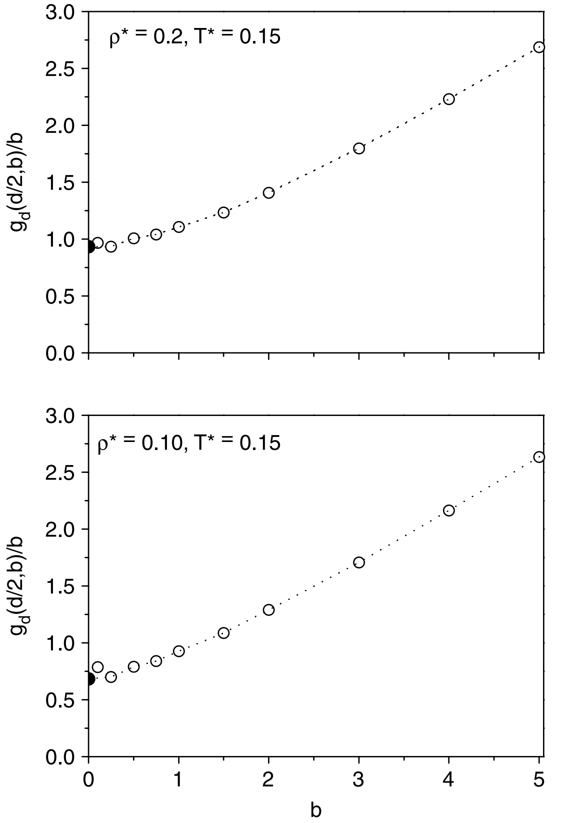

Figure 2. The Monte Carlo simulation results for $g_d(d/2, b)/b$ vs. b at the reduced temperature $T^* = 0.15$ and reduced densities $\rho^* = 0.1$ (lower panel) and 0.2 (upper panel). The dotted line joining the MC points is given simply to act as a visual aid. MC data from reference [12]. The open circles give the values of $g_d(d/2)/b$ and the solid circle gives the value of a.

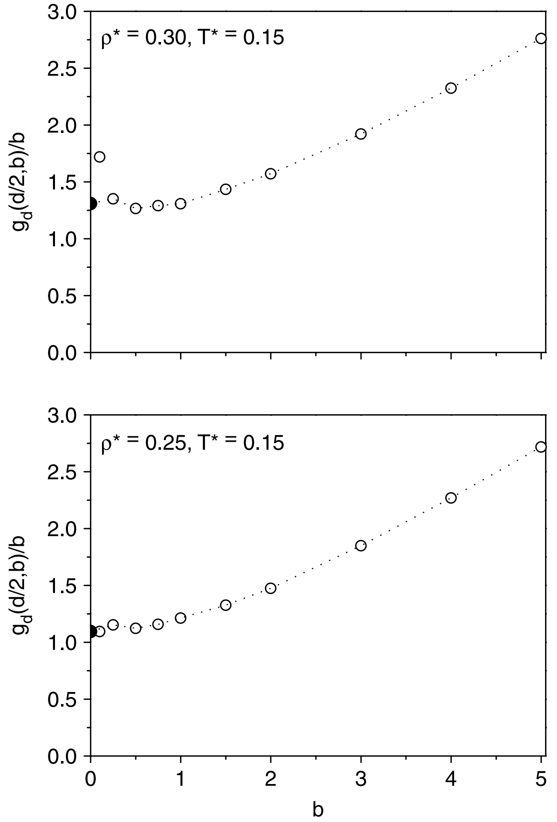

Figure 3. The Monte Carlo simulation results for $g_d(d/2, b)/b$ vs. b at the reduced temperature $T^* = 0.15$ and reduced densities $\rho^* = 0.25$ (lower panel) and 0.30 (upper panel). The dotted line joining the MC points is given simply to act as a visual aid. MC data for $\rho^* = 0.30$ from reference [12]. The open circles give the values of $g_d(d/2)/b$ and the solid circle gives the value of a.

However, good semi-empiricism can be good science so we are untroubled. Fundamentally, all science is semi-empirical.

In the GCS theory

$$g_d(d/2) = b. \tag{13}$$

Since $a = 1$ in the GCS theory, we could say that the GCS theory satisfies equation (11) in a self consistent manner. However, the issue is more subtle. The MSA yields equation 13 even though in this approximation $g_s(d/2, b = 0) \neq 1$. We have made plots of the hypernetted chain approximation (HNC/MSA version) results of Lozada-Cassou *et al.* [13] that are similar to the MC results presented here. These indicate that equation (13) is satisfied by the HNC/MSA theory. Since the MSA and HNC/MSA reduce to the GCS theory for vanishing ion diameter and $a \neq 1$ in these approximations, we believe that the GCS theory satisfies equation (13) without a hidden value of a. In any case, the presence of a value of a other than one in equation (1) or (2) does not imply an extension of equation (13). It would be desirable if an extension of equation (11) to large b can be devised. Merely replacing a by a^2 in equation (10) is unsatisfactory as the resulting coion contact value would not vanish at infinite b.

During the preparation of this manuscript we became aware of the contact value formula of Holovko *et al.* [14] for $g_d(d/2)$, CVF2, which follows from Born–Green–Yvon equation and which appears valid for all b. In contrast to the result reported here, the Holovko *et al.* result is non-local. The connection between our result and

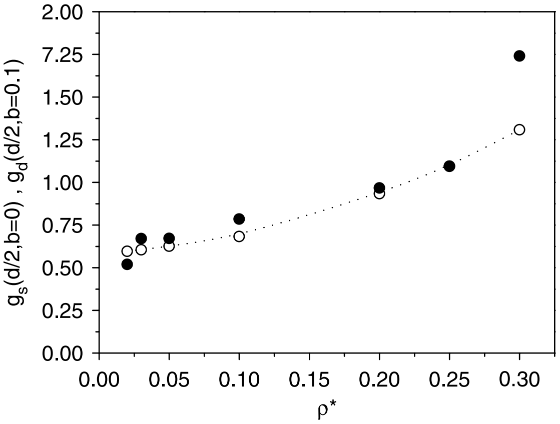

Figure 4. The Monte Carlo simulation results for $g_d(d/2, b)/b$ (open circles) and $g_s(d/2)$ (solid circles) vs. ρ^* at $b = 0.1$ and at the reduced temperature $T^* = 0.15$. The dotted line joining the MC points for $g_s(d/2)$ is given simply to act as a visual aid. MC data from reference [12] except for the state $\rho^* = 0.25$.

this non-local result is not obvious. The goal of understanding the relation between the local and non-local formulae thereby obtaining an extension of equation (11) will continue to occupy our attention.

Acknowledgements

LBB acknowledges an instutitional grant through Fondos Institucionales Para la Investigacion (FIPI), University of Puerto Rico. We are grateful to Dr S. Lamperski of A. Mickiewicz University, Poznań, Poland, for providing us with an independent check for a couple of MC states through his grand canonical MC simulation, and to M. Alawneh of Brigham Young University for checking one of our simulation runs.

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