

Simple Expressions for Contact Values of Density Profiles in a Planar Double Layer

Douglas Henderson

*Department of Chemistry and Biochemistry, Brigham Young University,
Provo, Utah 84602*

Lutful Bari Bhuiyan*

*Laboratory for Theoretical Physics, Department of Physics, University of Puerto Rico,
San Juan 00931, Puerto Rico*

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Abstract: Exact, or even accurate, results are very valuable for developing improved statistical mechanical theories of, for example, the double layer formed by the ions in an electrolyte near a charged electrode. In this paper we consider the primitive model of the double layer. For simplicity, we assume the electrolyte to be binary and symmetric. In our previous work, we proposed an exact local expression for the contact value of the total ion density, which is valid for all electrode charges, and local expressions for the individual ion density contact values for an electrode with a small charge. Previously, no local expression was known for the individual density contact values at high electrode charge. On the basis of our work and a recent paper by Lou and Lee [*J. Chem. Theory Comput.* **2009**, *5*, 1079–1083], we suggest local, empirical expressions for these contact values and test them by comparison with our extensive simulation results. The simulations are performed in the canonical ensemble with the ‘charged sheets’ method being utilized to treat long-range electrostatic interactions. The simulation results for the various contact quantities are seen to validate the empirical results for all electrode charges treated. The results are also likely to be (i) useful pointers for simulation of more complex, realistic models and (ii) relevant for experiments in that most electrochemistry occurs near the electrode where the classical Gouy–Chapman–Stern theory may not be adequate.

1. Introduction

If an electrode is inserted into an electrolyte, a charged layer is formed near the electrode. This layer is conventionally called the electric double layer even though modern work has shown that it may consist of multiple layers of differently charged ions. The study of this problem is both interesting and important because of its relevance for a plethora of industrial and biological systems. The electric double layer is commonly described using the primitive model (PM) in which the ions are treated as charge hard spheres and the solvent is treated as a dielectric continuum characterized by

the permittivity ϵ . If the ions are of equal size, this model is called the restricted primitive model (RPM). We treat here the RPM planar double layer and, for simplicity, restrict ourselves to double layers formed by binary symmetric $z:z$ valency electrolytes of charge ze , $-ze$, where z is the ion valence, e the magnitude of the electron charge, and d the common ionic diameter. The electrode is treated as a flat, smooth surface with a uniform charge density of σ and is assumed to have the same dielectric constant as the electrolyte so that polarization may be neglected.

The quantities of major importance in a theory of the electric double layer are the density profiles, $\rho_i(x) = \rho_i g_i(x)$, where i is the ion species, $\rho_i = \rho_i(\infty)$ is the bulk density of an ion of species i , and x is the perpendicular distance from

* To whom correspondence should be addressed. E-mail: beena@beena.cnnnet.clu.edu.

the electrode. The quantity $g_i(x)$ is the electrode–ion singlet distribution function. Both charge profiles and potential profiles may be obtained from the density profiles. The classical and traditional theory of the double layer is the seminal Gouy–Chapman–Stern (GCS)^{1–3} theory, which is based on the assumption that the ions are essentially free, devoid of mutual (interionic) correlations and that the ionic size may be neglected (except to define a distance of closest approach to the electrode). In the RPM, the distance of closest approach is $d/2$.

Exact, or at least accurate, expressions for the density or charge profiles are very valuable in gaining insight into the accuracy of a theory and developing new theories. A fundamental expression is the charge neutrality theorem in which the total integrated charge in the double layer is equal in magnitude but opposite in sign to the charge of the electrode. Although fundamental, it is not very helpful since any decent theory will satisfy this condition. Contact value theorems or exact sum rules are more helpful. Some years ago, Henderson and Blum⁴ and Henderson et al.⁵ obtained an exact contact value theorem for the total density profile $\rho(x) = \sum_i \rho_i g_i(x)$. For a binary symmetric electrolyte, we may define the sum and difference profiles by $g_{\text{sum}}(x) = [g_1(x) + g_2(x)]/2$ and $g_{\text{diff}}(x) = [g_1(x) - g_2(x)]/2$, respectively. The total density profile is obtained from $g_{\text{sum}}(x)$, while the charge profile is obtained from $g_{\text{diff}}(x)$. Without loss of generality, we assume the electrode to have a negative surface charge and define species 1 and 2 to be the counterions (+) and co-ions (−), respectively. With these definitions, the Henderson et al. theorem reads

$$g_{\text{sum}}(d/2) = a + \frac{b^2}{2} \quad (1)$$

Here $a = p/\rho k_B T$, with p , k_B , and T , being the pressure, Boltzmann constant, and temperature, respectively, $b = 4\pi\beta ze\sigma/\epsilon\kappa$ is a dimensionless variable for the electrode charge, and $\beta = 1/k_B T$. The parameter κ is the usual Debye–Hückel screening parameter and defined by $\kappa^2 = 4\pi\beta z^2 e^2 \rho/\epsilon$. As mentioned, eq 1 is exact and, thus, valid for all electrode charge. It is also local.

Until recently, eq 1 was the only contact value theorem for the double layer. What is needed is a contact theorem for $g_{\text{diff}}(x)$. Very recently, Holovko et al.^{6,7} obtained the exact contact value theorem for this quantity. For symmetric valency RPM electrolytes their expression can be written as

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

where $\phi(x)$ is the potential profile. Equation 2 is exact, valid for all electrode charge, but nonlocal and difficult to use.^{8,9} At about the same time, Henderson and Boda¹⁰ suggested an expression for $g_{\text{diff}}(d/2)$ at small electrode charge (small b). It is

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

This result was not derived; it was obtained from an examination of simulation results for a wide range of states. Thus, it cannot be regarded as exact but does seem accurate.¹¹ Additionally, it

is local. This result accounts for the low contact values of $g_{\text{diff}}(x)$ when the coupling constant $\beta z^2 e^2/\epsilon d$ is large and a is small.

From eqs 1 and 3, the following local expressions for the $g_i(d/2)$ can be obtained

$$g_1(d/2) = g_+(d/2) = a + ab + \frac{b^2}{2} + O(b^3) \quad (4)$$

$$g_2(d/2) = g_-(d/2) = a - ab + \frac{b^2}{2} + O(b^3) \quad (5)$$

Bhuiyan et al.¹² pointed out that the product $g_+(x)g_-(x)$ is of interest because it is identically equal to 1 in the GCS theory. Hence, any departures of this product from unity give one insight into ways in which the GCS theory may be improved. From the above equations, we obtain the contact theorem

$$g_+(d/2)g_-(d/2) = a^2 + (a - a^2)b^2 + O(b^4) \quad (6)$$

which is accurate at small electrode charge.¹² An inherent difficulty with this relation is that at high electrolyte concentrations ($a > 1$), the second term on the right-hand side becomes negative, which in turn can lead to unphysical negative values for $g_+(x)g_-(x)$. Note that eqs 3–6 reduce to the corresponding GCS expressions when $a = 1$, the ideal gas limit. Clearly, accurate local expressions for $g_{\text{diff}}(d/2)$, $g_i(d/2)$, and $g_+(d/2)g_-(d/2)$ would be very useful. This is the subject of this note.

2. Theory and Simulations

2.1. New Expression. The biggest problem in generalizing eqs 5 and 6 is obtaining expressions that go to zero at large b without passing through negative values. Since the $g_i(x)$ are probabilities and normalized densities, they must be positive and, hence, $g_+(x)g_-(x)$ must be positive. Recently, Lou and Lee¹³ applied what they call a modified Poisson–Boltzmann theory to obtain an analytic expression for $g_+(x)g_-(x)$. In this theory the steric effect of the ions is taken into account by combining the classical mean field GCS theory with a lattice-gas type approximation for the ionic exclusion volume term. Since in the double-layer literature the term-modified Poisson–Boltzmann theory is used to denote a more elaborate but nonanalytic theory, we prefer to call the Lou–Lee theory a simplified, improved Poisson–Boltzmann theory. Note that the interionic correlations are still neglected in this theory. In any case, they obtain

$$g_+(d/2)g_-(d/2) = \exp(-\rho^* b^2) \quad (7)$$

where $\rho^* = \rho d^3$, $\rho = \sum_i \rho_i$. They claim that this result is accurate for large b .

Equation 7 provides a key to generalizing eq 6. We cannot just use the first two terms of the right-hand side of eq 6 as a prefactor to the exponential since, as indicated earlier, these may lead to negative values for $g_+(d/2)g_-(d/2)$. We suggest

$$g_+(d/2)g_-(d/2) = (a^2 + ab^2) \exp\left(-\frac{b^2 \left(1 + \frac{\rho^* b^2/2}{1 + \alpha b^2}\right)}{1 + \alpha b^2}\right) \quad (8)$$

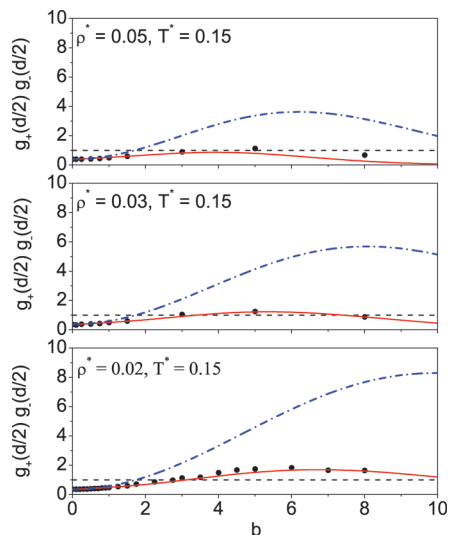


Figure 1. Product $g_+(d/2)g_-(d/2)$ as a function of b in a 1:1 RPM planar double layer at the reduced temperature $T^* = 0.15$ and reduced electrolyte density $\rho^* = 0.02$ (bottom), 0.03 (middle), and 0.05 (top). The symbols are the MC simulation data¹¹ while the solid and dash-dotted lines are the results from eq 8 with $\alpha = 1/2$ and 1, respectively. The dashed line represents the GCS result.

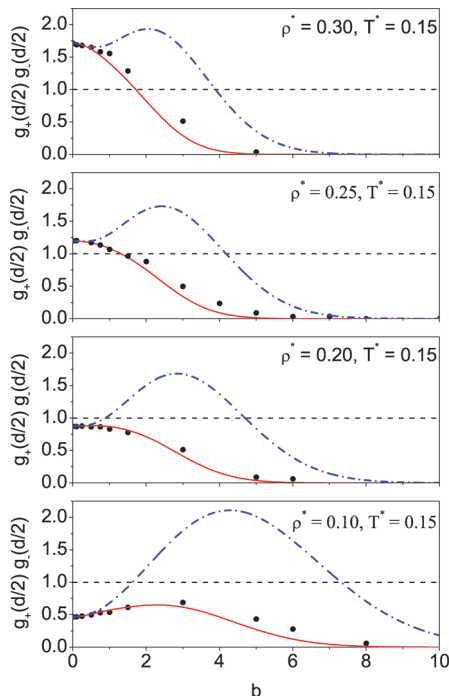


Figure 2. Same as Figure 1 but at reduced density: from bottom to top, $\rho^* = 0.1, 0.2, 0.25$, and 0.3 .

where α is a parameter. Equation 8 reduces to eq 6 if b is small. When b is large, the argument of the exponential in eq 8 is $-b^2\rho^*/2\alpha$. We tried two values for α , 1 and $1/2$, with $\alpha = 1/2$ turning out to be the better choice. Note that at large b and $\alpha = 1/2$, eq 8 is consistent with the Lou-Lee expression (eq 7).

From eq 8 we obtain

$$g_{\text{diff}}(d/2) = \sqrt{[g_{\text{sum}}(d/2)]^2 - g_+(d/2)g_-(d/2)} \quad (9)$$

where $g_{\text{sum}}(d/2)$ is given by eq 1,

$$g_1(d/2) = g_+(d/2) = a + \frac{b^2}{2} + g_{\text{diff}}(d/2) \quad (10)$$

and

$$g_2(d/2) = g_-(d/2) = a + \frac{b^2}{2} - g_{\text{diff}}(d/2) \quad (11)$$

Because $g_+(d/2)g_-(d/2)$ and $g_+(d/2)$ are always positive, $g_-(d/2)$ is guaranteed to be positive, and eq 11 tends to zero as $b \rightarrow \infty$.

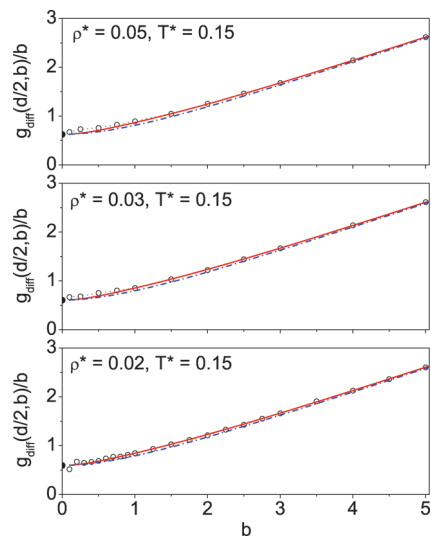


Figure 3. $g_{\text{diff}}(d/2, b)$ as a function of b in a 1:1 RPM planar double layer at the reduced temperature $T^* = 0.15$ and reduced electrolyte density $\rho^* = 0.02$ (bottom), 0.03 (middle), and 0.05 (top). The open circles are the MC simulation data,⁸ and the solid circle is the MC value of $a = g_{\text{sum}}(d/2, b = 0)$. The solid and dash-dotted lines are the results from eq 9, where the values $\alpha = 1/2$ and 1, respectively, have been used in $g_+(d/2)g_-(d/2)$.

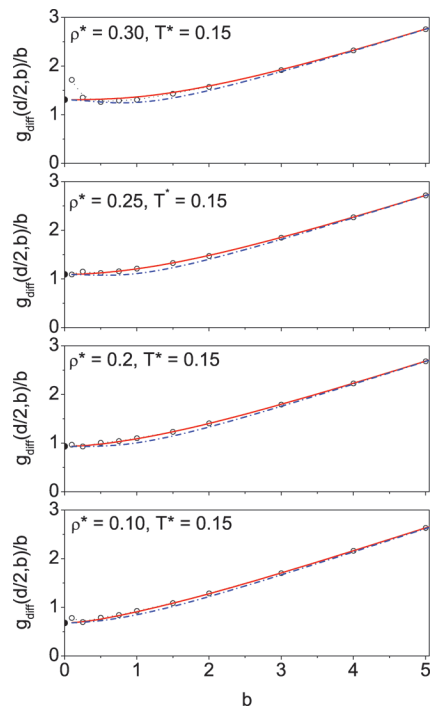


Figure 4. Same as Figure 3 but at reduced density: from bottom to top, $\rho^* = 0.1, 0.2, 0.25$, and 0.3 .

2.2. Monte Carlo Simulations. The MC simulations were performed in the canonical (NVT) ensemble following the Metropolis algorithm. A rectangular parallelepiped of sides $l_x, l_y = l_z$ was chosen as the central MC box with one y - z face being the planar charged wall at $x = 0$ and the other face at $x = l_x$ being uncharged. The traditional Ewald treatment of ionic interactions is cumbersome and computationally inconvenient for a planar system. In contrast, in such a geometry, the parallel *charged sheets* method pioneered by Torrie and Valleau¹⁴ to account for the long-range nature of the Coulomb interactions is attractive and convenient to use. The technique has subsequently been used successfully by other groups.^{15,16} Furthermore, in a recent work on electric double-layer capacitance Crozier et al.¹⁷ tested the charged sheets technique against a corrected 3D Ewald calculation using molecular dynamics and found the results from the two algorithms to be within the statistical error of each other for charged hard spheres. We employed the charged sheets method in conjunction with the usual minimum image plus periodic boundary conditions along the y and z axes. Note that Torrie and Valleau employed the grand canonical (μ VT) ensemble. The target bulk concentration was achieved through adjustments to the MC cell length l_x . The typical number of configurations sampled was on the order of 10^8 out of which the first 10^7 were used to equilibrate the system. The statistical uncertainty in reproducing the target bulk concentration was about $\pm 2\%$.

3. Results and Discussion

We present our empirical results for a range of physical states to test the predictions of eqs 8 and 9 against ‘exact’ simulation data. It is convenient to discuss results in terms of universal reduced parameters such as the reduced temperature $T^* = (\epsilon k_B T d) / (z^2 e^2)$ (reciprocal of the coupling parameter) and the reduced density $\rho^* = \rho d^3$. The specific values used are $T^* = 0.15$ and $\rho^* = 0.02, 0.03, 0.05, 0.1, 0.2, 0.25$, and 0.3 . Although the reduced temperature $T^* = 0.15$ corresponds to a 1:1 solution at 75 K, for a 2:2 solution this represents room temperature, ~ 300 K. The values for the product $g_+(d/2)g_-(d/2)$ and $g_{\text{diff}}(d/2)$ from eqs 8 and 9, respectively, are compared with our previously published simulation results^{11,12} for the above range of states in Figures 1–4. In the figures results corresponding to both $\alpha = 1$ and $1/2$ are shown for comparative purposes.

The agreement of eqs 8 and 9 using $\alpha = 1/2$ is very good. Using $\alpha = 1$ consistently gives values for $g_+(d/2)g_-(d/2)$ that are too large relative to the simulations and show a maximum for all cases studied. The MC data show such maxima only for $a < 1$, and for $a > 1$ they decrease monotonically. Thus, for $\alpha = 1$, $g_+(d/2)g_-(d/2)$ is qualitative only at low electrolyte concentrations when $a < 1$. This feature notwithstanding (for $\alpha = 1$) the values for $g_{\text{diff}}(d/2)$ are reasonable and follow the simulation data quite closely. This suggests that we need to take a holistic approach rather than focus on individual quantities such as $g_{\text{diff}}(d/2)$. Equation 8 with $\alpha = 1/2$ is a very promising expression. We are fairly confident of eq 3; it is appealing

because it is consistent with the observed (in simulations) dewetting of the electrode at low charge and large coupling constant. However, lacking a more convincing justification, eq 8 can only be regarded as a useful, but empirical, local result. Nonetheless, there is no denying its accuracy. We note that obtaining sensible results is a nontrivial exercise. Because of the square root in eq 9, an imaginary result can be obtained easily.

A final remark or two on the empirical nature of the results is in order. Empirical results, per se are, in general, useful for assessing simulations and inspiring theoretical development. The simulation data are seen to validate the present results at all electrode charges treated, and the latter are thus likely to be useful pointers for simulations of more complex, realistic models. The various contact condition results presented here can be relevant for experiments also in view of the fact that most electrochemistry occurs at or near the electrode interface, the region where the classical GCS theory is not very accurate, being more a theory for integrated quantities.

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