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Comment on “Contact conditions for the charge in the theory of the electrical double layer”

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Comment on "Contact conditions for the charge in the theory of the electrical double layer" [J. Chem. Phys. 123, 234705 (2005)]

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Exact results in any field, including statistical mechanics, are both aesthetically pleasing and very valuable in assessing theoretical approximations. One such result is the contact value theorem of Henderson *et al.*[1,2] in the electric double layer for the part of the contact value of the density profile that is common to all the species of ions, normalized to unity at large distance, $g_{sm}(d/2)(=\frac{1}{2}(g_{\text{counterion}}(d/2)+g_{\text{coion}}(d/2))$, for the ions near a planar charged electrode,

$$g_{sm}(d/2) = a + \frac{b^2}{2}, \tag{1}$$

where d is the ion diameter, assumed here for simplicity to be the same for all species, $a=p/\rho k_B T$, p is the bulk pressure, $\rho(=\Sigma_i \rho_i)$ is the number density of the ions, and k_B and T are the Boltzmann constant and temperature, respectively. Lastly, $b=4\pi q\sigma/\kappa k_B T$ is the dimensionless electrode charge density, whose dimensioned value is σ with κ being the usual bulk Debye–Hückel parameter defined through

$$\kappa^2 = \frac{4\pi q^2 \rho}{\epsilon k_B T}. \tag{2}$$

For simplicity, we assume that the electrolyte is symmetric and the magnitude of the ionic charge q is the same for all species. Although Eq. (1) is of value, a contact value theorem for that part of the density profile that gives the electrostatic response of the ions, $g_{df}(d/2)(=\frac{1}{2}(g_{\text{counterion}}(d/2)-g_{\text{coion}}(d/2))$ would be of even more value. Recently, two such results have been given. One is the low electrode charge formula of Henderson and Boda,[3]

$$g_{df} = (d/2) = ab. \tag{3}$$

The other is the formula of Holovko *et al.*,[4,5]

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

where $\beta=1/k_B T$ and $\phi(t)$ is the mean electrostatic potential at a perpendicular distance t from the electrode. The result of Henderson and Boda is semiempirical based on simulation results[3] but has the important advantage of being local. The result of Holovko *et al.* is rigorous but nonlocal.

In this Comment, we examine these two expressions for $g_{df}(b/2)$ using the extensive recent simulation results of Bhuiyan *et al.*[6] Our emphasis here is on low values of b since Eq. (3) is valid only in this regime. Values for $g_{df}(d/2)$ are plotted in Fig. 1 for a case for which a differs appreciably from unity. It is seen that Eq. (3) gives the initial slope somewhat more accurately than does Eq. (4). We have no reason to believe that this is due to anything other than the fact that Eq. (4) is nonlocal. At larger b (even beyond the range of b shown in Fig. 1), Eq. (4) is satisfactory.

A more extensive examination of Eq. (3) can be found elsewhere.[7,8] A detailed analysis of a semiempirical extension of Eqs. (3) and (4) will be published soon.

A derivation of the formal connection between Eqs. (3) and (4) is desirable. In their Response (to this Comment), Holovko *et al.*[9] give a plausible and interesting argument for obtaining Eq. (3) from Eq. (4). They suggest replacing $g_{sm}(z)$ by its contact value together with the linearized Gouy–Chapman theory for the contact potential. Neither approximation is very accurate. Indeed at low temperatures and low b, $g_{sm}(z)$ is far from being a constant, with $g_{sm}(z)<1$ near the electrode. Holovko *et al.* argue that the two approximations compensate. This may be so; however, we believe that their argument is sufficient but not necessary. We have found

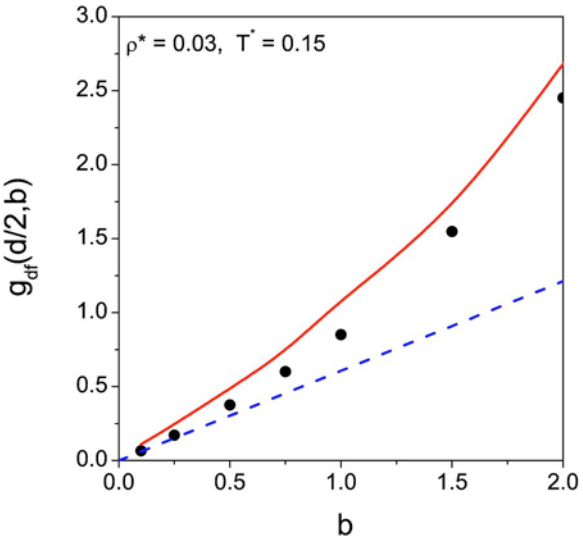

FIG. 1. (Color online) The $g_{df}(d/2,b)$ as a function of b at reduced density ρ^* $(=\rho d^3)=0.03$ and reduced temperature $T^*(=k_B T_\epsilon/q^2)=0.15$ (which is characteristic of a 2:2 electrolyte in a waterlike solvent at room temperature). The symbols are results from the formula of Henderson and Boda (Ref. 3) [Eq. (3)] using Monte Carlo (MC) data of Ref. 6, while the solid line represents the result of Holovko *et al.* (Ref. 4) [Eq. (4)] utilizing the same MC data. The dashed line has the slope $a=0.606$ for the chosen physical parameters.

with our simulations that Eq. (3) is accurate over a wide range of densities and temperatures. While not impossible, it would be surprising for this compensation to be accurate under such a spectrum of conditions.

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