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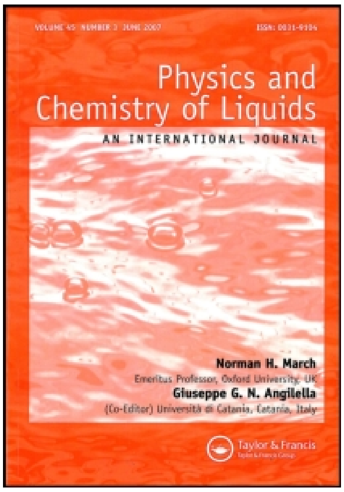

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An Improved Approximation for the Primitive Model of the Electric Double Layer

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Letter

An Improved Approximation for the Primitive Model of the Electric Double Layer

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The primitive model for the one sided electrode interface consists of an electrode which is perfectly smooth and flat, and an electrolyte formed by charged hard spheres, all immersed in a dielectric continuum.

The early work of Gouy,[1] Chapman[2] and Stern[3] is based on such a model, and in recent times it has received considerable attention by a number of researchers. Extensive computer simulations have been performed by Torrie, Valleau and coworkers.[4] The approximate integral equations which have been used to compute the density and voltage profiles and differential capacitance can be divided into four groups. Mean Spherical Approximation (MSA) and its generalization (GMSA),[5,6] the Hypernetted Chain (HNC) and derived equations,[7,8] the Modified Poisson–Boltzmann's (MPB)[9] and the Born–Green–Yvon (BGY)[10,11] type theories.

In this communication we present a new approximation for the BGY equation. This approximation is based on the fact that the correct form of the inhomogeneous pair correlation function should be[12,13,14]

$$g(1, 2) = F(r_{12}) + f(z_1)f(z_2)G(R_{12}) \qquad r_{12}^2 = R_{12}^2 + z_{12}^2 \tag{1}$$

This form of the inhomogeneous pair correlation function is obtained in

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the three dimensional case in the weak coupling (low surface charge) limit, and is rigorously true for the two dimensional one component plasma at reduced temperature $\beta e^2 = 2$.[13]

In previous work[11] the modified Croxton–McQuarrie ansatz produces regions in which the pair correlation function $g_{ij}(1, 2)$ between ions i at r_1 and j at r_2 is negative.

We are proposing a simple ansatz which corrects this deficiency. For the pair correlation function we assume:

$$g(1, 2) = A(z_1, z_2)\overset{\text{PY}}{h}(r_{12}) + f_i(z_1)f_j(z_2)\overset{\text{Bulk}}{h_{ij}}(r_{12})$$

where

$$\begin{aligned} A(z_1, z_2) &= A \quad &&\text{if} \quad z_1, z_2 < 2\sigma, \\ &= 0 \quad &&\text{if} \quad z_1 \text{ or } z_2 \geq 2\sigma, \end{aligned}$$

and σ is the hard sphere diameter.

This ansatz is of the required form (1). The functions $f_i(x)$ are obtained by requiring that the electroneutrality theorems be satisfied:[14,15]

$$-e_i = \sum_j e_j \int \mathrm{d}r_2 \, \rho_j(2) h_{ij}(1, 2)$$

where

$$h_{ij}(1, 2) = g_{ij}(1, 2) - 1$$

$$g_{ij}(1, 2) = \rho_{ij}(1, 2)/\rho_i(1)\rho_j(2)$$

The costant A is chosen in such a way to suppress the unphysical region of $g_{ij}(1, 2)$.

The density profile is obtained from the BGY equation

$$k_B T \mathbf{\nabla}_1 \ln \rho_i(1) + e_i \phi(1) = \mathbf{I}_i^F(1) + e_i \mathbf{E}_i^F(1)$$

where

$$\mathbf{I}_i^F(1) = k_B T \int \mathrm{d}2 \left\{ \sum_j \rho_j(2) g_{ij}(1, 2)\, \delta(r_{12} - \sigma_{ij}) \right\}$$

$$\mathbf{E}_i(1) = \int \mathrm{d}2 \sum_j e_j \rho_j(2) h_{ij}(1, 2) \frac{\mathbf{r}_{12}}{r_{12}^3}$$

In our case $\sigma_{ij} = \sigma$.

We solve this equation by a method described elsewhere.[11]

The results for 2 molar 1–1 electrolyte at surface charge $\sigma^* = 0.396$ Coul/m^2 ($b = \beta e E/k_{\text{Debye}} = 4.238$) and with $\sigma = 4.25$ Å, are shown in Figure 1. The bulk correlation functions are obtained by solving the HNC approximation and are rather accurate.[16]

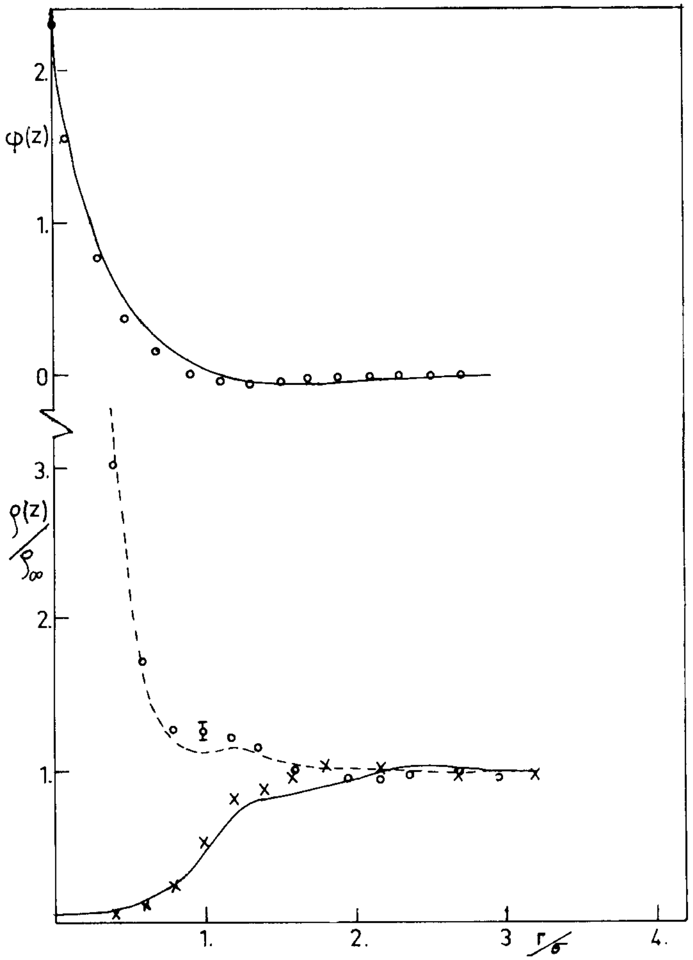

FIGURE 1 *Top*: electrostatic potential profile at 2 M and $\sigma^* = 0.396$; circles, MC results (Ref. 4); continuous line, present theory. *Bottom*: Density profiles at 2 M and $\sigma^* = 0.396$. Coion density profile: crosses, MC results, continuous line, theory. Counterion profile: circles, MC results, dashed line, theory.

We remark that the agreement visible in the figure between the theory and the MC results is obtained without any adjustable parameter and that the qualitative features are not very sensitive to the value of A. A change of about 50% in A will shift the contact potential from 2.31 to 2.39.

Furthermore we notice that all the qualitative features of the MC calculations are reproduced by the theory, including a shoulder at about 1.5 σ, which is not the case with other theories.

The calculations require about 5–6 iterations and we check both electroneutrality and contact theorem[11]

$$\frac{\beta P}{\rho} = \sum_i \rho_i(0) - b^2$$

which are satisfied to a precision of 0.3 %. This should be considered the overall accuracy of our calculations.

We have also performed the calculation for higher concentration. The results for 3 M are shown in Figure 2. Unfortunately we have no computer

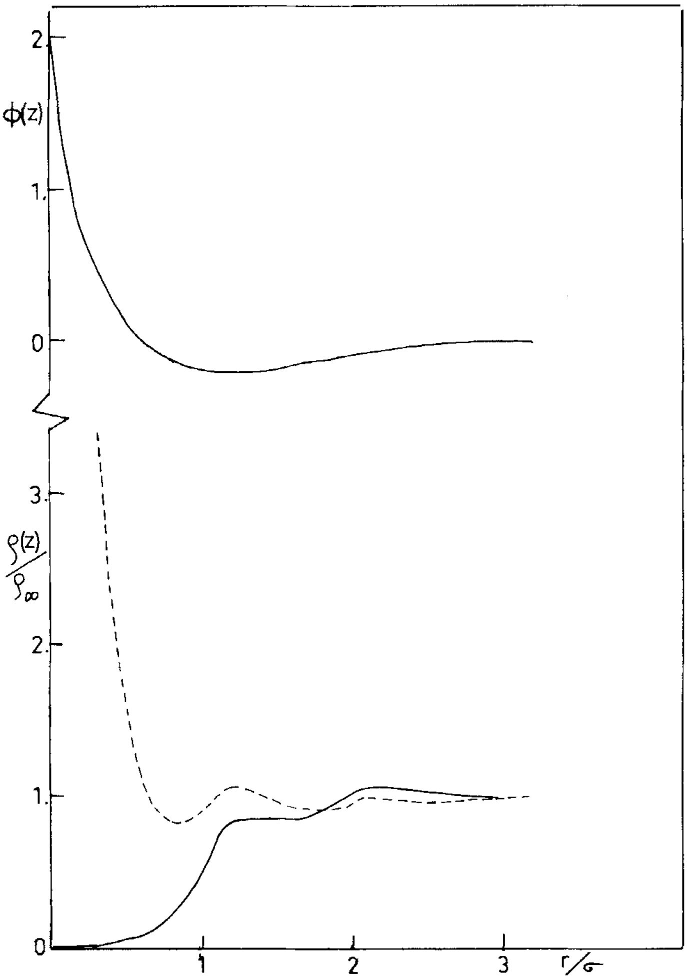

FIGURE 2 Electrostatic potential and density profiles at 3 M with $\sigma^* = 0.396$. Same symbols as in Figure 1.

simulations to compare to. But again our calculation satisfies the contact theorem very accurately. The qualitative trends observed in the 2 M case are enhanced in this case. We see a stronger dip in the potential and stronger oscillations in the density profiles. These features appear also in the 4 M case, not reported here.

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