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A local HNC/HNC approximation for the 2:2-RPM electrolytes at a charged wall

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A local HNC/HNC approximation is proposed and applied to 2:2 electrolytes near a charged hard wall. The results are compared with Monte Carlo data and other theories such as HNC/HNC, HNC/MSA, BGY, and MPB5. A remarkable improvement of the density profiles and of the diffuse layer potential is obtained. We show that the HNC closure for the ion-ion correlations, when used in the local scheme, always gives better results than those obtained from the MSA closure. The necessary algorithm for solving the local HNC/HNC equations is also presented.

I. INTRODUCTION

The electrode/electrolyte solution interface or "double layer," a great problem in electrochemistry, has been studied by statistical mechanic methods mainly with a very simple model, the so-called primitive model (PM). In this model the ions are assumed to be hard spheres with embedded point charges, the solvent is simulated by an inert continuum with a dielectric constant ϵ and the electrode is regarded as a smooth impenetrable wall with a uniform charge density ω . The use of the model in a Monte Carlo simulation with the correct choice of parameters is successful in describing the thermodynamic behavior of simple aqueous electrolyte solutions.¹

The theoretical investigations of the primitive model double layer have recently been collected by Carnie and Torrie.² The earliest approaches go back to the pioneering works of Gouy,³ Chapman,⁴ and Stern.⁵ They described the double layer structure using the Poisson-Boltzmann equation for the mean electrostatic potential and introducing the ionic size only to define a distance of closest approach to the charged surface.

The recent approaches are instead based on the integral equation theories of liquid state physics. These can be classified into three broad groups: the hypernetted chain (HNC),^{6,7} the Born-Green-Yvon (BGY),^{8,9} and the modified Poisson Boltzmann (MPB)¹⁰ based theories, all of which account for the finite ion size and for the correlations between the ions. These two aspects will produce, for certain values of the electrolyte bulk density and of the electrode charge density, an oscillatory behavior in the density profile near the surface, a feature never shown by the Stern-Gouy-Chapmann theory.

The Monte Carlo simulations that will constitute our experimental background have been performed by the group of Torrie and Valleau.^{2,11} The quantities usually determined are the ion density profiles, $\rho_\alpha(z)$, the mean electrostatic potential, $\psi(z)$, and the differential capacitance, C_D .

For the 1:1 electrolytes the agreement between the various theories and the Monte Carlo data is good only for regions of small surface charge density but it even deteriorates gradually when decreasing the electrolyte bulk density from 2 to 0.01 M. For the 2:2 electrolytes no theory so far was able

to reach a quantitative success¹² and consequently this system appears to be a severe test for any theoretical approach.

In what follows we concentrate only on HNC-based theories. The HNC theory divides into two branches, HNC/MSA and HNC/HNC, according to the approximation scheme used to describe the particle-particle correlations inside the electrolyte solution. The wall-particle correlations are described in both cases by the HNC closure of the otherwise exact Ornstein-Zernike equation for nonuniform systems.

The HNC-theories for the double layer start from the integral equations for the ion density profiles^{6,7}:

$$\rho_\alpha(z) = \rho_\alpha^{\text{Bulk}} \exp\left\{-V_\alpha(z)/k_B T + \sum_\beta \int d\mathbf{r}_1 [\rho_\beta(\mathbf{r}_1) - \rho_\beta^{\text{Bulk}}] c_{\alpha\beta}(\mathbf{r}, \mathbf{r}_1)\right\} \quad (1)$$

in which $V_\alpha(z)$ is the external potential due to the charged surface. Equation (1) can be solved iteratively, when the direct ion-ion correlation functions $c_{\alpha\beta}(\mathbf{r}, \mathbf{r}_1)$ are known. The $c_{\alpha\beta}$ are required throughout the strongly inhomogeneous region near the electrode surface. Previously these ion-ion correlations have been approximated by those of the neutral bulk electrolyte of density $\rho^\beta = \{\rho_\alpha^{\text{Bulk}}\}$:

$$c_{\alpha\beta}(\mathbf{r}, \mathbf{r}_1) \simeq c_{\alpha\beta}(|\mathbf{r} - \mathbf{r}_1|; \rho^\beta). \quad (2)$$

In homogeneous systems, the $c_{\alpha\beta}$ can be evaluated analytically in the mean spherical approximation (MSA) and numerically in the HNC approximation. In general, the HNC approximation gives the better structure.^{13,14} Therefore the expectation is that the HNC/HNC must provide a better description than the HNC/MSA of the double layer. However, we know that for both 1:1 and 2:2 electrolytes this is never so (see Figs. 2 and 5 of Ref. 12). At elevated surface charge densities both procedures fail to describe the layering of the counterions in the 1:1 electrolytes.² In the 2:2 case the disagreement with Monte Carlo density profiles has been found also for low charge densities.¹² At higher surface charges no solutions have been obtained for the HNC/HNC equations.

All these shortcomings can be traced back to the approximation of Eq. (2). An idea to improve it is provided by introducing a "local density" concept.¹⁵⁻¹⁷ The particle-

particle direct correlations are evaluated for the composition of the system in the double layer region, where there are nearly only ions of one kind and the ionic surrounding is strongly different from that of the neutral bulk system. Then, the essential step in the local HNC/MSA and HNC/HNC approximations is

$$c_{\alpha\beta}(\mathbf{r}, \mathbf{r}_1) \simeq c_{\alpha\beta}(|\mathbf{r} - \mathbf{r}_1|; \bar{\rho}(z)). \quad (3)$$

$c_{\alpha\beta}(|\mathbf{r} - \mathbf{r}_1|; \bar{\rho}(z))$, assumed spherically symmetric, is now taken from nonneutral homogeneous systems of local composition $\bar{\rho}(z) = \{\bar{\rho}_\alpha(z)\}$.^{17,18} The densities $\bar{\rho}_+(z)$ and $\bar{\rho}_-(z)$ are evaluated averaging the density profiles $\rho_\alpha(z)$ around z . A similar idea has been recently used by Tarazona¹⁹ and by Curtin and Ashcroft²⁰ to describe the freezing transition of hard spheres, which is another example of a strongly varying density situation.

In this paper we investigate a 2:2 electrolyte using the local HNC/HNC approximation. All the unwanted features (poor agreement with Monte Carlo data of the diffuse layer potential, bad description of the coion density profile near the electrode and break down in the solution of the HNC/HNC equations) shown by the HNC/MSA and HNC/HNC approximations are eliminated. We will also show definitely that the local HNC/HNC scheme has to be preferred over the local HNC/MSA approximation, the main reason being the better description of the particle-particle correlations in homogeneous systems by the HNC method.

In Sec. II we give the equations of the theory and we define the averaged densities $\bar{\rho}_\alpha(z)$, whereas the necessary algorithm for the solution of the equations is described in Sec. III. Section IV is devoted to the comparison of the Monte Carlo data with the local HNC/HNC results. A comparison with the HNC/MSA and HNC/HNC results is also presented. The conclusions are given in Sec. V.

II. LOCAL HNC/HNC EQUATIONS

The equilibrium densities, $\rho_\alpha(\mathbf{r})$, in a nonhomogeneous multicomponent system in the presence of an external field can be expressed by the exact equation^{7,16}:

$$\begin{aligned} \rho_\alpha(\mathbf{r}) = & \rho_{\alpha 0}(\mathbf{r}) \exp\left\{-[u_\alpha(\mathbf{r}) - u_{\alpha 0}(\mathbf{r})]/k_B T\right. \\ & + \sum_\beta \int_0^1 d\lambda \int d\mathbf{r}_1 c_{\alpha\beta} \\ & \left. \times (\mathbf{r}, \mathbf{r}_1; [\rho(\lambda)]) \frac{\partial \rho_\beta(\mathbf{r}_1; \lambda)}{\partial \lambda}\right\}, \quad (4) \end{aligned}$$

where

$$u_\alpha(\mathbf{r}) = V_\alpha(\mathbf{r}) - \mu_\alpha.$$

Here $V_\alpha(\mathbf{r})$ is the interaction potential between the ion α and the external field and μ_α is the chemical potential. λ is a parameter to vary the density profile $\rho_\alpha(\mathbf{r}; \lambda)$ from the initial state $\rho_{\alpha 0}(\mathbf{r})$ ($\lambda = 0$) to the final state $\rho_\alpha(\mathbf{r})$ ($\lambda = 1$). $c_{\alpha\beta}(\mathbf{r}, \mathbf{r}_1; [\rho(\lambda)])$ is the direct correlation function between ions of species α and β , at position \mathbf{r} and \mathbf{r}_1 , respectively, and it is a functional of the density profiles $\rho(\lambda)$. k_B is the Boltzmann constant.

If we consider an electrolyte in front of a planar charged

hard wall and if we choose the initial conditions:

$$V_{\alpha 0}(\mathbf{r}) = 0, \quad \rho_{\alpha 0}(\mathbf{r}) = \rho_\alpha^B$$

and a linear integration path²¹

$$\rho_\alpha(\lambda) = \rho_\alpha^B + \lambda [\rho_\alpha(\mathbf{r}) - \rho_\alpha^B]$$

we can rewrite Eq. (4) in the form¹⁶

$$\begin{aligned} \rho_\alpha(z) = & \rho_\alpha^B \exp\left\{-\frac{Z_\alpha e}{k_B T} \psi(z)\right. \\ & + \sum_\beta \int d\mathbf{r}_1 [\rho_\beta(z_1) - \rho_\beta^B] \\ & \left. \times \int_0^1 d\lambda c_{\alpha\beta}^{\text{SR}}(\mathbf{r}, \mathbf{r}_1; [\rho(\lambda)])\right\}, \quad z \geq \sigma/2 \\ \rho_\alpha(z) = & 0, \quad z < \sigma/2 \end{aligned} \quad (5)$$

which is still an exact equation. z is the distance from the wall, σ is the ionic diameter, Z_α are the valences, e is the electronic charge, and $\mathbf{r} = (0, 0, z)$. $c_{\alpha\beta}^{\text{SR}}(\mathbf{r}, \mathbf{r}_1; [\rho(\lambda)])$ are the short-range direct correlation functions defined by

$$\begin{aligned} c_{\alpha\beta}^{\text{SR}}(\mathbf{r}, \mathbf{r}_1; [\rho(\lambda)]) = & c_{\alpha\beta}(\mathbf{r}, \mathbf{r}_1; [\rho(\lambda)]) \\ & + \frac{Z_\alpha Z_\beta e^2}{k_B T \epsilon |\mathbf{r} - \mathbf{r}_1|}. \end{aligned} \quad (6)$$

$\psi(z)$ is the mean electrostatic potential and it satisfies the Poisson equation:

$$\psi''(z) = -\frac{4\pi}{\epsilon} \sum_\alpha Z_\alpha e \rho_\alpha(z) \quad (7)$$

with the boundary conditions:

$$\begin{aligned} \psi'(z) = & -\frac{4\pi}{\epsilon} \omega, \quad z = 0, \\ \psi(z) \rightarrow & 0, \quad z \rightarrow \infty, \end{aligned} \quad (8)$$

where ω is the charge density on the electrode. The boundary conditions are equivalent to the overall charge neutrality condition:

$$\omega = -\int_0^\infty dz \sum_\alpha Z_\alpha e \rho_\alpha(z). \quad (9)$$

Integrating Eq. (7), $\psi(z)$ can be put also in the form

$$\psi(z) = \frac{4\pi}{\epsilon} \int_z^\infty dy (z-y) \sum_\alpha Z_\alpha e \rho_\alpha(y) \quad (10)$$

and it is the first moment of the charge distribution in the double layer region.

Provided there is a scheme for the evaluation of the ion-ion direct correlation functions [Eq. (6)], Eqs. (5) and (7) form a closed set of equations which in principle can be solved. In practice the behavior of

$$\int_0^1 d\lambda c_{\alpha\beta}^{\text{SR}}(\mathbf{r}, \mathbf{r}_1; [\rho(\lambda)]) \quad (11)$$

is unknown and we need some approximation for it.

Previously this integral has been approximated by the direct correlation function determined at the homogeneous bulk densities ρ_α^B , $c_{\alpha\beta}^{\text{SR}}(|\mathbf{r} - \mathbf{r}_1|; \rho_\alpha^B)$. Knowing that near the charged wall the "local" composition of the electrolyte, $\rho_\alpha(z)$, is different from that in the bulk, ρ_α^B , and that the

direct correlation functions depend on the density, we approximate the integral (11) in the following way:

$$\int_0^1 d\lambda c_{\alpha\beta}^{\text{SR}}(\mathbf{r}, \mathbf{r}_1; [\rho(\lambda)]) \simeq c_{\alpha\beta}^{\text{SR}}(|\mathbf{r} - \mathbf{r}_1|; \bar{\rho}(z)). \quad (12)$$

Here $\bar{\rho}(z) = \{\bar{\rho}_\alpha(z)\}$ are averaged densities around z . The ion-ion direct correlation functions are now evaluated for the homogeneous system of composition $\bar{\rho}_+(z)$ and $\bar{\rho}_-(z)$. $\bar{\rho}_\alpha(z)$ is defined by the equation¹⁶

$$\bar{\rho}_\alpha(z) = \begin{cases} \frac{1}{2\Delta\sigma} \int_{z-\Delta}^{z+\Delta} dy \int_{y-\sigma/2}^{y+\sigma/2} dx \rho_\alpha(x), & z \geq \Delta \\ \frac{1}{(z+\Delta)\sigma} \int_0^{z+\Delta} dy \int_{y-\sigma/2}^{y+\sigma/2} dx \rho_\alpha(x), & z < \Delta. \end{cases} \quad (13)$$

The first integration (integration over x) determines the local mean density and the second averages it around the position z . The criteria for the choice of the averaging range Δ are discussed in the next section.

Using in Eq. (5) the local approximation (12) and carrying out the integration parallel to the wall, the local HNC equations for the density profile then take the form^{16,17}

$$\begin{aligned} \rho_\alpha(z) = \rho_\alpha^B \exp \left\{ -\frac{Z_\alpha e}{k_B T} \psi(z) \right. \\ \left. + 2\pi \sum_\beta \int_{-\infty}^{+\infty} dy [\rho_\beta(y) - \rho_\beta^B] \right. \\ \left. \times \int_{|z-y|}^{+\infty} ds s c_{\alpha\beta}^{\text{SR}}(s; \bar{\rho}_+(z), \bar{\rho}_-(z)) \right\}, \quad z \geq \sigma/2 \\ \rho_\alpha(z) = 0, \quad z < \sigma/2. \end{aligned} \quad (14)$$

III. THE ALGORITHM FOR THE LOCAL HNC/HNC METHOD

For the numerical solution of the local HNC/HNC equations we proceed as follows. We define a grid of densities:

$$\begin{aligned} \rho_+ = \rho_+^1, \dots, \rho_+^n, \\ \rho_- = \rho_-^1, \dots, \rho_-^m. \end{aligned} \quad (15)$$

Typical chosen values for the density grid lie between zero and the close packed density for the counterion profile and between zero and two times the bulk density for the coion profile.

We solve the bulk HNC equations for the homogeneous but nonneutral systems specified by all the pairs of densities in the grid. The method used by us is the mixing procedure of Ng²² which is one of the most reliable in our range of densities.

The outputs obtained from the solution of the HNC equations are the short range direct correlation functions $c_{\alpha\beta}^{\text{SR}}(z; \rho_+^k, \rho_-^L)$ and from these we construct the integrated version needed in Eq. (14):

$$C_{\alpha\beta}(|z-y|; \rho_+^k, \rho_-^L) = 2\pi \int_{|z-y|}^{+\infty} ds s c_{\alpha\beta}^{\text{SR}}(s; \rho_+^k, \rho_-^L). \quad (16)$$

We perform the calculation of $C_{\alpha\beta}(|z-y|; \rho_+^k, \rho_-^L)$ once and for all and store all the results in a matrix indexed by the density grid (15). By linear interpolation between the grid points, we will find $C_{\alpha\beta}(|z-y|; \bar{\rho}_+(z), \bar{\rho}_-(z))$ for a given composition, $\bar{\rho}_+(z)$, $\bar{\rho}_-(z)$, of the system in the double layer. Now, the iteration procedure to solve Eqs. (14) starts and we proceed as follows.

We begin solving the modified Gouy Chapman (MGC) equations to get the input $\rho_\alpha(z)$ densities. We evaluate $\bar{\rho}_\alpha(z)$ from Eq. (13). For each z , we select $C_{\alpha\beta}(|z-y|; \bar{\rho}_+(z), \bar{\rho}_-(z))$ by linear interpolation between the grid points of the stored matrix $C_{\alpha\beta}(|z-y|; \rho_+^k, \rho_-^L)$ and determine the convolution integrals in Eq. (14). The mean potential $\psi(z)$ is evaluated from Poisson's equation (7) by Runge-Kutta method satisfying the boundary conditions (8) and it is added to the convolution integrals. New values of $\rho_\alpha(z)$ are obtained from Eq. (14) and they become the input of the next iteration step. More precisely the iteration scheme is

$$\bar{\rho}_\alpha^{(n)}(z) = \begin{cases} \frac{1}{2\Delta\sigma} \int_{z-\Delta}^{z+\Delta} dy \int_{y-\sigma/2}^{y+\sigma/2} dx \rho_\alpha^{(n)}(x) \\ \frac{1}{(z+\Delta)\sigma} \int_0^{z+\Delta} dy \int_{y-\sigma/2}^{y+\sigma/2} dx \rho_\alpha^{(n)}(x) \end{cases},$$

$C_{\alpha\beta}(|z-y|; \bar{\rho}_+^{(n)}(z), \bar{\rho}_-^{(n)}(z))$ from a linear interpolation procedure between the grid points of the matrix $C_{\alpha\beta}(|z-y|; \rho_+^k, \rho_-^L)$,

$$\begin{aligned} \varphi_\alpha^{(n)}(z) = \sum_\beta \int_{-\infty}^{+\infty} dy [\rho_\beta^{(n)}(y) - \rho_\beta^B] \\ \times C_{\alpha\beta}(|z-y|; \bar{\rho}_+^{(n)}(z), \bar{\rho}_-^{(n)}(z)), \end{aligned}$$

$\psi^{(n)}(z)$ from the Poisson's equation

$$\psi^{(n)}(z) = -\frac{4\pi}{\epsilon} \sum_\alpha Z_\alpha e \rho_\alpha^{(n)}(z),$$

$$\rho_\alpha^{(n+1)}(z) = \rho_\alpha^B \exp \left\{ -\frac{Z_\alpha e}{k_B T} \psi^{(n)}(z) + \varphi_\alpha^{(n)}(z) \right\}.$$

For an electrolyte of given bulk density, the Δ parameter is determined only by fitting the diffuse layer potential to the Monte Carlo data at the highest surface charge. This value is used along the whole ω range. For the 0.5 and 0.05 M 2:2 electrolytes we have found, respectively, $\Delta = 1.5\sigma$ and $\Delta = 4\sigma$. We note that these values scale proportional to the Debye-Hückel length as has been proposed in Refs. 16 and 17.

The algorithm is quickly performed and after ≈ 10 iterations we reach a convergence of

$$\left\{ \frac{1}{L} \sum_\alpha \int_0^L dz \left| \frac{\rho_\alpha^{\text{out}}(z)}{\rho_\alpha^B} - \frac{\rho_\alpha^{\text{in}}(z)}{\rho_\alpha^B} \right|^2 \right\}^{1/2} < 10^{-5}$$

in which L is the maximum distance from the wall up to which all functions have been evaluated. We have chosen L equal to 10 Debye-Hückel lengths. The total charge neutrality [Eq. (9)] is satisfied within 1%. The contact value of the density, given in the HNC/HNC approximation by⁷

$$\sum_{\alpha} \rho_{\alpha}(\sigma/2) = \frac{2\pi\omega^2}{k_B T \epsilon} + \sum_{\alpha} \rho_{\alpha}^B - 2\pi \sum_{\alpha, \beta} \rho_{\alpha}^B \rho_{\beta}^B \times \int_0^{\infty} dt t^2 c_{\alpha\beta}^{SR}(t; \rho^B)$$

has generally a deviation less than 1%.

IV. RESULTS

We now present the application of the local HNC/HNC approximation to 2:2 electrolytes and test the accuracy of our scheme by comparing the theoretical results with the Monte Carlo simulations for the 0.5 and 0.05 M systems. The values of the fixed parameters used in both the Monte Carlo simulations and our calculations are: $T = 298$ K, $\epsilon = 78.5$, $\sigma = 4.25$ Å. All the results will be expressed by the dimensionless units $\psi^*(z) \equiv e\psi(z)/k_B T$ and $\omega^* \equiv \sigma^2 \omega/e$. The distances from the wall are in units of σ with the origin at the wall.

In Fig. 1 are shown the theoretical results of the local HNC/HNC, local HNC/MSA, HNC/HNC, and HNC/MSA schemes and the Monte Carlo data for the diffuse layer potential $\psi^*(\sigma/2)$ vs the surface charge density ω^* for two bulk concentrations. The good agreement of the local HNC/HNC results with those from the simulation data is evident, especially for the 0.05 M case. In contrast to the HNC/HNC we do not obtain any break down in the solution of the equations at elevated ω^* .

From Fig. 1 we also see that the local HNC/HNC results are always in better agreement with simulation data than the local HNC/MSA results, the trend being verified for the 1:1 and 2:1 electrolytes, too (see Refs. 16 and 17). With the introduction of the proper local densities $\bar{\rho}_{\alpha}(z)$ for the evaluation of the homogeneous direct correlation functions, the different results of the local HNC/HNC and local HNC/MSA approximations are simply reflecting the different ability of $c_{\alpha\beta}^{MSA}$ and $c_{\alpha\beta}^{HNC}$ to describe the ion-ion correlations in nonneutral homogeneous systems. We conclude that the local scheme eliminates any fortuitous cancellation of errors, which previously produced HNC/MSA results better than HNC/HNC.¹²

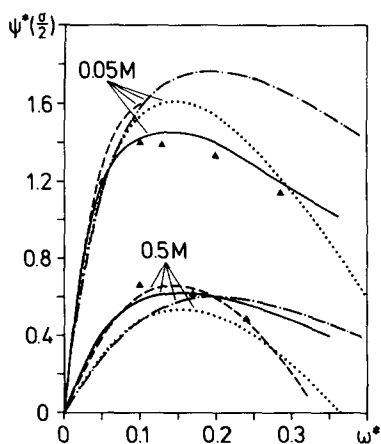


FIG. 1. Diffuse layer potential $\psi^*(\sigma/2)$ as a function of the surface charge density ω^* for 2:2 electrolytes.— local HNC/HNC, --- HNC/HNC, ---- local HNC/MSA, ... HNC/MSA, ▲ MC data from Ref. 12.

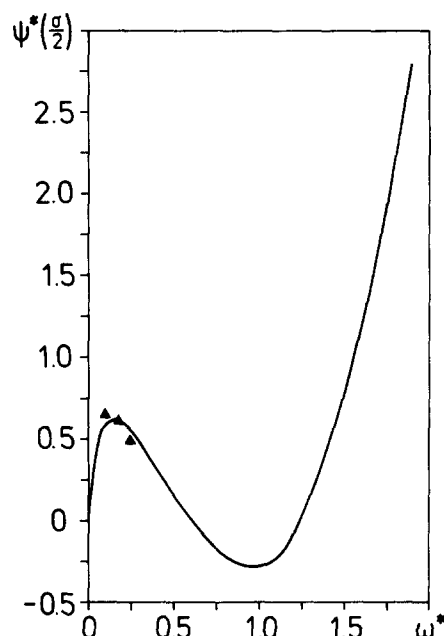


FIG. 2. Diffuse layer potential $\psi^*(\sigma/2)$ as a function of the surface charge density ω^* for 2:2, 0.5 M electrolyte in the local HNC/HNC scheme for extremely high charges. ▲ MC data from Ref. 12.

In the relatively small ω^* region explored, the excluded volume effects such as layering in the counterion profile are playing no role because the ions (doubly charged) are very effective in screening the electrical charge on the wall. The only gross visible feature in the region of small ω^* in Fig. 1 is a maximum in the $\psi^*(\sigma/2)$ functions. As ω^* is gradually increased from the zero value, the electrolyte system first of all builds a plane of ions with a charge opposite to that on the electrode (counterions) (Fig. 6). Increasing ω^* towards the maximum in $\psi^*(\sigma/2)$, it builds an inversely charged region (Fig. 3). As ω^* continues to increase, so does the extent of this charge inversion (Fig. 4), leading to a decrease of $\psi^*(\sigma/2)$. The charge inversion is very evident in the 2:2 electrolytes because the strong correlation between the doubly charged ions drags into the double layer more ions with the same charge as the electrode (co-ions), than in the 1:1 case.

At very high surface charge density (Fig. 2), the packing effects will come into the play. The first layer gets filled with counterions, the double layer region will expand and

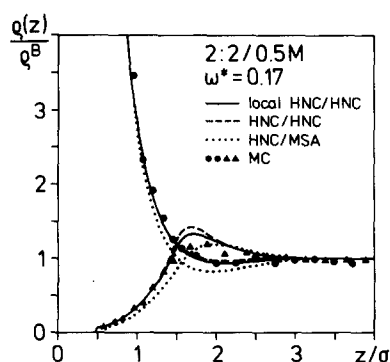


FIG. 3. Ion density profiles $\rho_{\alpha}(z)/\rho_{\alpha}^B$ for the 2:2 electrolyte at 0.5 M and $\omega^* = 0.17$. MC data from Ref. 2.

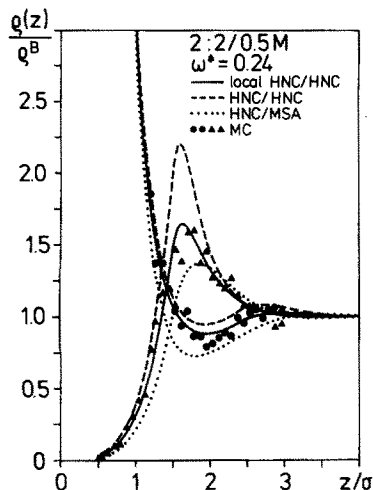


FIG. 4. Ion density profiles $\rho_\alpha(z)/\rho_\alpha^B$ for the 2:2 electrolyte at 0.5 M and $\omega^* = 0.24$. MC data from Ref. 12.

$\psi^*(\sigma/2)$ will rise again. This behavior is predicted only by the local HNC/HNC method and it would be desirable to have MC data for these extreme surface charge densities.

The density profiles for two 0.5 M systems are shown in Figs. 3 and 4. In Fig. 3 the electrode charge density ω^* is 0.17, whereas in Fig. 4 it is 0.24, the highest charge for which there are Monte Carlo data. From Fig. 3 we see that the local HNC/HNC is decreasing the height of the coion profile that is usually overestimated by the HNC/HNC approach. This behavior is more evident in Fig. 4. Here, the first maximum in the coion profile is strongly reduced with respect to the HNC/HNC and the minimum in the counterion profile is a little depressed. As a result, good agreement with the Monte Carlo data is obtained also for the potential $\psi^*(z)$. Thus, the local HNC/HNC scheme recognizes that fewer coions are near the counterions compared to the bulk situation. In Figs. 3 and 4 are also shown the HNC/MSA results. In this case it is evident that the introduction of a local HNC/MSA approximation, with its decreased (+ -) correlations, will move the density profiles in the wrong direction.²³

In Fig. 5 we show the mean electrostatic potential pro-

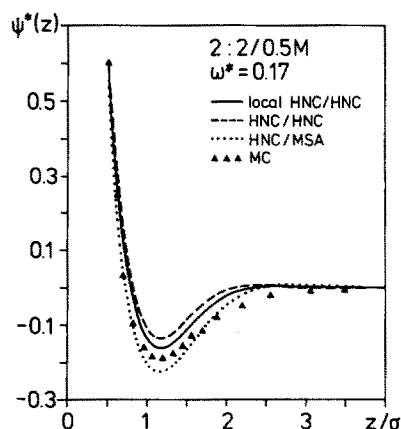


FIG. 5. Mean potential profile $\psi^*(z)$ for the case of Fig. 3. MC data from Ref. 2.

file, $\psi^*(z)$, for the 0.5 M and $\omega^* = 0.17$ case. The nonmonotonic behavior of the mean potential due to the charge inversion (Fig. 3) is reproduced.

The density profiles for the 0.05 M cases are shown in Figs. 6 and 7. In Fig. 6 $\omega^* = 0.0975$. For this small charge density there is no charge inversion. The agreement of the local scheme with the simulation data is remarkable. In Fig. 7 are presented the density profiles for the increased charge density $\omega^* = 0.284$. The MC data show a maximum in the co-ion profile around $z = 2\sigma$ and from this point on the profiles for both kinds of ions are very close to each other. This means that beyond two ionic diameters from the wall the system is locally neutral. The mean potential profile (Fig. 8) is reflecting this curious behavior and it reaches a value of almost zero at this same z distance. The local HNC/HNC approximation again follows closely the Monte Carlo data.

In the literature, for the 2:2 systems there are also some results coming from the MPB5 theory¹⁰ and the BGY theory.⁹ The MPB5 theory fails in describing the maximum in the diffuse layer potential vs ω^* and the agreement of the BGY theory with the Monte Carlo data is also not as good as in our calculations.

We conclude that in the local HNC/HNC approximation all three quantities, $\psi_{\sigma/2}^*(\omega^*)$, $\psi^*(z)$, and $\rho_\alpha(z)$, are, at the same time, following closely the Monte Carlo data as they indeed must.

V. CONCLUSIONS

In this paper we have developed and extensively applied the local HNC/HNC approximation to 2:2 electrolytes near a charged wall. The results are accurate for the range of parameters explored, i.e., for the reduced electrode charge density ω^* lying in the interval 0–0.4 and for the 0.5 and 0.05 M densities. The published Monte Carlo simulations available for comparison are in this range.

The Monte Carlo density profiles are well reproduced by the theory. No over or under estimation of the coion profile and no break down in the solution of the equations are present. The diffuse layer potential results plotted against the surface charge correctly describe the maximum shown by the simulation, which, from the structural point of view, indicates the presence of an inversely charged region. The

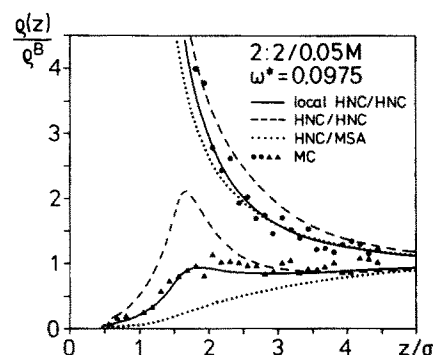


FIG. 6. Ion density profiles $\rho_\alpha(z)/\rho_\alpha^B$ for the 2:2 electrolyte at 0.05 M and $\omega^* = 0.0975$. MC data from Ref. 12.

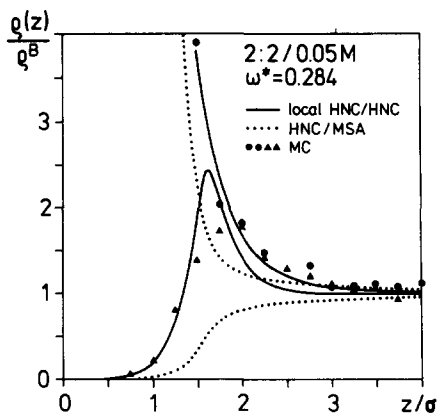


FIG. 7. Ion density profiles $\rho_\alpha(z)/\rho_\alpha^B$ for the 2:2 electrolyte at 0.05 M and $\omega^* = 0.284$. MC data from Ref. 2.

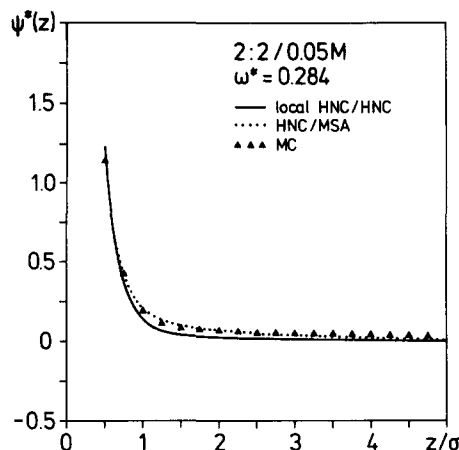


FIG. 8. Mean potential profile $\psi^*(z)$ for the case of Fig. 7. MC data from Ref. 2.

good performance of the local approximation is also reflected in the mean potential results.

The success of the method is due to the evaluation of the direct correlation functions at averaged densities $\bar{\rho}_\alpha(z)$ that in the double layer are different from the bulk densities. This improvement becomes more and more effective for higher values of the charge density on the electrode. In the low ω^* region, the deviation of $\bar{\rho}_\alpha(z)$ from the bulk densities ρ_α^B is small, and we recover the already good results of the standard schemes.

The local HNC/HNC results are better than the local HNC/MSA results, as has also been verified for the 1:1 and 1:2 electrolytes.^{16,17} This systematic analysis of the three systems indicates, in our opinion, the absence of any accidental error compensation.

The averaging parameter Δ is the only parameter introduced into the theory. At each bulk concentration, Δ is fixed by fitting the Monte Carlo result for the diffuse layer potential at the highest surface charge. The values so obtained agree with an empirical scaling rule based on the Debye-Hückel screening length (see Refs. 16 and 17), which allows a systematic extension of the averaging procedure to systems where no MC data are available.

We note that other averaging procedures leading to $\bar{\rho}_\alpha(z)$ have been suggested for simple liquids (see Refs. 19 and 20). Work in this direction for the double layer is in progress.

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