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Weighted-density-functional theory of nonuniform ionic fluids: Application to electric double layers

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A weighted-density-functional theory is developed for inhomogeneous ionic fluids and applied to the structure of the electric double layer using the restricted primitive model where the ions are considered to be charged hard spheres of equal diameter. The formalism is nonperturbative with both hard-sphere and electrical contributions to the one-particle correlation function evaluated through a suitably averaged weighted density, the only input being the second-order direct correlation functions of the corresponding uniform system. Numerical results on the ionic density profile and the mean electrostatic potential near a hard wall at several surface charge densities are shown to compare well with available simulation results.

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I. INTRODUCTION

Density-functional theory (DFT) has established itself as a highly powerful tool for studying the equilibrium properties of nonuniform fluids [1], which include a wide class of problems, viz. the liquid surface [2], freezing of liquids [3] and many other interfacial phenomena [4]. One can also study the structure of classical uniform fluids using a density-functional approach [5,6]. DFT has, however, been restricted mostly to neutral liquids [7–9] and its application to ionic or dipolar liquids has attracted attention rather recently [10,11].

In a density-functional approach, one employs the single-particle density as the basic variable for the description of a many-particle system. For this purpose, the grand potential for the system is first to be expressed in terms of the density, which on minimization leads to the expression for the equilibrium density distribution.

The exact functional form of the grand potential is, however, not known in general, and therefore the crux of the problem lies in finding a suitable approximation to express this functional in terms of the density. Most of the variants of DFT that are normally used correspond to different schemes of this approximation procedure. In many cases, the form of the functional is known for a uniform system, and this knowledge is often used to construct the functional for the corresponding nonuniform system.

The simplest approach that is followed is a Taylor-series expansion of the functional with respect to the inhomogeneity around the homogeneous bulk density. This perturbative approach has been employed in many problems and has been partially successful as well. However, since the series is usually truncated at the second-order term, in most of the cases this perturbative approach might lead to considerable inaccuracy especially if the inhomogeneity is not weak.

Nonperturbative approaches to DFT have therefore been proposed recently. The commonly used ones are based on the weighted-density approach and its generalizations. The two recent successful theories based on a weighted-density scheme are due to Tarazona [12,13] and Curtin and Ashcroft [7] and Denton and Ashcroft [8,9]. In a weighted-density approach (WDA), either the excess free energy or its functional derivative (the first-order correlation function) for the nonuniform fluid is approximated by that of the corresponding uniform fluid of a different smoothed average density, determined from suitable weighted averages of the actual nonuniform density of the system. In the Tarazona version of the WDA, it is the excess free energy which is approximated and the associated weight function is expressed as a truncated density expansion where the coefficients are determined by fitting the corresponding direct correlation function to that from the Percus-Yevic approximation. The WDA of Ashcroft *et al.*, however, approximates the first-order correlation function and the weight function is given by an analytical expression in terms of the first- and second-order correlation functions of the uniform system. Both these approaches have recently been employed quite successfully to the study of structure of hard-sphere fluids and their mixtures near a hard-wall potential [9,14]. The predicted inhomogeneous density of the fluid near the surface provides important information about the essential features of the interface.

Another nonuniform system that is of much interest is the electric double layer (EDL) [15,16], the region of inhomogeneous ionic distribution in an electrode-electrolyte interface, resulting from the charge separation under the influence of the electric field produced by the surface charge. The structure of the EDL is known to play an important role in various electrochemical, colloidal, and biological phenomena, and its understanding and prediction have attracted a great deal of attention over the years.

The simplest and most thoroughly studied model for the EDL is the restricted primitive model (RPM), where the electrolyte is assumed to consist of ions which are charged hard spheres of equal diameter, immersed in a solvent which is treated as a continuum isotropic dielec-

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tric medium. The electrode is considered to be an infinite planar, polarizable and impenetrable hard wall containing a uniform surface charge density.

The purpose of the present work is to introduce a suitable nonperturbative weighted-density approach to DFT of nonuniform ionic fluids and apply it to study the structure of the EDL. Although recently there has been interest in applying DFT to the study of the EDL, these studies have mostly used a combination of the WDA and the perturbative schemes. Thus Davis *et al.* [10,11] uses the Tarazona model of the WDA to the hard-sphere contribution to the correlation function, while for the ionic part they use second-order perturbation expansion around the bulk density. Groot [4,17], on the other hand, has determined a coarse-grained density for the ions considering both hard-sphere and ionic contributions but uses it as a zeroth-order density to carry out a perturbation expansion around it.

Our objective in this work is to introduce a fully nonperturbative version of DFT for the inhomogeneous ionic distribution near the electrode-electrolyte interface by generalizing and extending the WDA of Denton and Ashcroft [9] to ionic systems. After developing the theory in Sec. II, we present the results of numerical calculations in Sec. III. Finally, we offer a few concluding remarks in Sec. IV.

II. THEORY

We consider a system consisting of two ionic components (α and β) dissolved in a solvent (considered as a uniform dielectric continuum), and distributed under the influence of an external potential (denoted as $u_\alpha(\mathbf{r})$ for the αth component). The grand-potential functional for this system at fixed temperature (T), volume, external potential and chemical potential (μ_α for the αth component) is given by

$$\Omega[\{\rho_\alpha\}]=F[\{\rho_\alpha\}]+\sum_\alpha\int d\mathbf{r}\,u_\alpha(\mathbf{r})\rho_\alpha(\mathbf{r})-\sum_\alpha\int d\mathbf{r}\,\mu_\alpha\rho_\alpha(\mathbf{r})\ , \tag{1}$$

where $F[\{\rho_\alpha\}]$ is the intrinsic Helmholtz free-energy functional, $\rho_\alpha(\mathbf{r})$ being the nonuniform single-particle density of component α and the summation is over both the components. The true equilibrium density distribution of each component corresponds to the minimum of the grand potential with respect to the component densities and is determined by the equation

$$\mu_\alpha=u_\alpha(\mathbf{r})+\frac{\delta F[\{\rho_\alpha\}]}{\delta\rho_\alpha(\mathbf{r})}\ . \tag{2}$$

The free-energy functional $F[\{\rho_\alpha\}]$ consists of an ideal-gas free-energy functional representing the free energy of the nonuniform system in absence of internal interactions and an excess free-energy contribution F_{ex}, viz.

$$F[\{\rho_\alpha\}]=(1/\beta)\sum_\alpha\int d\mathbf{r}\,\rho_\alpha(\mathbf{r})[\ln(\rho_\alpha(\mathbf{r})\lambda_\alpha^3)-1]+F_{\text{ex}}[\{\rho_\alpha\}]\ , \tag{3}$$

where $\beta=(k_BT)^{-1}$, k_B being the Boltzmann constant, and λ_α is the de Broglie wavelength of the αth component.

The excess free energy $F_{\text{ex}}[\{\rho_\alpha\}]$ originates from internal interactions within the system and is in general unknown. It defines the direct correlation functions of different order through functional derivatives, the most important ones being the first- and second-order correlation functions defined, respectively, as

$$c_\alpha^{(1)}(\mathbf{r}_1)=-\beta\frac{\delta F_{\text{ex}}[\{\rho_\alpha\}]}{\delta\rho_\alpha(\mathbf{r}_1)}\ , \tag{4}$$

$$c_{\alpha\beta}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=-\beta\frac{\delta^2F_{\text{ex}}[\{\rho_\alpha\}]}{\delta\rho_\alpha(\mathbf{r}_1)\delta\rho_\beta(\mathbf{r}_2)}=\frac{\delta c_\alpha^{(1)}(\mathbf{r}_1)}{\delta\rho_\beta(\mathbf{r}_2)}\ . \tag{5}$$

For a system consisting of charged hard spheres (q_α being the charge of the αth species), the direct Coulomb interaction contribution can be extracted and the excess free energy can be expressed as

$$F_{\text{ex}}[\{\rho_\alpha\}]=(1/2\epsilon)\sum_\alpha\sum_\beta q_\alpha q_\beta\int\int d\mathbf{r}_1 d\mathbf{r}_2\rho_\alpha(\mathbf{r}_1)\rho_\beta(\mathbf{r}_2)/|\mathbf{r}_1-\mathbf{r}_2|+F_{\text{ex}}^{\text{HS}}[\{\rho_\alpha\}]+F_{\text{ex}}^{\text{el}}[\{\rho_\alpha\}]\ , \tag{6}$$

where ϵ is the dielectric constant of the medium. The corresponding separation in the correlation functions leads to the results

$$c_\alpha^{(1)}(\mathbf{r}_1)=(\beta/\epsilon)q_\alpha\int d\mathbf{r}'\sum_\beta q_\beta\rho_\beta(\mathbf{r}')/|\mathbf{r}_1-\mathbf{r}'|+c_\alpha^{(1)\text{HS}}(\mathbf{r}_1;[\{\rho_\alpha\}])+c_\alpha^{(1)\text{el}}(\mathbf{r}_1;[\{\rho_\alpha\}])\ , \tag{7}$$

$$c_{\alpha\beta}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=(\beta/\epsilon)q_\alpha q_\beta/|\mathbf{r}_1-\mathbf{r}_2|+c_{\alpha\beta}^{(2)\text{HS}}(\mathbf{r}_1,\mathbf{r}_2)+c_{\alpha\beta}^{(2)\text{el}}(\mathbf{r}_1,\mathbf{r}_2)\ , \tag{8}$$

where the middle terms on the right-hand side (rhs) are the contribution to the correlation functions solely due to hard-sphere (HS) interactions, the first terms indicate explicit Coulomb interactions, and the third terms represent extra electrical contributions arising from the coupling of Coulombic and hard-sphere interactions.

In the RPM model of the planar electric double layer, the density variation is along the z direction (i.e., perpendicular to the electrode surface) and the external potential $u_\alpha(z)$ consists [11,15] of Coulomb potential due to the surface charge density σ and the hard-sphere potential, viz.

$$u_\alpha(z)=q_\alpha u_{\text{Coul}}(z)+u_{\text{HS}}(z)\ , \tag{9}$$

with

$$u_{\text{Coul}}(z)=-2\pi\sigma z/\epsilon-2\pi\sigma z/[\epsilon+u_{\text{HS}}(z)]\ , \tag{10a}$$

$$u_{\rm HS}(z)=\begin{cases}\infty \ \text{ for } z<d/2 & \text{(10b)}\\ 0 \ \text{ for } z>d/2\ , & \text{(10c)}\end{cases}$$

where d is the diameter of the hard spheres.

Using Eqs. (3)–(9), Eq. (2) can be rewritten as

$$\begin{aligned}\mu_\alpha&=(1/\beta)\{\ln[\rho_\alpha(\mathbf{r})\lambda_\alpha^3]+c_\alpha^{(1)}(\mathbf{r};[\{\rho_\alpha\}])\}+u_\alpha(\mathbf{r})\\ &=(1/\beta)\{\ln[\rho_\alpha(\mathbf{r})\lambda_\alpha^3]+c_\alpha^{(1)\rm HS}(\mathbf{r};[\{\rho_\alpha\}])\\ &\qquad+c_\alpha^{(1)\rm el}(\mathbf{r};[\{\rho_\alpha\}])\}\\ &\quad+u_{\rm HS}(z)+q_\alpha\psi(z)\ ,\end{aligned}\tag{11}$$

where $\psi(z)$ denotes the mean electrostatic potential due to the surface charge (i.e., $u_{\rm Coul}$) and the ionic distribution [see the first term on the rhs of Eq. (7) representing the direct Coulomb part of $c_\alpha^{(1)}$]. Here the quantities $c_\alpha^{(1)\rm HS}(\mathbf{r};[\{\rho_\alpha\}])$ and $c_\alpha^{(1)\rm el}(\mathbf{r};[\{\rho_\alpha\}])$ denote, respectively, the hard-sphere and the electrical-hard-sphere coupling contributions to the first-order correlation function. Since the ionic density varies only along the z direction, $\psi(z)$ obtained from the solution of the corresponding Poisson equation in one dimension is given by the simplified expression

$$\begin{aligned}\psi(z)=&-(4\pi\sigma/\epsilon)z-(4\pi/\epsilon)z\int_0^z dz'\sum_\alpha q_\alpha\rho_\alpha(z')\\ &-(4\pi/\epsilon)\int_z^\infty dz'z'\sum_\alpha q_\alpha\rho_\alpha(z')\ ,\end{aligned}\tag{12a}$$

which can also be rewritten as

$$\psi(z)=(4\pi/\epsilon)\int_z^\infty dz'(z-z')\sum_\alpha q_\alpha\rho_\alpha(z')\tag{12b}$$

using the electroneutrality condition given by

$$\int_0^\infty dz'\sum_\alpha q_\alpha\rho_\alpha(z')+\sigma=0\ .\tag{13}$$

Evaluating the chemical potential μ_α using the bulk phase density ρ_α^0 in Eq. (11) and substituting this value in the same equation, one obtains

$$\begin{aligned}\rho_\alpha(z)=\rho_\alpha^0\exp(&-\beta q_\alpha\psi(\mathbf{r})+c_\alpha^{(1)\rm HS}(\mathbf{r};[\{\rho_\alpha\}])\\ &+c_\alpha^{(1)\rm el}(\mathbf{r};[\{\rho_\alpha\}])-c_\alpha^{(1)\rm HS}([\{\rho_\alpha^0\}])\\ &-c_\alpha^{(1)\rm el}([\{\rho_\alpha^0\}]))\ ,\end{aligned}\tag{14}$$

which determines the density in the region $z>d/2$. For $z<d/2$, however, the density vanishes, i.e., $\rho_\alpha(z)=0$.

Although Eq. (14) is the key equation for obtaining the density profiles of the ions, it is incomplete due to the lack of knowledge about the explicit expressions of $c_\alpha^{(1)\rm HS}$ and $c_\alpha^{(1)\rm el}$ for nonuniform density distributions. Since these are known for a uniform system of charged hard spheres, we propose to use this knowledge to obtain an approximation scheme for the corresponding inhomogeneous system in the presence of an external field. For uncharged hard-sphere systems, such an approach has formed the basis of the WDA of Curtin and Ashcroft [7] and Denton and Ashcroft [8,9], where $c^{(1)}(\rho(\mathbf{r}))$ for a nonuniform system is obtained by evaluating the expression of $\tilde{c}^{(1)}$ for a corresponding uniform system with an effective density $\bar{\rho}(\mathbf{r})$, i.e.,

$$c^{(1)}(\rho(\mathbf{r}))=\tilde{c}^{(1)}(\bar{\rho}(\mathbf{r}))\ .\tag{15}$$

Here the effective weighted density $\bar{\rho}$ is defined through an appropriate weighted average of the actual nonuniform density of the system as

$$\bar{\rho}(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r}))\ ,\tag{16}$$

with a suitably chosen weight function $w(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r}))$. (Throughout this work, we use the notation $\tilde{c}^{(1)}$ and $\tilde{c}^{(2)}$ to denote the correlation functions for the uniform system.)

We now propose a new WDA route to Eq. (14) for the nonuniform ionic liquid system under consideration through generalization and extension of Eqs. (15) and (16). For a uniform neutral ionic system, analytical expressions are available for both $\tilde{c}_{\alpha\beta}^{(2)\rm HS}(\mathbf{r}_1,\mathbf{r}_2)$ and $\tilde{c}_{\alpha\beta}^{(2)\rm el}(\mathbf{r}_1,\mathbf{r}_2)$. To obtain the corresponding first-order quantities $\tilde{c}_\alpha^{(1)\rm HS}([\{\rho_\alpha^0\}])$ and $\tilde{c}_\alpha^{(1)\rm el}([\{\rho_\alpha^0\}])$, we first express $c_\alpha^{(1)}$ as the sum $c_{\alpha\alpha}^{(1)}+c_{\alpha\beta}^{(1)}$, and the expressions for the contributions from α and β components for a uniform system, viz. $\tilde{c}_{\alpha\alpha}^{(1)}$ and $\tilde{c}_{\alpha\beta}^{(1)}$ are obtained through functional integrations of the second-order correlation functions $\tilde{c}_{\alpha\alpha}^{(2)}$ and $\tilde{c}_{\alpha\beta}^{(2)}$.

The proposed WDA is then based on replacing both the first-order correlation functions $c^{(1)\rm HS}$ and $c^{(1)\rm el}$ in Eq. (14) by their homogeneous counterparts evaluated with appropriate effective densities. Thus, we write

$$c_\alpha^{(1)\rm HS}(\mathbf{r};[\{\rho_\alpha\}])=\tilde{c}_{\alpha\alpha}^{(1)\rm HS}(\bar{\rho}_{\rm HS}^{(\alpha)}(\mathbf{r}))+\tilde{c}_{\alpha\beta}^{(1)\rm HS}(\bar{\rho}_{\rm HS}^{(\beta)}(\mathbf{r}))\ ,\tag{17a}$$

$$c_\alpha^{(1)\rm el}(\mathbf{r};[\{\rho_\alpha\}])=\tilde{c}_{\alpha\alpha}^{(1)\rm el}(\bar{\rho}_{\rm el}^{(\alpha)}(\mathbf{r}))+\tilde{c}_{\alpha\beta}^{(1)\rm el}(\bar{\rho}_{\rm el}^{(\beta)}(\mathbf{r}))\ ,\tag{17b}$$

where

$$\begin{aligned}\bar{\rho}_{\rm HS}^{(\alpha)}(\mathbf{r})=&\int d\mathbf{r}'\rho_\alpha(\mathbf{r}')w_{\alpha\alpha}^{\rm HS}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\rm HS}^{(\alpha)}(\mathbf{r}))\\ &+\int d\mathbf{r}'\rho_\beta(\mathbf{r}')w_{\alpha\beta}^{\rm HS}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\rm HS}^{(\alpha)}(\mathbf{r}))\\ &+\int d\mathbf{r}'\rho_\alpha(\mathbf{r}')w_{\alpha\alpha}^{\rm el}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\rm HS}^{(\alpha)\rm el}(\mathbf{r}))\\ &+\int d\mathbf{r}'\rho_\beta(\mathbf{r}')w_{\alpha\beta}^{\rm el}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\rm HS}^{(\alpha)\rm el}(\mathbf{r}))\end{aligned}\tag{18a}$$

and

$$\begin{aligned}\bar{\rho}_{\rm el}^{(\alpha)}(\mathbf{r})=&\int d\mathbf{r}'\rho_\alpha(\mathbf{r}')w_{\alpha\alpha}^{\rm HS}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\rm el}^{(\alpha)\rm HS}(\mathbf{r}))\\ &+\int d\mathbf{r}'\rho_\beta(\mathbf{r}')w_{\alpha\beta}^{\rm HS}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\rm el}^{(\alpha)\rm HS}(\mathbf{r}))\\ &+\int d\mathbf{r}'\rho_\alpha(\mathbf{r}')w_{\alpha\alpha}^{\rm el}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\rm el}^{(\alpha)}(\mathbf{r}))\\ &+\int d\mathbf{r}'\rho_\beta(\mathbf{r}')w_{\alpha\beta}^{\rm el}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\rm el}^{(\alpha)}(\mathbf{r}))\ ,\end{aligned}\tag{18b}$$

with similar expressions for $c_\beta^{(1)\rm HS}(\mathbf{r};[\{\rho_\alpha\}])$, $c_\beta^{(1)\rm el}(\mathbf{r};[\{\rho_\alpha\}])$, $\bar{\rho}_{\rm HS}^{(\beta)}(\mathbf{r})$, and $\bar{\rho}_{\rm el}^{(\beta)}(\mathbf{r})$ to be obtained by interchanging α and β in Eqs. (17) and (18).

The correlation functions $c_\alpha^{(1)\rm HS}(\mathbf{r};[\{\rho_\alpha\}])$ and $c_\alpha^{(1)\rm el}(\mathbf{r};[\{\rho_\alpha\}])$ are evaluated in Eqs. (17) using the effective densities $\{\bar{\rho}_{\rm HS}^{(\alpha)}(\mathbf{r})\}$ and $\{\bar{\rho}_{\rm el}^{(\alpha)}(\mathbf{r})\}$. The quantity

$\bar{\rho}_{\mathrm{HS}}^{(\alpha)}(\mathbf{r})$ can thus be physically interpreted as the effective total density of a locally uniform fluid to which the actual nonuniform fluid is mapped so that the contribution to the hard-sphere part of the one-particle correlation function arising from the correlation with particles of the αth component is correctly reproduced when the expression for the uniform system is evaluated with this density. Analogously, $\bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r})$ is the effective total density of a locally uniform and locally neutral fluid, whose electrical part of the one-particle correlation function arising from the correlation with particles of the αth component is the same as that of the actual nonuniform and locally nonneutral fluid. The effective weighted densities corresponding to the βth component, i.e., $\bar{\rho}_{\mathrm{HS}}^{(\beta)}(\mathbf{r})$ and $\bar{\rho}_{\mathrm{el}}^{(\beta)}(\mathbf{r})$ can also be similarly interpreted. Since these mappings are done at every point $\mathbf{r}$, the weighted densities are $\mathbf{r}$ dependent.

Two other effective densities $\bar{\rho}_{\mathrm{HS}}^{(\alpha)\mathrm{el}}(\mathbf{r})$ and $\bar{\rho}_{\mathrm{el}}^{(\alpha)\mathrm{HS}}(\mathbf{r})$ (which are essentially "off-diagonal" effective densities) are also introduced in Eqs. (18) to evaluate w^{el} and w^{HS}, respectively, appearing in the expressions of $\bar{\rho}_{\mathrm{HS}}^{(\alpha)}(\mathbf{r})$ and $\bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r})$. We propose to choose these two effective density quantities as equal to zero, $\bar{\rho}_{\mathrm{HS}}^{(\alpha)}(\mathbf{r})$ or $\bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r})$ and obtain thereby different WDA schemes.

We follow the approach of Ashcroft and derive expressions for the weight functions by requiring that the first functional derivative of Eqs. (17) with respect to the densities ρ_α or ρ_β would yield the exact appropriate two-particle correlation functions in the limit of uniform density. This leads to the results

$$\begin{aligned} w_{\alpha\alpha}^{\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) &= w_{\alpha\beta}^{\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) \\ &= w_{\beta\alpha}^{\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) = w_{\beta\beta}^{\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) \\ &= w_{\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) , \end{aligned} \tag{19a}$$

$$\begin{aligned} w_{\alpha\alpha}^{\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) &= -w_{\alpha\beta}^{\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) \\ &= -w_{\beta\alpha}^{\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) \\ &= w_{\beta\beta}^{\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) \\ &= (\tfrac{1}{2}) w_{\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) , \end{aligned} \tag{19b}$$

where the weight functions w_{HS} and w_{el} are given by

$$w_{\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) = \tilde{c}^{(2)\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r})) \Big/ \int d\mathbf{r}' \tilde{c}^{(2)\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r})) , \tag{20a}$$

$$w_{\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}) = \tilde{c}^{(2)\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r})) \Big/ \int d\mathbf{r}' \tilde{c}^{(2)\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r})) . \tag{20b}$$

The expressions for the weighted densities can now be rewritten as

$$\bar{\rho}_{\mathrm{HS}}^{(\alpha)}(\mathbf{r}) = \int d\mathbf{r}' w_{\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\mathrm{HS}}^{(\alpha)}(\mathbf{r}))[\rho_\alpha(\mathbf{r}')+\rho_\beta(\mathbf{r}')] + \tfrac{1}{2}\int d\mathbf{r}' w_{\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\mathrm{HS}}^{(\alpha)\mathrm{el}}(\mathbf{r}))[\rho_\alpha(\mathbf{r}')-\rho_\beta(\mathbf{r}')] , \tag{21a}$$

$$\bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r}) = \int d\mathbf{r}' w_{\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\mathrm{el}}^{(\alpha)\mathrm{HS}}(\mathbf{r}))[\rho_\alpha(\mathbf{r}')+\rho_\beta(\mathbf{r}')] + \tfrac{1}{2}\int d\mathbf{r}' w_{\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r}))[\rho_\alpha(\mathbf{r}')-\rho_\beta(\mathbf{r}')] , \tag{21b}$$

with similar expressions for $\bar{\rho}_{\mathrm{HS}}^{(\beta)}(\mathbf{r})$ and $\bar{\rho}_{\mathrm{el}}^{(\beta)}(\mathbf{r})$ obtained easily by interchanging α and β.

We now discuss different choices for the two "off-diagonal" effective densities $\bar{\rho}_{\mathrm{HS}}^{(\alpha)\mathrm{el}}(\mathbf{r})$ and $\bar{\rho}_{\mathrm{el}}^{(\alpha)\mathrm{HS}}(\mathbf{r})$. Since $c_\alpha^{(1)\mathrm{HS}}(\mathbf{r};[\{\rho_\alpha\}])$ has a purely hard-sphere contribution, one might assume that the effective density $\bar{\rho}_{\mathrm{HS}}^{(\alpha)}$ with which $\tilde{c}_\alpha^{(1)\mathrm{HS}}(\bar{\rho})$ is evaluated should not have a contribution from w^{el}. This corresponds to the choice

$$\bar{\rho}_{\mathrm{HS}}^{(\alpha)\mathrm{el}}(\mathbf{r}) = 0 , \tag{22a}$$

which yields $\bar{\rho}_{\mathrm{HS}}^{(\alpha)}(\mathbf{r}) = \bar{\rho}_{\mathrm{HS}}^{(\beta)}(\mathbf{r})$ and consequently $c_\alpha^{(1)\mathrm{HS}}(\mathbf{r};[\{\rho_\alpha\}]) = c_\beta^{(1)\mathrm{HS}}(\mathbf{r};[\{\rho_\beta\}])$. Also, for calculating $\bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r})$ using Eq. (18b), one can assume that w_{HS} should be evaluated with an effective density which does not have an explicit contribution from the electrical part; i.e., one assumes

$$\bar{\rho}_{\mathrm{el}}^{(\alpha)\mathrm{HS}}(\mathbf{r}) = \bar{\rho}_{\mathrm{HS}}^{(\alpha)}(\mathbf{r}) . \tag{22b}$$

This prescription, which employs Eqs. (22a) and (22b) for the two "off-diagonal" effective densities, is denoted here as scheme A.

In an alternative scheme (scheme B), we use Eq. (22a) for $\bar{\rho}_{\mathrm{HS}}^{(\alpha)\mathrm{el}}(\mathbf{r})$, but $\bar{\rho}_{\mathrm{el}}^{(\alpha)\mathrm{HS}}(\mathbf{r})$ is assumed to be given by Eq. (22c), i.e.,

$$\bar{\rho}_{\mathrm{el}}^{(\alpha)\mathrm{HS}}(\mathbf{r}) = \bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r}) . \tag{22c}$$

In yet another scheme (scheme C), we assume Eq. (22c) for $\bar{\rho}_{\mathrm{el}}^{(\alpha)\mathrm{HS}}(\mathbf{r})$, but $\bar{\rho}_{\mathrm{HS}}^{(\alpha)\mathrm{el}}(\mathbf{r})$ also is assumed to be given by the same quantity, i.e.,

$$\bar{\rho}_{\mathrm{HS}}^{(\alpha)\mathrm{el}}(\mathbf{r}) = \bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r}) . \tag{22d}$$

While schemes A, B, and C are fully nonperturbative in nature, we propose another approach (scheme D) in the spirit of the recent work of Davis and co-workers [11] where the electrical part is evaluated perturbatively, i.e., one employs [instead of Eq. (17b)] the equation

$$c_\alpha^{(1)\mathrm{el}}(\mathbf{r};[\{\rho_\alpha\}]) = c_\alpha^{(1)\mathrm{el}}([\{\rho_\alpha^0\}]) + \int d\mathbf{r}' \tilde{c}_{\alpha\alpha}^{(2)\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\rho_0)[\rho_\alpha(z')-\rho_\alpha^0] + \int d\mathbf{r}' \tilde{c}_{\alpha\beta}^{(2)\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\rho_0)[\rho_\beta(z')-\rho_\beta^0] , \tag{23}$$

with $\rho_0=\rho_\alpha^0+\rho_\beta^0$, although the contribution $c_\alpha^{(1)\mathrm{HS}}(\mathbf{r};[\{\rho_\alpha\}])$ is calculated using Eq. (17a) with $\bar{\rho}_{\mathrm{HS}}^{(\alpha)}(\mathbf{r})$ of Eq. (18a) and Eq. (22a) of Scheme A. The difference of Scheme D with the work of Davis and co-workers [11] is that here we obtain the weight function using the approach of Ashcroft rather than that of Tarazona.

One now requires the expressions for the correlation functions $\tilde{c}^{(2)\mathrm{HS}}$ and $\tilde{c}^{(2)\mathrm{el}}$ for a uniform charged hard-sphere system, which has been solved within the mean spherical approximation (MSA) by Waisman and Lebowitz [18]. The expressions for the correlation functions in the region $|\mathbf{r}-\mathbf{r}'|<d$ are given by

$$\tilde{c}_{\alpha\beta}^{(2)\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\rho_0)=a_0+a_1(|\mathbf{r}-\mathbf{r}'|/d)+a_3(|\mathbf{r}-\mathbf{r}'|/d)^3\ , \tag{24}$$

with $a_0=(2a_3/\eta)=-(1+2\eta)^2/(1-\eta)^4$, $a_1=6\eta(1+\eta/2)^2/(1-\eta)^4$, $\eta=(\pi/6)\rho_0 d^3$, and

$$\tilde{c}_{\alpha\beta}^{(2)\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\rho_0)=-(\beta q_\alpha q_\beta/\epsilon)\times[(2B/d)-(B/d)^2|\mathbf{r}-\mathbf{r}'|-1/|\mathbf{r}-\mathbf{r}'|]\ , \tag{25}$$

where

$$B=[x+1-(1+2x)^{1/2}]/x$$

and

$$x=d\left[(4\pi\beta/\epsilon)\sum_\alpha \rho_\alpha q_\alpha^2\right]^{1/2} .$$

The quantities $\tilde{c}^{(2)\mathrm{HS}}(|\mathbf{r}-\mathbf{r}'|;\rho_0)$ and $\tilde{c}^{(2)\mathrm{el}}(|\mathbf{r}-\mathbf{r}'|;\rho_0)$ are zero for $|\mathbf{r}-\mathbf{r}'|>d$.

The corresponding expressions for $\tilde{c}_{\alpha\beta}^{(1)\mathrm{HS}}$ and $\tilde{c}_{\alpha\beta}^{(1)\mathrm{el}}$, obtained by functional integrations of Eqs. (24) and (25), respectively, are given by

$$\tilde{c}_{\alpha\beta}^{(1)\mathrm{HS}}=-\tfrac{1}{4}(14\eta-13\eta^2+5\eta^3)/(1-\eta)^3+\tfrac{1}{2}\ln(1-\eta)\ , \tag{26}$$

$$\tilde{c}_{\alpha\beta}^{(1)\mathrm{el}}=(q_\beta/q_\alpha)((x^2/12)+(2X/3)+\tfrac{1}{9}[(1+2x)^{3/2}-1]-2[(1+2x)^{1/2}-1]-\ln\{(2/x)[(1+2x)^{1/2}-1]/[(1+2x)^{1/2}+1]\})\ . \tag{27}$$

Equation (27) implies that $\tilde{c}_{\alpha\alpha}^{(1)\mathrm{el}}=\int d\mathbf{r}\int d\rho\,\tilde{c}_{\alpha\alpha}^{(2)}(r;\rho)=-\tilde{c}_{\alpha\beta}^{(1)\mathrm{el}}$ and consequently $\tilde{c}_\alpha^{(1)\mathrm{el}}$ evaluated as the sum $\tilde{c}_{\alpha\alpha}^{(1)\mathrm{el}}+\tilde{c}_{\alpha\beta}^{(1)\mathrm{el}}$ is nonzero only when the two components are evaluated at two different weighted densities $\bar{\rho}_{\mathrm{el}}^{(\alpha)}$ and $\bar{\rho}_{\mathrm{el}}^{(\beta)}$. Although this is the case in the present scheme for the inhomogeneous system, for a uniform ionic liquid, the quantity $\tilde{c}_\alpha^{(1)\mathrm{el}}$ (and also $F_{\mathrm{ex}}^{\mathrm{el}}$) when evaluated in this manner vanishes, implying that the chemical potential of each ionic species is only hard-sphere-like and therefore cannot predict the liquid-gas transition of the ionic solution. This rather unphysical consequence is, however, due to the approximation involved in the MSA result for $\tilde{c}_{\alpha\beta}^{(2)\mathrm{el}}$.

An alternative route to $F_{\mathrm{ex}}^{\mathrm{el}}$ through the energy equation, i.e. using the pair distribution function, can predict the nonzero contribution for the electric part for the uniform ionic fluid, viz.

$$F_{\mathrm{ex}}^{\mathrm{el}}=-(12\beta\pi d^3)^{-1}[3x^2+6x+2-2(1+2x)^{3/2}]\ . \tag{28}$$

One can obtain $\tilde{c}_\alpha^{(1)\mathrm{el}}$ using Eq. (28) in Eq. (4), but the same, however, will be inconsistent with Eq. (5) and $\tilde{c}_{\alpha\beta}^{(2)\mathrm{el}}$ of the MSA solution. Such inconsistencies arising from approximate theories are many and have been discussed in the literature [19].

Since in the proposed WDA the consistency between $\tilde{c}_\alpha^{(1)}$ and $\tilde{c}_{\alpha\beta}^{(2)}$ is a necessity, this additional contribution to $\tilde{c}_\alpha^{(1)\mathrm{el}}$ using Eqs. (4) and (28) cannot be evaluated using a weighted-density procedure. However, if one chooses to evaluate this term at the bulk density even for the inhomogeneous system, it will not contribute to the density distribution as obtained from Eq. (14) and hence this term can as well be dropped, as has been done here.

Equations (14) and (17)–(21) thus provide the prescription for the calculation of the density profile through the present WDA scheme. Since the density variation is only along the z direction, simplification can be achieved by rewriting Eq. (16) as

$$\bar{\rho}(z)=\int_0^\infty dz'\rho(z')\bar{w}(|z-z'|;\bar{\rho}(z))\ , \tag{29}$$

with the planar averaged weight function $\bar{w}(|z-z'|;\bar{\rho}(z))$ defined as

$$\bar{w}(|z-z'|;\bar{\rho}(z))=\int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dy'w(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(z))\ , \tag{30}$$

where the integrations can be performed analytically, leaving only a one-dimensional integral in Eq. (29) to be evaluated numerically. The integrals in the denominators of Eqs. (20) can also be evaluated analytically.

III. RESULTS AND DISCUSSION

The nonlinear integral equations [Eq. (14)] for density are solved numerically using iterative methods with modified Guoy-Chapman (MGC) density for the EDL as the initial density input for several values of the surface charge density σ and concentration for 1:1 and 2:2 electrolytes. A uniform mesh was used for discretization and a simple trapezoidal rule was used for numerical integrations. The results have been obtained for the three fully nonperturbative schemes A, B, and C of the proposed WDA as well as scheme D, which evaluates the electrical contribution through a perturbation expression. The convergence criterion has been chosen so that the norm defined as $(\sum_\alpha\sum_{i=1}^N\{[\rho_\alpha^{(n+1)}(z_i)-\rho_\alpha^{(n)}(z_i)]/\rho_\alpha^0\}^2/2N)^{1/2}$, with N as the number of mesh points, is a small number (e.g., $<10^{-5}$) after the nth iteration. The electroneutrality condition [Eq. (13)] was also satisfied up to the desired accuracy.

The parameter values used in our calculations are the same as those used for simulation [20] and also by Davis and co-workers [11] and are $T=298$ K, $d=4.25$ Å, and $\epsilon=78.5$. For convenience, dimensionless reduced quantities are used. Thus, the potential and the surface charge density are measured in units of $(\beta e)^{-1}$ and (e/d^2), respectively, where e is the magnitude of the electronic charge. Thus we define $\psi^*(z)=\beta e\psi(z)$ and $\sigma^*=\sigma d^2/e$. The distances are measured in terms of (z/d) and the reduced density of ions is defined as $\rho_\alpha^*(z)=\rho_\alpha(z)d^3$.

The density distributions for the ions and the mean electrostatic potentials calculated for the schemes A, B, C, and D are compared with the results from computer simulation [11,20] for concentrations $0.1M$, $1.0M$, and $2.0M$ for 1:1 and $0.5M$ for 2:2 electrolytes for different values of the surface charge densities ($\sigma^*=0.30$, 0.42, 0.55, 0.70, 0.396, and 0.1704). Of special importance in EDL theory is the diffuse layer potential (ψ_0), which is the value of the electrostatic potential at the closest approach to the charged surface, i.e., $\psi(d/2)$. Our calculated results on ψ_0 are compared in Table I with predictions from simulation, MGC theory and also the work of Davis and co-workers [11]. Although the predicted values are lower than the corresponding simulation results in most of the cases, results of scheme A show an overall good agreement. Scheme C also yields better values for this quantity in general, although there is an overprediction to some extent. Although the results are quite comparable or even better than many methods, the lack of very good agreement may be due to the fact that while approximating the electrical part of the correlation function of a nonuniform system by that of the corresponding uniform system, the same for a locally nonneutral system is being approximated by that of a locally neutral system. The results of scheme D, which is similar to the work of Davis and co-workers [11] (except for the use of the model of Ashcroft for the hard-sphere part instead of that of Tarazona), are observed to be lower than their results.

In Figs. 1 and 2 we plot, respectively, the density profiles of both the ions and the mean electrostatic potential in dimensionless forms for $c=0.1M$ and $\sigma^*=0.30$ for a 1:1 electrolyte. The results of schemes A, B, and C are indistinguishable and agree quite well with results of Monte Carlo (MC) simulation. Scheme D, however, shows some deviation.

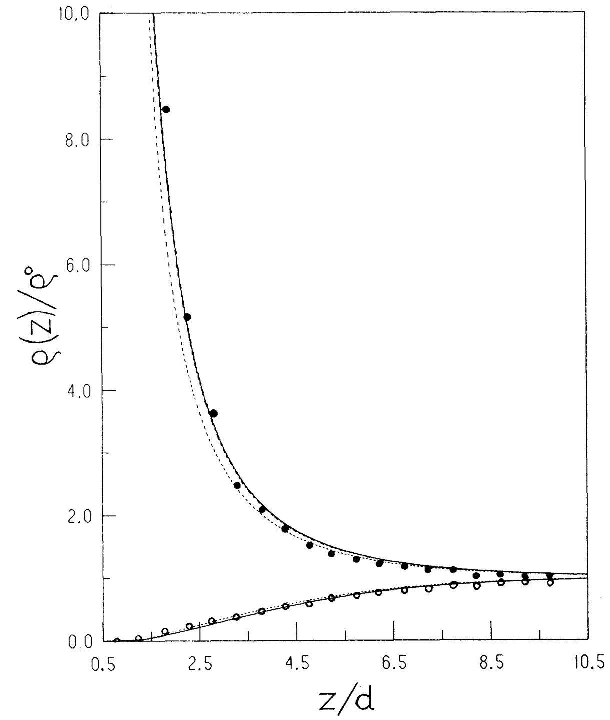

FIG. 1. Reduced ion density profiles for a 1:1 electrolyte at $c=0.1M$ and $\sigma^*=0.30$. The upper curves refer to counterions and the lower curves to co-ions. Calculated results are shown using scheme A (——), scheme B (– – – -), scheme C (—··—··—), and scheme D (— — —). Simulation results are shown as circles.

While at the low concentrations considered in Fig. 1 all the results show monotonic behavior, structure appears in the density profile at higher values of concentration and surface charge density. Thus, the plots of density in Figs. 3–5 corresponding to $c=1M$ and $\sigma^*=0.42$, 0.55, and 0.70, respectively, clearly reveal that with an increase in surface charge, a layering effect due to hard-sphere exclusion sets in and the structure at $z=3d/2$ is quite clear.

TABLE I. Diffuse layer potential $\psi_0^*=\psi^*(d/2)=\beta e\psi(d/2)$.

Conc.					Schemes from present work			
(M)	σ^*	MC[a]	MGC[b]	Tarazona[c]	A	B	C	D
				1:1 electrolyte				
0.1	0.30	4.63	5.34	4.54	4.81	4.78	4.85	4.44
1.0	0.42	3.08	3.74	2.88	3.03	2.94	3.22	2.79
1.0	0.55	4.15	4.26	3.61	3.76	3.58	4.26	3.39
1.0	0.70	5.71	4.74	4.79	4.79	4.50	5.92	4.30
2.0	0.396	2.29	2.99	1.88	1.89	1.80	2.08	1.79
				2:2 electrolyte				
0.5	0.1704	0.63	1.36	0.532	0.577	0.568	0.574	0.527

[a] Results from Monte Carlo simulation (Refs. [11] and [20]).

[b] Results from modified Gouy-Chapman theory.

[c] Results calculated by Davis and co-workers (Ref. [11]).

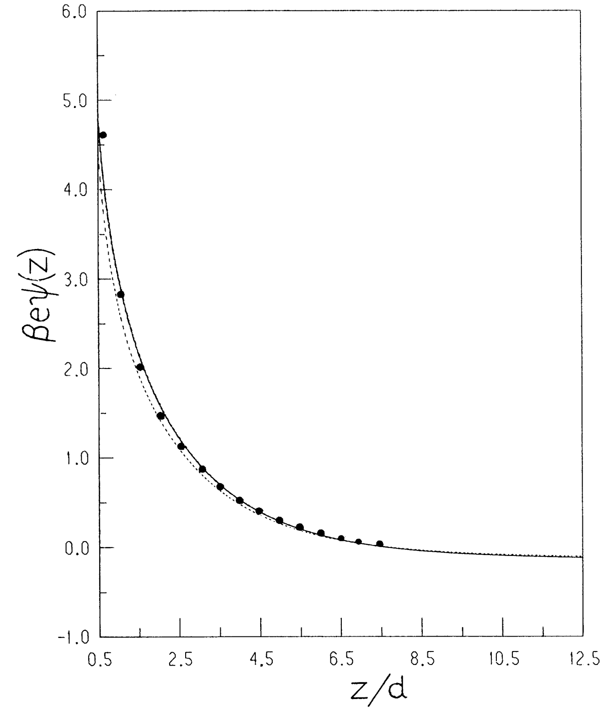

FIG. 2. Mean electrostatic potential in dimensionless form for a 1:1 electrolyte at $c=0.1M$ and $\sigma^*=0.30$. Calculated results are shown using scheme A (——), scheme B (—-—-), scheme C (—··—··—), and scheme D (— — —). Simulation results are shown as circles.

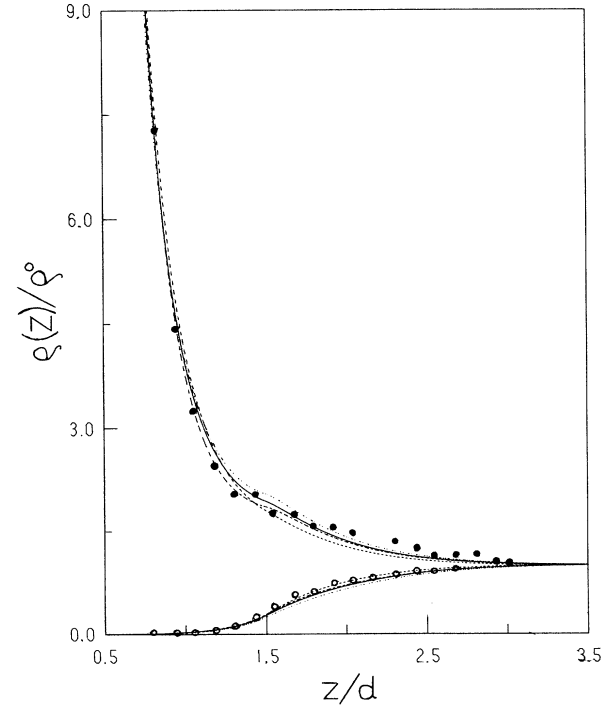

FIG. 3. Reduced ion density profiles for a 1:1 electrolyte at $c=1M$ and $\sigma^*=0.42$. The key is the same as in Fig. 1.

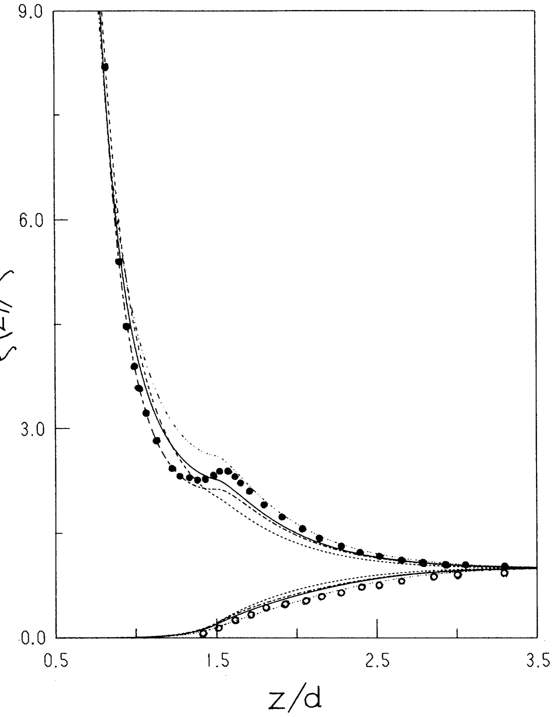

FIG. 4. Reduced ion density profiles for a 1:1 electrolyte at $c=1M$ and $\sigma^*=0.55$. The key is the same as in Fig. 1.

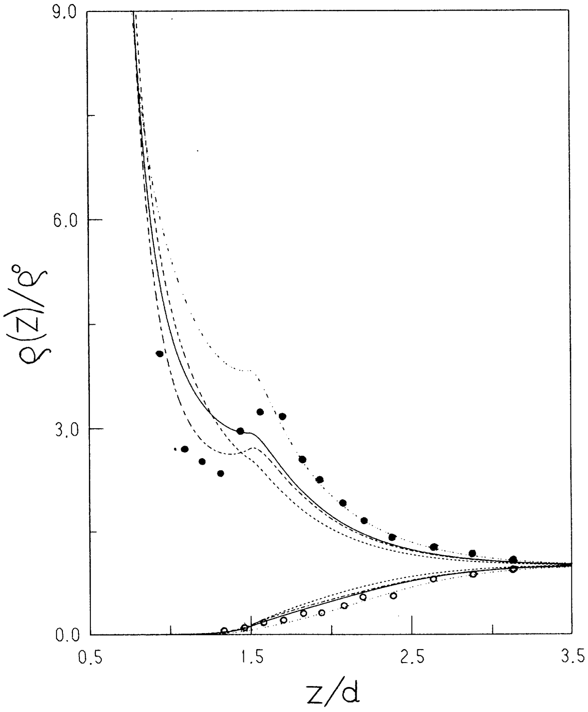

FIG. 5. Reduced ion density profiles for a 1:1 electrolyte at $c=1M$ and $\sigma^*=0.70$. The key is the same as in Fig. 1.

While results of scheme B agrees better with the MC results for $z<3d/2$, results of scheme C agrees better in the region $z>3d/2$. Scheme A, however, shows an overall good agreement on the average and the layering effect is most poorly reproduced by scheme D. For the potential plotted in Fig. 6 corresponding to $c=1M$ and $\sigma^*=0.70$ (the same as in Fig. 5), however, it is scheme C, the results for which agree better with the MC results.

At higher concentration ($c=2M$), the interesting case of charge inversion as well as oscillation in the potential profile is predicted by all the schemes, as seen, respectively, from plots of Figs. 7 and 8 for $\sigma^*=0.396$. The charge inversion is more prominent even at a moderate concentration ($c=0.5M$) in the case of a 2:2 electrolyte (see Fig. 9) due to stronger electrostatic interaction as compared to the case of a 1:1 electrolyte. The plots of density and potential profiles shown, respectively, in Figs. 9 and 10 for $\sigma^*=0.1704$ and $c=0.5M$ of a 2:2 electrolyte indicate that results of different schemes do not differ significantly for this case.

It is important to study whether the present WDA model satisfies the contact theorem for ionic fluids, viz.

$$\beta(p+2\pi\sigma^2/\epsilon)=\sum_{\alpha}\rho_\alpha(d/2)\ , \tag{31}$$

where p is the bulk equilibrium pressure and $\rho_\alpha(d/2)$ is the density at contact for the αth species. Since a direct

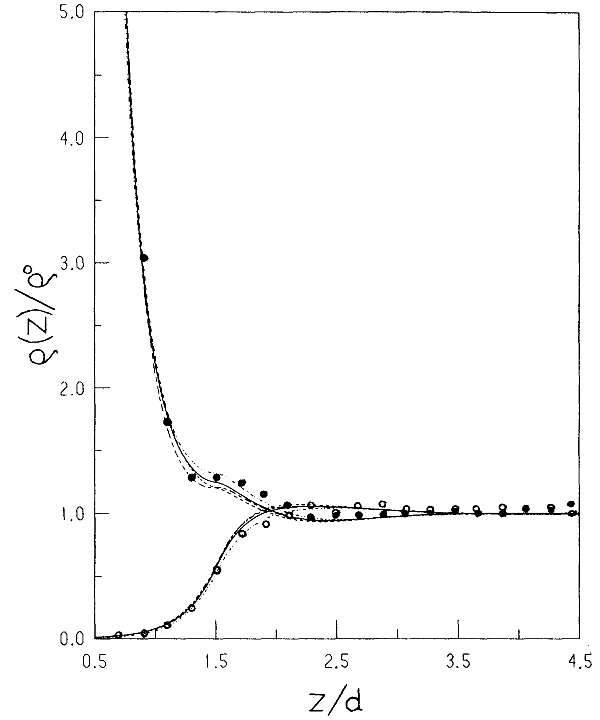

FIG. 7. Reduced ion density profiles for a 1:1 electrolyte at $c=2M$ and $\sigma^*=0.396$. The key is the same as in Fig. 1.

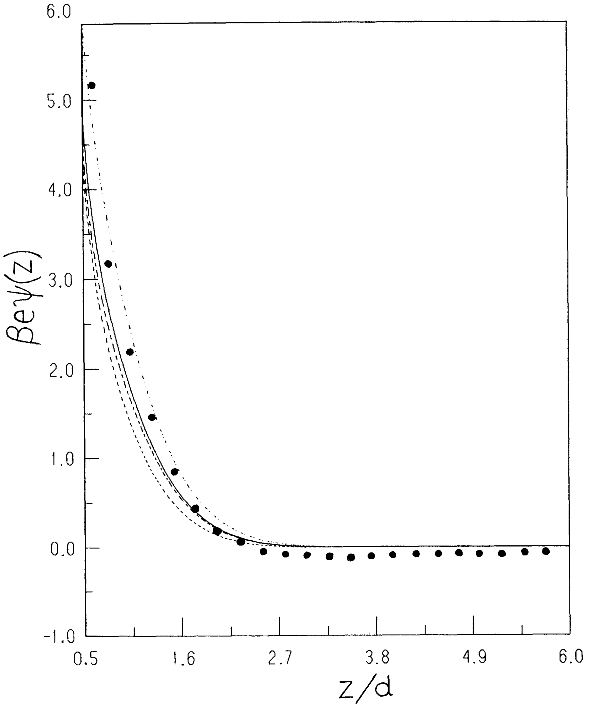

FIG. 6. Mean electrostatic potential in dimensionless form for a 1:1 electrolyte at $c=1M$ and $\sigma^*=0.70$. The key is the same as in Fig. 2.

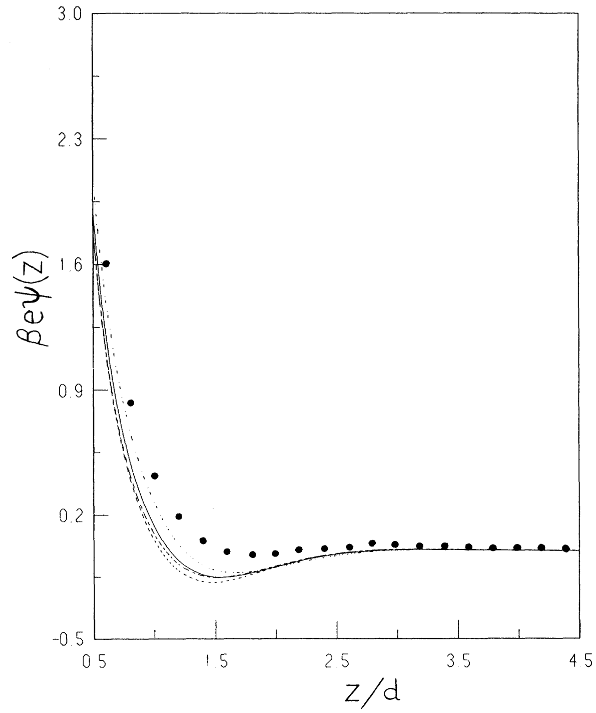

FIG. 8. Mean electrostatic potential in dimensionless form for a 1:1 electrolyte at $c=2M$ and $\sigma^*=0.396$. The key is the same as in Fig. 2.

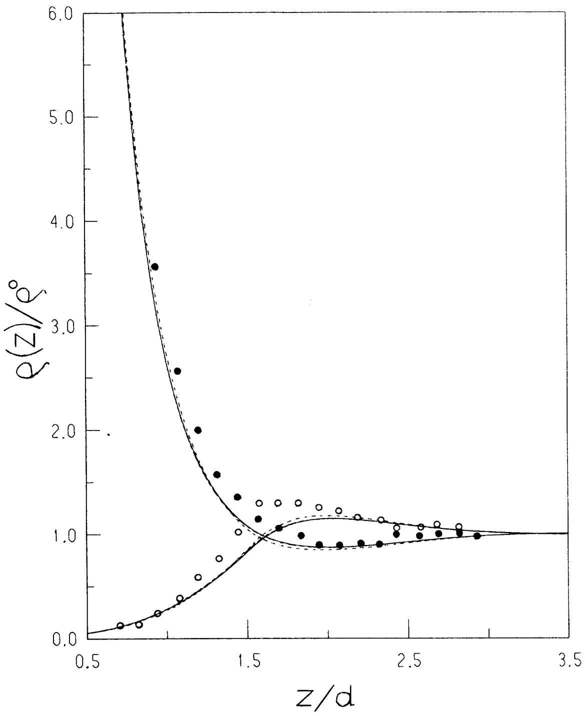

FIG. 9. Reduced ion density profiles for a 2:2 electrolyte at $c=0.5M$ and $\sigma^*=0.1704$. The key is the same as in Fig. 1.

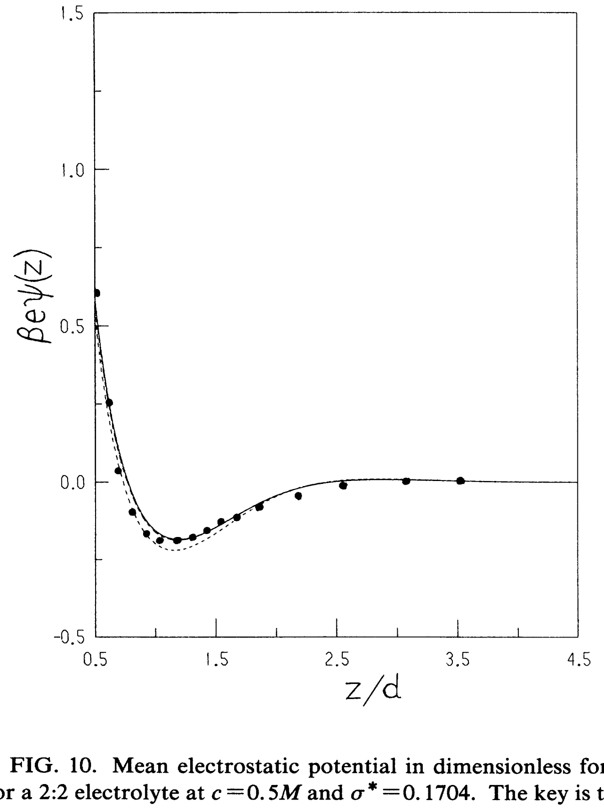

FIG. 10. Mean electrostatic potential in dimensionless form for a 2:2 electrolyte at $c=0.5M$ and $\sigma^*=0.1704$. The key is the same as in Fig. 2.

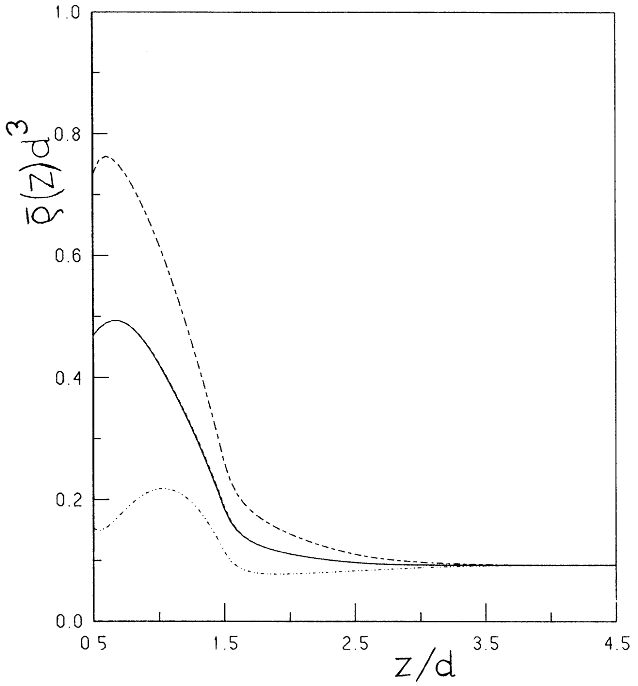

FIG. 11. Reduced weighted-density profiles for a 1:1 electrolyte at $c=1M$ and $\sigma^*=0.70$, calculated using scheme A. ——, $\bar{\rho}^{(\alpha)}_{\mathrm{HS}}(z)d^3$; —··—··—, $\bar{\rho}^{(\alpha)}_{\mathrm{el}}(z)d^3$ (co-ion); — — —, $\bar{\rho}^{(\beta)}_{\mathrm{el}}(z)d^3$ (counterion).

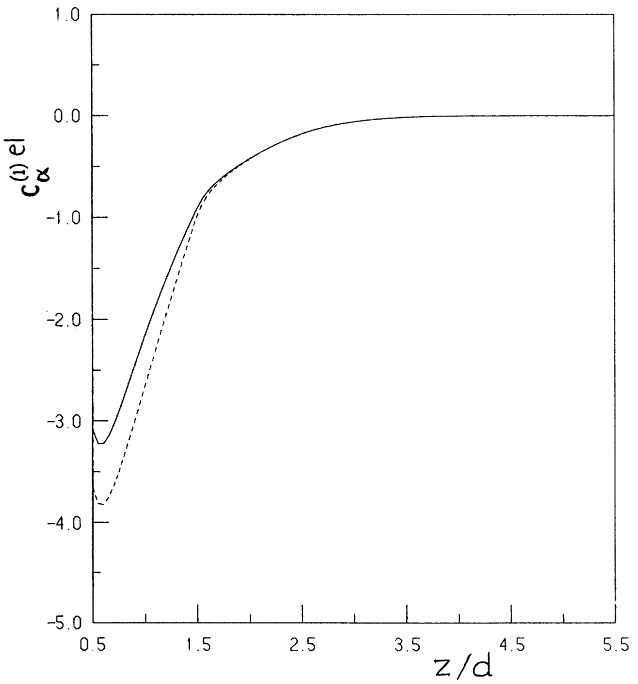

FIG. 12. Plot of the electrical contribution to the one-particle correlation function $[c_\alpha^{(1)\mathrm{el}}(z)]$. ——, weighted-density prescription of Eq. (17b) and self-consistent density of scheme A; — — —, calculated from perturbation expression of Eq. (23) but using the same density as above.

derivation of the contact theorem for the present WDA model has not yet been possible, we attempt here to verify whether our calculated densities satisfy Eq. (31). Thus, at $c=0.1M$ and $\sigma^*=0.30$, the quantity $[\sum_\alpha \rho_\alpha(d/2)/\sum_\alpha \rho_\alpha^0]$ as predicted by Eq. (31) is 103.7, whereas the same calculated from the present WDA densities of Schemes A, B, C, and D are 104.9, 105.3, 104.6, and 104.5, respectively. The proposed WDA thus yields a density which satisfies the contact theorem to a rather good accuracy.

The main feature of the proposed WDA is the evaluation of the electrical contribution to the one-particle correlation function $c_\alpha^{(1)\mathrm{el}}(\mathbf{r})$ through the weighted densities $\bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r})$ and $\bar{\rho}_{\mathrm{el}}^{(\beta)}(\mathbf{r})$. The corresponding hard-sphere contribution $c_\alpha^{(1)\mathrm{HS}}(\mathbf{r})$ uses the weighted densities $\bar{\rho}_{\mathrm{HS}}^{(\alpha)}(\mathbf{r})$ and $\bar{\rho}_{\mathrm{HS}}^{(\beta)}(\mathbf{r})$ (which are identical in Schemes A and B). In order to obtain further insight, we have plotted in Fig. 11 these effective densities corresponding to the self-consistent solution of Scheme A. Although at large distance all of them approach the same limiting bulk density ($\rho_0^*=0.0925$ for $c=1M$), they vary drastically near the wall. The spatial variation of $\bar{\rho}_{\mathrm{HS}}^{(\alpha)}(r)$ is more in comparison to that of the corresponding quantity for neutral fluids [9]. The quantity $\bar{\rho}_{\mathrm{el}}^{(\beta)}(\mathbf{r})$ corresponding to the counterions is higher than that for co-ions, viz. $\bar{\rho}_{\mathrm{el}}^{(\alpha)}(\mathbf{r})$. This indicates that the effective locally uniform fluid is not locally neutral and provides a net nonvanishing contribution to $c_\alpha^{(1)\mathrm{el}}(\mathbf{r})$ through Eq. (17b). Since this quantity is of importance in the present work, we have plotted in Fig. 12 the quantity $c_\alpha^{(1)\mathrm{el}}(\mathbf{r})$ from the WDA of Scheme A and compared the same with that obtained by evaluating the perturbation expression of Eq. (23) using the same density of Scheme A. The latter seems to yield values of larger magnitude.

IV. CONCLUDING REMARKS

We have formulated a weighted-density approach to the density-functional theory of inhomogeneous ionic liquids. The WDA proposed recently by Curtin and Ashcroft [7] and Denton and Ashcroft [8,9] has led to effective schemes for the study of nonuniform neutral fluids. The present work is essentially a generalization and extension of the WDA to nonuniform ionic systems. Application to the case of charged hard spheres near a hard wall with nonzero surface charge, i.e., the restricted primitive model of the electric double layer, is discussed.

The results on the ionic density distribution as well as diffuse double-layer potential using the present WDA schemes show that the evaluation of the electrical contribution of a nonuniform and locally non-neutral solution using the correlation functions of a uniform and locally neutral electrolyte is a good approximation for low surface charges. At higher surface charges also, the appearance of the layering effect as well as charge inversion at higher concentration for a 1:1 electrolyte and at moderate concentration for a 2:2 electrolyte indicates the success of the model. Among the three different fully nonperturbative schemes A, B, and C proposed here, scheme A is perhaps more suitable and provides results in better overall agreement with simulation data for both density distribution and potential characteristics. While the present study has been restricted to the RPM of the EDL, further generalizations and application to more elaborate models are of interest and are currently under investigation.

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