

## Weighted-density-functional theory of electrode-electrolyte interface: Beyond the primitive model

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A weighted-density-functional theory is developed for an inhomogeneous electrolyte solution near a planar charged electrode using a nonprimitive three-component model consisting of one neutral and two charged hard-sphere components representing the solvent and the ions, respectively. Both the hard-sphere and electrical contributions to the one-particle correlation function are obtained nonperturbatively by evaluating the direct-correlation functions of the corresponding uniform system using appropriate effective densities. Numerical results on the density profiles of the ions and the solvent molecules and also the mean electrostatic potential near the electrode surface at several surface-charge densities are presented to obtain insight into the layering and charge-inversion phenomena occurring at the interface.

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### I. INTRODUCTION

Density-functional theory (DFT) has been highly successful in predicting the equilibrium properties of nonuniform fluids [1–3]. Although most of the earlier studies have been concerned with neutral liquids [2,3], in recent years there has been growing interest in applying DFT to nonuniform ionic liquids [4–8].

An inhomogeneous ionic distribution arises in many electrochemical, colloidal, and biological phenomena. In an electrode-electrolyte solution interface, for example, the electric field produced by the surface charge leads to an inhomogeneous distribution of ions producing an electric double layer [9] (EDL). Theoretical studies of EDL are mostly based on models, the simplest one being the restricted primitive model (RPM), where the ions of the electrolyte are assumed to be charged hard spheres of equal diameter, and the solvent is treated as a continuum isotropic dielectric medium. The planar electrode surface is considered to be a polarizable and impenetrable hard wall carrying a uniform surface-charge density.

The EDL, however, is actually a three-component system [7], where the molecular nature of the solvent plays an important role in determining the distribution of the ions near the electrode surface and thus the structure of the EDL. Our objective here is to develop a density-functional theory of an inhomogeneous mixture of positive and negative ions (treated as charged hard spheres as in the RPM) and the solvent molecules (represented as neutral hard spheres) and thus obtain the structure of EDL corresponding to a more realistic three-component model [7]. A consideration of the molecular nature of the solvent is crucial for explaining many experimental observations [10]. For example, the oscillation of the force between two surfaces immersed in an electrolyte solution with a change in the distance between them, has been attributed to the solvent structure [11] and cannot be ex-

plained using a continuum model of the solvent.

The central theme in a density-functional approach is that the grand potential for the system is expressible in terms of its single-particle density and attains a minimum value for the true equilibrium density distribution. Because of the lack of knowledge concerning the general functional form of the grand potential in terms of the density in general, approximations are, however, essential. In some cases the functional form is known for a uniform system and this knowledge often serves as a basis for constructing the functional for the corresponding nonuniform system, using a perturbative or nonperturbative approach.

The perturbative approach usually involves a second-order-functional Taylor expansion in density inhomogeneity and is suitable only for weakly inhomogeneous systems. In a nonperturbative procedure such as a weighted-density approach (WDA), the first-order correlation function (or other analogous quantity) for the nonuniform fluid is approximated locally by that of the corresponding uniform fluid of an effective density, obtained from a suitable weighted average of the actual inhomogeneous density distribution. In a recent work [8], we have generalized and extended the WDA approach of Curtin, Denton, and Ashcroft (CDA) [2,3,12] of neutral liquids to the case of ionic liquids and thus obtained the structure of EDL within the framework of RPM.

In the present work, we extend it further to a mixture of charged and neutral hard spheres and develop a fully nonperturbative-weighted-density approach to the DFT of a nonuniform electrolyte solution where the molecular nature of the solvent is explicitly introduced and apply it to study the structure of EDL corresponding to a nonprimitive model. Earlier works on DFT of EDL have mostly used a combination of WDA and the perturbative schemes. In recent works, Davis and co-workers [5,7] have evaluated the ionic part through second-order perturbation expansion around the bulk density although the

Tarazona [13] scheme of weighted averaging has been used to obtain the hard-sphere contribution to the correlation function. Kierlik and Rosinberg [6] have also considered second-order perturbation expansion around the bulk density for the electrical contribution but their nonlocal-weighted-density approach for the hard-sphere part employs interesting density-independent weight functions. Groot [4,14,15], however, determined an effective density for the ions considering both hard-sphere and ionic contributions, which is used as a zeroth-order density for carrying out a perturbation expansion. In what follows, we first develop the theory in Sec. II proposing the nonperturbative-weighted-density-functional schemes for density calculation and present the numerical results in Sec. III. We offer a few concluding remarks in Sec. IV.

## II. THEORY

We consider an electrolyte solution consisting of two ionic components and a neutral solvent, with an inhomogeneous density distribution due to the influence of an external potential arising from a planar charged electrode surface. The three species are considered to be hard spheres with the hard-sphere diameter, charge, and density distribution of the component  $\alpha$  denoted by  $d_\alpha$ ,  $q_\alpha$ , and  $\rho_\alpha(r)$ , respectively. In our notation  $\alpha=0$  refers to the solvent (i.e.,  $q_0=0$ ) while  $\alpha=1$  and 2 denote the positive and negative ions, respectively. For simplicity we consider only symmetric electrolytes, i.e.,  $q_1=-q_2$  and also assume that the ions have the same hard-sphere diameters, i.e.,  $d_1=d_2$ . The grand potential functional for this system at temperature  $T$  can be written as

$$\Omega[\{\rho_\alpha\}] = \frac{1}{\beta} \sum_\alpha \int d\mathbf{r} \rho_\alpha(\mathbf{r}) \{ \ln[\rho_\alpha(\mathbf{r}) \lambda_\alpha^3] - 1 \} + \frac{1}{2\epsilon} \sum_\alpha \sum_\beta q_\alpha q_\beta \int \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_\alpha(\mathbf{r}_1) \rho_\beta(\mathbf{r}_2) / |\mathbf{r}_1 - \mathbf{r}_2| + F_{\text{ex}}^{\text{HS}}[\{\rho_\alpha\}] + F_{\text{ex}}^{\text{el}}[\{\rho_\alpha\}] + \sum_\alpha \int d\mathbf{r} [u_\alpha(\mathbf{r}) - \mu_\alpha] \rho_\alpha(\mathbf{r}), \quad (1)$$

where  $\beta=(k_B T)^{-1}$ ,  $k_B$  being the Boltzmann constant, and  $\lambda_\alpha$ ,  $u_\alpha(r)$ , and  $\mu_\alpha$  represent, respectively, the de Broglie wavelength, external potential, and chemical potential corresponding to the  $\alpha$ th component and  $\epsilon$  is the dielectric constant of the medium.

The first term on the right-hand side (rhs) of Eq. (1) represents the ideal-gas contribution to the free energy. The excess free-energy contributions  $F_{\text{ex}}^{\text{HS}}[\{\rho_\alpha\}]$  and  $F_{\text{ex}}^{\text{el}}[\{\rho_\alpha\}]$  originate from solely mutual hard-sphere interactions and electrical contributions, respectively, the latter including the coupling of Coulombic and hard-sphere interactions, but excluding the direct Coulomb part included in the second term on the rhs of Eq. (1). The first- and second-order correlation functions defined as their functional derivatives, given by

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

$$c_{\alpha\beta}^{(2)\text{HS}}(\mathbf{r}_1, \mathbf{r}_2) = -\beta \frac{\delta^2 F_{\text{ex}}^{\text{HS}}[\{\rho_\alpha\}]}{\delta \rho_\alpha(\mathbf{r}_1) \delta \rho_\beta(\mathbf{r}_2)}, \quad (3)$$

and similar expressions for the electrical part, play important roles in the DFT of liquids.

For the planar electric double layer under consideration, the density variation is along the (perpendicular)  $z$  direction, and the external potential  $u_\alpha(z)$  consists [9] of Coulomb potential due to the surface-charge density  $\sigma$  and the hard-sphere potential  $u_\alpha^{\text{HS}}(z)$  where the latter is infinite for  $z < d_\alpha/2$  and zero otherwise.

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

$$\mu_\alpha = \frac{\delta \Omega[\{\rho_\alpha\}]}{\delta \rho_\alpha(\mathbf{r})}, \quad (4)$$

$$= (1/\beta) \ln[\rho_\alpha(\mathbf{r}) \lambda_\alpha^3] + u_\alpha^{\text{HS}}(z) + q_\alpha \psi(z) + (1/\beta) (c_\alpha^{(1)\text{HS}}(\mathbf{r}; [\{\rho_\alpha\}]) + c_\alpha^{(1)\text{el}}(\mathbf{r}; [\{\rho_\alpha\}])) ,$$

where  $\psi(z)$ , the mean electrostatic potential due to the external surface charge and the internal ionic distribution, satisfies the corresponding Poisson equation in one dimension and can be written as

$$\psi(z) = -(4\pi\sigma/\epsilon)z - (4\pi/\epsilon)z \int_0^z dz' \sum_\alpha q_\alpha \rho_\alpha(z') - (4\pi/\epsilon) \int_z^\infty dz' z' \sum_\alpha q_\alpha \rho_\alpha(z'), \quad (5)$$

which can be represented in other forms using the electroneutrality condition given by

$$\int_0^\infty dz' \sum_\alpha q_\alpha \rho_\alpha(z') + \sigma = 0. \quad (6)$$

Writing Eq. (4) for the bulk-phase density  $\rho_\alpha^0$  of component  $\alpha$  and combining with the same equation for  $\rho_\alpha(z)$ , one can write

$$\begin{aligned} \rho_\alpha(z) = & \rho_\alpha^0 \exp(-\beta q_\alpha \psi(\mathbf{r}) + c_\alpha^{(1)\text{HS}}(\mathbf{r}; [\{\rho_\alpha\}]) \\ & + c_\alpha^{(1)\text{el}}(\mathbf{r}; [\{\rho_\alpha\}]) \\ & - c_\alpha^{(1)\text{HS}}([\{\rho_\alpha^0\}]) - c_\alpha^{(1)\text{el}}([\{\rho_\alpha^0\}]) \end{aligned} \quad (7)$$

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

The density profiles of the ions as well as the solvent can be calculated using Eq. (7) once the correlation functions  $c_\alpha^{(1)\text{HS}}$  and  $c_\alpha^{(1)\text{el}}$  for a nonuniform density distribution is known. In the absence of exact expressions for these quantities, we propose an approximation scheme based on the knowledge of the same for a uniform mixture of charged and neutral hard spheres within the framework of WDA, according to which,  $c^{(1)}(\rho(\mathbf{r})) = \tilde{c}^{(1)}(\bar{\rho}(\mathbf{r}))$ , where  $\tilde{c}^{(1)}$ , the correlation function for the corresponding uniform system, is evaluated at an effective density  $\bar{\rho}$ , a weighted average of the actual nonuniform density of the system.

For a uniform mixture of charged and neutral hard spheres, analytical expressions are available for both  $\tilde{c}_{\alpha\beta}^{(2)\text{HS}}(\mathbf{r}_1, \mathbf{r}_2)$  and  $\tilde{c}_{\alpha\beta}^{(2)\text{el}}(\mathbf{r}_1, \mathbf{r}_2)$ , where the electrical part vanishes when either  $\alpha$  or  $\beta$  refers to the neutral component. The corresponding first-order quantities  $\tilde{c}_{\alpha\beta}^{(1)\text{HS}}(\mathbf{r}; [\{\rho_\alpha^0\}])$  and  $\tilde{c}_{\alpha\beta}^{(1)\text{el}}(\mathbf{r}; [\{\rho_\alpha^0\}])$  are obtained through functional integration of the second-order correlation functions  $\tilde{c}_{\alpha\beta}^{(2)\text{HS}}$  and  $\tilde{c}_{\alpha\beta}^{(2)\text{el}}$ . One thus have  $\tilde{c}_\alpha^{(1)} = \sum_\beta \tilde{c}_{\alpha\beta}^{(1)}$ , valid for hard-sphere as well as electrical contributions.

We propose to obtain both the first-order correlation functions  $c_\alpha^{(1)\text{HS}}$  and  $c_\alpha^{(1)\text{el}}$  in Eq. (7) for the nonuniform system by evaluating their homogeneous counterpart components at suitable effective densities, viz.,

$$\begin{aligned} c_\alpha^{(1)\text{HS}}(\mathbf{r}; [\{\rho_\alpha\}]) &= \tilde{c}_\alpha^{(1)\text{HS}}(\bar{\rho}_{\text{HS}}^{(\alpha)}(\mathbf{r})) \\ &= \sum_{\beta=0}^2 \tilde{c}_{\alpha\beta}^{(1)\text{HS}}(\bar{\rho}_{\text{HS}}^{(\alpha)}(\mathbf{r})), \end{aligned} \quad (8a)$$

$$c_\alpha^{(1)\text{el}}(\mathbf{r}; [\{\rho_\alpha\}]) = \sum_{\beta=1}^2 \tilde{c}_{\alpha\beta}^{(1)\text{el}}(\bar{\rho}_{\text{el}}^{(\beta)}(\mathbf{r})), \quad (8b)$$

for  $\alpha=0,1,2$ , where the effective densities  $\bar{\rho}_{\text{HS}}^{(\alpha)}(\mathbf{r})$  and  $\bar{\rho}_{\text{el}}^{(\alpha)}(\mathbf{r})$  are defined as the weighted averages

$$\bar{\rho}_{\text{HS}}^{(\alpha)}(\mathbf{r}) = \sum_{\beta=0}^2 \int d\mathbf{r}' \rho_\beta(\mathbf{r}') w_{\alpha\beta}^{\text{HS}}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}_{\text{HS}}^{(\alpha)}(\mathbf{r})) \quad (9a)$$

and

$$\begin{aligned} \bar{\rho}_{\text{el}}^{(\alpha)}(\mathbf{r}) &= \sum_{\beta=0}^2 \int d\mathbf{r}' \rho_\beta(\mathbf{r}') w_{\alpha\beta}^{\text{HS}}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}_{\text{HS}}^{(\alpha)\text{el}}(\mathbf{r})) \\ &+ \sum_{\beta=1}^2 \int d\mathbf{r}' \rho_\beta(\mathbf{r}') w_{\alpha\beta}^{\text{el}}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}_{\text{el}}^{(\alpha)}(\mathbf{r})), \end{aligned} \quad (9b)$$

where

$$\bar{\rho}_{\text{HS}}^{(\alpha)\text{el}}(\mathbf{r}) = \sum_{\beta=1}^2 \int d\mathbf{r}' \rho_\beta(\mathbf{r}') w_{\alpha\beta}^{\text{HS}}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}_{\text{HS}}^{(\alpha)\text{el}}(\mathbf{r})). \quad (9c)$$

The physical interpretations of the effective densities  $\bar{\rho}_{\text{HS}}^{(\alpha)}(\mathbf{r})$  and  $\bar{\rho}_{\text{el}}^{(\alpha)}(\mathbf{r})$  are simple. Thus, the contribution to the hard-sphere part of the one-particle correlation function (corresponding to the  $\alpha$  component) of a nonuniform fluid is assumed to be given by that of a corresponding uniform fluid of effective total density  $\bar{\rho}_{\text{HS}}^{(\alpha)}(\mathbf{r})$ . Similarly,  $\bar{\rho}_{\text{el}}^{(\alpha)}(\mathbf{r})$  is the effective total density of a locally uniform and locally neutral fluid such that the electrical part of the one-particle correlation function  $c_\beta^{(1)\text{el}}$ , arising from correlation with particles of the  $\alpha$ th component, is the same as that of the actual nonuniform and locally non-neutral fluid. The correspondence to uniform fluids is done at every point separately and hence the weighted densities are clearly position dependent. It may be noted that as implied by Eq. (8a), the contributions to the hard-sphere correlation function  $c_\alpha^{(1)\text{HS}}$  is obtained by summing all three components  $\tilde{c}_{\alpha\beta}^{(1)\text{HS}}$  for  $\beta=0,1,2$  evaluated at the same effective density  $\bar{\rho}_{\text{HS}}^{(\alpha)}(\mathbf{r})$ . For the electrical part,  $c_\alpha^{(1)\text{el}}$ , however, for a nonuniform density which is locally non-neutral (which is the case when the external potential acting on the positive and negative ions differ), the two components  $\tilde{c}_{\alpha\beta}^{(1)\text{el}}$  for  $\beta=1,2$  are evaluated at two different effective densities  $\bar{\rho}_{\text{el}}^{(1)}(\mathbf{r})$  and  $\bar{\rho}_{\text{el}}^{(2)}(\mathbf{r})$ , respectively [see Eq. (8b)]. This clearly leads to a nonzero contribution to the quantity  $c_\alpha^{(1)\text{el}}$  through WDA of Eq. (8b).

We now derive explicit expressions for the weight functions in the spirit of the CDA approach, i.e., by demanding that the first functional derivatives of Eqs. (8) with respect to the densities  $\rho_\alpha$  or  $\rho_\beta$  in the limit of homogeneous density provide the exact appropriate two-particle correlation functions. The resulting expressions for the weight functions  $w_{\alpha\beta}^{\text{HS}}$  and  $w_{\alpha\beta}^{\text{el}}$  are given by

$$w_{\alpha\beta}^{\text{HS}}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}) = \frac{\tilde{c}_{\alpha\beta}^{(2)\text{HS}}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho})}{\frac{\partial}{\partial \bar{\rho}} [\tilde{c}_\alpha^{(1)\text{HS}}(\bar{\rho})]}, \quad (10a)$$

$$w_{\alpha\beta}^{\text{el}}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}) = \frac{\frac{1}{2} \tilde{c}_{\alpha\beta}^{(2)\text{el}}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho})}{\frac{\partial}{\partial \bar{\rho}} [\tilde{c}_{\alpha\alpha}^{(1)\text{el}}(\bar{\rho})]}. \quad (10b)$$

It is clear that  $w_{\alpha\beta}^{\text{HS}} = w_{\beta\alpha}^{\text{HS}}$  and  $w_{\alpha\beta}^{\text{HS}} = w_{\alpha'\beta'}^{\text{HS}}$  if  $d_\alpha = d_{\alpha'}$  and  $d_\beta = d_{\beta'}$ . Similarly,  $w_{\alpha\beta}^{\text{el}} = w_{\beta\alpha}^{\text{el}}$  and  $w_{\alpha\alpha}^{\text{el}} = w_{\beta\beta}^{\text{el}}$  for  $\alpha, \beta = 1, 2$ . Other components of  $w_{\alpha\beta}^{\text{el}}$  involving the solvent component ( $\alpha$  or  $\beta = 0$ ) vanish. Equation (10b) corresponds to  $w_{\alpha\alpha}^{\text{el}} = -w_{\alpha\beta}^{\text{el}}$ , and clearly indicates that weight functions  $w_{\alpha\beta}^{\text{el}}$  integrate to  $\frac{1}{2}$ , while  $w_{\alpha\beta}^{\text{HS}}$  integrates to unity. The expressions for the weighted density  $\bar{\rho}_{\text{el}}^{(\alpha)}$  can thus be rewritten as

$$\bar{\rho}_{\text{el}}^{(\alpha)}(\mathbf{r}) = \bar{\rho}_{\text{HS}}^{(\alpha)\text{el}}(\mathbf{r}) + \int d\mathbf{r}' w_{\alpha\alpha}^{\text{el}}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}_{\text{el}}^{(\alpha)}(\mathbf{r})) [\rho_{\alpha}(\mathbf{r}') - \rho_{\beta}(\mathbf{r}')] , \quad (11)$$

with a similar expression for  $\bar{\rho}_{\text{el}}^{(\beta)}$  obtained easily by interchanging  $\alpha$  and  $\beta$ , for  $\alpha, \beta = 1, 2$ .

Equations (7)–(10) thus provide a set of equations for calculating the density distribution. Apart from this fully non-perturbative approach, we propose another partially perturbative scheme in the spirit of the recent work of Davis and co-workers [5,7] where  $c_{\alpha}^{(1)\text{HS}}(\mathbf{r}; [\{\rho_{\alpha}\}])$  is calculated through WDA using Eq. (8a) with  $\bar{\rho}_{\text{HS}}^{(\alpha)}$  of Eq. (9a) but the electrical part (for  $\alpha = 1, 2$ ) is evaluated perturbatively, i.e., one employs [instead of Eq. (8b)] the equation

$$c_{\alpha}^{(1)\text{el}}(\mathbf{r}; [\{\rho_{\alpha}\}]) = \bar{c}_{\alpha}^{(1)\text{el}}([\{\rho_{\alpha}^0\}]) + \sum_{\beta=1}^2 \int d\mathbf{r}' \bar{c}_{\alpha\beta}^{(2)\text{el}}(|\mathbf{r}-\mathbf{r}'|; \{\rho_{\alpha}^0\}) [\rho_{\beta}(\mathbf{r}') - \rho_{\beta}^0] . \quad (12)$$

The present prescription differs from that of Tang *et al.* [5] in that the weight function here corresponds to the CDA approach, rather than the Tarazona approaches [13] used by them.

The analytical expressions for the correlation functions  $\bar{c}_{\alpha\beta}^{(2)\text{HS}}$  and  $\bar{c}_{\alpha\beta}^{(2)\text{el}}$  for a uniform mixture of charged and neutral hard spheres are obtainable from the works of Lebowitz [16] and Ashcroft and Langreth [17]. The main expressions are

$$\bar{c}_{\alpha\alpha}^{(2)\text{HS}}(|\mathbf{r}-\mathbf{r}'|; \{\rho_{\alpha}^0\}) = a_{\alpha} + b_{\alpha} |\mathbf{r}-\mathbf{r}'| + d |\mathbf{r}-\mathbf{r}'|^3 , \quad (13)$$

for  $|\mathbf{r}-\mathbf{r}'| < d_{\alpha}$  and zero otherwise, while

$$\bar{c}_{\alpha\beta}^{(2)\text{HS}}(|\mathbf{r}-\mathbf{r}'|; \{\rho_{\alpha}^0\}) = a_{\gamma} + \Theta(R) [bR^2 + 4\lambda R^3 + dR^4] / |\mathbf{r}-\mathbf{r}'| , \quad (14)$$

for  $|\mathbf{r}-\mathbf{r}'| < d_{\alpha\beta}$  and zero otherwise. Here  $\Theta$  denotes the Heaviside step function,  $\lambda = |d_{\alpha} - d_{\beta}|/2$ ,  $R = |\mathbf{r}-\mathbf{r}'| - \lambda$ ,  $d_{\alpha\beta} = (d_{\alpha} + d_{\beta})/2$ , and the  $\gamma$  component refers to the component of smaller diameter. The exact expressions of the coefficients  $a_{\alpha}$ ,  $b_{\alpha}$ ,  $b$ , and  $d$  in terms of the bulk packing fraction, concentration ratio, and diameter ratio are given in the work of Ashcroft and Langreth [17]. Similarly, for the electrical part [18] (assuming  $d_1 = d_2$ ), one has

$$\bar{c}_{\alpha\beta}^{(2)\text{el}}(|\mathbf{r}-\mathbf{r}'|; \{\rho_{\alpha}^0\}) = -(\beta q_{\alpha} q_{\beta} / \epsilon) [(2B/d_{\alpha}) - (B/d_{\alpha})^2 |\mathbf{r}-\mathbf{r}'| - 1 / |\mathbf{r}-\mathbf{r}'|] , \quad (15)$$

for  $|\mathbf{r}-\mathbf{r}'| < d_{\alpha}$  and zero otherwise, where  $B = [x + 1 - (1 + 2x)^{1/2}] / x$ , and  $x = d_{\alpha} [(4\pi\beta/\epsilon) \sum_{\alpha} \rho_{\alpha} q_{\alpha}^2]^{1/2}$ . Equation (15) is valid for  $\alpha, \beta = 1, 2$  and for either  $\alpha$  or  $\beta = 0$ , one has  $\bar{c}_{\alpha\beta}^{(2)\text{el}} = 0$ .

Using these expressions for  $\bar{c}_{\alpha\beta}^{(2)}$ , on functional integration one obtains explicit expressions for  $\bar{c}_{\alpha\beta}^{(1)}$ . Also, since the density depends only on the  $z$  coordinate, one can calculate the effective densities as

$$\bar{\rho}(z) = \int_0^{\infty} dz' \rho(z') \bar{w}(|z-z'|; \bar{\rho}(z)) , \quad (16)$$

with the planar averaged weight functions  $\bar{w}_{\alpha\beta}(|z-z'|; \bar{\rho}(z))$  given by the simplified expressions

$$w_{\alpha\beta}^{\text{HS}}(z) = 2\pi [(a_{\gamma}/2)(d_{\alpha\beta}^2 - z^2) + (b/3)d_{\gamma}^3 + d\lambda d_{\gamma}^4 + (d/5)d_{\gamma}^5 + \Theta(z-\lambda) \{ (b/3)(z-\lambda)^3 + \lambda d(z-\lambda)^4 + (d/5)(z-\lambda)^5 \}] [4\pi(ma_{\gamma} + nb + pd)]^{-1} , \quad (17a)$$

for  $0 < z < d_{\alpha\beta}$  and zero otherwise. Similarly,

$$w_{\alpha\beta}^{\text{el}}(z) = 2\pi [(\beta q_{\alpha} q_{\beta} / \epsilon) \{ (d_{\alpha} - z) - (B/d_{\alpha})(d_{\alpha}^2 - z^2) + \frac{1}{3}(B/d_{\alpha})^2 (d_{\alpha}^3 - z^3) \}] \times (4\pi[(\beta q_{\alpha} q_{\beta} / \epsilon) \{ 1/2 - (B/3d_{\alpha}) + (B^2/4d_{\alpha}^2) \}])^{-1} , \quad (17b)$$

for  $0 < z < d_{\alpha}$  and zero otherwise. Here the quantities  $m$ ,  $n$ , and  $p$  are given by

$$m = \frac{1}{3}u^3 , \quad (18a)$$

$$n = \frac{1}{4}u^4 - \frac{2}{3}u^3v + \frac{1}{2}u^2v^2 - \frac{1}{12}v^4 , \quad (18b)$$

$$p = 4v \{ \frac{1}{5}u^5 - \frac{3}{4}u^4v + u^3v^2 - \frac{1}{2}u^2v^3 + \frac{1}{20}v^5 \} + \frac{1}{6}u^6 - \frac{4}{5}u^5v + \frac{3}{2}u^4v^2 - \frac{4}{3}u^3v^3 + \frac{1}{2}u^2v^4 - \frac{1}{30}v^6 , \quad (18c)$$

where  $u = \frac{1}{2}[(d_{\gamma}/d_{\alpha}) + 1]$  and  $v = \frac{1}{2}[(d_{\gamma}/d_{\alpha}) - 1]$ . With these expressions for  $\bar{c}_{\alpha\beta}^{(2)\text{HS}}$  and  $\bar{c}_{\alpha\beta}^{(2)\text{el}}$ , the present prescription thus provides a means to the calculation of the inhomogeneous density profiles of the ions as well as the solvent molecules in the electrode-electrolyte interface region.

### III. RESULTS AND DISCUSSION

We have employed iterative numerical methods to solve the nonlinear integral equations [Eq. (7)] to obtain the density profiles of the two ions and the solvent. We have used a simple discretization scheme with a uniform mesh and trapezoidal rule for numerical integration. The initial trial density for the ions was the modified Guoy-Chapman (MGC) density for the EDL while for the solvent the average bulk density has been used as the initial input. For convenience, various quantities are transformed to the corresponding dimensionless forms. Thus the distance ( $z^* = z/d_1$ ) is measured in units of the hard-sphere diameter, which is chosen here as  $d_0 = d_1 = d_2 = 4.25 \text{ \AA}$ . The density quantities are expressed as  $\rho_{\alpha}^* = (\rho_{\alpha} d_1^3)$ . The reduced surface-charge den-

sity  $\sigma^* = (\sigma d_1^2 / e)$  and the reduced electrostatic potential  $\psi^* = \beta e \psi(z)$ , where  $e$  is the magnitude of the electronic charge. The calculations are performed for a temperature of 298 K and  $\epsilon = 78.5$ . The convergence criterion chosen is that for  $N$  mesh points, the norm defined as  $[\sum_{\alpha} \sum_{i=1}^N ([\rho_{\alpha}^{(n+1)}(z_i) - \rho_{\alpha}^{(n)}(z_i)] / \rho_{\alpha}^0)^2 / 3N]^{1/2}$  is a small number (e.g.,  $< 10^{-5}$ ) after the  $n$ th iteration. The accuracy to which the electroneutrality condition is satisfied is also checked by evaluating the left-hand side (lhs) of Eq. (6).

The reduced bulk density for the solvent has been fixed at  $\rho_0^{0*} = 0.8$  and different concentrations for the ions (0.1M, 1M, and 2M for 1:1 and 0.5M for 2:2 electrolyte) have been chosen in order to study the effect of bulk concentration of the ions. The effect of the surface-charge density is also studied by carrying out the calculations at different values of  $\sigma^*$ . Since the results of computer simulation for this model electrolyte solution are not available, we have compared our calculated results with those obtained by the same scheme but by considering the solvent to be merely a continuous dielectric medium. The comparison of the results thus obtained for the molecular solvent model (MSM) and the continuum-solvent model (CSM) using the same method provides insight into how the exclusion of the ions is caused by the solvent molecules.

It is to be noted that throughout this work, the density plots correspond to the plots of  $[\rho_{\alpha}(z) / \rho_{\alpha}^0]$ , i.e., density relative to the bulk density of the corresponding component. The actual reduced densities can be obtained by multiplication with  $\rho_0^{0*} = 0.8$  for the solvent and  $\rho_{\alpha}^{0*} = 0.04624$  (for  $c = 1M$ ) for the ions ( $\alpha = 1, 2$ ).

We have plotted the density profiles of the two ions and the solvent in dimensionless forms  $[\rho_{\alpha}(z) / \rho_{\alpha}^0]$  for  $c = 0.1M$  of a 1:1 electrolyte and  $\sigma^* = 0.10$  and 0.60 in Figs. 1 and 2, respectively. The layering effect is very predominant, with density oscillations being damped at larger distance. At very low  $\sigma^*$  ( $= 0.10$ ), even co-ions are found at  $z^* = 0.5$ , but as  $\sigma^*$  increases, co-ions are almost completely excluded from the first layer. This is a direct consequence of the increase of electrostatic interaction. Another important effect is the increase in the density of the first minimum of the counterion density at  $z^* = 1.0$ . For CSM, there is an increase in counterion density near the surface as  $\sigma^*$  is increased, although only monotonic behavior is observed for the density.

As the concentration is increased, e.g., at  $c = 1M$ , the density plot of Fig. 3 for  $\sigma^* = 0.70$  clearly reveals that apart from the density oscillation which is a layering effect due to hard-sphere exclusion, another important effect of charge inversion sets in beyond the first two layers of the counterions and the solvent. The co-ions are almost completely excluded from the first layer at such higher values of  $\sigma^*$ . The tendency of merging of the first two layers of the counterion at higher values of  $\sigma^*$  however is not observed. In the CSM result, a weak structure in counterion density due to layering effect is observed at  $z^* = 1.5$ , but the charge inversion does not appear.

At a still higher concentration ( $c = 2M$  and  $\sigma^* = 0.39602$ ), charge inversion is observed (see Fig. 4) prior to the second layer itself. For the CSM result, a less

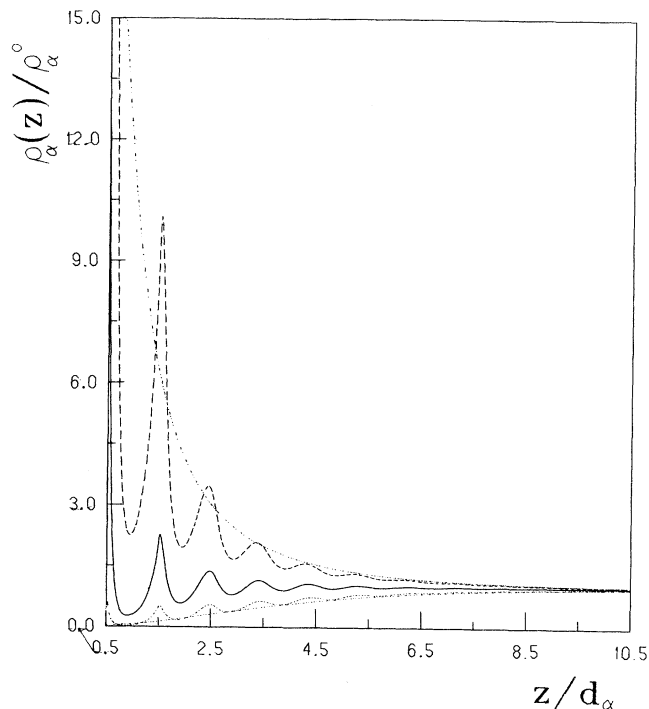


FIG. 1. Reduced density profiles for a 1:1 electrolyte at  $c = 0.1M$  and  $\sigma^* = 0.10$ . ---, counterion density using MSM; (- · - · -), co-ion density using MSM; (—), solvent density using MSM; (- · · · - · - · -), counterion (upper curve) and co-ion (lower curve) densities using CSM.

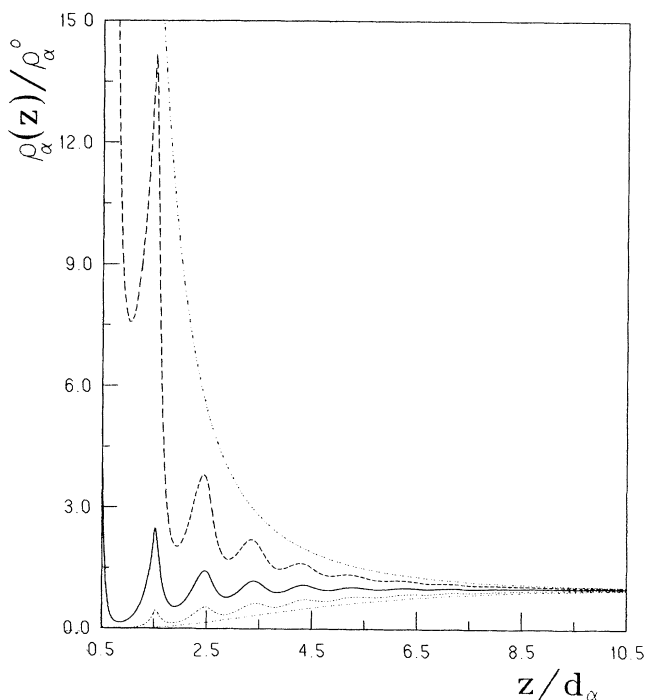


FIG. 2. Reduced density profiles for a 1:1 electrolyte at  $c = 0.1M$  and  $\sigma^* = 0.60$ . Key same as in Fig. 1.

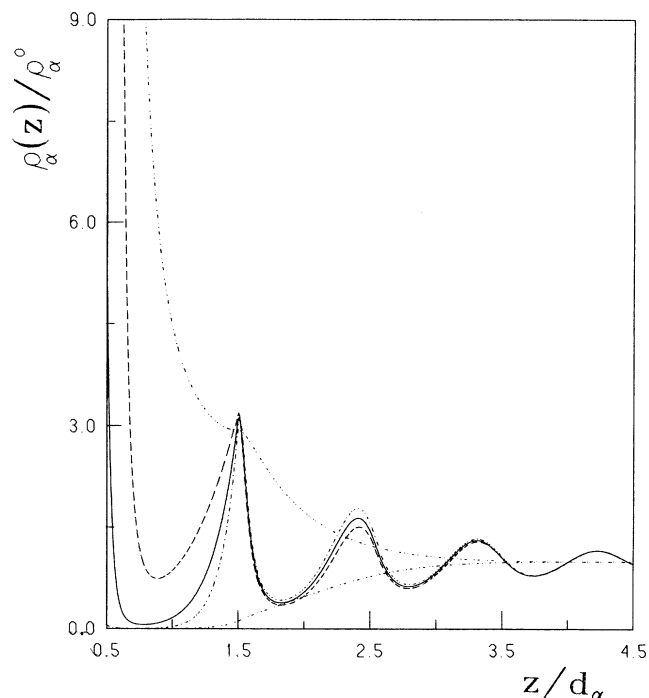


FIG. 3. Reduced density profiles for a 1:1 electrolyte at  $c = 1M$  and  $\sigma^* = 0.70$ . Key same as in Fig. 1.

pronounced charge inversion is observed beyond the second layer. For a 2:2 electrolyte, the charge inversion is prominent for both MSM and CSM results even at a moderate concentration ( $c = 0.5M$ ) (see Fig. 5 for  $\sigma^* = 0.1704$ ) due to stronger electrostatic interaction.

The layering effects are consequences of hard-sphere correlations leading to exclusions of ions or solvent mole-

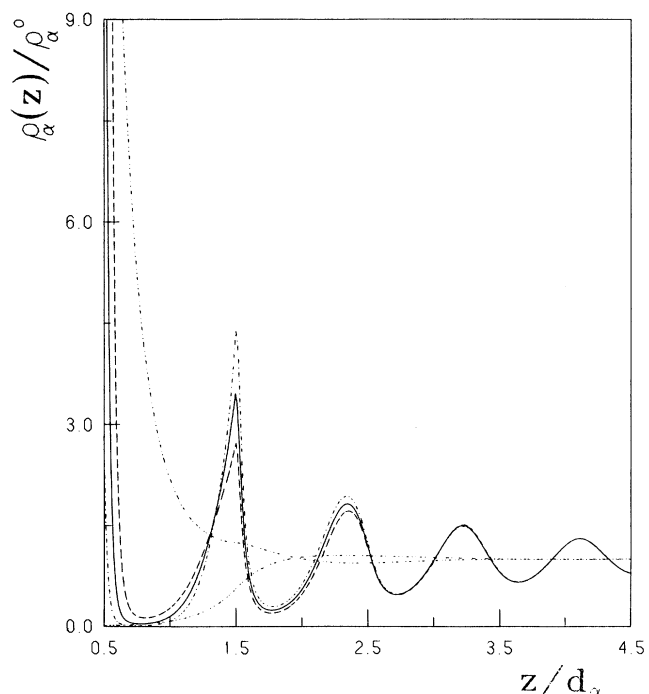


FIG. 4. Reduced density profiles for a 1:1 electrolyte at  $c = 2M$  and  $\sigma^* = 0.39602$ . Key same as in Fig. 1.

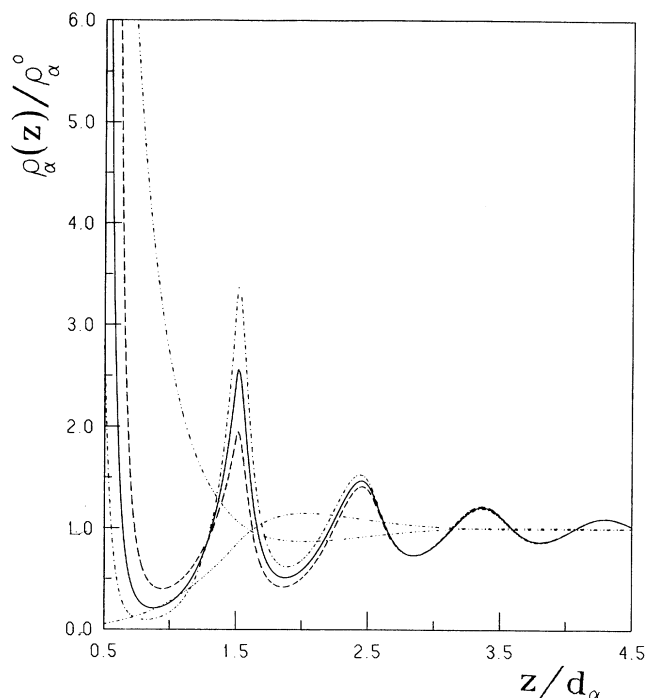


FIG. 5. Reduced density profiles for a 2:2 electrolyte at  $c = 0.5M$  and  $\sigma^* = 0.1704$ . Key same as in Fig. 1.

cules in different regions and thus appear through the  $c^{(1)HS}$  and  $c^{(1)el}$  terms. The charge inversion, however, is reflected in the mean electrostatic potential itself. Thus, plots of  $\psi^*(z)$  in Figs. 6–8 corresponding to the density plots of Figs. 2–4, respectively, show clearly inversion of  $\psi^*(z)$  in some region. Thus, although at low concentration ( $c = 0.1M$ ), the plot of  $\psi^*(z)$  in Fig. 6 is monotonic, at  $c = 1M$  (see Fig. 7),  $\psi^*(z)$  changes sign and passes through a minimum at negative value, and the depth has been found to increase with increase in  $\sigma^*$ . For  $c = 2M$  (1:1 electrolyte),  $\psi^*(z)$  is negative near the surface itself and becomes positive at larger distances (see Fig. 8). The same trend is observed for even  $c = 0.5M$  for a 2:2 electrolyte and the depth of the minima becomes greater as  $\sigma^*$  increases. In all the potential plots, comparison is made with the results of CSM, for which the potential inversion is predicted only at higher concentration ( $c = 2M$ ) for the 1:1 electrolyte (see Fig. 8) or moderate concentration ( $c = 0.5M$ ) for the 2:2 electrolyte while in other cases, the potential is monotonic.

While so far we have discussed results from the proposed (fully) nonperturbative scheme alone, we have also carried out calculations for the partially perturbative scheme where the electrical contribution is calculated using perturbation expression [Eq. (12) instead of Eq. (8b)]. These results for both MS and CSM are included in all the potential plots and the trends are qualitatively almost the same as those of the nonperturbative scheme, although differences in the potential-inversion phenomena are observed in a few cases. One result of density profiles using this perturbative scheme corresponding to the external parameters used for Fig. 3 is shown in Fig. 9.

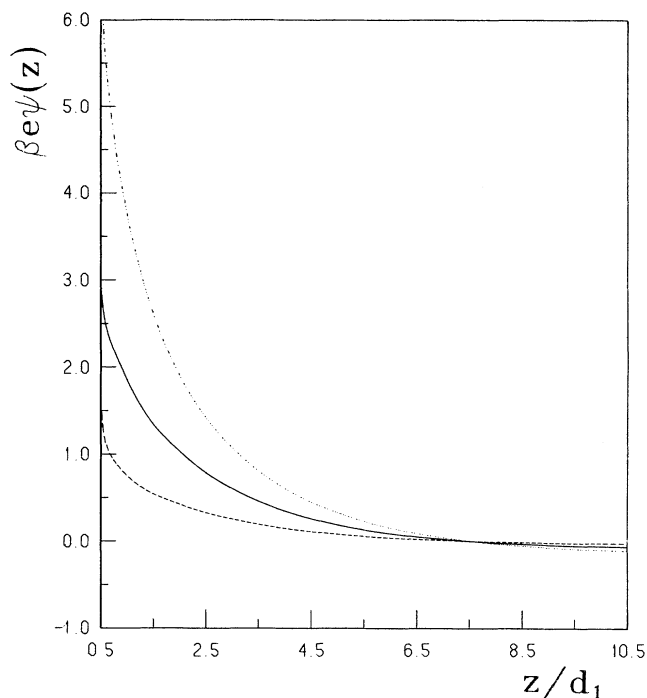


FIG. 6. Mean electrostatic potential in dimensionless form for a 1:1 electrolyte at  $c=0.1M$  and  $\sigma^*=0.60$ . (—), MSM result; (-·-·-·), CSM result; (- - -), MSM result (using perturbation scheme).

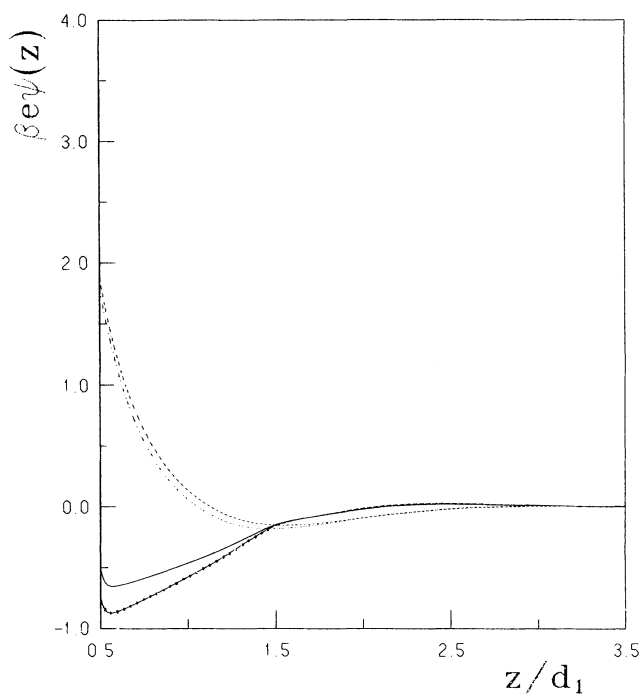


FIG. 8. Mean electrostatic potential in dimensionless form for a 1:1 electrolyte at  $c=2M$  and  $\sigma^*=0.39602$ . Key same as in Fig. 7.

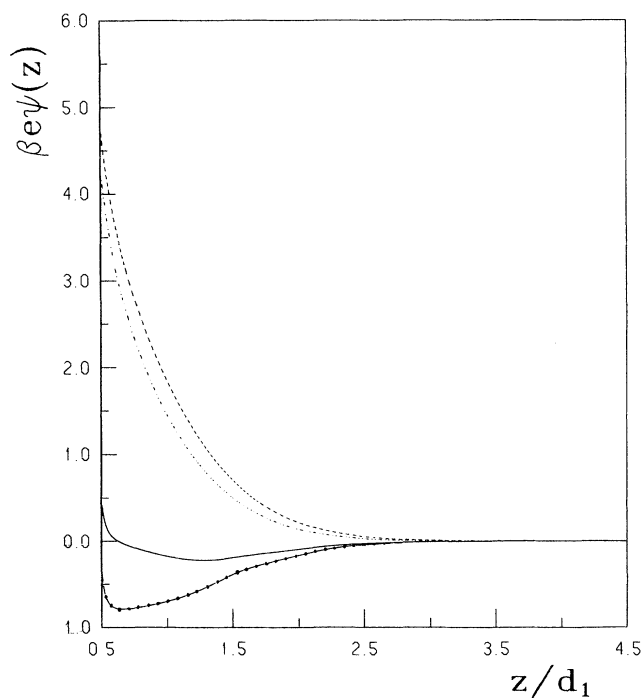


FIG. 7. Mean electrostatic potential in dimensionless form for a 1:1 electrolyte at  $c=1M$  and  $\sigma^*=0.70$ . (—), MSM result; (- - -), CSM result; (-·-·-·), MSM result (using perturbation scheme); (-·-·-·), CSM result (using perturbation scheme).

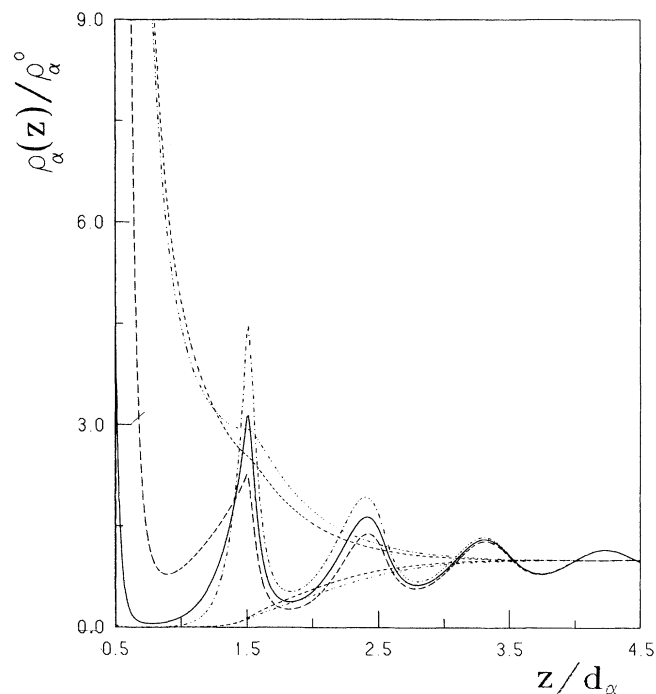


FIG. 9. Reduced density profiles for a 1:1 electrolyte at  $c=1M$  and  $\sigma^*=0.70$ . (- - -), counterion density using MSM and perturbation scheme; (-·-·-·), co-ion density using MSM and perturbation scheme; (—), solvent density using MSM and perturbation scheme; (- - -), counterion (upper curve) and co-ion (lower curve) densities using CSM and perturbation scheme; (-·-·-·), counterion (upper curve) and co-ion (lower curve) densities using CSM.

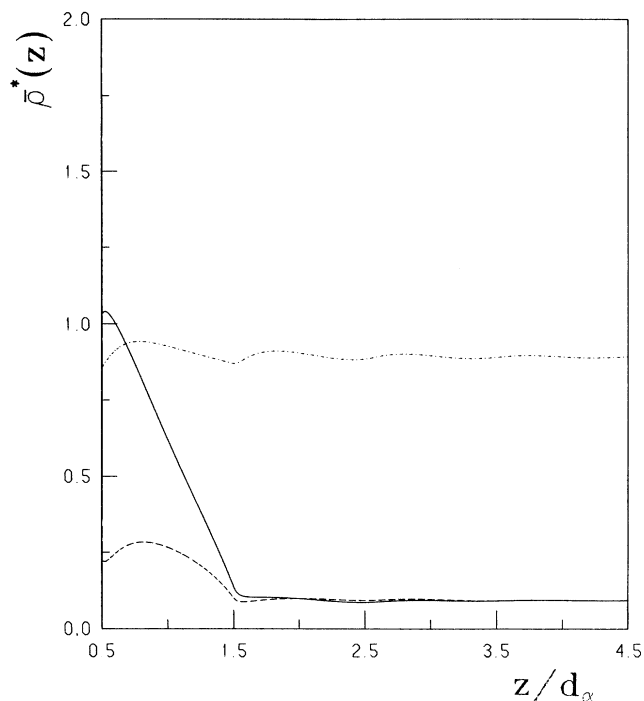


FIG. 10. Weighted reduced density profiles of MSM of a 1:1 electrolyte at  $c = 1M$  and  $\sigma^* = 0.70$ . (—),  $\bar{\rho}_{el}^{(\alpha)*}$  for counterions ( $\alpha=2$ ); (---),  $\bar{\rho}_{el}^{(\alpha)*}$  for co-ions ( $\alpha=1$ ); (-.-.-),  $\bar{\rho}_{hs}^{(\alpha)*}$  for  $\alpha=0, 1$ , or 2.

The densities obtained using this scheme for both CSM and MSM are shown here along with the CSM results of the fully nonperturbative scheme for comparison (note that these last CSM results are included in Figs. 1–5). The results are qualitatively similar although quantitative details differ. The MSM with perturbation scheme is in the spirit of the work of Tang, Scriven, and Davis [7] differing only in the hard-sphere weight functions which correspond to CDA here instead of Tarazona [5] as used by them.

Since the effective density  $\bar{\rho}$ , plays an important role in the present theory, we have plotted  $\bar{\rho}^*$  ( $=\bar{\rho}d_1^3$ ) profiles of MSM in Fig. 10 for  $\sigma^* = 0.70$  and  $c = 1M$  of a 1:1 electrolyte. It is to be noted that in these plots the effective densities are absolute and not relative to the corresponding bulk densities. The structures in the profiles of  $\bar{\rho}$  are

manifested in the oscillations of the calculated density profiles of the solvent and the ions.

It may be noted that the oscillating density profiles observed in the present three-component model have a direct consequence on the experimental observation of oscillation in the force between two surfaces separated by an electrolyte solution, as the distance between them is varied. The force between the two electrode surfaces can be expressed in terms of the contact density at the surface. With increase in separation the contact density shows the same oscillation as that in the midplane region due to hard-sphere exclusion by the solvent. Thus it is the oscillating density profile near the electrode surface as studied here using MSM, which is responsible for the oscillating force between the electrode surfaces observed experimentally [10].

#### IV. CONCLUDING REMARKS

We have developed in this work a fully nonperturbative-weighted-density approach to the density-functional theory of an inhomogeneous ionic solution, where the molecular nature of the solvent is taken into account explicitly. The present work is essentially a generalization and extension of our earlier work [8] on a nonuniform ionic system using a continuum model for the solvent. The present theory is applied to the electrode-electrolyte interface using a nonprimitive model of the electric double layer.

The present WDA evaluates the correlation-function components of a nonuniform and locally non-neutral electrolyte solution using the same components of a uniform and locally neutral electrolyte solution of suitable density. While computer-simulation results for the molecular solvent model are not available for comparison, the layering effect and charge inversion predicted by the present model when compared with the results of continuum-solvent model provide considerable insight into the exclusion and redistribution of the ions induced by the solvent molecules. Insight has also been obtained into the oscillations observed in the force between two surfaces placed in an electrolyte solution, in terms of the oscillatory density profiles of the present study incorporating the molecular nature of the solvent.

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