

Weighted-density-functional theory of solvation forces in liquids

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The weighted-density-functional theory developed by us recently [Phys. Rev. E **47**, 4088 (1993)] for inhomogeneous ionic fluids is employed to calculate the solvation forces between two planar charged surfaces with an electrolyte solution confined between them. The restricted primitive model corresponding to charged hard-sphere ions with continuum solvent as well as the molecular solvent model with charged and neutral hard spheres representing the ions and the solvent, respectively, are used to represent the constituents of the electric double layer formed near each of the two charged hard walls. The forces on the walls are evaluated from the density distributions of the ions (and the solvent) obtained from the proposed fully nonperturbative weighted density approach using position-dependent effective densities. Neutral liquids and their mixtures are also studied as special cases. The calculated solvation forces as well as the density distributions are shown to compare quite well with available computer simulation results. A rigorous first-principles calculation of the interaction energies between colloidal particles through this approach is thus shown to be possible.

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I. INTRODUCTION

The density functional theory (DFT) proposed formally by Hohenberg, Kohn, and Mermin [1] is a versatile and general approach for describing a many-particle system in terms of its single-particle density [2]. The theory has thus been a powerful tool for studying the equilibrium [3] and dynamical [4] properties of many-electron quantum systems as well as the structure [5] of nonuniform neutral and ionic classical fluids [6,7] arising, for example, in fluid-solid interfaces.

In DFT, single-particle density is the basic variable and the grand potential of an inhomogeneous many-particle system characterized by an external potential is a unique functional of the density distribution, assuming a minimum value at the true density. The exact form of this functional is, however, unknown for an arbitrary inhomogeneous density distribution. An important property of this unknown functional (other than the explicitly known potential-dependent part) is that it is universal and hence the knowledge of this functional for a density distribution corresponding to any suitable external potential should enable one to calculate the same for any other arbitrary density. Unfortunately, this knowledge is often restricted to some systems with uniform density and hence the expression will not be sufficiently general to be applicable directly to inhomogeneous densities. One can therefore adopt a perturbative approach involving a functional Taylor expansion with respect to the density inhomogeneity. Alternatively, one can demand that the system with an inhomogeneous density distribution can be locally mapped to a corresponding uniform system with a different position-dependent effective density, which in turn is determined from suitable weighted averages of the actual inhomogeneous density function. Among these so-called nonperturbative weighted density approaches (WDA), the two successful ones for neutral liquids are

due to Tarazona [8] and Denton and Ashcroft [9], who evaluate respectively the expressions for the excess free-energy density and the first-order correlation function of the uniform system using the effective density [10]. Very recently, we have extended and generalized the WDA of Denton and Ashcroft [9], formulated [11–13] a WDA for inhomogeneous ionic solutions, and also have applied the formalism to two models for the electric double layer (EDL) [14] in an electrode-electrolyte interface. In the restricted primitive model (RPM), the electrolyte consists of charged hard-sphere ions of equal size immersed in a continuum solvent, while in the three-component nonprimitive molecular solvent model (MSM), one considers the neutral hard spheres to represent the solvent, in addition to the charged hard-sphere ions. In both cases, the electrode is modeled as a uniformly charged infinite planar, polarizable, and impenetrable hard wall. While our theory [11–13] is fully nonperturbative, there have also been other approaches involving a partially perturbative procedure [15,16].

In the present work, we apply our theory to the case of an electrolyte solution confined between two such charged planar surfaces. This system of interacting double layers has been of much current interest since the forces between the two surfaces have been measured [17] experimentally and are found to oscillate [18] between attraction and repulsion as a function of the distance between the walls. This so-called solvation or structural force [18] observed for ionic as well as neutral liquids arises essentially from the tendency of formation of an integral number of layers in the confined space between the two surfaces. It has important consequences in determining the interaction between charged colloidal particles [19] in a suspension, for which the inadequacy of the conventional Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory [20] (especially at shorter distances) has been well known. The DLVO theory corresponds to a

continuum approximation and does not reflect these oscillations due to the molecular nature, although these are crucial for a proper theoretical understanding of various interfacial phenomena. A systematic improvement of the DLVO potential in an alternative direction has also been obtained [21] through systematic many-body corrections using a density-functional theory for the counterions, even with the point charge model. The oscillating solvation force has also been predicted by computer simulation for neutral liquids [22] as well as an RPM electrolyte [23], although simulation results are not yet available for the more realistic three-component MSM of an electrolyte solution. Integral equation theories [24] have also been used for the study of solvation forces, but they cannot be applied to more complicated systems, and simpler approaches are therefore needed. Since DFT is a versatile theory for studying an inhomogeneous density distribution, we propose to apply this theory to predict the solvation force between two planar surfaces in pure as well as a mixture of neutral liquids and also in an electrolyte solution using both RPM and MSM. The results can directly be used to obtain the forces between colloidal particles in a suspension, since planar surfaces are good approximations for two such large spheres. After developing in Sec. II the weighted density-functional theory for the calculation of the density distribution and the solvation forces in ionic (and also neutral as a special case)

systems, we present the numerical results in Sec. III, and concluding remarks in Sec. IV.

II. WEIGHTED DENSITY-FUNCTIONAL THEORY FOR IONIC AND NEUTRAL LIQUIDS

We consider an electrolyte solution consisting of two ionic and one neutral (solvent) components, modeled as charged and neutral hard spheres, respectively, confined between two infinite parallel planar uniformly charged hard walls of surface charge density σ . The quantities ρ_α^0 , d_α , and q_α are the bulk density, the hard-sphere diameter, and the ionic charge corresponding to the component α . Here, $\alpha=1$ and 2 are used to represent the positive and negative ions and $\alpha=0$ the solvent component. Clearly, $q_0=0$ and for symmetric electrolytes with identical hard-sphere diameters, which we consider here for simplicity, one has $q_1=-q_2$ and $d_1=d_2$. Assuming the two walls to be located at $z=0$ and $z=h$, respectively, the resulting external potential $u_\alpha(z)$ and the inhomogeneous density distribution $\rho_\alpha(z)$ of each component α in the confined region vary only along the perpendicular (z) direction.

Within the framework of DFT of an inhomogeneous liquid mixture, the grand potential Ω for this system at temperature T can be expressed [10] as the density functional given by

$$\begin{aligned} \Omega[\{\rho_\alpha\}] = & (k_B T) \sum_\alpha \int d\mathbf{r} \rho_\alpha(\mathbf{r}) \{ \ln[\rho_\alpha(\mathbf{r}) \lambda_\alpha^3] - 1 \} + (1/2\epsilon) \sum_\alpha \sum_\beta q_\alpha q_\beta \int \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_\alpha(\mathbf{r}_1) \rho_\beta(\mathbf{r}_2) / |\mathbf{r}_1 - \mathbf{r}_2| \\ & + F_{ex}^{hs}[\{\rho_\alpha\}] + F_{ex}^{el}[\{\rho_\alpha\}] + \sum_\alpha \int d\mathbf{r} [u_\alpha(\mathbf{r}) - \mu_\alpha] \rho_\alpha(\mathbf{r}) + 2\pi\sigma^2 h / \epsilon, \end{aligned} \quad (1)$$

and the pressure acting on each wall can be obtained from the definition

$$p(h) = - \left. \frac{\partial \Omega}{\partial h} \right|_{T, \{\mu_\alpha\}}. \quad (2)$$

Here, k_B is the Boltzmann constant, λ_α and μ_α represent, respectively, the de Broglie wavelength and chemical potential corresponding to the α th component, and ϵ is the dielectric constant of the medium. The last term in Eq. (1) represents the direct Coulomb interaction between the two charged surfaces, and the other energy components have their usual significance [11–13].

Minimizing the grand potential of Eq. (1) with respect to density and evaluating the chemical potential for the uniform bulk density, one obtains the expression for the equilibrium density distribution for species α in the region $d_\alpha/2 < z < h - d_\alpha/2$ between the two walls, given by

$$\begin{aligned} \rho_\alpha(z) = & \rho_\alpha^0 \exp \left[- \frac{q_\alpha \psi(z)}{k_B T} + c_\alpha^{(1)hs}(z; \{\rho_\alpha\}) - c_\alpha^{(1)hs}(\{\rho_\alpha^0\}) \right. \\ & \left. + c_\alpha^{(1)el}(z; \{\rho_\alpha\}) - c_\alpha^{(1)el}(\{\rho_\alpha^0\}) \right], \end{aligned} \quad (3)$$

where $\psi(z)$, the mean electrostatic potential arising from

the external surface charges and the internal ionic distributions, is given by

$$\psi(z) = (4\pi/\epsilon) \int_z^{h/2} dz' (z - z') \sum_\alpha q_\alpha \rho_\alpha(z') + \psi(h/2), \quad (4)$$

with the midplane potential $\psi(h/2)$ determined from the electroneutrality condition

$$\int_0^h dz' \sum_\alpha q_\alpha \rho_\alpha(z') + 2\sigma = 0. \quad (5)$$

The quantities $c_\alpha^{(1)hs}(\mathbf{r}_1)$ and $c_\alpha^{(1)el}(\mathbf{r}_1)$ in Eq. (3) represent, respectively, the hard-sphere and electrical contributions to the first-order correlation function defined as the functional derivatives

$$c_\alpha^{(1)}(\mathbf{r}_1) = -(k_B T)^{-1} \delta F_{ex}[\{\rho_\alpha\}] / \delta \rho_\alpha(\mathbf{r}_1). \quad (6)$$

The expression for pressure $p(h)$ at the surface due to the confined liquid, as given by Eq. (2), can now be evaluated using Eq. (1) for the grand potential and Eq. (3) for the density distribution in the region $d_\alpha/2 < z < h - d_\alpha/2$, to obtain

$$p(h) = (k_B T)^{-1} \sum_\alpha \rho_\alpha(d_\alpha/2; h) - 2\pi\sigma^2/\epsilon, \quad (7)$$

where $\rho_\alpha(d_\alpha/2; h)$ represents the contact density of

species α when the wall separation is h . One finally obtains the force per unit area between the two walls immersed in the liquid as the difference

$$f(h) = p(h) - p(\infty) \\ = (k_B T)^{-1} \left[\sum_{\alpha} \rho_{\alpha}(d_{\alpha}/2; h) - \sum_{\alpha} \rho_{\alpha}(d_{\alpha}/2; \infty) \right], \quad (8)$$

where $p_0 [= p(\infty)]$ represents the pressure of the coexisting bulk fluid, corresponding to an infinite separation between the walls. Equation (8) for $f(h)$ can easily be evaluated from the density distributions of the ionic and solvent components obtained from Eq. (3).

Exact explicit expressions for the density functionals for the first-order correlation functions $c_{\alpha}^{(1)hs}$ and $c_{\alpha}^{(1)el}$ in the density equation (3) are however not known for a nonuniform density distribution. We have recently proposed [11,12] an approximation scheme for evaluating them from the knowledge of the same for the corresponding system of uniform density. In this WDA, both the quantities $c_{\alpha}^{(1)hs}$ and $c_{\alpha}^{(1)el}$ for the nonuniform system are obtained from their homogeneous counterpart components evaluated at suitable effective densities, i.e.,

$$c_{\alpha}^{(1)hs}(\mathbf{r}; \{\rho_{\alpha}\}) = \bar{c}_{\alpha}^{(1)hs}[\bar{\rho}_{hs}^{(\alpha)}(\mathbf{r})] \\ = \sum_{\beta=0}^2 \bar{c}_{\alpha\beta}^{(1)hs}[\bar{\rho}_{hs}^{(\alpha)}(\mathbf{r})], \quad (9a)$$

$$c_{\alpha}^{(1)el}(\mathbf{r}; \{\rho_{\alpha}\}) = \sum_{\beta=1}^2 \bar{c}_{\alpha\beta}^{(1)el}[\bar{\rho}_{el}^{(\beta)}(\mathbf{r})], \quad (9b)$$

where the first-order correlation function components $\bar{c}_{\alpha\beta}^{(1)hs}$ and $\bar{c}_{\alpha\beta}^{(1)el}$ for a uniform system are obtained through functional integration of the corresponding second-order correlation functions $\bar{c}_{\alpha\beta}^{(2)hs}$ and $\bar{c}_{\alpha\beta}^{(2)el}$, and one has $\bar{c}_{\alpha}^{(1)} = \sum_{\beta} \bar{c}_{\alpha\beta}^{(1)}$. The effective densities $\bar{\rho}_{hs}^{(\alpha)}(\mathbf{r})$ and $\bar{\rho}_{el}^{(\alpha)}(\mathbf{r})$ are obtained from weighted averages of the actual nonuniform density distributions, viz.,

$$\bar{\rho}_{hs}^{(\alpha)}(\mathbf{r}) = \sum_{\beta=0}^2 \int d\mathbf{r}' \rho_{\beta}(\mathbf{r}') w_{\alpha\beta}^{hs}[|\mathbf{r}-\mathbf{r}'|; \bar{\rho}_{hs}^{(\alpha)}(\mathbf{r})] \quad (10a)$$

and

$$\bar{\rho}_{el}^{(\alpha)}(\mathbf{r}) = \bar{\rho}_{hs}^{(\alpha)el}(\mathbf{r}) \\ + \sum_{\beta=1}^2 \int d\mathbf{r}' \rho_{\beta}(\mathbf{r}') w_{\alpha\beta}^{el}[|\mathbf{r}-\mathbf{r}'|; \bar{\rho}_{el}^{(\alpha)}(\mathbf{r})], \quad (10b)$$

where

$$\bar{\rho}_{hs}^{(\alpha)el}(\mathbf{r}) = \sum_{\beta=1}^2 \int d\mathbf{r}' \rho_{\beta}(\mathbf{r}') w_{\alpha\beta}^{hs}[|\mathbf{r}-\mathbf{r}'|; \bar{\rho}_{hs}^{(\alpha)el}(\mathbf{r})]. \quad (10c)$$

The expressions for the weight functions $w_{\alpha\beta}^{hs}$ and $w_{\alpha\beta}^{el}$ have also been derived [12] and are given by

$$w_{\alpha\beta}^{hs}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}) = \bar{c}_{\alpha\beta}^{(2)hs}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}) / \{(\partial/\partial\bar{\rho})[\bar{c}_{\alpha}^{(1)hs}(\bar{\rho})]\}, \quad (11a)$$

$$w_{\alpha\beta}^{el}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}) = \frac{1}{2} \bar{c}_{\alpha\beta}^{(2)el}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}) / \{(\partial/\partial\bar{\rho})[\bar{c}_{\alpha}^{(1)el}(\bar{\rho})]\} \quad (11b)$$

for $\alpha, \beta=0, 1, 2$ and $\alpha, \beta=1, 2$, respectively. Other components of $w_{\alpha\beta}^{el}$ involving the solvent component (α or $\beta=0$) vanish.

For the uniform mixture of charged and neutral hard spheres (corresponding to the MSM) under consideration, analytical expressions for the correlation functions $\bar{c}_{\alpha\beta}^{(2)hs}$ and $\bar{c}_{\alpha\beta}^{(2)el}$ have been obtained by Ashcroft and Langreth [25] and Waisman and Lebowitz [26] and can be used to calculate the weight functions as well as the other quantities. The main expressions have been reported elsewhere [12]. As limiting cases, one can obtain the expressions for RPM electrolyte and also for neutral liquids and their mixtures.

Thus, using the equations for density, potential, correlation functions and weighted densities, one can easily calculate the inhomogeneous density distribution of the ions and the solvent molecules in the interfacial regions near the two walls. Using the calculated densities (values at contact) in Eq. (8), the solvation forces between two surfaces immersed in liquids can be obtained.

III. RESULTS AND DISCUSSION

We have solved the nonlinear integral equation (3) for density along with Eqs. (4) and (9)–(11), using discretization with a uniform mesh and iterative numerical procedures until convergence is reached. The trial densities used for the two ions and the solvent correspond to a superposition of the modified Guoy-Chapman densities [14] for the EDL at the two walls and the average bulk density, respectively. The midplane potential $\psi(h/2)$ in Eq. (4) is determined by requiring that the electroneutrality condition of Eq. (5) is satisfied in each iteration. The sol-

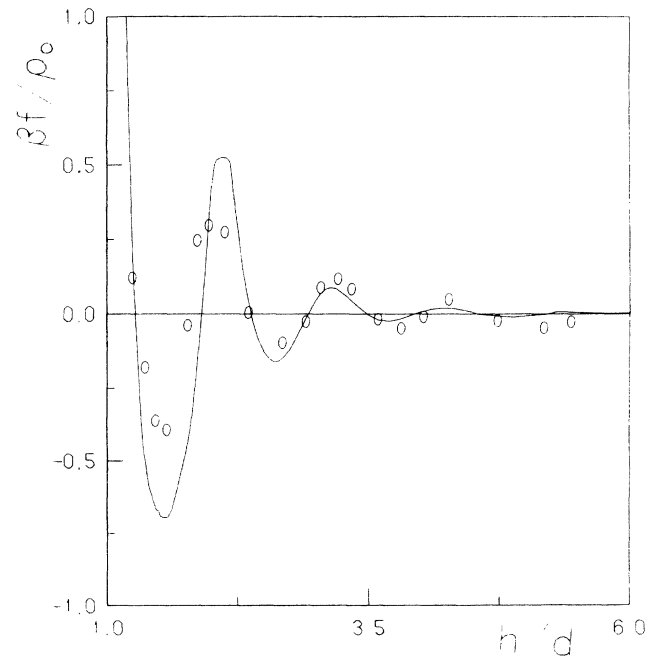


FIG. 1. Solvation force in a neutral liquid vs the wall separation ($\rho_0^* = 0.50$). Continuous curve, present calculation; circles, Monte Carlo simulation.

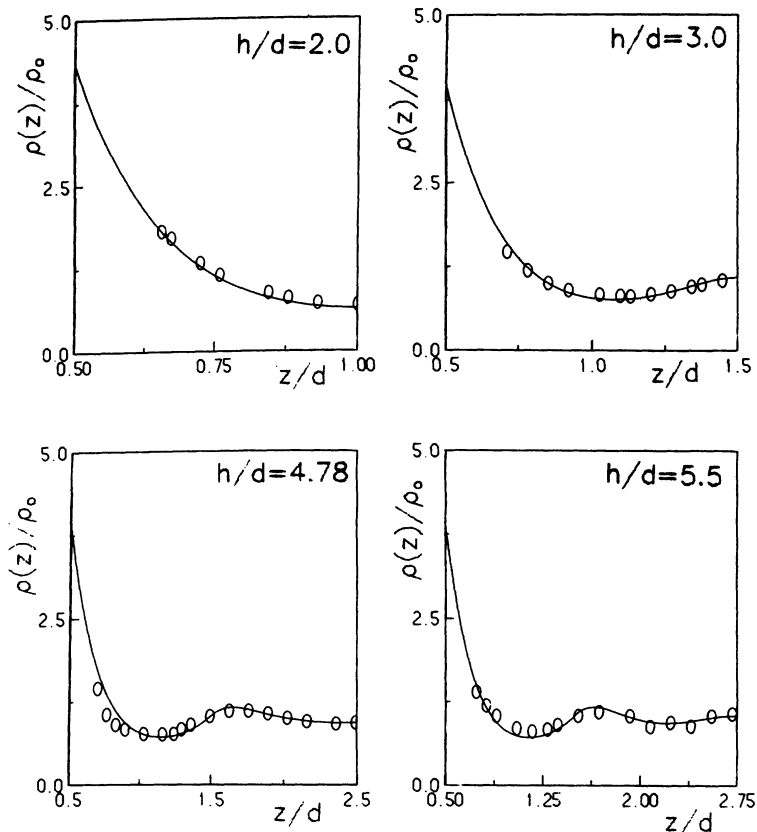


FIG. 2. Calculated density profiles for hard spheres at selected values of wall separation. Continuous curve, present calculation; circles, Monte Carlo simulation (system parameters same as in Fig. 1).

vation force is then obtained from Eq. (8), by substituting the calculated component contact densities $[\rho_\alpha(d_\alpha/2)]$ for finite (h) as well as infinite wall separations. The values of temperature and the dielectric constant used in the calculation are $T=298$ K and $\epsilon=78.5$ (corresponding to water). The dimensionless reduced quantities, viz., $z^*(=z/d_1)$ for distance, $\rho_\alpha^*(=\rho_\alpha d^3)$ for density, $\sigma^*(=\sigma d^2/e)$ for surface charge density, and $\psi^*(z)=\beta e \psi(z)$ for the potential are used as usual for convenience.

Although our main concern is the double layer force in ionic solutions, as special cases we have studied the simpler neutral liquids as well. Thus, we have considered four cases; viz., (i) a one-component neutral liquid ($d_0=d$; $\rho_1^0=\rho_2^0=0$, but $\rho_0^0=\rho_0$); (ii) a two-component neutral liquid mixture ($q_1=-q_2=0$; $d_1=d_2\neq d_0$; $\rho_1^0=\rho_2^0\neq 0$ and $\rho_0^0\neq 0$); (iii) a symmetric RPM electrolyte ($q_1=-q_2$; $d_1=d_2$; $\rho_1^0=\rho_2^0\neq 0$, but $\rho_0^0=0$); and (iv) a symmetric MSM electrolyte ($q_1=-q_2$; $d_1=d_2=d_0$; $\rho_1^0=\rho_2^0\neq 0$ and $\rho_0^0\neq 0$). In the neutral liquid mixture of case (ii), the components $\alpha=1$ and 2 (with $q_1=-q_2=0$) together are considered to represent one liquid and the component $\alpha=0$ is the other liquid. In case (iii), the solvent is a continuum dielectric and it is the density of solvent hard spheres, which is zero.

For the neutral liquid [case (i)], we have chosen the bulk density and the hard-sphere diameter as $\rho_0^*=0.50$ and $d=4.2$ Å. The density profile is calculated as a func-

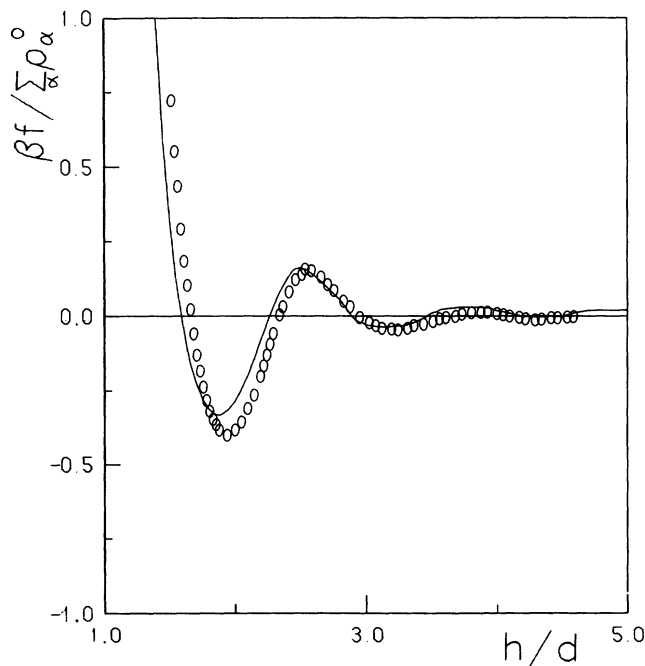


FIG. 3. Solvation force in a neutral liquid mixture vs the wall separation ($\rho_A^0=0.10$, $\rho_B^0=0.30$, $d_B/d_A=1.2$). Continuous curve, present calculation; circles, calculation by Grimson (Ref. [27]).

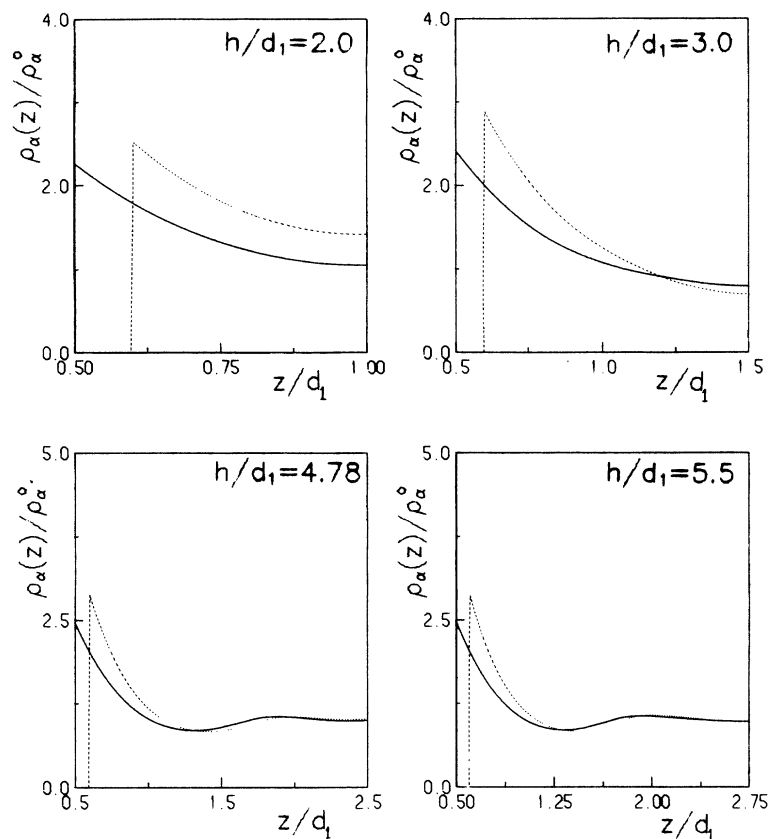


FIG. 4. Calculated density profiles for mixture of hard spheres at selected values of wall separation. —, component with smaller diameter; ---, component with larger diameter (system parameters same as in Fig. 3).

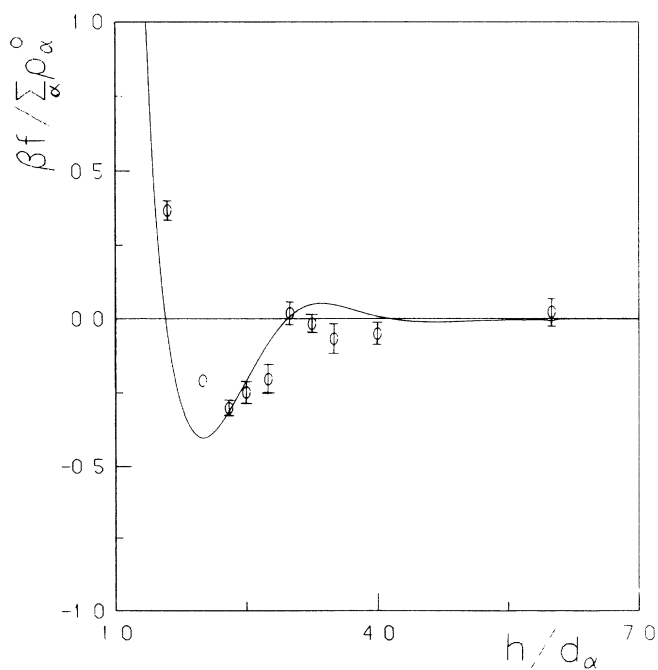


FIG. 5. The double layer force in a 2:2 RPM electrolyte vs the wall separation ($c = 0.971M$, $\sigma^* = 0.10$). Continuous curve, present calculation; circles, Monte Carlo simulation.

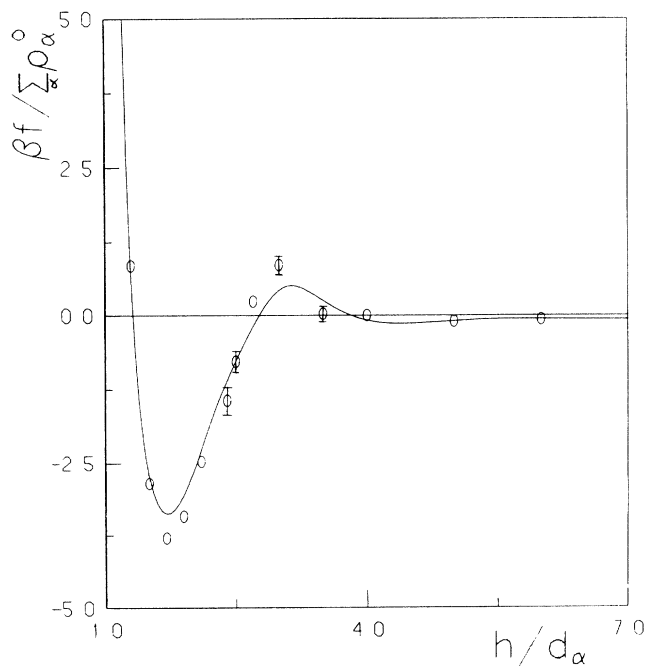


FIG. 6. The double layer force in a 2:2 RPM electrolyte vs the wall separation ($c = 0.971M$, $\sigma^* = 0.30$). Continuous curve, present calculation; circles, Monte Carlo simulation.

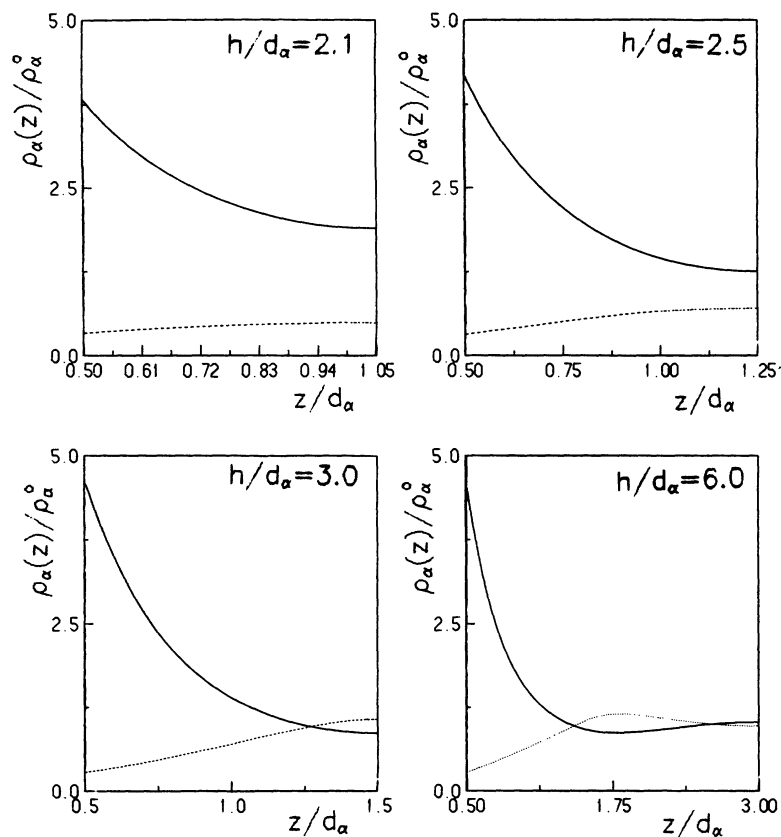


FIG. 7. Density profiles of the ions at selected values of wall separation. —, calculated results for counterions; ---, calculated results for co-ions (system parameters same as in Fig. 5).

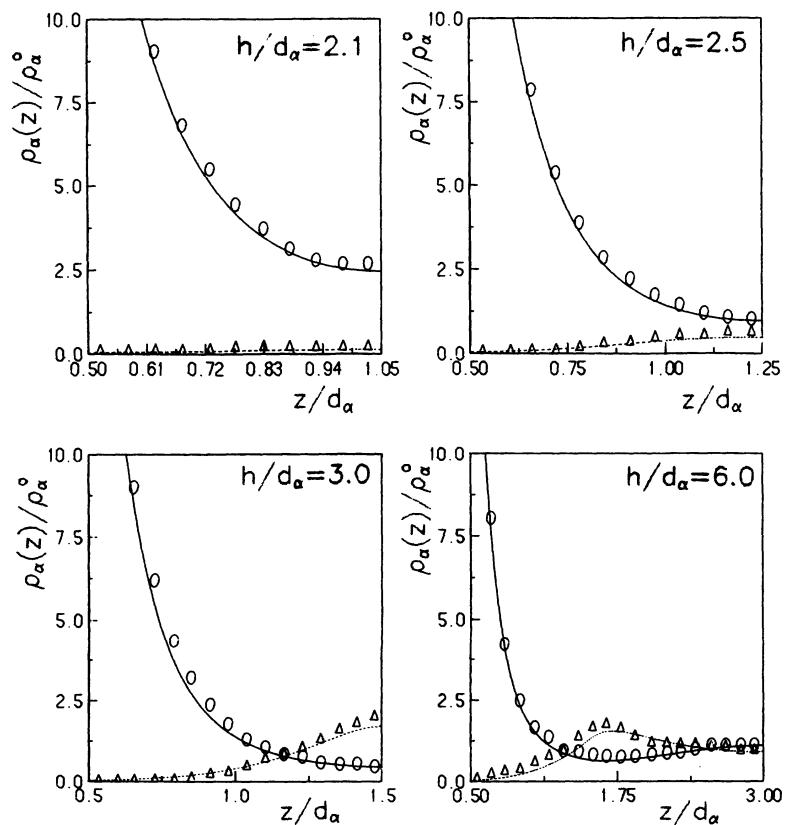


FIG. 8. Density profiles of the ions at selected values of wall separation. —, calculated results for counterions; ---, calculated results for co-ions. Circles, Monte Carlo simulation for counterions; triangles, Monte Carlo simulation for co-ions (system parameters same as in Fig. 6).

tion of the wall separation h and the solvation force obtained thereby is plotted in Fig. 1. Also shown are the results of Monte Carlo simulation [22], which clearly show quite good overall agreement. The force shows oscillations between repulsion and attraction, with a periodicity close to the value of the hard-sphere diameter, which clearly suggests that the phenomenon is a consequence of packing in a restricted region. To obtain further insight into this aspect, we have plotted in Fig. 2 the density profiles at selected values of the wall separation, along with the corresponding simulation results which show very good agreement. The changes in the appearance of structure as h is varied are well correlated with the oscillations in the force curve of Fig. 1.

For the hard-sphere liquid mixture [case (ii)], we consider the bulk densities of the two components A and B as $\rho_A^* = 0.10$ and $\rho_B^* = 0.30$ with the diameter ratio $d_B/d_A = 1.2$, i.e., $d_1 = d_2 = 4.2 \text{ \AA}$, $d_0/d_1 = 1.2$, $q_1 = -q_2 = 0$, $\rho_0^* = 0.30$ and $\rho_1^* = \rho_2^* = 0.05$ in the present notation. The plot of the calculated solvation force shown in Fig. 3 is compared with the calculations of Grimson [27], since simulation results are not available. Here, the solvation force is contributed by two contact densities corresponding to two different distances from each wall, as is clear from the plots of the density profiles at several values of h shown in Fig. 4. The dependence of the periodicity of the oscillating force on the diameter ratio of the two components can be understood

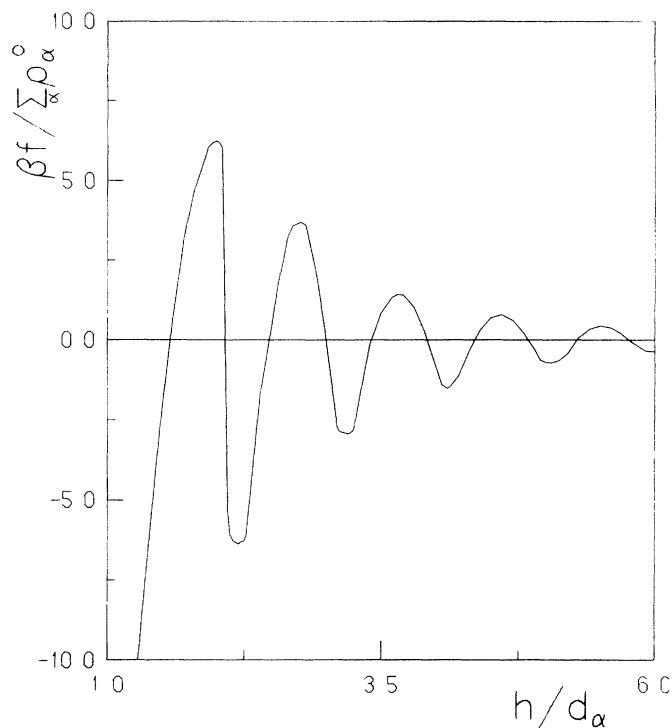


FIG. 9. The double layer force in a 2:2 MSM electrolyte vs the wall separation ($c = 0.971M$, $\rho_0^* = 0.80$, $\sigma^* = 0.10$).

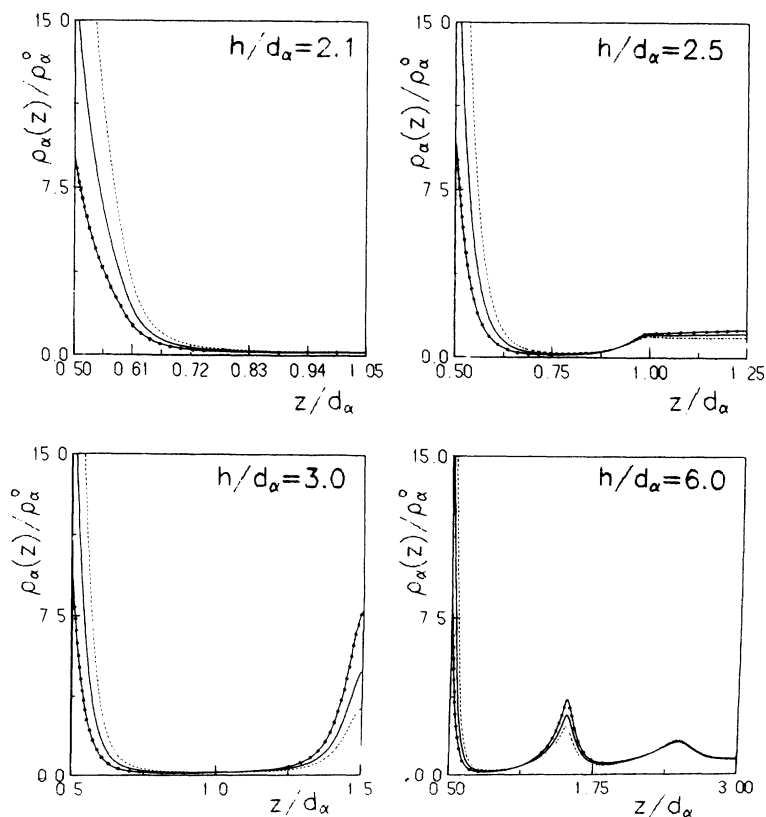


FIG. 10. Calculated density profiles of the ions and the solvent molecules at selected values of wall separation. ---, counterions; —●—, co-ions; —, solvent molecules (system parameters same as in Fig. 9).

from the nature of the oscillations of the two component densities of Fig. 4. In both these cases of neutral liquid and the mixture, the force is repulsive at a very short distance and then alternates between attraction and repulsion as h is increased.

For an RPM electrolyte [case (iii)], we have chosen a 2:2 electrolyte of concentration $C=0.971M$, the hard-sphere radius $d_1=d_2=4.2 \text{ \AA}$, and two cases of surface charge densities $\sigma^*=0.1$ and $\sigma^*=0.3$. The calculated solvation forces plotted as a function of h in Figs. 5 and 6 show quite good (especially at higher σ^*) overall agreement with the simulation results of Valleau, Ivkov, and Torrie [23], also shown in the figures. Here also, the force is repulsive at a very short distance, but as h increases, it passes through attractive and repulsive regions, finally remaining attractive at higher h . The density distributions of both the ions corresponding to $\sigma^*=0.10$ and $\sigma^*=0.30$ are plotted in Figs. 7 and 8, respectively, and the results of Fig. 8 are also shown to agree quite well with the simulation results [23]. The interesting phenomena of charge inversion in the density profiles as h increases provides an explanation of the oscillatory nature of the forces in Figs. 5 and 6.

For the MSM electrolyte [case (iv)], we have chosen the same system parameters as in case (iii), but with the additional bulk density $\rho_0^*=0.8$ corresponding to the solvent hard spheres. The calculated forces plotted in Fig. 9 show pronounced oscillations as compared to the RPM electrolyte (see Fig. 5). The corresponding density oscillations as plotted in Fig. 10 are also much enhanced (compare Fig. 7), which is also clearly reflected in the highly oscillatory nature of the force. An interesting feature of the MSM is that in Fig. 9, the force is attractive at smaller h in contrast to the repulsive behavior observed in Figs. 1, 3, 5, and 6. This is a direct consequence of accumulation of large excess of counterions near the wall for small wall separation (see the trends in the density plots of Fig. 10). Although the density plots in Fig. 10 could not be compared with simulation results, an important effect due to the presence of neutral hard spheres in MSM is that even the co-ions accumulate near the surface in contrast to only depletion observed for RPM (see Figs. 6 and 8).

IV. CONCLUDING REMARKS

The nonlocal weighted density-functional approach proposed recently [11–13] for nonuniform ionic solutions is shown here to be able to predict the main features of the solvation or structural forces in ionic (and also neutral) liquids, justifying the suitability of the approximations used [28]. The calculated solvation forces in all cases are of a decaying oscillatory nature with a periodicity roughly equal to the sizes of the ions or the solvent molecules. This establishes the role of volume exclusion due to the finite size of the molecules in a restricted space in determining the oscillations of the force. Insight is also obtained into the relative importance of the hard-sphere and electrostatic correlations through the variation in the surface-induced density inhomogeneities as a function of the distance between two walls immersed in neutral and ionic liquids.

The present formalism and the results are directly applicable for the calculation of the interaction between colloidal particles [20], since the surface of the colloidal particles can be considered to be planar due to their large size in comparison with the solvent molecules. Löwen, Hansen, and Madden [21] have recently calculated the force between colloidal macroions through a different density-functional approach for a point charge model of the counterions and reported a Car-Parrinello-type simulation of colloidal suspension. While the approach of Löwen, Hansen, and Madden [21] as well as the present one incorporate many-body effects through a self-consistent density-functional formalism, our concern has been to study the effect of finite size of the ions and the solvent molecules on the solvation force. We are currently extending the formalism to the case of dipolar hard spheres to represent a polar solvent like water and it would also be worthwhile to investigate whether the surface induced inhomogeneity affects the solvation dynamics in a dipolar liquid.

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