

Solvation forces in ionic and neutral liquids: A density functional approach

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Abstract. The solvation forces between two planar charged surfaces in ionic solutions, corresponding to charged and neutral hard spheres representing the ions and the solvent, respectively, are studied here using a weighted density functional theory for inhomogeneous Coulomb systems developed by us recently. The hard sphere contributions to the one-particle correlation function are evaluated nonperturbatively using a position-dependent effective density, while the electrical contributions are obtained through a perturbative expansion around this weighted density. The calculated results on the solvation forces between two charged hard walls compare well with available simulation results for ionic systems. For a neutral system, the present results show good agreement with the experimentally observed oscillating forces for two mica surfaces in octamethylcyclotetrasiloxane. The present approach thus provides a direct route to the calculation of interaction energies between colloidal particles.

Keywords. Density functional theory; solvation force; electric double layer; weighted density approach.

1. Introduction

Theoretical understanding of various interfacial phenomena requires knowledge about the nature of the forces acting between solid surfaces or solute particles in a liquid (solvent) medium (Israelachvili 1992). An important example is the force between the charged colloidal particles in a suspension (for recent reviews, see Pusey 1991, Sood 1991), for which the well-known theory of Derjaguin, Landau, Verwey and Overbeek (DLVO) (see Verwey and Overbeek 1948) provides the simplest expression in terms of the contributions due to Coulomb repulsion between the two double layers and the attractive van der Waals interaction. Although suitable at large separations, this theory based on a continuum approximation for the solvent completely fails to predict the oscillating (i.e. alternating repulsive and attractive) nature of the interactions arising at short distances due to the molecular nature and hence the organised structure of the solvent and the ions near the surface. This so called solvation force has been experimentally measured (Horn and Israelachvili 1980; Israelachvili 1985, 1987, 1992) in a wide variety of systems involving ionic as well as neutral solutions and has also been predicted by computer simulation results for simple systems (Valleau *et al* 1991). There have been attempts in recent years to predict the solvation force in neutral and ionic liquids through the integral equation theories (Hansen and McDonald 1986; Henderson and Lozada-Cassou 1986). It is

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however rather difficult to apply these theories to more complicated systems and simpler approaches are thus demanded. The solvation forces arise as a result of the packing of the solvent molecules in a restricted space between the two surfaces, and thus theories suitable for the study of the structure of the solid-liquid interface should be suitable for understanding this phenomena. One such theory is the density functional theory (DFT) (Hohenberg and Kohn 1964; Mermin 1965; March and Deb 1987) which has been highly successful in predicting the equilibrium properties of non-uniform fluids (for excellent recent reviews, see Evans 1992, Henderson 1992) with wide applications in the study of liquid surface (Evans 1979), freezing of liquids (Ramakrishnan and Yussouff 1979), electric double layer (EDL) (Grimson and Rickayzen 1981; Groot 1988; Tang *et al* 1990, 1992; Kierlik and Rosinberg 1991; Patra and Ghosh 1993, 1994) all of which play important roles (Rowlinson and Widom 1982) in various electrochemical, colloidal and biological phenomena.

In a density functional approach, the single-particle density determines in principle the exact grand potential (Mermin 1965) for a many-particle system as a unique functional, which attains a minimum value at the true density. Since the exact form of this functional is unknown for an arbitrary inhomogeneous density distribution, suitable approximations are to be developed. The functional is however known for some systems with uniform density, and in such cases an approximation to the same for the corresponding non-uniform system can be obtained using, for example, a simple perturbative second-order functional Taylor expansion (Lebowitz and Percus 1963) in density inhomogeneity or, alternatively, by replacing the density argument in the expressions by a position-dependent effective density, obtained through suitable averaging of the actual inhomogeneous density distribution.

For inhomogeneous neutral fluids, two successful approaches in the latter category are the weighted density approaches (WDA) of Tarazona (1985) and Denton and Ashcroft (1991). In our recent works (Patra and Ghosh 1993), we have developed new weighted density procedures for inhomogeneous ionic liquids by extending the method of Denton and Ashcroft (1991), and applied them to the study of the structure of the electrode-electrolyte interface (Carnie and Torrie 1984), using the simple models of charged and neutral hard spheres for the ions and the solvent, respectively, distributed in the field of a charged hard wall. Apart from this molecular solvent model (MSM), we have also studied the simpler restricted primitive model (RPM) corresponding to a continuum dielectric solvent. The nature of the density and potential distributions provided considerable insight into the layering and charge inversion phenomena near the surface and it was clear that consideration of the molecular nature of the solvent might be crucial for explaining many experimental observations (Israelachvili 1987, 1992), a typical example being the oscillation of the force between two surfaces immersed in an electrolyte solution with change in their separation.

The objective of the present work is to study this solvation force between two surfaces immersed in a fluid in presence as well as absence of an added electrolyte. The solvent molecules and the ions are modelled respectively as neutral and charged hard spheres with suitable values for the effective diameters and the solid surfaces are considered as planar, which is a good approximation even for two large spheres such as colloidal particles in a suspension. As special cases, the RPM electrolyte as well as the neutral liquid system are also investigated. We first develop the theory in § 2, proposing the weighted density functional schemes for the calculation of the

density distribution and the force. The numerical results are then presented in §3, with concluding remarks in §4.

2. Theory

The system that we consider is an electrolyte solution consisting of two ionic components and a neutral solvent, modelled for simplicity as charged and neutral hard spheres, respectively, and confined between two infinite parallel planar uniformly charged hard walls.

The density distribution of each component α in the enclosed region are inhomogeneous along the perpendicular x -direction due to the influence of the external potential $u_\alpha(x)$ arising from the two walls, located at $x=0$ and $x=h$ respectively. Here $\alpha=0, 1$ and 2 represent the solvent, and the positive and negative ions, respectively. The density functional theory of Hohenberg and Kohn (1964) and Mermin (1965) enables one to express the grand potential Ω as a functional of the density given by

$$\Omega[\{\rho_\alpha\}] = F[\{\rho_\alpha\}] + \sum_\alpha \int d\mathbf{r} [u_\alpha(\mathbf{r}) - \mu_\alpha] \rho_\alpha(\mathbf{r}) + 2\pi\sigma^2 h/\epsilon, \quad (1)$$

where $F[\{\rho_\alpha\}]$ is the intrinsic Helmholtz free energy functional, μ_α and $\rho_\alpha(\mathbf{r})$ are the chemical potential and non-uniform single particle density of component α . The last term in (1) is the direct Coulomb interaction between the two charged surfaces, with uniform surface charge density σ at each wall and ϵ is the dielectric constant of the medium. The free-energy functional $F[\{\rho_\alpha\}]$ can be written as the sum

$$F[\{\rho_\alpha\}] = F_{id}[\{\rho_\alpha\}] + F_{ex}[\{\rho_\alpha\}], \quad (2)$$

consisting of an explicitly known ideal gas (noninteracting) free energy functional $F_{id}[\{\rho_\alpha\}]$, given by

$$F_{id}[\{\rho_\alpha\}] = (1/\beta) \sum_\alpha \int d\mathbf{r} \rho_\alpha(\mathbf{r}) [\ln(\rho_\alpha(\mathbf{r})\lambda_\alpha^3) - 1], \quad (3)$$

with $\beta(=k_B T)^{-1}$ and λ_α representing the inverse temperature and the de Broglie wavelength of the α th component, respectively, and an excess free energy contribution F_{ex} , originating from internal interactions within the system, the exact form of which is unknown in general.

For the present system consisting of a mixture of charged hard spheres (q_α , d_α and ρ_α^0 denoting respectively charge, diameter and the bulk density of species α), one can separate out the direct Coulomb interaction and the excess free energy can be expressed as

$$F_{ex}[\{\rho_\alpha\}] = (1/2\epsilon) \sum_\alpha \sum_\beta q_\alpha q_\beta \iint d\mathbf{r}_1 d\mathbf{r}_2 \rho_\alpha(\mathbf{r}_1) \rho_\beta(\mathbf{r}_2) / |\mathbf{r}_1 - \mathbf{r}_2| + F_{ex}^{hs}[\{\rho_\alpha\}] + F_{ex}^{el}[\{\rho_\alpha\}], \quad (4)$$

where F_{ex}^{hs} corresponds to hard sphere interactions, while F_{ex}^{el} represents the coupling

of Coulombic and hard sphere interactions. For simplicity, in this work we consider only symmetric electrolytes (i.e. $q_\alpha = -q_\beta$).

The true equilibrium density distribution of each component for a fixed external potential (at fixed h) corresponds to the minimum of the grand potential with respect to the respective densities and is determined by the equation

$$\begin{aligned}\mu_\alpha &= u_\alpha(\mathbf{r}) + \delta F[\{\rho_\alpha\}]/\delta\rho_\alpha(\mathbf{r}) \\ &= (1/\beta)[\ln(\rho_\alpha(\mathbf{r})\lambda_\alpha^3) + c_\alpha^{(1)}(\mathbf{r};[\{\rho_\alpha\})] + u_\alpha(\mathbf{r}),\end{aligned}\quad (5)$$

where the first-order correlation function $c_\alpha^{(1)}$ is defined as the functional derivative of the excess free energy, viz.

$$\begin{aligned}c_\alpha^{(1)}(\mathbf{r}) &= -\beta\delta F_{ex}[\{\rho_\alpha\}]/\delta\rho_\alpha(\mathbf{r}) \\ &= (\beta/\varepsilon) \int d\mathbf{r}' \sum_\beta q_\beta \rho_\beta(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| \\ &\quad + c_\alpha^{(1)hs}(\mathbf{r};[\{\rho_\alpha\}) + c_\alpha^{(1)el}(\mathbf{r};[\{\rho_\alpha\})\end{aligned}\quad (6)$$

The second-order direct correlation function $c_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is also defined as the second derivative given by

$$c_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = (\beta/\varepsilon)q_\alpha q_\beta/|\mathbf{r}_1 - \mathbf{r}_2| + c_{\alpha\beta}^{(2)hs}(\mathbf{r}_1, \mathbf{r}_2) + c_{\alpha\beta}^{(2)el}(\mathbf{r}_1, \mathbf{r}_2).\quad (7)$$

For the confined double layer systems under consideration, the external potential $u_\alpha(x)$ is contributed by the Coulomb potential due to the surface charge densities (σ) at each wall and the hard sphere potential $u_\alpha^{hs}(x)$ which is infinite for $x < d_\alpha/2$ and $x > h - d_\alpha/2$, but zero otherwise.

The pressure acting on each wall can be defined in terms of the grand potential as

$$p(h) = -(\partial\Omega/\partial h)_{T, \{\mu_\alpha\}},\quad (8)$$

which can be simplified on using (1)–(5) and the fact that the density is zero outside the region $d_\alpha/2 < x < h - d_\alpha/2$ (a consequence of the hard walls), to obtain

$$p(h) = \beta^{-1} \sum_\alpha \rho_\alpha(d_\alpha/2) - 2\pi\sigma^2/\varepsilon.\quad (9)$$

The force per unit area between the two walls immersed in the liquid is the difference between the pressure at the surface $p(h)$ due to the confined liquid and the pressure of the coexisting bulk fluid $p_0(=p(\infty))$ corresponding to an infinite separation between the walls, viz.

$$\begin{aligned}f(h) &= p(h) - p(\infty) \\ &= \beta^{-1} \left[\sum_\alpha \rho_\alpha(d_\alpha/2; h) - \sum_\alpha \rho_\alpha(d_\alpha/2; \infty) \right],\end{aligned}\quad (10)$$

where $\rho_\alpha(d_\alpha/2; h)$ represents the contact density of species α when the two walls are separated by h . Thus the force can easily be calculated once the density distributions of the ionic and solvent components are obtained.

The equation for the density distribution of species α in the region $d_\alpha/2 < x < h - d_\alpha/2$, obtained by combining (5) for $\rho_\alpha(x)$ and for the bulk density ρ_α^0 , is given by

$$\rho_\alpha(x) = \rho_\alpha^0 \exp \left\{ -\beta q_\alpha \psi(x) + c_\alpha^{(1)hs}(x; [\{\rho_\alpha\}]) - c_\alpha^{(1)hs}([\{\rho_\alpha^0\}]) + c_\alpha^{(1)el}(x; [\{\rho_\alpha\}]) - c_\alpha^{(1)el}([\{\rho_\alpha^0\}]) \right\}, \quad (11)$$

where $\psi(x)$, the mean electrostatic potential due to the external surface charges and the internal ionic distributions, is the solution of the corresponding Poisson's equation in one dimension with suitable boundary conditions, and is given by

$$\begin{aligned} \psi(x) = & -(4\pi/\epsilon)\sigma x - (4\pi/\epsilon) \int_0^x dx' \sum_\alpha q_\alpha \rho_\alpha(x') \\ & - (4\pi/\epsilon) \int_x^{h/2} dx' x' \sum_\alpha q_\alpha \rho_\alpha(x') + \psi(h/2), \end{aligned} \quad (12)$$

or the alternative expression

$$\psi(x) = (4\pi/\epsilon) \int_x^{h/2} dx' (x - x') \sum_\alpha q_\alpha \rho_\alpha(x') + \psi(h/2), \quad (13)$$

where $\psi(h/2)$ is determined by demanding that the density distribution satisfies the electroneutrality condition

$$\int_0^h dx' \sum_\alpha q_\alpha \rho_\alpha(x') + 2\sigma = 0. \quad (14)$$

The density equation (11) is however not complete without knowledge about the correlation functions $c_\alpha^{(1)hs}$ and $c_\alpha^{(1)el}$. Since exact explicit expressions for these density functionals are not known for a non-uniform density distribution, we have recently proposed approximation schemes for obtaining them using the known correlation functions $\tilde{c}_{\alpha\beta}^{(2)hs}(\mathbf{r}_1, \mathbf{r}_2)$ and $\tilde{c}_{\alpha\beta}^{(2)el}(\mathbf{r}_1, \mathbf{r}_2)$ for a mixture of charged and neutral hard spheres of uniform density and evaluating the corresponding first order quantities $\tilde{c}_\alpha^{(1)}$ at suitable effective densities. Since details have been reported elsewhere (Patra and Ghosh 1994), we will mention here only the relevant final equations.

The hard sphere contribution $c_\alpha^{(1)hs}$ in (11) for the non-uniform system is thus obtained here by evaluating its homogeneous counterpart at suitable effective densities, $\bar{\rho}_\alpha^{hs}(\mathbf{r})$, viz.

$$c_\alpha^{(1)hs}(\mathbf{r}; [\{\rho_\alpha\}]) = \tilde{c}_\alpha^{(1)hs}(\bar{\rho}_\alpha^{hs}(\mathbf{r})), \quad (15)$$

where $\{\bar{\rho}_\alpha^{hs}(\mathbf{r})\}$ are defined as the weighted averages

$$\bar{\rho}_\alpha^{hs}(\mathbf{r}) = \sum_\beta \int d\mathbf{r}' \rho_\beta(\mathbf{r}') w_{\alpha\beta}^{hs}(\mathbf{r}, \mathbf{r}'; \bar{\rho}_\alpha^{hs}(\mathbf{r})). \quad (16)$$

Equation (15) implies that the contribution to the hard sphere part of the one-particle correlation function (corresponding to component α) of a non-uniform fluid at a

point \mathbf{r} is assumed to be given by that of a corresponding uniform fluid of effective total density $\bar{\rho}_\alpha^{hs}(\mathbf{r})$. While this evaluation is fully nonperturbative, the electrical part is evaluated perturbatively by employing

$$c_\alpha^{(1)el}(\mathbf{r}; [\{\rho_\alpha\}]) = \tilde{c}_\alpha^{(1)el}([\{\rho_\alpha^0\}]) + \sum_\beta \int d\mathbf{r}' \tilde{c}_{\alpha\beta}^{(2)el}(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}_\alpha^{ion}(\mathbf{r})) [\rho_\beta(\mathbf{r}') - \bar{\rho}_\alpha^{ion}(\mathbf{r})], \quad (17)$$

where the two-particle correlation function is evaluated at an effective density $\{\bar{\rho}_\alpha^{ion}(\mathbf{r})\}$ for the ions, obtained from (16) by summing over the ionic components, ($\beta = 1$ and 2).

Now, demanding that the functional derivatives of (15) yield the exact two-particle correlation functions in the limit of homogeneous density, one obtains the explicit expressions for the weight functions $w_{\alpha\beta}^{hs}(|\mathbf{r} - \mathbf{r}'|)$ given by

$$w_{\alpha\beta}^{hs}(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}) = \tilde{c}_{\alpha\beta}^{(2)hs}(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}) / [(\partial/\partial\bar{\rho})(\tilde{c}_\alpha^{(1)hs}(\bar{\rho}))]. \quad (18)$$

The ingredients in the theory are thus the correlation functions $\tilde{c}_{\alpha\beta}^{(2)hs}$ and $\tilde{c}_{\alpha\beta}^{(2)el}$ for a mixture of charged and neutral hard spheres of uniform density. For simplicity we specialise here only in the case of identical diameters ($d_\alpha = d$) for which the mean spherical approximation (MSA) solutions (Waisman and Lebowitz 1972; Hansen and McDonald 1986) for the correlation functions are given by

$$\tilde{c}_{\alpha\beta}^{(2)hs}(r; \{\rho_\alpha^0\}) = a_0 + a_1(r/d) + a_3(r/d)^3, \quad (19)$$

$$\tilde{c}_{\alpha\beta}^{(2)el}(r; \{\rho_\alpha^0\}) = -(\beta q_\alpha q_\beta / \epsilon) [(2B/d) - (B/d)^2 r - 1/r], \quad (20)$$

in the region $r < d$, and are zero for $r > d$. Here, $a_0 = (2a_3/\eta) = -(1 + 2\eta)^2/(1 - \eta)^4$; $a_1 = 6\eta(1 + \eta/2)^2/(1 - \eta)^4$, $\eta = (\pi/6) \sum_\alpha \rho_\alpha^0 d^3$, and $B = [x + 1 - (1 + 2x)^{1/2}]/x$, $x = d[(4\pi\beta/\epsilon) \sum_\alpha \rho_\alpha^0 q_\alpha^2]^{1/2}$. The expression for the first order correlation function $\tilde{c}_{\alpha\beta}^{(1)hs}$ obtained by functional integration of (19) is given by

$$\tilde{c}_{\alpha\beta}^{(1)hs} = -(1/4)(14\eta - 13\eta^2 + 5\eta^3)/(1 - \eta)^3 + (1/2)\ln(1 - \eta). \quad (21)$$

Since the density variation is only along the x -direction, integrations over the y - and z -coordinates are performed analytically leaving only one-dimensional integrals to be evaluated numerically.

With the expressions ((19)–(21)) for the correlation functions for the uniform system, the present prescription ((11)–(18)) thus provides a route to the calculation of the inhomogeneous density distribution of the ions as well as the solvent molecules in the interfacial region. Using the calculated values of the contact densities in (10), one can therefore evaluate the solvation forces between surfaces immersed in liquids.

3. Results and discussion

The nonlinear integral equations (11) along with (12) for $\psi(x)$ and (15)–(18) for WDA are discretized using a uniform mesh and simple schemes for numerical integration. For convenience, dimensionless representations are used, i.e. the distance

is measured in units of the hard sphere diameter d , and the density, surface charge density and the electrostatic potential are expressed respectively as the reduced quantities $\rho_\alpha^* = (\rho_\alpha d^3)$, $\sigma^* = (\sigma d^2/e)$ and $\psi^*(x) = \beta e \psi(x)$, where e is the magnitude of the electronic charge. The resulting equations are solved iteratively with suitably chosen trial densities for each component, until convergence is reached as judged by the criterion that the norm defined as $\left[\sum_\alpha \sum_{i=1}^N \{(\rho_\alpha^{(n+1)}(z_i) - \rho_\alpha^{(n)}(z_i))/\rho_\alpha^0\}^2/N \right]^{1/2}$ with N denoting the number of mesh points, is a small number (e.g. $< 10^{-5}$). The forms for the trial densities that are found suitable for the two ions are the superposition of the modified Guoy–Chapman densities (Carnie and Torrie 1984) for the EDL at the two walls, while for the solvent, the average bulk density can be used. In (12), the value of the mid-plane potential $\psi(h/2)$ is chosen such that in each iteration the resulting density profiles satisfy the electroneutrality condition of (14). Using the calculated contact densities $\rho_\alpha(d/2)$ for all the components at a wall separation h as well as an infinite separation (i.e. the result for a single wall), the force is obtained from (10).

We have carried out three sets of calculations. The first case is a symmetric

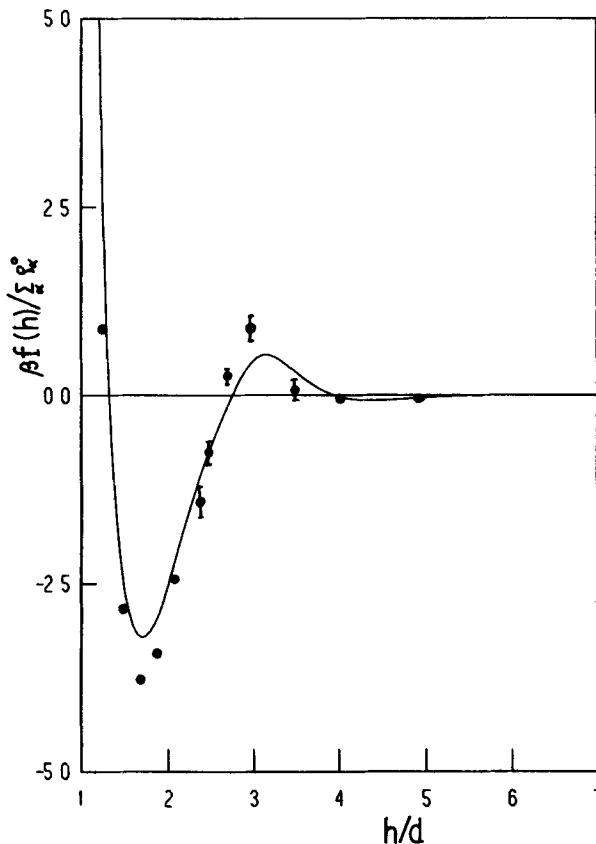


Figure 1. The double layer force in an RPM electrolyte vs the wall separation (see text for system parameters). Continuous curve: present calculation; circles: Monte Carlo simulation by Valteau *et al* (1991).

($q_1 = -q_2$) RPM electrolyte with the density of solvent hard spheres as zero but a continuum dielectric as the solvent. In the second case, we consider the MSM with non-zero densities for both the ions and the solvent. In the third case, the electrolyte density is assumed to be zero, corresponding to a neutral liquid. All the calculations correspond to a temperature of 298 K and the dielectric constant chosen is that of water, i.e. $\epsilon = 78.5$.

For the RPM electrolyte, we have chosen the same system parameters as those used in the computer simulation by Valleau *et al* (1991), i.e. a 2:2 electrolyte of concentration $C = 0.971$ M, the hard sphere radius $d = 4.2$ Å, and the surface charge density $\sigma^* = 0.3$. In figure 1, we have plotted the force obtained from the present density functional calculation as a function of the wall separation h . Also shown in the figure are the simulation results (Valleau *et al* 1991), which clearly indicate overall good agreement. While the force is repulsive at a very short distance, it first becomes attractive with a minimum and then passing through a repulsive region becomes attractive again as the walls are further separated. Insight into this behaviour can be gained from figure 2, where we have plotted the density distributions (calculated

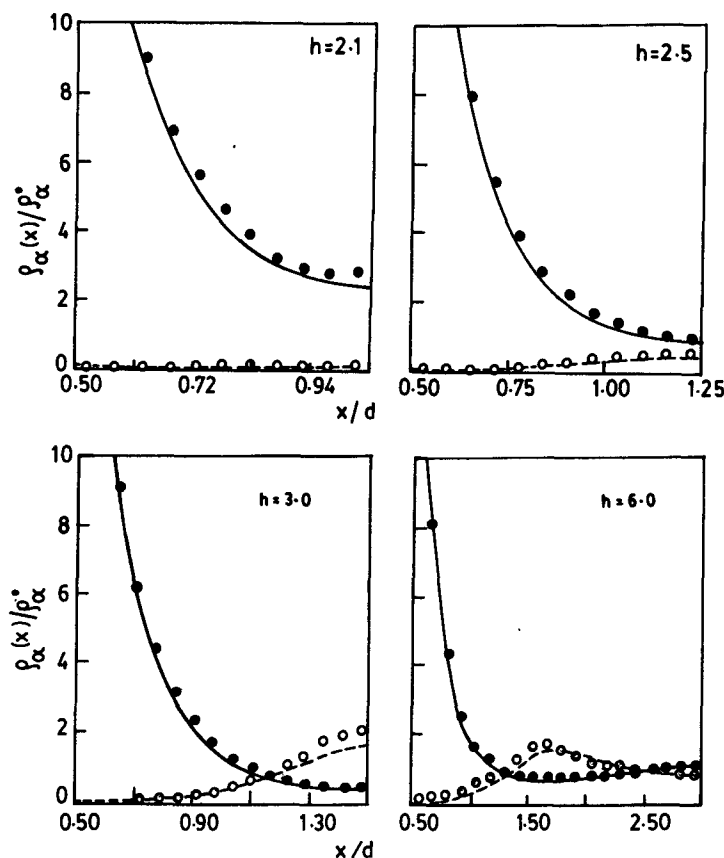


Figure 2. Density profiles of the ions at selected values of wall separation, (—): calculated results for counter-ions; (---): calculated results for co-ions; circles: Monte Carlo simulation by Valleau *et al* (1991) (system parameters as in figure 1).

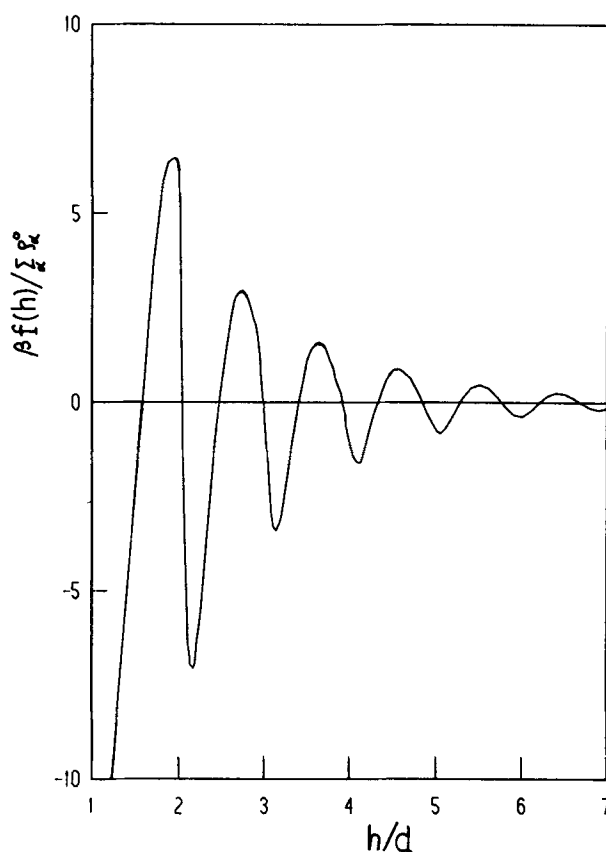


Figure 3. The calculated double layer force in a MSM electrolyte vs the wall separation (see text for system parameters).

as well as simulation results) of the positive and negative ions at selected values of h . There is an almost complete exclusion of the co-ions from the surface region at smaller values of h ; but this co-ion concentration increases with increase in h , leading to a charge inversion and the density at the mid-plane region finally approaches the bulk density.

In order to understand the effect of incorporating the molecular nature of the solvent, we have considered the same system as above with additional neutral hard spheres of the same radius representing the solvent of bulk density $\rho_0^{0*} = 0.8$. For this MSM, the calculated results on the force are plotted in figure 3, showing much more pronounced oscillations in the force with change in h . This is again a consequence of the enhanced oscillations in the density distributions plotted in figure 4 for the same values of h as used in figure 2. An interesting feature of the density profiles is that even the co-ions are attracted towards the surface in contrast to the depletion observed in the case of the RPM electrolyte (see figure 2). This is clearly a consequence of the presence of neutral hard spheres of relatively higher concentration.

It is also of interest to study the wall pressure due to the neutral hard spheres alone and compare the results with those of the MSM electrolyte as well as the

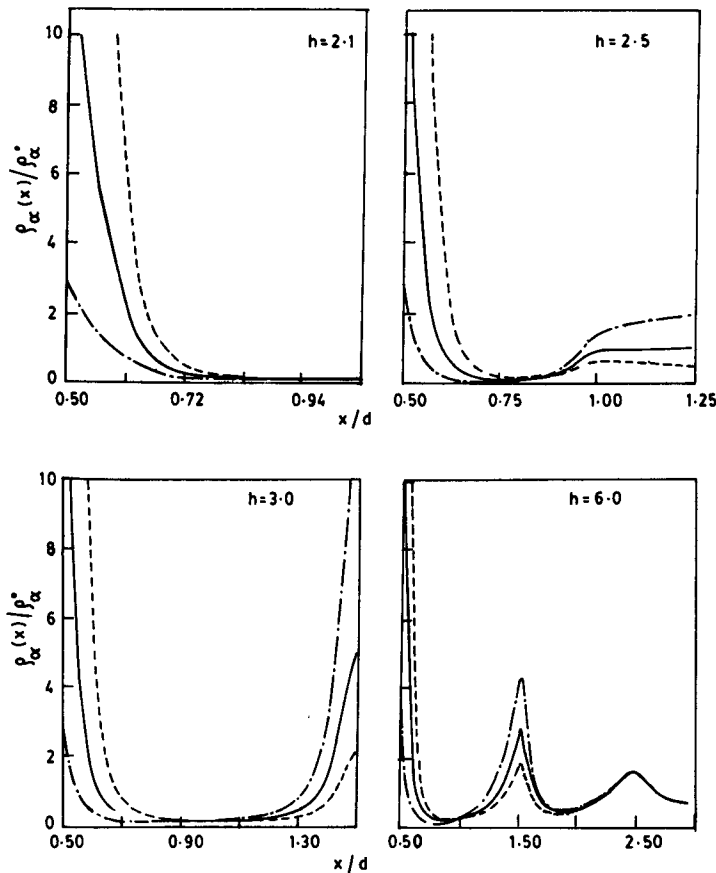


Figure 4. Calculated density profiles of the ions and the solvent molecules at selected values of wall separation; (-----): counter-ions, (-·-·-·): co-ions, (—): solvent molecules (system parameters as in figure 3).

experimentally observed forces in neutral liquids. With a view to reproducing the experimentally observed (Horn and Israelachvili 1980) oscillating forces between two mica surfaces immersed in octamethylcyclotetrasiloxane, a liquid of nonpolar nearly spherical molecules of diameter ≈ 0.85 nm (Horn and Israelachvili 1987), we use the present scheme to calculate the forces in a hard sphere neutral liquid of density $\rho_0^* = 0.68$, which is close to the typical values of 0.7 or 0.8 normally used for liquids. The calculated forces are numerically integrated to obtain the interaction energy (per unit area) $E(h)$ between the two walls and the results are plotted in figure 5 along with the experimental results of Horn and Israelachvili (1980). (It may be noted that the quantity F/R plotted in figure 1 of their paper is divided by 2π to obtain the interaction energy $E(h)$ plotted here and h is measured in units of $d = 0.85$ nm). Considering the fact that no adjustable parameter is used here except that the bulk density chosen is somewhat arbitrary, the agreement between the calculated and the experimental results is very good. Also plotted in the figure is the van der Waals interaction energy

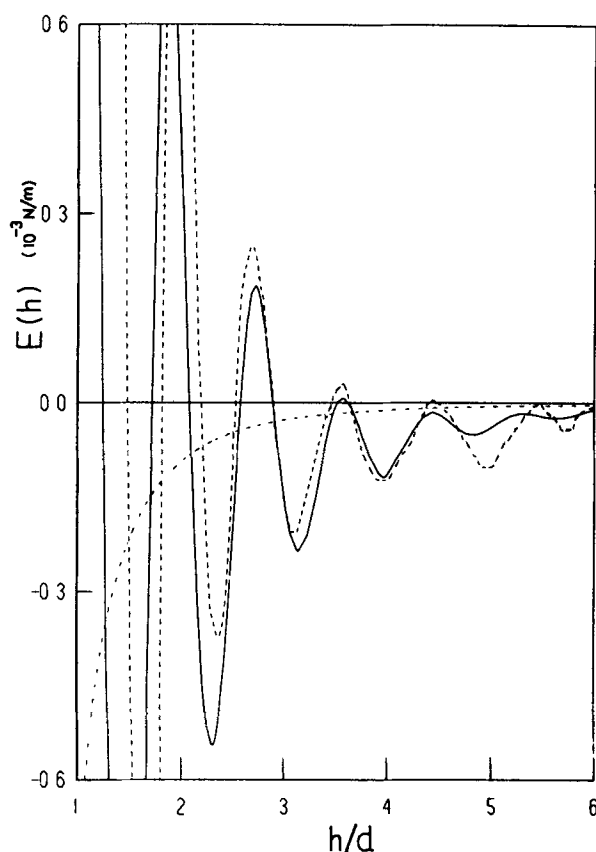


Figure 5. Interaction energy between two walls in a neutral liquid vs. the wall separation; (—): present calculation for hard spheres ($\rho^* = 0.68$); (---): experimental results of Horn and Israelachvili (1980); (-·-·-): van der Waals interaction energy.

(using Hamaker constant $A = 1.4 \times 10^{-20}$ J) between the walls for comparison. The density profiles are also plotted in figure 6 for selected values of h .

The solvation force in all cases shows oscillations with a periodicity nearly equal to the sizes of the ions or the solvent molecules, which clearly emphasizes that the volume exclusion due to the finite size of the molecules is responsible for this important effect. The manner in which the density oscillations set in as the walls are separated in all the three sets of studies provides useful insight into the relative importance of hard sphere exclusion and the electrostatic interaction.

4. Concluding remarks

The success of the recently proposed nonlocal weighted density functional approach (Patra and Ghosh 1993, 1994) for non-uniform ionic solutions, in predicting the solvation or structural forces due to the surface-induced inhomogeneity in the density distribution of the liquid confined between two walls immersed in it further establishes

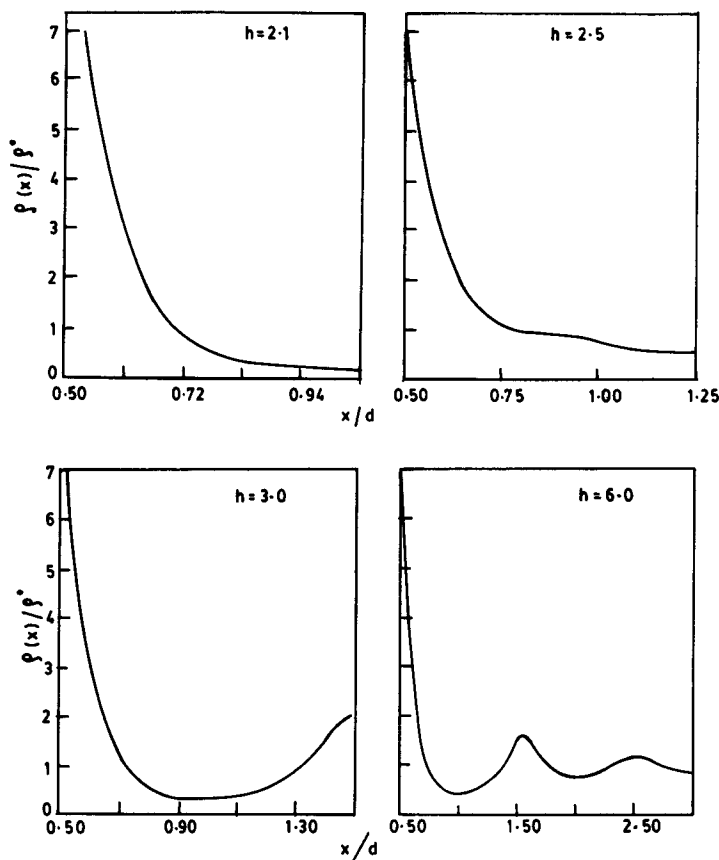


Figure 6. Calculated density profiles for hard spheres at selected values of wall separation, (system parameters as in figure 5).

the suitability of the approximations used. The theory was earlier shown to be successful in predicting the structure of the electrode–electrolyte interface for RPM as well as MSM electric double layer.

Although we have considered the surfaces to be planar, the present results are directly applicable to the interaction between the colloidal particles, since the sizes of the latter are much larger compared to the sizes of the solvent molecules. The fact that the basic features of even the experimental results in a real liquid are so well predicted using such a simple model is quite encouraging. We are currently applying the present formalism to the case of dipolar hard spheres which would be a more realistic model for the solvent in aqueous electrolyte solutions.

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