# Density functional approach to solvent-induced interactions in neutral liquids: Comparison with experimental results

Chandra N. Patra and Swapan K. Ghosh
*Heavy Water Division, Bhabha Atomic Research Centre, Bombay 400085, India*
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The solvent-induced interaction between two planar hard surfaces in a neutral hard sphere liquid is studied through two recent versions of weighted density approaches to density functional theory. The experimental results of Israelachvili [Acc. Chem. Res. **20**, 415 (1987)] and co-workers [Horn and Israelachvili, Chem. Phys. Lett. **71**, 192 (1980)] on the interaction energies between two mica surfaces in liquid tetradecane and also octamethylcyclotetrasiloxane are shown to be well reproduced by the present calculation using suitable values of effective hard sphere diameters and the actual bulk densities for these two liquids.

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In recent years, there has been growing interest in the study of forces [1] between macroscopic surfaces immersed in neutral or ionic liquids. A proper understanding of these forces is very important in connection with a wide variety of interfacial phenomena. Experimental measurements [2-4] have revealed that the general qualitative behavior of this force (or the corresponding interaction energy) as a function of the distance between the two surfaces is of decaying oscillatory nature, although detailed quantitative aspects differ from system to system. This so called solvation or structural force [2,4] arises because the liquid molecules tend to form an integral number of layers between the two surfaces, and whenever the distance between them differs from an integral multiple of the molecular diameter, the liquid responds with an excess attractive or repulsive force on the walls. The solvation force is thus determined by the structure of the solid-liquid interface at the walls, and hence, for a quantitative prediction of this force and the corresponding interaction energy, we are prompted to employ density functional theory (DFT) [5] which has been highly successful in predicting the structure of inhomogeneous neutral and ionic fluids [6-11] at interfaces.

The density functional approach, although exact in principle, has to invoke approximations for practical applications, since the exact forms of the energy density functionals are not known in general. For inhomogeneous classical neutral fluids, the most successful approximate approaches [6] are the weighted density approaches (WDA) of Tarazona [7] and Denton and Ashcroft [8], while the generalization of the latter proposed by us recently [11] for ionic fluids has been suitable for describing the structure of the electrode-electrolyte interface [11,12] as well as the solvation force [13], in good agreement with available simulation results for the restricted primitive model of an electrolyte solution.

In the present work, our objective is to employ DFT to understand and predict the experimental results for solvent-induced interaction energies reported in the literature. For this purpose, we have chosen as examples the measurements of Israelachvili and co-workers [2,3] on the interaction between two mica surfaces immersed in neutral liquids, viz. liquid octamethlylcyclotetrasiloxane (OMCTS) and tetradecane. For simplicity, the liquid molecules are modeled here as neutral hard spheres of suitable effective diameters and bulk density, and the solid surfaces are considered as planar hard walls. An analogous model has been used earlier by Attard and Parker [4] to predict the solvation force for OMCTS using integral equation theories.

The density functional theory of Hohenberg, Kohn, and Mermin [5] uses the single-particle density $\rho(r)$ as the basic variable, which in principle determines the exact grand potential $\Omega$ for a many-particle system characterized by an external potential $u(r)$. For a fixed $u(r)$, the density functional $\Omega[\rho]$ is unique and attains a minimum value at the true density. The theory thus provides a prescription for calculating the inhomogeneous density distribution $\rho(r)$. The system of interest here is a neutral hard sphere liquid of molecular diameter $d$ and bulk density $\rho_0$, confined between two infinite parallel planar hard walls located at $z=0$ and $h$, respectively, which causes the external potential $u(z)$ as well as the surface-induced inhomogeneous density $\rho(z)$ to depend only on the perpendicular $z$ coordinate. The grand potential (per unit area in the $x$-$y$ plane) for this system at temperature $T$ can be written as the density functional

$$\Omega[\rho(z)]=(k_BT)\int_0^h dz\,\rho(z)\{\ln[\rho(z)\lambda^3]-1\} + F_{ex}[\rho(z)]+\int_0^h dz[u(z)-\mu]\rho(z)\ , \quad (1)$$

where the first and second terms on the right hand side represent the ideal and excess free energy functionals, respectively, $k_B$ and $\lambda$ are the Boltzmann constant and the de Broglie wavelength, and $\mu$ is the chemical potential. The true density distribution in the confined region corresponds to a minimization of the grand potential with respect to the density, leading to the equation

$$\mu=u(z)+(k_BT)\{\ln[\rho(z)\lambda^3]-c^{(1)}(z)\}\ , \quad (2)$$

where $c^{(1)}(z)$ is the first order direct correlation function defined by the functional derivative

$$c^{(1)}(z)=-(k_BT)^{-1}\delta F_{ex}[\rho(z)]/\delta\rho(z)\ . \quad (3)$$

Evaluating $\mu$ using the bulk density $\rho_0$, Eq. (2) leads to an explicit expression for the density $\rho(z)$ viz.

 

$$\rho(z)=\rho_0\exp\{c^{(1)}(z;[\rho(z)])-c^{(1)}(\rho_0)\}\ , \tag{4}$$

valid in the region $d/2<z<h-d/2$, but zero otherwise, since the external potential $u(z)$ is infinite for $z<d/2$ and $z>h-d/2$ and zero elsewhere.

The grand potential also determines the pressure acting on each wall, through the relation

$$p(h)=-(\partial\Omega/\partial h)_{T,\mu}\ , \tag{5a}$$

which can be simplified (see, for example, Ref. [10]) by using Eqs. (1)–(3) and $F_{ex}[\rho(z)]=-(k_BT)\int_0^h dz\,\rho(z)\int_0^1 d\lambda\,c^{(1)}[\lambda\rho(z)]$, to obtain the result

$$p(h)=(k_BT)\rho(d/2;h)\ , \tag{5b}$$

where $\rho(d/2;h)$ represents the contact density for a wall separation $h$. For the walls immersed in the liquid, the net force per unit area is the difference between the pressure $p(h)$ due to the confined liquid and the bulk pressure $p_0[=p(\infty)]$ corresponding to an infinite separation between the walls (i.e., a single wall) viz.

$$\begin{aligned}f(h)&=p(h)-p(\infty)\\&=(k_BT)[\rho(d/2;h)-\rho(d/2;\infty)]\ .\end{aligned} \tag{6}$$

The interaction energy (per unit area) is then obtained through the integral

$$E(h)=\int_h^\infty f(h')dh'\ . \tag{7}$$

Although Eqs. (4), (6), and (7) together provide a scheme for the calculation of the solvation force and hence the interaction energy, approximations are to be introduced for the quantity $c^{(1)}$ in the density equation (4), since its exact functional form for an inhomogeneous density distribution is unknown. For a uniform density, however, analytical solution for a hard sphere system is available within the Percus-Yevick approximation, and is employed here through the WDA approach.

In WDA, a position-dependent effective density $\bar\rho(z)$, defined as a weighted average of the actual nonuniform density of the system viz.

$$\bar\rho(z)=\int d\underline{r}'\rho(z')w(|\underline{r}-\underline{r}'|;\bar\rho(z))\ , \tag{8}$$

is used to evaluate expressions for the uniform system for obtaining an estimate of the same for nonuniform density.

In the WDA of Denton and Ashcroft [8], one directly approximates the first order correlation function viz.

$$c^{(1)}(z;[\rho(z)])=\bar c^{(1)}(\bar\rho(z))\ , \tag{9}$$

while in the Tarazona [7] approach, it is the excess free energy density which is evaluated using the effective density, which corresponds to a first order correlation function obtained as

$$c^{(1)}(z;[\rho(z)])=-(k_BT)^{-1}\left[\bar f_{ex}(\bar\rho(z))+\int d\underline{r}'\rho(z')[\delta\bar f_{ex}(\bar\rho(z'))/\delta\bar\rho(z')][\delta\bar\rho(z')/\delta\rho(z)]\right]\ . \tag{10}$$

where $f_{ex}$ is defined as $F_{ex}=\int d\mathbf{r}\,\rho(\mathbf{r})f_{ex}(\mathbf{r};[\rho(z)])$. The notations $\bar c^{(1)}$, $\bar c(2)$ and $\bar f_{ex}$ refer here to the hard sphere system of uniform density. The quantities $c^{(1)}$ and $f_{ex}$ used in the present study correspond to the compressibility and the Carnahan-Starling equation of state [14], respectively.

Explicit expressions for the weight function $w(|\mathbf{r}-\mathbf{r}'|)$ have been derived in both the approaches, and are given by

$$w(|\mathbf{r}-\mathbf{r}'|;\bar\rho)=\bar c^{(2)}(|\mathbf{r}-\mathbf{r}'|;\bar\rho)/\{(\partial/\partial\bar\rho)[\bar c^{(1)}(\bar\rho)]\} \tag{11}$$

for the Denton and Ashcroft [8] approach, and by the second order expansion

$$\begin{aligned}&w(|\mathbf{r}-\mathbf{r}'|;\{\bar\rho(\mathbf{r})\})\\&\quad=w^{(0)}(|\mathbf{r}-\mathbf{r}'|)+w^{(1)}(|\mathbf{r}-\mathbf{r}'|)\bar\rho(\mathbf{r})\\&\qquad+w^{(2)}(|\mathbf{r}-\mathbf{r}'|)(\bar\rho(\mathbf{r}))^2\end{aligned} \tag{12}$$

for the Tarazona [7] approach. The expressions for the density-independent functions $w^{(i)}$ have been given by Tarazona [7].

In Eq. (8), the integrations of $w(|\mathbf{r}-\mathbf{r}'|)$ over $x'$ and $y'$ coordinates are performed analytically, and only a one-dimensional integral involving the density $\rho(z)$ is to be evaluated numerically to obtain the effective density. Explicit expressions for these planar-averaged weight functions are reported elsewhere [8,12].

Thus we have two prescriptions for the calculation of the inhomogeneous density distributions in the wall-fluid interfaces, and thereby the solvation forces as well as the interaction energies between surfaces immersed in liquids. For convenience, the WDA of Denton and Ashcroft [8], corresponding to Eqs. (4), (8), (9), and (11), is designated here as scheme A, and that of Tarazona [7] corresponding to Eqs. (4), (8), (10), and (12) as scheme B.

The nonlinear density equation (4) and the effective density expression (8) of WDA corresponding to schemes A and B , are discretized using a uniform mesh, and the resulting equations are solved iteratively using the bulk density as the initial trial density, until convergence is reached. For convenience, we measure the distances in units of the hard sphere diameter $d$, and the density as the dimensionless reduced density $\rho^*=(\rho d^3)$. From the calculated contact densities $\rho(d/2;h)$ at different values of the wall separation $h$ (including $h=\infty$ corresponding to a single wall), the force $f(h)$ is evaluated with the help of Eq. (6), and hence the interaction energy $E(h)$ is obtained through numerical integration using Eq. (7).

Our objective here has been to compare the calculated interaction energies for the hard sphere hard wall system with the experimentally observed interaction between two mica surfaces immersed in a neutral liquid. In order to reproduce the experimental results reported by Israelachvili and co-workers [2,3] for the liquids OMCTS and tetradecane, we have used the reduced bulk densities ($\rho_0^*$)

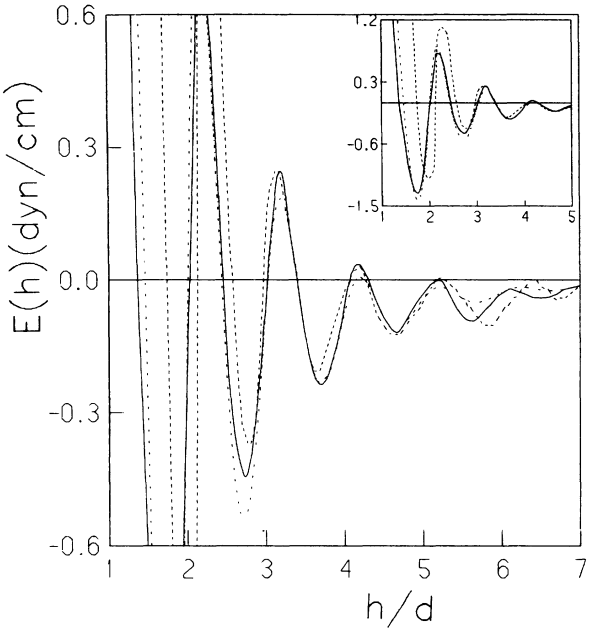


FIG. 1. Interaction energy between two walls in a neutral liquid vs the wall separation. (——): present calculation using scheme A for hard spheres ($\rho^*=0.68$). (—·—·—·): calculation using scheme B (results from Ref. [15]). (----): experimental results for liquid OMCTS.

as 0.68 and 0.60, respectively, at $T=298$ K. These are obtained by using the actual densities of the two liquids viz. 0.956 and 0.763 gm/ml, with hard sphere diameters chosen to be as 7.05 and 6.38 Å, respectively. The reported effective diameter for nearly spherical OMCTS molecule is 8.5 Å, and the present effective hard sphere

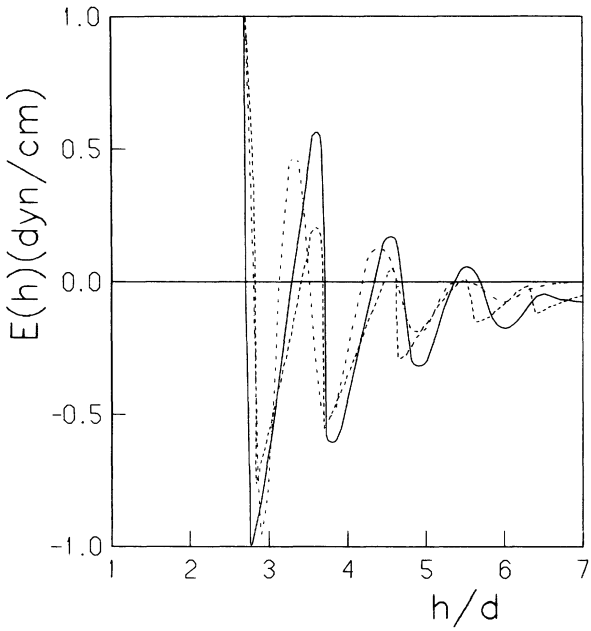


FIG. 2. Interaction energy between two walls in a neutral liquid vs the wall separation. (——): present calculation using scheme A for hard spheres ($\rho^*=0.60$). (—·—·—·): present calculation using scheme B. (----): experimental results for liquid tetradecane.

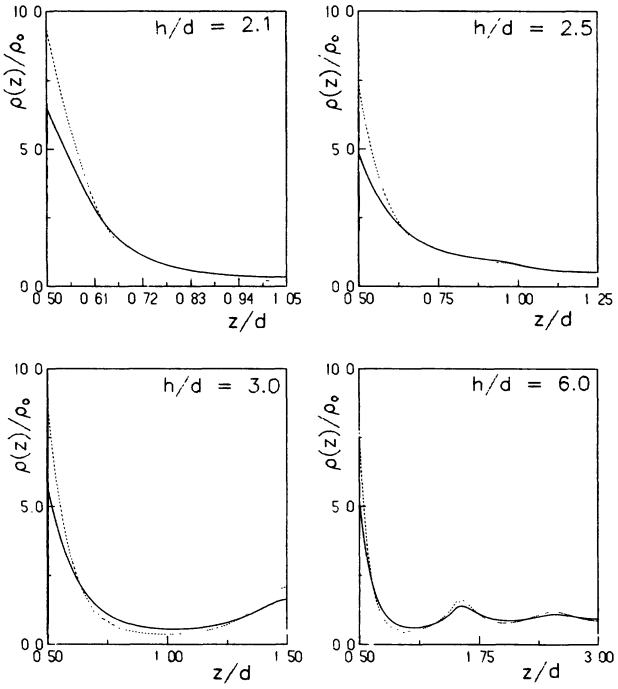


FIG. 3. Calculated density profiles for hard spheres at selected values of the wall separation (system parameters same as in Fig. 1). (——): calculation using scheme A. (----): calculation using scheme B.

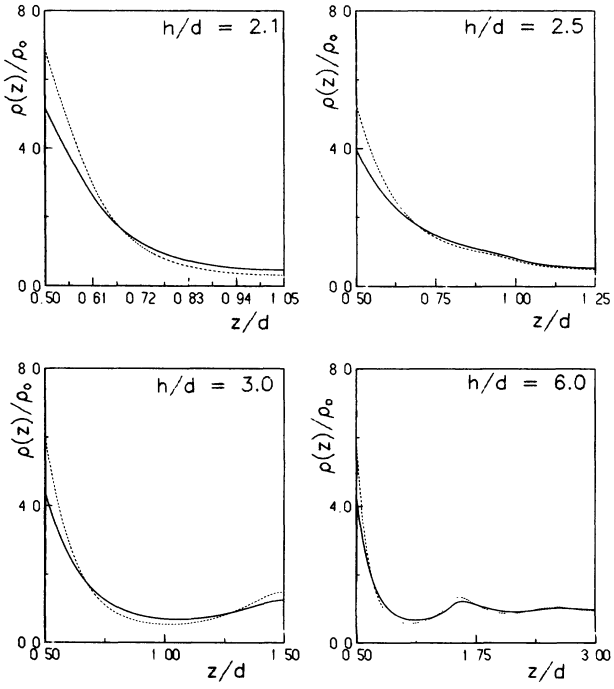


FIG. 4. Calculated density profiles for hard spheres at selected values of the wall separation (system parameters same as in Fig. 2). (——): calculation using scheme A. (----): calculation using scheme B.

diameter is thus somewhat lower. For the tetradecane molecule, however, the effective hard sphere diameter is higher than the reported value of $4.2\pm0.3$ Å. This is because, in this case, the molecule is nearly cylindrical and the reported diameter corresponds to that of the cylinder. The effective hard sphere diameter, on the other hand, is a result of consequences arising from the diameter as well as the length of the cylindrical molecule, and is thus higher in this case. Modeling the tetradecane molecules as hard spheres, however, is relatively less suitable, and consequently the deviation of the calculated results is also observed to be more in this case.

The calculated interaction energy (per unit area) has been plotted in Fig. 1 for OMCTS, and in Fig. 2 for tetradecane, along with the corresponding experimental results of Israelachvili and co-workers [2,3]. [The quantity $F/R$ reported by Israelachvili and co-workers has been divided by $2\pi$ to obtain $E(h)$ plotted in the present work.] The experimental results for the forces or interaction energies are oscillatory in nature, and are reproduced very well by the present calculations. In general, it is observed that the results of scheme B are better than those of Scheme A, which might be a consequence of the fact that the contact theorem [14] is better satisfied [11] in the former approach. The agreement between calculated and experimental results can be considered to be very good if we take into account the fact that except for the values of the effective hard sphere diameter, no adjustable parameter has been used. Attard and Parker [4] have also used adjustable hard sphere diameter and integral equation theories to obtain forces in agreement with the experimental results for OMCTS. The oscillations are consequences of the problem of packing in a confined region, and have a periodicity approximately equal to the molecular sizes. To obtain further insight, we have plotted the density profiles in Figs. 3 and 4 for four selected values of $h$. The formation of intermediate layers corresponding to the density maxima at higher values of $h$ is quite clear. Also, the contact density predicted by scheme A is lower than that of scheme B. However, since Eq. (6) represents a difference quantity, the force predicted by scheme A is not necessarily always lower than that of scheme B.

It is highly encouraging that the basic features of the experimental results for solvent-induced interaction in a real liquid are reproduced so well using such a simple hard sphere model for the liquid. One can thus conclude that the nonlocal weighted density functional approaches as employed here provide a powerful tool for studying the surface-induced inhomogeneity in the density distribution of a liquid confined between two walls, and thereby predicting the resulting solvent or structural forces quite accurately. Applications to other related problems, viz. the interaction in a colloidal suspension (see, for example, Ref. [16] for a different density functional approach), are of considerable interest.

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