Full Length Research Paper

Solvation force in a hard-sphere Yukawa fluid confined between walls

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We apply a general density functional theory for calculating solvation force between two walls immersed in a fluid of particles. Solvation force is obtained for the hard-sphere Yukawa fluid confined between hard and attractive walls. To determine the density profile, we use the density functional theory proposed by Yi and Kim. This theory is based on the density functional approximation, which in turn is based on both the weighted-density approximation of Tarazona and the density functional approximation of Rickayzen and Augousti (1984). The calculated density profile is used to obtain the solvation force exerted by the fluid on the walls. We show the effect of varying wall and particle interactions on the solvation force. As the result indicates, the solvation force depends on temperature, separation of the walls and on the wall potential.

Key words: Density functional theory, solvation force, Yukawa potential, colloidal systems.

INTRODUCTION

In studying the structure and stability of surface coating and colloidal systems, like paints, emulsions, etc, we need the interaction of the fluid molecules and colloidal particles. When two big colloidal particles or surfaces approach each other closer than a few nanometers, the structure of the confined fluid can differ dramatically from that in the bulk. Common to these processes is the presence of fluid films that are under strong influence of confining colloidal particles or walls. The solvation force is the normal force exerted by the fluid on the confining walls. This force has a complicated dependance on potential between particles, density, temperature, and distance separation of colloidal particles (Verwey et al., 1948; Moradi and Kavosh, 2001a; Lajovie and Jamnik, 2007). Since the size of the colloid particles, from the microscopic viewpoint is very large compared with the size of the fluid molecules, the boundary between fluid particles can be assumed to be flat (Grimson et al., 1980; Archer, 2003). Thus to find the solvation force, we suppose two large parallel plates filled with the fluid. At first, we calculate the density profile of the fluid confined by parallel walls and then we use this density profile to find the solvation force.

In the last two decades, many theoretical methods have been proposed to discuss the properties of inhomogeneous fluids (Olesky and Hansen, 2006; Zhou, 2009; Roth et al., 2002). Yi and Kim (1997) used the density functional perturbative approximation and calculated density profiles of the hard-sphere attractive Yukawa fluid confined by parallel walls. Having compared the results with modified version of the Lovett-Mou-Buff-Wertheim (LMBW-1) and computer simulation. Jong-Ho Yi showed that the density functional perturbative approximation is better than the LMBW-1 due to its reasonably good agreement with the computer simulation (Yi and Kim, 1997). This theory is based on both the weighted-density approximation (WDA) of Tarazona (1985) and the density functional approximation (DFA) of Rickayzen and Augousti (1984).

In this article, we first use this theory to find the density profile of hard-sphere Yukawa fluid at various temperatures as well as wall potentials and then we calculate the corresponding solvation force.

DENSITY FUNCTIONAL PERTURBATIVE APPROXIMATION

To obtain solvation force, the density profile of a fluid confined by the walls is required. We consider the hard-sphere Yukawa fluid confined between two parallel planar walls separated by distance *h*.

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The grand canonical potential, $\Omega[\rho]$, at temperature T and one-particle density $\rho(\mathbf{r})$, is given by (Moradi and Kavosh, 2001a),

$$\Omega[\rho] = F_{ex}[\rho] + \int d\mathbf{r}\rho(\mathbf{r})[U(\mathbf{r}) - \mu] + \beta^{-1}\int d\mathbf{r}\rho(\mathbf{r})\{\ln[\Lambda^3\rho(\mathbf{r})] - 1\} \quad (1)$$

Where $F_{ex}[\rho]$ is the excess free energy functional originated from the particle interaction, $U(\mathbf{r})$ the external potential, μ the equilibrium chemical potential of the system, $\beta = 1/k_BT$, and Λ the thermal de Broglie wavelength. With the minimization of the grand canonical potential respect to $\rho(\mathbf{r})$ we have,

$$\frac{\delta\Omega[\rho]}{\delta\rho(\mathbf{r})} = 0 \Rightarrow \ln[\Lambda^3\rho(\mathbf{r})] + \beta\frac{\delta F_{ex}[\rho]}{\delta\rho(\mathbf{r})} + \beta[U(\mathbf{r}) - \mu] = 0 \quad (2)$$

If we use the definition of one-particle direct correlation function (DCF) of the inhomogeneous fluid,

$$c^{(1)}(\mathbf{r};[\rho]) = -\beta\frac{\delta F_{ex}[\rho]}{\delta\rho(\mathbf{r})} \quad (3)$$

we will have

$$\rho(\mathbf{r}) = \Lambda^{-3}e^{\beta\mu}\exp[-\beta U(\mathbf{r}) + c^{(1)}(\mathbf{r};[\rho])] \quad (4)$$

For the homogeneous bulk density, $\rho_\circ$, of the system, Equation (4) becomes

$$\rho_\circ = \Lambda^{-3}e^{\beta\mu}\exp[c^{(1)}(\rho_\circ)] \quad (5)$$

where $c^{(1)}(\rho_\circ)$ is one-particle DCF of the homogeneous fluid. By combining Equations (4) and (5), one obtains the density profile equation as follows.

$$\rho(\mathbf{r}) = \rho_\circ\exp[-\beta U(\mathbf{r}) + c^{(1)}(\mathbf{r};[\rho]) - c^{(1)}(\rho_\circ)] \quad (6)$$

To calculate the density profile, the external potential and the DCF of the hard-sphere Yukawa fluid can be divided into the hard-sphere part (*hs*) and the attractive part (*att*), such as

$$\rho(\mathbf{r}) = \rho_\circ\exp[-\beta U_{hs}(\mathbf{r}) + c_{hs}^{(1)}(\mathbf{r};[\rho]) - c_{hs}^{(1)}(\rho_\circ)]$$
$$\times\exp[-\beta U_{att}(\mathbf{r}) + c_{att}^{(1)}(\mathbf{r};[\rho]) - c_{att}^{(1)}(\rho_\circ)] \quad (7)$$

We, on the one hand, used the WDA of Tarazona for calculating the hard-sphere part, which is known to give excellent results (Tarazona, 1985; Moradi and Kavosh, 2001b; Moradi and Kavosh, 2001c) and on the other hand, the modified hyper-netted chain approximation, proposed by Rickayzen and Augousti (1984) to calculate the attractive part.

In the WDA of Tarazona the DCF of a hard-sphere fluid is given as (Roth et al., 2002):

$$c(\mathbf{r},\mathbf{r}') = -\frac{2\Delta\psi'(\rho_\circ)}{k_BT}\left.\frac{\delta\bar{\rho}(\mathbf{r})}{\delta\bar{\rho}(\mathbf{r}')}\right|_{\rho_\circ} - \frac{\Delta\psi''(\rho_\circ)\rho_\circ}{k_BT}\int d\mathbf{r}''\left.\frac{\delta\bar{\rho}(\mathbf{r}'')}{\delta\bar{\rho}(\mathbf{r})}\right|_{\rho_\circ}\left.\frac{\delta\bar{\rho}(\mathbf{r}'')}{\delta\bar{\rho}(\mathbf{r}')}\right|_{\rho_\circ}$$
$$-\frac{\Delta\psi'(\rho_\circ)\rho_\circ}{k_BT}\int d\mathbf{r}''\left.\frac{\delta^2\bar{\rho}(\mathbf{r}'')}{\delta\bar{\rho}(\mathbf{r}')\delta\bar{\rho}(\mathbf{r}'')}\right|_{\rho_\circ} \quad (8)$$

Where $\Delta\psi'(\rho_\circ)$ and $\Delta\psi''(\rho_\circ)$ are the first and second derivatives of the excess free energy per particle, with respect to $\bar{\rho}(\mathbf{r})$ in the bulk. The excess free energy per particle is derived from the quasi-exact Carnahan Starling equation of state (Carnahan and Starling, 1970). To avoid purely local treatment of narrow peaks in $\rho(\mathbf{r})$ and to reach a really good description of direct correlation, Tarazona (1985) suggested and applied the function $\bar{\rho}(\mathbf{r})$ as

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}\bar{\rho}(\mathbf{r})w(|\mathbf{r} - \mathbf{r}'|, \bar{\rho}(\mathbf{r})) \quad (9)$$

where the, $w(|\mathbf{r} - \mathbf{r}'|, \bar{\rho}(\mathbf{r}))$ is a weight function and normalizes to unit (Moradi and Kavosh, 2001b; Kim and Suh, 1997).

Rickayzen and Augousti (1984) expanded DCF around bulk density. Their expansion considers DCF up to the second order term, that is:

$$c_{att}^{(1)}(\mathbf{r};[\rho]) = c_{att}^{(1)}(\rho_\circ) + \int d\mathbf{s}c_{att}^{(2)}(|\mathbf{r} - \mathbf{s}|;\rho_\circ)[\rho(\mathbf{s}) - \rho_\circ]$$
$$+\frac{1}{2}\int d\mathbf{s}\int d\mathbf{t}c_{att}^{(3)}(\mathbf{r},\mathbf{s},\mathbf{t},\rho_\circ)[\rho(\mathbf{s}) - \rho_\circ][\rho(\mathbf{t}) - \rho_\circ] + \cdots \quad (10)$$

In this approximation, we need to know two-particle and three-particle DCFs. For the two-particle DCF we have

$$c_{att}^{(2)}(r;\rho_\circ) = c_{Yu}^{(2)}(r;\rho_\circ) - c_{hs}^{(2)}(r;\rho_\circ) \quad (11)$$

Where $c_{hs}^{(2)}(r;\rho_\circ)$ is the two-particle DCF of hard-sphere system and is calculated of the Percus-Yevick approximation for the hard sphere fluid (Percus and Yevick, 1958). The first part, that is, $c_{Yu}^{(2)}(r;\rho_\circ)$ is the two-particle DCF of the hard-sphere Yukawa fluid, which is calculated within the mean filed spherical approximation and yields quite a good result up to higher densities (Yi and Kim, 1997; Waisman, 1973; Hoye and Stell, 1976).

$$c_{Yu}^{(2)}(r;\rho_\circ) = a - br/\sigma - \eta ar^3/2\sigma^3 - v\sigma[1 - \exp(-\lambda r/\sigma)]/\lambda r \quad (12)$$
$$- v^2\sigma^2[\cosh(\lambda r/\sigma) - 1]/[2\beta\varepsilon_f\lambda^2\exp(\lambda)]r \qquad r < \sigma$$
$$= \beta\varepsilon_f\sigma\exp[-\lambda(r - \sigma)/\sigma]/r \qquad r > \sigma$$

where σ is the diameter of the hard sphere fluid particles and a, b, v and others are parameters which are defined implicitly (Olivars-Rivas et al., 1997). However, the three-particle DCF is not known, but it is not very sensitive when the separation of any two of the coordinates, $|\mathbf{r}-\mathbf{u}|$, is greater than a molecular diameter. In the density functional approximation of Rickayzen and Augousti (1984), they chose three-particle DCF in the following simple form (Yi and Kim, 1997):

$$c_{att}^{(3)}(\mathbf{r},\mathbf{s},\mathbf{t},\rho_\circ) = B\left(\frac{6}{\pi\sigma^3}\right)^3\int d\mathbf{u}\theta\left(\frac{\sigma}{2} - |\mathbf{r} - \mathbf{u}|\right)\theta\left(\frac{\sigma}{2} - |\mathbf{s} - \mathbf{u}|\right)\theta\left(\frac{\sigma}{2} - |\mathbf{t} - \mathbf{u}|\right) = BL_1 \quad (13)$$

where $\theta(x)$ is the Heaviside step function and parameter B is a constant. We should choose B in such a way that it provides us with the exact pressure, P, in the equation of state for the homogeneous bulk fluid. Then, we obtain

$$B = \frac{\rho_\circ^2\beta\Delta\psi'(\rho_\circ) + \rho_\circ - \frac{1}{2}\rho_\circ^2\int dr\, c_{att}^{(2)}(r;\rho_\circ) - \beta P}{\rho_\circ^3 L_1} \quad (14)$$
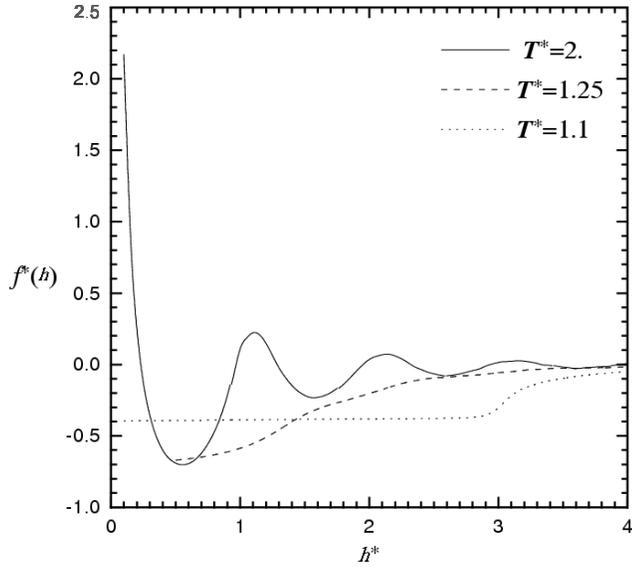
Figure 1. Solvation force of a hard-sphere Yukawa fluid confined between hard walls as a function of reduced separation of the walls, $h^* = h/\sigma$, for $\rho_\circ^* = \rho_\circ \sigma^3 = 0.7$ and the reduced temperatures given on the figure.

After combining Equations 7 to 14 together and the application of numerical iteration we can calculate density profiles of the hard-sphere Yukawa fluid.

SOLVATION FORCE

Solvation force, f_s, is equal to the normal pressure between the walls, but we should note that the external potential and the fluid number density varies along one dimension only, say, the z direction. Thus, the external potential is given by

$$U(z) = \begin{cases} u_{ext}(z) + u_{ext}(h-z) & 0 \langle z \langle h \\ 0 & otherwise \end{cases} \quad (15)$$

where $u_{ext}(z)$ is the wall potential. In the ensemble or time average, force per unit area exerted by the fluid on each wall is (Moradi and Kavosh, 2001a; Magda et al., 1985):

$$f_s = \frac{-1}{2A} \left\langle \sum_{i=1}^{N} \left[\frac{du_{ext}(z_i)}{dz_i} + \frac{du_{ext}(h-z_i)}{dz_i} \right] \right\rangle, \quad (16)$$

where the pointed bracket denotes an ensemble average. We write the solvation force in terms of the number density as:

$$f_s(h) = -\int_0^h \rho(z) \frac{du_{ext}(z)}{dz} dz = -\int_0^{h/2} \rho(z) \frac{du_{ext}(z)}{dz} dz - \int_0^{h/2} \rho(z) \frac{du_{ext}(h-z)}{dz} dz. \quad (17)$$

If the number density and the wall potential are given, the solvation force could be obtained. When $u_{ext}(z)$ is zero, that is, when the fluid is confined by hard walls, the solvation forces is (Grimson and Rickayzen, 1982; Moradi and Kavosh, 1999):

$$f_s(h) = \frac{\rho(h) - \rho(\infty)}{\beta} \quad (18)$$

where $\rho(h)$ and $\rho(\infty)$ are the densities at the hard walls where the distances between the walls is h and infinity respectively.

RESULTS AND DISCUSSION

We solve the integral Equation (7) to find the density profile of a hard-sphere Yukawa fluid for the reduced bulk density $\rho_\circ^* = \rho_\circ \sigma^3 = 0.7$ and at given reduced temperatures, $T^* = 1/\beta\varepsilon_f$, 2.0, 1.25 and 1.1 for different wall separations. Two types of the wall-fluid interaction, βu_{ext}, have been considered.

Hard-sphere Yukawa fluid confined between hard walls

In this case the interaction between the wall and the fluid is

$$u_{ext}(z) = \begin{cases} 0 & z \rangle 0 \\ \infty & z \rangle 0 \end{cases} \quad (19)$$

The solvation force in this case can be obtained from Equation (18). The reduced solvation force $f^*(h) = \beta f_s(h)\sigma^3$, as a function of reduced distance between walls, $h^* = h/\sigma$, is plotted in Figure 1. As the figure shows, at lower temperatures, the reduced solvation force is negative and if the separation of the walls is increased, the solvation force tends toward zero. At high temperature, the trend towards zero is still the same but the changing pattern is oscillatory.

Hard-sphere Yukawa fluid confined between walls with an attractive tail

In this case the interaction between the wall and the fluid is given by

$$u_{ext}(z) = \begin{cases} 0 & z \rangle 0 \\ -\beta\varepsilon_w \exp[-\lambda z/\sigma] & z \rangle 0 \end{cases} \quad (20)$$

where in these calculations we choose $\varepsilon_w = 5\varepsilon_f$. The solvation force in this case can be obtained from Equation (17). In this calculation when the separation of the walls goes to 6σ, the solvation force approaches to zero. To minimize the errors, we calculate shifted and reduced solvation force, $f^*(12) = (f_s(z) - f_s(12))\sigma^3/\varepsilon_w$, as a function of the reduced separation of the walls, h^*. The results are plotted in Figure 2. As it is indicated by Figures 1 to 3, the solvation force depends on the temperature and on the wall potential.
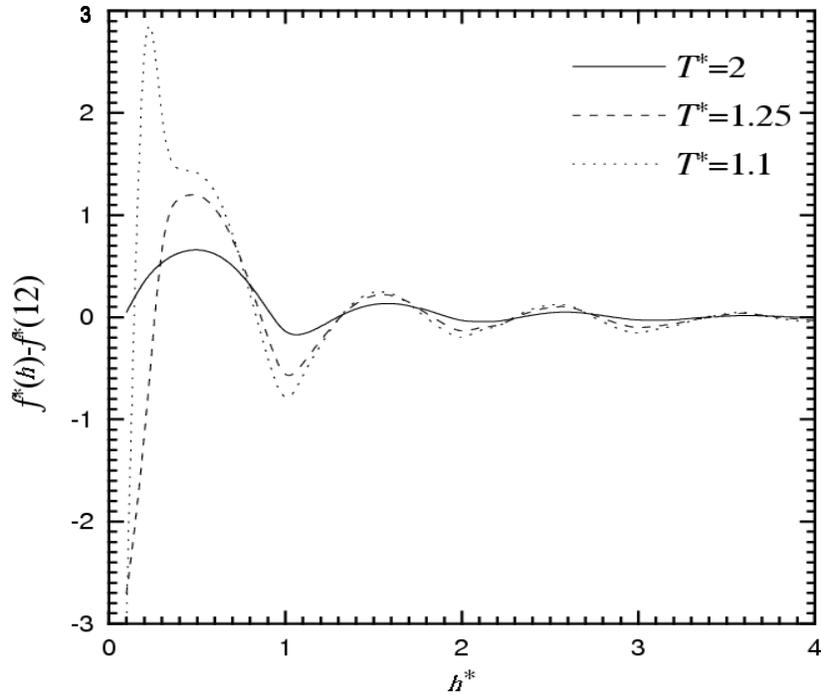
Figure 2. Shifted and reduced solvation force, $f^*(z)$- $f^*(12)$, for a hard-sphere Yukawa fluid confined between walls with an attractive tail as a function of $h^* = h/\sigma$, for $\rho_{\circ}^* = \rho_{\circ}\sigma^3 = 0.7$ and the reduced temperatures given on the figure.
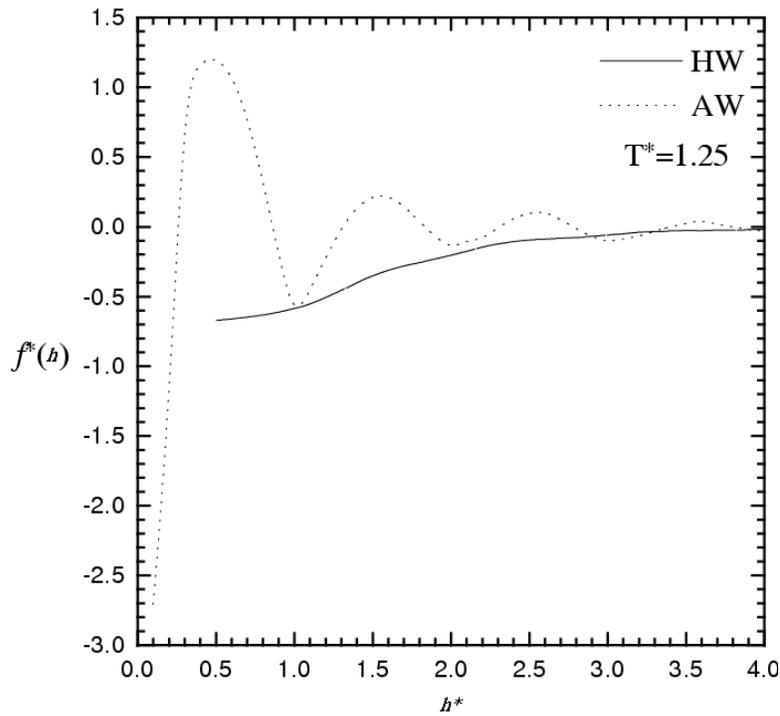
Figure 3. Solvation force as a function of reduced separation of the walls, $h^* = h/\sigma$, for $\rho_{\circ}^* = \rho_{\circ}\sigma^3 = 0.7$ and reduced temperatures T^*=1.25. The solid line corresponds to the hard walls, and dotted line to attractive Yukawa walls.

Conclusions

We performed simulations in the grand canonical ensemble of a hard-sphere Yukawa fluid confined between two parallel planar walls separated by distance *h*. We computed the solvation force exerted by the fluid on the walls. We found a large difference in the solvation force for hard-sphere Yukawa fluid confined between hard walls and attractive tail walls. For hard-sphere Yukawa fluid confined between hard walls, we found at high temperature an oscillatory behaviour in the solvation force with periodicity close to the diameter of the hard sphere fluid, but with decrease temperature, the oscillations are decreased and solvation force is shifted to the attractive region in Figure 1. However, we see oscillatory behaviour in hard-sphere Yukawa fluid confined between attractive tail walls even in low temperatures. In addition, when we increase the distance between the walls, we find that the density profile becomes broader and then the solvation force decreases. When the distance between the walls is greater than 8 times the particle diameter the fluid particles, the pressure exerted by the fluid on the walls is equal to the pressure exerted by the fluid outside the plates. As was mentioned in the introduction, if we can find the solvation force, we can get the required information about the particles' interactions in the corresponding colloid system.

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