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Structural properties of confined sticky hard-sphere fluids

Ji-Young Hwang and Soon-Chul Kim
Department of Physics, Andong National University, Andong, 760-749 Korea

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A simple density-functional approximation, which is based on both the hybrid weighted-density approximation of Leidl and Wagner and the density-functional approximation of Calleja *et al.*, has been developed to study the structural properties of sticky hard-sphere fluids. The approximation has been applied to calculate the density profiles of sticky hard-sphere fluids confined in structureless hard walls, and the results have been compared with those from the available computer simulation and some other approximations. The calculated density profiles have shown that the approximation is better than the Choudhury-Ghosh and Kim-Suh approximations, and they compare very well with the results from the computer simulation. [S1063-651X(98)09206-X]

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Over the last decade, numerical studies have addressed problems involving model fluids confined in special symmetrical systems [1,2]. It is known that for confined hard-sphere fluids, the weighted-density approximations [3,4] describe their structural properties very well compared with the well-known standard integral equations. However, at the lower temperature the weighted-density approximations fail to describe the structural properties of the real systems with the attractive potential. For example, for the confined sticky hard-sphere fluid the weighted-density approximations yield very poor results at the lower τ values compared with the computer simulation, where τ is the stickiness parameter related to the strength of adhesion and to the temperature of the system [5]. It is actually very difficult to use the usual perturbation theories [6] of a liquid for a sticky hard-sphere fluid because of the special intermolecular potential $\phi(r)$;

$$\exp[-\beta\phi(r)] = \frac{R}{12\tau}\,\delta(r-R^{-}) + \theta(r-R), \tag{1}$$

where R is the diameter of the sticky hard sphere, $\delta(x)$ Dirac's delta function, and $\theta(x)$ the Heaviside step function. Thus relatively few studies have yet considered the structural properties of the confined sticky hard-sphere fluid. Jamnik and Bratko [7,8] studied the wall-fluid correlations on the basis of the solution to the Percus-Yevick–Ornstein-Zernike equation to predict the density profiles of sticky hard-sphere fluid confined in structureless hard walls. Choudhury and Ghosh [9,10] proposed the simple density-functional approximation, which is based on both the higher-order weighted-density approximation for the reference term and the density-functional Taylor series expansion of one-particle direct correlation function for the remaining contribution, to study the structural properties of the confined sticky hard-sphere fluid. They have shown that for the strong adhesiveness these approximations are in poor agreement with the results from the computer simulation. On the other hand, Kim and Suh [11] have recently proposed the density-functional approximation, which is based on both the hybrid weighted-density approximation of Leidl and Wagner [4] and the higher-order weighted-density approximation of Denton and Ashcroft [12], to predict the density profiles of confined sticky hard-sphere fluids. The calculated results have shown that the Kim-Suh approximation is better than the Choudhury-Ghosh approximation. However, for the strong adhesiveness the agreement with the computer simulation slightly deteriorates with increasing fluid densities. Thus we have here addressed these problems.

In this Brief Report, we will develop the density-functional approximation, which is based on both the hybrid weighted-density approximation of Leidl and Wagner for the reference term and the density-functional approximation of Calleja *et al.* [2] for the remaining term, to study the structural properties of sticky hard-sphere fluids. We apply it to predict the density profiles of sticky hard-sphere fluids confined by hard walls and compare with those from some other approximations.

In the density-functional theory, the grand canonical potential $\Omega[\rho]$ and intrinsic (Helmholtz) free energy functional $F[\rho]$, both unique functionals of the one-particle density $\rho(\vec{r})$, are related as

$$\Omega[\rho] = F[\rho] + \int d\vec{r}\;\rho(\vec{r})[u_{\mathrm{ext}}(\vec{r}) - \mu], \tag{2}$$

where μ is the chemical potential of the system and $u_{\mathrm{ext}}(\vec{r})$ an external potential. The equilibrium particle density distribution of the inhomogeneous fluid corresponds to the minimum of the grand canonical potential satisfying $\delta\Omega[\rho]/\delta\rho(\vec{r}) = 0$, which leads to the Euler-Lagrange equation; $\mu - u_{\mathrm{ext}}(\vec{r}) = \delta F[\rho]/\delta\rho(\vec{r})$. For an inhomogeneous fluid in contact with a homogeneous bulk fluid, its chemical potential μ is equal to that of the homogeneous bulk fluid and hence the Euler-Lagrange equation leads to an expression for the density profile equation given by

$$\ln\left[\frac{\rho(\vec{r})}{\rho_b}\right] = -\beta u_{\mathrm{ext}}(\vec{r}) + c^{(1)}(\vec{r};[\rho]) - c^{(1)}(\rho_b), \tag{3}$$

where ρ_b is the homogeneous bulk density of the system, $c^{(1)}(\vec{r};[\rho])$ the one-particle direct correlation function (DCF) for the inhomogeneous fluid, and $c^{(1)}(\rho_b)$ the one-particle DCF for the homogeneous bulk fluid.

However, since the exact form of $c^{(1)}(\vec{r};[\rho])$ is unknown, some kinds of approximations must inevitably be introduced. For this, we follow the basic idea of Choudhury and Ghosh [9], which was proposed to study the structural properties of the confined sticky hard-sphere fluid. We divide the excess free energy functional $F_{\rm ex}[\rho]$ with the reference term $F_{\rm ref}[\rho]$ (hard-sphere-like) and the remaining contribution $\Delta F[\rho]$ as

$$F_{\rm ex}[\rho]=F_{\rm ref}[\rho]+\Delta F[\rho]. \tag{4}$$

As an approximation for the reference term $F_{\rm ref}[\rho]$, we adopt the hybrid weighted-density approximation (HWDA) of Leidl and Wagner [4], which is known to give excellent results for the hard-sphere system and is computationally easier than the weighted-density approximations based on the local density [3]. In the HWDA theory, $F_{\rm ref}[\rho]$ is assumed as

$$F_{\rm ref}[\rho]=\int d\vec{r}\ \rho(\vec{r})f_{\rm ref}[\overline{\rho(\vec{r})}], \tag{5}$$

where

$$\overline{\rho(\vec{r})}=\int d\vec{s}\ \rho(\vec{s})\omega(|\vec{r}-\vec{s}|,\hat{\rho}[\rho]), \tag{6}$$

with

$$\hat{\rho}[\rho]=\frac{1}{N}\int d\vec{r}\ \rho(\vec{r})\int d\vec{s}\ \rho(\vec{s})\omega(|\vec{r}-\vec{s}|,\hat{\rho}[\rho]), \tag{7}$$

where $\omega(|\vec{r}-\vec{s}|,\rho)$ is the weighting function for the reference term, N the number of particles of the system, and $f_{\rm ref}(\rho)$ the free energy per particle. The weighted densities $\overline{\rho(\vec{r})}$ and $\hat{\rho}[\rho]$ become the homogeneous bulk density ρ_b for the homogeneous system.

A unique specification of $\omega(|\vec{r}-\vec{s}|,\rho_b)$ follows from requiring that the defining relationship between the two-particle DCF $c^{(2)}_{\rm ref}(|\vec{r}-\vec{s}|,\rho_b)$ and the second functional derivative of $F_{\rm ref}[\rho]$ with respect to $\rho(\vec{r})$ be as follows:

$$\begin{aligned}c^{(2)}_{\rm ref}(|\vec{r}-\vec{s}|,\rho_b)=&-2\beta f'_{\rm ref}(\rho_b)\omega(|\vec{r}-\vec{s}|,\rho_b)\\&-\rho_b\beta f''_{\rm ref}(\rho_b)\int d\vec{t}\ \omega(|\vec{r}-\vec{t}|,\rho_b)\\&\times\omega(|\vec{t}-\vec{s}|,\rho_b),\end{aligned} \tag{8}$$

where the prime denotes the derivative with respect to the density ρ_b. Then, $c^{(2)}_{\rm ref}(|\vec{r}-\vec{s}|,\rho_b)$ is related to the two-particle DCF $c^{(2)}(|\vec{r}-\vec{s}|,\rho_b)$ as

$$c^{(2)}_{\rm ref}(|\vec{r}-\vec{s}|,\rho_b)=c^{(2)}(|\vec{r}-\vec{s}|,\rho_b)-\Delta c^{(2)}(|\vec{r}-\vec{s}|,\rho_b), \tag{9}$$

where $\Delta c^{(2)}(|\vec{r}-\vec{s}|,\rho_b)$ is the two-particle DCF corresponding to the remaining contribution. We can also decompose the corresponding one-particle DCF $c^{(1)}_{\rm ref}(\rho_b)$ as

$$c^{(1)}_{\rm ref}(\rho_b)=c^{(1)}(\rho_b)-\Delta c^{(1)}(\rho_b), \tag{10}$$

where $\Delta c^{(1)}(\rho_b)$ is the one-particle DCF corresponding to the remaining contribution. In this approximation, the density profile equation, Eq. (3), can be rewritten as

$$\begin{aligned}\ln\left[\frac{\rho(\vec{r})}{\rho_b}\right]=&-\beta u_{\rm ext}(\vec{r})+c^{(1)}_{\rm ref}(\vec{r};[\rho])+\Delta c^{(1)}(\vec{r};[\rho])\\&-c^{(1)}_{\rm ref}(\rho_b)-\Delta c^{(1)}(\rho_b),\end{aligned} \tag{11}$$

where the one-particle DCFs $c^{(1)}_{\rm ref}(\vec{r};[\rho])$ and $c^{(1)}_{\rm ref}(\rho_b)$ become, from Eqs. (5)–(7),

$$\begin{aligned}c^{(1)}_{\rm ref}(\vec{r};[\rho])=&-\beta f_{\rm ref}[\overline{\rho(\vec{r})}]-\int d\vec{s}\ \rho(\vec{s})\beta f'_{\rm ref}[\overline{\rho(\vec{s})}]\\&\times\omega(|\vec{r}-\vec{s}|,\hat{\rho}[\rho]),\end{aligned} \tag{12}$$

and

$$c^{(1)}_{\rm ref}(\rho_b)=-\beta f_{\rm ref}(\rho_b)-\rho_b\beta'_{\rm ref}(\rho_b). \tag{13}$$

As the approximation for the remaining term $\Delta c^{(1)}(\vec{r};[\rho])$, we introduce the density-functional approximation of Calleja *et al.* and Kim and Suh [2,13], which is based on the density-functional Taylor series expansion of the excess free energy functional corresponding to the remaining contribution. If we retain terms only up to the second order in the functional Taylor series expansion, one obtains the one-particle DCF $\Delta c^{(1)}(\vec{r};[\rho])$, after some manipulation,

$$\begin{aligned}\Delta c^{(1)}(\vec{r};[\rho])=&\Delta c^{(1)}(\rho_b)+\int d\vec{s}\ \Delta c^{(2)}(|\vec{r}-\vec{s}|,\rho_b)\\&\times[\rho(\vec{s})-\rho_b]+3\int d\vec{s}\int d\vec{t}\ L(\vec{r},\vec{s},\vec{t})\\&\times[\rho(\vec{s})-\rho_b][\rho(\vec{t})-\rho_b],\end{aligned} \tag{14}$$

where the kernel $L(\vec{r},\vec{s},\vec{t})$ is related to the three-particle DCF of the system [13,14]. It is noted that with $L(\vec{r},\vec{s},\vec{t})=0$, Eqs. (11) and (14) lead to the Choudhury-Ghosh approximation. However, the three-particle DCF is not known so we need an approximation for the kernel $L(\vec{r},\vec{s},\vec{t})$. In fact, it appeared that the kernel $L(\vec{r},\vec{s},\vec{t})$ is not very sensitive when the separation of any two of the coordinates, $|\vec{r}-\vec{s}|$, is greater than a molecular diameter R. Thus we have chosen a practically simple form as

$$L(\vec{r},\vec{s},\vec{t})=B\int d\vec{u}\ a(|\vec{r}-\vec{u}|)a(|\vec{s}-\vec{u}|)a(|\vec{t}-\vec{u}|), \tag{15}$$

with

$$a(r)=\frac{6}{\pi R^3}\theta\left(\frac{R}{2}-r\right). \tag{16}$$

The constant B, which depends on the properties of the homogeneous bulk fluid, is determined by the equation of state of the system [13]

$$\beta P=\rho_b+\rho_b^2\beta f'_{\rm rep}(\rho_b)-\frac{\rho_b^2}{2}\int d\vec{s}\ \Delta c^{(2)}(|\vec{r}-\vec{s}|,\rho_b)+B\rho_b^3, \tag{17}$$

where P is the pressure of the system. Combining Eqs. (11)–(14), one obtains the density profile equation

$$\begin{aligned}\ln\left[\frac{\rho(\vec r)}{\rho_b}\right] =& -\beta u_{\rm ext}(\vec r) - \beta f_{\rm ref}[\overline{\rho}(\vec r)] \\ &- \int d\vec s\ \rho(\vec s)\beta f'_{\rm ref}[\overline{\rho}(\vec s)]\,\omega(|\vec r-\vec s|,\hat\rho) + \beta f_{\rm ref}(\rho_b) \\ &+ \rho_b\beta f'_{\rm ref}(\rho_b) + \int d\vec s\ \Delta c^{(2)}(|\vec r-\vec s|,\rho_b) \\ &\times[\rho(\vec s)-\rho_b] + 3B\int d\vec s\ a(|\vec r-\vec s|)\,\overline{\delta\rho(\vec s)^2}, \qquad (18)\end{aligned}$$

where

$$\overline{\delta\rho(\vec r)^2} = \left[\int d\vec s a(|\vec r-\vec s|)[\rho(\vec s)-\rho_b]\right]^2. \qquad (19)$$

Let us consider the fluid confined in planar slits consisting of two walls located at $z=-L/2-R/2$ and $z=L/2+R/2$, where the walls are parallel to the plane $(x,y,0)$. In this case, the fluid-wall interaction $\beta u_{\rm ext}(z)$ is given by a hard core one,

$$\beta u_{\rm ext}(z) = \begin{cases} 0 & \text{for } -L/2<z<L/2 \\ \infty & \text{otherwise.}\end{cases} \qquad (20)$$

Due to the planar symmetry of the problem the density distribution varies only along the z direction; $\rho(\vec r)=\rho(z)$ and $\overline{\rho}(\vec r)=\overline{\rho}(z)$.

To calculate the density profiles of the sticky hard-sphere fluid confined in hard walls, Baxter's Percus-Yevick (PY) expression for the two-particle DCF $c^{(2)}(r,\rho_b)$ of sticky hard-sphere fluid in the homogeneous phase has been used [5]. Following the suggestion of Choudhury and Ghosh [9], we have chosen the reference term (hard-sphere-like) and the remaining contribution as

$$c^{(2)}_{\rm ref}(r,\rho_b) = \left[-A_0 - A_1\left(\frac{r}{R}\right) - \frac{\eta}{2}A_0\left(\frac{r}{R}\right)^3\right]\theta(R-r), \qquad (21)$$

and

$$\Delta c^{(2)}(r,\rho_b) = -\frac{\eta}{12}\lambda^2\left(\frac{R}{r}\right)\theta(R-r) + \frac{\lambda}{12}\,\delta(r-R^-), \qquad (22)$$

where $\eta=\pi\rho_b R^3/6$ is the packing fraction, $A_0=(1+2\eta-\xi)^2/(1-\eta)^4$, $A_1=-3\eta(2+\eta)^2+2\xi(1+7\eta+\eta^2)-\xi^2(2+\eta)/2(1-\eta)^4$, $\xi=\lambda\eta(1-\eta)$, $\lambda=6/\eta[\nu-(\nu^2-\gamma)^{1/2}]$, $\nu=\tau+\eta/(1-\eta)$, and $\gamma=\eta(2+\eta)/6(1-\eta)^2$. To calculate the constant B, the equation of state [15] for the sticky hard-sphere fluid, via the compressibility equation, has been used:

$$\frac{\beta P}{\rho_b} = \frac{1+\eta+\eta^2}{(1-\eta)^3} - \frac{\xi(2+\eta)}{2(1-\eta)^3} + \frac{\xi^3}{36\eta(1-\eta)^3}. \qquad (23)$$

The compressibility sum rule has been used to calculate the excess free energy $f_{\rm ref}(\rho_b)$ corresponding to the reference term [15]. The weighting function $\omega(r,\rho_b)$ has numerically been obtained by solving Eq. (8) for the known $f_{\rm ref}(\rho_b)$ and $c^{(2)}_{\rm ref}(r,\rho_b)$. The integrals have been performed by the trapezoidal method with spacing $\Delta z=0.01$. The iteration is stopped when the successive values, $\rho_n(z)R^3$, $\rho_{n+1}(z)R^3$ of the density profile satisfy $\int_{-L/2R}^{L/2R} d(z/R)[\rho_{n+1}(z)R^3-\rho_n(z)R^3]^2<10^{-10}$.

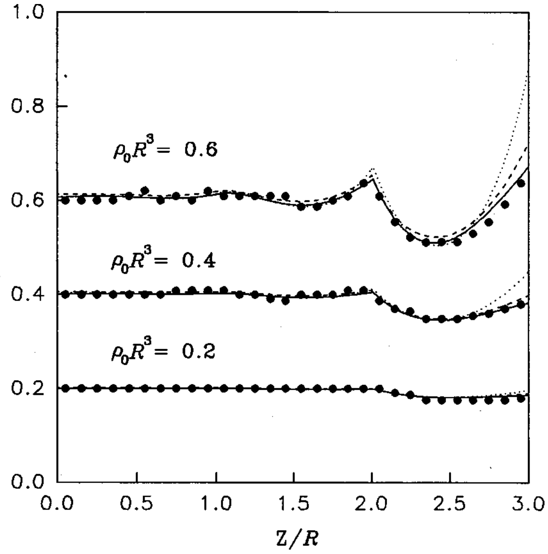

FIG. 1. Density profiles of the sticky hard-sphere fluid confined in the gap of width $L=6R$ hard walls at different bulk density $\rho_b R^3$ $(=0.6$, 0.4, and 0.2) with the strong adhesiveness $\tau(=0.2)$. The solid circles are taken from the computer simulation [8]. The solid lines correspond to the present approximation. The dotted lines and dashed lines correspond to the Choudhury-Ghosh (the present approximation with $B=0$) [9] and the Kim-Suh approximations [11], respectively.

The resulting density profiles for the confined sticky hard-sphere fluid $\rho(z)R^3$ with the gap of width $L=6R$ have been displayed against z/R at three different values of the bulk densities $\rho_b R^3(=0.2$, 0.4, and 0.6) with the strong adhesiveness $\tau(=0.2)$ in Fig. 1 and compared with those from the

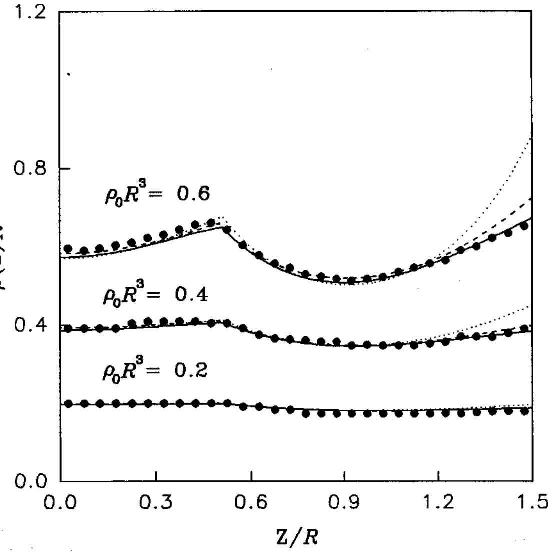

FIG. 2. As for Fig. 1 except that the gap is $L=3R$.

computer simulation. It is noted that in the original Choudhury-Ghosh approximation Choudhury and Ghosh [9] used the higher-order weighted-density approximation [12] based on the approximation of the one-particle direct correlation functional. It is known that for the hard-sphere fluid the HWDA is better than the higher-order weighted-density approximation of Denton and Ashcroft. As can be seen from Fig. 1, the Choudhury-Ghosh approximation is less satisfactory even for the lower densities. Figure 1 also shows that the present approximation is better than the Kim-Suh approximation and comparable with the computer simulation; the Kim-Suh approximation yields higher values of the fluid density at the walls compared with the computer simulation. The good agreement with the computer simulation perhaps comes from the fact that the strength parameter B in Eq. (18) is chosen to satisfy the equations of state, Eq. (17), for the homogeneous sticky hard-sphere fluid. The above choice of B ensures that if ρ_w is the liquid wall density at a hard wall, the exact relation, $\beta P_w = \rho_w$, is satisfied when the wall separation L goes to infinity. This indicates that for the confined sticky hard-sphere fluid the present approximation provides a proper representation of the intermolecular correlation.

In Fig. 2, the calculated density profiles of the sticky hard-sphere fluid confined in a planar wall with a gap of $L=3R$ have been displayed. The calculated results also show that the present approximation is better than the Kim-Suh approximation and compares with the computer simulation; at higher densities the Choudhury-Ghosh and Kim-Suh approximations yield higher values of the fluid density near the hard wall compared with the computer simulation and the disagreement with the computer simulation deteriorates with the increase of the strength adhesiveness. Once again, for the confined sticky hard-sphere fluid the present approximation yields reasonably good results compared with the computer simulation, whereas for the Choudhury-Ghosh and Kim-Suh approximations the agreements get worse at the hard walls. On the other hand, the above result indicates that the present success will provide impetus to extend the density-functional approach to the study of inhomogeneous fluids with anisotropic adhesion or to more realistic interaction potentials. Further investigation for these realistic systems is in progress.

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