

## Density functional approximations for confined classical fluids

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(Received 14 May 1998)

A density functional approximation, which is based on both the density functional Taylor series expansion of the one-particle direct correlation function and the exact contact value theorem for a hard wall, has been proposed to study the structural properties of confined classical fluids. The approximation has been applied to calculate the density profiles of sticky hard-sphere fluids confined in structureless hard walls. The calculated density profiles have shown that the present approximation compares very well with the results from the computer simulation. Furthermore, a density functional perturbative approximation, which is based on both the weighted-density approximation for the repulsive part of potential and the present approximation for the attractive part of potential, has been developed to predict the density profiles of model fluids with the attractive part of potential and has been applied to calculate the density profiles of hard-sphere Yukawa fluids near a planar slit. The calculated results also show that the proposed perturbative approximation is a significant improvement upon those of the modified version of the Lovett-Mou-Buff-Wertheim, and compares very well with the computer simulation. [S1063-651X(98)04210-X]

PACS number(s): 61.20.Gy, 61.20.Ne

### I. INTRODUCTION

The structural properties of fluid confined in special symmetrical systems have been a subject of long-standing theoretical and practical interest [1,2]. Many theoretical methods have been proposed to describe the structural properties of confined model fluids. It is known that the density functional approximations simulate the structural properties of confined fluids reasonably well compared with the 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 such as a confined sticky hard-sphere fluid. Thus, relatively few studies have yet been considered for the structural properties of a confined sticky hard-sphere fluid. Jamnik *et al.* [3,4] had studied the wall-fluid correlations on the basis of the solution to the Percus-Yevick-Ornstein-Zernike equation to study the density profiles of sticky hard-sphere fluids confined in hard walls. Kim and Suh [5] have recently used the density functional perturbative approximation, which is based on both the hybrid weighted-density approximation of Leidl and Wagner [6] and the higher-order weighted-density approximation of Denton and Ashcroft [7], to calculate the density profiles of confined sticky hard-sphere fluids. They have shown that the Kim-Suh approximation is better than the Choudhury-Ghosh approximation [8,9], 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. However, for the strong adhesiveness the agreement with the computer simulation is slightly unsatisfactory. Thus, we here address these problems and propose a simple density functional approximation based on the contact value theorem for a hard wall to study the structural properties of confined sticky hard-sphere fluids.

For model systems with the attractive part of the potential, the most successful class of approximate theories both from the point of view of numerical accuracy and of intuitive appeal is the density functional perturbative approximations based on the liquid theory. Among many different approximations, Kim and Suh [10] have recently developed the density functional perturbative approximation, which can be considered as the extended Choudhury-Ghosh approximation [8,9], to study the structural properties of confined model fluids. They [10,11] have shown that the proposed approximation well describes the structural properties of confined square-well and hard-sphere Yukawa fluids with the attractive potential compared with the computer simulation. In this approximation, the constant “*B*” appearing in the density profile equation is determined to satisfy the equation of state of a model system. Here, one interesting thing is that the exact contact value theorem for a hard wall can be used to determine the constant “*B*” appearing in the density functional perturbative approximation. Another is whether or not the density functional perturbative approximation based on the contact value theorem for a hard wall describes well machinery results compared with those of other approximations.

The purpose of the present paper is to develop the density functional approximation and the density functional perturbative approximation, which are based on both the density functional Taylor series expansion of one-particle direct correlation function and the contact value theorem for a hard wall, to study the density profiles of confined sticky hard-sphere and hard-sphere Yukawa fluids. In Sec. II, we propose the density functional approximation for simple fluids and the density functional perturbative approximation for model fluids with the attractive potential. We apply, in Sec. III, the proposed approximations to calculate the density profiles of confined sticky hard-sphere and hard-sphere Yukawa fluids, and compare their results with those of other approximations. Finally, we briefly discuss the strengths and weaknesses of the proposed approximations in actual applications.

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## II. THEORY

### A. Density functional approximation

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

$$\Omega[\rho] = F[\rho] + \int d\vec{r} \rho(\vec{r}) [u_{\text{ext}}(\vec{r}) - \mu], \quad (1)$$

where  $\mu$  is the equilibrium chemical potential of the system and  $u_{\text{ext}}(\vec{r})$  is an external potential [1]. The intrinsic free energy functional  $F[\rho]$  can be generally written as the ideal contribution  $F_{\text{id}}[\rho]$  plus the excess free energy functional  $F_{\text{ex}}[\rho]$  originating from the particle interaction

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

where  $\beta F_{\text{id}}[\rho] = \int d\vec{r} \rho(\vec{r}) \{\ln[\Lambda^3 \rho(\vec{r})] - 1\}$ ,  $\beta = 1/k_B T$ , and  $\Lambda$  is the thermal de Broglie wavelength.

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,  $\mu - u_{\text{ext}}(\vec{r}) = \delta F[\rho]/\delta\rho(\vec{r})$ . For an inhomogeneous fluid in contact with a homogeneous bulk fluid, its chemical potential  $\mu$  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

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

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

Since the exact form of  $c^{(1)}(\vec{r};[\rho])$  for a model fluid is unknown, some kinds of approximations must inevitably be introduced. For this, we use the density functional Taylor series expansion of the one-particle DCF  $c^{(1)}(\vec{r};[\rho])$  with respect to the bulk density  $\rho_b$ . Then, we obtain

$$c^{(1)}(\vec{r};[\rho]) = c^{(1)}(\rho_b) + \sum_{n=2}^{\infty} \frac{1}{(n-1)!} \int d\vec{s} \cdots \int d\vec{t} c^{(n)}(\vec{s}, \dots, \vec{t}, \rho_b) [\rho(\vec{r}) - \rho_b] \cdots [\rho(\vec{t}) - \rho_b], \quad (4)$$

where  $c^{(n)}(\vec{r}, \dots, \vec{t}, \rho_b)$  is the  $n$ -particle DCF of the system. If we retain terms only up to the second order in the density functional Taylor series expansion, we obtain

$$\begin{aligned} c^{(1)}(\vec{r};[\rho]) &= c^{(1)}(\rho_b) + \int d\vec{s} c^{(2)}(|\vec{r}-\vec{s}|, \rho_b) [\rho(\vec{s}) - \rho_b] \\ &+ \frac{1}{2} \int d\vec{s} \int d\vec{t} c^{(3)}(\vec{r}, \vec{s}, \vec{t}, \rho_b) [\rho(\vec{s}) - \rho_b] \\ &\times [\rho(\vec{t}) - \rho_b]. \end{aligned} \quad (5)$$

However, the three-particle DCF  $c^{(3)}(\vec{r}, \vec{s}, \vec{t}, \rho_b)$  is not known so we need an approximation for the three-particle

DCF. In the density functional approximation proposed by Rickayzen *et al.* [12,13], it appeared that the three-particle DCF  $c^{(3)}(\vec{r}, \vec{s}, \vec{t}, \rho_b)$  is not very sensitive when the separation of any two of the coordinates,  $|\vec{r}-\vec{s}|$ , is greater than a molecular diameter  $R$ . Following the Rickayzen's argument [12,13], we chose a practically simple form as

$$c^{(3)}(\vec{r}, \vec{s}, \vec{t}, \rho_b) = B \int d\vec{u} a(|\vec{r}-\vec{u}|) a(|\vec{s}-\vec{u}|) a(|\vec{t}-\vec{u}|) \quad (6)$$

with

$$a(r) = \frac{6}{\pi R^3} \theta\left(\frac{R}{2} - r\right), \quad (7)$$

where the strength  $B$  is an unknown constant and  $\theta(x)$  the Heaviside step function. In this case, the density profile equation becomes, from Eqs. (3), (5), and (6),

$$\begin{aligned} \ln\left[\frac{\rho(\vec{r})}{\rho_b}\right] &= -\beta u_{\text{ext}}(\vec{r}) + \int d\vec{s} c^{(2)}(|\vec{r}-\vec{s}|, \rho_b) [\rho(\vec{s}) - \rho_b] \\ &+ \frac{B}{2} \int d\vec{s} a(|\vec{r}-\vec{s}|) \overline{\delta\rho(\vec{s})^2}, \end{aligned} \quad (8)$$

with

$$\overline{\delta\rho(\vec{s})^2} = \left[ \int d\vec{t} a(|\vec{s}-\vec{t}|) [\rho(\vec{t}) - \rho_b] \right]^2. \quad (9)$$

To determine a constant  $B$ , we use the exact contact value theorem for a structureless hard wall at  $z = -R/2$ , where  $R$  is the diameter of a model fluid.[1] Due to the planar symmetry, the density distribution varies only along the  $z$  direction:  $\rho(\vec{r}) = \rho(z)$ . The contact value theorem states that

$$\beta P = \rho(z=0), \quad (10)$$

where  $P$  is the pressure of the system. For a structureless planar slit the density profile  $\rho(z=0)$  at a hard wall becomes, from Eq. (8),

$$\begin{aligned} \ln\left[\frac{\rho(z=0)}{\rho_b}\right] &= \int_0^\infty dz' c^{(2)}(z', \rho_b) [\rho(z') - \rho_b] \\ &+ \frac{B}{2} \int_0^\infty dz' a(z') \overline{\delta\rho(z')^2}, \end{aligned} \quad (11)$$

where  $c^{(2)}(z, \rho_b) = 2\pi \int_0^\infty dR R c^{(2)}([R^2 + z^2]^{1/2}, \rho_b)$  and  $a(z) = 2\pi \int_0^\infty dR R a([R^2 + z^2]^{1/2}, \rho_b)$ . Then, Eqs. (10) and (11) yield

$$\frac{B}{2} = \frac{\ln(\beta P/\rho_b) - \int_0^\infty dz' c^{(2)}(z', \rho_b) [\rho(z') - \rho_b]}{\int_0^\infty dz' a(z') \overline{\delta\rho(z')^2}}. \quad (12)$$

Taken together, Eqs. (8) and (12), constitute the density profile equation for the density functional approximation, and provide an exact route to calculating the density profiles of model fluids provided the two-particle DCF  $c^{(2)}(|\vec{r}-\vec{s}|, \rho_b)$  is known. It is noted that in the density functional approximation of Rickayzen *et al.* [12,13], the authors had

used the equation of state,  $\beta P = -\beta\Omega(\rho)/V$ , for the homogeneous phase to determine the constant  $B$  appearing in their approximations.

### B. Density functional perturbative approximation

It is generally known that for model systems with an attractive part of the potential the density functional perturbative approximations well describe the structural properties of confined model fluids compared with the standard integral equations. Following the density functional perturbative theory, the pair interaction potential  $u(r)$  of a model fluid can be divided into the hard-sphere part  $u_{\text{hs}}(r)$  and the attractive part  $u_{\text{att}}(r)$  such as

$$u(r) = u_{\text{hs}}(r) + u_{\text{att}}(r), \quad (13)$$

where the attractive part  $u_{\text{att}}(r)$  is treated as the perturbative term for a hard-sphere part. Then, the one-particle DCF  $c^{(1)}(\vec{r};[\rho])$  can be written as

$$c^{(1)}(\vec{r};[\rho]) = c_{\text{hs}}^{(1)}(\vec{r};[\rho]) + c_{\text{att}}^{(1)}(\vec{r};[\rho]), \quad (14)$$

where  $c_{\text{hs}}^{(1)}(\vec{r};[\rho])$  and  $c_{\text{att}}^{(1)}(\vec{r};[\rho])$  denote the one-particle DCFs corresponding to the hard-sphere and the attractive contributions, respectively. For a homogeneous fluid, Eq. (14) becomes

$$c^{(1)}(\rho_b) = c_{\text{hs}}^{(1)}(\rho_b) + c_{\text{att}}^{(1)}(\rho_b), \quad (15)$$

since  $\rho(\vec{r}) = \rho_b$  for a homogeneous state. In this approximation, the density profile equation becomes, from Eqs. (3), (14), and (15),

$$\ln \left[ \frac{\rho(\vec{r})}{\rho_b} \right] = -\beta u_{\text{ext}}(\vec{r}) + c_{\text{hs}}^{(1)}(\vec{r};[\rho]) - c_{\text{hs}}^{(1)}(\rho_b) + c_{\text{att}}^{(1)}(\vec{r};[\rho]) - c_{\text{att}}^{(1)}(\rho_b). \quad (16)$$

As the approximation for an attractive contribution  $c_{\text{att}}^{(1)}(\vec{r};[\rho])$ , we use the density functional Taylor series ex-

pansion of the one-particle DCF  $c_{\text{att}}^{(1)}(\vec{r};[\rho])$  with respect to the bulk density  $\rho_b$  and retain terms only up to the second order in the density functional Taylor series expansion. Then,  $c_{\text{att}}^{(1)}(\vec{r};[\rho])$  becomes

$$\begin{aligned} c_{\text{att}}^{(1)}(\vec{r};[\rho]) &= c_{\text{att}}^{(1)}(\rho_b) + \int d\vec{s} c_{\text{att}}^{(2)}(|\vec{r}-\vec{s}|, \rho_b) [\rho(\vec{s}) - \rho_b] \\ &\quad + \frac{1}{2} \int d\vec{s} \int d\vec{t} c_{\text{att}}^{(3)}(\vec{r}, \vec{s}, \vec{t}, \rho_b) [\rho(\vec{s}) - \rho_b] \\ &\quad \times [\rho(\vec{t}) - \rho_b]. \end{aligned} \quad (17)$$

Since the exact form of the three-particle DCF corresponding to the attractive contribution is unknown, we chose a simple form as

$$c_{\text{att}}^{(3)}(\vec{r}, \vec{s}, \vec{t}, \rho_b) = B \int d\vec{u} a(|\vec{r}-\vec{u}|) a(|\vec{s}-\vec{u}|) a(|\vec{t}-\vec{u}|). \quad (18)$$

Then, the density profile equation becomes, from Eqs. (6), (16), and (17),

$$\begin{aligned} \ln \left[ \frac{\rho(\vec{r})}{\rho_b} \right] &= -\beta u_{\text{ext}}(\vec{r}) + c_{\text{hs}}^{(1)}(\vec{r};[\rho]) \\ &\quad - c_{\text{hs}}^{(1)}(\rho_b) + \int d\vec{s} c_{\text{att}}^{(2)}(|\vec{r}-\vec{s}|, \rho_b) [\rho(\vec{s}) - \rho_b] \\ &\quad + \frac{B}{2} \int d\vec{s} a(|\vec{r}-\vec{s}|) \overline{\delta\rho(\vec{s})^2}. \end{aligned} \quad (19)$$

Since the constant  $B$  is still unknown, we use the exact contact value theorem for a hard wall;  $\beta P = \rho(z=0)$ . Then, the constant  $B$  is simply given as, after some manipulations,

$$B/2 = \left[ \ln(\beta P/\rho_b) - c_{\text{hs}}^{(1)}(z=0;[\rho]) + c_{\text{hs}}^{(1)}(\rho_b) - \int_0^\infty dz' c_{\text{att}}^{(2)}(z', \rho_b) [\rho(z') - \rho_b] \right] / \left[ \int_0^\infty dz' a(z') \overline{\delta\rho(z')^2} \right], \quad (20)$$

where  $c_{\text{att}}^{(2)}(z, \rho_b) = 2\pi \int_0^\infty dR R c_{\text{att}}^{(2)}([R^2 + z^2]^{1/2}, \rho_b)$ .

Taken together, Eqs. (19) and (20) constitute the density profile equation for the density functional perturbative approximation. Once again, Eqs. (19) and (20) provide an exact route to calculate the density profiles of model fluids provided  $c_{\text{hs}}^{(1)}(\vec{r};[\rho])$  and  $c_{\text{att}}^{(2)}(|\vec{r}-\vec{s}|, \rho_b)$  are known.

## III. RESULTS AND DISCUSSION

### A. Sticky hard-sphere fluids in planar slits

As an application of the density functional approximation proposed in Sec. II A, we consider a sticky hard-sphere fluid confined in structureless planar slits. For a sticky hard-sphere fluid, the intermolecular potential  $\beta u(r)$  [14] is given as

$$\exp[-\beta u(r)] = \frac{R}{12\tau} \delta(r-R^-) + \theta(r-R), \quad (21)$$

where  $\tau$  is the stickiness parameter related to the strength of adhesion and to the temperature of the system,  $R$  the diameter of sticky hard sphere, and  $\delta(x)$  Dirac's delta function. For a confined sticky hard-sphere fluid, it is known that at lower  $\tau$  values the weighted-density approximations [15] yield very poor results compared with the computer simulation.

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

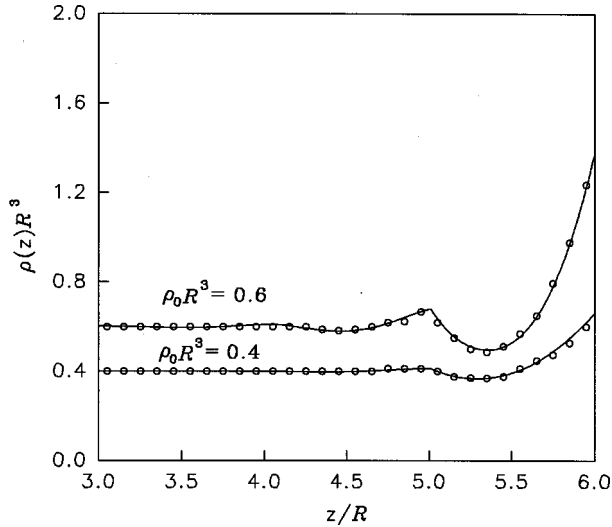


FIG. 1. Density profiles of sticky hard-sphere fluids confined in the gap of with  $L=6R$  hard walls at different bulk density  $\rho_b R^3$  ( $=0.6$  and  $0.4$ ) with the adhesiveness  $\tau=0.5$ . The open circles are taken from the computer simulation [4]. The solid lines correspond to the proposed approximation.

$$\beta u_{\text{ext}}(z) = \begin{cases} 0 & 0 < z < L \\ \infty & \text{otherwise.} \end{cases} \quad (22)$$

To calculate the density profiles of confined sticky hard-sphere fluids, Baxter's Percus-Yevick (PY) expression for the two-particle DCF  $c^{(2)}(r, \rho_b)$  of a sticky hard-sphere fluid in the homogeneous phase has been used,

$$c^{(2)}(r, \rho_b) = \left[ -A_0 - A_1 \left( \frac{r}{R} \right) - \frac{\eta}{2} A_0 \left( \frac{r}{R} \right)^3 \right] \theta(R-r) - \frac{\eta}{12} \lambda^2 \left( \frac{R}{r} \right) \theta(R-r) + \frac{\lambda}{12} \delta(r-R^-), \quad (23)$$

where  $\eta = \pi \rho_b R^3 / 6$  is the packing fraction,  $A_0 = (1 + 2\eta - \xi)^2 / (1 - \eta)^4$ ,  $A_1 = -3\eta(2 + \eta)^2 + 2\xi(1 + 7\eta + \eta^2)$

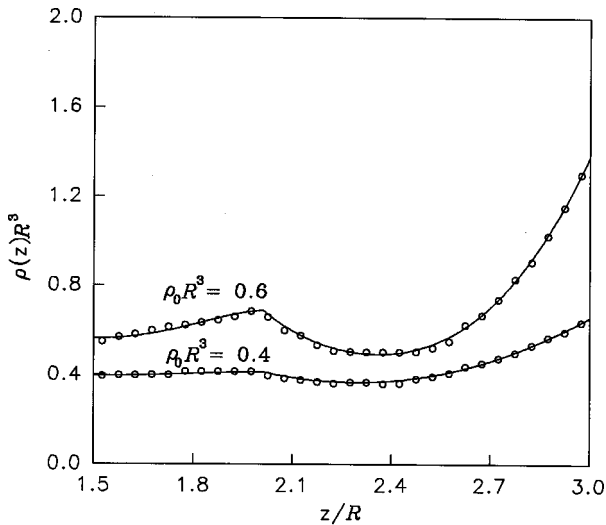


FIG. 2. Same as Fig. 1, but for  $L=3R$ .

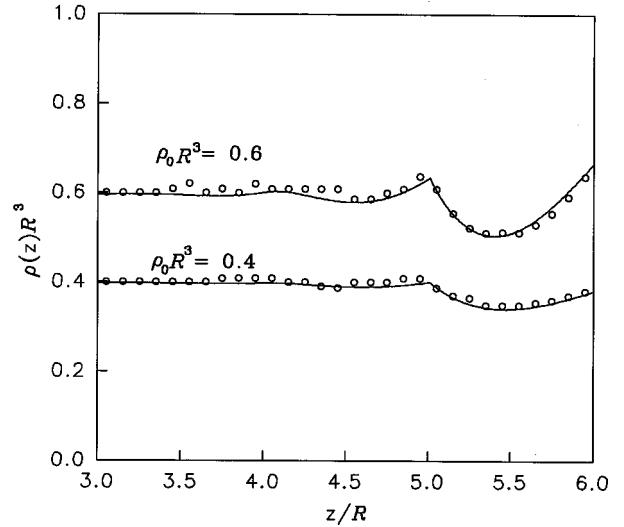


FIG. 3. Same as Fig. 1, but for  $\tau=0.2$ .

$-\xi^2(2 + \eta)/2(1 - \eta)^4$ ,  $\xi = \lambda \eta(1 - \eta)$ ,  $\lambda = 6/\eta[\nu - (\nu^2 - \gamma)^{1/2}]$ ,  $\nu = \tau + \eta/(1 - \eta)$ , and  $\gamma = \eta(2 + \eta)/6(1 - \eta)^2$  [14]. To calculate a constant  $B$  appearing in Eq. (6), the equation of state [16] for a sticky hard-sphere fluid, via the compressibility equation, has been used

$$\frac{\beta P}{\rho_b} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} - \frac{\xi(2 + \eta)}{2(1 - \eta)^3} + \frac{\xi^3}{36\eta(1 - \eta)^3}. \quad (24)$$

The resulting density profiles for a confined sticky hard-sphere fluid with the gap of widths  $L=6R$  and  $L=3R$  have been displayed against  $z/R$  at two different values of the bulk densities  $\rho_b R^3$  ( $=0.4$  and  $0.6$ ) in Figs. 1 and 2. As can be seen from Figs. 1 and 2, for the weak adhesiveness  $\tau=0.5$  the agreement with the present approximation and the computer simulation is excellent.

In Figs. 3 and 4, the calculated results for a sticky hard-sphere fluid confined in a planar wall with gaps of  $L=6R$  and  $L=3R$  have been displayed. The calculated results show that even for the strong adhesiveness  $\tau=0.2$  the present approximation is in excellent agreement with the computer

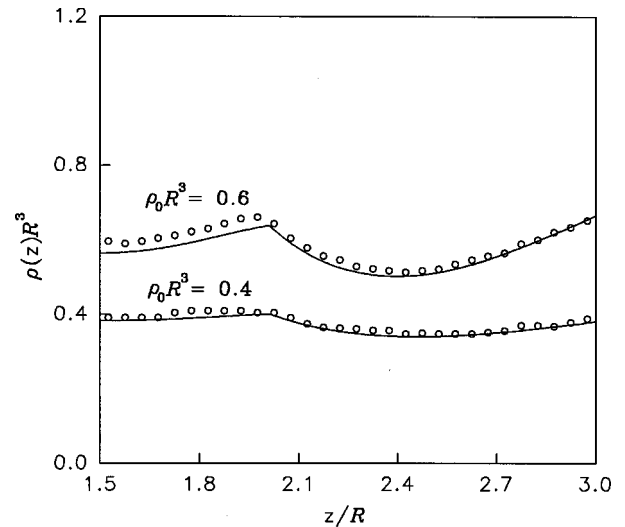


FIG. 4. Same as Fig. 1, but for  $L=3R$  and  $\tau=0.2$ .

simulation. The comparisons with other approximations, which are the Choudhury-Ghosh [8] and Kim-Suh approximations [5], also show that the present approximation is better than the Choudhury-Ghosh and Kim-Suh approximations, even if we did not display their results in Figs. 3 and 4 for clarity; 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 decreasing  $\tau$  values. On the other hand, these results also suggest that for a confined sticky hard-sphere fluid the density functional approximation of Rickayzen *et al.* [12,13] yields excellent results compared with the computer simulation, because in this case the constant  $B$  is determined to satisfy the equation of state of the system.

### B. Hard-sphere Yukawa fluids near a planar slit

As an application of the density functional perturbative approximation developed in Sec. II B, we consider a hard-sphere Yukawa fluid near a planar slit [17]. For a hard-sphere Yukawa fluid, the hard-sphere part  $u_{\text{hs}}(r)$  is given as

$$\beta u_{\text{hs}}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma, \end{cases} \quad (25)$$

and the attractive part  $u_{\text{att}}(r)$  is given as

$$\beta u_{\text{att}}(r) = \begin{cases} 0, & r < \sigma \\ -\beta \epsilon_F \sigma \exp[-\lambda(r-\sigma)/\sigma]/r, & r > \sigma, \end{cases} \quad (26)$$

where the parameter  $\epsilon_F$  is the depth of the fluid-fluid potential,  $\lambda$  the range parameter, and  $\sigma$  the diameter of the hard sphere.

As an approximation for the hard-sphere part  $c_{\text{hs}}^{(1)}(\vec{r};[\rho])$  appearing in Eq. (19), we have used the weighted-density approximation (WDA) of Tarazona [15], which is known to give excellent results for a hard-sphere fluid. In the WDA of Tarazona,  $c_{\text{hs}}^{(1)}(\vec{r};[\rho])$  is simply given as

$$c_{\text{hs}}^{(1)}(\vec{r};[\rho]) = -\beta f_{\text{hs}}[\bar{\rho}(\vec{r})] - \int d\vec{s} \rho(\vec{s}) \beta f'_{\text{hs}}(\bar{\rho}(\vec{s})) \frac{\delta \bar{\rho}(\vec{s})}{\delta \rho(\vec{r})} \quad (27)$$

with

$$\frac{\delta \bar{\rho}(\vec{s})}{\delta \rho(\vec{r})} = \frac{\omega(|\vec{r}-\vec{s}|, \bar{\rho}(\vec{s}))}{1 - \int d\vec{t} \rho(\vec{t}) \omega'(|\vec{s}-\vec{t}|, \bar{\rho}(\vec{s}))}, \quad (28)$$

where  $f_{\text{hs}}(\rho)$  is the excess free energy per particle corresponding to the hard-sphere system and the prime denotes the derivative with respect to the density. The weighted density  $\bar{\rho}(\vec{r})$  appearing in Eq. (27) is assumed as

$$\bar{\rho}(\vec{s}) = \int d\vec{t} \rho(\vec{t}) \omega[|\vec{s}-\vec{t}|, \bar{\rho}(\vec{s})], \quad (29)$$

where  $\omega(|\vec{r}-\vec{s}|, \rho_b)$  is the weighting function for the hard-sphere part. As the weighting function, we have here employed a simple expansion

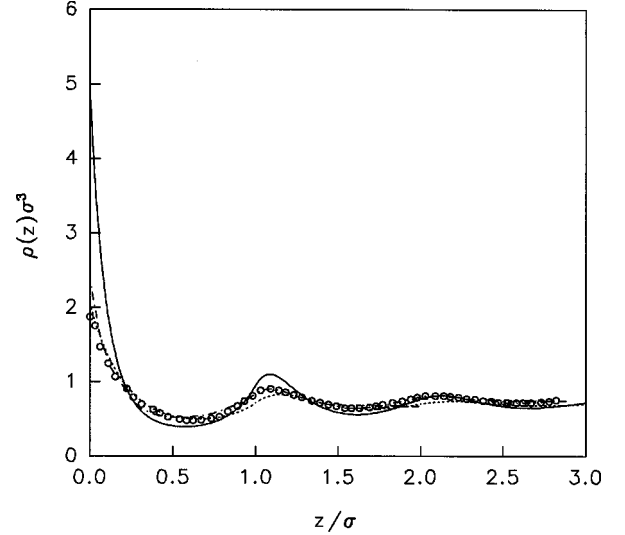


FIG. 5. Density profiles for hard-sphere Yukawa fluids near a hard wall ( $\rho_b \sigma^3 = 0.7$  and  $T^* = 2.0$ ). The solid lines are for a ratio  $\epsilon_W/\epsilon_F = 5$ . The open circles and dotted lines are from the computer simulation [19] and the proposed perturbative approximation, respectively. The dash-dotted lines are the results of LMBW-1 [19].

$$\omega(r, \rho_b) = \omega_0(r) + \omega_1(r) \rho_b + \omega_2(r) \rho_b^2, \quad (30)$$

where detailed expressions are given in Ref. [15].

As the excess free energy corresponding to the hard-sphere contribution,  $f_{\text{hs}}(\rho)$ , the quasixact Carnahan-Starling equation of state has been used;  $\beta f_{\text{hs}}(\rho) = \eta(4 - 3\eta)/(1 - \eta)^2$ , where  $\eta = \eta \rho \sigma^3/6$  is the packing fraction [18]. To calculate the two-particle DCF  $c_{\text{hs}}^{(2)}(|\vec{r}-\vec{s}|, \rho_b)$  for a hard-sphere Yukawa fluid, the mean spherical approximation (MSA) has been used, because the MSA yields quite good results up to the higher densities

$$c_{\text{hs}}^{(2)}(r, \rho_b) = \begin{cases} -a - br/\sigma - \eta ar^3/2\sigma^3 - v\sigma[1 - \exp(-\lambda r/\sigma)]/\lambda r \\ -v^2[\cosh(\lambda r/\sigma) - 1]/[2\beta \epsilon_F \lambda^2 \exp(\lambda)], & r < \sigma \\ \beta \epsilon_F \sigma \exp[-\lambda(r-\sigma)/\sigma]/r, & r > \sigma, \end{cases} \quad (31)$$

where  $a$ ,  $b$ , and  $v$  are parameters, which are defined implicitly [17,19]. As the two-particle DCF  $c_{\text{hs}}^{(2)}(|\vec{r}-\vec{s}|, \rho_b)$  for a hard-sphere fluid, we have used an analytic solution of the Percus-Yevick (PY) approximation [20]. To determine a constant  $B$  appearing in Eq. (17); the bulk pressure  $\beta P$  (energy route) for a hard-sphere Yukawa fluid given by Olivares-Rivas *et al.* [19,21] has been used. Through these calculations, the hard-sphere Yukawa potential with a range parameter  $\lambda = 1.8$  has been used to compare with the computer simulation.

For a hard-sphere Yukawa fluid near a planar slit, two types of wall-fluid interactions  $\beta u_{\text{ext}}(z)$  have been considered: (i) for a structureless hard wall given as

$$\beta u_{\text{ext}}(z) = \begin{cases} 0, & 0 < z \\ \infty, & z > 0, \end{cases} \quad (32)$$

and (ii) for the wall with an attractive tail

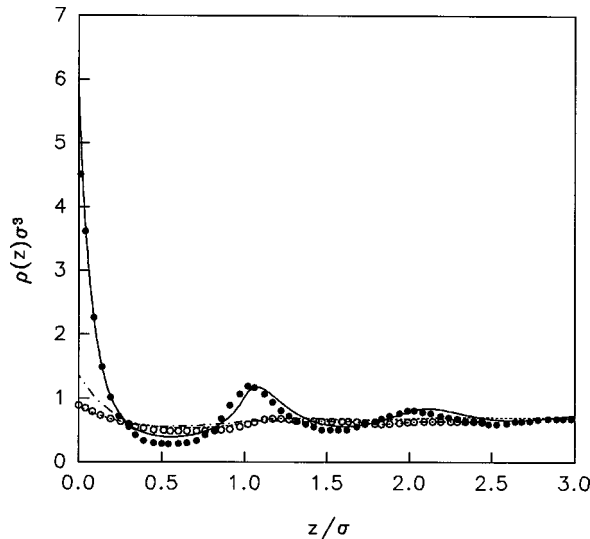


FIG. 6. Density profiles for hard-sphere Yukawa fluids ( $\rho_b\sigma^3 = 0.7$  and  $T^* = 1.25$ ). The upper set is for a ratio  $\epsilon_W/\epsilon_F = 5$ . The lower set is for a hard wall  $\epsilon_W/\epsilon_F = 0$ . The solid and open circles are from the computer simulation [19]. The solid and dotted lines are from the proposed perturbative approximation. The dash-dotted lines are the results of LMBW-1 [19].

$$\beta u_{\text{ext}}(z) = \begin{cases} 0, & 0 < z \\ -\beta\epsilon_W \exp[-\lambda z/\sigma], & z > 0. \end{cases} \quad (33)$$

The density profiles ( $\rho_b\sigma^3 = 0.7$  and  $T^* = k_B T/\epsilon_F = 0.2$ ) for hard-sphere Yukawa fluids near a hard wall are displayed in Fig. 5 with the computer simulation [19]. At a high temperature, the proposed perturbative approximation shows a reasonably good agreement with the computer simulation. The comparison with the modified version of the Lovett-Mou-Buff-Wertheim (LMBW-1) [19] shows that the proposed perturbative approximation is better than the LMBW-1. It is noted that Yi and Kim [11] have recently used the density functional perturbative approximation, which is based on both the weighted-density approximation and the density functional approximation of Rickayzen *et al.*, [12], to study the density profiles of confined hard-sphere Yukawa fluids. The comparison shows that the proposed perturbative approximation yields almost the same results as the Yi-Kim results, even if we did not display their results in the figures for clarity.

For lower temperatures ( $T^* = 1.25$  and  $T^* = 1.1$ ), approaching the liquid-vapor transition temperature, the calculated results have been displayed in Figs. 6 and 7. The comparisons with the computer simulation also show an excellent agreement. Furthermore, the density profiles for an

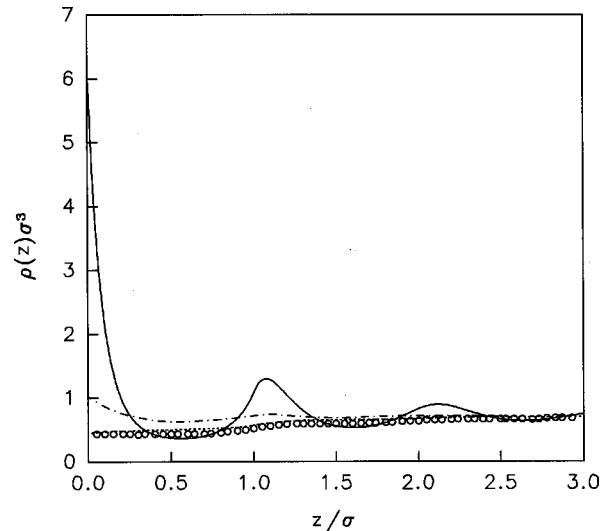


FIG. 7. Same as Fig. 5, but for  $T^* = 1.1$ .

attractive Yukawa wall with  $\epsilon_W/\epsilon_F = 5$  have been displayed in Figs. 5, 6, and 7. As can be seen from Fig. 6 ( $T^* = 1.25$ ), the proposed perturbative approximation shows good agreement with the computer simulation. With increasing the temperature, the contact values of the density profiles decrease because of the increase of the attractive wall potential. This effect is much the same as that of the hard-sphere fluid near a wall [1].

In summary, we have here proposed the density functional approximation and the density functional perturbative approximation, which are based on the exact contact value theorem for a hard wall, to study the structural properties of sticky hard-sphere and hard-sphere Yukawa fluids confined in planar slits. The calculated results show that the present approximations yield an excellent agreement with the computer simulation. Theory presented here can generally be used as a reference system for the study of a bulk sticky hard-sphere fluid and for a perturbative analysis in the study of a bulk hard-sphere Yukawa fluid. On the other hand, the present approximations can be applied to study the structural properties of model fluids or binary mixtures confined in a spherical and cylindrical pore. We will leave these problems to a future study.

#### ACKNOWLEDGMENTS

This paper was partially supported by the Korea Science and Engineering Foundation (Grant No. KOSEF-981-0205-018-1), and by the Basic Science Research Institute Program (Grant No. BSRI 97-2405).

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