Thermodynamic perturbative approach for simple fluids:
Structure of a confined square-well fluid

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An approximation, which is based on both the weighted-density approximation (WDA) of Tarazona [Phys. Rev. A **31**, 2672 (1985)] for the repulsive part of the model potential, and the density-functional approximation (CNPR) of Calleja *et al.* [Mol. Phys. **59**, 973 (1991)] for the attractive part of the model potential, has been proposed to study the structural properties of simple fluids and is abbreviated as WDA-CNPR. The WDA-CNPR approximation can be considered as an extended Choudhury-Ghosh approximation, which is based on the density-functional expansion of a one-particle direct correlation function corresponding to the attractive part of the model potential. It has been applied to predict the density profiles of a confined square-well fluid, and compared with the computer simulation. The calculated results show that for the square-well fluid confined in planar slits the WDA-CNPR approximation is a significant improvement upon those of the Choudhury-Ghosh approximation, and compares well with the computer simulation. For the weak fluid-wall interaction a very good agreement between the results of theory and computer simulation are obtained, but the agreement deteriorates with the increase of the fluid-wall interaction. [S1063-651X(97)11208-9]

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I. INTRODUCTION

Over the last decade, numerical studies have already addressed problems involving the model fluids confined in special symmetrical systems [1–3]. Many theoretical methods have been proposed to describe the structural properties of confined model fluids such as the hard-sphere and Lennard-Jones fluids. For the study of the structural properties of hard-sphere fluid; two kinds of approximate theories, which are the integral equations based on the liquid theories and the weighted-density approximations based on either the local or hybrid weighted densities, are well known. It is known that for the confined hard-sphere fluid the weighted-density approximations based on the local density describe their structural properties very well compared with well-known integral equations such as the Percus-Yevick and hypernetted chain functional approximations. However, at lower temperature these kinds of weighted-density approximations fail to describe the structural properties of the real systems with attractive potentials such as the square-well and Lennard-Jones fluids.

The crux of the problem lies in the fact that the exact form of the free-energy functional $F[\rho]$ or grand-canonical potential $\Omega[\rho]$ is still unknown. To find a reliable approximation to $F[\rho]$ (or, $\Omega[\rho]$) is now a major activity in density-functional approximations. For a model system 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 are perturbation approximations based on the liquid theory. Among many different perturbative theories, there are well-known perturbation theories such as the mean-field density-functional theory (MFDFT) and density-functional perturbation theory (DFPT) [4]. These approximations are quite successful for the prediction of the structural properties of confined Lennard-Jones fluid [5,6]. It is known that, for the structural properties of a confined square-well fluid, these approximations yield the oscillatory structure on the bulk liquid side of liquid-vapor interfacial profiles, i.e., the simplified choice made for the attractive contribution of square-well fluid yields an unwanted approximate bulk equation of state [7–9]. Song and Kim [9] recently applied the density-functional approximation of Choudhury and Ghosh [10], which is based on the density-functional expansion of a one-particle direct correlation function corresponding to the attractive part of the square-well potential, to study the structural properties of a confined square-well fluid. They showed that the Choudhury-Ghosh approximation describes well on the average the structural properties of confined square-well fluids compared with the available computer simulation. However, the agreement with the computer simulation is less satisfactory for higher densities and for the strong fluid-wall interaction. Thus it seems to be interest to extend the Choudhury-Ghosh approximation to study the structural properties of confined square-well fluid and other simple fluids. On the other hand, the structural properties of confined square-well fluid have not been studied much compared with those of confined Lennard-Jones fluid [11].

In this paper, we will propose a density-functional approximation (the WDA-CNPR approximation) which is based on both the weighted-density approximation (WDA) of Tarazona [12,13] for the repulsive part of the model potential and the density-functional approximation (CNPR) of Calleja *et al.* [11] for the attractive part of model potential, to

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study the structural properties of simple fluids. We drive the density profile equation for the WDA-CNPR approximation. We show that in the second-order approximation in the density the WDA-CNPR approximation leads to the Choudhury-Ghosh approximation. In Sec. III, we apply the WDA-CNPR approximation to calculate the density profiles of the square-well fluid confined in planer walls, and compare the results of WDA-CNPR approximation with those of other approximations. Finally, we briefly discuss the strengths and weaknesses of the proposed WDA-CNPR approximation in the actual applications.

II. WDA-CNPR APPROXIMATION

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 $\rho(\mathbf{r})$, are related as

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

where μ is the chemical potential of the system and $u_{\text{ext}}(\mathbf{r})$ an external potential. The Helmholtz 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

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

where the ideal part is known exactly,

$$\beta F_{\text{id}}[\rho] = \int d\mathbf{r} \, \rho(\mathbf{r})\{\ln[\Lambda^3 \rho(\mathbf{r})] - 1\}, \qquad (3)$$

where $\beta = 1/k_B T$ is the inverse temperature and $\Lambda = h(2\pi m k_B T)^{-1/2}$ the thermal de Broglie wavelength.

Since little is known about the exact form of $F_{\text{ex}}[\rho]$ for the model system with the attractive part of the potential, we need to approximate the excess free-energy functional. For this, we introduce the perturbative theory which is well known in the liquid theory. Following the perturbative theory, the pair interaction potential $u(r)$ of a model system can be divided by the reference part $u_{\text{rep}}(r)$ corresponding to the repulsive part of the model potential plus the attractive part $u_{\text{att}}(r)$ corresponding to the attractive part of the model potential:

$$u(r) = u_{\text{rep}}(r) + u_{\text{att}}(r). \qquad (4)$$

In this case, the excess free-energy functional $F_{\text{ex}}[\rho]$ for the model system can be approximated as the repulsive contribution $F_{\text{rep}}[\rho]$ corresponding to the repulsive part of the model potential plus the attractive contribution $F_{\text{att}}[\rho]$ originating from the attractive part of the model potential,

$$F_{\text{ex}}[\rho] = F_{\text{rep}}[\rho] + F_{\text{att}}[\rho]. \qquad (5)$$

Since the exact forms of $F_{\text{rep}}[\rho]$ and $F_{\text{att}}[\rho]$ are still unknown, some kinds of approximations for $F_{\text{rep}}[\rho]$ and $F_{\text{att}}[\rho]$ must inevitably be introduced. It is well known that weighted-density approximations based on either the local density or the globally averaged density describe well the

structural properties of hard-sphere fluids [2,3]. Thus, as an approximation for the repulsive contribution $F_{\text{rep}}[\rho]$, we adopt the WDA of Tarazona [12,13], which is known to give excellent results for the hard-sphere system. In the WDA of Tarazona, $F_{\text{rep}}[\rho]$ is assumed to be

$$F_{\text{rep}}[\rho] = \int d\mathbf{r} \, \rho(\mathbf{r}) f_{\text{rep}}[\bar{\rho}_{\text{rep}}(\mathbf{r})], \qquad (6)$$

with the weighted density $\bar{\rho}_{\text{rep}}(\mathbf{r})$,

$$\bar{\rho}_{\text{rep}}(\mathbf{r}) = \frac{2\bar{\rho}_0(\mathbf{r})}{[1 - \bar{\rho}_1(\mathbf{r})] - \{[1 - \bar{\rho}_1(\mathbf{r})]^2 - 4\bar{\rho}_0(\mathbf{r})\bar{\rho}_2(\mathbf{r})\}^{1/2}}, \qquad (7)$$

where

$$\bar{\rho}_i(\mathbf{r}) = \int d\mathbf{s} \, \rho(\mathbf{s})\omega_i(|\mathbf{r} - \mathbf{s}|) \quad \text{for } i = 0, \, 1, \text{ and } 2, \qquad (8)$$

and $f_{\text{rep}}(\rho)$ is the excess free energy per particle corresponding to the repulsive part of the model potential, and $\omega_i(|\mathbf{r} - \mathbf{s}|)$ is the weighting function and only a function of the coordinate. Since the excess free energy $f_{\text{rep}}(\rho)$ per particle is also difficult to obtain exactly, approximations have to be made. In the actual calculation, the excess free energy corresponding to the hard-sphere contribution is taken by the quasiexact Carnahan-Starling equation of state. The weighting function $\omega_i(|\mathbf{r} - \mathbf{s}|)$ is given by requiring close agreement, over a range of densities, of the two-particle direct correlation function (DCF) that predicted by the Percus-Yevick approximation for the homogeneous hard-sphere fluid [12]:

$$\omega_0(r) = \frac{3}{4\pi\sigma^3} \, \theta(|\mathbf{r}| - \sigma), \qquad (9)$$

$$\omega_1(r) = 0.475 - 0.648\left(\frac{|\mathbf{r}|}{\sigma}\right) + 0.113\left(\frac{|\mathbf{r}|}{\sigma}\right)^2, \quad |\mathbf{r}| < \sigma$$

$$= 0.288\left(\frac{\sigma}{|\mathbf{r}|}\right) - 0.924 + 0.764\left(\frac{|\mathbf{r}|}{\sigma}\right) - 0.187\left(\frac{|\mathbf{r}|}{\sigma}\right)^2,$$

$$\sigma < |\mathbf{r}| < 2\sigma$$

$$= 0, \quad |r| > 2\sigma \qquad (10)$$

$$\omega_2(r) = \frac{5\pi\sigma^3}{144}\left[6 - 12\left(\frac{|\mathbf{r}|}{\sigma}\right) + 5\left(\frac{|\mathbf{r}|}{\sigma}\right)^2\right]\theta(|\mathbf{r}| - \sigma), \qquad (11)$$

where σ is the diameter of the hard sphere, and $\theta(r)$ is the Heaviside step function and is equal to 1 if $r > \sigma$ and 0 otherwise. Then the weighting function $\omega_i(|\mathbf{r} - \mathbf{s}|)$ satisfies the following normalization condition:

$$\int d\mathbf{s}\omega_i(|\mathbf{r} - \mathbf{s}|) = 1 \quad \text{for } i = 0$$

$$= 1 \quad \text{for } i = 1 \text{ and } 2. \qquad (12)$$

Let us consider an approximation for the attractive contribution $F_{\text{att}}[\rho]$ corresponding to the attractive part of the

model potential. As an approximation of $F_{att}[\rho]$, here we employ the density-functional approximation proposed by Calleja *et al.* [11] (hereafter, we will call it the CNPR approximation) to predict the structural properties of the confined hard-sphere and Lennard-Jones fluids. Following the CNPR approximation [11], the excess free-energy functional corresponding to the attractive part of model potential can be written as

$$\beta F_{att}[\rho] = -\int d\mathbf{r} \int d\mathbf{s}\, K(|\mathbf{r}-\mathbf{s}|)\rho(\mathbf{r})\rho(\mathbf{s})$$
$$-B\int d\mathbf{r}\int d\mathbf{s}\int d\mathbf{t}\, L(\mathbf{r},\mathbf{s},\mathbf{t})\rho(\mathbf{r})\rho(\mathbf{s})\rho(\mathbf{t}),$$
$$(13)$$

where $K(|\mathbf{r}-\mathbf{s}|)$ and $L(\mathbf{r},\mathbf{s},\mathbf{t})$ are kernels symmetric in their arguments, and B is an unknown constant. The kernels $K(|\mathbf{r}-\mathbf{s}|)$ and $L(\mathbf{r},\mathbf{s},\mathbf{t})$ are related to the two-particle DCF $c_{att}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho)$ and three-particle DCF $c_{att}^{(3)}(\mathbf{r},\mathbf{s},\mathbf{t},\rho)$ corresponding to the attractive part of the model potential, respectively. Notice here that $c_{att}^{(3)}(\mathbf{r},\mathbf{s},\mathbf{t},\rho)$ is the three-particle DCF for the homogeneous fluid [see Eqs. (14) and (15)]. With $B=0$, that is, in the absence of the term of third order in the density, it can be shown that Eqs. (6) and (13) lead to the Choudhury-Ghosh approximation, which was proposed by Choudhury and Ghosh [10] to study the structural properties of colloidal suspension and sticky hard-sphere fluid. Thus the CNPR approximation combined with the WDA of Tarazona can be considered as an extended Choudhury-Ghosh approximation. However, the three-particle DCF $c_{att}^{(3)}(\mathbf{r},\mathbf{s},\mathbf{t},\rho)$ is not known, so we need an approximation for the kernel $L(\mathbf{r},\mathbf{s},\mathbf{t})$. In fact, it appeared that the kernel $L(\mathbf{r},\mathbf{s},\mathbf{t})$ is not very sensitive when the separation of any two of the coordinates, $|\mathbf{r}-\mathbf{s}|$, is greater than a molecular diameter σ [14–16]. Thus we have chosen a practically simple form of the kernel as

$$L(\mathbf{r},\mathbf{s},\mathbf{t}) = \int d\mathbf{u}\, a(|\mathbf{r}-\mathbf{u}|)a(|\mathbf{s}-\mathbf{u}|)a(|\mathbf{t}-\mathbf{u}|), \quad (14)$$

with

$$a(|\mathbf{r}|) = \frac{6}{\pi\sigma^3}\,\theta\!\left(\frac{\sigma}{2}-|\mathbf{r}|\right), \quad (15)$$

where $\theta(x)$ is the Heaviside step function and is equal to 1 if $r > \sigma/2$, and 0 otherwise. The constant B appeared in $F_{att}[\rho]$, which depends on the properties of the homogeneous bulk fluid, and is determined by the equation of state of the system.

Then the grand-canonical potential is given, from Eqs. (1), (3), (6), and (13), as

$$\beta\Omega[\rho] = \int d\mathbf{r}\,\rho(\mathbf{r})\{\ln[\Lambda^3\rho(\mathbf{r})]-1\} + \int d\mathbf{r}\,\rho(\mathbf{r})[\beta u_{ext}(\mathbf{r})$$
$$-\beta\mu] + \int d\mathbf{r}\,\rho(\mathbf{r})\beta f_{rep}[\bar{\rho}_{rep}(\mathbf{r})]$$
$$-\int d\mathbf{r}\int d\mathbf{s}\, K(|\mathbf{r}-\mathbf{s}|)\rho(\mathbf{r})\rho(\mathbf{s})$$
$$-B\int d\mathbf{r}\int d\mathbf{s}\int d\mathbf{t}\, L(\mathbf{r},\mathbf{s},\mathbf{t})\rho(\mathbf{r})\rho(\mathbf{s})\rho(\mathbf{t}). \quad (16)$$

The equilibrium particle density distribution of the inhomogeneous fluid corresponds to the minimum of the grand-canonical potential satisfying $\delta\Omega[\rho]/\delta\rho(\mathbf{r})=0$, which leads to the Euler-Lagrange equation, from Eq. (1),

$$\beta\mu - \beta u_{ext}(\mathbf{r}) = \beta\,\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}. \quad (17)$$

From Eq. (16), one obtains the equilibrium particle density distribution $\rho(\mathbf{r})$ given by

$$\ln\!\left[\frac{\rho(\mathbf{r})}{\rho_1}\right] = -\beta u_{ext}(\mathbf{r}) - \beta f_{rep}[\bar{\rho}_{rep}(\mathbf{r})]$$
$$-\int d\mathbf{s}\,\rho(\mathbf{s})\beta f'_{rep}[\bar{\rho}_{rep}(\mathbf{s})]\,\frac{\delta\bar{\rho}_{rep}(\mathbf{s})}{\delta\rho(\mathbf{r})}$$
$$+2\int d\mathbf{s}\, K(|\mathbf{r}-\mathbf{s}|)\rho(\mathbf{s})$$
$$+3B\int d\mathbf{s}\int d\mathbf{t}\, L(\mathbf{r},\mathbf{s},\mathbf{t})\rho(\mathbf{s})\rho(\mathbf{t}), \quad (18)$$

with

$$\frac{\delta\bar{\rho}_{rep}(\mathbf{s})}{\delta\rho(\mathbf{r})}$$
$$= \frac{\omega_0(|\mathbf{r}-\mathbf{s}|) + \omega_1(|\mathbf{r}-\mathbf{s}|)\bar{\rho}_{rep}(\mathbf{s}) + \omega_2(|\mathbf{r}-\mathbf{s}|)\bar{\rho}_{rep}(\mathbf{s})^2}{1 - \bar{\rho}_1(\mathbf{s}) - 2\bar{\rho}_2(\mathbf{s})\bar{\rho}_{rep}(\mathbf{s})},$$
$$(19)$$

where $\rho_1 = \Lambda^{-3}\exp(\beta\mu)$. If the inhomogeneous fluid is in contact with the homogeneous bulk fluid, its chemical potential $\beta\mu$ is equal to that of the homogeneous bulk fluid. Then Eq. (18) becomes

$$\ln\!\left[\frac{\rho_b}{\rho_1}\right] = -\beta f_{rep}(\rho_b) - \rho_b\beta f'_{rep}(\rho_b) + 2\rho_b\int d\mathbf{s}\, K(|\mathbf{r}-\mathbf{s}|)$$
$$+3B\rho_b^2\int d\mathbf{s}\int d\mathbf{t}\, L(\mathbf{r},\mathbf{s},\mathbf{t}), \quad (20)$$

where ρ_b is the homogeneous bulk density of the system. Combining Eqs. (18) and (20) and eliminating the chemical potential $\beta\mu$ (or, ρ_1), one obtains the equilibrium particle density distribution (or, density profile equation) given by

$$\ln\left[\frac{\rho(\mathbf{r})}{\rho_b}\right] = -\beta u_{\text{ext}}(\mathbf{r}) + \beta f'_{\text{rep}}(\rho_b) + \rho_b \beta f'_{\text{rep}}(\rho_b)$$

$$- \beta f_{\text{rep}}[\bar{\rho}_{\text{rep}}(\mathbf{r})]$$

$$- \int d\mathbf{s}\, \rho(\mathbf{s}) \beta f'_{\text{rep}}[\bar{\rho}_{\text{rep}}(\mathbf{s})] \frac{\delta\bar{\rho}_{\text{rep}}(\mathbf{s})}{\delta\rho(\mathbf{r})}$$

$$+ 2\int d\mathbf{s}\, K(|\mathbf{r}-\mathbf{s}|)[\rho(\mathbf{s})-\rho_b]$$

$$+ 3B\int d\mathbf{s}\int d\mathbf{t}\, L(\mathbf{r},\mathbf{s},\mathbf{t})[\rho(\mathbf{s})\rho(\mathbf{t})-\rho_b^2]. \quad (21)$$

Since the two-particle DCF $c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b)$ corresponding to the attractive part of model potential is defined by

$$c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b) = -\lim_{\rho(\mathbf{r})\to\rho_b} \frac{\delta^2 \beta F_{\text{att}}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{s})}, \quad (22)$$

the two-particle DCF $c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b)$ for the homogeneous bulk fluid becomes, from Eq. (13),

$$c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b) = 2K(|\mathbf{r}-\mathbf{s}|) + 6B\rho_b \int d\mathbf{t}\, L(\mathbf{r},\mathbf{s},\mathbf{t}). \quad (23)$$

The two-particle DCF $c^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b)$ for the model system is related to the two-particle DCF $c_{\text{rep}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b)$, corresponding to the repulsive part of the model potential

$$c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b) = c^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b) - c_{\text{rep}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b), \quad (24)$$

where $c_{\text{rep}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b)$ is defined as

$$c_{\text{rep}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b) = -\lim_{\rho(\mathbf{r})\to\rho_b} \frac{\delta^2 \beta F_{\text{rep}}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{s})}. \quad (25)$$

Then, the density profile equation, Eq. (21), becomes, from Eqs. (14) and (23),

$$\ln\left[\frac{\rho(\mathbf{r})}{\rho_b}\right] = -\beta u_{\text{ext}}(\mathbf{r}) + \beta f'_{\text{rep}}(\rho_b) + \rho_b \beta f'_{\text{rep}}(\rho_b)$$

$$- \beta f_{\text{rep}}[\bar{\rho}_{\text{rep}}(\mathbf{r})]$$

$$- \int d\mathbf{s}\, \rho(\mathbf{s}) \beta f'_{\text{rep}}[\bar{g}r_{\text{rep}}(\mathbf{s})] \frac{\delta\bar{\rho}_{\text{rep}}(\mathbf{s})}{\delta\rho(\mathbf{r})}$$

$$+ \int d\mathbf{s}\, c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b)[\rho(\mathbf{s})-\rho_b]$$

$$+ 3B\int d\mathbf{u}\, a(|\mathbf{r}-\mathbf{u}|)\overline{\delta\rho(\mathbf{u})}^2, \quad (26)$$

with

$$\overline{\delta\rho(\mathbf{s})} = \int d\mathbf{t}\, a(|\mathbf{s}-\mathbf{t}|)[\rho(\mathbf{t})-\rho_b]. \quad (27)$$

Here, we can check that, with $B=0$, Eq. (26) leads to the Choudhury-Ghosh approximation [10]. The strength parameter B in Eq. (26) is chosen to satisfy the equation of state for the homogeneous bulk fluid. The pressure P of the homogeneous fluid obtained from the functional (16) is given by

$$\beta P = -\beta\Omega[\rho]/V$$

$$= -\rho_b \ln[\rho_b/\rho_1] + \rho_b - \rho_b^2 \beta f_{\text{rep}}(\rho_b)$$

$$+ \rho_b^2 \int d\mathbf{s}\, K(|\mathbf{r}-\mathbf{s}|) + B\rho_b^3 \int d\mathbf{s}\int d\mathbf{t}\, L(\mathbf{r},\mathbf{s},\mathbf{t}), \quad (28)$$

where V is the volume of the system. From Eqs. (14), (23) and (28), one obtains the equation of state as

$$\beta P = \rho_b + \rho_b^2 \beta f'_{\text{rep}}(\rho_b) - \frac{\rho_b^2}{2}\int d\mathbf{s}\, c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b) + B\rho_b^3. \quad (29)$$

since $\int d\mathbf{s}\int d\mathbf{t}\, L(\mathbf{r},\mathbf{s},\mathbf{t}) = 1$. When B is chosen in this way, all the functions and parameters of the fluid in this approximation are determined by the properties of the homogeneous fluid. Taken together, Eqs. (26) and (29), constitute the density profile equation for the WDA-CNPR approximation. Equations (26) and (29) provide an exact route to calculate the density profiles of confined model fluids provided the two-particle DCF $c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b)$ is known; for the given P (or, the given B), Eq. (26) has to be solved by the numerical iteration.

III. RESULTS AND DISCUSSION

As a simple application of the WDA-CNPR approximation, we consider the square-well system with the well depth ϵ. In this case, the intermolecular potential $\beta u(r)$ is given as

$$\beta u(r) = \infty, \quad 0 < r < \sigma$$

$$= -\beta\epsilon, \quad \sigma < r < \sigma + \delta$$

$$= 0, \quad r > \sigma + \delta. \quad (30)$$

where δ is the well width of the attractive potential. Following the perturbative theory, we divide the square-well potential by the repulsive part (the hard-sphere part) plus the attractive part, respectively:

$$\beta u_{\text{rep}}(r) = \infty, \quad 0 < r < \sigma$$

$$= 0, \quad r > \sigma \quad (31)$$

and

$$\beta u_{\text{att}}(r) = 0, \quad 0 < r < \sigma$$

$$= -\beta\epsilon, \quad \sigma < r < \sigma + \delta$$

$$= 0, \quad r > \sigma + gd. \quad (32)$$

Then the excess free energy $F_{\text{rep}}[\rho]$ corresponding to the repulsive part of the square-well potential is presented by the hard-sphere contribution, whereas the attractive part $F_{\text{att}}[\rho]$ is treated as the perturbative term. In the numerical calculation, the excess free energy corresponding to the hard-sphere contribution, $f_{\text{rep}}(\rho)$, is taken by the quasiexact Carnahan-Starling equation of state [17]

$$\beta f_{\text{rep}}(\rho) = \frac{\eta(4-3\eta)}{(1-\eta)^2}, \qquad (33)$$

where $\eta = \pi\rho\sigma^3/6$ is the packing fraction. We have used an analytic solution of the Percus-Yevick approximation for the hard-sphere fluid [18,19] as the two-particle DCF $c_{\text{rep}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho)$ corresponding to the repulsive part of the square-well potential, since the Percus-Yevick results are comparable with the computer simulation up to $\rho\sigma^3 = 0.8$. For the two-particle DCF $c^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho)$ of the square-well fluid, the mean spherical approximation (MSA) [4,20] for the square-well fluid has been used, because (i) it is easy to solve the MSA numerically compared with any other integral equations [4], and (ii) the MSA yields quite good results up to $\rho\sigma^3 = 0.8$. To determine the constant B that appeared in Eq. (29), the bulk pressure βP for the square-well fluid obtained from the computer simulation of Henderson and van Swol [7] was used as input. Through these calculations, the square-well potential (the well depth $\beta\epsilon = 1.0$) with the cut-off at $\delta = 0.5\sigma$ was used to compare with the available computer simulation [7,8].

Let us consider the square-well fluid confined in planar slits consisting of the structureless hard walls. In this case, the spacial dependence of quantities is on z only, not on x and y, because of the symmetry of the problem: $\rho(\mathbf{r}) = \rho(z)$, $\omega_i(z,\rho) = 2\pi\int_0^\infty dR\ \omega_i([R^2+z^2]^{1/2},\rho)$, $c_{\text{att}}^{(2)}(z,\rho) = 2\pi\int_0^\infty dR\ c_{\text{att}}^{(2)}([R^2+z^2]^{1/2},\rho)$, and so on. The wall-fluid interaction (the external potential) $\beta u_{\text{ext}}(z)$ is given as

$$\beta u_{\text{ext}}(z) = 0, \quad 0 < z < L$$
$$= \infty \quad \text{otherwise}, \qquad (34)$$

where $\rho(z)$ is defined in the range of $0 < z < L$.

The density profiles $\rho(z)\sigma^3$ of the confined square-well fluid ($\delta = 0.5\sigma$, $\beta\epsilon = 1.0$) at four different densities ($\rho\sigma^3 = 0.678$, 0.741, 0798, and 0.819) are displayed in Figs. 1–4 with those of the Choudhury-Ghosh approximation and the computer simulation [7]. At lower densities, the WDA-CNPR approximation is better than the Choudhury-Ghosh approximation, and shows an excellent agreement with the computer simulation. For example, the Choudhury-Ghosh approximation near a hard wall is in poor agreement with the computer simulation even at the low density ($\rho_b\sigma^3 = 0.678$, which is above but quite close to the critical density $\rho_b\sigma^3 = 0.648$), as can be seen from Fig. 1. However, at higher densities, the slight discrepancy between the WDA-CNPR approximation and computer simulation can be seen near the second maximum ($z \sim \sigma$) and near the third maximum ($z \sim 2\sigma$), even if the excellent agreement shows at the hard wall. In the WDA-CNPR approximation, the excellent agreement near a hard wall comes perhaps from the property of the CNPR approximation; i.e., the constant B in Eq. (29) is determined to satisfy the equation of state for the homogeneous square-well fluid. At higher densities, the poor agreement with the computer simulation can be seen in the Choudhury-Ghosh approximation. We can think that at higher densities these discrepancies perhaps come from (i) the calculation of $c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho)$ by both the MSA approximation for the square-well fluid and the Percus-Yevick approximation for the hard-sphere fluid, and (ii) the CNPR ap-
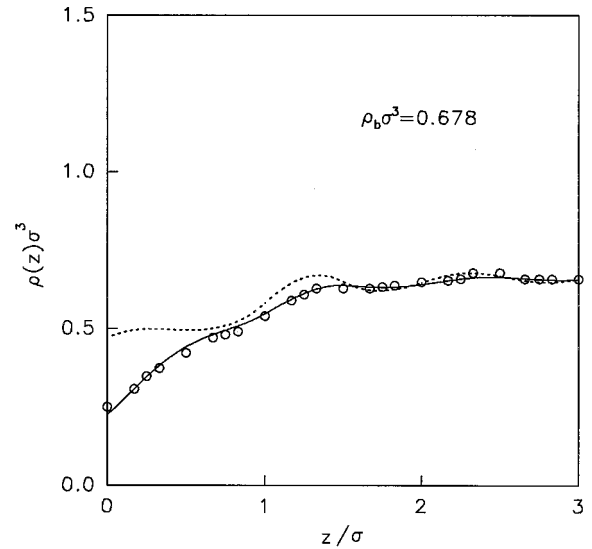

FIG. 1. Density profiles of the confined square-well fluid ($\delta = 0.5\sigma$, $\beta\epsilon = 1.0$) in the gap of width $L = 11.18\sigma$ at $\rho\sigma^3 = 0.678$. The solid and dotted lines are from the WDA-CNPR and Choudhury-Ghosh approximations, respectively. The open circles are from the computer simulation [7].

proximation corresponding to the attractive part of square-well system, because of the weak dependence on the local density $\rho(\mathbf{r})$ of the two-particle DCF $c_{\text{att}}^{(2)}(\mathbf{r},\mathbf{s};[\rho])$ as

$$c_{\text{att}}^{(2)}(\mathbf{r},\mathbf{s};[\rho]) = c_{\text{att}}^{(2)}(|\mathbf{r}-\mathbf{s}|,\rho_b)$$
$$+ 6B\int d\mathbf{t}\ L(\mathbf{r},\mathbf{s},\mathbf{t})[\rho(\mathbf{t})-\rho_b]. \qquad (35)$$

Thus, as the first trial to reduce the disagreement with the computer simulation, it is expected to use the modified hypernetted chain approximation [21], which is better than the MSA, to calculate the two-particle DCF of square-well fluid. However, the overall picture shows that the WDA-CNPR approximation is a significant improvement upon those of
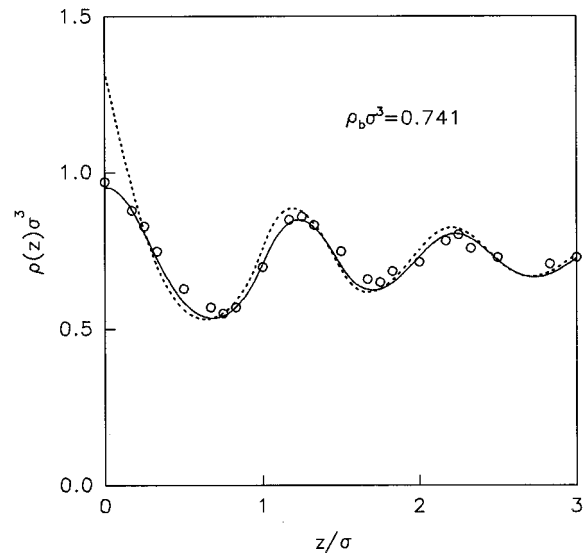

FIG. 2. As in Fig. 1, but for $L = 10.55\sigma$ and $\rho\sigma^3 = 0.741$.
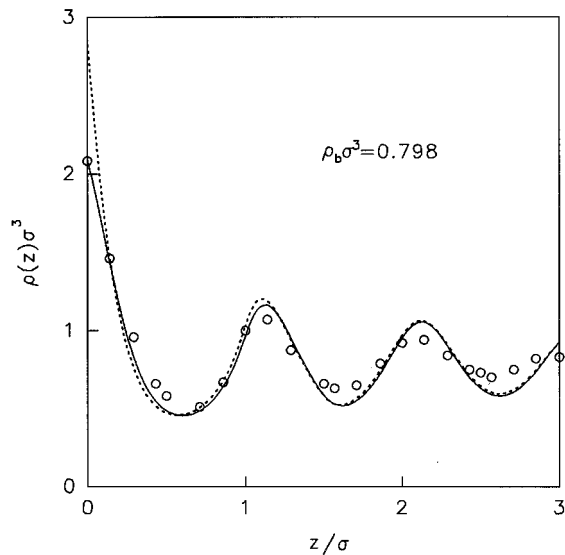
FIG. 3. As in Fig. 1, but for $L=10.18\sigma$ and $\rho\sigma^3=0.798$.

the Choudhury-Ghosh approximation, and gives good results for the hard walls near or above the critical density.

In Figs. 5, 6, and 7, the density profiles in the wall-liquid interfacial region of our square-well wall system have been represented, in which the fluid-wall potential is given as

$$\beta u_{\text{ext}}(z)=-\beta\epsilon_w, \quad 0<z<\sigma/2$$
$$=0, \quad z>\sigma/2, \tag{36}$$

and ϵ_w represents the well depth of the fluid-wall potential. In this case, the density $\rho(z)\sigma^3$ is defined in the range of $0<z<\infty$. The separation of $L=16\sigma$ is taken to calculate the density profiles of square-well fluid; for $L=16\sigma$, the exact relation [4,15], $\beta P_w=\rho_w$, is satisfied, so that a separation of 16σ can be considered as an infinite separation, where ρ_w is the liquid wall density at a hard wall. As can be seen from Figs. 5, 6, and 7, the density near a square-well wall de-
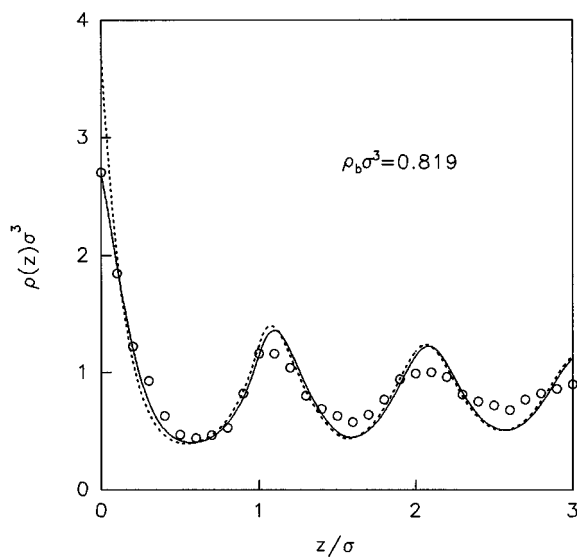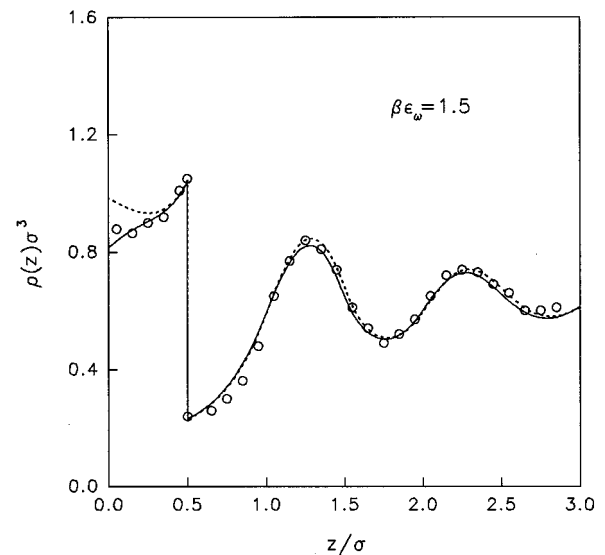

FIG. 5. Density profiles of the square-well fluids near a square-well wall with the fluid-wall interaction $\beta\epsilon_w=1.5$ and at $\rho\sigma^3=0.648$. The solid and dotted lines are from the WDA-CNPR and the Choudhury-Ghosh approximations, respectively. The open circles are from the computer simulation [7,8].

creases relatively with the increase of fluid-wall interaction because of the attractive fluid-wall interaction near a square-well wall. For the weak fluid-wall interaction ($-\beta\epsilon=-1.5$), the WDA-CNPR approximation shows an excellent agreement with the computer simulation [8], whereas in the Choudhury-Ghosh approximation the poor agreement can be seen near the square-well wall. For the strong fluid-wall interaction ($-\beta\epsilon_w=-1.0$, which is the position of drying transition), the agreement between the WDA-CNPR approximation and computer simulation is less satisfactory near a square-well wall ($0<z<\sigma/2$). However, the overall picture shows that the WDA-MWDA approximation, on the average, compares well with results from the computer simulation. The calculated results also show that the WDA-CNPR

FIG. 4. As in Fig. 1, but for $L=10.06\sigma$ and $\rho\sigma^3=0.819$.
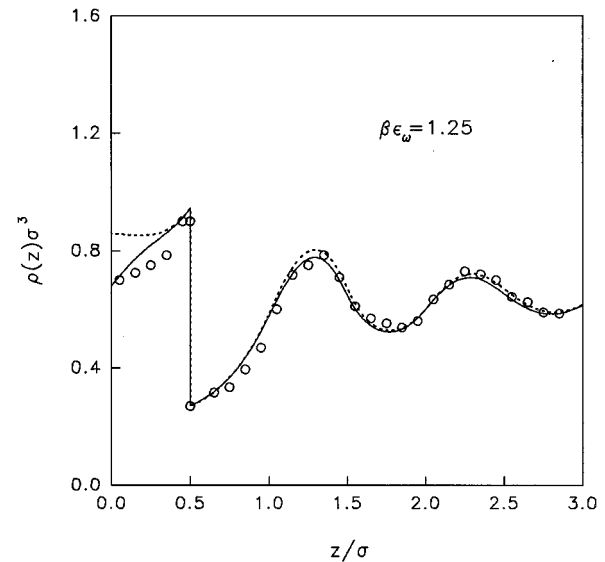

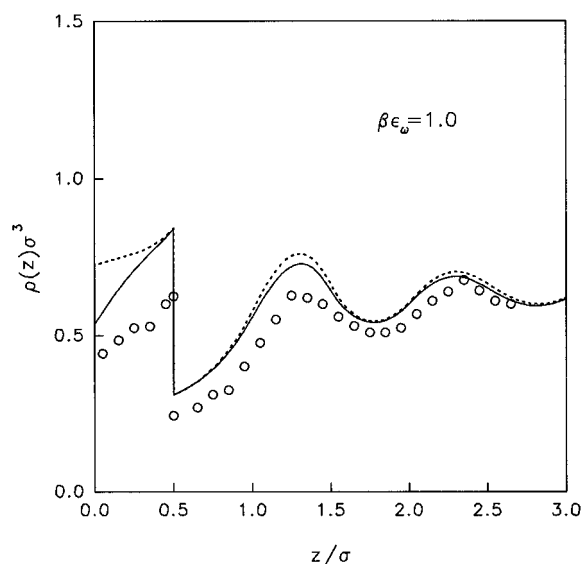FIG. 6. As in Fig. 5, but for $\beta\epsilon_w=1.25$ and $\rho\sigma^3=0.639$.

FIG. 7. As in Fig. 5, but for $\beta\epsilon_w = 1.0$ and $\rho\sigma^3 = 0.651$.

approximation is a significant improvement upon those of the Choudhury-Ghosh approximation. Even if we did not show the results of van Swol and Henderson [8] in Figs. 5–7 for clarity, the comparison shows that the WDA-CNPR approximation is comparable with those of van Swol and Henderson [8], who proposed a weighted-density approximation (WDA) density-functional theory based on the direct input of the desired bulk equation of state, because, for the structural properties of the confined square-well fluid, the usual perturbation theories such as the MFDFT and DFPT approximations possess a qualitative flaw, to varying degrees of quantitative significance [8,9]. In the WDA density-

functional theory, the bulk equation of state for the square-well fluid has been obtained by fitting the simulation isotherms possessing a relatively modest amount of molecular simulation data. The present approximation needs only the two-particle DCF for the square-well fluids as input, thus we believe that the present approximation is computationally easier than the WDA density-functional theory if the two-particle DCF's for the model systems are known.

In summary, we proposed the WDA-CNPR approximation, which can be considered as an extended Choudhury-Ghosh approximation, to study the structural properties of square-well fluid confined in planar slits. The calculated results show that the WDA-CNPR approximation shows good agreement with the computer simulation, even if the agreement is less satisfactory for the strong fluid-wall interaction. On the other hand, we can basically apply the WDA-CNPR approximation to study the structural properties of simple fluids with the attractive part of potential such as the Lennard-Jones system. As a comment, it is known that weighted-density approximations based on the local densities fail to describe the structural properties of the sticky hard-sphere fluid [22] with the extreme pair potential, whereas the CNPR approximation shows an excellent agreement with the computer simulation [23–25]. Thus it is also very interesting to apply the WDA-CNPR approximation to study the structural properties of sticky hard-sphere fluid: We will leave these problems to a future study.

ACKNOWLEDGMENTS

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