

# New Weighted Density Functional Theory Based on Perturbative Approach

Niharendu Choudhury and Swapan K. Ghosh\*

Theoretical Chemistry Section, RC & CD Division, Chemistry Group, Bhabha Atomic Research Centre, Mumbai 400 085, India

Received: September 24, 2002; In Final Form: April 28, 2003

A new weighted density functional theory for inhomogeneous fluids is developed by combining the functional Taylor expansion of the perturbative approach with the nonperturbative weighted density concept. In this approach, the functional Taylor expansion of the one-particle direct correlation function (DCF) is truncated at second order and the effect of a subset of the higher order terms is taken into account by evaluating the third-order DCF at a suitable weighted density, determined by demanding the fourth order DCF to be reproduced from the proposed expansion in the homogeneous limit. The present approach uses as input the two-particle DCF of the corresponding uniform fluid along with an approximation to the three-particle DCF. The proposed theory is applied to hard sphere as well as Lennard-Jones fluids in confined geometries, and the calculated density profiles for both the systems are shown to be in very good overall agreement with the available simulation data.

## I. Introduction

Understanding the structure of fluids at interfaces<sup>1</sup> is of prime importance because of its connection with a large variety of phenomena in surface science, such as adsorption in porous material, wetting, catalysis, capillary condensation, etc. The basic difference between a fluid at an interface and that in the bulk arises because of confinement of the fluid particles in the former case that induces inhomogeneity in the particle density distribution. For the theoretical study of such a non-uniform many-particle system, an ideal, efficient, and powerful theoretical tool that uses the single-particle density as the basic variable is provided by the so-called density functional theory (DFT).<sup>2</sup>

In classical DFT,<sup>3,4</sup> the grand potential of a many-particle inhomogeneous system is expressed as a functional of its single-particle density distribution. For a fixed external potential, this functional is unique and satisfies the variational principle, i.e., its minimization leads to the true equilibrium density distribution. However, the exact form of the interparticle interaction dependent part of the free energy functional is not known in general for an inhomogeneous system, and therefore, search for a suitable approximation of this quantity has been a very active field of research for the last two decades. Various approximate versions of DFT existing in the literature may be classified into two broad categories, namely, the perturbative approach<sup>4,5</sup> based on a functional Taylor expansion of either the free energy or the one-particle direct correlation function (DCF) of the inhomogeneous systems around that of the homogeneous system and the nonperturbative weighted density approach (WDA)<sup>4,6–11</sup> based on the mapping of the inhomogeneous fluid into a homogeneous fluid of an effective density. Because of the lack of knowledge of the higher order DCFs even for the homogeneous fluid, which are required as input in the perturbative approach, the scope of this approach has been rather limited. Even though it has been successful in many cases,<sup>5</sup> its validity has always been questioned because of the unknown error

induced because of truncation. However, a systematic improvement in the perturbative framework is possible by incorporating higher order terms by some approximate means. In fact, the third and higher order terms in the functional Taylor expansion have been included, and the method turns out to be successful not only for pure hard sphere fluids and their mixtures<sup>12–14</sup> but for Lennard-Jones fluids<sup>15,16</sup> and colloidal suspensions<sup>17</sup> as well. It is worth noting that the standard bridge function approach<sup>18–20</sup> in the integral equation theory of homogeneous fluids amounts to a perturbative DFT with the contribution involving second order DCF treated exactly and all of the higher order terms incorporated into the so-called bridge function. Recently, using the concept of the universality of the free energy functional, the bridge function based approach has been extended to the case of inhomogeneous fluids with successful applications<sup>21–24</sup> to several simple model systems including the hard sphere and Lennard-Jones fluids. Zhou<sup>25</sup> has also shown that this concept of universality can be used to incorporate the radial distribution function of the bulk phase into the density functional approximation.

In the usual nonperturbative weighted density approaches, one maps either the free energy or the one-particle DCF of the nonuniform system to that of a homogeneous system (which are often known for suitable interparticle interactions) evaluated at some effective density obtained through a suitable averaging of the actual inhomogeneous density distribution. These WDA schemes are assumed to include a subset of all of the higher order contributions and are found to be suitable for treating a variety of problems involving inhomogeneous fluids.<sup>4</sup> Weighted density functionals based on geometric measure and known as fundamental measure functionals<sup>26,27</sup> are also available and are widely used in various problems. In WDA, it is not explicitly known which are the various higher order terms that have been included. Recently, an attempt has been made<sup>28</sup> to correlate various terms of a functional Taylor expansion of the one-particle DCF obtained in the Denton-Ashcroft (DA) WDA to those from conventional functional Taylor perturbative expansion around the homogeneous fluid. In most of the WDA

\* To whom correspondence should be addressed. E-mail: skghosh@magnum.barc.ernet.in.

approaches, either the free energy or the one-particle DCF is approximated and the weight function is obtained by demanding the correct two-particle DCF to be reproduced from the approximated free energy or one-particle DCF in the homogeneous limit. This condition ensures that the functional Taylor expansion of the approximated quantity about the uniform fluid is exact up to the term containing the two-particle DCF. It is however interesting to investigate the effect of the inclusion of the three-particle and higher order DCFs in WDA. In fact, attempts have been made to include terms beyond the two-particle DCF by Ashcroft et al.<sup>29,30</sup> in their position-independent WDA, which is found to be useful in describing the freezing transition in one-component plasma.<sup>30</sup> However, inclusion of higher order terms beyond the two-particle DCF has not been considered so far in the position-dependent WDA calculations. It is, therefore, of interest to investigate the effect of the inclusion of the terms beyond second order in a WDA based approach.

In the present work, we have formulated a new WDA based approach which includes a subset of certain higher order terms exactly. In what follows, we develop the theoretical formalism in section II, and applications of the theoretical approach to the case of hard sphere as well as LJ fluids are described in section III. Finally a few concluding remarks are included in section IV.

## II. Density Functional Theory of an Inhomogeneous Fluid

DFT of an inhomogeneous many-particle system under the influence of an external potential  $u(\mathbf{r})$  starts by expressing the grand potential  $\Omega$  as a functional of its single particle density distribution  $\rho(\mathbf{r})$ , viz.

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

where  $\beta = 1/k_B T$ , with  $k_B$  as the Boltzmann constant, represents the inverse temperature,  $\Lambda$  denotes the thermal de Broglie wavelength, and  $\mu$  represents the chemical potential. The first term in the above expression represents the ideal gas contribution to the free energy, whereas the quantity  $F_{\text{ex}}[\rho]$  is the excess Helmholtz free energy arising from interparticle interactions. For a fixed  $u(\mathbf{r})$  and  $\mu$ , the grand potential satisfies the variational principle and leads, on minimization, to an expression for the true equilibrium density distribution  $\rho(\mathbf{r})$ , given by

$$\rho(\mathbf{r}) = \rho_0 \exp\{-\beta u(\mathbf{r}) + c^{(1)}(\mathbf{r};[\rho]) - c_0^{(1)}(\rho_0)\} \quad (2)$$

as obtained after equalization of the chemical potential of the inhomogeneous system with that of the bulk phase of density  $\rho_0$ , with which the inhomogeneous fluid is considered to be in equilibrium. Here,  $c^{(1)}(\mathbf{r};[\rho])$  represents the one-particle DCF, the first member in the hierarchy of  $n$ -particle DCF's defined as

$$c^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = -\beta \frac{\delta^n F_{\text{ex}}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2) \dots \delta \rho(\mathbf{r}_n)} \quad (3)$$

and  $c_0$  refers to its uniform fluid counterpart. Although eq 2 provides an exact expression for the density profile, the exact functional form of neither the one-particle DCF appearing in this equation nor  $F_{\text{ex}}[\rho]$  is in general known for an inhomogeneous system and in fact, various approximations proposed for these and related quantities have led to different versions of DFT.

In the present approach, we begin with the conventional functional Taylor expansion of the one-particle DCF as given by

$$\Delta c^{(1)}(\mathbf{r};[\rho]) \equiv c^{(1)}(\mathbf{r};[\rho]) - c_0^{(1)}(\rho_0) = \int d\mathbf{r}_2 c_0^{(2)}(\mathbf{r}, \mathbf{r}_2; \rho_0)(\rho(\mathbf{r}_2) - \rho_0) + \frac{1}{2} \int d\mathbf{r}_2 d\mathbf{r}_3 c_0^{(3)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; \rho_0)(\rho(\mathbf{r}_2) - \rho_0)(\rho(\mathbf{r}_3) - \rho_0) + \text{higher order terms} \quad (4)$$

where the quantities  $c_0^{(2)}$  and  $c_0^{(3)}$  denote the homogeneous fluid counterparts of the second and third-order DCFs  $c^{(2)}$  and  $c^{(3)}$ , respectively. Although this expansion containing infinite terms is exact in principle, for practical implementation, its truncation becomes essential in view of the lack of knowledge about the higher order DCFs even for the homogeneous phase. In this work, we propose to truncate the series at second order in density inhomogeneity (i.e., retain terms containing up to third-order DCF) and propose to include the effect of certain higher order terms along the lines of WDA. For this purpose, we follow Zhou<sup>31,32</sup> closely and note that eq 4 truncated at the second term will be exact if the third-order DCF in the above equation is evaluated<sup>33</sup> at some inhomogeneous density distribution  $[\rho_0 + \lambda(\rho(\mathbf{r}) - \rho_0)]$  with  $\lambda$  between 0 and 1, instead of the homogeneous bulk density  $\rho_0$ . This provides essentially an extension of the work of Zhou<sup>31,32</sup> which is based on the second-order DCF to a formalism based on the third-order DCF. Equation 4, within this prescription, can be written as

$$c^{(1)}(\mathbf{r};[\rho]) = c_0^{(1)}(\rho_0) + \int d\mathbf{r}_2 c_0^{(2)}(\mathbf{r}, \mathbf{r}_2; \rho_0)(\rho(\mathbf{r}_2) - \rho_0) + \frac{1}{2} \int d\mathbf{r}_2 d\mathbf{r}_3 c^{(3)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; [\rho_0 + \lambda(\rho(\mathbf{r}) - \rho_0)])(\rho(\mathbf{r}_2) - \rho_0)(\rho(\mathbf{r}_3) - \rho_0) \quad (5)$$

We now propose to obtain the third-order DCF  $c^{(3)}$  for the inhomogeneous density appearing in eq 5 in the spirit of WDA by evaluating the corresponding homogeneous phase quantity  $c_0^{(3)}$  at a weighted density  $\bar{\rho}(\mathbf{r})$ , viz.

$$c^{(3)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; [\rho_0 + \lambda(\rho(\mathbf{r}) - \rho_0)]) = c_0^{(3)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; \bar{\rho}(\mathbf{r})) \quad (6)$$

where the weighted density  $\bar{\rho}(\mathbf{r})$  is defined as

$$\begin{aligned} \bar{\rho}(\mathbf{r}) &= \int d\mathbf{r}_2 w(\mathbf{r}, \mathbf{r}_2; \rho_0) [\rho_0 + \lambda(\rho(\mathbf{r}_2) - \rho_0)] \\ &= \rho_0 + \lambda \int d\mathbf{r}_2 w(\mathbf{r}, \mathbf{r}_2; \rho_0)(\rho(\mathbf{r}_2) - \rho_0) \end{aligned} \quad (7)$$

using a weight function  $w(\mathbf{r}, \mathbf{r}_2)$  normalised to unity and evaluated, for simplicity, at the bulk density. It may be noted that this form of the weighted density has also been used by Zhou.<sup>31,32</sup> Clearly in the homogeneous limit of  $\rho(\mathbf{r}) \rightarrow \rho_0$ ,  $\bar{\rho}(\mathbf{r})$  reaches the bulk density  $\rho_0$  irrespective of the value of the parameter  $\lambda$ . The final equation for the first-order DCF  $c^{(1)}(\mathbf{r};[\rho])$  of eq 5 is thus given by

$$c^{(1)}(\mathbf{r};[\rho]) = c_0^{(1)}(\rho_0) + \int d\mathbf{r}_2 c_0^{(2)}(\mathbf{r}, \mathbf{r}_2; \rho_0)(\rho(\mathbf{r}_2) - \rho_0) + \frac{1}{2} \int d\mathbf{r}_2 d\mathbf{r}_3 c_0^{(3)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; \bar{\rho}(\mathbf{r}))(\rho(\mathbf{r}_2) - \rho_0)(\rho(\mathbf{r}_3) - \rho_0) \quad (8)$$

The weight function  $w(\mathbf{r}, \mathbf{r}_2)$  as well as the value of the parameter  $\lambda$  are obtained by demanding that the approximate functional as given by eq 8 reproduces the correct fourth order DCF in the homogeneous limit. Thus, eq 8, on successive functional

differentiation for three times followed by evaluation in the homogeneous limit  $\rho(\mathbf{r}) \rightarrow \rho_0$ , yields the fourth order DCF  $c_0^{(4)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$  given by

$$c_0^{(4)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \lambda [c_0^{(3)'}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)w(\mathbf{r}, \mathbf{r}_4) + c_0^{(3)'}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_4)w(\mathbf{r}, \mathbf{r}_3) + c_0^{(3)'}(\mathbf{r}, \mathbf{r}_3, \mathbf{r}_4)w(\mathbf{r}, \mathbf{r}_2)] \quad (9)$$

where the symbol  $c_0^{(3)'}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3) [= \int d\mathbf{r}_4 c_0^{(4)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)]$  denotes the simple derivative of  $c_0^{(3)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; \rho_0)$  with respect to the bulk density  $\rho_0$ . Now integrating eq 9 over  $\mathbf{r}_4$ ,  $\mathbf{r}_3$ , and  $\mathbf{r}_2$  coordinates successively, one obtains  $\lambda = 1/3$  and also the weight function  $w(\mathbf{r} - \mathbf{r}_2)$  given by

$$w(\mathbf{r} - \mathbf{r}_2; \rho_0) = \frac{c_0^{(2)''}(\mathbf{r} - \mathbf{r}_2; \rho_0)}{c_0^{(1)'''}(\rho_0)} \quad (10)$$

where again a prime on  $c_0^{(2)}$  and  $c_0^{(1)}$  signifies a derivative with respect to  $\rho_0$  and the number of primes indicate the order of the derivative. Once the weight function is specified by eq 10, one can proceed to calculate the weighted density  $\bar{\rho}(\mathbf{r})$  according to eq 7, as

$$\bar{\rho}(\mathbf{r}) = \rho_0 + \frac{1}{3} \frac{1}{c_0^{(1)'''}(\rho_0)} \int d\mathbf{r}_2 c_0^{(2)''}(\mathbf{r} - \mathbf{r}_2; \rho_0) (\rho(\mathbf{r}_2) - \rho_0) \quad (11)$$

For a given external potential  $u(\mathbf{r})$ , eqs 2, 8, and 11 together constitute a closed self-consistent set of equations for the density profile  $\rho(\mathbf{r})$  and the weighted density  $\bar{\rho}(\mathbf{r})$ , which can easily be solved iteratively, if the input functions  $c_0^{(2)}$ ,  $c_0^{(3)}$  and their density derivatives for the corresponding homogeneous fluid are known. Although the input function  $c_0^{(2)}(\mathbf{r} - \mathbf{r}_2)$  is often known within some standard approximation such as Percus–Yevick (PY), mean spherical approximation, etc. for various model potentials, the three-particle DCF  $c_0^{(3)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)$  is not known exactly for most of the model potentials and therefore an approximation of this quantity is essential. In the present case, we approximate  $c_0^{(3)}$ , following Zhou and Ruckenstein<sup>14</sup> and using the present weight function, as

$$c_0^{(3)}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3; \rho_0) = w(\mathbf{r}, \mathbf{r}_2; \rho_0) w(\mathbf{r}, \mathbf{r}_3; \rho_0) c_0^{(1)''}(\rho_0) \approx B \left( \frac{c_0^{(1)''}}{[c_0^{(1)'''}]^2} \right) c_0^{(2)''}(\mathbf{r}, \mathbf{r}_2; \rho_0) c_0^{(2)''}(\mathbf{r}, \mathbf{r}_3; \rho_0) \quad (12)$$

where  $B$  is a parameter that is determined by forcing the wall theorem to be satisfied by the resulting density profile. Similar kinds of approximations for  $c_0^{(3)}$  have earlier been used by various authors,<sup>14,28</sup> whereas a more accurate representation of this quantity has also been available<sup>15,16</sup> in terms of an integral involving three second-order DCFs. Introducing the form of  $c_0^{(3)}$  as given by eq 12, one can rewrite eq 8 as

$$\Delta c^{(1)}(\mathbf{r}; [\rho]) = \gamma(\mathbf{r}; \rho_0) + \frac{B}{2} \left( \frac{c_0^{(1)''}}{[c_0^{(1)'''}]^2} \right) [\gamma_d(\mathbf{r}; \bar{\rho}(\mathbf{r}))]^2 \quad (13)$$

where  $\gamma(\mathbf{r})$  and  $\gamma_d(\mathbf{r})$  are given respectively as

$$\gamma(\mathbf{r}; \rho_0) = \int d\mathbf{r}_2 c_0^{(2)}(\mathbf{r} - \mathbf{r}_2; \rho_0) [\rho(\mathbf{r}_2) - \rho_0] \quad (14)$$

and

$$\gamma_d(\mathbf{r}; \bar{\rho}(\mathbf{r})) = \int d\mathbf{r}_2 c_0^{(2)''}(\mathbf{r} - \mathbf{r}_2; \bar{\rho}(\mathbf{r})) [\rho(\mathbf{r}_2) - \rho_0] \quad (15)$$

**A. Hard Sphere Fluids near Hard Walls.** We first consider the simple case of a pure hard sphere fluid confined in a planar slit consisting of two planar hard walls. Because of the planar symmetry of the problem, the density inhomogeneity is only in the perpendicular  $z$  direction. For a hard sphere fluid of particle diameter  $d$  confined between two hard walls located at  $z = z_0$  and  $z_f$  which defines the wall separation or pore size  $H = z_f - z_0$ , the external potential is symmetric, viz.

$$u(z) = 0 \text{ for } z_0 + d/2 \leq z \leq z_f - d/2 \quad (16)$$

and infinite otherwise. The density equation (2) for the above external potential may then be rewritten as

$$\rho(z) = \rho_0 \exp[\Delta c^{(1)}(z; [\rho])] \quad (17)$$

for  $z_0 + d/2 \leq z \leq z_f - d/2$  and zero otherwise. In this equation,  $\Delta c^{(1)}(z; [\rho])$  is the planar averaged quantity corresponding to  $\Delta c^{(1)}(\mathbf{r}; [\rho])$  of eq 13 and can be expressed as

$$\Delta c^{(1)}(z; [\rho]) = \gamma(z; \rho_0) + \frac{B}{2} \left( \frac{c_0^{(1)''}}{[c_0^{(1)'''}]^2} \right) [\gamma_d(z; \bar{\rho}(z))]^2 \quad (18)$$

where the quantity  $\gamma(z; \rho_0)$  is given by planar-averaging of eq 14 as

$$\gamma(z; \rho_0) = \int_{-\infty}^{\infty} dz' [\rho(z') - \rho_0] f(|z - z'|) \quad (19)$$

with the function  $f(s)$  defined as

$$f(s) = 2\pi \int_s^{\infty} ds' s' c_0^{(2)}(s'; \rho_0) \quad (20)$$

The other quantity  $\gamma_d(z; \bar{\rho}(z))$  is given by an equation similar to eq 19 with  $f(s)$  replaced by  $f_d(s)$ , which is defined as

$$f_d(s) = 2\pi \int_s^{\infty} ds' s' c_0^{(2)''}(s'; \bar{\rho}(z)) \quad (21)$$

For a pure hard sphere fluid, the second-order DCF  $c_0^{(2)}(|\mathbf{r} - \mathbf{r}'|)$  for the bulk phase is known analytically within the PY approximation and is given by  $c_0^{(2)}(r) = a + b(r/d) + c(r/d)^3$  with the density dependent coefficients  $a$ ,  $b$ , and  $c$  expressed by simple standard expressions<sup>18</sup> in terms of the packing fraction  $\eta = (\pi/6)\rho_0 d^3$ . To determine the parameter  $B$ , as has already been mentioned earlier, one has to know the bulk pressure and in the present case the expression for the bulk pressure used is obtained from the well-known Carnahan–Starling equation of state<sup>18</sup> given by

$$\frac{\beta P}{\rho_0} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (22)$$

The exact expression of the parameter  $B$  determined by equating  $\beta P$  with  $\rho(z = d/2)$ , the density at the interface, as predicted by the density equation (17), is given by

$$B = 2 \left( \frac{[c_0^{(1)'''}]^2}{c_0^{(1)''}} \right) \frac{[\ln(\beta P/\rho_0) - \gamma(d/2; \rho_0)]}{[\gamma_d(d/2; \bar{\rho}(d/2))]} \quad (23)$$

Because  $B$  is expressed here in terms of the density at contact  $\rho(z = d/2)$ , it has to be determined self-consistently with the density equation (17) along with eqs 18–23.

**B. Lennard-Jones Fluid near Hard Walls.** We consider here a Lennard-Jones fluid confined between two parallel hard walls separated from each other by  $H$  with the walls located at  $z = z_0$  and  $z_f$  for which the external potential  $u(z)$  is given by eq 16. We also consider LJ fluid in front of a planar hard wall for which the external potential is given by  $u(z) = 0$  for  $z \geq z_0 + d/2$  and infinite otherwise. In the case of LJ fluid, the interparticle potential  $\phi(r)$  is given by

$$\phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (24)$$

where  $\sigma$  is the distance at which the potential is zero and  $\epsilon$  is the depth of the potential. It is customary to split this potential into a short ranged repulsive part and a relatively long ranged attractive component  $\phi^{\text{att}}(r)$ . Because of this splitting, one can easily partition the quantity  $\Delta c^{(1)}(\mathbf{r};[\rho])$  for this system into a short-range part  $\Delta c_{\text{SR}}^{(1)}$  and an attractive component  $\Delta c_{\text{att}}^{(1)}$ , viz.

$$\Delta c^{(1)}(\mathbf{r};[\rho]) = \Delta c_{\text{SR}}^{(1)}(\mathbf{r};[\rho]) + \Delta c_{\text{att}}^{(1)}(\mathbf{r};[\rho]) \quad (25)$$

where the latter is often estimated within the mean field approximation (MFA) as

$$\Delta c_{\text{att}}^{(1)}(\mathbf{r};\rho) = -\int d\mathbf{r}' [\rho(\mathbf{r}') - \rho_0] \phi^{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \quad (26)$$

It is also a common practice to replace the short-range repulsive part of the potential by a reference hard sphere fluid with some suitable effective hard sphere diameter. The temperature-dependent effective diameter of the reference hard sphere system in the present case has been obtained from the analytical expression<sup>34</sup>

$$d_{\text{eff}} = \frac{\alpha_1 T^* + \alpha_2}{\alpha_3 T^* + \alpha_4} \quad (27)$$

where  $T^* (=k_B T/\epsilon)$  is the dimensionless temperature and  $\alpha_i$ 's are constants. The values of the parameters  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ , and  $\alpha_4$  are chosen<sup>16,35,36</sup> as 0.3837, 1.0320, 0.4293, and 1.0, respectively. The quantity  $\Delta c_{\text{SR}}^{(1)}(\mathbf{r};[\rho])$  appearing in eq 25 is the same as that of the hard sphere system given by eq 18 with an effective diameter  $d_{\text{eff}}$ . To obtain the attractive part of the potential  $\phi_{\text{att}}$ , several splitting prescriptions<sup>18</sup> such as the McQuarrie and Katz scheme,<sup>37</sup> the Barker and Henderson scheme,<sup>38</sup> the Weeks, Chandler, and Anderson (WCA) scheme,<sup>39</sup> etc. are available in the literature. Here, we split the potential according to the WCA prescription<sup>39</sup> at the minimum of the potential  $r_{\text{min}} (=2^{1/6}\sigma)$  such that the attractive part of the potential  $\phi^{\text{att}}$  is represented as

$$\begin{aligned} \phi^{\text{att}}(r) &= -\epsilon, r < r_{\text{min}} \\ &= \phi(r), r > r_{\text{min}} \end{aligned} \quad (28)$$

In the present case of inhomogeneous LJ fluid, one can easily write the planar averaged quantity  $\Delta c^{(1)}(z)$  as

$$\Delta c^{(1)}(z;[\rho]) = \gamma^{\text{HS}}(z;\rho_0) + \frac{B}{2} \left( \frac{c_{\text{OHS}}^{(1)''}}{[c_{\text{OHS}}^{(1)''}]^2} \right) [\gamma_d^{\text{HS}}(z;\bar{\rho}(z))]^2 + \Delta c_{\text{att}}^{(1)}(z;[\rho]) \quad (29)$$

where  $\Delta c_{\text{att}}^{(1)}(z;[\rho])$  is defined as

$$\Delta c_{\text{att}}^{(1)}(z;[\rho]) = -\int dz' [\rho(z') - \rho_0] \phi^{\text{att}}(|z - z'|) \quad (30)$$

with  $\phi^{\text{att}}(z)$  given by

$$\phi^{\text{att}}(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \phi^{\text{att}}(\sqrt{x^2 + y^2 + z^2}) \quad (31)$$

and all of the quantities with subscript HS refer to the hard sphere part of those quantities. Thus, for the calculation of the density profiles of the LJ fluid, in addition to  $c_0^{(2)}$ ,  $c_0^{(1)}$ , and their various density derivatives for the effective hard sphere system, the pressure of the LJ fluid is also required as an input parameter. As in the case of pure hard sphere fluid,  $c_{\text{OHS}}^{(2)}$ ,  $c_{\text{OHS}}^{(1)}$ , and their various density derivatives are obtained from the analytical expressions within PY approximation and for the pressure of LJ fluid, we have used the analytical expression of Nicolas et al.<sup>40</sup> obtained from a 32-parameter fitting of several computer simulation data. For the LJ fluid, the expression for the parameter  $B$  given by eq 23 is thus modified by the presence of the attraction term in  $\Delta c^{(1)}(z)$  and is given by

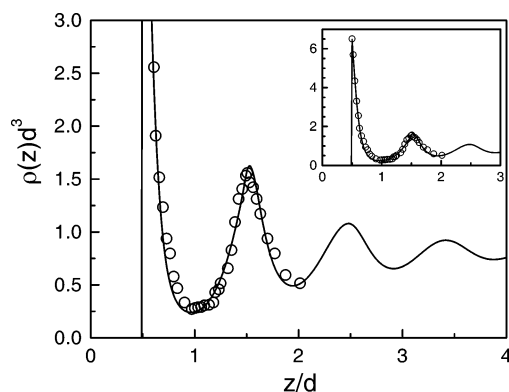
$$B = 2 \left( \frac{[c_{\text{OHS}}^{(1)'''}]^2}{c_{\text{OHS}}^{(1)''}} \right) \frac{[\ln(\beta P/\rho_0) - \gamma^{\text{HS}}(d/2;\rho_0) + \Delta c_{\text{att}}^{(1)}(z;[\rho])]}{[\gamma_d^{\text{HS}}(d/2;\bar{\rho}(d/2))]} \quad (32)$$

### III. Results and Discussion

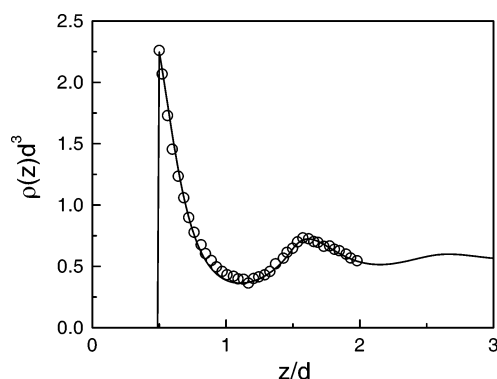
The nonlinear integral equation (17) along with eqs 18–21 for the density profile of the hard sphere fluid near hard walls and eq 17 along with eqs 29–31 for the LJ fluid confined between slit pores have been solved using a self-consistent iterative procedure using  $\rho(z) = \rho_0$  as the initial guess. The one-dimensional integrals appearing in these equations have been evaluated numerically by means of a simple discretization scheme with a uniform mesh using trapezoidal rule. The convergence criterion for the iterative procedure has been such that the average mean square density deviation between successive iterations is very small. The distance from the wall and the densities are measured in the dimensionless forms  $z/d$  and  $\rho(z)d^3$  respectively for the hard sphere systems while  $z/\sigma$  and  $\rho(z)\sigma^3$  respectively are employed for the LJ fluid. The temperature for the LJ fluid is expressed in the dimensionless form in terms of the potential depth  $\epsilon$ , i.e.,  $T^* = k_B T/\epsilon$ .

**A. Density Profiles of Hard Sphere Fluids Confined in Slit Pores.** We present the results of our calculation for the density profiles  $\rho(z)d^3$  of a pure hard sphere fluid confined between two parallel plates for different values of the bulk densities  $\rho_0$ . The calculated results for a pure hard sphere fluid of density  $\rho_0 d^3 = 0.81$  confined in a slit pore of width  $H = 11d$  is shown in Figure 1. The density profile obtained from the present approach is found to be oscillatory with a period of oscillation equal to the hard sphere diameter. For comparison, we have included in the same figure the results from computer simulation by Snook and Henderson<sup>41</sup> and the present results are found to show very good agreement with those from simulation. It is to be noted that in the present approach the density profile is made to satisfy the contact theorem, according to which the density at the contact should be equal to the bulk pressure and, as a result, the calculated density at the contact is in very good agreement (see inset) with the simulation, although it is generally highly overestimated by various theories such as Denton–Ashcroft (DA) WDA,<sup>8,11</sup> second order functional Taylor expansion, etc., which fail to satisfy this theorem. Not only is the height of the first peak in very good agreement with simulation, but the height of the second peak, which is again overestimated by DA WDA,<sup>11</sup> is also in very good agreement with the simulation results. To investigate the effect of change





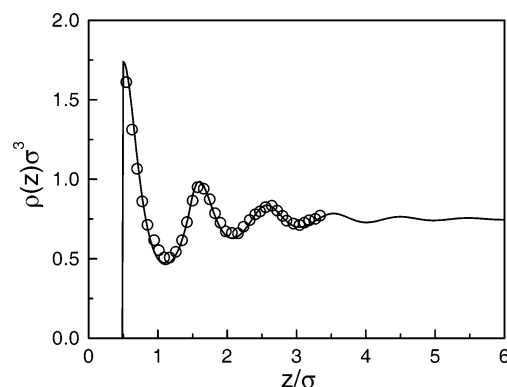
**Figure 1.** Plot of the density profile  $\rho(z)d^3$  vs  $z/d$  for a pure hard sphere fluid of bulk density  $\rho_0 d^3 = 0.81$ , confined in a slit pore consisting of two hard walls of width  $H = 11d$ . The result from the present approach is shown by the solid line and the symbols correspond to the simulation data of Snook and Henderson.<sup>41</sup>



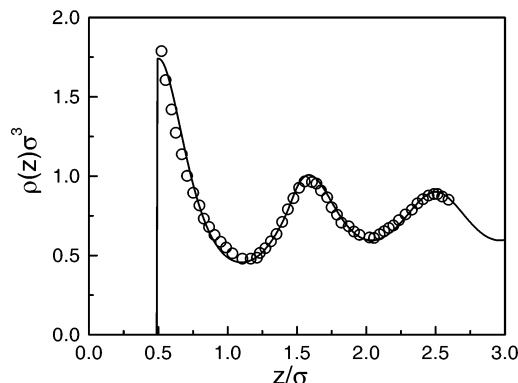
**Figure 2.** Plot of the density profile  $\rho(z)d^3$  vs  $z/d$  for a pure hard sphere fluid of bulk density  $\rho_0 d^3 = 0.57$ , confined in a slit pore consisting of two hard walls of width  $H = 11d$ . The key is the same as in Figure 1.

in the bulk density, we have plotted in Figure 2 the results of our calculation for the hard sphere fluid of another bulk density  $\rho_0 d^3 = 0.57$  confined in a pore of the same width  $H = 11d$  along with the simulation results<sup>41</sup> and a very good agreement is observed in this case also.

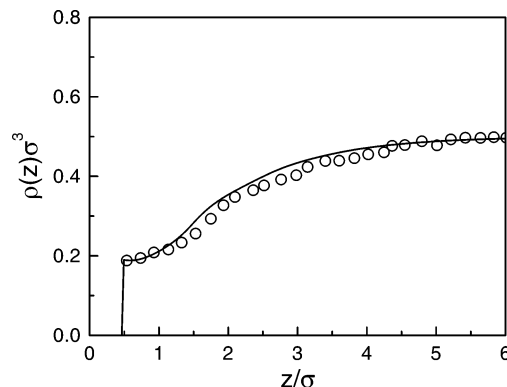
**B. Density Profiles for Lennard-Jones Fluids in Front of a Hard Wall and Confined in a Slit Pore.** The applicability of the present density functional theory for inhomogeneous systems as proposed here is also applied to the case of a Lennard-Jones fluid confined in a planar slit made up of two parallel hard walls as well as in front of a hard wall. As has already been mentioned, the LJ system has been treated here in the light of perturbation theory<sup>18,42</sup> in which one considers the splitting of the potential into a repulsive reference system and an attractive part. Here, we utilize the WCA splitting scheme and treat the attractive part in the mean-field approximation. We present the results from the present theory as well as the available simulation studies<sup>43</sup> for the density profiles of a LJ fluid of bulk density  $\rho_0 \sigma^3 = 0.75$  and reduced temperature  $T^* = 1.304$  confined in a slit pore of width  $H = 13\sigma$  in Figure 3 and the same system confined in a narrower pore of width  $H = 5\sigma$  in Figure 4. It is to be noted that in a pore width of  $H$  the distance accessible to the fluid particles is  $H - \sigma$ . As these figures show, the agreement of our results with those from the simulation is quite good in both the cases. To test our theoretical approach further, we have chosen a few more cases for which it has been shown<sup>44</sup> that Tarazona WDA<sup>6</sup> for the reference hard sphere part in combination with MFA for the attractive part of the potential is unable to predict the density profiles near a hard wall correctly. In Figure 5, we have plotted the density profile



**Figure 3.** Plot of the density profiles  $\rho(z)\sigma^3$  vs  $z/\sigma$  for a Lennard-Jones fluid of bulk density  $\rho_0 \sigma^3 = 0.75$  at reduced temperature  $T^* = 1.304$ , confined in a slit pore consisting of two hard walls of width  $H = 13\sigma$ . The result from the present approach is shown by the solid line and the symbols denote the simulation data.<sup>43</sup>

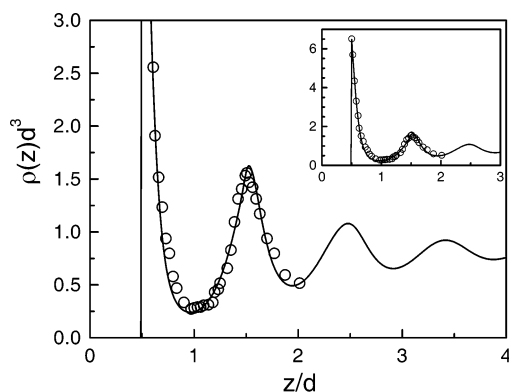


**Figure 4.** Plot of the density profiles  $\rho(z)\sigma^3$  vs  $z/\sigma$  for a Lennard-Jones fluid of bulk density  $\rho_0 \sigma^3 = 0.75$  at reduced temperature  $T^* = 1.304$ , confined in a slit pore consisting of two hard walls of width  $H = 5\sigma$ . The key is the same as in Figure 3.



**Figure 5.** Plot of density profiles  $\rho(z)\sigma^3$  vs  $z/\sigma$  for a Lennard-Jones fluid in contact with a hard wall at a reduced temperature of  $T^* = 1.35$  and bulk density of  $\rho_0 \sigma^3 = 0.5$ . The result from the present approach is shown by the solid line and the symbols denote the simulation data<sup>45</sup> (reproduced from ref 44).

calculated from the present approach for a LJ system of bulk density  $\rho_0 \sigma^3 = 0.5$  at the temperature  $T^* = 1.35$  along with the available simulation results.<sup>45</sup> Although we have not plotted the results of the Tarazona approach with MFA here, the same has been shown to be in complete disagreement with the simulation results in Figure 4 of ref 44. The results from the present approach, which also uses MFA for the attractive part, however, show very good agreement with the simulation. The importance of the attractive interaction among the particles is evident at this relatively low bulk density. The attraction between



**Figure 6.** Plot of density profiles  $\rho(z)\sigma^3$  vs  $z/\sigma$  for a Lennard-Jones fluid in contact with a hard wall at a reduced temperature of  $T^* = 1.35$  and bulk density of  $\rho_0\sigma^3 = 0.82$ . The key is the same as in Figure 5.

the particles in this case nullifies the strong short range structure induced by the pair repulsion, which generally induces a strong structure due to larger particle accumulation near the wall in the case of hard sphere–hard wall systems. The density profile in this case starts from a very low value at the wall and increases continuously to approach the bulk value far away from the wall, indicating the formation of a vapor layer near the wall surface. Most of the particles in this case tend to be away from the surface to the bulk because of stronger attraction among themselves. When the bulk density is increased to  $\rho_0\sigma^3 = 0.82$  as shown in Figure 6, however, strong oscillations in the density profile are observed, indicating that in this case, because of larger bulk density, the short-range repulsive force makes larger contribution and the attractive force is completely overshadowed by it. The present results for the density profile are found to compare fairly well with the corresponding simulation results.<sup>45</sup> In ref 44, it has been shown that, in both Tarazona WDA with MFA for attractive force and with more accurate treatment for the same, oscillations far away from the walls are too high as compared to the simulation results. In the present approach, however, smaller oscillations far away from the wall predicted by the simulation are fairly well reproduced. The peak height at the wall surface is slightly over predicted by the present approach as compared to the simulation. However, the density at the contact in our approach is determined by the bulk pressure, and use of a more accurate bulk pressure might improve the result, particularly at the contact.

Although not shown here, comparison of our result with the available simulation results<sup>43</sup> at low temperatures is not encouraging. Our results do not agree quite well, particularly near the walls. This disagreement may be due to several reasons: In their work,<sup>43</sup> the (NVT) MC simulation has been performed and the effect of open system (GCMC simulation) is taken into account by taking the bulk density as obtained from the density integral of their theoretically predicted  $\rho(\mathbf{r})$ . Thus, the bulk density they are using in simulation is quite different from the actual bulk density. It is further evident from the fact that density at the contact as obtained from this simulation is quite different from the bulk pressure as given by the accurate Nicolas et al. equation.<sup>40</sup> Thus, the chemical potentials in the theory and simulation may be different.

#### IV. Concluding Remarks

In the present work, a new density functional approach that combines both perturbative and nonperturbative weighted density approaches has been presented. Retaining terms up to

the ones containing third-order DCF in the functional Taylor expansion of the one particle DCF of the inhomogeneous fluid and evaluating the third-order DCF at an effective weighted density obtained by demanding the fourth order DCF to be reproduced in the homogeneous limit by the approximate one particle DCF, it is ensured that a subset of certain exact higher order terms has been taken into account. The three particle DCF of the homogeneous fluid required as input in this theory has been approximated by a simple form expressed in terms of the product of two second-order DCF related quantities of the homogeneous fluid along with a multiplicative parameter, which is determined by enforcing the density profile to satisfy an important sum rule known as the wall theorem. Applications of this theory to the hard sphere fluids as well as LJ fluids in confined geometries have been considered here, and the illustrative numerical results on the density profiles are shown to be in very good agreement with the corresponding computer simulation results. In a very recent study, this approach has also been extended and applied to hard sphere mixtures.<sup>46</sup> Further extensions and applications of this approach to other kind of systems with different interparticle potentials and other types of confinement geometries are in progress.

**Acknowledgment.** It is a pleasure to thank Dr. T. Mukherjee and Dr. J. P. Mittal for their kind interest and encouragement.

#### References and Notes

- (1) For a review, see: *Fundamentals of Inhomogeneous Fluids*; Henderson, D., Ed.; Marcel Dekker: New York, 1992.
- (2) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864. Mermin, N. D. *Phys. Rev. A* **1965**, *137*, 1441. Saam, W. F.; Ebner, C. *Phys. Rev. A* **1977**, *15*, 2566.
- (3) Evans, R. *Adv. Phys.* **1979**, *28*, 143.
- (4) For a review, see: Evans, R. In *Fundamentals of Inhomogeneous Fluids*; Henderson, D., Eds.; Marcel Dekker: New York, 1992.
- (5) Ramakrishnan, T. V.; Yussouff, M. *Phys. Rev. B* **1979**, *19*, 2775. For a review, see: Singh, Y. *Phys. Rep.* **1991**, *207*, 351. Haymet, A. D. J.; Oxtoby, D. W. *J. Chem. Phys.* **1981**, *74*, 2559. Haymet, A. D. J.; *Annu. Rev. Phys. Chem.* **1987**, *38*, 89.
- (6) Tarazona, P. *Mol. Phys.* **1984**, *52*, 81; *Phys. Rev. A* **1985**, *31*, 2672.
- (7) Curtin, W. A.; Ashcroft, N. W. *Phys. Rev. A* **1985**, *32*, 2909; *Phys. Rev. Lett.* **1986**, *56*, 2775.
- (8) Denton, A. R.; Ashcroft, N. W. *Phys. Rev. A* **1989**, *39*, 426.
- (9) Tan, Z.; Marini Bettolo Marconi, U.; van Swol, F.; Gubbins, K. E. *J. Chem. Phys.* **1989**, *90*, 3704.
- (10) Denton, A. R.; Ashcroft, N. W. *Phys. Rev. A* **1990**, *42*, 7312; *Phys. Rev. A* **1991**, *44*, 1219.
- (11) Denton, A. R.; Ashcroft, N. W. *Phys. Rev. A* **1991**, *44*, 8242.
- (12) Rickayzen, G.; Augousti, A. *Mol. Phys.* **1984**, *52*, 1355. Rickayzen, G.; Kalpaxis, P.; Chacon, E. *Mol. Phys.* **1994**, *101*, 7963.
- (13) Choudhury, N.; Ghosh, S. K. *J. Chem. Phys.* **1999**, *110*, 8628.
- (14) Zhou, S.; Ruckenstein, E. *Phys. Rev. E* **2000**, *61*, 2704.
- (15) Calleja, M.; North, A. N.; Powles, J. G.; Rickayzen, G. *Mol. Phys.* **1991**, *73*, 973.
- (16) Choudhury, N.; Ghosh, S. K. *Phys. Rev. E* **2001**, *64*, 021206.
- (17) Choudhury, N.; Ghosh, S. K. *J. Chem. Phys.* **1998**, *108*, 7493.
- (18) Hansen, J. P.; McDonald, I. R. *Theory of simple liquids*, 2nd ed.; Academic: London, 1986.
- (19) Caccamo, C. *Phys. Rep.* **1996**, *274*, 1.
- (20) Choudhury, N.; Ghosh, S. K. *J. Chem. Phys.* **2002**, *116*, 8517.
- (21) Zhou, S.; Ruckenstein, E. *J. Chem. Phys.* **2000**, *112*, 5242, 8079.
- (22) S. Zhou, *J. Chem. Phys.* **2000**, *113*, 8719; *Phys. Rev. E* **2001**, *63*, 051203; *Phys. Rev. E* **2001**, *64*, 011112.
- (23) Choudhury, N.; Ghosh, S. K. *J. Chem. Phys.* **2001**, *114*, 8530.
- (24) Kim, S.-C.; Suh, S.-H. *J. Chem. Phys.* **2002**, *117*, 9880.
- (25) Patra, C. N.; Ghosh, S. K. *J. Chem. Phys.* **2002**, *117*, 8933.
- (26) Zhou, S. *J. Chem. Phys.* **2001**, *115*, 2212; *Phys. Rev. E* **2001**, *63*, 061206.
- (27) Rosenfeld, Y. *Phys. Rev. Lett.* **1989**, *63*, 980.
- (28) Kierlik, E.; Rosinberg, M. L. *Phys. Rev. A* **1990**, *42*, 3382.
- (29) Choudhury, N.; Patra, C. N.; Ghosh, S. K. *J. Phys. Condens. Matter* **2002**, *14*, 11955.
- (30) Likos, C. N.; Ashcroft, N. W. *J. Chem. Phys.* **1993**, *99*, 9090.

- (30) Likos, C. N.; Ashcroft, N. W. *Phys. Rev. Lett.* **1992**, *69*, 316; **1992**, *69*, 3141E.
- (31) Zhou, S. *New J. Phys.* **2002**, *4*, 36.
- (32) Zhou, S. *J. Phys. Chem. B* **2002**, *106*, 7674; *Chem. Phys.* **2003**, *289*, 309.
- (33) Volterra, V. *Theory of Functionals*; Dover: New York, 1959; p 26. See also: *Density Functional Theory of Atoms and Molecules*; Parr, R. G., Yang, W., Eds.; Oxford University Press: New York, 1989; p 249.
- (34) Lu, B. Q.; Evans, R.; Telo da Gama, M. M. *Mol. Phys.* **1985**, *55*, 1319.
- (35) Kierlik, E.; Rosinberg, M. L. *Phys. Rev. A* **1991**, *44*, 5025. Kierlik, E.; Rosinberg, M. L.; Finn, J. E.; Monson, P. A. *Mol. Phys.* **1992**, *75*, 1435.
- (36) Verlet, L.; Weis, J. J. *Phys. Rev. A* **1982**, *5*, 939.
- (37) McQuarrie, D. A.; Katz, J. L. *J. Chem. Phys.* **1966**, *44*, 2398.
- (38) Barker, J.; Henderson, D. *J. Chem. Phys.* **1967**, *47*, 7414.
- (39) Weeks, J. D.; Chandler, D.; Anderson, H. C. *J. Chem. Phys.* **1971**, *54*, 5237.
- (40) Nicolas, J. J.; Gubbins, K. E.; Strett, W. B.; Tildesley, D. J. *Mol. Phys.* **1979**, *37*, 1429.
- (41) Snook, I. K.; Henderson, D. *J. Chem. Phys.* **1978**, *68*, 2134.
- (42) Barker, J. A.; Henderson, D. *J. Chem. Phys.* **1967**, *47*, 4714; *Rev. Mod. Phys.* **1976**, *48*, 587.
- (43) Powles, J. G.; Rickayzen, G.; Williams, M. L. *Mol. Phys.* **1988**, *64*, 33.
- (44) Tang, Z.; Scriven, L. E.; Davis, H. T. *J. Chem. Phys.* **1991**, *95*, 2659.
- (45) Balabanic, C.; Borstnik, B.; Milcic, R.; Rubcic, A.; Sokolic, F. Static and Dynamic Properties of Liquids. In *Springer Proceedings in Physics*; Davidovic, M., Soper, A. K., Eds.; Springer: Berlin, 1989; Vol. 40, p 70.
- (46) Choudhury, N.; Ghosh, S. K. *J. Chem. Phys.* **2003**, *118*, 1327.