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A new perturbative weighted density functional theory for an inhomogeneous hard-sphere fluid mixture

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Abstract

A new approach to the structure of the inhomogeneous fluid mixture is developed within the framework of density functional theory by expanding the Denton–Ashcroft weighted density-based expression for the first-order direct correlation function as a Taylor series in the weighted density inhomogeneity. The connection of this expansion with the conventional functional Taylor perturbative approach is investigated. A truncation of the proposed expansion coupled with the use of a scaled parameter to mimic the effect of the neglected higher-order contributions, determined self-consistently by forcing the wall theorem to be satisfied, is implemented. The theory is employed to predict the structure of a pure hard-sphere fluid as well as a hard-sphere mixture near a hard wall and the agreement with the available simulation results is found to be very good.

1. Introduction

Density functional theory (DFT) [1] has established itself as a versatile and powerful tool for the study of the structure of inhomogeneous classical fluids [2] and their mixtures, associated with a number of systems and phenomena, such as fluids at interfaces, adsorption in pores, capillary condensation, nucleation, freezing, wetting and various other interfacial phenomena. In DFT, one starts by expressing the grand potential of a many-particle system as a functional of its single-particle density distribution and then minimizes it under the condition of a fixed external potential to obtain the equilibrium density profile. Due to the lack of knowledge of the exact form of part of the free energy functional, however, there have been approximate versions of DFT which may be broadly classified into two categories [3], namely functional perturbative approaches and nonperturbative weighted density approaches (WDA) [4–8] which also include geometry-based functionals [7, 8]. While the success of the perturbative approach has been

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limited by the nonavailability of knowledge of the higher-order direct correlation functions (DCF), a systematic improvement [9] is possible in this framework at least in principle. On the other hand, the WDA schemes evaluate the excess free energy densities [4] or the first-order DCFs [5, 6] using an effective weighted density obtained through a suitable averaging of the actual inhomogeneous density distribution and have been extended to a large variety of systems [10–12]. WDA is assumed to include the higher-order contributions in an average approximate manner by incorporating some of these terms exactly while neglecting the others. It will thus be of interest to develop a perturbative analysis of the WDA approach and attempt to correlate the contributions of different order with the corresponding terms in the conventional functional Taylor perturbative expansion. Also, often some of the important theorems are not satisfied by some of the WDA-based density at the interface and in the absence of any parameter they cannot be enforced in these WDA approaches as prescribed. On the other hand, some of these theorems have been imposed in a functional perturbation scheme by using a parameter in the third-order DCF, determined by forcing the wall theorem to be satisfied. Also, for homogeneous fluids, there is the standard bridge function approach [13] in the integral equation theory, which amounts to a perturbative DFT with the higher-order terms (beyond second order) together forming the bridge function. This approach has recently been successfully employed in the case of inhomogeneous fluids as well [14] and it will be of interest to explore the connection of this approach to the WDA-based approaches.

The purpose of the present work is thus twofold. We first propose a Taylor series perturbative expansion of the Denton–Ashcroft (DA) WDA-based first-order DCF and show its connection with the conventional functional perturbation expansion as well as the bridge function approach. The expansion is then truncated at a finite order and a parameter is used to compensate for the neglect of the remaining terms which is determined by forcing the wall theorem to be satisfied. Thus, the present perturbative WDA approach might be considered to be a hybrid of the perturbative and nonperturbative prescriptions.

The plan of the rest of the paper is as follows. In section 2, we develop the theoretical formalism and discuss in section 3 the numerical results for a one-component hard-sphere fluid as well as a binary hard-sphere fluid mixture at a hard-wall interface. Finally we offer a few concluding remarks in section 4.

2. Density functional theory for an inhomogeneous binary fluid mixture

The system under consideration is a two-component fluid mixture with the inhomogeneous density distributions $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ arising as a consequence of the respective fixed external potentials $u_1(\mathbf{r})$ and $u_2(\mathbf{r})$ corresponding to the two components. In DFT, the grand potential $\Omega[\rho_1, \rho_2]$ of this system is proved to be a unique functional of the component densities and is expressed as

$$\begin{aligned} \Omega[\rho_1, \rho_2] = & \beta^{-1} \sum_{i=1}^2 \int d\mathbf{r} \rho_i(\mathbf{r}) \{ \ln[\rho_i(\mathbf{r}) \Lambda_i^3] - 1 \} + F_{ex}[\rho_1, \rho_2] \\ & + \sum_{i=1}^2 \int d\mathbf{r} [u_i(\mathbf{r}) - \mu_i] \rho_i(\mathbf{r}), \end{aligned} \quad (1)$$

where β ($=1/k_B T$, with k_B as the Boltzmann constant) is the inverse temperature and Λ_i and μ_i represent respectively the thermal de Broglie wavelength and chemical potential of the i th component. Here, the first term on the right-hand side (rhs) corresponds to the ideal-gas free energy while the functional $F_{ex}[\rho_1, \rho_2]$ representing the excess free energy arising from

interaction is a universal functional of the densities for a fixed interparticle potential and defines the first-order DCF as the functional derivative given by

$$c_i^{(1)}(\mathbf{r}; [\rho_1, \rho_2]) = -\beta \frac{\delta F_{ex}[\rho_1, \rho_2]}{\delta \rho_i(\mathbf{r})}, \quad (2)$$

which appears in the density equation for the i th component given by

$$\rho_i(\mathbf{r}) = \rho_i^0 \exp\{-\beta u_i(\mathbf{r}) + c_i^{(1)}(\mathbf{r}; [\rho_1(\mathbf{r}), \rho_2(\mathbf{r})]) - \tilde{c}_i^{(1)}(\rho_1^0, \rho_2^0)\} \quad (3)$$

where the quantity $\tilde{c}^{(1)}$ denotes the DCF in the bulk phase. This equation is obtained by minimizing the grand potential given by equation (1) and equating the component chemical potentials of the inhomogeneous system to their bulk phase values since the fluid mixture is considered to be in equilibrium with the bulk fluid of uniform bulk densities ρ_1^0 and ρ_2^0 away from the source of inhomogeneity. It may be noted that the form of equation (3) is the same as the Boltzmann distribution for an ideal gas and all the effects of interparticle interactions enter through the DCF $c_i^{(1)}(\mathbf{r}; [\rho_1, \rho_2])$ which plays the role of an effective one-particle potential in DFT just as the Kohn–Sham potential does in quantum DFT [15] for many-electron systems.

The different versions of DFT correspond to various approximations proposed for the last two terms on the rhs in equation (3) involving the first-order DCF $c_i^{(1)}(\mathbf{r}; [\rho_1, \rho_2])$, the exact functional form of which is unknown for an inhomogeneous density distribution. The conventional functional Taylor perturbative expansion expresses this quantity (retaining terms up to second order in density inhomogeneity) as

$$\begin{aligned} c_i^{(1)}(\mathbf{r}; [\rho_1, \rho_2]) - \tilde{c}_i^{(1)}([\rho_1^0, \rho_2^0]) &= \sum_{j=1}^2 \int d\mathbf{r}' \tilde{c}_{ij}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho_1^0, \rho_2^0]) (\rho_j(\mathbf{r}') - \rho_j^0) \\ &+ \frac{1}{2} \sum_{j=1}^2 \sum_{k=1}^2 \iint d\mathbf{r}' d\mathbf{r}'' \tilde{c}_{ijk}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}''; [\rho_1^0, \rho_2^0]) (\rho_j(\mathbf{r}') - \rho_j^0) (\rho_k(\mathbf{r}'') - \rho_k^0) \end{aligned} \quad (4)$$

where the quantities $c_{ij}^{(2)}$ and $c_{ijk}^{(3)}$ denote the second- and third-order DCFs defined respectively as

$$c_{ij}^{(2)}(\mathbf{r}, \mathbf{r}') = -\beta \frac{\delta^2 F_{ex}[\rho_1, \rho_2]}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}')} \quad (5)$$

and

$$c_{ijk}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = -\beta \frac{\delta^3 F_{ex}[\rho_1, \rho_2]}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}') \delta \rho_k(\mathbf{r}'')} \quad (6)$$

and $\tilde{c}_{ij}^{(2)}$ and $\tilde{c}_{ijk}^{(3)}$ in equation (4) correspond to the homogeneous fluid mixture. A nonperturbative WDA such as that of DA [5, 6] however employs the mapping

$$c_i^{(1)}(\mathbf{r}; [\rho]) = \tilde{c}_i^{(1)}(\bar{\rho}_i(\mathbf{r}); x) \quad (7)$$

and evaluates the expressions for the first-order DCF of the homogeneous system at the effective weighted densities $\bar{\rho}_i(\mathbf{r})$ defined through an averaging over the density distribution as given by

$$\bar{\rho}_i(\mathbf{r}) = \sum_{j=1}^2 \int d\mathbf{r}' w_{ij}(\mathbf{r}, \mathbf{r}'; [\rho_1^0, \rho_2^0]) \rho_j(\mathbf{r}') \quad (8)$$

and the bulk concentration $x = \rho_2^0 / (\rho_1^0 + \rho_2^0)$. Here the weight function $w_{ij}(\mathbf{r}, \mathbf{r}')$, as obtained by demanding the correct second-order DCFs to be obtained by taking the functional derivative of equation (7) in the homogeneous limit, is given by

$$w_{ij}(\mathbf{r}, \mathbf{r}') = \tilde{c}_{ij}^{(2)}(\mathbf{r}, \mathbf{r}') / \int d\mathbf{r}' \tilde{c}_{ij}^{(2)}(\mathbf{r}, \mathbf{r}') \quad (9)$$

where the integral in the denominator accounts for the correct normalization of the weight function. It may be noted that the weight function in equation (8) is evaluated here at the bulk densities [16] instead of the weighted densities used in the original DA approach. Thus, we have the functional perturbative as well as the WDA-based approaches obtained by using equations (4) and (7) respectively in the density equation (3).

We now propose to employ the Taylor series expansion of the WDA-based quantity ($\tilde{c}_i^{(1)}(\bar{\rho}_i(\mathbf{r})) - \tilde{c}_i^{(1)}(\rho^0)$) in powers of the weighted density inhomogeneity ($\bar{\rho}_i(\mathbf{r}) - \rho^0$) and write

$$\begin{aligned} \Delta c_i^{(1)}(\mathbf{r}) &= \tilde{c}_i^{(1)}(\bar{\rho}_i(\mathbf{r})) - \tilde{c}_i^{(1)}(\rho^0) = \tilde{c}_i^{(1)'}(\bar{\rho}_i(\mathbf{r}) - \rho^0) + \frac{1}{2}\tilde{c}_i^{(1)''}(\bar{\rho}_i(\mathbf{r}) - \rho^0)^2 \\ &\quad + \frac{1}{6}\tilde{c}_i^{(1)'''}(\bar{\rho}_i(\mathbf{r}) - \rho^0)^3 + \text{higher-order terms} \end{aligned} \quad (10)$$

where the primes on \tilde{c}_i denote the derivatives of different order with respect to the bulk density and these quantities are also evaluated at this density. It may be noted that the expansion here is around the total bulk density $\rho^0 = \rho_1^0 + \rho_2^0$ unlike in equation (4) involving the component densities, since the weighted density $\bar{\rho}_1(\mathbf{r})$ and $\bar{\rho}_2(\mathbf{r})$ essentially represent the total effective densities needed to mimic the inhomogeneous fluid locally. We now use a truncated version of this expansion and also proceed to demonstrate the interrelation with the conventional functional perturbation as well as the bridge function approach by considering the specific cases of inhomogeneous hard-sphere fluid and its mixtures separately.

2.1. One-component hard-sphere fluid near a hard wall

We first consider the simple case of a one-component hard-sphere fluid near a hard wall for which the density inhomogeneity is only in the perpendicular z -direction due to the planar symmetry of the problem. For the wall position at $z = 0$, the external potential $u(z) = 0$ for $z > d/2$ and is infinite for $z < d/2$, where d is the hard-sphere diameter. The general density equation (3) can be rewritten in the simple form

$$\rho(z) = \rho^0 \exp[\Delta c^{(1)}(z; [\rho])] \quad (11)$$

for $z > d/2$ and $\rho(z) = 0$ otherwise. Here the first-order DCF contribution $\Delta c^{(1)}(z; [\rho])$ to the density equation (11) is given in the proposed expansion (equation (10)) by

$$\begin{aligned} \Delta c^{(1)}(z; [\rho]) &= \tilde{c}^{(1)}(\bar{\rho}(z)) - \tilde{c}^{(1)}(\rho^0) \\ &= \tilde{c}^{(1)'}(\bar{\rho}(z) - \rho^0) + \frac{1}{2}\tilde{c}^{(1)''}(\bar{\rho}(z) - \rho^0)^2 + \frac{\lambda}{6}\tilde{c}^{(1)'''}(\bar{\rho}(z) - \rho^0)^3 \end{aligned} \quad (12)$$

where the primed quantities are evaluated at the bulk density and we have used a truncation at third order introducing a multiplicative factor λ in this term as a compensation for the neglect of the higher-order terms. We propose to evaluate this constant by demanding the resulting density at the surface to satisfy the wall theorem relating the bulk pressure to the contact density at the wall.

For a hard-sphere fluid, the second-order DCF $c^{(2)}(|\mathbf{r} - \mathbf{r}'|)$ for the bulk phase is known within the Percus–Yevick (PY) approximation and is given by $\tilde{c}^{(2)}(r) = a + br/d + c(r/d)^3$ for $r < d$ (and zero otherwise), with the density-dependent coefficients a , b and c expressed by simple standard expressions in terms of the packing fraction $\eta = (\pi/6)\rho^0 d^3$ and the expression for the bulk pressure is given by the compressibility equation of state given by

$$\frac{\beta P}{\rho^0} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}. \quad (13)$$

Equating βP with $\rho(d/2)$, the density at the interface, as predicted by the density equation (equations (11) and (12)), one obtains the following explicit expression of the parameter λ :

$$\lambda = \frac{6(\ln(\beta P/\rho^0) - \tilde{c}^{(1)' }(\bar{\rho}(d/2) - \rho^0) - \frac{1}{2}\tilde{c}^{(1)'' }(\bar{\rho}(d/2) - \rho^0)^2)}{\tilde{c}^{(1)''' }(\bar{\rho}(d/2) - \rho^0)^3}. \quad (14)$$

In the integral equation theory of homogeneous fluids, one defines an indirect correlation function $\gamma(r)$ which is also used to express the bridge function $B(\gamma(r))$. In the present inhomogeneous case, the analogous quantity $\gamma(z)$ can be defined [14, 17] as

$$\gamma(z) = \int d\mathbf{r}' \tilde{c}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho^0])(\rho(z') - \rho^0) \quad (15)$$

which on comparison with the expression of the weighted density $\bar{\rho}(z)$ as obtained from equations (8) and (9) and given by

$$\bar{\rho}(z) = \frac{1}{\tilde{c}^{(1)' }} \int d\mathbf{r}' \tilde{c}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho^0])\rho(z') \quad (16)$$

clearly leads to the result

$$\gamma(z) = \tilde{c}^{(1)' }[\bar{\rho}(z) - \rho^0]. \quad (17)$$

Comparing equation (12) with the conventional functional perturbation expression (equation (4)) rewritten for the one-component case as

$$\begin{aligned} \Delta c^{(1)}(z; [\rho]) &= \int d\mathbf{r}' \tilde{c}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho^0])(\rho(z') - \rho^0) \\ &+ \frac{1}{2} \iint d\mathbf{r}' d\mathbf{r}'' \tilde{c}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}''; [\rho^0])(\rho(z') - \rho^0)(\rho(z'') - \rho^0) \end{aligned} \quad (18)$$

it is evident that the first term in equation (12) is identical to $\gamma(z)$ defined in equation (17) and representing the first correction term in equation (18). The second term in equation (12) can be shown to be identical to the term involving the third-order DCF $\tilde{c}^{(3)}$ in equation (18) if the latter is approximated as the product of two second-order DCFs given by

$$\tilde{c}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}''; [\rho^0]) = \frac{\tilde{c}^{(1)'' }}{[\tilde{c}^{(1)' }]^2} \tilde{c}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho^0])\tilde{c}^{(2)}(\mathbf{r}, \mathbf{r}''; [\rho^0]). \quad (19)$$

It may be noted that this form of the third-order DCF has been obtained earlier and used by Zhou and Ruckenstein [18], while a more accurate representation [9] has also been available in terms of an integral involving three second-order DCFs. The last term in equation (12) corresponds to a term involving the fourth-order DCF in the conventional functional perturbation approach (neglected in equation (18)) and we have employed a parameter λ in this term which is determined by the pressure condition as already mentioned.

One can also combine the last two terms in equation (12) which essentially represent a bridge function and re-express them approximately as a Verlet modified bridge function [19] in the form

$$B[\gamma(z)] = \frac{1}{2} \frac{\tilde{c}^{(1)'' }}{[\tilde{c}^{(1)' }]^2} \gamma^2 \left(1 - \frac{\lambda}{3} \frac{\tilde{c}^{(1)'' }}{\tilde{c}^{(1)' } \tilde{c}^{(1)'' }} \gamma \right)^{-1}. \quad (20)$$

Thus, the present approach based on a perturbative expansion of the WDA result shows clear correspondence with the various other approximate approaches available and also provides a route to the inhomogeneous density distribution satisfying the contact theorem.

2.2. Binary hard-sphere fluid mixture near a hard wall

We now consider a binary hard-sphere fluid mixture characterized by the diameter ratio $\alpha (=d_1/d_2)$ with d_1 being the diameter of the smaller spheres, the concentration $x = \rho_2^0/\rho^0$ and the bulk packing fraction η defined as

$$\eta = \frac{\pi}{6}[\rho_1^0 d_1^3 + \rho_2^0 d_2^3] = \frac{\pi}{6}[x + (1-x)\alpha^3]\rho^0 d_2^3. \quad (21)$$

For the uniform hard-sphere mixture, Lebowitz's solution [20] of the PY integral equation provides the second-order DCF $\tilde{c}_{ij}^{(2)}(|\mathbf{r} - \mathbf{r}'|)$ and also the bulk pressure which is given by

$$\frac{\beta P}{\rho^0} = \frac{(1 + \xi_3 + \xi_3^2)}{(1 - \xi_3)^3} - 3\eta_1 x \left(\frac{1}{\alpha} - 1\right)^2 \frac{[(1 + \frac{1}{\alpha}) + d_2 \xi_2]}{(1 - \xi_3)^3} \quad (22)$$

where $\eta_1 = (\pi/6)\rho_1^0 d_1^3$ and $\xi_n = (\pi/6)\sum_{i=1}^2 \rho_i^0 d_i^n$. Also the partial pressures of the individual components have been obtained within the scaled particle theory by Lebowitz *et al* [21] and for the i th component, the partial pressure p_i is given by

$$\beta p_i = \frac{\rho_i^0}{(1 - \xi_3)} + \left[\frac{\pi}{6} \beta P - \frac{\xi_0}{(1 - \xi_3)} \right] \frac{\rho_i^0 d_i^2}{\xi_2} \quad i = 1, 2. \quad (23)$$

For the hard-sphere mixture near a hard wall located at $z = 0$, the external potential $u_i(z)$ is again infinite for $z < d_i/2$ and zero otherwise. The equation for the equilibrium density profile (i.e. equation (3)) can be rewritten for this case as

$$\rho_i(z) = \rho_i^0 \exp[\Delta c_i^{(1)}(z)] \quad (24)$$

where the quantity $\Delta c_i^{(1)}(z)$ can be expressed in the present perturbative WDA prescription by rewriting equation (10) (and retaining terms up to the third power) as

$$\Delta c_i^{(1)}(z) = \tilde{c}_i^{(1)'}(\bar{\rho}_i(z) - \rho^0) + \frac{1}{2}\tilde{c}_i^{(1)''}(\bar{\rho}_i(z) - \rho^0)^2 + \frac{\lambda_i}{6}\tilde{c}_i^{(1)'''}(\bar{\rho}_i(z) - \rho^0)^3 \quad (25)$$

with the weighted density $\bar{\rho}_i(z)$ given by the final expression

$$\bar{\rho}_i(z) = \sum_{j=1}^2 \frac{1}{\tilde{c}_{ij}^{(1)'}} \int d\mathbf{r}' \tilde{c}_{ij}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho_1^0, \rho_2^0]) \rho_j(z') \quad (26)$$

where $\tilde{c}_{ij}^{(1)'}$ represents the integral $\int d\mathbf{r}' \tilde{c}_{ij}^{(2)}(\mathbf{r}, \mathbf{r}')$. The parameters λ_i for each component as determined by equating the component density quantities at the wall with the respective bulk partial pressures given by equation (23) are given by the expressions

$$\lambda_i = \frac{6(\ln(\beta p_i/\rho_i^0) - \tilde{c}_i^{(1)'}(\bar{\rho}_i(d/2) - \rho_i^0) - \frac{1}{2}\tilde{c}_i^{(1)''}(\bar{\rho}_i(d/2) - \rho_i^0)^2)}{\tilde{c}_i^{(1)'''}(\bar{\rho}_i(d/2) - \rho_i^0)^3}. \quad (27)$$

For the inhomogeneous fluid mixture, the indirect correlation function $\gamma_i(z)$ can be expressed as

$$\gamma_i(z) = \sum_{j=1}^2 \int d\mathbf{r}' \tilde{c}_{ij}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho_1^0, \rho_2^0]) [\rho_j(z') - \rho_j^0] \quad (28)$$

and on comparison with the weighted density equation (26), leads to an interrelation between the two quantities in terms of cross-contributions involving the components. Clearly, the first term of the new perturbative WDA expression (equation (25)) represents the second-order perturbative correction $\gamma_i(z)$ in the conventional functional Taylor expansion with some additional cross-term contributions arising from the fact that the latter involves expansion around the component bulk densities. The interpretations of the other terms are also similar but, unlike in the pure fluid case, there are cross-terms in the case of mixtures. The bridge function can also be extracted in the form of equation (20) in the case of mixtures.

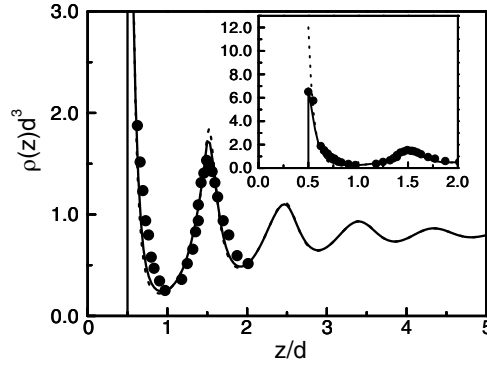


Figure 1. A plot of density profile $\rho(z)d^3$ versus z/d for a one-component hard-sphere fluid of bulk density $\rho^0 d^3 = 0.81$ near a hard wall. Solid curve: present scheme; dotted line: weighted density approximation of DA; circles : simulation. The inset shows the density profile at and near contact.

3. Results and discussion

The density profiles of the one-component hard-sphere fluid as well as the hard-sphere mixtures have been calculated through numerical solution of equations (11) and (12) for the former and equations (24) and (25) for the latter. The trapezoidal rule with a uniform mesh has been used for the one-dimensional numerical integration and the respective bulk density quantities have been used as the initial inputs for the self-consistent iterative procedure. The distances from the wall and the density quantities are measured in dimensionless forms as z/d and $\rho(z)d^3$ respectively for the pure fluid and z/d_1 and $\rho_i(z)d_1^3$ for the fluid mixture.

The calculated density profile of a hard-sphere fluid of bulk density $\rho^0 d^3 = 0.81$ near a hard wall is shown in figure 1 along with the simulation results [22] as well as the results calculated by us using the DA WDA [6]. The wall theorems have been imposed through the parameters λ and λ_i appearing in the density equations. The positions and heights of the peaks of the oscillatory density profiles predicted by the present theory are found to be in excellent agreement with the available simulation results. This shows the applicability of the present perturbative WDA approach to the case of pure hard-sphere fluids at interfaces.

For the hard-sphere fluid mixture near a wall, we consider the density profiles $\rho_i(z)d_1^3$ of the two components calculated for different values of the bulk packing fraction η , bulk concentration x and the diameter ratio α . In figure 2(a), we have plotted the calculated density profiles of the two components for the system parameters $\alpha = 1/3$, $\eta = 0.3435$ and $x = 0.7144$ along with the available simulation results [23] as well as the results from the DA WDA [6]. It is observed that the present results show clearly better agreement with simulation not only at contact but also at the second peak as well as elsewhere. The densities of the components approach the respective bulk density limits far away from the wall. The calculated concentration profile $\rho_1(z)/(\rho_1(z) + \rho_2(z))$ of the first component (smaller size) for the same system parameters has been plotted in figure 2(b) along with the simulation results and again the agreement is found to be quite good. Thus, it is clear that the results based on the present approach are found to be in better agreement with simulation for the systems studied here.

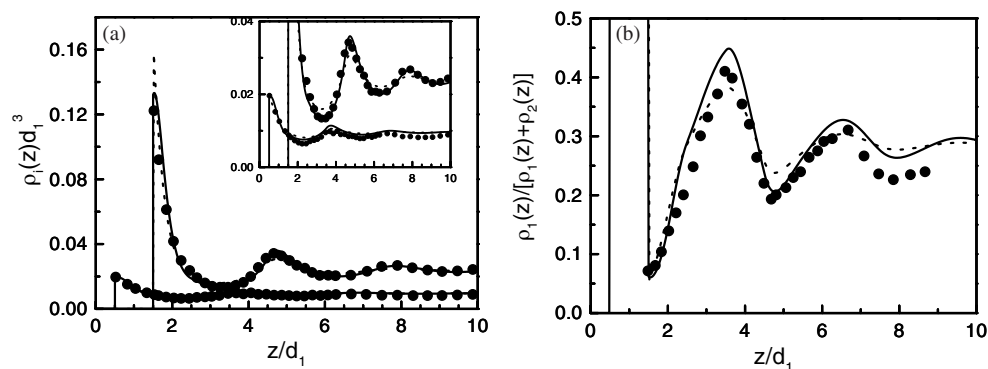


Figure 2. (a) A plot of the density profiles $\rho_i(z)d_1^3$ versus z/d_1 for a hard-sphere mixture near a hard wall with $\alpha = 1/3$, $\eta = 0.3435$ and $x = 0.7144$. Bottom curves: $\rho_1(z)$; upper curves: $\rho_2(z)$. Solid curve: present scheme; dotted curve: weighted density approximation of DA; circles: simulation. (b) A plot of the concentration profiles $\rho_1(z)/[\rho_1(z) + \rho_2(z)]$ versus z/d_1 for a hard-sphere mixture near a hard wall. The parameters are the same as in figure 2(a). Solid curve: present scheme; dotted curve: weighted density approximation of DA; circles: simulation.

4. Concluding remarks

A density functional approach based on a perturbative expansion of the WDA expression has been developed here for a one-component fluid as well as a binary fluid mixture. For a pure fluid an explicit order-by-order analysis of the WDA scheme has been presented and the truncated expansion has been scaled to force the wall theorem to be satisfied by the resulting density profile. For the mixture as well, a similar correspondence has been discussed although here a few cross-terms appear to be present. Application to the hard-sphere fluid as well as the hard-sphere fluid mixture has been considered and illustrative numerical results on density profiles are shown to be in good agreement with the simulation results. Extensions and applications of the present theory to other kinds of system with soft interparticle potentials are possible by using, for example, a thermodynamic perturbation approach [24] with a hard-sphere reference system. Further studies in these directions are in progress.

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References

- [1] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864
Mermin N D 1965 *Phys. Rev. A* **137** 1441
Saam W F and Ebner C 1977 *Phys. Rev. A* **15** 2566
- [2] For a review, see
Henderson D (ed) 1992 *Fundamentals of Inhomogeneous Fluids* (New York: Dekker)
- [3] For a review, see
Evans R 1992 *Fundamentals of Inhomogeneous Fluids* ed D Henderson (New York: Dekker)
- [4] Tarazona P 1984 *Mol. Phys.* **52** 81
Tarazona P 1985 *Phys. Rev. A* **31** 2672
- [5] Denton A R and Ashcroft N W 1989 *Phys. Rev. A* **39** 426

- [6] Denton A R and Ashcroft N W 1991 *Phys. Rev. A* **44** 8242
- [7] Rosenfeld Y 1989 *Phys. Rev. Lett.* **63** 980
- [8] Kierlik E and Rosinberg M L 1990 *Phys. Rev. A* **42** 3382
- [9] Choudhury N and Ghosh S K 1999 *J. Chem. Phys.* **110** 8628
Rickayzen G and Augousti A 1984 *Mol. Phys.* **52** 1355
- [10] Patra C N and Ghosh S K 1993 *Phys. Rev. E* **47** 4088
Patra C N and Ghosh S K 1993 *Phys. Rev. E* **48** 1154
Patra C N and Ghosh S K 1994 *J. Chem. Phys.* **102** 2556
Patra C N and Ghosh S K 2002 *J. Chem. Phys.* **116** 9846
- [11] Choudhury N and Ghosh S K 1996 *J. Chem. Phys.* **104** 9563
Choudhury N and Ghosh S K 1996 *Phys. Rev. E* **53** 3847
Choudhury N and Ghosh S K 1997 *J. Chem. Phys.* **106** 1576
Choudhury N and Ghosh S K 1998 *Phys. Rev. E* **57** 1939
Choudhury N and Ghosh S K 2002 *J. Chem. Phys.* **116** 384
- [12] Denton A R and Ashcroft N W 1989 *Phys. Rev. A* **39** 4701
Choudhury N and Ghosh S K 1995 *Phys. Rev. E* **51** 4503
- [13] Caccamo C 1996 *Phys. Rep.* **274** 1
Duh D-M and Henderson D 1996 *J. Chem. Phys.* **104** 6742
- [14] Choudhury N and Ghosh S K 2001 *J. Chem. Phys.* **114** 8530
- [15] Parr R G and Yang W 1989 *Density Functional Theory of Atoms and Molecules* (New York: Oxford University Press)
- [16] Patra C N and Ghosh S K 2002 *J. Chem. Phys.* **116** 8509
- [17] Zhou S and Ruckenstein E 2000 *J. Chem. Phys.* **112** 8079
- [18] Zhou S and Ruckenstein E 2000 *Phys. Rev. E* **61** 2704
- [19] Choudhury N and Ghosh S K 2002 *J. Chem. Phys.* **116** 8517
- [20] Lebowitz J L 1964 *Phys. Rev.* **133** A895
- [21] Lebowitz J L, Helfand E and Praestgaard E 1965 *J. Chem. Phys.* **43** 774
- [22] Snook I K and Henderson D 1978 *J. Chem. Phys.* **68** 2134
- [23] Tan Z, Marini Bettolo Marconi U, van Swol F and Gubbins K E 1989 *J. Chem. Phys.* **90** 3704
- [24] Hansen J-P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)