Vol 16 No 5, May 2007
1009-1963/2007/16(05)/1167-09

Chinese Physics

© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Density functional approximation for van der Waals fluids: based on hard sphere density functional approximation*

Zhou Shi-Qi(周世琦)†

Laboratory of Green Packaging and Biological Nanotechnology and

Institute of Modern Statistical Mechanics, Hunan University of Technology, Zhuzhou 412008, *China*

(Received 31 July 2006; revised manuscript received 23 October 2006)

A universal theoretical approach is proposed which enables all hard sphere density functional approximations (DFAs) applicable to van der Waals fluids. The resultant DFA obtained by combining the universal theoretical approach with any hard sphere DFAs only needs as input a second-order direct correlation function (DCF) of a coexistence bulk fluid, and is applicable in both supercritical and subcritical temperature regions. The associated effective hard sphere density can be specified by a hard wall sum rule. It is indicated that the value of the effective hard sphere density so determined can be universal, i.e. can be applied to any external potentials different from the single hard wall. As an illustrating example, the universal theoretical approach is combined with a hard sphere bridge DFA to predict the density profile of a hard core attractive Yukawa model fluid influenced by diverse external fields; agreement between the present formalism's predictions and the corresponding simulation data is good or at least comparable to several previous DFT approaches. The primary advantage of the present theoretical approach combined with other hard sphere DFAs is discussed.

Keywords: statistical mechanics, inhomogeneity
PACC: 9160K, 8260L

1. Introduction

During the last few decades, classical density functional theory (DFT) had witnessed considerable progress, most of which happens in the field of hard sphere density functional approximation (DFA), so it is reasonable to conclude that the theory for hard sphere DFA has been highly successful.[1] To name some of successful hard sphere DFAs, we have a long-history functional perturbation expansion approximation (FPEA),[1,2] and the weighted density-type approximation (WDA), which include several different versions, i.e. the Tarazona version,[3] Ashcroft's version,[4] and Rosenfeld's fundamental measure version.[5] We also have a so-called bridge DFA (BDFA),[6] a Lagrangian theorem-based DFA (LTDFA)[7] and its adjustable parameter free version.[8] All of the above-mentioned hard sphere DFAs perform well for hard sphere fluid under the influence of diverse external potentials. Especially, the LTDFA holds a desirable self-correction property as discussed in a recent paper.[9] Although the bridge DFA and the LTDFA are approximations for the nonuniform first-order direct correlation function (DCF), they also can be employed in the calculation of free energy of the nonuniform systems.[8,10] Unfortunately, extension of the hard sphere DFAs to van der Waals fluids is far from successful. There exist several routes for applying the hard sphere DFAs to the van der Waals fluids: the density functional mean field approximation (DFMFA), the density functional perturbation approximation (DFPA),[11−13] and the partitioned density functional approximation.[14−16] Besides these standard methodologies, there also exists a DFA based on the radial distribution function (RDF), denoted by RDF-based DFA.[17] Finally, some researchers also employ directly the hard sphere DFAs to the van der Waals fluids by substituting the hard sphere second-order DCF and excess Helmholtz free energy expressions appearing in the hard sphere DFAs by the corresponding van der Waals fluid's ones.[18] With regard to the accuracy and the application of these methods, one can conclude that the DFMFA is very low in accuracy; the DFPA can improve the DFMFA in some cases, but also becomes unsatis-

*Project supported by the National Natural Science Foundation of China (Grant No 20673150).
†E-mail: chixiayzsq@yahoo.com

factory when the coexistence bulk density and temperature are low. One of the versions of the partitioned DFA[15] can be very accurate by incorporating an adjustable parameter into itself,[7] but the formalism cannot work when the temperature is below the critical temperature since the formalism needs as input the bulk second-order DCF of many state points at the same temperature with different bulk densities which sometimes enter into the unstable region bounded by a binodal line. It is well-known that a fluid will phase separate into a low-density gas phase and a high-density liquid phase when the bulk state is in the unstable region where the Ornstein–Zernike (OZ) integral equation (IE) has no physical solution. Although the RDF-based DFA can be very accurate, and can be applied at subcritical temperatures, its development is hampered by the many-value property of the DFA from the bulk RDF, therefore its application is now limited to the cases where the required bulk RDF is from the non-renormalization OZ IE theory.[19] However, it was known that the bulk RDF of high accuracy comes from renormalization OZ IET.[20] Therefore, before the bottle-neck is eliminated, there is a long time when the RDF-based DFA can draw little attention. In regard to the direct application of the hard sphere WDAs to the van der Waals fluids,[18] the resultant formalism will break down due to the same reason as that in Ref.[15]. One can also notice that previous DFAs[11,12,15,21−26] for nonuniform van der Waals fluids had been only verified by simulation data taken from safe regions of the bulk phase diagram, i.e. the regions far away from the critical point, or far away from the binodal line. Therefore, their behaviours in regions near critical point and gas–liquid coexistence line are not known yet.

The aim of the present work is to propose a theoretical approach which enables the hard sphere DFAs to apply to the van der Waals fluids under the influence of diverse external fields so that the resultant DFA for the van der Waals fluids will be applicable in both supercritical and subcritical temperature regions. Especially, we will employ simulation data for 'dangerous' regions to confirm the validity of the present DFA, i.e. the coexistence bulk fluid is near the critical temperature or the gas–liquid coexistence line, since the 'dangerous' regions can be a strict test standard for any DFAs for the van der Waals fluids. It also should be noted that the external potentials employed in the present calculation are of a hard wall type which can serve as a far stricter test standard than that of a soft wall type.

2. Universal theoretical approach for extending hard sphere DFAs to the van der Waals fluids

We will employ a recently proposed BDFA[6] as an illustrating example to show the validity of the present universal theoretical approach, in which a hard core attractive Yukawa (HCAY) model potential will be employed as the target potential since enough simulation data were reported for the HCAY model fluid under the influence of various external fields.[27] Especially, these simulation data mainly corresponds to the coexistence bulk fluid situated in the 'dangerous' regions. It is also shown that the nonuniform HCAY model fluid may be the only one whose density distribution profile is the most difficult to predict theoretically accurately, this fact can be found clearly from the far larger scaling of ordinate of the figures than the actual range of the ordinate change.[12,16,21,22,24,25]

The BDFA[6] specifies the first-order DCF, $C^{(1)}(\boldsymbol{r};[\rho])$, of the nonuniform fluid as follows:

$$C^{(1)}(\boldsymbol{r};[\rho]) = C_0^{(1)}(\rho_{\rm b}) + \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b}) \times C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}) + B\Big(\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1-\rho_{\rm b}\Big) \times C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b})). \quad (1)$$

Here $C_0^{(1)}(\rho_{\rm b})$ is the corresponding uniform first-order DCF, $C_0^{(2)}(r;\rho_{\rm b})$ is the second-order DCF of the coexistence bulk fluid with density $\rho_{\rm b}$ and interaction potential $u(\boldsymbol{r})$. Substituting Eq.(1) into a single-component density profile equation,[28]

$$\rho(\boldsymbol{r}) = \rho_{\rm b}\exp\{-\beta\varphi_{\rm ext}(\boldsymbol{r}) + C^{(1)}(\boldsymbol{r};[\rho]) - C_0^{(1)}(\rho_{\rm b})\}, \quad (2)$$

one has

$$\rho(\boldsymbol{r}) = \rho_{\rm b}\exp\Big\{-\beta\varphi_{\rm ext}(\boldsymbol{r}) + \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b}) \times C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}) + B\Big(\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b}\Big) \times C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}))\Big\}, \quad (3)$$

where $\varphi_{\rm ext}(\boldsymbol{r})$ is an external potential responsible for the generation of the nonuniform density distribution $\rho(\boldsymbol{r})$. B denotes the bridge functional of the corresponding coexistence uniform fluid. It should be noted

that the bridge functional B in the BDFA should be expressed as a functional of the indirect correlation function of the uniform fluid. For nonuniform hard sphere fluid, a well-known Verlet-modified bridge functional,[29]

$$B_{\rm VM}(\gamma) = -0.5\gamma^2/(1+0.8\gamma), \tag{4}$$

is combined with the hard sphere BDFA, i.e.

$$\begin{aligned} C^{(1)}(\boldsymbol{r};[\rho]) = C_0^{(1)}(\rho_{\rm b}) + \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b}) \\ \times C_{0{\rm hs}}^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}) + \Big(\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b}\Big) \\ \times C_{0{\rm hs}}^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b})). \end{aligned} \tag{1'}$$

Here $C_{0{\rm hs}}^{(2)}(r;\rho_{\rm b})$, the second-order DCF of the coexistence hard sphere fluid of bulk density $\rho_{\rm b}$, provides the most accurate prediction for $\rho(\boldsymbol{r})$ and surface tension[6,10] under diverse external potentials. However, straightforward application of the BDFA to nonuniform Lennard-Jones (LJ) fluid[15] only produces qualitatively correct prediction, but quantitatively incorrect; its direct application to nonuniform penetrable sphere fluid with bounded interaction[23] is also only quantitatively correct in the high temperature case.

To calculate the density distribution $\rho(\boldsymbol{r})$ by using Eq.(2), the key point is to obtain the expression $C^{(1)}(\boldsymbol{r};[\rho]) - C_0^{(1)}(\rho_{\rm b})$ as a functional of the density distribution $\rho(\boldsymbol{r})$. A formal 'Taylor series' expansion of the $C^{(1)}(\boldsymbol{r};[\rho])$ around the coexistence bulk fluid of density $\rho_{\rm b}$ can be written as

$$\begin{aligned} C^{(1)}(\boldsymbol{r};[\rho]) = C_0^{(1)}(\rho_{\rm b}) + \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}) \\ + \sum_{n=3}^{\infty}\frac{1}{(n-1)!}\int {\rm d}\boldsymbol{r}_1\int {\rm d}\boldsymbol{r}_2\ldots\int {\rm d}\boldsymbol{r}_{n-1}\prod_{m=1}^{n-1}[\rho(\boldsymbol{r}_m)-\rho_{\rm b}]C_0^{(n)}(\boldsymbol{r},\boldsymbol{r}_1,\ldots,\boldsymbol{r}_{n-1};\rho_{\rm b}), \end{aligned} \tag{5}$$

Comparing Eq.(5) with Eq.(1), one can have

$$\begin{aligned} \sum_{n=3}^{\infty}\frac{1}{(n-1)!}\int {\rm d}\boldsymbol{r}_1\int {\rm d}\boldsymbol{r}_2\ldots\int {\rm d}\boldsymbol{r}_{n-1}\prod_{m=1}^{n-1}[\rho(\boldsymbol{r}_m)-\rho_{\rm b}]C_0^{(n)}(\boldsymbol{r},\boldsymbol{r}_1,\ldots,\boldsymbol{r}_{n-1};\rho_{\rm b}) \\ = B\Big(\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b})\Big). \end{aligned} \tag{6}$$

As discussed just now, for a nonuniform hard sphere fluid, Eq.(6) together with the bridge functional specified by Eq.(4) can be very accurate for calculation of density distribution $\rho(\boldsymbol{r})$ and surface tension prediction as shown in Refs.[6] and [10]. However, for a nonuniform LJ fluid, even if one chooses diverse forms of bridge functional B, Eq.(6) combined with Eqs.(5) and (2), i.e. the BDFA Eq.(1), can only describe the density distribution $\rho(\boldsymbol{r})$ of a LJ fluid of high density and high temperature under external fields.[30] When the bulk density and temperature are lowered, its performance rapidly deteriorates.[15,30] Recalling that in the partitioned DFT,[15] it was proved that if the tail part $C_{0{\rm tail}}^{(2)}(r;\rho_{\rm b})$ of the bulk second-order DCF $C_0^{(2)}(r;\rho_{\rm b})$ is independent of the density argument or is only very weakly dependent on the density argument, the bridge functional B for the tail part (denoted by $B_{\rm tail}$) can be exactly zero or approximately zero. Then, following the spirit of the partitioned DFT, and approximating the hard core part $C_{0{\rm hc}}^{(2)}(r;\rho_{\rm b})$ by the hard sphere DFA, here the BDFA, we have

$$\begin{aligned} & C^{(1)}(\boldsymbol{r};[\rho]) - C_0^{(1)}(\rho_{\rm b}) \\ = & \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C_{0{\rm hc}}^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}) \\ & + B\Big[\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C_{0{\rm hc}}^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b})\Big] \\ & \times \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C_{0{\rm tail}}^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}). \end{aligned} \tag{7}$$

Equation (7) makes use of the weak density-dependence of the tail part $C_{0{\rm tail}}^{(2)}(r;\rho_{\rm b})$ on the density argument, i.e. setting $B_{\rm tail}=0$.

In Ref.[31] Eq.(7) is substituted into the density profile Eq.(2) to calculate the density distribution $\rho(\boldsymbol{r})$ of an adhesive hard sphere fluid confined between two hard walls. It was found that the prediction will be-

come unsatisfactory when the adhesive parameter is reduced and therefore the adhesive hard sphere fluid becomes less like the hard sphere fluid. To improve the performance in the case of low adhesive parameter, one has to employ the high-order FPEA[2] to cure the inappropriateness of Eq.(7) in the case of low adhesive parameter. Although it was concluded incorrectly in Ref.[24] that the high-order FPEA was integrated to improve the second-order FPEA for the tail part. In another paper,[25] the present author has corrected the statement in Ref.[24] and concludes that the high-order FPEA is integrated to improve the inappropriateness of the hard sphere DFAs, here, the hard sphere BDFA, for the hard core part. In fact, even other WDA was substituted for the BDFA in Eq.(7), the above observation also appears as shown in Ref.[26]. When a LTDFA[7] is substituted for the BDFA in Eq.(7) to calculate the density distribution $\rho(\boldsymbol{r})$ of an LJ fluid near a single hard wall,[15] it is found that the accuracy can be very high if the adjustable parameter in the LTDFA is specified by a hard wall sum rule, but the adjustable parameter's value largely deviates from 0.5 required by the adjustable parameter free version of the LTDFA.[8] In a recent paper,[9] the author found that the LTDFA has a self-correction property which enables the LTDFA-based DFA for nonuniform polymer melt to behave quite well even with a not very accurate bulk second-order DCF as input. Therefore, it can be concluded that it is not a suitable procedure to employ the hard sphere DFA with the hard sphere second-order DCF $C^{(2)}_{0\rm hs}(r;\rho_{\rm b})$ substituted by the hard core part $C^{(2)}_{0\rm hc}(r;\rho_{\rm b})$ of the considered fluid second-order DCF to treat the hard core part. The success of the partitioned DFT[15] is due to the self-correction property of the LTDFA. If one assumes that the hard sphere DFA is strictly suitable only for the hard sphere fluid, considering the above statement, and that the hard core part of the van der Waals interaction potential can be replaced by an effective hard sphere fluid, one should substitute the hard core part $C^{(2)}_{0\rm hc}(r;\rho_{\rm b})$ of the considered fluid second-order DCF by the hard sphere second-order DCF $C^{(2)}_{0\rm hs}(r;\rho_{\rm hs})$ but with an effective hard sphere density $\rho_{\rm hs}$ different from the density $\rho_{\rm b}$ of the considered fluid, and then substitute the resultant $C^{(2)}_{0\rm hs}(r;\rho_{\rm hs})$ for the $C^{(2)}_{0\rm hs}(r;\rho_{\rm b})$ appearing in the hard sphere BDFA (1′). With this idea in mind, we have

$$\begin{aligned}
&C^{(1)}(\boldsymbol{r};[\rho]) - C^{(1)}_0(\rho_{\rm b}) \\
&= \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C^{(2)}_{0\rm hc}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}) \\
&\quad + B\Big[\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C^{(2)}_{0\rm hs}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm hs})\Big] \\
&\quad \times \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C^{(2)}_{0\rm tail}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}) \\
&= \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C^{(2)}_{0}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}) \\
&\quad + B\Big[\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C^{(2)}_{0\rm hs}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm hs})\Big]. \qquad (8)
\end{aligned}$$

Equation (8) is actually equivalent to an improvement of the second-order FPEA by adding a term into the second-order FPEA. In the case of the BDFA, the added term is

$$B\Big[\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C^{(2)}_{0\rm hs}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm hs})\Big],$$

which is exactly the omitted terms resulting from expanding $C^{(1)}(\boldsymbol{r};[\rho])$ around the coexistence bulk fluid of density $\rho_{\rm b}$, and truncating the series at the lowest order, i.e. the left side of Eq.(7) with $\rho_{\rm b}$ replaced by $\rho_{\rm hs}$. Since any DFA, whether it is for the excess Helmholtz free energy or for the $C^{(1)}(\boldsymbol{r};[\rho])$, certainly means an approximation to the left side of Eq.(6), the present theoretical method for applying the hard sphere DFAs to the van der Waals fluids, can be implemented with any other hard sphere DFAs. It is based on this consideration that we denote the present procedure as 'universal theoretical approach for extending hard sphere DFA to the van der Waals fluids'. In the present preliminary investigation, we only study the property of the universal theoretical approach based on the hard sphere BDFA, i.e. we will investigate the prediction accuracy of Eq.(8) for nonuniform HCAY model fluid using the following density profile:

$$\rho(\boldsymbol{r}) = \rho_{\rm b}\exp\Big\{-\beta\varphi_{\rm ext}(\boldsymbol{r}) + \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C^{(2)}_0(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}) + B\Big[\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_{\rm b})C^{(2)}_{0\rm hs}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm hs})\Big]\Big\}. \qquad (9)$$

The HCAY potential is of the following form:

$$\begin{aligned}
\beta u(r) &= \infty\,, && r/\sigma < 1, \\
&= -\beta\varepsilon\sigma\exp[-\kappa^*(r-\sigma)/\sigma]/r, && r/\sigma > 1,
\end{aligned} \qquad (10)$$

where σ is the hard core diameter of the HCAY particle, and is used as a length unit; ε is the interaction amplitude parameter, which is related to the reduced temperature $T^* = kT/\varepsilon$, κ^* is the reduced screening parameter. The present Eq.(8) needs as input the second-order DCF $C_0^{(2)}(r;\rho_b)$ of the bulk HCAY system in coexistence with the nonuniform HCAY fluid under consideration. In the present calculation, we employ a nonlinear optimized random phase approximation (ORPA)[32] for the OZ IE for $C_0^{(2)}(r;\rho_b)$. For the specification of the effective reduced hard sphere density $\rho_{hs}\sigma^3$, we try to determine it by the virial pressure self-consistency, i.e. we follow the Percus test particle method and apply Eq.(9) to a special external potential which is due to a bulk HCAY particle situated at the origin, then the reduced density distribution $\rho(\boldsymbol{r})/\rho_b$ is exactly the bulk RDF. From the obtained RDF one can determine the virial pressure of the bulk system. Letting the virial pressure obtained from Eq.(9) equal to the virial pressure predicted from the nonlinear ORPA, one can determine the effective reduced hard sphere density $\rho_{hs}\sigma^3$. In some density range of the coexistence fluid, one can determine the effective reduced hard sphere density $\rho_{hs}\sigma^3$ successfully, but in other cases, a solution does not always exist. Even if we replace the equality between the two virial pressures by minimizing the difference between the two virial pressures, the $\rho_{hs}\sigma^3$ determined is physically meaningless. By much practice, we find that the most suitable procedure for the specification of $\rho_{hs}\sigma^3$ is based on a hard wall sum rule which specifies the bulk pressure P by a hard wall contact density ρ_w,

$$P = \rho_w kT, \tag{11}$$

where ρ_w can be obtained from $\rho(0.5\sigma)$ in Eq.(9) when the external potential has the following form:

$$\begin{aligned} \varphi_{ext}(z) &= \infty, \quad z/\sigma < 0.5 \\ &= 0, \quad 0.5 < z/\sigma. \end{aligned} \tag{12}$$

Although the hard wall sum rule is valid only for a fluid in contact with a single hard wall, the specified value of $\rho_{hs}\sigma^3$ from this special case can also be used in other external potential cases, and this property is called the universality of the associated adjustable parameter $\rho_{hs}\sigma^3$. Since the universality of the adjustable parameter associated with a theoretically derived DFA depends strongly on the suitability of the DFA, it needs verification. In Ref.[33] based on enough simulation data, we have verified the universality of the adjustable parameter and find that only if the DFA is suitable, and the externally imported second-order bulk DCF is highly accurate, will the universality hold.

To see whether the present Eq.(9) is valid for diverse external potentials, we investigate the density profile $\rho(\boldsymbol{r})$ due to a single hard wall as well as two hard walls separated by a distance $H\sigma$, a large hard sphere with radius $R\sigma$, a spherical cavity with a hard wall of radius $R\sigma$, and a bulk HCAY particle. The external potentials due to these hard bodies and the soft body take the following mathematical forms:

$$\begin{aligned} \varphi_{ext}(z) &= \infty, \quad z/\sigma > H, \\ &= 0, \quad 0 < z/\sigma < H, \end{aligned} \quad \text{for two hard walls} \tag{13}$$

$$\begin{aligned} \varphi_{ext}(\boldsymbol{r}) &= \infty, \quad |\boldsymbol{r}|/\sigma < R, \\ &= 0, \quad |\boldsymbol{r}|/\sigma > R; \end{aligned} \quad \text{for a large hard sphere} \tag{14}$$

$$\begin{aligned} \varphi_{ext}(\boldsymbol{r}) &= \infty, \quad |\boldsymbol{r}|/\sigma < R, \\ &= 0, \quad |\boldsymbol{r}|/\sigma > R; \end{aligned} \quad \text{for a spherical cavity} \tag{15}$$

$$\varphi_{ext}(\boldsymbol{r}) = u(r). \quad \text{for a bulk particle} \tag{16}$$

It should be pointed out that there exist several previous DFT approaches,[12,16,21,22,24,25] which predict the density profile for HCAY model fluid near a single hard wall or a soft wall, in which the coexistence bulk fluid with reduced range parameter $\kappa^* = 1.8$ exists only at the state points with bulk reduced density $\rho_b\sigma^3 = 0.7$ and reduced temperatures $T^* = 2, 1.25, 1.1$. Although the dimensionless density profile changes within 2 units in the cases investigated, the ordinates of the figures reported

in Refs.[12,16,21,22,24,25] range from zero to six or seven. Therefore, practical agreement between the simulation and theory is not so perfect as concluded in these papers. In the present work, in case that the prediction is very accurate, the ordinate never has such a large range. When comparing the performance of the previous DFT approaches[12,16,21,22,24,25] with the present formalism, we have to take into account the difference of scales in these papers. If the prediction is not very accurate, in order to make a fair comparison between the previous DFT approaches and the present work, we should take the same ordinate scaling as in the previous works.

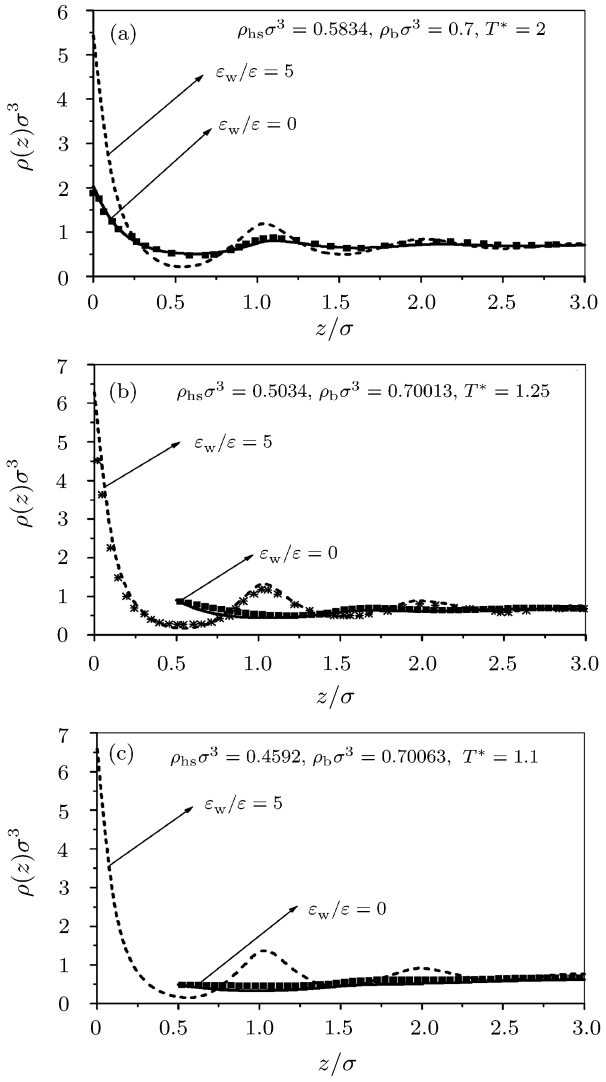


Fig.1. Density profile for the HCAY fluid near a single hard and soft wall. The lines correspond to the predictions of the present formalism Eqs.(9), and the symbols stand for the corresponding computer simulation data from Ref.[22]. The three figures differ from one another in temperatures. To make the figures clearer, Figs.(b) and (c) are shifted 0.5σ along the x direction.

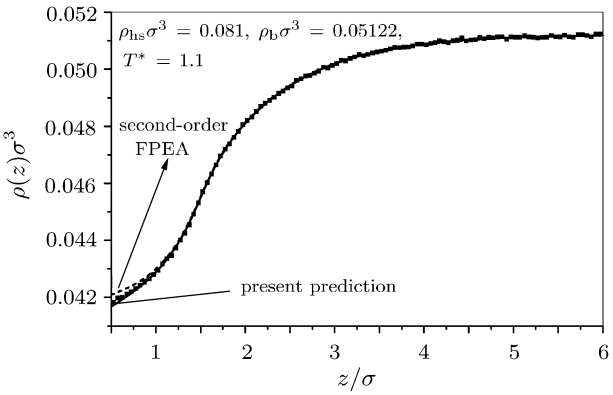


Fig.2. The same as in Fig.1 except for different coexistence bulk densities. The prediction from the second-order is FPEA also presented.

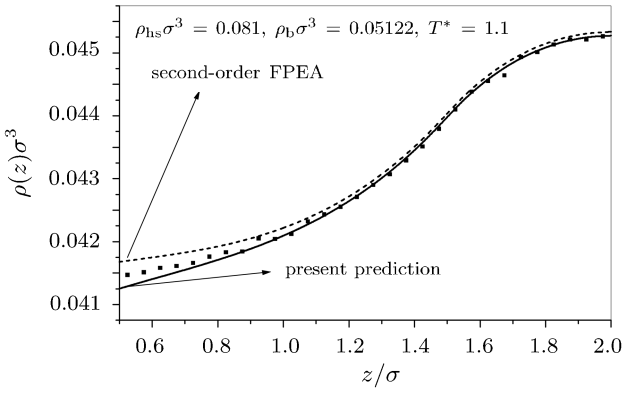


Fig.3. The same as in Fig.2 but the external potential is due to two hard walls separated by a distance 4σ.

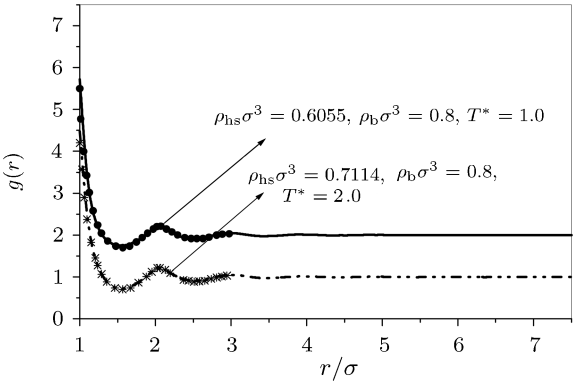


Fig.4. The radial distribution function for two state points indicated in the figure. The lines correspond to the predictions of the present formalism Eqs.(9), the symbols stand for the corresponding computer simulation data taken from Ref.[34].

In Fig.1, we plot the density profile of the HCAY fluid near a single hard wall or hard wall plus an attractive tail, and the corresponding simulation data[22] for the coexistence bulk fluid state points as investigated in Refs.[12,16,21,22,24,25], here the coordinate

scaling is the same as before. From Fig.1 one can see that the present prediction accuracy is comparable to previous ones.

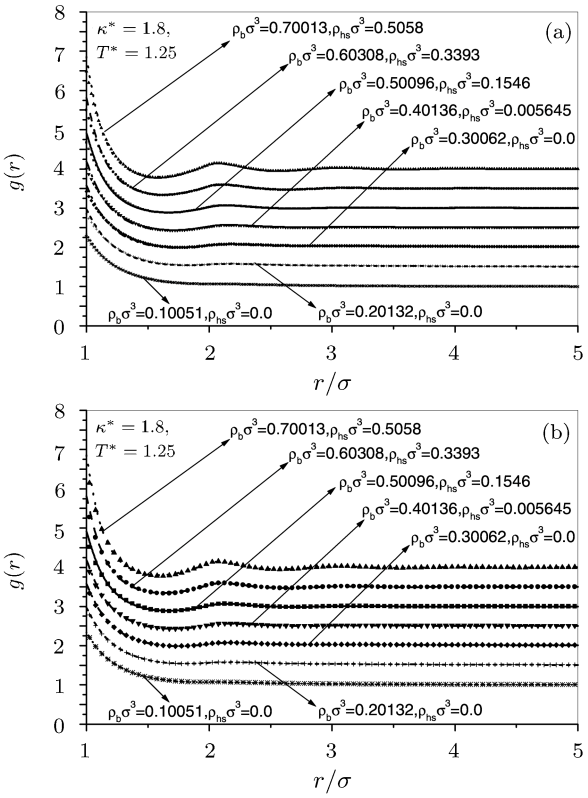


Fig.5. The same as in Fig.4 except for different bulk state points indicated in the figures. The symbols stand for the predictions from the numerical solution of the nonlinear ORPA in Ref.[32] (a) and the simulation data in Ref.[27] (b).

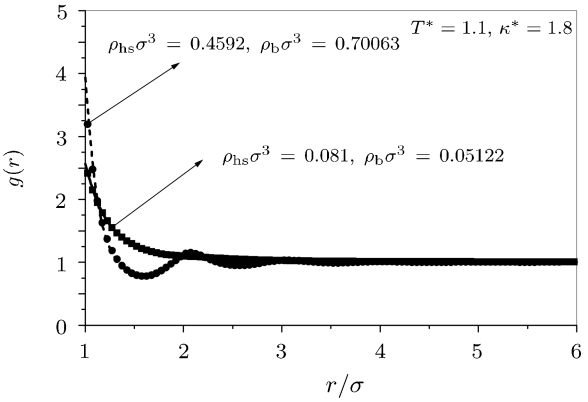


Fig.6. The same as in Fig.5(b) except for different bulk state points.

In Figs.2–10, we compare the present density profile predictions for HCAY model fluid under the influence of several external fields as given by Eqs.(13–16) with the corresponding simulation data provided in Ref.[27]. After a careful scrutiny one can conclude that in all the hard external potential cases, the prediction accuracy can be very high when the coexistence bulk density is low no matter whether the temperature is supercritical or subcritical. However, when the coexistence bulk density is high, the prediction accuracy is only comparable to several previous DFT approaches no matter whether the temperature is supercritical or subcritical. When the external potential is of an attractive tail, the prediction accuracy can be high for both low and high coexistence fluid bulk densities.

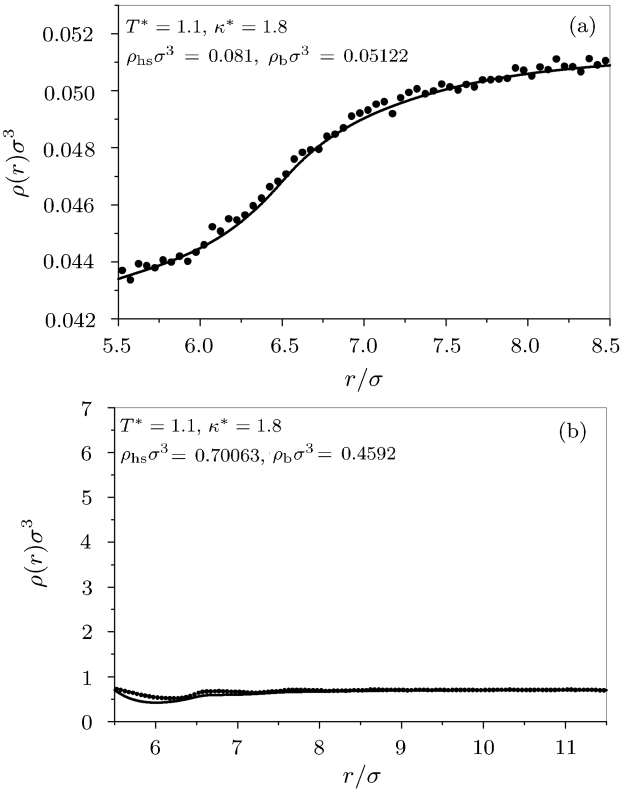


Fig.7. Density profiles for the HCAY fluid near a large hard sphere of $R = 5.5\sigma$. The lines correspond to the predictions of the present formalism Eqs.(9), the symbols stand for the corresponding computer simulation data taken from Ref.[27]. The coexistence bulk states are indicated in the figures.

Therefore one can conclude that the present DFA is a very useful theoretical tool for the investigation of wetting transition induced by an external potential with an attractive ingredient. One also can see that the performance of the present formalism somewhat deteriorates when the external potential is due to the hard spherical cavity. This comes from the fact that the hard spherical cavity represents the highest degree of confinement, whereas the present formalism is based on the expansion around the bulk fluid, the

higher degree of confinement certainly incurs a large disagreement between the bulk density and the density profile under consideration. Therefore the present formalism becomes more inappropriate when the degree of confinement increases. It should be pointed out that the required hard sphere fluid bulk second-order DCF is based on the well-known Percus–Yevick (PY) approximation.[1]

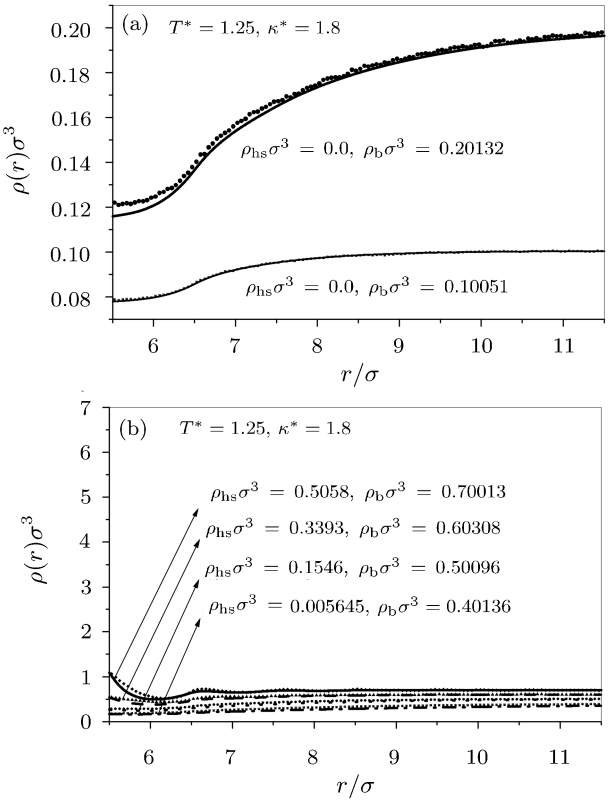


Fig.8. The same as in Fig.7 except for different coexistence bulk state points as indicated in the figures.

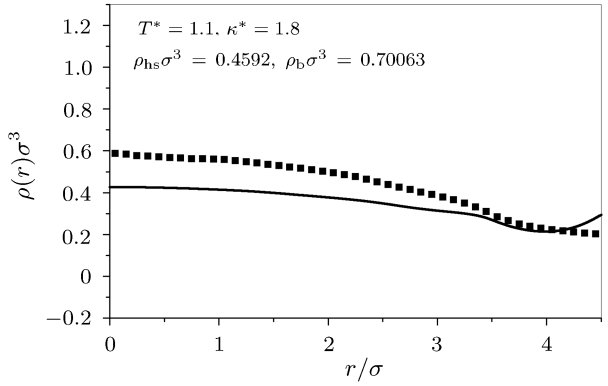


Fig.9. Density profiles for the HCAY fluid confined by a cavity with a hard wall of radius$R=4.5\sigma$. The lines correspond to the predictions of the present formalism Eqs.(9), and the symbols stand for the corresponding computer simulation data taken from Ref.[27]. The coexistence bulk states are indicated in the figure.

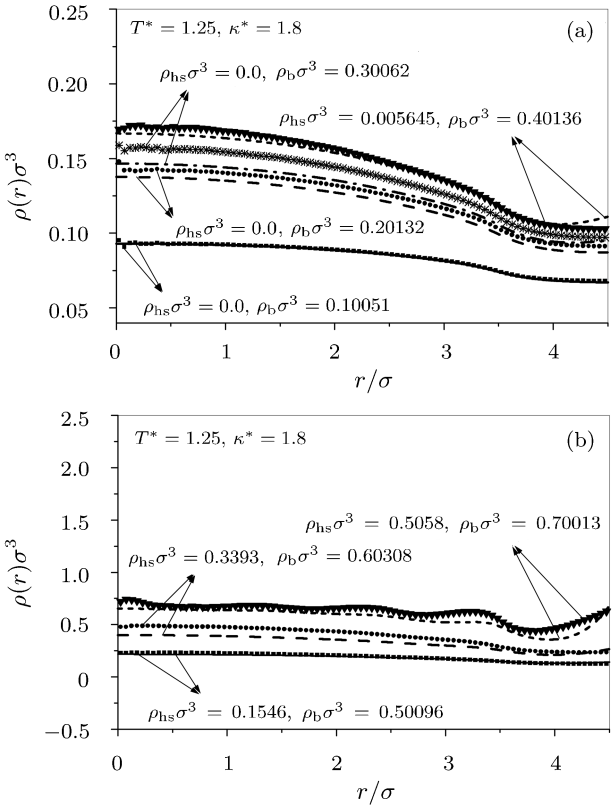


Fig.10. The same as in Fig.9 except for different coexistence bulk state points indicated in the figures.

3. Discussion and concluding remarks

The present paper proposes a universal theoretical method with which any hard sphere DFAs can be applied to the van der Waals fluids. As an example, the present paper employs the hard sphere BDFA to investigate the solid–liquid interface structural behaviour of the HCAY model fluid. The prediction accuracy is good or at least comparable to that in several previous DFT approaches. Possibly, when the adjustable parameter free version of the LTDFA[8] is combined with the present universal theoretical method, the greatest advantage of the present theoretical method can be shown up. As shown in Ref.[15], when the LTDFA is substituted into the partitioned DFT, the resultant DFT for nonuniform LJ fluid is very accurate. However, the LTDFA-based partitioned DFT[15,16] will break down in the case of subcritical temperature since the approach needs as input the bulk second-order DCF of many density points, while the OZ IE will not have a physical solution when the density point lies in the region

bounded by a binodal line. Since the present universal theoretical approach only concerns itself with the bulk second-order DCF of the coexistence fluid state point and the second-order DCF of the effective hard sphere fluid, where the coexistence fluid is certainly stable, i.e. it certainly lies in a single phase region corresponding to either monophase gaseous state (low densities) or monophase liquid state (high densities), the needed bulk second-order DCF of the coexistence fluid state point certainly exists. Therefore, the resultant DFT approach based on LTDFA or other WDAs will also apply in the subcritical temperature region. What then is the difference between the present formalism and that in Ref.[25]? The DFA in Ref.[25] is also based on the expansion around the bulk density, but the hard core part is truncated at the third-order terms whereas the tail part is truncated at the second-order ones. The present formalism distinguishes itself from the DFA in Ref.[25] by two points: one is to treat the hard core part by infinite-order, instead of the third-order level; the other is that the treatment is based on the effective hard sphere fluid instead of the hard core part in Ref.[25].

Further exploration of the present theoretical approach combined with other hard sphere DFAs, and their application to some interesting phenomena such as drying transition, wetting transition, especially application of the resultant DFT approach in a recent universal theoretical framework for calculation of solvent-mediated potential[35−42] will be reported in future publications.

References

[1] Henderson D 1992 *Fundamentals of Inhomogeneous Fluids*, (New York: Dekker)
[2] Zhou S and Ruckenstein E 2000 *Phys. Rev.* E **61** 2704
[3] Tarazona P 1984 *Mol. Phys.* **52** 81
[4] Denton A R and Ashcroft N W 1991 *Phys. Rev.* A **44** 8242
[5] Rosenfeld Y 1989 *Phys. Rev. Lett.* **63** 980
[6] Zhou S and Ruckenstein E 2000 *J. Chem. Phys.* **112** 8079
[7] Zhou S 2002 *New J. Phys.* **4** 36
[8] Zhou S 2003 *Phys. Lett.* A **319** 279
[9] Zhou S 2005 *Chem. Phys.* **310** 129
[10] Zhou S 2004 *Chem. Phys. Lett.* **385** 208
[11] Tang Z Scriven L E and Davis H T 1991 *J. Chem. Phys.* **95** 2659
[12] Tang Y 2004 *J. Chem. Phys.* **121** 10605
[13] You F Q, Yu Y X and Gao G H 2005 *J. Phys. Chem.* B **109** 3512
[14] Quesada-Perez M, Martin-Molina A and Hidalgo-Alvarez R 2004 *J. Chem. Phys.* **121** 8618
[15] Zhou S 2003 *Phys. Rev.* E **68** 061201
[16] Zhou S 2002 *J. Phys. Chem.* B **106** 7674
[17] Zhou S and Zhang X 2002 *Chin. Phys.* **11** 1051
[18] Marr D W and Gast A P 1993 *J. Chem. Phys.* **99** 2024
[19] Rogers F J and Young D A 1984 *Phys. Rev.* A **30** 999
[20] Duh D M and Haymet A D J 1995 *J. Chem. Phys.* **103** 2625
[21] Yi J H and Kim S C 1997 *J. Chem. Phys.* **107** 8147
[22] Olivares-Rivas W, Degreve L, Henderson D and Quintana J 1997 *J. Chem. Phys.* **106** 8160
[23] Kim S C and Suh S H 2002 *J. Chem. Phys.* **117** 9880
[24] Yoon T H and Kim S C 1998 *Phys. Rev.* E **58** 4541
[25] Zhou S 2003 *Commun. Theor. Phys.* (Beijing, China) **40** 721
[26] Choudhury N and Ghosh S K 1997 *J. Chem. Phys.* **106** 1576
[27] Zhou S and Jamnik A 2005 *J. Chem. Phys.* **122** 064503
[28] Evans R 1979 *Adv. Phys.* **28** 143
[29] Verlet L 1980 *Mol. Phys.* **41** 183
[30] Zhou S and Ruckenstein E 2000 *J. Chem. Phys.* **112** 5242
[31] Zhou S 2001 *J. Phys. Chem.* B **105** 10360
[32] Pini D Parola A and Reatto L 2002 *Mol. Phys.* **100** 1507
[33] Zhou S and Jamnik A 2005 *J. Chem. Phys.* **123** 124708
[34] Shukla K P 2000 *J. Chem. Phys.* **112** 10358
[35] Zhou S 2004 *Chem. Phys. Lett.* **399** 315
[36] Zhou S 2004 *Chem. Phys. Lett.* **399** 323
[37] Zhou S 2006 *Phys. Rev.* E **74** 011402
[38] Zhou S 2005 *Chin J. Chem. Phys.* **18** 679
[39] Zhou S 2005 *J. Colloid and Interface Sci.* **288** 308
[40] Gou C L 2006 *Chin Phys.* **15** 1239
[41] Zheng S B 2005 *Chin. Phys.* **14** 1825
[42] Wang Y L, Zhou Z X, Yuan C X, Jiang X Q and Qin R H 2006 *Chin. Phys.* **15** 156