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How to Extend the Bridge Density Functional Approximation to the Confined Non-hard Sphere Fluid

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A theoretical method was proposed to extend a bridge density functional approximation (BDFA) for the non-uniform hard sphere fluid to the non-uniform Lennard-Jones (LJ) fluid. The DFT approach for LJ fluid is simple, quantitatively accurate in a wide range of coexistence phase and external field parameters. Especially, the DFT approach only needs a second order direct correlation function (DCF) of the coexistence bulk fluid as input, and is therefore applicable to the subcritical temperature region. The present theoretical method can be regarded as a non-uniform counterpart of the thermodynamic perturbation theory, in which it is not at the level of the free energy but at the level of the second order DCF.

Key words: Density functional theory, Bridge density functional approximation, Hard sphere fluid, Correlation function

I. INTRODUCTION

A so-called bridge density functional approximation (BDFA) was recently proposed [1], its performance is excellent for both of the density profile calculation [1] and the surface tension calculation [2] of a non-uniform hard sphere fluid. A main advantage of the BDFA is its simplicity and high accuracy, it may be the simplest one among the available hard sphere density functional approximation (DFA). However, the high accuracy will be lost when it is applied directly to the non-hard sphere fluid under the influence of the external fields [3]. Since the DFAs for the hard sphere fluid are highly matured, the applicability of a DFA to the non-hard sphere fluid is very important for its general acceptance by the academic circles. A numercial version [4] of the BDFA was also proposed by the present author, in which we extracted the bridge function from the numerical solution of an Ornstein-Zernike (OZ) integral equation theory (IET). In Ref.[4], the employed OZ IET was based on a well-known Rogers-Young approximation for the bridge function, the numerical version of the BDFA was applied to the non-uniform hard core attractive Yukawa fluid. The RY approximation is very suitable for fluids with purely repulsive potentials, the extension to fluids with a hard core plus an attractive tail, has to invoke a so-called renormalization of an indirect correlation function (ICF) [5,6]. The renormalization-based OZ IETs [5,6] drew a lot of reasearch activities in recent years, their predictions for bulk structure functions, i.e. the radial distribution function (RDF) and the second order direct correlation function (DCF), and the bulk thermodynamic properties, are very accurate. Thus, in the framework of the BDFA (both the original version and the numerical version), extending the renormalization-based OZ IET for the non-hard sphere fluids to the corresponding non-uniform case is a very important and very pressing task. However, based on the renormalization-based OZ IETs, a direct extension of the BDFA confronted with difficulty, which made the BDFA violate the boundary condition which declared that the density distribution should be reduced to the bulk coexistence density when it was far away from the external field. To overcome the difficulty, a lot of work should be done. The simplicity and excellent performance of the BDFA motivated us to propose a theoretical method, which enabled the BDFA also suitable for the non-uniform non-hard sphere fluid. We also employed the non-uniform Lennard-Jones fluid as a sample potential to test the proposed method.

II. THEORETICAL METHODS

BDFA specifies the non-uniform first order DCF $C^{(1)}(\mathbf{r};[\rho])$ of a single component system as the following form

$$C^{(1)}(\mathbf{r};[\rho]) = C_0^{(1)}(\rho_b) + \int d\mathbf{r}_1[\rho(\mathbf{r}_1) - \rho_b] \cdot C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b) + B\left\{\int d\mathbf{r}_1[\rho(\mathbf{r}_1) - \rho_b] \cdot C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b)\right\} \quad (1)$$

here $C_0^{(1)}(\rho_b)$ is the corresponding uniform first order DCF, $C_0^{(2)}(\mathbf{r};\rho_b)$ is the second order DCF of the coexistence bulk fluid with bulk density ρ_b. Substituting Eq.(1) into the single component density equation

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Eq.(2),

$$\rho(\mathbf{r}) = \rho_b \exp\left[-\beta\varphi_{\text{ext}}(\mathbf{r}) + C^{(1)}(\mathbf{r};[\rho]) - C_0^{(1)}(\rho_b)\right] \quad (2)$$

one arrives at

$$\begin{aligned}\rho(\mathbf{r}) = \rho_b \Big\{ & \exp -\beta\varphi_{\text{ext}}(\mathbf{r}) + \int \mathrm{d}\mathbf{r}_1[\rho(\mathbf{r}_1) - \rho_b] \\ & \cdot C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b) + B\Big[\int \mathrm{d}\mathbf{r}_1\big(\rho(\mathbf{r}_1) - \rho_b\big) \\ & \cdot C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b)\Big]\Big\} \end{aligned} \quad (3)$$

here $\varphi_{\text{ext}}(\mathbf{r})$ is an external potential responsible for the generation of the non-uniform density distribution $\rho(\mathbf{r})$, B denotes the bridge function of the corresponding coexistence uniform fluid. For the non-uniform hard sphere fluid, the well-known Verlet-modified bridge function B_{VM} provides the most accurate prediction for $\rho(\mathbf{r})$ and surface tension [1,2] under various external potentials,

$$B_{\text{VM}}(\gamma) = -0.5\gamma^2/(1+0.8\gamma) \quad (4)$$

For the present theoretical calculation, we truncate and shift the Lennard-Jones (LJ) potential denoted by Eq.(5) to be in agreement with the available simulation data for non-uniform LJ fluid,

$$u_{\text{LJ}}(r) = 4\varepsilon\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right] \quad (5)$$

i.e. the employed potential in the theoretical calculation and simulation is of a following form,

$$\begin{aligned} u_{\text{LJ}}^C(r) &= u_{\text{LJ}}(r) - u_{\text{LJ}}(r_c) & r \le r_c \\ &= 0 & r \le r_c \end{aligned} \quad (6)$$

here, σ is a size parameter of the LJ particle, and ε an energy parameter.

To obtain the second order DCF, we should numerically solve a renormalization-based OZ IET based on Duh and Haymet [6], in which a modified Verlet-modified bridge function [7] should be employed in the Duh and Haymet's theory. Since Ref.[7] indicated that the combination of the renormalization strategy of Duh and Haymet with the modified Verlet-modified bridge function generated even better performance than that of the combination of the same renormalization strategy with the bridge function proposed in Ref.[6]. However, when one directly applied BDFA to the LJ fluid near a hard wall [3], i.e. the second order DCF $C_0^{(2)}(r;\rho_b)$ in Eq.(3), that is corresponding to the coexistence bulk LJ fluid, the prediction for the density profile was in poor agreement with the simulation results. Thus we proposed a theoretical method to extend BDFA to the non-uniform LJ fluid.

The fact that BDFA is very accurate for the non-uniform hard sphere fluid motivates me to map the LJ fluid onto that of the hard sphere fluid. Since the second order DCF is a key factor for the construction of any DFAs, one should map the second order DCF of the LJ fluid onto the hard sphere fluid. The key point is how to map and how to determine the mapped hard sphere density ρ_{map}. According to Ref.[3,8], if the tail part of the second order DCF is weakly dependent on the density argument. For the present theoretical calculation, we truncate and shift the LJ potential denoted by Eq.(5) to be in agreement with the available simulation data for non-uniform LJ fluid,, one can employ the lowest order functional perturbation expansion approximation (FPEA) to treat the weakly-density-dependent part of the second order DCF, the strongly-density-dependent core part can be treated by the DFA originally devised from the non-uniform hard sphere fluid. Considering that BDFA is only suitable for the hard sphere fluid, we have to map the core part onto some hard sphere fluids with appropriate mapped hard sphere density. We proposed that the second order DCF of the core part should be equal to the mapped second order DCF of the hard sphere fluid, which may determine the mapped density. If we choose the space integration of the second order DCF as the mapping quantity, then,

$$\int_0^{\sigma} \mathrm{d}r 4\pi r^2 C_{0hs}^{(2)}(r;\rho_{\text{map}}) = \int_0^{r_{\text{cut}}} \mathrm{d}r 4\pi r^2 C_0^{(2)}(r;\rho_b) \quad (7)$$

here $C_{0hs}^{(2)}(r;\rho_{\text{map}})$ is the second order DCF of the hard sphere fluid with density ρ_{map} and the hard sphere diameter σ, $C_0^{(2)}(r;\rho_b)$ is the second order DCF of the LJ fluid under consideration, r_{cut} is a separation distance at which the LJ fluid is divided into core part and the tail part. Obviously r_{cut} should be near the distance at which the potential crosses zero point. The complete specification of r_{cut} needs an additional equation which is not yet available at the present stage. However, in the present investigation, the main aim is to test the feasibility of the proposed theoretical method. One can choose an appropriate r_{cut} to see wether the density profile is in agreement with the 'exact' simulational results.

According to the partitioned DFT approach [3,8], the tail part can be treated by the lowest order FPEA. Then the density profile equation is

$$\begin{aligned}\rho(\mathbf{r}) = \rho_b \exp\Big\{ & -\beta\varphi_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}_1[\rho(\mathbf{r}_1) - \rho_b] \\ & \cdot C_{0hs}^{(2)}(|\mathbf{r}-\mathbf{r}_1|_{|\mathbf{r}-\mathbf{r}_1|<\sigma};\rho_{\text{map}}) + B\Big[\int d\mathbf{r}_1(\rho(\mathbf{r}_1) \\ & -\rho_b)C_{0hs}^{(2)}\left(|\mathbf{r}-\mathbf{r}_1|_{|\mathbf{r}-\mathbf{r}_1|<\sigma};\rho_{\text{map}}\right)\Big] + \int d\mathbf{r}_1 \\ & \cdot[\rho(\mathbf{r}_1) - \rho_b]C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|_{|\mathbf{r}-\mathbf{r}_1|>r_{\text{cut}}};\rho_b)\Big\} \end{aligned} \quad (8)$$

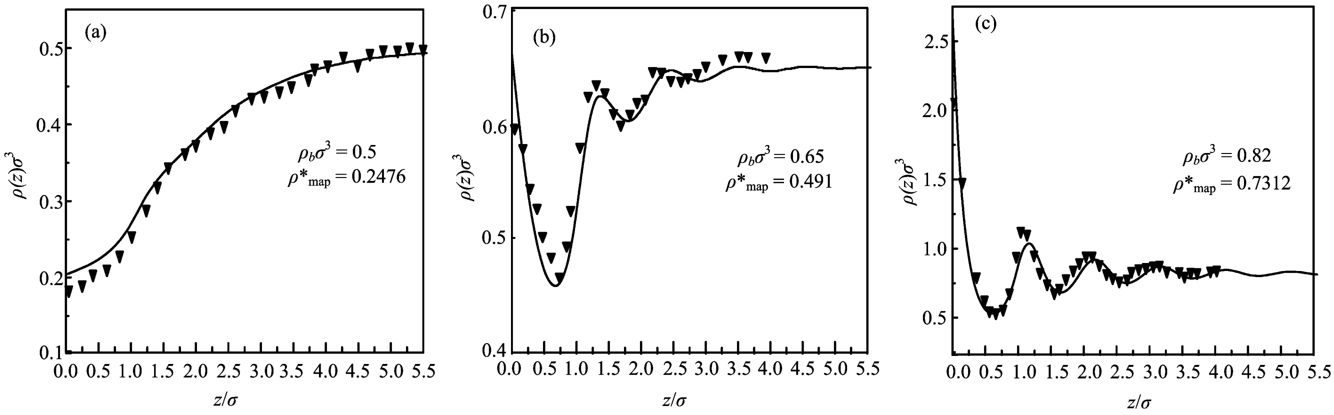

FIG. 1 Density profile for a LJ (truncated and shifted at $r_c^*=r_c/\sigma=4$) fluid in contact with a hard wall at $T^*=1.35$ and $r_{\rm cut}=1.16\sigma$. The symbols are for the MC data [10] reproduced from Ref.[11], the lines are for the present theoretical predictions.

We can choose the space integration of the second order DCF as a mapping quantity. The reason is that the space integration of the second order DCF is exactly the density derivative of the first order DCF, it is reasonable that the density derivatives of the hard core part of the first order DCF of the LJ fluid and the mapped hard sphere fluid are equal. At the same time, the space integration of the second order DCF determines the magnitude of the quantity $\int {\rm d}\mathbf{r}_1[\rho(\mathbf{r}_1)-\rho_b]C_{0hs}^{(2)}[|\mathbf{r}-\mathbf{r}_1|_{|\mathbf{r}-\mathbf{r}_1|<\sigma};\rho_{\rm map}]$ or similar other quantities in Eq.(8), if the density distribution $\rho(\mathbf{r}_1)$ is reduced to a constant. It is necessary for the mapped hard sphere fluid and the original LJ fluid to produce the same result in the limit case.

To test the validity of the present theoretical method, we applied the Eq.(8) to the LJ fluid under the influence of several external fields. It is well-known that the hard wall external fields (such as a single hard wall, a hard slit pore, or a large hard sphere particle etc.) set up the criteria for a DFA, while an attractive external field can also be the strict criteria for a DFA, since even a crude mean field approximation combined with a DFA for the hard sphere fluid can also produce density profile in satisfactory agreement with simulation data when the external field includes an attractive potential. Therefore, the present work concentrates on the hard wall external fields whose mathematical expressions are as follows, for the single hard wall

$$\varphi_{\rm ext}(z)=\begin{cases}\propto & (z/\sigma<0)\\ 0 & (z/\sigma>0)\end{cases} \quad (9)$$

for the two hard walls:

$$\varphi_{\rm ext}(z)=\begin{cases}\propto & (z/\sigma<0 \quad \text{or} \quad z/\sigma>H)\\ 0 & (0<z/\sigma<H)\end{cases} \quad (10)$$

for the hard sphere:

$$\varphi_{\rm ext}(\mathbf{r})=\begin{cases}\propto & (|\mathbf{r}|<R)\\ 0 & (|\mathbf{r}|>R)\end{cases} \quad (11)$$

As discussed in Ref.[9] for the case of the non-uniform adhesive hard sphere fluid, the formation of the oscillatory local density distribution was negatively affected by the so-called hard wall-induced packing effect, which modifies the local environment of near-surface particles by reducing the number of the short-ranged interaction. These near-surface particles are in contact with other particles, and have the adhesive interaction between the fluid particles, which forces the fluid particles to move away from the interface. Thus they have more chance to keep close touch with each other owing to the energetically favorable adhesive interaction and offseting the so-called packing effect, which forces the fluid particles to move towards the interface. Such analysis also applied in the LJ fluid near a hard wall. When the coexistence bulk density is low, the interparticle attractive interaction will force the LJ particle to move away from the surface, and this driving force dominates over the packing effect which forces the LJ particle to move towards the surface. Thus, the net effect is that the equilibrium density distribution becomes lower near the surface than that away from the surface. On the other hand, when the coexistence bulk density is high, the hard surface-induced packing effect will dominate over the interparticle attractive interaction-induced depletion effect, the net effect is that the particles are agglomerated near the hard surface. A good DFA should predict the transformation from the depletion to accumulation when the coexistence bulk density changes from a low value to a high value.

In Fig.1, the above phenomena from the present theoretical prediction and the corresponding simulation [10] are is presented at reduced temperature $T^*=1.35$ and several bulk densities. For this case, agreement between theory and simulation is very satisfactory, and the performance is significantly superior to that of a direct application of BDFA [3] and a non-uniform version of the second order thermodynamic perturbation theory [11]. The present performance for case in Fig.1 is also in comparison with the DFT approach [12]. It should be noted that the optimum value of the separation distance $r_{\rm cut}$ is found to be near 1.16σ for cases in Fig.1-Fig.3. In Fig.2, we presented the theoretical predictions and the corresponding simulation results available in literature [13] at two kinds of subcritical temperatures. The prediction accuracy for this case is lower than that for case in Fig.1, but still is qualitatively correct and acceptable. It should be noted that all of the published DFT approaches seems to be unable to predict correctly for this case. The third order perturbatibe DFT in Ref.[13] even is qualitatively not correct for case in Fig.2 (b). In Ref.[14], the comparison of the DFT's results with simulation data presented in Fig.2 is not encouraging, failure of the theory is attributed to an inequality between bulk density used in simulation and the actual coexistence bulk density. All of the other available DFT approaches including a recent one [12] did not give a comparison of the theoretical prediction with the simulation data for case in Fig.2. In Fig.3, we presented a

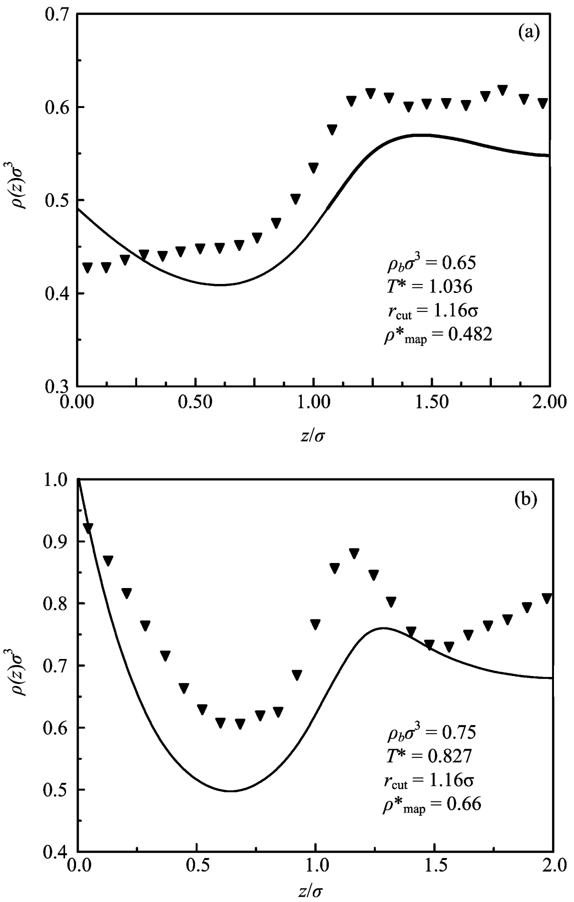

FIG. 2 Density profile for a LJ (truncated and shifted at $r_c^*=r_c/\sigma=2.5$) fluid confined between two hard walls with width $H=4\sigma$, The reduced temperature and coexistence bulk density are shown in figures. The symbols are for the MC data reproduced from Ref.[13], the lines are for the present theoretical predictions.

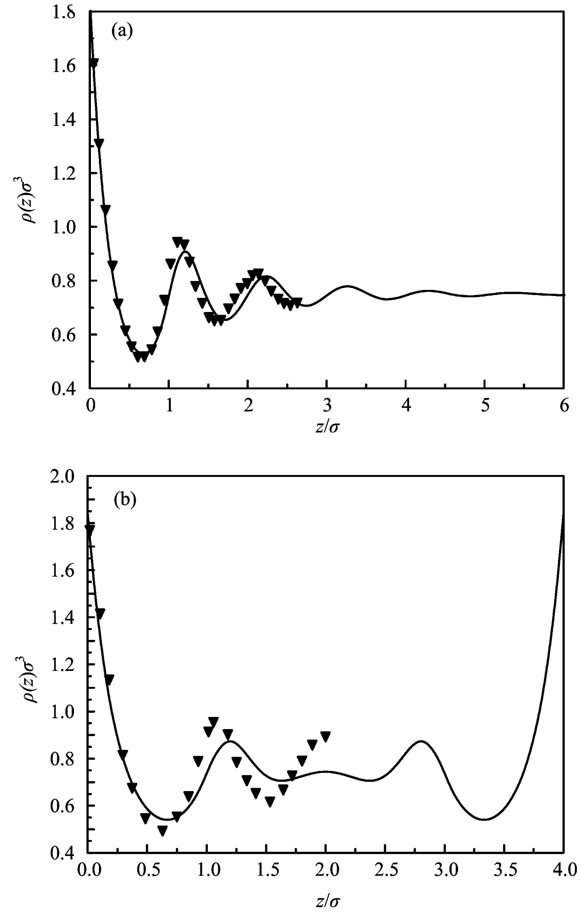

FIG. 3 Density profile for a LJ (truncated and shifted at $r_c^*=r_c/\sigma=2.5$) fluid confined between two hard walls with width $H=12\sigma$, The reduced temperature and coexistence bulk density are shown in figures. The symbols are for the MC data reproduced from Ref.[13], the lines are for the present theoretical predictions. $\rho_b\sigma^3$=0.75, T^*=1.304, $r_{\rm cut}$=1.16σ, $\rho*_{\rm map}$=0.6413.

comparison between the theoretical prediction and the simulation data at the supercritical temperature (for $r_c^*=r_c/\sigma=2.5$, the critical temperature of the fluid is about $1.12kT/\varepsilon$ [16]) and the coexistence bulk fluid is at a liquid state. For this case, the agreement between the theoretical calculation and the simulation calculation is good for the external field of a single hard wall ($H=12\sigma$ is wide enough for the result to be the same with that of a single hard wall), but the theory underestimate the oscillatory amplitude for the external field when the two hard walls are seperated by 4σ. In Fig.4, the external field is formed due to the changing size of a hard sphere particle, the LJ particle around a hard sphere particle can simulate the hydrophobic effect [15]. As discussed above, the interparticle attractive interaction tends to push the particles away from the hard wall, this tendency can be strengthened by increasing the size of the external field particle. The number of the neighbor would decrease as the hard sphere diame-

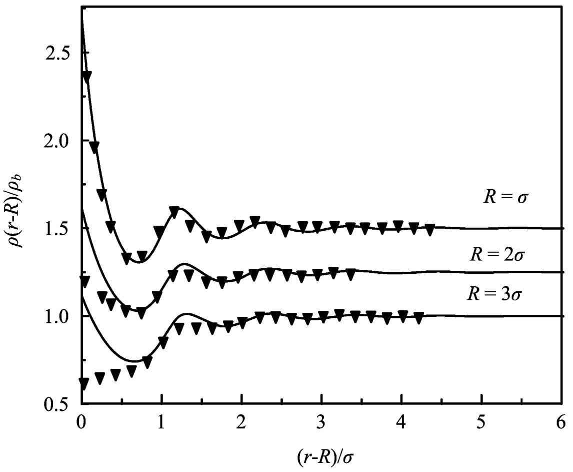

FIG. 4 Density profile for a LJ fluid truncated and shifted at $r_c^*=r_c/\sigma=2.5$ near a large hard sphere with different R as shown in the figures. The symbols are for the MC data reproduced from Ref.[15], the lines are for the present theoretical predictions. $\rho_b\sigma^3=0.7$, $T^*=0.85$, $r_{\rm cut}=1.16\sigma$, $\rho*_{\rm map}=0.5664$.

ter increased, thus the LJ particles have to move away from the surface to increase the interaction between the LJ particles and other bulk particles, which will reduce the total energy. The simulation data (reproduced from [15]) in Fig.4 and Fig.5 reflect the tendency, in which one can see that the agreement between the theoretical predictions and the simulation results is dependent on the value of the separating distance $r_{\rm cut}$. Although the choosing of $r_{\rm cut}=1.16\sigma$ can work quite well for all of the cases above discussed, it is not so good for the cases $R=2\sigma$, 3σ. However, a smaller value of $r_{\rm cut}$ can predict the density distribution in very good agreement with the simulation results for all of the field particle sizes.

III. CONCLUSION

The present work proposed a theoretical method to extend BDFA for hard sphere fluid to the non-hard sphere fluid. Its predictions for the non-uniform LJ fluid density distribution are very satisfactory compared with those of the published DFT approaches. The theoretical method has an advantage over other DFT approaches published. The first one is its simplicity, the time used in the present approach is not more than that in the second order perturbative DFT. The second one is that it is easy to input the parameter. The present approach does not require the analytical second order DCF, which is necessary in the approach in Ref.[12]. One can obtain the second order DCF of coexistence bulk fluid numerically, thus the present approach can apply not only in the model fluids whose second order DCF can be obtained analytically, but also in the arbitrary interaction potential fluids [17-20]. What the present work had the input mode of the numerical second order DCF also provides the possibility of excellent performance. In subcritical temperature region, the coexistence fluid is either stable liquid phase or stable gas phase, the phase point of the coexistence fluid is certainly outside the unstable region surrounded by a spinodal line. The OZ integral equation for the coexistence fluid is certainly solvable. The third one is its applicability to the subcritical temperature region. The key point is how to determine the separating distance $r_{\rm cut}$, as shown in Fig.4 and Fig.5. The accuracy of the prediction for some cases can be very sensitive to the choosing of $r_{\rm cut}$. We will investigate the application of the present approach and explore the theoretical determination of the separating distance. It should also be pointed out that the present method can also apply in other DFAs of the non-uniform hard sphere fluid. The present method is based on dividing the second order DCF into core part and tail part at the level of the second order DCF, while thermodynamic perturbation theory [21] is at the level of the free energy. The calculation of the density profile requires the non-uniform first order DCF as the input, therefore the present method is much simpler than that of the DFT approach [11] based on the thermodynamic perturbation theory. The present theoretical method can be regarded as a non-uniform counterpart of the thermodynamic perturbation theory [21] at the level of the second order DCF instead of the level of the free energy.

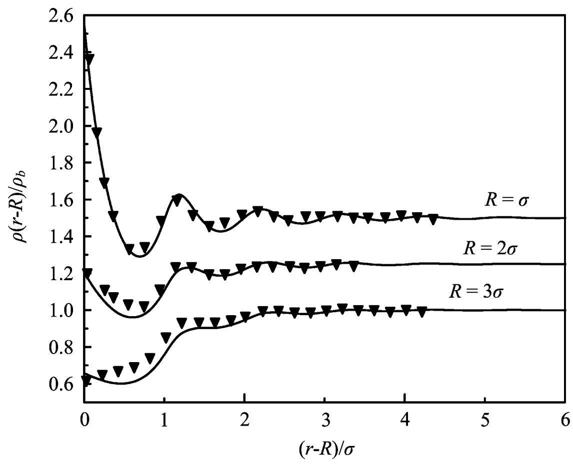

FIG. 5 Density profile for a LJ fluid truncated and shifted at $r_c^*=r_c/\sigma=2.5$ near a large hard sphere with different R as shown in the figures. The symbols are for the MC data reproduced from Ref.[15], the lines are for the present theoretical predictions. $\rho_b\sigma^3=0.7$, $T^*=0.85$, $r_{\rm cut}=1.16\sigma$, $\rho*_{\rm map}=0.6091$.

IV. ACKNOWLEDGEMENTS

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