Perturbation Density Functional Theory for Density Profile of A Nonuniform and Uniform Hard Core Attractive Yukawa Model Fluid

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The nonuniform first-order direct correlation function (DCF) for a hard-core attractive Yukawa model fluid (HCAYMF) was expanded around bulk density and truncated at the lowest order. The truncation was made formally exact by applying the functional counterpart of Lagrangian theorem of the differential calculus to the functional expansion. To calculate the density profile of a nonuniform HCAYMF, the uniform second-order DCF from the mean spherical approximation for HCAYMF was employed; the resulting density functional theory (DFT) was computationally simpler and quantitatively more accurate than the previous weighted density approximation (WDA) + functional perturbation expansion approximation (FPEA) DFT, which divided the interaction potential into a short-ranged hard-sphere-like part and a long-ranged interaction part and treated the former by the WDA and the latter by third-order FPEA. The present DFT also was employed to calculate the radial distribution function of bulk HCAYMF and bulk hard-sphere fluid; the calculated results were in good agreement with simulation data.

I. Introduction

The physical properties of fluids at the solid−fluid interface are of considerable practical importance regarding their connection with phenomena such as freezing, adsorption, wetting transition, and capillary condensation (for a review, see ref 1). Over the past decade, density functional theory (DFT) has witnessed great progress and established itself as a powerful tool for these nonuniform systems. Among various versions of the existing DFTs,[2−5] perturbation DFT (PDFT)[2] was often employed for calculation of density distribution profile; a common procedure for the PDFT to be employed for non-hard-sphere nonuniform fluids is to divide the interaction potential under consideration into a short-ranged hard-sphere-like part and a long-ranged interaction part. Then the short-ranged hard-sphere-like part was approximated by the hard-sphere model, which was attacked by the existing DFTs such as the various WDA and the recently proposed DFT based on the universality principle of the free energy density functional;[2−6] the long-ranged interaction part was treated by various PDFT.[7−11]

The model potential considered in the present work is that of a hard core interacting with an attractive Yukawa tail

$$\begin{aligned} \beta u(r) &= \infty && r/\sigma < 1 \\ &= -\beta\epsilon\sigma \exp[-\lambda(r-\sigma)/\sigma]/r && r/\sigma > 1 \end{aligned} \quad (1)$$

where σ is the diameter of the hard core, $\beta = 1/(k_B T)$ is the inverse temperature, ϵ is the strength of the Yukawa interaction at hard contact, and λ is the inverse screening length. One feature of this hard-core Yukawa model potential is that the range of interaction can be varied by changing the parameter λ, hence allowing it to be used to model many different systems qualitatively. An often-cited value of the parameter $\lambda = 1.8$ (with positive value of ϵ) is claimed to yield results comparable with those obtained from the Lennard-Jones potential parametrized for liquid argon.[12] The potential in eq 1 with large value of λ often is used as a good model for the effective pair potential between the macroparticles in a charge-stabilized colloidal suspension (with negative value of ϵ).[13] The potential in eq (1) is also well-known as the repulsive part of the Derjaguin−Landau−Verwey−Overbeek (DLVO) potential when ϵ is smaller than zero.

Unlike the uniform hard-core attractive Yukawa model fluid, its nonuniform counterpart has only recently received some attention. The first who addressed this problem were W. Olivares-Rivas et al.,[14]who employed the grand canonical Monte Carlo simulation and a modified single integral equation; then T. H. Yoon and S. C. Kim[9] proposed the weighted density approximation (WDA) + third-order functional perturbative expansion approximation (FPEA) DFT, which employed the WDA by Tarazona to handle the short-ranged hard-sphere-like part and the third-order FPEA[2] to treat the long-ranged interaction part and achieved far better predictions than that of the modified single integral equation.[14] Because the weighted density[7,8] was coupled with the weighting function, the third-order FPEA was computationally more intensive than the second-order one and an adjustable parameter had to be determined by iteration, so the DFT by T. H. Yoon and S. C. Kim was computationally demanding. So what is welcomed is one computationally simpler and quantitatively more accurate DFT, which is the aim of the present work.

The details of the present DFT were presented in section II and its validity was tested by applying it to calculate the density profile of a hard-core attractive Yukawa model fluid exerted by two different external potentials and the radial distribution function of the corresponding bulk fluid and bulk hard-sphere fluid in the same section II. Finally, in section III, we discussed the proposed DFT.

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II. Formally Exact Second-Order Perturbation Density Functional Theory

In the formalism of DFT, the density profile equation of a nonuniform single-component fluid reads as follows:

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

where $C^{(1)}(\mathbf{r};[\rho])$ is the nonuniform first-order direct correlation function (DCF), $C_0^{(1)}(\rho_b)$ is its uniform counterpart, $\beta\varphi_{ext}(\mathbf{r})$ is the external potential responsible for the nonuniform density distribution $\rho(\mathbf{r})$, ρ_b is the bulk density to which the nonuniform density distribution $\rho(\mathbf{r})$ reduces at which the external potential disappears.

The present paper was largely concerned with calculation of the density profile of inhomogeneous fluids, so it is convenient to carry out the functional perturbation expansion at the level of the first-order DCF, although it is also possible to proceed at the level of the excess Helmholtz free energy density functional.

A formal "Taylor series" expansion of the nonuniform first-order DCF, $C^{(1)}(\mathbf{r};[\rho])$, around the uniform system of bulk density ρ_b can always be written down as follows:

$$C^{(1)}(\mathbf{r};[\rho]) = C_0^{(1)}(\rho_b) + \int d\mathbf{r}_1(\rho(\mathbf{r}_1) - \rho_b) \times C_0^{(2)}(|\mathbf{r} - \mathbf{r}_1|;\rho_b) + \sum_{n=3}^{\infty} \frac{1}{(n-1)!} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ldots \int d\mathbf{r}_{n-1} \prod_{m=1}^{n-1} [\rho(\mathbf{r}_m) - \rho_b] C_0^{(n)}(\mathbf{r},\mathbf{r}_1, \ldots,\mathbf{r}_{n-1};\rho_b) \quad (3)$$

Here, each functional derivative, that is, the expansion coefficient $C_0^{(n)}(\mathbf{r},\mathbf{r}_1, \ldots,\mathbf{r}_{n-1};\rho_b)$ $n \geq 2$, is evaluated at the initial density ρ_b. We will not strive to make approximations for the expansion coefficients of the higher orders as done in previous literature;[2e] instead, we truncated the series at the first order (it can also be said that at the second order from the view of the expansion at the level of the excess Helmholtz free energy density functional), but to make the truncation an accurate representation, one can evaluate the last functional derivative not at the initial ρ_b but at some $\rho_b + \chi(\rho - \rho_b)$ with χ between 0 and 1.[15] The procedure is exactly the functional counterpart of the Lagrangian theorem of the differential calculus, which states that eq 4 is exact if the value of χ is correctly chosen. According to the above procedure, eq 3 reduces to

$$C^{(1)}(\mathbf{r};[\rho]) = C_0^{(1)}(\rho_b) + \int d\mathbf{r}_1 (\rho(\mathbf{r}_1) - \rho_b) C^{(2)}(\mathbf{r},\mathbf{r}_1;[\rho_b + \chi(\rho - \rho_b)]) \quad (4)$$

In the preceding equations, the subscript 0 corresponds to the uniform case and its absence to the corresponding nonuniform case. It should be noted that the expansion coefficient $C_0^{(2)}$ was replaced by $C^{(2)}$ in eq 4 because of the substitution of the bulk density ρ_b by the nonuniform density field $\rho_b + \chi(\rho - \rho_b)$; this replacement has to be done to be in agreement with the definition of the DCF. Equation 4 is exact, and it does not include any approximation. However, it should be noted that the functional counterpart of the Lagrangian theorem of the differential calculus, when the series was truncated at the first order, is actually the functional counterpart of the Lagrangian mean theorem. Substituting eq 4 into eq 2 leads to

$$\rho(\mathbf{r}) = \rho_b \exp\{-\beta\varphi_{ext}(\mathbf{r}) + \int d\mathbf{r}_1 (\rho(\mathbf{r}_1) - \rho_b) C^{(2)}(\mathbf{r},\mathbf{r}_1;[\rho_b + \chi(\rho - \rho_b)])\} \quad (5)$$

To proceed numerically, one has to approximate the nonuniform second-order DCF, $C^{(2)}(\mathbf{r},\mathbf{r}_1;[\rho_b + \chi(\rho - \rho_b)])$ and choose the appropriate mixing parameter χ. For the former, we extend the WDA[16] for the nonuniform first-order DCF by Ashcroft et al. to the nonuniform second-order DCF; that is, we make the approximation

$$C^{(2)}(\mathbf{r},\mathbf{r}_1;[\rho_b + \chi(\rho - \rho_b)]) = C_0^{(2)}(|\mathbf{r} - \mathbf{r}_1|;\tilde{\rho}(\mathbf{r}')) \quad (6)$$

where the weighted density $\tilde{\rho}$ is defined as follows:

$$\tilde{\rho}(\mathbf{r}) = \int d\mathbf{r}' (\chi(\rho(\mathbf{r}') - \rho_b) + \rho_b) w(|\mathbf{r} - \mathbf{r}'|;\tilde{\rho}(r)) \quad (7)$$

The weighting function $w(|\mathbf{r} - \mathbf{r}'|;\tilde{\rho}(\mathbf{r}))$ will be specified later in the present paper. One new problem is how to choose the position vector $\mathbf{r}'$ in eq 6. The numerical value of $C^{(2)}(\mathbf{r},\mathbf{r}_1;[\rho_b + \chi(\rho - \rho_b)])$ is related with two points $\mathbf{r}$ and $\mathbf{r}_1$, so it is reasonable to make the position vector $\mathbf{r}'$ in eq 6 also related with the two points $\mathbf{r}$ and $\mathbf{r}_1$. Taking account of the symmetry of the position vectors $\mathbf{r}$ and $\mathbf{r}_1$, then the natural procedure is to make the position vector $\mathbf{r}'$ in eq 6 related with the mean value of the two points $\mathbf{r}$ and $\mathbf{r}_1$, that is, eq 6 reduces to

$$C^{(2)}(\mathbf{r},\mathbf{r}_1;[\rho_b + \chi(\rho - \rho_b)]) = C_0^{(2)}(|\mathbf{r} - \mathbf{r}_1|;\tilde{\rho}((\mathbf{r} + \mathbf{r}_1)/2)) \quad (8)$$

Such choosing about the position vector $\mathbf{r}'$ appeared in a similar approximation for the nonuniform radial distribution function $g(\mathbf{r},\mathbf{r}_1;[\rho])$.[17]

As usual, the mixing parameter χ could be specified by the hard-wall sum rule, which specifies the bulk pressure P by the hard-wall contact density, ρ_w

$$P = \rho_w kT \quad (9)$$

where ρ_w can be obtained from $\rho(0.0)$ in eq 5 when the external potential has the following form:

$$\varphi_{ext}(z) = \infty \qquad z/\sigma < 0.0$$
$$= 0 \qquad 0.0 < z/\sigma \quad (10)$$

Although the hard-wall sum rule is valid only for a fluid in contact with a single hard wall, the specified value of χ from this special case can also be used for other cases of the external potential, such as a spherical cavity of a soft wall, at the same bulk thermodynamic state. The reasoning is as follows: the χ is included in eq 4; $C^{(1)}(\mathbf{r};[\rho])$ is the functional derivative of the excess Helmholtz free energy density functional with respective to the density distribution; the excess Helmholtz free energy density functional is independent of the external potential; thus, $C^{(1)}(\mathbf{r};[\rho])$ is also independent of the external potential. This means that a certain value of χ suitable for some external potential (for example, a single hard wall) is also suitable for any other external potentials (for example, a spherical cavity) at the same bulk thermodynamic state point[6,18] because the eqs 4, 6, and 7 had expressed $C^{(1)}(\mathbf{r};[\rho])$ as a functional of the density distribution by the weighted density. To exemplify the universality of χ, we will calculate the density distribution profile for a hard-core attractive Yukawa model fluid subjected to three different external fields from the value of χ determined for the same model fluid near a single hard wall at the same bulk state point.

For the hard-core attractive Yukawa model fluid, the required bulk second-order DCF was employed from the mean spherical approximation[19]

$$C_0^{(2)}(r,\rho_b) = -a - br/\sigma - \eta a r^3/2\sigma^3 - v\sigma[1-\exp(-\lambda r/\sigma)]/\lambda r - v^2[\cosh(\lambda r/\sigma) - 1]/[2\beta\epsilon\lambda^2 \exp(\lambda)] \quad r < \sigma$$
$$= \beta\epsilon\sigma \exp[-\lambda(r-\sigma)/\sigma]/r \quad r > \sigma \tag{11}$$

where the parameters a, b, v are defined implicitly by three coupled nonlinear equations, which can be solved numerically. Substituting eqs 11 and 6 into eq 5, one arrives at

$$\rho(\mathbf{r}) = \rho_b \exp\{-\beta\varphi_{ext}(\mathbf{r}) + \int d\mathbf{r}_1 (\rho(\mathbf{r}_1) - \rho_b) C^{(2)}_{0hs-like}(|\mathbf{r}-\mathbf{r}_1|;\tilde{\rho}(|\mathbf{r}+\mathbf{r}_1|/2)) + \int d\mathbf{r}_1 (\rho(\mathbf{r}_1) - \rho_b) C^{(2)}_{0long}(|\mathbf{r}-\mathbf{r}_1|)\} \tag{12}$$

where $C^{(2)}_{0hs-like}$ and $C^{(2)}_{0long}$ can be obtained from dividing of $C_0^{(2)}(r,\rho_b)$ as follows:

$$C^{(2)}_{0hs-like}(r,\rho_b) = -a - br/\sigma - \eta a r^3/2\sigma^3 - v\sigma[1-\exp(-\lambda r/\sigma)]/\lambda r - v^2[\cosh(\lambda r/\sigma) - 1]/[2\beta\epsilon\lambda^2 \exp(\lambda)] \quad r/\sigma < 1$$
$$= 0 \quad r/\sigma > 1 \tag{13}$$

$$C^{(2)}_{0long}(r) = 0 \quad r/\sigma < 1$$
$$= \beta\epsilon\sigma \exp[-\lambda(r-\sigma)/\sigma]/r \quad r/\sigma > 1 \tag{14}$$

We divide $C_0^{(2)}(r,\rho_b)$ as above, because the resulting long-ranged part $C^{(2)}_{0long}$ is disconnected from the density argument, then it is not necessary to calculate the weighted density for the calculation of the long-ranged part $C^{(2)}_{0long}$ of the second-order DCF. Now we concentrate on specification of the weighting function appearing in eq 7. Following the spirit of the SWDA,[20] which employed the normalized second-order DCF as weighting function and made the bulk density ρ_b as the density argument of the weighting function, we can specify the weighting function $w(|\mathbf{r}-\mathbf{r}'|;\tilde{\rho}(\mathbf{r}))$ by

$$w(|\mathbf{r}-\mathbf{r}'|;\tilde{\rho}(\mathbf{r})) = C^{(2)}_{0hs-like}(|\mathbf{r}-\mathbf{r}'|;\rho_b)/\int d\mathbf{r}\, C^{(2)}_{0hs-like}(\mathbf{r};\rho_b) \tag{15}$$

where we employed the normalized short-ranged part, $C^{(2)}_{0hs-like}$, of the second-order DCF as weighting function, not the normalized whole second-order DCF, $C_0^{(2)}$, for two reasons. First, the weighted density $\tilde{\rho}$ in eq 12 appears as the density argument of $C^{(2)}_{0hs-like}$, so it is reasonable to employ the normalized $C^{(2)}_{0hs-like}$ not the normalized $C_0^{(2)}$ as the weighting function. Second, $C^{(2)}_{0hs-like}$ is short-ranged, but $C_0^{(2)}$ is long-ranged; employing the normalized $C^{(2)}_{0hs-like}$ as the weighting function can reduce the computational task for the weighted density largely. In the calculation of the DFT, it is well-known that the calculation of the weighted density is the most time-consuming process. Choosing of the normalized long-ranged part of the whole second-order DCF as weighting function appeared in a previous paper,[21] which employed the WDA[16] to calculate the long-ranged part of the nonuniform whole first-order DCF of adhesive hard-sphere fluid; the present choosing is similar to that of ref 21. The weighting function corresponding to prescription for the WDA[16]and SWDA[20] is employed in present case on the basis of the fact that two recently proposed DFT approaches[5c,e] by the present author also employed the weighting function for the SWDA to cases different from one for which SWDA is suitable to translate the radial distribution function of bulk hard-sphere fluid and Lennard-Jones fluid into the nonuniform density distribution and achieved good prediction acuracy. The present DFT simplified the calculation in the following three ways. First, we employed and extended the SWDA for nonuniform first-order DCF to its second-order counterpart; the calculational simplicity of the SWDA lies in the fact that its weighted density is decoupled from the weighting function. Second, the uniform second-order DCF was divided naturally into short-ranged and long-ranged parts; then making use of the independence of the long-ranged part on the density argument makes the calculation of the weighted density for the long-ranged part of the nonuniform second-order DCF unnecessary. Third, instead of the normalized whole second-order DCF, we employed the normalized short-ranged part of the whole second-order DCF as the weighting function; the short-ranged part of the second-order DCF, $C^{(2)}_{0hs-like}$, is only nonzero within a diameter unit, so the integration region is largely reduced compared with the original integration region (depending on the value of ϵ and λ, the integration region will be a sphere of radius 10σ or more). From ref 22, we can know that one can approximate reasonably the nonuniform second-order DCF through the uniform second-order DCF. So our extension of the WDA for nonuniform first-order DCF to its second-order counterpart is reasonable.

About the bulk pressure P for the uniform hard-core attractive Yukawa model fluid, we employed the recently proposed equation of state[23]

$$\frac{P-P_0}{\rho_b kT} = -\eta\frac{\beta\epsilon}{\Phi_0}\left[\frac{\partial\alpha_0}{\partial\eta} - \frac{\alpha_0}{\Phi_0}\frac{\partial\Phi_0}{\partial\eta}\right] + \frac{\lambda^3}{6\eta}\left[F(x) - F(y) - (x-y)\frac{dF(y)}{dy}\right] - \frac{\lambda^3}{6}\left\{\frac{\partial x}{\partial\eta}\left[\frac{dF(x)}{dx} - \frac{dF(y)}{dy}\right] - \frac{\partial y}{\partial\eta}(x-y)\frac{d^2F(y)}{dy^2}\right\} \tag{16}$$

where P_0 is the bulk pressure of the hard-sphere fluid of bulk density ρ_b; in ref [23], it was from the Carnahan−Startling empirical equation of state[24]

$$\frac{P_0}{\rho_b kT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{17}$$

$\eta = \pi\rho_b\sigma^3/6$ is the bulk packing fraction. The analytical expressions for the partial derivatives and the relation of the symbols of Φ_0, α_0, x, and y with the potential parameters λ and ϵ can be found in ref 23; also, the definition of function F can be found there.

To test the above procedure numerically, we applied the present formally exact second-order perturbation DFT approach to a hard-core attractive Yukawa model fluid near a single structureless hard wall and a single wall with an attractive tail. For the former case, the external potential is of the same form as in eq 10. For the latter case, it is in the following form:

$$\varphi_{ext}(z) = \infty \quad z/\sigma < 0$$
$$= -\beta\epsilon_w \exp[-\lambda z/\sigma] \quad 0 < z/\sigma \tag{18}$$

Through the present calculation, the hard-core attractive Yukawa model potential with a range parameter $\lambda = 1.8$ had been used to compare with the computer simulation result available in the literature. The calculated density distribution profiles ($\rho_b\sigma^3 = 0.7$ and $T^* = kT/\epsilon = 2$) were plotted in Figure

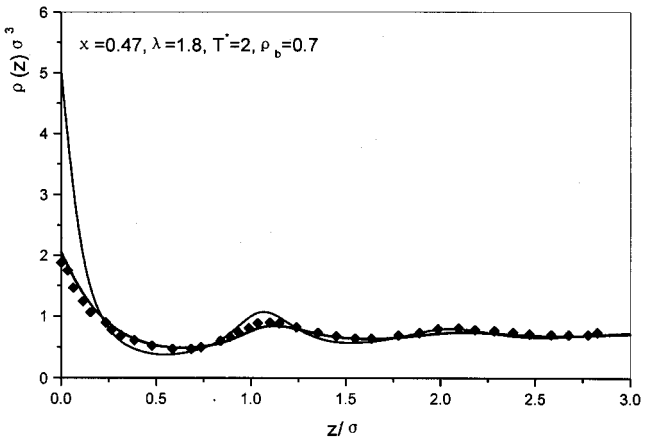

Figure 1. Density profiles for the hard-core attractive Yukawa model fluid of $\rho_b = 0.7$, $T^* = 2.0$, and $\lambda = 1.8$ near a hard wall (the upper curve is for the case of a hard wall with an attractive tail with $\epsilon_w/\epsilon = 5$). The lines correspond to the predictions of the present DFT, the symbols stand for the corresponding computer simulation data from ref 14 for the case of $\epsilon_w/\epsilon = 0.0$.

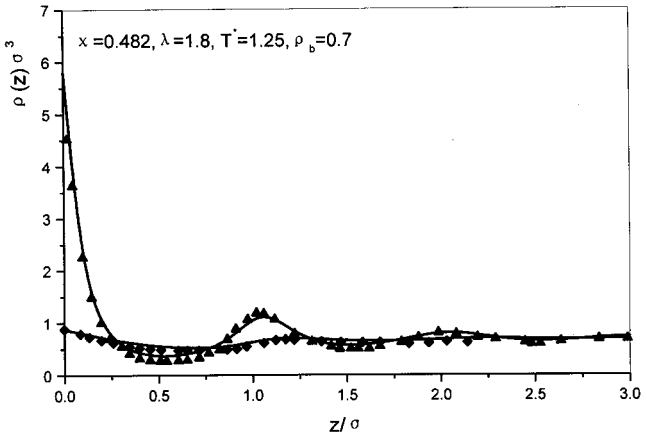

Figure 2. Density profiles for the hard-core attractive Yukawa model fluid of $\rho_b = 0.7$, $T^* = 1.25$, and $\lambda = 1.8$ near a hard wall (the upper curve is for the case of a hard wall with an attractive tail with $\epsilon_w/\epsilon = 5$). The lines correspond to the predictions of the present DFT, the symbols stand for the corresponding computer simulation data from ref 14.

1 with the corresponding computer simulation data.[14] For the high temperature, the present formally exact second-order perturbative DFT shows a good agreement with the simulation data; the present predictions are even better than that of a previous weighted density approximation (WDA) + functional perturbative expansion approximation (FPEA) DFT,[9] which divided the interaction potential into a short-ranged hard-sphere-like part and a long-ranged interaction part and treated the former by the computationally intensive WDA and the latter by the third-order FPEA, even if we did not display their results in the present figure for clarity. It is well-known that the previous WDA + FPEA + DFT is better than the modified version of the Lovett−Mou−Buff−Wertheim (LMBW-1)[14] for the predictions of the density distribution profile. For lower temperatures ($T^* = 1.25$ and $T^* = 1.1$) approaching the liquid−vapor transition temperature, the calculated results were displayed in Figures 2 and 3. The comparison with the computer simulation data also showed an excellent agreement. Furthermore, the density profiles for an attractive Yukawa wall with $\epsilon_w/\epsilon = 5$ were displayed in Figures 1−3. As is well-known, with decreasing temperatures, the hard wall contact values of the density profile decrease; when the temperature is low enough,

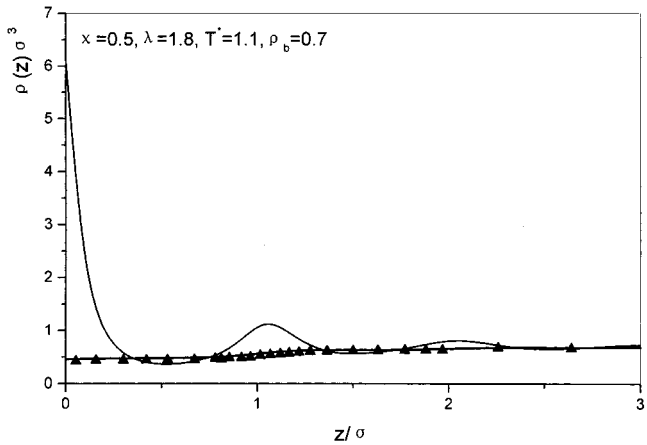

Figure 3. Density profiles for the hard-core attractive Yukawa model fluid of $\rho_b = 0.7$, $T^* = 1.1$, and $\lambda = 1.8$ near a hard wall (the upper curve is for the case of a hard wall with an attractive tail with $\epsilon_w/\epsilon = 5$). The lines correspond to the predictions of the present DFT, the symbols stand for the corresponding computer simulation data from ref 14 for the case of $\epsilon_w/\epsilon = 0.0$.

the depletion layer near the hard wall appears. This is due to the fact that increasing of the attractive well depth forces the fluid particles to move away from the wall to have more chances for the interaction among the fluid particles, which is energetically more favorable than the interaction with the hard wall. Even this phenomenon can be predicted by the so simple second-order perturbation DFT. However, it should be noted that one recently proposed DFT[5f] based on the numerically obtained bridge functional also predicted the density distribution profile of the same hard-core attractive Yukawa model fluid with the same potential parameters and external potential parameters as in Figures 1 and 2 in same good agreement with the corresponding simulation data. But when the bulk parameters are near the critical bulk parameters, the numerical solution of the OZ equation becomes more and more difficult; as a result, the DFT in ref 5f cannot be employed successfully to predict the density distribution profile for the potential parameters in Figure 3.

To further test the universality of χ, that is, that the value of χ determined for the bulk hard-core attractive Yukawa model fluid near a single structureless hard wall for certain state point can be used for the calculation for any other case of the external potentials (i.e., different geometry or different external potential parameters or both) for the same state point, we applied the present approach to calculate the radial distribution function of the bulk hard-core attractive Yukawa model fluid. Following the test particle trick by Percus,[25] the radial distribution function, $g(\mathbf{r})$, of the bulk fluid can be related to the nonuniform density distribution, $\rho(\mathbf{r})$, by the following relation

$$\rho(\mathbf{r}) = \rho_b g(\mathbf{r}) \tag{19}$$

where the external potential responsible for the generation of $\rho(\mathbf{r})$ results from a so-called test particle chosen from the bulk and situated at the origin; the interaction potential between the test particle and any other particle in the bulk is exactly the external potential,

$$\begin{aligned} \varphi_{ext}(\mathbf{r}) &= \infty && |\mathbf{r}|/\sigma < 1 \\ &= -\beta\epsilon\sigma \exp[-\lambda(r-\sigma)/\sigma]/r && |\mathbf{r}|/\sigma > 1 \end{aligned} \tag{20}$$

In Figures 4 and 5, the calculated radial distribution functions were displayed with the corresponding simulation data[26] for λ

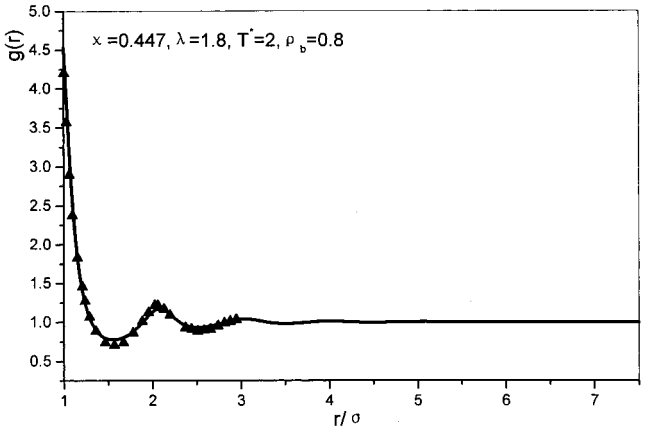

Figure 4. Comparison of the radial distribution function of the hard-core attractive Yukawa model fluid from the present DFT and the Monte Carlo simulation with parameters as shown in the figure.[26]

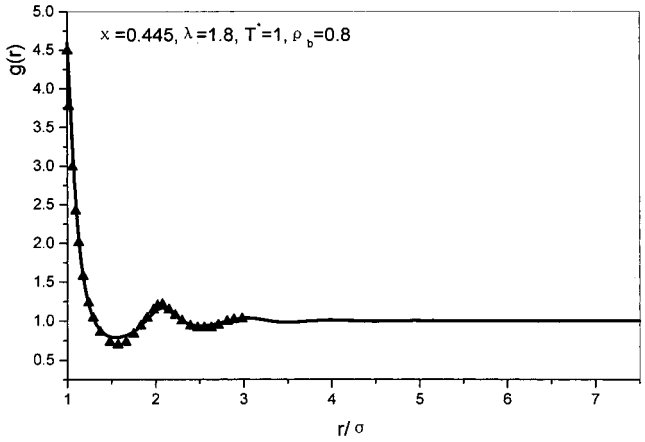

Figure 5. Comparison of the radial distribution function of the hard-core attractive Yukawa model fluid from the present DFT and the Monte Carlo simulation with parameters as shown in the figure.

$= 1.8$, $\rho_b\sigma^3 = 0.8$, and $T^* = 1.0$ and $T^* = 2.0$ respectively. The prediction accuracy for the radial distribution function is as good as that shown in Figures 1−3. Because the external potential generated from a spherical particle is completely different from that of a single structureless hard wall, the good accuracy shown in Figures 4 and 5 indicated the universality of the mixing parameter χ, that is, its independence from the external potential. It is interesting to note that the present formally exact second-order perturbation DFT for the hard-core attractive Yukawa model fluid can be used to calculate the radial distribution function of the bulk hard-sphere fluid by choosing appropriate potential parameters. In principle, when $T^* = \infty$ or $\lambda = \infty$ or both, the hard-core Yukawa potental reduces to the hard-sphere potential exactly; at the same time the MSA reduces to the PY approximation exactly. Actually, to solve the three coupled nonlinear equations defining the parameters a, b, and υ from the present Fortran77 program, we chose $T^* = 10^8$ and $\lambda = 18$ to reduce the hard-core Yukawa potental to the hard-sphere potential. In fact, for the chosen value of $T^* = 10^8$ and $\lambda = 18$, the resulting second-order DCF from eq 11 is equal to the PY approximation second-order DCF for all bulk densities. Numerical results also showed that for the chosen value of $T^* = 10^8$ and $\lambda = 18$ the pressure from eq 16 for the hard-core attractive Yukawa model fluid exactly reduces to the pressure from the Carnahan−Startling empirical equation of state, that is, the left side of eq 16 exactly reduces to zero. In Figures 6−8, the calculated radial distribution functions from the present DFT approach were displayed with the corresponding simulation data[27] for the bulk hard-sphere fluid. It was shown that the agreement with the simulation data is also good even for very high bulk hard-sphere density, such as $\rho_b\sigma^3 = 0.8$.

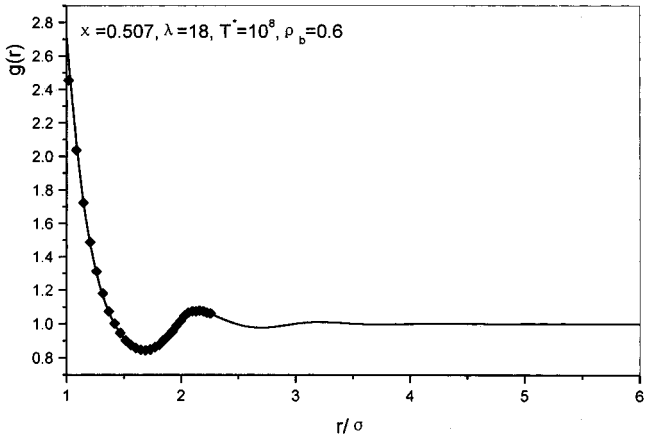

Figure 6. Comparison of the radial distribution function of the hard sphere model fluid from the present DFT for the hard-core attractive Yukawa model fluid with $T^* = 10^8$ and $\lambda = 18$ and bulk density as shown in the figure and the Monte Carlo simulation.[27]

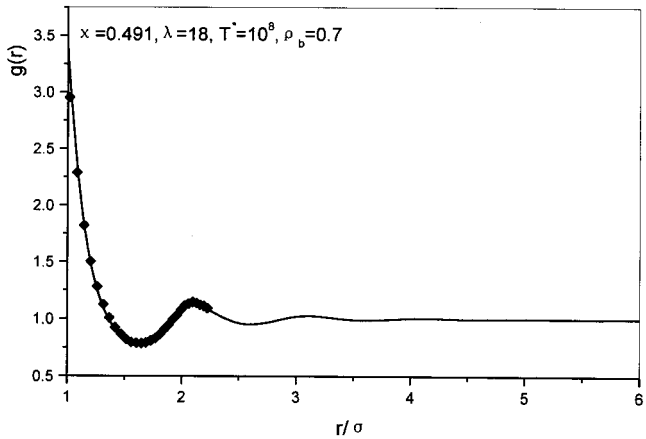

Figure 7. Comparison of the radial distribution function of the hard sphere model fluid from the present DFT for the hard-core attractive Yukawa model fluid with $T^* = 10^8$ and $\lambda = 18$ and bulk density as shown in the figure and the Monte Carlo simulation.[27]

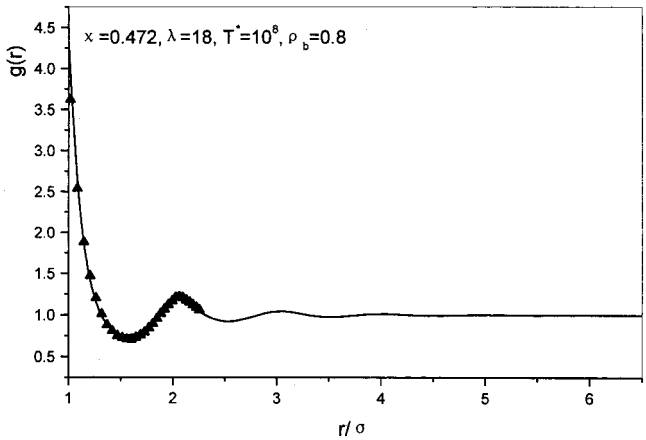

Figure 8. Comparison of the radial distribution function of the hard sphere model fluid from the present DFT for the hard-core attractive Yukawa model fluid with $T^* = 10^8$ and $\lambda = 18$ and bulk density as shown in the figure and the Monte Carlo simulation.[27]

III. Discussion and Summaries

Formally, the present formally exact second-order perturbation DFT for nonuniform hard-core attractive Yukawa model fluid is like the current WDA + FPEA + DFTs, which treated the hard-sphere-like part with WDA devised for the nonuniform hard-sphere model fluid and treated the long-ranged part with third-order functional perturbation expansion approximation. But essentially they are completely different and include different approximations. First, the previous WDA + FPEA + DFTs approximated the hard-sphere-like part with a hard sphere treated by the WDA devised for the hard-sphere model. So there appeared two approximations. The hard-sphere-like part, the second-order DCF of which is $C^{(2)}_{0\mathrm{hs-like}}$, is not equal to the real hard-sphere model fluid; this can be understood from the difference between $C^{(2)}_{0\mathrm{hs-like}}$ for the value of the potential parameters, which does not reduce the hard-core attractive Yukawa model fluid to the hard-sphere fluid and for the real hard-sphere model fluid PY second-order DCF $C^{(2)}_{0\mathrm{hs}}$.[28]

$$C^{(2)}_{0hs}(r,\rho_b) = a + b(r/\sigma) + c(r/\sigma)^3 \qquad r < \sigma$$
$$= 0 \qquad r > \sigma \qquad (21)$$

where the coefficients a, b, and c can be found in ref 28 as a function of bulk density ρ_b.

But the WDA employed the hard-sphere model fluid quantities, such as the PY hard-sphere first-order and second-order DCF, the PY excess Helmholtz free energy per particle, or the excess Helmholtz free energy per particle from the Carnanhan−Startling equation of state, as the input parameters. This is the first approximation, that is, approximating the hard-sphere-like part by the hard-sphere model fluid. The second approximation comes from the WDA itself; the WDA itself is not exact for the nonuniform hard-sphere fluid, but it is only an approximation. The third approximation comes from treating the long-ranged part by the truncated functional perturbation expansion approximation; the functional perturbation expansion has to be truncated due to the lack of the higher-order expansion coefficients, that is, the uniform DCFs order higher than two. Basically, the present DFT is also the truncated functional perturbation expansion; the truncation was carried out at the lowest order, but the truncation was made formally exact by applying the Lagrangian theorem of the differential calculus to the functional expansion. Because the present expansion was carried out for the interaction potential as a whole, it can be said that the present DFT is not associated with the dividing of the interaction potential. The formal similarity between the present DFT and the above-mentioned WDA + FPEA + DFT is due to the form of the MSA second-order DCF for the hard-core attractive Yukawa model fluid. When the parameters $T^* = \infty$ or $\lambda = \infty$ or both, the long-ranged part, $C^{(2)}_{0\mathrm{long}}$, of the hard-core attractive Yukawa model MSA second-order DCF naturally reduces to zero and its short-ranged part, $C^{(2)}_{0\mathrm{hs-like}}$, exactly reduces to the hard-sphere model PY second-order DCF, $C^{(2)}_{0\mathrm{hs}}$, so it is reasonabe to regard $C^{(2)}_{0\mathrm{hs-like}}$ as the hard-sphere-like part, and the residue, that is, $C^{(2)}_{0\mathrm{long}}$, as the long-ranged part. Because the long-ranged part $C^{(2)}_{0\mathrm{long}}$ is independent of the density argument, for the long-ranged part, the formally exact truncated functional perturbation expansion is reduced to the ordinary second-order functional perturbation expansion approximation formally. But this kind of density-independence approximation for the long-ranged part of the MSA second-order DCF was compensated for by the short-ranged hard-sphere-like part $C^{(2)}_{0\mathrm{hs-like}}$ the nonuniform counterpart of which was made formally exact in the present DFT approach by the Lagrangian theorem of the differential calculus, so the present DFT approach is completely different from the ordinary second-order functional perturbation expansion approximation. Equation 4 is based on the Lagrangian theorem, so it is exact and does not include any approximation; the unique approximation included in the present DFT is approximating the nonuniform second-order DCF by its uniform counterpart with an appropriate weighted density as its density argument the validity of which was tested in ref 22. The present specification of the weighting function follows the spirit of the SWDA the calculational simplicity of which makes the present DFT approach computationally modest. Surely, the SWDA is a simplified WDA, but the error of its application in the present approach can be reduced largely by adjusting the numerical value of the mixing parameter χ, that is, the mixing parameter χ from the Lagrangian theorem was also used as an adjustable parameter in the present physical theory to reduce the error resulting from the statistical mechanics approximation made. The number of the approximations included in the present DFT is reduced largely compared with the previous WDA + FPEA + DFT, so it is not surprising for the present DFT to predict more accurately than the former one. To conclude, the present formally exact second-order perturbative DFT for nonuniform hard-core attractive Yukawa model fluid is both computationally simpler and quantitatively more accurate than the previous one, its extension to other nonuniform interaction potential fluids and their mixture is straightforward, and we will report the corresponding calculation results in some separate papers.

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