

Structure of a Confined Square-Well Fluid

Shiqi Zhou*

Research Institute of Modern Statistical Mechanics, Zhuzhou Institute of Technology, Wenhua Road, Zhuzhou City 412008, People's Republic of China

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Square-well fluid under the influence of an external field is investigated by means of density functional theory. The attractive part of the square-well potential is treated by the mean field approximation, while the repulsive part is approximated by the hard sphere potential of the same bulk density with the investigated square-well fluid. When the square-well fluid is confined due to an external field, the hard sphere model fluid, approximating the repulsive part, becomes nonuniform and is then treated by a recently proposed density functional approximation by the present author (*New J. Phys.* **2002**, *4*, 36). The associated mixing parameter is determined in the present case by the hard wall sum rule for the square-well fluid. The prediction accuracy for the density distribution by the present work is comparable with that of a recently proposed weighted density approximation plus a third-order perturbation expansion approximation in the low bulk density case and is higher than that in the higher bulk density cases. The greatest advantage of the present approach is that the required input function is the bulk Percus–Yevick hard sphere direct correlation function, which is conveniently available. Thus numerical solution of the Ornstein–Zernike equation for bulk square-well fluid is avoided. Evidence for the continuity and differentiability of the density functional $C^{(1)}(\mathbf{r};[\rho])$ is given.

I. Introduction

The interparticle interaction potential in many uncharged colloidal dispersions of practical interest consists of harsh repulsions and strong attractions, both of which are often short ranged. Such interaction can be modeled reasonably well by the adhesive hard sphere (AHS) potential¹ and square-well (SW) potential.² The advantage of employing the AHS model to model the colloidal interaction is that it allows one to take advantage of the analytical solution of the Percus–Yevick (PY) integral equation for the AHS potential.³ However, the AHS model presents two limitations. First, the system of monodisperse AHS potential is not thermodynamically stable. The second limitation of AHS potential as a representation of a realistic short ranged interaction lies in the fact that it is unable to distinguish two situations with the same adhesiveness and density, but different interaction strength and/or range. To mimic the particle interaction in colloidal systems in a more realistic way, one can assume that the particles interact via the SW potential⁴

$$\begin{aligned}\beta u(r) &= \infty, & r < \sigma \\ &= -\beta\epsilon, & \sigma < r < \sigma + \delta \\ &= 0, & r > \sigma + \delta\end{aligned}\quad (1)$$

where σ is the diameter of the hard core, ϵ is the well depth, and δ is the well width. The equilibrium properties of the SW fluid depend on the values of three dimensionless parameters: the reduced density $\rho_b\sigma^3$, the reduced temperature $k_B T/\epsilon$ (k_B being the Boltzmann constant), and the reduced well width parameter δ/σ . Because the SW model potential includes two potential parameters, well depth parameter ϵ and well width parameter δ , while the AHS model potential has only one potential parameter, the adhesiveness, the SW model potential

can be more useful in uncovering and describing a much richer spectrum of the realistic colloidal interaction potential parameters. As an example, one may consider the works in ref 2, in which the SW model has been used to describe the structure factors of the inverted micellar and microemulsion system.

Despite the mathematical simplicity of the SW potential, no analytical solution of the conventional integral equations for fluids is known.^{5,6} The mean spherical approximation of Sharma and Sharma⁷ provides only an analytical expression for the structure factor, but it is not consistent with the hard core exclusion constraint. For extremely short-range potential ($\delta \leq 0.05\sigma$), there exists an analytic (yet approximate) solution of the PY closure for the direct correlation function (DCF) of the SW fluid by Nezbeda.⁸ The condition of extremely small well width parameter δ limits largely the application of the analytical solution. The nonexistence of the analytical solution for the bulk SW potential fluid with wide application range explains why, compared with other model potential fluid, so much less research work had been carried out for the confined SW fluid by the powerful density functional theory (DFT), for the DFT requires the bulk fluid second-order DCF as an input. Studies of the nonuniform SW fluid include that by Henderson and van Swol⁹ and that by Kim and Suh,¹⁰ the details of which will be discussed in detail later in present paper. Recently a DFT for confined atomic fluid was proposed¹¹ which is based on the functional perturbation expansion of the first-order DCF of the nonuniform fluid $C^{(1)}(\mathbf{r};[\rho])$ combined with the functional counterpart of the well-known Lagrangian theorem of differential calculus to make the truncated expansion series formally exact. The new version of classical DFT was then extended to another confined interaction potential fluid: Lennard-Jones fluid;¹² adhesive hard sphere fluid;¹³ hard core attractive Yukawa potential fluid;¹⁴ binary component hard sphere fluid.¹⁵ The main goal of the present paper is to extend the new version of DFT to the SW potential fluid. In addition, some readers of this series think

* Corresponding author. E-mail address: chixiayzsq@yahoo.com.

that the mixing parameter λ in the new version should be a function of the space position \mathbf{r} , not a constant, as has been done in this series of papers. The present paper will clear up this argument in Appendix A. In section II, the new version is recapitulated, and then it is combined with the mean field approximation for the attractive part of the square-well potential and the PY hard sphere second-order DCF to construct the DFT for the SW fluid. In section III, the calculated results are compared with the available simulation data; the present DFT is also compared with the previous two versions for the confined SW fluid. Finally, in section IV some concluding remarks are made. In Appendix B, evidence of the continuity and differentiability of the density functional $C^{(1)}(\mathbf{r};[\rho])$ will be given; the continuity and differentiability of the density functional $C^{(1)}(\mathbf{r};[\rho])$ is very crucial for the application of Lagrangian theorem.

II. Formulation of DFT for Confined SW Fluid

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

$$\rho(\mathbf{r}) = \rho_b \exp\{-\beta\varphi_{\text{ext}}(\mathbf{r}) + C^{(1)}(\mathbf{r};[\rho]) - C^{(1)}_0(\rho_b)\} \quad (2)$$

where $\varphi_{\text{ext}}(\mathbf{r})$ is the external potential responsible for generation of the density distribution $\rho(\mathbf{r})$ and $C^{(1)}_0(\rho_b)$ is the uniform counterpart of $C^{(1)}(\mathbf{r};[\rho])$. The subscript 0 denotes the uniform case; its absence denotes the nonuniform case. The relation of $C^{(1)}(\mathbf{r};[\rho])$ and $C^{(1)}_0(\rho_b)$ to the excess Helmholtz free energy density functional $F_{\text{ex}}[\rho]$ is as follows.

$$C^{(1)}(\mathbf{r};[\rho]) = \frac{-\beta\delta F_{\text{ex}}[\rho]}{\delta\rho(\mathbf{r})} \quad (3)$$

$$C^{(1)}_0(\rho_b) = \lim_{\rho(\mathbf{r}) \rightarrow \rho_b} \frac{-\beta\delta F_{\text{ex}}[\rho]}{\delta\rho(\mathbf{r})} \quad (4)$$

As usual, one can treat the attractive part and the repulsive part of the square-well potential separately. We divide the SW potential (1) into attractive and repulsive part as follows.

$$\begin{aligned} \beta u_{\text{att}}(r) &= -\beta\epsilon, \quad r < \sigma + \delta \\ &= 0, \quad r > \sigma + \delta \end{aligned} \quad (5)$$

and

$$\begin{aligned} \beta u_{\text{rep}}(r) &= \infty, \quad r < \sigma \\ &= 0, \quad r > \sigma \end{aligned} \quad (6)$$

Correspondingly, the excess Helmholtz free energy and the first-order DCF of uniform and nonuniform fluid can also be separated into the attractive part and the repulsive part as follows.

$$F_{\text{ex}}[\rho] = F_{\text{ex}}^{\text{rep}}[\rho] + F_{\text{ex}}^{\text{att}}[\rho] \quad (7)$$

$$F_{0\text{ex}}(\rho_b) = F_{0\text{ex}}^{\text{rep}}(\rho_b) + F_{0\text{ex}}^{\text{att}}(\rho_b) \quad (8)$$

$$C^{(1)}(\mathbf{r};[\rho]) = C^{(1)}_{\text{rep}}(\mathbf{r};[\rho]) + C^{(1)}_{\text{att}}(\mathbf{r};[\rho]) \quad (9)$$

$$C^{(1)}_0(\rho_b) = C^{(1)}_{0\text{rep}}(\rho_b) + C^{(1)}_{0\text{att}}(\rho_b) \quad (10)$$

Substituting eqs 9–10 into eq 2 gives rise to

$$\rho(\mathbf{r}) = \rho_b \exp\{-\beta\varphi_{\text{ext}}(\mathbf{r}) + C_{\text{rep}}^{(1)}(\mathbf{r};[\rho]) - C_{0\text{rep}}^{(1)}(\rho_b) + C_{\text{att}}^{(1)}(\mathbf{r};[\rho]) - C_{0\text{att}}^{(1)}(\rho_b)\} \quad (11)$$

No coupling term results from the above separation of the correlation functions due to the fact that the correlation functions are the functional derivative of the excess Helmholtz free energy density functional $F_{\text{ex}}[\rho]$ with respect to the density distribution $\rho(\mathbf{r})$ and $F_{\text{ex}}[\rho]$ is additive. According to the definition of the functional derivative, the functional derivative of the sum of two quantities is equal to the sum of the functional derivative of each quantity.

In the present preliminary study on SW fluid, to indicate the validity of the new version DFT, we adopt the simplest approximation for the attractive part, the mean field approximation; i.e.

$$F_{\text{ex}}^{\text{att}}[\rho] = (1/2) \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') u_{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \quad (12)$$

Combining eq 12 with eqs 3 and 4, one can obtain the attractive part of the first-order DCF of nonuniform and uniform fluid.

$$C_{\text{att}}^{(1)}(\mathbf{r};[\rho]) = - \int d\mathbf{r}' \rho(\mathbf{r}') \beta u_{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \quad (13)$$

$$C_{0\text{att}}^{(1)}(\rho_b) = -\rho_b \int d\mathbf{r}' \beta u_{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \quad (14)$$

Thus

$$C_{\text{att}}^{(1)}(\mathbf{r};[\rho]) - C_{0\text{att}}^{(1)}(\rho_b) = - \int d\mathbf{r}' (\rho(\mathbf{r}') - \rho_b) \beta u_{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \quad (15)$$

About the treatment of the repulsive part, we employ the recently proposed DFT version¹¹ which is based on the functional counterpart of Lagrangian theorem and will be detailed as follows. We also will give a simplified proving about the continuity and differentiability of the density functional $C^{(1)}(\mathbf{r};[\rho])$, as required by the Lagrangian theorem.

We expand the nonuniform first-order DCF $C^{(1)}(\mathbf{r};[\rho])$ around the uniform system of bulk density ρ_b .

$$\begin{aligned} C^{(1)}(\mathbf{r};[\rho]) &= C^{(1)}_0(\rho_b) + \int d\mathbf{r}_1 (\rho(\mathbf{r}_1) - \rho_b) C^{(2)}_0(|\mathbf{r} - \mathbf{r}_1|; \rho_b) + \\ &\quad \sum_{n=3}^{\infty} \frac{1}{(n-1)!} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \dots \int d\mathbf{r}_{n-1} \prod_{m=1}^{n-1} [\rho(\mathbf{r}_m) - \rho_b] \\ &\quad C^{(n)}_0(\mathbf{r}, \mathbf{r}_1, \dots, \mathbf{r}_{n-1}; \rho_b) \end{aligned} \quad (16)$$

Here each functional derivative, i.e., the expansion coefficient $C^{(n)}_0(\mathbf{r}, \mathbf{r}_1, \dots, \mathbf{r}_{n-1}; \rho_b)$, $n \geq 2$, is evaluated at the initial ρ_b . When such a series is terminated, it can be made an accurate representation by having the last functional derivative evaluated not at the initial ρ_b but at some $\rho_b + \lambda(\rho - \rho_b)$, with λ between 0 and 1;^{16a,b} this is actually a functional counterpart of the well-known Lagrangian theorem of differential calculus which states that the following eq 17 is exact if the value of λ is correctly chosen. According to the above procedure, we truncated the series at the first order, and then eq 16 reduces to

$$C^{(1)}(\mathbf{r};[\rho]) = C^{(1)}_0(\rho_b) + \int d\mathbf{r}_1 (\rho(\mathbf{r}_1) - \rho_b) C^{(2)}_0(\mathbf{r}, \mathbf{r}_1; [\rho_b + \lambda(\rho - \rho_b)]) \quad (17)$$

It should be noted that the expansion coefficient $C_0^{(2)}$ in eq 16 was replaced by $C^{(2)}$ in eq 17 because of substitution of the bulk density ρ_b by the nonuniform density field $\rho_b + \lambda(\rho - \rho_b)$; this replacement has to be done to be in agreement with the definition of the DCF. Equation 17 is exact, and it does not include any approximation. It should be noted that the mixing parameter λ should be a constant value, not a field, as held by the current tendency. In fact, the functional counterpart of the Lagrangian theorem of differential calculus has been regarded as a mathematical theorem; the reader can refer to the refs 16a,b. We give a detailed account of the functional counterpart of the Lagrangian theorem of differential calculus in Appendix A. The Lagrangian theorem applies for the function or functional which is continuous and differentiable. The continuity and differentiability of $C^{(1)}(\mathbf{r};[\rho])$ with arbitrary density distribution $\rho(\mathbf{r})$ can be proved as follows. According to the spirit of weighted density approximation,¹⁷ the thermodynamic or structural functions of a nonuniform system with nonuniform density distribution $\rho(\mathbf{r})$ can be approximated by their uniform counterpart with the density argument being substituted by the so-called weighted density $\bar{\rho}(\mathbf{r})$

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) \quad (18)$$

From eq 18, one can see that the weighted density $\bar{\rho}(\mathbf{r})$ is actually the convolution integral of the actual density distribution function $\rho(\mathbf{r})$ and weighting function w . According to the mathematical properties of convolution integral, no matter the function form of $\rho(\mathbf{r})$ and w , $\bar{\rho}(\mathbf{r})$ is always continuous. One can also know that, with another bulk parameter fixed, $C_0^{(1)}(\rho_b)$ is always a continuous function of its density argument. To conclude, $C^{(1)}(\mathbf{r};[\rho])$ is always a continuous functional of the density distribution function $\rho(\mathbf{r})$ and is differentiable, so one can always apply the functional counterpart of the Lagrangian theorem to the above density functional $C^{(1)}(\mathbf{r};[\rho])$; i.e., eq 17 is always formally exact and suitable for various density distributions $\rho(\mathbf{r})$. However, it should be noted that ref 9a also points out the continuity of $\bar{\rho}(\mathbf{r})$ and $C^{(1)}(\mathbf{r};[\rho])$ without having to resort to the mathematical properties of convolution integral and that a local density approximation (LDA) does not satisfy the continuity of $\bar{\rho}(\mathbf{r})$ and $C^{(1)}(\mathbf{r};[\rho])$ and, hence, explains the well-known problems with LDA-DFT. In Appendix B, we give a different proof of the continuity of $C^{(1)}(\mathbf{r};[\rho])$. Now we apply eq 17 to the structural function $C_{\text{rep}}^{(1)}(\mathbf{r};[\rho])$ of the repulsive part of the SW potential eq 6 and approximate the structural function $C_{\text{rep}}^{(2)}(\mathbf{r}, \mathbf{r}_1; [\rho_b + \lambda(\rho - \rho_b)])$ of the repulsive part by that of the exact hard sphere potential $C_{\text{PY,HS}}^{(2)}(\mathbf{r}, \mathbf{r}_1; [\rho_b + \lambda(\rho - \rho_b)])$, where the subscript PY,HS denotes the PY approximation for the hard sphere model potential. It has to be noted that this is an approximation; although eq 6 is exactly the hard sphere potential, it is related to the attractive part, so the structural and thermodynamic functions of the repulsive part are not exactly the same as that of the pure hard sphere potential model fluid. To conclude, we have

$$C_{\text{rep}}^{(1)}(\mathbf{r};[\rho]) = C_{0\text{rep}}^{(1)}(\rho_b) + \int d\mathbf{r}' (\rho(\mathbf{r}') - \rho_b) C_{\text{PY,HS}}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho_b + \lambda(\rho - \rho_b)]) \quad (19)$$

Substituting eqs 15 and 19 into eq 11, one has

$$\rho(\mathbf{r}) = \rho_b \exp\{-\beta\varphi_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' (\rho(\mathbf{r}') - \rho_b) C_{\text{PY,HS}}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho_b + \lambda(\rho - \rho_b)]) - \int d\mathbf{r}' (\rho(\mathbf{r}') - \rho_b) \beta u_{\text{att}}(|\mathbf{r} - \mathbf{r}'|)\} \quad (20)$$

Now we apply directly the relevant approximation from ref 11 to the present case; i.e.

$$C_{\text{PY,HS}}^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho_b + \lambda(\rho - \rho_b)]) = C_{0\text{PY,HS}}^{(2)}(|\mathbf{r} - \mathbf{r}'|; \tilde{\rho}((\mathbf{r} + \mathbf{r}')/2, \lambda)) \quad (21)$$

where

$$\tilde{\rho}((\mathbf{r} + \mathbf{r}')/2, \lambda) = \frac{\int d\mathbf{r}'' [\rho_b + \lambda(\rho(\mathbf{r}'') - \rho_b)] C_{0\text{PY,HS}}^{(2)}(|(\mathbf{r} + \mathbf{r}')/2 - \mathbf{r}''|; \rho_b)}{\int d\mathbf{r} C_{0\text{PY,HS}}^{(2)}(\mathbf{r}; \rho_b)} \quad (22)$$

As usual, the mixing parameter λ can be specified by a hard wall sum rule which specifies the bulk pressure P by a hard wall contact density ρ_w

$$P = \rho_w kT \quad (23)$$

ρ_w can be obtained from $\rho(0.0\sigma)$ in eq 20 when the external potential has the following form

$$\begin{aligned} \varphi_{\text{ext}}(z) &= \infty, & z/\sigma < 0.0 \\ &= 0, & 0.0 < z/\sigma \end{aligned} \quad (24)$$

where P for the SW fluid obtained from the computer simulation of Henderson and van Swol¹⁸ was used as input. According to the universality of mixing parameter λ (as discussed in detail by the present author^{11,14,19,20}), i.e., the independence of the numerical value of λ on the external potential, one can employ the specified value of λ from this special case for other cases of the external potentials, such as a spherical cavity, a soft wall, etc., at the same bulk thermodynamic state, even though the hard wall sum rule is valid only for a fluid in contact with a single hard wall.

III. Comparison of Density Distribution Profile Prediction with Simulation Data

Through the following calculations, the SW potential with the well depth $\beta\epsilon = 1.0$ and the well width $\delta = 0.5\sigma$ was used to compare with the available computer simulation results.^{9,18} We first consider the SW potential fluid confined in planar slits consisting of structureless hard walls. In this case, the external potential is given as

$$\begin{aligned} \varphi_{\text{ext}}(z) &= \infty, & \text{otherwise} \\ &= 0, & 0 < z < L \end{aligned} \quad (25)$$

The density distribution profiles $\rho(z)\sigma^3$ from the present method for the confined SW fluid ($\beta\epsilon = 1.0$ and $\delta = 0.5\sigma$) at four different bulk densities ($\rho_b\sigma^3 = 0.678, 0.741, 0.798, 0.819$) are displayed in Figures 1–4 with the corresponding simulation data; the corresponding numerical values of the mixing parameter λ are also displayed in Figures 1–4. One can see that, as required by the Lagrangian theorem, the mixing parameter λ is surely between 0 and 1. Compared with the predictions by ref

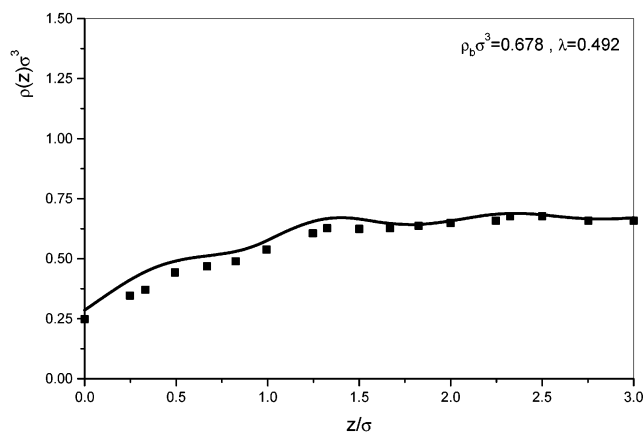


Figure 1. Density profiles of the confined SW fluid ($\delta = 0.5\sigma$, $\beta\epsilon = 1.0$) in the slit of width $L = 11.18\sigma$ at $\rho_b\sigma^3 = 0.678$. The line is from the present DFT. The symbols are from the computer simulation.¹⁸

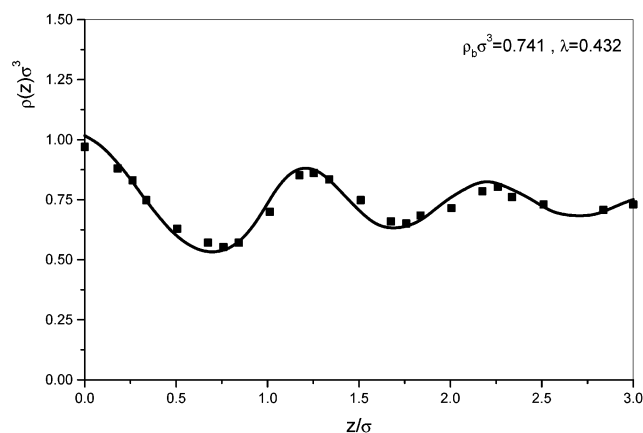


Figure 2. As in Figure 1, but for $L = 10.55\sigma$ and $\rho_b\sigma^3 = 0.741$.

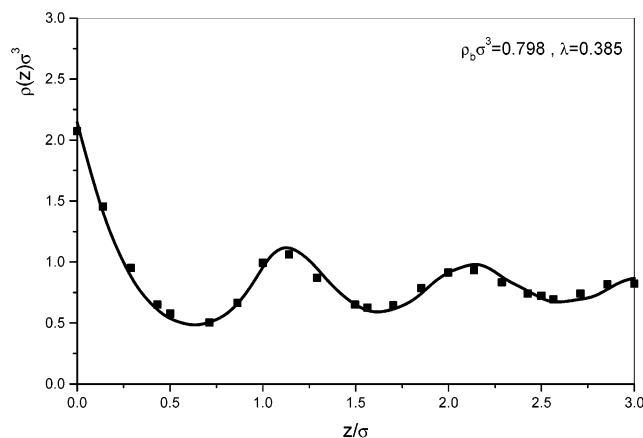


Figure 3. As in Figure 1, but for $L = 10.18\sigma$ and $\rho_b\sigma^3 = 0.798$.

10, which are not plotted in the same Figures 1–4 for clarity, at higher bulk densities (see Figures 2–4), the present predictions are more accurate than that from ref 10; this result can be expected since the mean field approximation becomes more accurate when the density becomes higher where the repulsive part of the SW potential dominates over the attractive part, while the repulsive part was treated effectively in the present work by the new version DFT. At lower density (see Figure 1), the present accuracy is also comparable with that from ref 10.

To avoid the suspicion that the present good predictions result from the associating adjustable parameter λ , we will test the performance of the present method for the density profiles in the wall–fluid interfacial region of the SW wall system whose

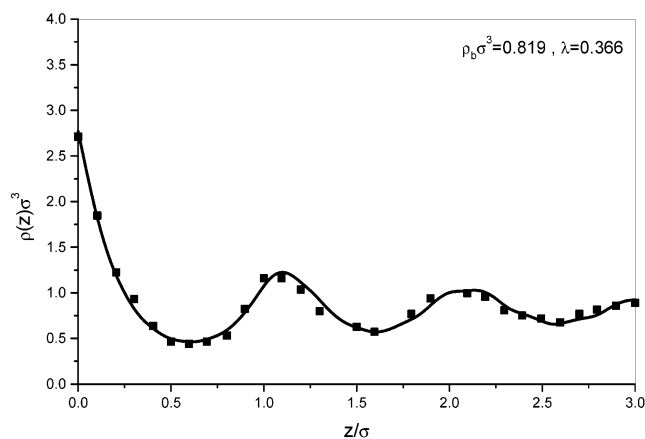


Figure 4. As in Figure 1, but for $L = 10.06\sigma$ and $\rho_b\sigma^3 = 0.819$.

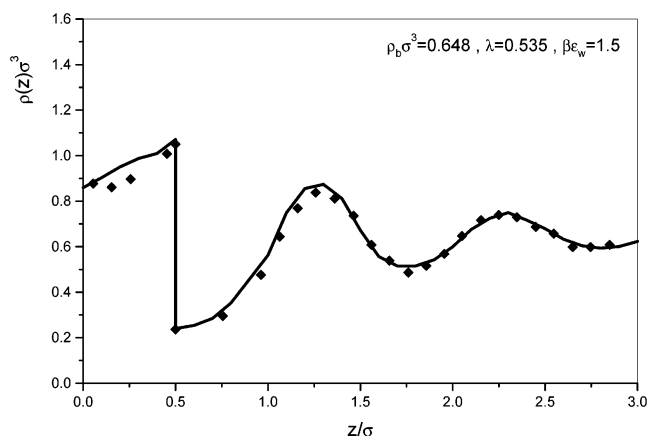


Figure 5. Density profiles of the confined SW fluid ($\delta = 0.5\sigma$, $\beta\epsilon = 1.0$) near a SW wall with the SW–wall interaction $\beta\epsilon_w = 1.5$ and at $\rho_b\sigma^3 = 0.648$. The line is from the present DFT. The symbols are from the computer simulation.^{9,18}

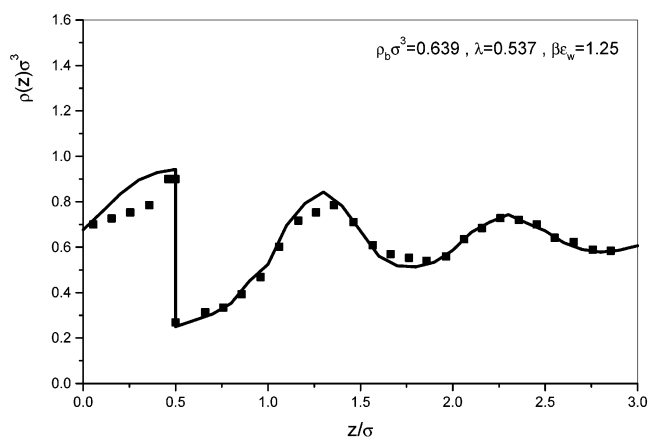


Figure 6. As in Figure 5, but for $\beta\epsilon_w = 1.25$ and $\rho_b\sigma^3 = 0.639$.

external potential is of the following form

$$\begin{aligned} \varphi_{\text{ext}}(z) &= -\epsilon_w, & 0.0 < z < \sigma/2 \\ &= 0, & \sigma/2 < z \end{aligned} \quad (26)$$

As can be seen from Figures 5–7, the density profile near a SW wall increases with the increase of the fluid–wall attractive interaction from $\beta\epsilon_w = 1.0$ to $\beta\epsilon_w = 1.5$: when away from the position of drying transition ($\beta\epsilon_w = 1.0$), the same good agreement with the simulation data is obtained (see Figures 5 and 6), and near the drying transition (see Figure 7), the agreement with simulation data is poor for two cases of the

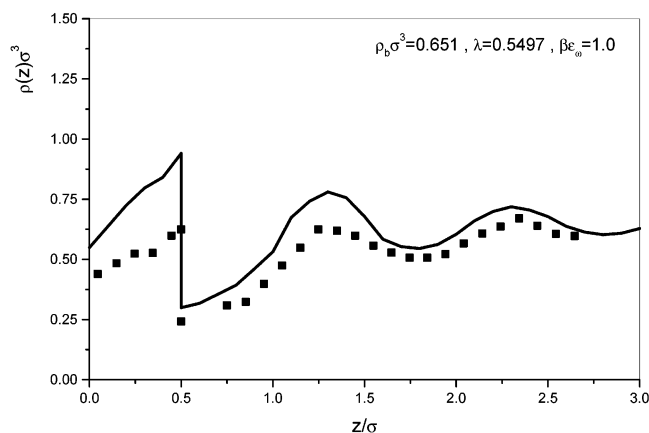


Figure 7. As in Figure 5, but for $\beta\epsilon_w = 1.0$ and $\rho_b\sigma^3 = 0.651$.

present DFT and that in ref 10; this clearly indicates that the mean field approximation is poor near the continuous phase transition point.

With regard to the self-consistency of determining λ by a one hard wall sum rule and then employing the so specified λ for other external potential cases, we have the following argument. If one employs an accurate equation of state for the left side of eq 23, this means that the density functional approximation under consideration (i.e. eqs 15, 19, 21, and 22 in the present case) can reduce to the bulk equation of state. If the density functional approximation under consideration is very accurate, then when one applies the same density functional approximation to the bulk fluid by the test particle method due to Percus, as is the case in ref 11, the same accurate bulk equation of state should be obtained by the virial route based on the obtained radial distribution function $g(\mathbf{r}) = \rho(\mathbf{r})/\rho_b$. Since the obtained $g(\mathbf{r})$ can produce the accurate bulk equation of state, then one can deduce that the obtained $g(\mathbf{r})$ should be very accurate; this is exactly the case of ref 11. It should be noted that this kind of desirable case depends on whether the density functional approximation under consideration is very accurate. However in the present case, the desirable case in ref 11 does not appear. As one can see, Figure 7 only predicts the overall shape of the density profile; obviously the density profile displayed in Figure 7 predicts a drying transition different from the simulated one. This is obviously due to the density functional approximation under consideration; i.e., eqs 15, 19, 21, and 22 are not very accurate for the case of Figure 7 (the inappropriateness of the present density functional approximation is mainly manifested in the mean field approximation for the attractive part of the interaction potential). To conclude, we point out that the present declaration of the universality of λ is physically founded and the self-consistency of λ depends on the accuracy of the density functional approximation under consideration. Conversely, from the self-consistency of λ , one can deduce whether the considered density functional approximation is appropriate.

With regard to the computational complexity, the present approach is the simplest compared with that in refs 9 and 10. Both the present approach and that in ref 9 treat the attractive part by mean field approximation, but the latter approach treats the repulsive part by local weighted density approximation¹⁷ at the level of the excess Helmholtz free energy $F_{\text{ex}}[\rho]$; in this approximation since the weighting function and weighted density are coupled together, its computational task is obviously enormous. On the other hand, although the present approach also is concerned with one kind of weighted density approximation, i.e., the simple weighted density approximation (SWDA),²¹

the SWDA is carried out at the level of second-order DCF; furthermore its weighting function and weighted density are decoupled, so the present approach is computationally largely simplified. In particular, an adjustable parameter is naturally integrated into the present approach; its incorporation into the formalism makes the SWDA-based DFT achieve higher accuracy than that of the computationally more complex WDA, as can be seen from ref 11. The DFT in ref 10 treats the repulsive part by the same approximation as in ref 9, but its treatment on the attractive part is rather sophisticated. Concretely speaking, it concerns the third-order perturbation expansion of the attractive part of the first-order DCF around the bulk density; the second-order DCF in the second-order term of the expansion is the difference between the bulk SW fluid second-order DCF (obtained by numerically solving the OZ equation combined with the mean spherical approximation in ref 10) and the PY hard sphere fluid second-order DCF; and the third term concerns an intuitive and symmetry-based consideration kernel function. However, the more sophisticated formalism only achieves the same accuracy as that in the present approach, even in the low-density case, which is not the case most suitable for the present mean field approximation; for the higher density case the present accuracy is far higher than that in ref 10.

IV. Concluding Remarks

About the DFT for the nonuniform, non-hard-sphere interaction potential fluid, there does not exist a well-accepted method. A commonly adopted method is mean field approximation⁹ and thermodynamics perturbation method.²² Both of these two routes fail near the wetting or drying point. Other approaches include WDA for the attractive part,²³ but its input parameter is the bulk second-order DCF which is often obtained from the integral equation theory (IET); it is well-known that the IETs also fail near the vapor–liquid point, so this route is also not satisfactory. Recently the present author proposed a version of DFT²⁴ which treats the interaction potential as a whole and constructs the density functional approximation by incorporating the bulk radial distribution function $g(r)$. Obviously, this formalism enjoys the same shortcoming as that in ref 23. Since $g(r)$ has to be obtained by solving numerically the Ornstein–Zernike (OZ) integral equation, near the vapor–liquid point the OZ equation cannot be solved by the current algorithm. In fact the absence of the solution often is regarded as an indicator of the phase transition. So it can be said that although the DFT for a hard sphere is highly developed, the studies on the attractive part by DFT are still at a very rudimentary stage, and this should be the center point of future DFT study.

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Appendix A

Let Δf be a finite change in f . A formal Taylor series expansion of functional $F[f + \Delta f]$ can then be written:

$$F[f + \Delta f] = F[f] + \sum_{n=1}^{\infty} \frac{1}{n!} \int \dots \int \frac{\delta^{(n)} F}{\delta f(x_1) \delta f(x_2) \dots \delta f(x_n)} \times \Delta f(x_1) \Delta f(x_2) \dots \Delta f(x_n) dx_1 dx_2 \dots dx_n \quad (\text{A1})$$

Here, each functional derivative is evaluated at the initial f . When such a series is terminated, it can be made into an accurate representation by having the last functional derivative evaluated not at the initial f but at some $f + \lambda\Delta f$, with λ between 0 and 1.^{16a,b}

We truncate the series in eq A1 at the first order. When $F[f + \Delta f]$ and f are substituted by $C^{(1)}(\mathbf{r};[\rho])$ and ρ_b , respectively, Δf has to be substituted by $\rho - \rho_b$. According to definition, when $\rho \rightarrow \rho_b$, $C^{(1)}(\mathbf{r};[\rho])$ reduces to $C_0^{(1)}(\rho_b)$. Thus, $F[f]$ should be substituted by $C_0^{(1)}(\rho_b)$, and $f + \lambda\Delta f$ should be substituted by $\rho_b + \lambda(\rho - \rho_b)$. With all of the above substitution and according to the definition of direct correlation function,

$$C^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho]) = \delta C^{(1)}(\mathbf{r}; [\rho]) / \delta \rho(\mathbf{r}') \quad (\text{A2})$$

eq A1 reduces to eq 17.

Appendix B

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

$$\rho(\mathbf{r}) = \rho_b g(\mathbf{r}) \quad (\text{A3})$$

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; i.e.

$$\varphi_{\text{ext}}(\mathbf{r}) = u(\mathbf{r}) \quad (\text{A4})$$

Then eq 2 reduces to

$$g(\mathbf{r}) = \exp\{-\beta u(\mathbf{r}) + C^{(1)}(\mathbf{r}; [\rho]) - C_0^{(1)}(\rho_b)\} \quad (\text{A5})$$

Comparing eq A5 with the closing relation for the Ornstein–Zernike (OZ) integral equation

$$g(\mathbf{r}) = \exp\{-\beta u(\mathbf{r}) + \int d\mathbf{r}' [g(\mathbf{r}') - 1] C_0^{(2)}(\mathbf{r}, \mathbf{r}'; \rho_b) + B(\mathbf{r})\} \quad (\text{A6})$$

and employing eq A3, one can find that

$$C^{(1)}(\mathbf{r}; [\rho]) - C_0^{(1)}(\rho_b) = \int d\mathbf{r}' [\rho(\mathbf{r}') / \rho_b - 1] C_0^{(2)}(\mathbf{r}, \mathbf{r}'; \rho_b) + B(\mathbf{r}) \quad (\text{A7})$$

In eq A7, $\int d\mathbf{r}' [\rho(\mathbf{r}') / \rho_b - 1] C_0^{(2)}(\mathbf{r}, \mathbf{r}'; \rho_b)$, i.e., the indirect correlation function $\gamma(\mathbf{r})$, is the convolution integral of two functions $C_0^{(2)}(\mathbf{r}, \mathbf{r}'; \rho_b)$ and $\rho(\mathbf{r}') / \rho_b - 1$. According to the mathematical properties of a convolution integral, no matter the function form of $C_0^{(2)}(\mathbf{r}, \mathbf{r}'; \rho_b)$ and $\rho(\mathbf{r}') / \rho_b - 1$, $\gamma(\mathbf{r})$ is always a continuous functional of the density distribution $\rho(\mathbf{r})$. $B(\mathbf{r})$ in eq A7 is usually expressed as a function of $\gamma(\mathbf{r})$, as is the case of the HNC approximation, the PY approximation, the VM approximation, the MS approximation, the BPGG approximation, and the RY approximation and its variant, i.e., HMSA; $B(\mathbf{r})$ is also a continuous functional of the density distribution $\rho(\mathbf{r})$. Thus, one can conclude that $C^{(1)}(\mathbf{r}; [\rho])$ is a continuous functional of the density distribution $\rho(\mathbf{r})$. The OZ equation and its closing relation eq A6 are applicable to various cases of interaction potentials and particle shapes, so the spectrum of $u(\mathbf{r})$ to which eqs A6 and A7 and the OZ equation are applicable is in coincidence with the spectrum of $\varphi_{\text{ext}}(\mathbf{r})$. Both $u(\mathbf{r})$ and $\varphi_{\text{ext}}(\mathbf{r})$ can be arbitrary. Thus, one can conclude that $C^{(1)}(\mathbf{r}; [\rho])$ is a continuous functional of arbitrary density distribution $\rho(\mathbf{r})$.

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