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Transformation from Rogers-Young approximation to the density functional approach for nonuniform fluids: Numerical recipe

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A numerical recipe is devised to extend the methodology [J. Chem. Phys. **112**, 8079 (2000)] to nonhard-sphere nonuniform fluids where analytical expressions for the functional relationship of the bridge function as a function of indirect correlation function do not exist, the numerical recipe is also based on the universality of the free-energy density functional. As an example, the recipe is employed to calculate the density profile of a colloidal suspension near a single charged hard wall and the hard-sphere Yukawa fluid near a single hard wall and a single hard wall with an attractive tail, the agreement of the predictions of the theory with the simulation data is good. The difference of the present methodology from that of the weighted density approximation is discussed.

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I. INTRODUCTION

Information about the structural properties of fluids in confined geometries (nonuniform fluids [1,2]) is important for both applied and basic research due to their relevance to practical application, as well as their association with some interesting phenomena such as selective adsorption from mixtures, solvation forces in fluids, etc. The most important characteristic of nonuniform fluids is the nonuniform density distribution near the interfacial region resulting from the interaction between fluid particles and external field such as ''a wall.'' Usually, the theoretical approaches employed can be divided into two categories, viz. the integral equation theory [3] (IET) and the density functional theory [4–6] (DFT), IET for nonuniform fluids is computationally complicated because the Ornstein-Zernike equation with the suitable closure relations such as the Percus-Yevick (PY), hypernetted chain (HNC), or rescaled mean spherical approximation (RMSA) has to be solved for the particle-particle, as well as, wall-particle correlation. Furthermore, IET cannot capture the interesting phase transitions such as wetting phenomena. The DFT provides a suitable theoretical formalism for nonuniform fluids by expressing the nonuniform system grand potential as a function of single-particle density distribution [7,8], which, on minimization, yields the equilibrium density distribution and the free energy. Also an approximation has to be incurred for the unknown part of the free-energy density functional, i.e., the excess free energy. In the classical DFT, three different versions of approximation for the nonuniform system excess free energy or its functional derivative were proposed. One such version is the functional perturbative expansion approximation [9–11] (PEA) of the excess free energy of the nonuniform system around the uniform system in powers of the density deviation between nonuniform density distribution and bulk density with the coefficients representing the direct correlation functions (DCF's) of the uniform system, In most of the early studies, the expansion was truncated at the second order due to the lack of knowledge of the higher-order DCF's of even the uniform bulk fluid, but recently some studies developed a higher-order expansion approximation by making use of approximate higher-order DCFs [12–14]. Another such version is the so-called weighted density approximation (WDA) and its variants [15–18], which are actually mappings of nonuniform systems onto uniform counterparts and approximately include contributions to the free-energy density functional from all orders in density difference. In the WDA approach, it is the excess free energy or its functional derivative (the first-order DCF) for the nonuniform fluids that is approximated by that of the corresponding uniform fluid at a smoothed average density that is actually a suitable weighted average of the physical density of the system under consideration. However, it should be noted that a completely new DFT formalism [19,20] was proposed recently, which resulted from the use of the conception of the universality of the free-energy density functional, but the method is now limited only to the nonuniform hard-sphere system due to the fact that there exists the analytical expression only for the hard-sphere bridge functional that is expressed as a functional of the indirect correlation function γ (ICF) of the corresponding uniform system, so it is interesting to observe how this methodology evolves. Beyond the above three main DFT types, there also exist other DFT formalisms, especially the fundamental measure theory by Rosenfeld [21,22], which is based on geometrical considerations and specifies the excess free energy by reproducing the PY equation of state and second-order DCF of the hard-sphere fluid. A characteristic of the original WDA is that the weighted density and weighting function are coupled together [23], this entails iterative calculation, thus, tremendous computer time is required. This shortcoming becomes very obvious when the methods of WDA type are extended to the case of mixtures. Furthermore, the input parameters include the excess free-energy per particle and the excess chemical potential or the first-order DCF of the corresponding uniform system, but it is usually difficult to obtain these parameters for the nonhard-

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sphere system, for example, the hard-sphere Yukawa system, or the colloidal suspension system with the DLVO potential as the interparticle interaction potential. Regarding the PEA, it is usually not easy to obtain the accurate input parameters, i.e., the higher-order DCF's of the corresponding uniform system, thus, usually the PEA is less accurate than the approaches of the WDA type. Within the framework of DFT, the WDA and the PEA are also combined to attack the problem of the long-range interaction potential system, for example, the Lennard-Jonnes fluid [24,25], the electrical double-layer system [26,27] etc. The suggested methodology in Ref. [19] collects all of the orders beyond the second order in the form of the bridge function and only requires the second-order DCF and the bridge function of the uniform system as inputs. These inputs can be easily obtained from the integral equation theory for the corresponding uniform system, so the new methodology should be easy to use for various nonuniform fluids. A necessary condition specified in Ref. [19] for the methodology to be used is that the functional form of the bridge functional must be the one that expresses the bridge functional as a function of indirect correlation function γ and the γ is then substituted by a combination of the Ornstein-Zernike equation for the uniform system and the Percus identity Eq. (3). But in most cases, the bridge functional in the IET is usually not expressed as a function of the indirect correlation function analytically in, for example, the mean spherical approximation (MSA) [3], the Rogers-Young approximation (RY) [28] etc., thus, this necessary condition limits the application of the methodology to the nonuniform hard-sphere fluid only. The necessary condition comes from the requirement that the theoretical prediction should not be dependent on the choice of the origin of the coordinate system. To widen the applicability of the methodology, the present paper devises a numerical procedure to carry out the condition computationally. As an example, the numerical procedure will be used to predict the density distribution profile of nonuniform colloidal suspension and hard-sphere Yukawa fluid.

II. DENSITY FUNCTIONAL APPROACH FOR THE NONUNIFORM FLUIDS

In the formalism of DFT, the density profile equation of a nonuniform single component fluid is

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

where $\varphi_{\mathrm{ext}}(\mathbf{r})$ is the external potential responsible for the generation of the density distribution $\rho(\mathbf{r})$, $\beta=1/kT$ with k the Boltzmann constant and T the absolute temperature and ρ_b is the bulk density. To calculate the density distribution profile, the difference between the first-order DCF of the nonuniform and uniform system $C^{(1)}(\mathbf{r};[\rho])$ and $C_0^{(1)}(\rho_b)$ is needed. In the methodology from Ref. [19], $C^{(1)}(\mathbf{r};[\rho(\mathbf{r})])$ was expanded around the uniform system of bulk density ρ_b as follows:

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

where $C_0^{(n)}(\mathbf{r},\mathbf{r}_1,\dots,\mathbf{r}_{n-1};\rho_b)$ is the n order DCF of a uniform system of bulk density ρ_b. Even in a uniform system, there is a nonuniform density profile around each molecule located in origin given by [29]

$$\rho(\mathbf{r})=\rho_b g(\mathbf{r}), \quad (3)$$

where $g(\mathbf{r})$ is the radial distribution function of the bulk fluid. Thus, for this special type of inhomogeneity, Eq. (2) acquires the following form

$$\begin{aligned} C^{(1)}&(\mathbf{r};[\rho_b g(\mathbf{r})]) \\ &=C_0^{(1)}(\rho_b)+\int d\mathbf{r}_1[\rho_b g(\mathbf{r})-\rho_b]C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b) \\ &\quad+\sum_{n=3}^{\propto}\frac{\rho_b^{(n-1)}}{(n-1)!}\int d\mathbf{r}_1\int d\mathbf{r}_2\dots\int d\mathbf{r}_{n-1} \\ &\quad\times\prod_{m=1}^{n-1}h(\mathbf{r}_m)C_0^{(n)}(\mathbf{r},\mathbf{r}_1,\dots\mathbf{r}_{n-1};\rho_b), \end{aligned} \quad (4)$$

where $h(\mathbf{r})=g(\mathbf{r})-1$ is the total correlation function of the bulk fluid. The third term in the right-hand side of the above equation represents the bridge functional [30], which is denoted as $B[\gamma(\mathbf{r})]$ in Ref. [19], where $\gamma=h-C_0^{(2)}$, is the indirect correlation function of the uniform system. $\gamma(\mathbf{r})$ is chosen as the argument of the bridge function to delete the dependence of the calculated density distribution profile on the coordinate origin. Consequently, Eq. (4) can be rewritten as

$$\begin{aligned} C^{(1)}(\mathbf{r};[\rho_b g(\mathbf{r})])=C_0^{(1)}(\rho_b)+\int d\mathbf{r}_1[\rho_b g(\mathbf{r}_1)-\rho_b] \\ \times C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b)+B[\gamma(\mathbf{r})]. \end{aligned} \quad (5)$$

Because the density functional $F_{\mathrm{ex}}(\mathbf{r};[\rho(\mathbf{r})])$ (hence $C^{(1)}\{\mathbf{r};[\rho(\mathbf{r})]\}=-\beta\delta F_{\mathrm{ex}}\{\mathbf{r};[\rho(\mathbf{r})]\}/\delta\rho(\mathbf{r})$) is universal for any systems involving only additive pair interactions and is independent of the external potential responsible for the inhomogeneity, one can conclude that $C^{(1)}\{\mathbf{r};[\rho(\mathbf{r})]\}$ for a general nonuniform system has the same form as Eq. (5). Let us recall that $\rho(\mathbf{r})$ was replaced by $\rho_b g(\mathbf{r})$ for the special inhomogeneity that provided Eqs. (4) and (5). It is then clear that for a general nonuniform system, $g(\mathbf{r})$ in Eq. (5) should be replaced by $\rho(\mathbf{r})/\rho_b$. Consequently, the following form for $C^{(1)}\{\mathbf{r};[\rho(\mathbf{r})]\}$ for a general nonuniform system is obtained:

$$C^{(1)}\{\mathbf{r};[\rho(\mathbf{r})]\}=C_0^{(1)}(\rho_b)+\int d\mathbf{r}_1[\rho(\mathbf{r}_1)-\rho_b] C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b)+B[\gamma(\mathbf{r})]. \tag{6}$$

In Ref. [19], $\gamma(\mathbf{r})$ was substituted by the Ornstein-Zernike (OZ) equation

$$h(r)=C_0^{(2)}(r;p_b)+\rho_b\int d\mathbf{r}_1 h(\mathbf{r}_1)C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b). \tag{7}$$

Thus, one arrives at the following Eq. (8) for $C^{(1)}\{\mathbf{r};[\rho(\mathbf{r})]\}$ for a general nonuniform system

$$C^{(1)}\{\mathbf{r};[\rho(\mathbf{r})]\} =C_0^{(1)}(\rho_b)+\int d\mathbf{r}_1[\rho(\mathbf{r}_1)-\rho_b]C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b) +B\left[\int d\mathbf{r}_1[\rho(\mathbf{r}_1)-\rho_b]C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b)\right]. \tag{8}$$

In Ref. [19], the PY and VM approximation for the hard-sphere bridge function were employed to calculate the density distribution profile of nonuniform hard-sphere fluid, good agreement with computer simulation data was obtained. For other fluids, there does not exist an analytical expression for the bridge functional $B[\gamma(\mathbf{r})]$, so, to apply the same methodology to these fluids, we devise the following numerical recipe.

To obtain the second order DCF, we solve numerically the OZ equation (7) combined with the Rogers-Young (RY) approximation. Now we apply the test particle method [29], i.e., choose a particle (called test particle) from the bulk and make it located at the origin. The interaction potential $u(r)$ between the test particle and other particle in the bulk is regarded as external potential, then, and the resulting density distribution is related to the bulk $g(\mathbf{r})$ by Eq. (3). Substituting Eqs. (8) into Eq. (1), we obtain

$$\rho(r)=\rho_b\exp\left\{-\beta u(r)+\int d\mathbf{r}_1[\rho(\mathbf{r}_1)-\rho_b] \times C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b)+B\left[\int d\mathbf{r}_1[\rho(\mathbf{r}_1)-\rho_b] \times C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho_b)\right]\right\}. \tag{9}$$

A combination of Eqs. (3), (7), (9) leads to the following equation

$$g(\mathbf{r})=\exp\{-\beta u(\mathbf{r})+\gamma(\mathbf{r})+B[\gamma]\}. \tag{10}$$

Equation (10) is actually the equation defining the bridge function B in the IET, but in the present paper it is derived out from the DFT framework combined with the test particle method. From the numerical solution of $g(r)$, γ, and Eq. (10), we can obtain numerically the bridge function as a functional of γ, that is, $B[\gamma]$. The numerically obtained functional relationship $B[\gamma]$ can then be inserted into Eq. (8) to determine the universal $C^{(1)}\{\mathbf{r};[\rho(\mathbf{r})]\}$ for arbitrary external field.

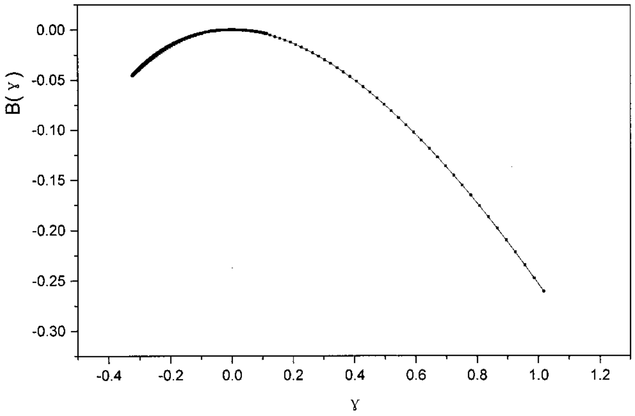

FIG. 1. The curve of B as a function of γ for hard-sphere Yukawa fluids ($\rho_b\sigma^3=0.7$ and $T^*=k_BT/\varepsilon_F=2.0$, $\lambda=1.8$).

Equations (1), (7), (8), (10) constitute the present DFT formalism. The concrete calculation procedure for the density distribution profile is as follows

(1) Solve the OZ equation combined with the RY approximation (with specified bulk parameters) to obtain the radial distribution function g, the second-order DCF $C_0^{(2)}$, and the IDF γ.

(2) Equation (10) is used to obtain numerically the functional relationship $B[\gamma]$, then the obtained functional relationship and the second-order DCF $C_0^{(2)}$ are employed in Eq. (8).

(3) Equation (1) is combined with Eq. (8) to calculate the density distribution profile for the specified bulk parameters and external potential parameters.

In the calculation performed for the specified bulk parameters, we can obtain many points (γ versus $B[\gamma]$) of the function $B[\gamma]$, rearrange these points according to the numerical value of γ from small value to large value, then plot these points into a figure, we can see that it is a smooth curve. When the numerical value of $\int d\mathbf{r}_1[\rho(\mathbf{r}_1)-\rho^b]C_0^{(2)}(|\mathbf{r}-\mathbf{r}_1|;\rho^b)$ for the case of a nonuniform fluid falls into the above numerical range of γ from the IET for the corresponding uniform fluid, we can use the three-point interpolation procedure to specify the functional relationship $B[\gamma]$, when beyond the above numerical range of γ, we can choose three points with appropriate separation at the two ends of the above curve, respectively, then we can also use the three-point interpolation procedure with those six points chosen to specify the part of functional relationship $B[\gamma]$ beyond the two ends of the above curve. As an example, we plot the functional relationship $B[\gamma]$ corresponding to a hard-sphere Yukawa fluid with interaction potential represented by Eq. (11) ($\rho_b\sigma^3=0.7$, $T^*=k_BT/\varepsilon_P=2.0$, and $\lambda=1.8$) and obtained from the RY approximation in Fig. 1.

From Eq. (8), we know that the universal density functional $C^{(1)}$ is related to the second order DCF $C_0^{(2)}$. Thus, for

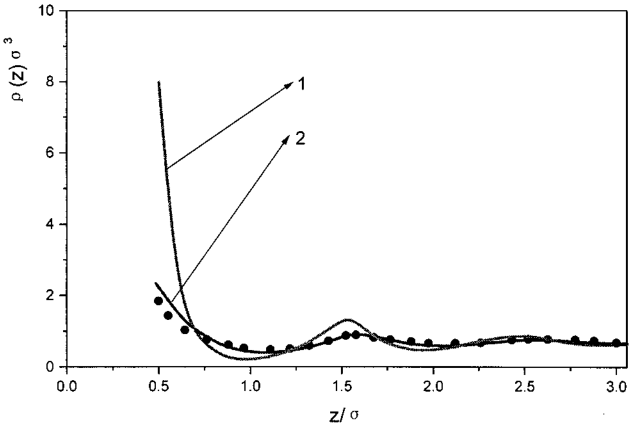

FIG. 2. Density profiles for hard-sphere Yukawa fluids ($\rho_b\sigma^3=0.7$ and $T^*=k_BT/\varepsilon_F=2.0$, $\lambda=1.8$) near a single wall. The curve 1 is for a hard wall with an attractive tail with a ratio $\varepsilon_W/\varepsilon_F=5$, the curve 2 is for a hard wall, the dots are the computer simulation data (Ref. [33]) for the case of curve 2.

different specified bulk parameters, the functional relationship $B[\gamma]$ should be calculated, respectively. In the present paper, we use the RY approximation to obtain the input parameter $C_0^{(2)}$ and $B[\gamma]$, because the OZ equation combined with the RY approximation provides the best agreement with the computer simulation data for the radial distribution function g. To show the accuracy of the present numerical recipe, we calculate the density distribution profile of the nonuniform hard-sphere Yukawa fluid and colloidal suspension.

For the hard-sphere Yukawa fluid, the interaction potential is:

$$\begin{aligned}\beta u(r) &= -\beta\varepsilon_F\sigma\exp[-\lambda(r-\sigma)/\sigma]/r, \quad && r>\sigma\\ &=\propto, && r<\sigma,\end{aligned}\tag{11}$$

where the parameter σ represents the diameter of hard sphere, ε_F the depth of the fluid-fluid interaction potential, and λ the range parameter.

For the case of the hard-sphere Yukawa fluid near a hard wall located at $z=0$, the external potential is:

$$\begin{aligned}\beta\varphi_{ext}(z) &= 0, \quad && z>\sigma/2\\ &=\propto, && z<\sigma/2,\end{aligned}\tag{12}$$

For the case of the hard-sphere Yukawa fluid near a hard wall with an attractive tail located at $z=0$, the external potential is:

$$\begin{aligned}\beta\varphi_{\mathrm{ext}}(z) &= -\beta\varepsilon_w\exp[-\lambda(z-\sigma/2)/\sigma], \quad && z>\sigma/2\\ &=\propto, && z<\sigma/2,\end{aligned}\tag{13}$$

where ε_v is the depth of the fluid-external field interaction potential.

For the case of colloidal suspension, as has been mentioned, the large macroparticles in the colloidal suspension are modeled as highly charged hard spheres of diameter σ and the small ions and solvent are assumed to provide only a charged neutralizing dielectric continuum background of dielectric constant ε, the interaction potential between two charged macroparticles $u(r)$ is represented by the DLVO potential and is given by [31,32]

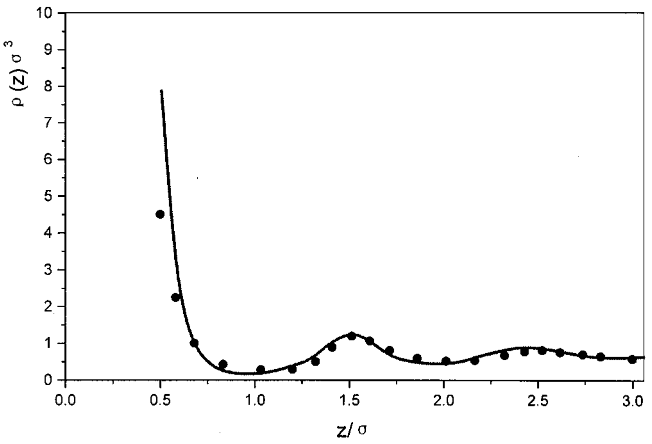

FIG. 3. Density profiles for hard-sphere Yukawa fluids ($\rho_b\sigma^3=0.7$ and $T^*=k_BT/\varepsilon_F=1.25$, $\lambda=1.8$) near a single hard wall with an attractive tail with a ratio $\varepsilon_W/\varepsilon_F=5$, the dots are the computer simulation data (Ref. [33]).

$$\begin{aligned}\beta u(r) &= \gamma\frac{e^{-kx}}{x} \quad && r>\sigma \quad (x>1)\\ &=\propto && r<\sigma \quad (x<1),\end{aligned}\tag{14}$$

where $x=r/\sigma$ with r representing the interparticle distance, in the above equation, γ and $k=\kappa\sigma$ are the Coulomb coupling strength and the inverse screening length, given, respectively, as

$$\gamma=\frac{\beta Z^2e^2}{\varepsilon\sigma(1+\kappa\sigma/2)^2}e^{\kappa\sigma},\tag{15}$$

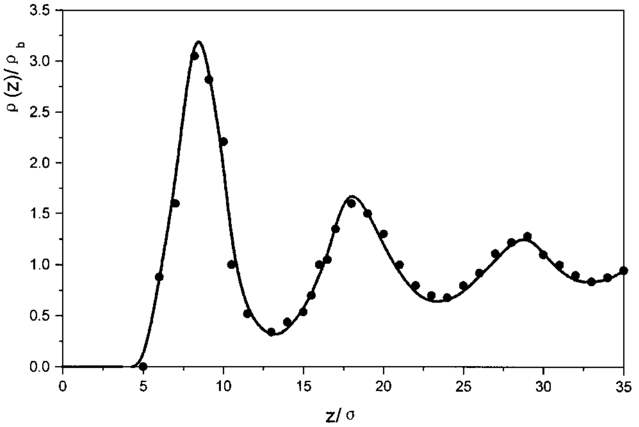

FIG. 4. Density profiles $\rho(z)/\rho_b$ vs z/σ for a model colloidal suspension ($\eta=\rho_b\sigma^3\pi/6=0.00042$ $k=0.15$, $\gamma=580$) near a single charged hard wall with $K_w=200$, the dots are the computer simulation data (Ref. [34]).

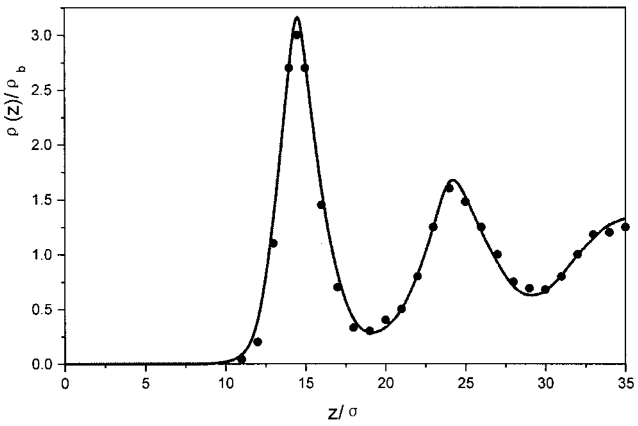

FIG. 5. The same as in Fig. 4, but with $K_w = 500$.

$$\kappa^2 = \frac{4\pi\beta}{\varepsilon}[\rho_b Z e^2 + \Sigma n_\alpha Z_\alpha^2 e^2], \tag{16}$$

where ρ_b is the average bulk density of the macroparticles of charge Ze with e the electronic charge and n_α the number density of the ions of type α with charge $Z_\alpha e$.

For the colloidal suspension in the field of a single charged wall situated in $z = -0.5\sigma$, the external field is given by

$$\Phi_{\mathrm{ext}}(z) = \beta^{-1} K_w \exp(-\kappa Z), \tag{17}$$

where K_w is the depth of the fluid-external field interaction potential.

The above bulk parameters and the external potential parameters are chosen to be in agreement with those resulting in the corresponding simulation data [33,34]. Figures 2–5 show that the predictions from present numerical recipe are in good agreement with the corresponding computer simulation data.

In all of the calculation in the present paper, the OZ equation is solved combined with the RY approximation [28] in which

$$g(r) = \exp[-\beta u(r)]\left\{1 + \frac{\exp[\gamma(r) f(r)] - 1}{f(r)}\right\}, \tag{18}$$

$$f(r) = 1 - \exp(-\alpha r), \tag{19}$$

where α is the adjustable parameter used to achieve thermodynamic consistency.

III. DISCUSSION AND CONCLUDING REMARKS

The WDA version of the DFT, like the present approach, is also a summation of all terms in a perturbative expansion that is exact to second order and has approximate kernels (the higher-order DCFs) at all higher orders by forcing the WDA to reproduce the uniform fluid second-order DCF $C_0^{(2)}$. The difference between the two approaches is in the nature of how the higher-order terms are being approximated. The WDA accomplishes this through a lower-level, and more approximate, assumption on the form of the excess free energy or the first-order DCF of nonuniform fluid and only uses information from $C_0^{(2)}$, the higher-order DCFs$C_0^{(n)}$ $(n \geqslant 3)$ can be obtained by the functional derivative in the WDA, but due to the approximation of $C_0^{(2)}$, the excess free energy and the first-order DCF of uniform fluid, the error accumulation is resulted, so even the $C_0^{(3)}$ obtained in WDA is only qualitatively correct, not to say $C_0^{(n)}$ $(n \geqslant 4)$. Contrary to the WDA, the present formulation is based on the functional perturbative expansion, and the expansion is not truncated, all of the expansion terms are taken into account with the help of the bridge function concept, so the present formulation is exact mathematically, and it provides the possibility to include all of the expansion terms exactly, its approximation results from the approximation in the bridge function in the IET. There are two different main points of the present formulation from the WDA, the first one is that the WDA is a physically intuitive idea, we are willing to use the WDA, because its predictions are in good agreement with the computer simulation data, but presently, there does not exist strict mathematical proof for the WDA, the present formalism is mathematically robust, furthermore, its strict form embodies the physical content of universality. The second one is that the WDA is specified by the second-order DCF $C_0^{(2)}$ of the corresponding bulk fluid only, but the present formulation is specified by both the radial distribution function g and the second order DCF $C_0^{(2)}$ of the corresponding bulk fluid, so more information is incorporated into the present approach.

The present formulation provides a numerical recipe to translate the integral equation theory for uniform fluids to density functional theory for nonuniform fluids. It is a numerical extension of the methodology suggested in Ref. [19], in the present recipe, it is not necessary for the bridge functional to be expressed as a functional of the indirect correlation function analytically, so it greatly extends the applicability of the methodology suggested in Ref. [19], all of the input parameters of the present recipe can be obtained from numerically solving OZ equation, in fact, there are many successful integral equation theories for various uniform fluids, only if the bridge functional of the integral equation theory can be expressed numerically as a function of the indirect correlation function smoothly, then the integral equation theory can be transformed into the density functional theory for nonuniform fluids to calculate the density distribution profile. So, the present numerical version of the methodology suggested in Ref. [19] really builds a bridge from the IET to DFT for many nonuniform fluids. The application of the present recipe to other nonuniform phenomena, especially the most challenging of the nonuniform problems, for example, the freezing transition, will be reported in a forthcoming paper.

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