

Reformulation of density functional theory for generation of the nonuniform density distribution

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The concept of universality of the free energy density functional and the weighted density approximation are combined to provide the density distribution profile of nonuniform fluids from the predictions of integral equation theory for the corresponding uniform fluids. To obtain the expression for the free energy as a function of the density distribution, the present formalism expresses the difference of the first order direct correlation function of a nonuniform fluid with respect to its uniform fluid counterpart as a function of the weighted density, which is also a function of the space position. The input parameters used in the present approach are the radial distribution function and the second order direct correlation function of the corresponding uniform fluid. All of these parameters can be easily obtained from numerical solution of Ornstein-Zernike integral equation theory. The present approach is based on the formalism of classical density functional theory (DFT) and its application to two kinds of fluid under different external potentials is presented. The agreement of the theoretical predictions with the corresponding computer simulation data is good. The present formulation of DFT can treat fluids of different interaction potential under nonzero external fields in a unified way.

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I. INTRODUCTION

An accurate description of the structure and thermodynamics of nonuniform fluids [1,2] is of basic as well as practical importance for its relevance in various phenomena such as selective adsorption from mixtures, solvation forces in fluids, etc. Research on nonuniform fluids has largely involved calculation of the nonuniform density distribution profile of the fluid particles, the most important characteristic of the nonuniform fluid, which results from interaction between the fluid particles and an external field such as a "wall." Although the integral equation theory (IET) method [3], originally devised for uniform fluids, was also extended to be applicable to nonuniform fluids [1], lower accuracy, complexity of the numerical solution and inability to capture the interesting phase transitions such as wetting phenomena limited its application as a standard method in the field of nonuniform fluid statistical thermodynamics.

The main approach for nonuniform fluids is classical density functional theory (DFT), which was introduced into classical statistical mechanics in the early 1960s [4–6]. Classical DFT has its quantum counterpart (quantum DFT), originally devised for the simplified solution of complicated quantum many-body problems [7,8]. After the development of perhaps two dozen versions, classical DFT has evolved into four main types of methodology [9]. One is the functional perturbative expansion approximation [10–12] (PEA) of the nonuniform system's excess free energy around the uniform system in powers of the density deviation between the nonuniform density distribution and the 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. Recently, some studies developed a higher-order expansion approximation by making use of approximate higher-order DCF's [13–15]. Another such version is the so-called weighted density approximation (WDA) and its variants [16–19], which are actually mappings of nonuniform systems onto their 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) of the nonuniform fluid that is approximated by that of the corresponding uniform fluid at a smoothed average density, which is actually a suitable weighted average of the physical density of the system under consideration. The third version of DFT is the fundamental measure theory by Rosenfeld [20,21], which is based on geometrical considerations and specifies the excess free energy by reproducing the Percus-Yevick (PY) equation of state and the second order DCF of the hard sphere fluid. The fourth version [22–24] proposed recently, resulted from the use of the concept of the universality of the free energy density functional and collected all orders beyond the second of the functional perturbative expansion in the form of a bridge functional. A characteristic of the original WDA is that the weighted density and weighting function are coupled together. This fact requires iterative calculation, and thus tremendous computer time is required. This shortcoming becomes very obvious when methods of the WDA type are extended to the case of mixtures [25–27]. 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 non-hard-sphere interaction potential fluids; thus, to treat the non-hard-sphere interaction potential system under nonzero external field, a perturbative method has to be employed, an intensive computational task. On the other hand, the PEA version of DFT requires high-order DCF's beyond the second of the uniform system as

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input. However, accurate expressions for these higher-order DCFs are usually not available. The suggested methodology in Ref. [22] requires only the second order DCF and the bridge functional of the uniform system as inputs and these inputs can be easily obtained from Ornstein-Zernike integral equation theory for the corresponding uniform system, so this methodology should be easy to use for various nonuniform fluids.

A necessary condition specified in Ref. [22] for the methodology to be used is that the form of the bridge functional must be one that expresses it as a functional of the indirect correlation function γ . γ is then substituted by a combination of the Ornstein-Zernike equation for the uniform system and the Percus identity [Eq. (8) below]. But in most cases the bridge functional in IET cannot be expressed as a functional of the indirect correlation function analytically; an approximation is needed; for example, the hypernetted chain approximation [3], the mean spherical approximation [3], the Rogers-Young (RY) approximation [28], etc. Thus, the necessary condition limits the application of the methodology to nonuniform hard sphere fluids only. The condition comes from the requirement that theoretical predictions should not be dependent on the choice of origin of the coordinate system and cannot be removed.

To widen the applicability of the methodology proposed in Ref. [22], a numerical version of it was presented [29], but this numerical version is still not applicable to some fluids, such as Lennard-Jones fluids, where the bridge functional in the IET cannot be expressed as a functional of the indirect correlation function even numerically and with a single value. To apply the methodology based on the universality of the free energy density functional to various fluids in principle and overcome the shortcomings of previous versions of DFT, we reformulate the classical DFT also by using the universality of the free energy density functional, but the present formulation avoids the use of the bridge functional concept. Instead, it uses the concept of the weighted density to incorporate the functional dependence of the free energy on space position, but the input parameters include only the radial distribution function and the second order direct correlation function of the corresponding uniform fluids.

The plan of the present paper is as follows. In Sec. II, we describe the present reformulation of classical DFT in detail. In Sec. III, we apply the reformulation to several examples of nonuniform fluids to predict the density distribution and compare the predictions with corresponding computer simulation data to show the validity and accuracy of the present procedure. In Sec. IV, there is some discussion and concluding remarks about the essential points of the present DFT methodology.

II. REFORMULATION OF THE CLASSICAL DFT BASED ON THE UNIVERSALITY OF THE FREE ENERGY DENSITY FUNCTIONAL AND THE CONCEPT OF WEIGHTED DENSITY

We consider a many-particle system (pure component) at fixed temperature $kT = \beta^{-1}$ and chemical potential μ under the influence of an external potential $\varphi_{\text{ext}}(\mathbf{r})$. The grand po-

tential Ω_{min} of a system in thermal equilibrium is obtained by the basic variational principle [30]

$$\Omega_{\text{min}} = \min \Omega[\rho], \quad (1)$$

where $\rho(\mathbf{r})$ is the single particle density distribution. The grand potential functional $\Omega[\rho]$ is expressed as

$$\Omega[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r})[\varphi(\mathbf{r}) - \mu]. \quad (2)$$

The Helmholtz free energy functional $F[\rho]$ may be divided into two independent parts: an ideal gas part $F_{\text{id}}[\rho]$ which is exactly known and is given as

$$F_{\text{id}}[\rho] = \beta^{-1} \int d\mathbf{r} \rho(\mathbf{r}) \{ \ln[\rho(\mathbf{r})\lambda^3] - 1 \} \quad (3)$$

where λ is the thermal de Broglie wavelength, and an excess part $F_{\text{ex}}[\rho]$ which is not exactly known, but serves to generate the hierarchy of direct correlation functions

$$C^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n; [\rho]) = -\beta \delta^n F_{\text{ex}}[\rho] / \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2) \dots \delta\rho(\mathbf{r}_n). \quad (4)$$

The equilibrium density profile of a nonuniform system is obtained by the Euler-Lagrange equation resulting from the variational principle Eq. (1):

$$\mu = \varphi_{\text{ext}}(\mathbf{r}) + \delta F_{\text{id}}[\rho] / \delta\rho(\mathbf{r}) + \delta F_{\text{ex}}[\rho] / \delta\rho(\mathbf{r}). \quad (5)$$

For the case of the grand canonical ensemble we consider here, the chemical potential of the nonuniform fluid is equal to that of the bulk fluid [where $\varphi_{\text{ext}}(\mathbf{r}) = 0$ and $\rho(\mathbf{r}) = \rho_b$]. This leads to the density profile equation

$$\rho(\mathbf{r}) = \rho_b \exp\{-\beta\varphi_{\text{ext}}(\mathbf{r}) + C^{(1)}(\mathbf{r}; [\rho(\mathbf{r})]) - C_0^{(1)}(\rho_b)\}, \quad (6)$$

where $C_0^{(n)}$ is the uniform fluid counterpart of $C^{(n)}$. Now we choose a particle situated at the origin of the bulk fluid by following the test particle method due to Percus [31]. For this special type of inhomogeneity when the external potential $\varphi_{\text{ext}}(\mathbf{r})$ is equal to the interaction potential between particles $u(\mathbf{r})$,

$$\varphi_{\text{ext}}(\mathbf{r}) = u(\mathbf{r}), \quad (7)$$

the single particle density function is given by

$$\rho(\mathbf{r}) = \rho_b g(\mathbf{r}), \quad (8)$$

where $g(\mathbf{r})$ is the radial distribution function of the corresponding bulk fluid. Substituting Eqs. (7) and (8) into Eq. (6) leads to

$$g(\mathbf{r}) = \exp\{-\beta u(\mathbf{r}) + C^{(1)}(\mathbf{r}; [g(\mathbf{r})\rho_b]) - C_0^{(1)}(\rho_b)\} \quad (9)$$

for a specified uniform fluid. The radial distribution function $g(\mathbf{r})$ can be obtained from the IET for uniform fluids, which is a combination of the Ornstein-Zernike (OZ) equation

$$h(\mathbf{r}) = C_0^{(2)}(\mathbf{r}; \rho_b) + \rho_b \int d\mathbf{r}_1 h(\mathbf{r}_1) C_0^{(2)}(\mathbf{r}, \mathbf{r}_1; \rho_b) \quad (10)$$

and a closure equation relating the correlation functions with the bridge functional $B(\mathbf{r})$,

$$g(\mathbf{r}) = \exp\{-\beta u(\mathbf{r}) + h(\mathbf{r}) - C_0^{(2)}(\mathbf{r}; \rho_b) + B(\mathbf{r})\}. \quad (11)$$

Each version of the IET corresponds to a definition for the bridge functional. Because $F_{\text{ex}}[\rho]$ and thus $C^{(1)}(\mathbf{r}; [\rho(\mathbf{r})])$, its functional derivative with respect to $\rho(\mathbf{r})$, is, for a given interaction potential, a universal functional [32] of the density distribution $\rho(\mathbf{r})$ and is independent of the external potential responsible for the generation of the density distribution $\rho(\mathbf{r})$, we can specify the functional form of $C^{(1)}(\mathbf{r}; [\rho(\mathbf{r})])$ from the specific case where the external potential is the interaction potential between a particle situated at the origin and the bulk particles. To do so, we first define a weighted density $\bar{\rho}(\mathbf{r})$ according to the second order direct correlation function

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' f C_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b) \rho(\mathbf{r}'), \quad (12)$$

where the coefficient f can be specified by the normalization condition

$$\rho_b = \int d\mathbf{r}' f C_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b) \rho_b. \quad (13)$$

Thus

$$f = 1 \left/ \int d\mathbf{r}' C_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b) \right. \quad (14)$$

Following the sum rule derived from the uniform fluid limit of Eq. (4),

$$\int d\mathbf{r}' C_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b) = C_0^{(1)'}(\rho_b), \quad (15)$$

we obtain

$$f = 1/C_0^{(1)'}(\rho_b), \quad (16)$$

where $C_0^{(1)'}(\rho_b)$ is the derivative of the first order DCF of the uniform fluid with respect to the argument ρ_b .

From Eqs. (12) and (16), we obtain

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') C_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b) / C_0^{(1)'}(\rho_b). \quad (17)$$

If we define

$$w(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_b) = \frac{C_0^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_b)}{C_0^{(1)'}(\rho_b)} \quad (18)$$

then Eq. (17) reduces to

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|; \rho_b). \quad (19)$$

Equation (19) is actually equivalent to the simple weighted density approximation (SWDA) [33]. Now we define the functional $C^{(1)}(\mathbf{r}; [\rho(\mathbf{r})])$ as a function of the weighted density $\bar{\rho}(\mathbf{r})$ denoted as $G(\bar{\rho}(\mathbf{r}))$, that is,

$$C^{(1)}(\mathbf{r}; [\rho(\mathbf{r})]) = G(\bar{\rho}(\mathbf{r})). \quad (20)$$

The form of the function G is determined as follows. Substituting Eq. (20) into Eq. (6) and employing Eqs. (7) and (8) lead to

$$g(\mathbf{r}) = \exp\{-\beta u(\mathbf{r}) + G(\bar{\rho}(\mathbf{r})) - C_0^{(1)}(\rho_b)\}. \quad (21)$$

From the numerical solution of the OZ equation (10), we can get the radial distribution function $g(\mathbf{r})$, which can be combined with Eqs. (8) and (17) to calculate the weighted density $\bar{\rho}(\mathbf{r})$. Then the weighted density obtained is substituted into Eq. (21) to arrive at the following equation:

$$\begin{aligned} C^{(1)}(\mathbf{r}; [\rho(\mathbf{r})]) - C_0^{(1)}(\rho_b) &= G(\bar{\rho}(\mathbf{r})) - C_0^{(1)}(\rho_b) \\ &= \ln[g(\mathbf{r})] + \beta u(\mathbf{r}). \end{aligned} \quad (22)$$

For a specified uniform fluid with specific interaction potential $u(\mathbf{r})$ and bulk density ρ_b , we can calculate the weighted density $\bar{\rho}(\mathbf{r})$ at different space points. From Eq. (22), we can get the form of the function G , that is, the functional form of $C^{(1)}(\mathbf{r}; [\rho(\mathbf{r})])$ with respect to the density distribution function $\rho(\mathbf{r})$. The universality of the functional form of $C^{(1)}(\mathbf{r}; [\rho(\mathbf{r})])$ enables us to substitute Eq. (22) into Eq. (6) to obtain the nonuniform fluid density distribution $\rho(\mathbf{r})$ under an arbitrary external potential $\varphi_{\text{ext}}(\mathbf{r})$.

It should be noted that the profile of the radial distribution function $g(\mathbf{r})$ oscillates, so it is possible that at some space points, for example, \mathbf{r}_1 and \mathbf{r}_2 , the calculated weighted density has the same value but $g(\mathbf{r}_1)$ and $g(\mathbf{r}_2)$ are different, so G becomes a many-valued function of $\bar{\rho}(\mathbf{r})$ at some points of $\bar{\rho}(\mathbf{r})$. This is surely the case for the present example of a hard sphere fluid and a Lennard-Jones fluid. For these cases, we chose the space points of the radial distribution function profile $g(\mathbf{r})$ for which the calculated weighted density is near and below the bulk density. The calculated weighted density is then exactly in the numerical range needed for the iterative solution of Eq. (6). Then a smooth curve, as shown in Fig. 7 below for the case of the Lennard-Jones fluid state point $\rho_b \sigma^3 = 0.75$, $kT/\epsilon = 1.304$, can be obtained. We can use a three-point interpolation procedure with three points obtained as above as inputs to specify the functional relationship $G[\rho(\mathbf{r})]$ for the iterative solution of Eq. (6) for a nonuniform density distribution with any external potential. The weighted density is an average of the actual density distribution and the weighting function has a smoothing effect on the oscillatory density profile. Thus, by choosing a good initial value, for example, the predictions of second order perturbative DFT or the SWDA, for the iterative solution of Eq. (6), we can expect that the calculated weighted densities from the density distribution profile of Eq. (6) will fall into the required numerical range even if the external potential is so

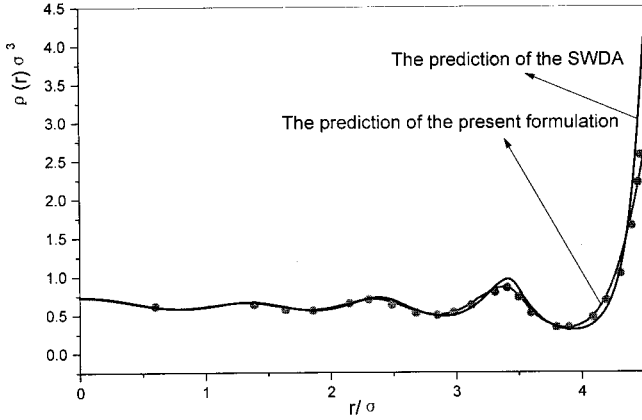


FIG. 1. Density profiles of a hard sphere fluid ($\rho_b\sigma^3=0.62$) confined in a spherical cavity with a hard wall $R=4.5\sigma$. The lines correspond to the predictions of the theory and the points to the corresponding computer simulation data [35].

large that strong oscillation of the density distribution profile results. This is surely the case for the figures presented below.

III. NUMERICAL SOLUTION AND COMPARISON WITH COMPUTER SIMULATION RESULTS

First, we apply the above formulation of DFT to two cases: (1) a hard sphere fluid confined in a spherical cavity with a hard wall of radius, R , and (2) a hard sphere fluid near a hard wall. For case (1), the external potential $\varphi_{\text{ext}}(\mathbf{r})$ responsible for the generation of the density distribution $\rho(\mathbf{r})$ has the form

$$\varphi_{\text{ext}}(\mathbf{r}) = \begin{cases} \infty, & |\mathbf{r}|/\sigma > R \\ 0, & |\mathbf{r}|/\sigma < R, \end{cases} \quad (23)$$

and for case (2)

$$\varphi_{\text{ext}}(z) = \begin{cases} \infty, & z/\sigma < 0.5 \\ 0, & 0.5 < z/\sigma. \end{cases} \quad (24)$$

To proceed numerically, the second order DCF of the uniform hard sphere fluid is needed. In the present paper, the PY result [34] is employed. To solve the OZ equation for $g(\mathbf{r})$, the RY approximation [28] is employed because it provides the most accurate data for $g(\mathbf{r})$. A numerically iterative and self-consistent procedure is employed to solve the nonlinear integral equation (6). $\rho(\mathbf{r}) = \rho_b$ is chosen as initial value for solution of the SDWA version of DFT, and the predictions of the SWDA version are used as initial values for solution of the present reformulation of DFT.

In Figs. 1 and 2, the predictions of the present formulation are plotted with the predictions of the SWDA and the corresponding computer simulation data [35] for case (1). It is shown that the accuracy of the present formulation is far superior to that of the SWDA, and the present predictions coincide with the corresponding computer simulation data almost point by point. I also compared the predictions of the present formulation with those of the most accurate DFTs

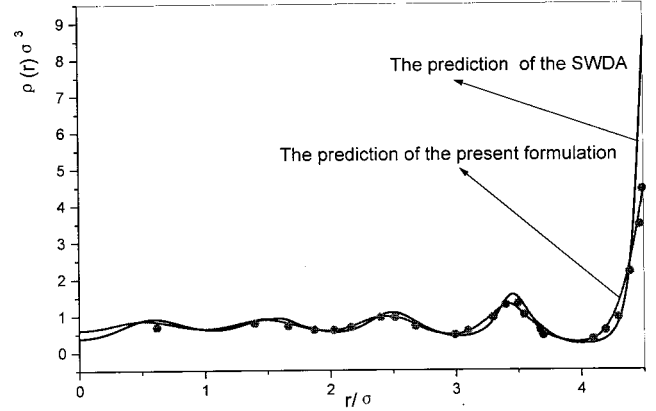


FIG. 2. As in Fig. 1 but $\rho_b\sigma^3=0.75$.

[22,36] in the literature and found that the present predictions are superior. To make the figures clear, the predictions of these two DFTs are not plotted in the same figures. We also compare the predictions of the present reformulation based on the RY and PY approximations for the radial distribution function $g(\mathbf{r})$. It was found that the results based on the RY approximation are superior to those based on the PY approximation. It is well known that the PY approximation is less accurate than the RY approximation for prediction of the RDF of the bulk fluid. This fact indicates further the importance of incorporation of knowledge of the bulk fluid radial distribution function $g(\mathbf{r})$ into the DFT approximation.

In Figs. 3 and 4, we compare the predictions of the present formulation of DFT with the corresponding computer simulation data [37] for case (2). The agreement is also good.

To further test the present formulation, we apply it to an additional case: a Lennard-Jones fluid confined between two hard walls at separation H . For this case, the external potential has the form

$$\varphi_{\text{ext}}(z) = \begin{cases} \infty, & z/\sigma < 0.5 \text{ and/or } z/\sigma > H + 0.5 \\ 0, & 0.5 < z/\sigma < H + 0.5. \end{cases} \quad (25)$$

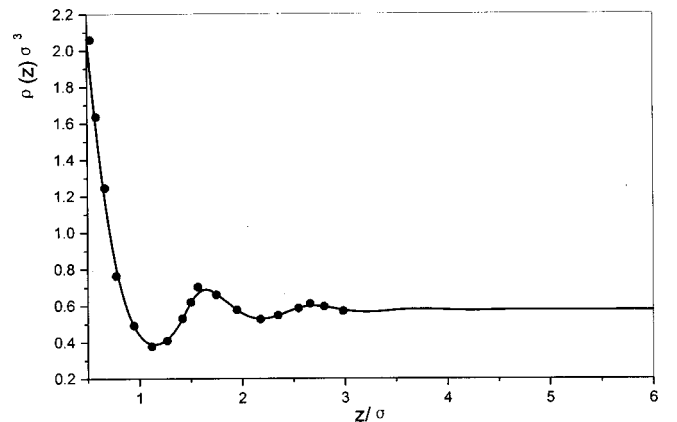
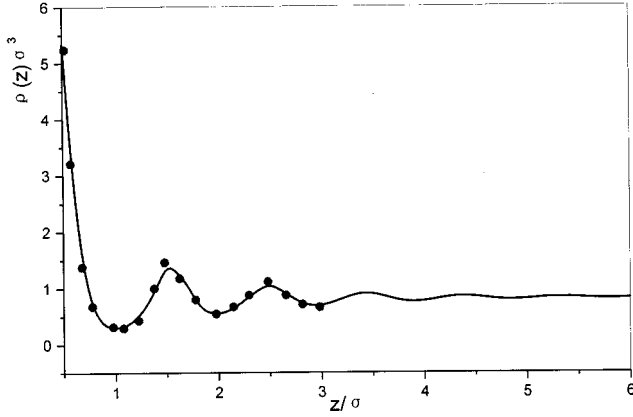


FIG. 3. Density profiles of a hard sphere fluid ($\rho_b\sigma^3=0.575$) near a hard wall. The line corresponds to the predictions of the present formulation and the points to the corresponding computer simulation data [37].


 FIG. 4. As in Fig. 3 but $\rho_b\sigma^3=0.813$.

To proceed computationally, the quantities $C_0^{(2)}(r;\rho_b)$ and $g(r)$ are needed. In the present paper, they are obtained by solving numerically the OZ equation (10) and the closing equation (11). To proceed numerically with Eqs. (10) and (11), we use the thermodynamically self-consistent Rogers-Young approximation [28]. For the Lennard-Jones fluid, the interaction potential $u(r)$ has the form

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (26)$$

where σ and ϵ characterize the interaction range and strength, respectively.

The density profile equation (6) is plotted and compared with the corresponding computer simulation results [38] in Figs. 5 and 6 for $H/\sigma = 12$ and 4, respectively. In Figs. 5 and 6, the bulk parameters are $\rho_b\sigma^3 = 0.75$ and $kT/\epsilon = 1.304$. We plotted the functional relationship of $C^{(1)}(\mathbf{r};[\rho(\mathbf{r})]) - C_0^{(1)}(\rho_b)$ as a function of the weighted density $\bar{\rho}(\mathbf{r})$, which is also a function of space position, in Fig. 7. We used the result of second order perturbative DFT as the initial value for the iterative solution of the present version of DFT. One can see that the predictions of the present method for this

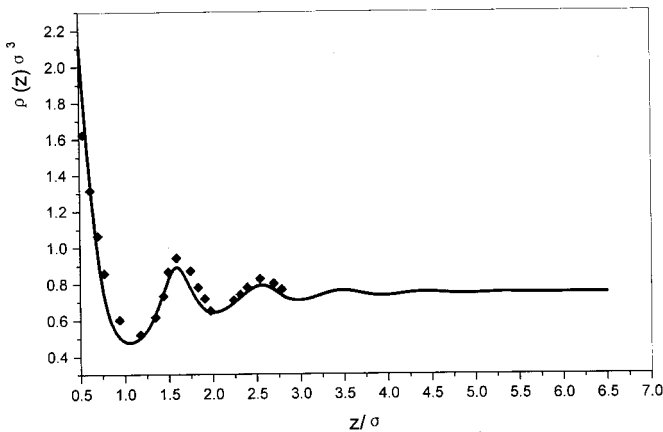
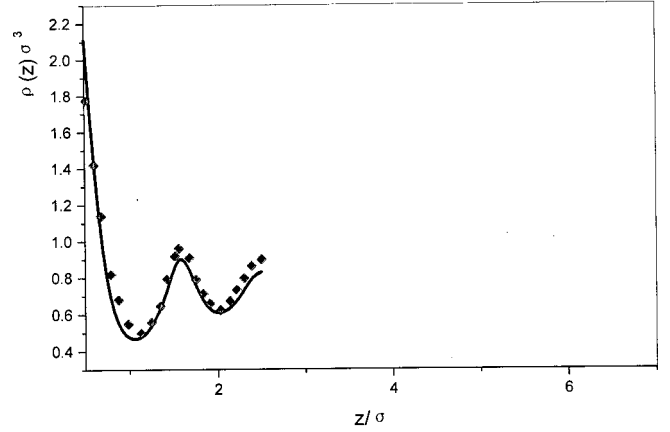


FIG. 5. Density profiles of a Lennard-Jones fluid ($\rho_b\sigma^3=0.75$, $kT/\epsilon=1.304$) confined between two hard walls with $H/\sigma=12$. The dots represent the corresponding Monte Carlo results [38]. Only half the slit is shown.


 FIG. 6. As in Fig. 5 but with $H/\sigma=4$.

case are also in good agreement with the computer simulation results. This fact shows further not only the validity of the present reformulation of DFT for fluids of various interaction potential, but also that it is not necessary to employ a computationally intensive perturbative method for long range potential fluids. With an accurate numerical solution of the OZ equation, nonuniform long range potential fluids can be studied in the present formalism of DFT in the same manner as nonuniform hard sphere fluids.

IV. CONCLUDING REMARKS

The present version of DFT is based on the universality of the free energy density functional $F_{\text{ex}}[\rho]$ and hence of its functional derivative $-\beta\delta F_{\text{ex}}[\rho]/\delta\rho(\mathbf{r})$, the quantity that is required to produce the density distribution of nonuniform fluids. The universality means that its mathematical form is independent of the particular external field, so we can obtain its universal form from some specific external field. In the present paper, the interaction potential of bulk fluid particles

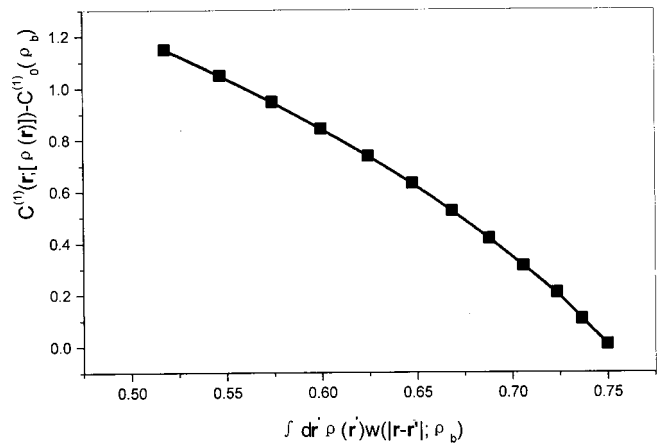


FIG. 7. The difference between the first order direct correlation function of a nonuniform fluid $C^{(1)}(\mathbf{r};[\rho(\mathbf{r})])$ and its uniform fluid counterpart $C_0^{(1)}(\rho_b)$ as a function of the weighted density $\int d\mathbf{r}' \rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|;\rho_b)$. The curve corresponds to the bulk parameters $\rho_b\sigma^3=0.75$ and $kT/\epsilon=1.304$.

is chosen as this external field. Then, by the test particle method, we relate the nonuniform fluid under the special external field to the corresponding bulk fluid. The knowledge of the bulk fluid can easily be obtained from integral equation theory, so we can obtain knowledge of nonuniform fluids from the predictions of integral equation theory for the corresponding uniform fluids by the present formulation of DFT. Previous studies on classical DFT employed knowledge of only the second order direct correlation function of bulk fluids, but structural information of the radial distribution function of bulk fluids was not used. The present paper provides a systematic procedure to incorporate effectively knowledge of the structure of the radial distribution function of bulk fluids into the DFT. Obviously, the accuracy of the present formulation of DFT is strongly dependent on the accuracy of the radial distribution function of the bulk fluid.

Compared with other versions of DFT, the most notable advantage of the present one is that it requires only the radial distribution function $g(\mathbf{r})$ and the second order direct corre-

lation function $C_0^{(2)}(\mathbf{r}, \mathbf{r}_1; \rho_b)$ of the bulk fluid as input. They can be obtained easily from numerical solution of the OZ equation. Another related advantage is that nonuniform fluids with different interaction potentials can be treated in a unified way, and it is not necessary to resort to the computationally complicated perturbative method for long range potential fluids.

With regard to its application to phase transitions, we only discuss the problem in general. The present reformulation of DFT differs from previous versions only by incorporating the radial distribution function of the homogeneous fluid, which previous versions did not do. However, the radial distribution function and the DCF of a homogeneous fluid are coupled together by the OZ equation and are two parallel concepts, so the present reformulation can do all the things that previous versions can do. Our formalism should work well for the transition problems for which previous versions of DFT work.

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- [1] *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Marcel Dekker, New York, 1992).
- [2] R. F. Cracknell, K. E. Gubbins, M. Maddox, and D. Nicholson, *Acc. Chem. Res.* **28**, 281 (1995).
- [3] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1986).
- [4] J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 116 (1963).
- [5] F. H. Stillinger and F. P. Buff, *J. Chem. Phys.* **37**, 1 (1962).
- [6] D. Mermin, *Phys. Rev. A* **137**, A1441 (1965).
- [7] P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, B864 (1964).
- [8] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [9] *Chemical Application of Density Functional Theory*, edited by B. B. Laird, R. B. Ross, and T. Ziegler (American Chemical Society, Washington, DC, 1996).
- [10] T. V. Ramakrishnan and M. Yussouff, *Phys. Rev. B* **19**, 2775 (1979).
- [11] G. Rickayzen and A. Augousti, *Mol. Phys.* **52**, 1355 (1984).
- [12] M. Calleja, A. N. North, J. G. Powels, and G. Rickayzen, *Mol. Phys.* **73**, 973 (1991).
- [13] J. H. Yi and S. C. Kim, *J. Chem. Phys.* **107**, 8147 (1997).
- [14] T. H. Yoon and S. C. Kim, *Phys. Rev. E* **58**, 4541 (1998).
- [15] S. Zhou and E. Ruckenstein, *Phys. Rev. E* **61**, 2704 (2000).
- [16] P. Tarazona, *Phys. Rev. A* **31**, 2672 (1985).
- [17] A. R. Denton and N. W. Ashcroft, *Phys. Rev. A* **39**, 426 (1989).
- [18] A. R. Denton and N. W. Ashcroft, *Phys. Rev. A* **39**, 4701 (1989).
- [19] R. L. Davidchack and B. B. Laird, *Phys. Rev. E* **60**, 3417 (1999).
- [20] Y. Rosenfeld, *Phys. Rev. Lett.* **63**, 980 (1989).
- [21] Y. Rosenfeld, *Phys. Rev. E* **50**, R3318 (1994).
- [22] S. Zhou, *J. Chem. Phys.* **112**, 8079 (2000).
- [23] S. Zhou, *Eur. Phys. J. E* **3**, 343 (2000).
- [24] S. Zhou, *J. Chem. Phys.* **113**, 8719 (2000).
- [25] S. J. Smithline and A. D. J. Haymet, *J. Chem. Phys.* **86**, 6486 (1987).
- [26] A. R. Denton and N. W. Ashcroft, *Phys. Rev. A* **44**, 8242 (1991).
- [27] C. N. Patra and S. K. Ghosh, *J. Chem. Phys.* **100**, 5219 (1994).
- [28] F. J. Rogers and D. A. Young, *Phys. Rev. A* **30**, 999 (1984).
- [29] S. Zhou, *Phys. Rev. E* **63**, 051203 (2001).
- [30] R. Evans, *Adv. Phys.* **28**, 143 (1979).
- [31] J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and A. L. Lebowitz (Benjamin, New York, 1964), p. 113.
- [32] J. T. Chayes and L. Chayes, *Commun. Math. Phys.* **93**, 57 (1984).
- [33] S. Zhou, *J. Chem. Phys.* **110**, 2140 (1999).
- [34] E. Thiele, *J. Chem. Phys.* **39**, 474 (1963); M. S. Wertheim, *Phys. Rev. Lett.* **19**, 321 (1963).
- [35] M. Calleja, A. N. North, J. G. Powels, and G. Rickayzen, *Mol. Phys.* **73**, 973 (1991).
- [36] S. C. Kim and S. H. Suh, *J. Chem. Phys.* **104**, 7233 (1996).
- [37] R. D. Groot, N. M. Faber, and J. P. Van der Eerden, *Mol. Phys.* **62**, 861 (1987).
- [38] J. G. Powles, G. Rickayzen, and M. L. Williams, *Mol. Phys.* **64**, 33 (1988).