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Universality principle and the development of classical density functional theory*

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The universality principle of the free energy density functional and the 'test particle' trick by Percus are combined to construct the approximate free energy density functional or its functional derivative. Information about the bulk fluid radial distribution function is integrated into the density functional approximation directly for the first time in the present methodology. The physical foundation of the present methodology also applies to the quantum density functional theory.

Keywords: density functional theory, free energy density functional
PACC: 6430, 6250, 6390

1. Introduction

A macroscopic matter system is composed of an enormous number of particles, for example, molecules. We call this a many-body problem. The particles interact with one another by inter-particle forces which are governed by classical mechanics or quantum mechanics. The description of the gross physical and chemical properties of a many-body system, from the microscopic inter-particle interaction forces, has been an important subject of physics during the last two centuries, and will continue to be in this century. The solution to this problem is to be found in statistical mechanics which offers a prescription for averaging the inter-particle interaction forces to obtain values for the macroscopically measurable quantities. So methods of the statistical mechanics theory are applicable to the study of properties of macroscopic matter systems. Some of the examples are listed as follows: solutions (including complex charged colloids, electrolytes, biological fluids, polyelectrolyte solutions), phase transition, plasmas, liquid crystals and solids, etc. In each of the fields, the phenomena can be divided into two types. The first is uniform phenomena in which the density distribution $\rho(\boldsymbol{r})$ ($\boldsymbol{r}$ denotes space position) of the particles is uniform, thus $\rho(\boldsymbol{r})$=const. Generally speaking, there is no external potential acting on the particles of a matter system; the bulk solution is one of the examples of this type. The other is non-uniform phenomena in which $\rho(\boldsymbol{r})$ varies with the space positions and, generally speaking, there is an external potential acting on the particles; one of the examples of this type is the well-known electrical double layer. The main and basic approach for non-uniform phenomena is the density functional theory (DFT), the classical version of which was introduced into the classical statistical mechanics around 1963.[1−3] The classical DFT has its quantum counterpart (quantum DFT), originally devised for the simplified solution of the complicated quantum many-body problem.[4,5]

After several decades of development, the DFT (both classical and quantum) has evolved into a powerful theoretical tool for the calculation of uniform as well as non-uniform phenomena in many fields with reliability and without excessive computation. It can be employed to calculate the electronic structure[6] of atoms, molecules and solids to construct the theories of high-temperature superconductivity[7] and semiconductivity.[8] Also, it has been applied successfully to the freezing of a variety of classical liquids;[9] or even liquids (helium) with a significant quantum characteristic.[10,11] It can explain the phase behaviours of solutions containing macromolecules, from food colloids to DNA,[12,13] to reveal the ori-

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gin of the attractive interaction between like-charge colloids,[14−16] to describe the adsorption of a polyelectrolyte on a charged surface or binding to ionic surfactant, which is a very common case in molecular biology and a very good model for the process of delivering genes into cells.[17,18] Finally, it also finds widespread application in wetting transition, capillary condensation, liquid crystals, catalysis, the process of nucleation and crystal growth, separation of mixtures and many other interfacial phenomena.[19] We may expect that, with the development of the uniform polymer fluid integral equation theory (IET), the DFT will be extended for calculation of the bio-macromolecular configuration and protein folding thermodynamics.[20] Thus, a new development in DFT methodology could give a great push to all the studies in the abovementioned practical fields, as well as the basic research of statistical mechanics.

In this paper, we report on a methodology with which the calculation in classical DFT can be simplified, the accuracy of prediction can be improved, with only a minimum of input parameters needed, and various fluids with different interaction potentials can be treated in a unified way. Especially, all of the input parameters of this methodology can be obtained from the IET for a uniform fluid, which has been the most efficient theoretical tool for structural and thermodynamical calculations in statistical mechanics since its inception in 1914.[21] So, the present methodology really builds a bridge from the IET for uniform phenomena to DFT for non-uniform phenomena. Our discussion is largely based on the classical DFT, but its physical foundation also applies to the quantum DFT (discussed at the end of the paper). To begin our discussion, we simply review some basic terminologies and recent progresses in the classical DFT.

2. The methodology

From the point of view of statistical thermodynamics, the structural and thermodynamical properties of a many-body system are determined by the excess Helmholtz free energy $F_{\rm ex}$ of the system, which is an important component of the system grand potential Ω. In the DFT, $\rho(\boldsymbol{r})$ is chosen as the basic variable, and Ω is expressed as a functional of $\rho(\boldsymbol{r})$. Then, all the properties of the system in thermal equilibrium are obtained from the grand potential $\Omega_{\rm min}$ of the thermal equilibrium system resulting from the basic variational principle[22]

$$\Omega_{\rm min} = \min\Omega[\rho]. \tag{1}$$

The functional $\Omega[\rho]$ is expressed as

$$\Omega[\rho] = F[\rho] + \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r})[\varphi_{\rm ext}(\boldsymbol{r}) - \mu], \tag{2}$$

where μ denotes the chemical potential, and $\varphi_{\rm ext}(\boldsymbol{r})$ denotes the external potential acting on the particles.

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

$$F_{\rm id}[\rho] = \beta^{-1}\int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r})\{\ln[\rho(\boldsymbol{r})\lambda^3] - 1\}, \tag{3}$$

where λ is the thermal de Broglie wavelength, and $kT = \beta^{-1}$ is the temperature. The other is an excess part $F_{\rm ex}[\rho]$ which is not exactly known, but serves to generate the hierarchy of the direct correlation functions (DCFs) of non-uniform fluids

$$\begin{aligned} &C^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n; [\rho]) \\ &= -\beta\delta^n F_{\rm ex}[\rho]/\delta\rho(\boldsymbol{r}_1)\delta\rho(\boldsymbol{r}_2)\cdots\delta\rho(\boldsymbol{r}_n), \end{aligned} \tag{4}$$

where $\rho(\boldsymbol{r})$ is obtained by the Euler–Lagrange equation resulting from the variational principle Eq.(1)

$$\mu = \varphi_{\rm ext}(\boldsymbol{r}) + \delta F_{\rm id}[\rho]/\delta\rho(\boldsymbol{r}) + \delta F_{\rm ex}[\rho]/\delta\rho(\boldsymbol{r}). \tag{5}$$

For the case of the grand canonical ensemble considered by the DFT, μ of a non-uniform fluid is equal to that of the bulk fluid (where $\varphi_{\rm ext}(\boldsymbol{r})$=0 and $\rho(\boldsymbol{r}) = \rho_{\rm b}$). This leads to the density profile equation

$$\begin{aligned} \rho(\boldsymbol{r}) =& \rho_{\rm b}\exp\{-\beta\varphi_{\rm ext}(\boldsymbol{r}) \\ &+ C^{(1)}(\boldsymbol{r}; [\rho(\boldsymbol{r})]) - C_0^{(1)}(\rho_{\rm b})\}, \end{aligned} \tag{6}$$

where $C_0^{(n)}$ is the uniform fluid counterpart of $C^{(n)}$.

All statistical mechanics theories include approximations. In the DFT, the approximation can be made at two levels, depending on the calculated quantities. If one wants to predict the phase behaviour of a fluid in confined geometry or freezing points of liquid–solid, etc, the approximations are generally made at the level of $F_{\rm ex}[\rho]$. The earliest proposed approximation is the functional perturbative expansion approximation (FPEA) around the bulk fluid with bulk density $\rho_{\rm b}$ truncated at the second order[9]

$$\begin{aligned} F_{\rm ex}[\rho] =& \beta F_{\rm ex}(\rho_{\rm b}) - \sum_{n=1}^{\infty}\frac{1}{n!}\int {\rm d}\boldsymbol{r}_1\cdots\int {\rm d}\boldsymbol{r}_n \\ &\times C_0^{(n)}(\boldsymbol{r}_1\cdots, r_n; \rho_{\rm b})\nabla\rho(\boldsymbol{r}_1)\cdots\rho(\boldsymbol{r}_n), \end{aligned} \tag{7}$$

where $\nabla\rho(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \rho_{\rm b}$. Recently, some high-order FPEAs have been proposed (see Refs.[23]–[27] and references therein). Obviously, in the FPEA, $\beta F_{\rm ex}(\rho_{\rm b})$, $C_0^{(n)}$ are the input parameters. Generally, the uniform fluid second-order DCF $C_0^{(2)}$ can be obtained from the Ornstein–Zernike (OZ) integral equation[21,28]

$$h(r) = C_0^{(2)}(r;\rho_{\rm b}) + \rho_{\rm b}\int {\rm d}\boldsymbol{r}_1 h(\boldsymbol{r}_1)C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_{\rm b}), \tag{8}$$

combined with a closure equation relating the correlation functions with the bridge function $B(\boldsymbol{r})$

$$g(\boldsymbol{r}) = \exp\{-\beta u(\boldsymbol{r}) + h(\boldsymbol{r}) - C_0^{(2)}(\boldsymbol{r};\rho_{\rm b}) + B(\boldsymbol{r})\}, \tag{9}$$

where $h = g - 1$ is the bulk fluid total correlation function, and g is the bulk fluid radial distribution function.

Each version of the IET corresponds to an approximation to $B(\boldsymbol{r})$. Some of the famous approximations for $B(\boldsymbol{r})$ can be found in Ref.[28]. For a uniform hard-sphere fluid, $\beta F_{\rm ex}(\rho_{\rm b})$ and $C_0^{(1)}$ can be obtained from the numerically very accurate equation of state (especially the famous Carnahan–Starling equation[29]), but for a non-hard-sphere fluid, it is difficult to obtain these two input parameters. So the mean-field perturbation method[30] is often resorted to in this case. At the level of $F_{\rm ex}[\rho]$, there also exists the weighted density approximation (WDA)

$$F_{\rm ex}[\rho] = \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r})f(\overline{\rho}(\boldsymbol{r})), \tag{10}$$

where $f(\rho_{\rm b})$ is the excess free energy per particle of the corresponding uniform fluid with bulk density $\rho_{\rm b}$, and $\overline{\rho}(\boldsymbol{r})$ is a weighted average of $\rho(\boldsymbol{r})$,

$$\overline{\rho}(\boldsymbol{r}) = \int {\rm d}\boldsymbol{r}'\rho(\boldsymbol{r}')w(|\boldsymbol{r}-\boldsymbol{r}'|;\overline{\rho}(\boldsymbol{r})). \tag{11}$$

Originally, the weighting function $w(|\boldsymbol{r}-\boldsymbol{r}'|;\overline{\rho}(\boldsymbol{r}))$ was chosen as[31]

$$w(r) = {\rm Heaviside}(\sigma - r)3/\sigma^3 4\pi, \tag{12}$$

but lately, it has been specified by forcing Eq.(4) to reproduce $C_0^{(2)}$ in the limit of a uniform fluid.[32] Concerning the recent advance of the WDA, one can consult recent papers[33–35] and references therein. The WDA suffers from a computationally intensive shortcoming as well as the same shortcomings as the FPEA. At the level of $F_{\rm ex}[\rho]$, there also exists the fundamental measure theory (FMT) proposed by Rosenfeld and coworkers,[36–39] which is based on geometrical considerations and specifies $F_{\rm ex}[\rho]$ by reproducing the Percus–Yevick (PY) equation of state and the PY $C_0^{(2)}$ of the hard-sphere fluid. The FMT is also devised for the non-uniform hard-sphere fluid, and it has the same shortcomings as the above FPEA and WDA.

If the main calculated quantity is $\rho(\boldsymbol{r})$, one can often make an approximation at the level of $C^{(1)}$. One version[40] of the WDA belongs to this type:

$$C^{(1)}(\boldsymbol{r};[\rho]) = C_0^{(1)}(\overline{\rho}(\boldsymbol{r})). \tag{13}$$

Then, substituting Eq.(13) into Eq.(6), one can calculate $\rho(\boldsymbol{r})$ for an arbitrary $\varphi_{\rm ext}(\boldsymbol{r})$.

To maximally reduce the input parameters and improve the accuracy, we devise the following methodology, based on the universality principle of $F_{\rm ex}[\rho]$.[41] The universality principle indicates that $F_{\rm ex}[\rho]$ and its functional derivative $C^{(1)}$ are a universal functional for the systems involving pairwise additive interactions, independent of the external potential responsible for the formation of $\rho(\boldsymbol{r})$. Thus, one can specify the universal functional form of $F_{\rm ex}[\rho]$ and $C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})])$ by a specific external potential which results from a test particle chosen from the bulk and situated at the origin. The interaction potential between the test particle and other bulk particles is regarded as the special external potential[42]

$$\varphi_{\rm ext}(\boldsymbol{r}) = u(\boldsymbol{r}). \tag{14}$$

In the special inhomogeneous case, $\rho(\boldsymbol{r})$ is related to $g(\boldsymbol{r})$ by

$$\rho(\boldsymbol{r}) = \rho_{\rm b}g(\boldsymbol{r}). \tag{15}$$

The concrete procedures to specify the functional form of $C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})])$ differ from each other, depending on the calculated quantities and the input parameters available. We devise four procedures in this paper.

In procedure I, we define $\overline{\rho}(\boldsymbol{r})$ by using $C_0^{(2)}(r;\rho_{\rm b})$ as

$$\overline{\rho}(\boldsymbol{r}) = \int {\rm d}\boldsymbol{r}' f C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}'|;\rho_{\rm b})\rho(\boldsymbol{r}'), \tag{16}$$

where the constant f can be specified by the normalization condition

$$\rho_{\rm b} = \int {\rm d}\boldsymbol{r}' f C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}'|;\rho_{\rm b})\rho_{\rm b}. \tag{17}$$

Thus

$$f = \left[\int {\rm d}\boldsymbol{r}' C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}'|;\rho_{\rm b})\right]^{-1}, \tag{18}$$

using the language of the WDA and the present weighting function $w = fC_0^{(2)}$.

Since $\overline{\rho}(\boldsymbol{r})$ is a function of $\boldsymbol{r}$, if we define $C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})])$ as a function of $\overline{\rho}(\boldsymbol{r})$ denoted by $G(\overline{\rho}(\boldsymbol{r}))$, then, we have specified the functional $C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})])$:

$$C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})]) = G(\overline{\rho}(\boldsymbol{r})). \tag{19}$$

The key point is how to determine the functional form of G.

Substituting Eq.(19) into Eqs.(6) and (15) leads to

$$g(\boldsymbol{r}) = \exp\{-\beta u(\boldsymbol{r}) + G(\overline{\rho}(\boldsymbol{r})) - C_0^{(1)}(\rho_{\rm b})\}. \tag{20}$$

From a numerical solution of the OZ equation (8), we can obtain $g(\boldsymbol{r})$ and $C_0^{(2)}(r;\rho_{\rm b})$, which can be combined with Eqs.(16) and (18) to calculate $\overline{\rho}(\boldsymbol{r})$. Then the obtained $\overline{\rho}(\boldsymbol{r})$ is substituted into Eq.(20) to arrive at the following equation

$$\begin{aligned} &C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})]) - C_0^{(1)}(\rho_{\rm b}) \\ =&G(\overline{\rho}(\boldsymbol{r})) - C_0^{(1)}(\rho_{\rm b}) = \ln[g(\boldsymbol{r})] + \beta u(\boldsymbol{r}). \end{aligned} \tag{21}$$

In procedure II, we explain the procedure for constructing $C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})])$. One can expand $C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})])$ around the corresponding uniform fluid with bulk density $\rho_{\rm b}$, then truncate the series at the second order

$$\begin{aligned} &C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})]) \\ =&C_0^{(1)}(\rho_{\rm b}) + \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1) - \rho_{\rm b}) \\ &\times C_0^{(2)}(|\boldsymbol{r} - \boldsymbol{r}_1|;\rho_{\rm b}) + {\rm Re(sidue)}. \end{aligned} \tag{22}$$

In Eq.(22), the discarded part of the series is denoted by Re(sidue). To express the $C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})])$ as a functional of $\rho(\boldsymbol{r})$, one can express Re(sidue) as a function of $\int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1) - \rho_{\rm b})C_0^{(2)}(|\boldsymbol{r} - \boldsymbol{r}_1|;\rho_{\rm b})$, then use the same step of procedure I to specify the functional form of Re(sidue).

For a hard-sphere fluid, there exists an analytical expression for $C_0^{(1)}(\rho_{\rm b})$. One can also devise procedure III:

$$C^{(1)}(\boldsymbol{r};[\rho]) = \chi[\rho_{\rm b};\overline{\rho}(\boldsymbol{r})]C_0^{(1)}(\overline{\rho}(\boldsymbol{r})). \tag{23}$$

Substituting Eq.(23) into Eq.(6) and employing Eqs.(14) and (15), we obtain

$$\begin{aligned} g(\boldsymbol{r}) =&\exp[-\beta u(r) + \chi[\rho_{\rm b};\overline{\rho}(\boldsymbol{r})] \\ &\times C_0^{(1)}(\overline{\rho}(\boldsymbol{r})) - C_0^{(1)}(\rho_{\rm b})]. \end{aligned} \tag{24}$$

Then following the same step as in procedure I, one can specify the function form of $\chi[\rho_{\rm b};\overline{\rho}(\boldsymbol{r})]$ with respect to $\overline{\rho}(\boldsymbol{r})$.

To test the validity of procedures I–III, first we apply procedure I to one case of a Lennard–Jones (LJ) fluid confined between two hard walls at a separation H. For this case, the external potential has the form

$$\begin{aligned} \varphi_{\rm ext}(z) = \propto \quad & z/\sigma < 0.5 \ \text{ or } \ z/\sigma > H - 0.5; \\ =0 \quad & 0.5 < z/\sigma < H - 0.5. \end{aligned} \tag{25}$$

To proceed computationally, the quantities $C_0^{(2)}(r;\ \rho_{\rm b})$ and $g(r)$ are needed, which are obtained by solving numerically the OZ equation (8) combined with Eq.(9) and the thermodynamically self-consistent Rogers–Young (RY) approximation,[43] due to the fact that the RY approximation provides the accurate data of $g(\boldsymbol{r})$. The interaction potential $u(r)$ for the LJ fluid has the following form

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], \tag{26}$$

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

It has to be noticed that $g(\boldsymbol{r})$ oscillates, so it is possible that at some space points, e.g. $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, the calculated $\overline{\rho}(\boldsymbol{r})$ has the same value, but $g(\boldsymbol{r}_1)$ and $g(\boldsymbol{r}_2)$ are different. Therefore, G becomes a non-single value function of $\overline{\rho}(\boldsymbol{r})$ at some points of $\overline{\rho}(\boldsymbol{r})$. This is surely the case for the present example of the LJ fluid. For these cases, we choose the space points of $g(\boldsymbol{r})$ from which the calculated $\overline{\rho}(\boldsymbol{r})$ is near and below the bulk density which is exactly the numerical range of $\overline{\rho}(\boldsymbol{r})$ needed for the iterative solution of Eq.(6). Then a smooth curve can be obtained, as shown in Fig.1(a), for the case of the LJ fluid state point of $\rho_{\rm b}\sigma^3$=0.75, kT/ε=1.304. We can use the interpolation procedure to specify the functional relationship G for the iterative solution of Eq.(6) for $\rho(\boldsymbol{r})$ with arbitrary $\varphi_{\rm ext}(\boldsymbol{r})$. Since $\overline{\rho}(\boldsymbol{r})$ is an average of the actual $\rho(\boldsymbol{r})$ and the weighting function has a smoothening function on the oscillatory density profile, by choosing a good initial value, for example, the prediction of the second-order perturbative DFT, for the iterative solution of Eq.(6), one can expect that with the iterative intermediate value of $\rho(\boldsymbol{r})$ of Eq.(6) or with $\rho(\boldsymbol{r})$ from the final solution of Eq.(6) as inputs, the calculated $\overline{\rho}(\boldsymbol{r})$ falls into the above numerical range even if $\varphi_{\rm ext}(\boldsymbol{r})$ is so large that strong oscillation of density distribution profile results. This is surely the case for the present calculation. The calculated results are plotted in Fig.1.

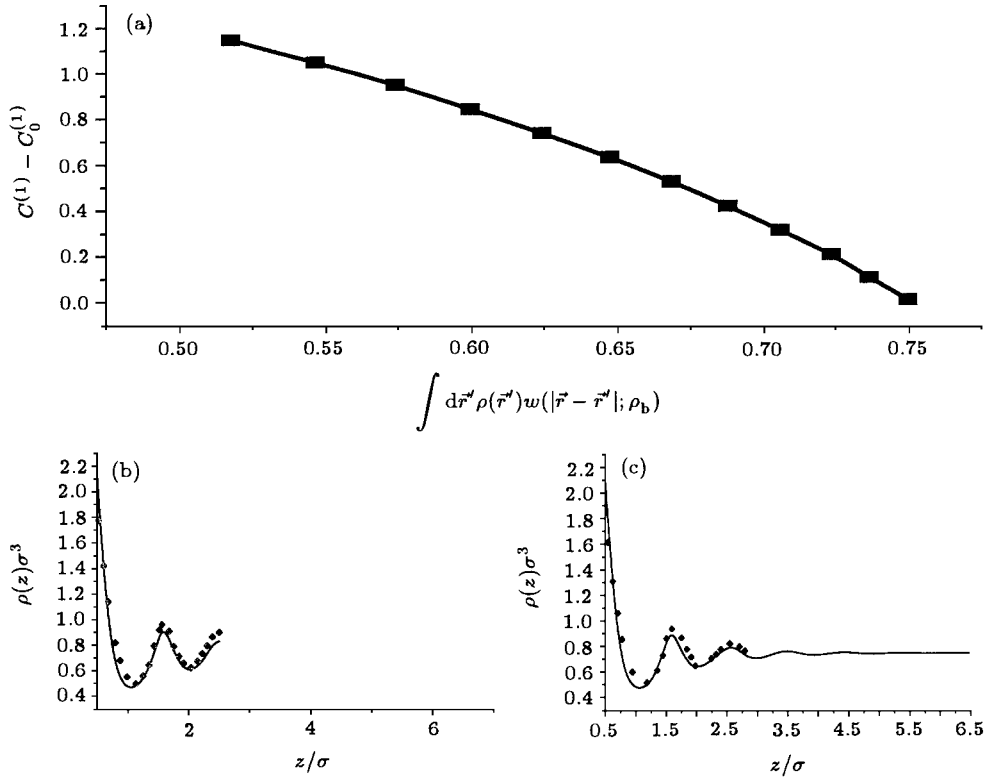


Fig.1. (a) The difference between $C^{(1)}(\vec{r}; [\rho(\vec{r})])$ and $C_0^{(1)}(\rho_b)$ as a function of $\int d\vec{r}' \rho(\vec{r}') w(|\vec{r} - \vec{r}'|; \rho_b)$. The present curve corresponds to the LJ bulk parameters $\rho_b\sigma^3$=0.75, kT/ε=1.304. (b) The density profile of a LJ fluid ($\rho_b\sigma^3$=0.75, kT/ε=1.304) confined between two hard walls with H/σ=5. The dots represent the corresponding Monte Carlo results.[44] The curve is for the predictions of procedure I. Only half the slit is shown. (c) The same as in (b) but with H/σ=13.

Secondly, procedure II is also applied to the above non-uniform LJ fluid. It is interesting that the functional relationship of $C_0^{(2)}(|\boldsymbol{r} - \boldsymbol{r}_1|; \rho_b)$ with respect to $\int d\boldsymbol{r}_1(\rho(\boldsymbol{r}_1) - \rho_b)$ for the bulk LJ fluid of many different state points is the same as that shown in Fig.2(a). We employ the curve from the LJ fluid state point $\rho_b\sigma^3$=1.45, kT/ε=1.95, as shown in Fig.2(b), to calculate $\rho(\boldsymbol{r})$, as shown in Figs.2(c) and 2(d).

Figures 1(b) and 1(c) and Figs.2(c) and 2(d) show that the predictions of the present procedures I and II are in very good agreement with the corresponding computer simulation data, even for the complex long-range potential fluid as a whole.

Thirdly, procedure III is applied to a hard-sphere fluid near a hard wall. In this case, the external potential $\varphi_{ext}(\boldsymbol{r})$ has the form

$$\begin{aligned} \varphi_{ext}(z) &= \propto \quad z/\sigma < 0.5; \\ &= 0 \qquad 0.5 < z/\sigma. \end{aligned} \tag{27}$$

To proceed numerically, the first-order and second-order DCFs of a uniform hard-sphere fluid are needed, which are provided by the PY results.[45,46] To solve the OZ equation for $g(\boldsymbol{r})$, the RY approximation is also employed for the same reason as in procedures I and II. Figures 3(a) and 3(b) show that curves of $\chi[\rho_b; \overline{\rho}(\boldsymbol{r})]$ with respect to $\overline{\rho}(\boldsymbol{r})$ are smooth at the end of the small numerical value of $\overline{\rho}(\boldsymbol{r})$, but oscillate weakly at the end of the large numerical value of $\overline{\rho}(\boldsymbol{r})$ when $\chi[\rho_b; \overline{\rho}(\boldsymbol{r})]$ is very near to 1.

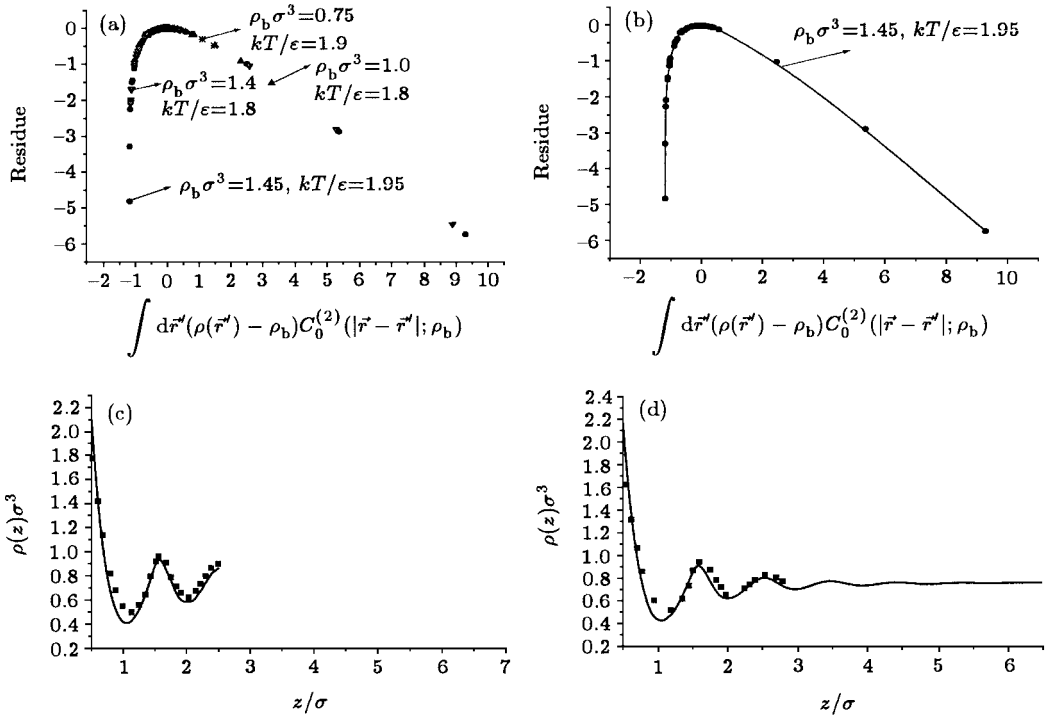


Fig.2. (a) Residue as a function of $\int d\vec{r}_1(\rho(\vec{r}_1)-\rho_b)C_0^{(2)}(|\vec{r}-\vec{r}_1|;\rho_b)$ for the bulk LJ fluid of several state points. (b) Residue as a function of $\int d\vec{r}_1(\rho(\vec{r}_1)-\rho_b)C_0^{(2)}(|\vec{r}-\vec{r}_1|;\rho_b)$ for the bulk LJ fluid of state point $\rho_b\sigma^3$=1.45, kT/ε=1.95. (c) The same as in Fig.1(b) but the curve is for the predictions of procedure II. (d) The same as in (c) but with H/σ=13.

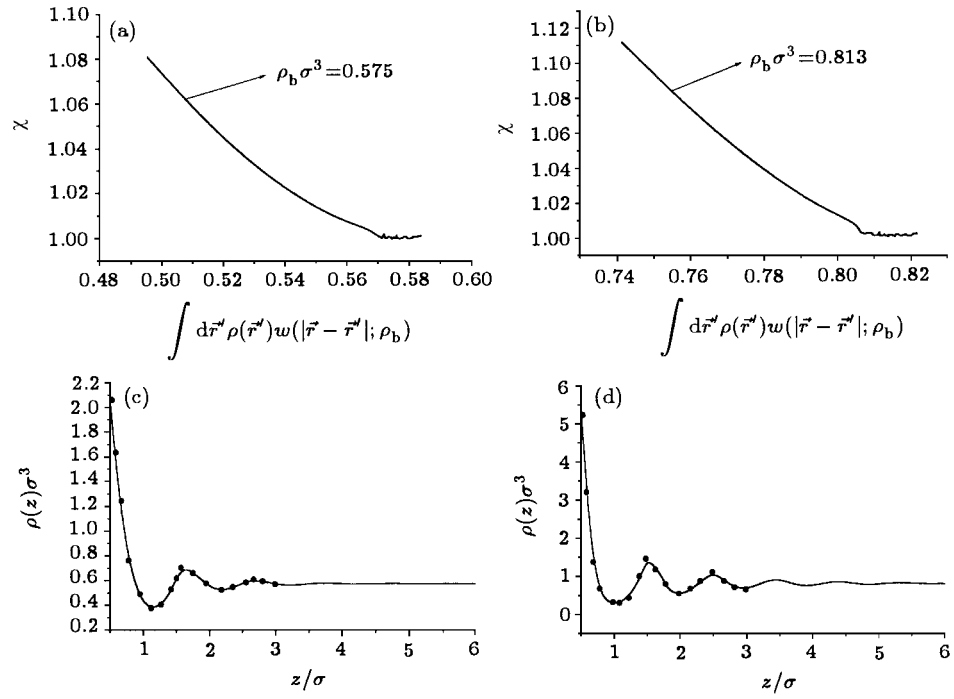


Fig.3. (a) The prediction for $\chi[\rho_b;\overline{\rho}(\vec{r})]$ using procedure III as a function of $\int d\vec{r}'\rho(\vec{r}')w(|\vec{r}-\vec{r}'|;\rho_b)$ for the bulk hard-sphere fluid of $\rho_b\sigma^3$=0.575. (b) Same as in (a) but with $\rho_b\sigma^3$=0.813. (c) The density profile of a hard-sphere fluid ($\rho_b\sigma^3$=0.575) near a hard wall: the line corresponds to the prediction of procedure III, the dots denote the corresponding computer simulation data.[47] (d) Same as in (c) but with $\rho_b\sigma^3$=0.813.

To make the numerical solution of procedure III stable, we let $\chi[\rho_b;\overline{\rho}(\boldsymbol{r})]$ equal 1 when the curve begins to oscillate weakly, and we use the interpolation procedure to specify the smooth part of the curve. In this case, the agreement of the theoretical prediction with the simulation data is also very good. Now we apply procedure III to a hard-sphere fluid confined in a spherical cavity with a hard wall of radius R. The external potential has the following form

$$\varphi_{\rm ext}(\boldsymbol{r}) = \infty \quad |\boldsymbol{r}|/\sigma > R;$$
$$= 0 \quad |\boldsymbol{r}|/\sigma < R. \tag{28}$$

In this case, the theoretical predictions coincide with the simulation data almost point by point, as shown in Figs.4(a) and 4(b). For comparison, the predictions of the simple weighted density approximation (SWDA)[48] are also plotted in Figs.4(a) and 4(b).

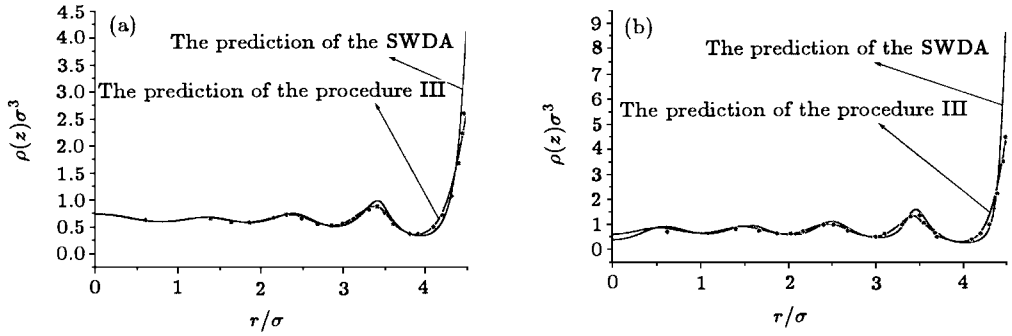


Fig.4. (a) The density profiles of a hard-sphere fluid ($\rho_b\sigma^3$=0.62) confined in a spherical cavity with a hard wall of radius R=4.5. The points denote the corresponding computer simulation data.[49] (b) Same as in (a) but with $\rho_b\sigma^3$=0.75.

Obviously, the present methodology can also be applied at the level of $F_{\rm ex}[\rho]$ (procedure IV). As an example, we introduce a WDA[32] based on an approximation to $F_{\rm ex}[\rho]$

$$F_{\rm ex}[\rho] = \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r}) f(\overline{\rho}(\boldsymbol{r})). \tag{29}$$

In the original paper,[32] the weighting function and the weighted density are coupled together, and the expression for the weighting function is very complicated. Now, we employ the present definition of $\overline{\rho}(\boldsymbol{r})$ and correct Eq.(29) with the density functional factor $\chi[\rho_b;\overline{\rho}(\boldsymbol{r})]$

$$F_{\rm ex}[\rho] = \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r})\chi[\rho_b;\overline{\rho}(\boldsymbol{r})] f(\overline{\rho}(\boldsymbol{r})). \tag{30}$$

By the functional derivative of Eq.(30), one can obtain an expression for $C^{(1)}(\boldsymbol{r};[\rho])$. Then substituting into Eq.(6), one also can use the information of $g(\boldsymbol{r})$ to obtain the expression of $\chi[\rho_b;\overline{\rho}(\boldsymbol{r})]$ following the same step as in procedure I. The numerical performance of Eq.(30) should be tested, and we will report this in a separate paper. The above four procedures indicate that there are many routes to carry out the present methodology numerically.

In recent years, the extension of classical DFTs to quantum systems has been proposed (see Refs.[50] and [47] and references therein). The bottleneck in the development of the Kohn-Sham (KS) method of the electronic DFT is how to construct a suitable approximation for the exchange-correlation (ec) energy functional $E[\rho]$ or the corresponding multiplicative xc-potential $\nu_{\rm ec}(\boldsymbol{r};[\rho])$

$$\nu_{ec}(\boldsymbol{r}[\rho]) = \frac{\delta E_{\rm ec}[\rho]}{\delta\rho(\boldsymbol{r})}. \tag{31}$$

The quantum analogue of Eq.(29) gives the ground-state exchange-correlation energy functional[51]

$$E_{\rm ec}(\boldsymbol{r};[\rho]) = \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r})\varepsilon_{\rm ec}(\overline{\rho}(\boldsymbol{r})), \tag{32}$$

where $\varepsilon_{\rm ec}(\overline{\rho}(\boldsymbol{r}))$ is the ec energy per particle of a uniform electron gas with an effective electron gas density $\overline{\rho}(r)$. Similar to Eq.(30) and with reference to Eq.(32), one can write

$$E_{\rm ec}[\rho] = \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r})\chi[\rho_b;\overline{\rho}(r)]\varepsilon_{\rm ec}(\overline{\rho}(\boldsymbol{r})). \tag{33}$$

To carry out Eq.(33) numerically, we need the quantum analogue of $C_0^{(2)}$ and $g(\boldsymbol{r})$ which can be obtained from the quantum analogue of the IET. In either quantum or classical DFT, what is used directly is the potential, i.e. the first-order DCF for the classical system, and the multiplicative xc-potential $\nu_{\rm ec}(\boldsymbol{r};[\rho])$ for

the quantum system. From the definition of $\nu_{\rm ec}(\boldsymbol{r};[\rho])$, we know that the classical analogue of $\nu_{\rm ec}(\boldsymbol{r};[\rho])$ is the first-order DCF, so the above four procedures for the classical DFT can be extended to the quantum case. The unique required inputs are the quantum analogue of $C_0^{(2)}$ and $g(\boldsymbol{r})$, which can be obtained by quantum Monte Carlo simulation[52] and the quantum IET.[28]

3. Concluding remarks

The basic idea of the present methodology is that, based on the universality principle and test particle method, the universal functional form of $F_{\rm ex}[\rho]$ or its functional derivative $C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})])$ can be extracted from the IET for a bulk fluid. Furthermore, by using the functional integration of $C^{(1)}(\boldsymbol{r};[\rho(\boldsymbol{r})])$ based on the procedures I–III, one can obtain the excess Helmholtz free energy density function $F_{\rm ex}[\rho]$. Although the present methodology and the DFTs in Refs.[23]–[27] are all based on the universality principle of $F_{\rm ex}[\rho]$, the ways in which the universality principle is employed are different. The DFTs in Refs.[23]–[27] use the bulk bridge functional as the input, and at the same time the bridge functional has to be expressed as a function of the indirect correlation function. Therefore, the DFTs in Refs.[23]–[27] are suitable only for the hard-sphere and hard-sphere-chain fluids due to the fact that only the bridge functional of these fluids can be accurately expressed as a function of the indirect correlation function. The present methodology differs from that employed in Refs.[23]–[27] mainly in the incorporation of the knowledge of $g(\boldsymbol{r})$ into the approximate density functional, and does not depend on the bridge functional concept. So the present methodology is applicable to the general interaction potential fluid. This advantage is not shared by any other DFTs available previously in the literature. Previous DFTs have only employed explicitly the knowledge of $C_0^{(2)}(\boldsymbol{r},\rho_{\rm b})$ to construct the density functional. In statistical mechanics theories, approximations have to be made, so it is possible that the theoretical prediction for one quantity is good, but the prediction for another quantity is bad. In the IET, the PY approximation can predict well $C_0^{(2)}(\boldsymbol{r};\rho_{\rm b})$, while its prediction for $g(\boldsymbol{r})$ is inferior to the RY approximation. Because an approximate theory itself is not theoretically completely self-consistent, so one cannot conclude that the previous DFT incorporates $g(\boldsymbol{r})$ into itself only because $C_0^{(2)}(\boldsymbol{r};\rho_{\rm b})$ is connected with $g(\boldsymbol{r})$ by the OZ equation.

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