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# Specification of Density Functional Approximation by Radial Distribution Function of Bulk Fluid*

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***Abstract*** *A systematic methodology is proposed to deal with the weighted density approximation version of classical density functional theory by employing the knowledge of radial distribution function of bulk fluid. The present methodology results from the concept of universality of the free energy density functional combined with the test particle method. It is shown that the new method is very accurate for the predictions of density distribution of a hard sphere fluid at different confining geometries. The physical foundation of the present methodology is also applied to the quantum density functional theory.*

**PACS numbers:** 05.20.-y
**Key words:** density functional theory, weighted density approximation, radial distribution function

## 1 Introduction

Density functional theory (DFT) has being devised to study the properties of non-uniform interacting many-particle systems.[1] In this approach, it is the single-particle density distribution (the basic variable) with respect to which the free energy of non-uniform system is minimized, its minimization at equilibrium provides both the density distribution and the free energy of the system. In the classical DFTs, three different versions of approximations for the non-uniform system free energy or the potential (the functional derivative of the non-uniform system free energy with respect to the density variation) were proposed. One of the versions is the functional Taylor expansion of excess free energy of non-uniform system around the uniform system in powers of the density deviation between non-uniform density distribution and bulk density with the coefficients representing the direct correlation functions (DCFs) of the uniform system.[2] In most of the early studies, the expansion was truncated at the second order due to the lack of the knowledge of the higher-order DCFs of even the uniform bulk fluid. Recently some studies developed the higher-order expansion approximation by making use of approximate higher-order DCFs.[3−5] Another version is the so-called weighted density approximation (WDA) which is actually mappings of non-uniform systems onto uniform counterparts and approximately includes the contributions to excess free energy density functional from all the orders in density difference.[6−8] In the WDA approach, it is the excess free energy or its functional derivative (the first-order DCF) of the non-uniform system which is approximated by that of the corresponding uniform fluid at a smooth average density which is actually a suitable weighted average of the physical density of the system under consideration. Beyond the above two main DFT types, there also exists other DFT formalism, especially the fundamental measure theory by Rosenfeld,[9] 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. However, it should be noted that a completely new DFT[10] was proposed recently by the present author which resulted from the use of the universality of the free energy density functional.[11] This type of DFT requires the bridge function of the bulk fluid as input, furthermore, the required bridge function has to be expressed as a function of the indirect correlation function of the corresponding bulk fluid. But there does not exist this form of bridge function for many fluids at the present time, up to now, this form of bridge function exists only for hard sphere fluid. So it is interesting to observe how this methodology evolves. One characteristic of the original WDA is that the weighted density and weighting function are coupled together, this fact entails iterative calculation, thus tremendous computer time is required. This shortcoming will becomes very obvious when the methods of WDA type are extended to the case of mixture.[8] To simplify the calculation, the Tarazona version[7] and the Ashcroft *et al.*[7] version of the WDA are decoupled respectively,[12,13] both of the decoupled WDAs produced predictions comparable to that of their original versions. Especially the decoupled simple WDA (SWDA) from Ref. [13] based on an approximation directly to the first-order DCF was extended to the case of mixture and electrical double layer,[14] also comparable results with computer simulation data were obtained for these complicated cases. However, to make the decoupled WDAs more practical, it is good to make them more accurate but still keep their simplicity. In all of the previous WDAs, only the second-order DCF of the uniform fluid was used to specify the weighting function.

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The concept of the radial distribution function (RDF) of the bulk fluid is parallel with that of the second DCF of uniform fluid. But, regretfully the knowledge of the RDF of the uniform fluid has not been employed explicitly to specify the approximations in the design of all previous WDAs. (Although the RDF of the uniform fluid is related to the second-order DCF of uniform fluid by the Ornstein–Zernike (OZ) equation, the OZ equation has to be combined with some approximate closure to produce the approximate second-order DCF, approximate theory itself is not completely self-consistent. Thus by an indirect way of an exact OZ equation and an approximate second-order DCF, it is difficult to say that the versions of the WDA type incorporate explicitly the radial distribution function into itself). The aim of the present paper is to devise a new method to improve on the accuracy of the decoupled WDAs by employing explicitly the knowledge of the RDF of the bulk fluid besides the second-order DCF of the bulk fluid. The physical foundation of the method is also the universality of the free energy density functional, its implementation needs to perform the test particle method.[15] As an example, we incorporate the present method into the SWDA and compare its predictions with those of the SWDA and the corresponding computer simulation data for the case of a hard sphere fluid in a spherical cavity or near a hard wall. The present paper is largely about the classical system, but we also give a brief discussion about the application of the present idea in the context of quantum density functional theory.

## 2 The Present Methodology

Because the universal form of the free energy density functional is not known, we can only make use of the universality principle to improve on the accuracy of some approximation. We choose the WDA, because in WDA the basic variable is the weighted density which has been a functional of the actual physical density. Thus, only if we can express the free energy or the potential as a function of the weighted density, we express the free energy or the potential as a functional of density distribution. Furthermore, the ad hoc WDA incorporates the correlation of the non-uniform fluid into itself, and the WDAs have been used widely and successfully in both the classical DFT and electronic DFT, if the new methodology is combined with the WDAs, it can be extended to quantum case straightforwardly. To explore a computationally simplest DFT, we choose the SWDA on which our discussion is based.

In the WDA of Ref. [7], an approximation to the first order DCF $C^{(1)}(\boldsymbol{r};[\rho])$ of a non-uniform system was made,

$$C^{(1)}(\boldsymbol{r};[\rho]) = C_0^{(1)}(\bar{\rho}(\boldsymbol{r}))\,, \tag{1}$$

where $C_0^{(1)}(\bar{\rho}(\boldsymbol{r}))$ is the first-order DCF of an effective uniform fluid with density $\bar{\rho}(\boldsymbol{r})$ which is defined as a weighted average of the actual physical density $\rho(\boldsymbol{r})$ according to

$$\bar{\rho}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}'\rho(\boldsymbol{r}')w(|\boldsymbol{r}-\boldsymbol{r}'|;\bar{\rho}(\boldsymbol{r}))\,, \tag{2}$$

where the weighted density $\bar{\rho}(\boldsymbol{r})$ and the weighting function $w(|\boldsymbol{r}-\boldsymbol{r}'|;\bar{\rho}(\boldsymbol{r}))$ are coupled together. To decouple them, we replace the weighting function $w(|\boldsymbol{r}-\boldsymbol{r}'|;\bar{\rho}(\boldsymbol{r}))$ of Ref. [7] by $w(|\boldsymbol{r}-\boldsymbol{r}'|;\tilde{\rho}(\boldsymbol{r}))$ where $\tilde{\rho}(\boldsymbol{r})$ is also an weighted average of the actual physical density $\rho(\boldsymbol{r})$. Thus, in the present paper, equation (2) is changed as

$$\bar{\rho}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}'\rho(\boldsymbol{r}')w(|\boldsymbol{r}-\boldsymbol{r}'|;\tilde{\rho}(\boldsymbol{r}))\,. \tag{3}$$

To ensure that the present approximation is exact in the limit of uniform fluid ($\rho(\boldsymbol{r})\to\rho_b$), the weighting function $w(|\boldsymbol{r}-\boldsymbol{r}'|;\tilde{\rho}(\boldsymbol{r}))$ is required to satisfy the normalization condition

$$\int \mathrm{d}\boldsymbol{r}'w(|\boldsymbol{r}-\boldsymbol{r}'|;\tilde{\rho}(\boldsymbol{r})) = 1\,. \tag{4}$$

The final determination of the weighting function follows the requirement that the second-order DCF $C_0^{(2)}(r;\rho_b)$ of the uniform fluid is recovered from the approximation according to

$$\lim_{\rho\to\rho_b}\Big\{\frac{\delta C^{(1)}(\boldsymbol{r}_1;[\rho])}{\delta\rho(\boldsymbol{r}_2)}\Big\} = C_0^{(2)}(|\boldsymbol{r}_1-\boldsymbol{r}_2|;\rho_b)\,. \tag{5}$$

Substituting Eq. (1) into Eq. (5), we arrive at

$$C_0^{(2)}(|\boldsymbol{r}_1-\boldsymbol{r}_2|;\rho_b) = \lim_{\rho\to\rho_b}\Big[C_0^{(1)'}(\bar{\rho}(\boldsymbol{r}_1))\Big\{\int \mathrm{d}\boldsymbol{r}'\delta(\boldsymbol{r}_2-\boldsymbol{r}')w(|\boldsymbol{r}_1-\boldsymbol{r}'|;\tilde{\rho}(\boldsymbol{r}_1)) + \int \mathrm{d}\boldsymbol{r}'\rho(\boldsymbol{r}')w'(|\boldsymbol{r}_1-\boldsymbol{r}'|;\tilde{\rho}(\boldsymbol{r}_1))\frac{\delta\tilde{\rho}(\boldsymbol{r}_1)}{\delta\rho(\boldsymbol{r}_2)}\Big\}\Big]\,. \tag{6}$$

Exchanging the sequence of derivative and integration, equation (6) can be simplified as

$$C_0^{(2)}(|\boldsymbol{r}_1-\boldsymbol{r}_2|;\rho_b) = C_0^{(1)'}(\rho_b)\Big\{w(|\boldsymbol{r}_1-\boldsymbol{r}_2|;\rho_b) + \rho_b\lim_{\rho\to\rho_b}\frac{\delta\tilde{\rho}(\boldsymbol{r}_1)}{\delta\rho(\boldsymbol{r}_2)}\lim_{\rho\to\rho_b}\frac{\mathrm{d}}{\mathrm{d}\tilde{\rho}}\int \mathrm{d}\boldsymbol{r}'w(|\boldsymbol{r}_1-\boldsymbol{r}'|;\tilde{\rho}(\boldsymbol{r}_1))\Big\}\,. \tag{7}$$

Due to the normalization condition of the weighting function, equation (7) can be further simplified as

$$w(|\boldsymbol{r}_1-\boldsymbol{r}_2|;\rho_b) = \frac{C_0^{(2)}(|\boldsymbol{r}_1-\boldsymbol{r}_2|;\rho_b)}{C_0^{(1)'}(\rho_b)}\,. \tag{8}$$

The above derivation does not depend on the definition of argument $\tilde{\rho}(\boldsymbol{r})$, so we have greater freedom to choose the argument $\tilde{\rho}(\boldsymbol{r})$, at the same time still keep the same simple form of the weighting function of Eq. (8). We note

that the form of the weighting function of the present decoupled WDA is the same as that of the WDA of Ashcroft *et al.*[7] and the SWDA.[13] If we choose $\tilde{\rho}(\boldsymbol{r})$ to be equivalent to $\bar{\rho}(\boldsymbol{r})$, the WDA of Ashcroft *et al.*[7] is recovered, choose $\tilde{\rho}(\boldsymbol{r})$ to be equivalent to $\rho_b$, the SWDA[13] is recovered. The shortcoming of the SWDA lies in the fact that its weighting function $w(|\boldsymbol{r}-\boldsymbol{r}'|;\rho_b)$ is the same at the different regions of the density distribution. But the gradient of density distribution changes as the space position $\boldsymbol{r}$ does. To remedy the shortcoming of the SWDA, we use a density functional factor $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$ to correct the SWDA, that is

$$C^{(1)}(\boldsymbol{r};[\,\rho]) = \chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]C_0^{(1)}(\,\bar{\rho}(\boldsymbol{r}))\,. \tag{9}$$

Thus all of the errors resulting from the crude approximation of the SWDA is embodied in the factor $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$. What is the key point is how to choose the form of $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$. $C^{(1)}(\boldsymbol{r};[\,\rho])$ is related to the excess free energy density functional $F_{\rm ex}[\,\rho]$ by the following relation

$$C^{(1)}(\boldsymbol{r};[\,\rho]) = -\beta\frac{\delta F_{\rm ex}[\,\rho]}{\delta\rho(\boldsymbol{r})}\,, \tag{10}$$

where $\beta = 1/kT$ with $k$ the Boltzmann constant and $T$ the absolute temperature. $F_{\rm ex}[\,\rho]$ being universal means that $C^{(1)}(\boldsymbol{r};[\,\rho])$ is also universal, thus $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$ is universal. The universality of $F_{\rm ex}[\,\rho]$ means that the form of $F_{\rm ex}[\,\rho]$ is independent of the form of the external field responsible for the formation of the non-uniform density distribution $\rho(\boldsymbol{r})$. Only if we specify the form of $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$ for some special external field, can we use the same form of $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$ to the other cases of external field. From the view point of test particle method,[15] the uniform system can be regarded as a special non-uniform system, this kind of non-uniformity results from choosing a particle from bulk system and putting the particle (called test particle) at the origin of coordinate, then the test particle is regarded as external field whose action on the other particle under consideration is responsible for the formation of non-uniform density distribution $\rho(\boldsymbol{r})$ around the test particle which is related to the radial distribution function $g(\boldsymbol{r})$ of the corresponding bulk fluid as follows:

$$\rho(\boldsymbol{r}) = \rho_b g(\boldsymbol{r})\,, \tag{11}$$

where $\rho_b$ is the bulk density.

For a classical fluid at a fixed temperature $kT = \beta^{-1}$ and bulk density $\rho_b$ under the influence of an external field $\varphi_{\rm ext}(\boldsymbol{r})$, the density profile equation is given in the DFT as follows:

$$\rho(\boldsymbol{r}) = \rho_b\exp[-\beta\varphi_{\rm ext}(\boldsymbol{r}) + C^{(1)}(\boldsymbol{r};[\,\rho]) - C_0^{(1)}(\rho_b)]\,. \tag{12}$$

Now the SWDA with the correction factor is applied to the above special inhomogeneity whose external field is the interaction potential of the bulk particles, i.e.,

$$\varphi_{\rm ext}(\boldsymbol{r}) = u(\boldsymbol{r})\,. \tag{13}$$

To show the power of the present methodology, we use hard sphere fluid as an example,

$$u(\boldsymbol{r}) = \begin{cases} \infty, & r < \sigma\,, \\ 0, & r > \sigma\,. \end{cases} \tag{14}$$

Substituting Eqs (9), (11), and (13) into Eq. (12) leads to

$$g(\boldsymbol{r}) = \exp\{-\beta u(\boldsymbol{r}) + \chi[\,\rho_b;\bar{\rho}\,(\boldsymbol{r})] \times C_0^{(1)}(\bar{\rho}\,(\boldsymbol{r})) - C_0^{(1)}(\rho_b)\}\,, \tag{15}$$

where $\bar{\rho}(\boldsymbol{r})$ is determined by Eqs (3) and (8) with $\tilde{\rho}(\boldsymbol{r})$ in Eq. (3) being chosen as $\rho_b$ as required by the SWDA. To determine the form of $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$ at different bulk densities, $g(\boldsymbol{r})$ of different bulk densities is needed. In the present paper, the OZ integral equation

$$h(\boldsymbol{r}) = C_0^{(2)}(\boldsymbol{r};\rho_b) + \rho_b\int \mathrm{d}\boldsymbol{r}_1 h(\boldsymbol{r}_1)C_0^{(2)}(\boldsymbol{r}_1;\rho_b) \tag{16}$$

is combined with the equation defining the bridge function $B(\boldsymbol{r})$,

$$g(\boldsymbol{r}) = \exp[-\beta u(\boldsymbol{r}) + h(\boldsymbol{r}) - C_0^{(2)}(\boldsymbol{r};\rho_b) + B(\boldsymbol{r})]\,, \tag{17}$$

to obtain $g(\boldsymbol{r})$, where $h(\boldsymbol{r}) = g(\boldsymbol{r}) - 1$ is the total correlation function. To solve Eqs (16) and (17), an approximation relating the bridge function $B(\boldsymbol{r})$ to the second DCF and total correlation function is needed. There exist many such approximations in literature, such as the PY approximation, the hypernetted-chain (HNC) approximation and the RY approximation etc.[16,17] Anyone of the above approximations can be combined with Eqs (16) and (17) to determine the $g(\boldsymbol{r})$ of different bulk densities, then the obtained $g(\boldsymbol{r})$ can be inserted into Eq. (15) to determine the form of $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$. Upon the acquirement of $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$, the SWDA with the correct factor is completely specified. To show the effect of incorporation of the knowledge of bulk fluid $g(\boldsymbol{r})$ into the weighted density type approximation, we will apply the above formulation of the present methodology to two cases: (i) a hard sphere fluid confined in a spherical cavity with a hard wall of radius $R$, (ii) a hard sphere fluid near a hard wall.

For case (i), the external potential $\varphi_{\rm ext}(\boldsymbol{r})$ responsible for the generation of the density distribution $\rho(\boldsymbol{r})$ has the form

$$\varphi_{\rm ext}(\boldsymbol{r}) = \begin{cases} \infty, & |\boldsymbol{r}|/\sigma > R\,, \\ 0, & |\boldsymbol{r}|/\sigma < R\,, \end{cases} \tag{18}$$

while for case (ii), it is

$$\varphi_{\rm ext}(z) = \begin{cases} \infty, & z/\sigma < 0.5\,, \\ 0, & 0.5 < z/\sigma\,. \end{cases} \tag{19}$$

To proceed numerically, the first- and second-order DCFs of uniform hard sphere fluid are needed. In the present paper, the PY result[16] is employed for these two functions. To solve the OZ equation for $g(\boldsymbol{r})$, the RY approximation[17] is employed due to the fact that the RY

approximation provides the most accurate data of $g(\boldsymbol{r})$ for bulk hard sphere fluid.

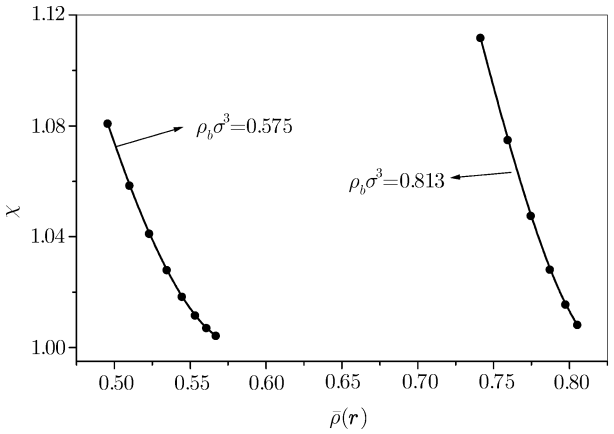


**Fig. 1** Part of the curve of the function relationship of $\chi[\rho_b;\bar{\rho}(\boldsymbol{r})]$ with respect to $\bar{\rho}(\boldsymbol{r})$ for bulk hard sphere fluid of $\rho_b\sigma^3 = 0.575$ and $\rho_b\sigma^3 = 0.813$ respectively.

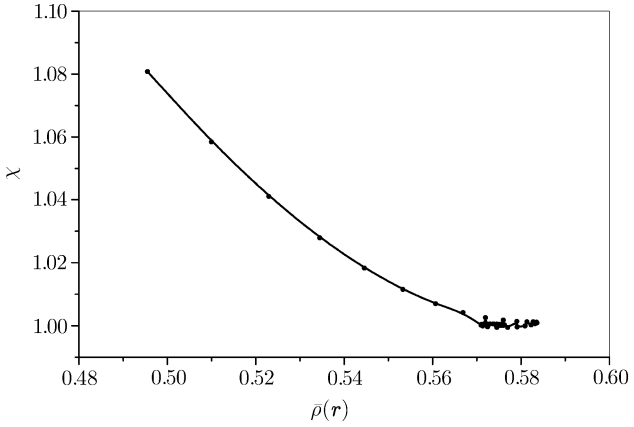


**Fig. 2** The function relationship of $\chi[\rho_b;\bar{\rho}(\boldsymbol{r})]$ with respect to $\bar{\rho}(\boldsymbol{r})$ for bulk hard sphere fluid of $\rho_b\sigma^3 = 0.575$.

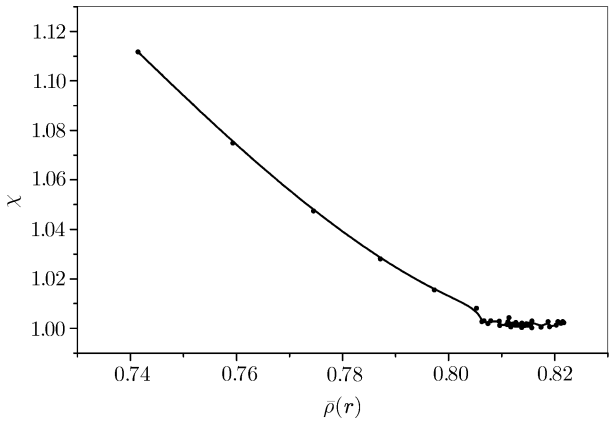


**Fig. 3** The function relationship of $\chi[\rho_b;\bar{\rho}(\boldsymbol{r})]$ with respect to $\bar{\rho}(\boldsymbol{r})$ for bulk hard sphere fluid of $\rho_b\sigma^3 = 0.813$.

It has to be noticed that the profile of the radial distribution function $g(\boldsymbol{r})$ oscillates, so it is possible that at some space points, for example, $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, the calculated weighted densities have the same value, but $g(\boldsymbol{r}_1)$ and $g(\boldsymbol{r}_2)$ are different. This is sure for the present case, so the curve $\chi[\rho_b;\bar{\rho}(\boldsymbol{r})]$ becomes a many-valued function of $\bar{\rho}(\boldsymbol{r})$ at some points of $\bar{\rho}(\boldsymbol{r})$. We choose space points in the whole space of $g(\boldsymbol{r})$ (for two state points of hard sphere fluid based on the RY approximation) from $r/\sigma = 1$ to $r/\sigma = 10.2$ with separation 0.05 $\sigma$, then a curve of $\chi[\rho_b;\bar{\rho}(\boldsymbol{r})]$ with respect to $\bar{\rho}(\boldsymbol{r})$ was obtained which is smooth (see Fig. 1) at the end of small $\bar{\rho}(\boldsymbol{r})$, but oscillates weakly at the end of large $\bar{\rho}(\boldsymbol{r})$ when the numerical value of $\chi[\rho_b;\bar{\rho}(\boldsymbol{r})]$ is very near to 1 as shown in Figs 2 and 3. To make the numerical solution of Eq. (12) stable, we make $\chi[\rho_b;\bar{\rho}(\boldsymbol{r})]$ equal 1 when the curve oscillates weakly, and use the three points interpolation procedure to specify the smooth part of the curve for the non-uniform fluid case. By choosing a good initial value, for example, the prediction of the second-order perturbative DFT or the SWDA, for the iterative solution of Eq. (12), all of the calculated weighted densities during the iteration process fall into the above numerical range of the calculated weighted densities from the IET for the corresponding uniform fluid. In fact, even if the bulk density is chosen as the initial value for the iterative solution of Eq. (12), all of the calculated weighted densities also fall into the above numerical range. We think that it is due to the smoothening function of the weighting action on the oscillatory density distribution profile.

In Figs 4 $\sim$ 7, the predictions of the present formulation are plotted with the predictions of the SWDA and the corresponding computer simulation data.[18,19] It is shown that the accuracy of the present formulation is far superior to that of the SWDA, and the present predictions can coincide with the corresponding computer simulation data almost point by point. We also compared the predictions of the present formulation with that of the most accurate DFTs[10,12] in literature, 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 formulation based on the RY and PY approximations respectively, it was found that the result based on the RY approximation is superior to that based on the PY approximation, it is well known that the PY approximation is less accurate than the RY approximation for the prediction of the RDF of the bulk fluid. This fact indicates furthermore the importance of the incorporation of $g(\boldsymbol{r})$ into the weighted density type approximation. Although the results based on the RY approximation are not consistent (it uses the PY second-order DCF and the RY radial distribution function), the results based on the RY approximation are more accurate than those based on the PY approximation. We explain this phenomenon as follows. Approximate statistical mechanics theory itself is not completely consistent, some approximation is good for some correlation functions, but not for other correlation functions. For example, the PY approximation is good for the second-order DCF, but RY approximation

is better for the radial distribution function than the PY approximation.

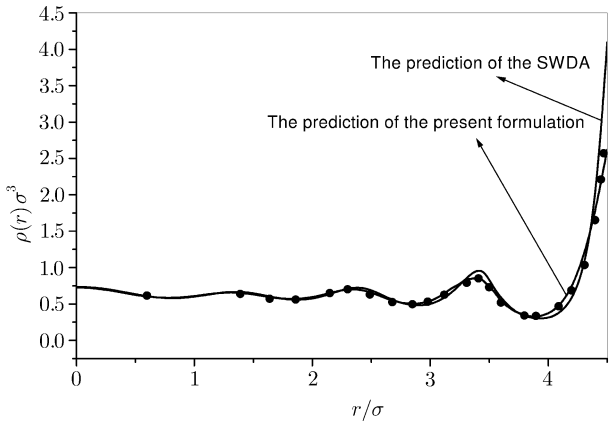


**Fig. 4** Density profiles of a hard sphere fluid ($\rho_b\sigma^3 = 0.62$) confined in a spherical cavity with a hard wall $R = 4.5\sigma$. The lines correspond to the predictions of the theory. The points stand for the corresponding computer simulation data.[18]

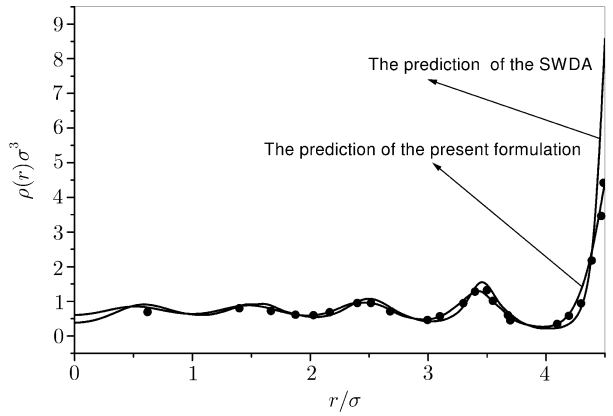


**Fig. 5** The same as Fig. 4 but for $\rho_b\sigma^3 = 0.75$.

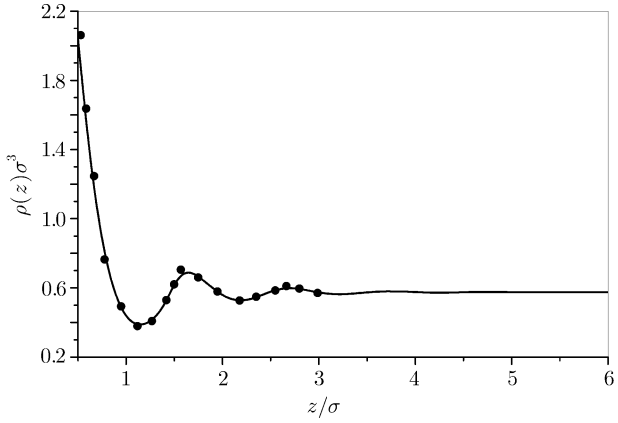


**Fig. 6** Density profiles of a hard sphere fluid ($\rho_b\sigma^3 = 0.575$) near a hard wall. The line corresponds to the predictions of the present formulation. The points stand for the corresponding computer simulation data.[19]

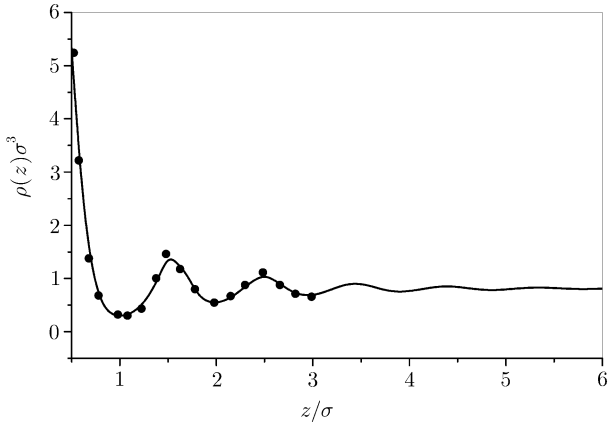


**Fig. 7** The same as Fig. 3 but $\rho_b\sigma^3 = 0.813$.

The present calculation suggests a route along which the information of $g(\boldsymbol{r})$ of uniform fluid is integrated in the density functional form to get better density functional approximation. Its implementation is not unique due to the fact that there exist many versions of WDA. As an example, we can introduce a WDA[6] based on an approximation to the excess free energy per particle of the uniform system

$$F_{\rm ex}[\,\rho] = \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r}) f(\bar{\rho}(\boldsymbol{r}))\,, \tag{20}$$

where $f(\bar{\rho}(\boldsymbol{r}))$ is the excess free energy per particle of an effective uniform fluid with weighted density $\bar{\rho}(\boldsymbol{r})$. In the original paper,[6] the weighting function and the weighted density are coupled together, the expression for the weighting function is very complicated. Its decoupled form was proposed,[12] but the second DCF was not used to specify the weighting function. As in the SDWA, we define the weighted density by Eq. (3) with $\tilde{\rho}(\boldsymbol{r})$ in Eq. (3) being replaced by $\rho_b$, then by requiring the excess free energy functional to reproduce the second-order DCF of the uniform system, we can acquire the largely simplified formulae for the weighting function

$$\begin{aligned} &2f'(\rho_b)\hat{w}(k;\rho_b) + \rho_b f''(\rho_b)\hat{w}^2(k;\rho_b) \\ &\quad + \beta^{-1}\hat{C}_0^{(2)}(k;\rho_b) = 0\,, \end{aligned} \tag{21}$$

where the carrot stands for the Fourier transform. Now we correct Eq. (20) with the density functional factor $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$,

$$F_{\rm ex}[\,\rho] = \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r})\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})] f(\bar{\rho}(\boldsymbol{r}))\,, \tag{22}$$

the correction factor $\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]$ can be determined as the above procedure designed for the SWDA-correction factor. The numerical performance of Eq. (22) should be tested, we will report in a separate paper. The present two reformulations of weighted density-type approximation indicate that there exist many routes to employ the information of $g(\boldsymbol{r})$ of the uniform fluid to improve on the weighted density-type approximation.

In recent years, the extensions of classical DFTs to quantum system were proposed (see Ref. [20] and the

references therein), the flask neck constituting the development of the Kohn–Sham method of DFT is the construction of a suitable approximation for the exchange-correlation (xc) energy functional $E_{\rm xc}[\,\rho]$ or the corresponding multiplicative xc-potential $v_{\rm xc}(\boldsymbol{r};[\,\rho])$

$$v_{\rm xc}(\boldsymbol{r};[\,\rho]) = \frac{\delta E_{\rm xc}[\,\rho]}{\delta\rho(\boldsymbol{r})}\,. \tag{23}$$

The quantum analog of Eq. (22) gives the ground state xc energy functional

$$E_{\rm xc}[\,\rho] = \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r})\chi[\,\rho_b;\bar{\rho}(\boldsymbol{r})]\epsilon_{\rm xc}(\bar{\rho}(\boldsymbol{r}))\,, \tag{24}$$

where $\epsilon_{\rm xc}(\bar{\rho}(\boldsymbol{r}))$ is the xc energy per particle of the uniform electron gas with an effective electron gas density $\bar{\rho}(\boldsymbol{r})$. To carry out numerically Eq. (24), we need the quantum DCF and the radial distribution function which can be obtained from the quantum analog of the IET. Either quantum DFTs or classical DFTs, what is used directly is the potential, i.e., the first DCF for the case of classical system and the multiplicative xc-potential $v_{\rm xc}(\boldsymbol{r};[\,\rho]\,)$ for the case of quantum system. From the definition of $v_{\rm xc}(\boldsymbol{r};[\,\rho]\,)$, we know that the classical analog of $v_{\rm xc}(\boldsymbol{r};[\,\rho]\,)$ is the first-order DCF, so the above SWDA-correction factor can be extended to the quantum case. The required inputs are the quantum analog of the second- and first-order DCFs which can be obtained by quantum Monte Carlo simulation[21,22] and integral equation theory.[16]

## 3 Concluding Remarks

All the previous formulations of the weighted density-type approximations use the same essential inputs, namely, the second-order DCF of the uniform fluid, but $g(\boldsymbol{r})$ of the uniform fluid is not explicitly employed. Otherwise, the SWDA with the correct factor should not be more accurate than the SWDA. The present contribution indicates clearly that incorporation of $g(\boldsymbol{r})$ of the uniform fluid into the weighted density-type approximation can greatly improve on the prediction accuracy and points out a new direction in an effort to generate better approximate density functional by incorporating the knowledge of $g(\boldsymbol{r})$ of the uniform fluid from IET for uniform system. However, it should be noted that a generalized DFT[23] was proposed, the key point of the generalized DFT is the determination of the scaling function. Obviously the present paper also suggests a systematic method to specify the scaling function.

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