A self-consistent approach for modelling the interfacial properties and phase diagrams of Yukawa, Lennard-Jones and square-well fluids

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A self-consistent density-functional approach is presented for describing the phase behaviour and interfacial tensions of van der Waals fluids represented by the hard-core Yukawa (HCY), Lennard-Jones (LJ) and square-well (SW) potentials. The excess Helmholtz energy functional is formulated in terms of a modified fundamental measure theory (MFMT) for the short-ranged repulsion and a density-gradient expansion for the van der Waals attractions. Analytical expressions for the direct correlation functions of uniform fluids are utilized to take into account the effect of van der Waals’ attraction on intermolecular correlations. For bulk phases, the density functional theory is reduced to an equation of state (EOS) that provides accurate saturation pressures and vapour–liquid phase diagrams. Near the critical region, the long-range fluctuations can be corrected by using the renormalization group (RG) theory. With the same set of molecular parameters, the theory also yields satisfactory surface tensions and interfacial density profiles at all relevant temperatures.

1. Introduction

The vapour–liquid phase diagrams and interfacial tensions represent two kinds of thermophysical properties that are important for a plethora of engineering applications [1]. Conventionally, different theoretical models are used to calculate phase diagrams and interfacial properties. While the phase behaviour of a fluid can be described by a van der Waals-type cubic equation of state or a more sophisticated statistical-thermodynamic theory, interfacial properties are often represented by a different theoretical framework such as the square-gradient theory. Different sets of molecular parameters may be required for the same fluid. However, as demonstrated over a century ago by van der Waals and Kohn-Stamm [2], such inconsistency is certainly not an inherited limitation of statistical mechanics, based on which both bulk and interfacial theories are formulated. In recent years, there has been rejuvenated interest in establishing a self-consistent approach to quantitatively describe both bulk and interfacial properties using a single set of molecular parameters [3–9].

In principle, a classical density functional theory (DFT) is applicable to correlating both bulk and interfacial properties [10, 11]. Following the ideas proposed in van der Waals’ original work, Bongiorno and Davis constructed a virtual DFT where the repulsive part of the free energy functional is formulated in terms of a local density approximation (LDA) while the attractive part is calculated in the framework of the Weeks–Chandler–Anderson (WCA) first-order perturbation theory [12]. Although the modified van der Waals theory yields satisfactory vapour pressures as well as surface tensions of argon over a broad range of temperatures, it fails to reproduce the exact results predicted by the linear-response theory at limiting conditions. Besides, the square-gradient approximation is inadequate for capturing the density oscillations as expected for liquids near a hard wall. A more concise theory based on quadratic density expansion was proposed by Ebner et al. [13] who, to the authors’ assertion, were the first to introduce the terminology of DFT into the statistical mechanics of classical fluids. Although this theory overcomes a number of limitations of the modified van der Waals theory, its numerical performance is satisfactory neither for the bulk phase diagram nor for the surface tensions. In general, the quadratic approximation is not very accurate for systems with both attractive and repulsive components in the intermolecular potential and it is insufficient to predict the phase
transitions. Later applications of the density functional theory to modeling the interfacial properties of fluids are primarily focused on various weighted density approximations (WDA) for the repulsive part of the Helmholtz energy functional [10] while the attractive contribution is taken into account using the mean-field approximation [14], perturbation theory [15–17] or density expansions [18, 19]. One major problem with the mean-field approximation is that for uniform fluids, the Helmholtz energy functional reduces to an equation of state that is only qualitative under most circumstances. Moreover, it under predicts the critical temperature which results in unphysical surface tensions in the critical region. Both the perturbation approaches and density expansions for the attractive Helmholtz energy functional yield satisfactory results for the bulk phase diagram as well as interfacial properties. However, these approaches involve direct or pair correlation functions that must be solved numerically from the Ornstein–Zernike equation. As a result, implementation of these more sophisticated methods is often computationally challenging and the assessment of the assumptions involved in these theories is quite difficult.

The purpose of this work is to develop a numerically accurate, yet computationally convenient density-functional theory, that is applicable to predicting both bulk and interfacial properties using a single set of molecular parameters. While the main focus here is on simple fluids represented by three conventional intermolecular potentials: hard-core attractive Yukawa (HCY) potential, Lennard-Jones (LJ) potential and square-well (SW) potential, we wish to extend similar procedures for more sophisticated systems in the future work by introducing the repulsive part of the attractive Helmholtz energy functional $F[\rho(\mathbf{r})]$ through the Legend transformation

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] - \mu \int \rho(\mathbf{r}) \, d\mathbf{r},$$

where $d\mathbf{r}$ represents an infinitesimal volume.

For a simple fluid in which the intermolecular potential consists of a short-ranged repulsion and a long-ranged van der Waals attraction, the Helmholtz energy functional can be formally expressed as

$$F[\rho(\mathbf{r})] = F^{\text{id}}[\rho(\mathbf{r})] + F^{\text{at}}[\rho(\mathbf{r})] + F^{\text{disp}}[\rho(\mathbf{r})],$$

where $F^{\text{id}}[\rho(\mathbf{r})]$ corresponds to that for an ideal gas with the same density profile, and $F^{\text{at}}[\rho(\mathbf{r})]$ and $F^{\text{disp}}[\rho(\mathbf{r})]$ stand for the contributions due to the repulsion and dispersion attractions respectively. The Helmholtz energy functional of an ideal gas is known exactly

$$F^{\text{id}}[\rho(\mathbf{r})] = kT \int d\mathbf{r} \{ \rho(\mathbf{r}) [\ln \rho(\mathbf{r}) A^3 - 1] \},$$

where $k$ is the Boltzmann constant, $T$ is the absolute temperature and $A$ denotes the thermal wavelength.

2.1. Hard-sphere model for the short-ranged repulsion

The Helmholtz energy functional due to the short-ranged repulsions can be represented by that for hard spheres. In this work, this term is described by the mean-field approximation (MFT) proposed by Yu and Wu [24] and independently by Roth et al. [25]. This modification preserves all the advantages of the original MFT and gives improved structural and thermodynamic properties of hard-sphere fluids in the bulk and at inhomogeneous conditions as well. As in the original MFT [26], MFMT conjectures that the excess intrinsic Helmholtz energy functional can be expressed in the form of

$$F^{\text{hs}}[\rho(\mathbf{r})] = kT \int d\mathbf{r} [f^{\text{hs}}[n_\alpha(\mathbf{r})]],$$

where the local Helmholtz density $f^{\text{hs}}[n_\alpha(\mathbf{r})]$ is a function of six scalar and vector weighted densities $n_\alpha(\mathbf{r})$ defined as

$$n_\alpha(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') w^{(\alpha)}(\mathbf{r} - \mathbf{r}').$$
The weight functions \( w^{(a)}(r) \) with the indices \( a = 0, 1, 2, 3, V_1, V_2 \) are linked to the geometry of a single particle of radius \( R \)

\[
w^{(2)}(r) = \delta(R - r), \quad w^{(3)}(r) = \Theta(R - r), \quad w^{(V)}(r) = (r/R)\delta(R - r),
\]

(7)

\[
n_0(r) = \frac{n_2(r)}{4\pi R^2}, \quad n_1(r) = \frac{n_2(r)}{4\pi R}, \quad n_{V_1}(r) = \frac{n_{V_2}(r)}{4\pi R}.
\]

(8)

While the local Helmholtz density \( f^{hs}[n_a(r)] \) in the original FMT is formulated in the framework of the scaled-particle theory, MFMT takes the advantages of the more accurate Carnahan–Starling equation of state for hard spheres [27]. The local Helmholtz density is divided into scalar (denoted by the superscript S) and vector (denoted by the superscript V) contributions

\[
f^{hs}[n_a(r)] = f^S[n_a(r)] + f^V[n_a(r)],
\]

(9)

with

\[
f^S[n_a] = -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \left[ \frac{\ln(1 - n_3)}{36\pi n_5^2} + \frac{1}{36\pi n_3(1 - n_3)^2} \right] n_3^2,
\]

(10)

\[
f^V[n_a] = -\frac{n_{V_1} \cdot n_{V_2}}{1 - n_3} - \left[ \frac{\ln(1 - n_3)}{12\pi n_5^2} + \frac{1}{12\pi n_3(1 - n_3)^2} \right] n_3 n_{V_1} \cdot n_{V_2}.
\]

(11)

The scalar part is identical to that from the Carnahan–Starling equation of state [27]. In the limit of a uniform fluid, the two vector-weighted densities \( n_{V_1}(r) \) and \( n_{V_2}(r) \) as well as the vector Helmholtz energy vanish and equation (9) becomes identical to that from the Carnahan–Starling equation [27].

Both hard-core Yukawa (HCY) and square-well (SW) potentials have distinctive separation between the short-ranged repulsion and the longer-ranged van der Waals attractions. However, for the LJ potential

\[
u(r) = 4\varepsilon \left( \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right)
\]

(12)

where \( \sigma \) and \( \varepsilon \) are the size and energy parameters as usual and both repulsive and attractive components span the entire range of intermolecular separations. To apply the hard-sphere model, the short-ranged repulsion and longer-ranged attraction are split following the method proposed by Barker and Henderson [28]

\[
u_{rep}(r) = \begin{cases} 
4\varepsilon \left( \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right), & r < \sigma, \\
0, & r > \sigma,
\end{cases}
\]

\[
u_{at}(r) = \begin{cases} 
0, & r < \sigma, \\
4\varepsilon \left( \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right), & r > \sigma.
\end{cases}
\]

The short-ranged repulsion as given by equation (13) can be approximated by a hard-sphere potential with an effective diameter of

\[
d = \int_0^{\sigma} (1 - \exp(-\beta u_{rep}(r))) dr.
\]

Equation (15) can be accurately reproduced by [29]

\[
d = \frac{1 + 0.29777T^*}{1 + 0.331637T^* + 1.0477 \times 10^{-3}T^*},
\]

(16)

where \( T^* = kT/\varepsilon \). Equation (15) is attainable by minimizing the difference in free energy between the reference fluid with only the short-ranged repulsion and the effective hard-sphere fluid.

2.1.2. Quadratic density expansion for the attractive interactions

We apply the quadratic density expansion for the attractive part of the Helmholtz energy functional

\[
\int d\rho \left[ \frac{\rho^2}{4} + \frac{kT}{4} \int d\rho \left( \phi(\rho) - \phi(\rho') \right)^2 \right] ^{1/2},
\]

(17)

where \( \phi_0^{dis}[\rho(r)] \) is the attractive Helmholtz energy of a uniform fluid of density \( \rho(r) \) and \( \phi(\rho(r) - \rho(r'))^2 \) denotes the attractive part of the direct correlation function at an average density of

\[
\tilde{\rho} = \frac{\rho(r) + \rho(r')}{2}.
\]

The Helmholtz energy densities of bulk HCY and LJ fluids have been derived from mean-spherical approximations (MSA) [30, 31]. For a bulk SW fluid, an analytical expression of \( \phi_0^{dis}[\rho(r)] \) can also be obtained by using the first-order perturbation theory [32]. The analytical expressions for the direct correlation functions of bulk Yukawa and LJ fluids were recently reported by Tang [33]. These equations provide an essential input for the implementation of our DFT. However, for SW fluids
the reported analytical expressions of DCF [34, 35] are applicable only when the attraction is short ranged.

It should be emphasized that the quadratic expansion applied in this work is different from that in the classical density functional theory by Ebner et al. [13] or the conventional square-gradient approaches. Here the expansion does not apply to the repulsive part of the Helmholtz functional, which is already represented by an accurate non-local density-functional theory for hard spheres. Unlike conventional quadratic theories, our approach is able to predict the phase transitions at least in principle.

2.2. Renormalization-group (RG) theory

Although a non-mean-field DFT is able to account for the short-range correlations due to the intermolecular forces, it is generally inadequate to represent the long-range fluctuations near the critical point of vapour–liquid equilibrium. For that purpose, we employ a renormalization-group (RG) theory of classical fluids originally proposed by White and Zhang [36–40]. During the renormalization-group iteration, a sequence of corrections to the Helmholtz energy density, \( \delta f_n \), \( n = 1, 2, \ldots \), are added to the initial Helmholtz energy density, \( f_0(\rho) = f_0[\hat{\rho}(r)] \), which ignores the contributions due to long-wavelength fluctuations. The recursion equation is given by [41]

\[
f_n(\rho) = f_{n-1}(\rho) + \delta f_n(\rho),
\]

where the differential Helmholtz energy density \( \delta f_n \) is calculated from

\[
\delta f_n(\rho) = -K_n \ln \frac{Q_n^x}{Q_n^r}, \quad 0 \leq \rho < \rho_{\max}/2,
\]

with

\[
K_n = \frac{1}{\beta V_{p,n}} = \frac{1}{2\pi \beta L^3},
\]

\[
Q_n^x(\rho) = \int_0^\rho dx \exp \left\{ -f_n^x(\rho + x) + f_n^x(\rho - x) - 2f_n^r(\rho) \right\},
\alpha = s, l,
\]

\[
f_n^s(\rho) = f_{n-1}(\rho) + \alpha \rho^2,
\]

\[
f_n^l(\rho) = f_{n-1}(\rho) + \alpha \rho^2 \frac{\psi \sigma^2}{2^{n+1} L^2}, \quad \left( L = \frac{L}{\sigma} \right).
\]

In equations (20)–(24), \( \rho_{\max} \) is the maximum possible molecule density, and \( \alpha \) and \( \tilde{\omega}^2 \) depend on the intermolecular potential \( u(r) \):

\[
\alpha = -\frac{1}{2} \int u(|r - r'|) \, dr
\]

and

\[
\tilde{\omega}^2 = -\frac{1}{3 \sigma \alpha r} \int r^2 u(|r - r'|) \, dr.
\]

Table 1 gives the analytical expressions of \( \alpha \) and \( \tilde{\omega} \) for the potentials investigated in this work. The parameters \( L \) and \( \psi \) are obtained by fitting to the critical temperature and pressure from simulations. The values of these parameters for the three model fluids are also listed in table 1. In principle, the RG iteration can also be applied to the Helmholtz energy density in the DFT theory to take into account the long-range fluctuations. However, we did not include RG in the minimization of the grand potential for numerical concerns.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Hard-core Yukawa (HCY)</th>
<th>Lennard-Jones (LJ)</th>
<th>Square-well (SW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u(r) )</td>
<td>( \begin{cases} \infty, &amp; r \leq \sigma \ -e^{-\lambda(r/\sigma - 1)} &amp; r &gt; \sigma \end{cases} )</td>
<td>( 4\pi \left( \frac{a\rho^2 - \sigma^6}{\rho^6} \right) )</td>
<td>( \begin{cases} \infty, &amp; r \leq \sigma \ -e^{-\lambda(r/\sigma - 1)} &amp; \sigma &lt; r \leq \lambda \sigma \ 0, &amp; r &gt; \lambda \sigma \end{cases} )</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>( 2\pi e \frac{1 + \lambda}{\lambda^2} )</td>
<td>( 5.58 e )</td>
<td>( 2\pi e \frac{\lambda}{3} )</td>
</tr>
<tr>
<td>( \tilde{\omega}^2 )</td>
<td>( \frac{1}{3} \left( 6 + 6 \lambda + 3 \lambda^2 + \lambda^3 \right) )</td>
<td>( 1.27 )</td>
<td>( \frac{\lambda}{5} )</td>
</tr>
<tr>
<td>( \psi )</td>
<td>10.0</td>
<td>8.0</td>
<td>7.0</td>
</tr>
<tr>
<td>( 1/L )</td>
<td>0.6</td>
<td>0.5</td>
<td>0.5</td>
</tr>
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</table>
3. Results and discussion

3.1. Vapour–liquid phase diagrams

For bulk phase-equilibrium calculations, the DFT reduces to an equation of state that is equivalent to a conventional perturbation theory. With the RG correction, the Helmholtz free energy has no analytical expression. As a result, both pressure and chemical potential as required in the vapour–liquid equilibrium calculations must be obtained via numerical methods.

Figures 1–3 present the vapour–liquid coexistence curves and the saturation pressures of model van der Waals fluids in comparison with the simulation results from the literature. Also shown in these figures are the results from the corresponding equations of state without the RG correlation. As expected, the analytical

Figure 1. (a) Phase diagrams and (b) the reduced saturation pressures ($\rho^* = \rho \sigma^3$) of hard-core Yukawa (HCY) fluids with $\lambda = 1.8$, 3.0 and 4.0. (Symbols: simulation data [42, 43], lines: —: with RG correction, - - - -: without RG correction.)

Figure 2. (a) Phase diagrams and (b) the reduced saturation pressures ($\rho^* = \rho \sigma^3$) of Lennard-Jones (LJ) fluids. Here $R$ stands for the cut off length, and $L$ is the box length. (Symbols: simulation data, ◊ [44], O [45]; lines: —: with RG correction, - - - -: without RG correction.)
theories predict much too high critical temperatures. With the RG correlation, the equations of state are able to represent both the bulk phase behaviour and thermodynamic properties accurately.

3.2. Surface tension

Using the coexisting vapour and liquid densities obtained from the phase-diagram calculations, we can calculate the equilibrium density $\rho(r)$ across the vapour–liquid interface from the DFT. Because the density varies only in the direction perpendicular to the interface ($z$ direction), the Euler–Lagrange equation becomes:

$$
\left( \frac{\partial f^{id}[\rho(z)]}{\partial \rho(z)} + \frac{\partial f^{hs}[\rho(z)]}{\partial \rho(z)} + \frac{\partial f^{dis}[\rho(z)]}{\partial \rho(z)} \right) - \mu = 0. \tag{27}
$$

Detailed expressions for the partial derivatives appearing on the left-hand side of equation (27) are given in the appendix.

Equation (27) is solved using the standard Picard method. Specifically, the initial guess for the density profile is given by

$$
\rho(z) = \begin{cases} 
\rho^V, & z \leq 0, \\
\rho^L, & z > 0.
\end{cases} \tag{28}
$$

The density $\rho(z)$ is updated using equation (27) and the process is continued until a convergence is achieved.

Figures 4 to 6 present, respectively, the interfacial density profiles for the HCY fluids with $\lambda = 1.8$, the LJ fluid and the SW fluid with $\lambda = 1.5$. In all cases, the density profile varies smoothly between the bulk densities as predicted from the classical square-gradient theory. We did not find simulation data for a direct comparison of the predicted density profiles. However, as shown in table 2, the surface thicknesses of the HCY
fluid predicted from the present theory agree well with those from molecular simulations [46]. Here the thickness of the interfaces is calculated by the so-called ‘10%-to-90%-width’ method, i.e. the width of the interface is defined as the distance over which the density changes from \( \rho^\text{v} + 0.1(\rho^\text{l} - \rho^\text{v}) \) to \( \rho^\text{v} + 0.9(\rho^\text{l} - \rho^\text{v}) \) [47].

Once we have the interfacial density profile, the surface tension can be calculated from

\[
\gamma = \int_{-\infty}^{\infty} \left[ f(\rho(z)) - \rho(z) \mu + P \right] dz, \tag{29}
\]

where \( P \) stands for pressure. Figure 7 depicts the surface tensions of the HCY fluids obtained from three density functional approaches: (1) LDA and MFA, (2) the density-gradient theory and (3) the current work. With accurate liquid and vapour densities as the input, all three approaches correctly capture the

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**Table 2. Surface thickness of HCY fluids obtained by the 10%-90% rule.**

<table>
<thead>
<tr>
<th>( T^* )</th>
<th>Theory</th>
<th>MD [46]</th>
<th>MC [46]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>3.23</td>
<td>2.83</td>
<td>2.77</td>
</tr>
<tr>
<td>0.95</td>
<td>3.63</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>4.5</td>
<td>4.06</td>
<td>3.79</td>
</tr>
<tr>
<td>1.05</td>
<td>5.03</td>
<td>4.55</td>
<td>4.42</td>
</tr>
<tr>
<td>1.1</td>
<td>6.03</td>
<td>6.03</td>
<td>5.98</td>
</tr>
<tr>
<td>1.15</td>
<td>7.43</td>
<td>7.18</td>
<td>9.35</td>
</tr>
</tbody>
</table>

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**Legend:** 
- ●: MC value [46], ■: MD values [46]; lines: — predicted by the current DFT, – – predicted by the density gradient theory [8] and - - - predicted by MFA and LDA.)

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**Figure 5.** Interfacial density profiles of LJ fluids predicted from the density functional theory.

**Figure 6.** Interfacial density profiles of SW fluids with \( \lambda = 1.5 \) predicted from the density functional theory.

**Figure 7.** The reduced surface tensions (\( \gamma^* = \gamma \sigma^2 / \epsilon \)) of HCY fluids with \( \lambda = 1.8, 3.0 \) and 4.0. (Symbols: ● MC value [46], ■: MD values [46]; lines: — predicted by the current DFT, – – predicted by the density gradient theory [8] and - - - predicted by MFA and LDA.)
qualitative features of the dependence of the interfacial tension as a function of temperature. However, by comparison with the corresponding results from molecular simulations, we find that the quantitative performance of the first approach is poor for both phase equilibria and surface tensions. In this approach, both the long-range and short-range correlations are ignored. Whereas the second approach gives satisfactory results for the surface tensions and it is reducible to an accurate bulk equation of state, as in a typical density-gradient theory, it is unable to capture the density oscillations near a hard surface and the phase transitions. In contrast, the third approach is numerically more satisfactory by correctly taking into account both the long-range and short-range correlations. Figure 8 compares the surface tensions predicted from the current DFT with the results from simulations for the LJ fluid. For the SW fluids, as mentioned earlier, the available DCFs in the literature are applicable only when the attraction is short-ranged ($\lambda < 1.15$). Figure 9 presents only the surface tensions predicted from LDA and MFA. We find that as the range of attraction increases, the first-order perturbation theory becomes less satisfactory. We expect that the numerical performance can be further improved if a more accurate direct correlation function for the corresponding bulk fluids is available.

4. Conclusions

We have shown that with the direct correlation functions for the bulk fluids as the input, it is feasible to construct a density functional theory that yields accurate bulk phase behaviour and interfacial properties using a single set of molecular parameters. For simple fluids as represented by conventional intermolecular potentials, analytical expressions for the direct correlation functions have been reported before. Extension of similar approaches to more complicated systems is also feasible at least in principle. For systems containing spherical particles, the direct correlation functions may be obtained by numerically solving the Ornstein–Zernike (OZ) equation using a conventional closure such as the hypernetted-chain (HNC) approximation. Although the OZ equation may lose solution inside the vapour–liquid coexistence, approximate direct correlation functions can be attained by interpolation or extrapolation techniques. An alternative way to avoid the problem is by using a reference system that involves only the physically stable bulk phases as defined in the Gibbs dividing interface. In that case, direct correlation functions are always numerically attainable. For polymeric fluids, the direct correlation functions can also be attained by solving the PRISM equations [48]. Alternatively,
as demonstrated in our previous publications [21, 22],
the Helmholtz energy functional can be formulated
in terms of non-local density approximations. In
both approaches, a self-consistent molecular theory
for both bulk and interfacial properties can be
achieved.

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Appendix: Detailed expressions for equation (28)
The partial derivatives of the ideal-gas and hard-
sphere Helmholtz energy densities with respect to
two number densities are given by

\[ \frac{\partial f_{id}^{\alpha}(\rho(z))}{\partial \rho(z)} = kT \ln \left[ \rho(z)A^\alpha \right], \quad (A1) \]
\[ \frac{\partial f_{id}^{\alpha}(\rho(z))}{\partial \rho(z)} = \int_{z-R}^{z+R} \sum_{\alpha} \frac{\partial f_{id}^{\alpha}(n_{\alpha}(z'))}{\partial n_{\alpha}(z')} W^{(\alpha)}(z, z') \, dz', \quad (A2) \]

where \( f_{id}^{\alpha}(\rho(z)) \) is the attractive Helmholtz energy
density of a uniform fluid with density \( \rho(z) \). Accordingly, on the
LDA, \( \partial f_{id}^{\alpha}(\rho(z))/\partial \rho(z) \) is given by

\[ \frac{\partial f_{id}^{\alpha}(\rho(z))}{\partial \rho(z)} = \gamma_{id}(\rho(z)) \rho(z)^2 + Z_{id}(\rho(z)), \quad (A3) \]

where \( Z_{id}(\rho(z)) \) is the compressibility factor due to
the attractive contribution in the uniform fluid. Using the
weighted densities as appeared in the fundamental
measure theory, we may express \( \partial f_{id}^{\alpha}(\rho(z))/\partial \rho(z) \) as

\[ \frac{\partial f_{id}^{\alpha}(\rho(z))}{\partial \rho(z)} = \int_{z-R}^{z+R} \sum_{\alpha} \frac{\partial f_{id}^{\alpha}(n_{\alpha}(z'))}{\partial n_{\alpha}(z')} W^{(\alpha)}(z, z') \, dz'. \quad (A5) \]

In our calculations, only \( \alpha = 3 \) is taken into account
in equation (A5). We find that it is sufficient to achieve
the smooth but convergent density profiles.

\[ \frac{\partial f_{id}^{\alpha}(\rho(z))}{\partial \rho(z)} = \frac{f_1^{\alpha}(\rho(z) + \Delta \rho(z)) - f_1^{\alpha}(\rho(z) - \Delta \rho(z))}{2 \Delta \rho(z)}, \quad (A6) \]
\[ f_1^{\alpha}(\rho(z)) = \frac{kT}{4} \int [\rho(z) - \rho(z')] c((z - z')^2; \rho) \, dz', \quad (A7) \]

where the average direct correlation function
\( c((z - z'); \rho) \) is expressed as:

\[ \int_0^{2\pi} \int_{\mid \theta, r \mid} c((z - z'); \rho) \, \rho \, dr. \quad (A8) \]

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