Homogeneous properties of the renormalized density functional theory

Soon-Chul Kim

Department of Physics, Andong National University, Andong, 760-749, Korea

Abstract. We extend the renormalized density fucntional theory (RDFT), which was proposed by Groot and Van der Eerden, by using the Percus condition, and apply this to hard-sphere fluids which have a hard repulsive potential. The low-density expansion is used to calculate the fourth virial coefficient and the second-order pair correlation function for hard-sphere fluids, in which it disagrees with the exact virial expansion of the system. We compare these results with those of the standard integral equations and other weighted-density approximation theory approaches to the theory of fluids. The extended RDFT also shows that this fails at low temperatures for systems whose intermolecular potential has an attractive part, as do other weighted-density approximations.

1. Introduction

Much theoretical work has recently concentrated on how to approximate the free-energy functional, and how to apply these approximations to actual physical phenomena, i.e. the equation of state, the freezing problems which is the first-order liquid-to-solid transition, interfacial problems, elastic properties of solids, and so on. Even though many methods for approximating the free-energy functional for an inhomogeneous system have been proposed, we can generally classify these into three groups. In the first group the free-energy functional for an inhomogeneous system is written as a perturbation of the free energy about a given uniform reference homogeneous system. In the second group of approximations (Tarazona 1985, Denton and Ashcroft 1989a, b) the free-energy functional is written as a function of an effective or weighted density which is itself a locally averaged functional of the local density. Several different methods of averaging have been proposed but all make use of some properties of a reference homogeneous state and a particular assumed weighted-density function. A third group of approximations (Groot 1987, Groot and Van der Eerden 1987) are based upon the free-energy functional expansion about a 'coarse-grained' density, where the weighting function is determined by the extremal condition with respect to a 'coarse-grained' density. These approximations also have to assume knowledge of a reference homogeneous state.

However, in the free-energy version of the weighted-density approximation (WDA), we have already proposed a method of extending the WDA theories to determine the equation of state of systems for a large class of intermolecular potentials (Jones and Kim 1989, Kim and Jones 1989). Therefore, it is worthwhile to investigate its properties,

even though the renormalized density functional theory (RDFT) seems to be more complicated than the traditional methods. In section 2, we summarize the RDFT and show how to extend this theory by using the Percus condition which was used to derive the Percus–Yevick (PY) and hypernetted-chain (HNC) equations. We apply the extended RDFT theory to the hard-sphere system and obtain the fourth virial coefficient and the second-order pair distribution function. Finally we briefly discuss its properties and informal problem of the WDAS.

2. Extension of the RDFT theory

In the RDFT, the free-energy functional form $F[\rho]_{RDFT}$ is given by

$$\beta F[\rho]_{RDFT} = \int dr\, \rho(r) [\ln \rho(r) - 1 + \psi(\rho_0(r))]$$

$$- \int dr \int ds\, \rho(r) G(r, s, \rho_0(r)) [\rho(s) - \rho_0(r)] \tag{2.1}$$

where $G(r, s, \rho_0(r))$ represents the two-point coupling, and $\psi(\rho_0(r))$ is the excess free energy per particle at density $\rho_0(r)$. In equation (2.1), $\rho_0(r)$ plays the role of a free variable. Making equation (2.1) stationary with respect to $\rho_0(r)$, $\rho_0(r)$ becomes

$$\rho_0[\rho](r) = \int dr\, G'(r, s, \rho_0(r))\rho(s) \Big/ \int ds\, G'(r, s, \rho_0(r)) \tag{2.2}$$

where G' is the derivative with respect to the second argument $\rho_0(r)$. By taking the functional derivative with respect to the density functional, the weighting function $w(r, s, \rho(r))$ is given as

$$w(r, s, \rho_0(r)) = \delta\rho_0(r)/\delta\rho(s) = G'(r, s, \rho_0(r)) \Big/ \int ds\, G'(r, s, \rho_0(r)) \tag{2.3}$$

and also satisfies the normalization condition $\int w(r, s, \rho(r)) = 1$.

Together equations (2.1)–(2.3) constitute the basic equations of the RDFT. For the first functional derivative of equation (2.1) with respect to $\rho(r)$,

$$\delta\beta F[\rho]_{RDFT}/\delta\rho(x) = \ln \rho(x) + \psi(\rho_0(r)) + \int dr\, \rho(r)\psi'(\rho_0(x)) \frac{\delta\rho_0(r)}{\delta\rho(x)}$$

$$- \int dr \int dt\, \rho(r) G(r, t, \rho_0(r)) [\rho(t) - \rho_0(r)] \frac{\delta\rho_0(r)}{\delta\rho(x)}$$

$$- \int dt\, G'(x, t, \rho_0(x)) [\rho(t) - \rho_0(x)]$$

$$- \int dr \int dt\, \rho(r) G(r, t, \rho_0(r)) \left(\delta(t - x) - \frac{\delta\rho_0(r)}{\delta\rho(x)} \right). \tag{2.4}$$

By taking the second functional derivative and imposing the reproduction of the bulk

direct correlation, the direct correlation function is given at $\rho(r) = \rho_0(r) = \rho$; after some manipulation,

$$c^{(2)}(r-s, \rho) = 2G(r-s, \rho) + \rho \int dt \, G'(r-t, \rho)G'(t-s, \rho) \Big/ \int dt \, G'(r-t, \rho).$$

$$(2.5)$$

Integrating over r and using the normalization condition gives the compressibility sum rule for uniform fluids:

$$\int dr \, c^{(2)}(r, \rho) = 2 \int dr \, G(r, \rho) + \rho \int dr \, G'(r, \rho).$$

$$(2.6)$$

To extend this theory, we consider the Percus (1964) condition which was used to derive the PY and HNC equations. The Percus condition is simply the statement that there is an exact relationship between the pair correlation function $g(r, t)$ of the system with no external potential and the density distribution of the same system in an external potential $u(r) = \varphi(r, t)$ provided by a fixed particle at t:

$$\rho(r)g(r, t)|_0 = \rho(r)|_{u(r)=\varphi(r,t)} \quad (2.7)$$

where the subscripts indicate that quantities on the left are evaluated in a zero external field while the local density on the right is evaluated in the external field $u(r) = \varphi(r, t)$. From equations (2.4), (2.7) and the exact relation for the free-energy functional (Evans 1979, Jones 1987) given by

$$\delta\beta F[\rho]/\delta\rho(r) = -\beta u(r) + \beta\mu - 3\beta \ln \Lambda \quad (2.8)$$

eliminating the chemical potential μ between a homogeneous and an inhomogeneous state gives

$$\beta\varphi(x-t) = -\ln g(x-t) - \psi(\rho) - \rho\psi'(\rho) + \psi(\rho_0(x-t))$$

$$+ \rho\psi'(\rho_0(x-t)) \int dr \, g(r-t)w(r-x, \rho_0(r-t))$$

$$- \int dr \int ds \, G(r-s, \rho_0(s-t))[\rho g(s-t) - \rho_0(r-t)]$$

$$\times w(r-x, \rho_0(r-t)) - \int dr \, G'(r-x, \rho_0(r-t))[\rho g(r-t)$$

$$- \rho_0(x-t)] - \rho \int dr \int ds \, g(r-t)G(r-s, \rho_0(r-t))$$

$$\times [\delta(r-t) - w(r-x, \rho_0(r-t))] \quad (2.9)$$

where Λ is the thermal de Broglie wavelength, and $\rho_0(r-t)$ is given by, from equation (2.2),

$$\rho_0(r-t) = \rho \int w(r-s, \rho_0(r-t))g(s-t) \, dt. \quad (2.10)$$

On the other hand, we can easily obtain the relation between the excess free energy

$\psi(\rho)$ and the two-point coupling $G(r, \rho)$ by using the following exact relation for the uniform fluids:

$$\partial c^{(1)}/\partial\rho = \int dr\, c^{(2)}(r, \rho). \tag{2.11}$$

Then, from equations (2.6), (2.9) and the exact compressibility equation (Groot 1987), one obtains

$$\psi'(\rho) = -\int dr\, G(r, \rho). \tag{2.12}$$

Here, note that equation (2.12) is a very useful relation to simplify the extended RDFT and, in particular, to derive the second-order pair correlation function $g_2(r)$ of equation (2.15) in a low-density approximation. In addition we have the usual Ornstein–Zernike relation between $c^{(2)}(r, \rho)$ and $g(r, \rho)$:

$$c^{(2)}(r - t, \rho) - [g(r - t) - 1] + \rho \int ds\, [g(r - s) - 1]c^{(2)}(s - t, \rho) = 0. \tag{2.13}$$

Now the unknown functions $\psi(\rho)$, $w(r, \rho)$ (or $G(r, \rho)$), $c^{(2)}(r, \rho)$ and $g(r, \rho)$ must satisfy equations (2.3), (2.9), (2.10) and (2.13).

Since it is very difficult to solve these equations generally, we consider a low-density expansion to investigate the properties of an extended RDFT as a simple application. Now, if we assume that the four unknown functions can be expanded in a power series in the density (Jones and Kim 1989), then we can readily show that the above equations uniquely determine all coefficients in the expansions for any intermolecular potential $\varphi(r)$. In this case, the extended RDFT also gives the correct virial expression for $g_0(r)$ and $g_1(r)$, where $g_0(r)$ and $g_1(r)$ denote the first two terms in the density expansion of the pair correlation function $g(r, \rho)$:

$$g(r, \rho) = g_0(r) + \rho g_1(r) + \rho^2 g_2(r) + \rho^3 g_3(r) + \ldots. \tag{2.14}$$

However, the extended RDFT gives a different expression for $g_2(r)$, as do other free-energy theories and standard integral equations. After a lengthy but straightforward calculation, $g_2(r)$ becomes in terms of the usual Mayor graphs

$$g_2(r)/g_0(r) = -(1/3B_3)\left(\begin{array}{c}\text{graph}\end{array}\right)^2 + 2\begin{array}{c}\text{graph}\end{array} + \begin{array}{c}\text{graph}\end{array} \Big/ B_3 + \begin{array}{c}\text{graph}\end{array} \tag{2.15}$$

where B_3 is the third virial coefficient and is given in terms of the Mayor functions, i.e. $f(r) = \exp[-\beta\varphi(r)] - 1$:

$$B_3 = -\tfrac{1}{3}\int dr \int ds \int dt\, f(r - s)f(r - t)f(s - t). \tag{2.16}$$

In table 1, we compare our results with those of the WDA (Tarazona 1985, Jones and Kim 1989), the modified weighted density approximation (MWDA) (Denton and Ascroft 1989a, b, Kim and Jones 1989), the PY equation, the HNC equation, the YBG equation and the exact virial expansion. B_4 is the formal virial coefficient of pressure and is computed both from the compressibility and from the pressure equation of state. For $r \geq 1$, the extended RDFT results for $g_2(r)/g_0(r)$ give a reasonable result but are somewhat worse than those of any other theories at small r. For the fourth virial coefficient B_4, computed by either the pressure or the compressibility methods, the extended RDFT

Table 1. Results for the hard-sphere fluids with unit diameter ($B_2 = 4\pi/3$): c, compressibility method; p, pressure method.

	B_4/B_2^3	$g_2(0)/g_0(0)$	$g_2(1)/g_0(1)$	$g_2(2)/g_0(2)$
Exact†	0.2869	12.885	1.259	−0.407
RDFT	0.2076(c)	3.000	1.201	−0.407
	0.2738(p)			
WDA‡	0.2935(c)	13.269	1.266	−0.402
	0.2887(p)			
MWDA§	0.2492(c)	12.885	1.518	−0.407
	0.3460(p)			
HNC†	0.2092(c)	16.998	1.953	−0.407
	0.4453(p)			
PY†	0.2969(c)	8.225	1.097	−0.407
	0.2500(p)			
YBG†	0.3424(c)	14.256	0.988	−0.407
	0.2252(p)			

† Integral equation values are taken from Baker and Henderson (1976) and Ree *et al* (1966).
‡ Jones and Kim (1989).
§ Kim and Jones (1989).

results are much worse than the WDA result and somewhat worse than the PY equation. Judging either by agreement with the exact result or the consistency of the pressure and compressibility B_4-values the extended RDFT is substantially less accurate than the WDA and somewhat less accurate than the PY equation. On the other hand, the extended RDFT theory also fails at low temperatures for systems whose intermolecular potential has an attractive part, as does the WDA theory, because $B_3 = 0$ at a particular temperature (Baker and Henderson 1976). This suggests that there is some structure flaw, perhaps the assumed form of the free-energy functional (Percus 1988). Here we have two surprising results. The first is that the original RDFT gives a good result in the analysis of the density profile of hard-sphere fluids near a hard wall (Groot 1987, Groot and Van der Eerden 1987), but the extended RDFT (i.e. uniform fluids) does not do so. Therefore, we could think that the former result possibly comes from the use of an exact direct correlation function $c^{(2)}(r, \rho)$ as input. The second is that the extended RDFT result is less accurate than the WDA theory, but this is a very difficult problem to understand and further study is still needed in future.

3. Conclusions

In the previous section, we show that knowledge of the intermolecular potential puts constraints on the RDFT, which take the form of a small number of non-linear integral equations of unusual type and which completely determine the theories. In the extended RDFT, a low-density expansion is made, and we show that the extended RDFT is substantially less accurate than the WDA. The major problem of all weighted-density theories is that they are not applicable to systems whose intermolecular potentials have an attractive region. This suggests that there is some structure flaw as indicated by Percus (1988).

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