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LETTER TO THE EDITOR

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Abstract. We propose the modified renormalized density functional theory (MRDFT) based on a global average of the density, and investigate some properties of this theory. In this approximation, the weighting function and the weighted density are determined by minimizing the free-energy functional with respect to the 'coarse-grained' density as a free variable. We show that this approximation also leads to the usual hypernetted chain (HNC) equation of state for the homogeneous systems as do the weighted density approximation theories based on the global average of the density, even though their free-energy functional forms and the weighting functions are basically different. From the derivation in the present work and comparison with the weighted density approximation theories based on the global average of the density, we also obtain the required conditions for the weighted density approximation theories based on a global average of the density to satisfy the usual HNC equation of state for the homogeneous systems.

Many kinds of density functional approximation theories have been proposed recently to describe the problems of inhomogeneous dense fluids of various sorts—for example, the liquid–solid transition (Baus 1987 and references therein), fluid interfaces (Evans 1979, 1989), and so on. These applications have been both qualitatively and, to varying degrees, quantitatively successful. Among many free-energy functional approximations for the inhomogeneous systems, the renormalized density functional theory (RDFT) proposed by Groot and Van der Eerden (1987) seems to be the successful model, because the weighting function and the weighted density are determined by minimizing the free-energy functional with respect to the 'coarse-grained' density, unlike in other well-known weighted density approximation theories (Tarazona 1985, Denton and Ashcroft 1989, Zeng and Oxtoby 1990). However, the RDFT results (Kim 1990) for the equation of state of the hard-sphere fluids with a strongly repulsive potential are somewhat less accurate than those of the original weighted density approximation (WDA) theory which was proposed by Tarazona (1985), even though the latter obtained a reasonable result for the hard-sphere interfacial problem. Therefore, for better understanding of this formalism we propose the modified renormalized density functional theory (MRDFT) based upon a global average of the density rather than a local density itself, and investigate some properties of this theory. We will show that this approximation also leads to the usual HNC equation of state for the homogeneous systems as do the weighted density approximation theories (Denton and Ashcroft 1989, Zeng and Oxtoby 1990)

based on the global average of the density. Finally, from this derivation and comparison with the weighted density approximation theories based on the global average of the density, we will derive the required conditions for the weighted density approximation theories based on a global average of the density to satisfy the usual HNC equation of state for the homogeneous systems.

As the starting point, we consider the Helmholtz free-energy functional $F[\rho]$ of the one-particle density, which can be expressed quite generally in the form

$$F[\rho] = k_B T \int dr\, \rho(r) \left[\ln \rho(r) - 1 \right] + \int dr\, \rho(r) \psi[\rho] \tag{1}$$

where the first term on the right-hand side of (1) represents the ideal part of the free energy, $\psi[\rho]$ a local excess free-energy functional per particle which arises from the contribution of the intermolecular interaction to the free-energy functional, and k_B is the Boltzmann constant. Since the relation between the excess free energy and the chemical potential μ of the non-ideal part (Evans 1979, Groot 1987) is formally given by

$$\psi[\rho] = \int_0^1 d\zeta\, \mu[\zeta\rho] \tag{2}$$

we can expand the chemical potential μ around that of a uniform reference fluid with the 'coarse-grained' density $\hat\rho$. Then the chemical potential becomes, neglecting the higher terms greater than $n \geq 3$,

$$\mu[\rho] = \mu(\hat\rho) - k_B T \int dr_1\, c^{(2)}(r - r_1, \hat\rho)[\rho(r_1) - \hat\rho]. \tag{3}$$

Substituting (2) and (3) into (1) and defining $f(\hat\rho)$ and the two-point coupling function $G(r - r_1, \hat\rho)$ as

$$f(\hat\rho) = \int_0^1 d\zeta\, \mu(\zeta\hat\rho) \tag{4a}$$

and

$$G(r - r_1, \hat\rho) = \int_0^1 d\zeta\, \zeta c^{(2)}(r - r_1, \zeta\hat\rho) \tag{4b}$$

we can rewrite the free-energy functional (1) in the form

$$F[\rho] = k_B T \int dr\, \rho(r)[\ln \rho(r) - 1] + N f(\hat\rho)$$
$$- k_B T \left(\int dr\, \rho(r) \int dr_1\, \rho(r_1) G(r - r_1, \hat\rho) - N\hat\rho \int dr\, G(r, \hat\rho) \right) \tag{5}$$

where N is the number of particles in the system and is given by

$$N = \int dr\, \rho(r). \tag{6}$$

To obtain the weighted density $\hat\rho$ (hereafter, we will call the 'coarse-grained' density

the weighted density) and the weighting function W, minimizing the free-energy functional (5) with respect to $\hat{\rho}$ and using the exact compressibility equation (Groot 1987, Groot and Van der Eerden 1987)

$$\partial f(\hat{\rho})/\partial \hat{\rho} = -k_B T \int \mathrm{d}r\, G(r, \hat{\rho}) \tag{7}$$

the weighted density and the weighting function are given in the forms

$$\hat{\rho} = (1/N) \int \mathrm{d}r\, \rho(r) \int \mathrm{d}r_1\, \rho(r_1) W(r - r_1, \hat{\rho}) \tag{8}$$

and

$$W(r - r_1, \hat{\rho}) = G'(r - r_1, \hat{\rho}) \Big/ \int \mathrm{d}r_1 G'(r_1, \hat{\rho}) \tag{9}$$

respectively. Here the prime on G denotes the derivative with respect to $\hat{\rho}$. Taking the integration over r, we have a normalization condition

$$\int \mathrm{d}r\, W(r, \hat{\rho}) = 1. \tag{10}$$

A relation between the two-point coupling function $G(r, \hat{\rho})$ and the two-particle direct correlation function (DCF) $c^{(2)}$ follows from the defining relationship between the two-particle DCF and the second functional derivative of the excess free-energy functional $F_{ex}[\rho]$ with respect to $\rho(r)$. Explicitly, we have for homogeneous states, from (5),

$$c^{(2)}(r, \rho) = 2G(r, \rho) - (1/V)\beta \rho f''(\rho) \tag{11}$$

where V is the volume of the system. Integrating over r gives the compressibility sum rule

$$\int \mathrm{d}r\, c^{(2)}(r, \rho) = -2\beta f'(\rho) - \beta \rho f''(\rho) \tag{12}$$

where we used (7) to derive the above results.

Taken together, (5), (8), (10), (11) and (12) constitute the MRDFT theory as formulated in the RDFT theory.

Now, to investigate the homogeneous properties of MRDFT theory we use the Percus identity (Percus 1964) that was used in deriving the usual HNC and Percus–Yevick equations of state. His main idea is that the pair distribution function $g(r - t)$ of a system at chemical potential μ and zero external potential is simply related to the local density $\rho(r)$ of the same system with an external potential $u(r)$ provided by a fixed particle at t interacting with the system particles by the intermolecular potential $\varphi(r - t)$. Specifically,

$$\rho g(r - t)|_{u(r)=0} = \rho(r)|_{u(r) = \varphi(r-t)} \tag{13}$$

where the subscripts are meant to indicate that quantities on the left are evaluated in zero external field $u(r) = 0$ while the local density on the right is evaluated in the external field $u(r) = \varphi(r - t)$. Furthermore, this Percus identity gives a basic connection between

the theories of the uniform and non-uniform fluids, which can be concisely expressed by the following relation (Kim and Jones 1990, Jones and Kim 1989)

$$c^{(1)}(\rho) = c^{(1)}(r:[\rho g]) - \ln g(r) - \beta\varphi(r). \tag{14}$$

Here $c^{(1)}(r:[\rho g])$ is the one-particle DCF of a fluid whose density is made locally non-uniform by the equivalent external potential $u(r)$ arising from the presence of a particle fixed at the origin. By taking the first functional derivative of the excess free energy with respect to $\rho(r)$, the one-particle direct correlation functional becomes, from (5), (7) and (8):

$$c^{(1)}(r:[\rho]) = -\beta f(\hat{\rho}) + \beta\hat{\rho}f'(\hat{\rho}) + 2\int dr_1\,\rho(r_1)G(r-r_1,\hat{\rho})$$

$$+ (\delta\hat{\rho}/\delta\rho(r))\int dr_1\,\rho(r_1)\int dr_2\,\rho(r_2)G'(r_1-r_2,\hat{\rho})$$

$$- (\delta\hat{\rho}/\delta\rho(r))\hat{\rho}\int dr_1\,\rho(r_1)\int dr_2\,G'(r_1-r_2,\hat{\rho}). \tag{15}$$

For the uniform case $\hat{\rho} = \rho$ and (15) simply gives

$$c^{(1)}(\rho) = -\beta[f(\rho + \rho f'(\rho)]. \tag{16}$$

Now consider the non-uniform case $c^{(1)}(r:[\rho g])$. Let $\hat{\rho}'$ be the corresponding global average from (8). Using (8) and (13) in (15) gives, after a little calculation

$$c^{(1)}(r:[\rho g]) = -\beta\{f(\hat{\rho}') - \hat{\rho}'f'\} + 2\rho\int dr_1\,G(r-r_1,\hat{\rho}')g(r_1) + O(1/N) \tag{17}$$

where $O(1/N)$ indicate several terms which will vanish in the thermodynamic limit. It is very easy to show from (8) that $\hat{\rho}' = \rho + O(1/N)$ so that when (11) is used, and the thermodynamic limit of (17) is taken, we have

$$c^{(1)}(r:[\rho g]) = -\beta[f(\rho) + \rho f'(\rho)] + \rho\int dr_1\,c^{(2)}(r-r_1,\rho)[g(r_1) - 1]. \tag{18}$$

With (16) and (18), (14) yields

$$\ln g(r) = -\beta\varphi(r) + \rho\int dr_1\,c^{(2)}(r-r_1,\rho)[g(r_1) - 1]. \tag{19}$$

Finally the Ornstein–Zernike relation with (18) leads to the usual hypernetted chain equation

$$\ln g(r) = -\beta\varphi(r) + \rho\int dr_1\,[g(r-r_1) - 1][g(r_1) - 1 - \ln g(r_1) - \beta\varphi(r_1)]. \tag{20}$$

This is exactly the same result as those of the weighted density approximation theories (Denton and Ashcroft 1989, Zeng and Oxtoby 1990, Kim and Jones 1990, Kim 1991) which were used in the analysis of the freezing problem of hard-sphere liquids. Here notice that the weighting function $d_2(r, \lambda\rho)$ and the weighted density $\hat{\rho}$ in the Zeng–Oxtoby approximation theory (Zeng and Oxtoby 1990) depend on the 'charging parameter' λ. This result means that the last term of (5) does not contribute to the property of homogeneous systems, and this is clear from (15).

From the derivation in the present work and comparison with the weighted density approximation theories based on a global average of the density, it is clear that the

conditions required for the weighted density approximation theories based on a global average of the density to satisfy the usual HNC equation of state for the homogeneous systems are the following:

(i) $F_{ex}[\rho] = \mathcal{F}(\hat{\rho})$, where $\hat{\rho}$ is the weighted density based on a global average of the density; $\hat{\rho} = (1/N)\int dr\,\rho(r)\int ds\,\rho(s)W(r-s,\hat{\rho}[\rho])$.

(ii) The weighting function $W(r,\hat{\rho})$ is normalized in the homogeneous limit: $\int dr\,W(r,\rho) = 1$.

(iii) The second derivative of the excess free-energy functional $F_{ex}[\rho]$ with respect to the density yields the correct $c^{(2)}(r,\rho)$ in the homogeneous limit

$$\lim_{\rho(r)\to\rho} \frac{\delta^2 \beta F_{ex}[\rho]}{\delta\rho(r)\,\delta\rho(s)} = -c^{(2)}(r-s,\rho). \tag{21}$$

These conditions mean that such a derivation does not require the specific forms of the excess free energy $\mathcal{F}(\hat{\rho})$ and the weighting function $W(r,\rho)$: the latter does not depend on the 'charging parameter' λ of the weighting function $d_2(r,\lambda\rho)$ in the Zeng–Oxtoby approximation theory (Zeng and Oxtoby 1990), and does not depend on the specific form of the excess free energy in the MRDFT theory. Notice here that the generalized effective liquid approximation (GELA) theory which was proposed by Lutsko and Baus (1990a, 1990b) also satisfies these conditions.

On the other hand, the MRDFT theory is also expected to give an undesirable property for the n-particle DCF $c^{(n)}$ for $n \geqslant 3$ as do the weighted density approximation theories (Curtin and Ashcroft 1986, Denton and Ashcroft 1989, Kim and Jones 1990, Kim 1991) which were based on a global average of the density, because this theory is similarly based. Actually, one can show that all the n-particle DCFs for $n \geqslant 3$ vanish. This is because the functional derivatives of the weighted density $\hat{\rho}$ with respect to $\rho(r)$ for homogeneous systems vanish in the thermodynamic limit. This is clear from the form of (8), and this is a common property of the weighted density approximation theories based on a global average of the density. However, as we can see in the Zeng–Oxtoby approximation theory (Zeng and Oxtoby 1990), it is expected to give the different results for the freezing problem of the hard-sphere liquids, in which the solid is treated as a liquid with an effective liquid density.

In summary, we have considered the MRDFT theory based upon a global average of the density, and determined the weighted density and the weighting function by minimizing the free-energy functional with respect to the 'coarse-grained' density. We have shown that, just like the weighted density approximation theories based on a global average of the density, the MRDFT theory also leads to the usual HNC equation of state for homogeneous systems. From these results, we have obtained the required conditions for the weighted density approximation theories based on a global average of the density to satisfy the HNC equation of state for the homogeneous systems. As we can see from these results, an interesting question is: what forms of approximation for the homogeneous systems would correspond to other usual approximations for the uniform fluids, namely the Percus–Yevick and Yvon–Born–Green approximations? We will leave this problem as one for future study with the application of MRDFT theory.

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