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Weighted-density approximations for non-uniform classical fluids and their applications

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Abstract. We reformulate the weighted-density approximation based on a global average of the density by using the unified density-functional approach for non-uniform classical fluids which was introduced by Zeng and Oxtoby. We show that the modified weighted-density approximation (MWDA) of Denton and Ashcroft and the weighted-density approximation of Zeng and Oxtoby can be approximated as second-order truncations of exact functional expansions. Through this reformulation, we propose a new version of the modified weighted-density approximation (NMWDA) depending on the charging parameter λ and briefly discuss a basic question arising from the density-functional expansions. We show that for homogeneous systems the NMWDA and the weighted-density approximation including the higher-order contributions also lead to the usual hypernetted-chain equation of state, and the homogeneous properties of the weighted-density approximation do not depend on the detailed forms of n-particle hierarchy functions. Finally, we apply the NMWDA to the liquid–solid transition. The numerical results obtained are compared with those of computer simulations and other approximations and show good agreement with computer simulations.

1. Introduction

In a recent paper, Lutsko (1991) had reformulated three kinds of weighted-density approximation (Baus and Colot 1985, Denton and Ashcroft 1989, Lutsko and Baus 1990a, b) based on a global average of the density and shown that these approximations are second-order truncations of exact Taylor functional expansions. The essential idea underlying this reformulation is that the direct correlation functional of an inhomogeneous system can be expressed as that of a homogeneous system by means of a density-functional expansion. This reformulation also suggests a new version for the well known weighted-density approximations which are currently used in the actual applications. On the other hand, this reformulation raises some questions

(i) about the expansion of the direct correlation function for a given order parameter (e.g. $\Delta\rho(r,\lambda) = \lambda\rho(r) - \hat{\rho}[\rho]$),

(ii) about the application to simple liquid systems, i.e. the weighted-density approximation including the higher-order contributions also leads to the usual hypernetted-chain (HNC) equation of state for a homogeneous system, and

(iii) about the application to the freezing problem, i.e. which approximations give the better results.

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In this paper, we shall introduce the unified density-functional approach (Zeng and Oxtoby 1990) for non-uniform classical fluids to reformulate the weighted-density approximation based on a global average of the density. In section 2, we shall reformulate the modified weighted-density approximation (MWDA) of Denton and Ashcroft (1989) and the weighted-density approximation of Zeng and Oxtoby using the density-functional expansion. Through this reformulation, we shall propose a new version of the modified weighted-density approximation (NMWDA) depending on the charging parameter and briefly discuss a basic question arising from the density-functional expansion of the n-particle hierarchy functional d_n. In sections 3 and 4, we shall apply the NMWDA and the weighted-density approximation including the higher-order contributions to simple liquid systems and show that these approximations also lead to the usual HNC equation of state. Finally we shall apply the NMWDA to the freezing problem of hard-sphere liquids and compare our results with those of other proposed approximations.

2. Reformulation of the weighted-density approximation based on a global average of the density

We now consider the excess (Helmholtz) free energy based on a global average of the density in the form

$$\beta F[\rho]_{ex} = N f(\bar{\rho}) \tag{1}$$

where $\beta = 1/k_B T$, $N = \int d\boldsymbol{r}\, \rho(\boldsymbol{r})$ and $f(\rho)$ denotes the excess free energy per particle originating from the particle interaction. It is well known that $F[\rho]_{ex}$ is the generating functional of the n-particle direct correlation functions (DCFs) $c^{(n)}$ (Percus 1964, Hansen and McDonald 1986):

$$c^{(n)}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n; [\rho]) = -\delta^n \beta F[\rho]_{ex} / \delta\rho(\boldsymbol{r}_1) \ldots \delta\rho(\boldsymbol{r}_n). \tag{2}$$

Following the unified density-functional approach (Zeng and Oxtoby 1990) for non-uniform classical fluids, we define the n-particle hierarchy functional d_n using the generating functional $\bar{\rho} = N\bar{\rho}$:

$$d_n(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n; [\rho]) = \delta^n \bar{\rho}[\rho] / \delta\rho(\boldsymbol{r}_1) \ldots \delta\rho(\boldsymbol{r}_n). \tag{3}$$

Taking the functional integration from an initial density $\rho_i(\boldsymbol{r}) = 0$ (note that $\rho[\rho_i] = 0$) to a final density $\rho(\boldsymbol{r})$ along a linear path $\rho_\lambda = \lambda\rho(\boldsymbol{r})(0 < \lambda < 1)$, we obtain for $n = 2$

$$\begin{aligned}\bar{\rho}[\rho] &= \int d\boldsymbol{r}_1\, \rho(\boldsymbol{r}_1) \int d\boldsymbol{r}_2\, \rho(\boldsymbol{r}_2) \int_0^1 d\lambda \int_0^\lambda d\lambda'\, d_2(\boldsymbol{r}_1, \boldsymbol{r}_2; [\lambda'\rho]) \\ &= \int d\boldsymbol{r}_1\, \rho(\boldsymbol{r}_1) \int d\boldsymbol{r}_2\, \rho(\boldsymbol{r}_2) \int_0^1 d\lambda\, (1-\lambda) d_2(\boldsymbol{r}_1, \boldsymbol{r}_2; [\lambda\rho])\end{aligned} \tag{4}$$

where λ is the 'charging' parameter. In the last step, we have used the identity

$$\int_0^1 d\lambda \int_0^\lambda d\lambda'\, h(\lambda') = \int_0^1 d\lambda\, (1-\lambda) h(\lambda) \tag{5}$$

valid for any $h(\lambda)$. In order to compare with the previous approximations (Denton and Ashcroft 1989, Zeng and Oxtoby 1990), we introduce the weighted density $\hat{\rho}$ and weighting functional $w(\boldsymbol{r}_1, \boldsymbol{r}_2; [\rho])$

$$\hat{\rho}[\rho] = \frac{1}{N} \int d\boldsymbol{r}_1 \, \rho(\boldsymbol{r}_1) \int d\boldsymbol{r}_2 \, \rho(\boldsymbol{r}_2) w(\boldsymbol{r}_1, \boldsymbol{r}_2; [\rho]) \tag{6}$$

where

$$w(\boldsymbol{r}_1, \boldsymbol{r}_2; [\rho]) = \int_0^1 d\lambda \, (1-\lambda) d_2(\boldsymbol{r}_1, \boldsymbol{r}_2; [\lambda\rho]). \tag{7}$$

We first consider the type of MWDA used by Denton and Ashcroft. To recover the MWDA of Denton and Ashcroft, we somewhat more generally expand $d_2(\boldsymbol{r}_1, \boldsymbol{r}_2; [\lambda\rho])$ about a reference density $\hat{\rho}[\rho]$, rather than about a fixed reference liquid density ρ_R (Percus 1964, Evans 1979, Lutsko 1991):

$$d_2(\boldsymbol{r}_1, \boldsymbol{r}_2; [\lambda\rho]) = d_2(\boldsymbol{r}_1 - \boldsymbol{r}_2, \hat{\rho}[\rho]) + \sum_{n=3}^{\infty} \frac{1}{(n-2)!} \int d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_n \, d_n(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n, \hat{\rho}[\rho]) \times \Delta\rho(\boldsymbol{r}_3; \lambda) \, \Delta\rho(\boldsymbol{r}_4; \lambda) \ldots \Delta\rho(\boldsymbol{r}_n; \lambda) \tag{8}$$

where

$$\Delta\rho(\boldsymbol{r}; \lambda) = \lambda\rho(\boldsymbol{r}) - \hat{\rho}[\rho]. \tag{9}$$

Note here that d_n does depend on the 'charging' parameter λ. Then, the weighting functional w becomes, from equation (7),

$$w(\boldsymbol{r}_1, \boldsymbol{r}_2; [\rho]) = \tfrac{1}{2} d_2(\boldsymbol{r}_1 - \boldsymbol{r}_2, \hat{\rho}[\rho] + \int_0^1 d\lambda \, (1-\lambda) \sum_{n=3}^{\infty} \frac{a}{(n-2)!} \times \int d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_n \, d_n(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n, \hat{\rho}[\rho]) \times \Delta\rho(\boldsymbol{r}_3; \lambda) \, \Delta\rho(\boldsymbol{r}_4; \lambda) \ldots \Delta\rho(\boldsymbol{r}_n; \lambda). \tag{10}$$

In the uniform limit $\rho(\boldsymbol{r}) \to \rho$, equation (10) becomes

$$w(\boldsymbol{r}_1 - \boldsymbol{r}_2, \rho) = \tfrac{1}{2} d_2(\boldsymbol{r}_1 - \boldsymbol{r}_2, \rho) + \int_0^1 d\lambda \, (1-\lambda) \sum_{n=3}^{\infty} \frac{[(\lambda-1)\rho]^{n-2}}{(n-2)!} \times \int d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_n \, d_n(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n, \rho). \tag{11}$$

Taking the integration over $\boldsymbol{r}_2$ and comparing with equation (6), we can obtain the useful relations for a homogeneous state:

$$\int d\boldsymbol{r}_2 \, d_2(\boldsymbol{r}_1 - \boldsymbol{r}_2, \rho) = 2 \tag{12}$$

$$\int_{n-1} \ldots \int d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_n \, d_n(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n, \rho) = 0 \qquad \text{for } n \geqslant 3. \tag{13}$$

On the other hand, we can also obtain equations (12) and (13) from the successive derivatives of the excess free energy with respect to the density and the sum rule for the DCF. Neglecting the higher-order terms $n \geqslant 3$, we have

$$w(\boldsymbol{r}_1 - \boldsymbol{r}_2, \rho[\rho]) \simeq \tfrac{1}{2} d_2(\boldsymbol{r}_1 - \boldsymbol{r}_2, \hat{\rho}[\rho]) \tag{14}$$

and, in the uniform limit $\rho(\boldsymbol{r}) \to \rho$, equation (11) satisfies the normalization condition

$$\int \mathrm{d}\boldsymbol{r}\, w(\boldsymbol{r}, \rho) = 1. \tag{15}$$

This is the weighting function of the MWDA which was originally introduced by Denton and Ashcroft (1989).

Secondly, we consider two types of weighted-density approximation depending on the charging parameter λ. To recover the Zeng–Oxtoby approximation in the same way as the MWDA, we first of all expand $d_2(\boldsymbol{r}_1, \boldsymbol{r}_2; [\lambda\rho])$ about a reference density $\hat{\rho}[\lambda\rho]$:

$$d_2(\boldsymbol{r}_1, \boldsymbol{r}_2; [\lambda\rho]) = d_2(\boldsymbol{r}_1 - \boldsymbol{r}_2, \hat{\rho}[\lambda\rho]) + \sum_{n=3}^{\infty} \frac{1}{(n-2)!} \int \mathrm{d}\boldsymbol{r}_3 \ldots \mathrm{d}\boldsymbol{r}_n\, d_n \times (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n, \hat{\rho}[\lambda\rho]) \Delta\rho(\boldsymbol{r}_3; \lambda)\, \Delta\rho(\boldsymbol{r}_4; \lambda) \ldots \Delta\rho(\boldsymbol{r}_n; \lambda) \tag{16}$$

where

$$\Delta\rho(\boldsymbol{r}; \lambda) = \lambda\rho(\boldsymbol{r}) - \hat{\rho}[\lambda\rho]. \tag{17}$$

Neglecting the higher-order terms $n \geqslant 3$, we obtain the Zeng–Oxtoby approximation:

$$w(\boldsymbol{r}_1, \boldsymbol{r}_2; [\rho]) \simeq \int_0^1 \mathrm{d}\lambda\, (1 - \lambda) d_2(\boldsymbol{r}_1 - \boldsymbol{r}_2, \rho[\lambda\rho]) \tag{18}$$

and, in the uniform limit,

$$\int \mathrm{d}\boldsymbol{r}\, w(\boldsymbol{r}, \rho) = \int \mathrm{d}\boldsymbol{r} \int_0^1 \mathrm{d}\lambda\, (1 - \lambda) d_2(\boldsymbol{r}, \lambda\rho) = 1 \tag{19}$$

where the higher-order terms $n \geqslant 3$ automatically cancel, because $\hat{\rho}[\lambda\rho] \to \lambda\rho$. Through this reformulation, we have shown that the MWDA and the Zeng–Oxtoby approximation can, in fact, be expressed as second-order truncations of exact density-functional expansions, albeit beginning with different reference densities. These are clear from their original assumptions as are other weighted-density approximations (Lutsko 1991).

On the other hand, this reformulation also suggests the NMWDA. To obtain the NMWDA, we consider a density-functional expansion of $d_2(\boldsymbol{r}_1, \boldsymbol{r}_2; [\lambda\rho])$ about a reference density $\lambda\hat{\rho}[\rho]$:

$$d_2(\boldsymbol{r}_1, \boldsymbol{r}_2; [\lambda\rho]) = d_2(\boldsymbol{r}_1 - \boldsymbol{r}_2, \lambda\hat{\rho}[\rho]) + \sum_{n=3}^{\infty} \frac{1}{(n-2)!} \int \mathrm{d}\boldsymbol{r}_3 \ldots \mathrm{d}\boldsymbol{r}_n\, d_n \times (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n, \lambda\hat{\rho}[\rho]) \Delta\rho(\boldsymbol{r}_3; \lambda)\, \Delta\rho(\boldsymbol{r}_4; \lambda) \ldots \Delta\rho(\boldsymbol{r}_n; \lambda) \tag{20}$$

where

$$\Delta\rho(r;\lambda) = \lambda(\rho(r) - \hat{\rho}[\rho]). \tag{21}$$

Neglecting the higher-order terms $n \geqslant 3$, the weighting function becomes

$$w(r_1, r_2[\rho]) \simeq \int_0^1 d\lambda\,(1-\lambda) d_2(r_1 - r_2, \lambda\hat{\rho}[\rho]). \tag{22}$$

This is the weighting function of the NMWDA depending on the charging parameter λ. We can see that for a homogeneous state the higher-order terms $n \geqslant 3$ do not contribute. Note here that the MWDA is similar to the modified effective-liquid approximation (MELA) (Baus 1987, Laird and Kroll 1990) which was introduced by Baus except the two-particle hierarchy function $d_2(r_1 - r_2, \lambda\hat{\rho}[\rho])$. However, the MELA has the disadvantage that for a homogeneous state it does not yield the correct $c^{(2)}(r_1 - r_2, \rho)$. Once again, we can expand $d_2(r_1 - r_2, \lambda\hat{\rho}[\rho])$ about a reference density $\hat{\rho}[\rho]$ as follows (Groot 1987):

$$d_2(r_1 - r_2, \lambda\hat{\rho}[\rho]) = d_2(r_1 - r_2, \hat{\rho}[\rho]) + \sum_{n=3}^{\infty} \frac{(\lambda-1)^{n-2}}{(n-2)!} (\hat{\rho}[\rho])^{n-2} \times \int dr_3 \ldots dr_n\, d_n(r_1, \ldots, r_n, \hat{\rho}[\rho]) \tag{23}$$

which is still exact. Taking only the first term, this approximation yields the MWDA of Denton and Ashcroft. However, we cannot say that the MWDA is a second-order approximation of the NMWDA, because if we take equation (14) we can equally well rewrite it so that the sum appears on the left-hand side. A question arising from this reformulation is which approximations in the actual applications give the better results. This is, in fact, not an easy problem, as indicated by Lutsko (1991) and Rosenfeld (1991), because all approximations are based on powers of the order parameter and the reference density used to derive these approximations appears as more or less an arbitrary rather than a fixed reference liquid density. This is actually related to the question of the convergence of the underlying expansion of $d_2(r_1, r_2; [\lambda\rho])$. Therefore, we can see that a good approximation in actual applications depends on how we choose an adequate reference density or how fast the series converge. We still need to study this problem further.

3. Applications to simple liquid systems

As an application of the NMWDA, we first consider simple liquid systems (Kim and Jones 1990, Brenan and Evans 1991, Denton and Ashcroft 1991, Kim 1991). Since the weighted density is given as

$$\hat{\rho}[\rho] = \frac{1}{N} \int dr_1\, \rho(r_1) \int dr_2\, \rho(r_2) \int_0^1 d\lambda\,(1-\lambda) d_2(r_1 - r_2, \lambda\hat{\rho}[\rho]) \tag{24}$$

and in a homogeneous state the weighting function $w(r, \rho)$ of the NMWDA satisfies

$$\int dr\, w(r, \rho) = \int dr \int_0^1 d\lambda\,(1-\lambda) d_2(r, \lambda\rho) = 1 \tag{25}$$

we can show that the NMWDA also leads to the usual HNC equation of state as do the MWDA and the Zeng–Oxtoby approximation (Kim 1991). Furthermore, we can prove that the weighted-density approximation (i.e. equation (10)) including the higher-order contributions also leads to the usual HNC equation of state and show that the homogeneous properties of the weighted-density approximation do not depend on the detailed forms of the n-particle hierarchy functions d_n. From equations (6) and (10), $c^{(1)}(\boldsymbol{r};[\rho])$ and $c^{(2)}(\boldsymbol{r},\rho)$ are given as

$$\beta^{-1}c^{(2)}(\boldsymbol{r},\rho) = 2f'(\rho)w(\boldsymbol{r},\rho) + (1/V)\rho f''(\rho) \tag{26}$$

and

$$\begin{aligned}\beta^{-1}c^{(1)}(\boldsymbol{r};[\rho]) = f(\hat{\rho}) + f'(\hat{\rho})\Bigg(&\frac{1}{N}\int d\boldsymbol{r}_1\,\rho(\boldsymbol{r}_1)\int d\boldsymbol{r}_2\,\rho(\boldsymbol{r}_2)w(\boldsymbol{r}_1,\boldsymbol{r}_2;[\rho]) \\ &- 2\int d\boldsymbol{r}_2\,\rho(\boldsymbol{r}_2)w(\boldsymbol{r}_1,\boldsymbol{r}_2;[\rho])\Bigg) \\ &\times\left(1-\frac{1}{N}\int d\boldsymbol{r}_1\,\rho(\boldsymbol{r}_1)\int d\boldsymbol{r}_2\,\rho(\boldsymbol{r}_2)w'(\boldsymbol{r}_1,\boldsymbol{r}_2;[\rho])\right)^{-1}\end{aligned} \tag{27}$$

where the weighted density is

$$\begin{aligned}\hat{\rho}[\rho] = \frac{1}{N}\int d\boldsymbol{r}_1\,\rho(\boldsymbol{r}_1)\int d\boldsymbol{r}_2\,\rho(\boldsymbol{r}_2)\Bigg(&\tfrac{1}{2}d_2(\boldsymbol{r}_1-\boldsymbol{r}_2,\hat{\rho}[\rho]) + \sum_{n=3}^{\infty}\frac{1}{(n-2)!}\int_0^1 d\lambda\,(1-\lambda) \\ &\times\int d\boldsymbol{r}_3\ldots d\boldsymbol{r}_n\,d_n(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n,\hat{\rho}[\rho]) \\ &\times\Delta\rho(\boldsymbol{r}_3;\lambda)\,\Delta\rho(\boldsymbol{r}_4;\lambda)\ldots\Delta\rho(\boldsymbol{r}_n;\lambda)\Bigg).\end{aligned} \tag{28}$$

Substituting equation (26) into equation (27) and using the exactly known relation (Kim and Jones 1990)

$$c^{(1)}(\rho) = c^{(1)}(\boldsymbol{r};[\rho g]) - \ln[g(\boldsymbol{r},\rho)] - \beta\phi(\boldsymbol{r}) \tag{29}$$

we can obtain the HNC closure after some manipulation. Here $g(\boldsymbol{r},\rho)$ is the pair correlation function, and $\phi(\boldsymbol{r})$ the intermolecular potential of the system. Therefore, we can conclude that the homogeneous property of the weighted-density approximation does not depend on the detailed forms of the n-particle hierarchy functions d_n. This result coincides with that of Kim (1991) and confirms once again that, if the three required conditions suggested in Kim's (1991) paper are satisfied, the weighted-density approximations lead to the HNC equation of state. Furthermore, we can easily prove that these kinds of weighted-density approximation do not generate the n-particle direct correlation functions for $n \geqslant 3$, because

$$\lim_{\rho(\boldsymbol{r})\to\rho}\{\delta^n\hat{\rho}[\rho]/\rho(\boldsymbol{r}_1)\ldots\rho(\boldsymbol{r}_n)\} \to 0 \text{ (in the thermodynamic limit).} \tag{30}$$

Table 1. Freezing parameters for the hard-sphere liquid–solid transition: average solid density ρ_s, liquid density ρ_L, change $\Delta\rho$ in density and Lindemann parameter $L = (3/\alpha a^2)^{1/2}$ for the FCC solid with a being the FCC lattice constant given by $a = (\rho_s/4)^{1/3}$, where σ is the hard-sphere diameter.

	$\rho_s\sigma^3$	$\rho_L\sigma^3$	$\Delta\rho\sigma^3$	L
Simulation [a]	1.041	0.943	0.10	0.126
NMWDA [b]	1.009	0.910	0.10	0.123
MWDA [c]	1.036	0.910	0.13	0.097
Zeng–Oxtoby approximation [d]	0.974	0.873	0.11	0.115
Weighted-density approximation [e]	1.02	0.881	0.14	0.101
GELA [f]	1.041	0.945	0.00	0.100

[a] From Hoover and Ree (1968).
[b] From this work.
[c] From Denton and Ashcroft (1989).
[d] From Zeng and Oxtoby (1990).
[e] From Curtin and Ashcroft (1985) and Curtin (1989).
[f] From Lutsko and Baus (1990a, b).

4. Application to the hard-sphere solid

As the second application of the NMWDA, the liquid–solid transition (Baus 1987, Singh 1991) can be considered. In Fourier space, equations (5) and (16) lead to a non-linear equation for $\hat{\rho}[\rho]$:

$$\hat{\rho}[\rho] = \rho_s\left(1 - \sum_{G=0} \frac{\rho G^2}{\rho_s^2} \int_0^1 d\lambda\,(1-\lambda)\frac{c^{(2)}(G; \lambda\hat{\rho}[\rho])}{f'(\lambda\hat{\rho}[\rho])}\right) \tag{31}$$

where ρ_s denotes the Fourier components of the density at the reciprocal lattice vectors G of the solid. For the analysis of the hard-sphere liquid–solid transition, we have assumed a face-centred cubic (FCC) lattice and also used a Gaussian parametrization for modelling the hard-sphere FCC crystal. For the hard-sphere fluid, $c^{(2)}$ is obtained from the Percus–Yevick approximation (Thiele 1963, Wertheim 1963):

$$\begin{aligned} c^{(2)}(k,\eta) = (4\pi/k^3)[a(y\cos y - \sin y) + (6\eta b/y)(y^2\cos y - 2y\sin y - 2\cos y + 2) \\ + (\eta a/2y^3)(y^4\cos y - 4y^3\sin y - 12y^2\cos y + 24y\sin y + 24\cos y - 24)] \end{aligned} \tag{32}$$

where $\eta = (\pi/6)\rho\sigma^3$ is the packing fraction of hard spheres of diameter σ, $a = (1+2\eta)^2/(1-\eta)^4$, $b = -(1-\eta/2)^2/(1-\eta)^4$ and $y = k\sigma$. For the uniform hard-sphere liquid the Carnahan–Starling (CS) (1969) approximation was used to calculate the total free energy of the liquid:

$$\beta F_{Lq}(\rho) = \ln\rho + 3\ln\Lambda - 1 + \eta(4-3\eta)/(1-\eta)^2. \tag{33}$$

These CS results are virtually identical with the computer results of the hard-sphere liquid.

In table 1, our results for the analysis of the freezing problem of hard-sphere liquids are compared with those of the molecular dynamics (Hoover and Ree 1968), the MWDA (Denton and Ashcroft 1989), the weighted-density approximation (Curtin and Ashcroft 1985, Curtin 1989) and the generalized effective-liquid approximation (Lutsko and Baus 1990a, b). Here the Lindemann parameter $L = (3/\alpha a^2)^{1/2}$ for an FCC crystal with the lattice constant $\rho_s = 4/a^3$ is also represented in the above theories. Our results show good agreement with the results of computer simulation.

5. Discussion and results

We have reformulated the weighted-density approximation on the basis of a global average of the density by using the unified density-functional approach and proposed an NMWDA. We have shown that for homogeneous systems the NMWDA and weighted-density approximation based on the exact density-functional expansion also lead to the HNC equation of state, as do the MWDA and the Zeng–Oxtoby approximation based on second-order truncations of expansions, and the homogeneous properties of weighted-density approximations do not depend on the detailed forms of the n-particle hierarchy functions d_n. For the freezing problem of hard-sphere systems the NMWDA shows good agreement with computer simulations as do other weighted-density approximation theories.

On the other hand, this reformulation raises the question of the density-functional expansion about an arbitrarily chosen reference density. This question basically depends on the convergence of the order parameter (and hence $\Delta\rho(r;\lambda)$) and is related to the fact that some theories work better than others when applied to the freezing problem. We still need to study this problem further.

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References

Baus M 1987 *J. Stat. Phys.* **48** 1129
Baus M and Colot J L 1985 *Mol. Phys.* **55** 653
Brenan G P and Evans R 1991 *Mol. Phys.* **73** 789
Carnahan N F and Starling K E 1969 *J. Chem. Phys.* **51** 635
Curtin W A 1989 *Phys. Rev.* B **39** 6775
Curtin W A and Ashcroft N W 1985 *Phys. Rev.* A **32** 2909
Denton A R and Ashcroft N W 1989 *Phys. Rev.* A **39** 4702
—— 1991 *Phys. Rev.* A **44** 1219
Evans R 1979 *Adv. Phys.* **28** 143 and references therein
Groot R D 1987 *Mol. Phys.* **60** 45
Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* 2nd edn (London: Academic)
Hoover W G and Ree F M 1968 *J. Chem. Phys.* **49** 3609
Kim S C 1991 *J. Phys.: Condens. Matter* **3** 2187
Kim S C and Jones G L 1990 *Phys. Rev.* A **41** 2222
Laird B B and Kroll D M 1990 *Phys. Rev.* A **42** 4810
Lutsko J F 1991 *Phys. Rev.* A **43** 4124
Lutsko J F and Baus M 1990a *Phys. Rev. Lett.* **64** 761
—— 1990b *Phys. Rev.* A **41** 6647
Percus J K 1964 *The Equilibrium Theory of Classical Fluids* ed H L Frish and J L Lebowitz (New York: Benjamin) p 33
Rosenfeld Y 1991 *Phys. Rev.* A **43** 5424
Singh Y 1991 *Phys. Rep.* **207** 351
Thiele E 1963 *J. Chem. Phys.* **39** 474
Wertheim M S 1963 *Phys. Rev. Lett.* **19** 321
Zeng X C and Oxtoby D W 1990 *Phys. Rev.* A **41** 7094