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Modified weighted-density-functional theory of nonuniform classical liquids

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A new formulation of the weighted-density approximation (WDA), as currently applied in the theory of nonuniform classical liquids, is presented. This *modified* weighted-density approximation retains a key feature of the original approximation by including correlations, at least approximately, to all orders in the functional expansion of the excess free energy. It continues to require as input *only* the two-particle direct correlation function of the uniform liquid. In contrast to the original WDA, however, practical implementation of the modified WDA demands considerably less computational effort. When applied to the freezing of the hard-sphere liquid, the results obtained previously with the original WDA, already in good agreement with simulation, are reproduced quite accurately. It is concluded that in its new formulation the WDA is now just as simple to implement as the widely used Ramakrishnan-Yussouff theory. But as with the original WDA the new formulation more accurately describes the freezing of hard spheres and is more soundly based in the sense of including correlations to all orders.

I. INTRODUCTION

Over the past decade the density-functional method has gained wide recognition as a fruitful approach to the study of freezing transitions and other phenomena involving nonuniform classical liquids. The basic assumption of all density-functional theories is that the thermodynamic potential of a *nonuniform* system may be approximated using known structural and thermodynamic properties of the corresponding *uniform* system. What distinguishes the various theories from one another is the detailed manner in which each formulates the approximation. A widely known density-functional theory is that of Ramakrishnan and Yussouff[1] (RY), which is based upon a functional Taylor series expansion of the excess Helmholtz free energy about the density of a uniform liquid. The essential approximation made in the RY theory is a *truncation* of this expansion, for practical reasons usually at second order, all succeeding higher-order terms being ignored entirely. In applications to the freezing transition in a variety of systems this theory has had mixed success.[2-4] Although an appealing feature of the RY theory is its computational simplicity, the truncation approximation upon which the theory is based has to date been given no *a priori* justification in the context of highly nonuniform systems, and in fact there are good reasons to doubt its general validity.[5]

Other density-functional theories have been proposed,[6-11] all of which are characterized by the use of a uniform reference system whose "effective" density is chosen according to varying criteria. One such theory is the weighted-density-functional theory of Curtin and Ashcroft[11] (CA), which, as its name suggests, is based upon a "weighted-density approximation" (WDA). A key feature of the WDA is its implicit inclusion of a subset of exact terms to *all* orders in the functional expansion of the excess Helmholtz free energy. Although generally more accurate than the RY theory,[11-15] the weighted-density-functional theory also requires significantly more computational effort to implement. It is the purpose of this paper to present a modified formulation of the WDA, which retains the key features of the original formulation, but which makes the weighted-density-functional theory just as simple to implement as the RY theory.

The remainder of the paper is organized as follows. In Sec. II we briefly review the WDA as originally formulated in the CA theory, and then describe our modified formulation. In Sec. III we apply the modified weighted-density-functional theory to the freezing of hard spheres and demonstrate that it accurately reproduces the results obtained previously with the original formulation. In Sec. IV we compare both the original and the modified formulation of the weighted-density-functional theory with the RY theory on the basis of the terms that each includes in the functional expansion of the excess free energy, and point out a similarity between the modified formulation and another recently proposed theory. Finally, in Sec. V we summarize and conclude.

II. THEORY

A. Weighted-density approximation

The excess Helmholtz free energy $F_{\mathrm{ex}}[\rho]$, a unique functional[16] of the one-particle density ρ, can be expressed quite generally in the form

$$F_{\mathrm{ex}}[\rho]=\int d\mathbf{r}\,\rho(\mathbf{r})f(\mathbf{r};[\rho]) , \tag{1}$$

which serves to *define* a local excess free energy *per particle* $f(\mathbf{r};[\rho])$. The CA theory is based upon a weighted-density approximation (WDA) for $F_{\mathrm{ex}}[\rho]$. In the following we review only the essential features of this approximation and refer the reader to Ref. 11 for further details and a discussion of the physical motivation.

The WDA for $F_{\rm ex}[\rho]$ can be expressed as

$$F_{\rm ex}^{\rm WDA}[\rho]=\int d\mathbf{r}\,\rho(\mathbf{r})f_0(\bar{\rho}(\mathbf{r}))\ , \tag{2}$$

where f_0 denotes the excess free energy per particle of a *uniform* liquid and $\bar{\rho}(\mathbf{r})$ is the "weighted density," defined as a *weighted average* of the one-particle density $\rho(\mathbf{r})$ with respect to a weight function w, according to

$$\bar{\rho}(\mathbf{r})\equiv\int d\mathbf{r}'\rho(\mathbf{r}')w(\mathbf{r}-\mathbf{r}';\bar{\rho}(\mathbf{r}))\ . \tag{3}$$

The self-consistency with respect to $\bar{\rho}(\mathbf{r})$ in this definition is a crucial feature of the WDA, a point we return to below after specifying the form of the weight function. To ensure that the approximation becomes exact in the limit of a uniform system [$\rho(\mathbf{r})\rightarrow\rho_0$, where ρ_0 is the density of the uniform system], the weight function must satisfy the "normalization condition"

$$\int d\mathbf{r}'w(\mathbf{r}-\mathbf{r}';\bar{\rho}(\mathbf{r}))=1\ . \tag{4}$$

A *unique* specification of w follows from requiring that the defining relationship between the n-particle direct correlation function (DCF) $c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n;[\rho])$ and the nth functional derivative of $F_{\rm ex}[\rho]$ with respect to ρ,

$$c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n;[\rho])=-\beta\frac{\delta^n F_{\rm ex}[\rho]}{\delta\rho(\mathbf{r}_1)\cdots\delta\rho(\mathbf{r}_n)}\ , \tag{5}$$

where $\beta\equiv 1/k_BT$, is satisfied *exactly* for $n=2$ in the uniform limit. Explicitly, $F_{\rm ex}^{\rm WDA}[\rho]$ is required to satisfy the relation

$$c_0^{(2)}(\mathbf{r}-\mathbf{r}';\rho_0)=-\beta\lim_{\rho\rightarrow\rho_0}\left[\frac{\delta^2F_{\rm ex}^{\rm WDA}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right]\ , \tag{6}$$

where $c_0^{(2)}$ is the two-particle DCF of the uniform system. Thus, by substituting $F_{\rm ex}^{\rm WDA}[\rho]$ [from Eq. (2)] into Eq. (6), one obtains the equation

$$\begin{aligned}-\beta^{-1}c_0^{(2)}(\mathbf{r}-\mathbf{r}';\rho_0)={}&2f_0'(\rho_0)w(\mathbf{r}-\mathbf{r}';\rho_0)+\rho_0f_0''(\rho_0)\int d\mathbf{r}''w(\mathbf{r}-\mathbf{r}'';\rho_0)w(\mathbf{r}'-\mathbf{r}'';\rho_0)\\&+\rho_0f_0'(\rho_0)\int d\mathbf{r}''[w'(\mathbf{r}-\mathbf{r}'';\rho_0)w(\mathbf{r}'-\mathbf{r}'';\rho_0)+w(\mathbf{r}-\mathbf{r}'';\rho_0)w'(\mathbf{r}'-\mathbf{r}'';\rho_0)]\ ,\end{aligned} \tag{7}$$

in which primes on f_0 and w denote derivatives with respect to density. In Fourier space Eq. (7) takes the form of a differential equation:

$$\begin{aligned}-\beta^{-1}c_0^{(2)}(k;\rho_0)={}&2f_0'(\rho_0)w(k;\rho_0)+\rho_0f_0''(\rho_0)w(k;\rho_0)^2\\&+2\rho_0f_0'(\rho_0)w'(k;\rho_0)w(k;\rho_0)\ .\end{aligned} \tag{8}$$

Assuming that $c_0^{(2)}$ and f_0 are both known for the uniform interacting liquid, Eq. (8) can be solved numerically for w. As noted above, the self-consistency requirement in Eq. (2) is crucial. The reason is that it can be shown to guarantee that the identity

$$c_0^{(n)}(k,0,\ldots,0;\rho_0)=\frac{\partial^{n-2}}{\partial\rho_0^{n-2}}c_0^{(2)}(k;\rho_0)\ , \tag{9}$$

relating the Fourier transforms of the n-particle uniform liquid DCF $c_0^{(n)}$ and the two-particle function $c_0^{(2)}$, *is satisfied exactly.*

Taken together, Eqs. (2), (3), (4) and (8), constitute the WDA as formulated in the CA theory. We turn now to a computationally simpler reformulation of the WDA.

B. Modified weighted-density approximation

The reformulation of the WDA involves essentially one new concept. Whereas the original WDA is an approximation for the quantity $f(\mathbf{r};[\rho])$, interpreted as the *local* excess free energy per particle, the new formulation focusses instead directly upon the *global* excess free energy per particle $F_{\rm ex}[\rho]/N$, where N is the number of particles in the system. Since $F_{\rm ex}[\rho]/N$ is independent of position—in contrast to $f(\mathbf{r};[\rho])$—the new formulation must necessarily involve a *position-independent* weighted density. We denote this new weighted density by the symbol $\hat{\rho}$ to distinguish it from the original position-dependent weighted density $\bar{\rho}(\mathbf{r})$. Then the *modified* weighted-density approximation (MWDA) for $F_{\rm ex}[\rho]/N$ can be expressed as

$$F_{\rm ex}^{\rm MWDA}[\rho]/N\equiv f_0(\hat{\rho})\ , \tag{10}$$

where, by analogy with the definition of $\bar{\rho}(\mathbf{r})$ [Eq. (3)], we *define* $\hat{\rho}$ by

$$\hat{\rho}\equiv\frac{1}{N}\int d\mathbf{r}\,\rho(\mathbf{r})\int d\mathbf{r}'\rho(\mathbf{r}')\tilde{w}(\mathbf{r}-\mathbf{r}';\hat{\rho})\ . \tag{11}$$

Since, as will be seen below, the weight function that appears in Eq. (11) actually differs somewhat from the original weight function, we also assign it a new symbol $\tilde{w}$. As was the case in the original WDA, the requirement of self-consistency—now with respect to $\hat{\rho}$—in Eq. (11) is again a crucial feature of the MWDA as it ensures that Eq. (9) remains satisfied exactly. From a comparison of Eqs. (3) and (11), it may be observed that $\hat{\rho}$ can be identified as a form of further averaging of the original weighted density $\bar{\rho}(\mathbf{r})$. It is important to emphasize, however, that this identification is only approximate, since (i) the weight function $\tilde{w}$ that appears in Eq. (11) differs from the weight function w in Eq. (3), and (ii) the density arguments of $\tilde{w}$ and w are actually different.[17]

To ensure that the approximation in the MWDA again becomes exact in the limit of a uniform system, the new weight function $\tilde{w}$ must also be normalized [cf. Eq. (4)]:

$$\int d\mathbf{r}'\tilde{w}(\mathbf{r}-\mathbf{r}';\hat{\rho})=1\ . \tag{12}$$

A unique specification of $\tilde{w}$ now follows by imposing the same requirement as in the original WDA—namely, that $F_{\rm ex}^{\rm MWDA}[\rho]$ satisfy Eq. (6) exactly. This results in a very simple expression for $\tilde{w}$ [cf. Eq. (7)], specifically,[18]

$$\tilde{w}(\mathbf{r}-\mathbf{r}';\rho_0)=\frac{-1}{2f_0'(\rho_0)}\left[\beta^{-1}c_0^{(2)}(\mathbf{r}-\mathbf{r}';\rho_0)+\frac{1}{V}\rho_0 f_0''(\rho_0)\right] , \qquad (13)$$

where V is the volume of the system, or in Fourier space [cf. Eq. (8)],

$$\tilde{w}(k;\rho_0)=\frac{-1}{2f_0'(\rho_0)}[\beta^{-1}c_0^{(2)}(k;\rho_0)+\delta_{k,0}\rho_0 f_0''(\rho_0)] . \qquad (14)$$

In a given application, of course, the density argument of $\tilde{w}(k)$ will be determined by the crucial self-consistency requirement [see Eq. (11)]. For $k=0$, the δ-function term in Eq. (14) ensures that the compressibility rule,

$$-\beta^{-1}c_0^{(2)}(k=0;\rho_0)=2f_0'(\rho_0)+\rho_0 f_0''(\rho_0) , \qquad (15)$$

is satisfied identically, as in the original WDA. For $k\neq 0$, $\tilde{w}(k)$ is simply proportional to $c_0^{(2)}(k)$, the Fourier transform of the (Ornstein-Zernike) two-particle direct correlation function, which, as noted previously, is assumed known.

Together, Eqs. (10), (11), (12), and (14) constitute the MWDA. They correspond directly to Eqs. (2), (3), (4), and (8), respectively, in the original WDA. There are two reasons why this new formulation of the WDA will be much simpler in practice to implement than the original. First, in the MWDA the weight function $\tilde{w}$ is simply proportional to the two-particle DCF, whereas in the WDA the weight function w is obtained only by solving a differential equation [compare Eqs. (14) and (8)]. Second, in contrast to $F_{\text{ex}}^{\text{WDA}}$, the computation of $F_{\text{ex}}^{\text{MWDA}}$ does *not* require the evaluation of a volume integral [compare Eqs. (10) and (2)]. These aspects will be illustrated in Sec. III where we test the MWDA by applying it to the freezing of hard spheres.

III. FREEZING OF THE HARD-SPHERE LIQUID

We begin by repeating the analysis of Ref. 11 of the hard-sphere-liquid–fcc-solid transition, but using the MWDA instead of the WDA. To do this, we determine the excess free energy of the hard-sphere fcc solid in the MWDA, add to this the exact ideal-gas part of the free energy, minimize the total with respect to a single variational parameter, and then compare with the "known" liquid free energy to determine the characteristic parameters of the freezing transition.

The first step is to compute the weighted density $\hat{\rho}$ of the solid. This computation is most easily performed in Fourier space, where the volume integrals of Eq. (11) transform into summations over the reciprocal-lattice vectors (RLV's) of the solid. Thus,

$$\hat{\rho}=\rho_s+\frac{1}{\rho_s}\sum_{\mathbf{G}\neq 0}\rho_{\mathbf{G}}^2\tilde{w}_{\mathbf{G}}(\hat{\rho}) , \qquad (16)$$

where ρ_s is the average solid density, and $\rho_{\mathbf{G}}$ and $\tilde{w}_{\mathbf{G}}$ denote the Fourier components at RLV $\mathbf{G}$ of the solid density and the weight function, respectively. At this point it is important to note that to date all density-functional theories of freezing require the lattice symmetry of the solid phase to be *specified*,[19] as will be done here. Following Ref. 11, we then assume an fcc lattice and parametrize the solid density $\rho_s(\mathbf{r})$ as a sum of normalized Gaussians, centered about the lattice sites at positions $\mathbf{R}$. Thus, we take

$$\rho_s(\mathbf{r})\equiv(\alpha/\pi)^{3/2}\sum_{\mathbf{R}}e^{-\alpha|\mathbf{r}-\mathbf{R}|^2} , \qquad (17)$$

with Fourier components

$$\rho_{\mathbf{G}}=\rho_s e^{-G^2/4\alpha} . \qquad (18)$$

The "localization parameter" α determines the width of the Gaussians. It is thus a measure of nonuniformity, $\alpha=0$ corresponding to the limit of a uniform liquid (infinitely wide Gaussians), and increasing values of α corresponding to increasing localization of the atoms about their respective lattice sites (increasingly narrow Gaussians). In particular, at freezing α directly determines the Lindemann parameter L, which is defined as the ratio of the rms displacement of an atom from its lattice site to the nearest-neighbor distance in the solid at coexistence. For the fcc lattice, $L=(3/\alpha a^2)^{1/2}$, where $a=(4/\rho_s)^{1/3}$ is the fcc lattice constant. Substitution of $\rho_{\mathbf{G}}$ [from Eq. (18)] and $\tilde{w}_{\mathbf{G}}$ [from Eq. (14)] into Eq. (16) results in the expression

$$\hat{\rho}(\rho_s,\alpha)=\rho_s\left[1-\frac{1}{2\beta f_0'(\hat{\rho})}\sum_{\mathbf{G}\neq 0}e^{-G^2/2\alpha}c_0^{(2)}(\mathbf{G};\hat{\rho})\right] , \qquad (19)$$

where $c_0^{(2)}(\mathbf{G};\hat{\rho})$ denotes the Fourier component at RLV $\mathbf{G}$ and density $\hat{\rho}$ of the uniform liquid two-particle DCF. Note that this is an *implicit* equation for $\hat{\rho}$, with $\hat{\rho}$ appearing both on the left side and on the right side as the density argument of f_0' and $c_0^{(2)}$. As in Ref. 11, we adopt for f_0 and $c_0^{(2)}$ the Percus-Yevick (PY) approximations[20]

$$f_0(\eta)=\frac{3}{2}\left[\frac{1}{(1-\eta)^2}-1\right]-\ln(1-\eta) \qquad (20)$$

and

$$c_0^{(2)}(k;\eta)=\frac{4\pi}{k^3}\left[a(y\cos y-\sin y)+6\eta\frac{b}{y}(y^2\cos y-2y\sin y-2\cos y+2)+\tfrac{1}{2}\eta\frac{a}{y^3}(y^4\cos y-4y^3\sin y-12y^2\cos y+24y\sin y+24\cos y-24)\right] , \qquad (21)$$

where $\eta=(\pi/6)\rho\sigma^3$, $a=(1+2\eta)^2/(1-\eta)^4$, $b=-(1+\eta/2)^2/(1-\eta)^4$, and $y=k\sigma$ with σ being the hard-sphere diameter. For given average solid density ρ_s and localization parameter α, Eq. (19) is now easily solved for $\hat{\rho}$ by iteration.[21] As Fig. 1 illustrates, for fixed ρ_s, $\hat{\rho}(\rho_s,\alpha)$ is a monotonically *decreasing* function of α. Thus, the more localized the atoms, the *lower* the corresponding density

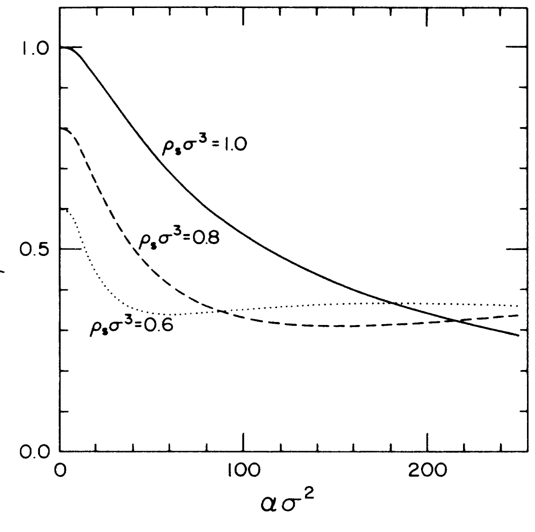

FIG. 1. Weighted density $\hat{\rho}$ vs localization parameter α for three different average densities of the fcc hard-sphere solid.

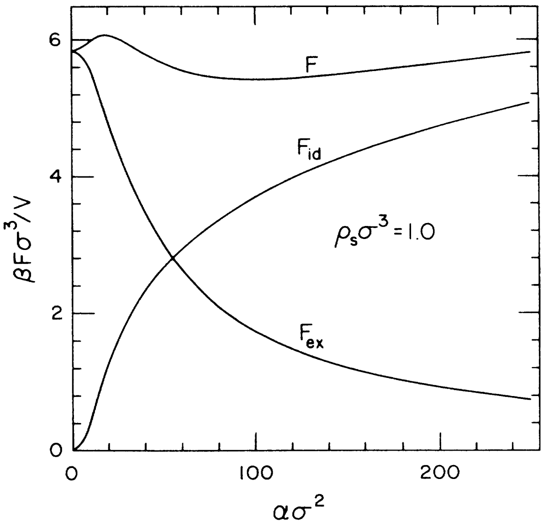

FIG. 2. Excess, ideal-gas, and total free energies vs localization parameter α for the fcc hard-sphere solid at average solid density $\rho_s\sigma^3=1.0$.

of the uniform reference liquid. It should be noted that although the PY approximation is known to become increasingly inaccurate with increasing density, in the MWDA f_0 and $c_0^{(2)}$ are evaluated at the density $\hat{\rho}$, which near the freezing transition turns out to be relatively small (see Fig. 1). Thus, use of the PY approximation for f_0 and $c_0^{(2)}$ is in fact quite justified.

Having computed $\hat{\rho}$, the next step in the freezing analysis is to substitute $\hat{\rho}$ into Eq. (10) to compute F_{ex}^{MWDA}. The *total* free energy F of the solid is then obtained by adding to F_{ex}^{MWDA} a nonuniform-ideal-gas contribution of the form

$$F_{id}[\rho_s]=\beta^{-1}\int d\mathbf{r}\,\rho_s(\mathbf{r})\{\ln[\rho_s(\mathbf{r})\lambda^3]-1\}\ , \qquad (22)$$

where λ is the thermal de Broglie wavelength. In the limit of negligible overlap between neighboring Gaussians ($\alpha\sigma^2>50$), which is certainly the case near freezing, F_{id} is very accurately approximated by

$$\beta F_{id}(\rho_s,\alpha)/N=\tfrac{3}{2}\ln(\alpha/\pi)+3\ \ln(\lambda)-\tfrac{5}{2}\ . \qquad (23)$$

Figure 2 illustrates the dependence on α of the excess, ideal-gas, and total free energies of the solid. Notice that F_{id} *increases* monotonically with α, favoring delocalization of the atoms, while F_{ex}^{MWDA} *decreases* monotonically with α, favoring localization. Evidently, the average solid density $\rho_s\sigma^3=1.0$ is sufficiently high that at a nonzero value of α the total free energy of the solid exhibits a minimum *below* the liquid free energy, indicating that the solid is indeed the thermodynamically stable phase.

Figure 3 exhibits the density dependence of the liquid and solid total free energies and of the localization parameter α which minimizes the solid free energy. As in Ref. 11, the liquid free energy has been computed using the Carnahan-Starling approximation,[22] which is known to be highly accurate even at densities near freezing. Since the two free energy curves cross, the theory predicts a freezing transition. The densities of the coexisting phases are easily determined from Fig. 3 by a common tangent construction. They are presented in Table I together with the results of Ref. 11 and simulation. Also compared in Table I are the results for the latent heat and the Lindemann parameter, two quantities which are rather poorly predicted by the RY theory. Table II gives a further comparison of the free energy and the pressure over a range of densities near freezing. It is apparent that the results of the MWDA for the freezing of hard spheres are very close to those of the original WDA, and that both are in quite good agreement with simulation. The largest discrepancies between the two approximations are seen to be in the pressure, but these are still no more than a few percent. What is especially significant is that the MWDA gives results of essentially the same accuracy as

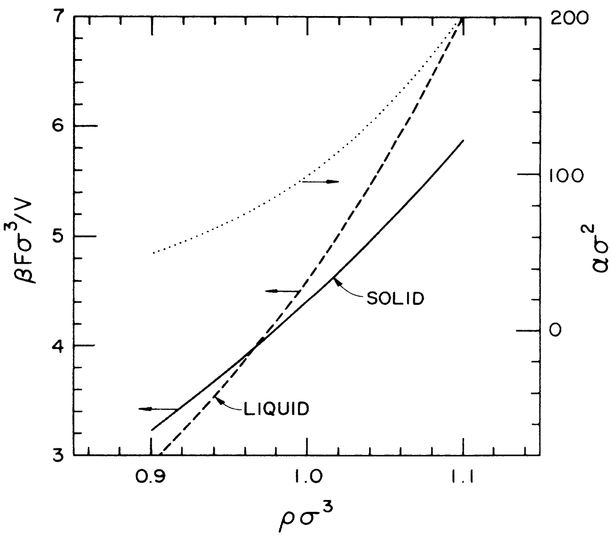

FIG. 3. Total free energies of the liquid and fcc solid phases of the hard-sphere system.

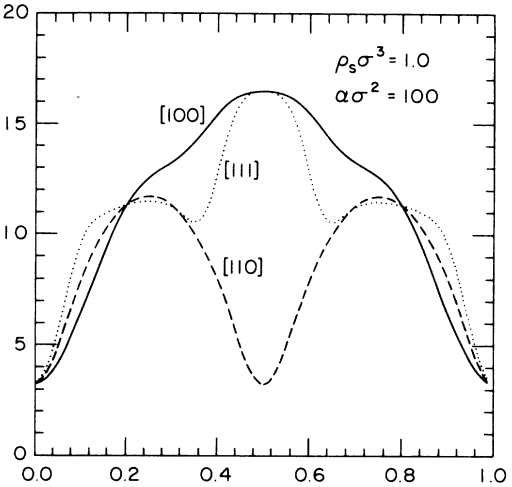

FIG. 4. Modified weighted-density approximation for the one-particle direct correlation function $c^{(1)}_{\mathrm{MWDA}}(\mathbf{r};[\rho])$ of the fcc hard-sphere solid along the three symmetry directions of the cubic unit cell.

TABLE I. Freezing parameters for the hard-sphere-liquid–fcc-solid transition: average solid density ρ_s, liquid density ρ_l, change in density $\Delta\rho$, latent heat per particle Δs, and Lindemann parameter $L=(3/\alpha a^2)^{1/2}$ for the fcc solid, where σ is the hard-sphere diameter and a is the fcc lattice constant.

	$\rho_s\sigma^3$	$\rho_l\sigma^3$	$\Delta\rho\sigma^3$	$\Delta s/k_B$	L
Simulation[a]	1.04	0.94	0.10	1.16	0.126
MWDA	1.036	0.910	0.13	1.35	0.097
WDA[b]	1.045	0.916	0.13	1.41	0.093
RY[c]	1.147	0.967	0.18	2.24	0.055

[a] See Ref. 24.

[b] See Ref. 23.

[c] See Refs. 4 and 5.

the WDA, but requires considerably less computational effort.

A feature of the MWDA particularly worth mentioning is that it also provides a simple approximation for the *one-particle* DCF (or excess chemical potential) $c^{(1)}(\mathbf{r};[\rho])$ of the nonuniform system. According to Eq. (4), $c^{(1)}(\mathbf{r};[\rho])$ is defined by

$$c^{(1)}(\mathbf{r};[\rho])\equiv-\beta\frac{\delta F_{\mathrm{ex}}[\rho]}{\delta\rho(\mathbf{r})} . \tag{24}$$

Thus, by substituting $F^{\mathrm{MWDA}}_{\mathrm{ex}}[\rho]$ into Eq. (24) we obtain the approximation

$$-\beta^{-1}c^{(1)}_{\mathrm{MWDA}}(\mathbf{r};[\rho])$$
$$=f_0(\hat\rho)+f_0'(\hat\rho)\frac{2\left[\rho_s+\sum\limits_{\mathbf{G}\neq0}\rho_{\mathbf{G}}w_{\mathbf{G}}(\hat\rho)e^{i\mathbf{G}\cdot\mathbf{r}}\right]-\hat\rho}{\left[1-\dfrac{1}{\rho_s}\sum\limits_{\mathbf{G}}\rho_{\mathbf{G}}^2w_{\mathbf{G}}'(\hat\rho)\right]} , \tag{25}$$

which is easily computed. In comparison, the WDA also gives an approximation for $c^{(1)}(\mathbf{r};[\rho])$, but in a form which is numerically intractable. Figure 4 shows a typical plot of $-\beta^{-1}c^{(1)}_{\mathrm{MWDA}}(\mathbf{r};[\rho])$ for the hard-sphere fcc solid along the three symmetry directions of the cubic unit cell. Notice that $-\beta^{-1}c^{(1)}_{\mathrm{MWDA}}(\mathbf{r};[\rho])$ is lowest at the lattice sites where the density is highest, and highest in the interstitial regions where the density is lowest. This qualitative behavior is in accord with the physical interpretation of $-\beta^{-1}c^{(1)}(\mathbf{r};[\rho])$ as an "effective one-body potential" which acts to self-consistently determine the equilibrium density $\rho_{\mathrm{eq}}(\mathbf{r})$, the latter interpretation following from the fundamental relation[16]

$$\rho_{\mathrm{eq}}(\mathbf{r})=z\exp\{-\beta\phi_{\mathrm{ext}}(\mathbf{r})+c^{(1)}(\mathbf{r};[\rho_{\mathrm{eq}}])\} , \tag{26}$$

where z is the fugacity and $\phi_{\mathrm{ext}}(\mathbf{r})$ an external potential, if present.

We conclude this section with some remarks on the application of the MWDA to systems with other-than-hard-sphere pair potentials. As illustrated above, application of the MWDA (as of the original WDA) requires knowledge of the functions $c_0^{(2)}$ and f_0 over a wide range of densities of the *uniform* interacting liquid. For a system whose pair potential is purely repulsive (e.g., the hard-sphere system) these functions are well defined at all densities below the freezing transition. It may be observed, however, that for a system whose pair potential

TABLE II. Free energy per particle F/N and ratio of pressure P to average solid density ρ_s for the hard-sphere fcc solid over a range of average solid densities.

	$\beta F/N$			$\beta P/\rho_s$		
$\rho_s\sigma^3$	MWDA	WDA[a]	Simulation[b]	MWDA	WDA[a]	Simulation[c]
1.000	4.412	4.449	4.661	8.51	8.83	10.25
1.025	4.629	4.674	4.868	8.96	9.40	10.81
1.050	4.853	4.908	5.099	9.61	10.09	11.49
1.075	5.090	5.156	5.354	10.58	11.06	12.30
1.100	5.347	5.423	5.663	11.90		13.26

[a] See Ref. 23.

[b] See Ref. 11.

[c] See Ref. 25.

includes also an attractive part, there could exist a range of densities, characterized by equilibrium two-phase (liquid-vapor) coexistence, over which $c_0^{(2)}$ and f_0 are undefined. As demonstrated in Refs. 6 and 12, however, it is possible to treat such a system by expanding the excess free energy F_{ex} about that of a *reference* system with a purely repulsive potential (e.g., the hard-sphere system). The MWDA can then be applied solely to the reference system, with the attractive contribution to F_{ex} treated as a perturbation and approximated by independent means (e.g., by a mean-field approximation).

IV. DISCUSSION

The results of Sec. III demonstrate that in their *quantitative* predictions the MWDA and the WDA are practically equivalent—at least in the case of the freezing of hard spheres. A formal basis for comparing the two approximations—with each other and with the RY theory—is provided by the functional Taylor series expansion of the excess Helmholtz free energy about the density of the uniform liquid. Using the definition of the n-particle DCF $c^{(n)}$ from Eq. (5), the expansion can be expressed in the form

$$\begin{aligned}\beta F_{\mathrm{ex}}[\rho]=\beta F_{\mathrm{ex}}(\rho_l)-c_0^{(1)}(\rho_l)\int d\mathbf{r}[\rho(\mathbf{r})-\rho_l]-\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'c_0^{(2)}(\mathbf{r}-\mathbf{r}';\rho_l)[\rho(\mathbf{r})-\rho_l][\rho(\mathbf{r}')-\rho_l]\\ -\frac{1}{3!}\int d\mathbf{r}\int d\mathbf{r}'\int d\mathbf{r}''c_0^{(3)}(\mathbf{r}-\mathbf{r}'',\mathbf{r}'-\mathbf{r}'';\rho_l)[\rho(\mathbf{r})-\rho_l][\rho(\mathbf{r}')-\rho_l][\rho(\mathbf{r}'')-\rho_l]-\cdots ,\end{aligned} \tag{27}$$

where ρ_l is the liquid density. As noted in the Introduction, expansion (27) is the basis of the RY theory, where $F_{\mathrm{ex}}[\rho]$ is approximated by a truncation of the expansion—usually at second order, since until recently very little was known about $c_0^{(3)}$ and higher-order DCF's.[26] Although the MWDA and WDA are not *explicitly* based upon expansion (27), it is nevertheless possible to formally expand the approximate functionals $F_{\mathrm{ex}}^{\mathrm{MWDA}}$ and $F_{\mathrm{ex}}^{\mathrm{WDA}}$ by evaluating the approximate higher-order DCF's from Eq. (5). From Sec. II, it is clear that the pair of resulting expansions *must* be alike in two important respects. First, both are "exact" to second order—that is, to the extent that $c_0^{(2)}$ is known exactly—as ensured by the requirement that Eq. (6) is satisfied exactly. Second, both include a subset of *exact* higher-order terms, specifically those terms that can be derived from $c_0^{(2)}$ via Eq. (9). In addition, both expansions include approximate higher-order terms that cannot be derived from $c_0^{(2)}$, and it is only in the precise form of these approximate terms that the two expansions differ. In contrast, in the RY theory the expansion—though also exact to second order where it is usually truncated—does not systematically include *any* of the higher-order terms.

Finally we point out that an approximation rather similar to the MWDA has recently been proposed by Stoessel,[27] but on the basis of quite a different motivation—namely, the desire to generalize to nonuniform systems the Carnahan-Starling approximation[22] for uniform liquids. Stoessel approximates the excess free energy per particle of the nonuniform system by

$$F_{\mathrm{ex}}[\rho]/N \equiv f_0^{\mathrm{CS}}(\eta[\rho]) , \tag{28}$$

where f_0^{CS} is the Carnahan-Starling uniform liquid free energy and $\eta[\rho]$ is a "generalized" packing fraction, defined by

$$\eta[\rho] \equiv -\frac{1}{8N}\int d\mathbf{r}\rho(\mathbf{r})\int d\mathbf{r}'\rho(\mathbf{r}')f(\mathbf{r},\mathbf{r}') , \tag{29}$$

where $f(\mathbf{r},\mathbf{r}')$ is the Mayer function, given by

$$f(\mathbf{r},\mathbf{r}')=\exp[-\beta\phi(\mathbf{r},\mathbf{r}')]-1 , \tag{30}$$

and $\phi(\mathbf{r},\mathbf{r}')$ is the pair potential. Notice that the definition of $\eta[\rho]$ is of precisely the same *form* as the definition of $\hat{\rho}$ in the MWDA [see Eq. (11)]. The specification of the weight function in the two approximations, however, is quite different. Whereas in Stoessel's approximation the weight function is proportional to the Mayer function, in the MWDA the weight function is proportional to the two-particle DCF [Eq. (13)], but with a carefully prescribed density argument [see Eq. (11)]. It is worth noting, however, that in the *low-density limit* the two-particle DCF reduces to the Mayer function and the two approximations then become equivalent. Since Stoessel's approximation does *not* involve a self-consistency requirement—in the sense that the weight function does not depend upon the generalized packing fraction—the corresponding functional expansion of $F_{\mathrm{ex}}[\rho]$ does *not* include the exact higher-order terms that are included by the MWDA and WDA. Nevertheless, when applied to the hard-sphere fcc and amorphous solids, Stoessel's approximation gives pressures that agree surprisingly well with simulation. The results for the free energy, however, are rather poor: indeed the free energy of the solid is consistently lower than that of the liquid, and thus no freezing transition is observed. For comparison, we have computed the pressure and free energy of the hard-sphere fcc solid in the MWDA using Stoessel's form of the weight function. In the case of hard spheres, Stoessel's weight function is simply a normalized step function (constant for $|\mathbf{r}-\mathbf{r}'|<\sigma$, zero for $|\mathbf{r}-\mathbf{r}'|>\sigma$), which differs significantly from the MWDA weight function [Eq. (13)] at densities as high as those near freezing. We confirm that when this form of the weight function is used the pressure of the solid is only slightly affected, whereas the free energy is indeed significantly reduced relative to the results presented in Sec. III, to the extent that, as noted, no freezing transition is actually observed.

V. SUMMARY AND CONCLUSIONS

In summary, we have presented a new formulation of the weighted-density approximation (WDA) as embodied in the weighted-density-functional theory of Curtin and Ashcroft. The new modified weighted-density approximation (MWDA) considerably simplifies the practical implementation of the theory, yet maintains good agreement with simulation when applied to the freezing of hard spheres. Furthermore, on the basis of the functional expansion of the excess free energy, the formal justification for the new approximation is in fact just as strong as for the original, since in both cases the expansion includes the same subset of *exact* higher-order terms. The two approximations differ in the precise form of the *approximate* higher-order terms which each includes. (In fact, at third order the MWDA actually includes only exact terms, whereas the WDA includes both the same exact terms *and* additional approximate terms, and consequently the WDA is better able to approximate the three-particle direct correlation function.[26]) These approximate higher-order terms, however, apparently are not important for describing the freezing of hard spheres, as evidenced by the close quantitative agreement between the two approximations demonstrated in Sec. III. Whether or not this same level of agreement holds more generally can be established only by comparing the results of the two approximations for a variety of phenomena and systems. In particular, though the MWDA can be easily applied to most bulk phase phenomena, application to *interfacial* phenomena, where the density nonuniformity is of *finite* range, may not be as straightforward. We mention that we have already generalized the new approximation to binary mixtures and applied it to the freezing of hard-sphere mixtures with favorable results. This work will be the subject of a future publication.[28] Finally, we reiterate that compared with the Ramakrishnan-Yussouff theory, the weighted-density-functional theory is evidently more soundly based, more accurately describes the freezing of hard spheres, and—with this new formulation of the weighted-density approximation—is now just as simple to implement.

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$$f_0\left[\frac{1}{N}\int d\mathbf{r}\,\rho(\mathbf{r})\int d\mathbf{r}'\rho(\mathbf{r}')\tilde{w}(\mathbf{r}-\mathbf{r}';\hat{\rho})\right] \rightarrow \frac{1}{N}\int d\mathbf{r}\,\rho(\mathbf{r})f_0\left[\int d\mathbf{r}'\rho(\mathbf{r}')\tilde{w}(\mathbf{r}-\mathbf{r}';\hat{\rho})\right],$$

then one recovers an equation which has the same *structure* as Eq. (2) [though it is not identical to Eq. (2) because of the difference between the weight functions $\tilde{w}$ and w].

[18] In deriving Eq. (13) we have made use of the facts that (i) $\int d\mathbf{r}'\tilde{w}'(\mathbf{r}-\mathbf{r}';\rho_0)=0$, from Eq. (12), and (ii) $\delta N/\delta\rho(\mathbf{r})=1$, since $N=\int d\mathbf{r}\,\rho(\mathbf{r})$.

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