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Weighted-density-functional theory of inhomogeneous liquids and the freezing transition

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Starting from an exact expression for the Helmholtz free-energy functional of an inhomogeneous classical liquid, an approximate functional is presented which depends on a *weighted average of the physical density.* It retains the nonlocal character of the exact expression, but requires only the properties of the homogeneous liquid. A physical choice of the weighting function used to construct the weighted density is made by appealing to the structure of the homogeneous liquid. The resulting weighted-density approximation (WDA) corresponds to an approximation for some of the third- and higher-order terms in a density-functional expansion of the true free energy, the first-, second-, *and* a subset of higher-order terms being retained exactly. In this respect the theory differs crucially from earlier functionals based on weighted-density ideas. As an application of the WDA, the freezing of simple liquids is considered within the framework of mean-field theory and is briefly compared to previous theories. In particular, the freezing transition of the hard-sphere system is studied using the WDA formalism, the resulting freezing parameters and the equation of state for the solid being in good agreement with computer-simulation studies.

I. INTRODUCTION

The theory of classical liquids has progressed rapidly in recent years largely as a consequence of the advent of functional methods[1,2] and the availability of computer-simulation data.[3] The thermodynamic potentials of these systems are all unique[4] functionals of density, or of an external potential, and the formal statements which can be made as a result of this uniqueness have provided a guide for approximate functional theories. In addition, functional perturbation theory introduces a systematic approach to the study of both uniform and inhomogeneous liquids. For inhomogeneous systems, the natural expansion variable is, of course, the one-particle density $\rho(\mathbf{r})$. The free energy $F[\rho]$ also can be modeled by a local-density approximation, which consists of approximating F by $F_{\mathrm{LD}}=\int d\mathbf{r}\, f(\rho(\mathbf{r}))$, where f is the free-energy density of a homogeneous liquid. On occasion, the first nonlocal correction to F_{LD} is also included. The application of such approximate functions usually requires an accurate knowledge of the properties of homogeneous liquids over a wide range of densities. The success of these approaches is, however, mixed. For example, calculations of the liquid-vapor surface tensions and surface profiles of simple liquids and monovalent metals are in reasonable agreement with experimental results where available.[5,6] On the other hand, results for liquids in contact with a rigid wall are on the whole less encouraging, since it is not clear that the oscillations in the density profile near the wall or the subsequent wetting phenomena are accurately described.[7] Nevertheless, the functional ideas have been sufficiently successful that they have been extended to consider the formation of a solid from a liquid, about which we will have much more to say below.

Work on the liquid-based theory of freezing has tended to view the emerging solid as a grossly inhomogeneous liquid with a rapidly varying one-particle density $\rho(\mathbf{r})$ reflecting the lower symmetry of a lattice.[8-13] In what follows, we will also retain this statistical (i.e., non-phonon-based) view of the solid. Given such a picture, a number of recent approaches to freezing have applied functional perturbation theory,[9,10] with the uniform system taken as the zeroth or unperturbed system. Generally the key objective is the determination of the solid and liquid coexistence conditions. In the calculations reported in the literature, they are often found to agree quite well with experiment. Yet, in spite of this agreement, the application of low-order perturbation theory (i.e., linear response) to a case in which the density variation typical of a solid is *a priori* strongly varying would not appear to be well founded. Indeed, for the hard-sphere system it has already been found[14] that the partial inclusion of the next-higher-order terms in a direct density expansion has rather important consequences in the calculations of its freezing transition.

The primary purpose of this paper is to provide a foundation for a functional description of the inhomogeneous liquid which, as we shall see, circumvents some of the above difficulties. We present an approximate free-energy functional which is constructed in such a way that the free-energy density of an inhomogeneous liquid at a given point is interpreted as that of a homogeneous system, but taken at an auxiliary density which depends parametrically on the chosen point. The appropriate density is obtained approximately by weighting the physical density over a physically relevant range about the given point. The resultant weighted-density approximation (WDA) thus accounts by construction for the short-ranged, nonlocal effects present in a real, interacting inhomogeneous liquid at the given point. The approximate functional has no local-density piece and for this reason is expected to give much better results for highly inhomogeneous systems (such as the developing solid) than functional approximations involving local-density contributions. We note here that the functional we will discuss is similar to one used by Tarazona;[13] although *ad hoc*, Tarazona's scheme succeeded in locating a first-order phase transition for simple liquids in qualitative agreement with simulation studies. In addition, good results for the liquid in contact with a hard wall were also obtained. However, the status of this approach has not been established, in the sense that the chosen free-energy functional is somewhat arbitrary and has not, as yet, been shown to result from a well-defined approximation of the exact functional. We mention here that the WDA also has an analog in the electron-gas problem (where effective densities are frequently employed) as an approximate exchange-correlation energy functional and has been analyzed in that context.[15]

The secondary aim of this paper is the determination of the liquid-solid transition in simple systems, which we pursue through an application of the WDA. This approximation does lead to such a transition, and we find the freezing parameters for the classical hard-sphere solid to be in reasonable agreement with computer-simulation studies. More importantly, the physical picture of freezing which emerges is one which depends solely on the nature of the weighted density with no further crucial or *ad hoc* approximations invoked. At sufficiently high average densities the solid phase becomes stable relative to the liquid of the same density. The reason for this is that in spite of the loss of the communal-like entropy present in the liquid resulting from the localization of the particles to lattices sites, there is a *gain* in entropy from localization (the entropy is less negative) resulting from a decrease in particle interactions, each particle sensing to a far lesser extent the presence of its now localized neighbors. This more than offsets the lost entropy. The excess free energy of the solid is interpreted in the WDA as that of an effective liquid of much *lower* density than the average solid density. It is precisely such a low-density liquid that is required to approximate the correlations in the solid, and the description arises naturally in the WDA, as we shall see below. The picture presented here goes beyond the scope of the simple cell theories of the solid by approximately including correlations between near particles, correlations which are naturally built into a phonon-based description of the solid. As we shall see, the resulting equation of state and free energy for the solid are both good.

In the next section we will begin by examining the exact free-energy functional of an inhomogeneous liquid and then describe in detail the approximation we make to obtain a weighted-density functional. We then proceed to derive an explicit expression for the optimal weighting function, optimal meaning here that all known relations between two-point functions and functional derivatives of the free energy are preserved in the homogeneous liquid limit. We are then able to provide an interpretation of the content of the WDA. In Sec. III we present the functional approach to freezing, discuss previous approximate freezing theories, and briefly compare them to the WDA, for which arguments can be given to show that it is the preferred approach, to date. In Sec. IV we study the freezing of the classical hard-sphere liquid within the WDA and compare our results to computer-simulation studies. Section V presents further discussion and conclusions.

II. FORMALISM: THE WEIGHTED-DENSITY APPROXIMATION (WDA)

We shall restrict our discussion to simple monatomic systems in which the particles interact through pairwise, spherically symmetric potentials $\phi(r)$. For N atoms in a volume V the underlying microscopic Hamiltonian is thus

$$H=\sum_{i}^{N} P_i^2/2m+\tfrac{1}{2}\sum_{i}^{N}\sum_{j}^{N}{}'\phi(\mathbf{r}_i-\mathbf{r}_j)\ . \tag{1}$$

At temperature T ($\beta=1/kT$) and for single-particle density $\rho(\mathbf{r})$ the intrinsic Helmholtz free energy, a unique[4] functional of the one-particle density $\rho(\mathbf{r})$, may be written exactly as

$$F[\rho]=F_{\text{id}}+\tfrac{1}{2}\int\int d\mathbf{r}_1 d\mathbf{r}_2\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\phi(\mathbf{r}_1-\mathbf{r}_2)\times\int_0^1 d\alpha\, g(\mathbf{r}_1,\mathbf{r}_2;\alpha)\ , \tag{2}$$

where α is introduced as a coupling constant for the pair potential. In (2), $g(\mathbf{r}_1,\mathbf{r}_2;\alpha)$ is the pair correlation function for an *inhomogeneous* system with single-particle density $\rho(\mathbf{r})$ and pair potential $\alpha\phi(\mathbf{r})$; it is also a functional of $\rho(\mathbf{r})$. F_{id} is the ideal-gas part of F. We rewrite F in the compact form

$$F[\rho]=F_{\text{id}}+\int d\mathbf{r}_1\rho(\mathbf{r}_1)\Psi[\rho;\mathbf{r}_1]\ , \tag{3}$$

where

$$\Psi[\rho;\mathbf{r}_1]=\tfrac{1}{2}\int d\mathbf{r}_2\rho(\mathbf{r}_2)\phi(\mathbf{r}_2-\mathbf{r}_1)\int_0^1 d\alpha\, g(\mathbf{r}_2,\mathbf{r}_1;\alpha) \tag{4}$$

is the excess free energy per particle of the inhomogeneous liquid at $\mathbf{r}_1$. It is clearly a functional of the density.

Since little is known about the details of $g(\mathbf{r}_1,\mathbf{r}_2;\alpha)$ and $\Psi[\rho;\mathbf{r}_1]$ for inhomogeneous systems, practical approximations usually involve a knowledge of the properties of homogeneous liquids. For homogeneous systems, the functional $\Psi[\rho;\mathbf{r}_1]$ becomes merely a function of the density, $\Psi(\rho)$. Therefore, the most desirable approximation to $\Psi[\rho;\mathbf{r}_1]$ using only homogeneous liquid information is one in which the uniform reference density $\bar{\rho}(\mathbf{r}_1)$, at which $\Psi(\rho)$ is evaluated, is itself a functional of the one-particle density *and* satisfies

$$\Psi[\rho;\mathbf{r}_1]=\Psi(\bar{\rho}(\mathbf{r}_1))\ , \tag{5}$$

which guarantees that F is evaluated exactly. For the hard-sphere system $\Psi(\rho)$ is a monotonic function of density over the entire range of densities and the identification (5) is unambiguous, in principle. In any case, the identification is intractable in practice. To proceed further, it is necessary to obtain the density $\bar{\rho}(\mathbf{r})$ of the equivalent homogeneous system, which must be a functional of the real density. We take $\bar{\rho}(\mathbf{r}_1)$ to be a weighted average of the real density which we write, following Tarazona,[13] in the form

$$\bar{\rho}(\mathbf{r})=\int d\mathbf{r}'w(\mathbf{r}'-\mathbf{r};\bar{\rho}(\mathbf{r}))\rho(\mathbf{r}')\ . \tag{6}$$

Equation (6) introduces into the theory a weighting function $w(r;\rho)$ which has an essential dependence on the density $\tilde{\rho}(\mathbf{r})$ to be discussed below. The function w should be chosen physically not only to best approximate the free energy F but also to reflect the range of nonlocality in the exact functional (4). The weighted-density approximation (WDA) thus consists of writing $F[\rho]$ as

$$F_{\mathrm{WD}}[\rho]=F_{\mathrm{id}}+\int d\mathbf{r}_1\rho(\mathbf{r}_1)\Psi(\bar{\rho}(\mathbf{r}_1)) \; . \tag{7}$$

Here,

$$\Psi(\bar{\rho}(\mathbf{r}_1))=\tfrac{1}{2}\bar{\rho}(\mathbf{r}_1)\int d\mathbf{r}_2\phi(\mathbf{r}_2-\mathbf{r}_1) \times\int_0^1 d\alpha\, g^h_{\bar{\rho}(\mathbf{r}_1)}(\mathbf{r}_2-\mathbf{r}_1;\alpha) \tag{8}$$

has the interpretation that it is the exact interaction part of the free energy per particle of a *homogeneous* liquid of constant density $\bar{\rho}(\mathbf{r}_1)$ and pair correlation function $g^h_{\bar{\rho}(\mathbf{r}_1)}$. Now, $\bar{\rho}(\mathbf{r}_1)$ appears in two places in (8). However, we may substitute (6) for the $\bar{\rho}(\mathbf{r}_1)$ prefactor, interchange integrations, and relabel coordinates to obtain

$$\Psi(\bar{\rho}(\mathbf{r}_1))=\tfrac{1}{2}\int d\mathbf{r}_2\rho(\mathbf{r}_2)w(\mathbf{r}_2-\mathbf{r}_1;\tilde{\rho}(\mathbf{r}_1)) \times\left[\int d\mathbf{r}_3\phi(\mathbf{r}_3-\mathbf{r}_1) \times\int_0^1 d\alpha\, g^h_{\bar{\rho}(\mathbf{r}_1)}(\mathbf{r}_3-\mathbf{r}_1;\alpha)\right] , \tag{9}$$

so that $\bar{\rho}(\mathbf{r}_1)$ only appears in the evaluation of g^h. Equation (9) may be compared directly to (4), and we observe that the WDA is actually an approximation only for

$$\phi(\mathbf{r}_2-\mathbf{r}_1)\int_0^1 d\alpha\, g(\mathbf{r}_2,\mathbf{r}_1;\alpha)$$

rather than for the full free energy per particle, $\Psi[\rho,\mathbf{r}_1]$. Note that the term in large parentheses in (9) also depends only on the coordinate $\mathbf{r}_1$ and hence the range of nonlocality in (9) is precisely the range of the weight function.

It is now necessary to prescribe the weighting function $w(r;\rho)$. We first observe that the choice $w(\mathbf{r})=\delta(\mathbf{r})$ leads to the well-known local-density approximation (LDA). The LDA is not expected to be physically acceptable for the case of a rapidly varying density, as is the situation we face for a solid developing out of a liquid. For a less singular choice, w will clearly serve to smooth out the sharp density variations (which are overemphasized in the LDA) to a degree determined by its spatial range. The free-energy density at $\mathbf{r}$ will thus depend not only on $\rho(\mathbf{r})$, but also on an average of the density in some region about $\mathbf{r}$. As noted, little is known about the exact properties of the inhomogeneous liquid, and so we will extract the optimum form for w by appealing to the homogeneous limit of (7). In particular, we insist that w be chosen so that the known relation between the direct correlation function $c^{(2)}(\mathbf{r};\rho_0)$ and the second functional derivative in density of the excess Helmholtz free energy $-\Phi=F-F_{\mathrm{id}}$ be strictly obeyed for the homogeneous liquid of density ρ_0.

The direct correlation function of the inhomogeneous liquid is, generally,

$$c^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\rho)=\beta\frac{\delta^2\Phi[\rho]}{\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_1)} \; . \tag{10}$$

The complex expression for $c^{(2)}$ resulting from the use of $\Phi=\Phi_{\mathrm{WD}}$ simplifies considerably in the homogeneous limit since many terms involving density derivatives of w vanish identically. For example,

$$\int d\mathbf{r}'\rho(\mathbf{r}')\partial w/\partial\tilde{\rho}\rightarrow\rho_0(\partial/\partial\tilde{\rho})\left[\int d\mathbf{r}' w(\mathbf{r}'-\mathbf{r};\tilde{\rho})\right]=0 \; ,$$

where we have used the normalization requirement

$$\int d\mathbf{r}' w(\mathbf{r}'-\mathbf{r};\tilde{\rho}(r))=1 \tag{11}$$

independent of $\mathbf{r}$ and $\tilde{\rho}(\mathbf{r})$. The uniform liquid direct correlation function is given by

$$c^{(2)}(\mathbf{r}_2-\mathbf{r}_1;\rho_0)=-\beta(\partial\Psi/\partial\rho_0)w(\mathbf{r}_2-\mathbf{r}_1;\rho_0)-\beta\rho_0(\partial^2\Psi/\partial\rho_0^2)\int d\mathbf{r}'' w(\mathbf{r}-\mathbf{r}'';\rho_0)w(\mathbf{r}_2-\mathbf{r}'';\rho_0)$$
$$-\beta\rho_0(\partial\Psi/\partial\rho_0)\int d\mathbf{r}''\{[\partial w(\mathbf{r}_2-\mathbf{r}'';\tilde{\rho}(\mathbf{r}''))/\partial\tilde{\rho}][\delta\tilde{\rho}(\mathbf{r}'')/\delta\rho(\mathbf{r}_1)]+[\partial w(\mathbf{r}_1-\mathbf{r}'';\tilde{\rho}(\mathbf{r}''))/\partial\tilde{\rho}][\delta\tilde{\rho}(\mathbf{r}'')/\delta\rho(\mathbf{r}_2)]\}.$$

For strongly inhomogeneous systems (such as a solid), the choice of $\tilde{\rho}(\mathbf{r})=\bar{\rho}(\mathbf{r})$ as the density argument in the weight function is *required* for important reasons to be discussed below. Hence,

$$\frac{\delta\tilde{\rho}(\mathbf{r})}{\delta\rho(\mathbf{r}_1)}=\frac{w(\mathbf{r}_1-\mathbf{r};\bar{\rho}(r))}{1-\int d\mathbf{r}''\rho(\mathbf{r}'')\partial w(\mathbf{r}''-\mathbf{r}_1;\bar{\rho}(\mathbf{r}_1))/\partial\bar{\rho}}\rightarrow w(\mathbf{r}_1-\mathbf{r};\rho_0) \; ,$$

and so $w(\mathbf{r}'-\mathbf{r})$, which only depends on $|\mathbf{r}'-\mathbf{r}|$, must satisfy

$$c^{(2)}(\mathbf{r}_2-\mathbf{r}_1;\rho_0)=-2\beta(\partial\Psi/\partial\rho_0)w(\mathbf{r}_2-\mathbf{r}_1;\rho_0)-\beta\rho_0(\partial^2\Psi/\partial\rho_0^2)\int d\mathbf{r}'' w(\mathbf{r}''-\mathbf{r}_2;\rho_0)w(\mathbf{r}''-\mathbf{r}_1;\rho_0)$$
$$-\beta\rho_0(\partial\Psi/\partial\rho_0)\int d\mathbf{r}''[w(\mathbf{r}_1-\mathbf{r}'';\rho_0)\partial w(\mathbf{r}_2-\mathbf{r}'';\rho_0)/\partial\rho_0+w(\mathbf{r}_2-\mathbf{r}'';\rho_0)\partial w(\mathbf{r}_1-\mathbf{r}'';\rho_0)/\partial\rho_0] \; . \tag{12}$$

Alternatively, after Fourier transformation the condition on $w(k,\rho_0)$ is

$$c^{(2)}(k;\rho_0)=-2\beta(\partial\Psi/\partial\rho_0)w(k;\rho_0) -\beta\rho_0(\partial^2\Psi/\partial\rho_0^2)w^2(k;\rho_0) -2\beta\rho_0(\partial\Psi/\partial\rho_0)w(k;\rho_0)\partial w(k;\rho_0)/\partial\rho_0 \; . \tag{13}$$

In particular, for $k\rightarrow 0$, the compressibility rule reads

$$c^{(2)}(0;\rho_0)=-2\beta\partial\Psi/\partial\rho_0-\beta\rho_0\partial^2\Psi/\partial\rho_0^2 \; , \tag{14}$$

which is independent of the weight function, since $w(k=0,\rho_0)=1$.

We are now in a position to examine the content of the

WDA. With w determined from (12), a functional expansion of $-\Phi=F_{\mathrm{WD}}-F_{\mathrm{id}}$ about a uniform reference density is guaranteed to be identical to an expansion of the true Φ to second order in density differences. Explicitly, the approximate free energy is

$$\begin{aligned} F_{\mathrm{WD}}=F_{\mathrm{id}}-\frac{1}{2\beta}\int d\mathbf{r}\,d\mathbf{r}'c^{(2)}(\mathbf{r}'-\mathbf{r};\rho_0) \\ \times[\rho(\mathbf{r})-\rho_0][\rho(\mathbf{r}')-\rho_0] \\ -\frac{1}{6\beta}\int d\mathbf{r}\,d\mathbf{r}'d\mathbf{r}''c^{(3)}_{\mathrm{WD}}(\mathbf{r}'',\mathbf{r}',\mathbf{r};\rho_0)[\rho(\mathbf{r})-\rho_0] \\ \times[\rho(\mathbf{r}')-\rho_0][\rho(\mathbf{r}'')-\rho_0]+\cdots\ . \end{aligned}$$

The higher-order direct correlation functions for the homogeneous liquid, $c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_{n-1};\rho_0)$, which appear in the higher-order terms of the functional expansion, correspond *within the* WDA to well-defined approximations and are obtained by taking further functional derivatives of Φ_{WD} and then taking the homogeneous limit $\rho(\mathbf{r})\to\rho_0$. Given that the higher-order direct correlation functions are difficult to evaluate even for simple liquid approximations (e.g., the Percus-Yevick approximation), the $c^{(n)}_{\mathrm{WD}}$ for $n>2$ are not easy to compare with their exact values. However, the exact relationship between $c^{(2)}(k,\rho_0)$ and $c^{(n)}(k,k',\ldots;\rho_0)$ given by

$$c^{(n)}(k,0,\ldots;\rho_0)=(\partial^{n-2}/\partial\rho_0^{n-2})c^{(2)}(k;\rho_0) \qquad (15)$$

is preserved for all n. Now the WDA can be constructed to preserve the direct correlation function $c^{(2)}$ exactly for both of the physically acceptable choices of density argument in the weight function, namely $\tilde{\rho}(\mathbf{r})=\rho_0$ and $\tilde{\rho}(\mathbf{r})=\bar{\rho}(\mathbf{r})$. However, it is *only* the choice $\tilde{\rho}(\mathbf{r})=\bar{\rho}(\mathbf{r})$ that leads to higher-order correlation functions[16] which *also* satisfy (15). Since $c^{(2)}$ is assumed known, *all* two-point functions and hence all the thermodynamic functions of the homogeneous liquid are reproduced exactly in the WDA. The WDA is thus an approximation which (i) is exact to lowest orders in the density variations, in the limit of nearly constant density but with arbitrarily rapid spatial fluctuations, (ii) includes terms to all[17] higher orders in a density expansion by providing approximate expressions for the three- and higher-point correlation functions [the subset of terms involving (15) being included exactly] and thus uses *all* available information from the two-point functions of the homogeneous liquid, (iii) retains an implicit functional dependence of Ψ on $\rho(\mathbf{r})$, and (iv) is expressible in a fairly simple, compact form, namely (7). In addition, the WDA is devoid of a local-density contribution to the excess free energy (i.e., w has no δ-function piece). It therefore differs fundamentally from previous approximations which also satisfy (i) in the nearly homogeneous limit but retain a local correction to the excess free energy, even in the highly inhomogeneous liquid.[5]

The nonlinear differential equation (13) for $w(k;\rho_0)$, which has been previously encountered in the electron-gas context,[15] is difficult to solve. For the classical liquid, neither of the desired boundary conditions [$w(k=0,\rho_0)=1$ and $w(k\to\infty;\rho_0)\to 0$] can be transformed into boundary conditions in the *density* variable. For fixed k and density, however, we may guess the desired solution to (13) and then iterate until satisfactory convergence is found. Our first estimate for $w(k,\rho_0)$ is obtained by solving the quadratic equation which results when the derivative term in (13) is neglected. The proper root is determined by the $k=0$ and $k\to\infty$ boundary conditions at fixed density. In practice, computation of the neglected term using the initial solution and then iterating results in convergence within 5–10 iterations to 1 part in 10^4. The resultant $w(k,\rho_0)$ differs from the initial estimate by at most 10% for the densities we consider. Figure 1 presents our results for $w(k,\rho_0)$ as calculated within the Percus-Yevick approximation[18] for a hard-sphere liquid with hard-sphere diameter σ which provides a convenient analytic form for the direct correlation function[19] (see Sec. IV). Figure 2 shows $w(r,\rho_0)$, the Fourier transform of

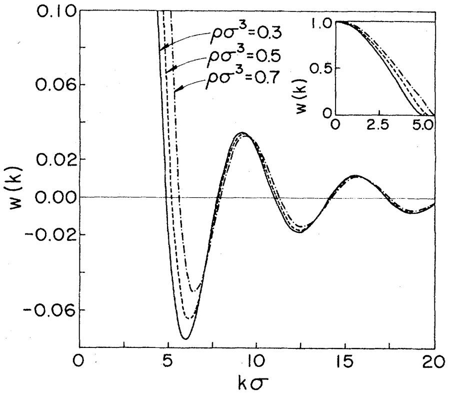

FIG. 1. Fourier transform of the weight function, $w(k)$, vs $k\sigma$ for the hard-sphere liquid in the Percus-Yevick approximation at densities $\rho\sigma^3=0.3$, 0.5, and 0.7, respectively. $w(k)$ is obtained from Eq. (12) and requires $c^{(2)}(k)$, the two-particle direct correlation function of the uniform liquid, as input. Note that $w(k)\ll 1$ for $k\sigma>5$ at all densities. The oscillations in $w(k)$ shift to slightly larger k with increasing density. Inset: $w(k)$ vs $k\sigma$ for $k\sigma<5$. Note the change in scale. $w(k=0)=1$ is required by normalization and the compressibility sum rule.

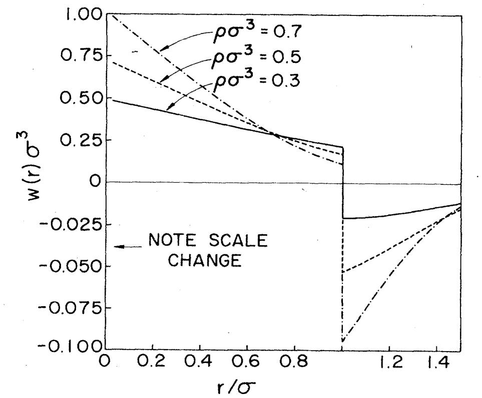

FIG. 2. Weight function in real space, $w(r)$ vs r/σ for the hard-sphere liquid in the Percus-Yevick approximation at densities $\rho\sigma^3=0.3$, 0.5, and 0.7, respectively. The basic length scale of $w(r)$ is the hard-sphere diameter σ, with $w(r)$ positive for $r/\sigma<1$ and $w(r)$ negative and small for $r/\sigma>1$. Note the scale change for $r/\sigma>1$. The range of $w(r)$ narrows with increasing density.

$w(k,\rho_0)$, at several densities, and it is clear that w possesses the range of the short-ranged function $c^{(2)}$ which, as noted originally by Ornstein and Zernike, is characteristic of the range of interactions in the liquid rather than the range of correlations. It follows that the averaging range of $\rho(\mathbf{r})$ [see Eq. (6)] is comparable to that of the short-range interactions that exist in a uniform fluid of density ρ_0 (e.g., on the scale of the *short*-range repulsive part of the pair potential). That this is physically reasonable may be seen by examining the exact functional with the simple low-density, density-independent approximation

$$g(\mathbf{r}_2,\mathbf{r}_1;\alpha)=e^{-\alpha\beta\phi(\mathbf{r}_2-\mathbf{r}_1)} .$$

The coupling constant integral in (2) may be carried out exactly for this g and the resulting free energy is

$$F=F_{\mathrm{id}}+\tfrac{1}{2}\int\int d\mathbf{r}_1 d\mathbf{r}_2\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)(1-e^{-\beta\phi(\mathbf{r}_2-\mathbf{r}_1)}) ,$$

which may be compared to (7) to tandem with (9). The weight function which appears in (9) (and which is shown for several densities in Fig. 2) is qualitatively similar to the short-ranged quantity $1-e^{-\beta\phi}$, which, for the hard-sphere potential, is simply equal to 1 for $|\mathbf{r}_2-\mathbf{r}_1|<\sigma$ and zero elsewhere. The detailed behavior of w is, of course, quite important in actual applications.

Equations (6) and (7) [with Eqs. (12) or (13) prescribing the choice of weight function] constitute the basis of the weighted-density functional formalism to be used below in an application to freezing. The application of this method to inhomogeneous systems proceeds by minimizing $F_{\mathrm{WD}}[\rho]$ with respect to a suitably parametrized density in order to find the appropriate density profile and free energy. As is usual with approximate density-functional techniques, no strict variational principle applies to the approximate functional. Instead, F_{WD} is to be viewed as a thermodynamic potential which is assumed to take its maximum equilibrium value at some density.

III. FUNCTIONAL THEORY OF FREEZING

We turn now to the application of the WDA to the freezing of a homogeneous, simple liquid into a solid structure characterized by an inhomogeneous one-particle density. The discussion is valid for all types of solids: crystalline, quasicrystalline, or glassy, and application of the WDA to each is only limited by the ability to accurately parametrize the one-particle density appropriate to the solid of interest.

We begin with the grand potential $\Omega[\rho]$ for a liquid of density $\rho(\mathbf{r})$, chemical potential μ, and initially in the presence of a one-body potential $V_{\mathrm{ext}}(r)$:

$$\Omega[\rho]=F[\rho]-\mu\int d\mathbf{r}\rho(\mathbf{r})+\int d\mathbf{r}\rho(\mathbf{r})V_{\mathrm{ext}}(\mathbf{r}) . \tag{16}$$

The equilibrium density $\rho_0(\mathbf{r})$ for this system is found by applying the condition

$$[\delta\Omega/\delta\rho(\mathbf{r})]_{\rho_0(\mathbf{r})}=0 , \tag{17}$$

which requires that $\rho_0(\mathbf{r})$ satisfies

$$\delta F/\delta\rho_0(\mathbf{r})-\mu+V_{\mathrm{ext}}(\mathbf{r})=0 . \tag{18}$$

If we write

$$F=F_{\mathrm{id}}-\Phi=\beta^{-1}\int d\mathbf{r}\rho(\mathbf{r})\{\ln[\Lambda\rho(\mathbf{r})]-1\}-\Phi[\rho] \tag{19}$$

(with Λ the cube of the thermal wavelength), then (18) becomes

$$\rho_0(\mathbf{r})=\Lambda^{-1}\exp[-\beta\mu-\beta V_{\mathrm{ext}}(\mathbf{r})+c^{(1)}(\mathbf{r};\rho(\mathbf{r}))] \tag{20}$$

and the corresponding grand potential is

$$\Omega[\rho_0]=-\Phi[\rho_0]+\beta^{-1}\int d\mathbf{r}\rho_0(\mathbf{r})[c^{(1)}(\mathbf{r};\rho_0(\mathbf{r}))-1] . \tag{21}$$

Here,

$$c^{(1)}(\mathbf{r},\rho)=\beta\delta\Phi[\rho]/\delta\rho(\mathbf{r}) \tag{22}$$

is the one-body *effective* potential acting upon a particle but having its origin in the totality of interactions with all other particles. It is the first member of the hierarchy of direct correlation functions, of which the Ornstein-Zernike function $c^{(2)}$ [Eq. (9)] is the second. The gradient of the natural logarithm of (20) leads to the first member of the Yvon-Born-Green hierarchy.

A number of approaches to freezing into a crystalline solid are based on the general mean-field results discussed above.[8–10,12–14] We note that the mean-field theory embodied in (20) and (22) should be an acceptable theory of the solid phase and hence of the liquid-solid transition since the freezing transition is first order, implying the existence of a latent heat and a resultant suppression of fluctuation effects. The dynamic solid is described by a one-particle density $\rho_s(\mathbf{r})$ which possesses the space-group symmetry of the assumed structure. In terms of the reciprocal-lattice vectors $\{\mathbf{G}\}$ characterizing the solid structure of interest, the density is expressed as

$$\rho_s(\mathbf{r})=\rho_s+\sum_{\mathbf{G}}{}'\rho_G e^{i\mathbf{G}\cdot\mathbf{r}} . \tag{23}$$

In several recent theories,[9,10] (20) is approximately solved for $\rho_s(\mathbf{r})$ (i.e., $\rho_s,\{\rho_G\}\neq 0$) in the limit $V_{\mathrm{ext}}\to 0$. This is achieved by expanding the effective one-body potential $c^{(1)}$ about its value for the uniform liquid at the coexisting liquid density ρ_l to first order in the difference $\rho(\mathbf{r})-\rho_l$. Subsequently, the set of $\{\rho_G\}$ is obtained self-consistently, but usually only for a few of the smallest or most important reciprocal-lattice vectors. Freezing is then asserted to occur for that particular density $\rho_s(\mathbf{r})$ which (a) satisfies (20) after expanding $c^{(1)}$, and (b) satisfies $\Omega[\rho_s]=\Omega[\rho_l]$ after expanding both $c^{(1)}$ and Φ in (21) to lowest orders in the density difference.

The subsequent equations are

$$\rho_G=(\rho_l/V)\int d\mathbf{r}\,e^{i\mathbf{G}\cdot\mathbf{r}}\exp\left[-\int d\mathbf{r}'c^{(2)}(\mathbf{r}'-\mathbf{r};\rho_l)\times[\rho_s(\mathbf{r})-\rho_l]\right]$$

for each ρ_G retained and

$$\Omega[\rho_1]=\Omega[\rho_1]-(1/\beta)\int d\mathbf{r}[\rho_s(\mathbf{r})-\rho_1]$$
$$+(1/2\beta)\int d\mathbf{r}\,d\mathbf{r}'c^{(2)}(\mathbf{r}'-\mathbf{r};\rho_1)$$
$$\times[\rho_s(\mathbf{r}')-\rho_1][\rho(\mathbf{r})-\rho_1]\ . \qquad (24)$$

It should be noted that at this level of approximation the only input required by the theory is the crystal structure and the quantity $c^{(2)}(k=0,\rho_1)$. Generally the density change observed at freezing and the solid density itself are given reasonably well by this limited first-order expansion method. However, it is not easily extended to higher orders because the requisite $c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n;\rho_1)$ are not readily available. The inadequacy of retaining only the low-order corrections to the LDA is a well-known difficulty for the electron-gas problem. Correspondingly, for the classical fluid, Haymet[14] has shown that the inclusion of a limited set of third-order terms, involving of course $c^{(3)}$, does have important consequences on the predictions of the theory. Moreover, in expanding about the coexisting liquid density rather than the average solid density, there is complete neglect of contributions to the free energy of the form

$$\Delta\Omega=[c_0^{(n+1)}/n!+(n-1)c_0^{(n)}/n!]\eta^n,\quad n>1 \qquad (25)$$

attributable to the nonzero fractional density change $\eta=(\rho_s-\rho_1)/\rho_1$ upon freezing. Here, $c_0^{(n)}$ is the Fourier transform of the nth-order direct correlation function with all $n-1$ wave vectors set to zero, and is related to $c^{(2)}(k=0,\rho_1)$ by (14). The terms $\Delta\Omega$ are not negligible, and it is therefore highly desirable to include corrections to all higher orders whenever possible.

To compare the WDA approach to those of the density expansion theories of freezing, we first note that the WDA is exact to the same order as the theories which reduce to (24). However, it also incorporates higher-order terms, some terms being included exactly. The theories of freezing based on density expansions may be recovered from our approach by expanding $c^{(1)}$ about ρ_s, truncating at first order and then *further* expanding the uniform liquid quantities $c^{(1)}(\rho_s)$ and $c^{(2)}(\rho_s)$ about the liquid density ρ_1. Evidently, the WDA (with the properly chosen weight function) provides a somewhat better basis for studying the freezing transition than theories based on functional expansions about the uniform liquid, despite the fact that only information about the uniform system is required in all theories to date. From a more physical point of view, the earlier theories implicitly assume [through the use of only $c^{(2)}(\mathbf{r}_2-\mathbf{r}_1;\rho_1)$] that the structure of a high-density liquid is able to accurately describe that of a solid. We will see, via the inclusion of the higher-order terms previously neglected, that if some uniform liquid is to be chosen so as to best describe a solid, that liquid should be a much *lower* density than the coexisting liquid density.

The WDA functional is an approximation for the functional $\Phi[\rho]$ and thus makes a particular but approximate statement about the form of $c^{(1)}(\mathbf{r},\rho(\mathbf{r}))$, which appears in (20). In principle, the equivalents of (20) and (21) can be studied directly *without* resort to further expansion. As an alternative procedure, the density $\rho_s(\mathbf{r})$ of the dynamic solid can be parametrized and F minimized directly with respect to $\rho_s(\mathbf{r})$ at constant average density ρ_s, and μ and Ω both calculated at the minimizing density. For fixed T, freezing is attained when the chemical potentials and pressures of the two phases are equal, i.e.,

$$\mu(\rho_s)=\mu(\rho_1)\ \text{and}\ \Omega(\rho_s)/V=\Omega(\rho_1)/V\ , \qquad (26)$$

thereby giving the coexistence densities and the solid density profile. The procedure just described has been carried out by Tarazona, who initially used a simple density-independent weight function w. More recently[13] he employed an improved form for w which included some density dependence. While these choices do lead to a freezing transition, the $F[\rho]$ assumed in Tarazona's work still requires physical justification, and although the results are reasonable, it remains difficult to see why. In particular, it is not clear why weight functions appropriate to *low*-density liquids give reasonable results for *high*-density systems. We show below that even for a physically motivated weight function, corresponding to the choice of $\bar{\rho}(\mathbf{r})=\rho_s$, freezing does *not* result even though the resultant functional is *exact* to second order, includes terms to all orders, and seems physically reasonable. We remark, however, that the important corrections of (25), arising from an expansion about ρ_s, are included exactly for *any* weight function used since the compressibility (14) from which all terms in (25) are derived is independent of w. Further, the relation of the WDA approach to the theory embodied in the approximate forms of (24) has not been previously established We have now provided this connection and have shown why the WDA as applied to the freezing transition is to be preferred.

IV. FREEZING OF HARD SPHERES

The classical hard-sphere (HS) liquid is a traditional testing ground for liquid theories because of the availability of accurate computer simulations[3] and thermodynamic functions.[19–22] The HS liquid provides a satisfactory description of many aspects of real *dense* liquids and for this reason has also been a basis for perturbation theory. Of particular interest here is the liquid-fcc solid transition observed in simulation studies near $\rho_1\sigma^3=0.94$. In the following, we discuss (i) the thermodynamics of the uniform HS liquid to be used in describing the inhomogeneous solid, (ii) the parametrization of the solid density and relevant length scales in the solid, (iii) the structure of the weighted density, and (iv) the freezing transition for hard spheres, using the WDA as described in the preceding sections. Although the hard-sphere system is chosen, the general features of the weighted density, its role in determining the freezing transition and the physics underlying the transition itself are not limited to the hard-sphere system.

A. Thermodynamics of hard spheres

The hard-sphere potential is

$$\phi(r)=\begin{cases}\infty, & r<\sigma\\ 0, & r>\sigma\end{cases} \qquad (27)$$

and the excess Helmholtz free energy is thus entirely entropic. There is no temperature scale and the only relevant quantity is the packing fraction $\eta=(\pi/6)\rho\sigma^3$. The equation of state (EOS) for the uniform liquid is best described by the semiempirical form suggested by Carnahan and Starling,[20]

$$\frac{\beta P}{\rho}=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\ , \tag{28}$$

where P is the thermodynamic pressure. However, the Percus-Yevick (PY) approximation provides an accurate equation of state, as derived from the compressibility, *and* an analytic form for the direct correlation function,[19] namely,

$$\frac{\beta P}{\rho}=\frac{1+\eta+\eta^2}{(1-\eta)^3} \tag{29}$$

and

$$c^{(2)}(r;\rho_0)=\begin{cases}a+b(r/\sigma)+c(r/\sigma)^3, & r<\sigma\\ 0, & r>\sigma\end{cases} \tag{30}$$

where

$$a=-(1+2\eta)^2(1-\eta)^{-4}\ ,$$

$$b=6\eta(1+\tfrac{1}{2}\eta)^2(1-\eta)^{-4}\ ,$$

and

$$c=\tfrac{1}{2}\eta a\ .$$

The excess Helmholtz free energy per particle Ψ may be obtained by integrating the equation

$$\beta P/\rho=1+\eta\partial(\beta\Psi)/\partial\eta\ . \tag{31}$$

To employ the WDA, we require $c^{(2)}$ for the homogeneous liquid. We will use (31) for $c^{(2)}$ and the corresponding equation of state (30) in determining Ψ. Despite the high *average* solid density of $\eta_s\approx0.5$, the Percus-Yevick EOS will prove to be quite accurate at the *weighted densities* of importance in the freezing problem.

B. The solid density

To parametrize the solid density, we assume the one-particle solid density to be a sum of identical Gaussians centered on the solid lattice sites.[23] The lattice structure must be specified *a priori;* we use a single parameter α to determine the width of each Gaussian. The precise form is[24,12,13]

$$\rho_s(\mathbf{r})=(\alpha/\pi)^{3/2}\sum_{R}\exp[-\alpha(\mathbf{r}-\mathbf{R})^2]\ . \tag{32}$$

Here, $\alpha=0$ corresponds to a constant density, i.e., a uniform liquid. We also observe that $\alpha\sigma^2\gg1$ corresponds to sharp, nonoverlapping peaks centered on the lattice sites. The solid density may also be written as a sum over the reciprocal-lattice vectors (RLV) $\mathbf{G}$ of the solid [see Eq. (23)] as

$$\rho_s(\mathbf{r})=\rho_s+\rho_s\sum_{\mathbf{G}}\exp(-\pi^2G^2/\alpha)e^{i\mathbf{G}\cdot\mathbf{r}}\ . \tag{33}$$

Both real and Fourier space representations will be useful, as we shall see. For a fcc lattice, the lattice constant a is related to the density by $a=(4/\rho_s)^{1/3}$. The nearest-neighbor distance is thus $d=a/\sqrt{2}=1.12\sigma$ at $\rho_s\sigma^3=1.0$, and the smallest reciprocal-lattice vector, $(2\pi/a)(1,1,1)$, has the magnitude $G_1=6.89/\sigma$ at $\rho_s\sigma^3=1.0$. Lastly, all real-space integrations may be reduced to integrals over the region $0\leqq z\leqq y\leqq x\leqq a/2$ by elementary symmetry considerations.

C. The weighted density

The general behavior of the weighted density may be ascertained by simple arguments. The weight function w has a range σ. Since the nearest neighbors of a given lattice site $\mathbf{R}$ are more distant than σ, at large values of α, $\bar\rho_s(\mathbf{R})$ has important contributions mainly from the peak at $\mathbf{R}$. The remainder of the region of integration in (6) lies in the very-low-density interstitial regions. Thus, $\bar\rho_s(\mathbf{R})$ must be *lower* than the average density ρ_s. In contrast, near the edge of the Wigner-Seitz cell, two or more lattice peaks are well within the range of w, and $\bar\rho_s(\mathbf{r})$ may be *larger* than the average density in the interstitial regions. The fact that $w<0$ for $r>\sigma$ accentuates the difference between lattice site and cell-edge weighted densities, although the average density remains unaltered.

The calculation of the self-consistent weighted density, at fixed α and ρ_s, is most conveniently carried out using the RLV description of the solid. Using (23), Eq. (6) takes the form

$$\bar\rho(\mathbf{r})=\rho_s+\sum_{\{G\}}\rho_G w(\mathbf{G};\bar\rho_s(\mathbf{r}))e^{i\mathbf{G}\cdot\mathbf{r}}\ , \tag{34}$$

where $\rho_G=\rho_s\exp(-\pi^2G^2/\alpha)$. Since all the reciprocal-lattice vectors of the solid are larger than $2\pi/\sigma$, the $w(G;\bar\rho_s(\mathbf{r}))$ are quite small in comparison to unity (see Fig. 1), the variations in $\bar\rho_s(\mathbf{r})$ will clearly be much less drastic than those of the physical density $\rho_s(\mathbf{r})$. In addition, larger G's are actually less important since both $w(G)$ and ρ_G decrease with increasing G. In practice, a careful truncation of the sum in (34) is required. We have examined the weighted density at a lattice site,

$$\bar\rho_s(\mathbf{R})=\rho_s+\sum_{G}w(G;\bar\rho_s(\mathbf{R}))\rho_G\ ,$$

to determine the number of shells (RLV's equivalent by symmetry) which must be retained. Since $w(G)$ oscillates in sign, groups of shells either add or subtract from $\bar\rho_s(\mathbf{R})$, and the truncation should be performed with care in order to take advantage of the cancellation between positive and negative contributions to the weighted density. By restricting the sum to the first 29 shells of RLV's, we find that $\bar\rho_s(\mathbf{R})$ is *underestimated* by at most 1% of the exact value for the range of densities and α's we consider.

Figure 3 shows the weighted density along the [100], [110], and [111] symmetry lines of the solid at $\rho_s\sigma^3=1.0$ and $\alpha\sigma^2=91.2$. The real solid density normalized to its peak value and calculated using (32) is also plotted. As discussed, the weighted density is a *local minimum* at the lattice sites where the real density is very large $[\rho_s(\mathbf{R})\sigma^3=156.6]$. The dips in $\bar\rho_s(\mathbf{r})$ near the cell edges in

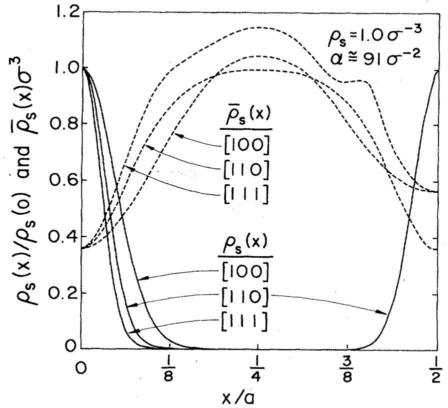

FIG. 3. The weighted density $\bar{\rho}_s(x)$ (— — —) and the normalized real solid density $\rho_s(x)/\rho_s(0)$ (———) vs x/a along the [100], [110], and [111] symmetry directions of the fcc solid. The average solid density is $\rho_s\sigma^3=1.0$, the localization parameter is $\alpha\sigma^2=91$, and the peak solid density is $\rho_s(0)\sigma^3=156.6$. The weighted density is a *local minimum* at the lattice site $x=0$ and $\bar{\rho}_s(x)$ is considerably smaller than ρ_s over the region where $\rho_s(x)$ is appreciable. The [110] densities are symmetric about $x/a=0.25$, as required. The decrease in the weighted density seen in the [100] and [111] directions for $x/a>0.25$ is due to the truncation in the sums over Fourier components in Eq. (33), but has no physical consequences because $\rho_s(x)$ is vanishingly small in this region.

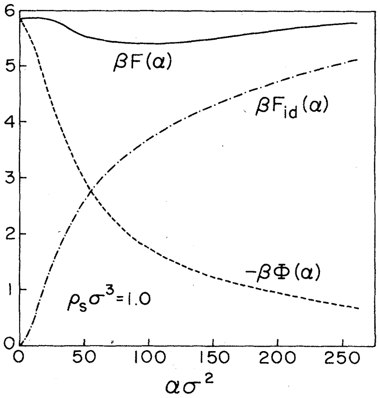

FIG. 4. Localization-dependent part of the Helmholtz free energy $\beta F(\alpha)$ vs localization parameter $\alpha\sigma^2$. Also shown are the ideal gas contribution $\beta F_{id}(\alpha)$, an increasing function of α, and the interaction contribution $-\beta\Phi(\alpha)$, a decreasing function of α. The total free energy $\beta F(\alpha)=\beta F_{id}(\alpha)-\beta\Phi(\alpha)$ may thus exhibit a local minimum for $\alpha\neq 0$, indicating the existence of a (meta-) stable solid phase.

the [100] and [111] directions are a result of the truncation in the sum over RLV's but have no physical consequences because the solid density is vanishingly small in those interstitial regions. The solution for $\bar{\rho}_s(r)$ of the self-consistent equation (34), after truncation, requires an iterative procedure at each **r**. We calculate $\bar{\rho}_s(\mathbf{R})$ to 1 part in 10^4 and use the result as input to calculate $\bar{\rho}_s(\mathbf{r})$. After two iterations, the weighted density has converged to within 1% of its fully iterated value.

D. The stable solid and the freezing transition

The existence of a (meta-) stable solidlike structure depends on a delicate balance between those free-energy contributions favoring uniformity ($\alpha=0$) and those favoring strong localization ($\alpha\rightarrow\infty$). At fixed ρ_s, the Helmholtz free energy will always have a minimum for $\alpha=0$ corresponding to the uniform liquid since an arbitrarily small density variation will always increase F relative to that of the uniform liquid. But it is also possible for F to be a local minimum for $\alpha\neq 0$, which may be understood by examining the α-dependent contributions to F. Only two terms in (19) depend on α. The first of these derives from the local, ideal-gas part of F,

$$\beta F_{id}(\alpha)=\int d\mathbf{r}\,\rho_s(\mathbf{r})\ln[\rho_s(\mathbf{r})/\rho_s]\ , \tag{35}$$

which is a monotonically *increasing* function with increasing α, as shown in Fig. 4. Accordingly, $\beta F_{id}(\alpha)$ favors the uniform liquid over any inhomogeneous configurations. The second term depending on α is the excess free energy

$$-\beta\Phi(\alpha)=\beta\int d\mathbf{r}\,\rho_s(\mathbf{r})\Psi(\bar{\rho}_s(\mathbf{r})) \tag{36}$$

also shown in Fig. 4. This is monotonically *decreasing* with increasing α, and therefore favors very strong localization of the particles about the lattice sites. The interesting behavior of $-\beta\Phi(\alpha)$ results from the structure of the weighted density. The integrand in (36) is dominated by $\rho_s(\mathbf{r})$, and therefore only the volume within $1/\sqrt{\alpha}$ of a lattice site contributes appreciably to $-\beta\Phi(\alpha)$. However, this volume is precisely the region where the weighted density, and hence $\Psi(\bar{\rho}_s(\mathbf{r}))$, is a minimum (see Fig. 3) and hence $-\beta\Phi(\alpha)$ decreases as α increases. The physical interpretation of this contribution to F is that as localization increases, each particle feels the effects of its neighbors to a lesser extent than in the liquid because the neighbors are *localized* at distances slightly *larger* (10%) than the typical correlation distance for the liquid. The in-

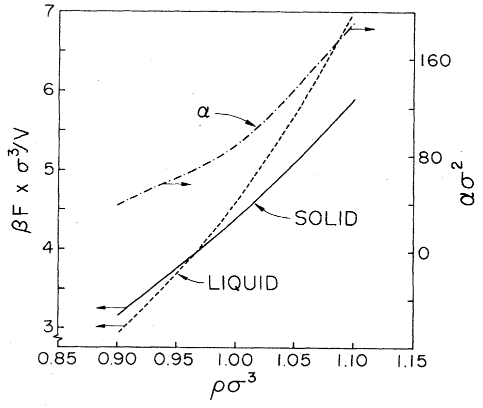

FIG. 5. Helmholtz free energy βF vs $\rho\sigma^3$ for the locally stable solid (———) and liquid (— — —). The $\rho\ln\Lambda$ part of βF is not included. For $\rho\sigma^3<0.96$ the liquid βF is the global minimum. However, above $\rho\sigma^3>0.96$, the solid phase has the lower free energy. The localization parameter α corresponding to the solid phase is also shown at each density. The chemical potential and pressure of each phase may be obtained from $\beta F/V$ using the relations $\beta\mu=(\partial/\partial\rho)(\beta F/V)$ and $-\beta P=\beta F/V-\rho\beta\mu$.

TABLE I. Liquid-solid coexistence data for the hard-sphere solid. The Lindemann parameter L is related to the structural parameter α by $L=(3/\alpha a^2)^{1/2}$ for the fcc lattice.

	ρ_s	ρ_l	$\rho_s-\rho_l$	$\Delta s/k_B$	Lindemann parameter L	Peak in $S(k)$ k	$S(k)$
Simulation	1.04	0.94	0.10	1.16	0.126	7.15	2.85
Theory	1.025	0.905	0.12	1.31	0.104	6.90[a]	2.82[a]

[a] Using the Percus-Yevick form for $S(k)$. Using the more accurate Verlet-Weis parametrization (Ref. 22) would lead to a slight increase in k and a slight decrease in $S(k)$ at the peak.

teraction contribution to the free energy of the dense, highly localized liquid is evidently comparable to that of a uniform liquid of much *lower* density. A lower effective density near the lattice sites is just what is required to best model the solid correlations by those of a liquid and arises naturally in the WDA functional description of the inhomogeneous liquid. We will discuss this point in some detail in Sec. V.

The two contributions to $F(\alpha)$ discussed above add and can lead in principle to a minimum in $F(\alpha)$ at finite α, reflecting the competition of the local and nonlocal terms in the free energy (see Fig. 4). As the solid density is varied, the values of α and F at which F is a minimum change. Figure 5 presents the solid free-energy minima as a function of the average density ρ_s, along with the free energy of a homogeneous liquid of the same density. In addition, the localization parameter α is shown at each density. The liquid free energy is calculated using the Carnahan-Starling equation of state, which is considerably more accurate than the Percus-Yevick EOS for the *high*-density liquid. At about $\rho\sigma^3=0.96$ there is a change from the liquid being the global minimum to the solid being the global minimum in the free energy. We have not examined the absolute stability of the solid phase.

Two important points may be noted at this juncture. First, we can now determine the consequences of choosing a weight function which depends on ρ_s rather than on $\bar{\rho}_s(r)$. Such a choice would lead to a higher weighted density at the lattice sites, for which $-\beta\Phi(\alpha)$ is larger, implying the occurrence of the solid phase to be less favorable. In fact, *$F(\alpha)$ possesses no local minimum* at $\alpha\neq 0$ if the weight function depends only on the *average density* ρ_s. For freezing calculations, this observation points out the importance of using the self-consistently-determined weight function [i.e., $\tilde{\rho}(\mathbf{r})=\bar{\rho}(\mathbf{r})$], which gives the best approximation for the higher-order correlation functions, even though the real-space scale of the weight function is roughly σ for all reasonable densities. In essence, the self-consistent w allows for the range of lower densities required to describe the solid to be obtained while the alternative choice for w artificially restricts the weighted densities to values closer to the average density. Second, since the important contributions to $-\beta\Phi(\alpha)$ are from weighted densities much *smaller* than the average solid density [e.g., from Fig. 3, $0.3<\bar{\rho}_s(r)\sigma^3<0.5$ in the region where $\rho_s(\mathbf{r})$ is appreciable], the error introduced by using the Percus-Yevick EOS for the solid is actually quite small, and is much smaller than the error incurred by using the PY approximation at densities near $\rho_s\sigma^3=1.0$.

To locate the hard-sphere freezing transition, we first calculate the chemical potential and grand free energy per unit volume of the solid phase from

$$\mu(\rho_s)/V=\partial/\partial\rho[F(\rho_s)/V]$$

and

$$\omega(\rho_s)=\Omega(\rho_s)/V=F(\rho_s)/V-\rho_s\mu(\rho_s)\ .$$

The corresponding quantities for the uniform liquid at density ρ_l are easily calculated from the Carnahan-Starling EOS. The coexisting solid and liquid densities are those satisfying $\mu(\rho_s)=\mu(\rho_l)$ and $\omega(\rho_s)=\omega(\rho_l)$, as mentioned earlier. We find $\rho_s\sigma^3=1.025-1.03$ and $\rho_l\sigma^3=0.905$—0.908 at coexistence, and hence a density change upon freezing of $\rho_s\sigma^3-\rho_l\sigma^3=0.12$. Table I presents our results for various thermodynamic quantities and those obtained from computer simulation. The satisfactory agreement between theory and simulation holds not only at coexistence but over a wide density range, as shown in Table II, which compares the free energy and EOS obtained for the solid in the WDA with those of simulation. The theory consistently deviates from "experiment" by only 5% and 10% for the free energy and EOS,

TABLE II. Free energy per particle and equation of state for the hard-sphere solid at various densities.

Solid density ρ_s	Free energy per particle $\beta F/N$ Theory	Simulation[a]	Equation of state $\beta P/\rho_s$ Theory	Simulation
1.000	4.391	4.661	9.14	10.26
1.025	4.623	4.868	9.62	10.84
1.050	4.861	5.099	10.16	11.54
1.075	5.108	5.354	10.89	12.28
1.100	5.370	5.663	11.62	13.12

[a] Extrapolated at lower densities from the data of Ref. 3(c) using the form suggested in Ref. 25.

respectively. Improvements in the form of a better direct correlation function and EOS for the liquid[20-22] are possible, but may not substantially improve the agreement with simulation since the functional employed is only approximate at the outset. The general agreement, however, is quite good and is to be attributed to the accuracy of the functional we have used.

V. DISCUSSION AND CONCLUSIONS

We have formulated and discussed the foundations of a weighted-density functional theory for classical inhomogeneous liquids. By optimally choosing the weight function, we have shown that the WDA corresponds to an approximate resummation of a functional expansion in density of the *exact* excess Holmholtz free energy which preserves all the two-point correlation functions of the homogeneous liquid. At the present stage of development of inhomogeneous liquid theory, the WDA appears to be the best approximation which can be made by using *only* the known properties of homogeneous liquids. It results in an expression for the excess free energy which has a particularly simple form, involving an integral over the exact excess energy of a *homogeneous* liquid but evaluated at a weighted density. The latter is a nonlinear functional of the physical density which preserves the nonlocality inherent in the exact functional. In applying the WDA to a study of the freezing transition, we find that the WDA is preferable to previous approaches based on truncated density expansions because the WDA retains terms to all order in a density expansion, the first two terms of which are given exactly.

We have also provided a detailed analysis of the freezing of the hard-sphere liquid for which, as in most simple systems, the liquid-to-solid transition is dominated by entropy considerations. At sufficiently large average densities, the solid structure is thermodynamically preferred to a uniform liquid of the same density because localization of the particles about lattice sites leads to a higher entropy from interactions despite an obvious loss of entropy due to localization. The increase in interaction entropy is accurately reflected in the structure of the weighted density, which is a minimum where the real density is a maximum, and hence implies that the localized particles have an excess entropy corresponding to that of a uniform liquid of much lower density.

We have alluded a number of times to the importance of a *low*-density liquid in describing the solid. To understand why such a density is appropriate, we must compare the particle pair correlations of the liquid, $\rho_l^{(2)}$, and the solid $\rho_s^{(2)}$. The pair correlation function $\rho^{(2)}$, defined as the joint probability of two different particles being simultaneously within $d\mathbf{r}_1$ of $\mathbf{r}_1$ and $d\mathbf{r}_2$ of $\mathbf{r}_2$, may be expressed as

$$\rho^{(2)}(\mathbf{r}_2,\mathbf{r}_1)=\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)g(\mathbf{r}_2,\mathbf{r}_1) ,$$

which serves to define g. In the homogeneous liquid, the one-particle density is a constant and hence all the structural information in $\rho_l^{(2)}$ is also contained in g_l. In the hard-sphere liquid, as an example, g is necessarily zero inside the hard core and has a peak at $r=\sigma^+$ which grows rapidly and sharpens with increasing density. Although g_l approaches its uncorrelated value $g_l=1$ at large distances, it greatly exceeds this value at σ^+ for high densities, being expressable in the PY approximation as

$$g_l(\sigma^+)=(1+\tfrac{1}{2}\eta)/(1-\eta)^2 .$$

Subsidiary oscillations in g_l corresponding to further neighbor correlations also grow with increasing density.

In contrast, the structure in $\rho^{(2)}$ of the solid is dominated by the highly structured *one*-particle density which, even in the supposed absence of two-particle correlations, gives $\rho_s^{(2)}$ the long-range order characteristic of the solid. The additional correlations contained in g_s are only those resulting from the presence of the hard core (which is perhaps not to crucial since the localized particles are separated by more than σ) and from the correlations $\langle\mathbf{u}(\mathbf{R})\cdot\mathbf{u}(\mathbf{R}')\rangle$ between the displacements $\mathbf{u}(\mathbf{R})$ and $\mathbf{u}(\mathbf{R}')$ of particles at the different lattice sites $\mathbf{R}$ and $\mathbf{R}'$, respectively. In fact, the Einstein model, which gives a reasonable description of the high-temperature solid, assumes $g_s=1$, i.e., that *no* pair correlations between particles exist. Within a harmonic approximation for the solid, g_s may be obtained from $\langle\mathbf{u}(\mathbf{R})\cdot\mathbf{u}(\mathbf{R}')\rangle$ (although this is not usually carried out) and is a relatively featureless function in comparison to its liquid counterpart g_l. In the hard-sphere system, which is highly anharmonic, one expects $g_s(\mathbf{r})$ to be zero for $r<\sigma$ but to remain otherwise devoid of any structure comparable to that of the dense liquid. If one is to now ask for what density of liquid would g_l be most similar to g_s (aside from the lattice structure which will be built into g_s), the answer is clearly a *low* density since liquids of densities comparable to that of the solid are too highly structured in physically inappropriate regions.

The weighted density at which g_l is evaluated in (9) models the required behavior quite well. Near the lattice sites, which are the only important regions in the solid, the weighted density is small and the solid correlations are likely to be best represented. Although the weighted density rises in the interstitial regions to satisfy normalization requirements, the free energy is unaffected by its behavior away from the lattice sites. Now the excess entropy cannot be expressed only in terms of the low-order correlation function g at $\alpha=1$ (in contrast to other thermodynamic quantities such as the internal energy and pressure). Hence, the effective liquid density which appears in the WDA is one which attempts to account for all the correlations simultaneously and cannot be determined only by examining g_s. However, the above discussion gives a definite interpretation of the role of the weighted density and indicates why the results obtained for the excess entropy are so good.

The ability to describe theoretically the excess entropy in non-phonon-based views of the solid has long been a problem. The "free-volume" theory,[24] often compared to the early simulation results, assumes that localizing the particles to individual cells and neglecting correlation motion is sufficient to describe the solid phase. This model corresponds to an effective potential $c^{(1)}$ which is zero at points in a cell more than σ away from the near-neighbor sites and infinite elsewhere. The free-volume theory, although asymptotically exact in the limit of close packing of hard spheres, does not adequately describe the free energy of the solid phase at near coexistence densities primarily because the correlations are neglected. A lack of knowledge of correlation effects also hampered the early developments of the statistical theory of solids, as represented in the work of Brout.[8] (Brout's work did, however, show how phonons evolve from the liquid view of the solid.) The liquid-based WDA goes beyond a simple anharmonic Einstein model of particle interactions by assuming the short-ranged, multiparticle correlations in the solid to be liquidlike. The effective potential in the WDA is thus a minimum at the cell centers but increases away from $\mathbf{R}=0$. And while it does rise sharply at points a distance σ from the near-neighbor sites, it is not infinite, which reflects the fact that with correlated motion included there exists a finite probability for particles to be within σ of the near *sites*. Since the short-ranged correlations are most important to the entropy of the solid at high temperatures, the neglect of the long-wavelength correlations in the liquid-based approach (corresponding to the small q phonons of the solid) does not lead to substantial errors. As a result, the WDA predicts free energies which are only 5% smaller and an EOS which is only about 10% lower than the simulation values over the range $1.0 \leqq \rho_s \sigma^3 \leqq 1.1$. While it has been recognized that the internal energy of a solid could be well-approximated by replacing g_{solid} by g_{liquid} at the same density,[25] our scheme is apparently the first in which the solid *free energy* is also accurately obtainable within a liquid approximation.

As expected, an attractive potential, although crucial to the existence of the liquid-vapor transition, is not required to obtain a liquid-solid transition. The inclusion of an attractive interaction between particles has not yet been considered here. It would, of course, impose a temperature scale on the problem but should not otherwise affect the basic picture of freezing presented here. The WDA formalism, of course, is generally applicable to one-component liquids with pairwise interactions of any form.

Finally, the WDA has been introduced as a general approximation for inhomogeneous liquids *without* any specific assumptions made on the nature of the inhomogeneities. Nonetheless, even for the most inhomogeneous of systems (the dynamic solid) the results we present are good and suggest that the entire range of inhomogeneities from nearly uniform liquid to highly inhomogeneous liquid is within the scope of the WDA. In particular, with a better understanding of the solid phase from the viewpoint of liquid-state theory, the extremely interesting properties of the solid-liquid and solid-vapor interfaces may now be accessible theoretically. Our future work lies in this direction.

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