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Density-Functional Theory and Freezing of Simple Liquids

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A theory for the Helmholtz free-energy functional F of inhomogeneous simple liquids is presented in which hard-sphere perturbation theory is utilized to separate F into primarily entropic and internal-energy contributions. The entropy of the hard-sphere reference system is obtained from the weighted-density approximation and the internal energy is determined from an expansion about the uniform-liquid value. The thermodynamic functions of a model Lennard-Jones solid, liquid, and vapor are then calculated and the resulting ρ - T phase diagram is found to be in good agreement with all aspects of simulation studies, including the Lindemann parameter along the freezing curve.

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In an application of the theory of inhomogeneous liquids¹⁻³ the dynamic solid is viewed as a highly inhomogeneous liquid characterized by a spatially varying one-particle density $\rho(\mathbf{r})$ possessing the symmetry of a crystal. This constitutes a very stringent test for any approximate liquid theories because the density $\rho(\mathbf{r})$ is very sharply peaked on a scale much narrower than the characteristic length scale σ of the repulsive, short-range interparticle interactions. This we know from the smallness of the Lindemann parameter at the melting point. But the excess Helmholtz free energy $F[\rho]$, a unique functional⁴ of $\rho(\mathbf{r})$, is inherently *nonlocal* on at least the same characteristic scale σ . Consequently,

expansions of F about uniform-liquid¹ and local-density approximations are suspect in such grossly inhomogeneous systems. As an alternative, we have recently proposed³ an approximation which builds in the appropriate nonlocality of $F[\rho]$ by means of a weight function w :

$$F^{\text{WDA}}[\rho] = \int d^3r \rho(\mathbf{r}) f^l(\bar{\rho}(\mathbf{r})),$$
$$\bar{\rho}(\mathbf{r}) = \int d^3r' w(\mathbf{r}' - \mathbf{r}; \bar{\rho}(\mathbf{r}')) \rho(\mathbf{r}'), \quad (1)$$

where f^l is the excess free energy per particle of a homogeneous liquid. The function w is determined by the requirement that (1) reduce to the truncated perturbation result⁴

$$F[\rho] = F^l(\rho_0) - \frac{1}{2\beta} \int d^3r d^3r' c^{(2)}(\mathbf{r}' - \mathbf{r}; \rho_0) \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}')$$

in the limit $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0 < \rho_0$, where perturbation theory is valid. This condition leads to an equation for w in terms of $c^{(2)}(r; \rho_0)$ and f^l and its derivatives with respect to density. The resulting w reflects the range of the nonlocality, which is also the range of $c^{(2)}$, the direct correlation function of the liquid at temperature T ($\beta = 1/kT$), and density ρ_0 . But, in contrast to the truncated perturbation expansion, (1), the weighted-density approximation, or WDA, remains useful even for the solid since it embodies an approximate summation of *all* terms in a perturbation expansion. In partic-

ular, the dependence of w on $\bar{\rho}(\mathbf{r})$ implies a self-consistency that allows a subset of higher-order terms in the perturbation expansion to be retained exactly.³ This WDA has been applied to study the thermodynamics of the hard-sphere (HS) solid and excellent results have been obtained. We note that similar weighted-density functionals have recently been proposed by Tarazona,⁵ and also by Meister and Kroll.⁶

Here, we present a systematic extension of the WDA to systems characterized by potentials for which

hard-sphere perturbation theory is an appropriate starting point. Freezing in such systems is expected to exhibit the same general behavior as in the HS system since it primarily involves the same geometric packing considerations arising from the strongly repulsive, short-ranged part of the potential. Accordingly, we expand the free energy about an appropriately chosen HS reference system, a common procedure for studying both uniform and inhomogeneous systems,⁷ and then use the WDA to calculate the reference system free energy. We further expand the internal energy about that of the isochoric liquid, which can be justified on the grounds that in any dense phase particles sit in nearly identical potential wells created by the potentials of neighboring particles. The resulting theory is

$$f[\rho] \approx f_{\text{HS}}[\rho; d] + (1/2N) \int d^3r d^3r' \phi(\mathbf{r}' - \mathbf{r}) \rho_{\text{HS}}^{(2)}[\mathbf{r}', \mathbf{r}; \rho, d], \quad (2)$$

where ϕ is the full pair potential. Here, $f_{\text{HS}}[\rho; d]$ and $\rho_{\text{HS}}^{(2)}[\mathbf{r}', \mathbf{r}; \rho, d]$ are the excess free energy per particle and pair distribution function of the HS system and are not, in general, known. We use the WDA for the HS reference energy and obtain an approximation to the second term in (2) as follows. We first expand the exact $f[\rho]$ about that of the liquid to all orders:

$$f[\rho] = f^l(\rho_0) - \sum_{n=2}^{\infty} \frac{1}{N\beta n!} \int d^3r_n \cdots d^3r_1 c^{(n)}(\mathbf{r}_n \cdots \mathbf{r}_1) \Delta\rho(\mathbf{r}_n) \cdots \Delta\rho(\mathbf{r}_1). \quad (3)$$

The $c^{(n)}$ are the n th-order direct correlation functions of the liquid, which we write as $c^{(n)} = c_{\text{HS}}^{(n)} + \Delta c^{(n)}$, defining $\Delta c^{(n)}$ as the difference between the actual $c^{(n)}$ of the full system and that of the HS reference system. We now (i) use the homogeneous limit of (2) for the liquid free energy, (ii) sum the hard-sphere contributions to all orders, (iii) approximate the HS reference energy using the WDA, and (iv) neglect the higher-order terms $\Delta c^{(n)}$ ($n > 2$), which have only minor effects on $f[\rho]$ since the main contributions due to $c_{\text{HS}}^{(2)}$ are retained to all orders. Following this sequence of steps we straightforwardly obtain the excess free energy of the inhomogeneous liquid as

$$f[\rho] = f_{\text{HS}}^{\text{WDA}}[\rho; d] + \frac{1}{2\rho_0} \int d^3r \phi(r) \rho_{\text{HS}}^{(2)l}(r) - \frac{1}{2\beta N} \int d^3r d^3r' \Delta c^{(2)}(\mathbf{r}' - \mathbf{r}) \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}'), \quad (4)$$

which is our main result. Here, $\rho_{\text{HS}}^{(2)l}$ is the pair distribution function of the HS liquid of diameter d . This approach is an expansion of the full liquid correlation functions about those of the HS liquid in which the main correction $\Delta c^{(2)}$ is kept; it is *not* a density expansion.

At large r we know that $\Delta c^{(2)} \approx -\beta\phi$. But, calculations of $c^{(2)}$ for the special case of the LJ potential¹⁰ at $\rho\sigma^3 = 0.84$, $kT/\epsilon = 0.75$ suggest that for *any* potential, the structure, magnitude, and even sign of $\Delta c^{(2)}(r < \sigma)$ are very sensitive to the choice of d . So, (i) to prevent particles from interacting with their own potential and (ii) to assure that all particles feel the potential well $\phi(r > d)$, as dictated by the exclusion of particles from the region $r < d$ by the exact $\rho_{\text{HS}}^{(2)l}$, we suggest the approximation

$$\Delta c^{(2)} = \begin{cases} 0, & 0 < r < r_{nn}/2, \\ -\beta\epsilon, & r_{nn}/2 < r < r_{\min}, \\ -\beta\phi(r), & r_{\min} < r, \end{cases} \quad (5)$$

where r_{nn} is the interparticle spacing, $-\epsilon$ the depth of

used to calculate the fcc solid thermodynamics of a model Lennard-Jones (LJ) system, with the properties of the uniform phases obtained in the homogeneous limit of the theory. The subsequent determination of the LJ phase diagram is, as far as we are aware, the first single theory to predict *accurately* the phase boundaries to temperatures as low as the LJ triple point and also to give results for latent heats and Lindemann parameters in good agreement with simulation results.^{8,9}

For any inhomogeneous liquid the *excess* free energy may be systematically expanded about a suitable reference system. If the reference system is that of hard spheres of diameter d , the excess free energy per particle may be written as

the potential well, and r_{\min} the location of the well minimum. The correlation "hole" for $r < r_{nn}$ is equivalent to the satisfaction of the sum rule $\int d^3r \rho(\mathbf{r}) g(\mathbf{r}', \mathbf{r}) = N - 1$ and prevents self-interaction effects.

To both liquid and solid excess energies must be added the ideal gas contribution

$$\beta f_{\text{id}}[\rho] = \ln(\rho_0 \Lambda^3) - 1 + \frac{1}{V} \int d^3r \frac{\rho(\mathbf{r})}{\rho_0} \ln \left(\frac{\rho(\mathbf{r})}{\rho_0} \right), \quad (6)$$

where Λ is the thermal wavelength. The last term on the right-hand side of (6) vanishes in the liquid and is positive for any spatial distortions in $\rho(\mathbf{r})$, reflecting the loss of entropy arising from the restriction of available phase space upon localizing particles.

We now turn to the particular case of the Lennard-Jones potential, which may be accurately parametrized by a sum of Yukawa potentials as¹¹

$$\phi_{\text{LJ}}(x) = (E/x) [e^{-a(x-1)} - e^{-b(x-1)}],$$

with $x = r/\sigma$ [$\phi_{LJ}(\sigma) = 0$], $a = 14.735$, $b = 2.6793$, and $E = 2.0199\epsilon$. We choose the HS diameter d to be independent of $\rho(\mathbf{r})$ by following the Barker and Henderson⁸ prescription

$$d(T) = \int_0^\sigma dr [1 - e^{-\beta\phi(r)}].$$

With d chosen this way, the first term in an expansion of the free energy of the purely repulsive part of the LJ potential system about that of the hard-sphere system vanishes. We use the Percus-Yevick approximation⁸ for $\rho_{HS}^{(2)l}$ and the Carnahan-Starling form⁸ for $f_{HS}^l(\rho_0)$.¹² With this input, the liquid free energy becomes an analytic function of the parameters. The free energy of the stable solid is obtained by minimizing the sum of (4) and (6) with respect to variations in $\rho(\mathbf{r})$ at fixed average density and for a given Bravais lattice. We assume the solid density to be a sum of identical Gaussians centered on the observed fcc lattice sites \mathbf{R} , namely

$$\rho(\mathbf{r}) = (\alpha/\pi)^{3/2} \sum_{\mathbf{R}} \exp[-\alpha(\mathbf{r} - \mathbf{R})^2]. \quad (7)$$

The parameter α determines the Gaussian widths and is the *only* parameter varied to minimize the solid energy. Clearly $\alpha = 0$ corresponds to a constant-density liquid while $\alpha\sigma^2 \gg 1$ corresponds to sharp, nonoverlapping peaks. The value of α obtained for the stable solid gives the rms displacement of the atoms their lattice sites which, for an fcc lattice, is $\langle r^2 \rangle^{1/2} = (3/2\alpha)^{1/2}$. Hence, α is also related to the Debye

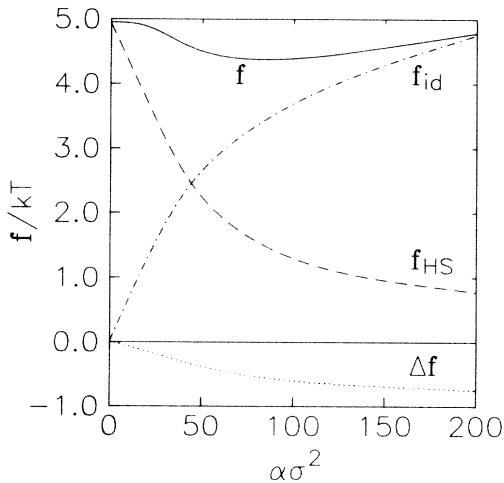


FIG. 1. Structure-dependent part of the free energy per particle, f , vs structural parameter $\alpha\sigma^2$ for the fcc Lennard-Jones solid at $kT = 0.75\epsilon$ and average density $\rho_0\sigma^3 = 1.0$. Also shown are the constituents of f : the ideal-gas entropy f_{id} , the hard-sphere energy f_{HS} calculated by use of the weighted-density approximation, and the structurally dependent contribution due to the attractive part of the pair potential Δf . The total $f = f_{id} + f_{HS} + \Delta f$ may exhibit a minimum for $\alpha \neq 0$ indicating the existence of a stable solid phase (shown) or a metastable phase.

temperature of the solid and to the Lindemann parameter $L = \{\langle r^2 \rangle^{1/2}/r_{nn}$ at $T = T_m$. Figure 1 shows the structurally dependent parts of $f[\rho]$ as functions of α at $kT = 0.75\epsilon$ and $\rho_0\sigma^3 = 1.0$. A minimum at $\alpha \neq 0$ may occur, primarily due to the competition between the monotonically increasing f_{id} and the monotonically decreasing f_{HS}^{WDA} .³ The contribution Δf from the attractive part of the potential has only the minor effect of shifting the minimum to slightly higher values of α . The dominant contribution to the internal energy is structure independent and *does not affect* the determination of the stable solid.

A stringent test of the present theory is at low T , where the internal energy is relatively large. At $kT = 0.75\epsilon$ and for various densities, we find that for both liquid and solid phases, differences between calculated and simulation⁹ free energies are almost entirely in the internal energy, the bulk of which is in the $\frac{1}{2} \int \phi \rho_{HS}^{(2)l}$ term of (4), and the calculated free energies per particle are too large by $\approx (0.4-0.5)kT/\epsilon$. The free energy of the HS *reference* solid is, however, very nearly the same as the simulation results for the fcc solid with pair potential $\phi(r < \sigma)$. Since the main discrepancy in both phases is attributable to the same approximation, the liquid-solid phase boundary is accurately predicted and is fairly insensitive to improvements on that approximation.

Figure 2 shows the phase diagram of the LJ system as calculated and also as determined by simulation studies.⁹ The agreement is very good, particularly for $kT < 1.35\epsilon$. The liquid-vapor curve is determined only from the liquid limit of the theory, providing a measure of the accuracy of liquid-phase HS perturba-

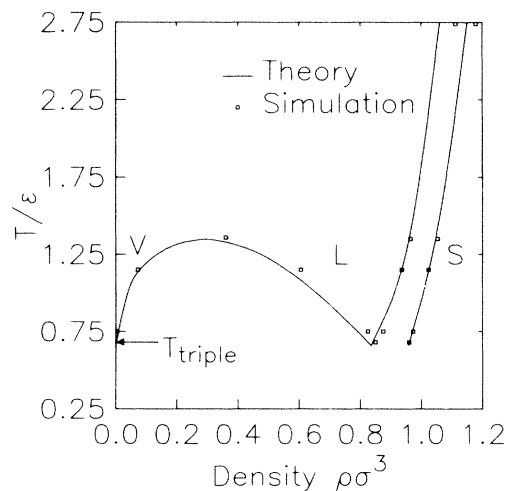


FIG. 2. Temperature-density phase diagram of the Lennard-Jones system as calculated by the present theory (solid line) and as found in simulation studies (squares). The Lindemann parameter L is found to be nearly constant, $\approx 0.12-0.13$, along the entire coexistence line.

TABLE I. Theory (simulation, Refs. 8 and 9) results for liquid and solid densities, pressure P , latent heat $T\Delta S$, and Lindemann parameter L along the Lennard-Jones liquid-solid coexistence curve. Calculated densities are accurate to within 0.005, pressures within 0.1, and latent heats within $\sim 10\%$.

kT/ϵ	$\rho_l\sigma^3$	$\rho_s\sigma^3$	$P\sigma^3/\epsilon$	$T\Delta S/\epsilon$	L
0.75	0.855 (0.875)	0.970 (0.973)	0.9 (0.67)	1.1 (1.31)	0.127 (0.145)
1.15	0.934 (0.936)	1.026 (1.024)	6.4 (5.68)	1.5 (1.46)	0.126 (0.139)
1.35	0.960 (0.964)	1.045 (1.053)	9.1 (9.00)	1.7 (1.88)	0.126 (0.137)
2.75 (2.74)	1.060 (1.113)	1.150 (1.150)	31.5 (32.2)	3.2 (2.69)	0.120 (0.149)

tion theory. Deviations at high T arise primarily from the well-known problem of choosing an appropriate d to represent the rapidly varying potential at $r \leq 0.95\sigma$. At high T , the phase boundary is governed *only* by the location of the underlying HS transition and d .

Coexistence data for the liquid and solid are compared to simulation data in Table I. The coexisting densities, pressures, latent heats, and Lindemann parameters L are all in good agreement with simulation.^{8,9} The latter implies that the Debye temperature is also given correctly for the solid, which in turn determines many temperature-dependent quantities such as the specific heat and the thermal expansion coefficient. This result is in sharp contrast to results obtained with the truncated perturbation expansion,^{1,13} which give satisfactory thermodynamic quantities such as the pressure but also give values of L at least a factor of 2 *smaller* than observed.¹⁴

It is important to examine the effects of alternative choices for $\Delta c^{(2)}$. We have done this by taking $\Delta c^{(2)} = -\epsilon$, $r < r_{\min}$, rather than the form given in Eq. (5). In this case, self-interaction effects are now deliberately included and these lower the free energy of the solid. The coexistence densities are thus also lowered, with the strongest deviations occurring at low T . At $kT = 0.75\epsilon$, coexistence occurs somewhere below $\rho_s\sigma^3 = 0.955$ and $\rho_l\sigma^3 = 0.835$. By $kT = 1.15\epsilon$, however, the coexisting densities are at $\rho_s\sigma^3 = 0.995$ and $\rho_l\sigma^3 = 0.905$, only a few percent smaller than previously determined.

The approach taken here to study the dynamic solid should be valid for the many systems characterized by

potentials for which hard-sphere perturbation theory is an appropriate starting point and for which the requisite $\Delta c^{(2)}$ may be similarly determined. As noted, the freezing transition is dominated by the change of excess entropy in the liquid into ideal gas entropy in the highly localized solid (see Fig. 1). The internal energy basically modulates the temperature and density dependence of the underlying hard-sphere transition. With the present theory of the freezing transition in non-HS systems, we are now in a position to study the many interesting problems involving solid-liquid boundaries, *which cannot be studied by use of phonon theory*. Solid-solid transitions are also within the scope of the theory and hence an understanding of the tendency of many materials to change from close-packed structures to a bcc structure just prior to melting¹⁵ may soon be within reach.

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