Density-Functional Theory of the Solid-Liquid Interface

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A density-functional theory for the structure and surface free energy γ of solid-liquid interfaces is presented which avoids perturbation and square-gradient approximations by the utilization of (i) the weighted-density approximation for the Helmholtz free-energy functional and (ii) a physical, two-parameter density profile of the interfacial region. The hard-sphere [100] fcc-liquid interface is found to be only four to five layers wide with $\gamma = 0.66kT/\sigma^2$, consistent with simulations on the similar $\epsilon(r/\sigma)^{-12}$ interface.

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The structure and energetics of the solid-liquid interface are of considerable importance in understanding a variety of phenomena including crystal growth, homogeneous nucleation, and dendritic growth. However, quantitative information, either experimental or theoretical, has so far been difficult to obtain. Computer simulations are extremely useful for the study of bulk phases but require considerable time to treat well-equilibrated, large-surface-area systems.[1,2] Moreover, the surface free energy has been obtained in only a few cases and only recently with high accuracy.[2] A theoretical study of the interface requires *a priori* that the coexisting solid and liquid be treated from the same general perspective, thereby precluding the use of the phonon theory usually used to study crystals. By describing the solid as an inhomogeneous liquid having a density $\rho_s(\mathbf{r})$ consisting of sharp peaks centered on the crystal lattice sites (the nonzero peak widths are due to thermal vibrations), the solid thermodynamics may be obtained, in principle, using density-functional (DF) ideas developed in the theory of inhomogeneous liquids[3] and liquid-state input. Since the thermal broadening in the solid is small (at melting, the Lindemann parameter is only about 0.1), $\rho_s(\mathbf{r})$ is very rapidly varying. The solid thus poses a stringent test of any DF theory based on liquid-state quantities. However, with a density functional capable of accurately predicting the solid structure and equation of state, both solid-liquid phase coexistence (equal pressure P, chemical potential μ, and temperature T in both phases) and the interfaces between them may be studied.

The interface between coexisting solid and liquid takes on the structure $\rho(\mathbf{r})$ which minimizes the excess grand potential functional $\Delta\Omega$ ($\Omega = -PV$),

$$\Delta\Omega = \int d^3r \left[\rho(\mathbf{r})\{kT[\ln(\rho(\mathbf{r})\Lambda^3) - 1] + f[\rho] - \mu\} + P\right], \tag{1}$$

subject to the constraints of liquid $[\rho(\mathbf{r}) = \rho_l]$ and solid $[\rho(\mathbf{r}) = \rho_s(\mathbf{r})]$ densities asymptotically on either side of the interface. In Eq. (1), $\rho(\ln\rho\Lambda^3 - 1)$ is the ideal-gas entropy and $f[\rho]$, the key unknown quantity, is the excess Helmholtz energy per particle and a nonlocal functional of the density. The interfacial free energy γ is precisely the excess free energy per unit area at the minimum, $\gamma = \Delta\Omega/A\,|_{\min}$, and so the structure and surface energy are obtained simultaneously and inseparably. Formally, the minimum may be found by solving the Euler-Lagrange equation $\delta(\Delta\Omega)/\delta\rho(\mathbf{r}) = 0$. Practical solutions to this problem, however, require an approximation for $f[\rho]$ which is accurate for rapidly varying densities and then a physical parametrization for $\rho(\mathbf{r})$, with the minimization carried out numerically.

Previous studies of the solid and solid-liquid interface taking the above general approach have assumed that the solid may be treated as a weakly perturbed liquid.[4,5] Lowest-order thermodynamic perturbation theory in $\rho(\mathbf{r}) - \rho_l$ is then used to approximate $f[\rho]$. Despite reasonable predictions of some solid and interfacial properties (with use of additional square-gradient approximations), the application of perturbation theory to the highly structured solid $[\rho(\mathbf{r}) - \rho_l \gg \rho_l]$ is suspect. In fact, perturbation theories predict much more rapidly varying solid densities than found in simulation studies. This unrealistic solid structure probably leads to artificially broadened interfaces and has an unknown effect on the calculated surface energies. Variations on this density-functional approach suffer from similar deficiencies[6] and related "improved" DF theories are not easily extended to the interface problem.[7] Finally, no interfaces between coexisting fcc solid and liquid phases have yet been studied, although these are the only systems which have been studied by simulation.

In this Letter, a density-functional theory for solid-liquid interfaces is presented which accurately predicts interfacial properties without the use of perturbation or square-gradient expansions. The Helmholtz free energy is approximated by use of the weighted-density approximation (WDA), which yields a nonlocal, nonperturbative functional of $\rho(\mathbf{r})$ and is, in principle, valid for arbitrary inhomogeneities.[8] In addition, a density profile providing a physically appealing description of the interfacial region is introduced which contains two variational parameters controlling the full interface width and rate of broadening of the solid density peaks, respectively. By a combination of the WDA with this parametrization, the surface free energy and profile may be calculated with no further key approximations. As an example, the hard-sphere [100] fcc-liquid interface is studied and is found to be fairly narrow, approximately four to five atomic layers wide, with a surface free energy of $\gamma=0.66kT/\sigma^2$, results comparing well with simulation studies of the similar $(r/\sigma)^{-12}$ [100] fcc interface and demonstrating that this approach may be used to obtain *quantitative* information on interfacial properties.

The WDA approximation[8] for $f[\rho]$ is given by the two equations

$$f[\rho(\mathbf{r})]=f^l(\bar{\rho}(\mathbf{r})), \tag{2a}$$

$$\bar{\rho}(\mathbf{r})=\int d^3r'w(\mathbf{r}'-\mathbf{r};\bar{\rho}(\mathbf{r}))\rho(\mathbf{r}'). \tag{2b}$$

Here, f^l is the free energy per particle of a uniform liquid, but evaluated at a weighted density $\bar{\rho}(\mathbf{r})$, thereby reflecting the nonlocality of the exact functional. By demanding that the WDA functional become exact in the limit of small density variations, the weight function $w(r;\rho)$ is completely specified in terms of f^l and the liquid direct correlation function $c^{(2)}(r;\rho)$. The WDA functional is not perturbative but rather, because of the self-consistent determination of $\bar{\rho}(\mathbf{r})$, can be viewed as an approximate sum of *all* terms in perturbation theory with some terms at each other retained *exactly*. In applications to crystalline solids, the WDA predicts the solid structure, thermodynamics, and solid-liquid coexistence conditions of the hard-sphere[8] and Lennard-Jones (LJ)[9] solids (with use of hard-sphere perturbation theory) in excellent agreement with simulation studies. The WDA is thus fully capable of handling the variations in $\rho(\mathbf{r})$ arising in the interface problem.

Now, the general physical attribute of the interface between crystal and liquid phases is that as the interface is traversed starting from the solid side, the sharp density peaks characteristic of the solid must decrease in height and broaden in a smooth manner. Upon approach of the uniform liquid, the density peaks overlap considerably and the density begins to resemble a weakly perturbed liquid. The primary factor governing the density profile is the overall width of the interface, the structural details roughly scaling with this width. To describe this behavior, $\rho(\mathbf{r})$ is first expressed in terms of the Fourier coefficients of the solid reciprocal-lattice vectors $\mathbf{G}$ (interface perpendicular to z) as

$$\rho(\mathbf{r})=\rho_l+(\rho_s-\rho_l)f_0(z)+\textstyle\sum_{\mathbf{G}}\rho_{\mathbf{G}}(z)e^{i\mathbf{G}\cdot\mathbf{r}}. \tag{3}$$

The interface is now characterized by the manner in which $\{f_0(z),\rho_G(z)\}$ vary from their solid phase values of $\{1,\rho_G\}$ to zero in the liquid. Since the rapid variations in the solid density broaden in the interface, the $\rho_G(z)$ of the larger G must decay to zero on a shorter length scale than those of the smaller G. Now the solid peaks are basically Gaussian, $\rho(\mathbf{r})\sim\exp[-\alpha(\mathbf{r}-\mathbf{R})^2]$, and so if the near-solid peaks are broadened Gaussians, $\rho(\mathbf{r})\sim\exp[-\alpha(z)(\mathbf{r}-\mathbf{R})^2]$, then the decay length of ρ_G scales like G^{-1}. Since the peaks may broaden less rapidly, the following general scaling form for the decay length z_G-z_0 of $\rho_G(z)$ is proposed:

$$z_G-z_0=(G_1/G)^\nu\Delta z,\quad 0\leq\nu\leq 1, \tag{4}$$

the exponent ν governing the rate of broadening of the peaks through the interface of width Δz (and allowing for no broadening if $\nu=0$). The $\rho_G(z)$ are next parametrized by a simple shape function,

$$\begin{aligned}\rho_G(z)&=\rho_G,\quad |z|<z_0,\\ &=\rho_G\{1+\cos[(z-z_0)\pi/(z_G-z_0)]\}/2,\quad z_0<|z|<z_G,\\ &=0,\quad z_G<|z|,\end{aligned} \tag{5}$$

in a slab geometry (solid phase in the region $|z|<z_0$, liquid in the region $|z|>z_0+\Delta z$, interface width Δz). The spatial variation of $f_0(z)$ is taken to be identical to that of $\rho_{G1}(z)$, where G_1 is the smallest G of the solid. With use of (4) and (5), each $\rho_G(z)$ decays smoothly from its solid value to zero over a length z_G-z_0 which is *proportional to the full interface width* Δz. The width Δz and exponent ν are the only parameters varied to minimize Eq. (1). It is evident from Fig. 1 (which shows the planar average of the minimum hard-sphere [100] fcc-liquid interface width $\nu=0.25$) that this simple description contains the essential physical features of the interface. The scaling in (4) gives physically reasonable, positive-definite interface profiles for $0\leq\nu\leq 0.8$ while the cosine functions in (5) closely mimic the exact hyperbolic tangent functions which obtain from ϕ^4 theories, especially in the middle of the interface where the ρ_G vary most rapidly. Also, for large G the decay length is potentially very short and may invalidate any assumptions of slow variations. The quantity z_0 is, in principle, a third variational parameter because the location of the interface relative to the underlying crystal lattice can vary, but here z_0 is fixed at the midpoint between [100] lattice planes. Of course, modifications to (4) and (5) to account for subtle details of the interfacial structure, such as slight lattice expansion or contraction, may be made, but only at the expense of further parameters and likely with only small corrections to the actual surface free energy, which is of as much, if not more, importance

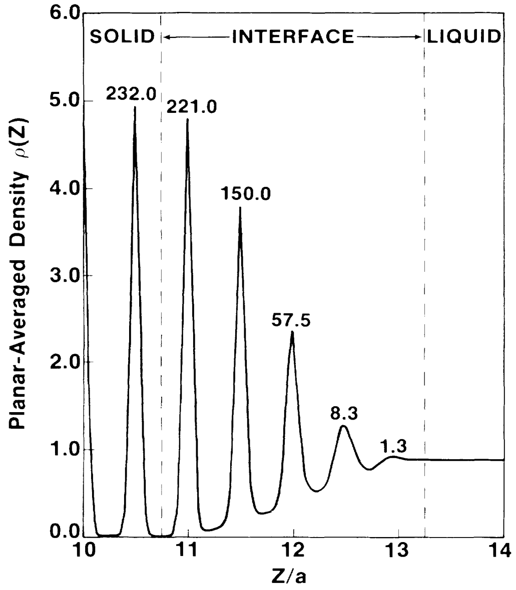

FIG. 1. Planar-averaged density $\rho(z)$ of the equilibrium hard-sphere [100] fcc-liquid interface obtained with use of the WDA and a scaling parametrization for the interfacial profile in which the length scales for the broadening and weakening of the solid peaks are the only variational parameters. The interfacial width is only four to five atomic layers (five shown) and the *local* densities at the lattice sites are also noted to emphasize the extreme variations in local density through the interface.

than the detailed structure. The scaling law for $z_G - z_0$ depends only on the magnitude of G and so this two-parameter form does not possess anisotropy, which could be introduced by making the scaling law depend on both $\mathbf{G}_\parallel$ and G_z independently, with at least one extra parameter. However, the functional used is nonlocal and, hence, "knows" the orientation of the interface, so that anisotropy in the interfacial properties can be considered within the present approach.

The minimization of Eq. (1) to obtain γ is now straightforward and we consider the hard-sphere [100] fcc-liquid interface as an example. In the following, the unit of length is the hard-sphere diameter σ and the unit of energy is kT. The features of the coexisting phases which are expected to most influence the interfacial properties are a fractional density change of 15.7% on freezing ($\rho_s\sigma^3 = 1.02$, $\rho_l\sigma^3 = 0.881$), a latent heat of $\Delta s = 1.46$, and a Lindemann parameter in the solid of 0.101, all in basic agreement with simulation studies.[10] Numerical details will be discussed in a longer paper.

The surface energy is found to be $\gamma = 0.66 \pm 0.02$, corresponding to a minimum for a width of four to five atomic layers (four to five layers of neither bulk solid nor bulk liquid density) and an exponent of $\nu \approx 0.25$. Near the minimum, γ is weakly dependent on the precise interface width. Results for $\nu = 0.5$ are only 0.05 larger while those for $\nu = 0$ are 0.17 larger, indicating $\nu > 0.25$. In addition, essentially identical results are obtained for interfaces in which z_0 is shifted by $a/4$. The planar-averaged density profile $\rho(z) = A^{-1}\int dx\,dy\,\rho(\mathbf{r})$ of the five-layer, $\nu = 0.25$ interface is shown in Fig. 1 and is, not surprisingly, considerably narrower than those obtained with use of perturbation theories.[5,6] Since the averaged profile does not show the considerable variations in 3D structure through the interface, the peak *local* densities at the lattice sites in each layer are noted. Even in the near-liquid layers, the density variations are nonnegligible for such narrow interfaces. The largest contributions to γ occur in the middle of the interface where the structure is still appreciable and most rapidly varying, and hence, the use of a nonperturbative functional such as the WDA, rather than perturbation and square-gradient approximations, is clearly necessary in studying this interface. Finally, it is interesting to note that small contributions to the excess free energy do come from the layers of bulk solid and liquid adjacent to the interfacial region because the functional is nonlocal on a scale of about σ.

Simulations have not been carried out on the hard-sphere [$\epsilon(r/\sigma)^{-n}$, $n = \infty$] interface but have been made on the closely related purely repulsive soft-sphere $\epsilon(r/\sigma)^{-12}$ system, which freezes into an fcc structure (and is a good approximation to the high-temperature Lennard-Jones system).[11] Since the freezing transition is dominated by entropic considerations, a qualitative comparison of these two systems is justified. Furthermore, some quantitative comparisons are reasonable because the important quantities $\Delta s = 1.0$ and $L = 0.14$ for the soft spheres are close to the corresponding hard-sphere values and the energy of fusion ($\simeq 0.12kT$) is small in the soft-sphere system. Cape and Woodcock[11] found the [100] interface to be seven layers wide, slightly broader than found here. The surface stress of the $\epsilon(r/\sigma)^{-12}$ interface, which is similar but not identical to the surface free energy since a solid can sustain shear, was determined to be $0.46 \pm 0.1(kT/\epsilon)^{1/6}kT/\sigma^2$. To make a quantitative comparison, we assume that a hard-sphere system having an effective diameter $d/\sigma = (\epsilon/kT)^{1/n}(1 + B/n)$ ($B = 0.5772\ldots$) approximates well the properties of the $\epsilon(r/\sigma)^{-n}$ system.[12] By scaling our results in this manner, we find $\gamma = 0.60(kT/\epsilon)^{1/6}kT/\sigma^2$, which is close to the simulation values. The simulation results also indicate that the averaged density and structure are varying on the same length scale, so that the assumption of $f_0(z) \propto \rho_{G1}(z)$ made here seems reasonable. A further comparison of simulated $(r/\sigma)^{-12}$ and LJ [100] interfaces shows them to be very similar in structure.[11] The WDA has been used to study LJ freezing,[9] and so the present approach is clearly applicable to the LJ system. In fact, the attractive potential contributions play only a minor role in the LJ freezing transition and structural results similar to those obtained here are thus expected.

In conclusion, a physical parametrization of the interfacial density profile has been presented which, in combination with the flexible WDA functional for the Helmholtz free energy, allows for the determination of interfacial properties *without any assumptions of slow density variations.* Results for the hard-sphere [100] fcc-liquid interface show both the capabilities of this approach and the necessity of allowing for rapidly varying interfacial structures. The present approach may be used to study other potential systems, particularly those amenable to hard-sphere perturbation theory. Accurate surface tensions, surface structures, and the anisotropies in these quantities with varying crystal face are thus now obtainable for a variety of materials.

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