bcc Symmetry in the Crystal-Melt Interface of Lennard-Jones Fluids Examined through Density Functional Theory

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Using a density functional theory for Lennard-Jones fluids, we find significant bcc (body-centered-cubic) character in both the planar interface between the stable fcc (face-centered-cubic) crystal and the stable liquid and at the interface of the critical fcc nucleus in a metastable liquid. We introduce an order parameter that continuously distorts a crystal with fcc symmetry to one with bcc symmetry. Our results suggest that metastable phases may have large effects on equilibrium interfaces and on rates of first-order phase transitions. [S0031-9007(96)01498-6]

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In a first-order phase transition away from the spinodal, the stable phase first appears in a metastable background phase via nucleation. The work of formation of a nucleus depends on the free energies of the stable and metastable phases and on a surface free energy determined by the structure of the interface. A recent computer-simulation study by ten Wolde *et al.* [1] of Lennard-Jones fluids has indicated that on the surface of a fcc (face-centered-cubic) critical nucleus in a background of metastable liquid lies a layer with bcc (body-centered-cubic) symmetry. This finding has important implications for the calculation of interfacial surface free energies used in nucleation theories. Their findings also indicate that at small undercoolings precritical bcc crystallites form and then transform into the critical fcc nucleus.

These phenomena were prefigured by Ostwald [2] in his “step” rule of 1897, which postulated that the crystallite formed is not necessarily the most stable thermodynamically but is the state closest to the liquid. Refining this rule, Stranski and Totomanow [3] argued that the state with the lowest free energy barrier to nucleation will be the one found. More recently, Alexander and McTague [4] and Klein and Leyvraz [5] have suggested that a metastable bcc phase can easily be formed from the undercooled liquid.

A host of computer simulations have examined the possibility of bcc nuclei forming in the metastable liquid [6–12]. One simulation reported the formation of bcc nuclei [6]; others reported no such findings [7–12]. Swope and Andersen [12] found both bcc and fcc precritical crystallites at an undercooling of 50% of the melting temperature; however, only the fcc crystallites became postcritical. Recently, ten Wolde *et al.* [1] studied the formation of crystallites at moderate undercoolings (20% of the melting temperature) and found evidence for precritical bcc crystallites forming and then transforming to a critical fcc crystallite.

On the density functional theory front [13], Curtin and Runge [14] utilized a weighted-density-functional approximation (WDA) to find metastable hard sphere solids with bcc structure. The density functional results are in good agreement with their Monte Carlo simulations of hard sphere solids. In this Letter, we introduce an order parameter that monitors the Bain’s distortion [15] which continuously transforms a crystal of fcc symmetry into a crystal of bcc symmetry. This order parameter allows us to model the continuous symmetry change across an interface of the fcc solid and the liquid in our density functional calculations for the Lennard-Jones fluid. Our free energy functional has a square-gradient form, with the parameters determined by a modified weighted density approximation (MWDA) applied locally through the liquid-solid interface. We find a planar interface with significant bcc character, as well as strong bcc character surrounding the critical fcc nucleus in the undercooled system.

We write the microscopic density, $\tilde{\rho}(\mathbf{r})$, as a Fourier expansion in reciprocal lattice vectors (the symmetry of these reciprocal lattice vectors is discussed below),

$$\tilde{\rho}(\mathbf{r}) = \rho + \rho_s \sum_i m_i e^{i\mathbf{k}_i \cdot \mathbf{r}}, \tag{1}$$

where ρ is the average density, ρ_s is the average density of the solid, the Fourier coefficients m_i are structural order parameters that measure the crystallinity of the solid, and the $\mathbf{k}_i$'s are reciprocal lattice vectors. ρ ranges from the density of the liquid to the density of the solid, and m_i ranges from zero (in the liquid) to one (in a zero-temperature perfect crystal). We approximate the density as a sum of Gaussians,

$$\tilde{\rho}(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_i e^{-\alpha(\mathbf{r}-\mathbf{R}_i)^2}, \tag{2}$$

where a_0 is the lattice constant, the $\mathbf{R}_i$'s are the real-space lattice sites, and α determines the width of the Gaussians (the mean-square amplitude of vibrations about the crystal sites). In our Gaussian approximation, all of the m_i's are coupled to the first one, m_1,

$$m_i = (m_1)^{(\mathbf{k}_i/\mathbf{k}_1)^2}. \tag{3}$$

Thus, ρ describes the change in the average density, and m_1 (which we write as m from here on) describes the change in structural order.

In specifying the symmetry of the crystal lattice, we look for a model that continuously distorts the fcc lattice into a bcc lattice. We introduce an order parameter χ that monitors the Bain's distortion [15] in the $\hat{v}$ direction (see Fig. 1). The set of real-space lattice vectors that span the bcc-fcc lattices are

$$a_1 = \frac{a_0}{2}\left(\hat{u} + \frac{\chi\hat{v}}{\sqrt{2}}\right), \qquad a_2 = \frac{a_0}{2}\left(\hat{t} + \frac{\chi\hat{v}}{\sqrt{2}}\right), \tag{4}$$

and

$$a_3 = \frac{a_0}{2}(\hat{t} + \hat{u}), \tag{5}$$

where $\chi = 1$ defines the bcc lattice and $\chi = \sqrt{2}$ the fcc lattice. The reciprocal lattice vectors k_i in Eq. (1) are linear combinations of the following vectors:

$$b_1 = \frac{2\pi}{a_0}\left(-\hat{t} + \hat{u} + \frac{\sqrt{2}\,\hat{v}}{\chi}\right),$$
$$b_2 = \frac{2\pi}{a_0}\left(\hat{t} - \hat{u} + \frac{\sqrt{2}\,\hat{v}}{\chi}\right), \tag{6}$$

and

$$b_3 = \frac{2\pi}{a_0}\left(\hat{t} + \hat{u} - \frac{\sqrt{2}\,\hat{v}}{\chi}\right). \tag{7}$$

Three order parameters, ρ (change in density), m (crystallinity), and χ (lattice symmetry of the solid) vary through the crystal-melt interface.

In studying phase transitions, it is convenient to employ the grand canonical potential, Ω, which allows fluctuations in the number density at fixed chemical potential. In density functional theory, Ω is a functional of the microscopic density $\tilde{\rho}(\mathbf{r})$. In modeling a Lennard-Jones fluid (argon) we use a square-gradient approximation for the nonlocal contributions to the grand canonical potential. To simplify our calculations and obtain a qualitative picture of the liquid-solid interface, we keep the density ρ constant, so that the grand canonical potential functional for the equilibrium planar interface is

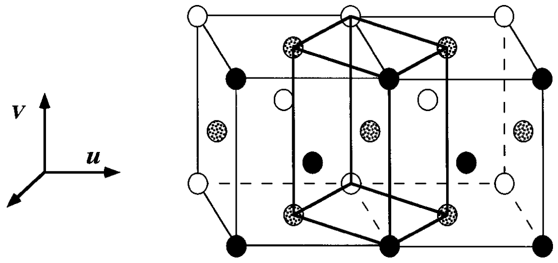

FIG. 1. Two fcc (face-centered-cubic) cells are shown outlined with thin black lines. The solid circles are atoms at the front of the cubes; the dot-filled circles are in the midplane; and the open circles are in the back. After undergoing a Bain's distortion along the v axis, the cube outlined with thick dark lines becomes bcc (body-centered cubic).

$$\begin{aligned}\frac{\Omega}{\rho_s k_B T_f} &= \int d\mathbf{r}\,\omega[\chi(\mathbf{r}), m(\mathbf{r})] \\ &+ \frac{1}{2}\int d\mathbf{r}\,K^2_{mm}[\chi(\mathbf{r}), m(\mathbf{r})]\left(\frac{\partial m}{\partial z}\right)^2 \\ &+ \frac{1}{2}\int d\mathbf{r}\,K^2_{\chi\chi}[\chi(\mathbf{r}), m(\mathbf{r})]\left(\frac{\partial \chi}{\partial z}\right)^2 \\ &+ \int d\mathbf{r}\,K^2_{m\chi}[\rho(\mathbf{r}), m(\mathbf{r})]\left(\frac{\partial \chi}{\partial z}\right)\left(\frac{\partial m}{\partial z}\right),\end{aligned} \tag{8}$$

where k_B is the Boltzmann constant, T_f is the coexistence temperature, ω is the local free energy, and the K^2_{jk}'s are square-gradient coefficients obtained by expanding the free energy with respect to $(\partial m/\partial z)$ and $(\partial\chi/\partial z)$,

$$\begin{aligned}K^2_{jk} &= \frac{k_B T}{2V(\rho_s k_B T_f)}\int d\mathbf{r} \\ &\times \int d\mathbf{r}'(z - z')^2 c^{(2)}\,\frac{\partial\rho(\mathbf{r})}{\partial j}\,\frac{\partial\rho(\mathbf{r}')}{\partial k},\end{aligned} \tag{9}$$

where V is the volume and $c^{(2)}$ is the direct correlation function.

To construct the local grand canonical potential density, ω, we adopt a compromise between simply expanding the free energy about the liquid density and truncating it at second order [16,17] and using the full weighted density approximation [18]. We follow the approach proposed by Ohnesorge *et al.* [19] that separates the Lennard-Jones potential into a hard sphere and an attractive tail. The hard sphere free energy is then calculated using the MWDA [20]. For details of the free energy functional, see Refs. [19] and [21].

Throughout our calculations, we hold the density ρ constant (a_0 changes). At the coexistence temperature, $T = 83.1$ K, we choose $\rho = 0.888$ so that the free energy of the solid is equal to that of the liquid. The local grand canonical free energy surface is shown in Fig. 2. Note the stable fcc solid at $\chi = 1.414$ and $m = 0.818$, the metastable bcc solid at $\chi = 1$ and $m = 0.750$, and the liquid at $m = 0$ (the value of χ is irrelevant for the liquid).

The planar equilibrium interface is found by minimizing the grand canonical potential functional,

$$\frac{\delta\Omega}{\delta\tilde{\rho}(\mathbf{r})} = 0. \tag{10}$$

This gives two ordinary differential equations describing the evolution of m and χ across the interface,

$$\frac{\delta\Omega}{\delta m(z)} = 0, \qquad \frac{\delta\Omega}{\delta\chi(z)} = 0. \tag{11}$$

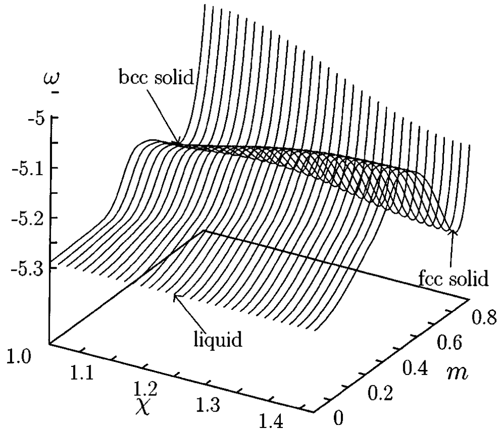

FIG. 2. The local grand canonical free energy density ω at $T = 83.1$ K and $\rho = 0.888$. Note the stable fcc solid ($\chi = 1.414, m = 0.818$), the metastable bcc solid ($\chi = 1.0, m = 0.750$), and the stable liquid ($m = 0$). The metastable bcc solid creates a saddle point near $\chi = 1.0$.

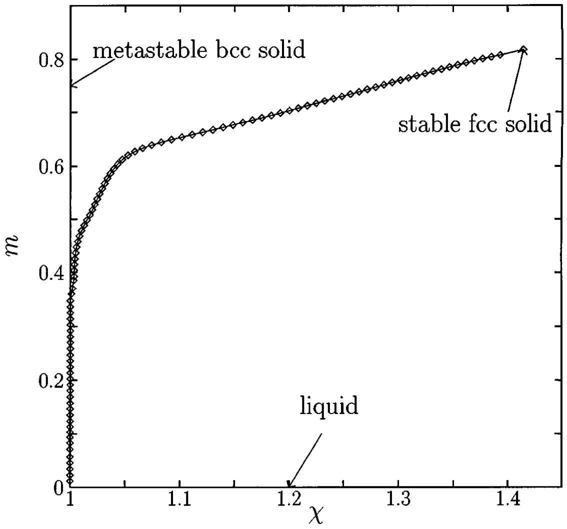

FIG. 3. A plot of the two order parameters m and χ as they depend parametrically on position z through a planar equilibrium crystal-melt interface. Note that the symmetry of the lattice changes from fcc to bcc before m approaches the liquid value.

We solve the equations using a Runge-Kutta variable step-size routine [22], with the following boundary conditions:

$$m_{z\to-\infty} = m_{\text{solid}}, \quad m_{z\to+\infty} = 0,$$

$$\chi_{z\to-\infty} = \sqrt{2}\,. \tag{12}$$

Figure 3 shows the two order parameters m and χ as they depend parametrically on the position z through a planar equilibrium crystal-melt interface. Note the significant bcc character in the interface as the crystal becomes less ordered (m decreases): the value of χ evolves quickly from 1.414 to 1. The presence of the metastable bcc state creates a saddle point (evident in Fig. 2) which serves as the lowest free energy barrier between the crystal and the liquid; the equilibrium interfacial profile passes close to this saddle point. The simpler path in which only m changes at fixed χ is of higher free energy. Our results confirm those of ten Wolde *et al.* [1], who found residual bcc character in the crystal-liquid interface. A qualitative description of our results is that the fcc solid is "wetted" by a bcc layer. Because the density is held constant, the calculated surface free energy γ is $0.19\epsilon/\sigma^2$, which is somewhat outside the range of values from simulations, $0.34\epsilon/\sigma^2$ [23], and from free minimization of the free energy functional, $0.29\epsilon/\sigma^2$ [24].

In general, the presence of metastable states in the vicinity of two stable states creates saddle points that provide lower free energy barriers for the equilibrium profiles to cross. This was also seen by Ohnesorge *et al.* [19] in the surface melting of Lennard-Jones vapor-solid interfaces, where a metastable liquid layer lies between the stable solid and the stable vapor. In a system with many metastable states (such as in ice) and depending on the geometry of the free energy surface, the interface may be quite complicated as the equilibrium interfacial profile passes close to one or more of these metastable phases.

We now ask how this bcc character in the interface affects the nucleation of Lennard-Jones fluids. In density functional theory, the critical nucleus is obtained by finding the extremum (saddle point) of the grand canonical potential functional,

$$\frac{\delta\Omega}{\delta\tilde{\rho}(\mathbf{r})} = 0\,. \tag{13}$$

From the above equation, two ordinary differential equations describe the evolution of m and χ in a spherically symmetric nucleus, where $m = 0$ as r (distance from the center of the nucleus) approaches $+\infty$,

$$\frac{\delta\Omega}{\delta m(r)} = 0, \qquad \frac{\delta\Omega}{\delta\chi(r)} = 0\,. \tag{14}$$

As the liquid-solid interface is undercooled, the system is kept under nonequilibrium conditions by constraining the density to be 0.888. There is again significant bcc character in the interface. As the undercooling increases, the interface with bcc character moves toward the center, until at $T = 50.0$ K, the nucleus is essentially all surface and the critical nucleus has essentially bcc symmetry. This is in accord with the results of ten Wolde [1], who found clusters that were small enough to be surface dominated by bcc order. Our work and that of Ref. [1] show that bcc symmetry appearing between the fcc solid and the liquid is quite common both for equilibrium interfaces and for critical nuclei.

Further work is needed to incorporate the effects of density on these interfaces and to look at the role of strain in neighboring fcc and bcc crystalline regions. At small undercoolings, ten Wolde *et al.* [1] found bcc nuclei forming and then changing into the more stable fcc nuclei. However, at large undercoolings Swope and Andersen [12] found that only the stable fcc crystallites became postcritical. Further work is needed to understand the limits of Ostwald's "step rule."

Our suggestion that metastable states may play a critical role in nucleation dynamics could have much broader implications for other kinds of first-order phase transitions. Perepezko [25] has observed that both fcc and bcc crystals form at comparable rates over a range of compositions in nickel-vanadium alloys; this is surprising because the driving force depends on composition, so the nucleation rates should be exponentially different from one another. A possible mechanism is a single (largely bcc) critical nucleus that subsequently grows into either a bcc or a fcc crystal. Smits *et al.* [26] have shown that nucleation rates for colloidal crystals depend strongly on the range of the repulsive potential (through changes in the polymer coating) and have suggested the possibility that metastable bcc transition complexes may accelerate the nucleation. This is exactly the scenario present in our work.

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