Supercooling of surface modified liquids

A. Weinstein and S. A. Safran

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

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We present a simple model of surface modified first-order phase transitions, based on the density-functional theory of freezing. Motivated by recent experiments of surface induced freezing, we show how supercooling may in fact be inhibited below a certain temperature which depends on the lattice mismatch between the monolayer and the nucleated crystal, as well as on the macroscopic strength of the surface treatment. We also apply the model to systems which tend to surface-freeze above the melting point, and correlate their surface-freezing and supercooling temperatures.

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Systems which undergo first-order phase transitions often remain in metastable states for long times before reaching their equilibrium stable phase. Nucleation of the stable phase can be accelerated by the presence of perturbations, such as random defects or impurities, which reduce the free-energy barrier between metastable and equilibrium phases. While the mechanism of bulk nucleation (homogeneous and heterogeneous) has been extensively [1,2] studied, the phenomenon of controlled nucleation, initiated by surface modifications, has only recently [3] been demonstrated. In a series of experiments it was shown that crystallization of ice can be induced by monolayers of amphiphilic long-chain alcohols, $C_nH_{2n+1}OH$, on the surface of supercooled water drops. These molecules self-aggregate in a two-dimensional crystal structure [4] which closely matches the attached face of the to-be-nucleated lattice, hence leading to ice nucleation. By changing the chain length, n, the measured freezing temperature was varied from $-20\,°C$ to nearly $0\,°C$. The chain length is correlated with various properties of the monolayer—the misfit between the lattices, the strength (i.e., crystallinity) of the monolayer, and its coherence length. Understanding the effects of these properties on the stability of supercooled liquids is of both theoretical and practical interest, with applications such as cloud seeding (where ice formation is induced by surface additives) and fuel stabilization (where wax formation can be prevented by such additives).

As a first step in analyzing the problem, Refs. [5,6] used a generic, Ginzburg-Landau model for a first-order phase transition to study the effects of an ordered surface on the stability of metastable bulk. The minimal supercooling temperature was calculated as a function of the surface order parameter and a characteristic domain size. In this model, a scalar order parameter represents the "crystallinity" of the system, and the possibility of imperfect lattice matching between the monolayer and the solid is not treated. In fact, the mismatch is an important parameter which is varied systematically in water-alcohol experiments, and is expected to play an important role in surface nucleation. The work we present here accounts for lattice mismatch effects by allowing deviations from the ideal crystal structure. The supercooling temperature is found to vary as the square of the mismatch—a prediction that can be tested experimentally.

Our approach is based on the density-functional theory of freezing, originally formulated [7] by Ramakrishnan and

Yussouff, that relates the density to a set of order parameters (OP's), corresponding to the known crystalline structure of the solid phase. The free energy is expressed as a functional of the density; the solid is treated as a perturbation of the homogeneous fluid. The microscopic properties enter via the direct correlation function, $c(r)$, whose Fourier transform is related [14] to the structure factor by $\rho_0 c(q) = 1-[1/S(q)]$, where ρ_0 is the liquid density. The theory was generalized, by Haymet and Oxtoby [8], to include spatially varying order parameters, enabling calculations such as the critical size of a crystal nucleus [9] and crystal nucleation rate [10]. Multicomponent OP's have also been used [11,12] in fields such as surface melting and liquid films, but here we extend the application of density-functional theory to surface induced freezing. Rather than assuming perfect lattice matching and using scalar order parameters which represent only the amplitude of the density waves, we introduce *complex* OP's whose phases represent small deviations from the crystal periodicity. In this manner, the effects of misfitting surface modification on the supercooled bulk can be studied. We also use our theory to predict correlations between *surface freezing* and the inhibition of supercooling which has application to recent experiments [13] in alkanes.

The density of the system is expanded in terms of the lattice symmetry of the solid:

$$\rho(\vec{r})=\rho_0\left[1+\eta(\vec{r})+\sum_G \mu_G(\vec{r})\exp(i\vec{G}\cdot\vec{r})\right],\qquad(1)$$

where η is the fractional density change and $\{\vec{G}\}$ are the reciprocal lattice vectors (RLV's) of the solid. The coefficients μ_G, along with η, are the OP's of the theory, which are assumed to be slowly varying in space, and vanish in the liquid phase. It is shown in Ref. [8] that the difference in the thermodynamic potential between a homogeneous liquid and a nonuniform system (e.g., a solid-liquid interface) is given by

$$\Delta\Omega=\int d\vec{r}\left[\tilde{\Omega}(\eta,\mu_G)+\frac{1}{2}\xi_0^2(\vec{\nabla}\eta)^2+\frac{1}{2}\sum_G \xi_G^2|\hat{G}\cdot\vec{\nabla}\mu_G|^2\right]\qquad(2)$$

measured in units of k_BT. $\hat{G}$ denotes a unit vector in the direction of $\vec{G}$. The bulk energy density, $\tilde{\Omega}(\eta,\mu_G)$, depends

both on the local OP's, and on the correlation function $c(G)$ which, in principle, can be measured in the liquid phase. The other two terms represent energy penalty for spatial variations of the OP's, with the coefficients ξ_G^2 proportional to $c''(G)$. The competition between logarithmic-entropy terms and two-body correlations gives to $\tilde{\Omega}$, below the melting temperature, a characteristic "double-well" structure in OP-energy space, with one minimum at the origin (metastable liquid) and another one at finite values of μ_G and η (stable crystal). Considering a system of liquid plus surface monolayer, the *total* free energy includes, in addition to Eq. (2), a surface term, f_0, which accounts for the monolayer-liquid coupling and other surface effects. The various stable and metastable phases of the system are determined by functionally minimizing the total energy with respect to all the order parameters. One first minimizes $\Delta\Omega$ for fixed values of OP's on the surface; afterwards the total free energy is minimized with respect to these surface values. For weak modifications of the surface, the system can retain its supercooled state by remaining in a local minimum of the energy, characterized by OP's that, although finite at the surface, vanish far into the bulk. However, we expect that for large enough surface values of the OP's, such profiles become unstable and the local minimum disappears, i.e., *supercooling ceases to exist.*

In many [7] cases, only one or two sets of RLV's (which are related by point-group transformations) are dominant in the freezing process. Hence we consider only a single set, $\{\vec{k}\}$, of RLV's. The corresponding OP's can be written in a complex form: $\mu_k(\vec{r})=\psi_k(\vec{r})e^{i\varphi_k(r)}$, where ψ_k is the amplitude of crystallinity and φ_k represents a deviation from the ideal crystal structure. Following Refs. [8–10] we assume that ξ_0 is negligible and use a bulk free-energy density, denoted by f, which is already minimized with respect to the local density change η. The total free energy now has the form

$$F=\int d\vec{r}\left\{f(\mu_k)+\sum_k\left[\frac{1}{2}\xi^2(\hat{k}\cdot\vec{\nabla}\psi_k)^2+\frac{1}{2}\xi^2\psi_k^2(\hat{k}\cdot\vec{\nabla}\varphi_k)^2\right]\right\}$$
$$+f_0(\mu_k(0))\tag{3}$$

where f has a typical double-well structure in $\{\mu_k\}$. Minimizing F, one obtains two coupled equations for the amplitude and phase of each order parameter:

$$\frac{\partial f}{\partial\psi_k}+\xi^2\psi_k(\hat{k}\cdot\vec{\nabla}\varphi_k)^2-\xi^2(\hat{k}\cdot\vec{\nabla})^2\psi_k=0,\tag{4a}$$

$$2(\hat{k}\cdot\vec{\nabla}\psi_k)(\hat{k}\cdot\vec{\nabla}\varphi_k)+\psi_k(\hat{k}\cdot\nabla)^2\varphi_k=0.\tag{4b}$$

Note that Eq. (4b) requires that the function $\psi_k^2(\hat{k}\cdot\vec{\nabla}\varphi_k)$ can only vary in the plane perpendicular to $\hat{k}$.

In what follows, we consider for simplicity a system whose stable phase is a bcc crystal [7,15]. We expect that the mechanism by which a surface modification destabilizes a supercooled liquid does not depend on the exact structure of the to-be-nucleated solid. There are 12 vectors in the dominant set of shortest RLV's, which, for a surface in the plane $z=0$, can be represented by only two OP's: μ and $\mu_\|$ for the directions $(\hat{x}+\hat{z})$ and $(\hat{x}+\hat{y})$ correspondingly. The other

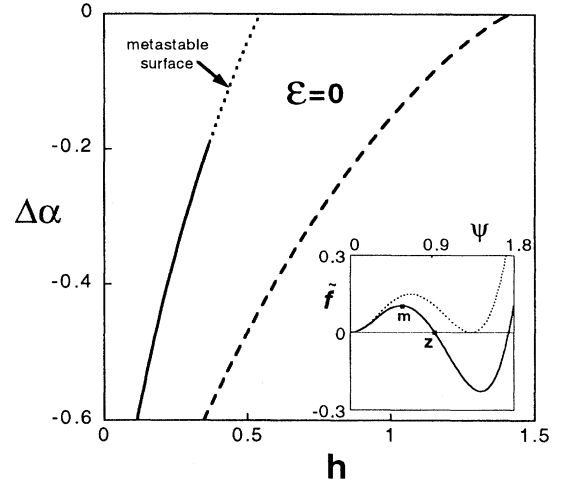
FIG. 1. Minimal supercooling temperature $\Delta\alpha$ vs field h, with no mismatch ($\varepsilon=0$), for $a=1$ (dashed line) and $a=0$ (solid and dotted line). The dotted line represents surface metastability. The inset shows the effective energy density $\tilde{f}$ (with $\varepsilon=0$) at the melting temperature (dotted) and at $\alpha=0.9\alpha_m$ (solid line).

OP's are related by symmetry. We assume an ideal, infinite monolayer with small mismatch and strong coupling to the underlying liquid. In this case the first layer of the liquid is ordered with a homogeneous periodicity, close [16] to that of the monolayer, and the amplitudes ψ and $\psi_\|$ vary only in the z direction. Equations (4b) are solved for the phases: $\varphi_\|=(\sqrt{3}/2)\varepsilon(x+y)$ and $\varphi=(\sqrt{3}/2)\varepsilon(x-z)$ (the prefactor is chosen for convenience), so that Eqs. (4a) acquire the simple form

$$\frac{\partial f}{\partial\psi_\|}+3\varepsilon^2\psi_\|=0,\tag{5a}$$

$$\frac{\partial f}{\partial\psi}-\frac{\partial^2}{\partial z^2}\psi=0.\tag{5b}$$

The mismatch parameter ε represents the fractional change between the periodicity of the crystal and that of the first layer, and the coordinates $\vec{r}$ are scaled by $\xi/\sqrt{2}$. Equation (5a) is algebraic and yields $\psi_\|$ as a function of ψ. Substituting this in Eq. (5b), one easily evaluates the first integral:

$$\frac{1}{2}\left(\frac{\partial\psi}{\partial z}\right)^2=\tilde{f}(\psi)\equiv f(\psi)+\frac{3}{2}\varepsilon^2\psi_\|^2(\psi),\tag{6}$$

where $\tilde{f}$ is an effective energy density which is a function of ψ only (see inset of Fig. 1). The constant of integration is set to zero since both ψ and its gradient vanish as $z\to\infty$. Minimization of the total free energy with respect to the surface value of the OP, $\psi_0\equiv\psi(z=0)$, leads to the boundary condition:

$$\left(\frac{\partial\psi}{\partial z}\right)_{z=0}=\frac{\partial f_0}{\partial\psi_0}.\tag{7}$$

In the supercooling region, Eqs. (6) and (7) can be solved simultaneously, yielding metastable profiles of ψ which decay away from the surface and vanish at infinity. Below a certain temperature such solutions cease to exist, presumably indicating instability of the supercooled liquid and nucleation of the solid phase.

To demonstrate this instability we approximate the bulk energy f by a fourth-order polynomial in ψ and $\psi_{\parallel}$, which provides a generic model for first-order phase transitions. We emphasize that by doing this we do not mean that the OP's are small; rather, this is just a convenient way to fit the double well. A similar model (for one OP) was assumed [17,18] by studies of critical surface phenomena in systems with first-order bulk transitions, and was also suggested in Ref. [8] for the liquid-solid interface. We take

$$f = \frac{3\alpha}{2}(2\psi^2 + \psi_{\parallel}^2) - 2\psi^2\psi_{\parallel} + \frac{1}{4}(2\psi^4 + \psi_{\parallel}^4), \qquad (8)$$

where the normalization of the third- and forth-order coefficients is set by a proper scaling of f and ψ. α is a positive constant which can be linearized in temperature close to the melting point. This expression takes into account the symmetry (of a bcc lattice) and shows the expected double-well structure in OP-energy space: for α smaller than the melting temperature, $\alpha_m = 8/27$, the absolute minimum of f is at a finite value of the OP ($\psi = \psi_{\parallel} = 1 + \sqrt{1 - 3\alpha}$), but there is another local minimum at $\psi = 0$. Equation (5a) is now exactly solvable, and the inset of Fig. 1 shows the resulting effective energy, $\tilde{f}$, at $\alpha = \alpha_m$ and below (for $\varepsilon = 0$).

The surface coupling energy is taken [17] to have the form

$$f_0 = -h\psi_0 + \frac{a}{2}\psi_0^2, \qquad (9)$$

where the first term is the "field" induced by the ordered monolayer, and the quadratic term represents a tendency of the bare surface to be disordered (both a and h are positive). In principle, f_0 also depends on the phase, and the value of ε is determined by minimization of F. However, as a first approximation we assume that the bulk contribution to this is small and it is sufficient to minimize f_0 by itself, so that ε is just the mismatch between the monolayer and the lattice.

Combining Eqs. (6) and (7), the boundary condition becomes $h = a\psi_0 + \sqrt{2\tilde{f}(\psi_0)}$. For a fixed temperature the right hand side of this equation is maximal at a certain ψ_0 between the maximum of $\tilde{f}$ (point m in Fig. 1) and its zero (point z). This is an upper bound on h, above which there are no metastable solutions. The argument can be reversed — for a given value of h there is a lower bound on temperature, below which supercooling is inhibited. In Fig. 1 we plot this minimal supercooling temperature [in dimensionless units: $\Delta\alpha \equiv (\alpha - \alpha_m)/\alpha_m$] as a function of the coupling field, h, for an ideal case of perfect matching ($\varepsilon = 0$). The onset of instability is characterized by two limiting cases: When $a \to 0$ it coincides with ψ_0 maximizing $\tilde{f}$ (point m), i.e., the system becomes unstable as the bulk energy barrier is crossed by the first layer. When $a \gg 1$ the instability occurs close to $\tilde{f}(\psi_0) = 0$ (point z). In this case supercooling persists even
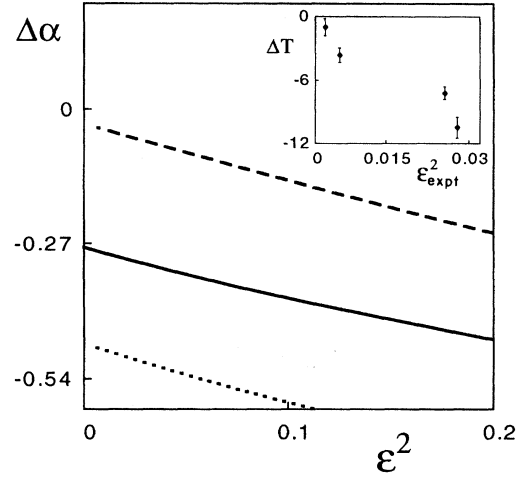

FIG. 2. Minimal supercooling temperature vs lattice mismatch ε, for $h = 1.3$, $a = 1$ (dashed line); $h = 0.3$, $a = 0$ (solid); and $h = 0.5$ $a = 1$ (dotted). The inset shows the measured freezing temperature vs average mismatch (experimental data taken from Ref. [6]).

beyond the barrier, stabilized by the gradient term in F. The dotted part of the curve in Fig. 1 represents a region of surface metastability, in which the surface layer may undergo a first-order transition into a more ordered state [18].

When the monolayer ordering does not match the crystal structure the instability curves are shifted toward lower temperatures. Figure 2 shows the dependence of the minimal supercooling temperature on the square of the mismatch parameter, ε, for various choices of the confining potential. The almost linear dependence is explained by the approximately equal value of the two order parameters, ψ and $\psi_{\parallel}$, in most of the range. Assuming they are equal, the coefficient of the quadratic term in $\tilde{f}$ becomes $\tilde{\alpha} \equiv \alpha + (\varepsilon^2/3)$, so that the mismatch simply shifts the temperature parameter by $\varepsilon^2/3$. It is not entirely straightforward to compare this prediction with the available experimental data, mainly because of the anisotropic mismatch but also due to a simultaneous change of other monolayer parameters, such as the coherence length and crystallinity, along with the mismatch [4]. Nevertheless, the inset of Fig. 2 shows the measured freezing temperature versus the average mismatch (for odd carbon number alcohol chains).

Our theory also predicts the supercooling behavior of systems which tend to surface-freeze above their melting point. An example of current interest [13] is the abrupt formation of a highly ordered surface layer in n-alkanes prior to bulk freezing. The temperature difference between surface and bulk freezing varies with chain length, and disappears for chains which are either too long or too short. We expect that the free energy of the surface layer is characterized by a double-well structure which shows an ordering transition at higher temperature than the bulk. This energy is modeled by a fourth-order polynomial in the surface order parameter ψ_s:

$$f_s = A\left[\frac{\alpha_s}{2}\left(\frac{\psi_s}{s}\right)^2 - \frac{1}{3}\left(\frac{\psi_s}{s}\right)^3 + \frac{1}{4}\left(\frac{\psi_s}{s}\right)^4\right]. \qquad (10)$$

α_S is a chain-length dependent parameter which is assumed to be linear in temperature, and the constants A and s scale f_s and ψ_s with respect to the bulk. The bulk energy density and the coupling energy are given by Eqs. (8) and (9), and the influence of the surface layer is expressed by taking in Eq. (9): $h \equiv c\psi_s$, where c is a coupling constant. For $\alpha_s < 2/9$, $\alpha > 8/27$ the surface is ordered, but the bulk free energy is still minimal for a liquid phase. To find the stable and metastable configurations of the system one should minimize the total free energy, $F + f_s$, with respect to ψ, ψ_0, and ψ_s. In practice, we assume that A is large enough so that ψ_s can be determined by separate minimization of f_s; F is then minimized for a fixed value of ψ_0, which is finally determined by another minimization. Naively one might think that any surface-freezing would prevent supercooling. In fact, our calculation shows that it depends on the value of the surface OP, ψ_s. High surface-freezing temperature is correlated with a more ordered monolayer, which suppresses supercooling more efficiently. This qualitative picture does not depend on the specific choice of parameters in f_s and f_0. In Fig. 3 we plot the minimal supercooling temperature $\Delta\alpha_{sc}$ vs the surface freezing temperature $\Delta\alpha_{sf}$. Perfect lattice matching ($\varepsilon = 0$) is assumed between the surface layer and the frozen bulk because of their molecular identity. The dashed line demonstrates how the instability curve is shifted down when a finite mismatch ($\varepsilon = 0.2$) is introduced. This suggests a mechanism for preserving the fluidity of these systems to lower temperatures, e.g., by the inclusion of surface active contaminants which distort the structural fit between surface and bulk.
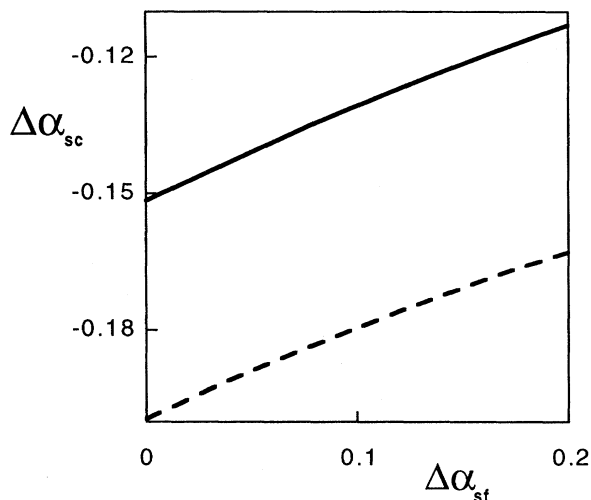

FIG. 3. Minimal supercooling temperature $\Delta\alpha_{sc}$ vs surface freezing temperature $\Delta\alpha_{sf}$ in the absence of mismatch (solid line) and with $\varepsilon = 0.2$ (dotted line). The parameters used in the coupling and surface energy are $s = 0.8, c = 0.5, a = 0.7$.

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