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Incomplete symmetry breaking and anomolous crystallization kinetics at close-packed crystal-liquid interfaces

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Stacking faults in close-packed planes are commonly observed during crystallization. In this paper we demonstrate that this behavior can be described in terms of a simple theoretical description of crystallization kinetics that couples two structural order parameters. We establish that the packing degeneracy that permits such faults also gives rise to a striking kinetic effect. The close-packed surface can freeze only when the symmetry of the two possible in-layer packings is broken, either by fluctuations or longer-range interactions. In the absence of long-range interactions, growth can take place only once the supercooling exceeds a critical depinning value, associated with a second-order phase transition in a single surface layer.
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I. INTRODUCTION

At small enough deviations from the melting temperature, the nonequilibrium dynamics of a crystal liquid are governed by the kinetics of the structural rearrangements and not the macroscopic transport of heat or impurities. The behavior of the interface in this range of small supercoolings therefore provides insight into the complex collective relaxation of the microscopic processes involved in ordering.

In this paper we examine a microscopic theory of freezing and melting that incorporates a two-order-parameter description of the crystalline structure. Interfacial growth described in terms of a single order parameter provides a rather generic picture relating interfacial motion with the chemical potential difference between the two phases. In the case of crystal growth, we only begin to understand how the complex collective process of molecular ordering influences the interfacial dynamics once we have taken into account the complexity of the final crystal structure. In theoretical terms, this translates as incorporating a multiple-order-parameter description of the crystal phase. Even in situations where we believe a bulk crystal structure can be successfully described by a single order parameter defined as the Fourier amplitude of a set of symmetry-related reciprocal lattice vectors, the presence of an interface will typically break this symmetry and hence generate multiple independent order parameters.

In the case of particles with only short-range interactions, we show that this slight increase in detail is sufficient to generate a rich range of dynamic behavior, dependent largely on the basic symmetries rather than the particular model system or approximations. In a previous study [1] it was shown that the close-packed crystal-liquid interface is unable to freeze in the absence of fluctuations. By way of contrast, a higher-index surface freezes easily, indicating an extreme anisotropy in interfacial kinetics. In this paper we show that crystallization proceeds at the close-packed surface with the inclusion of stacking faults, in the presence of fluctuations, for temperatures below a depinning temperature T_{dp}. The explanation of the persistence of this pinning in the presence of fluctuations for $T_{\mathrm{dp}}<T<T_m$ (T_m being the melting point) is a central result of this paper.

The incomplete symmetry breaking of interest here is related to the sort of degeneracies found, for example, between hard-sphere crystals of face-centered cubic (fcc) and hexagonal-close-packed structures. This degeneracy can be characterized by the energy equivalence of two possible sets of sites on the close-packed (111) surface (see Fig. 1). This equivalence is a product of the short range of interaction. Two distinct crystal packings may have the same number of nearest neighbors per particle (and hence equivalent potential energy when interactions are short ranged), but will differ in the number of more distant neighbors per particle. The sort of stacking degeneracies described here can thus be thought of as arising from a lack of coupling of the in-layer order in adjacent close-packed planes. Such a picture is certainly relevant to the case of crystallization in hard-sphere colloidal suspensions. Pusey *et al.* [2] have established with light scattering the presence of a significant density of stacking faults in these crystals. In this paper we examine the kinetic con-

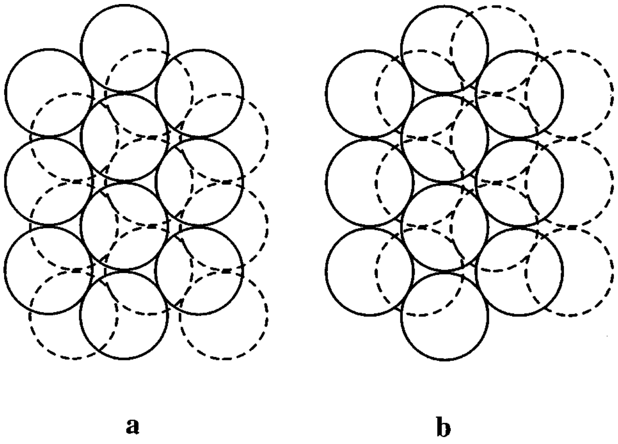

FIG. 1. (a) and (b) Sketches of the two possible sets of sites (indicated by solid circles) for the next layer on a (111) surface (indicated by dashed circles). In the case of particle-particle interactions that extend only as far as the nearest neighbors, these two stackings (conventionally labeled *B* and *C*) are equivalent in energy.

sequences of a similar stacking degeneracy found at the (100) interface of a simple cubic crystal in a lattice model.

The kinetic consequences of this lack of complete coupling between adjacent planes have been considered by Burke, Broughton, and Gilmer [4] with respect to molecular-dynamics simulations of growth into the liquid at the (111) surface of a fcc crystal of Lennard-Jones particles. They found that, unlike the (100) surface, the (111) growth rate exhibited a temperature dependence suggestive of diffusion control. They noted that growth on this surface depended upon collective fluctuations in which domains of particles in the surface plane shifted their registry between the two possible sets of sites. Würth *et al.* [3] invoke similar behavior to explain the crystallization kinetics observed in suspensions of charged polystyrene particles.

Deviations away from the planar surface tend to reduce the effective anisotropy of growth rates. In dynamic Monte Carlo simulations of a lattice model exhibiting a crystal-liquid transition [5], no difference was observed between the dynamics of the close-packed surface and a high-index surface during freezing. The presence of microfacets of the close-packed planes on the high-indexed surface led the authors to conclude that growth was dominated by the close-packed (and slower) surface in both cases. Anomalous behavior was still noted, however, in the temperature dependence of growth rate at small supercoolings. In this case no growth was observed until a temperature of $T_{\mathrm{dp}} = 0.994T_m$ was reached. At this supercooling the growth rate appeared to under go a small ''jump'' and then exhibited a linear dependence on supercooling as the temperature was decreased further. The authors presented a qualitative argument to account for this behavior based on the idea that as growth of the uncoupled planes consists of a series of two-dimensional ordering transition in the surface plane, it was the critical temperature of this transition rather than the freezing temperature of the three-dimensional crystal that governed growth kinetics. The results of molecular dynamics simulation studies of freezing in Si [6] suggest similar pinning of a supercooled crystal surface.

In the following section we discuss the derivation of the equations of motion of order parameters for crystalline order of a *cubic* crystal in a model liquid based on a fcc lattice. It is argued below that many of the results presented in Sec. IV depend on the general symmetries of the model, not on the specific nature of the interactions or crystal structure.

II. THEORY

While the qualitative features of the results presented here are not expected to depend significantly on the specific model liquid and approximate equations of motion for the interface, some explicit choices do need to be made in order to carry out the numerical analysis. Following our previous study [1], we shall use a lattice-gas model with crystal and dense liquid phases on which to base the derivation of the free-energy functional. While our major results are due to the symmetry of the equations of motion rather than the specific couplings between structural order parameters in the free-energy functional, the magnitude of the effects described here will certainly depend on the details of each specific system.

The mean-field free energy of the fcc lattice gas can be written in terms of four scalar density fields $\{\phi_i\}$ corresponding to the density of particles on each of the four interpenetrating cubic lattices that constitute the fcc lattice. The ordered crystal corresponds to all the particles residing on one of these cubic sublattices, while a uniform distribution of particles among all four sublattices represents the liquid phase. With a nearest-neighbor interaction of J_1 and next-nearest-neighbor interactions of J_2 we can write the mean-field free energy of the uniform system W_u as

$$\frac{W_u}{N_s} = k_B T \sum_{i=1}^{4} [(1-\phi_i)\ln(1-\phi_i) + \phi_i \ln(\phi_i)] + 4J_1 \sum_{i\neq j}^{4} \sum_{j=1}^{4} \phi_i\phi_j + 6J_2 \sum_{i=1}^{4} \phi_i^2 - \mu \sum_{i=1}^{4} \phi_i, \quad (1)$$

where μ is the chemical potential and N_s is the number of sites on a sublattice.

The density fields $\{\phi_i\}$ can be transformed into a set of density wave amplitudes $\{\eta_i\}$ and the total density c, defined as

$$\begin{aligned} \eta_1 &= (\phi_1+\phi_2)-(\phi_3+\phi_4),\\ \eta_2 &= (\phi_1+\phi_3)-(\phi_2+\phi_4),\\ \eta_3 &= (\phi_1+\phi_4)-(\phi_2+\phi_3),\\ c &= \phi_1+\phi_2+\phi_3+\phi_4. \end{aligned} \quad (2)$$

Here η_1 is the mean amplitude of a density wave along the [100] direction, η_2 the mean amplitude along the [010] direction, η_3 the mean amplitude along the [001] direction, and c the total density. We restrict our attention to the case $c=1$.

In the case of the bulk crystal, $\eta_1=\eta_2=\eta_3$ by symmetry. In the presence of an interface normal to the [100] direction this symmetry is lifted, leaving us with two independent order parameters: $p=\eta_1$, the amplitude of the density wave normal to the interface, and $q=\eta_2=\eta_3$, the in-layer order parameter. The free energy W_u can be written in terms of these two order parameters,

$$\frac{W_u}{N_s} = k_B T \sum_{i}^{4} S_i + 3(J_1+J_2)c^2/2 - (J_1-3J_2)(p^2+2q^2)/2 - \mu c, \quad (3)$$

where the S_i's are

$$
\begin{aligned}
S_1&=\left[(4-c-p-2q)\ln\left(\frac{4-c-p-2q}{4}\right)\right.\\
&\qquad\left.+(c+p+2q)\ln\left(\frac{c+p+2q}{4}\right)\right]\bigg/\,4,\\
S_2&=\left[(4-c-p+2q)\ln\left(\frac{4-c-p+2q}{4}\right)\right.\\
&\qquad+(c+p-2q)\ln\left(\frac{c+p-2q}{4}\right)\bigg/\,4,\\
S_3&=\left[(4-c-p)\ln\left(\frac{4-c-p}{4}\right)+(c-p)\ln\left(\frac{c-p}{4}\right)\right]\bigg/\,4\\
&=S_4.
\end{aligned}
\tag{4}
$$

For the (111) interface, the symmetry between the order parameters is retained and the interface is specified by a single parameter $p=\eta_1=\eta_2=\eta_3$. All equations for the (111) surface can be obtained from the above equations by substituting $p=q$.

In connecting the free-energy functional with the time dependence of the order parameter fields we assume the generalized Langevin expression [7]

$$\frac{\partial\phi_i(z,t)}{\partial t}=-\Gamma\,\frac{\delta W}{\delta\phi_i(z,t)}+R_i(z,t). \tag{5}$$

W is the free-energy functional of the four *nonuniform* densities and the functional differentiation on the right-hand side can be regarded as the chemical potential of the ith sublattice of a nonuniform system. At equilibrium this derivative is zero and we get stationary profiles. The kinetic coefficient Γ is assumed to be independent of the value of the densities and the R_i's are random fluctuations with average properties specified below.

For the case of the planar crystal-liquid interface, the chemical potentials can be expressed as a sum of a local and a nonlocal part

$$\frac{\delta W}{\delta\phi_i(z)}=\frac{\partial W_u}{\partial\phi_i(z)}+\kappa\gamma_i(z). \tag{6}$$

The nonlocal contributions can be written explicitly in terms of the spatial variations of the order parameters p and q,

$$
\begin{aligned}
\gamma_1(z)&=(J_2-8J_1)\Delta p(z)/4+J_2\Delta q(z)/2,\\
\gamma_2(z)&=(J_2-8J_1)\Delta p(z)/4-J_2\Delta q(z)/2,\\
\gamma_3(z)&=(J_2-8J_1)\Delta p(z)/4=\gamma_4,
\end{aligned}
\tag{7}
$$

with the difference operation defined as

$$\Delta p(z)=p(z+1)+p(z-1)-2p(z). \tag{8}$$

The coefficient κ is introduced here to provide a simple scaling of the characteristic length in the problem.

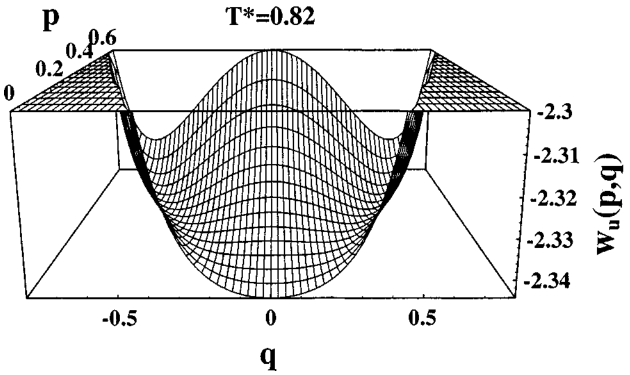

FIG. 2. Free energy $\omega_u(p,q)$ for a uniform system characterized by order parameters p and q at $T^*=0.82$, the melting temperature. Note the ''forked valley'' topology in going from the disordered liquid (0,0) to the two-degenerate-crystal minima at (0.464,0.464) and (0.464,−0.464).

Substituting the chemical potentials into the kinetic equations leads us to the final form of the equations of motion

$$\frac{\partial p}{\partial t}=-\Gamma\left(16\,\frac{\partial W_u}{\partial p}+\kappa(J_2-8J_1)\Delta p\right)+R_p(z,t), \tag{9}$$

$$\frac{\partial q}{\partial t}=-\Gamma\left(4\,\frac{\delta W_u}{\delta q}+\kappa J_2\Delta q\right)+R_q(z,t). \tag{10}$$

In the following analysis the temperature is presented in units of J_1/k_B (i.e., the reduced temperature $T^*=k_BT/J_1$), the free energy is in units of J_1, distance is measured in lattice spacings, and time is presented in units of $1/\Gamma J_1$. Unless otherwise stated $\kappa=1.0$ and a time step of $\Delta t=10^{-5}$ in the reduced units is used.

The stochastic terms $R_p(z,t)$ and $R_q(z,t)$ are introduced to model the effect of fluctuations in the dynamics of the order parameters. This noise satisfies

$$
\begin{aligned}
&\langle R_\alpha(z,t)\rangle=0,\\
&\langle R_\alpha(z_1,t_1)R_\beta(z_2,t_2)\rangle=\Theta_\alpha^2T^*\,\delta_{\alpha\beta}\delta(z_1-z_2)\,\delta(t_1-t_2).
\end{aligned}
\tag{11}
$$

III. RESULTS

The free energy $w_u(p,q)=W_u(p,q)/N$, for the uniform system is plotted in Figs. 2 and 3. The ''forked valley'' topology in the space of (p,q) is a direct consequence of the presence of two-degenerate-crystal structures. At the coexistence temperature $T_m^*=0.82$ [Fig. 3(b)] the free energy at the liquid minimum at (0,0) is equal to that at the two-crystal minima (0.464,0.464) and (0.464,−0.464). Increasing the temperature [Fig. 3(c)] we see the rapid disappearance of the local minima associated with the superheated solid, while on supercooling [Fig. 3(c)] we find that the liquid persists as a metastable state until a spinodal is reached at around $T^*\approx0.76$. The symmetry of w_u with respect to q is a reflection of the symmetry of the two in-layer packings associated with $q<0$ and $q>0$ and is independent of the range of particle interactions. The nonlocal term in W is responsible for the lifting of this symmetry.

We begin with the close-packed (100) surface in the absence of next-nearest-neighbor interactions, i.e., $J_2=0$. The equilibrium interface corresponds to the stationary solution of Eqs. (9) and (10) at $T^*=0.82$ and is plotted in Fig. 4 with

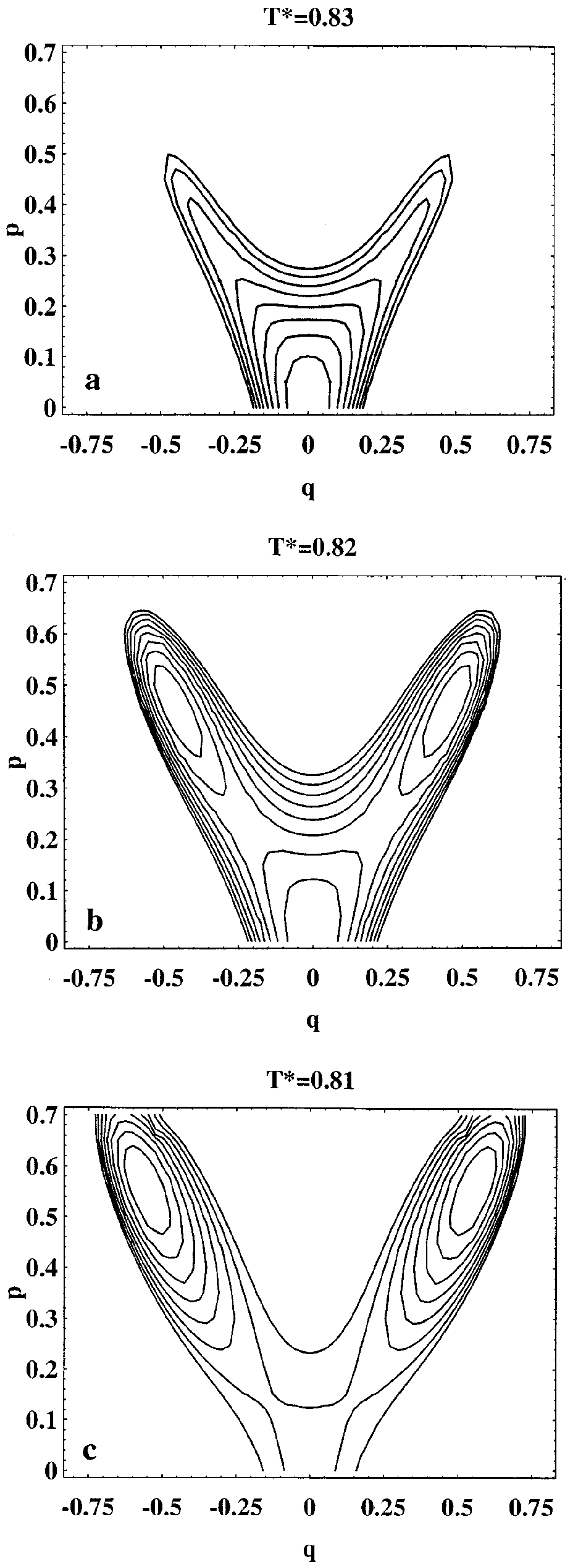

FIG. 3. Contour plots of the free energy $w_u(p,q)$ for a uniform system calculated at (a) $T^*=0.83$, showing the equilibrium liquid minimum only; (b) $T^*=0.82$, showing the minima corresponding to the coexisting liquid and solid phases; and (c) $T^*=0.81$, depicting the two equilibrium solid phases with the liquid minimum now a metastable state.

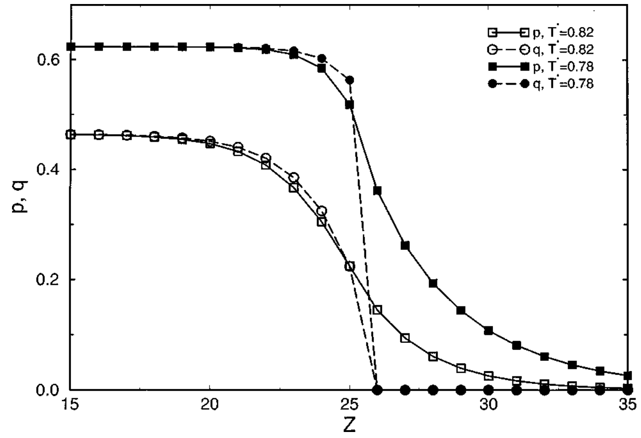

FIG. 4. Interfacial profiles of the order parameters p and q for stationary (100) surfaces at equilibrium $T^*=0.82$ and under supercooling $T^*=0.78$. Note the distortion of the latter due to the pinning of the $q=0$ region of the inlayer order profile.

$\kappa=1.0$. With $J_2=0$, the time development of the in-layer order q, given in Eq. (10), is uncoupled to the in-layer order in adjacent layers. From the symmetry of the uniform potential in Fig. 3, it is clear that $\partial w_u/\partial q=0$ whenever $q=0$. As a result

$$\frac{\partial q(z,t)}{\partial t}=0 \quad \forall p \ \text{ when } q=0 \tag{12}$$

and the interface, unable to induce in-layer order in the liquid in the absence of fluctuations, cannot grow. The role of the liquid portion of the q profile in pinning the interface is clear from the supercooled profile at $T^*=0.78$ in Fig. 4. The steady-state velocity of the (100) surface, averaged over a displacement of 15 lattice spacings, is plotted in Fig. 5 as a function of temperature. The asymmetry between freezing and melting at this surface is obvious. The *melting* interface does not need to induce in-plane order in the liquid and so is unaffected by the pinning described here.

The equation of motion of the (111) surface, at the same level of structural detail, involves only a single order parameter p. This order parameter must retain the coupling be-

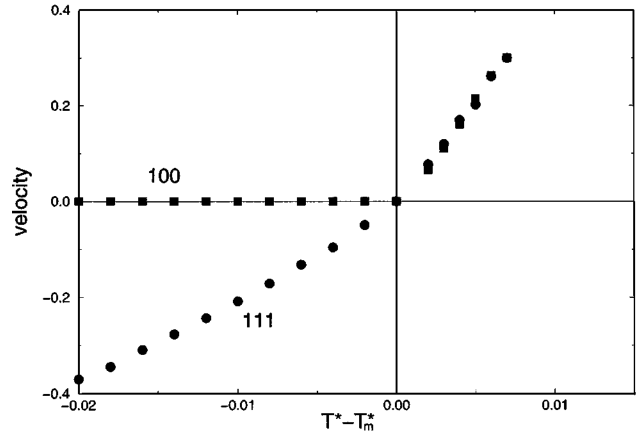

FIG. 5. Interfacial velocity as a function of temperature for the (100) and (111) surfaces in the absence of fluctuations with $\kappa=1.0$. Note the complete arrest of the supercooled (100) surface. Velocity is in units of (lattice spacing) $\times\Gamma J_1$.

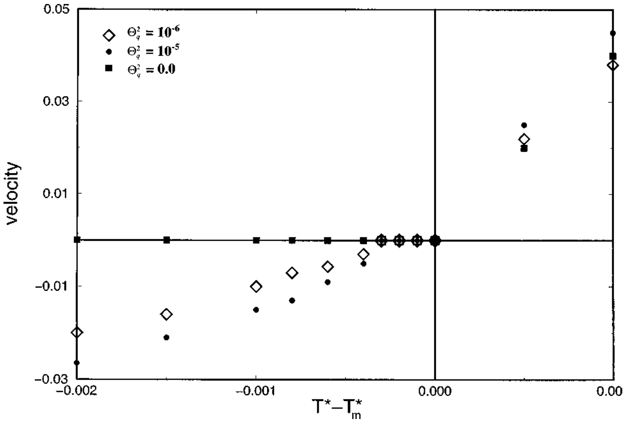

FIG. 6. Velocities of the (100) interface as a function of temperature for a range of fluctuation amplitudes Θ_q^2 with $\kappa=1.0$. Velocity is in units of (lattice spacing) $\times \Gamma J_1$.

tween adjacent (111) layers and hence does not experience the pinning of the supercooled (100) surface. The result is a substantial anisotropy of the crystallization rate while leaving the rate of melting isotropic. Note in Fig. 5 that the *nonlinear* dependence of interface velocity on temperature of the (111) surface is different for melting and for freezing. This is a reflection of the difference in $\partial^2 W_u / \partial p^2$ at the crystal and liquid minima.

In the case of the (100) interface, this asymmetry between freezing and melting extends down to the melting point itself in a singular fashion, with the derivative of the interfacial velocity with respect to temperature being discontinuous at T_m. It has been argued [8] that such a singularity would be unphysical as it would violate microscopic reversibility. This argument, however, only excludes a singularity resulting from an unphysical asymmetry between the rates at which particles bind and unbind from the surface. The singularity described here refers only to the steady-state interfacial velocity and so avoids placing such unphysical constraints on the microscopic kinetics.

The asymmetric pinning of the (100) surface is the result of the disordered layers ‘‘inability’’ to lift the symmetry of the two in-layer packings. As the density p of a disordered layer increases, the free energy w_u changes along the $q=0$ line from being a local minimum to a local maximum. The latter unstable state should be susceptible to any amplitude of fluctuations in the in-layer order q. Interfacial velocities of the (100) surface with $\kappa=1.0$ in the presence of a range of fluctuation amplitudes Θ_q^2 are plotted in Fig. 6. Each velocity is obtained from the translation of the surface of at least 15 layer spacings. We draw the readers attention to three important features of these results. (i) The surface remains pinned in the presence of the fluctuations for temperatures in the range $T_{\mathrm{dp}} < T^* < T_m$. The depinning temperature T_{dp} is a decreasing function of the amplitude of fluctuations. (ii) The (100) surface *does* freeze in the presence of fluctuations in the in-layer order parameter q, the crystal so grown consisting of a random stacking faults. The freezing velocity v is, for small supercoolings, of the form

$$v \propto g(\Theta_q^2)(T_{\mathrm{dp}} - T^*) \quad \text{for } T^* \leqslant T^{\mathrm{dp}}, \tag{13}$$

where $g(x)$ is an increasing function of x. (iii) The melting velocity is not significantly effected by the fluctuations. These three results are in qualitative agreement with the simulations of freezing in the lattice model [5].

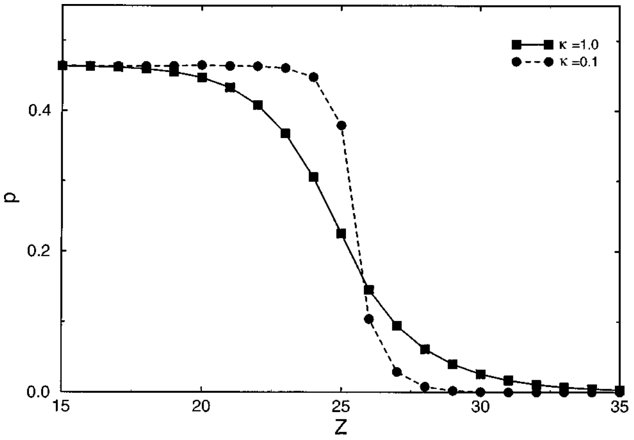

FIG. 7. Role of the coefficient κ in determining the number of layers in the interfacial region at equilibrium $T^* = 0.82$. Varying κ between 0.1 and 1.0, we find that the interfaces vary in thickness between 5 and 15 layers.

The persistence of pinning in the presence of fluctuations in this simple theory, noted as ‘‘observation (i),’’ poses a puzzle. Consider the crystal-liquid interface as being represented by a ‘‘trajectory’’ in (p,q) space. In order for the interface to freeze or melt an arbitrary volume element in the path of the interface must move along the trajectory either from liquid to solid or solid to liquid, respectively. For the supercooled (100) interface without fluctuations, such an arbitrary volume element is unable to move from the $q=0$ line, hence the surface is pinned. Now the high-p end of the $q=0$ portion of the pinned interface lies on either a ‘‘saddle’’ $(\partial^2 w_u / \partial q^2 = 0)$ or the ‘‘ridge crest’’ $(\partial^2 w_u / \partial q^2 < 0)$ of the potential surface w_u (see Figs. 2 and 3). Fluctuations in the q axis will nudge such a precariously pinned point off along the trajectory to the crystal state. The fact that the nudge is to the positive or negative q with equal probability results in the (100) stacking faults. So, in light of this picture, the puzzle is why do we see *any* persistent pinning when fluctuations are present. To answer this we need to consider the effect of the discretization of the order parameter field.

The numerical treatment of the equations of motion for continuous order parameter fields involves finite differences as a practical necessity. In the case of crystal order (and $\kappa=1.0$), however, there is a strong case for identifying the discrete intervals along the surface normal at which the values of the p and q fields are recorded as the physical crystal layers themselves. In the latter view it is only the values of the order parameters at these discrete locations that contain physically relevant information. The number of such layers that can be found in the interfacial region is a real physical characteristic of crystal-liquid interfaces. The coefficient κ has been included into our equations of motion to allow the simple adjustment of the thickness of the interface in terms of crystal layers. Examples of equilibrium surfaces at $T^* = 0.82$ with small and large κ are shown in Fig. 7. Note the variation in the number of layers in each interface ranging from 5 to 15 layers. By comparison, simulations of the close-packed (111) surface of a fcc crystal of Lennard-Jones particles [10] result in an equilibrium surface consisting of

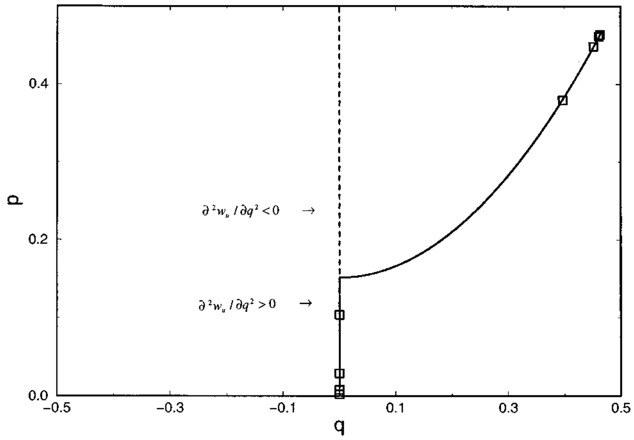

FIG. 8. Sketch of the interface as a trajectory in the space (p,q). The solid curve indicates the loci of points corresponding to *minima* of w_u with respect to q. The squares are the (p,q) values associated with the discrete layers through the equilibrium interface with $\kappa=0.1$ depicted in Fig. 7. The vertical dashed line indicates *maxima* of the potential with respect to the in-layer order parameter. The interface remains stable with respect to fluctuations in q until a supercooling is reached at which one of the discrete points on the $q=0$ line is pushed in the region in which $\partial^2 w_u / \partial q^2 < 0$, denoted by the dashed line.

approximately ten layers while simulations of the close-packed surface of silicon [6] show a narrower interface, roughly five layers in thickness. Higher-index interfaces typically consist of considerably more layers than the close-packed surfaces, simply by virtue of the smaller layer spacing.

This discrete picture has two important consequences for interfacial dynamics. First, the discrete steps break the symmetry of space resulting, at equilibrium, in only a discrete periodic set of stable equilibrium positions for the interface with free-energy barriers between them. Away from equilibrium, we find that interfacial motion involves jumps of the interfacial position between these long-lived positions. This behavior was discussed by Cahn in the 1960s in terms of the presence of a periodic set of free-energy barriers to the displacement of the crystal interface and the transition between lateral to continuous growth for a diffuse interface [9]. We find it here for both melting and freezing. It is the second consequence of the discrete layers, discussed below, which is central to the existence of a depinning temperature T_{dp}.

To understand this connection, it is useful to return to the description of the interface as a trajectory in (p,q) space. Our arbitrary volume element no longer moves continuously along this path, but instead it jumps between the discrete sites, the number of which corresponds to the number of layers in the interface (see Fig. 8). Now, in order for fluctuations to depin the surface they must find one of these ''sites'' along the $q=0$ line in a region where $\partial^2 w_u / \partial q^2 < 0$. Points for which $\partial^2 w_u / \partial q^2 > 0$ will be stable with respect to fluctuations in q, the local free-energy curvature ensuring that the interface will act to restore itself following a fluctuation. For a continuous interface there would always be a point through the interface at which $q=0$ and $\partial^2 w_u / \partial q^2 < 0$ and hence fluctuations can depin the surface at any temperature below the melting point. For discrete sites there is no such inevitability. In fact, as the temperature approaches T_m from below the length of the interface trajectory that corresponds to unstable $q=0$ vanishes and along with it goes the probability of finding one of the discrete crystal layers in that region. As a result, the interface has to be supercooled in order to ''push'' one of the discrete disordered layers into the unstable region. The depinning temperature T_{dp} is the measure of the minimum supercooling needed to accomplish this necessary distortion of the interface. As the interface approaches the continuous limit (i.e., large κ), the magnitude of the push required vanishes and T_{dp} approaches T_m. Conversely, a narrow crystal-liquid interface with a width of only a few layers, found for a small κ, exhibits a depinning temperature significantly lower than the melting temperature, as shown in Fig. 9. We also note the appearance of a small region of pinning of the superheated crystal-liquid interface with decreasing κ and hence interfacial width. We shall return to this feature and its connection with Cahn's model [9] in the following section.

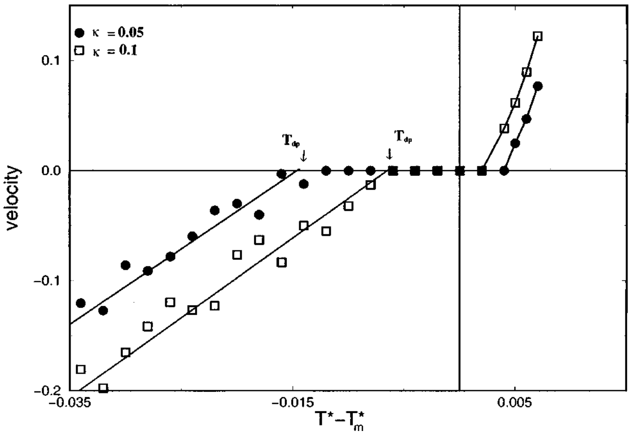

FIG. 9. Temperature dependence of the velocity of the (100) interface at small supercoolings and superheatings in the presence of noise $(\Theta_q^2 = 10^{-6})$. The depinning temperature T_{dp} is indicated. Note that while T_{dp} approaches T_m with increasing κ a considerable asymmetry persists between the behavior of the interface above and below T_m. Velocity is in units of (lattice spacing) $\times \Gamma J_1$.

Including next-nearest-neighbor interactions (here in the form of nonzero values of J_2) lifts the residual symmetry between the two possible choices of inlayer order. In Fig. 10 we show the effect on interfacial velocities of adding a next-nearest-neighbor interaction. This extra potential-energy contribution will shift T_m and, more importantly for our present discussion, introduce a coupling between adjacent layers and so allow the inlayer order in one layer to weight the choice of the in-layer order in the next. The freezing surface now exhibits a regular steplike advance in the absence of fluctuations, the waiting time at each step determined by the strength of the next-nearest-neighbor interactions. The crystal grown in the presence of fluctuations will include stacking faults at a density determined by the relative magnitudes of J_2 and Θ_q^2. When $J_2 \gg \Theta_q^2$, the density of faults will be small with the choice of in-layer packing, q positive or negative, determined by the state of the crystal at the initial time. As Θ_q^2 increases in magnitude, the growth is eventually dominated by the fluctuations and the density of stacking faults approaches 0.5, the value found in the crystal with nearest-neighbor interactions only.

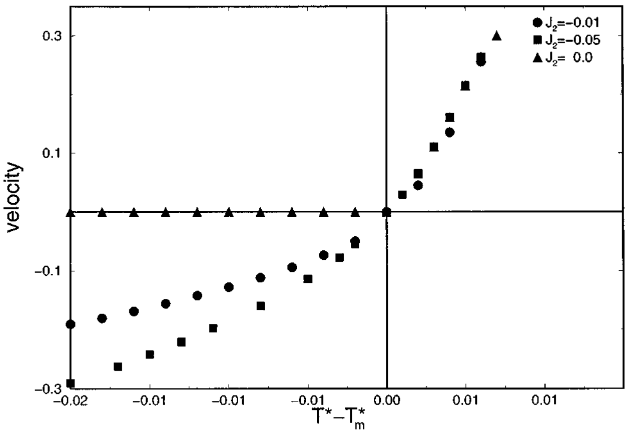

FIG. 10. Velocity of the (100) interface as a function of the temperature for a range of second-nearest-neighbor interaction strengths J_2 with $\kappa=1.0$. Velocity is in units of (lattice spacing) $\times \Gamma J_1$.

IV. CONCLUSION

Stacking faults in close-packed planes are commonly observed during crystallization of particles whose interaction potential is short ranged with respect to the lattice spacing [2]. In this paper we have demonstrated that this behavior can be described in terms of a simple theoretical description of crystallization kinetics that couples two structural order parameters. As our major result, we establish that the packing degeneracy that permits such faults also gives rise to a striking kinetic effect arising from the inability of the specific crystal surface to fully break the symmetry of the adjacent liquid. The close-packed surface can freeze only when the symmetry of the two possible in-layer packings is broken, either by fluctuations or longer-range interactions. In the absence of long-range interactions, growth can take place only once the supercooling exceeds a critical depinning value, associated with a second-order phase transition in a single surface layer.

This phenomenon differs qualitatively from the interface dynamics identified by Cahn [9] over 30 years ago. Cahn's insight was that the transition between nucleated (here one can read ''fluctuation dependent'') and continuous growth could be described for a diffuse interface in terms of the periodic variation of the free energy with interfacial displacement with respect to the lattice origin. This potential is responsible for the possibility of an equilibrium roughening transition, even for diffuse interfaces [11,12]. The amplitude of this periodic free energy increases with decreasing surface width [11] and so is identical with the steplike dynamics that arises naturally in the theory presented here. For small enough supercoolings or superheatings, this periodic free energy will pin the surface in the absence of fluctuations. This ''periodic'' pinning differs in four significant ways from the pinning due to ''incomplete symmetry breaking'' described in this paper.

(i) The periodic pinning applies equally to both melting and freezing while the incomplete symmetry breaking mechanism applies principally to freezing alone. (For narrow interfaces, we *do* observe some pinning of the melting interface, indicating that the periodic pinning mechanism is present but of very much smaller amplitude than that due to the symmetry breaking mechanism.)

(ii) Even in the absence of fluctuations, periodically pinned surfaces will freeze once a critical supercooling is exceeded. No such freezing occurs at the surface pinned by incomplete symmetry breaking.

(iii) Surface pinning via the incomplete symmetry breaking mechanism depends sensitively upon the details of coupling between the various structural order parameters, while that due to the periodic component of the free energy arises from the periodicity of the crystal density along the surface normal alone.

(iv) Finally, the incomplete symmetry breaking mechanism, unlike the periodic pinning, has been shown to depend explicitly upon the short range of the particle interactions.

Qualitatively, these results depend only upon general symmetry arguments. As such, we present them as a generic feature of interfacial dynamics involving crystalline order. The existence of a pinning temperature T_{dp} in the presence of fluctuations due to incomplete symmetry breaking, as described here, is in qualitative agreement with simulations of nonequilibrium crystal-liquid interfaces in the fcc lattice gas [5]. Our results suggest that this asymmetric pinning is most likely to be observed for crystal-liquid interfaces that consist of only a few layers. Simulation results indicate that the close-packed surface of silicon meets this criterion. The simulations of crystallization of silicon to date [6] suggest that such a pinning may be present. It would be interesting to carry out careful long-time molecular-dynamic simulations of such an interface at *small* deviations from coexistence in order to establish whether similar dynamic asymmetries can be observed. Extending these results, we would also expect to observe considerably larger fluctuations of in-layer structure at the close-packed surfaces than those found at high-index interfaces [1,5].

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