Kinetic Depinning Transitions

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A simple model for the kinetics of two interacting interfaces moving at a prescribed rate is proposed. It is a kinetic generalization for problems like wetting, pinning, surface segregation, or surface reordering during solidification. Various types of nonequilibrium phase transitions are predicted.

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Equilibrium phase transitions at coupled interfaces have recently received great attention.[1-5] The common basis for the problems of wetting,[1] pinning,[2-4] surface-induced disordering,[5] etc., is a model where a fluctuating internal interface between two coexisting phases interacts with a stiff external surface or boundary. In a ferromagnetic system, for example, this external boundary is the surface while the internal interface separates a down-spin region near the surface from an up-spin region in the bulk. A simple phenomenological model for this situation was given in Ref. 5.

A different problem at first sight seems to be the phenomenon of kinetic disordering,[6-8] where an ordered two-component crystal becomes disordered if the growth rate exceeds a critical value. The earliest observation of this phenomenon was made by a computer simulation.[6] (The experimental situation is less clear, basically because of the competing effect of polycrystalline growth.) In this Letter we present a simple phenomenological model as an extension to Ref. 5 which gives a unified picture of the two classes of phenomena and in addition predicts different types of nonequilibrium phase transitions, depending on the phase diagram and spatially inhomogeneous kinetics of the system under consideration. The last point may be particularly important for applications in laser annealing of compound material.[9] As a final point we note that the mechanism of propagating pattern selection[10] also becomes relevant in this problem.

For simplicity we will describe our analysis in the language of kinetic disordering. Assume a two-component crystal with two identical sublattices to grow from a completely disordered liquid phase. Assume the liquid to cover the half-infinite space $z<0$, the solid covering $z>0$, z being the spatial coordinate normal to the solid-liquid interface (= external boundary). Inside the solid, close to the solid-liquid interface, the solid is assumed to be also disordered ($M=0$), its order increasing around $z=z_0$ towards the saturation value ($M=1$) at $z\to+\infty$, as seen in Fig. 1. In the equilibrium case this is essentially the model proposed in Ref. 5. Here we have chosen the slightly simpler boundary condition $M(z=0)=0$ compared with Ref. 5, since in our case the disordered liquid $[M(z<0)=0]$ directly serves as the nutrient phase. But now we assume that the crystal is growing, the solid-liquid interface at $z=0$ moving at constant rate V to the left. Here $z_0>0$ denotes the distance from this interface in the moving coordinate system. As an explicit model we assume dissipative kinetics for the (nonconserved) order parameter M:

$$0=\frac{\partial M}{\partial t}=-\kappa\frac{\delta F}{\delta M}-V\frac{\partial M}{\partial z}, \tag{1}$$

where κ is a mobility (to be discussed later), the zero on the left-hand side denotes stationarity, and the V term represents the transformation to the moving coordinate system z. F is a Ginzburg-Landau free energy

$$F=\int_0^\infty dz\left\{\frac{1}{2}\left(\frac{\partial M}{\partial z}\right)^2+f(M)\right\}, \tag{2}$$

with

$$f(M)=\begin{cases}\pm(M^2-M_0^2), & M\leq M_0;\\ (M-1)^2-(M_0-1)^2, & M>M_0;\end{cases}$$

$$0<M_0<\tfrac{1}{2}.$$

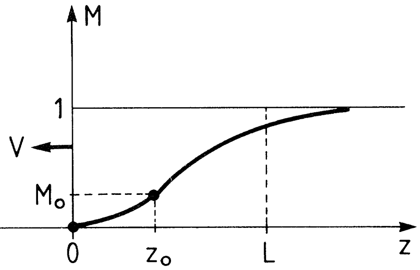

FIG. 1. Schematic plot of the order-parameter profile $M(z)$. The surface at $z\leq 0$ moves with prescribed velocity V to the left; the internal profile follows at a distance z_0.

Irrelevant constants are set equal to unity.

The plus sign in $f(M)$ denotes case (A) in Fig. 2, the minus sign case (B). In case (B), the disordered state $M = 0$ is unstable (spinodal decomposition), in case (A) it is metastable, the stable state in both cases being $M = 1$. The value of M_0 and the realization of either (A) or (B) depends on the phase diagram of the particular system. Case (A) corresponds to a phase diagram where the disordered solid is metastable, while in case (B) it is unstable. Around z_0 an interface between the disordered and the ordered solid will be formed.

When we look for stationary solutions, the equation of motion (3) to be solved is simply

$$\frac{\partial^2 M}{\partial z^2} - V\frac{\partial M}{\partial z} = \frac{\partial f(M)}{\partial (M)} \tag{3}$$

with boundary conditions $M(z = 0) = 0$ and $M(z \to \infty) = 1$. This is identical to a simple damped oscillator, where $\tau = -z$ corresponds to time, M takes the role of the time-dependent coordinate, and $U \equiv -f(M)$ is a potential. The velocity V corresponds to the damping constant. Since the derivative of $f(M)$ at $M(z_0) = M_0$ is discontinuous, we have to require continuity for $M(z)$ and $\partial M(z)/\partial z$ at z_0 as internal matching conditions.

The qualitative behavior of the system (3) is easily visualized in terms of this mechanical analog of a particle moving in an external potential U, keeping in mind that the potential U has the opposite sign from f. At $z = +\infty$ ($\tau = -\infty$) the "particle" starts at the unstable equilibrium point $M = 1$ (Fig. 2), reaches $M = M_0$ at z_0, and finally should reach $M = 0$ at $z_0 = 0$ (or "time" $\tau = 0$). While without doubt the path from $M = 1$ to $M = M_0$ is always possible for arbitrary damping V, V must be small enough to allow the particle to pass from $M(z_0) = M_0$ to $M = 0$ in finite time. This condition defines the value of z_0.

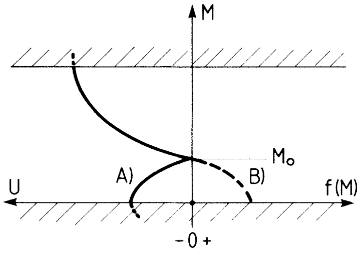

FIG. 2. Potential $f(M)$ depending on the order parameter M. Case (A) is an unsymmetric double-well potential, (B) a single-well potential with maximum at $M = 0$.

If V is very small the particle passes the point $M = 0$ in both cases (A) and (B) at some value of z, which can be set to zero by shifting z_0. Hence the boundary condition $M(0) = 0$ can be fulfilled. This is no longer the case if V is too large. In case (A) of Fig. 2 the particle does not reach the point $M = 0$—a local maximum in the potential U—any more and finally becomes trapped at M_0. The critical value V_A above which this occurs is

$$V_A = \frac{2\sqrt{2}(1-2M_0)}{[1-(1-2M_0)^2]^{1/2}}. \tag{4}$$

In case (B) we have to discriminate between two possibilities, depending on whether

$$M_0 \geq M^* \tag{5a}$$

or

$$M_0 < M^* \tag{5b}$$

with $M^* = 1 - 1/\sqrt{2}$, as discussed below. First we note, that for arbitrary values of $V > 0$, in case (B) the particle will ultimately be trapped at $M = 0$ in contrast to case (A). For small values of V it performs damped oscillations about this point. If V is slightly larger than a critical value

$$V_B = \sqrt{8}, \tag{6a}$$

it approaches $M = 0$ only asymptotically, without ever passing it [under condition Eq. (5a)], or passing it at most once [Eq. (5b)]. But even in the latter case the particle will not pass $M = 0$ if $V > \tilde{V}_B$,

$$\tilde{V}_B = \frac{4M_0^4 - 8M_0^3 + 8M_0^2 - 4M_0 + 1}{2M_0^3 - 3M_0^2 + M_0} \times 2 \tag{6b}$$

and $\tilde{V}_B > V_B$.

Therefore, if V is larger than the respective critical value, we have no stationary solution for the motion of the two coupled interfaces a distance z_0 apart. Approaching V_A or either of V_B and $\tilde{V}_B$ from below, the intermediate layer $0 < z < z_0$ diverges:

$$\text{Case (A):}\quad z_0 \sim -\ln(V_A - V); \tag{7}$$

$$\text{Case (B):}\quad z_0 \sim (V_B - V)^{-1/2} \tag{8a}$$

$$\sim -\ln(\tilde{V}_B - V) \tag{8b}$$

[depending on the model situation, Eqs. (5a) and (6a) or (5b) and (6b)].

The physical interpretation of this effect is simply understood. At small growth rates V an ordered crystal is formed from the liquid with an intermediate disordered solid layer of thickness z_0 near the solid-liquid interface. As V approach-

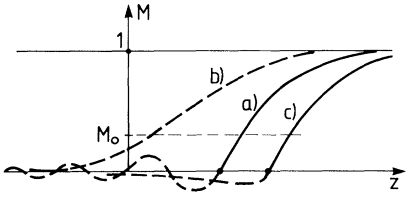

FIG. 3. Three possible moving profiles for an infinite system with potential (B) (Fig. 2). (a) An oscillating (slow) profile; (b), (c) two "overdamped" (fast) profiles. (The positions of the three profiles along the z axis here are arbitrary.)

es the critical velocity V_A or either of V_B and $\tilde{V}_B$, the thickness of the disordered layer diverges, Eqs. (7) and (8). For larger values of V a steady state is not reached, but the disordered layer increases continuously in thickness. This is our nonequilibrium phase transition. It is "sharp" in the sense that the metastable states involved in the analysis are very long living, justifying a Ginzburg-Landau approach. This is not a crucial assumption in case (A), but in case (B) we have to worry about spinodal decomposition.

Instead of going into details here, we would like to add a modification of the kinetic equation (1). Close to the solid-liquid interface one may expect a region of fairly high mobility, while deeper in the solid the mobility is drastically reduced, e.g., by the lower temperature. We may model this by setting $\kappa = 1$ at $0 < z < L$ (Fig. 1) and κ changing rapidly to $\kappa = 0$ for $z > L$. The bulk of the growing crystal then maintains the order $M(z = L)$ all the way out to $z \to \infty$. The qualitative behavior in case (B) will not be dramatically changed, except that the mechanism of spinodal decomposition becomes irrelevant as L becomes small.

In case (A), however, we expect a change in the nature of the transition. For $z_0 > L$, there is no reason for the system to deform the order-parameter profile from $M(z) = 0$, $z \geqslant 0$, , since this is at least a local minimum of the potential $f(M)$. This implies a first-order transition for the bulk of the crystal from $M > 0$ to $M = 0$ as soon as $z_0 \lesssim L$, because of the competition of energies $F(M(z < z_0))$ and $F(M(z_0 < z < L))$. Clearly, if $z_0 \gtrsim L$ the system will remain in the state $M = 0$. Experimentally there does not seem to exist any systematic investigation. It should not be hard to determine the critical growth rate V_A, V_B. To identify quantitatively the predicted logarithmic singularity, however, may not be easy, since it has to be discriminated from a first-order transition. So we leave this to future discussion.

To summarize, we have obtained a fairly general formulation for the kinetic disordering transition for systems with nonconserved order parameter. Modifications to include diffusion are easily possible in the frame of this piecewise linear model. As a final point we note that the critical velocity V_B [Eq. (6a)] is identical to the ultimately selected[10] velocity arising in the problem of propagating pattern selection. Note, however, that our solutions [case (B)], Fig. 3(a), correspond to the dynamically inaccessible states of Ref. 10 because of the boundary condition $M(z = 0) = 0$.

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