Dynamical Mechanism for the Formation of Metastable Phases

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Rapid temperature quenches have long been known to produce metastable thermodynamic phases. We study Landau-Ginzburg models of phase transitions for free energies having three local minima and show that metastable phases can be formed via a dynamic instability that splits the front separating the stable high- and low-temperature phases. Even though quenching may nucleate the stable phase, the splitting instability we discuss will favor the formation of the metastable phase.

For at least a century, it has been known that rapidly cooling a liquid may produce a solid phase whose crystalline structure differs from that obtained by slowly freezing the same liquid [1]. Although these metastable phases obviously correspond to local but not to global minima of the free energy, little has been said about the precise mechanism by which these phases are formed. Why does quenching produce metastable phases? What driving force (undercooling, cooling rate, or front velocity) is needed to produce the new phase? Is it always possible to produce a given metastable phase by a fast-enough quench? The considerable amount of empirical data collected about metastable phases has led to a qualitative picture: When a material is cooled rapidly enough, the stable phase might not have time to form. One finds instead a close-by phase, which, although higher in free energy, can form more rapidly.

In this Letter, we describe a model in which these elusive notions are mapped onto more precise theoretical constructs, whose relation to materials parameters is known. Specifically, we show that, in Landau-Ginzburg models of phase transitions [2], fronts separating the stable high- and low-temperature phases can split apart into two independently moving fronts. The first front separates the phase that is stable at high temperatures (phase 0) from the metastable phase (phase 1). The second separates the metastable phase from that stable at low temperatures (phase 2). Because the 01 front moves faster than the 12 front, a macroscopically large region of the metastable phase 1 is created. The mechanism explains how metastable phases can grow given that the stable phase has already been nucleated, but does not address the possibility of nucleating directly the metastable phase.

To see the mechanism in its simplest setting, we study an infinite, one-dimensional spatial domain ($-\infty < x < \infty$). We assume that phases 0, 1, and 2 may be described by a single, nonconserved order parameter q. The free energy $F(q)$ has three local minima at $q = 0$, 1, and 2. The minimum at $q = 0$ represents a disordered phase (e.g., a liquid), that at $q = 2$ a stable phase (e.g., the equilibrium low-temperature solid phase), and that at $q = 1$ a metastable phase 1 (e.g., a solid phase with a different crystal structure, a martensite [3], or a quasicrystal [4]).

The order parameter $q(x,t)$ obeys a deterministic Landau-Ginzburg equation, which reads

$$\tau_0 q_t = q_{xx} - \frac{dF(q(x,t))}{dq(x,t)} . \tag{1}$$

Both x and q are scaled to be dimensionless. The potential $F(q)$ and the various coefficients, which are set to unity here, can be obtained from microscopic density-functional theories [5]. For $F(q)$, we choose

$$\frac{dF}{dq} = q[q - (0.5 - b)](q-1)(q-1.5)(q-2) . \tag{2}$$

By construction, the potential $F(q)$ always has minima at $q = 0$, 1, and 2. The control parameter $b \propto T_{02} - T$, where T_{02} is the coexistence temperature between phases 0 and 2. Thus, $b = 0$ corresponds to the usual melting temperature. When $0 < b < 0.5$, the stable solid phase ($q = 2$) invades the liquid (freezing). The liquid and solid spinodal points are at $b = \pm 0.5$. Over the range $-0.5 < b < 0.5$, phase 2 has a lower free energy than phase 1, which is thus always metastable. In Eq. (1), the time scale τ_0 sets the relaxation rate of order-parameter fluctuations and will be assumed to be independent of both the temperature and q. We set $\tau_0(q,b) = 1$ in the following.

We first examine solutions of Eqs. (1) and (2) that describe fronts propagating at constant velocity v. In the moving frame, $x \to x - vt$ and $q_t \to -vq_x$. The equation of motion becomes

$$q_{xx} + vq_x - \frac{dF(q(x))}{dq(x)} = 0 . \tag{3}$$

As has often been recognized [5], this equation describes the motion of a particle moving under the influence of a potential $-F$. A 02 front corresponds to a particle that starts out on "hill" 0 at a "time" $x = -\infty$ and ends up on hill 2 at $x = \infty$. The friction coefficient is just the front velocity v. Although the 02 front corresponds to the usual transition to the stable phase, clearly one can also construct 01 and 12 fronts that connect the metastable phase to the liquid and solid phases, respectively.

We solved Eq. (3) numerically to find the steady-state velocities of the three different fronts. The infinite x domain is first mapped to the interval $(-1, 1)$ by the

tanh map $x' = \tanh x/x_0$. The width x_0 was set adaptively so that the last finite points enclosed a region equal to 3 times the front width. The discretized equations were then solved by Newton's method, for $N = 100$ and 1000 points. The latter grid was necessary only when the region over which the order parameter varied significantly became large.

Figure 1 shows the three front velocities plotted against the control parameter b. The most striking feature is the interesection of $v_{01}(b)$, $v_{12}(b)$, and $v_{02}(b)$ all at the same value of $b = b_c \approx 0.15419$. Although steady-state 01 and 12 fronts exist for all values of b up to the spinodal point $b = 0.5$, where the liquid phase becomes absolutely unstable, the steady-state 02 front ceases to exist when $b > b_c$. This critical value b_c of the control parameter corresponds to a physically achievable undercooling.

To understand why there is no 02 steady-state front when $b > b_c$, we first show that $v_{01} < v_{02}$ and $v_{02} < v_{12}$ for all b, provided that v_{02} exists. Consider, in the mechanical analogy described above, a particle that moves from hill 2 to hill 1 (see inset to Fig. 1). Because hill 1 is lower than hill 2, a friction v_{12} must be imposed to get the particle to stop at hill 1. To go from hill 2 past hill 1 to hill 0, the friction must now be reduced, so that $v_{02} < v_{12}$. Alternatively, starting from the lowest hill 0, we need more "negative friction" to go from 0 to 2 past 1 than we do to go simply from 0 to 1. Thus, $v_{02} > v_{01}$, and our result is proved.

The crucial point now is that v_{01} and v_{12} are independent quantities. In particular, they can cross, as they do in our example at b_c. Since v_{02} must lie between the two velocities, we see immediately that no steady-state 02 front exists for $b > b_c$. At b_c, $v_{01} = v_{12} = v_{02}$ and we can imagine constructing the 02 profile by putting the 01 and 12 solutions together, back to back. In this case, although the 01 and 12 fronts each have widths of order unity (in our scaling), the 02 front has an infinite shelf of the metastable phase 1. Thus, as $b \to b_c$, we expect that the particle will spend more and more "time" going over

hill 1, and that the width of the 02 front will diverge. Figure 2 confirms this expectation and shows that the width $w_{02} \propto \ln(b_c - b)$. A similar divergence is predicted in nonequilibrium studies of surface melting [6].

Beyond b_c, solutions connecting phases 0 and 2 are time dependent in all uniformly translating reference frames. To follow the front motion numerically, we integrated Eq. (1) using Crank-Nicholson time stepping for the q_{xx} term and Adams-Bashforth time stepping for the free-energy terms, resulting in stability and $O(t^2)$ accuracy. The initial condition was the stationary solution found for $b = 0$. The simulation then corresponds to an instantaneous quench from coexistence to some finite undercooling. The splitting of the initial 02 front into independent 01 and 12 fronts is shown for $b = 0.18$ in the inset to Fig. 3. The width $w_{02}(t)$ is shown in Fig. 3 for different quench temperatures. When $b < b_c$, w_{02} converges to a constant. When $b > b_c$, it diverges linearly for large times. We have checked that the asymptotic rate of divergence satisfies

$$\frac{dw_{02}}{dt} = v_{01}(b) - v_{12}(b). \tag{4}$$

This, then, is our mechanism for the formation of metastable states: In the presence of the metastable phase, the 02 front can be thought of as a combined 01 and 12 front. As long as the rear part (12) moves faster than the leading part (01), the 02 front moves as a "bound state" with a velocity intermediate between v_{01} and v_{12}. When the rear is unable to keep up with the leading edge, the 02 state splits into two quasi-independent 01 and 12 fronts: A macroscopic quantity of phase 1 is created.

One might worry that the case of a single order parameter is special in that the 02 trajectory must pass directly over the metastable phase. With two order parameters, this is not so. Indeed, let q_1 and q_2 be two nonconserved order parameters. The free energy is then a surface, with three wells that are not normally collinear. Thus, 02 trajectories need not—and usually will not—pass directly
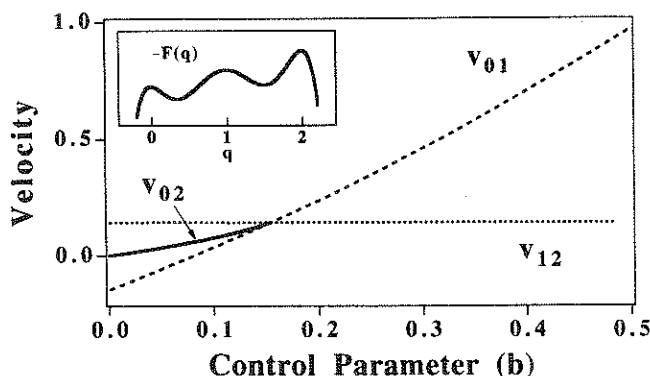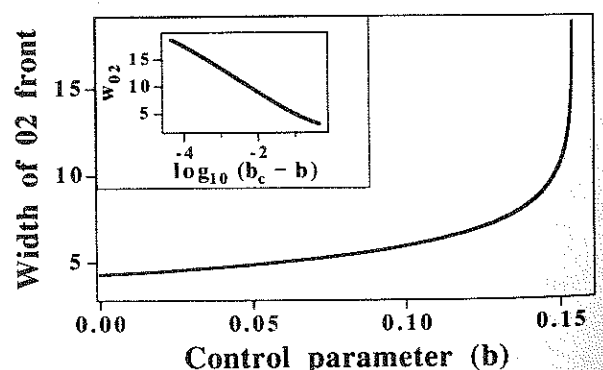

FIG. 1. Calculated velocities of the 01, 12, and 02 fronts as a function of b. Inset: Minus the free energy vs the order parameter q. The curve is minus the integral of Eq. (2) for $b = b_c$.

FIG. 2. Width of the 02 front as b_c is approached. Inset: The divergence is shown to be logarithmic. The width $w_{02} = x_a - x_b$, where $q(x_a) = 0.5$ and $q(x_b) = 1.5$.
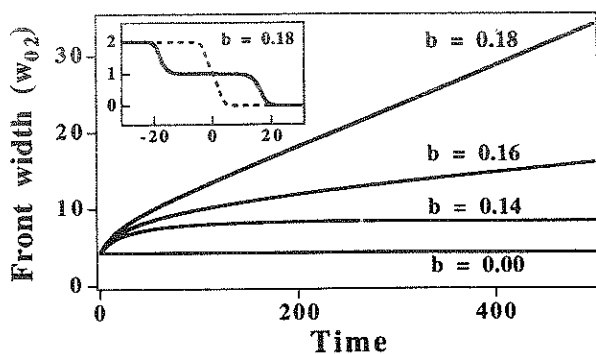
FIG. 3. Width of the 02 profile vs time for $b=0$, 0.14, 0.16, and 0.18. Inset: Splitting of the 02 front for $b=0.18$. Order parameter q vs position x. The dashed curve is the initial stationary solution for $b=0$. The solid curve shows a profile for $t=10000$ time units.

over well 1. Nevertheless, we can show explicitly that in at least one case, the same splitting instability occurs. Our equations of motion are now

$$(q_i)_t = (q_i)_{xx} - \frac{dF(q_1,q_2)}{dq_i}, \quad i=1,2. \qquad (5)$$

Since a polynomial form for the free energy is cumbersome, we choose instead a sum of three Gaussians,

$$F(q_1(x,t),q_2(x,t))$$

$$= -\sum_{j=1}^{3} h_j \exp\{-[(q_1-q_{1j})^2+(q_2-q_{2j})^2]/w\}, \qquad (6)$$

where the positions of the three Gaussian peaks (q_{1j},q_{2j}) are set so that there are wells at $(0,0)$, $(1,0)$, and $(1,1)$, which are analogous to wells 0, 1, and 2, above. The width $w=0.3$. Since our arguments depend only on the qualitative shape of the free energy, the exact analytical form is unimportant. The well depths (or hill heights, for the mechanical analogy) are $h_1=1$, $h_2=h_3-0.1$, $h_3=1+b$, where b is again a control parameter that is proportional to the deviation of temperature from the solid-liquid coexistence value.

In analogy to the one-order-parameter case, we find that for $b \le b_c \approx 0.168$, the front moves at constant velocity, and there is no metastable phase. By contrast, for $b > b_c$, an ever-widening region of the $(1,0)$ phase is created. There are some subtleties, however. First, since trajectories representing the front in order-parameter space do not pass directly over the $(1,0)$ hill, the value of b_c is no longer given exactly by the generalization of the condition that $v_{01} > v_{12}$, although that relation continues to hold approximately. Second, the metastable phase must not lie too far from the line in order-parameter space connecting $(0,0)$ with $(1,1)$. In the mechanical analogy, it is clear that if the metastable hill is very far from the other two, it cannot influence the particle dynamics. And third, there can be multiple solutions connecting $(0,0)$ with $(1,1)$ [7]. These can lead to hysteresis in the behavior of fronts as b is varied. The two-order-

parameter case will be discussed in detail in a future article [8]. In particular, we are in the process of determining just "how close" the intermediate state must be to the other two phases in the order-parameter space in order for the splitting instability to occur. But what is important here is that the splitting instability can exist even when there are multiple order parameters.

We have thus shown that metastable wells in the free energy lead naturally to a front-splitting instability that generates macroscopic quantities of the metastable phase. One might object that the metastable phase will only be a kind of transient because the stable phase will always be present and will eventually replace the metastable phase. The issue is how long is "eventually," for materials are often processed in just such a way as to minimize this effect. Common techniques such as rapid cooling from the vapor or the liquid state (often called "splat cooling") [9] depend on rapid temperature changes and large departures from thermodynamic equilibrium. As mentioned above, the basic time scale τ_0 is actually a function of both the order parameter and the temperature. It will get large either because the ordered phase has slow kinetics, or because a phase with fast kinetics has been sufficiently undercooled (as happens in the glass transition [10]). For the particular case of metastable crystal structure in solids, the time scale τ_0 in the solid phases is several orders of magnitude larger than it is in the liquid. This means that the velocity scale for v_{12} will be correspondingly smaller than that for v_{01}. Once the 01 front separates from the 12 front, the velocity scale of the separating subfronts will continue to be set by v_{01}, implying rapid creation of the metastable phase, while the 12 front between the two solid phases moves slowly, for *all* temperatures.

We end with four notes. First, in the simplest case, fronts split when $v_{01} > v_{12}$. For small departures from equilibrium, $v_{01} \propto \Delta F_{01}$ and $v_{12} \propto \Delta F_{12}$, where ΔF_{ij} is the free-energy difference between phases i and j. Thus, we expect to see the splitting instability when $\Delta F_{01} \gg \Delta F_{12}$. This condition formalizes the intuition that metastable phases can form only if they are "close by" the stable phase. For an undercooled liquid, the free energy of the metastable solid phase would be just slightly higher than that of the stable solid phase (ΔF_{12} small), whereas both phases would have substantially lower free energies than the liquid ($F_2 \lesssim F_1 \ll F_0$ and ΔF_{01} large).

Second, for the splitting instability to occur, not only must there be a third well in the free-energy space, but also the front velocities v_{01} and v_{12} must become equal as the control parameter is varied. Since one typically varies one—or possibly, two—control parameters, it is clear that in a given experimental situation (e.g., fast quenching), it may not be possible to produce the given metastable phase. Thus, in an important sense, the mechanism is necessarily nongeneric.

Third, the splitting mechanism differs from the "entropy-production" principle [11,12] discussed recently in

the context of pattern selection, and it should be possible to distinguish experimentally between these two mechanisms.

Fourth, certain aspects of the splitting instability have been anticipated in studies of kinetic-depinning transitions [13], surface melting [6], and fronts separating stable from unstable phases [14,15]. However, the work on surface melting was for a solid-liquid-vapor system near a triple point, and the more general applicability to phases that are always metastable was not mentioned. That on unstable fronts was in the context of amplitude equations for bifurcations; the applicability to thermodynamic phase transitions was not mentioned. Although amplitude equations are similar to the Landau equations discussed above, they often have complex coefficients and thus cannot be derived from a free energy. But for real coefficients (and triple-well potentials), one should be able to see the "instability version" of front splitting.

In conclusion, we have described how strong undercooling can lead to a front-splitting instability that produces macroscopic quantities of a metastable phase. Because our mechanism is highly specific, many tests can be envisioned. For example, certain pattern transitions observed in previous experiments on directional solidification of liquid crystals [16] and on textures of cholesteric liquid crystals in frustrated geometries [17,18] perhaps are due to the front-splitting instability. Detailed calculations are under way.

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