Interfacial Dynamics at a First-Order Phase Transition Involving Strain: Dynamical Twin Formation

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Dynamical growth aspects of symmetry-breaking, first-order phase transitions for which the primary order parameter is a second-rank tensor, e.g., strain describing diffusionless structural phase transitions, are considered. It is found that a single domain does not always grow inside the parent phase matrix, but instead a perpetually twinning interface propagates through the system, a result of the system attempting to minimize its kinetic energy.

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In order for one to describe systems which undergo a symmetry-breaking first-order phase transition, both the nucleation and growth processes must be accounted for. The latter is usually associated with the propagation of interfaces separating the high-temperature parent phase and the low-temperature product phase, and the growth laws describing this motion are often amenable to classification via universality. As with all transitions, the number of components of the order parameter, and the symmetries of the system, strongly influence the behavior at the transition [1]. The most common theoretical approach involves the use of time-dependent Ginzburg-Landau theory (TDGLT) which associates a thermodynamic force with an approach to equilibrium governed by a viscous damping term, i.e., it is essentially an overdamped description of the dynamics. At long times, this description is generally considered to be adequate.

This Letter examines systems which undergo structural phase transitions for which a discontinuous change of shape of the unit cell signifies the transition and the primary order parameter is a second-rank tensor, namely, strain. The interfacial motion that we find, studied with purely *deterministic* dynamics, contrasts sharply with the TDGLT approach discussed above. The overdamped (i.e., diffusive) limit, in which the mass density is set to zero, leads to an infinite sound velocity. This means that a disturbance is "communicated" instantaneously to the whole solid. The point of this Letter is to display the very complicated interfacial dynamics found when the physical (underdamped) hydrodynamic limit is employed.

A one-dimensional deterministic model will be considered which lacks the geometrical difficulties of more general ferroelastic systems [2]. However, experiments usually show that after the transition has occurred, arrays of twins (viz., two symmetry-related crystal shapes being periodically alternated along a single axis) are found (e.g., see Fig. 2b of Ref. [3]), and thus our model is sufficiently general to address the question: What are the dynamics that lead to this ordered polydomain product phase? Up until now, only the energetics of such static configurations [4] have been considered, even though a number of experimental papers [5,6] have provided evidence that factors such as the degree of undercooling can indeed influence the final morphology. After presenting our theoretical work we shall return to the experiments for comparison.

It is standard that in TDGLT the growth interface is described by a moving kink-type solitary wave which connects only one variant of the low-temperature phase with the parent matrix. Except for certain pathological boundary conditions [7], no such single solitary wave solutions exist for the strained system at nonzero undercooling and finite damping. Instead, the growth front can be described by (a) a perpetually twinning interface which has a localized kinetic energy, but cannot be classified as a usual propagating kink, or (b) two kinks connecting different strains of opposite sign moving at different speeds. A phase diagram will be presented showing how the competition between inertia, damping, and undercooling determines which of the two types of motion described above [(a) or (b)] will be obtained. The boundary in phase space between these two types of solutions can be approximated by comparing the growth velocity with the sound velocity of the parent phase.

We shall focus on the simplest first-order symmetry-breaking transition for which strain is the primary order parameter, viz., only a single strain is involved in the transition, and the product phase is only doubly degenerate. A single (vector) displacement field $u(x)$ is used, which depends on one spatial variable x. The strain is then simply $e \equiv u_x$. Further, an on-site ϕ^6 Landau free energy is employed for which $e=0$ corresponds to the high-temperature parent phase, while $e=\pm e_m$ correspond to the doubly degenerate, low-temperature product phase. Thus, the free-energy functional $F[e(x,t)]$ that we use is

$$F[e(x,t)] = F_0(T) + \int [f_L(e) + \tfrac{1}{2} D e_x^2] dx \,, \qquad (1)$$

where T is the temperature, and the local Landau free-energy density $f_L(e)$ is an expansion for small strain:

$$f_L(e) = \tfrac{1}{2} A \delta T e^2 - \tfrac{1}{4} B e^4 + \tfrac{1}{6} C e^6 \,. \qquad (2)$$

The coefficients A, B, C, and D are positive constants, and $\delta T = T - T_c$, where T_c is the instability temperature of the parent phase. The minima of $f_L(e)$ define the stable equilibrium values of the strain for a homogeneous system. In particular, if the temperature is above the first-order transition temperature T_1, there is only one absolute minimum located at $e=0$ (the parent phase), and if the temperature drops below T_1, the parent phase be-

comes metastable and two new absolute minima develop, which are the two variants of the product phase. Finally, for $T < T_c$, the parent phase becomes unstable. Our analysis will only be concerned with the growth of the product phase when $T_c < T < T_1$. This potential represents a variety of structural (so-called martensitic) phase transitions [8], such as the 2D square-to-rectangular transition, and the 3D tetragonal-to-orthorhombic transition.

For this range of temperatures, the free energies of the homogeneous phases are different, so the interface separating the nucleated domain of (low free energy) the product phase from the background (higher free energy) parent phase would be constantly accelerated unless the motion is damped, removing the energy gained via the larger volume fraction of the product phase after the interface propagates [9]. Thus, we include the sound-wave viscosity following from the Rayleigh dissipation function R for the elastic field, $R = \int \frac{1}{2} \gamma e_t^2 dx$. Last, and most importantly for the dynamics presented in this Letter, we include the kinetic energy density $T = \frac{1}{2} \rho u_t^2$, where ρ is the mass density, finally leading to the equation of motion

$$\Lambda e_{tt} = [\delta T e - e^3 + e^5 - e_{xx} + e_t]_{xx}, \qquad \Lambda \equiv \rho D/\gamma^2. \tag{3}$$

The rescaling of the variables used to obtain the equation of motion is given by

$$\tilde{e} = \left(\frac{C}{B}\right)^{1/2} e, \quad \tilde{x} = \frac{B}{\sqrt{CD}} x, \quad \tilde{T} = \frac{C\alpha}{B^2} T, \quad \tilde{t} = \frac{B^2}{\gamma C} t, \tag{4}$$

where the tildes have been dropped in Eq. (3). We therefore obtain a two-parameter model which depends on a rescaled undercooling (δT) and a rescaled mass coefficient (Λ).

To proceed we have considered the initial $t = 0$ state to be a single nucleation center in the parent phase which is large enough to overcome the barrier to grow into the product phase. Our results do not depend qualitatively on the choice of the initial strain field, so we choose a pulse which is both static and symmetric about $x = 0$ (e.g., an asymmetric nucleus leads to the same kind of interfacial dynamics). Since the equation of motion is also symmetric about this point, we need only examine $x > 0$. Then, we integrate Eq. (3) numerically to obtain the mean-field dynamics for this model.

In the overdamped ($\Lambda = 0$) limit, one can obtain an analytic solution for the interface in the form of a kink-type propagating solitary wave given by

$$e(x,t) = \frac{\pm e_m}{\{1 + \exp[(x - vt)/l]\}^{1/2}}, \tag{5}$$

where $e_m = 0.5(1 + \sqrt{1 - 4\delta T})$ is the martensitic strain. The speed v and width l are uniquely determined by the undercooling δT. (This, as was mentioned earlier, corresponds to the TDGLT; e.g., the speed v is determined by balancing the energy gained from the newly transformed state, with the energy lost from the dissipative forces.) After a short transient, our initial pulse rapidly approaches a steady-state profile consisting of two kinks, one moving to the right at a speed v, and one moving to the left at the same speed [see Fig. 1(a)]. Analysis of the displacement field [found by integrating $e(x,t)$] reveals that a finite velocity (u_t) develops everywhere in the parent phase. In the overdamped limit (zero mass density) this solution is perfectly acceptable. However, if the mass density is nonzero, such motion would correspond to an infinite kinetic energy. That this solution is not realized in the physical hydrodynamic description is a direct consequence of the finite propagation time of the elastic field found for $\rho \neq 0$. Instead, we *empirically* find that the displacement field far from the interface must remain fixed, and thus the parent phase is "bent" in the immediate vicinity of the growth front. The resulting profile can differ quite dramatically from the overdamped solution, as is seen in Figs. 1(b)–1(d).

The growth of the product phase, therefore, induces a stress on the parent phase at the interface. This gives rise

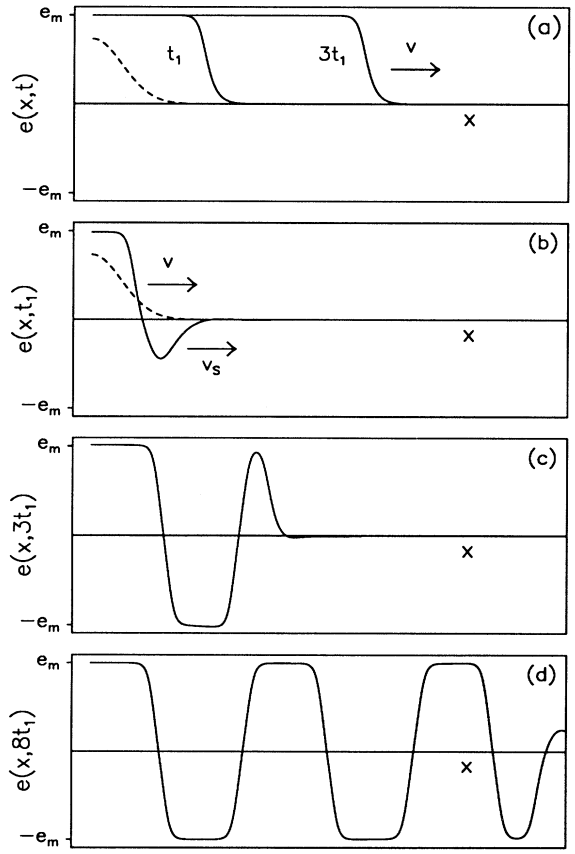

FIG. 1. Strain profile vs position at three different times for $\delta T = 0.04$. (a) The overdamped solution ($\Lambda = 0$); (b)–(d) the evolution of a perpetually twinning interface when $\Lambda = 1$. The dashed line is the initial ($t = 0$) profile.

to a local "twinning force" which creates a strain opposite in sign to the originally nucleated pulse. As a consequence, if one starts with the $e=e_m$ state, the $e=-e_m$ state is produced to the right of the interface [see Figs. 1(b)–1(d)]. This new variant of the product phase starts to grow until the process repeats itself in reverse. The moving interface separating product from parent alternately leaves behind a structure consisting of *both* of the doubly degenerate low-temperature variants connected by *static* domain walls. It is easy to show that the kinetic energy for this type of growth is localized in the vicinity of the interface, thereby minimizing the total mechanical energy. Notice that this is a purely dynamic effect and that the remaining twinned structure is not the lowest static energy configuration. The spacing between the domain walls is determined by the *dynamical* parameter Λ and the undercooling δT. We shall refer to this process as autocatalytic twin formation, and our explanation is one that contrasts with static theories based on nonlinear elastic restoring forces [3].

The magnitude of the stress induced in the parent phase depends strongly on the growth velocity, and hence the parameters δT and Λ. One finds that as the velocity is decreased, the resulting twinning force is no longer strong enough to overcome the energetic barrier for nucleation of the opposing variant. In this case, the profile seen in Fig. 2 develops. This profile consists of two kink-type solitons connecting values of the strain that do not correspond to energy minima, and are solely determined by the dynamics. (Of course, these structures cannot persist when the outer interface reaches the boundary, and indeed upon reflection from a free boundary, we have found that twinning can occur. Boundary effects for strain in finite systems are quite restrictive [10]; however, a twinned product phase necessarily lowers the surface stresses that must be present to stabilize the static martensite [11].)

This leads us to the twinning/no-twinning phase diagram shown in Fig. 3. First, in $(\Lambda,\delta T)$ phase space, we have numerically determined that only for sufficiently large undercooling (small δT) and small damping will autocatalytic twinning occur. Then we have found that this behavior has a simple explanation in the form of a geometrical relation between the induced strain (e_2) in the parent phase, the growth speed (v), and the speed of sound (v_s) ($=\sqrt{\delta T/\Lambda}$ in a linear theory), namely,

$$e_2=e_m v/(v_s-v)\,. \tag{6}$$

These quantities are labeled in Fig. 2. This equation can be derived from the condition that the displacement field remain fixed far from the growth region for the profile shown in Fig. 2. As the growth speed approaches the speed of sound, the strain e_2 will exceed the spinodal strain (e_i) determined by $\partial^2 f(e)/\partial e^2=0$, viz., $e_i=0.1(3-\sqrt{9-20\delta T})$. If the strain e_2 does not reach this critical value, twinning does not occur, and the profile shown in Fig. 2 is obtained. Otherwise, the strain becomes unstable and the system starts to autocatalytically twin, as shown in Figs. 1(b)–1(d). In the overdamped limit (along the $\Lambda=0$ axis), the speed of sound is infinite, and hence the strain e_2 is identically zero; Fig. 1(a) is thus seen to be the $v_s\to\infty$ limit of Fig. 2 [cf. Eq. (6)].

Based on the above, one can expect the boundary between twinning and no-twinning in phase space to be ap-

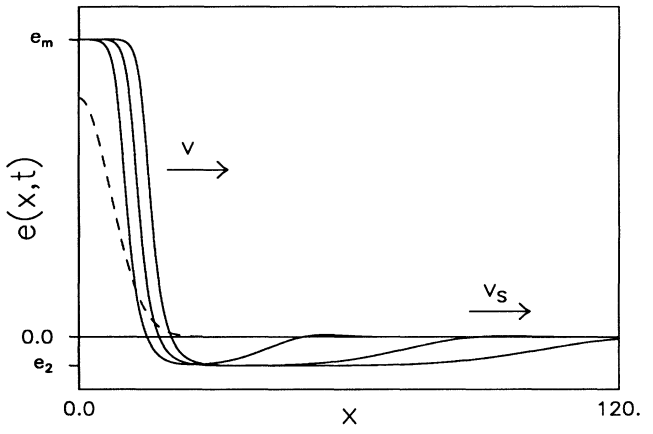

FIG. 2. Two-kink solution for the evolution of the strain field for $\delta T=0.15$ and $\Lambda=1$. The initial profile (dashed line) and three subsequent times are plotted as a function of position x. The new phase is growing to the right at velocity v, and the velocity of the forward kink with amplitude e_2 is approximately given by the speed of sound in the parent phase, v_s.

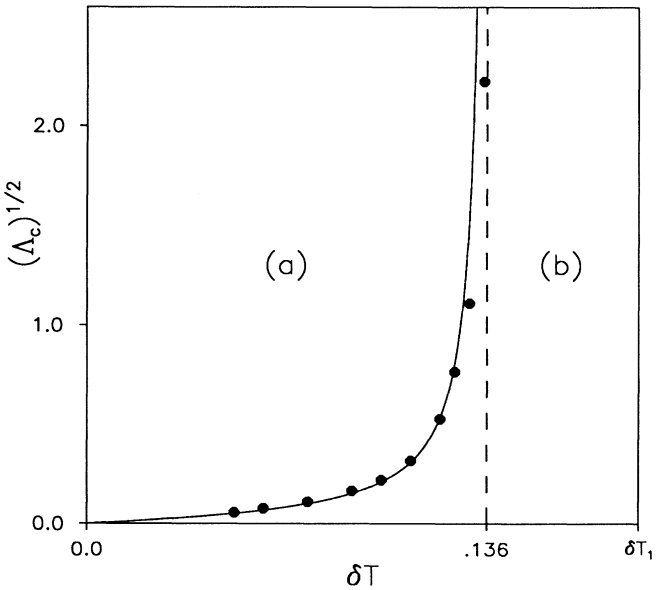

FIG. 3. Critical value of the renormalized mass density, Λ_c, vs the undercooling δT. When Λ exceeds Λ_c one obtains autocatalytic twin formation, (a). Otherwise, the strain evolves as in Fig. 2, (b). Numerical results are shown along with the theoretical curve obtained from Eq. (7) (solid line). $\delta T_1=0.1875$ is the transition temperature in rescaled units.

proximated by setting $e_2 = e_i$ in Eq. (6), and then solving for $\Lambda_c^{1/2}(\delta T)$ (which defines the critical value of Λ at which twinning occurs). We need only calculate the growth speed. This is not a trivial matter, but a rough estimate can be made if we turn to the energy balance condition $dE_{\text{mech}}/dt = -2R$, where E_{mech} is the total mechanical energy. The left-hand side can be calculated exactly for the profile in Fig. 2, and we will approximate the right-hand side with the Rayleigh dissipation function R for the overdamped kink, viz., Eq. (5). Combining Eq. (6) and the energy balance equation, and including nonlinear corrections to the speed of the forward kink ($\approx v_s$), we then obtain

$$\Lambda_c^{1/2} = \frac{-e_m^4 e_i (\delta T - e_i^2 + e_i^4)^{1/2}}{4\sqrt{3}(e_m + e_i)[\delta T e_i - \frac{3}{4} e_i^3 + \frac{2}{3} e_i^5 + \frac{1}{2}\delta T e_m - \frac{1}{4} e_m^3 + \frac{1}{6} e_m^6]}, \tag{7}$$

where e_m and e_i are functions of δT. This curve is plotted in Fig. 3 along with results from the numerics; clearly, the agreement is superb. Also note that Eq. (7) diverges when $\delta T \cong 0.136$. Between this temperature and the transition temperature ($\delta T_1 = \frac{3}{16}$ in our rescaled units) twinning will not occur for any value of Λ.

We now consider the more familiar model B dynamics [1], and use it to display the complete dependence of our twinning results on how the finite propagation time, imposed by the inertia of the displacement field, leads to a type of conservation law. Consider a system with a conserved scalar order parameter that includes a nonzero transit time [12] for the current to propagate in the system, denoted by τ. The continuity and constitutive equations are then

$$\Phi_t = \nabla \cdot \mathbf{J}, \quad \left[\tau \frac{\partial}{\partial t} + 1\right] \mathbf{J} = \nabla \frac{\delta F}{\delta \Phi}. \tag{8}$$

The resulting equation of motion for Φ is

$$\tau \Phi_{tt} = \nabla^2 \frac{\delta F}{\delta \Phi} - \Phi_t, \tag{9}$$

which, except for the damping term, is *identical* in form to Eq. (3). When integrated, the interfacial dynamics for this system is found to have the same topology as that of either Figs. 1(b)–1(d) or Fig. 2. Then, if one lets the effective inertia of this system vanish, viz., $\tau \to 0$, one obtains the usual overdamped TDGLT. However, the resulting interfacial deterministic dynamics *still* mimics (the topology of, anyways) a perpetually twinning interface. This is because the local conservation law is always imposed for model B dynamics, irrespective of whether or not a relaxation time is included. For our strain system the nonlocal conservation law corresponds to the boundaries remaining fixed only for a nonzero mass density. This latter *empirical* conservation result is a direct consequence of the finite propagation time of the elastic field, but is no longer obeyed when the inertia is set to zero [see Fig. 1(a)].

In conclusion, we have shown that the inclusion of the inertia of the displacement field when considering the interfacial dynamics for symmetry-breaking, first-order phase transitions involving strain as the primary order parameter leads, in some cases, to autocatalytic twin formation. It will be difficult to test this idea experimentally, simply because the typical speeds of sound in a metallic solid are of order 2000 m/s; no direct observation of the interfaces could thus be accomplished. However, related experiments [5,6] for order-disorder transitions which involve a concomitant discontinuous change of shape of the unit cell, and where diffusion is required and which thus proceed much more slowly, have indeed shown that a large undercooling does lead to enhanced twin formation [5], in agreement with our Fig. 3. In fact, the complete nucleation and growth sequence displaying this twin formation has been seen using *in situ* electron micrographs [6]. In our simulations of such a coupled system (which also included the coupling to the thermal field and the expulsion of the latent heat) this behavior was also found, and the twins were formed dynamically; these results will be reported elsewhere [13].

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