Role of Elastic Compatibility in Martensitic Texture Evolution

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Abstract

We employ the time-dependent Ginzburg-Landau (TDGL) method to analyze the time evolution of strain fields in a model for materials with martensitic phase transformations. The free energy functional is expressed in terms of the components of the strain tensor, and its functional derivatives with respect to these components give their rate of change. However, the components of the strain tensor are not independent fields; rather, they are related by the Saint-Venant compatibility condition. This condition imposes constraints on the variations of the strain tensor components needed to obtain the equations of motion. Incorporating these constraints in the TDGL procedure introduces extra terms that effectively act as long-range, anisotropic elastic interactions. The latter govern the types of elastic textures that may emerge during a martensitic transformation. The results from the numerical solution of these evolution equations exhibit fine and coarse tweed, twinning, and tip-splitting.

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I. INTRODUCTION.

There is great contemporary interest in the behavior of materials which undergo martensitic phase transitions, partially driven by the important distortive transformations observed and exploited in, for example, ferroelectrics, ceramics and shape-memory alloys. We are interested here in a subset of martensites, the so-called "ferroelastic martensites". The phase transformations in these substances involve changes in the shape of the crystalline unit cell, partial softening with temperature of frequencies of long-wavelength acoustic phonons, and anomalies in the temperature dependence of elastic constants, along with the formation of lamellar, wedge-like and hierarchical structures below the transformation temperature (Barsch and Krumhansl, 1984, 1988; Salje, 1990).

In these materials the changes in the shape of the unit cell on going from the high-temperature (austenite) structure to the low-temperature (martensite) structure can occur in several different ways. Thus there are different "variants" of the low-temperature structure, and these different distortions are related to each other via an element of the symmetry group of the high-temperature phase. Different experiments on these systems show a variety of interesting phenomena. Many of these experiments do not directly involve or pass through the phase transition, but depend only on the fact that there are these different variants in the low-temperature phase. In these experiments several of the possible variants are present simultaneously in the sample. These different variants have to accommodate to each other to maintain the integrity of the sample. The resulting competition as the system tries to achieve a local minimum state of the free energy produces complex patterns at the mesoscale length scale in the mixture of the different variants. Theoretical attempts to predict these patterns have motivated the development of new methods in the calculus of variations (see for example Ball and James, 1992 and the references therein).

Our goal in this paper is to attempt a description of the time evolution leading to these patterns. Our approach is to use time-dependent Landau-Ginzburg (TDGL) equations of motion. This method requires knowledge of the free energy functional of the relevant coarse-grained dynamical field(s). This Landau-Ginzburg (LG) functional is constructed from terms involving small powers of both the fields and the gradients of the fields which are invariant under the symmetry operations of the high temperature structure (the parent phase). The functional derivatives of this free energy with respect to the fields then give their rates of change. In the absence of noise sources, this scheme gives solutions that approach the local minima of the LG functional, which are the possible metastable equilibrium states.

In the situation considered here, the appropriate coarse-grained fields are components of the strain tensor, and so we employ a LG functional which depends on these tensor components. But in applying the canonical TDGL procedure, we find it is necessary to incorporate a new feature. In order not to over-count the number of degrees of freedom of the system, all of the components of the strain tensor can not be independent dynamical fields; there must be constraint equations relating them. These constraints must be taken into account in evaluating the rates of change of the independent dynamical fields from the GL functional, and we have been able to do that. These constraints give rise to additional terms in the equations of motion beyond what one might have intuitively expected. These additional terms are in many respects equivalent to having a long-range, anisotropic self-interaction for that component of the strain whose values actually distinguish the different low-temperature variants, that is for *the* order parameter of the phase transition.

In Section II we describe the origin of the constraints and how they affect the TDGL equations, and in Section III we describe the specific model that we use. Then in Section IV we present our results and follow that with our conclusions in Section V.

II. ELASTIC COMPATIBILITY

We treat the solid as an elastic continuum, for which the fundamental dynamical variable is the displacement field $\mathbf{u}$, a function of position $\mathbf{x}$ and time t. The Landau-Ginzburg (LG) free energy that we use is a functional of the elastic strain, a symmetric tensor field,

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \sum_k \frac{\partial u_k}{\partial x_i}\frac{\partial u_k}{\partial x_j}\right) \tag{2.1}$$

(i, j, k denote Cartesian components). The last term in Eq. (2.1), a nonlinear function of the displacement field, is required to make the strain tensor vanish for displacements which are just finite rotations. For physical situations in which both $\mathbf{u}$ and $\nabla\mathbf{u}$ are small it is often omitted, an approximation known as "geometrical linearity", and we shall make that approximation also. The remaining terms then vanish only for displacements which are infinitesimal rotations. For a comparison between the geometrically nonlinear and linear theories within the context of martensitic transformations see Bhattacharya, 1993.

In d-dimensions the displacement field has d independent components at any point $\mathbf{x}$, whereas a symmetric tensor nominally has $d(d+1)/2$ independent components. Because the strain tensor is composed of derivatives of a vector field, there must be relations or constraints among its components, so that all components can not vary in arbitrary ways. In the approximation of "geometrical linearity" these constraints are expressed by the Saint-Venant compatibility relation (Navier, 1864; Gurtin 1984; Baus and Lovett, 1990)

$$\nabla \times (\nabla \times \epsilon) = 0 \tag{2.2}$$

This equation in an identity expressing equality of certain combinations of mixed partial derivatives which arise from the form of ϵ in Eq. (2.1).

Other authors (Kartha, Krumhansl, Sethna and Wickham, 1995; Jacobs, 1995) have pointed out the importance of the compatibility relations. They have chosen to account for them by calculating directly in terms of displacements and then subsequently differentiating to obtain the strains. Here we shall incorporate the constraints directly in the equations of motion for the strains.

Our goal here is to describe martensitic transformations for which the parent phase (austenite) has square symmetry. The following linear combinations of the strain tensor components directly describe simple strains in that symmetry:

$$e_1 = \frac{1}{\sqrt{2}}\left(\epsilon_{11} + \epsilon_{22}\right), \tag{2.3}$$

$$e_2 = \epsilon_{12}, \tag{2.4}$$

$$\phi = \frac{1}{\sqrt{2}} \left(\epsilon_{11} - \epsilon_{22}\right). \tag{2.5}$$

The component e_1 describes bulk dilatation (change in volume without change in shape), e_2 describes shear distortion (change in shape without change in volume), and ϕ describes "deviatoric" strain (change from square to rectangular shape without change of volume). This ϕ component of the strain tensor is the order parameter for the martensitic transformation of interest (Barsch and Krumhansl, 1988). The compatibility constraint [Eq. (2.2)], restricted to 2D and expressed in terms of these linear combinations, reduces to one equation,

$$\nabla^2 e_1 - \sqrt{8}\frac{\partial^2 e_2}{\partial x \partial y} - \left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2}\right)\phi = 0. \tag{2.6}$$

Therefore only two of the three fields e_1, e_2, and ϕ, are independent. We choose the bulk volume change e_1 to be the dependent field and vary e_2 and ϕ independently. We make this choice because the e_1 component describes homogeneous volume changes which are not so important for understanding the structure which develops below the transition temperature. Also, in 2D there is a sense in which the other two components, e_2 and ϕ, are equivalent to each other and therefore should be treated equivalently. This sense is that the last two terms in Eq. (2.6) can be interchanged by rotating the coordinate system by 45°.

In 3D Eq. (2.2) would give rise to three equations relating the symmetry-adapted strain components. Although it is possible in principle to deal with these equations, the execution of this procedure would be difficult. Therefore for the sake of illustration and simplicity, we proceed here with the 2D situation.

We now suppose we have a free energy functional F which depends on these three strain components. Since we have chosen e_2 and ϕ to be the independent components in order to be consistent with the constraint Eq. (2.6), our LG equations of motion are

$$\frac{\partial e_2}{\partial t} = -\frac{\delta F}{\delta e_2(\mathbf{x})}, \qquad \frac{\partial \phi}{\partial t} = -\frac{\delta F}{\delta \phi(\mathbf{x})}. \tag{2.7}$$

The evolution of e_1 is determined from the solution of these equations through the constraint, Eq. (2.6). Typically in LG equations, there is a kinetic coefficient multiplying the functional derivatives on the right-hand-side. For simplicity we have assumed that the two kinetic coefficients are the same. Then we have moved those factors to the left side of the equations and combined them with t to define a dimensionless time variable.

Typically one assumes that the LG free energy depends on the gradient of the order parameter, that is, on $\nabla\phi$ in this problem. Thus it has the form

$$F[e_1, e_2, \phi] = \int d^2x f(e_1(\mathbf{x}), e_2(\mathbf{x}), \phi(\mathbf{x}), \nabla\phi). \tag{2.8}$$

(The notation d^2x denotes a two-dimensional integral over $\mathbf{x}$.) Although other authors have taken the free energy to depend on the gradient of the other two strain components as well (Jacobs, 1992), such dependence goes beyond the simplest LG theory. Apart from this assumption about the dependence on the gradients of the strain components, the specific form of the LG functional does not matter at this point.

According to Eq. (2.7), we need the functional derivatives of the LG functional F with respect to variations in the independent fields e_2 and ϕ. Variations in these two fields induce variations in e_1 through the constraint, Eq. (2.6). The variation in F due to variations in $e_2(\mathbf{x})$ is thus

$$\delta F = \int d^2x' \frac{\partial f}{\partial e_1(\mathbf{x}')} \delta e_1(\mathbf{x}') + \int d^2x \frac{\partial f}{\partial e_2(\mathbf{x})} \delta e_2(\mathbf{x}). \tag{2.9}$$

Because the variation $\delta e_1(\mathbf{x}')$ is induced by the variation $\delta e_2(\mathbf{x})$, it is given by the functional derivative chain rule

$$\delta e_1(\mathbf{x}') = \int d^2x \frac{\delta e_1(\mathbf{x}')}{\delta e_2(\mathbf{x})} \delta e_2(\mathbf{x}). \tag{2.10}$$

We substitute this result into the first term of Eq. (2.9) and obtain

$$\delta F = \int d^2x \left[\frac{\partial f}{\partial e_2(\mathbf{x})} + \int d^2x' \frac{\delta e_1(\mathbf{x}')}{\delta e_2(\mathbf{x})} \frac{\partial f}{\partial e_1(\mathbf{x}')} \right] \delta e_2(\mathbf{x}). \tag{2.11}$$

We introduce the notation

$$\chi_{e_1 e_2}(\mathbf{x}' - \mathbf{x}) = \frac{\delta e_1(\mathbf{x}')}{\delta e_2(\mathbf{x})} \tag{2.12}$$

for this functional derivative. Then the functional derivative of the free energy with respect to the strain component $e_2(\mathbf{x})$ is

$$\frac{\delta F}{\delta e_2(\mathbf{x})} = \frac{\partial f}{\partial e_2(\mathbf{x})} + \int d^2x' \chi_{e_1e_2}(\mathbf{x}' - \mathbf{x}) \frac{\partial f}{\partial e_1(\mathbf{x}')}. \tag{2.13}$$

In a similar fashion, variation of the LG free energy with respect to the other independent strain component $\phi(\mathbf{x})$ gives

$$\frac{\delta F}{\delta \phi(\mathbf{x})} = \frac{\partial f}{\partial \phi(\mathbf{x})} - \sum_i \frac{d}{dx_i} \frac{\partial f}{\partial \left(\frac{\partial \phi}{\partial x_i}\right)} + \int d^2x' \chi_{e_1\phi}(\mathbf{x}' - \mathbf{x}) \frac{\partial f}{\partial e_1(\mathbf{x}')}, \tag{2.14}$$

where we introduced the notation

$$\chi_{e_1\phi}(\mathbf{x}' - \mathbf{x}) = \frac{\delta e_1(\mathbf{x}')}{\delta \phi(\mathbf{x})}. \tag{2.15}$$

The second term on the right-hand-side of Eq. (2.14 arises from the dependence of the LG free energy density on the gradient of the order parameter field, as is familiar in other variational calculations.

To complete the evaluation of the free energy functional derivatives, we need the functions in Eqs. (2.12) and (2.15). These are obtained from the constraint in Eq. (2.6), by taking the functional derivatives of that equation with respect to $e_2(\mathbf{x})$ and $\phi(\mathbf{x})$. We use the relations $\delta\phi(\mathbf{x})/\delta e_2(\mathbf{x}') = 0$, which expresses the independence of these two fields, and $\delta\phi(\mathbf{x}')/\delta\phi(\mathbf{x}) = \delta(\mathbf{x}' - \mathbf{x})$, and obtain

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \chi_{e_1e_2}(\mathbf{x}' - \mathbf{x}) = \sqrt{8} \frac{\partial^2}{\partial x \partial y} \delta(\mathbf{x}' - \mathbf{x}), \tag{2.16}$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \chi_{e_1\phi}(\mathbf{x}' - \mathbf{x}) = \left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2}\right) \delta(\mathbf{x}' - \mathbf{x}). \tag{2.17}$$

The solution of these two equations subject to appropriate boundary conditions gives the needed ingredients for completing the evaluation of the functional derivatives of the LG free energy.

For the rest of the paper we restrict the treatment to periodic boundary conditions (PBC), which allow a simple solution of Eqs. (2.16) and (2.17). There are of course other boundary conditions that are of interest in the context of martensitic transformations (Finlayson, 1997) and which we hope to investigate. However, solutions of Eqs. (2.16) and (2.17) are more difficult to obtain for those cases. In this paper we study the simplest situation.

The integral in Eq. (2.13) is a convolution. For PBC (or integration over all space), we express that convolution in terms of the Fourier transforms of its factors, using the Fourier transform convolution theorem:

$$\frac{\delta F}{\delta e_2(\mathbf{x})} = \frac{\partial f}{\partial e_2(\mathbf{x})} + \int \frac{d^2k}{(2\pi)^2} e^{i\mathbf{k}\cdot\mathbf{x}} \hat{\chi}_{e_1 e_2}(-\mathbf{k}) \left[\widehat{\frac{\partial f}{\partial e_1(\mathbf{x}')}}\right]_{\mathbf{k}}. \tag{2.18}$$

Here the caret denotes the Fourier transform of the given function, and the notation in the last factor is to denote the Fourier transform of the quantity in the brackets.

Similarly,

$$\frac{\delta F}{\delta \phi(\mathbf{x})} = \frac{\partial f}{\partial \phi(\mathbf{x})} - \sum_i \frac{d}{dx_i} \frac{\partial f}{\partial \left(\frac{\partial \phi}{\partial x_i}\right)} + \int \frac{d^2k}{(2\pi)^2} e^{i\mathbf{k}\cdot\mathbf{x}} \hat{\chi}_{e_1 \phi}(-\mathbf{k}) \left[\widehat{\frac{\partial f}{\partial e_1(\mathbf{x}')}}\right]_{\mathbf{k}}. \tag{2.19}$$

The Fourier transforms of Eqs. (2.16) and (2.17) are easily performed. The solutions are

$$\hat{\chi}_{e_1 e_2}(\mathbf{k}) = \hat{\chi}_{e_1 e_2}(-\mathbf{k}) = \frac{\sqrt{8} k_x k_y}{k_x^2 + k_y^2}, \tag{2.20}$$

$$\hat{\chi}_{e_1 \phi}(\mathbf{k}) = \hat{\chi}_{e_1 \phi}(-\mathbf{k}) = \frac{k_x^2 - k_y^2}{k_x^2 + k_y^2}. \tag{2.21}$$

When Eqs. (2.20) and (2.21) are substituted into Eqs. (2.18) and (2.19), we have evaluated the functional derivatives of the LG functional to the extent that is possible without specifying its form more precisely.

III. THE MODEL AND EQUATIONS OF MOTION

We take the following form for the LG free energy density of Eq. (2.8):

$$f = \frac{1}{2} A_1 e_1^2 + \frac{1}{2} A_2 e_2^2 + \frac{1}{2} \kappa \left(\nabla \phi\right)^2 + f_b(\phi). \tag{3.1}$$

where the "bulk" part of the free energy density contributed by the order parameter is

$$f_b(\phi) = (\tau - 1)\phi^2 + \phi^2(\phi^2 - 1)^2 - P\phi. \tag{3.2}$$

Here P is a stress, and τ is a dimensionless temperature. The stress P could be externally imposed or it could be induced by defects within the crystal. The first two terms of Eq. (3.1) describe linear elasticity for the e_1 and e_2 components of the strain. The "bulk" term f_b describes the nonlinear self-interactions of the order parameter. For $P = 0$, f_b is a symmetric function with one, two, or three minima, depending on the value of the dimensionless temperature τ (see Fig. 1). For $\tau < 0$, $\phi = 0$ is a local maximum, with the value $f_b(\phi = 0) = 0$, and there are two symmetric minima with negative values. For $0 < \tau < 1$, $\phi = 0$ is a minimum [still with $f_b(\phi = 0) = 0$], and there are two other symmetric minima for which the function is negative. At $\tau = 1$, f_b has three degenerate minima with value $f_b = 0$; this temperature is the first-order phase transition point. When $1 < \tau < 4/3$, $\phi = 0$ remains a minimum, and there are two (symmetric) minima at which the function is positive. Finally, for $4/3 < \tau$, the minimum at $\phi = 0$ is the only extremum. The effect of having $P \neq 0$ is to tilt f_b so that the extrema at non-negative ϕ values are no longer degenerate. The determination of the equilibrium state at several temperatures using Monte Carlo simulations by Kartha *et al.* employed this same functional form as Eqs. (3.1) and (3.2) with a τ that depended on the local composition (Kartha, Krumhansl, Sethna, and Wickham, 1995).

Because of the simple form of this LG function, the derivatives appearing in Eqs. (2.18) and (2.19) are

$$\frac{\partial f}{\partial e_i(\mathbf{x})} = A_i e_i(\mathbf{x}), \quad i = 1, 2. \tag{3.3}$$

With this form, the Fourier transform of $\partial f / \partial e_1(\mathbf{x})$ needed for Eqs. (2.18) and (2.19) is just $\hat{e}_1(\mathbf{k})$. This factor is the strain component that was chosen to be dependent on the other two components through the constraint, Eq. (2.6). We Fourier transform that equation to obtain $\hat{e}_1(\mathbf{k})$ in terms of the Fourier components of the other strain components and use that equation to eliminate $\hat{e}_1(\mathbf{k})$ from Eqs. (2.18) and (2.19).

By substituting these results into Eq. (2.7), we obtain our final equations of motion:

$$\frac{\partial e_2(\mathbf{x}, t)}{\partial t} = -A_2 e_2(\mathbf{x}, t)$$

$$- A_1 \int \frac{d^2k}{(2\pi)^2} e^{i\mathbf{k}\cdot\mathbf{x}} \left[\frac{8(k_x k_y)^2}{(k_x^2+k_y^2)^2} \hat{e}_2(\mathbf{k},t) + \frac{\sqrt{8} k_x k_y (k_x^2 - k_y^2)}{(k_x^2+k_y^2)^2} \hat{\phi}(\mathbf{k},t) \right], \tag{3.4}$$

$$\frac{\partial \phi(\mathbf{x},t)}{\partial t} = -\kappa \nabla^2 \phi - \left(2\tau\phi - 8\phi^3 + 6\phi^5 \right)$$
$$- A_1 \int \frac{d^2k}{(2\pi)^2} e^{i\mathbf{k}\cdot\mathbf{x}} \left[\frac{\sqrt{8} k_x k_y (k_x^2 - k_y^2)}{(k_x^2+k_y^2)^2} \hat{e}_2(\mathbf{k},t) + \frac{(k_x^2 - k_y^2)^2}{(k_x^2+k_y^2)^2} \hat{\phi}(\mathbf{k},t) \right]. \tag{3.5}$$

We solved these equations by a Runge-Kutta method. The form of the equations requires transforming between configuration and wavevector space on each timestep. Periodic spatial boundary conditions were employed (as mentioned previously). Various initial conditions were utilized and are illustrated in the next section. The runs displayed in the next section are for spatial discretizations of 256×256 grid points. We checked the adequacy of this spatial discretization by performing a small number of runs on a 2048×2048 grid. The only real difference we found is that the needle tips which appear with some of the initial conditions are somewhat clearer in the higher resolution case. We similarly checked the adequacy of our time step and again found no significant changes in the results. Finally, we mention that an additional feature in the program is that it is possible to have different values of the temperature parameter τ in different spatial sub-areas within the computational cell.

IV. RESULTS

In this section we describe results from our numerical solution of Eqs. (3.4) and (3.5). These results are presented in pictures showing the spatial dependence of the order parameter ϕ at different times. The solution of the equations of motion of course gives the evolution of all components of the strain tensor, but the pictures here show only the most important component, ϕ. These pictures are snapshots taken from movies which are more illustrative but can not be included in this paper (Kerr, 1997).

On these figures, the value of ϕ at each lattice site is encoded by a color scheme which is shown in the panel at the bottom of the figure. Blue indicates negative values near $\phi \approx -1$, describing one variant of martensite, red indicates values near $\phi \approx +1$, describing the other variant, and white is $\phi = 0$, describing austenite. These ϕ values for the different phases and variants are those shown in Fig. 1.

Figures 2 - 5 are from one simulation run. Figure 2 shows the initial conditions, which are uniformly random over an interval around $\phi = 0$. Comparing the range of colors in the figure to the range in the panel at the bottom of the figure, one sees that the interval is small compared to the interval between martensite variants. A feature of this simulation, visible in the subsequent figures, is that the left and right halves of the system are at different temperatures. The left half is held at $\tau > 4/3$, i.e. the temperature parameter of the local potential has a value such that $V_1(\phi)$ has only one minimum. That part of the system will tend to remain in the austenite phase. The local potential on the right-half of the system has $\tau < 1$, so that the degenerate martensite configurations are the preferred structures. The random initial conditions used for this simulation can be thought of as starting from an infinite initial temperature, in the sense that every possible value of the order parameter is equally probable. Thus this run is a quench of the system from a very high temperature to a particular spatially inhomogeneous state with lower temperature. This very nonequilibrium process is quite distinct from the more usual procedure of slow quasi-equilibrium cooling of a system.

The subsequent figures show that structure begins to evolve immediately after the quench. Most of this structure occurs in the "cooler" right-half of the system. However, one sees that the structures which evolve in the right-half penetrate into the "hotter" left-half of the crystal. This penetration effect demonstrates the elastic continuity across the interface arising from the compatibility requirement and illustrates the long range nature of the compatibility-induced interaction. The structure in Fig. 3 is similar to structure in some experimental micrographs made by transmission electron microscopy (Robertson and Wayman, 1983; Schryvers and Tanner, 1990; Tanner, Schryvers, and Shapiro 1990) that show a mottled structure known as "tweed" (see Semenovskaya and Khachaturyan, 1997; Bratkovsky et al., 1995; Kartha et al., 1995; and the references therein). Since the coherent structures in this figure are comparatively small, this structure is "fine tweed". Subsequent evolution, shown in Fig. 4, produces larger structures, which could be labeled "coarse tweed". This coarsening of the tweed structures as the system is cooled toward T_0 is consistent with experiment (Sugiyama, 1985). Also in this figure, some twin bands have also evolved, each of which is made up of one variant of martensite. At this stage there are two sets of twins, oriented along the (11) and $(1\bar{1})$ directions. In subsequent evolution, one of these sets wins over the other, so in Fig. 5 the twin set running parallel to the (11) direction occupies a substantially smaller volume of the system. The small "grain" then eventually disappears (not shown), leaving bands parallel only to the $(1\bar{1})$direction.

At about the center of the upper right-hand quarter of this picture, a thin sliver of austenite (white) material is visible. This small piece of austenite disappears before the end of this simulation run. Such small slivers of austenite frequently remain at the conclusion of several of our simulations. However we believe that they would eventually work their way out of the system if the simulation were run for longer times.

Figures 6 - 8 are from another simulation. In this simulation a narrow band along the left side of the system is held rigidly in the austenite phase, at $\phi = 0$. This is shown by the white band on the left in these three figures. The temperature of the rest of the system is in the martensite regime. The initial condition has one giant twin (wrapped around by PBC) meeting the austenite boundary at a 45° angle, as shown in the first figure. The evolution of this system consists in refinement of the initial twin into increasingly narrower and more numerous twins. This evolution becomes increasingly slow at longer time. Also in this run there are thin slivers of austenite along parts of the twin boundaries. We believe these would disappear if the simulation were continued to much later times.

The boundary between the twinned martensite region and the austenite region (the habit plane) in this simulation was chosen arbitrarily. We need to do this because of a special condition that arises in 2D simulations. In 3D systems, twinning arises as a result of minimizing a free energy with three minima, *viz.* two variants of martensite which satisfy a generalized compatibility relation (a rank-one connection) between them and austenite which is incompatible with the two martensite variants (Ball and James, 1987). In 2D, there *is* a rank-one connection between austenite and martensite, so there is no energetic incentive to form twins. In this simulation we forced an interface to exist by imposing a sharp temperature gradient.

The final set of figures, Figs. 9 - 11, shows the evolution of a system at low temperature under loading, i.e. the pressure P in the local potential is positive. This pressure biases the minimum of f_b at positive ϕ (red color) to be favored over the one at negative ϕ (blue color). The initial condition is a matrix of the two different variants. The short, narrow red strips in the first figure quickly grow out to meet the wider red regions, as shown in the second figure. Also, the long red bars widen, as seen in the third figure. In the third figure, the number of red strips between the bars has doubled, compared to the starting configuration; the narrower set of strips appeared out of the blue regions a few timesteps before this snapshot was taken. One more doubling of the number of these narrow strips occurs before the evolution concludes by having essentially the whole system become red. In this last figure one can observe nucleation events occurring where the tips meet the long interfaces, as more material feeds into the red region. Tip-splitting is also visible at the boundary with the long interfaces; tip-splitting has also been observed experimentally (Shimizu and Otsuka, 1975; Abeyaratne, Chu, and James, 1996). As observed in these experiments, our simulations show a slight bowing just before the event of fast tip splitting.

Finally we should mention that all our simulations of isothermal evolution seem to eventually evolve to a state where the entire specimen is in only one variant. In other words, we do not observe any equilibrium states consisting of a patchwork of twins as seen for example in the experiments (Chu, 1993). Possible explanations for this include: the constraining effect of our periodic boundary conditions (the experiments of Chu are performed under biaxial loading) and the absence of defects or compositional inhomogeneity in our simulations.

V. CONCLUSIONS

Our goal in this paper has been to follow the time dependence of deviatoric (rectangular) and shear elastic strains as they evolve towards a free energy local minimum, starting from appropriate (experimentally relevant) initial conditions. We employed the time-dependent Ginzburg-Landau method. Here the Landau-Ginzburg free energy is expressed in terms of the coarse-grained physical variables, and its functional derivatives with respect to those variables give the corresponding rates of change. In our system, the relevant variables are the local values of the components of the strain tensor.

The typical TDGL procedure must be augmented in this problem because the different components of the strain tensor are not independent fields. They are constrained by the Saint-Venant compatibility relation. We have been able to formally extend the TDGL procedure to include these constraints in a systematic way. In situations where periodic boundary conditions are applicable, we have explicitly carried the procedure through. It results in long-range, anisotropic elastic terms in the TDGL equations for the independent strain components. Appropriately incorporating other boundary conditions with these constraints in the TDGL formalism is an important task for future work.

The results from the numerical solution of the ensuing equations show several features that are also seen in experiments. These include fine and coarse tweed, appearance of the variants of the low-temperature phase in twinned configurations, and tip-splitting. We emphasize that the elastic patterns here were obtained subsequent to a nonequilibrium quench as opposed to the (usual) cooling under equilibrium conditions.

There are several questions remaining to be answered that can be studied within this framework. We have already mentioned the need to use different boundary conditions such as free or fixed. Another problem is to understand the effects of disorder on the time evolution. Including disorder effects is necessary in order to further understand the nature of tweed. It is known that values of martensitic transition temperatures are extremely sensitive to the degree of disorder (Sugiyama, Oshima, Fujita 1984; Sugiyama, 1985). It therefore seems highly likely that disorder is a prominent determinant of the pretransformation patterns in these materials. Indeed, our simulations (Figures 2 - 5) show the presence of transient (metastable) tweed-like states of very low energy even in the absence of any disorder or compositional fluctuations. Introducing even a small amount of disorder can therefore pin these states or possibly lead to a glassy evolution that is experimentally indistinguishable from equilibrium. It has been shown (Shenoy, 1997) that including terms in the LG functional which couple composition fluctuations to the order parameter ϕ and performing a Gaussian average over these fluctuations leads to fourth-order cross-gradient terms in our equations of motion. Further numerical work is necessary to demonstrate that these terms can lead to a more accurate understanding of the experimental phenomena.

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FIGURES

FIG. 1. The bulk contribution $f_b(\phi)$ of the LG functional, Eq. (3.2), for $P = 0$ and several values of τ. The decreasing sequence of τ values identifies the different curves from top to bottom. For each τ the minima of this function describe the possible spatially uniform stable and metastable states.

FIG. 2. Uniformly random initial conditions for ϕ around $\phi = 0$. In this simulation the system is held in a spatially inhomogeneous state by having different values for the dimensionless temperature τ in the left and right halves of the system. This inhomogeneity is not evident in the initial conditions but becomes so in the next figure.

FIG. 3. An early intermediate time configuration after quench from random initial conditions. It is evident in this picture that the value τ in $f_b(\phi)$, Eq. (3.2), has different values in the left and right halves of the system. On the left, $\tau > 4/3$ so only the austenite phase is possible, and on the right, $\tau < 0$, so the two martensite variants are the stable structures. The random initial condition has evolved into a "fine tweed" configuration.

FIG. 4. A later intermediate time configuration after quench from random initial conditions. The smaller-scale patterns here are "coarse tweed"; they are larger scale than the "fine" tweed of the previous figure. Twin boundaries have also emerged, separating the two martensite variants. At this time, the twins extend along both $\pm 45°$ directions.

FIG. 5. Late time configuration after quench from random initial conditions. The cooler half of the system has evolved almost entirely into twins. In the evolution after this picture, the small grain of twins running in the $+45°$ direction disappears.

FIG. 6. Initial conditions for a second simulation. There is a single large twin of the two martensite variants occupying most of the system. In a strip along the left side, the order parameter has the value $\phi = 0$. In the subsequent evolution, this strip is held rigidly at this value. The τ value in the rest of the figure is negative.

FIG. 7. Intermediate time configuration from the large twin initial condition. The single twin is starting to refine into narrower strips.

FIG. 8. Late time configuration from the large twin initial condition. The evolution has become very slow in this configuration.

FIG. 9. Initial conditions for a third simulation. This system has an applied stress, $P > 0$, which favors the red martensite variant over the blue. Again, this condition is not evident in the initial condition.

FIG. 10. Intermediate time configuration for the stressed system. At this time the short strips in the initial configuration have grown and just touched the wide red regions.

FIG. 11. Late time configuration for the stressed system. Note that the thin red strips between the two wide red bands divide into two categories: very narrow ones appear in between each pair of slighly wider ones. The wider ones have evolved from the short red bars in the initial state. The narrower ones appeared just a few time steps before this picture was made. Also note the tip-splitting where the thin strips meet the wide bands.