Modulation mechanism for first-order transformations with nonconserved order parameters

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The effect of energy conservation on the decomposition dynamics of unstable states is considered for systems with nonconserved order parameters. We demonstrate that close to the critical point of instability the dynamics of the order-parameter field is described by the nonlinear Cahn-Hilliard equation, leading to microstructure evolution by heat-transfer-controlled modulation. The results are applied to first-order displacive transitions, predicting an alternative transformation mechanism that follows a path of continuous strain modulation with finite wavelength.

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It is well known that conservation of energy can lead to heat-transfer-controlled kinetics for first-order phase transformations, which can be especially important when the transformation order parameter is not itself a conserved quantity. This gave rise to the so-called "phase-field model" (PFM) [1,2], which describes the conservation of energy by an inhomogeneous diffusion-type equation for temperature. In this Rapid Communication we examine the general problem of the effect of energy conservation on the decomposition dynamics of unstable and weakly metastable states of a system with a nonconserved order parameter. Initial conditions are known to play an important role in the isothermal disintegration of an unstable state [3]: Localized perturbation ultimately leads to the formation of a front moving with a characteristic velocity. However, nonlocalized initial conditions resulting from thermal fluctuations may lead to different types of dynamics [4]. In the case of a displacive structural transformation where the order parameter is a strain, it has been suggested [5] that a first-order transition might occur by a continuous strain-modulation mechanism controlled by heat transfer.

When field theory is used to describe dynamics of phase transitions it is assumed that the state of a system at a given time $t$ in addition to temperature $T$ and stresses $\sigma$ (pressure) must be described by one more function of the position vector $x$. We shall call it the order-parameter field (OPF) $\xi(x,t)$. The nonequilibrium Gibbs free energy of the system as a whole (effective Hamiltonian) is taken as the Ginzburg-Landau functional:

$$\Phi = \frac{1}{2} \int \tilde{\xi} d^3x, \quad \tilde{\xi} = \xi(\xi, T, \sigma) + \frac{\kappa}{2} (\nabla \xi)^2, \quad (1)$$

where $\tilde{\xi}$ is the Gibbs free energy per unit volume of a nonlocal medium with a homogeneous part $\xi(\xi, T, \sigma)$, and the parameter $\kappa > 0$ characterizes the nonlocal properties of the medium. The internal energy density $\tilde{\xi}$ and the specific heat $C$ of such a system relate to the free energy in the same way as for the local medium:

$$\tilde{\xi} = C \left( \frac{\partial \tilde{\xi}}{\partial T} \right)_T$$

Metiu, Kitahara, and Ross [6] showed that depending upon the nature of the ordering field, its evolution is governed by equations of different types: the Cahn-Hilliard equation (CHE) [7],

$$\frac{1}{\gamma} \frac{\partial \xi}{\partial t} = \nabla \left[ \frac{\partial \xi}{\partial \xi} - \kappa \nabla^2 \xi \right]$$

if this field obeys a conservation law, or the relaxation equation,

$$\frac{1}{\gamma} \frac{\partial \xi}{\partial t} = - \frac{\partial \xi}{\partial \xi} + \kappa \nabla^2 \xi$$

if it does not. Here $\gamma$ and $\gamma$ are positive constants. The latter case is addressed in this Rapid Communication.

Over the past several years much attention has been given to this problem in the presence of conservation of energy [1,2,8]. Umantsev and Roitburd [9] developed a thermodynamically consistent approach to the problem and derived the evolution equation for the energy of a nonlocal medium:

$$\frac{\partial \xi}{\partial T} = \nabla \left[ \frac{\partial \xi}{\partial \xi} - \kappa \nabla^2 \xi \right]$$

Recently Umantsev [10] studied the existence and thermodynamic stability of different equilibrium states of such a system under adiabatic conditions with constant pressure (energy conservation) and found that a homogeneous equilibrium state (HES) obeys the same relation as that under isothermal conditions $(\partial s/\partial \xi)_{\text{HES}} = - (\partial s/\partial \xi)_{\text{T}}/T = 0$, i.e., the state diagram is the same. However the stability of these states with respect to small uniform fluctuations (the thermodynamic stability) is governed by the positivity of different moduli: $(\xi_{\xi})$ for an isothermal system and $(\xi_{\xi} - \xi_{\xi T}/\xi_{TT})$ for an adiabatic one. The thermodynamic analysis gives the stability condition of...
the equilibrium states only with respect to small static fluctuations and does not fully describe the physical origin of instabilities mainly because it assumes little about the evolutionary processes in a system. Fife and Gill [2] studied the linear stability properties of the PFM. In this Rapid Communication we address the linear (normal modes) and weakly nonlinear dynamical analysis of HES of the general system described by Eqs. (4) and (5).

To examine the linear dynamic stability of the HES of an infinite system we superpose disturbances $\{\Delta \xi, \Delta T\}$ on it, substitute into Eqs. (4) and (5), linearize in disturbance quantities, represent these in terms of normal modes $\{\xi, T\} \exp(\beta t + i\mathbf{k} \cdot \mathbf{x})$ where $\mathbf{k}$ is the three-dimensional wave vector, and find that the amplitudes $\Sigma, \Theta$ of perturbations must satisfy the system of equations

$$\begin{align*}
\left[ \gamma \frac{\partial \phi_{tt}}{\partial \psi_{tt}} + \kappa |\mathbf{k}|^2 \right] \Sigma = -\phi_{tt} \Theta, \\
(\lambda |\mathbf{k}|^2 - T \phi_{tt} \beta) \Theta = T \phi_{tt} \beta \Sigma,
\end{align*}$$

(6)

where functions with a bar should be taken at equilibrium. Notice that both cross terms are proportional to $\phi_{tt}$ which may be called the interaction modulus. The system (6) has nontrivial solutions if its determinant vanishes:

$$\frac{C}{\gamma} \beta^2 + C \left[ \phi_{tt} \frac{\phi_{tt}}{\phi_{tt}} - \frac{\phi_{tt}}{\phi_{tt}} \right] \beta + \left( \frac{\lambda}{\gamma} + \kappa \right) \beta |\mathbf{k}|^2 + \lambda \phi_{tt} |\mathbf{k}|^2 + \lambda \kappa |\mathbf{k}|^4 = 0.

(7)

This compatibility condition relates the amplification rate $\beta$ to the wave number $k = |\mathbf{k}|$ of the perturbation. To determine the dynamic stability of the HES [real parts of all roots of (7)] must be positive, utilizing a polynomial form of Eq. (7), we apply the Routh-Hurwitz criterion which yields

$$\begin{align*}
\frac{C}{\gamma} &\geq 0, \\
\gamma \left[ \phi_{tt} - \frac{\phi_{tt}}{\phi_{tt}} \right] + (a + d) |\mathbf{k}|^2 &\geq 0, \\
\lambda |\mathbf{k}|^2 + (\gamma \phi_{tt} + d |\mathbf{k}|^2) &\geq 0,
\end{align*}$$

where $a = \lambda / \gamma$ and $d = \gamma \kappa$ are thermal and relaxation diffusivities, respectively [11]. Except for the trivial condition of positivity of the specific heat $C$, inequalities (8) show that the criterion of dynamic stability for an ideal insulator ($\lambda = 0$) coincides with the local thermodynamic one for the adiabatic system. The same can be said about the uniform mode ($\mathbf{k} = \mathbf{0}$) of a general system with $\lambda \neq 0$. For the absolute stability of HES (arbitrary $k$) the adiabatic and isothermal moduli must be positive. If conditions in a system change (e.g., temperature or energy decreases), the isothermal modulus changes its sign first since the adiabatic modulus is not less than the isothermal one. Hence the dynamical criterion of absolute stability takes the form ($\phi_{tt} > 0$) which differs from the local thermodynamic one for an adiabatic system. This happens because the normal-mode perturbations in general do not satisfy the energy conservation requirement, but satisfy the conditions of the microcanonical ensemble [12]. Thus adiabatic and isothermal systems have the same stable HES (phases), because their dynamical criteria of absolute stability coincide.

Now we shall study the destabilizing influence of different modes. Both branches of the dispersion relation (7) are real because its discriminant cannot be negative. Hence, there are no oscillating modes: All of them either grow or decay. The smaller branch is never positive. The larger one may have unstable modes and will be studied below. Equation (7) also shows that short waves ($k \to \infty$) are not active because their growth rates are always negative. The adiabatic modulus does not regulate the dynamical stability of the system but governs different unstable regimes: If it is positive the uniform wave mode is neutrally stable ($\beta = 0$) even if the isothermal modulus is negative. Otherwise, this mode has a positive growth rate. In the unstable region there always exists a "quasi-isothermal" packet of unstable modes with the cutoff wave number $k_c = (\phi_{tt} / \kappa)^{1/2}$ which destabilizes the HES even if its adiabatic modulus is positive.

Differentiating the amplification rate $\beta$ in (7) with respect to wave number $k$ and equating the derivative to zero, we obtain an equation for the fastest growing mode $k_m$.

$$\frac{\partial \phi_{tt}}{\phi_{tt}} \equiv M = \frac{1}{1 + R} + \frac{2R}{R - 1} + m (1 + R) \frac{m^2}{1 - 2m},$$

(9)

$$R = \frac{a}{d},$$

where $\lambda = \kappa k_m^2 / \phi_{tt}$ is a normalized square of the wave number of the fastest growing mode in the unstable region ($\phi_{tt} < 0$) and $R$ is the ratio of thermal and relaxation diffusivities. If $M = 0$ ($\phi_{tt} = 0$) Eq. (9) does not have solutions. However Eqs. (6) decouple and the uniform mode is the fastest. If $M > M^* = (1 + R)^{-1}$ there is at most one positive root of Eq. (9) in the unstable region. In the vicinity of this criterion the wave number of the fastest mode is small. For $M \to + \infty$, $m$ monotonically increases and the limiting value of $k_m$ is $(\phi_{tt} / 2k)^{1/2}$. Thus one can see that the appearance of the fastest mode with finite wave number is due to the coupling in Eqs. (4) and (5) which is otherwise ($\phi_{tt} = 0$) absent. These results of the linear spectrum study can be summarized in the plane ($\phi_{tt}, \phi_{tt}$) as represented in Fig. 1. The uniform mode is the fastest growing mode if $0 < M < M^*$ [the interaction modulus is small and the adiabatic modulus is strongly negative, case (a) of Fig. 1] which is similar to the isothermal system. If $M^* < M < 1$ [the adiabatic modulus is still negative, case (b) of Fig. 1] the fastest mode has finite wave number and the uniform mode grows also; the unstable branch is optical. For $M > 1$ [the interaction modulus is large and the adiabatic modulus is positive, case (c) of Fig. 1] the wave number of the fastest mode is finite but the uniform mode is neutral; the unstable branch is acoustic. Thus over this range of conditions ($M > 1$) the HES is unstable with respect to the continuous modulation of the OPF.

To examine the further nonlinear development of the unstable long waves near the absolute stability limit of the
of the Cahn-Hilliard type which governs the high-
temperature transformation around the spinodal point. Much work has been done on the spatio-temporal dy-
namics of this equation [7], which shows that the early stages of this process involve selection of a finite wavelength. A large coefficient $\Gamma = \lambda / T \phi_{TR} \sim \varepsilon^{-1}$ in Eq. (14) is independent of the relaxation constant $\gamma$ of Eq. (4) which means that such a decomposition is totally controlled by heat transfer. An analogous equation can be derived if the conservation of energy is replaced by the conservation of solute particles in a solution. In this case $\Gamma \sim DT / \varepsilon \mu^2$, where $D$ is the diffusivity, $\mu$ is the chemical potential, and $c$ is the concentration of a solute.

This analysis can be applied to various phase transitions such as ferromagnetic, ferroelectric, or structural. As an example we examine a single crystal capable of a martensitic displacive phase transformation. It is appropriate to view deviatoric strain as the order parameter of this kind of transition. For a simple model system with uniform shear deformation, the Gibbs free energy can be written in the form of a bistable potential [5,10]:

$$
\varphi(\xi, T, \sigma) = \varphi_1(T) + \frac{a}{2} \xi^2 \left[ h - \frac{1}{3} (h + 2) \xi^2 \right] - \sigma \xi,
$$

where $\varphi_1(T)$ is the Gibbs free energy of the unstrained parent (high-temperature) phase $\xi = 0$, $\sigma$ is an applied shear stress, $h$ is the scaled temperature, $T^*$ is the spinodal (instability) point of the parent phase, $T_0$ is the equilibrium point of the unstrained parent and product (low-
temperature, $\xi = 1$) phases, $L$ is the latent heat of the re-
action, and $a$ is a constant defining the height of the free-
energy density barrier at equilibrium. In Fig. 2 the condi-
tions of homogeneous equilibrium, $(\partial \varphi / \partial \xi)_{\xi,T} = a \xi (1 - \xi)(h - 2 \xi) - \sigma = 0$, are depicted in the plane $(h, \xi)$ for the stress-free (solid lines) and stressed system (thick

![FIG. 1. Stability diagram in the plane $\phi_{\xi\xi}$ vs $\phi_{TR}$.](image)

HES ($\phi_0 = 0$) we introduce a small parameter $\varepsilon$ which determines the departure from the spinodal point ($\phi_{\xi\xi} = 0$):

$$
\phi_{\xi\xi} = -n_1 e^2, \hspace{1em} \phi_{\xi\xi} = n_1^{1/2} e,
$$

and, as the growing wave numbers $k$ are small, we can use the spatiotemporal coordinates of the system (4) and (5):

$$
X = e x, \hspace{1em} \tau = e^2 t. \hspace{1em} \text{Analysis of the system (6) for a transition at high temperature,}
$$

$$
\bar{T} = \frac{n_1}{\varepsilon}
$$

shows that disturbances $\{\Delta \xi, \Delta T\}$ can be scaled as

$$
\xi = \bar{\xi} + e \nu \xi, \hspace{1em} T = \bar{T} + e^{\nu+1} n_1^{1/2} \theta, \hspace{1em} \nu > 0,
$$

where positive quantities $n_1$ and amplitudes $\xi, \theta$ are of the order of unity. The scaling (10) shows that $M \sim e^{-1}$ (the adiabatic modulus is positive), which means strong interaction between energy and OFP modes. The scaling (11) manifests the large entropy contribution to the free energy. The scaling (12) shows that the fastest modes for the breakdown of stability are “quasithermal,” as temperature deflection is of higher order than the deflection of the OFP $\xi$. Since deflections of thermal and order parameter fields are small we can evaluate $\varphi_{\xi}$ in (4) and $w_{\xi}$ in (5) using a Taylor series. For $\nu \gg 1$ one can get only

![FIG. 2. An equilibrium state diagram with solid lines representing the rescaled temperature $h$ of states vs the order parameter value $\xi$; the thick line depicts the stressed system. Double-solid lines denote stable states. Dashed curves represent the states with the same energy.](image)
lines) for the normalized stress $\sigma/a = 0.1$. Double-solid lines denote stable states of the system. An equilibrium state diagram of a stress-free system consists of the parent ($\xi = 0$), product ($\xi = 1$), and unstable “intermediate” ($\xi = h/2$) states. The latter corresponds to the free-energy crest. Below the spinodal point $h = 0$ the unstrained parent state becomes unstable while the “intermediate” state with $\xi < 0$ stabilizes [10].

Recently much interest of the materials-science community has been attracted to the fcc-fct transformation in the Fe-30 at. % Pd alloy. Estimates [13] show that this system has a very small interval between equilibrium and spinodal points: $(T_0 - T^*)/T_0 \approx 0.0134$, and a small latent heat, $L/CT_0 \approx 0.0386$. In Fig. 2, together with the equilibrium states, curves of states with constant energy (dashed curves) are depicted for the system whose parameters correspond to the Fe-30 at. % Pd alloy. For the unstable “intermediate” state of this alloy at $T = T_0$, $M = 2.16$, which shows that this material is a reasonable candidate for the finite wavelength modulation mechanism (see Fig. 1).

We may now describe two types of scenario in such system. If the uniform stress-free parent phase is quenched suddenly below the spinodal point and then thermally isolated (state $A$ in Fig. 2), the transformation will take the path of uniform deformation along the line of constant energy because, in association with high symmetry of the cubic parent phase, $\bar{\varphi}_{CT} = 0$ (interaction is absent) and finite wavelength decomposition below the spinodal point is not favored (Fig. 3). When the system reaches the “intermediate” crest state $B$ the modulation starts because the uniform mode is neutrally stable now and the system should obey Eq. (14). If the parent phase above the spinodal point $C$ is subjected to quick application of shear stress the system finds itself in disequilibrium and follows along the line of constant energies towards the crest state $D$. Here the decomposition again follows a path of continuous strain modulation with finite wavelength.

Thus we infer that for systems with a nonconserved order parameter, decomposition of an unstable state can occur by finite wavelength modulation governed by energy conservation, with a behavior directly analogous to the spinodal decomposition of a system with a conserved order parameter. In the case of a displacive structural transformation this corresponds to the transformation mechanism that has been termed quasimartensitic [5]. Such a mechanism of first-order transformation represents an alternative to isothermal nucleation and growth. Achieving the conditions necessary for this mechanism in a specific system will of course depend on the ability to suppress competing isothermal nucleation, which may be the case if the ratio of diffusivities $R$ is small. Depending upon the specific parameter values $(a, L, C, T_0, R)$ a system has several possibilities for the end state of the transition: (a) to completely transfer to a product state if the final temperature is below the equilibrium point; (b) to form an equilibrium mixture of two phases with temperature close to the equilibrium point; or (c) to find a “meta-stable” state with a large lifetime. Further work is underway to investigate these possibilities in physical systems.

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[4] Thermal fluctuations may also smooth out the critical point and help to surmount the barrier for the transition from a weakly metastable state, but this will be addressed elsewhere.
[11] One of these conditions coincides with that for CHE. That is similar to the phase-field model [2].