Compositional Patterning in Systems Driven by Competing Dynamics Of Different Length Scale

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We study an alloy system where short-ranged, thermally driven diffusion competes with externally imposed, finite-ranged, athermal atomic exchanges, as is the case in alloys under irradiation. Using a Cahn-Hilliard-type approach, we show that when the range of these exchanges exceeds a critical value labyrinthine concentration patterns at a mesoscopic scale can be stabilized. Furthermore, these steady-state patterns appear only for a window of the frequency of forced exchanges. Our results suggest that ion beams may provide a novel route to stabilize and tune the size of nanoscale structural features in materials.

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The spontaneous formation of steady-state patterns have been extensively observed in many equilibrium and nonequilibrium systems [1]. While for equilibrium systems (e.g., ferrofluids, block copolymer melts, etc.) patterning is a result of the competition between repulsive and attractive interactions of different length scales, in nonequilibrium systems (e.g., reaction-diffusion systems, etc.) steady-state patterning is often the result of the competition between several dynamical mechanisms. A conceptual connection between the two classes of systems can sometimes be realized with the construction of Lyapunov functionals and effective Hamiltonians, by which steady-state pattern formation in dynamical systems is interpreted as resulting from the competition between different types of *effective interactions*.

The kinetic Ising-type model with competing dynamics and its continuum mean field counterpart are instruments by which we hope to understand a whole class of nonequilibrium driven systems [2,3], ranging from fast ionic conductors to alloys under irradiation. The main ingredient of this model is the competition between two dynamics: one the one hand, a thermally driven mechanism trying to bring the system to thermodynamical equilibrium; on the other hand, externally imposed particle exchanges of a nature essentially athermal. The usual attempt has been to express the steady state of the system in terms of effective Hamiltonians and effective thermodynamic potentials. Garrido, Marro, and collaborators [4] were able to derive effective Hamiltonians for several types of 1D Ising models with competing dynamics. Rácz and collaborators [5] studied the relation between the range of the externally imposed exchanges and the range of the effective interactions. In the context of alloys under irradiation, using a kinetic Ising-type model, Vaks and Kamyshenko [6] derived a formal expression for the steady-state probability distribution in terms of effective interactions, while from a continuum perspective Martin [7] studied the corresponding dynamical phase diagram by an effective free energy. The possibility of patterning as a result of the competing dynamics has not been considered in these works. How-

ever, in the limiting case of arbitrary length external exchanges, patterning has been recently observed in mean field and Monte Carlo simulations [8]. In this situation, the coarsening of segregated phases (magnetic domains in the Ising case) saturates, leading to a steady-state labyrinthine patterning at a mesoscopic length scale. This microstructure is rationalized in terms of a competition between the attractive nearest neighbor interactions and a repulsive electrostaticlike effective interaction. These patterns do not appear if the external exchanges are short range, e.g., when they occur between nearest neighbors [9,10]. The behavior difference between these two limiting regimes raises the question of whether there exists a critical value for the range of external exchanges for patterning to occur. The main objective of this Letter is to address this question, which, besides having its own theoretical interest, is relevant to alloys under irradiation. Indeed, forced relocation of atoms in displacement cascades may extend beyond nearest neighbor distances, especially in the case of dense cascades or for open crystal structures [11].

To render the problem more concrete, let us consider a binary alloy with a positive heat of mixing under irradiation. Each time an external particle collides with the solid, a local atomic rearrangement is produced. This rearrangement has a ballistic component that mixes the atoms regardless of their chemical identity, trying to bring the system to a random solid solution. During this ballistic mixing, a number of exchanges of atomic positions occur, with an average relocation distance R. The frequency of these exchanges, Γ, is then proportional to the number of collision cascades per unit of time. The case $R \rightarrow \infty$, or *arbitrary-length ballistic exchanges*, has already been studied: The macroscopic governing equation is identical to that describing a binary alloy undergoing a chemical reaction $A \rightleftharpoons B$ [12] and the one describing a block copolymer melt [13]. From the studies of these systems, the physics of this case is well understood. In terms of the frequency of forced exchanges Γ, it has been shown that, while high values bring the system to a random solid solution, there is a critical value below which the

homogeneous concentration profile becomes unstable towards phase separation. As in spinodal decomposition, enriched regions form and coarsen. However, the characteristic length of the domains l, instead of growing indefinitely towards a macroscopic phase separation, saturates at a mesoscopic scale, l_∞. For Γ values close to the critical value, the steady-state concentration profile has a sinusoidal-wave appearance, with diffuse interfaces, which is referred to as the weak-segregation regime. For smaller Γ values, the concentration profile presents sharper interfaces, with a square-wave-like appearance, which is referred to as the strong-segregation regime. In each regime, the characteristic length has been shown to follow a power law with the exchange frequency $l_\infty \sim \Gamma^{-\phi}$, with an exponent ϕ of $1/4$ for the weak- and $1/3$ for the strong-segregation regime [13].

In the case of ballistic exchanges of a finite range R, there should still be a critical value $\Gamma(R)$ below which the system phase separates. The question is whether phase coexistence takes place at a macroscopic or a mesoscopic scale. In principle, we can predict that, if certain Γ equilibrate a wavelength l for arbitrary length exchanges, finite-range exchanges must also generate patterns when $R \gg l$. It is, however, difficult to determine *a priori* the exact conditions under which coarsening will saturate as a function of R and Γ. In this Letter we show that given a certain R there is an interval $[\Gamma_1(R), \Gamma_2(R)]$ for the stabilization of patterns. Above Γ_2 the homogeneous concentration profile is stable, and below Γ_1 the coarsening continues with the time, with the system separating into macroscopic phases. The extent of this interval for patterning decreases with R, reaching a zero value at a critical, nonzero value R_c, when $\Gamma_1(R_c) = \Gamma_2(R_c) = \Gamma_c$. For ballistic mixing with a radius smaller than R_c, patterning is not possible. We also show that, given a mixing distance R, there is an upper bound for the wavelengths attainable as $\Gamma \to \Gamma_1^+(R)$. These conclusions are in agreement with recent kinetic Monte Carlo simulations of binary alloys under finite-range ballistic exchanges [14,15].

We study the problem using a Cahn-Hilliard-type description of one-dimensional fronts, simulating the walls of the labyrinthine patterns. We first investigate the dynamical trends of the system by a linear stability analysis, and then determine the long-time, steady-state behavior by a variational analysis. The equation describing the temporal evolution is composed of two terms, one for thermal diffusion and another one for ballistic mixing [7]:

$$\frac{\partial \psi}{\partial t} = \frac{\partial \psi^{\text{th}}}{\partial t} + \frac{\partial \psi^{\text{bal}}}{\partial t}. \tag{1}$$

Here we have chosen to represent the concentration field by a globally conserved order parameter $\psi(\mathbf{x})$ so that the homogeneous concentration profile (solid solution) corresponds to $\psi = 0$. In the previous equation, the first term is simply given by $M\nabla^2(\frac{\delta F}{\delta \psi})$, where F is the global equilibrium free energy, and we have assumed a constant mobility

M. As for the second term, we actually need to perform a derivation. For that purpose, let us consider first the ballistic mixing occurring one dimensionally between planes along a crystallographic direction. The rate of change of concentration in the plane i due to interchange of atoms with the planes labeled j is given by [7]

$$\frac{\partial \psi_i^{\text{bal}}}{\partial t} = -\Gamma \sum_j w_j (\psi_i - \psi_{i+j}) = -\Gamma(\psi_i - \langle \psi \rangle), \tag{2}$$

where w_j is a normalized weight function describing the distribution of ballistic exchange distances, and the brackets denote the corresponding (discrete) weighted spatial average. The extension to the continuum is immediate, and we write the governing equation as

$$\frac{\partial \psi}{\partial t} = M\nabla^2 \left(\frac{\delta F}{\delta \psi}\right) - \Gamma(\psi - \langle \psi \rangle_R). \tag{3}$$

where $w_R(\mathbf{x})$ is now a continuous function peaked around the origin with a width proportional to R, and the average denoted by the brackets is defined as

$$\langle \psi \rangle_R = \int w_R(\mathbf{x} - \mathbf{x}')\psi(\mathbf{x}')\, d\mathbf{x}'. \tag{4}$$

In the limit $R \to 0$, the ballistic term reduces to a Laplacian term, expressing diffusion. In limit $R \to \infty$, we recover the governing equation for the case of arbitrary-length ballistic exchanges.

In analogy to what was done in the case of arbitrary-length exchanges, we seek to find a Lyapunov functional for this problem [8,13], which we shall refer to as the effective free energy functional of the system [16]. This functional is given by $E = F + \gamma G$, and it is built so as to determine the kinetics: $\frac{\partial \psi}{\partial t} = M\nabla^2(\frac{\delta E}{\delta \psi})$. Here, G is a new term describing *effective interactions* related to the ballistic term, and to simplify the notation we use $\gamma = \Gamma/M$ for the rest of this paper. The functional E can be interpreted as a modification of the equilibrium free energy F, which, by being minimum at steady state, allows us to define a variational formulation.

For F, we use a Ginzburg-Landau free energy,

$$F = \int (-A\psi^2 + B\psi^4 + C|\nabla\psi|^2)\, d\mathbf{x}, \tag{5}$$

while G is expressed by a self-interaction of the form

$$G = \frac{1}{2} \int \int \psi(\mathbf{x})g(\mathbf{x} - \mathbf{x}')\psi(\mathbf{x}')\, d\mathbf{x}\, d\mathbf{x}', \tag{6}$$

with g being a kernel satisfying

$$\nabla^2 g(\mathbf{x} - \mathbf{x}') = -[\delta(\mathbf{x} - \mathbf{x}') - w_R(\mathbf{x} - \mathbf{x}')]. \tag{7}$$

To proceed further, at this point we need to make a choice of the weight function w_R. A Yukawa-type potential has been proposed by Goldenfeld [17]. This form fits

the observed distribution distances of ballistic exchanges for crystals under irradiation [11], while allowing us to handle part of the minimization problem analytically. In one dimension, $w_R(u) = R/2 \exp(-|u|/R)$.

Having stated the problem, we start by performing a stability analysis of Eq. (3). For small perturbations of the form $e^{\omega t + ikx}$ around a constant profile $\psi = 0$, it is straightforward to find the dispersion relation:

$$\frac{\omega(k)}{M} = 2Ak^2 - 2Ck^4 - \frac{\gamma R^2 k^2}{1 + R^2 k^2}. \quad (8)$$

A series of plots of this dispersion relationship for different values of γ is shown in Fig. 1. As in the case of arbitrary-length ballistic exchanges, there is a critical value γ_2 below which the homogeneous concentration profile becomes unstable. Below this value, there is a window of k values (k_1, k_2) for which the homogeneous solution is locally unstable, suggesting a wavelength selection. For smaller values of γ, the dispersion relation resembles the one of spinodal decomposition, suggesting macroscopic phase separation.

To confirm these predictions, we use a variational approach, based on minimizing the effective free energy functional E. Let us consider first the weak-segregation regime, where the choice of w_R allows us to solve the problem analytically, and then consider the strong-segregation regime, where we need to appeal to a numerical treatment.

In the weak-segregation regime, we can perform the minimization of E by considering a sine family of parametric functions, $\psi(x) = \alpha \sin(kx)$. We obtain the energy per unit length:

$$\langle E \rangle(\alpha, k) = -\alpha^2 \frac{A}{2} + \alpha^4 \frac{3B}{8} + \alpha^2 k^2 \frac{C}{2}$$
$$+ \alpha^2 \frac{\gamma R^2}{4(1 + k^2 R^2)}. \quad (9)$$

Minimization of this energy is performed analytically, and concentration patterning, indicated by solutions with nonzero values of k and α, is found for an interval in γ.
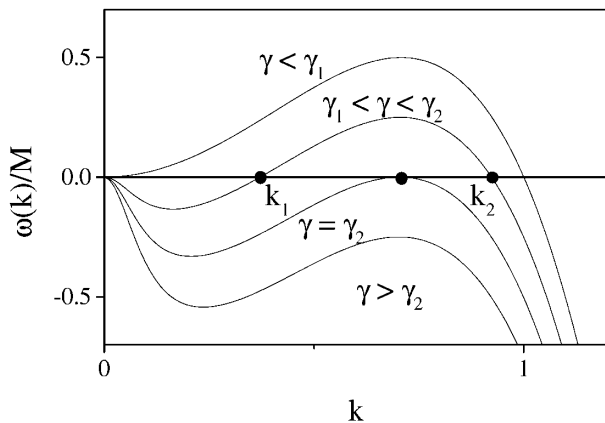

FIG. 1. Growth factor $\omega(k)$ for small perturbations of wave vector k.

In reality, the value of γ_1 predicted by this parametric function is an underestimation. Before that value is reached, the energy per unit length for the macroscopically separated system becomes lower than the energy per unit length for the sine profile. The crossover point determines the actual value of γ_1 in the weak-segregation regime approximation, where patterning occurs in the interval given by

$$\gamma_1 = \left(\frac{2\sqrt{3C} + \sqrt{6[(3 - \sqrt{6})AR^2 - (\sqrt{6} - 2)C]}}{3R^2} \right)^2,$$
$$\gamma_2 = (A + C/R^2)^2/2C. \quad (10)$$

This interval shrinks to zero at a critical value of $R_c = \sqrt{C/A}$, corresponding to $\gamma_c = 2A^2/C$. As a consequence of γ_1 being determined by a crossover of energies, a transition towards macroscopic phase separation occurs at a finite value of k. As a result, there is a bound in the wavelength of the patterns for a given R.

In the strong-segregation regime, we need to improve over the approximation of sine waves for a proper evaluation of γ_1 away from the critical point. To this purpose, we propose to minimize the effective free energy functional using the tanh-sine family of parametric functions $\psi(x) = \alpha \tanh[m/k \sin(kx)]$. The parameter m serves to change the wave profile continuously from a sinusoidal type to a tanhlike type with sharp interfaces, matching the concentration profile of an equilibrium interface.

The minimization can be performed analytically with respect to the parameter α, where we find that the values of γ and k which minimize the effective free energy
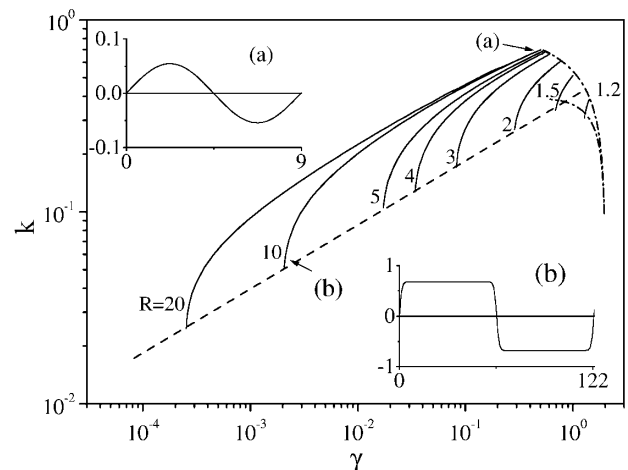

FIG. 2. Wave vector k as a function of γ for several values of R. Dashed-dotted lines mark the limits of patterning as predicted by the sine profiles in the weak-segregation regime. The dashed line corresponds to the large R power-law fit. Insets (a) and (b) show the concentration profile for $R = 10$ in the weak and strong segregation regimes, respectively.
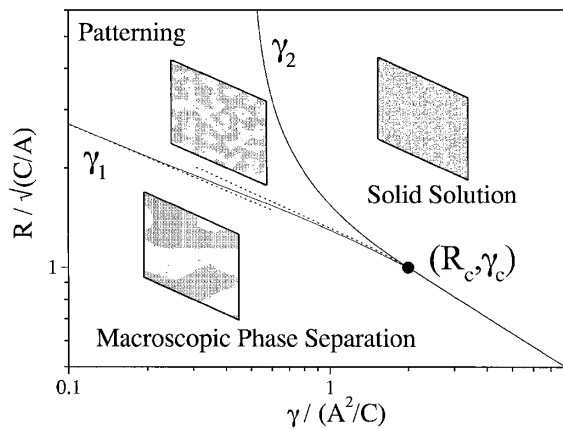
FIG. 3. Steady-state regimes as a function of R and γ. Asymptotics for γ_1 are indicated by dashed lines, for $R \sim R_c$ (sine profiles) and $R \gg R_c$ (power-law fits). Insets show cuts of 3D kinetic Monte Carlo simulations (to be presented elsewhere) of an fcc $A_{50}B_{50}$ alloy with ballistic exchanges of range $R \sim 5/\sqrt{2}$ lattice parameters [15].

are independent of the coefficient B, which only relates to the amplitude α. The remaining expression involves terms that cannot be obtained analytically, so we proceed with a numerical strategy. The effective free energy per unit length is then computed by numerical integration, and the actual minimization is performed by means of the subroutine MNFB from Netlib [18], based on a secant Hessian approximation. Figure 2 shows k versus γ plots for a series of values of R. The physical parameters A and C are set to unity. From this plot we obtain the dependency of γ_1 and the corresponding wave vector k_1 (related to the maximum attainable wavelength) as a function of R. A log-log plot of these quantities (not shown) can be almost perfectly fitted by the simple laws: $\gamma_1 = 2/R^3$ and $k_1 = 1/(2R)$. The latter relationship has the physical interpretation that R is the parameter determining the maximum wavelength. Furthermore, the combination of these two relationships yields the well-known power law of the $R \rightarrow \infty$ case: $k \propto \gamma^{1/3}$. For values of A and C not equal to 1, the corresponding dependencies can be derived by dimensional analysis, giving $\gamma_1 = 2\sqrt{AC}/R^3$ and $k_1 = 1/(2R)$. Figure 3 summarizes the steady-state regimes in the γ-R space. Patterning may occur in the present model when the range of the forced exchanges exceeds a critical value, with a maximum wavelength proportional to that range. In the case of alloys under irradiation, typical R values range from 2 to 10 Å, suggesting that patterns up to 100 Å could be stabilized. For a fixed irradiation flux and by changing the temperature (which implies changing M), patterning must appear just above the temperatures at which the system cannot

be brought to a solid solution by ion-beam mixing. For example, in the case of the Ag-Cu system, for irradiation with 1 MeV Kr ions and a flux of $2.5 \times 10^{13}/(\text{cm}^2 \text{ s})$, this means a temperature in the range of 298–398 K [19]. Experimental work to test these predictions is in progress.

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