

## Reaction-Controlled Morphology of Phase-Separating Mixtures

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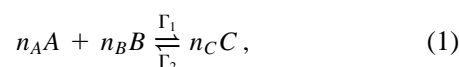
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The role of externally-controlled chemical reactions in the selection of patterns in phase-separating mixtures is presented. Linearized theory and computer simulation show that the initial long-wavelength instability characteristic of spinodal decomposition is suppressed by chemical reactions, which restrict domain growth to intermediate length scales even in the late stages of phase separation. Our findings suggest that such reactions may provide a novel way to stabilize and tune the steady-state morphology of phase-separating materials.

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Pattern formation in reaction-diffusion systems occurs throughout nature. It is well known, for example, that spiral waves and other interesting steady-state patterns can be generated by simple chemical reactions [1]. In contrast, transient patterns are formed during phase separation by spinodal decomposition in both small molecule and polymer mixtures [2,3]. These patterns, whose characteristic length scale depends on the specificity of the components of the mixture, coarsen and disappear when macroscopic phase separation is achieved at asymptotically long times. It would be desirable to devise a mechanism by which these phase-separating morphologies could be stabilized. In this Letter, we argue that chemical reactions can be used to stabilize and tune the characteristic length scale of patterns arising in phase-separating materials. Unlike the usual scenario of spinodal decomposition, where concentration fluctuations of all length scales larger than a certain critical length scale spontaneously grow with time, we show that chemical reactions introduce *two* cutoff lengths, thereby restricting the growth of fluctuations to a narrow range of length scales. Pattern tunability is achieved through appropriate selection of the rate constants governing the externally controlled chemical reactions [4]. Interestingly, our simplest model describing this phenomenon results in an equation identical in form to an empirical equation used to model microphase separation in block copolymer melts [5] and other systems [6] where short-range attractive and long-range repulsive interactions compete. However, unlike the majority of these pattern-selecting systems, chemical reactions offer a tremendous opportunity to control the final morphology of phase-separated materials, especially polymers. Since the kinetics of spinodal decomposition in polymer mixtures and small molecule mixtures is similar in many respects [7], for simplicity we focus here on the effect of chemical reactions on small molecule systems [8].

Consider a mixture of molecules of types *A* and *B* which has been quenched to a thermodynamically unstable state, and which simultaneously undergoes the reaction [4]



where  $\Gamma_1$  and  $\Gamma_2$  are the temperature-dependent forward and backward reaction rates, respectively, and the  $n_i$  are the stoichiometric coefficients. The equations of motion for the concentration  $\phi_i(\mathbf{x}, t)$  of component *i* are

$$\begin{aligned} \frac{\partial \phi_A}{\partial t} &= -\nabla \cdot \mathbf{J}_A - n_A \Gamma_1 \phi_A^{n_A} \phi_B^{n_B} + n_A \Gamma_2 \phi_C^{n_C} + h_A, \\ \frac{\partial \phi_B}{\partial t} &= -\nabla \cdot \mathbf{J}_B - n_B \Gamma_1 \phi_A^{n_A} \phi_B^{n_B} + n_B \Gamma_2 \phi_C^{n_C} + h_B, \\ \frac{\partial \phi_C}{\partial t} &= -\nabla \cdot \mathbf{J}_C + n_C \Gamma_1 \phi_A^{n_A} \phi_B^{n_B} - n_C \Gamma_2 \phi_C^{n_C} + h_C, \end{aligned} \quad (2)$$

where  $\mathbf{J}_i = -\sum_j M_{ij}(\delta F/\delta \phi_j)$ , *F* is the free energy functional appropriate to the mixture, and the  $h_i$ 's are reaction terms arising from spatial inhomogeneities. Alternate approaches to the coupling of diffusion and chemical reactions are possible [9]. In these equations, the local transport of heat and momentum, which in general couple to mass flow [10], has been ignored. The essential physics underlying the stabilization and tunability of pattern formation in phase-separating materials can be illustrated by considering a simpler, two-component system undergoing the following reaction:



The equation of motion for this immiscible, chemically reactive system is [11]

$$\frac{\partial \phi}{\partial t} = M \nabla^2 \frac{\delta F\{\phi\}}{\delta \phi} - \Gamma_1 \phi + \Gamma_2 (1 - \phi), \quad (4)$$

where we have dropped the subscript "A" on the local concentration  $\phi$  and assume incompressibility ( $\phi_A + \phi_B = 1$ ). Quenching below the spinodal temperature will result in demixing via spinodal decomposition and, simultaneously, mixing via the reaction  $A \rightleftharpoons B$ .

The free energy functional  $F\{\phi\}$  is typically written as the sum of the bulk free energy  $f(\phi)$ , which has a

double-well structure below the critical point, and the usual square-gradient approximation to the interfacial free energy [2,3,12]. For small molecules mixtures, Eq. (4) can be written as [13]

$$\frac{\partial \phi}{\partial t} = \Lambda \nabla^2 \left( \frac{\partial f}{\partial \phi} - 2\kappa \nabla^2 \phi \right) - (\Gamma_1 + \Gamma_2)\phi + \Gamma_2, \quad (5)$$

where  $\Lambda \equiv Mk_B T$  and  $f(\phi)$  has been divided by  $k_B T$ . We linearize Eq. (5) about the initial average concentration before the quench,  $\phi_0$ , and replace  $\phi$  by  $\phi_0 + \delta\phi$ , where  $\delta\phi$  is a small perturbation about  $\phi_0$  [2]. After Fourier transforming, we obtain

$$\begin{aligned} \frac{\partial \delta \tilde{\phi}_k}{\partial t} &= [2\kappa \Lambda k^2 (k_c^2 - k^2) - (\Gamma_1 + \Gamma_2)] \delta \tilde{\phi}_k \\ &+ [\Gamma_2 - (\Gamma_1 + \Gamma_2)\phi_0] \delta(k), \end{aligned} \quad (6)$$

where  $(\partial^2 f / \partial \phi^2)_{\phi_0} < 0$  in the two-phase region,  $k_c \equiv (|\partial^2 f / \partial \phi^2|_{\phi_0} / 2\kappa)^{1/2}$ , and  $\delta(k) = 0(1)$  when  $k \neq 0$  ( $k = 0$ ). For nonzero values of  $k$ , this equation is solved by a simple exponential function [14],

$$\delta \tilde{\phi}_k(t) = \delta \tilde{\phi}_k(0) e^{\omega(k)t}, \quad (7)$$

with the growth rate

$$\omega(k) = 2\kappa \Lambda k^2 (k_c^2 - k^2) - (\Gamma_1 + \Gamma_2). \quad (8)$$

Figure 1 shows the growth factor  $\omega(k)$  for spinodal decomposition both with and without chemistry. Without chemistry ( $\Gamma_1 = \Gamma_2 = 0$ ), the growth factor is the usual one predicted from Cahn's linear theory, with a cutoff at large wave vector  $k_c$ . Thus concentration fluctuations with  $k > k_c$  decay and those with  $k < k_c$  grow, with the maximum growth rate occurring for  $k_m = k_c / \sqrt{2}$ . However, the simultaneous occurrence of the reaction  $A \rightleftharpoons B$  decreases the usual growth factor by an amount proportional to the sum of the forward and backward reaction rates  $\Gamma_1$  and  $\Gamma_2$ . This shifts the small-wavelength cutoff to larger wavelengths, and introduces a large-wavelength cutoff. Thus concentration fluctuations at large wave-

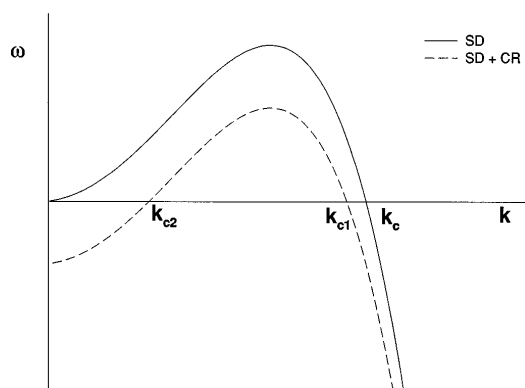


FIG. 1. Early-time growth factor  $\omega(k)$  vs wave vector  $k$ , both with (dotted line) and without (solid line) chemistry. In the absence of chemical reactions, concentration fluctuations at all wave vectors  $k < k_c$  grow. Chemical reactions introduce cutoffs both at large  $k$  and small  $k$ , so that growth occurs only for intermediate-wavelength fluctuations.

lengths (small  $k$ ) are suppressed by the reactions. Such suppression of long-wavelength fluctuations is a natural mechanism for pattern selection in a variety of systems [1,5,6], such as block copolymers. The mathematical origin of the similarity between spinodal decomposition with chemical reactions and ordering of block copolymers lies in the fact that a term linear in  $\phi$  in dynamics [Eq. (5)] can be absorbed into a redefined free energy functional as an additional nonlocal quadratic coupling of  $\phi$ 's [5,15].

Our analysis shows that due to the reactions, only fluctuations at an intermediate length scale grow initially. However, solution of the full nonlinear equation is necessary to explore the later stages of phase separation when the nonlinearities are important [15]. We numerically integrated Eq. (5) on a two-dimensional lattice with  $f(\phi)$ , the bulk free energy, taken as that for an incompressible, small molecule mixture,

$$\frac{f(\phi)}{k_B T} = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi), \quad (9)$$

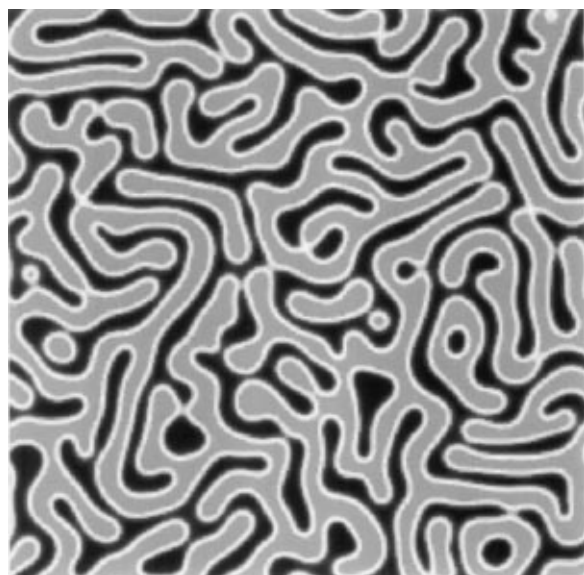
where the dimensionless interaction parameter  $\chi$  relates the interaction energies between the two species of molecules [12]. We take  $\kappa = \chi \lambda^2$ , where  $\lambda$  is the average range of the intermolecular interaction [12,16]. Equation (5) can then be written as

$$\begin{aligned} \frac{\partial \phi}{\partial t} &= \Lambda \nabla^2 \left[ \ln \left( \frac{\phi}{1 - \phi} \right) - 2\chi \phi - 2\chi \lambda^2 \nabla^2 \phi \right] \\ &- (\Gamma_1 + \Gamma_2)\phi + \Gamma_2. \end{aligned} \quad (10)$$

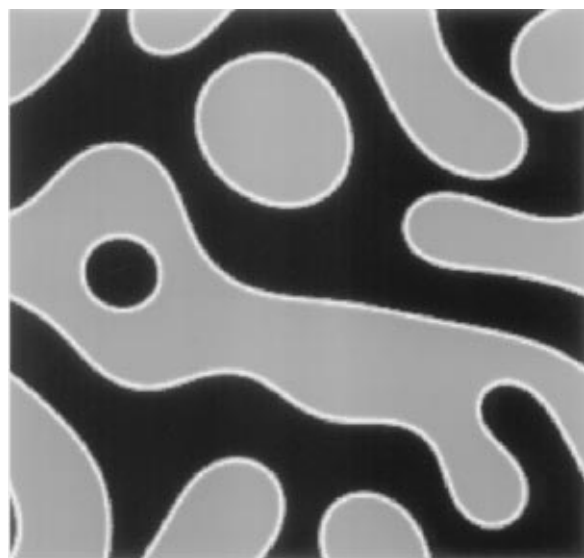
Our simulations were performed by discretizing Eq. (10) using a simple finite difference scheme in two dimensions. Computational details of the integration method will be given elsewhere [7].

The critical point of the free energy in Eq. (9) is given by  $\phi_c = 1/2$  and  $\chi_c = 2$ . The concentration at each lattice site was initialized to  $\phi = 1/2 \pm \delta\phi$ , where  $\delta\phi$  is a random number in the range  $[-0.0001, 0.0001]$ . Lattices of size  $256^2$  and larger were then quenched to  $\chi = 4.0$  for various choices of equal forward and backward reaction rates  $\Gamma_1$  and  $\Gamma_2$  (zero heat of reaction is implied). When  $\Gamma_1 = \Gamma_2 = 0$ , the system phase separates in the usual way [3,17]. This system is shown in Fig. 2 in the late stages of phase separation after a time (a)  $\tau = 512$  and (b)  $\tau = 2048$ . Figures 3(a) and 3(b) show the same system as in Fig. 2(b) at  $\tau = 2048$ , but with  $\Gamma_1 = \Gamma_2 = 0.05$  and  $0.2$ , respectively. Clearly, the steady-state, lamellar structure exhibited by the reactive systems in Figs. 3(a) and 3(b) is very different from the transient, interconnected, self-similar morphology of the nonreactive mixture in Fig. 2.

We measured the average domain size  $R(t)$  by calculating [18] the inverse of the first moment of the structure factor  $S(k, t)$ , for various choices of reaction rates. For each system, the reaction rates were chosen to be equal:  $\Gamma_1 = \Gamma_2 \equiv \Gamma$ . In the absence of chemistry ( $\Gamma = 0$ ) the



(a)



(b)

FIG. 2. Concentration field for  $256^2$  lattice at a time (a)  $\tau = 512$  and (b)  $\tau = 2048$  following a quench of Eq. (10) to the unstable region, in the absence of chemical reactions (i.e.,  $\Gamma_1 = \Gamma_2 = 0$ ).  $A$ -rich regions are shown black and  $B$ -rich regions are shown grey.

system exhibits the expected Lifshitz-Slyozov [19] growth law at late times,

$$R(t) \sim t^\alpha, \quad (11)$$

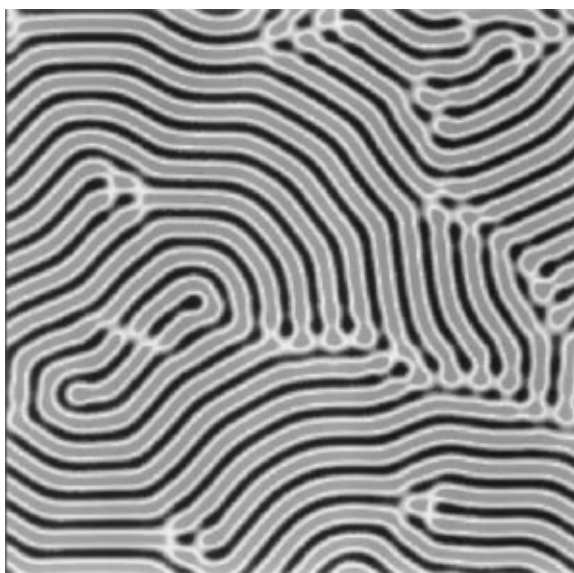
where  $\alpha = 0.32 \pm 0.02$  [17]. However, for nonzero reaction rate, the domain growth saturates at a certain steady-state value  $R_F$ . In the steady state, dimensional analysis of Eq. (10) shows that  $[t] = [1/\Gamma]$ , so that the domain size  $R_F$  should obey the scaling law

$$R_F \sim (1/\Gamma)^\alpha. \quad (12)$$

The steady-state inverse domain size  $R_F^{-1}$  is plotted double logarithmically against the reaction rate  $\Gamma$  in Fig. 4.



(a)



(b)

FIG. 3. Concentration field for  $256^2$  lattice at a time  $\tau = 2048$  following a quench of Eq. (10) to the unstable region, with reaction rates (a)  $\Gamma = 0.05$  and (b)  $\Gamma = 0.20$ .  $A$ -rich regions are shown black and  $B$ -rich regions are shown grey. Further evolution of the system tends to align domains, but the steady-state domain width has already been selected.

Indeed, we find that  $\alpha$  appears to be approaching  $1/3$  for small reaction rates [20]. Thus, the simultaneous presence of the chemical reaction  $A \rightleftharpoons B$  selects intermediate length scales for growth, even in the late stages of spinodal decomposition [21].

The suppression of long-wavelength fluctuations by the interplay between chemical reactions and thermodynamic instability provides a ubiquitous mechanism for pattern selection in nature. The underlying mechanism for pattern selection in typical reaction-diffusion systems arises from a competition between diffusion and chemical re-

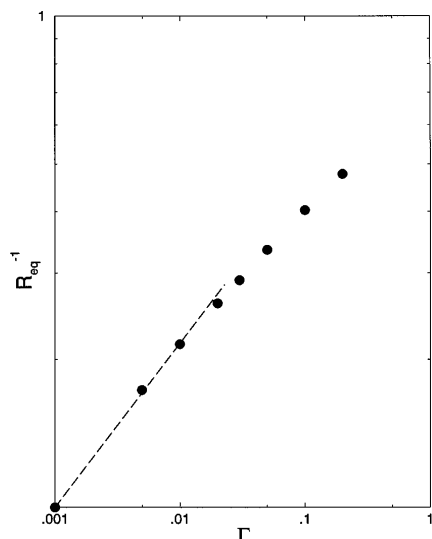


FIG. 4. Double logarithmic plot of equilibrium inverse average domain size  $R_F^{-1}$  vs  $\Gamma$ . The straight line has slope  $1/3$ .

action [1]. The length scale characterizing the transient patterns in spinodal decomposition of mixtures *without* chemical reactions is dictated by the competition between the square-gradient interfacial term and the thermodynamic instability inherent to the system. When externally-controlled chemical reactions and spinodal decomposition occur *simultaneously*, these two selection mechanisms combine to determine the length scale of the steady-state pattern. The two mechanisms can be tuned independently of one another, thereby allowing one to control the final microphase-separated structure of the material [4]. Generalization of the approach developed here to polymeric systems and more complicated chemical reactions promises to be of significant technological importance.

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