Chemically Controlled Pattern Formation in Phase-Separating Materials (*).

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Summary. — The role of 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 chemical 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 that a variety of steady-state patterns can be generated by simple chemical reactions[1] between diffusing species. In contrast, transient patterns are formed during phase separation of a thermodynamically unstable mixture[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 mesoscale structures occurring during spinodal decomposition in such mixtures could be stabilized. We have argued[4] 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 cut-off length spontaneously grow with time, we have shown that chemical reactions occurring during spinodal decomposition introduce *two* cut-off lengths, thereby restricting the growth of fluctuations to a narrow range of length scales.

Here we present a general approach to describe open systems with miscibility gaps whose molecules can additionally undergo externally induced chemical reactions. We focus specifically on the effect of reactions on thermodynamically unstable systems, *i.e.* when phase separation occurs by spinodal decomposition, but in general one can study the effect of chemistry on metastability (nucleation) as well [5]. In this approach, we start with a continuity equation for each component i relating the rate of change of the concentration $\phi_i(x, t)$ to the divergence of the current density J_i in the absence of chemical reactions. If molecules of species i diffuse under the influence of a force $\delta F/\delta\phi_j$ with a mobility M_{ij}, the current density can be written as $J_i = -\sum_j M_{ij} \nabla \delta F/\delta\phi_j$, where the form of the free-energy functional $F\{\phi_i, \phi_j, \phi_k, \ldots\}$ is system dependent. In general, stochastic noise terms that couple to the temperature and the mobilities can be included, as well as hydrodynamic forces. We will neglect these terms in the remainder of this treatment.

Chemical reactions are included by adding to the Langevin equations appropriate source and sink terms describing the particular reaction occurring in the system. We consider here thermodynamically open, non-equilibrium systems in which the demixing process and the reactions are decoupled. As an example, consider a mixture of molecules of type A and B which has been quenched to a thermodynamically unstable state, and which simultaneously undergoes the chemical reaction

$$\text{(1)} \qquad \nu_A A + \nu_B B \underset{\Gamma_2}{\overset{\Gamma_1}{\rightleftharpoons}} \nu_C C,$$

under an external force, where Γ_1 and Γ_2 are the forward and backward reaction rates, respectively, and ν_i is the stoichiometric coefficient of species i. The equations of motion for the local concentration $\phi_1(x, t)$ of component i are (*)

$$\text{(2)} \qquad \begin{cases} \dfrac{\partial \phi_A}{\partial t} = -\nabla \cdot J_A - \nu_A \Gamma_1 \phi_A^{\nu_A} \phi_B^{\nu_B} + \nu_A \Gamma_2 \phi_C^{\nu_C} + h_A, \\[2ex] \dfrac{\partial \phi_B}{\partial t} = -\nabla \cdot J_B - \nu_B \Gamma_1 \phi_A^{\nu_A} \phi_B^{\nu_B} + \nu_B \Gamma_2 \phi_C^{\nu_C} + h_B, \\[2ex] \dfrac{\partial \phi_C}{\partial t} = -\nabla \cdot J_C + \nu_C \Gamma_1 \phi_A^{\nu_A} \phi_B^{\nu_B} - \nu_C \Gamma_2 \phi_C^{\nu_C} + h_C, \end{cases}$$

where the h_i's are reaction terms related to spatial gradients (**).

(*) The systems we discuss here are considered to be open with respect to a thermal bath. Thus stochastic noise terms should be included in the Langevin equations of motion, in general. Since such terms are believed to have no effect on the late stage growth kinetics during spinodal decomposition in the absence of reactions, we neglect them here for simplicity.

(**) The functional form of the reaction terms assumes no intermediate reactions. This is not realistic when the stoichiometric coefficients are other than 1 or 2, and intermediate equations should then be considered.

Although A and B will begin to undergo spinodal decomposition following a quench to the unstable region, the chemical reaction may interfere with this process. The reaction in (1) could describe, *e.g.*, crosslinking of polymer chains, in which A and B refer to monomers on unlike chains and C refers to the crosslink, which can be taken to be immobile if the crosslinked chains belong to the gel phase. The reaction might also describe the formation of surfactant molecules where C is a dimer consisting of A and B. Depending on the reaction, the reactive terms in the Langevin equations, as well as the interaction energies, mobilities, and the free energy itself may all be different.

In principle, we can investigate the effect of any chemical reaction on the kinetics of spinodal decomposition with this approach by 1) linearizing the equations of motion to study the early-time growth of concentration fluctuations in momentum space, and 2) solving the coupled set of nonlinear equations numerically to study the late stage kinetics of spinodal decomposition and the steady-state pattern formation. The latter task is highly computer-intensive.

For illustrative purposes we consider here a binary mixture of molecules A and B, with respective concentrations ϕ_A and ϕ_B, in which the molecules undergo the simpler chemical reaction [4, 6]

$$(3) \qquad A \underset{\Gamma_2}{\overset{\Gamma_1}{\rightleftharpoons}} B .$$

The equations of motion for this immiscibile, chemically reactive system can be reduced to the single equation

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

where we have dropped the subscript «A» on the mobility M_A and the local coarse-grained concentration ϕ_A, and assume incompressibility ($\phi_A + \phi_B = 1$), a condition which forces $M_A = M_B$. When quenched to a temperature T less than the spinodal temperature, the binary mixture described by eq. (4) will *simultaneously* undergo demixing via spinodal decomposition and mixing via the reaction $A \rightleftharpoons B$.

For small-molecule systems, where the surface tension and mobility can be assumed to be independent of the local volume fraction, eq. (4) can be written as

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

where f is the homogeneous part of the free energy and $\kappa \nabla^2 \phi$ arises from the square gradient expansion. We linearize eq. (5) about the initial average concentration before the quench, ϕ_0, and replace ϕ by $\phi_0 + \delta\phi$, where $\delta\phi$ is a small perturbation about ϕ_0 [3]. Fourier transforming to $\boldsymbol{k}$-space, we find that the concentration fluctuations $\delta\tilde\phi(\boldsymbol{k}, t)$ grow or decay exponentially,

$$(6) \qquad \delta\tilde\phi(\boldsymbol{k}, t) = \delta\tilde\phi(\boldsymbol{k}, 0) \exp[\omega(k) t],$$

depending on the growth rate $\omega(k)$, which for $\phi_0 = 1/2$ and $\Gamma_1 = \Gamma_2 \equiv \Gamma$ is

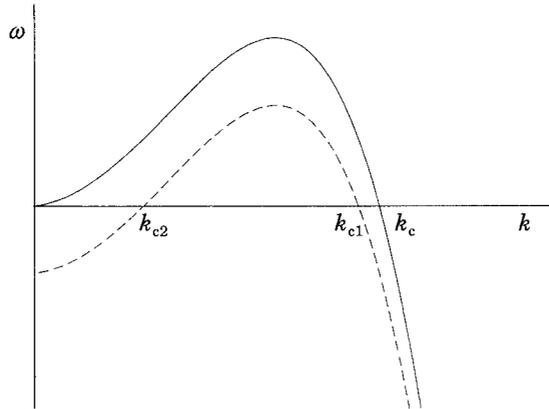$$(7) \qquad \omega(k) = \kappa M k^2 (k_c^2 - k^2) - 2\Gamma ,$$

Fig. 1. – Growth factor $\omega(k)$ vs wave vector k both with (dashed 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 cut-offs both at large k and small k, so that growth occurs only for intermediate-wavelength fluctuations.

where $k_c \equiv (|\partial^2 f/\partial \phi^2|_{\phi_0}/\kappa)^{1/2}$. Concentration fluctuations for which $\omega(k) < 0$ decay, while those for which $\omega(k) > 0$ grow. Figure 1 shows the growth factor $\omega(k)$ for spinodal decomposition both with (dashed line) and without (solid line) chemistry. Without chemistry ($\Gamma = 0$), the growth factor is the usual one predicted from Cahn's linear theory, with a cut-off at large wave vector k_c (small wavelength). 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 Γ_1 and Γ_2. This shifts the small wavelength cut-off to larger wavelengths, and *introduces a large wavelength cut-off*. Consequently, concentration fluctuations at large wavelengths (small k) are suppressed by the chemical reaction. *Such suppression of long-wavelength fluctuations is a natural mechanism for pattern selection in a variety of systems, and is predicted also for the more general chemical reaction described in eq. (1)*[1, 7].

Our analysis shows that the initial instability to long-wavelength concentration fluctuations normally observed during spinodal decomposition is suppressed by chemical reactions, so that only fluctuations at an intermediate length scale grow at early times. To explore the later stages of phase separation, we numerically integrated the nonlinear equation (4) on two-dimensional lattices of size 256^2 and larger for various choices of equal forward and backward reaction rates Γ_1 and Γ_2, with

$$(8) \qquad f(\phi) = \phi \ln \phi + (1 - \phi) \ln (1 - \phi) + \chi \phi (1 - \phi),$$

where the interaction parameter χ is given by a combination of the intermolecular interaction energies, and $\kappa = \chi a^2$ as for an incompressible, small molecule mixture (a is the interaction distance between molecules). When $\Gamma_1 = \Gamma_2 = 0$, the system phase separates in the usual way[3]. However, when the reactions are present, the domain growth is dramatically different, exhibiting a labyrinthine pattern as shown in fig. 2 and saturating at a steady-state domain width. In fact, we find that for small Γ the
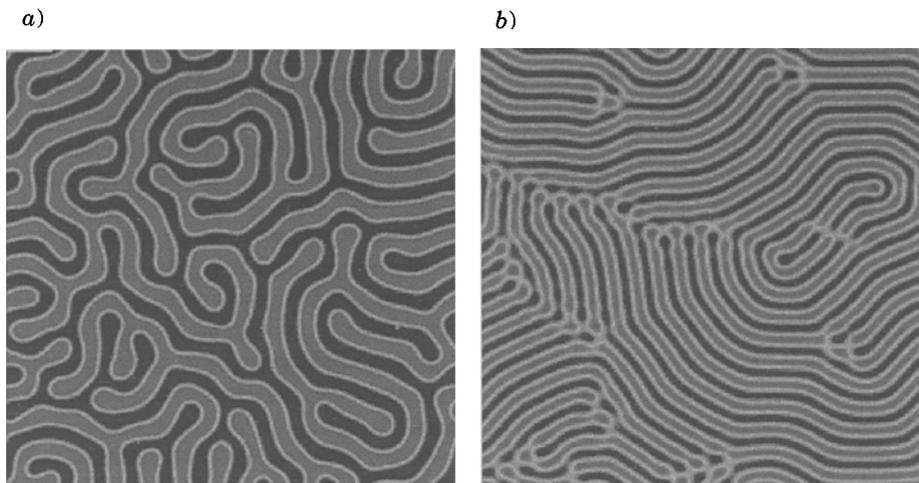
a) b)

Fig. 2. – Concentration field for 256^2 lattice at a time $\tau = 2048$ following a quench of eq. (5) to the unstable region ($\chi = 4$), 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.

average domain size $R(t)$ can be written in the following scaling form:

$$(9) \qquad\qquad R(t) = t^\alpha G(\Gamma t),$$

where $\alpha = 0.32 \pm 0.02$ [3,8], and the scaling function $G(x) = \text{const}$, $x \ll \infty$, and $G(x) = x^{-\alpha}$, $x \to \infty$. Thus, the simultaneous presence of the chemical reaction $A \rightleftharpoons B$ does indeed appear to select intermediate length scales for growth, and suppress concentration fluctuations at large wavelengths. The evolution of the pattern seems to follow a universal behavior, similar to the kinetics of systems in the absence of reactions.

A recent study [9] of the Ising/lattice-gas analogue of the reactive Cahn-Hilliard equation for the reaction $A \rightleftharpoons B$, eq. (5), with $f(\phi)$ given in eq. (8), for equal forward and backward reaction rates, showed that the effect of randomly converting spins (molecules) to the opposite species in addition to the usual Kawasaki exchange of nearest-neighbor spins (molecules) also results in steady-state lamellar patterns whose width decreases with increasing reaction rate. Moreover, the authors found a scaling relation for the domain size similar to that described here.

Interestingly, our simplest model describing the effect of chemical reactions on spinodal decomposition in a binary mixture, eq. (5), is identical in form to an empirical model of microphase separation in block copolymer melts [10] and other systems [11] where short-range attractive and long-range repulsive interactions compete. In those systems, which include magnetic films, ceramic compounds, dipolar fluids and amphiphilic monolayers, a balance between the two competing interactions produces steady-state patterns similar to those described here. The modified time-dependent Ginzburg-Landau (TDGL) equation for those systems was recently solved analytically in the limit of infinite-component order parameter, providing exact expressions for the time dependence of the structure factor $S(\boldsymbol{k}, t)$ and the peak position $k_m(t)$ [12]. It was found that for values of Γ less than a cut-off value Γ_c, the structure factor asymptotically approaches a delta function peaked

around a constant inverse domain size k_{eq} which depends on the mobility M, the interfacial square gradient coefficient κ, and Γ as $k_{eq} \propto (\Gamma/\kappa M)^{\alpha}$, where $\alpha = 1/4$, just as for the exponent characterizing domain growth in the unmodified, large-N TDGL model[13]. For $\Gamma \geq \Gamma_c$ the peak position of $S(k, t)$ approaches an asymptotic value $k_{\infty} = (-r/2\kappa)^{1/2}$ (where r is the coefficient of the quadratic term in the Landau expansion of the bulk free energy of mixing), while the amplitude of $S(k, t)$ goes to zero. The behavior predicted by the solution of the model in the limit of an infinite-component order parameter was found to be consistent in many respects with behavior observed in numerical simulations of the *scalar* model.

We have presented a general approach to studying the effect of chemical reactions on thermodynamically unstable materials. Application of the approach developed here to polymer blends or more complicated chemical reactions is straightforward, and promises to be of significant technological importance. Chemical reactions offer a tremendous opportunity to control the final morphology of phase-separated materials, particularly in polymer materials where a variety of chemical reactions could be induced through attachment of reactive groups along the backbone of the chains. In particular, the chemical reaction of reversible or irreversible crosslinking between either like or unlike species can be modeled with this approach. The results of this work will be published elsewhere.

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