Monte Carlo Simulations of Phase Separation in Chemically Reactive Binary Mixtures

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We present Monte Carlo simulations of a binary mixture simultaneously undergoing spinodal decomposition and the chemical reaction $A \rightleftharpoons B$. The competing processes give rise to novel, steady-state pattern formation with domain size scaling with reaction rate to a power, s, which equals the domain growth exponent, α, in the absence of chemical reactions. Our findings support recent numerical simulations of a Cahn-Hilliard-type model, suggesting that chemical reactions can be used to stabilize and tune patterns arising during phase separation.

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Simple chemical reactions have recently been suggested to dramatically affect domain growth during spinodal decomposition in binary mixtures [1]. In ordinary spinodal decomposition [2], a binary mixture of two species of molecules A and B will become unstable with respect to long-wavelength fluctuations in concentration when the mixture is quenched to temperatures below the critical temperature. The system subsequently phase separates into two coexisting, homogeneous phases—an A-rich phase and a B-rich phase—which have an interconnected morphology that coarsens with time. This process ultimately leads to macroscopic phase separation. The presence of chemical reactions alters this conventional picture. A chemical reaction such as

$$A \rightleftharpoons B \tag{1}$$

tends to spatially mix the two species, and when this reaction occurs simultaneously with spinodal decomposition, the phase separation process evolves into a steady-state pattern in which the demixing thermodynamic and mixing reactive processes balance. Understanding how these two competing processes give rise to pattern selection may have significant industrial importance in controlling the morphology of phase-separating materials [1].

The theoretical understanding of spinodal decomposition in binary mixtures is based mainly on the Cahn-Hilliard theory [2–4], which is readily modified to include reactions [1,5]:

$$\frac{\partial \phi}{\partial t} = \Lambda \nabla^2 \frac{\delta F\{\phi\}}{\delta \phi} - \Gamma_1 \phi + \Gamma_2 (1 - \phi). \tag{2}$$

Here ϕ is the local coarse-grained concentration of species A, Λ is the mobility of species A, Γ_1 and Γ_2 are the forward and backward reaction rates, respectively, and $F\{\phi\}$ is the Ginzburg-Landau-Wilson free energy functional, taken as the sum of the bulk free energy and the usual square-gradient approximation to the interfacial free energy [3]. A linear analysis of Eq. (2) in the absence of chemical reactions predicts the usual exponential growth of concentration fluctuations with a growth factor that has a cutoff at large wave vector k (small wavelength) [2,3]. However, it was recently shown [1] that the

simultaneous occurrence of the reaction $A \rightleftharpoons B$ decreases the growth factor. This shifts the small-wavelength cutoff to longer wavelengths, and introduces a long-wavelength cutoff. Thus, the initial instability to long-wavelength concentration fluctuations is suppressed by the chemistry, and only fluctuations at intermediate length scales grow. Numerical simulations of Eq. (2) show that the domain growth following a critical quench to the unstable region is indeed restricted, even at late times where nonlinear effects are important. The domains grow into a labyrinthine pattern of intermediate size that depends on the reaction rate [1]. In particular, for equal forward and backward reaction rates ($\Gamma_1 = \Gamma_2 \equiv \Gamma$), the steady-state domain size R_{eq} was found to be asymptotically proportional to a power of Γ:

$$R_{eq} \sim (1/\Gamma)^s, \tag{3}$$

where $s = 1/3$, the growth exponent for this universality class in the absence of chemical reaction [4].

Here we present lattice Monte Carlo (MC) simulations of a binary mixture with simultaneous Kawasaki exchange interactions and chemical "reactions." In the absence of reactions, this model is isomorphic to the spin-exchange kinetic Ising model, and was shown to be in the same universality class as Eq. (2) without the reaction terms in the late stages of spinodal decomposition [3,4]. We modify the usual Kawasaki model to include reactions $A \rightleftharpoons B$ with equal forward and backward reaction rates by randomly converting molecules (flipping spins) with probability p_r in addition to exchanging nearest-neighbor molecules (spins). Our goal is to determine whether this modified Kawasaki Ising model exhibits the same restricted domain growth as the modified Cahn-Hilliard equation, Eq. (2), when quenched to the unstable region at the critical concentration.

We have performed MC simulations on two-dimensional square lattices of size 316^2 to 3500^2, and three-dimensional simple cubic lattices of size 79^3 to 200^3. At time $t = 0$, each lattice is initialized at a temperature $T = \infty$ with a molecule randomly chosen to be A or B on every lattice site, such that each lattice
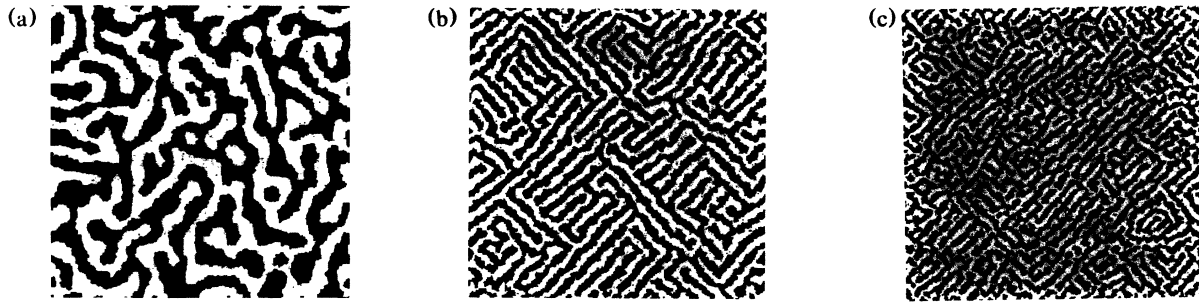
FIG. 1. Examples of 316×316 lattice configurations at $t = 3 \times 10^5$ MCS following a quench to $T \ll T_c$ for reaction probability $p_r =$ (a) 0, (b) 0.0001, and (c) 0.0005. Molecules of type A (B) are shown as black (white).

contains an equivalent number of A's and B's. Nearest-neighbor molecules interact with energy $-J$ ($+J$) if the molecules are of the same (different) species.

The temperature of the system is then quenched to $T = 0.5J/k_B$ and $T = 1.0J/k_B$ in two and three dimensions, respectively—well below the critical temperature T_c in the absence of chemical reactions [6]. The usual Kawasaki exchange dynamics are used to exchange nearest-neighbor molecules with the acceptance probability [7]

$$p_{\text{exch}} = \frac{e^{-\Delta E/k_B T}}{1 + e^{-\Delta E/k_B T}}, \qquad (4)$$

where $\Delta E \equiv E_{\text{final}} - E_{\text{initial}}$, the difference between the energy of the system before and after the exchange. In addition, a molecule can convert from A to B or vice versa with a temperature-independent probability p_r. This models a chemical reaction of the type $A \rightleftharpoons B$ with equal forward and backward reaction rate. Thus at each MC time step, both an attempted exchange of nearest-neighbor molecules and an attempted "reaction" is made at every lattice site. At $T < T_c$, the exchange of molecules will cause phase separation between the two species, while the temperature-independent reaction of molecules will tend to spatially randomize the system.

Figure 1 shows a two-dimensional 316^2 lattice at a time $t = 3 \times 10^5$ MCS per spin (where MCS is a Monte Carlo step) following the quench for three different chemical reaction probabilities $p_r = 0$, 0.0001, and 0.0005. The system with $p_r = 0$ shown in (a) exhibits the usual transient, interconnected morphology observed in binary mixtures undergoing spinodal decomposition in the absence of chemical reactions, and clearly contains larger and coarser domains than the systems with nonzero p_r shown in Figs. 1(b) and 1(c). We find that even a small reaction probability such as that used to generate the system in Fig. 1(b) causes the domain growth to be severely restricted. Figures 1(b) and 1(c) show that the A-rich and B-rich domains form diagonal, labyrinthine patterns, with the domain thickness decreasing with increasing reaction probability [8]. In fact, we find that the steady-state domain thickness is already established after

a time $t \ll 3 \times 10^5$ MCS. As the systems evolve further in time, significant changes in domain size are seen only in the system without chemical reactions.

In the usual "nonreactive" Ising model, it is known that the difference between the total energy of all nearest-neighbor pairs of molecules at any time t and at $t = \infty$ at the quench temperature depends on t as $|E(t) - E_\infty| \sim t^{-\alpha}$, where α is the same exponent that describes the time dependence of the average domain size [9]. Thus the energy difference is a measure of inverse domain size, since $R \sim t^\alpha$. For $p_r = 0$, we find an "effective" exponent $\alpha = 0.22 \pm 0.03$, consistent with previous MC studies [10,11]. Note that for longer simulation times, we expect α to asymptotically approach $1/3$ for the spin-exchange kinetic Ising model universality class.

However, for nonzero p_r we find that the magnitude of the energy saturates to a value $|E_{\text{eq}}|$ far below the equilibrium energy $|E_\infty|$ associated with that temperature in the absence of reactions. The energy difference $|E_{\text{eq}} - E_\infty|$ is plotted double-logarithmically versus p_r for the two-dimensional systems in Fig. 2. We find that the data are consistent with power-law behavior

$$|E_{\text{eq}} - E_\infty| \sim p_r^s, \qquad (5)$$

for small values of p_r, with $s = 0.22 \pm 0.02$. In terms of domain size [12], we find therefore that

$$R_{\text{eq}} \sim (1/p_r)^s. \qquad (6)$$

Note that scaling is only expected as p_r, and thus $|E_{\text{eq}} - E_\infty|$, becomes small. From Eq. (5) we expect our data to satisfy the following scaling relation:

$$|E(t) - E_\infty| = p_r^\alpha f(t p_r), \qquad (7)$$

where $f(x) = x^{-\alpha}$ for $x \ll \infty$ and $f(x) = \text{const}$ for $x \to \infty$. Figure 3 shows that this relation holds for $s = \alpha = 0.22$. For smaller values of p_r, which would allow the system to reach the $1/3$ scaling regime *before* saturation of the domain size, we expect to find $s = \alpha = 1/3$.

Our simulations thus support the contention that $s = \alpha$, a relation that was recently found by numerical simulations of Eq. (2) [1]. Since p_r has the units of inverse time, and the domain size in the absence of reaction scales as $R \sim t^\alpha$, the scaling in Eq. (6) with $s = \alpha$ seems rather
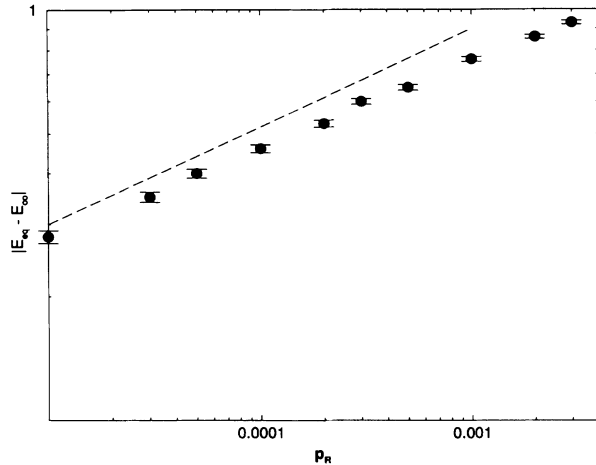
FIG. 2. Double-logarithmic plot of extrapolated energy difference $|E_{eq} - E_\infty|$ vs reaction probability p_r, calculated in $d = 2$. The dashed line has slope $1/4$.

natural. Thus the simultaneous presence of the chemical reaction $A \rightleftharpoons B$ during spinodal decomposition does indeed select intermediate length scales for growth and suppress concentration fluctuations at large length scales in this MC Ising model. The evolution of the pattern seems to follow a universal behavior, similar to the kinetics of systems in the absence of reactions.

In other systems where labyrinthine or lamellar morphologies are observed, typically one can identify a long-range repulsive force between like species that competes with a shorter-range, attractive interaction. In these systems, a balance between the two interactions produces stable, periodic structures. Magnetic films [13], ceramic compounds [14], dipolar fluids [15], amphiphilic monolayers [16], type I superconductors, and, in particular, block copolymers [17], all exhibit patterns similar to those observed here and in Ref. [1]. In fact, a phenomenological model of block copolymers [17] extends the usual time-dependent Ginzburg-Landau equation to include a long-range interaction term that describes the effect of the finite block length on phase separation. The reactive Cahn-Hilliard equation of Ref. [1] has been written [18] in precisely the same form as the time-dependent Ginzburg-Landau equation for the block copolymer model of Ref. [17]; the "block-length" parameter in the latter model plays the same role as the reaction rate. Thus the model of Ref. [17] for block copolymers, the model of Ref. [1] for a chemically reactive mixture, and presumably the model studied here are in the same universality class. It is interesting to note that the additional term in the block copolymer equation that describes the restriction of the finite block length on phase separation arises from an additional long-range force term in the free energy functional. Consequently, the effect of chemical reactions on a phase-separating binary mixture is similar to the effect of a long-range re-
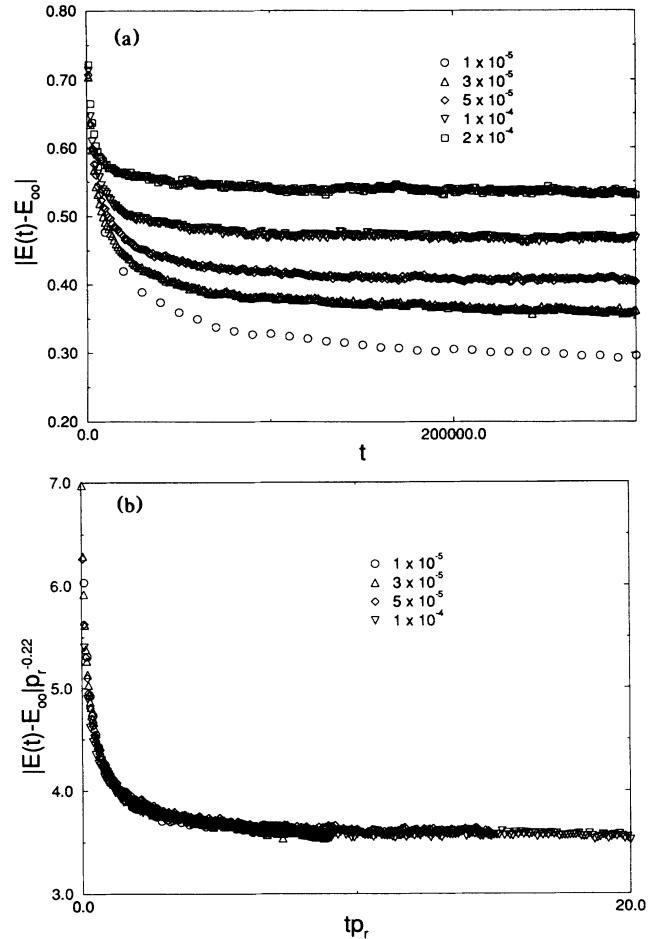

FIG. 3. (a) Energy difference $|E(t) - E_\infty|$ vs t for various reaction probabilities p_r, and (b) the data in (a) with the y axis divided by $p_r^{0.22}$ and the x axis multiplied by p_r, to confirm the scaling relation.

pulsive interaction between like species. Both compete with the thermodynamic unmixing process by tending to mix the system, and both give rise to novel, steady-state behavior where the characteristic domain size scales as a power law with the parameter describing the "strength" of the competing process.

One might also ask whether the reactions can be viewed as infinite-distance, temperature-independent exchanges since, on average, for every A that becomes a B, there is a B that becomes an A. To this end we repeated the simulations described above with random exchanges of any two molecules in the system [19], rather than random reactions, accompanying the local temperature-dependent Kawasaki dynamics. We found no discernable differences between these simulations and those described earlier [Figs. 1(b) and 1(c)].

We further note that when chemical reactions are included in the nonconserved spin-flip model with Glauber transition probabilities [7], no labyrinthine domain growth is observed. Instead, preliminary simula-

tions suggest that the effect of the reaction on a critical quench is similar to a shift in temperature. This is consistent with a linear analysis of the equivalent nonconserved coarse-grained model, namely Eq. (2) with $\Lambda \Delta^2$ replaced by $-\Lambda$. In this model, the chemical reaction $A \rightleftharpoons B$ decreases the early-time growth factor, but does not introduce a long-wavelength cutoff. In fact, the relevant equation can be rewritten by absorbing the chemistry terms into the free energy functional [18]. This results in a simple shifting of the linear and quadratic terms in the bulk free energy, again suggesting a mere temperature shift, with no novel pattern formation.

A related model which has attracted some attention [20] is that in which spins in an Ising model are flipped according to the Glauber finite temperature spin-flip transition probabilities, and locally exchanged with a temperature-independent probability—precisely the opposite of the model considered here. In that model, the second-order transition becomes a first-order transition as the rate of spin-exchange is increased beyond a critical value. It is even possible for that model to undergo a second-order phase transition in one dimension if the spin-exchange rate dominates the spin-flip rate. This one-dimensional behavior is not observed in the model considered here (with up to 8 million sites).

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[8] Diagonal orientation of the labyrinthine domains was also confirmed, even for large p_r, by calculation of appropriate correlation functions. This diagonality is due to the lattice type. A "reaction" of a molecule on the surface of a domain will not change the energy of the configuration if that molecule has equal number of like and unlike nearest neighbors. This is true independent of lattice type. However, on the square lattice, this is most efficiently accomplished if the domain is oriented at 45°; that is, this particular choice of angle minimizes the effect of a reaction by allowing for a sufficient number of molecules to have equal numbers of like and unlike neighbors, with a larger number of surface molecules required for a higher reaction rate. The width and stability of the diagonal, striplike domains is thus dependent on continued reactions. This diagonal orientation also allows for efficient restructuring of the domains through diffusion of the molecules.

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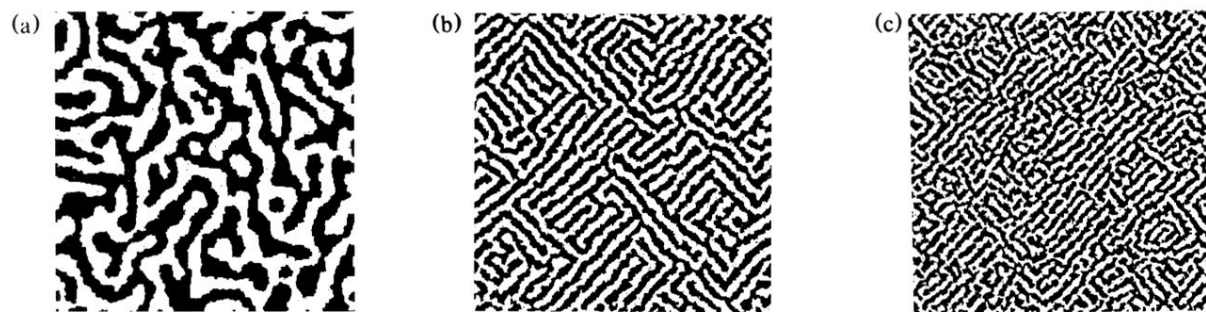
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