

## Kinetics of Phase Separation in the Presence of Two Disparate Energy Scales

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We develop a dynamical model for phase separation in a system with two disparate energy scales. Monte Carlo computer simulations of this model reveal a "pinning" of the structure factor during spinodal decomposition that obeys new scaling relations. We propose a mechanism for the pinning which allows us to predict exact values for the pinning exponents. Finally, we discuss our model in light of recent experiments.

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Considerable recent interest has focused on spinodal decomposition in a wide variety of physical systems. Theoretical efforts thus far have mainly concentrated on understanding the behavior of models such as the Ising lattice gas model [1], time-dependent Ginzburg-Landau models [2], and, most recently, cell dynamical models [3]. These models have proven successful in elucidating the basic spinodal decomposition process and have paved the way for applications of these types of models to systems with more complex interactions. Many experiments have recently focused on systems where such interactions give rise to phenomena that significantly alter the kinetics of phase separation from the usual kinetics of spinodal decomposition [4,5]. One example of a system that illustrates this principle is a solution of polymer chains that are simultaneously cross-linking and phase separating in poor solvent [5]. In the absence of cross-linking, the spinodal decomposition process is well understood, but phase separation in the presence of cross-linking gives rise to novel behavior. Here we develop a model for phase separation in systems with two different interaction energies, and show that a large difference between these energies leads to a "pinning" of the time-dependent structure factor and simple scaling properties.

The model contains monomers and solvent molecules on a lattice, with the key feature that nearest-neighbor monomers can interact with two different energies [6]. We assume that there are  $\Omega$  "weak" bonding configurations between monomers with interaction energy  $-J$ , and one "strong" bonding configuration with interaction energy  $-E$ . At any given time, each nearest-neighbor monomer-monomer pair must independently be in one of these  $\Omega+1$  possible bonding configurations.

During the course of the simulation, each bond is updated according to the standard Metropolis Monte Carlo (MC) scheme [7], by randomly choosing one of the  $\Omega+1$  configurations and calculating the Boltzmann factor  $\exp(-\Delta\epsilon/k_B T)$ , where  $\Delta\epsilon$  is the difference between the final bonding energy and the initial bonding energy of the pair. One MC step (MCS) includes an update of all monomer-monomer pair interactions, as well as an

attempted exchange of every nearest-neighbor monomer and solvent pair via Kawasaki dynamics [7,8].

In the infinite time limit, this model recovers the equilibrium properties of a model originally introduced to describe weak gels [9], and in the limit  $\Omega \rightarrow \infty$ , where no strong bonds ever form, recovers the kinetic properties of an Ising lattice gas [1,10]. All of the simulations were performed on a two-dimensional square lattice with 50% of the sites occupied by monomers; this is the critical concentration for this model.

The fraction of strong bonds present in the system in equilibrium at a temperature  $T$  is

$$n_b^{\text{eq}}(T) = \frac{e^{E/k_B T}}{e^{E/k_B T} + \Omega e^{J/k_B T}}. \quad (1)$$

We are interested in the regime  $E \gg J$  and  $E \gg k_B T$ , where, for the duration of the simulation, a strong bond rarely breaks. In this limit, the transition probability to go from one of the  $J$  bonding configurations to the  $E$  bonding configuration can be approximated by  $1/\Omega$ , and the probability to go from the  $E$  configuration to one of the  $J$  configurations by zero. Thus, on the time scale of our simulations, we are essentially placing bonds of infinite strength between monomers at a rate  $1/\Omega$ . At  $T = \infty$ ,  $n_b^{\text{eq}} = 1/(1 + \Omega) \simeq 0$  for large  $\Omega$ . Thus, following a quench from  $T = \infty$  to  $T = T_Q$ , we expect (and verify numerically) that the fraction of strong bonds increases with time as

$$n_b(t) \simeq n_b^{\text{eq}}(T_Q)(1 - e^{-t/\Omega}). \quad (2)$$

One probe in phase separation experiments is the dynamic structure factor,  $S(k, t)$ , which contains information on the time evolution of the various length scales  $k^{-1}$ . In ordinary spinodal decomposition, the characteristic wave vector moves to smaller values of  $k$  following a quench to the unstable region. One measure of this characteristic wave vector is the first moment of  $S(k)$ ,  $k_1 \equiv \sum_k k S(k) / \sum_k S(k)$  [10].

We performed quenches from  $T = \infty$  to a temperature  $T_Q = 0.88T_c^{\text{LG}}$ , where  $k_B T_c^{\text{LG}} = 0.567J$  is the critical

temperature for an Ising lattice gas with  $J$  interactions only. Figure 1(a) shows, for  $J = 1$ ,  $E = 10$  and different values of  $\Omega$ , the time dependence of  $k_1$ . Note from Eq. (1) that  $n_b^{\text{eq}}(T_Q) \approx 1$  for all finite values of  $\Omega$  considered.

For the  $\Omega = \infty$  case, which describes the Ising lattice gas since no strong bonds ever form, spinodal decomposition proceeds in the usual manner, and we find that for large  $t$ ,  $k_1 \sim t^{-\alpha}$  with  $\alpha = 0.25$  [1,11]. However, when  $\Omega$  is finite, in the limit  $E \gg J$  where strong bonds rarely break, we find that the phase separation process separates into two distinct time regimes and

$$k_1 \sim \begin{cases} t^{-\alpha}, & t \ll t_x, \\ \text{const}, & t \gg t_x, \end{cases} \quad (3)$$

where  $t_x$  is the crossover time that separates these two regimes [12]. For  $t \ll t_x$  phase separation is indistinguishable from phase separation in the Ising lattice gas,

since very few strong bonds are present in the system. For  $t \gg t_x$ , Fig. 1(b) shows that for large  $\Omega$ , the "frozen" wave vector behaves as

$$k_F \sim \Omega^{-\phi}, \quad (4)$$

with  $\phi = 0.17 \pm 0.01$ . Note that we expect to find scaling of  $k_F$  with  $\Omega$  only when  $\Omega$  is large enough that phase separation has reached the scaling regime before pinning occurs.

Figure 1(c) shows that for large  $\Omega$

$$t_x \sim \Omega^\psi, \quad (5)$$

with  $\psi = 0.70 \pm 0.03$ .

Our results are consistent with the scaling form

$$k_1 \sim t^{-\alpha} f(t/\Omega^\psi), \quad (6)$$

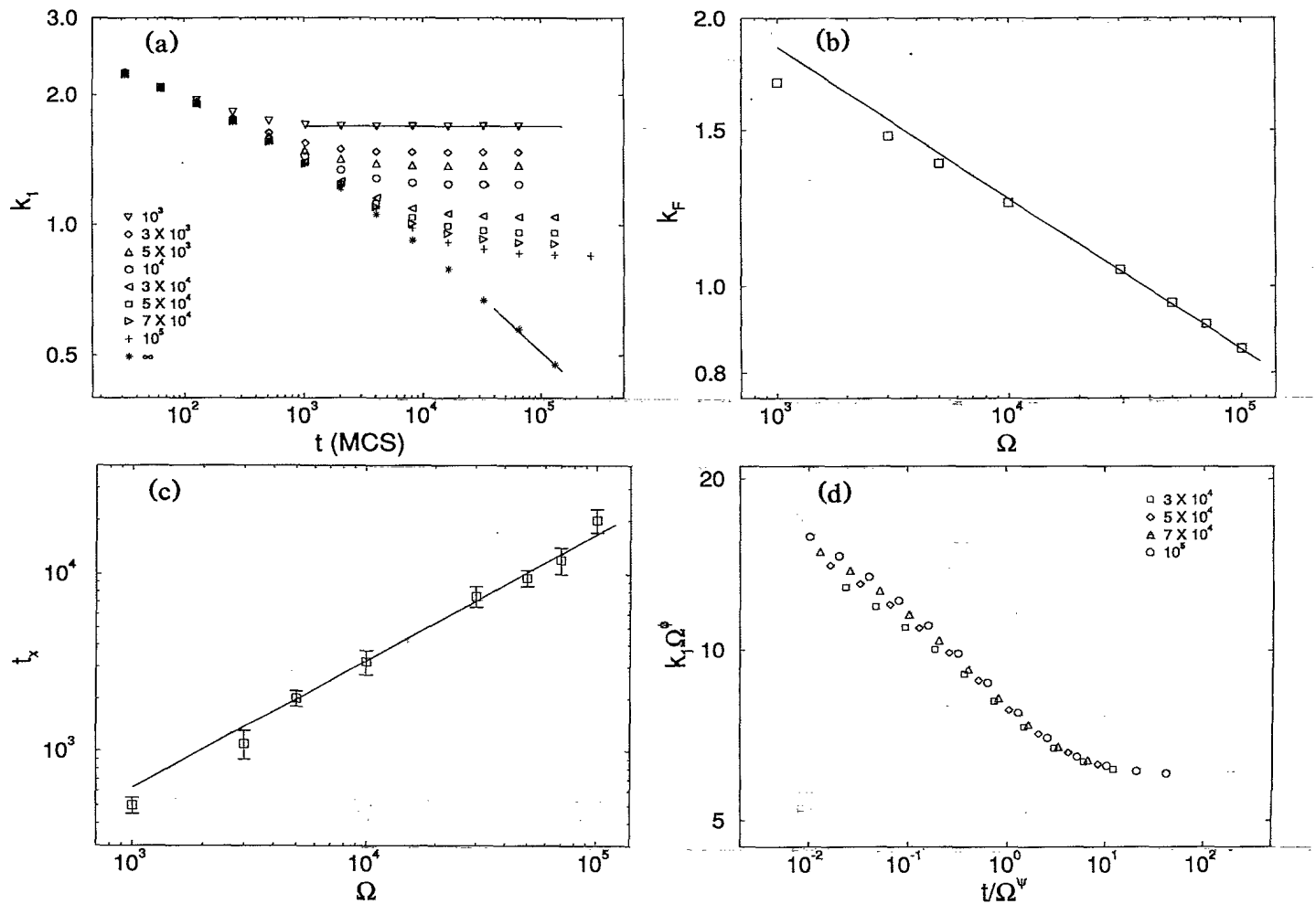


FIG. 1. (a) Double logarithmic plot of the first moment  $k_1$  of  $S(k)$  against time for various values of  $\Omega$ , following a critical quench to  $T = 0.88T_c^{\text{LG}}$ . The line through the  $\Omega = \infty$  data has slope 1/4. Each set of data is an average obtained from independent MC simulations of five  $256 \times 256$  lattices, spherically averaged. (b) Double logarithmic plot of  $k_F$  vs  $\Omega$  [obtained from (a)]. The line has slope 0.17. (c) Double logarithmic plot of  $t_x$  vs  $\Omega$  [obtained from (a)]. The line has slope 0.70. (d) Scaling plot of the data in (a), where  $k_1$  is scaled by  $\Omega^{-\phi}$ , with  $\phi = 0.17$ , and time  $t$  is scaled by  $\Omega^\psi$ , with  $\psi = 0.70$ .

with

$$f(x) = \begin{cases} \text{const}, & t \ll t_x, \\ x^\alpha, & t \gg t_x. \end{cases} \quad (7)$$

Note that this scaling form implies

$$\phi = \psi\alpha. \quad (8)$$

Equation (6) also predicts that  $k_1 \sim \Omega^{-\phi} g(t/\Omega t^\psi)$ , so that the data of Fig. 1(a) should collapse if  $k_1$  is scaled by  $\Omega^{-\phi}$ , and  $t$  is scaled by  $\Omega t^\psi$ . Figure 1(d) shows that all of the data with  $\Omega > 10^4$  indeed collapse onto a single universal curve.

To understand the mechanism governing the pinning as well as to predict the pinning exponents  $\phi$  and  $\psi$ , we propose that the pinning of a typical growing domain of weakly bonded monomers will occur when the radius  $\xi(t)$  of the domain becomes of the order of the average spacing between the strong bonds. If the bonds are randomly distributed, the average spacing between them is of order  $[n_b(t)]^{-1/d}$ . Thus at the crossover time,

$$[n_b(t_x)]^{-1/d} \sim \xi(t_x), \quad (9)$$

where  $n_b(t_x)$  is the fraction of bonds in the system at  $t_x$ ,  $\xi(t_x)$  is the characteristic domain size at the crossover time, and  $d$  is the system dimension. Since  $\xi \sim k_1^{-1} \sim t^\alpha$ , Eq. (9) implies that  $n_b(t_x) \sim t_x^{-\alpha d}$ . For large  $\Omega$ , Eq. (2) implies that  $n_b(t_x) \sim t_x/\Omega$ . Hence  $t_x \sim \Omega^\psi$ , with

$$\psi = \frac{1}{1 + \alpha d}. \quad (10)$$

For  $\alpha = 1/4$  and  $d = 2$ , Eq. (10) predicts

$$\psi = 2/3, \quad (11)$$

which agrees with the value  $\psi = 0.70 \pm 0.03$  found in our simulations. Moreover, with  $\psi = 2/3$  and  $\alpha = 1/4$ , Eq. (8) predicts

$$\phi = 1/6, \quad (12)$$

which compares well with the simulation value  $\phi = 0.17 \pm 0.01$ .

The proposed mechanism is reminiscent of behavior observed in systems with quenched disorder, where the presence of quenched impurities affects the phase separation of the system [13]. The strongly bonded monomers in our case act as quenched impurities since pairs of monomers are not moved by Kawasaki dynamics [7]. We propose that this idea can be used to explain pinning phenomena recently observed in polymer gels. In one experiment [5], phase separation and gelation occur simultaneously due to the different interaction energies present in the system—one associated with the interaction driving the phase separation of the polymer chains from the solvent (van der Waals interactions) and a sec-

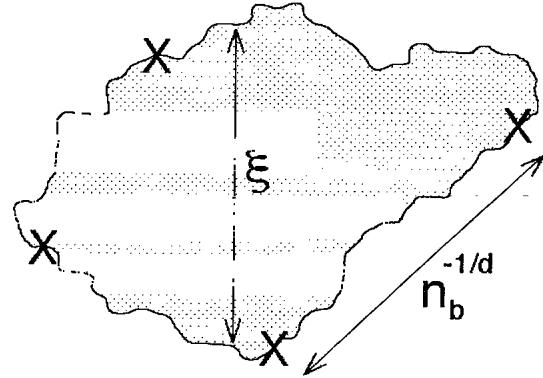


FIG. 2. Schematic representing the pinning criterion of Eq. (9); the crosses represent strongly bonded monomers. The onset of pinning occurs at the crossover time  $t = t_x$  when the average spacing between these monomers,  $n_b^{-1/d}$  (which is decreasing with time), becomes comparable to the average domain size,  $\xi(t)$  (which is increasing with time).

ond, stronger, energy associated with the interactions controlling the cross-linking (e.g., hydrogen bonding) between chains. This competition produces a pinning of the phase-separating mixture because the formation of cross-links between polymer chains arrests the phase separation of the chains from the solvent. In this experiment, the gelation time at which a cross-linked network appears precedes the crossover time at which the pinning occurs. We suggest, therefore, that since the cross-linked polymer chains belong to an infinite network, the cross-links are immobile and act as quenched impurities with respect to the chains. Additional phase separation beyond the gel time should be limited by the mesh size of the gel which in our model is the average spacing between "quenched" or strongly bonded monomers (Fig. 2). These monomers play the role of cross-links which in a gel are part of the infinite network.

In conclusion, we have developed a dynamical model of a system with two energy scales, and found that when one energy is sufficiently strong, a pinning of the structure factor occurs during spinodal decomposition. This pinning obeys new scaling relations and we have developed theoretical arguments that explain the nature of this scaling. In subsequent work, we will explore the generality of this model by applying it to a variety of physical systems.

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