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Dynamic approach to phase separation of a mixture of monomers and polymers

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We use a dynamic mean-field approximation to study the spinodal decomposition of a mixture of monomers and polymers. The system is modeled on a two-dimensional square lattice. A local mean-field concentration of polymers is employed in local dynamics in which possible switching of monomer and polymer on next-nearest-neighboring sites takes place according to the standard Monte Carlo updating rule. A dynamic equation for the local density is obtained, and spinodal curves are produced analytically for various degrees of polymerization by analyzing the stability of the uniform solution of the equation. We also determine the most unstable mode with respect to the uniform solution.

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I. INTRODUCTION

Phase separation in binary mixtures of small molecules and polymers is an interesting thermodynamic phenomenon involving a loss of stability of the mixed state [1,2]. Flory-Huggins mean-field theory [3,4], which is based on a combinatorial evaluation of the entropy of mixtures, has been successful in describing properties such as the coexistence curve (characteristic of equilibrium behavior) and spinodal decomposition (which relates to local and nonequilibrium behavior). In questions concerned with dynamic aspects of the approach to equilibrium, Cahn-Hilliard theory [5,6] has led to successful predictions about the initial pattern selection in the spinodal regime. These studies are all based on the thermal properties of the simplest possible mean-field approximation to the free energy of the system.

The general problem of phase separation is made more difficult by the fact that the dynamics used to study such behavior requires conservation of the order parameter. This order-parameter-conserved dynamics (an example being that introduced by Kawasaki [7]) is much more difficult to handle than that of a nonconserved one (for example, Glauber dynamics [8]). This is particularly true for spinodal decomposition, which is a concept whose very definition rests on the approximation scheme in which the local concentration is a well-defined quantity. As a consequence, even for a binary mixture, only a few exact results are available to describe spinodal decomposition in specific models, and most of these are restricted to zero temperature in one dimension [9,10] or on a Bethe lattice [11]. There are, however, a number of approximate results from a dynamical approach to phase separation [12,13]. In Ref. [12], Gobron introduced a pseudo-one-dimensional lattice gas model and applied an approximate master equation for the configurational distribution function to study dynamically the properties of spinodal decomposition of a binary mixture. His approach is not readily generalizable to the case of a mixture containing polymers, and has the apparent failing of yielding a spurious phase separation in one dimension.

In this paper, we introduce a more realistic two-dimensional lattice model to describe a mixture of monomers and polymers. We then use a dynamic mean-field approximation, which generalizes an approximation employed in the study of random Ising spin systems [14], to study both the spinodal decomposition and the initial pattern selection of the system by identifying the mode that is most unstable with respect to the uniform phase. The degree of polymerization, N, of the polymer in the mixture enters the formalism in a natural way. The paper is organized as follows: In Sec. II the model and a local switching dynamics are introduced. In Sec. III the dynamic mean-field approximation is employed to derive the dynamic equation for the local density of polymer. The stability is then analyzed and the spinodal curves produced in Sec. IV, and some conclusions are presented in Sec. V.

II. THE MODEL AND THE LOCAL SWITCHING DYNAMICS

We consider a mixture of monomers of type A and chain polymers of degree of polymerization N (≥ 2) composed of monomers of type B. The molar fraction of B monomers is assumed to be p. To study the spinodal decomposition of the mixture analytically, we introduce a lattice model, and for reasons of simplicity consider only a two-dimensional square lattice. Each site of the square lattice is occupied by one and only one unit of either type A or type B. A polymer chain is then represented by a sequence of monomers B, which are consecutively connected as nearest neighbors. A configuration of a polymer of degree eight on a square lattice is shown in Fig. 1(a). For each nearest-neighbor contact between A and B there is an energy cost of ϵ. A state of the mixture is then represented by the corresponding configuration of the lattice site occupancy by A and B. This is the lattice model of the mixture.

Next we introduce the dynamics that determines the time evolution of the system. A change of configuration is determined by the local switching, if allowed, of a pair of next-nearest-neighbor monomers of different types, according to the standard Monte Carlo updating rule. Let

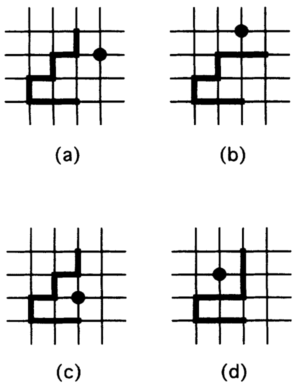

FIG. 1. This illustrates the changing of configurations by local switchings. Switching (a) to (b) is between a monomer of type A and a monomer of type B located at the end of a polymer chain. In switching (c) to (d) the monomer of type B is not located at a terminal position in the polymer chain.

E_i (E_f) be the energy of the configuration before (after) switching. The updating rule then says that the probability for an allowed switching to occur is unity if $E_f \leq E_i$, and is $e^{-\beta(E_f - E_i)}$ if $E_f > E_i$, where β is the inverse temperature. Because of the presence of bonds in the polymer chains, not every pair of next-nearest-neighbor monomers of different types are switchable. A switching is possible only if the detailed conformation of the polymer chain containing the B monomer permits the chain to retain its integrity after switching. The only two possible types of switching process are those shown in Fig. 1: Switching I [(a)–(b)] and Switching II [(c)–(d)].

It would now be possible to base a Monte Carlo simulation on the above model and dynamics. However, we take the alternative route of seeking an analytical solution to a mean-field theory based on this model.

III. DYNAMIC MEAN-FIELD APPROACH

Our first approximation is to assume, at time t, a local mean-field-like concentration, represented by $\varphi(x, y; t)$, of polymer at site (x, y), or, equivalently, the probability of finding a polymer segment B located at site (x, y) at time t. The time evolution of $\varphi(x, y; t)$ is, according to the dynamics described in Sec. II, given as (for $N \geq 2$)

$$\frac{\partial}{\partial t}\varphi(x,y;t) = \frac{2}{N}\sum_{\alpha_{\rm I}} P_{\rm I}(\varphi;\mu;\alpha_{\rm I}) + \left(1-\frac{2}{N}\right)\sum_{\alpha_{\rm II}} P_{\rm II}(\varphi;\mu;\alpha_{\rm II}) \ , \qquad (1)$$

where $P_{\rm I}(\varphi;\mu;\alpha_{\rm I})$ is the contribution from a switching $\alpha_{\rm I}$ of type I and the sum is over all possible switchings of type I, and similarly for $P_{\rm II}(\varphi;\mu;\alpha_{\rm II})$. (We will say more about these contributions and use a diagram to represent each of them later.) Here μ is a Boltzmann factor and is given by

$$\mu = e^{-2\beta\epsilon} \ . \qquad (2)$$

Several points require clarification about Eq. (1). First, the common factors $\frac{2}{N}$ and $(1 - \frac{2}{N})$ before the sum are mean-field countings of the probability that the chosen monomer of type B is located at one end or in the middle, respectively, of a polymer chain. For a mixture of monomers and dimers having $N = 2$, the second term vanishes, as is to be expected. Second, each sum contains both positive [for a case of "switching in," i.e. the site (x, y) chosen is occupied by a monomer of type A before a switching] and negative ("switching out") contributions. Third, since each site has four next-nearest neighbors, each sum contains all contributions from all possible switchings taking place between site (x, y) and its four next-nearest neighbors. Fourth, because the constrains of intrachain bonds apply to the polymer B, whether a switch (type I or II) is possible between a given pair of next-nearest-neighbor monomers of different types depends on the configuration of the occupancy of the nearest neighbors of the chosen site occupied by B, but not on that occupied by A [see Figs. 2(a) and (b)]. For example, Fig. 2(a) can contribute to both switching I and II, while Fig. 2(b) can only have a contribution to switching I.

Finally, we note that each individual contribution can be represented by a diagram. A complete list of all the

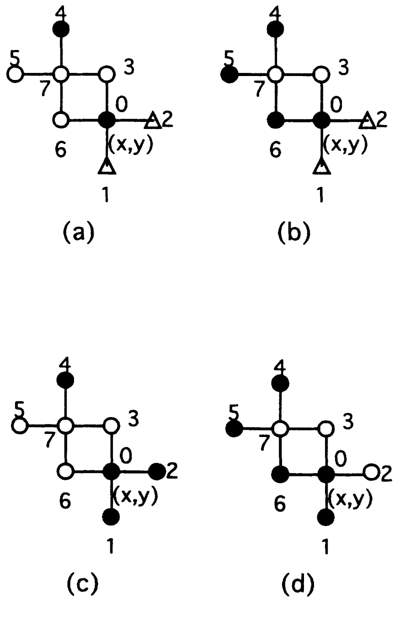

FIG. 2. (a) and (b) demonstrate two sets of configurations of the occupations of a pair of next-nearest neighbors (site 0 and site 7) and their nearest neighbors (sites 1 to 6) that can contribute to the time evolution of the local density of polymer at the chosen site 0 [i.e., site (x, y)]. Black and white dots represent sites occupied by monomers of type A and type B (that belonging to a polymer), respectively. A triangle indicates the site that can be occupied by a monomer of either type. (c) and (d) are two typical configurations belonging to the sets (a) and (b), respectively. Their contributions to the time evolution of the local density at site 0 are given in the text.

diagrams is rather lengthy, and so only two typical diagrams are shown in Figs. 2(c) and (d). Their corresponding contributions are for Fig. 2(c)

$$P_{\rm I}(\varphi;\mu;\alpha_{\rm I}) = (+)\left(\frac{2}{3}\right)(\bar\varphi_0\bar\varphi_1\bar\varphi_2\varphi_3\bar\varphi_4\varphi_5\varphi_6\varphi_7)\,(\mu) \tag{3}$$

and

$$P_{\rm II}(\varphi;\mu;\alpha_{\rm II}) = (+)\left(\frac{1}{3}\right)(\bar\varphi_0\bar\varphi_1\bar\varphi_2\varphi_3\bar\varphi_4\varphi_5\varphi_6\varphi_7)\,(\mu)\ , \tag{4}$$

and for Fig. 2(d)

$$P_{\rm I}(\varphi;\mu;\alpha_{\rm I}) = (+)(1)\,(\bar\varphi_0\bar\varphi_1\varphi_2\varphi_3\bar\varphi_4\bar\varphi_5\bar\varphi_6\varphi_7)\,(1)\ , \tag{5}$$

where φ_j, with $j = 0, 1 \ldots, 7$, is an abbreviation for the concentration $\varphi(x, y; t)$ at site j, and $\bar\varphi_j \equiv 1 - \varphi_j$. To clarify these expressions [Eq. (3)–Eq. (5)], we notice that each P is composed of four factors, each of which is enclosed in a pair of parentheses. The first factor is the sign which determines whether a switching is a "switching in" or "switching out". It is positive if site 0 is occupied by an A monomer, and negative if it is occupied by a B monomer. The second factor is, again, a mean-field counting of the geometrical packing of a polymer. Take Fig. 2(c) as an example. This factor is $\frac{2}{3}$ in $P_{\rm I}$ because a chain polymer whose end is at site 7 can go from site 7 to site 3, or to site 5, or to site 6, and only two of them (site 7 to site 3 and site 7 to site 6) allow a switching. The same factor is $\frac{1}{3}$ in $P_{\rm II}$ because in this case the packing pattern of a polymer is 3-7-5, or 3-7-6, or 5-7-6, and only pattern 3-7-6 allows a switching. The third factor is the probability of a given occupancy configuration. The last factor is related to the Boltzmann factor in the Monte Carlo updating rule, and is determined by the occupancy configuration of sites $0, 1, 2, 4, 5,$ and 7 only. This factor has only three possible forms: 1, μ, and μ^2. It is worth noting that both $P_{\rm I}$ and $P_{\rm II}$ are independent of the degree of polymerization N at this mean-field level of approximation.

Combining these considerations, we now know that the right hand side of Eq. (1) is a polynomial function of the φ (of degree seven, since the term containing a product of eight φ vanishes by symmetry), a quadratic function of μ, and a linear function of $\frac{1}{N}$.

While we now have in Eq. (1) a formal statement of a dynamic equation for the local concentration $\varphi(x, y; t)$, it is unfortunately too complicated to be solved analytically. However, an analysis of the local stability of the uniform solution in which φ is equal to the constant p is not beyond our reach.

IV. STABILITY ANALYSIS AND THE SPINODAL CURVES

In this section we determine the spinodal curve by finding the boundary of the region of stability of the solution for which φ is constant. To this end, we perturb the uniform solution in such a way that

$$\varphi(x, y; t) = p + \varepsilon e^{-\eta(k_x,k_y)t} e^{i(k_x x + k_y y)}\ , \tag{6}$$

where ε is a small perturbative variable, k_x (k_y) is the wave vector of the perturbative mode along the x (y) direction, and $\eta(k_x, k_y)$ is the spectrum of decay rates of the various modes. This spectrum is also a function of the polymer concentration p, the Boltzmann factor μ, and the degree of polymerization N. A stable uniform solution then exists only within the region for which $\eta > 0$. We now substitute Eq. (6) into Eq. (1), including all diagrams but keep terms only up to the first order in ε. We find, after some lengthy computer-aided analytic calculations, that

$$\eta(k_x, k_y) = (1 - \cos k_x \cos k_y)\,[a(p,\mu,N)(\cos k_x + \cos k_y) + b(p,\mu,N)]\ , \tag{7}$$

where

$$\begin{aligned} a(p,\mu,N) = {} & \mu^2\left[\frac{4}{3}(1-p)^2p^4 + \frac{16}{3}(1-p)^2p^3(2-p)\frac{1}{N}\right] \\ & + \mu\left[\frac{4}{3}(1-p)p^3(2-4p+3p^2) + \frac{16}{3}(1-p)p^2(3-8p+9p^2-3p^3)\frac{1}{N}\right] \\ & - \left[\frac{8}{3}(1-p)p^3(3-3p+p^2) + \frac{16}{3}(1-p)p^2(6-12p+9p^2-2p^3)\frac{1}{N}\right] \end{aligned} \tag{8}$$

and is always negative, and

$$\begin{aligned} b(p,\mu,N) = {} & \mu^2\left[\frac{2}{3}(1-p)^2p^4 + \frac{8}{3}(1-p)^2p^3(2-p)\frac{1}{N}\right] \\ & + \mu\left[\frac{4}{3}(1-p)p^3(2-4p+3p^2) + \frac{16}{3}(1-p)p^2(3-8p+9p^2-3p^3)\frac{1}{N}\right] \\ & + \left[\frac{2}{3}p^2(6-12p+14p^2-12p^3+5p^4)\right. \\ & \left. + \frac{8}{3}p(6-18p+30p^2-32p^3+20p^4-5p^5)\frac{1}{N}\right]\ , \end{aligned} \tag{9}$$

which is always positive within the physically meaningful region of the parameter space.

The stability boundary is found by first finding the minimum value of the spectrum with respect to the wave vector, and then setting this minimum equal to zero. When we exclude the case where $k_x = k_y = 0$, which is forbidden by reason of the conservation of order parameter, we find the nontrivial result to be

$$b(p,\mu,N) + 2a(p,\mu,N) = 0\ , \tag{10}$$

which determines a spinodal surface in the p-μ-N parameter space. It is worth pointing out that the stability boundary obtained in this discrete spatial formalism yields the same results as that obtained in a continuum spatial formalism because the first instability to occur as the temperature is lowered is at vanishingly small k. It is thus equivalent to expanding the right hand side of the dynamic equation with respect to the lattice spacing and keeping only terms up to second order. In this limit the dynamic equation is, in a linear stability analysis, a diffusion equation with a diffusion constant given by $b(p,\mu,N) + 2a(p,\mu,N)$.

We have plotted the spinodal curves in the μ-p parameter space for various degrees of polymerization in Fig. 3. We see that increasing the degree of polymerization N decreases the local stability of the uniform phase, as is the case in the Flory-Huggins mean-field theory. However, a qualitative difference appears at very low temperatures, where the Flory-Huggins theory predicts that a uniform phase of the mixture is unstable at zero temperature for all compositions p and degrees of polymerization N, while our approach suggests the uniform phase to be unstable only within part of the parameter space at zero temperature. The reason for this discrepancy lies in the phenomenon of "mobility freezing" that can occur at low temperatures in dynamic models, and which can prevent the system from phase separating at large length scales. When the polymer composition p is close to one (or zero), phase separation from a uniform phase to two phases requires a monomer (or polymer) to travel for a longer distance than is the case when the composition is near one-half. At zero temperature, any process that re-

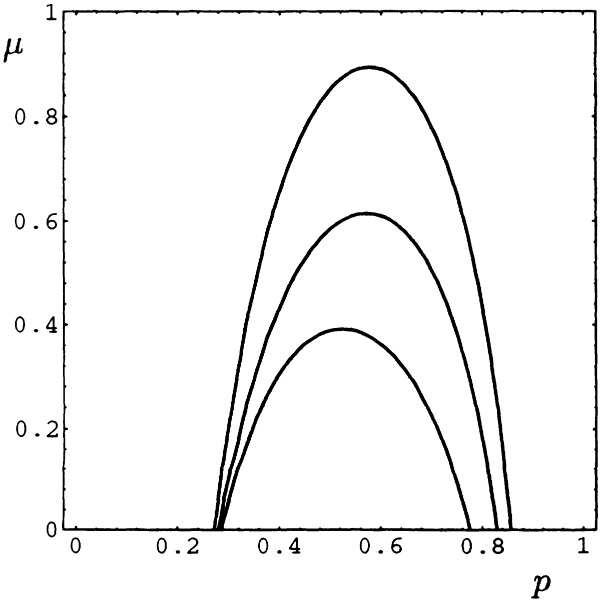

FIG. 3. The spinodal curves in the $\mu - p$ plane for various degrees of polymerization. From top to bottom, N is equal to ∞, 10, and 2, respectively.

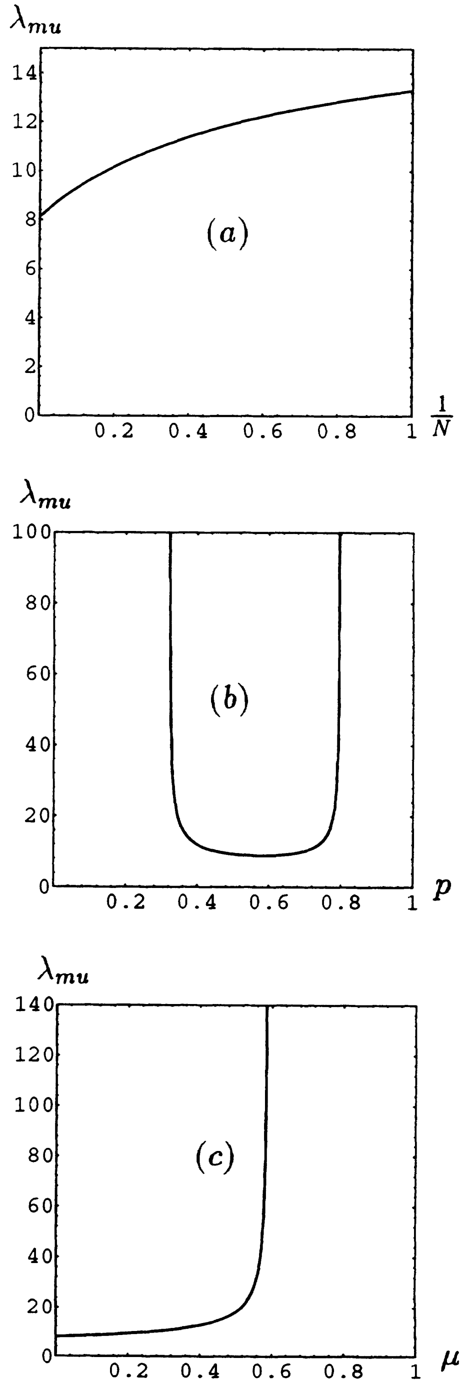

FIG. 4. This shows the variation of the wavelength λ_{mu} of the most unstable mode in different situations: (a) as a function of the inverse degree of polymerization $\frac{1}{N}$ at $p = 0.5$ and $\mu = 0.2$; (b) as a function of p at $\mu = 0.2$ and $\frac{1}{N} = 0.1$; and (c) as a function of μ at $p = 0.5$ and $\frac{1}{N} = 0.1$.

quires a monomer (or polymer) molecule to migrate for a large distance through a region dominated by the other species will essentially be eliminated, leaving the uniform phase as the stable one. Flory-Huggins mean-field theory does not involve local dynamics, and thus is not affected by this consideration.

Next we consider the initial patterns resulting from phase separation in the spinodal regime. These are determined by the wave vector for which the spectrum of $\eta(k)$ takes its most negative value. At the spinodal boundary this wave vector is isotropic, but for a deeper quench we find from Eq. (7) that the $(1,0)$ and $(0,1)$ directions are favored, and that the corresponding wavelength is

$$\lambda_{\rm mu}(p,\mu,N) = \frac{2\pi}{\arccos\left(\frac{b(p,\mu,N)}{-2a(p,\mu,N)}\right)} . \tag{11}$$

We have plotted this wavelength for the most unstable mode as a function of the different parameters while keeping other parameters fixed in Fig. 4. From Eq. (10) we find that this wavelength becomes infinite at the spinodal boundary.

The approach described above can also be used to investigate the phenomenon of polymerization-induced phase separation [15,16] by applying the method to a mixture of solvent monomers of type A and polymerizable monomers of type B that undergo a process of polymerization on a time scale that is slow compared to the diffusion process of the monomer. In this case there is a probability $Q(N,t)$ that a site known to be occupied by polymer at time t is occupied by one of degree of polymerization N. Then, in the derivation of the dynamic Eq. (1), for a given degree N each contribution to the time evolution of the local density of the polymers has an additional factor $Q(N,t)$, and there is a sum over N from one to infinity. For $N = 1$ (the case of an unpolymerized binary mixture), we need a more appropriate dynamics involving the local switching of a pair of different monomers that are nearest neighbors. The dynamic equation for $N = 1$ derived under this dynamics is different from that obtained from Eq. (1) by setting $N = 1$. If this difference is neglected, the polymerization-induced phase separation can then be studied by using Eq. (1) with $\frac{1}{N}$ replaced by its average $\langle 1/N \rangle$ with respect to the distribution $Q(N,t)$.

We have also studied the spinodal decomposition of a one-dimensional binary mixture using the dynamics for $N = 1$ described above. In this case the mode spectrum is given by

$$\eta(k) = 4[(1-2p+2p^2) - 2p(1-p)\cos k]\sin^2\frac{k}{2} + 4p(1-p)\mu\sin^2 k , \tag{12}$$

which is always positive. This indicates that the uniform phase is always stable, as was to be expected [14].

V. CONCLUSIONS

In conclusion, we have developed a two-dimensional lattice model to study the spinodal decomposition of a mixture of monomers (of type A) and polymers (composed of monomers of type B) with a degree of polymerization of N when there is an energy cost ϵ for each nearest-neighbor contact between monomer A and monomer B. A dynamic mean-field theory has been employed to generate the dynamic equation of the local mean-field-like density of polymer by using a local switching of monomer A and monomer B, while taking into account the polymer character of monomers of type B. The spinodal curves were obtained, and it was found that increasing the degree of polymerization decreases the local stability of a uniform phase of the mixture, in agreement with the Flory-Huggins mean-field theory [3,4]. However, at very low temperatures (for example, at zero temperature), the prediction of our theory is qualitatively in disagreement with that of Flory and Huggins, which predicts that the uniform phase of the mixture is always unstable for all compositions p. We account for this discrepancy in terms of the reduced mobility inherent in the local switching dynamics in our model.

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