

Monte Carlo study of phase separation in critical polymer blends

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Dynamics of phase separation in a polymer blend of critical composition is studied by Monte Carlo simulation of a microscopic lattice model. We find that dynamical scaling is obeyed by both the correlation function and the structure factor at late enough times, and that the asymptotic domain growth exponent is given by a modified Lifshitz-Slyozov law. We also compare the shape of the scaling function to the one previously obtained in a numerical study using a phenomenological Flory-Huggins-de Gennes free-energy functional.

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I. INTRODUCTION

Understanding the process of phase separation in polymer blends is important both for its fundamental aspect [1] and for specific materials applications [2,3]. A simple case is the binary homopolymer blend which consists of two types of polymer chains: one composed of a certain type of subunit, or *A*-type monomers, and the other constructed from *B*-type monomers. The kinetics of phase separation [4] in such a polymer blend can be followed experimentally [1,5,6] over a long period of time due to the slow diffusion of the polymer chains constituting the blend. It appears that a fundamental knowledge of the phase-separation process can lead to good control over the dynamics of phase separation through a proper choice of relevant parameters (such as the chain lengths and the relative extent of the two components) which, in turn, can significantly affect physical properties, creating practical importance in materials applications [7].

The theoretical understanding of phase separation in polymer blends is based largely on extension of methods used for small-molecule systems. The Cahn-Hilliard-Cook [4,8] approach to understanding demixing in the latter systems starts from the coarse-grained Ginzburg-Landau free-energy functional, which can be written in terms of the local concentration variable $\phi(\mathbf{r}, t)$, as

$$F_{\text{GL}} = \int d\mathbf{r} \left[f(\phi(\mathbf{r})) + \frac{\kappa}{2} |\nabla\phi(\mathbf{r})|^2 \right], \quad (1)$$

where $f(\phi)$, the Landau free-energy for a homogeneous system, is assumed to have the form

$$f(\phi) = -\frac{b}{2}\phi^2 + \frac{u}{4}\phi^4. \quad (2)$$

Here, b and u are phenomenological parameters of the model. The square-gradient term represents the energy caused to create an interface between domains and the parameter $\kappa = K\lambda^2$, where λ is an effective range of interaction between molecules.

The dynamics of the Cahn-Hilliard-Cook model takes the form of a Langevin equation. It is derived from the continuity equation expressing the conservation of mass and a mass current of the form

$$\mathbf{j} = \frac{\Lambda}{k_B T} \nabla\mu(\phi(\mathbf{r})) + \mathbf{j}_n(\mathbf{r}), \quad (3)$$

where Λ is the Onsager coefficient, the chemical potential (μ) is equal to the functional derivative of the free energy ($\mu = \delta F / \delta\phi$), and \mathbf{j}_n is the "thermal noise" mass flow. The Onsager coefficient measures the response of the system to local fluctuations in the chemical potential and is taken to be a constant. The resulting dynamical equation is

$$\frac{\partial\phi}{\partial t} = M \nabla^2 \frac{\delta F}{\delta\phi} + \eta(\mathbf{r}, t). \quad (4)$$

Here $M = \Lambda / k_B T$ and η is governed by the fluctuation-dissipation theorem

$$\langle \eta(\mathbf{r}, t), \eta(\mathbf{r}', t') \rangle = -2k_B T M \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (5)$$

This dynamical equation and the above free-energy functional form the basis for analytic studies of small-molecule systems. Both analytical [9,10] and numerical calculations [11,12] based on this model are found to be useful in understanding experimental results [13].

The extension of the Cahn-Hilliard-Cook model to polymer systems [14–16] involves two refinements to the free-energy functional. The first involves the free-energy $f(\phi)$ for the homogeneous system. Considering an ideal-gas form for the free-energy density of mixing, and an effective interaction parameter χ , one writes

$$f(\phi) = N^{-1} [\phi \ln\phi + (1-\phi) \ln(1-\phi)] + \chi\phi(1-\phi) \quad (6)$$

for a symmetric blend (where the length of both *A* and *B* chains is N). The other change in the free-energy functional is the addition of a concentration-dependent coefficient for the square-gradient term. The resulting Flory-Huggins-de Gennes free-energy functional is

$$\frac{F_{\text{FHdG}}[\phi]}{k_B T} = \int d\mathbf{r} \left[f(\phi) + \frac{a^2}{36\phi(1-\phi)} |\nabla\phi|^2 \right], \quad (7)$$

where a is the Kuhn length of the polymers. Starting from this free-energy functional, a Langevin equation, similar to Eq. (4), can be written for the polymer system as well. Note that the Onsager coefficient in this case is

expected to be a function of the volume fraction and the position vector. As a consequence of this, the spatial and temporal correlation for the thermal noise is more involved than the expression of Eq. (5). However, numerical simulations of Langevin equations with a constant Onsager coefficient [17] (which allows a simple form for the thermal noise correlation) seem to yield the correct asymptotic growth-law and scaling functions obtained in experiments [18] on critical polymer blends.

Similar to the small-molecule model, analytic studies of the phase-separation process have been carried out by linearizing the evolution equations for the order parameter. These theories are applicable only to early times. As mentioned above, numerical simulations have recently been performed [17,19,20] to probe the late-time dynamics of the phase-separation process. For critical quenches, the results of these simulations suggest that the growth law for the characteristic domain size $R(t)$ is given by the classical Lifshitz-Slyozov law [21], i.e., $R(t) \sim t^{1/3}$, independent of the final quench temperature. It was also found that the late times of the evolution process can be described by a scaling hypothesis [4,22] and that both the pair-correlation function and the structure factor obey dynamical scaling behavior at late times. Both the $t^{1/3}$ growth law and the scaling behavior for the structure factor have been confirmed in various experimental studies [5,6,23].

Despite this *a posteriori* support, it is important to note that the Flory-Huggins-de Gennes free-energy functional used in previous numerical studies describes equilibrium behavior in an inhomogeneous polymer blend at a phenomenological level, and it is not clear at all whether such a free-energy functional can be used in the nonequilibrium case of phase separation. The free-energy functional was postulated by de Gennes [14] by adding a square-gradient term to the Flory-Huggins free-energy for a homogeneous blend, and the prefactor of the square-gradient term was obtained by a random-phase approximation [24]. The difficulty of using such a model in conjunction with phase segregation has already been pointed out by several authors [25]. Also, the dynamics of the system postulated in the Cahn-Hilliard-Cook model does not have any rigorous justification for polymer blends [26]. Thus the theoretical approach toward phase separation as described in the previous section is totally phenomenological, and questions arise whether this is a satisfactory description of the phase-separation process in polymer mixtures.

In this paper, we take a totally different approach and carry out a Monte Carlo simulation of a model of phase separation in polymer blends which contains explicit chain structure for the molecules. Pioneering Monte Carlo simulation work in this model has been carried out by Sariban and Binder [27,28]. However, their results for the dynamics of spinodal decomposition are restricted to the early time regime [28]. On the other hand, we are interested in the large-scale, late-time structure formation in the model system. For this reason, we have carried out a Monte Carlo simulation in a reasonably large three-dimensional system (64^3) to a late time (our latest time is more than 20–30 times larger than that accessed in the

above simulation). We find that the system enters a dynamical scaling regime at sufficiently late times. In this scaling regime, we find that the microscopic model yields a growth exponent of $\frac{1}{3}$ as seen in experiments [5,6,23] and in previous studies [17] of coarse-grained models. We also find that the time-independent scaling function for the microscopic model is similar to that obtained in the coarse-grained model [17].

II. MODEL AND NUMERICAL PROCEDURE

Our simulation involves a simple model of polymer blends of critical composition (same number of *A*-type and *B*-type chains). Both species in the blend consist of chains of length N modeled as a self-avoiding walk of N bonds of unit length on a cubic lattice with periodic boundary conditions in all three directions. The chains obey the excluded-volume criterion so that no two monomers can occupy the same lattice site. The total monomer concentration of the blend is 0.80, which leaves 20% of the lattice sites vacant for possible movements. A model with a vacancy concentration of 0.20 behaves much like a blend, whereas the absence of any vacancies would imply that all sites are occupied by monomers, and no translational motion of the monomers is possible. Also, as discussed by Sariban and Binder [27,28], the actual ternary system considered here can be mapped onto the binary one by a suitable rescaling of parameters. The lattice used in this study has a side of $L = 64$ and chains of length $N = 32$. We have carried out several simulations for a 32^3 lattice as well in order to study possible finite-size effects.

In the most general case, the phase separation into domains can result both from an attraction between like monomers (ϵ_{AA} and ϵ_{BB}) and a repulsion between unlike monomers (ϵ_{AB}). In the limit of small vacancy concentration one expects that only the combination $\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2$ would matter. For finite vacancy contributions, however, Sariban and Binder [28] found that the attractive interaction between like monomers led to a collapse of chains and a dramatic lengthening of relaxation times. Inducing decomposition using only a repulsive interaction between like monomers ($\epsilon_{AA} = \epsilon_{BB} = 0, \epsilon_{AB} = \epsilon$) does not suffer from this drawback. Following Sariban and Binder, we also consider only a repulsive interaction between unlike monomers in our simulation and assign a repulsive interaction of strength $+\epsilon$ when two monomers of opposite species (*A-B*) are nearest neighbors.

The energetics are handled by the standard Metropolis algorithm; if a trial motion of a monomer causes a gain in system energy (ΔE), that move is accepted only if a random number is less than $\exp(-\Delta E/k_B T)$. The movements of the chains are implemented via a dynamic Monte Carlo method which uses three basic types of motion for the monomers: a local end relocation, kink jumps for middle monomers, and a crank-shaft motion [29]. Time is measured in units of Monte Carlo moves per monomer (MCM). No slithering-snake motions of the chains are explicitly included in the simulation, since this involves a movement of the whole chain and might

correspond to a different time scale than the monomer movements. However, it is possible that the *effective* motion of the chains in this dense system is reptationlike.

Although the dynamics of the Monte Carlo procedure is somewhat artificial, we expect that the large-scale, late-time behavior of the model will be similar to the dynamics of real, experimental polymer blends at intermediate times. We note that the model introduced here does not contain any hydrodynamic interactions, and thus the late-time behavior seen in experiments [5,6,23] on polymer blends [where the average domain size increases linearly with time, i.e., $R(t) \sim t$] cannot be obtained from the present model.

The polymer blend is initially generated by self-avoiding and mutually avoiding random walks alternating between *A* and *B* chains. The sample is then relaxed for 10 000 MCM in the absence of any repulsive interactions, i.e., at an infinite temperature. At a time denoted $t=0$ the system is quenched to a point deep inside the phase diagram [30] corresponding to $\varepsilon=1.0k_B T$. The phase separation then progresses and measurements of different probes are carried out every 1000 MCM until a final time of 100 000 MCM. The measurements are finally averaged over ten different realizations of the initial infinite temperature configurations (five of these initial conditions were carried beyond 50 000 MCM). We note that performing a Monte Carlo simulation of spinodal decomposition on a 64^3 lattice is a computationally demanding task. It took us about 3700 CPU hours of workstation computing, more than 22 CPU weeks, to produce these results. Execution would have been only about five times faster had the code been run on a Cray-YMP supercomputer since the Monte Carlo method for lattice chains is not strictly vectorizable.

Measurements of both blend and individual chain properties are made. For individual chains the radius of gyration and end-to-end distance are measured. The probability distribution of the radii of gyration for the chains at several times is presented in Fig. 1. Note that the chains undergo a slight but noticeable contraction immediately after the interaction is turned on, but this contraction does not progress with time. Thus, the chains do not collapse in the presence of the repulsive interactions considered here between unlike monomers. This result is in agreement with previous simulations of Sariban and Binder [28], where a chain collapse was seen only in the presence of attractive interactions between like monomers.

The structure formation in the binary blend is usually measured by the time-dependent structure factor $S(\mathbf{k}, t)$, which we define to be

$$S(\mathbf{k}, t) = \left\langle \frac{1}{n} \sum_{\mathbf{r}} \sum_{\mathbf{r}'} e^{i\mathbf{k} \cdot \mathbf{r}} [\sigma(\mathbf{r} + \mathbf{r}', t) \sigma(\mathbf{r}', t) - \langle \sigma \rangle^2] \right\rangle. \quad (8)$$

Here, $\sigma(\mathbf{r})$ is the local difference in concentration and takes the value $+1$ (-1), if the location \mathbf{r} is occupied by an *A* (*B*) type monomer; or zero, if the location \mathbf{r} is unoccupied. Note that both sums in the above equation run over the lattice of linear size L , and $n=L^3$ is the total number of points in the lattice. We expect the evolution

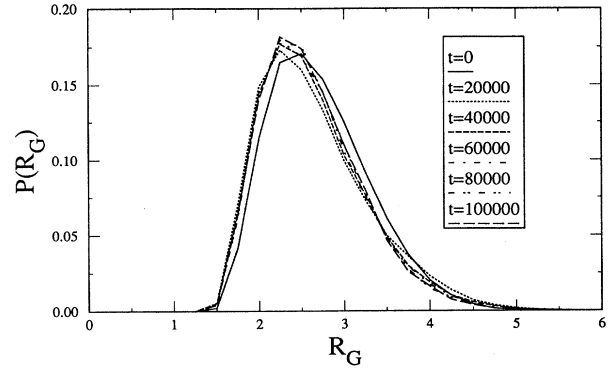


FIG. 1. Probability distribution of individual chain radii of gyration, R_G , at several times during the phase-separation process. The solid line is the distribution before the interaction is turned on. There is a slight contraction of chains after the quench.

process to be isotropic and compute the spherically averaged structure factor $S(k, t)$.

Although the location of the structure factor's maximum, k_m , is used experimentally to find the characteristic domain size at some time t , the discrete nature of the lattice in this model makes it difficult to precisely determine k_m . Previous work demonstrates that R_g , the first zero in the real-space correlation function, is a good measure for the average domain size [31,32]. In the present simulation also, we have found that R_g is statistically reliable, and for an average over ten runs, the statistical error in R_g is about 5%. In a discretized lattice the correlation function is the Fourier transformation of $S(\mathbf{k}, t)$ defined by

$$G(\mathbf{r}, t) = \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} S(\mathbf{k}, t). \quad (9)$$

Again a spherical average is taken since the system is isotropic. The correlation function is finally adjusted by normalizing the function to unity at $r=0$,

$$g(r, t) = G(r, t) / G(0, t). \quad (10)$$

The length R_g is then computed by fitting a cubic polynomial to the four points closest to the first sign change in $g(r, t)$ and finding the polynomial's root with a simple search.

It is well accepted now that the late stages of many growth processes can be described in terms of a dynamical scaling [4] with a time-dependent length. The scaling hypothesis states that at late times R_g is the only dominant length scale in the blend. If all distances can be scaled by this length scale, the rescaled pair correlation function can be written as

$$g(r, t) = \mathcal{G}[r/R_g(t)] \quad (11)$$

and the rescaled structure factor can be written as

$$S(k, t) = R_g^3(t) \mathcal{F}[kR_g(t)]. \quad (12)$$

If the scaling hypothesis is satisfied, then $\mathcal{G}[\rho]$ and $\mathcal{F}[X]$ should be time-independent functions.

III. RESULTS

After the critical quench, domains rich in either A - or B -type monomers form and grow. A typical configuration of the system at late times ($t = 100\,000$) is shown in Fig. 2. The growth of domain size with time can be seen in the movement of the first zero (which is a measure of the average domain size R_g) to longer lengths in the normalized correlation functions plotted in Fig. 3. The exponent of the growth rate of the domains is an important clue about the dominant growth mechanism. We present a log-log plot of R_g in Fig. 4. The linear dependence at late times suggests a power-law relation between R_g and t in this regime. A least-squares fit gives an effective exponent [31] of 0.30 ± 0.03 , although the exponent still seems to be increasing at late times. This exponent is close to the value of $\frac{1}{3}$ given by the Lifshitz-Slyozov evaporation-condensation mechanism. We note that the exponent found from the slope of the log-log plot is probably an effective exponent, since one expects that, at late times, the growth law is given by the form $R_g(t) = a + bt^{1/3}$ [31], and the additive term affects the slope of the log-log plot. In order to compute the asymptotic exponent we fit our data of $R_g(t)$ to a form $R_g(t) = a + bt^n$, treating a , b , and n as free parameters. This yields a value of $n = 0.35 \pm 0.05$ for the asymptotic exponent, which is consistent with the Lifshitz-Slyozov type growth. A similar growth-law exponent has been seen in previous numerical work on coarse-grained models [17] as well as in experiments on polymer blends [5,6,23] at intermediate times before hydrodynamic effects become important.

The dynamical scaling ansatz asserts that in an isotropic phase separation [33] such as this one, there should be

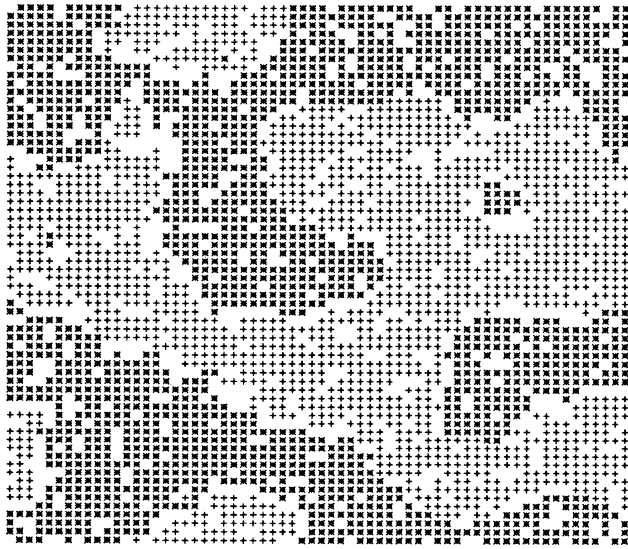


FIG. 2. A two-dimensional cross section (planar view) of a realization of the Monte Carlo model at $t = 100\,000$ MCM. The domains of $A(+)$ and $B(*)$ are quite distinct and interpenetrating. Note that the vacancies are often found at interface but are also found inside domains.

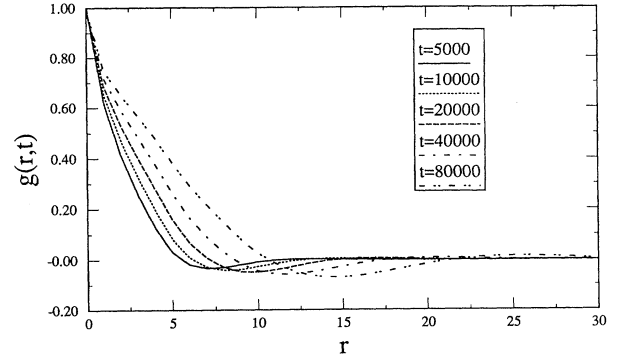


FIG. 3. Normalized pair correlation function $g(r,t)$ vs distance r for the Monte Carlo model at different times. The movement of the first zero of the function to the right reflects the growth in domain size as phase-separation proceeds.

only one important, time-dependent length scale in the system at late times. For the polymer blend, it is expected that once R_g becomes much larger than the interface thickness it will become the dominant length scale. In Fig. 5 the normalized, scaled pair-correlation function is plotted against rescaled distance $r/R_g(t)$ for several late times. Clearly the Monte Carlo model shows good scaling behavior at late times ($t > 20\,000$ MCM), with the rescaled correlation function for the several times all falling on the same curve.

The dynamical scaling ansatz for the structure factor [Eq. (12)] is tested in Fig. 6. We note that due to the lattice discretization, obtaining a clean scaling form for the structure factor is usually more difficult in numerical studies. However, as shown in Fig. 6, scaling seems to work reasonably well at late times as deviation from scaling is most apparent at earlier times. Data shown in Fig. 6 are replotted in Fig. 7 in a log-log form in order to compute the functional form of the structure factor for large values of the rescaled wave vector. We point out that there is a weak shoulder in the structure factor around $k \approx 2k_{\max}(t)$, which has also been observed in experi-

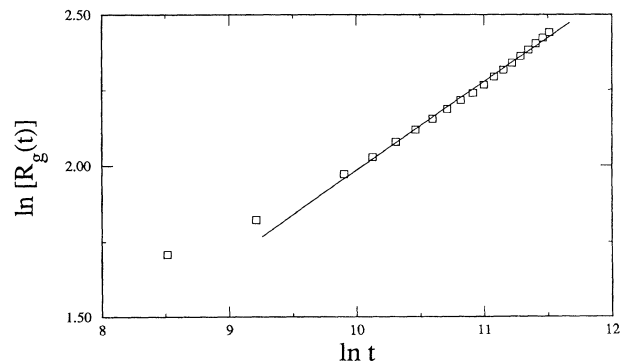


FIG. 4. Log-log plot of growth in the location of the first zero of the pair-correlation function R_g vs time. The straight line is a least-squares fit at late times (between $t = 20\,000$ and $t = 100\,000$), which gives an effective growth exponent of 0.30 ± 0.03 .

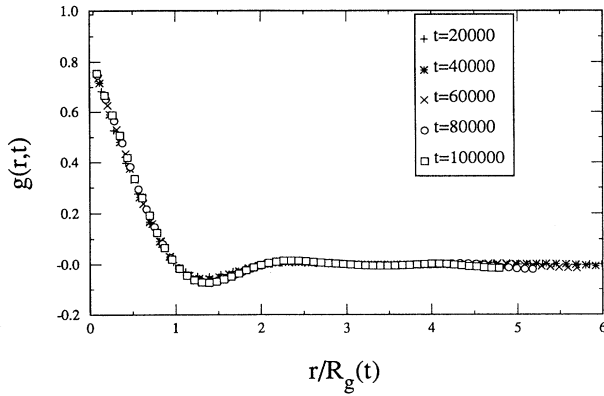


FIG. 5. Pair-correlation function $g(r,t)$ vs rescaled distance $r/R_g(t)$ for the Monte Carlo model at different times. The data symbols corresponding to different times fall on a single master curve suggesting dynamical scaling behavior at late times.

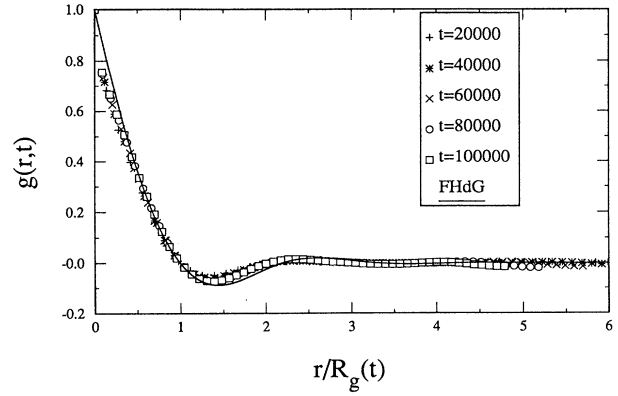


FIG. 8. Comparison of the time-independent scaling form of the pair-correlation functions for the Monte Carlo model and the coarse-grained Flory-Huggins-de Gennes model (taken from Ref. [17]).

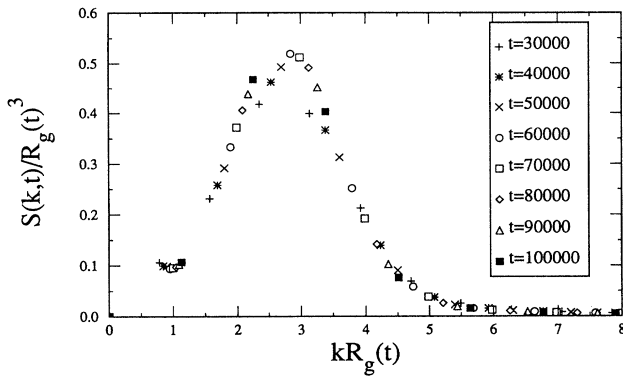


FIG. 6. Structure factor $S(k,t)$ rescaled with $R_g(t)$, the first zero of the pair-correlation function, as the characteristic length scale. The data points from different times fall onto the same curve.

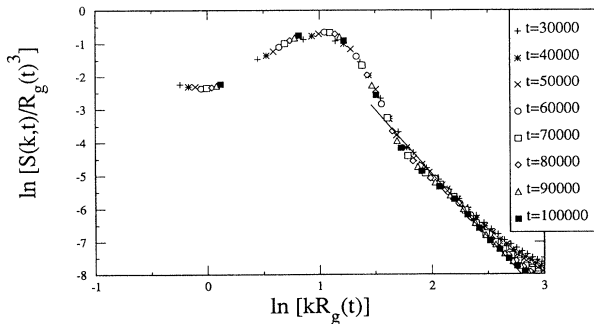


FIG. 7. Log-log plot of the rescaled structure factor for the Monte Carlo model. The solid line is a least-squares fit to the data as a test of Porod's law. The slope of this line yields an exponent of -3.85 . Note the weak shoulder at about twice the wave vector of the maximum.

ments [5,6] and on previous simulations on coarse-grained Langevin models [17]. For large k , one expects that the functional form of the structure factor is given by Porod's law [4,34]: $S(k) \sim k^{-4}$. The straight-line fit to the data in Fig. 7 for the latest time yields an exponent of -3.85 , which is close to the expected Porod law exponent of -4 . Thus we conclude that our results are consistent with Porod's law, although we do not have data over a large range of k .

Finally, we have compared the scaling function for the pair-correlation function obtained from the Monte Carlo simulation to the one obtained from a numerical study of the coarse-grained Flory-Huggins-de Gennes model. The result is shown in Fig. 8. In this figure we find that the two scaling functions are similar. Although there are some differences between the two scaling functions, a careful scrutiny of this figure reveals that the scaling function for the Monte Carlo model is still slowly converging to the scaling function for the coarse-grained model even at the latest times accessible in this simulation. We point out that numerically it is easier to enter the true, asymptotic scaling regime in coarse-grained models, whereas in a lattice model, it is extremely time-consuming to get into the asymptotic scaling regime. However, from the general grounds of universality and renormalization-group arguments [9], one would expect the two models to have the same large-scale, late-time behavior and that the asymptotic scaling functions in these two models would be the same.

IV. SUMMARY AND DISCUSSION

We have carried out a detailed Monte Carlo simulation of a lattice model of phase separation in polymer blends where the long chain structure of the polymer molecules is explicitly present in the model computations. We find that the asymptotic growth-law exponent of this model is given by the Lifshitz-Slyozov result. We also find that dynamical scaling is satisfied at late times. Comparing

these results to those obtained from numerical studies of a phenomenological coarse-grained model using the Flory-Huggins-de Gennes free-energy functional and the Langevin dynamical equation we find that both the asymptotic growth-law exponent and the asymptotic scaling functions are similar in these two models.

We point out that the phase diagram for the lattice model has recently been computed accurately [27], and this allows one to perform quenches to various off-critical locations inside the phase boundary. We expect that the Monte Carlo model calculations will be important for off-critical quenches as well, since the entropic effects may lead to a formation of new and unexpected structures for such quenches. For example, it has been argued by Kotnis and Muthukumar [20] that the entropic contribution to the Flory-Huggins-de Gennes free-energy functional (as manifested by the ϕ -dependent gradient term in this functional) plays an important role for off-critical quenches even in the unstable region of the phase diagram, if the equilibrium volume fraction of one of the components is smaller than the percolation threshold in three dimensions. In this case the situation becomes different (nonuniversal) from the small-molecule case because of the claimed entropic barrier [20] associated with chain transport between the separated domains of the minority phase. This arguably destroys the evaporation-condensation mechanism of Lifshitz-Slyozov growth, and domains "freeze" after a short-lived initial growth. A sharp "transnodal line" [20] would then exist which separates arrested growth and unarrested growth. The above picture is drawn from results of computer simulations of a coarse-grained model similar to the one described previously. In their model calculation, Kotnis and Muthukumar use a ϕ -dependent mobility. Since the

fluctuation-dissipation theorem is prohibitively complicated to work out for such a ϕ -dependent mobility, they did not include thermal fluctuations in their calculations. On the other hand, our recent study [19] with a constant mobility (in which case the thermal fluctuations can be taken into account relatively easily) shows that the freezing of domain growth is actually unstable against thermal fluctuations, even when the volume fraction of the minority phase is below the percolation threshold. Thus, it is not totally clear whether the entropic barriers suggested by Kotnis and Muthukumar actually survive in the presence of thermal noise. This fundamental question of whether there is an entropic barrier against domain growth which manifests into a possible transnodal line separating arrested and unarrested growth can be addressed in a Monte Carlo study by carrying out several different quenches at various temperatures and volume fractions. Since the chain structure of the polymer molecules will remain intact in this model study, definitive answers about entropic barriers can be answered in this simulation. The simulation results will be very important in understanding the mechanism behind the freezing behavior observed in some recent experiments [35,36]. Such studies are currently underway and the results will be presented elsewhere.

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- [1] T. Hashimoto, in *Current Topics in Polymer Science*, edited by R. M. Ottenbrite, L. A. Utracki, and S. Inoue (Hanser, Munich, 1987), Vol. II; *Phase Transitions* **12**, 47 (1988).
- [2] *Polymer Blends*, edited by D. R. Paul and S. Newman (Academic, New York, 1978), Vols. 1 and 2.
- [3] *Multicomponent Polymer Materials*, edited by D. R. Paul and L. H. Sperling (American Chemical Society, Washington, DC, 1986).
- [4] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8.
- [5] (a) T. Hashimoto, M. Takenaka, and H. Jinnai, *J. Appl. Cryst.* **24**, 457 (1991); (b) M. Takenaka and T. Hashimoto, *J. Chem. Phys.* **96**, 6177 (1992).
- [6] F. S. Bates and P. Wiltzius, *J. Chem. Phys.* **91**, 3258 (1989).
- [7] T. Hashimoto, H. Tanaka, and H. Hasegawa, in *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*, edited by M. Nagasawa (Elsevier, Amsterdam, 1988); T. Hashimoto, M. Takenaka, and T. Izumitani, *J. Chem. Phys.* **97**, 679 (1992).
- [8] J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958); H. E. Cook, *Acta Metall.* **18**, 297 (1970).
- [9] A. J. Bray, *Phys. Rev. Lett.* **62**, 2841 (1989).
- [10] G. F. Mazenko, *Phys. Rev. Lett.* **63**, 1605 (1989).
- [11] A. Chakrabarti, R. Toral, and J. D. Gunton, *Phys. Rev. B* **39**, 4386 (1989).
- [12] A. Shinozaki and Y. Oono, *Phys. Rev. Lett.* **66**, 173 (1991).
- [13] See, for example, B. D. Gaulin, S. Spooner, and Y. Morii, *Phys. Rev. Lett.* **59**, 668 (1987).
- [14] P. G. de Gennes, *J. Chem. Phys.* **72**, 4756 (1980).
- [15] P. Pincus, *J. Chem. Phys.* **75**, 1996 (1981).
- [16] K. Binder, *J. Chem. Phys.* **79**, 6387 (1983).
- [17] A. Chakrabarti, R. Toral, J. D. Gunton, and M. Muthukumar, *Phys. Rev. Lett.* **63**, 2072 (1989); *J. Chem. Phys.* **92**, 6899 (1990).
- [18] Note that the scaling function obtained in Ref. [17] compares quite well to the one found in experiments. See, for example, Ref. [5(a)].
- [19] G. Brown and A. Chakrabarti, *J. Chem. Phys.* **98**, 2451 (1993).
- [20] M. A. Kotnis and M. Muthukumar, *Macromolecules* **25**, 1716 (1992).
- [21] I. M. Lifshitz and V. V. Slyozov, *J. Phys. Chem. Solids* **19**, 35 (1961).
- [22] K. Binder and D. Stauffer, *Phys. Rev. Lett.* **33**, 1006 (1974).
- [23] The Lifshitz-Slyozov growth law is seen over intermediate

- times in experiments since the late-time behavior in experimental systems is controlled by hydrodynamic effects and the growth exponent changes over to unity [see, E. D. Siggia, *Phys. Rev. A* **20**, 595 (1979)].
- [24] More recently, self-consistent-field calculations [I. Szleifer and B. Widom, *J. Chem. Phys.* **90**, 7524 (1989); see also E. Helfand and Y. Tagami, *ibid.* **56**, 3592 (1971)] and density-functional theories [H. Tang and K. Freed, *J. Chem. Phys.* **94**, 1572 (1991)] are employed to obtain the prefactor of the square-gradient term.
- [25] M. Bahiana and Y. Oono, *Phys. Rev. A* **41**, 6763 (1990); K. Kawasaki and T. Ohta (unpublished).
- [26] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1988).
- [27] A. Sariban and K. Binder, *Macromolecules* **21**, 711 (1988).
- [28] A. Sariban and K. Binder, *Macromolecules* **24**, 578 (1991).
- [29] See, for example, K. Kremer and K. Binder, *Comput. Phys. Rep.* **7**, 259 (1988).
- [30] The critical value of ϵ for this vacancy concentration and chain length is $\epsilon_c = 0.03k_B T$. See Ref. [27].
- [31] D. A. Huse, *Phys. Rev. B* **34**, 7845 (1986).
- [32] T. M. Rogers, K. R. Elder, and R. C. Desai, *Phys. Rev. B* **37**, 9638 (1988); E. Gawlinski, J. Viñals, and J. D. Gunton, *ibid.* **39**, 7266 (1989).
- [33] The situation might be different when surface-effects are important. See, for example, G. Brown and A. Chakrabarti, *Phys. Rev. A* **46**, 4829 (1992).
- [34] G. Porod, in *Small-Angle X-ray Scattering*, edited by O. Glatter and O. Kratky (Academic, London, 1983).
- [35] T. Hashimoto, in *Dynamics of Ordering Process in Condensed Matter*, edited by S. Komura and H. Furukawa (Plenum, New York, 1988); T. Hashimoto, M. Takenaka, and T. Izumitani, *J. Chem. Phys.* **97**, 679 (1992).
- [36] A. Wong and P. Wiltzius (unpublished).