

Spinodal Decomposition in Polymer Mixtures

Amitabha Chakrabarti,^(1,2) Raúl Toral,^{(1),(a)} James D. Gunton,⁽¹⁾ and M. Muthukumar⁽³⁾

⁽¹⁾ *Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015*

⁽²⁾ *Center for Polymer Science and Engineering, Lehigh University, Bethlehem, Pennsylvania 18015*

⁽³⁾ *Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003*

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We present the first numerical study of spinodal decomposition in polymer mixtures in three dimensions for Flory-Huggins-de Gennes free energy, numerically integrating the time-evolution equations for the conserved order parameter. We study the time dependence of the domain size as well as the pair correlation function and structure factors for several quench temperatures. The results indicate that the growth law for the characteristic domain size is independent of the final quench temperature in contradiction with the recent experiments on model polymer systems. As well, it is shown that dynamical scaling is valid at sufficiently late times.

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The phenomenon of spinodal decomposition is the subject of many theoretical and experimental investigations in the field of small molecule or atomic systems, such as binary alloys, fluid mixtures, and inorganic glasses.¹ In recent years, such studies are also attracting much theoretical and experimental interest in the field of polymer mixtures,²⁻⁴ due to the ease with which the different regions of the phase diagram can be probed for widely varying time scales. The important objectives in the study of phase separation in polymer mixtures are (1) to look for *universality* in the kinetics of phase separation, i.e., to find whether the laws found for dynamics of small molecule systems work for polymeric systems as well, and (2) to discover possible unique characteristics originating from the presence of long-chain molecules.

The theoretical understanding of the process of phase separation,¹ in small molecule systems, is based mainly on the Cahn-Hilliard-Cook⁵ (CHC) formulation, which starts from the nonlinear Langevin equation with a Ginzburg-Landau-type free energy. Analytical studies of this field-theoretic model⁶ have been reasonably successful in describing the early-time behavior of the phase separation process but, due to their approximate nature, they are not as useful in the late stages. In the absence of analytical studies, numerical simulation plays a useful role in our ability to understand and to predict the late-time behavior of such a system. Numerical studies⁷⁻¹⁰ have suggested that the characteristic size of the domains shows a Lifshitz-Slyozov-type growth law (independent of the final temperature of quench, as long as this final temperature is much smaller than the critical temperature) and that the structure factor and the pair correlation functions show scaling forms at late times.

Recent experiments on the phase separation of isotopic polymer mixtures¹¹ have been interpreted to imply that (1) the growth law depends on the final temperature of quench and (2) the scaling behavior found in studies of small molecules does not seem to be valid. The authors of this paper also suggested that the so-called "violation"

of universal scaling is possibly due to the choice of the Ginzburg-Landau-type free energy in the theoretical studies, whereas the "true" free-energy functional for polymer mixtures is given by a Flory-Huggins-de Gennes expression. However, we note that in other studies with different polymer mixtures,^{2,12,13} scaling was suggested to hold for time scales similar to that of Ref. 11.

Analytical studies of spinodal decomposition in polymer mixtures have been carried out by several authors¹⁴ for early-time regimes. However, no such calculation is available for late times. It seems then, at this point, numerical simulations will continue to play a major role in understanding the late-time behavior of the phase separation process in polymer mixtures. Monte Carlo simulation techniques have been used to study early stages of phase separation in a lattice model of polymer mixtures in two and three dimensions.¹⁵ However, no similar study exists for the field-theoretic model with a Flory-Huggins-de Gennes free energy for the polymer mixtures.

In this Letter, we want to fill this gap by reporting results of a detailed numerical study in three dimensions starting from a full Flory-Huggins-de Gennes-type free energy and numerically integrating the time evolution equation of the conserved order parameter. We have carried out the simulations to late time and averaged over a large number of runs, for several final quench temperatures. We use a finite-difference scheme for both the spatial and temporal derivatives and compute, among other quantities, the structure factor and the pair correlation functions. We find that dynamical scaling is satisfied for both the pair correlation function and the structure factor at sufficiently late times, and that the growth law for the domain size is independent of the final temperature of quench.

We consider a mixture of two polymer species, *A* and *B*, with chain lengths $N_A = N_B = N$ and subunit size $a_A = a_B = 1$. We start from the equation relating the

time variation of the conserved concentration field $\varphi(\mathbf{r}, t)$ to the functional derivative of a (coarse-grained) free-energy functional plus a thermal noise in the following way:

$$\frac{\partial \varphi}{\partial t} = M \nabla^2 \frac{\delta F}{\delta \varphi} + \eta(\mathbf{r}, t), \quad (1)$$

where M is the mobility, assumed to be a constant. In order to study spinodal decomposition in polymer mixtures, we choose, for $F[\varphi]$, the full Flory-Huggins-de Gennes free energy (in units of $k_B T$) given by¹⁴

$$F[\varphi] = \int d\mathbf{r} \left[f(\varphi(\mathbf{r})) + \frac{1}{36\varphi(1-\varphi)} |\nabla\varphi|^2 \right], \quad (2)$$

$$\frac{\partial \varphi}{\partial \tau_1} = \frac{1}{2} \nabla_{\mathbf{x}}^2 \left[\frac{\chi_s}{2(\chi - \chi_s)} \ln \left(\frac{\varphi}{1-\varphi} \right) - \frac{2\chi}{\chi - \chi_s} \varphi + \frac{1-2\varphi}{36\varphi^2(1-\varphi)^2} (\nabla_{\mathbf{x}}\varphi)^2 - \frac{1}{18\varphi(1-\varphi)} \nabla_{\mathbf{x}}^2 \varphi \right] + \epsilon^{1/2} \xi(\mathbf{x}, \tau_1), \quad (4)$$

where the new noise ξ satisfies

$$\langle \xi(\mathbf{x}, \tau_1) \xi(\mathbf{x}', \tau_1') \rangle = -\nabla_{\mathbf{x}}^2 \delta(\mathbf{x} - \mathbf{x}') \delta(\tau_1 - \tau_1')$$

and $\epsilon = (\chi - \chi_s)^{1/2}$.

For the system studied in Ref. 11, the critical temperature and the χ parameter are known¹⁶ and these values are used as the input for the numerical studies. Thus by varying χ one can faithfully mimic the quench procedure at different final temperatures. We have taken $\chi = 0.326/T - 2.3 \times 10^{-4}$, $T_c = 62^\circ\text{C}$ and the quench temperatures 25, 40, 49, and 54.5°C . With these input parameters, we have numerically integrated Eq. (4) on a simple cubic lattice of size 50^3 with periodic boundary conditions. We have performed the numerical integration up to $\tau_1 = 500$ using a time step of 0.01. In order to average over the noise, we have performed twenty runs for each quench temperature. The specific details of the

where

$$f(\varphi(\mathbf{r})) = \frac{1}{N} [\varphi \ln \varphi + (1-\varphi) \ln(1-\varphi)] + \chi \varphi(1-\varphi). \quad (3)$$

χ is the temperature-dependent Flory interaction parameter, and the thermal noise $\eta(\mathbf{r}, t)$ satisfies the fluctuation dissipation theorem:

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

where $\langle \dots \rangle$ denotes an ensemble average.

In experimental studies,^{4,11-13} one defines a rescaled wave vector \mathbf{q} and a rescaled time τ as $\mathbf{q} = \mathbf{k}/k_m^0$ and $\tau = D_{\text{app}}(k_m^0)^2 t$. k_m^0 and D_{app} can be calculated from the linear theories as $(k_m^0)^2 = \frac{9}{2}(\chi - \chi_s)$ and $D_{\text{app}} = 2M(\chi - \chi_s)$, where $\chi_s = \chi(T = T_c) = 2/N$. In our numerical studies, we have used the following rescaled variables: $\mathbf{x} = (\chi - \chi_s)^{1/2} \mathbf{r}$ and $\tau_1 = 2M(\chi - \chi_s)^2 t$. Thus one finds from Eqs. (1)-(3) in terms of these reduced variables,

numerical integration will be given elsewhere.¹⁷

In order to study the growth law for the domain size and to examine the issue of scaling, we computed the spherically averaged structure factor $S(k, \tau_1)$ and the spherically averaged pair correlation function $g(x, \tau_1)$. We have defined the domain size $R_g(\tau_1)$ as the coordinate of the first zero of $g(x, \tau_1)$. We have also computed the location of the maximum of $S(k, \tau_1)$, $k_m(\tau_1)$. Our results for k_m are plotted in Fig. 1, for several values of the quench temperature, where we plot the data in a log-log scale in units of k_m^0 versus rescaled time τ , in order to compare with experimental results. Similarly, results for R_g are plotted in Fig. 2 in units of $(k_m^0)^{-1}$ vs τ . The determination of k_m is more unreliable than that of R_g , because k_m is computed by locating the maximum of the structure function, whereas R_g is found by comput-

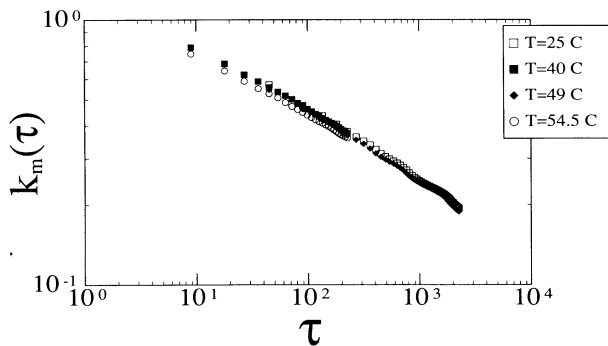


FIG. 1. The maximum of the structure factor k_m in units of k_m^0 vs rescaled time τ shown in a log-log scale for several quench temperatures. The growth-law exponent (0.28 ± 0.01), computed for $50 \leq \tau \leq 1000$, is independent of the quench temperature.

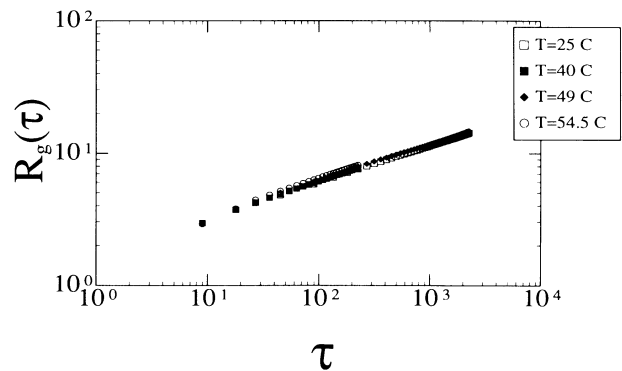


FIG. 2. The characteristic domain size R_g , calculated from the pair correlation function (see text) in units of $(k_m^0)^{-1}$, plotted against rescaled time τ for several quench temperatures. The qualitative behavior is the same as in Fig. 1.

ing the zero of the pair correlation function. Particularly at late times, the maximum of $S(k, \tau)$ is not precisely defined (see Fig. 3) due to the discretization of the Brillouin zone in a finite lattice such as considered here. This explains the small bends in the k_m vs τ curves for, say, $\tau > 500$. Another source of error is the statistical fluctuation of data coming from different runs. For the domain-size measures, the statistical errors are of the order of 5%. A complete analysis of the errors will be given elsewhere.¹⁷

In Figs. 1 and 2 we see that the growth-law exponent is independent of the quench temperature. This result is consistent with the claimed universal scaling of Refs. 12 and 13, but not with that of Ref. 11, where a quench-depth-dependent growth-law exponent is suggested for early to intermediate stages. The growth-law exponent calculated from the slope of these log-log plots is given by 0.28 ± 0.01 . This value of the growth exponent is in excellent agreement with the experimental result for intermediate to "transition" times.¹⁸ We point out that the physical mechanism governing the late-time behavior in the model corresponds to the so-called transition times in experimental systems, whereas the real-late-time behavior seen in the experiments is governed by hydrodynamic interactions. We also find that the peak of the structure factor $S(k = k_m, \tau)$ yields an effective growth-law exponent of 0.85 ± 0.02 ,¹⁷ in good agreement with recent experiments.¹⁸ However, we note that the exponents found from the log-log plots are probably effective exponents, since one expects¹⁹ that the growth law for domain size $R(\tau)$ is given by $R(\tau) = a + b\tau^n$. A fit to this expression of the R_g data between $\tau = 450$ and $\tau = 2250$ yields $n = 0.33 \pm 0.01$ for $T = 25^\circ\text{C}$ and $n = 0.33 \pm 0.02$ for $T = 49^\circ\text{C}$. This value of the exponent suggests that the Lifshitz-Slyozov mechanism describes the growth of domains in this time regime. We do not expect any change in the value of n at later times, since hydrodynamic interactions²⁰ are ignored in the present model.

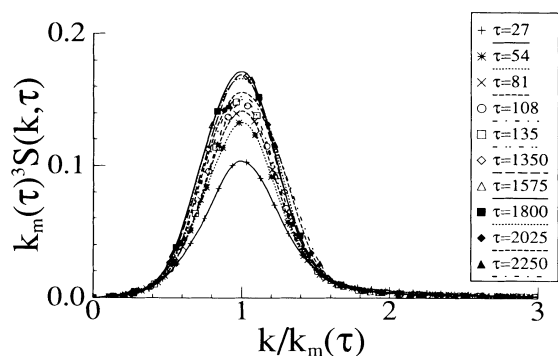


FIG. 3. Plot of the scaling function defined in Eq. (5) for the spherically averaged structure factor. Scaling is satisfied only at late times, i.e., $\tau \geq 1350$. The lines are spline fits which serve as a guide to the eye.

The dynamical scaling *Ansatz* predicts that at late times the structure factor should scale as

$$S(k, \tau) = k_m^{-3} F(k/k_m). \quad (5)$$

In order to study the scaling hypothesis we plot the data for the structure factor in Fig. 3, for several rescaled times τ after the quench. If the scaling hypothesis Eq. (5) is correct, all the data in Fig. 3 should fall on a single master curve. However, we note that the scaling hypothesis works only at very late time, as shown in this figure. In Fig. 3 the structure factor data are shown only for the quench temperature 25°C , but the same qualitative picture is found for all the other quench temperatures.

In order to study the functional form of the scaling curve, we plot the structure factor data in a log-log graph in Fig. 4. It is again clear from this figure that the scaling hypothesis works only at very late times ($\tau \geq 1350$) when all the curves fall on top of each other. Calculations over much larger times are necessary to study the scaling behavior more accurately. However, it is still interesting to note that the scaling function exhibits a weak shoulder around $k \approx 2k_m(\tau)$ which has also been observed in the most recent experimental systems.^{12,18} The straight line in Fig. 4 is the fit to the data for large- k values. We find that for large k , the scaling function goes as $k^{-3.6}$, which is close to the expected Porod's law behavior (k^{-4}). In recent experimental studies^{12,18} it has also been found that for late times the scaling function behaves as k^{-4} for large k .

In summary, we have studied the phase separation behavior in polymer mixtures by starting from the Flory-Huggins-de Gennes free-energy functional and numerically integrating the corresponding evolution equation for the conserved order parameter. We have carried out the calculations to late times and observe that the growth law for the characteristic domain size is independent of the quench depth contrary to Ref. 11. Nevertheless, our results are consistent with the claims of several other ex-

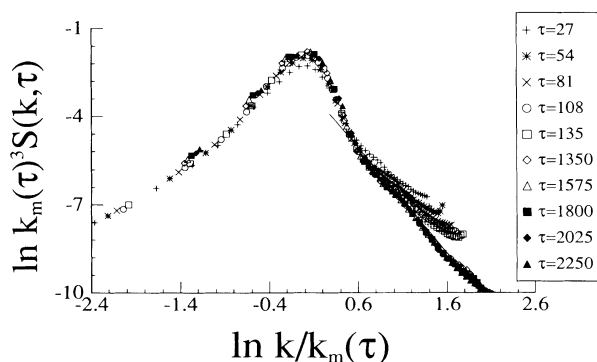


FIG. 4. Plot of the scaling function [Eq. (5)], in a log-log scale. The straight line is a fit to the data for large k , with a slope of -3.6 .

perimental investigations on different polymer mixtures. We also find that the dynamical scaling hypothesis is satisfied for both the structure factor and the pair correlation functions. However, scaling seems to be valid only at very late times. It will be interesting to carry out the calculations for a much larger time and for larger lattice sizes to study the scaling behavior more accurately. Also, it remains to be seen whether the quench-depth-dependent growth law observed in Ref. 11 arises from a wave-vector-dependent Onsager coefficient and/or a composition-dependent χ . We plan to address these questions in future publications.

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^(a)Permanent address: Departament de Fisica, Universitat de les Illes Balears, Palma de Mallorca, E-07010, Spain.

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