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Short-Range Fluctuations in the Spinodal Decomposition of Binary Polymer Mixtures

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ABSTRACT: Isothermal demixing after an instantaneous quench to below the spinodal of a binary polymer mixture was studied by using computer-simulation methods. Short-range fluctuations, corresponding to a large wavenumber q , were followed during the demixing. The results obtained provide a useful supplement to those based on a linearized version of Cahn's theory of spinodal decomposition (SD). The latter theory applies to *small* q regimes and to scattering experiments that cover a range of fluctuation wavelengths typically larger than the size of the polymer coils. However, fluctuations in wavelength on the order of the interaction range, i.e., the nearest-neighbor distance in the mixture, are not adequately described by the linearized theory; deviations are observed at very early stages of phase decomposition. In this regime thermodynamic, rather than diffusional, factors are paramount. In the present study spinodal decomposition for mixtures on a three-dimensional cubic lattice were simulated, and the corresponding kinetics were evaluated for a range of quench depths.

Introduction

The subject of polymer blends is now one of the most widely studied areas in the field of polymer material science. A thorough knowledge of the thermodynamics of polymer mixtures is necessary in the preparation and processing and in the control of the morphology of polymer blends. One special area of interest in the study of the thermodynamics of polymer mixtures is phase separation proceeding by spinodal decomposition (SC). In this process, a quench to an unstable region of the phase diagram is followed by a rapid appearance of a characteristic dimension, $2\pi/q$, throughout the system, where the parameter q is the wavelength of a sinusoidally modulated two-phase domain. The two-phase structure that appears is uniform and highly interconnected with a characteristic mesh size of concentration fluctuations. This process therefore differs from the nucleation process, which starts

nonuniformly at discrete isolated points.

Spinodal decomposition was first observed in mixtures of low molecular mass components,¹ and interest in this field was later extended to polymer mixtures.² Such mixtures are particularly well suited for these studies because of their high viscosity; thus the nucleation and growth mechanism that is characteristic for quenches to the metastable regime does not occur during the rapid quench from a stable through the metastable to the unstable regime of the phase diagram. Nishi et al.² were the first to apply the linearized Cahn-Hilliard¹ theory of SD used for mixtures of low molecular mass constituents to phase separation in polymer blends. Many studies have since appeared using light-scattering,^{3,4} X-ray,⁵ and small-angle neutron-scattering techniques⁶ for investigations of the concentration fluctuations in model systems. Scattering studies can investigate fluctuations in a $2\pi/q$ range that is larger than the typical size of a polymer coil, say, 100 Å. It is obvious that for fluctuations in this range the linearized SD theory developed for low molecular weight mixtures is applicable, and it has been found that

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the early stages of decomposition could be well accounted for in accord with the theory.

In this contribution we examine in contrast short-wavelength fluctuations in binary polymer mixtures. In the very early stages of decomposition, the kinetics of phase separation are controlled mainly by short-range interactions and not by diffusion processes. On the other hand, the linearized theory of SD is most applicable to longer wavelengths, the small- q domain, as has been discussed above. Given these limitations, it is of interest to examine short-wavelength fluctuations in the range of the segmental interaction distances at very early stages of SD which are mainly responsible for this regime. We have used a Monte Carlo (MC) simulation technique that is suitable for observing the very early stages of phase decomposition and is also applicable to small wavelength regimes, normally a delicate problem in experimental studies.

Theory

The theory has been well described, and only essential features are summarized. According to Cahn and Hilliard¹ the free energy F per volume element dv of an inhomogeneous mixture of small molecules is given by

$$F = \int [f(c) + k(\nabla c)^2 + \dots] dv \quad (1)$$

where $f(c)$ is the free energy density of the homogeneous mixture, c is the composition of the mixture in volume fraction units, and k is a positive constant. The second term describing excess free energy arises from the concentration gradient. The solution of a modified diffusion equation for the time, t , dependence of the concentration fluctuation, c , at a point r yields

$$c(r, t) - c_0 = \sum_q \exp(R(q)t) [A(q) \cos(qr) + B(q) \sin(qr)] \quad (2)$$

where $A(q)$ and $B(q)$ are the usual Fourier expansion coefficients, the amplification factor $R(q)$ is given by

$$R(q) = Dq^2 [-(\partial^2 f / \partial c^2) - 2kq^2] \quad (3)$$

q is the fluctuation wavenumber, c_0 is the initial value of the local composition, and D is the diffusion coefficient. From eq 3 it is obvious that when the mixture is stable to fluctuations ($\partial^2 f / \partial c^2$ being positive, a situation characteristic of nucleation and growth mechanisms of decomposition), the amplification factor is negative. On the other hand when the mixture is unstable to fluctuations ($\partial^2 f / \partial c^2$ being negative, characteristic of the SD mechanism), $R(q)$ is positive for values of q smaller than a critical value q_c ; hence, fluctuations can increase exponentially. In the SD regime there is thus a characteristic wavenumber q_m for fluctuations which increases rapidly with a corresponding maximum rate $R(q_m)$:

$$q_m^2 = q_c^2 / 2 = -(\partial^2 f / \partial c^2) / 4k \quad (4)$$

$$R(q_m) = -D(\partial^2 f / \partial c^2) / 8k \quad (5)$$

The intensity of the scattering observed experimentally from the fluctuations is proportional to the structure factor $S(q, t)$, a spatial Fourier transform of the concentration fluctuations. This is the quantity directly accessible by experiment.

The linearized theory was adapted to binary liquids composed of macromolecules^{7,8} by using the free energy of the blend obtained from an extended Flory-Huggins treatment and allowing for a slow spatial variation in composition. The relaxation rate obtained

$$R(q) = q^2 \Lambda(q) \left[2\chi - \frac{1}{Nc(1-c)} - \frac{a^2 q}{36c(1-c)} \right] \quad (6)$$

corresponds to eq 3. Here $\Lambda(q)$ is an Onsager transport coefficient and a is a constant of the order of monomeric dimensions. One of the major inadequacies of the Cahn-Hilliard theory, according to Cook,⁹ is associated with the omission of a term describing fluctuations in the stable mixture. Binder¹⁰ has modified the above approach taking into account such random thermal fluctuations. For the time dependence of the structure factor he obtained

$$S(q, t) = S(q, 0) \exp(-2t/\tau(q)) + S(q, \infty) [1 - \exp(-2t/\tau(q))] \quad (7)$$

where $-1/\tau(q) \equiv R(q)$. This expression satisfies the experimental condition that the fluctuations relax to the finite value $S(q, \infty)$ in the limit $t \rightarrow \infty$.

The time evolution of large wavelength fluctuations in the SD regime is controlled mainly by diffusion. Spinodal decomposition is accordingly often called diffusion-controlled phase separation. In the early stages of decomposition, however, the mixture is nearly homogeneous, and only small wavelength fluctuations are present. Demixing for this range of fluctuations with wavelength sizes in the monomer-monomer interaction range proceeds by a local adjustment⁷ of chains rather than by chain diffusion. The relaxation rate for the former process is greater than the relaxation of fluctuations with small q (proceeding in the later stages of SD) and is proportional to q^6 , differing from the standard q^2 dependency for diffusion.⁷ A change in $R(q)$ from exponential amplification to exponential decay is controlled entirely by thermodynamics, i.e., by the term in brackets on the right-hand side of eq 3. Thus the linear theory of the SD process cannot adequately describe phase separation in the early stages of demixing and in the range of small wavelengths. However, this region of SD is of interest if only because demixing ultimately originates from unfavorable interactions and necessarily starts in this range of fluctuation lengths.

Simulation Method

Quenches to an unstable region of a binary macromolecular mixture and the subsequent isothermal demixing process were followed by a Monte Carlo simulation technique. The simulation was performed for a set of macromolecules placed on a cubic lattice with $L = 22$ and with the usual periodic boundary conditions imposed. Equal chain lengths, $N_A = N_B = N = 20$, and compositions (volume fractions), $\phi_A = \phi_B = \phi = 0.4545$, were used for both types of chains. A small fraction of voids, $\phi_v = 0.0909$, afforded chain mobility. An interaction energy ϵ between adjacent A and B segments was applied with the usual steric restrictions, i.e., double occupancy of any lattice site was excluded. Standard reptation techniques¹¹ were used for moving the chains; this is the only method suited for simulations of lattice polymer systems at high densities. It may be noted that a more realistic algorithm for chain moves that should account for the cooperative nature of moves in dense ($2\phi \geq 0.9$), multichain systems is still lacking. The standard Metropolis algorithm was used to sample states with the correct thermodynamic distributions proportional to $\exp(-E/k_B T)$, where E is the energy of each configuration.¹² After an attempted move successfully satisfied the steric restrictions, it was accepted only if

$$\exp(-\Delta E/k_B T) \geq \xi \quad (8)$$

where ΔE is the change in total energy before and after

the attempted move and ξ is a random number between zero and unity. Thermodynamic averages were then calculated as arithmetic averages over acceptable configurations. Each time the configuration was rejected, the previous configuration was counted again in the average. When following the time evolution of the system, only spatial averages were calculated; thermodynamic averages were not included. Instead, the system was allowed to evolve according to eq 8, and instantaneous configurational properties were monitored continuously.

The calculations consisted of two stages: (1) The system was homogenized at a high temperature, $T \rightarrow \infty$, using $\epsilon' (\equiv \epsilon/k_B T) = 0$. Thus a zero interaction energy was applied to an arbitrary configuration, and the system was allowed to homogenize to equilibrium by using 3×10^7 reptation moves. The configurational properties reached the values corresponding to the polymer melt and were tested by calculating the mean-square end-to-end distance as previously described.¹³ (2) The quench into an unstable region outside the spinodal curve was then performed by an instantaneous change of ϵ' to a selected constant positive value in the range $0.05 < \epsilon' < 0.3$. This represented an instantaneous decrease of temperature (here assuming UCST behavior) to an unstable region of the phase diagram. It should be noted that the binodal and spinodal phase boundaries were crossed simultaneously because of the symmetry of the system. Thus the indications are that the consequent isothermal demixing will proceed by SD and not by nucleation and growth. The time after the quench was assumed to be proportional to the number of reptation moves required by the system to relax. It was of interest to investigate small wavelength fluctuations during the decomposition; thus we have been concerned with and calculated the instantaneous spatial average number of heterocontacts per monomer unit in the mixture, $N_{AB}(t)$.

Results and Discussion

We postulate that the average number of heterocontacts in the mixture is a measure of the small wavelength concentration fluctuations in the limit $2\pi/q \rightarrow a$. Quantitatively the distribution of concentration fluctuations in the mixture is given by the pair correlation function $G(r,t)$ and the structure factor $S(q,t)$ in the following forms:

$$G(r,t) = (1/n) \sum_i \eta(r_i,t) \eta(r_i+r,t) \quad (9)$$

$$S(q,t) = \sum_r \exp(iqr) G(r,t)$$

where the summations in (9) is over all monomer units in the mixture, n . The product of the occupation variable η at position r_i and $r_i + r$ is unity if a heteropair is encountered and zero otherwise. The search for heteropairs and the summation were made for each site r_i radially over all sites within a distance r . In the present case $r = a$; hence, $G(a,t)$ is simply twice the average number of nearest-neighbor heterocontacts $N_{AB}(t)$ in the mixture (each contact pair being counted twice in (9)). Notice that $G(a,t)$ then differs from the corresponding structure factor $S(q,t)$ only by a constant prefactor, and the time dependence of $S(q,t)$, $G(a,t)$, and $N_{AB}(t)$ is the same:

$$S(q,t) \propto G(a,t) = 2N_{AB}(t) \quad \text{for } r = a \quad (10)$$

Figures 1 and 2 depict the time dependences of $G(a,t)$ after the discontinuous temperature quenches to different depths below the spinodal have been applied. The interaction energy ϵ' was changed instantaneously from zero to a value in the range 0.05–0.3, which corresponds to the change in reduced temperature from infinity to a constant

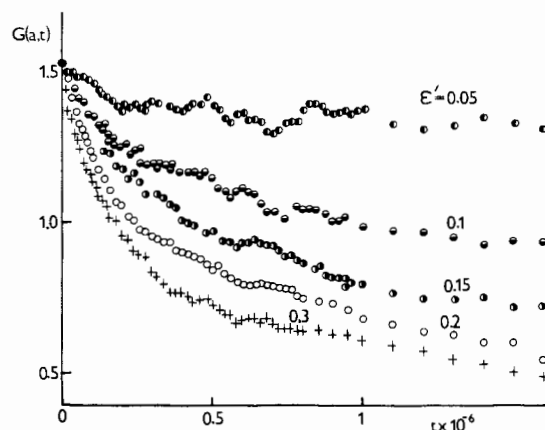


Figure 1. Initial time dependence of the short-range correlation function $G(a,t)$, defined in the text, for various quenches $0.05 \leq \epsilon' \leq 0.3$. The time is expressed in number of MC steps. (●) indicates the value corresponding to the homogeneous mixture for which $\epsilon' = 0$.

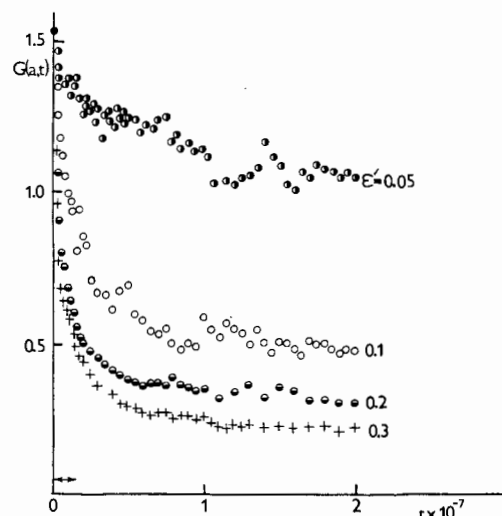


Figure 2. Complete demixing process shown in the same manner as in Figure 1. The initial region shown in expanded form in Figure 1 is indicated by arrows.

value $T' = 1/\epsilon'$. The consolute point for this finite system is reached for a value of $\epsilon' = 0.05$ as was shown in our previous study on the mixing/unmixing transition.¹³ This value of ϵ' was also obtained by interpolating values of critical temperatures in blends composed of chains with lengths $N = 4, 16$, and 32 calculated by Sariban and Binder¹⁴ ($k_B T_c / \epsilon = 1/\epsilon' = 20.1$ for $N = 20$). From Figures 1 and 2 one can recognize a general nonexponential decay in $G(a,t)$. The exponential-like decay in the expanded time scale shown in Figure 1 is present over only a small range of time in the overall demixing shown in Figure 2 and is followed by a long tailing effect. Substantial fluctuations in the decay curve and a slower relaxation are observed for the system quenched to the critical spinodal region ($\epsilon' = 0.05$). These fluctuations tend to diminish and disappear as deeper quenches below the spinodal were imposed. The fluctuations in the decay curve that are still present in Figure 1 are very probably due to finite size effects in the system. The fluctuations arise from the formation and release of constraints (entanglements) in the mixture that are not compensated for during demixing by an opposite process occurring somewhere else in the mixture as would be found in larger systems.

The kinetics of demixing according to eq 7 were evaluated by plotting the variable $Y = \ln \{ [G(a,t) - G(a,\infty)] / [G(a,0) - G(a,\infty)] \}$ as a function of time (Figure 3). From

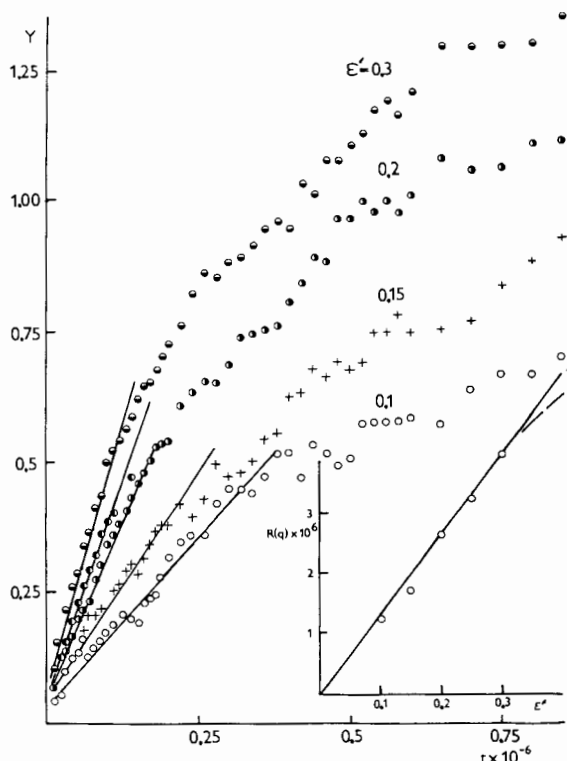


Figure 3. Semilog plot of the kinetic variable $Y \equiv [G(a,t) - G(a,\infty)]/[G(a,0) - G(a,\infty)]$ versus time for different temperature quenches below the spinodal. The insert depicts the variation of the rate factor $R(q)$, in inverse time units, with ϵ' .

the slope one may obtain the rate factor $R(q)$. It can be seen in Figure 3 that the deviations from linearity start in the very early stages of the decomposition. After the linear period, the rate decreases in a Ostwald ripening process which is caused by saturation effects. The period of linearity is only a small fraction (ca. $1/100$) of the overall demixing shown in Figure 2. This result agrees with observations by Hashimoto et al.,³ who found that at a given thermodynamic driving force (undercooling or superheating ΔT) deviations begin earlier for fluctuations with larger q than for those with smaller q . In the present case, working at large q limits, the deviations accordingly start at very early stages of decomposition. Also in agreement with the earlier observations³ we can confirm that at a given q , the greater the value of quench depth ΔT , the earlier the deviation begins. Thus Figure 3 shows a longer period of linearity for quenches with lower ϵ' . The asymptotic slopes of the short linear dependence of Y versus time satisfy the required proportionality of the rate factor to repulsion in the mixture, i.e., $R(q) \propto \chi$, according to eq 6. In fact Figure 3 shows $R(q)$ as a function of ϵ' ,

instead of χ , though this is equivalent because of the validity of the classical relation $\chi = \epsilon z/kT$, where z is the coordination number of the lattice. For repulsions of the order of $\epsilon' \leq 0.3$, we observe that the rate factor $R(q)$ is linearly proportional to repulsion. For larger values of ϵ' (not shown) a slowing is also observed for the initial slopes. Saturation in $R(q)$ versus ϵ' is analogous to that of χ versus ϵ' observed in the previous equilibrium study.¹³ However in this case in the initial stages of decomposition we observe saturation for larger positive ϵ' values than when reaching equilibrium since the present system is nearly homogeneous. While in the equilibrium study the leveling of the values began near the spinodal, $\epsilon' = 0.05$, in this case $R(q)$ is nonlinear with ϵ' for $\epsilon' > 0.3$. Following the kinetics at different quench depths also yields information about the major factors in the control of demixing. Inspection of eq 3 shows that the temperature dependence of $R(q)$ is determined by the two opposing temperature dependences of D and of the thermodynamic term in brackets in the equation. Since a deeper temperature quench by undercooling leads to a faster relaxation to equilibrium, we conclude that demixing is mainly controlled not by diffusion but by thermodynamics.

We have monitored the kinetics of phase separation in the unstable region and have shown that short wavelength fluctuations, from which the demixing originates (monomer-monomer repulsion) are not adequately described by the existing linearized diffusion theory of SD. This is in contrast to the behavior of the long wavelength fluctuations. The initial linear behavior is limited to very early stages of demixing, and the process may be said to be controlled by thermodynamics and not diffusion.

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