Structure Evolution during Spinodal Decomposition of Polymer Blends

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ABSTRACT: The evolution with time of the structure factor of a polymer mixture after a step from the one-phase region into a spinodal range is analyzed on the basis of the theory developed by Binder. The solution of the equation of motion which includes the effect of the random thermal forces provides a picture which differs in the short-time behavior from the predictions of the Cahn–Hilliard model. For all wave vectors q an increase in the intensity is expected; the point of intersection common to all curves which is characteristic for the Cahn–Hilliard model does not show up. It appears generally difficult to extract relaxation times for q values above the growth rate maximum from a time-dependent scattering experiment.

Introduction

In recent work on the kinetics of unmixing in polymer blends by Hashimoto et al.[1] and Snyder et al.[2] attempts were made to interpret the results of time-dependent light-scattering experiments on the basis of the Cahn–Hilliard theory of spinodal decomposition.[3] This theory, which first was developed to treat unmixing phenomena in metal alloys and inorganic glasses, was modified and extended by de Gennes[4] and Pincus[5] to be applicable for polymer blends. Hashimoto et al.[1] and Snyder et al.[2] compare their results with the theoretical predictions and find accordance for the early stages of unmixing.

The fact is that the Cahn–Hilliard treatment is incomplete, one shortcoming being the neglect of the random thermal forces responsible for the concentration fluctuations. Their effect has first been treated by Cook[6] and then included in all further treatments.[7] The large majority of experimental observations on metal alloys and inorganic glasses can be explained only by the extended theories.[7] The Cahn–Hilliard model here generally turned out to be insufficient.

In a recent paper Binder[8] thoroughly reconsidered the dynamics of concentration fluctions in polymer blends. The equations derived for the time dependence of the structure factor after a temperature jump do include the effect of thermal fluctuations. Applying these equations to the problem of interest, the structure evolution after a quenching step into the spinodal range, we are led to a picture which differs in some essential aspects from that given by the Cahn–Hilliard model. We begin with a summary of de Gennes', Pincus', and Binders' work and then present our results.

Cahn–Hilliard Model of Polymer Blend Unmixing

Starting from the Flory–Huggins expression for the free energy density of a polymer blend and extending it to account for slow spatial concentration variations, de Gennes[4] derived a relaxation equation for concentration fluctuations with wavenumber q (eq 3.5 in ref 4).

$$\frac{\mathrm{d}}{\mathrm{d}t}\delta\phi_q = -q^2\Lambda(q)\left(\frac{1}{N\phi(1-\phi)} + \frac{\sigma^2q^2}{36\phi(1-\phi)} - 2\chi\right)\delta\phi_q \tag{1}$$

Here a symmetrical blend is assumed with the same degree of polymerization $N_A = N_B = N$ and identical segment lengths $\sigma_A = \sigma_B = \sigma$ for both species. ϕ denotes the average volume fraction of polymer A, and χ the Flory–Huggins interaction parameter. $\delta\phi_q$ describes the amplitude of a concentration wave with wavelength $2\pi/q$. $\Lambda(q)$ is the Fourier transform of the Onsager coefficient which specifies the (nonlocal) linear relation between the flux of species A and the gradient of the chemical potential difference $\mu_A - \mu_B$.

$\delta\phi_q$ can be measured by a neutron-, X-ray-, or light-scattering experiment. The scattering intensity measured at q is determined by the structure factor

$$S(q) = \langle|\delta\phi_q|^2\rangle \tag{2}$$

If the solution of eq 1

$$\delta\phi_q(t) \sim \exp(-\tau_q^{-1}t)$$

with

$$\tau_q^{-1} = q^2\Lambda(q)\left(\frac{1}{N\phi(1-\phi)} - 2\chi + \frac{\sigma^2q^2}{36\phi(1-\phi)}\right) \tag{3}$$

is inserted into eq 2, the time dependence of the structure factor becomes

$$S(q,t) = S(q,0)\exp(-2\tau_q^{-1}t) \tag{4}$$

In the spinodal range the relaxation rate τ_q^{-1} changes its sign at a certain $q = q_c$. It is

$$\tau_q^{-1} < 0 \qquad \text{for } q < q_c$$

which means that the blend is unstable against concentration fluctuations with long wavelengths $q < q_c$. During the initial stage of phase separation, directly after a temperature (or pressure) step from the one-phase region into the spinodal range, structure factors $S(q,t)$ should shown an exponential increase for $q < q_c$, a decay for $q > q_c$, and a constant value for $q = q_c$. According to eq 3 the growth rate $-\tau_q^{-1}$ vanishes for $q = 0$ and then increases and goes over a maximum at $q_m = q_c/2^{1/2}$. It is the view of the Cahn–Hilliard model that the concentration waves with maximal growth rates at q_m will dominate the initial stages of unmixing and determine the length scale of the developing two-phase structure.

Equation of Motion for the Structure Factor

The Cahn–Hilliard treatment has a shortcoming: It does not yield the correct equilibrium structure factor in the one-phase region. Cook[6] removed this deficiency by including in the treatment the effect of random thermal forces. Binder[8] follows Cook's procedure and derives the following equation of motion for the structure factor $S(q,t)$ (eq 2.20 of ref 8):

$$\frac{\mathrm{d}S}{\mathrm{d}t}(q,t) = -2q^2\Lambda(q)\left[\left(\frac{1}{N\phi(1-\phi)} - 2\chi + \frac{\sigma^2q^2}{18\phi(1-\phi)}\right)S(q,t) - 1\right] \tag{5}$$

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Equation 5 has a nonvanishing stationary solution

$$\frac{dS}{dt} = 0 \rightarrow S_\chi(q) = 1/\left(\frac{1}{N\phi(1-\phi)} - 2\chi + \frac{\sigma^2 q^2}{18\phi(1-\phi)}\right) \tag{6}$$

In the one-phase region $S_\chi(q)$ is finite and positive for all q. The stationary solution here represents the structure factor in thermal equilibrium. It shows the well-known Ornstein–Zernicke form.

It is obvious that eq 5 correctly describes the structure relaxation after temperature steps within the one-phase region. The essential point made by Cook was that eq 5 should also be used for the initial stages of spinodal decomposition. For χ values in the spinodal range of the phase diagram the function $S_\chi(q)$ given by eq 6 shows a singularity at $q = q_c$, being negetive for smaller wavenumbers $q < q_c$ and positive for larger ones $q > q_c$. For $q > q_c$ the function $S_\chi(q)$ describes a metastable structure factor approached in the early stages of spinodal decomposition.

The equation of motion eq 5 is restricted to wavenumbers

$$q \ll R_G^{-1}$$

where R_G denotes the unperturbed radius of gyration of the polymer molecules

$$R_G^2 = N\sigma^2/6$$

A generalization and extension to a larger range of q values

$$q \ll \sigma^{-1}$$

is achieved[8] by replacing the Ornstein–Zernicke expression eq 6 by the complete equilibrium structure factor as given by the dynamical random phase approximation[9]

$$S_\chi^{-1}(q) = \frac{1}{N\phi(1-\phi)} f_D^{-1}(x) - 2\chi \tag{7}$$

where $f_D(x)$ denotes the Debye structure factor of noninteracting ideal chains

$$f_D = (2/x)[1 - (1 - \exp(-x))/x] \tag{8}$$

with

$$x = q^2 R_G^2$$

The general equation of motion thus obtained is

$$S(q,t)/dt = -2q^2\Lambda(q)S_\chi^{-1}(q)[S(q,t) - S_\chi(q)] \tag{9}$$

with $S_\chi^{-1}(q)$ being given by eq 7. Binder shows that the equation of motion eq 5 valid for low wavenumbers follows by a series expansion of $S_\chi^{-1}(q)$ in eq 7 up to second-order terms in q.

Equation 9 has the typical form of irreversible equations of motion in the linearization approximation and can be solved immediately:

$$S(q,t) = S_\chi(q) + (S(q,0) - S_\chi(q)) \exp(-2\tau_q^{-1}t) \tag{10}$$

$$\tau_q^{-1} = q^2\Lambda(q)S_\chi^{-1}(q) \tag{11}$$

Equation 10 describes a transition from an arbitrary initial state $S(q,0)$ away from equilibrium to a final state $S_\chi(q)$, the relaxation rates $2\tau_q^{-1}$ being those effective at the annealing temperature. In the one-phase region $S_\chi(q)$ constitutes the equilibrium structure factor; in the spinodal range it corresponds to a "virtual" structure factor, which sets the direction of change in the early stages of unmixing.

A comparison shows the approximations and neglects included in the Cahn–Hiliard model. For $q \ll R_G^{-1}$ the Cahn–Hilliard model yields the correct relaxation rates τ_q^{-1}. However, as shown by eq 10, they should be associated not with an exponential growth or decay of the initial structure factor $S(q,0)$ (eq 4), but with the transition to the (virtual) final structure factor $S_\chi(q)$. A neglect of $S_\chi(q)$ is only possible for

$$S(q,t=0) \gg |S_\chi(q)|$$

which is rarely the case. In particular, the condition for constancy of the intensity is changed. The Cahn–Hilliard model predicts

$$S(q,t) = \text{constant for } \tau_q^{-1} = 0 \tag{12}$$

which is the case for $q = q_c$. The condition set by Cook's treatment is different, namely, according to eq 10

$$S(q,0) = S_\chi(q) \tag{13}$$

We shall show that for polymers in the case of interest, a quenching step from the one-phase region into the spinodal range, this is never fulfilled.

Authors[4,5,8] use for the Onsager coefficient $\Lambda(q)$ that of ideal noninteracting chains which perform a Rouse or a reptation motion. The expressions given by Binder are

$$\Lambda(q) \simeq W\sigma^2\phi(1-\phi)f_D \quad \text{(Rouse motion)} \tag{14a}$$

$$\Lambda(q) \simeq \frac{Wd^2}{N}\phi(1-\phi)f_D \quad \text{(reptation)} \tag{14b}$$

Here W denotes the elementary jump rate of the segments; d gives the diameter of the tube, which restricts the reptative motion. The relaxation rates τ_q^{-1} follow from eq 11 together with eq 7:

$$\tau_q^{-1} \simeq \frac{6}{\tau_R} x\left(1 - \frac{\chi}{\chi_s} f_D(x)\right) \tag{15}$$

where $\chi_s = 1/2N\phi(1-\phi)$ denotes the value of χ at the spinodal (eq 26, Figure 2). The fundamental time τ_R is

$$\tau_R = N^2/W \quad \text{for Rouse motion}$$

or

$$\tau_R = N^2\sigma^2/(Wd^2) \quad \text{for reptation}$$

In both cases, Rouse motion and reptation, τ_R describes the time required by a polymer molecule to diffuse over a length comparable to its own size $N^{1/2}\sigma$. The two modes show a different molecular weight dependence. The temperature dependence $\tau_R(T)$ is the same for both models and enters via the segmental jump rate $W(T)$. Equation 15 is valid after all internal modes of the molecules have relaxed, i.e., for times $t > \tau_R$. The limiting behavior for small and larger x becomes

$$\tau_q^{-1} \simeq (6/\tau_R)\left(1 - \frac{\chi}{\chi_s}\right)x \quad \text{for } x \ll 1 \tag{16}$$

$$\tau_q^{-1} \simeq (6/\tau_R)x \quad \text{for } 1 \ll x\ (\ll\sigma^2) \tag{17}$$

For small values of x a critical slowing down is expected on approaching the spinodal. For large values of x the relaxation times lie in the order of τ_R and become independent of the interaction.

Time Dependence of Structure Factor in Quenching Experiments

Figure 1 shows the structure factor of polymer blends as given by the random phase approximation, eq 7, in a

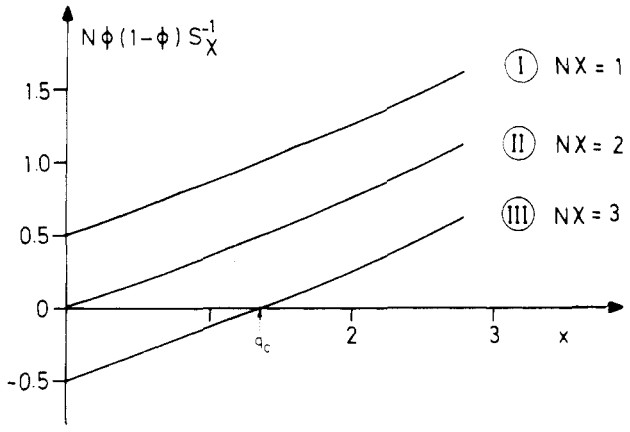

Figure 1. Structure factors of symmetric polymer blends as given by the random phase approximation eq 7: (I) one-phase region, (II) spinodal, (III) virtual structure factor in two-phase region.

plot of $N\phi(1-\phi)S_\chi^{-1}(q)$ vs. $x = q^2R_G^2$ for different values of $N\chi$ ($\phi = 0.5$). Curve I corresponds to the equilibrium situation in the one-phase region; S_χ^{-1} is positive for all q. Curve III is obtained in the spinodal region. Here the (virtual) structure factor becomes negative for $q < q_c$. Curve II is that found at the spinodal line, where $S_\chi^{-1}(q=0) = 0$, i.e., $S_\chi(q\to 0) \to \infty$.

Initiation of spinodal decomposition means that starting from the one-phase region, say curve I, a step is performed into the spinodal range, say to curve III. Since curves I and III are parallel to each other without a point of intersection, one has to expect for all q values an increase of the structure factor at the first stage of the unmixing process. There is no point q which fulfills Cook's condition for a constant intensity, eq 13. This is in striking contrast to the behavior of the Cahn–Hilliard model, which predicts a constant intensity at $q = q_c$ and a decay for large wavenumbers.

The initial growth rates

$$R(0) = \frac{\mathrm{d}\ln S}{\mathrm{d}t}(q,t=0) \tag{18}$$

can be easily calculated. We write down the equation of motion for the reciprocal structure factor

$$\frac{\mathrm{d}}{\mathrm{d}t}S^{-1}(q,t) = -S^{-2}\frac{\mathrm{d}}{\mathrm{d}t}S(q,t)$$

$$= S^{-1}(q,t)(2q^2)\Lambda(q)(S_\chi^{-1}(q) - S^{-1}(q,t))$$

and obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\ln S^{-1}(q,t) = 2q^2\Lambda(q)(S_\chi^{-1}(q) - S^{-1}(q,t)) \tag{19}$$

Considering that (eq 7)

$$S_\chi^{-1}(q) - S^{-1}(q,t=0) = -2(\chi - \chi_0) = \text{constant} \tag{20}$$

where χ_0 denotes the interaction parameter in the one-phase region before the temperature step and χ that in the spinodal raange after quenching, one arrives at the simple result

$$\frac{\mathrm{d}}{\mathrm{d}t}\ln S^{-1}(q,t=0) = -4q^2\Lambda(q)(\chi - \chi_0) = -R(0) \tag{21}$$

This result is qualitatively different from the prediction of the Cahn–Hilliard model

$$R(0) = -2\tau_q^{-1} = -2q^2\Lambda(q)S_\chi^{-1}(q)$$

First and most important, the initial growth rate $R(0)$ does not show critical behavior. The critical slowing down exhibited by the relaxation rate τ_q^{-1} is not reflected in $R(0)$. $R(0)$ is solely determined by the Onsager coefficient $\Lambda(q)$ and therefore is largely insensitive to the chain interactions. In terms of the initial growth rate $R(0)$ the spinodal curve does not constitute a point of discontinuity. The building up of critical fluctuations after a quench to a temperature near to the spinodal in the one-phase region will follow similar kinetics as the begin of unmixing at an adjacent temperature just underneath the spinodal curve.

The question arises how the relaxation rates τ_q^{-1} can be extracted from time-dependent scattering data. There are no problems for quenching experiments within the one-phase region. Here the relaxation rates follow from

$$\frac{\mathrm{d}\ln (S(q,t) - S_\chi(q))}{\mathrm{d}t} = -2\tau_q^{-1} \tag{22}$$

where

$$S_\chi(q) = S(q,t\to\infty)$$

This procedure cannot be simply transferred to studies of unmixing after quenches into the spinodal range. Here $S_\chi(q)$ is a virtual structure factor which cannot be measured in a direct way. In this case evaluation has to be based on later stages of spinodal decomposition rather than the initial growth rates $R(t=0)$. For

$$-\tau_q^{-1}t \gg 1 \tag{23}$$

eq 10 predicts an exponential growth

$$S(q,t) \sim \exp(-2\tau_q^{-1}t)$$

and therefore

$$\frac{\mathrm{d}\ln S(q,t)}{\mathrm{d}t} = -2\tau_q^{-1} \tag{24}$$

Principally this procedure is restricted to wavenumbers

$$q < q_c$$

since the prerequisite is

$$\tau_q^{-1} < 0$$

In practice it should work well for q values around the growth rate maximum at q_m.

Examples

Figure 2 shows the phase diagram of a symmetric polymer mixture.[9] The critical point is located at $\phi = 0.5$, $N\chi = 2$. The binodal is given by the equation

$$N\chi_b = \frac{1}{2\phi - 1}\ln\frac{\phi}{1-\phi} \tag{25}$$

and the spinodal given by

$$N\chi_s = \frac{1}{2\phi(1-\phi)} \tag{26}$$

We have calculated the evolution with time of the structure factor for different quenching experiments starting with an equilibrium state in the one-phase region (points I and II in Figure 2). Using eq 10 together with (eq 7)

$$S(q,0)^{-1} = \frac{1}{N\phi(1-\phi)}f_D^{-1}(x) - 2\chi_0$$

$$S_\chi(q)^{-1} = \frac{1}{N\phi(1-\phi)}f_D^{-1}(x) - 2\chi_1$$

where χ_0 is the interaction parameter in the initial one-

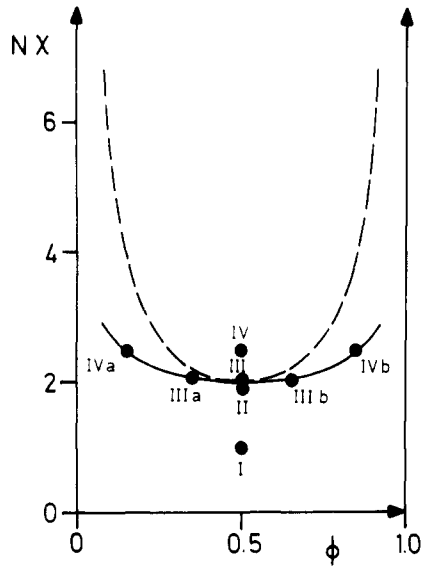

Figure 2. Phase diagram of symmetric polymer blend, the binodal being given by a continuous line, the spinodal by a broken line. The critical point is at $N\chi = 2$, $\phi = 0.5$.

phase state and χ_1 its value after quenching, a straightforward transformation gives

$$\frac{S}{N}\left(x,\tilde{t}=6\frac{t}{\tau_R}\right) = \phi(1-\phi)f_D(x)\frac{f_0(x)\exp(2\tilde{t}xf_1 + f_1 - f_0)}{f_0 f_1 \exp(2\tilde{t}xf_1)} \tag{27}$$

with

$$f_{1/0} = 1 - 2\phi(1-\phi)N\chi_{1/0}f_D(x) = 1 - \frac{\chi_{1/0}}{\chi_s}f_D(x)$$

The scale in q space is determined by the coil size ($x = R_G^2q^2$), and the time scale by the fundamental Rouse or reptation time τ_R. The time development of the structure factor depends on the interaction parameter before and after quenching, χ_0 and χ_1.

Figure 3a,b shows the evolution with time of the structure factor after quenching a system from $N\chi_0 = 1$ (point I in Figure 2) to $N\chi_1 = 2.5$ (spinodal range; point IV). Figure 3a depicts the initial stages ($t \sim \tau_R$), and Figure 3b the later stages in the time range $t \sim -\tau_{q_m}$. For all values of x an intensity increase is observed. Within times in the order of τ_R a peak appears at $x \approx 0.6$. The peak shifts to lower wavenumbers and approaches in the later stages of the development the location predicted by the Cahn–Hilliard model ($x_c = 0.68$; $x_m = x_c/2 = 0.34$). For $x > x_c$ the virtual structure factor $S_\chi(x)$ is approached, for $x \gtrsim 1$ within times in the order $t \sim \tau_R$, just as expected from eq 17.

The curves shown represent the first stages of spinodal decomposition which are then followed by coarsening processes. Coarsening finally leads to a macroscopic separation into two phases, with compositions as given by the points IVa,b on the binodal in Figure 2. The structure factor for this two-phase equilibrium state can be determined by eq 7, setting $N\chi = N\chi_1 = 2.5$ and $\phi = \phi_{binodal} = 0.15$ (or 0.85). As shown in Figure 3a, this final structure factor lies for all x values below the original values $S(q,t=0)$. We have therefore to expect for the overall time dependence of $S(q)$ for all wavenumbers after the initial increase a maximum and then a decrease down to the new equilibrium values.

Figure 4 shows the time dependence of the structure factor if the original one-phase state is located near to the spinodal (point II in Figure 2) and therefore exhibits strong concentration fluctuations. The quenching goes to $N\chi_1 = 2.5$ as in the previous case. Again for all x an intensity increase is observed. The short-time behavior is different from the first example. A shoulder rather than a peak appears (Figure 4a). The later stage of the structure evolution in the time range $t \sim -\tau_{q_m}$ (Figure 4b) corresponds again to that predicted by the Cahn–Hilliard model. At these times the original state becomes unimportant.

Figure 5 shows the results of a quenching experiment where the step goes to an unstable state near to the spinodal, $N\chi_0 = 1 \rightarrow N\chi_1 = 2.05$ (point III in Figure 2). In the short time range $t \sim \tau_R$ a peak shows up (Figure 5a). The further structure evolution is slow compared to the first examples. The Cahn–Hilliard regime is reached at much later times, which reflects the increase in $-\tau_{q_m}$, i.e., the critical slowing down. The two-phase equilibrium structure factor (calculated for the points IIIa,b on the binodal, Figure 2) here lies above $S(q,t=0)$. In this case a direct approach of the final structure factor is principally possible. Whether a direct approach occurs or the inten-

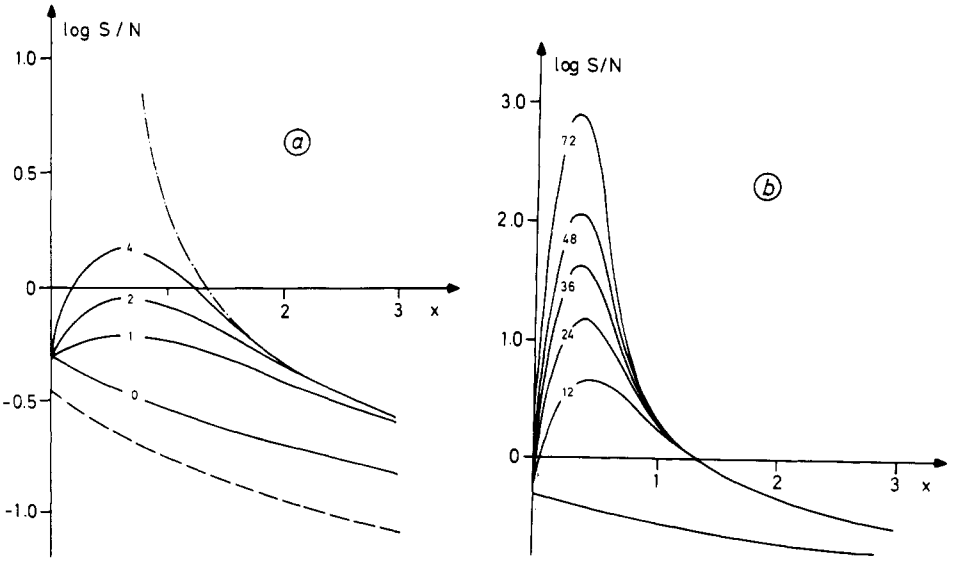

Figure 3. Time dependence of structure factor after a quench from $N\chi_0 = 1.0$ (one-phase region) to $N\chi_1 = 2.5$ (two-phase region). Times are given in units of $\tilde{t} = 6t/\tau_R$: (a) short-time behavior; (b) behavior in the time domain $t \sim -\tau_{q_m}$. The virtual structure factor $S_{\chi_1}(q)$ (–·–) and the two-phase equilibrium structure factor (– – –) are indicated.

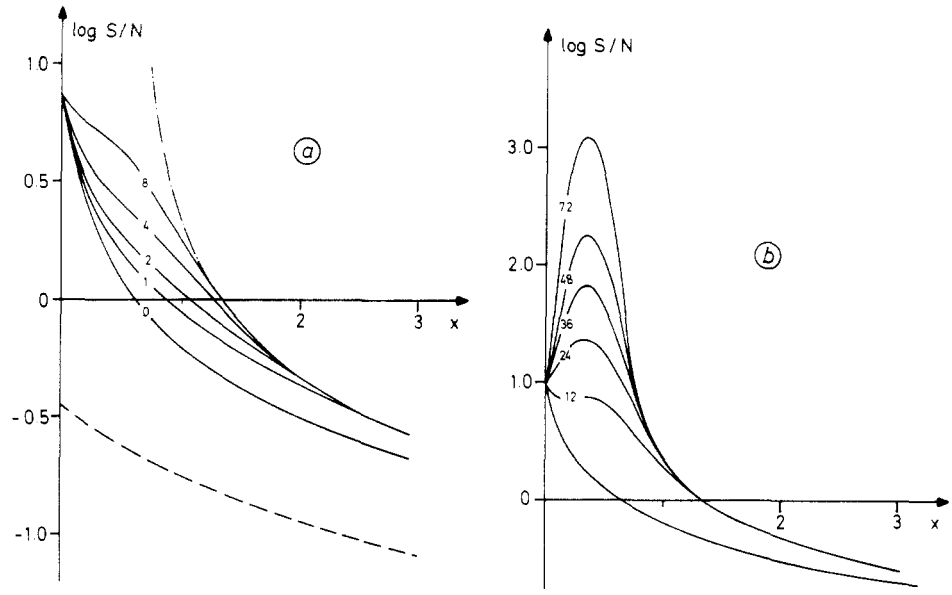

Figure 4. Time dependence of structure factor for a quenching experiment $N\chi_0 = 1.95 \rightarrow N\chi_1 = 2.5$: (a) short-time behavior; (b) time domain $t \sim -\tau_{q_m}$. Virtual structure factor S_{χ_1} (-·-) and two-phase equilibrium structure factor (---).

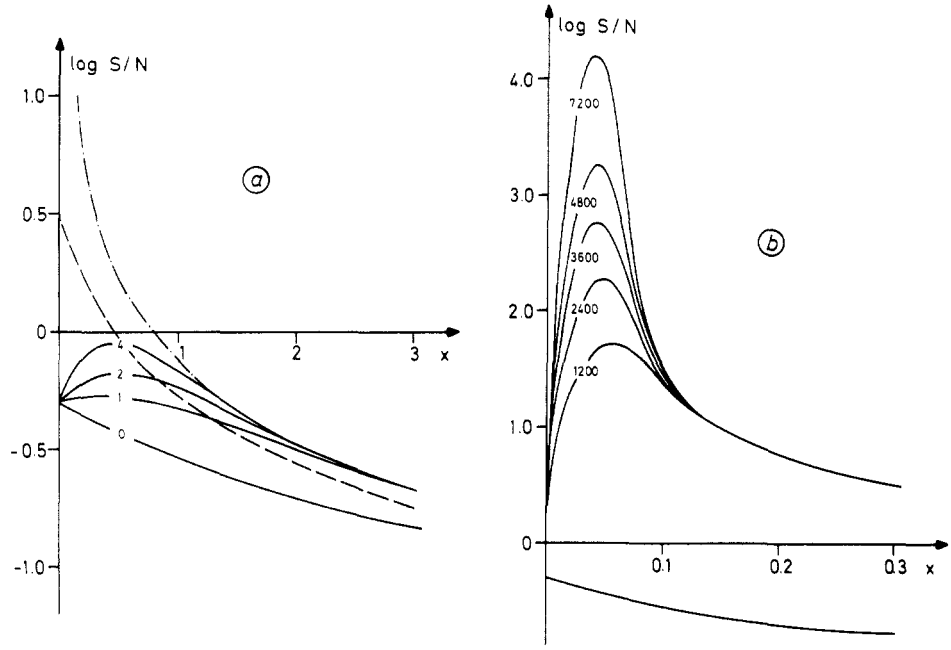

Figure 5. Time dependence of structure factor for a quenching experiment $N\chi_0 = 1.0 \rightarrow N\chi_1 = 2.05$: (a) short-time behavior; (b) time domain $t \sim -\tau_{q_m}$. Virtual structure factor $S_{\chi_1}(q)$ (-·-) and two-phase equilibrium structure factor (---).

sities are first going over a maximum will depend on the time of onset of coarsening.

Figure 6 finally shows the result of a quenching experiment within the one-phase region, $N\chi_0 = 1 \rightarrow N\chi_1 = 1.95$. The equation of motion here provides a complete description of the transition. It is interesting to note that the building up of the critical fluctuations is associated with the transient occurrence of a peak. As expected the initial kinetics are very similar to that of the spinodal decomposition at $N\chi_1 = 2.05$.

Conclusion

The analysis has shown that the unmixing of a polymer blend initiated by a quenching step across the spinodal in the first stages of evolution is associated for all wavenumbers q with an increase of the intensity. A point of intersection common to all curves $S(q,t)$ and an intensity decay for the higher wavenumbers, as it is predicted by the Cahn–Hilliard model, cannot be expected to occur.

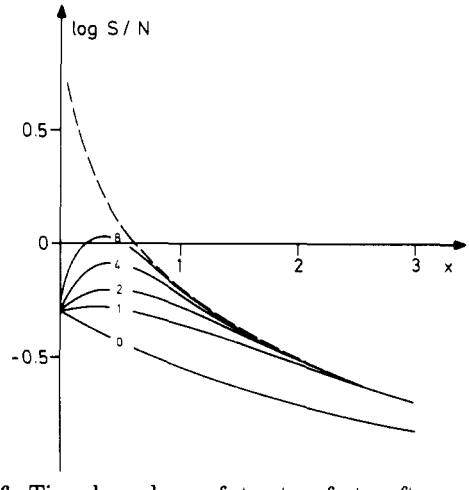

Figure 6. Time dependence of structure factor after a quenching step within the one-phase region ($N\chi_1 = 1.0 \rightarrow N\chi_1 = 1.95$).

It appears principally difficult to extract the relaxation times τ_q for $q > q_c$ from time-dependent scattering data. For experimental studies changes in the scattering intensity have to occur on the time scale of minutes. This can be accomplished for two different situations:

(a) Studies can be conducted, as Hashimoto et al.[1] and Snyder et al.[2] in their light-scattering experiments did, near to the critical temperature, where diffusion becomes slow. These experiments can yield relaxation times τ_q for q values up to the range around the growth rate maximum, provided that coarsening does not interfere. Relaxation times for higher q values are principally unattainable. For $qR_G > 1$ the structure usually has already relaxed before the measurements can start ($\tau_{x>1} \sim \tau_R \ll -\tau_{q_m}$); for $q > q_c$ the asymptotic equation (24) does not hold. The growth rates $R = \mathrm{d} \ln S(q,t)/\mathrm{d}t$ at times $t \gtrsim -\tau_{q_m}$, which are obtained by the experiment, will pass over a maximum at q_m and then continuously approach zero. Negative values of R, if they occur, are indicative of coarsening. They should not be associated with the exponential decay regime of the Cahn–Hilliard model.

(b) For suitable systems it is possible to perform a deep quench which transfers the blend to temperatures near to the glass transition. Here the fundamental diffusion time τ_R becomes sufficiently slow to enable time-dependent measurements. For deep quenches also the relaxation time at the growth rate maximum, $-\tau_{q_m}$, is on the order of τ_R (eq 17). In this case the structure evolution can be studied continuously from the initial stages up to the Cahn–Hilliard regime by using X-rays or neutrons. Analysis has to be based on the general equation of motion eq 9 rather than on the Cahn–Hilliard model. Relaxation times τ_q for $q > q_c$ can be determined only if the metastable structure factor $S_\chi(q)$ is reached before the onset of coarsening. We are performing studies on such deep quenches and shall give a report in a forthcoming paper.

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The Scanning Method with a Mean-Field Parameter: Computer Simulation Study of Critical Exponents of Self-Avoiding Walks on a Square Lattice

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ABSTRACT: The scanning method is a computer simulation technique for polymer chains applicable to a wide range of chain models (e.g., self-avoiding walks (SAWs), self-interacting SAWs, multiple-chain systems, chains which are subject to geometrical constraints such as boxes and tubes, etc.). In this paper we significantly improve the efficiency of the scanning method by incorporating a "mean-field" parameter. The method is applied to SAWs on a three-choice square lattice, where chains of up to 799 steps are studied. We obtain the critical exponents, $\gamma = 1.333$ (4) (which is smaller than Nienhuis's exact value), $\alpha = 0.5$ (1), and the connective constant $\mu = 2.6383$ (1). The data for the radius of gyration and for $\langle R^p \rangle$ (where R is the end-to-end distance and $p = 2$ and 4) are consistent with $\nu = 0.75$ and $\langle R^p \rangle \sim N^{p\nu}$. However, for $p < 0$, the behavior is different: $\langle R^p \rangle \sim N^{-f_p}$, where $f_p \neq \nu p$ and f_p is bounded from above by $f_\infty = 2\nu + (\gamma - 1) = 1.8437...$. For example, we obtain $\langle R^{-2} \rangle \sim N^{-1.4} \neq N^{-2\nu} = N^{-1.5}$. These results for $p < 0$ should be taken into account when calculating the diffusion coefficient with the help of Kirkwood's theory.

Introduction

The scanning method is a computer simulation technique for polymer chains that I recently suggested.[1,2] The method has been applied so far to self-avoiding walks (SAWs) on a square lattice and on a simple cubic lattice;[2] very recently it has also been employed for simulating a multiple-chain system.[3] The scanning method is a step-by-step construction procedure, based on scanning in each step for the possible future continuations of the chain, which consist of b steps. For SAWs this "looking-forward" procedure causes a considerable reduction in sample attrition, as compared to the direct Monte Carlo method;[4,5] the larger b is, the smaller the attrition. However, for a square lattice this procedure is limited in practice to $b \leq 10$, which means that only the immediate environment of a step can be scanned. Therefore, we introduce in this paper a "mean-field" parameter, which also takes into account the global shape of the chain. We describe two criteria, the minimum free energy principle and the criterion of minimum free energy fluctuation, which enable one to optimize this parameter. The method is applied again to SAWs on a square lattice. This model has attracted recently great interest in view of Nienhuis's analytical solution for the honeycomb lattice,[6] which is expected to be exact. He obtains $\nu = 0.75$ and $\gamma = 43/32$, where ν and γ are the critical exponents for the chain shape

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