

Spinodal decomposition of polymer films

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The dynamics of spinodal decomposition of a two-dimensional binary polymer liquid on a square lattice has been investigated by Monte Carlo simulation. Initial relaxation of the dynamic structure factor $S(q,t)$ is non-exponential, which is in agreement with the Ginzburg criterion for predicting non-classical behaviour in two dimensions.

(Keywords: Monte-Carlo simulations; polymer blends; decomposition; kinetics)

INTRODUCTION

Phase separation in two dimensions has received much attention in recent years^{1,2}. Such decomposition phenomena have been observed in a variety of physical, chemical and biological systems ranging from adsorbates on solid surfaces³ to mixed phospholipid bilayers⁴⁻⁶. Less attention has been paid to demixing processes of polymer films, although these are of significant industrial importance, e.g. in a variety of coating problems.

Theoretically two-dimensional decomposition is not yet fully understood. So far investigations on non-polymeric models only have been performed, by the Monte Carlo technique⁷⁻¹⁰ and by molecular dynamics^{11,12}; these have shown that two-dimensional systems deviate strongly from classical mean-field theory of kinetics following quenching as developed by Hillert¹³ and Cahn and Hilliard^{14,15}.

No corresponding investigations on two-dimensional polymer blends have been reported. Hence the purpose of the present work is on the one hand to demonstrate how segregation phenomena in dense polymer systems can successfully be performed by Monte Carlo methods, and on the other hand to compare the results with simulations of two-dimensional binary alloys and with theoretical predictions of polymer demixing processes¹⁶⁻²¹.

The theory of the dynamics of polymer blends is based on the extended¹⁹ (allowing for slow spatial variations) Flory-Huggins^{16,17,22} free energy

$$F/k_B T = \frac{\phi}{N_A} \ln \phi + \frac{(1-\phi)}{N_B} \ln(1-\phi) + \chi \phi(1-\phi) + \frac{a^2}{36\phi(1-\phi)} (\nabla\phi)^2 \quad (1)$$

where a is a typical size of a monomer, ϕ is the fraction of A-polymers, N_A , N_B are the degrees of polymerization of A and B; the interaction parameter χ is often positive and favours segregation, and in most cases assumed to be small and essentially independent of temperature^{17,22}.

The relaxation of ϕ is described by the standard phenomenological continuity equation

$$\partial\phi/\partial t + \text{div } \mathbf{J} = 0 \quad (2)$$

where \mathbf{J} is the local current of the A species, and is linearly related to the gradient of the chemical potential difference. The local chemical potential difference is given by the functional derivative of F with respect to ϕ . Equation (2) can then be written in terms of the Fourier components

$$\partial\phi(q,t)/\partial t = -[\Lambda(q)q^2/k_B T]\mu(q,t) + \eta(q,t) \quad (3)$$

Here an additional stochastic force has been introduced to ensure the correct statistical description of the system dynamics. Λ is related to the Onsager coefficient by a fluctuation-dissipation theorem as

$$\langle \eta(q,t)\eta(q',t') \rangle = \Lambda(q)q^2 \delta(t-t') \quad (4)$$

A linearization of equation (2) around the average concentration ϕ_0 using $\phi(q,t) = \phi_0 + \delta\phi(q,t)$ yields²⁴

$$\partial\langle |\phi(q,t)|^2 \rangle / \partial t = -2\omega(q)\langle |\phi(q,t)|^2 \rangle + 2\Lambda(q)q^2 \quad (5)$$

where $\omega(q)$ is the amplification factor defined as

$$\omega(q) = \Lambda(q)q^2 \left[\frac{1}{N_A\phi_0} + \frac{1}{N_B(1-\phi_0)} - 2\chi + \frac{a^2 q^2}{18\phi_0(1-\phi_0)} \right] \quad (6)$$

Note that the amplification factor changes sign at a certain q_c that depends on the length of the polymer chain. Fluctuations with wave vector q smaller than q_c are exponentially amplified, whereas those with q larger than q_c are exponentially damped. The maximum growth occurs at $q_m < q_c$ with the peak remaining stationary. Equation (5) has the solution related to the dynamic

structure factor $S(q,t)$

$$S(q,t) \equiv \langle |\phi(q,t)|^2 \rangle_T$$

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

More detailed derivations and discussions of the Cahn-Hilliard theory are given in ref. 21

The classical mean-field result of equation (6) is known to be nearly valid only for binary alloys ($N_A = N_B = 1$) with large but finite range of interactions²⁵ and for polymer blends ($N_A, N_B \gg 1$) in three dimensions¹⁸⁻²¹. This has been understood by means of the Ginzburg criterion²⁶⁻²⁸, which asserts mean-field behaviour if the mean square amplitude of fluctuations $\delta\Psi$ of the coarse-grained order parameter Ψ is smaller than the order parameter itself, $\langle [\delta\Psi(\mathbf{r})]^2 \rangle \ll \Psi^2$. In particular for polymer mixtures the Ginzburg criterion^{18,21} yields that the temperature width (with respect to the critical point T_c) of the non-classical region is

$$\Delta T^* \equiv T^* - T_c \sim T_c N^{-(d-2)/(4-d)} \quad (8)$$

which indicates mean-field behaviour for dimensions $d=3$ as soon as N is reasonably large, whereas non-classical behaviour is predicted for $d=2$ for any chain length. This last prediction is confirmed by Monte Carlo simulations presented in Results and Discussion.

MODEL AND SIMULATION TECHNIQUE

The single chain consists of $N-1$ flexible jointed segments (of the same length as the lattice constant) on a square lattice. The intermolecular energy between two adjacent polymer beads is $\varepsilon > 0$ if this is a contact between two different polymer species A and B, and zero otherwise. The steric interactions are taken into account as usual: double occupancy of any lattice site is excluded.

In order to simulate an infinite system of finite chains at a given concentration c , it is convenient to approximate the infinite system by infinitely many identical cells of linear dimension L (in units of the lattice constant) and imposing periodic boundary conditions between neighbouring cells. The concentration c is then simply given by the number of sites occupied by the chains per number of sites in one cell, which is $c = NN_p/L^2$; N_p is the number of chains per cell.

Technically different ensembles of chain configurations are generated by a modified reptation technique²⁹. Starting from an arbitrary configuration, one first selects at random one of the voids (i.e. unoccupied lattice sites). If one of the randomly selected nearest neighbour sites of this void is occupied by one of the two ends of one of the chains, the other end of the chain is moved to the void, thereby displacing this void to the former end point of the chain. The new state is accepted as usual according to the Metropolis sampling technique.

Reptation technique is presently the only method suitable for simulations of lattice polymer systems at very high concentrations. It should be noted that the most straightforward way to introduce a more realistic 'local' chain dynamics would be to consider chains in the continuum, e.g. freely jointed chains performing local kink jumps³⁰.

One particular system at concentration $c=0.976$ has been simulated. The system consists of $N_p=1476$ chains each $N=10$ sites long on a 123×123 square lattice. The fraction of A-type polymers is 50%. In order to follow decomposition processes, the system was quenched from infinite temperature to $T=1.0$ below the critical point $2.0 < T_c < 5.0$ (temperatures are given always in units of k_B/ε , i.e. $T \equiv k_B T/\varepsilon$). The exact location of the critical point T_c is not yet known, but from a few quenches to different temperatures we expect for our standard system $2.0 < T_c < 5.0$.

The collective structure factor $S_A(q,t)$ was computed from the Fourier transform of the pair-correlation function and spherically averaged²⁵

$$S_A(q,t) = \Sigma' S(q,t) / \Sigma' 1 \quad (9)$$

with $q = (2\pi/L)n$, where $n=1,2,\dots$; Σ' denotes that for a given n a spherical shell is taken as $n-1/2 \leq |q|L/2\pi \leq n+1/2$.

RESULTS AND DISCUSSION

Athermal equilibrium properties

To ensure that, before quenching the system, the initial configuration represents an equilibrated high temperature state, the structure factor $S(q)$ has been examined for various chain lengths at $T = \infty$. According to theory (see e.g. ref. 17) the scattering intensity is given by the Debye function

$$S(q) = (2N/x^2) [e^{-x} - 1 + x] \quad (10)$$

where $x = q^2 \langle S_N^2 \rangle$ and $\langle S_N^2 \rangle$ is the mean square radius of gyration. If $q^2 \langle S_N^2 \rangle \ll 1$ equation (10) gives the familiar Ornstein-Zernike form

$$S(q) = S(0) / (1 + q^2 \xi^2) \quad (11)$$

where $\xi^2 \propto \langle S_N^2 \rangle$. The data presented in Figure 1 are in agreement with equation (10) for $x < 2$, but deviate for larger values of x . There are two possible reasons for this discrepancy: the data clearly reflect for a large wave vector the artificiality of the underlying lattice structure; another reason for the discrepancy is probably the fact that in two-dimensional polymer melts the chain statistics become gaussian only in the limit of very long chains. Indeed we have $\langle S_N^2 \rangle / N \approx 0.22, 0.27, 0.31$ for $N=5, 10, 20$. A typical high temperature configuration is given in Figure 2a for $N=10$.

Spinodal decomposition

After having examined the high temperature behaviour of the polymer film the spinodal decomposition process is considered. The system was quenched from the athermal state to the temperature $T=1.0$, which is well inside the miscibility gap. All quenches were performed instantaneously.

Before examining the evolution of the structure factor it is illustrative as well as informative to consider a few configurations during the unmixing process. Figure 2a shows the one-phase homogeneous state from which the instantaneous quench was performed. After the system had evolved toward two-phase coexistence for about 4000 μs , Figure 2b was taken. Already A- and B-rich

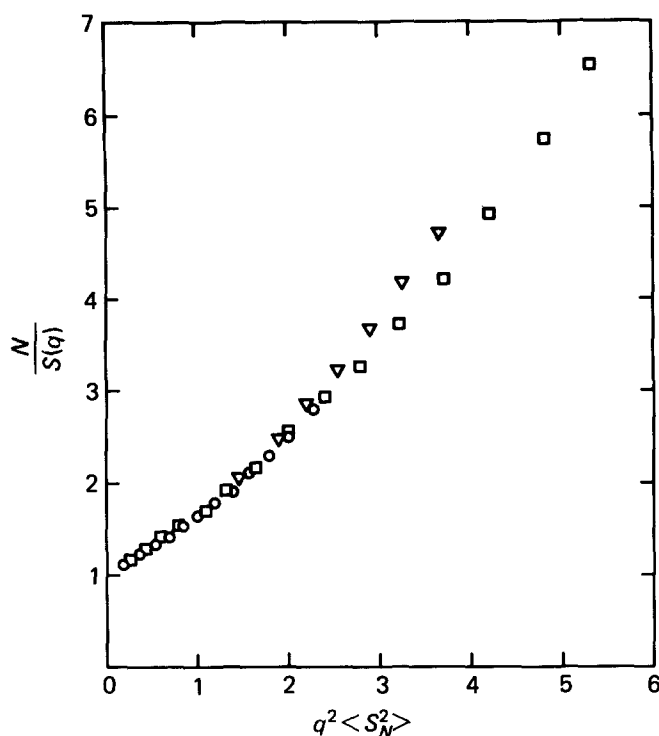


Figure 1 Scaling plot of the structure factor $N/S(q,0)$ versus $q^2 \langle S_N^2 \rangle$ at $T = \infty$ for $N=5$ (∇), 10 (\circ), 20 (\square)

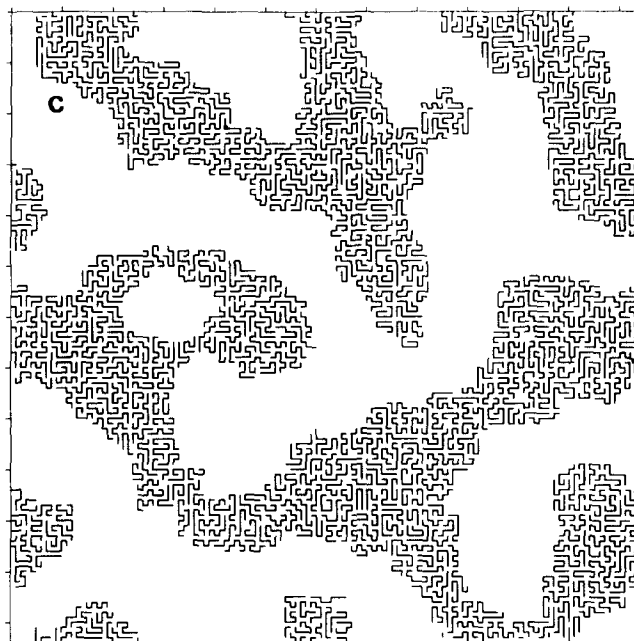
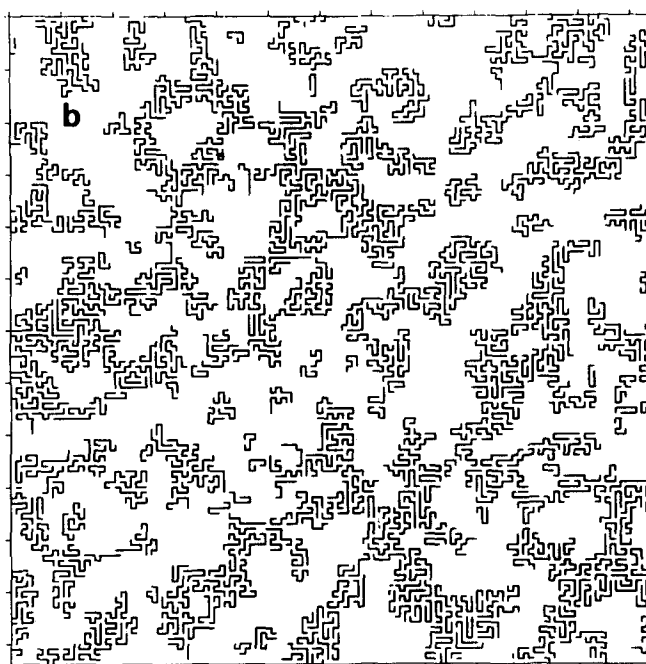
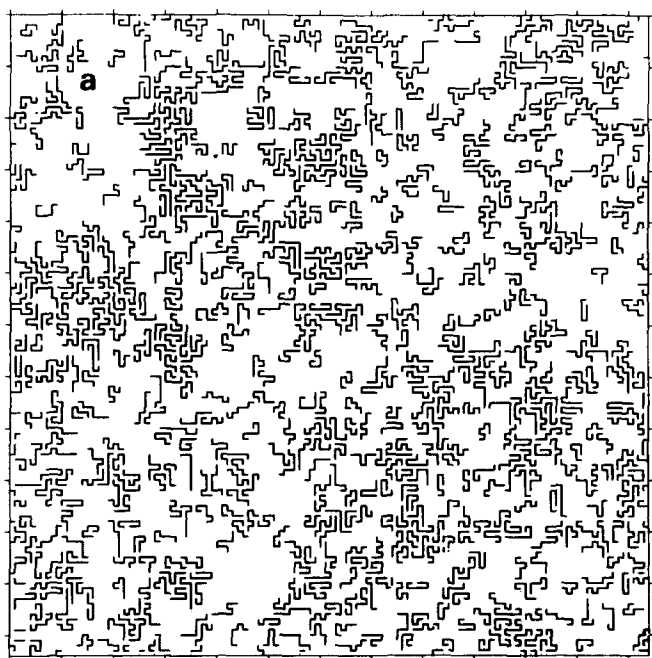


Figure 2 Configurations at different times of a system consisting of 1476 chains, each 10 sites long on a 123×123 square lattice. Only one type of the two polymer species is shown. The system has been quenched to $T = 1.0$. (a) Initial configuration at time $t = 0 \mu\text{s}$; (b) configuration at $t = 3750 \mu\text{s}$; (c) configuration at $t = 44500 \mu\text{s}$

domains have formed. Such domains are characteristic of the spinodal decomposition process. Note also the percolative nature of the domains. This can be seen even more strikingly in *Figure 2c*, which was taken at about $44000 \mu\text{s}$. The domains have coarsened considerably. Observe the compactness of the precipitate. In the later stages of unmixing the domains will coarsen even more until two-phase equilibrium is reached. In these late stages the growth is thought to be due to a mechanism of evaporation and condensation of small droplets.

Displayed in *Figure 3* is the change with time of the structure factor up to $3000 \mu\text{s}$. Owing to the wide spacing

between the wave vectors it is difficult to determine if the peak remains stationary, as predicted by the Cahn-Hilliard theory. The discreteness of the lattice hampers comparison with a continuous variable theory. The peak remains at a q vector for a certain time interval even though in reality it has shifted toward smaller q . The shift is observable only when it has reached the nearest lower q vector. This can only be achieved by simulating larger lattices $L \times L$, so that the spacing narrows according to $q = 2\pi/L$. However, it would require an extraordinary amount of computer time.

More instructive is the change of the structure factor at

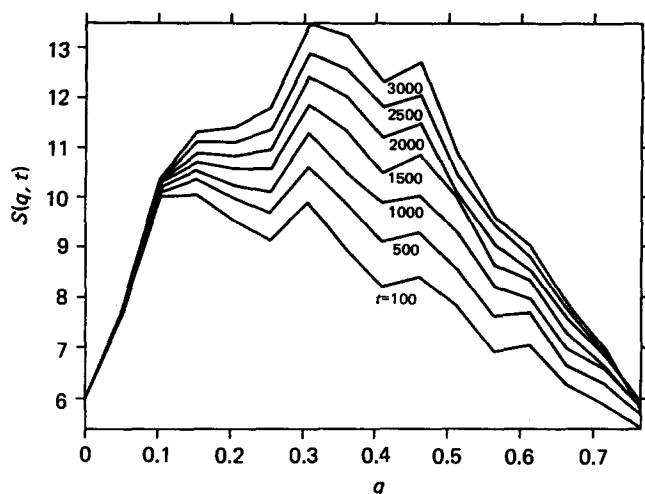


Figure 3 Structure factor $S(q, t)$ versus wavevector $q = 2\pi n/123$ at different times t as indicated. The system under consideration consists of 1476 chains comprising 10 sites each on a 123×123 square lattice. The system was quenched from $T = \infty$ to $T = 1.0$

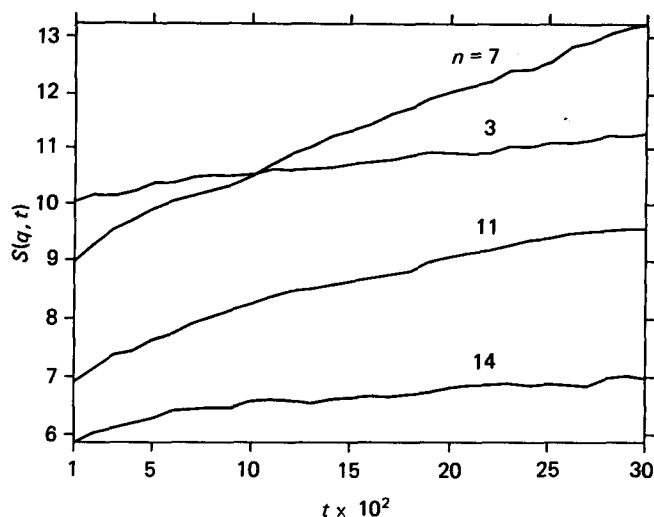


Figure 4 Structure factor $S(q, t)$ versus time for different wave vectors q as indicated. The system is the same as in Figure 3

fixed q as a function of time (cf. Figure 4 where the change with time is shown for four different wave vectors). The figure clearly shows that the structure factor does not increase exponentially with time. Rather, it increases very slowly. This is in disagreement with the Cahn–Hilliard theory, but is in accordance with the prediction of the Ginzburg criterion (8).

The changes with time bear a remarkable similarity to those found by Monte Carlo simulations of the two-dimensional nearest-neighbour Ising model^{7–12}. The model is a special case of that studied here. It corresponds to chains of length one. Hence, the simulations show that in two dimensions Cahn–Hilliard type behaviour can be observed only for systems with long-range interactions²⁵. It cannot be forced by making the chains longer, in contrast to the three-dimensional case^{17–21}. Three-dimensional binary polymer liquids with short range interactions and long chains would show, for short times following a quench, an exponential growth of the structure factor according to equation (7).

The slow growth of the structure factor suggests that the typical size of the precipitate increases very slowly. It would be interesting to follow the complete unmixing process, particularly for polymer systems since late time behaviour is not well understood.

SUMMARY

For the first time Monte Carlo simulation of spinodal decomposition of polymer mixtures has been performed. It has been demonstrated that even at very high concentration (in the present case $c = 0.976$) the dynamics of segregation processes can be simulated successfully. Although the present investigations were restricted to two dimensions (polymer film), the method can be applied as well to higher dimensions. Questions concerning single chain dynamics including reptational motion have not been considered. The resulting time-dependent collective structure factor exhibits strong non-exponential relaxation, which is in agreement with predictions using the Ginzburg criterion (8), according to which classical exponential relaxation is supposed to appear only in dimensions $d > 2$ for polymer mixtures.

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