

Computer simulation of the spinodal decomposition for a polydisperse polymer mixture

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A computer simulation of the dynamical evolution of the domain structure via spinodal decomposition was performed for a binary polymer blend in which one component has a bimodal molecular-weight distribution. The results indicated that the dynamical scaling law is valid for this polydisperse system.

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Recently many efficient methods [1–5] for simulating the time evolution of phase-separating domain structure via spinodal decomposition (SD) for binary mixtures have been reported. Chakrabarti *et al.* [5] proposed a method to simulate SD for binary symmetric polymer mixtures by using the Flory–Huggins–de Gennes (FHD) free-energy functional. They reported the *universality* in the dynamical behavior of polymer mixtures, such as the validity of the scaling postulate [6] and the dynamical scaling law [7,8] in the late stage SD, for the case in which the constituent polymers are monodisperse in molecular weight. However, actual polymers are polydisperse, and this property affects both static and dynamical behavior. The sensitive dependence of phase diagrams on polydispersity is a case in point [9]. For the early stage SD, Schichtel and Binder [10] reported a polydispersity effect. However, neither theory nor computer simulation works as yet been published concerning polydispersity effects on the late stage SD. The aim of this Rapid Communication is to present our computer solution to this problem, which was obtained by extending the method of Chakrabarti *et al.*

As a model of a polydisperse polymer mixture, we consider the system A - $B1$ - $B2$, in which A and Bn ($n = 1$ or 2) denote different polymer species, and $B1$ and $B2$ are the same polymer species having different molecular weights or polymerization indices. First, we derive the basic equations to simulate SD of the system, neglecting the thermal noise [11] and the hydrodynamic interactions [12]. Although the effects of the thermal noise and the hydrodynamic interactions are neglected, it does not mean at all that they are insignificant. These effects, especially those of the hydrodynamic interactions, on the spinodal decomposition for the polydisperse polymer mixtures should be fully explored in the future. If the volume fractions of A , $B1$, and $B2$ at a point \mathbf{r} and a time t are defined by $\phi_A(\mathbf{r}, t)$, $\phi_{B1}(\mathbf{r}, t)$, and $\phi_{B2}(\mathbf{r}, t)$, respectively, it follows from the incompressibility condition that

$$\phi_A(\mathbf{r}, t) + \phi_{B1}(\mathbf{r}, t) + \phi_{B2}(\mathbf{r}, t) = 1. \quad (1)$$

The continuity equations for A , $B1$, and $B2$ are given by

$$\frac{\partial \phi_A(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{J}_A = 0, \quad (2)$$

$$\frac{\partial \phi_{B1}(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{J}_{B1} = 0, \quad (3)$$

and

$$\frac{\partial \phi_{B2}(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{J}_{B2} = 0, \quad (4)$$

where \mathbf{J}_k ($k = A, B1$, and $B2$) is the flux of k . Onsager's theory gives the following relations between the flux and the chemical potential:

$$\mathbf{J}_A = -\Lambda_{AA} \nabla(\mu_A - \mu_{B2}) - \Lambda_{AB1} \nabla(\mu_{B1} - \mu_{B2}) \quad (5)$$

and

$$\mathbf{J}_{B1} = -\Lambda_{B1A} \nabla(\mu_A - \mu_{B2}) - \Lambda_{B1B1} \nabla(\mu_{B1} - \mu_{B2}), \quad (6)$$

where Λ_{ij} ($i, j = A, B1$, or $B2$) and μ_k ($k = A, B1$, or $B2$) are the Onsager coefficient and the chemical potential of k , respectively, and defined below. We note that the Onsager symmetric relations and the absence of bulk flow are used to derive Eqs. (5) and (6). Substituting Eqs. (5) and (6) into Eqs. (2) and (3), respectively, we obtain

$$\frac{\partial \phi_A(\mathbf{r}, t)}{\partial t} = \nabla \cdot \Lambda_{AA} \nabla(\mu_A - \mu_{B2}) + \nabla \cdot \Lambda_{AB1} \nabla(\mu_{B1} - \mu_{B2}) \quad (7)$$

and

$$\begin{aligned} \frac{\partial \phi_{B1}(\mathbf{r}, t)}{\partial t} &= \nabla \cdot \Lambda_{B1A} \nabla(\mu_A - \mu_{B2}) \\ &+ \nabla \cdot \Lambda_{B1B1} \nabla(\mu_{B1} - \mu_{B2}). \end{aligned} \quad (8)$$

Next, we consider the chemical potentials and the Onsager coefficients in Eqs. (7) and (8). According to the FHD theory, the free-energy functional $F\{\phi_A, \phi_{B1}, \phi_{B2}\}$ for A - $B1$ - $B2$ is given by

$$\begin{aligned} F\{\phi_A, \phi_{B1}, \phi_{B2}\} / k_B T &= \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_{B1}}{N_{B1}} \ln \phi_{B1} + \frac{\phi_{B2}}{N_{B2}} \ln \phi_{B2} \\ &+ \chi \phi_A (\phi_{B1} + \phi_{B2}) + \sum_{k=A, B1, B2} \frac{a_k^2}{36 \phi_k} (\nabla \phi_k)^2, \end{aligned} \quad (9)$$

where k_B is the Boltzmann constant, T the absolute temperature, χ the Flory-Huggins interaction parameter for the pair of A and B , and N_k and a_k the polymerization index and the statistical segment length of species k , respectively. The standard definition of μ_k gives

$$\mu_k = F + \sum_{j=A,B1,B2} \frac{\delta F}{\delta \phi_j} (\delta_{kj} - \phi_j), \quad (10)$$

where δ_{kj} is the Kronecker delta.

The Onsager coefficients for A - $B1$ - $B2$ have been formulated by Akcasu and Tombakoglu [13] using the random-phase approximation to give

$$\Lambda_{AA}^{-1} = \Lambda_{A0}^{-1} + (\Lambda_{B10} + \Lambda_{B20})^{-1}, \quad (11)$$

$$\Lambda_{B1B1}^{-1} = \Lambda_{B10}^{-1} + (\Lambda_{A0} + \Lambda_{B20})^{-1}, \quad (12)$$

and

$$\Lambda_{B1A}^{-1} = \Lambda_{AB1}^{-1} = - \left[\Lambda_{A0}^{-1} + \Lambda_{B10}^{-1} + \frac{\Lambda_{B20}}{\Lambda_{A0}\Lambda_{B10}} \right], \quad (13)$$

where Λ_{k0} is the bare mobility of k given by

$$\Lambda_{k0} = D_k N_k \phi_k, \quad (14)$$

and D_k is the self-diffusion coefficient of k . If D_k is given by the reptation theory [14], Λ_{k0} is represented by

$$\Lambda_{k0} = D_{lk} N_k^{-1} N_{ek} \phi_k, \quad (15)$$

where D_{lk} and N_{ek} are the monomeric diffusion coefficient of k and the polymerization index between entanglements of the k chains, respectively.

In order to reduce the computation time, we replaced $1/\phi_k$ in Eq. (9) and ϕ_k in Eq. (14) or Eq. (15) by $1/\langle \phi_k \rangle$ and $\langle \phi_k \rangle$, respectively, where $\langle \phi_k \rangle$ is the space average ϕ_k at $t=0$. Owing to this approximation, Eqs. (7) and (8) are simplified to

$$\begin{aligned} \frac{\partial \phi_A(\mathbf{r}, t)}{\partial t} = & \Lambda_{AA} \nabla^2 \left[\frac{\ln \phi_A + 1}{N_A} + \chi(\phi_{B1} + \phi_{B2}) - \frac{\ln \phi_{B1} + 1}{N_{B1}} - \chi \phi_A - \frac{a_A^2}{18 \langle \phi_A \rangle} \nabla^2 \phi_A + \frac{a_{B1}^2}{18 \langle \phi_{B1} \rangle} \nabla^2 \phi_{B1} \right] \\ & + \Lambda_{AB1} \nabla^2 \left[\frac{\ln \phi_{B1} + 1}{N_{B1}} - \frac{\ln \phi_{B2} + 1}{N_{B1}} - \frac{a_{B1}^2}{18 \langle \phi_{B1} \rangle} \nabla^2 \phi_{B1} + \frac{a_{B2}^2}{18 \langle \phi_{B2} \rangle} \nabla^2 \phi_{B2} \right] \end{aligned} \quad (16)$$

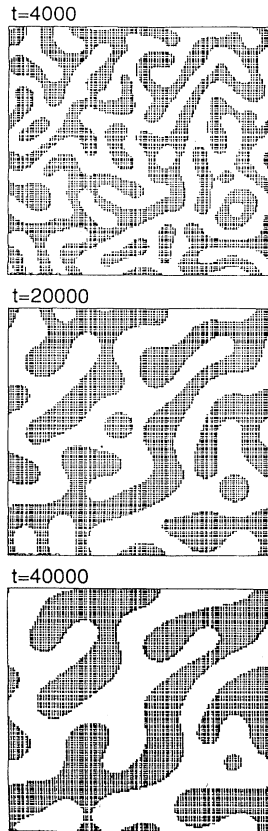


FIG. 1. Patterns for $\phi_A(\mathbf{r})$ at $t=4000$, 20000 , and 40000 sec, grown from a random mixed state. The regions $\phi_A(\mathbf{r}) > \langle \phi_A \rangle$ and $\phi_A(\mathbf{r}) < \langle \phi_A \rangle$ are filled and unfilled, respectively.

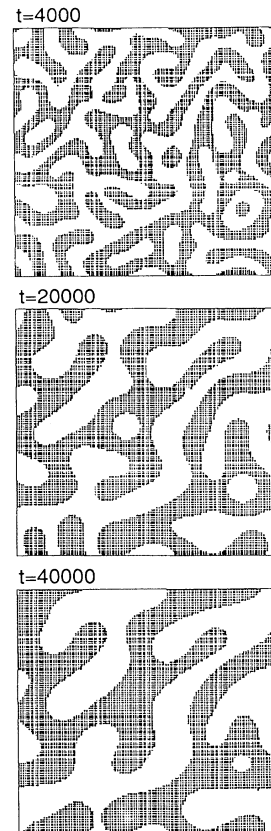


FIG. 2. Patterns for $\phi_{B1}(\mathbf{r})$ at $t=4000$, 20000 , and 40000 sec, grown from a random mixed state. The regions $\phi_{B1}(\mathbf{r}) > \langle \phi_{B1} \rangle$ and $\phi_{B1}(\mathbf{r}) < \langle \phi_{B1} \rangle$ are filled and unfilled, respectively.

and

$$\frac{\partial \phi_{B1}(\mathbf{r}, t)}{\partial t} = \Lambda_{B1A} \nabla^2 \left[\frac{\ln \phi_A + 1}{N_A} + \chi(\phi_{B1} + \phi_{B2}) - \frac{\ln \phi_{B1} + 1}{N_{B1}} - \chi \phi_A - \frac{a_A^2}{18 \langle \phi_A \rangle} \nabla^2 \phi_A + \frac{a_{B1}^2}{18 \langle \phi_{B1} \rangle} \nabla^2 \phi_{B1} \right] + \Lambda_{B1B1} \nabla^2 \left[\frac{\ln \phi_{B1} + 1}{N_{B1}} - \frac{\ln \phi_{B2} + 1}{N_{B1}} - \frac{a_{B1}^2}{18 \langle \phi_{B1} \rangle} \nabla^2 \phi_{B1} + \frac{a_{B2}^2}{18 \langle \phi_{B2} \rangle} \nabla^2 \phi_{B2} \right], \quad (17)$$

where

$$\Lambda_{AA} = \frac{D_A N_A \langle \phi_A \rangle (D_{B1} N_{B1} \langle \phi_{B1} \rangle + D_{B2} N_{B2} \langle \phi_{B2} \rangle)}{D_A N_A \langle \phi_A \rangle + D_{B1} N_{B1} \langle \phi_{B1} \rangle + D_{B2} N_{B2} \langle \phi_{B2} \rangle}, \quad (18)$$

$$\Lambda_{B1B1} = \frac{D_{B1} N_{B1} \langle \phi_{B1} \rangle (D_A N_A \langle \phi_A \rangle + D_{B2} N_{B2} \langle \phi_{B2} \rangle)}{D_A N_A \langle \phi_A \rangle + D_{B1} N_{B1} \langle \phi_{B1} \rangle + D_{B2} N_{B2} \langle \phi_{B2} \rangle}, \quad (19)$$

and

$$\Lambda_{AB1} = \Lambda_{B1A} = - \left[\frac{D_A N_A \langle \phi_A \rangle D_{B1} N_{B1} \langle \phi_{B1} \rangle}{D_A N_A \langle \phi_A \rangle + D_{B1} N_{B1} \langle \phi_{B1} \rangle + D_{B2} N_{B2} \langle \phi_{B2} \rangle} \right]. \quad (20)$$

We have numerically integrated Eqs. (16) and (17) on a 128×128 lattice with a time step 0.4 sec, using the periodic boundary conditions. The parameters chosen are $N_A = 1000$, $N_B = 500$, $N_{B2} = 1500$, $a_A = a_{B1} = a_{B2} = 0.7$ nm, $D_A = 2000$ nm²/sec, $D_{B1} = 8000$ nm²/sec, $D_{B2} = 888.8$

nm²/sec, and $\chi = 0.0025$. Furthermore, we chose $D_{1K} N_{ek}^{-1}$ to be 2×10^{-6} nm²/sec. With these parameters the weight-average polymerization index N_w , the number-average polymerization index N_n , and N_w/N_n for B are 1000, 750, and 1.25, respectively. The initial values of ϕ_k were given according to the Gaussian random numbers with $\langle \phi_A \rangle = 0.47$, $\langle \phi_{B1} \rangle = 0.265$, and $\langle \phi_{B2} \rangle = 0.265$. This initial condition makes the areas of A -rich and B -rich regions equal. We have run ten times up to 40 000 sec and ten runs are averaged. To see the growth of the domains and the self-similarity in the domain growth, we calculate the circularly averaged structure factor $I(q, t)$ as a function of time where q is the wave number.

Figures 1–3 show how $\phi_A(\mathbf{r}, t)$, $\phi_{B1}(\mathbf{r}, t)$, and $\phi_{B2}(\mathbf{r}, t)$ change with time, and reveal the appearance of bicontinuous patterns. The filled regions in both Figs. 2 and 3 can be superimposed on each other, indicating that the spatial distributions of $\phi_{B1}(\mathbf{r}, t)$ and $\phi_{B2}(\mathbf{r}, t)$ are identical. This is reasonable because we have not chosen the quench condition for the three-phase separation. The dy-

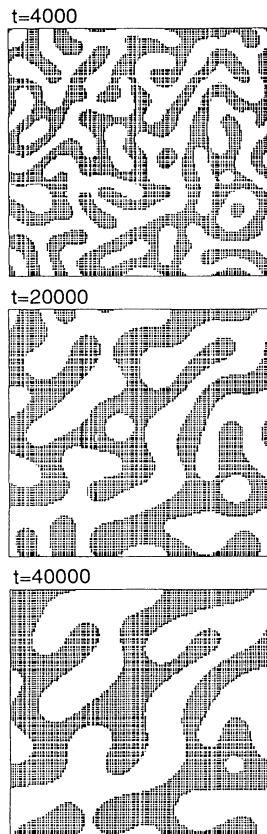


FIG. 3. Patterns for $\phi_{B2}(\mathbf{r})$ at $t = 4000, 20000$, and 40000 sec, grown from a random mixed state. The regions $\phi_{B2}(\mathbf{r}) > \langle \phi_{B2} \rangle$ and $\phi_{B2}(\mathbf{r}) < \langle \phi_{B2} \rangle$ are filled and unfilled, respectively.

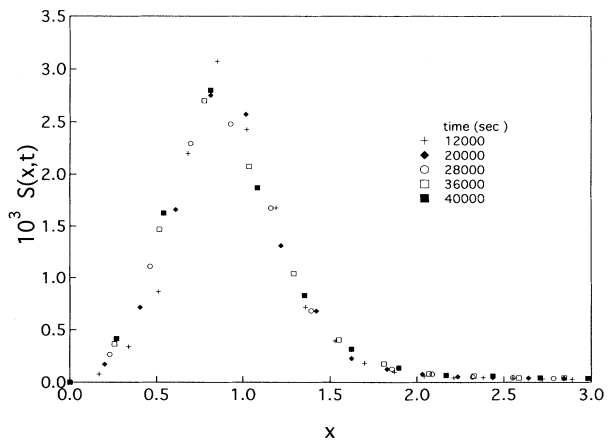


FIG. 4. Scaled structure factor $S(x, t)$ plotted as a function of the reduced wave number x .

namics of the phase separation in three phases is a very interesting problem, and will be discussed elsewhere [15].

In order to see whether the dynamical scaling law is valid or not, the scaled structure factor $S(x, t)$ calculated from

$$S(x, t) = q_1(t)^2 I(x, t) \quad (21)$$

is plotted against the reduced wave number

$$x = q/q_1(t) \quad (22)$$

in Fig. 4. Here $q_1(t)$ is defined by

$$q_1 = \frac{\int qI(q, t)dq}{\int I(q, t)dq} \quad (23)$$

We observe that the plots in the range $t = 12\,000$ – $40\,000$ sec are well superimposed, indicating that the dynamical scaling law is valid for the polydisperse polymer blend studied here.

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