

# Self-assembling morphology induced by nanoscale rods in a phase-separating mixture

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A symmetric binary mixture containing mobile nanoscale rods is quenched from a one-phase state into an unstable phase-separating region. Incorporating the motion of rods, the system undergoes spinodal decomposition to form a dropletlike structure. The rod-rod interaction and the preferential adsorption of one of the two immiscible phases onto the mobile rods play an important role in driving the system to self-assemble into this special structure. Within each cluster of the wetting phase, the rods align parallel to each other as in a nematic liquid crystal, while the rod orientations between these clusters are randomly distributed. However, an interconnected structure is recovered in the presence of hydrodynamic interaction. In the present phase-separating mixture with rods, the growth dynamics is examined in detail, and our simulations reveal a crossover from a rod-mobility-dependent to an independent regime. The system always exhibits slowing-down growth behavior where the well-known diffusive Lifshitz-Slyozov mechanism and hydrodynamic effects are both suppressed.

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## I. INTRODUCTION

When a binary mixture, initially prepared in a homogeneous fully mixed state (high-temperature phase), is suddenly quenched into the two-phase coexistence region, the system begins to phase separate, eventually forming two macroscopic phases, providing a wealth of interesting physical questions [1,2]. Depending on the composition, the morphology of the domains may be isolated droplets or interconnected bicontinuous phases, corresponding to nucleation and spinodal decomposition, respectively. It is widely accepted that the domain growth, at late time, obeys a power law of the form  $R(t) \sim t^n$ , where  $R(t)$  is the characteristic domain size at time  $t$ , and  $n$  is the growth exponent, which depends on the nature of the dynamics. In the limit of a dilute amount of one phase, the growth exponent  $n = 1/3$  is predicted by the mean field theories of Ostwald ripening, i.e., the Lifshitz-Slyozov (LS) coarsening mechanism [3]. On the other hand, the presence of hydrodynamic flows usually has an important influence on the domain growth and structural evolution. For systems with a symmetric composition, the flows are believed to accelerate the domain growth and lead to fast growth with  $R(t) \sim t$  in three dimensions or  $R(t) \sim t^{1/2}$  in two dimensions during the viscous regime, and  $R(t) \sim t^{2/3}$  for two- and three-dimensional systems during the inertial regime [1,4]. However, recent studies showed that, when hydrodynamic interaction is included, the scaling behavior is not clear even for such binary systems in the viscous regime [5].

While phase separation in a binary system has been studied extensively theoretically and experimentally [1,2], very little is known about the kinetics of phase separation in a binary mixture with the addition of a third component (e.g., colloidal particles). The introduction of mobile particles to binary fluids significantly increases the system complexity due to the additional particle-particle and particle-fluid interactions, and modifies their rheological properties. It is well

known that the morphology of polymer blends is one of the factors determining their characters, and studying how to control polymer blend morphology is an important subject in polymer engineering. In fact, in many technological applications, the use of colloidal or glass particles is a promising route to materials synthesis with the opportunity to create highly ordered structures on wide length scales. On the other hand, when a third component is introduced, the growth dynamics may be changed due to the interplay of several dynamic mechanisms. For example, ternary water-oil-surfactant mixtures always show the slowing-down growth of the coarsening process at late stages due to interface pinning by surfactant particles [6,7].

Recently, Tanaka *et al.* [8] provided an experimental study of the pattern evolution in a binary liquid into which mobile particles were introduced with different wettability to two immiscible phases, and found that the presence of mobile particles dramatically changes the morphology and growth kinetics of the phase separation. This phenomenon originates from the strong preferential wetting of the filler particle by one component of the blend. The presence of wetting strongly affects the structure evolution and growth dynamics [9]. However, the theoretical description of this problem is complicated by the interplay between phase separation and wetting dynamics. By combining cell dynamical systems and Langevin dynamics for particles, Ginzburg *et al.* [10] studied the phase separation in a binary mixture for low particle density with selective affinity of one of the species. It was found that the addition of hard particles greatly changes both the speed and the morphology of the phase separation. Furthermore, an interesting phenomenon was found by Peng *et al.* [11]: that when low volume fractions of nanoscale rods are immersed in a binary, phase-separating blend, the rods will self-assemble into needlelike, percolating networks. In addition, Lee *et al.* [12] observed filler-induced composition waves in phase-separating polymer blends.

In this paper, we present a simulation of a binary phase-separating mixture containing nanoscale rods that have preferential wettability to one of two immiscible phases. A model similar to that in Ref. [11] is used, and the rod-rod interaction

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is modified to exhibit an isotropic-nematic ordering for the rods. The effects of the third-component rods on the morphology and growth kinetics of phase separation are studied, and the interplay among the wetting effects, the motion of rods, and phase separation is examined. The present work is interesting from the practical point of view, because polymer blend materials are often filled with a third component that improves their mechanical, thermal, electrical, and/or optical properties [13]. The paper is organized as follows. Section II is devoted to the description of the model. In Sec. III the numerical results for pattern changes and the growth dynamics of phase separation are obtained and discussed. In Sec. IV, we briefly report the result of hydrodynamic effects. Finally, a brief summary is given in Sec. V.

## II. MODEL

In our two-dimensional simulation, we use a coarse-grained description of a phase-separating symmetric binary  $A$ - $B$  mixture which is described by a scalar order parameter  $\Psi$ , the local concentration difference between the  $A$  and  $B$  phases. For the  $A$ - $B$  binary mixture, we take the Cahn-Hilliard equation [2,14] to describe the time evolution of  $\Psi$ :

$$\frac{\partial \Psi}{\partial t} = M \nabla^2 \frac{\delta F(\Psi)}{\delta \Psi}, \quad (1)$$

where  $M$  is the transport coefficient.  $F(\Psi)$  represents the free energy of the system, and  $\delta F(\Psi)/\delta \Psi$  is the local chemical potential  $\mu$  driving phase separation.

As in Ref. [11], a third component is introduced by rigid rods whose center-of-mass position and orientation angle are represented by  $\mathbf{r}_i$  and  $\theta_i$ , respectively. These two variables obey the following motion equations:

$$\frac{\partial \mathbf{r}_i}{\partial t} = -M_r \frac{\partial F(\Psi)}{\partial \mathbf{r}_i}, \quad (2)$$

$$\frac{\partial \theta_i}{\partial t} = -M_\theta \frac{\partial F(\Psi)}{\partial \theta_i}. \quad (3)$$

Here,  $M_r$  and  $M_\theta$  represent the ‘‘motion’’ and ‘‘rotation’’ mobility coefficients, respectively.

The free energy function of the system  $F$  includes three parts [11], the fluid-fluid  $F_{GL}$ , fluid-rod  $F_{CPL}$ , and rod-rod interactions  $F_{RR}$ :  $F = F_{GL} + F_{CPL} + F_{RR}$ . The Ginzburg-Landau free energy  $F_{GL}$  describing the  $A$ - $B$  blend is given by

$$F_{GL} = \int d\mathbf{r} \left[ -\frac{1}{2} \Psi^2 + \frac{1}{4} \Psi^4 + \frac{1}{2} (\nabla \Psi)^2 \right], \quad (4)$$

where we assume that all variables have been rescaled into dimensionless units, and the third term on the right-hand side stands for the interfacial free energy derived from the spatial composition inhomogeneity. For the interaction between the rods with length  $L$  and the  $A$ - $B$  mixture, we use [11]

$$F_{CPL} = \int d\mathbf{r} \sum_i \int ds_i V(\mathbf{r} - \mathbf{s}_i) [\Psi(\mathbf{r}) - \Psi_w]^2, \quad (5)$$

where  $\mathbf{s}_i$  represent the points on the rods. Notice that in the present system  $\Psi = 1$  ( $-1$ ) corresponds to the  $A$ -rich ( $B$ -rich) phase. When  $\Psi_w$  is set to 1, it means that the rod is energetically favored in the  $A$  phase. We take the short-ranged wetting interaction  $V(\mathbf{r} - \mathbf{s}_i) = V_0 \exp(-|\mathbf{r} - \mathbf{s}_i|/r_0)$ , where  $V_0$  ( $>0$ ) is a parameter for the wetting strength and  $r_0$  represents a microscopic length scale. The rod-rod interaction  $F_{RR}$  is separated into two parts,  $F_r$  (motion-dependent part) and  $F_\theta$  (rotation-dependent part):

$$F_{RR} = F_r + F_\theta, \quad (6)$$

with

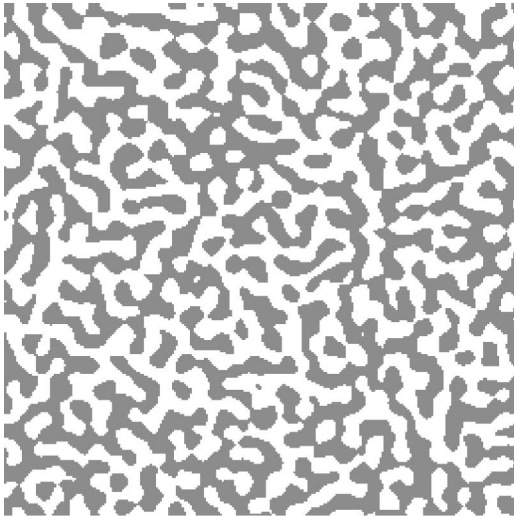
$$F_r = \sum_i \sum_j \begin{cases} 0, & |\mathbf{r}_i - \mathbf{r}_j| \geq 2L \\ -\chi_1 \frac{L^2}{|\mathbf{r}_i - \mathbf{r}_j|^\alpha}, & L \leq |\mathbf{r}_i - \mathbf{r}_j| < 2L \\ \chi_2 \frac{L(L - |\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|^\alpha} - \chi_1, & 0 < |\mathbf{r}_i - \mathbf{r}_j| < L, \end{cases} \quad (7)$$

$$F_\theta = \sum_i \sum_j \begin{cases} 0 & |\mathbf{r}_i - \mathbf{r}_j| \geq 2L \\ \chi_3 \frac{L^2 \sin^2(\theta_i - \theta_j)}{|\mathbf{r}_i - \mathbf{r}_j|^\alpha} & 0 < |\mathbf{r}_i - \mathbf{r}_j| < 2L. \end{cases} \quad (8)$$

The contribution from the motion-dependent part  $F_r$  causes the rods to congregate but keep some distance apart, while  $F_\theta$  tends to cause an isotropic-nematic ordering for the pure rod system.  $\chi_1$ ,  $\chi_2$ , and  $\chi_3$  describe the strengths of the interactions and  $\alpha$  represents the exponent of the decay of the interactions with distance. Notice that in Ref. [11] it was assumed that the rod-rod interaction is purely repulsive for  $|\mathbf{r}_i - \mathbf{r}_j| < L$ , and zero when  $|\mathbf{r}_i - \mathbf{r}_j| \geq L$ . Here we assume that the rod-rod interaction is repulsive when  $|\mathbf{r}_i - \mathbf{r}_j| < L$ , and attractive when  $L \leq |\mathbf{r}_i - \mathbf{r}_j| < 2L$ . When  $|\mathbf{r}_i - \mathbf{r}_j| \geq 2L$ , there is no interaction between rods. Under the present representation, the nearest-neighboring rods will prefer a balance position of distance  $L$  for the sake of the minimum of energy. Therefore, the rods can self-assemble to form locally parallel domain structure even in the absence of binary fluids, a result not provided by the model of Peng *et al.* [11]. When the density of the nanoscale rods becomes high, the present interaction form favors the formation of nematic structures. With the introduction of nanoscale rods to a phase-separating binary fluid, the self-assembly of rods will exhibit richer phenomena, as shown in the following section.

## III. RESULTS AND DISCUSSION

Our simulations are carried out in two dimensions with periodic boundary conditions, lattice constant  $\Delta r = 1$ , and lattice size of  $L_x = L_y = 256$ . The direct forward integration method is adopted to update the system. In our simulation, the initial distribution of  $\Psi$  is specified by random uniform



(a)  $t=1000$



(b)  $t=100000$

FIG. 1. Snapshots of phase separation in a binary mixture without solid additions and hydrodynamic interactions: (a)  $t=1000$ ; (b)  $t=100\,000$ . Phase A is represented by gray regions and phase B by white regions.

distributions in the range  $[-0.01, 0.01]$ , and 500 rigid rods of length  $L$  (the number density is 4.6%) are randomly dispersed in a symmetric binary fluid with a critical (50:50) composition; the motion of the rods is not restricted to lattice sites. We choose  $M=1.0$ ,  $L=6$ ,  $\chi_1=1.5$ ,  $\chi_2=3.0$ ,  $\chi_3=0.6$ ,  $\alpha=2$ ,  $V_0=1.0$ , and  $r_0=2$ . The time interval used is  $\Delta t=0.01$ . The results are averaged over ten independent runs for different initial conditions.

#### A. Pattern formation

Figures 1(a) and 1(b) show the pattern changes of phase separation for the case of a pure symmetric  $A$ - $B$  mixture

without the presence of rods. As we know, both  $A$ - and  $B$ -rich phases form an interconnected bicontinuous domain structure even at the late stages. On the other hand, we simulate the motion of rods in the absence of the  $A$ - $B$  binary mixture [see Figs. 2(a), 2(b), and 2(c)], and find that the assemble into discontinuous small domains with parallel rods, but at the late stages no obvious change is observed. Then we study the effects of the presence of rods on the domain morphology and growth dynamics of the binary mixture when the rods wet the bulk  $A$  phase. Figures 3(a) and 3(b) show the time evolution of phase separation at times in the simulation corresponding to  $t=1000$  and  $t=170\,000$ , respectively. The area shown in black indicates the wetting rods, while the gray and white regions stand for  $A$ -rich (wetting) and  $B$ -rich phase domains, respectively. Under the wetting interaction, the phase ordering process couples with the movement of rods. We see from Fig. 3 that the competition of the wetting dynamics and phase separation effectively breaks up the composition symmetry of the system and drives it into a dropletlike structure of the  $A$  phase enclosed by the  $B$  phase. The wetting rods prefer to be in the bulk of the wettable phase  $A$  because this is energetically favorable. Within each cluster, the rods are parallel as in a nematic liquid crystal; however, the rod orientations between these clusters are uncorrelated. The wetting of rods is expected to cause spatial heterogeneity for the phase-separating process, that is, the  $A$  component is attracted to condense around them in the early stage. On the other hand, under the  $F_{RR}$  interaction the rods with small spacings aggregate locally. As phase separation proceeds, such an assembly consequently attracts more  $A$  component, leading to the coarsening of the  $A$  domain. This progression directs the domain growth around the wetting rods and leads to the depletion of the  $A$  component in the particle-free region [15]. The heterogeneity is then amplified, which breaks up the composition symmetry, and finally the  $A$  domain forms a cluster morphology. In the present phase-separating process, we find that the motion mobility coefficient of the rods  $M_r$  plays a crucial role and dominates the structural evolution of the system. If we set  $M_r=0$ , namely, the center of mass of the rods is fixed, the  $A$  domain evolves into a percolating structure again [see Figs. 4(a) and 4(b)], while the morphology is still restricted due to the different positions of the rods. So we can conclude that the formation of the cluster structure is mainly due to the congregation of rods, and the patterning of the system can be controlled by changing the position of the rods. In addition, comparing Fig. 3(b) with Fig. 2(c), we can see that the aggregation of rods in Fig. 3(b) is easier than that in Fig. 2(c). This means that the phase-separating process will simultaneously cause more near-neighboring rods to assemble locally.

#### B. Growth behavior

In order to understand the influence of rigid rods on the growth dynamics of a binary blend, we investigate the growth behavior through the calculation of the characteristic length  $R(t)$ . The mean domain size  $R(t)$  is derived from the inverse of the first moment of the spherically averaged struc-

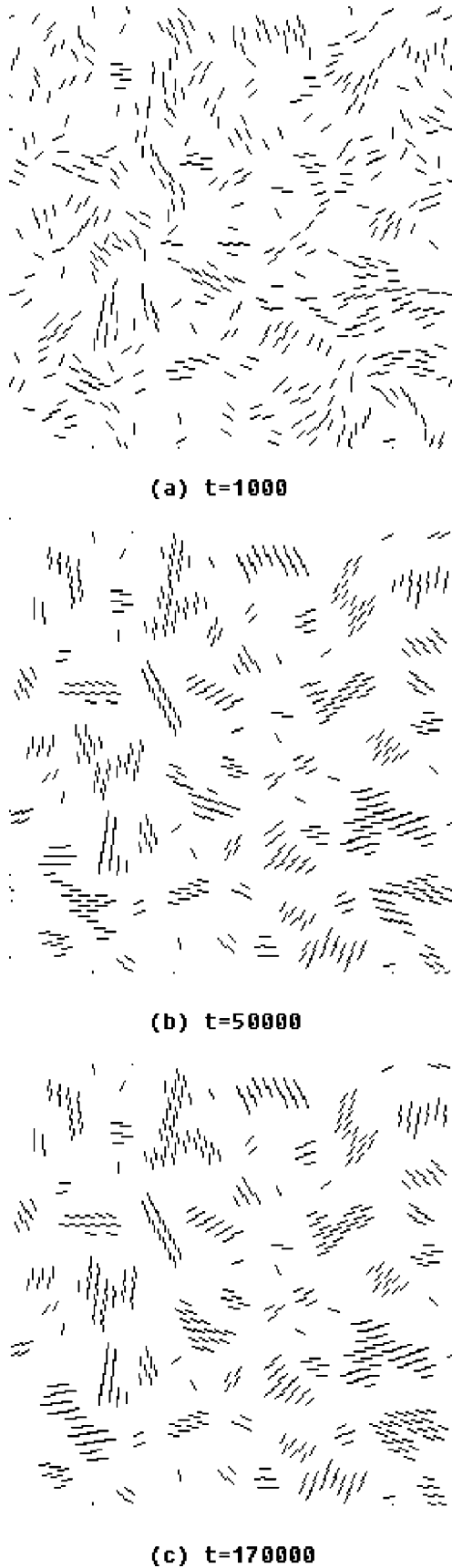


FIG. 2. The motion of rods without A-B binary mixture ( $M_r=0.5$  and  $M_\theta=1.0$ ). (a)  $t=1000$ ; (b)  $t=50000$ ; (c)  $t=170000$ .

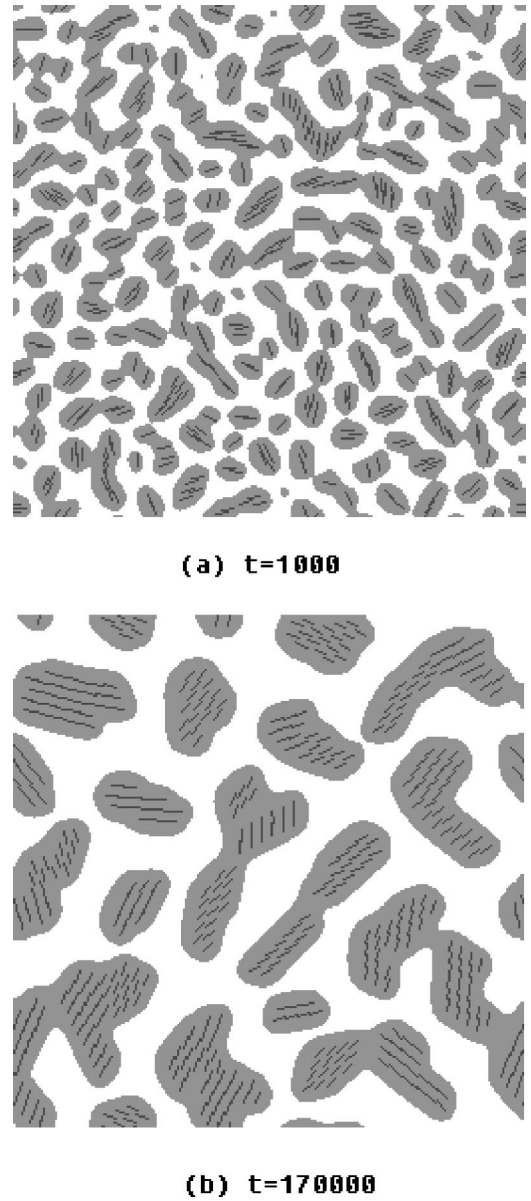
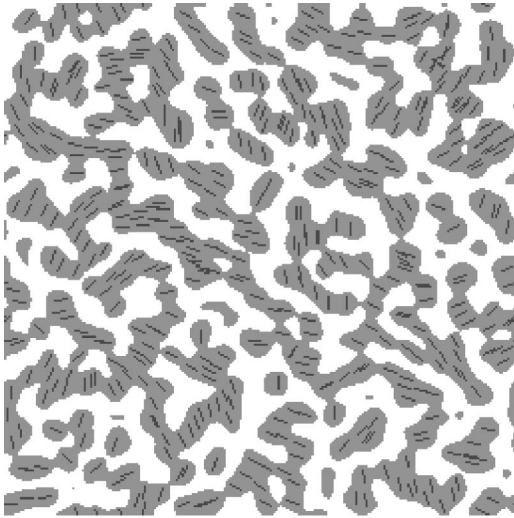
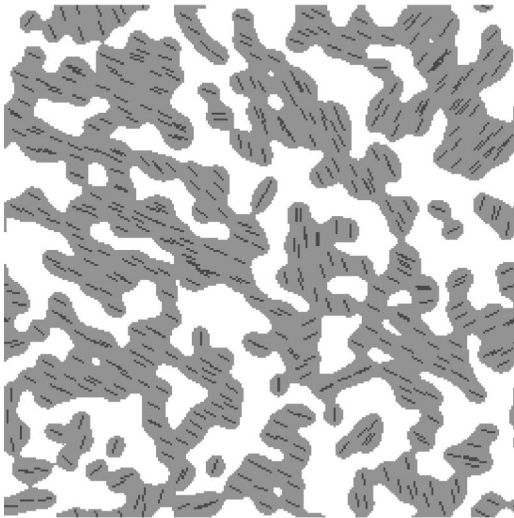


FIG. 3. Snapshots of order parameter patterns and rod positions for  $N=500$  rods of length  $L=6$  without hydrodynamic interaction ( $M_r=0.5$  and  $M_\theta=1.0$ ). Phase A is represented by gray regions, phase B by white regions, and nanoscale rods by black lines. (a)  $t=1000$ ; (b)  $t=170000$ .

ture factor  $\hat{S}(k,t)$  as  $R(t)=2\pi/\langle k(t) \rangle$ , where  $\langle k(t) \rangle = \sum_{k_n=0}^{k_c} k_n \hat{S}(k_n,t) / \sum_{k_n=0}^{k_c} \hat{S}(k_n,t)$  with  $k_c = \pi$ . The structure factor  $S(\mathbf{k},t)$  is defined as  $S(\mathbf{k},t) = \langle |\Psi_i(\mathbf{k},t)|^2 \rangle$ , where  $\Psi_i(\mathbf{k},t)$  is the Fourier component of  $\Psi_i(\mathbf{r},t)$ , and the sum runs over all lattice sites with  $\mathbf{k} = (2\pi/L)(m\mathbf{i} + n\mathbf{j})$ , in which  $m, n = 1, 2, 3, \dots, L$  and  $\langle \dots \rangle$  denotes the thermal average over a number of repeated runs from independent initial conditions. A further average may be taken to smooth the results—the spherically averaged structure factor, defined as  $\hat{S}(k,t) = \sum_{\mathbf{k}} S(\mathbf{k},t) / \sum_{\mathbf{k}} 1$ , where  $k = 2\pi n/L$ ,  $n = 0, 1, 2, \dots, L/2$ , and each sum for a given value of  $n$  is over a spherical shell defined by  $n - \frac{1}{2} \leq (L/2\pi)|\mathbf{k}| < n + \frac{1}{2}$ .



(a)  $t=1000$



(b)  $t=100000$

FIG. 4. Snapshots of phase separation when  $M_\theta=1.0$  but  $M_r=0$  (the center of mass of the rods is immobile): (a)  $t=1000$ ; (b)  $t=100\,000$ .

We now calculate the time evolution of the characteristic domain size for the “motion” mobility  $M_r=0.5$  and “rotation” mobility  $M_\theta=1.0$ . Figure 5 clearly reveals that the presence of rods slows down the process of phase separation by pinning the domain growth of the A phase, and the well-known Lifshitz-Slyozov power law is violated. On the other hand, the domain growth exponent  $n$  changes from 0.12 ( $\pm 0.003$ ) to 0.19 ( $\pm 0.004$ ) as time goes on. This crossover behavior may be attributed to the formation of a new structure, that is, the transition from a percolating domain to clusterlike morphology. At the early stages, the wetting dynamics becomes dominant so that a strong shape-pinning effect occurs as a result of the presence of rods, and a slowing-down growth is expected. As time elapses, the A component favor-

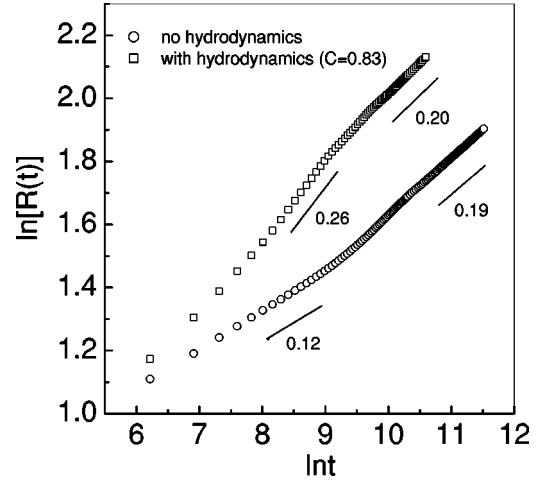


FIG. 5. Log-log plots of the average domain size  $R(t)$  vs time  $t$  with and without hydrodynamic interaction.

ing rigid rods thickens around the rods and directs the domain growth, leading to the formation of discontinuous dropletlike structures of the A phase. Correspondingly, the driving force for phase separation due to surface tension tends to force the A clusters into circular droplets, and the growth of the domain size  $R(t)$  becomes fast. However, the shape of the A phase domains is still far from circular since the presence and position of the rods restrict the space of shape modulation and consequently the interface motion is blocked. This geometrical confinement due to rods leads to suppression of the evaporation-condensation mechanism. From the energetic aspect, the interface tension drives phase separation tending to change the interface from irregular to a circular shape, but the rod-rod interaction keeps the shape of the A domain consisting of parallel rods; then the wetting interaction attracts the A component to form a similar morphology to the distributed shapes of the rods. Deformation of the oriented ordering domain of the rods has a higher potential barrier, and this greatly limits the interface motion.

To further understand the influence of the mobility of the rods, we perform simulations for different cases with  $M_r=0.5, 0.1,$  and  $0.05$ , and the results are plotted in Fig. 6. We find that at early time the domain growth depends on the rod motion, but the growth behavior becomes independent of the “motion” mobility at late time (the growth exponent  $n=0.19$ ). This means that in the late stage the motion mobility of the rods is no longer important to the growth behavior. A possible reason may be that at late time the cluster structure is almost formed, and the rods have found their positions which are spatially fixed. The growth dynamics is controlled only by the interplay between wetting and phase separation. Therefore the “motion” mobility is no longer the crucial factor that determines the domain growth at the late stage. What surprises us is the dependence of the early-time growth behavior on  $M_r$  (see Fig. 6). We can see from Fig. 6 that at early time the smaller the mobility is, the faster the domain grows (or the larger the domain size becomes). This fact is, however, somewhat at odds with the common wisdom according to which the movement of rods enhances coalescence and increases the growth process. To interpret this phe-

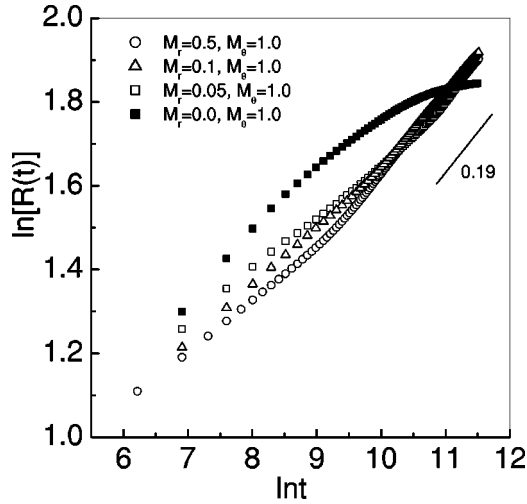


FIG. 6. Log-log plots of the average domain size  $R(t)$  vs time  $t$  for different values of  $M_r$ .

nomenon, we also simulate the case of fixed rod positions ( $M_r=0$ ) (Fig. 6). It grows more quickly than any other case with  $M_r \neq 0$  at the early stage, but interestingly continuous slowing-down behavior is observed at late stages. Comparing the morphologies of the cases  $M_r=0.5$  and  $M_r=0$  [see Fig. 2(a) and Fig. 3(a)], we find that, when  $M_r \neq 0$ , the movement of rods disturbs the growth of  $A$  domains caused by the wetting of rods at early times. In the case of  $M_r=0$ , the effect of the wetting is enlarged due to the absence of motion of the rods. The  $A$  domain is connected and the interface becomes smooth, favoring the growth of the  $A$  domain. However, in this case, the rods cannot self-assemble into a clusterlike morphology. At late stages, the domain growth gradually slows down as a result of gradual depletion of the  $A$  component around the rods. This case is similar to that of Refs. [10] and [16], where the hard particles are of very low mobility and become obstacles to the motion of interfaces. In the present model, the motion of rods destroys the usual domain coarsening LS mechanism and enforces a coarsening process adjusted to the motion of the rods. From the energy aspect, to decrease the rod-rod and rod-fluid energy, the interface energy is required to increase, leading to breakdown of the LS growth mechanism driven by surface tension.

We also investigated the dependence of growth dynamics on the “rotation” mobility coefficient  $M_\theta$ . The simulation reveals that in the whole process, the characteristic length  $R(t)$  is nearly independent of the value of  $M_\theta$  (see Fig. 7).

#### IV. HYDRODYNAMIC EFFECTS

At high viscosity, the fluid velocities are sufficiently small that hydrodynamic effects, which prevail in the viscous regime of phase separation in fluid mixtures, can be neglected. For low viscosity, however, hydrodynamics becomes relevant, and may change the domain morphology of the system. Therefore, in the coarsening process, the fluid will evolve through two competing growth mechanisms: thermodynamic diffusion and hydrodynamic flow. To take into ac-

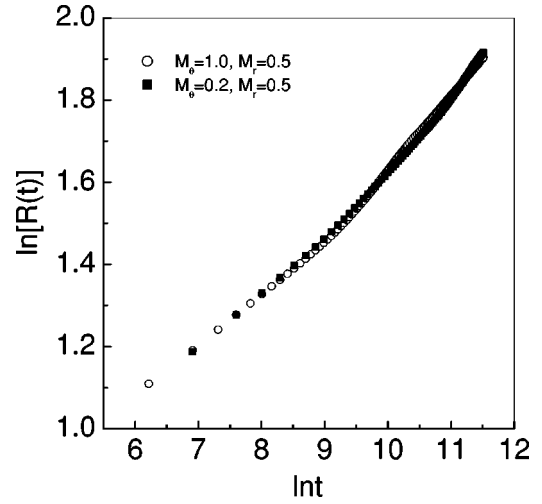


FIG. 7. Log-log plots of the average domain size  $R(t)$  vs time  $t$  for  $M_r=0.5$  with  $M_\theta=1.0$  and  $0.2$ .

count hydrodynamic interactions, we must modify the above model to couple with the Navier-Stokes equation [17]. The dynamics of the phase-separating process is governed by the time-dependent Cahn-Hilliard equation with the inclusion of an advection transport term,

$$\frac{\partial \Psi}{\partial t} + \mathbf{V} \cdot \nabla \Psi = M \nabla^2 \frac{\delta F(\Psi)}{\delta \Psi}, \quad (9)$$

where  $\mathbf{V}$  is the fluid velocity. By neglecting the inertial term in the Navier-Stokes equation [17], the velocity of fluid flow is given by

$$\nabla^2 \mathbf{V} = C \Psi \nabla \frac{\delta F(\Psi)}{\delta \Psi} + \nabla P, \quad (10)$$

$$\nabla \cdot \mathbf{V} = 0, \quad (11)$$

where  $P$  is the pressure and the parameter  $C$  represents the strength of the hydrodynamic effect [17]. In the present system, we are concerned with the case of strong wetting interactions between the  $A$  component and rods, and self-assembly of the rods is mainly controlled by the wetting effect and rod-rod interactions. Since the motion and rotation abilities of the rods are small, the effects on the rod motion due to hydrodynamic flow are irrelevant compared to the strong wetting interaction. Therefore, the viscous force acting on the rods from the velocity field of the fluid is negligible and we do not add advection terms to Eqs. (2) and (3).

We now use fast Fourier transform to update the values of the velocity field. The result shows that, at the late stage, the cluster structure of the  $A$  phase is destroyed, and instead the  $A$  domain again becomes percolating [see Figs. 8(a) and 8(b)]. The reason may be that in this case there exists an interplay among the rapid coarsening process caused by the hydrodynamic effect, the wetting effect, and the congregation of rods. At an early stage, the  $A$  domain is widely connected due to hydrodynamic effects, and this rapid coarsening process leads to difficulty in forming the dropletlike

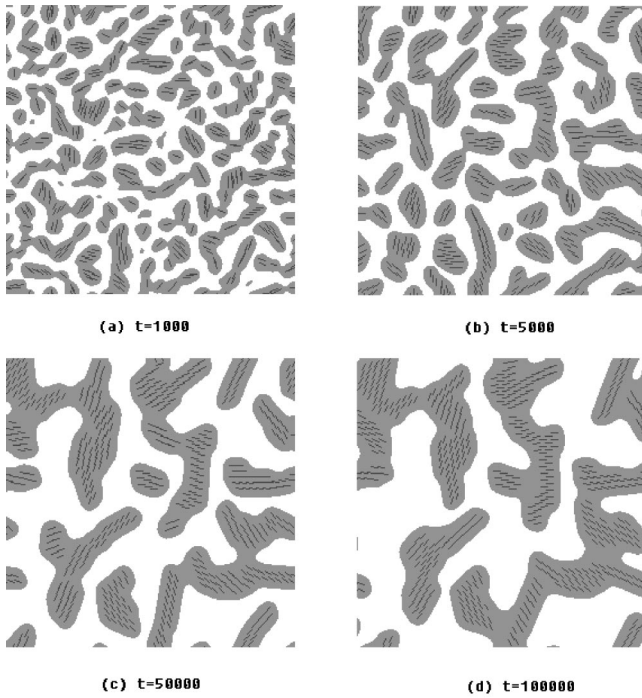


FIG. 8. Snapshots of phase separation in the presence of hydrodynamic interaction ( $C=0.83$ ) with  $M_r=0.5$  and  $M_\theta=1.0$ . (a)  $t=1000$ ; (b)  $t=5000$ ; (c)  $t=50\,000$ ; (d)  $t=100\,000$ .

structure of the  $A$  phase. The domain growth behavior is shown in Fig. 5. In the presence of hydrodynamics, the early-time growth process is much faster than that without hydrodynamic effects, but afterward it also crosses over to a slowing-down growth. We see from Fig. 5 that the growth exponent at late stages is not appreciably affected by hydrodynamic interactions (i.e., the growth exponent is almost the same,  $n=0.20\pm 0.004$ ). In this case, the presence of hydrodynamic interactions plays little role in the domain growth dynamics of the system despite the appearance of interconnected bicontinuous structures. We think that this may be attributed to modification of the rheological properties (e.g., fluidity) of the system. In the early stage, the borderline between two ordered fluid phases has large roughness, and the rods disturb the motion of interfaces near them and thus the hydrodynamic interaction has an important influence on the growth dynamics. As the interfacial area is gradually reduced and the rods form a relatively stable structure within the  $A$  phase, the presence of solid rods is expected to change the properties of the  $A$  phase by lowering the fluidity of the system, which tends to display a solidlike character. Therefore, the interface motion of the binary mixture is blocked, and thus the hydrodynamic effects are suppressed. This explains the slowing-down growth behavior despite the interconnected structure. In the present situation, on the one hand, hydrodynamic interactions will accelerate the phase separation of binary fluids, and the wetting phase  $A$  in turn affects the dispersion of rods through the strong wetting interaction between the rods and the  $A$  component. On the other hand, the motion of rods also influences the hydrodynamic flow, especially in the late regime where the rods are almost located at their fixed positions and the  $A$  domain

forms a relatively stable structure, so that the hydrodynamic flow becomes irrelevant. Notice that for such systems with third-component impurities there are no firm conclusions on the scaling behavior [15,16,18]. We should also point out that hydrodynamic effects are always suppressed due to the presence of third-component impurities such as surfactants and wetting particles [15,18–20], although the slowing-down mechanisms are different.

## V. SUMMARY

In summary, we systematically investigated the influences of third-component rods on the morphology and growth kinetics of phase separation. The rods immigrate into the bulk of the  $A$  phase to minimize the free energy of the system. Interestingly, the phase-ordering competition leads to a final morphology dependent on the rods' motion and hydrodynamic interactions. The results reveal that, due to the motion of nanoscale rods, the immiscible binary mixture will evolve into a cluster morphology if hydrodynamic interaction is neglected. On the one hand, the motion and position of the rods play an important role in determining the structure of the  $A$  domain; on the other hand, the phase-separating kinetics may simultaneously accelerate the congregating process of the rods. When hydrodynamic interaction is included, however, a rapid coarsening mechanism competes with the congregation process and destroys the dropletlike structure.

At early times, the growth behavior depends on the motion mobility of the rods, and the smaller the mobility  $M_r$ , the more quickly the domain grows. Then when the rods form a stable structure, the growth behavior crosses over to a mobility-independent region (the growth exponent  $n$  is  $\sim 0.19$ ). In the present process, the LS growth mechanism is suppressed because of geometrical confinement, giving rise to droplets that are noncircular. Similarly, hydrodynamic effects are also suppressed due to the lower fluidity of the system in the presence of the wetting effect of solid rods. The slowing-down growth behavior remains unchanged despite the interconnected structure as a result of hydrodynamic interactions. From the viewpoint of applications, the present study strongly indicates possibilities for modification of production performance through the addition of third-component rods to composite materials such as impurity-filled blends. For example, by adjusting the wetting interaction between the rods and the  $A$  component, we can improve the toughness of the final product by keeping systems from being destroyed when they are subjected to strong forces induced by flow, distortion, or dilution.

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