Simulation of Hard Particles in a Phase-Separating Binary Mixture

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We simulate the motion of spherical particles in a phase-separating binary mixture. By combining cell dynamical equations with Langevin dynamics for particles, we show that the addition of hard particles significantly changes both the speed and the morphology of the phase separation. At the late stage of the spinodal decomposition process, particles significantly slow down the domain growth, in qualitative agreement with earlier experimental data. [S0031-9007(99)09130-9]

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Phase separation plays a significant role in determining the morphology and properties of polymer composites, which typically involve a blend of various macromolecular fluids and solid "filler" particles [1]. Despite the utility of these composites, there is little understanding of the kinetic processes (including phase separation and wetting) that occur in the complex mixtures. While phase separation in binary systems has been studied extensively theoretically and experimentally [2,3], the influence of solid additives on the mixtures is still poorly understood. Recent studies have shed light on the interactions between a phase-separating fluid and a stationary wall [4], sphere [5], or substrate [6,7], but much less is known about the kinetics of mixtures that contain mobile particles. To address this problem, Tanaka *et al.* [8] examined the properties of a polymeric mixture undergoing a critical quench in the presence of small glass particles, which are preferentially wet by one of the components. Their results revealed that even a small concentration of hard particles significantly changes the morphology and dynamics of the phase-separation process. However, no theoretical or computational model was developed to characterize these changes.

In this Letter, we report the first simulations of hard mobile particles in a phase-separating binary mixture. Unlike earlier dynamical models of ternary systems (developed mostly for oil-water-surfactant mixtures [9–12]), we explicitly take into account the "excluded volume" interaction between the particles and the background fluid. Furthermore, we can vary the particle-fluid interactions, allowing for a richer range of behavior than that of a surfactant. Thus, the model presents a new means of exploring the physical properties of complex mixtures containing colloidal particles. Here, we consider particles that are preferentially wet by one of the two components and show that the boundary and excluded volume conditions at the particle surfaces significantly slow down the domain growth and change the morphology at the late stage of the phase separation.

We consider a phase-separating symmetric binary AB mixture that is characterized by the scalar order parameter Ψ. The phase separation dynamics are described by the Cahn-Hilliard equation

$$\frac{\partial \Psi}{\partial t} = \Gamma \nabla^2 \frac{\delta \mathcal{F}}{\delta \Psi} + \xi \, , \tag{1}$$

where Γ is a kinetic coefficient, ξ is a conserved zero mean Gaussian white noise with covariance $\langle \xi(\mathbf{r},t)\xi(\mathbf{r}',t')\rangle = -G_1 \nabla^2 \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$, and $\mathcal{F}$ is a free energy usually given by the Ginzburg-Landau functional

$$\mathcal{F} = \int d\mathbf{r} \left\{ -\frac{r}{2}\Psi^2 + \frac{u}{4}\Psi^4 + \frac{C}{2}(\nabla\Psi)^2 \right\}. \tag{2}$$

Into this system, we introduce spherical particles of radius R_0 that undergo Brownian motion. The particle dynamics are described by the following Langevin equation:

$$\dot{\mathbf{R}}_{\mathbf{i}} = M\mathbf{f}_{\mathbf{i}} + \eta_{\mathbf{i}} \, , \tag{3}$$

where M is the mobility, $\mathbf{f}_{\mathbf{i}}$ is the force acting on the ith particle due to all the other particles, and η represents Gaussian white noise with $\langle \eta_{\mathbf{i}\alpha}(\mathbf{r},t)\eta_{\mathbf{j}\beta}(\mathbf{r}',t')\rangle = G_2 \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\delta_{ij}\delta_{\alpha\beta}$. In this study, we neglect interactions between particles (i.e., $\mathbf{f}_{\mathbf{i}} = 0$) and only take into account the particles' diffusive motion. We also disregard osmotic effects (i.e., coupling between the particle motion and the order parameter field).

The simulation is carried out in two dimensions; our lattice is 256×256 sites in size, with periodic boundary conditions in both the x and y directions. A cell dynamical systems (CDS) method [13] is used in place of a direct forward integration of Eq. (1) to update the value of Ψ for the phase-separating AB mixture. Note that $\Psi = 1$ (-1) corresponds to the equilibrium order parameter for the A-rich (B-rich) phase. By employing CDS modeling [rather than a conventional discretization of Eq. (1)], we can significantly increase the computational speed of the simulation. To simulate the particle dynamics, we discretize Eq. (3)

and only allow the particles to move between different lattice sites. A "Kawasaki exchange" mechanism is used for each particle move: first, the order parameter values from all the cells to be occupied by a particle in its "new" position are moved to the "old" position; next, the boundary and excluded volume conditions are imposed for the order parameter at the "new" particle position. This mechanism ensures the conservation of the order parameter. Such dynamics may break down for high particle mobilities, so we considered only the case where the diffusion constant is rather low (almost all particle "jumps" are to neighboring sites). The discretized equations of motion have the following form:

$$\begin{aligned} \Psi(\mathbf{r}, t+1) &= F[\Psi(\mathbf{r}, t)] \\ &\quad - \langle\langle F[\Psi(\mathbf{r}, t)] - \Psi(\mathbf{r}, t)\rangle\rangle + \xi(\mathbf{r}, t), \\ F[\Psi(\mathbf{r}, t)] &= f(\Psi(\mathbf{r}, t)) + D[\langle\langle \Psi(\mathbf{r}, t)\rangle\rangle - \Psi(\mathbf{r}, t)], \\ f(\Psi) &= A \tanh(\Psi), \\ \mathbf{R_i}(t+1) &= \mathbf{R_i}(t) + M\mathbf{f_i} + \eta_\mathbf{i}(t), \end{aligned} \tag{4}$$

where $\langle\langle * \rangle\rangle$ is the isotropic spatial average over the nearest-neighbor and the next-nearest-neighbor sites, and $[\langle\langle * \rangle\rangle - *]$ can be thought of as a discrete generalization of the Laplacian.

At the surface of each particle, the lattice boundary conditions (specified order-parameter value and zero order-parameter flux) are imposed as $\Psi(\mathbf{r}, t) = \Psi_s$ and $\partial_n F(\mathbf{r}, t) = 0$, if $R_0 < |\mathbf{r} - \mathbf{R_i}(t)| \le R_0 + a$, where a is the lattice spacing and ∂_n denotes the "lattice" normal derivative. Here, we set $\Psi_s = 1$ so that the particles are "coated" by fluid A. The $\partial_n F = 0$ condition ensures zero flux of Ψ into the particles since F plays the role of a chemical potential.

The function F in Eq. (4) has a local driving term f and a term arising from the interaction with other sites; the map $f(\Psi)$ controls the local dynamics at each site. It is critical that f has a single unstable fixed point and two stable fixed points symmetrically located on each side of the unstable fixed point. Its exact functional form is not important for studying the universal properties of the phase separation dynamics [13]. Here, we select the map $f(\Psi) = A\tanh(\Psi)$, with $A < 1$ above the critical temperature, and $A > 1$ below.

We perform simulations for systems containing 0, 25, 50, 100, 150, 300, and 400 particles of radius 1 (all lengths are given in units of the lattice spacing a) [14]. Each system was averaged over 3 runs of 20 000 time steps each. For all systems, the following values of the parameters were used: $A = 1.3$, $D = 0.5$, $G_1 = 0$, $G_2 = 0.5$. The initial fluctuations of Ψ are Gaussian with a variance of 0.05. For all runs, the composition of the fluid is fixed at 50:50 (representing a critical mixture).

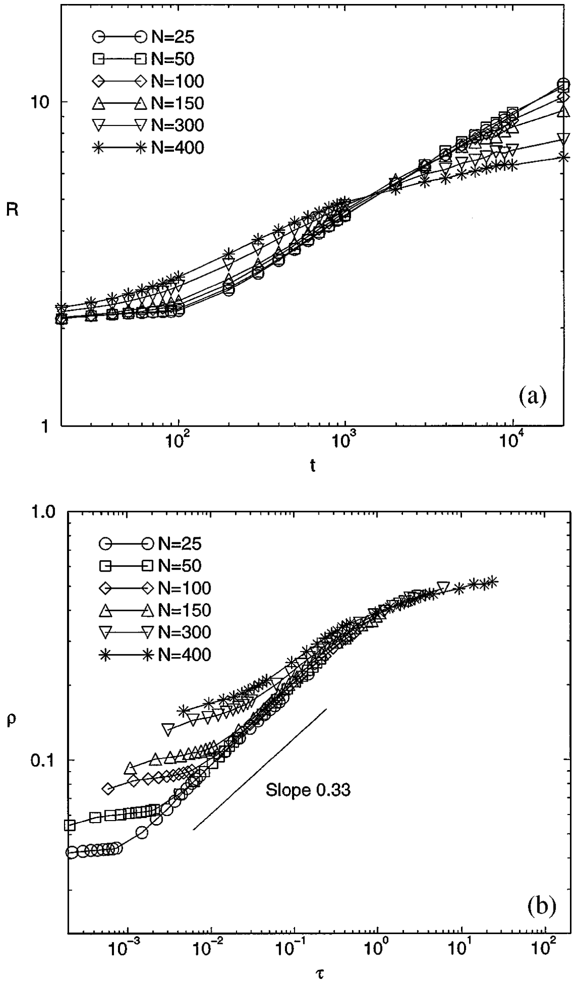

FIG. 1. Characteristic length as a function of time: (a) unscaled R vs t; (b) scaled coordinates $\rho = Rn^{1/2}/(1 + \alpha n)$ vs $\tau = tn^{3/2}$, where $n = N/L^2$ (data averaged over 3 runs). Growth exponent $\nu \approx 1/3$ in the early time range $10^{-2} < \tau < 10^0$.

The characteristic length $R(t)$ of the evolving domains is plotted as a function of time in Fig. 1(a). For $R(t)$ we use the "broken bond" formula [15], $R \sim L^d/\mathcal{A}(t)$, where L^d is the volume of the system and $\mathcal{A}(t)$ is the total interfacial "area." For $d = 2$ this becomes

$$R = \frac{L^2}{N_x + N_y}, \tag{5}$$

where L is the system size, N_x and N_y are the numbers of broken bonds (pairs of nearest neighbors with opposite signs of Ψ in the x and y directions, respectively). This measure of a characteristic length empirically yields the correct asymptotic behavior for both critical and off-critical quenches in binary mixtures.

The simulations reveal that the presence of particles slows down the domain growth in the late stage. It can be seen that for large particle numbers ($N > 100$), $R(t)$ undergoes a change from a Lifshitz-Slyozov [16] regime, with the growth exponent of 1/3, to a new regime. This new, slow-growth behavior is also characterized by a new morphology, different from the critical or slightly-off-critical pattern of bicontinuous domains [17]. The change in morphology can be seen by comparing order-parameter patterns and particle positions for the system $N = 300$

at times $t = 300$ [Fig. 2(a)] and $t = 3000$ [Fig. 2(b)]. The slower domain growth and altered structure of the mixture are qualitatively similar to the observations of Tanaka *et al.* [8].

In the early stage of phase separation, the formation of interfaces occurs as in a normal critical mixture, as would be expected as long as the concentration of particles is small, i.e., the interparticle distance is much larger than the particle radius. During this time, the initial domain growth satisfies the Lifshitz-Slyozov law, with the prefactor $E(n)$ smoothly depending on the particle density,

$$R(t) = E(n)t^{1/3}, \tag{6}$$

where $n = N/L^2$ is the particle density, and $E(n) = E_0(1 + \alpha n)$, with $E_0 \approx 0.4$ being a growth prefactor in a particle-free system. This growth continues until the characteristic domain size becomes comparable to the average interparticle distance $n^{-1/2}$. At that point, the wetting phase (A) percolates to form a single infinite domain [see Fig. 2(b)], and droplets of the B phase are trapped inside this domain. Further coarsening of B domains is inhibited by the particles acting as obstacles to the motion of interfaces.

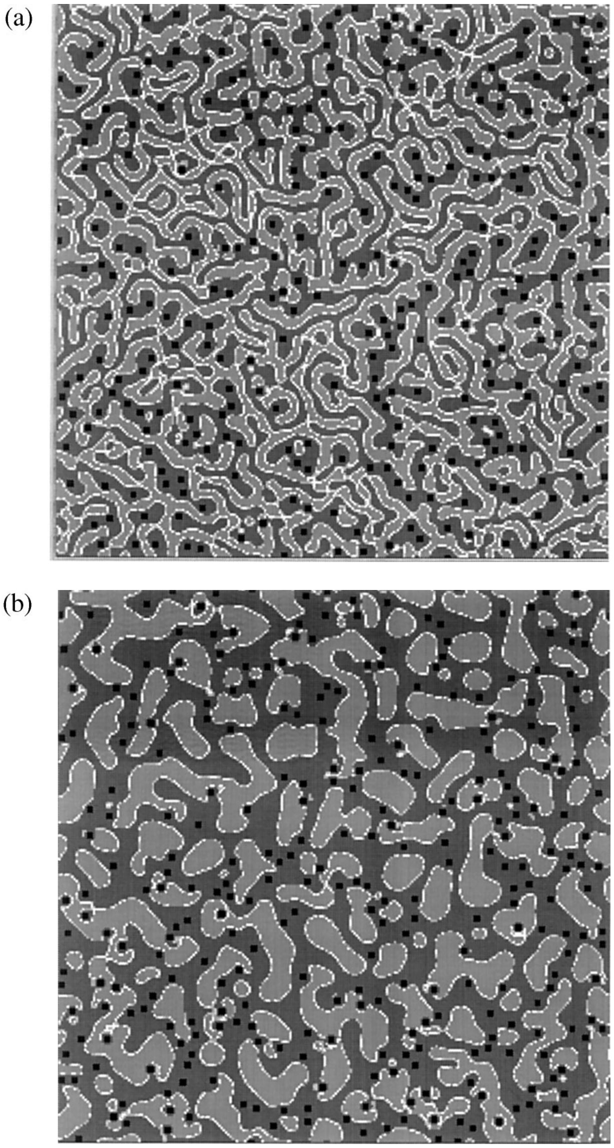

FIG. 2. Order-parameter patterns and particle positions for $N = 300$ particles at $t = 300$ (a) and $t = 3000$ (b). Black circles represent particles, dark grey regions are the A-phase domains, light grey regions are the B-phase domains, and white points are interfaces ($\Psi \approx 0$).

To describe the dependence of the characteristic size on both time and the particle density, we use the following scaling function:

$$R(t) = n^{-1/2}(1 + \alpha n)G(btn^{\gamma/2}), \tag{7}$$

where $b \approx 1$ is a "metrical factor," $G(x)$ behaves as $G(x) \approx G_0 x^{1/3}$ for small x ($b^{1/3}G_0 = E_0$), and $\gamma = 3$ (which is required to satisfy the transition to the Lifshitz-Slyozov growth law for $n \to 0$). There is clearly a slowing of growth at large time, and it is reasonable to assume $G(x) \sim x^{\delta}$ with a small power δ (or even logarithmic growth) for large x. A similar scaling form as Eq. (7) was used by Gyure *et al.* [18] to describe the dependence of the domain growth on the number of impurities in an Ising model. We introduce the additional factor $1 + \alpha n$ to account for the effective off-criticality induced by particles. To illustrate this scaling behavior, we plot the characteristic size in scaled coordinates $\rho = R(t)n^{1/2}/(1 + \alpha n)$ vs $\tau = tn^{3/2}$. For $\alpha = 13.1$, it can be seen [Fig. 1(b)] that all data fit reasonably well onto one master curve, with the exception of the $N = 400$ case, where additional n dependence is presumably required.

The observed slowing down of the domain growth is reminiscent of the interface pinning in Ising-type systems with quenched impurities [18–21]. In all those studies, impurities reduced local interfacial tension and thus enforced late-time pinning, with domain growth slowing down logarithmically, $R \propto (\ln t)^{\eta}$. A similar effect was also seen in the "hybrid" model of Kawakatsu *et al.* [12] for a binary mixture with surfactant molecules. On the other hand, our hard particles, which do not behave as surfactants and prefer to be in the bulk (A) phase, act as obstacles to the interface motion. When the characteristic domain size becomes comparable to the interparticle distance, interface coarsening becomes hindered by these obstacles, and the slowing down occurs. It is likely that at the very late stage the domain growth would stop completely (as indicated by the behavior of the $N = 400$ curve), however, it is difficult to verify this hypothesis computationally.

To elucidate the importance of wetting on the slowing down, we performed a simulation with hard, mobile particles and no preferential adsorption, i.e., with the following boundary conditions on the surface of the particles: $\partial_n \Psi(\mathbf{r}, t) = 0$, $\partial_n F(\mathbf{r}, t) = 0$. For $N = 300$ particles and no wetting, we observed no deviation from the Lifshitz-Slyozov growth law within the time scale of our simulations (20,000 time steps). This result indicates that the slowing down is clearly enhanced by the strong wetting and not merely by the effects of excluded volume or particle mobility. Indeed, nonwetting particles neither pin nor block interfaces, and thus have only minimal effect on the dynamics of the late-stage coarsening.

Although the simulations were performed for two-dimensional systems, we believe that the major features (the initial off-criticality and the late-stage slowing down) would be found in three dimensions as well. Indeed, in 3D, the particles still would represent a network of obstacles for the coarsening 2D interfaces. However, verifying this prediction remains a major computational challenge, even though the proposed model can be easily extended to three dimensions.

In the computations described here, we have not taken into account hydrodynamic interactions or the dependence of viscosity on the order parameter. We also have not considered systematically the dependence of the growth behavior on such factors as temperature (which manifests itself in the effective diffusion constant D_{eff}), the clustering of particles that could lead to additional domain pinning (an effect observed by Tanaka *et al.* [8] at very high particle densities), the dependence on the nature of the interparticle potential, and other features. These phenomena will be the subjects of future studies.

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