

Kinetic model of phase separation in binary mixtures with hard mobile impurities

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(Received 3 May 1999)

We develop a mean-field rate-equation model for the kinetics of phase separation in binary mixtures with hard mobile impurities. For impurities preferentially wet by one of the components, the phase separation is arrested in the late stage. The “steady-state” domain size depends strongly on both the particle diffusion constant and the particle concentration. We compare theoretical results with the simulation data and find good qualitative agreement. [S1063-651X(99)03510-2]

PACS number(s): 64.75.+g, 64.60.Ak, 66.30.Jt

I. INTRODUCTION

In the past decade, the use of solid filler particles to improve the physical properties of polymer blends has become widespread in the production of high-performance materials [1]. In particular, the fillers can increase the toughness, processibility, heat distortion temperature, and decrease the gas permeability of the blends [2]. Despite the utility of filled polymer systems, many aspects of the physical and mechanical behavior of these composites are still poorly understood. One of the most interesting and important questions deals with the structural evolution and final morphology of a binary polymer blend in the presence of the fillers. Understanding the influence of the particles on the thermodynamics and kinetics of binary mixtures is necessary for predicting the long-term stability and mechanical properties of the composites.

Phase separation in binary mixtures has been studied extensively [3]. In numerous experimental and computational studies, it has been shown that the characteristic domain size $R(t)$ grows asymptotically as $R(t) \sim t^\alpha$, with $\alpha = 1/3$ (Lifshitz-Slyozov law) [4]. Hydrodynamic effects increase the growth exponent and, for the long-time behavior of binary fluids, different values of α ranging from $1/2$ to 1 [3,5–7] have been suggested. The structure factor $S(\mathbf{k}, t) = \langle \Psi(\mathbf{k}, t) \Psi(-\mathbf{k}, t) \rangle$, where $\Psi(\mathbf{k}, t)$ is a Fourier transform of the order parameter $\Psi(\mathbf{r}, t)$, apparently obeys the dynamical scaling hypothesis,

$$S(\mathbf{k}, t) \approx R^d(t) \mathcal{F}(kR(t)), \quad (1)$$

where $\mathcal{F}(x)$ is a time-independent, universal scaling function. This observation has been confirmed by many numerical simulations and experiments [3,8,9].

The introduction of a third component in the form of solid mobile particles significantly increases the complexity of the problem. Particles introduce new length and time scales, generate new interfaces, and modify the morphology of the system at all stages. One can expect that the simple dynamical scaling hypothesis is no longer valid, and that many different forms of asymptotic behavior can be found depending on the particle-particle and particle-fluid interactions. Numerical studies of ternary water-oil-surfactant mixtures [10–12] showed many new and interesting features, e.g., the

slowing down of the coarsening process at the late stage due to interface pinning by the surfactant particles. However, numerical methods employed in these studies (hybrid model [10,11] and two-order parameter model [12,13]) are not suitable for describing hard filler particles because these models do not take into account the excluded volume and wetting interactions between the fillers and the polymer.

Recently, we proposed a new model to describe phase separation in a binary mixture with mobile hard particles that are preferentially wet by one of the two components [14]. This model combines the cell dynamical systems (CDS) equation of motion for the order parameter with Langevin dynamics for the hard particles. Excluded volume constraints are enforced for all particle jumps. On the boundary of each particle, zero-flux and constant-order parameter conditions are implemented at every time step. The model allows us to analyze the role of particles in the phase separation dynamics. We show that as the particle concentration is increased, the domain growth slows down progressively from the Lifshitz-Slyozov $t^{1/3}$ law. This result is in qualitative agreement with experimental observations of Tanaka *et al.* [15]. We also find that for large concentrations of particles, the domain growth stalls, and the final domain size is a complicated function of the particle concentration and the diffusion constant.

The observed result (slowing down of the domain growth at the late stage) bears a remarkable resemblance to some recent studies indicating the possibility of pinning in phase-separating systems with quenched disorder. Huse and Henley [16] suggested a theoretical mechanism of pinning (logarithmic slowing down) in Ising systems with nonconserved dynamics and static random impurities. Simulations by Srolovitz and Hassold [17] showed late-stage pinning in the nonconserved Ising system with mobile impurities. Guyre *et al.* [18] demonstrated the late-stage pinning in the conserved time-dependent Ginzburg-Landau kinetics with quenched impurities. Glotzer *et al.* [19] observed and theoretically described pinning in an Ising lattice gas with two disparate energy scales. Slowing down of the phase separation was experimentally observed for binary fluids in gels [20,21]. All these different systems exhibit different scaling laws and different pinning mechanisms; however, they all present strong evidence that any impurities in phase-separating binary mixtures tend to stop or significantly slow

down the phase-separation process at the late stage. The case of hard mobile particles with excluded volume has not yet been studied in this context. Understanding the behavior of this system is important for the description and classification of different pinning mechanisms in the phase-separation process.

In this paper, we present a simple rate-equation model describing the late-stage slowing down of the domain growth in binary mixtures with hard mobile particles, and compare theoretical predictions with computer simulation results. The model is described in Sec. II. In Sec. III, we describe the computational method [14] used to study the particle dynamics in a phase-separating mixture. Simulation results are compared with theoretical predictions. Finally, in Sec. IV we summarize our results and describe possible extensions of the model.

II. THEORY

A. Kinetic equations

We consider a phase-separating, binary AB mixture. The system is characterized by the order parameter $\Psi = \rho_A - \rho_B$ (ρ_A, ρ_B are the local densities of the A and B components). In this mixture, hard particles of radius R_0 are randomly dispersed. The particle concentration n is small, i.e., the interparticle distance $n^{-1/d} \gg R_0 > \xi$, where ξ is the width of an AB interface. Particles are preferentially wet by component A and move diffusively, with a diffusion constant D . The system separates into A -rich and B -rich domains. Let $N_-(t)$ and $n_-(t) = N_-(t)/L^d$ be the total number and the density of particles that are in B -rich domains at time t , and $N_+(t) = N - N_-(t)$, $n_+(t) = n - n_-(t)$ be the total number and the density of particles that are in A -rich domains. Here, L is the system size and d is the space dimensionality. In the following, we will set $d = 2$, although the theory can be easily extended to any dimensionality.

The densities n_+ and n_- change due to the motion of the particles and the interfaces. Such changes can be described as ‘‘reactions’’ of particles with interfacial segments. Since these ‘‘reactions’’ involve interfaces, they also affect the domain growth and coarsening rate. In particular, one can expect that when the number of particles and their mobility increase, the coarsening rate would slow down at the very late stage of the phase separation; this conclusion is confirmed by the simulations [14].

To derive kinetic equations for this system, we consider the two most elementary processes between particles and interfaces. In the first one [Fig. 1(a)], particles simply jump over the nearest interface. If we denote the particle in the A -rich phase as \mathcal{A} , the particle in the B -rich phase as \mathcal{B} , and the interface segment as \mathcal{C} , the reaction can be written as



with reaction constants k_1 and k_{-1} for the direct and the inverse reactions. In the second reaction [Fig. 1(b)], the boundary layer of a \mathcal{B} particle merges with the A domain, increasing the total length of the interface between the two domains. The reaction can be written as

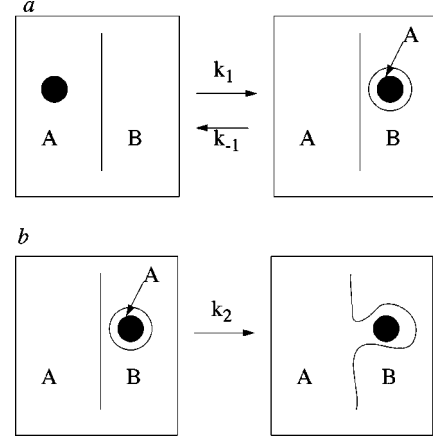


FIG. 1. Elementary processes in the particle-interface interaction: particle ‘‘jumps’’ over the interface (a); interface ‘‘overtakes’’ \mathcal{B} particle (b). Note that the particles are wet by component A .



where k_2 is the reaction constant and l is the number of the newly created interfacial segments. It can be intuitively seen that the reverse reaction can be disregarded since the probability of an interface spontaneously ‘‘surrounding’’ an \mathcal{A} particle is extremely small, especially at the late stage, where interfaces are relatively ‘‘flat.’’ (Taking the reverse reaction into account does not change the qualitative results but merely renormalizes the effective domain growth rate.)

To write down kinetic equations, we introduce a new variable, the ‘‘interface area density’’ $\sigma = S/L^d$ (where S is the total area of all AB interfaces and L is the system size). This variable is inversely proportional to $R(t)$, the characteristic domain size, $\sigma \approx 1/R(t)$ [22]. In the absence of particles, σ decreases according to the Lifshitz-Slyozov law: $\sigma \sim t^{-1/3}$. When particles are present, additional interfaces are created according to reaction (3), and the overall evolution of σ can be described by the following differential equation:

$$\frac{d\sigma}{dt} = -A\sigma^4 + k_2(l-1)n_-\sigma. \quad (4)$$

The proportionality constant A has dimensionality L^3T^{-1} and describes the growth of the characteristic size in a particle-free system. The concentration of the particles in the B phase is described by a second kinetic equation,

$$\frac{dn_-}{dt} = -k_2n_-\sigma - k_{-1}n_-\sigma + k_1n_+\sigma, \quad (5)$$

and $n_+ = n - n_-$. Equations (4) and (5) must be supplemented with initial conditions for $\sigma(t=0)$ and $n_-(t=0)$. Although these equations are highly nonlinear, and the general analytical solution cannot be obtained, we can study the fixed points and numerically describe the evolution of the system [23].

B. Dynamics

We analyze the evolution of the system numerically by integrating Eqs. (4) and (5). To perform the integration, we

first convert Eqs. (4) and (5) into the dimensionless form by introducing new variables, $\tau=t/T$, $x=n_-/n$, $y=\sigma R_0/R$, and parameters, $T=R_0^3/A$, $\lambda=k_2(l-1)R_0^2/A$, $\epsilon_1=k_1R_0^2/A$, and $\epsilon_{-1}=k_{-1}R_0^2/A$. The new dimensionless equations have a simple form,

$$\frac{dy}{d\tau} = -y^4 + 2\lambda\phi xy, \quad (6)$$

$$\frac{dx}{d\tau} = -(\lambda + \epsilon_1 + \epsilon_{-1})xy + \epsilon_1 y, \quad (7)$$

where ϕ is the two-dimensional ‘‘volume fraction’’ of the particles. We use a simple Euler scheme and forward integrate Eqs. (6) and (7) with a time step $d\tau=0.25$ in the range $0 < \tau < 10$ with the initial conditions $x(0)=0$, $y(0)=0.8$. We set $\lambda=1.0$, $\phi=0.16$, $\epsilon_{-1}=3.4\epsilon_1$, $A=0.023$, $R_0=2$, $T=350$, and perform calculations for $\epsilon_1=0.1, 0.2, 0.375, 0.75$, and 1. (The ratio ϵ_{-1}/ϵ_1 is selected to fit the simulation results for the dependence of the final domain size R^* on the diffusion constant D —see Sec. III.) The resulting ‘‘trajectories’’ $y(\tau)$ and $x(\tau)$ [or their dimensional analogs $R(t)$ and $n_-(t)$] are compared with the simulation data in Sec. III.

C. Fixed point

To find the fixed points of the system of Eqs. (4) and (5), we set the right-hand sides of both equations to zero. It is possible to solve the two equations exactly, and thus find that there is one stable fixed point:

$$n_-^* = \frac{k_1}{k_2 + k_1 + k_{-1}} n, \quad (8)$$

$$R^* = \frac{1}{\sigma^*} = \left(\frac{A}{k_2 l n_-^*} \right)^{1/3} = \left(\frac{A(k_2 + k_1 + k_{-1})}{k_1 k_2 n l} \right)^{1/3}. \quad (9)$$

Notice that, in general, the domain size saturates in this mean-field analysis for any finite concentration of particles. In order to elucidate the dependence of the final domain size on the diffusion constant D , we need to postulate the dependence of the rate constants k_1 , k_{-1} , and k_2 on D . Both k_1 and k_{-1} must be proportional to D because they are directly related to the ‘‘hopping probability’’ of particles near interfaces. On the other hand, k_2 has a contribution from the motion of an interface segment near a stationary particle, and thus can be considered D -independent (at least to a first approximation). With this in mind, we obtain

$$R^* = R_0 \left(\frac{\lambda + (\alpha_1 + \alpha_{-1})D}{2\phi\alpha_1 D} \right)^{1/3} \sim (A/Dn)^{1/3} (1 + \beta D)^{1/3}, \quad (10)$$

where $\alpha_1 = \epsilon_1/D$, $\alpha_{-1} = \epsilon_{-1}/D$, $\beta \sim R_0/A$, and λ has been defined above. These constants are independent of D and n .

It is easy to see from Eq. (10) that R^* decreases when either the particle density or the diffusion constant are increased. For large D ($D \gg \beta^{-1}$), R^* is D -independent; for small D ($D < \beta^{-1}$), $R^* \propto D^{-1/3}$. Note that for very small D , the model must break down. Indeed, once the characteristic size R^* becomes comparable with the interparticle distance

$n^{-1/2}$, we can no longer neglect the multiparticle processes (proportional to n^2 and higher-order terms in n). For such systems, interface pinning would presumably occur at $\bar{R} \sim n^{-1/2}$, preempting the steady state described by the current theory. This condition imposes a lower bound on the diffusion constant: $D > An^{1/2}$. Below this value, the final domain size is D -independent and equal to $n^{-1/2}$. Thus, the final domain size depends strongly on D in the region $An^{1/2} < D < A/R_0$. In this region, $R^* \propto D^{-1/3}$, while for $D \gg A/R_0$, R^* is almost D -independent.

The dependence of the final domain size on the particle concentration is also interesting. We find that for $D=0$, the final domain size is proportional to $n^{-1/2}$ [25]. This result is due to the fact that when the particles are immobile, the only relevant length scale is the interparticle distance $n^{-1/2}$. For nonzero D , there is a crossover between the ‘‘geometric’’ pinning $\bar{R} \sim n^{-1/2}$ and the ‘‘kinetic’’ steady-state size $R^* \sim (A/Dn)^{1/3}$. This crossover occurs near the particle concentration $\bar{n} \sim (D/A)^2$: when $n \gg \bar{n}$, the characteristic length is D -independent and scales as $n^{-1/2}$; when $n \ll \bar{n}$, the characteristic length scales as $(Dn)^{-1/3}$.

The results of the fixed-point calculation and the dependence of the final domain size on the particle number and the diffusion constant qualitatively resemble earlier experimental, theoretical, and numerical data. In their experiments, Tanaka *et al.* [15] showed that for a relatively high particle density, the characteristic domain size is frozen at the late stage. For smaller densities, the characteristic size exhibits a slow growth, with a growth exponent that is a function of the density, but always less than the Lifshitz-Slyozov exponent $\frac{1}{3}$. Similar features were found in numerical and theoretical models of phase ordering with quenched disorder. In particular, Huse and Henley [16] suggested that in an Ising-type system with a nonconserved dynamics, there is a logarithmic slowing down of the domain growth. This slowing down is due to interface pinning on quenched immobile impurities. Srolovitz and Hassold [17] independently found a similar behavior in their dynamical Monte Carlo simulations of the nonconserved Ising model with diffusing impurities with spin 0 (surfactantlike point particles). They also found that the final characteristic domain size depends on the diffusion constant; the increase in defect mobility leads to the decrease in the final domain size. Gyure *et al.* [18] analyzed the conserved time-dependent Ginzburg-Landau system with quenched immobile impurities and also found a slowing down at the late stage, consistent with the interface pinning model of Huse and Henley. Although all these studies offer qualitative support to our theory, it is not clear whether any of them are actually in the same universality class. Thus, to test predictions of the mean-field kinetic model in a more systematic way, we performed a series of simulations described in the next section.

III. SIMULATIONS

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,

$$\frac{\partial \Psi}{\partial t} = \Gamma \nabla^2 \frac{\delta \mathcal{F}}{\delta \Psi} + \xi, \quad (11)$$

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,

$$\mathcal{F} = \int d\mathbf{r} \left\{ -\frac{r}{2} \Psi^2 + \frac{u}{4} \Psi^4 + \frac{C}{2} (\nabla \Psi)^2 \right\}. \quad (12)$$

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

$$\dot{\mathbf{R}}_i = M \mathbf{f}_i + \boldsymbol{\eta}_i, \quad (13)$$

where M is mobility, \mathbf{f}_i is the force acting on the i th particle due to all the other particles, and $\boldsymbol{\eta}$ represents the Gaussian white noise $\langle \boldsymbol{\eta}_i(\mathbf{r}, t) \boldsymbol{\eta}_j(\mathbf{r}', t') \rangle = G_2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \delta_{ij} \delta_{\alpha\beta}$. In this study, we neglect interactions between particles (i.e., $\mathbf{f}_i = \mathbf{0}$) 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-system (CDS) method [26] is used 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 scheme), we can significantly increase the computational speed of the simulation. To simulate the particle dynamics, we discretize Eq. (13) 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 conservation of the order parameter. Such dynamics may break down for large 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:

$$\Psi(\mathbf{r}, t+1) = F[\Psi(\mathbf{r}, t)] - \langle \langle F[\Psi(\mathbf{r}, t)] - \Psi(\mathbf{r}, t) \rangle \rangle + \xi(\mathbf{r}, t),$$

$$F[\Psi(\mathbf{r}, t)] = f(\Psi(\mathbf{r}, t)) + \mathcal{D}[\langle \langle \Psi(\mathbf{r}, t) \rangle \rangle - \Psi(\mathbf{r}, t)],$$

$$f(\Psi) = A \tanh(\Psi),$$

$$\mathbf{R}_i(t+1) = \mathbf{R}_i(t) + M \mathbf{f}_i + \boldsymbol{\eta}_i(t), \quad (14)$$

where $\langle \langle * \rangle \rangle$ is the isotropic spatial average and $[\langle \langle * \rangle \rangle - *]$ can be thought of as a discretized generalization of the Laplacian. In the following studies we set $A = 1.3$, $\mathcal{D} = 0.5$, $M = 1.0$, and $G_1 = 0$.

The function F in Eq. (14) has a local driving term f and a term arising from the interaction with other sites; the map

$f(\Psi)$ controls the local dynamics of 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, as noted in Ref. [26]. Here, we select the map $f(\Psi) = A \tanh(\Psi)$, with $A < 1$ above the critical temperature and $A > 1$ below.

In addition to these equations, the following boundary condition is imposed in the vicinity of each particle: $\Psi(\mathbf{r}, t) = \Psi_s$ and $\partial_n F(\mathbf{r}, t) = 0$ if $R_0 < |\mathbf{r} - \mathbf{R}_i(t)| \leq R_0 + a$, where a is the lattice spacing and ∂_n denotes the normal derivative. Here, we set $\Psi_s = 1$ so that the particles are ‘‘coated’’ by fluid A . This condition can mimic either of two cases: (i) the filler particles have been pretreated with a polymer coating, or (ii) the adhesion between one of the two components (e.g., fluid A) and the surface of the particle is very strong compared to both kT and the surface adhesion of the other component. The $\partial_n F = 0$ condition ensures zero flux of Ψ into the particles since F plays the role of a chemical potential.

We performed a series of simulations on a 256×256 lattice, varying the particle number N from 0 to 300 and keeping the diffusion constant fixed at $D = 0.025$. These results have been reported elsewhere [14]. The characteristic domain size showed a marked slowing down for the systems with large values of N ($N > 150$); however, the simulation time ($T = 20\,000$ time steps) was insufficient to observe a complete saturation of the domain size, much less to determine the origin (kinetic or geometric) for the pinning mechanism.

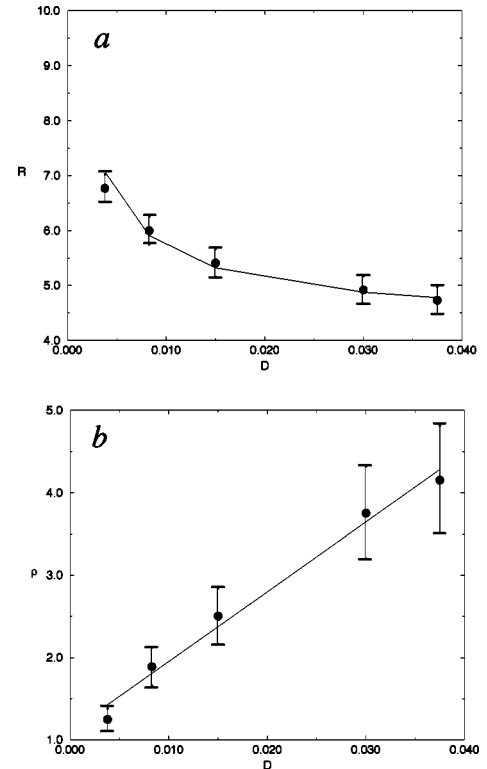


FIG. 2. Final domain size R^* vs diffusion constant D for the $N=600$ system: linear scale (a) and scaled coordinates $\rho = (R^*)^3 D$ vs D (b). Solid line represents the best fit, $\rho = (R^*)^3 D = 1.05 + 4.80D$. Vertical lines represent error bars.

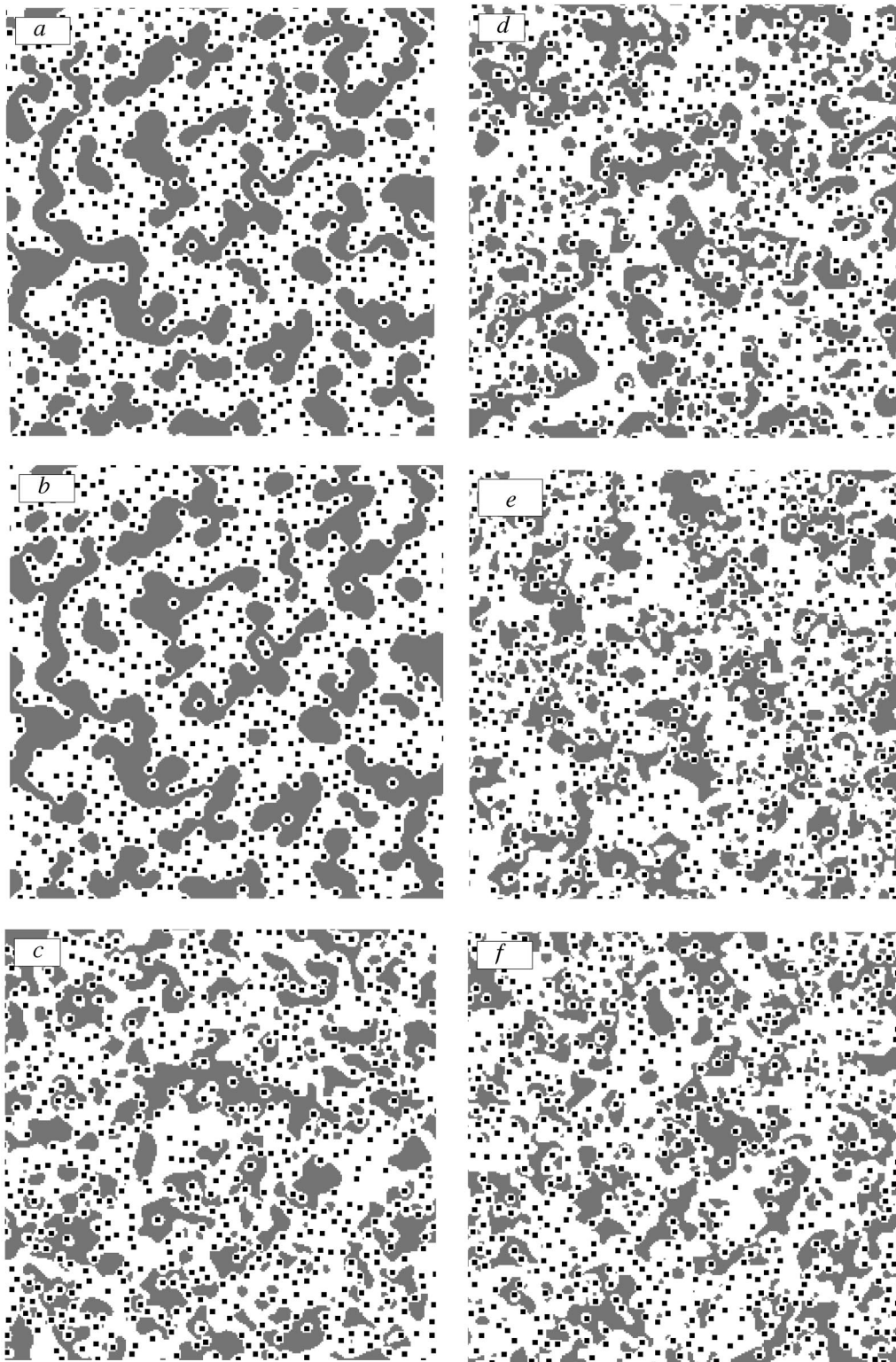


FIG. 3. Morphologies of a phase separating system with $N=600$ particles for different diffusion constants: $D=0.004$, $t=50\,000$ (a) and $t=80\,000$ (b); $D=0.015$, $t=50\,000$ (c) and $t=80\,000$ (d); $D=0.04$, $t=50\,000$ (e) and $t=80\,000$ (f). The white regions represent the A -rich phase, the dark regions correspond to the B -rich phase, and the small black squares represent the particles.

The difficulty in studying the late stage of the phase-separation process, and especially the saturation of the domain size, stems from the fact that the parameter space for such studies is very narrow. In the system we consider, for example, one cannot observe the slowing down of the domain growth until the number of particles is larger than N

$=200$; the “true” saturation is not observed until $N=500$ even up to $T=100\,000$ time steps. But, increasing the number of particles makes simulations extremely slow (since, at every time step, more and more operations are needed to ensure excluded volume constraints). As a result, the late-stage pinning can be studied only in a relatively narrow win-

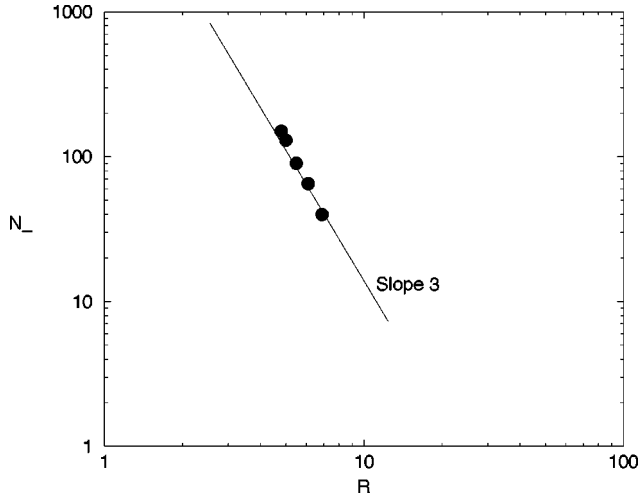


FIG. 4. Number of B particles in the “steady state” N_*^* vs the “steady-state” domain size, R^* (log-log plot). Solid line has a slope of -3 .

dow of particle concentrations ($500 < N < 800$) and the direct comparison of the theory and simulation is somewhat difficult. It is easier to vary the diffusion constant D ; however, when D becomes large ($D > 0.08$), the dynamics become unstable and dependent on specific rules of the order parameter updates during particle “jumps.” Indeed, the proposed lattice dynamics require that most particle moves occur only between the neighboring sites. Thus, the diffusion constant can be varied only in the region $0 < D < 0.08$.

To study the dependence of the characteristic domain size on the particle diffusion constant, we performed a set of simulations for the system with $N = 600$ ($\phi = 0.16$), for five different values of $D = 0.0038, 0.0076, 0.015, 0.030,$ and 0.038 . The domain growth slows down for all systems after approximately 20 000 timesteps. For every D , the results were averaged over two independent runs of 100 000 time steps each. In Fig. 2(a) we plot the dependence of the final domain size R^* on D and the best two-parameter fit from Eq. (10), with $\lambda = 1.0$, $\alpha_1 = 25.0$, and $\alpha_{-1} = 85.0$. The same data are replotted in Fig. 2(b) using the scaled coordinates $\rho = (R^*)^3 D$ versus D , in which the curve $\rho(D)$ should be a straight line according to Eq. (10). It can be seen that the agreement between the simulation data and the theory is reasonably good, albeit over a limited range (a factor of 10) in diffusion constant.

To better visualize the morphologies of the systems in the “steady-state” regime, snapshots of the configurations at $t = 50\,000$ and $t = 80\,000$ are shown for three different diffusion constants [Figs. 3(a)–3(f)]. It can be seen that for the smallest D [Figs. 3(a) and 3(b)], the majority of the domains did not change their shape or position. For the intermediate D [Figs. 3(c) and 3(d)], a small change in shape or position occurs for a significant fraction of all domains. Finally, for the largest D [Figs. 3(e) and 3(f)], most domains have somewhat changed their shape between the two snapshots. Note that the characteristic size does not change within the pairs, although clearly it is different for systems with different values of D . These pictures clearly illustrate the structural difference between the “geometric” pinning seen for the systems with immobile or slow particles [(a) and (b)] and the

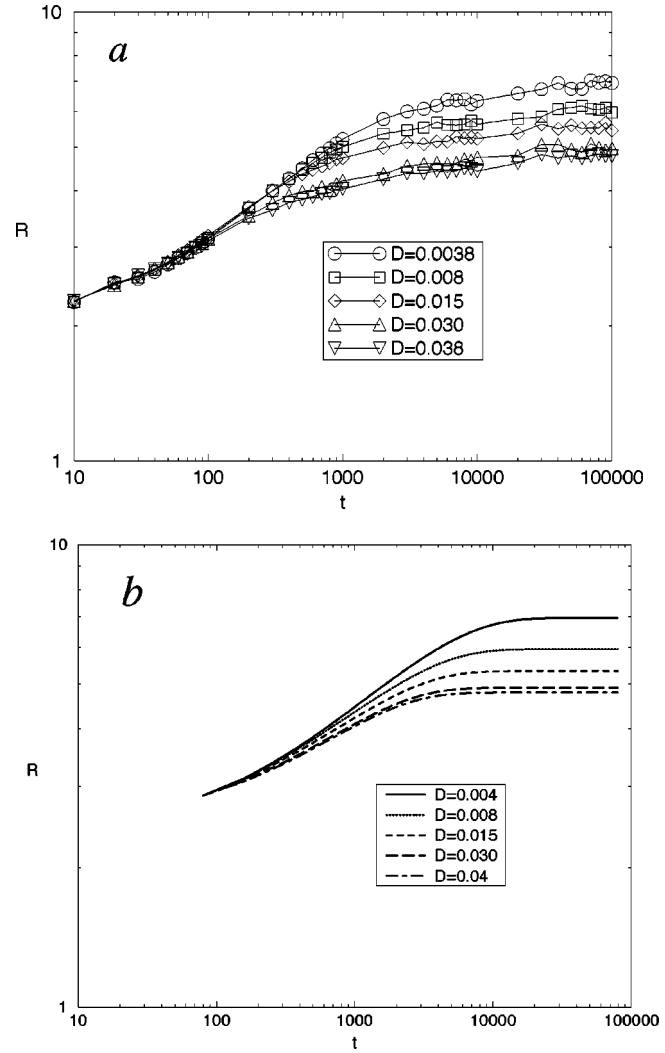


FIG. 5. Characteristic domain size $R(t)$ —simulation results (a) and calculations using Eqs. (4) and (5)(b).

dynamical “steady-state” saturation of the domain growth observed for the systems with fast particles [(c)–(f)].

Another important characteristic of the late-stage “steady state” is the concentration of particles in the “wrong” phase. In the simulations, we consider a particle to be in the “wrong” (B) phase if the total order parameter summed over all lattice sites adjacent to the particle’s “boundary layer” is negative. It can be seen from Eq. (8) that the dependence of N_*^* on R^* within the mean-field theory is described by an exact power law, $N_*^* \propto (R^*)^{-\delta}$, with $\delta = 3$. Within the mean-field approximation, this exponent is independent of the space dimensionality d . We plot the dependence of N_*^* on R^* , calculated for several values of D and for the fixed $N = 600$, in Fig. 4. The data clearly are consistent with the theoretical prediction of $\delta = 3$, although over a limited range in D .

Finally, we apply our mean-field rate-equation model to describe the dynamics of the system. Instead of looking only at the fixed point, we numerically integrate Eqs. (4) and (5) with initial conditions $N_-(t=0) = 0$, $\sigma(t=0) = 0.8$ to obtain the “trajectories” $R(t) = 1/\sigma(t)$ and $N_-(t)$. The details of the integration are described in Sec. II. In Figs. 5(a) and 5(b), simulated and theoretical trajectories $R(t)$ are plotted

for several values of D . It can be seen that the mean-field trajectories reproduce the general trends (the saturation domain size increases with a decrease in D ; the transition from the early growth regime to the late-stage regime occurs approximately at the same time for all the curves). But the mean-field calculations underestimate the width of the crossover region. This phenomenon is also seen in the calculation of the dependence of N_- on t , where the role of fluctuations is even more significant and the crossover region becomes even broader.

IV. CONCLUSIONS

We have developed a mean-field rate-equation model to describe the influence of hard mobile particles on the late stage of phase separation in binary mixtures. This model is based on an assumption that in a relatively dilute (low-particle-density) system, the influence of particles can be primarily attributed to their interactions with interfaces. Due to the asymmetry between the two phases (the particles are preferentially wet by component A), the interaction of a stationary “ B particle” with a moving interface has no inverse reaction (the interface cannot pass through an “ A particle”). This irreversible “reaction,” in combination with other (reversible) processes due to the particle diffusion, creates new interfaces and thus dynamically slows down the coarsening process. If the particles are sufficiently mobile, interface creation and annihilation offset each other, thereby forming a “steady state.” Although interfaces are highly mobile and domains change shape relatively rapidly, the characteristic size does not grow, and the overall morphology looks similar during the late-stage regime. This mechanism is different from the “geometrical” pinning described for the case of immobile impurities. In that case, interfaces simply cannot move because of the network of obstacles, and all domains remain unchanged for very long times. When the particles move sufficiently rapidly, the “steady state” behavior is observed, while when their motion is sufficiently slow, the “geometrical” pinning is observed.

The predictions of the kinetic theory have been tested by

computer simulations. Using the combined cell dynamical systems (CDS) and Langevin equations, we simulated phase separation in the presence of hard mobile filler particles and studied the dependence of the domain growth rate on the particle mobility, keeping the total number of particles fixed ($N=600$ on a 256×256 lattice). We observed a complete saturation of the domain growth at the late stage and determined the characteristic domain size at saturation. The dependence of this characteristic size on the particle diffusion constant shows a monotonic decrease, in qualitative agreement with theoretical predictions. We also measured the dependence of the number of particles in the “wrong” phase, N_- , on the characteristic size, R^* . The results for this dependence are consistent with the theoretical prediction, $N_- \propto (R^*)^{-3}$, albeit over a relatively limited range in R_* (a factor of 2). To verify the exponent δ , additional simulations and/or theoretical studies are necessary.

The proposed dependences of the “steady-state” domain size R^* on the diffusion constant D and the particle density n have a mean-field nature and are expected to break down for large n and/or for small D , when the interparticle correlations and the density fluctuations become important. It is also possible that some additional corrections should be introduced via the dependences of the kinetic coefficients A, k_1, k_{-1} , and k_2 on the “observables” D and n . Elucidation of these corrections would also require significant computational studies to increase the range of available densities and diffusion constants.

We plan to expand the proposed kinetic model to study the effects of other phenomena, such as wetting strength, flow field, and interparticle interaction, on the kinetics of phase separation. Such studies are currently underway.

D.J. gratefully acknowledges financial support from the NSF through Grant No. DMR9217935. D.J. and A.C.B. gratefully acknowledge support from the U.S. Army Office of Research. A.C.B. gratefully acknowledges the NSF for support through Grant No. DMR9709101, and the U.S. DOE for support through Grant No. DE-FG02-90ER45438.

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