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Phase separation in a simple model with dynamical asymmetry

Rajeev Ahluwalia*
Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India
and Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India

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We perform computer simulations of a Cahn-Hilliard model of phase separation that has dynamical asymmetry between the two coexisting phases. The dynamical asymmetry is incorporated by considering a mobility function that is order parameter dependent. Simulations of this model reveal morphological features similar to those observed in viscoelastic phase separation. In the early stages, the minority phase domains form a percolating structure that shrinks with time, eventually leading to the formation of disconnected regions that are characterized by the presence of random interfaces as well as isolated droplets. The domains grow as $L(t) \sim t^{1/3}$ in the very late stages. Although dynamical scaling is violated in the area shrinking regime, it is restored at late times. However, the form of the scaling function is found to depend on the extent of dynamical asymmetry. [S1063-651X(99)12101-9]

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I. INTRODUCTION

Phase separation phenomena in binary mixtures have been the subject of much recent research in condensed matter physics [1]. In a typical phase separation experiment, a binary mixture (such as an alloy, polymer blend, or a binary liquid mixture) is quenched from its one phase region into a region of its phase diagram where the constituent phases tend to segregate. The subsequent dynamics consists of the formation and growth of domains that are rich in either of the phases. It is now well established that, for mixtures the constituent phases of which have identical dynamical properties, the domain growth satisfies the dynamical scaling hypothesis in the late stages [2]. According to this hypothesis, the equal time structure factor of the appropriate order parameter satisfies the scaling law

$$S(\vec{k},t)=L(t)^{d}F(kL(t)), \tag{1}$$

where F is a scaling function and $L(t)$ is a time dependent length scale that can be associated with the mean size of the growing domains (d refers to the spatial dimension). The dynamical scaling implies that the evolution of domains is self-similar, i.e., domain size grows but the overall morphology does not change with time. The other interesting aspect is the functional form of the length scale $L(t)$. It is now conclusively established that for pure and isotropic systems, $L(t) \sim t^{\phi}$, where ϕ is the growth exponent that crucially depends on the nature of the dynamics. For example, in the case of a binary alloy where there is no intrinsic dynamical asymmetry between the two phases, the growth is driven by surface tension and is characterized by an exponent $\phi=1/3$ [1]. This is commonly referred to as the Lifshitz-Slyozov law, which also describes domain growth in polymer solutions and blends for shallow quenches. For binary liquids the hydrodynamic interactions are important and for this case, the growth exponent $\phi=1$ [3].

Recently, there have been some experiments investigating the role of dynamical asymmetry between the constituent phases of the phase separating system. The dynamical asymmetry usually arises when the characteristic relaxation times of the molecules of the coexisting phases are different. Tanaka has studied phase separation in deeply quenched semidilute polymer solutions [4] where the asymmetry arises due to the viscoelasticity of the polymer rich domains. In another interesting experiment, Tanaka [5] has investigated domain growth in a polymer blend that is quenched to a temperature that is close to the glass transition temperature of the minority species. The common feature of these systems is that the time scales of molecular motion of the minority phase are much slower relative to the other phase. This leads to unusual phase separation, which is now commonly referred to as viscoelastic phase separation.

The main features of viscoelastic phase separation are as follows. After an initial incubation regime during which no macroscopic phase separation occurs, domains of the more mobile majority phase nucleate and start growing. The growth of these domains eventually results in the formation of a thin spongelike percolating network of the minority phase (this is in contrast to usual phase separation where the minority phase forms isolated droplets). The growth of the majority phase domains also leads to an overall shrinking in the volume of the minority phase regions. The shrinking continues until the network breaks up into isolated droplets of the minority phase.

Taniguchi and Onuki [6] have studied this problem by simulating a viscoelastic model that incorporates the coupling between stress and diffusion [7] for a semidilute polymer solution. They were able to observe a spongelike network of the minority phase in their simulations. However, they were not able to see phase inversion (the eventual breaking up of the network into isolated minority phase domains) within the time scales of their simulations. Subsequently, Tanaka and Araki [8] simulated a viscoelastic model

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*Address correspondence to Materials Research Center, Indian Institute of Science, Bangalore 560 012, India. Electronic address: rajeev@mrc.iisc.ernet.in

[9] with the effects of bulk stress included. Using this model, they were able to demonstrate most of the experimentally observed features like the formation of the minority phase network, which eventually breaks down, leading to phase inversion.

Although, the viscoelastic models are crucial to explain the experimental observations of Tanaka, dynamical asymmetry can also be studied in framework of the usual Cahn-Hilliard theory of phase separation by making use of an order parameter dependent mobility. Sappelt and Jackle [10] have studied domain growth in a system where one of the phases freezes into a glassy state. They have considered an order parameter dependent mobility that is asymmetric about a fixed concentration. In their simulations, they found an unusual growth mechanism for concentrations where the less mobile glassy phase is the majority phase. However, they did not find a spongelike structure of the glassy phase for the case with low volume fraction of the glassy component.

In this paper, we study dynamically asymmetric phase separation within the framework of Cahn-Hilliard theory by choosing an appropriate mobility function. The mobility function used by us is different than that chosen by Sappelt and Jackle, who were investigating the interplay between spinodal-decomposition and glass transition [10]. In this work, we are specifically interested in describing the unusual coarsening behavior observed in viscoelastic phase separation experiments by Tanaka. We propose a simple model that can describe many of the features observed in Tanaka's experiments, from the point of view of pattern formation. Unlike the viscoelastic theories, we do not incorporate stress fields and the dynamics in our model is driven by surface tension only. The effect of dynamical asymmetry and the stress fields is incorporated by choosing the mobility function appropriately. We will give a detailed discussion of our modeling and its relation to the experiments in Sec. II.

The organization of this paper is as follows. In Sec. II, we introduce our dynamical model. We also explain the modeling of the order parameter dependent mobility and its physical significance. In Sec. III, we give numerical results for pattern evolution. We also show results for the domain growth law and the time-dependent structure factor. Section IV is devoted to a discussion of the results and the limitations of the model.

II. DYNAMICAL MODEL

The theory is formulated in terms of an order parameter that is the concentration difference between the two species. Since the concentration difference is a conserved quantity, the time evolution of a scaled dimensionless order parameter $\phi(\vec{x},t)$ is described by the equation

$$\frac{\partial\phi(\vec{x},t)}{\partial t}=\vec{\nabla}\cdot\{M(\phi(\vec{x},t))\vec{\nabla}[-\phi(\vec{x},t)+\phi(\vec{x},t)^3 -\nabla^2\phi(\vec{x},t)]\}, \tag{2}$$

where $\vec{x}$ and t are, respectively, the scaled space and time variables and $M(\phi)$ is the mobility function. This is the deterministic Cahn-Hilliard equation, which is also referred to as model B in the Halperin and Hohenberg system of classification [11]. In conventional theories of spinodal decomposition, the mobility function $M(\phi)$ is usually treated as a constant. However, recently there have been some studies where the effect of an order parameter dependent mobility on the dynamics of phase separation has been investigated [12].

At this stage, it is useful to discuss the mechanism of domain growth in viscoelastic phase separation. We consider the example of polymer in a solvent. For very deep quenches, molecular time scales of the polymer rich regions (minority phase) are much slower relative to the solvent (majority phase). This gives rise to viscoelastic stresses. The elastic stress in the early stages is responsible for the so-called incubation regime during which no macroscopic phase separation occurs as the stress fields tend to suppress diffusion. After the incubation period, holes of the solvent start nucleating in regions where the stress has locally relaxed. The holes start growing resulting in an increase in dynamical asymmetry as the more viscoelastic polymer rich regions are subjected to deformations due to the ongoing coarsening. Due to the high deformation rate, stress acts on the polymer rich regions that by now form a percolating network. The dynamics in this regime is governed by the viscoelastic stress rather than surface tension. As the stress relaxes, the polymer rich regions discharge the dissolved solvent resulting in volume shrinking of the polymer rich regions. In the very late stages, the system approaches equilibrium and consequently the deformation rate of the network decreases. This results in a weakening of the stress fields. In the absence of viscoelastic stress, the dynamics is governed by surface tension and so the network starts to break up into disconnected regions. Thus, the inherent asymmetry of molecular time scales between the two components does not influence the dynamics in late stages. To summarize, the dynamics in viscoelastic phase separation is characterized by a strong influence of dynamical asymmetry in the early stages. However, the effect of dynamical asymmetry gradually decreases as the system approaches equilibrium.

In this paper, we consider a model where the viscoelastic effects discussed above are mimicked through an order parameter dependent mobility. We state here that the model is not specific to polymer solutions but attempts to describe the unusual domain growth observed in viscoelastic phase separation within the general framework of the Cahn-Hilliard theory. We consider a mobility function of the type

$$M(\phi)=\frac{1}{1+\exp(\alpha\phi-\beta\phi^2)}, \tag{3}$$

where α and β are positive constants ($\beta>\alpha$). The motivation for choosing this particular form of the mobility is as follows. In the early stages of domain growth ϕ is small and for a large enough value of α, the mobility is a sharp step function around $\phi=0$. The negative quadratic term on the other hand provides a competing effect on the dynamical asymmetry as ϕ increases. This term is responsible for weakening of dynamical asymmetry in the late stages and is crucial to get phase inversion. The effect of this term on the dynamics is in some sense analogous to stress relaxation in viscoelastic systems.

III. NUMERICAL RESULTS

In this section, we give details of our numerical simulations of phase separation for an off-critical quench into the unstable region, using the above described model. We solve Eq. (2) with the mobility function given in Eq. (3) on an $N \times N$ square lattice with periodic boundary conditions. A simple Euler discretization is used with mesh size $\Delta x = 1.2$ and the smallest time step $\Delta t = 0.02$. The initial condition are given by

$$\phi(\vec{r},0) = \overline{\phi} + \delta\phi(\vec{r},0), \qquad (4)$$

where $\overline{\phi}$ is the off-criticality and $\delta\phi(\vec{r},0)$ represents random fluctuations uniformly distributed in the interval $[-0.005, 0.005]$. In the simulations reported in this paper, we choose $\overline{\phi} = -0.1$, which corresponds to a minority phase concentration of 0.45.

We first describe our results on pattern evolution on an $N \times N$ lattice with $N = 128$. We consider a quench corresponding to $(\alpha = 100, \beta = 160)$. In Fig. 1 we display the evolution of domains corresponding to $\overline{\phi} = -0.1$. The darker contrast regions correspond to the minority phase $(\phi > 0)$ and the brighter regions correspond to the majority phase $(\phi < 0)$. The shade varies with the extent of order, which is characterized by the local value of the order parameter. In the very early stages, the growth is strongly influenced by the dynamical asymmetry. At $t = 0$, the system is in a one phase state corresponding to $\overline{\phi} = -0.1$. As order parameter fluctuations start getting amplified, the growth of concentration in regions that are locally rich in the minority component is suppressed due to low mobility. However, regions that are rich in the majority component order much faster (this is in contrast to the usual phase separation where both minority and majority phases order rapidly and the minority phase forms isolated droplets). The snapshot at time $t = 50$ in Fig. 1 corresponds to this situation where we can see the emergence of local regions rich in the majority phase. These regions are more ordered as compared to the minority phase regions. However, the boundaries between the two phases are still not very sharp (this is analogous to the so-called incubation regime in viscoelastic phase separation). When the order parameter in the majority phase regions reaches its saturation value $\phi_{eq} = -1$ $(t \sim 100)$, well defined domains of the majority phase appear and start growing (keep in mind that the order parameter in the minority phase regions is yet to reach its saturation value of $\phi_{eq} = 1$). In this regime, the partially ordered minority phase regions form a percolating structure the area of which keeps on shrinking with time. This thinning is due to diffusion from the minority phase regions to the majority phase regions (the minority phase regions tend to expel the dissolved majority phase component and this results in the growth of order parameter within the minority phase regions). This behavior is analogous to the solvent discharge from the polymer rich domains in the elastic regime of viscoelastic phase separation.

The growth of the majority phase domains and the associated area shrinking can be clearly seen in the snapshots at times $t = 100$ and $t = 200$. As the order parameter in the minority phase grows, the negative quadratic term in the mobility starts dominating and the dynamics becomes faster. The order parameter in these regions rapidly saturates to the equilibrium value $\phi_{eq} = 1$ (the thick black patches in minority phase at time $t = 200$ correspond to such regions). At this stage, we should also remark that the negative quadratic term in the mobility is crucial to observe substantial area shrinking and eventual phase inversion. In the absence of this term, the mobility of the minority phase regions remains low for all time, thereby arresting the growth of order parameter [10].

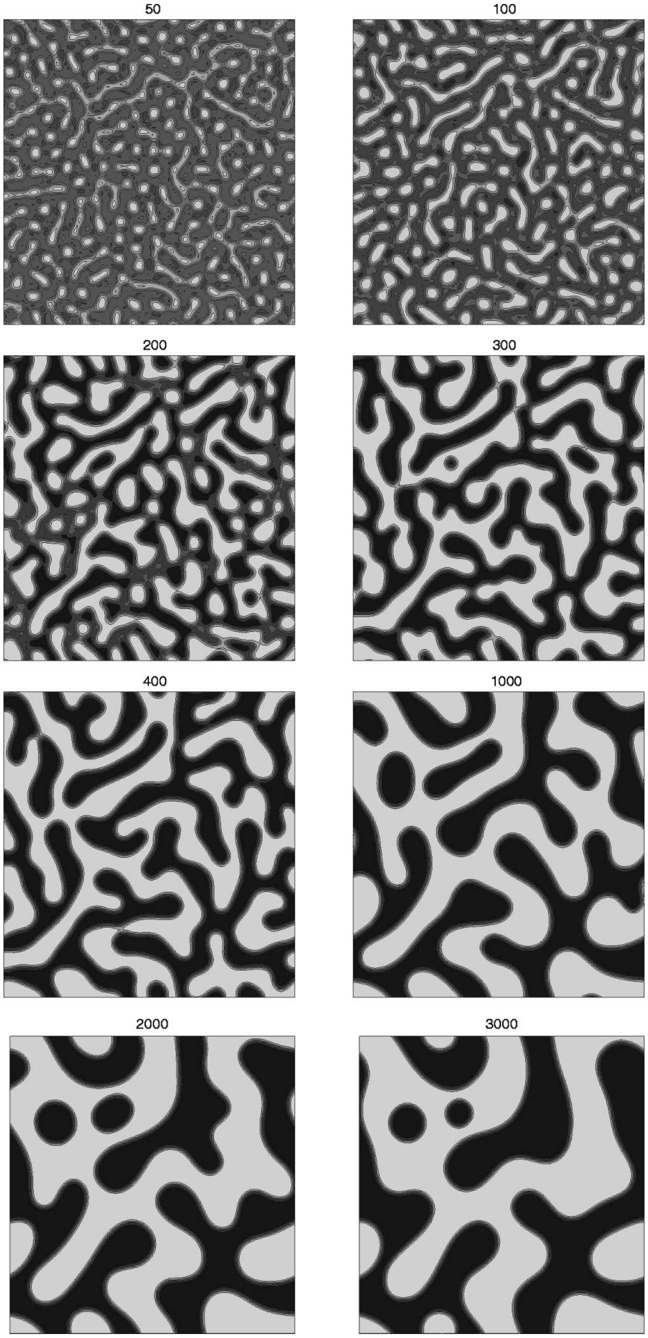

FIG. 1. Time evolution of the domains for the asymmetric mobility case. The dark contrast regions in the snapshots correspond to the minority phase regions $(\phi > 0)$ and the bright contrast regions correspond to the majority phase $(\phi < 0)$. The shade varies with the extent of ordering determined by the local value of the order parameter. The snapshots correspond to times $t = 50$, 100, 200, 300, 400, 1000, 2000, and 3000.

The area shrinking continues till the order parameter in most of the minority phase regions has also reached its saturation value $\phi_{eq}=1$. Notice that by this time, the asymmetry in the mobility has also disappeared as $M(\phi=1)=M(\phi=-1)$. Subsequently, the domain growth is expected to occur by the usual Lifshitz-Slyozov or evaporation-deposition mechanism, where there is a diffusion from regions of higher to lower curvature. Thus domains like to minimize the surface area and the connectivity of the minority phase regions is expected to break. This can be seen from the snapshots at times $t=300$ and $t=400$, where we can see the appearance of disconnected minority phase domains. At very late times, as shown in the snapshots at times 1000, 2000, and 3000, the morphology consists of disconnected random interfaces as well as isolated circular domains. Even after long times, we do not observe a fully droplet morphology that is characteristic of the dynamically symmetric cases for the present value of the initial composition. Thus, even in the regime that is not dominated by dynamical asymmetry, the pattern retains the memory of the percolating structure it had in the early stages. Similar behavior has been observed in simulations of a viscoelastic model by Tanaka and Araki [8] where the effect of the bulk as well as shear relaxational modulous has been incorporated.

We now present results pertaining to dynamical scaling. The quantity of interest here is the time-dependent structure factor defined as

$$S(\vec{k},t)=\frac{\langle \phi(\vec{k},t)\phi(-\vec{k},t)\rangle}{\frac{1}{N^2}\sum_k \langle \phi(\vec{k},t)\phi(-\vec{k},t)\rangle}, \tag{5}$$

where $\phi(\vec{k},t)$ is the fourier transform of $\phi(\vec{r},t)-\overline{\phi}$ and angular brackets refer to an average over initial conditions. The wave vector $\vec{k}$ ranges over the first Brillouin zone. For the results presented in this paper, we make use of the isotropy of the system and evaluate a spherically averaged structure factor that depends only on the magnitude of the wave vector.

We test whether the spherically averaged structure factor obeys the dynamical scaling form

$$S(k,t)=L(t)^d F(kL(t)), \tag{6}$$

where $L(t)$ is a length scale related to the mean size of the growing domains. We use the inverse of the first moment of the spherically averaged structure factor as a measure of this length scale, i.e., $L(t)\sim\langle k\rangle(t)^{-1}$, where

$$\langle k\rangle(t)=\frac{\int_0^{k_m} dkkS(k,t)}{\int_0^{k_m} dkS(k,t)}. \tag{7}$$

The upper cutoff is taken to be half the magnitude of the largest wave vector lying in the first Brillouin zone.

Before we describe our results on dynamical scaling and the structure factor, it is useful to identify the different regimes of growth. In Fig. 2, we plot the area fraction ϕ_A of the minority phase regions with the dimensionless time variable of our simulations. The quantity ϕ_A has been obtained by solving Eq. (2) on an $N\times N$ lattice ($N=256$) and computing the fraction of sites with $\phi>0$ at each time step. The data presented in Fig. 2 is obtained by averaging over 50 independent systems. We see that the area fraction initially increases above it's equilibrium value of 0.45. This corresponds to the fact that the minority phase forms a percolating matrix in the early stages. Subsequently, the area fraction ϕ_A rapidly decreases. This corresponds to the regime in which the concentration within the domains keeps on changing as there is a desorption from the minority phase to the majority phase leading to area shrinking. The area shrinking continues till the order parameter saturates to it's equilibrium value every where ($t\sim300$). The area fraction saturates close to the equilibrium value of 0.45 in the late stages. This regime can be clearly seen in Fig. 2 for times greater than $t\sim300$. The domain growth in this regime is characterized by the usual curvature driven mechanism. We should remark here that very similar time dependence of the volume fraction has been observed in deeply quenched polymer blends by Tanaka [5].

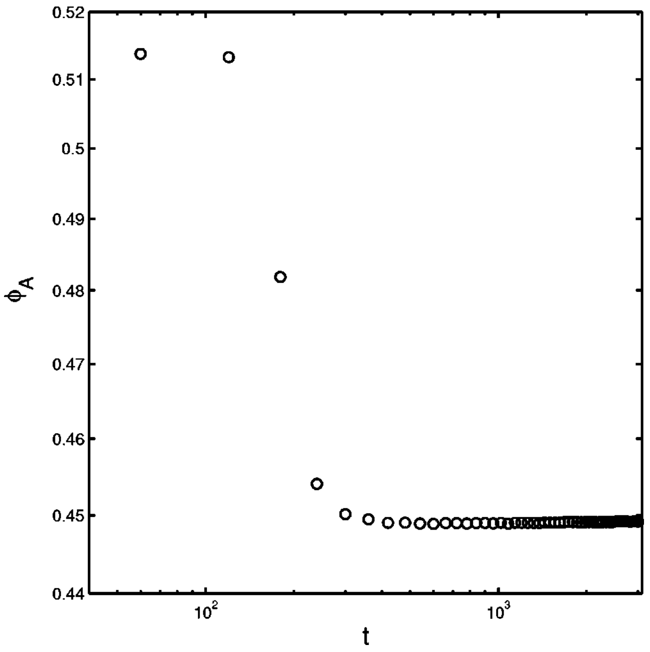

FIG. 2. Variation of the area fraction ϕ_A of the minority phase with the dimensionless time variable of the simulations.

We now present our results for the structure factor and the length scales. We have computed the spherically averaged structure factor and the associated length scale $L(t)$ on a 256×256 lattice by averaging over 50 independent initial conditions. In Fig. 3, we show the behavior of $L(t)$ with t (t is a dimensionless time variable) on a log-log scale. We observe an initial fast growth which corresponds to the area shrinking regime. The curve crosses over to a straight line that is nearly parallel to the solid line of slope 1/3, thereby indicating that our data conforms to a growth law $L(t)\sim t^{1/3}$ asymptotically. This growth law corresponds to the regime where both minority and majority phase regions are fully ordered and the evaporation-deposition mechanism is expected to apply.

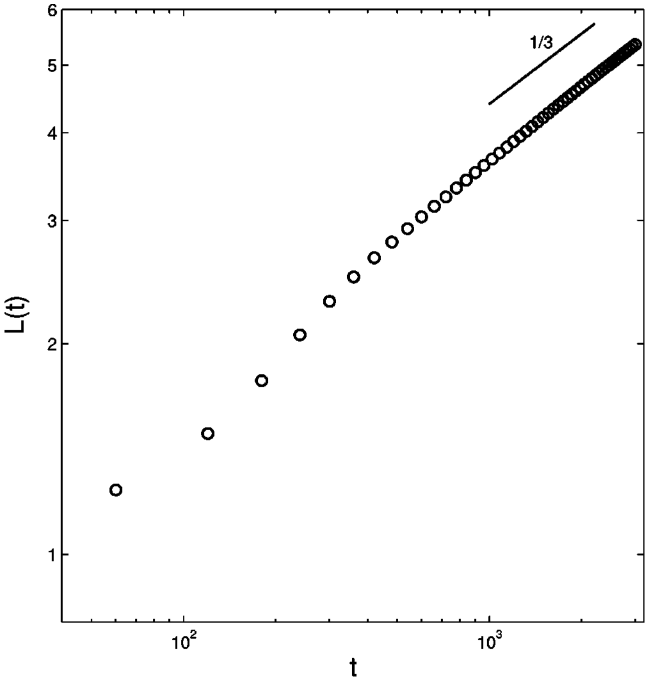

FIG. 3. Log-log plot of the mean domain size $L(t)$ (Inverse of the first moment of the spherically averaged structure factor) with the dimensionless time t of the simulations. The solid line has a slope 1/3 and serves as a guide to the eye.

To test for dynamical scaling hypothesis, we plot $L^{-2}(t)S(k,t)$ versus $kL(t)$ in Fig. 4, for times 60, 120, and 300. The datasets at times 120 and 300 fall within the area shrinking regime. We observe that there is no data collapse indicating a violation of dynamical scaling for these times. This can be understood if we consider the fact that in the area shrinking regime, the order parameter within the domains is not saturated but keeps on changing with time. However, there is a good data collapse at later times as shown in Fig. 5. The data at times 1500, 2100, and 3000 scales well (except in the tail where the finite interfacial width is responsible for deviations from scaling [13]). In this regime, the order parameter is saturated every where and growth takes place by usual evaporation-condensation mechanism.

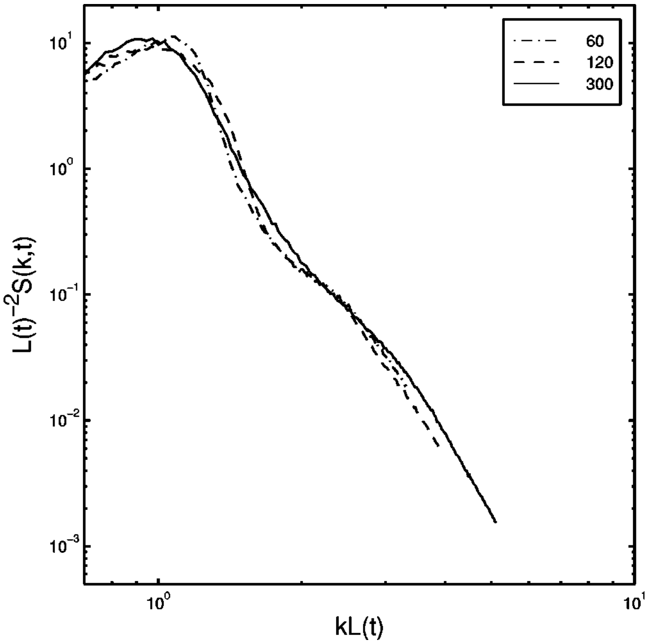

FIG. 4. Test for dynamical scaling in the early stages. We plot $L^{-2}(t)S(k,t)$ vs $kL(t)$ on a log-log scale for times $t=60$, 120, and 300.

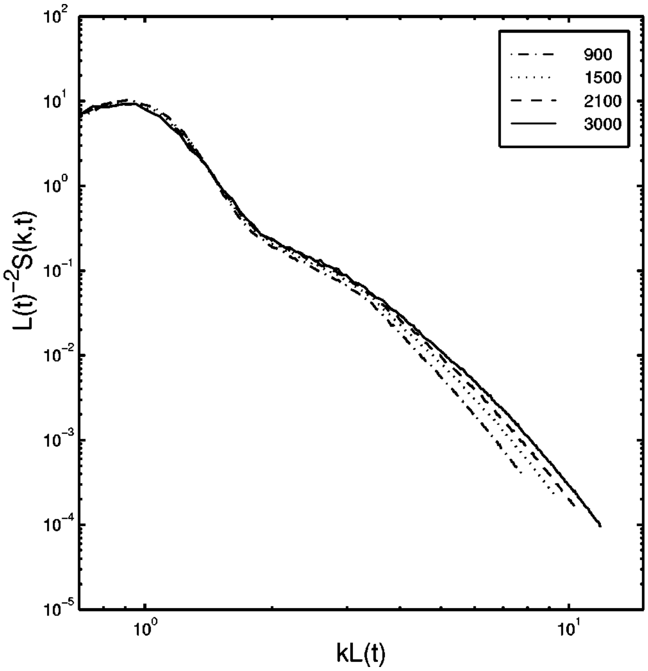

FIG. 5. Analogous to Fig. 4, but for times corresponding to $t=900$, 1500, 2100, and 3000.

It is interesting to compare the form of the scaling function with dynamical asymmetry to that with the symmetric mobility case. In Fig. 6, we plot $L^{-2}(t)S(k,t)$ with $kL(t)$ at

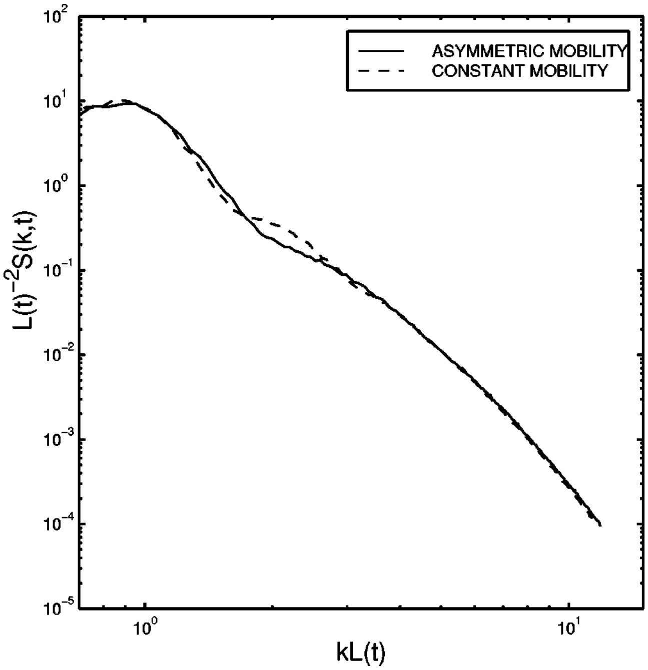

FIG. 6. Log-log plot of $L^{-2}(t)S(k,t)$ vs $kL(t)$ at time $t=3000$ for the aymmetric mobility case and the constant mobility case with $M(\phi)=1$.

time 3000 for the case of constant mobility and the dynamically asymmetric case considered in this paper (the data for the symmetric mobility case has been obtained for $M(\phi)=1$, with the same initial conditions and statistics as the asymmetric mobility case). We find that the two scaling functions have different form. In particular, the usual Porod's ''shoulder'' is less pronounced in the dynamically asymmetric case than in the constant mobility case. This suggests that the form of the scaled structure factor is dependent on the extent of the dynamical asymmetry, for the same value of the initial composition.

IV. SUMMARY AND DISCUSSION

In this paper, we have presented results of computer simulations of a simple Cahn-Hilliard type model that has dynamical asymmetry built in through an order parameter dependent mobility. The form of the mobility function is chosen so as to incorporate the effects of a strong dynamical asymmetry in the early stages along with a competing term that restores symmetry in the late stages. Our simple model captures many of the experimentally observed features that have also been observed in simulations on viscoelastic models. Our simulations reveal a morphology in which the minority phase forms a percolating structure in the early stages. The area of the minority phase matrix shrinks with time and eventually the matrix starts breaking up into disconnected regions.

We have also tested for the existence of dynamical scaling. We find that the structure factor does not scale very well in the area shrinking regime. However, it crosses over into a scaling form when the growth is determined by the evaporation deposition mechanism. Interestingly, the form of the scaling function is different than the constant mobility case. This suggests that the scaling behavior is dependent on the extent of the dynamical asymmetry (this can be checked in experiments by considering the dependence of the structure factor on the quench depth). The difference in the form of the scaling function arises due to the fact that the late stage morphology in the dynamically asymmetric case is different than that for the constant mobility case. However, the asymptotic growth law is same as that observed in constant mobility systems, i.e., $L(t)\sim t^{1/3}$.

Although we have been able to account for many of the experimental features, we do not claim this model to be an accurate description of viscoelastic phase separation. We have considered a very simple model that shows growth regimes similar to viscoelastic phase separation. The incorporation of stress fields is essential to obtain the thin network-like morphologies as observed in experiments, where as in our model, the domain shapes are determined by concentration gradients only. Nevertheless, we expect that our late stage results on the morphological features as well as the scaling behavior could be relevant to viscoelastic phase separation experiments, particularly in the time regime where the viscoelastic stresses have decayed.

We should also point out that the percolating minority phase structure is formed in our model only for a small range of compositions between $\bar{\phi}=-0.1$ and $\bar{\phi}=0.0$, only for a sufficiently large value of the asymmetry parameter α. In fact, for lower α, even for the same composition $\bar{\phi}=-0.1$, we do not get an initial percolating minority phase. The only effect of asymmetry for such cases is on the shape of the domains.

Finally, we remark that our choice of the mobility function is not unique. We could construct other forms of the mobility function that could give similar results. However, we expect that the associated phase separation to fall into the same dynamical universality class for all these models. In the present work, we have attempted to demonstrate that the unusual phase separation observed in viscoelastic systems is a more general phenomena, which is expected to show up in systems where there is a dynamical asymmetry that gradually decreases as the system approaches equilibrium.

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