

Phase separation in two-dimensional binary fluid mixtures: Spontaneous pinning effect

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The dynamics of phase separation, under asymmetric quench, is studied for binary mixtures by molecular dynamics simulations. We consider two kinds of systems, i.e., the small molecular liquid mixture and the flexible chain blend. The domain growth is found to be dependent crucially upon the relative composition of the mixture. For a near symmetric quench with volume fraction not far away from the critical value, we find that the domain growth is obviously slowed down (the spontaneous pinning effect) when the phase-separating structure undergoes the percolation-to-cluster transition. However, as the volume fraction of the minority phase is decreased, a pinning-depinning transition of the domain growth is observed for certain asymmetric quenches, due to the correlated motion of droplets. For sufficiently asymmetric quenches where the volume fraction of the minority phase is low, the domain growth is suppressed at late stages for the flexible polymer blend, in contrast to the fast growth for the small molecular system. The results are in good agreement with previous studies, and confirm the possibility of the intermittent or final pinning of phase separation for isolated droplets structure.

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Phase separation dynamics has been a subject of considerable study in recent years, not only from the technological but also from the theoretical point of view [1]. When a binary system is quenched into the coexisting region, the demixing process drives the formation and growth of two ordered phases. Typically, such spontaneous process can be well understood with a power law $R(t) \sim t^\alpha$, where $R(t)$ is the average domain size at time t . The growth exponent α is an important quantity which effectively reflects the growth mechanisms, and can take a characterized value by a given universality class. In fluid systems, the hydrodynamic flows usually have an important influence on the domain growth and structural evolution. For systems with a symmetric quench, the flows are believed to accelerate the domain growth and lead to the 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 [1,2]. Under the asymmetric quenches, phase separation dynamics is dependent crucially upon the relative composition of the mixture and hydrodynamic effects are believed to become less important with decreasing the volume fraction ϕ of the minority phase. For sufficiently asymmetric quenches where the volume fraction of the minority phase is rather low, isolated droplets structure is present at very early stages, and the domain growth is usually believed to be controlled by a *Brownian* coalescence mechanism [3] and a bulk diffusion mechanism [4], each of which gives the growth law $R(t) \sim t^{1/3}$. However, it was recently noted that the spontaneous motion of droplets also plays an important role for the structure evolution [5]. So far, it is not clear how the domain growth is influenced by such spontaneous motion which is spatially correlated, depending on the phase-separating structure.

Polymer blends are well suited to the investigation of phase separation because the time and size scales allow easy experimental monitoring. One striking observation is the

“spontaneous pinning” of domain growth when the minority phase evolves from the early-stage percolated domains into circular clusters (or droplets), i.e., the so-called percolation-to-cluster transition [6]. One interpretation is related with the enthalpic-barrier argument, which states that the transport of the components through the bulk is energetically unfavorable and the bulk-diffusive contribution to domain growth is therefore suppressed [6]. On the other hand, Crist [7] has pointed out that hydrodynamic effects must be considered for explaining the pinning behavior and attributes it to a cross-over behavior from the hydrodynamic regime to the other regime. This seems to be confirmed by a recent experiment [8]. However, there is still a lack of numerical evidence of the spontaneous pinning effect [9,10]. So far, the mechanism for the pinning effect is not available at this point.

In this paper we address the spontaneous pinning phenomenon by studying phase separation dynamics under asymmetric quenches, i.e., the systems have asymmetric compositions. The obtained results on two types of systems are compared and show that the domain growth presents qualitatively similar behaviors despite some trivial differences. It is shown that for near symmetric quenches with volume fraction not far away from the critical value, the domain growth is promoted by the hydrodynamic flows at early stages but is continuously slowed down. In particular, for certain asymmetric quenches, an intermittent pinning state is confirmly observed during the process, and after that phase separation becomes fast again. Such observation of a pinning-depinning transition qualitatively supports the experimental results, indicating that the hydrodynamic effects have significant influence on droplet motion and can suppress the coalescence of droplets temporarily. For sufficiently asymmetric quenches, suppressed domain growth is observed only for the flexible chain system, in contrast to the fast growth for small molecular systems. The reason for this discrepancy may be attributed to the different distances between droplets.

To simulate phase separation dynamics, we apply the molecular dynamics (MD) method similar to that previously

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employed by Toxvaerd and co-workers [11]. For a small molecular liquid mixture, the system is composed of two species of molecules (or monomers), labeled *A* and *B*. They interact with each other through the following two-component Lennard-Jones (LJ) potentials:

$$V(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \delta_{ij} \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two molecules *i* and *j*. $\delta_{ij} = 1$ or 0 , respectively, if the molecular pair is the same or different type. The immiscibility for the system is then introduced as the consequence of different pairwise interactions. The molecular mass μ , size σ , and interaction parameter ϵ are taken as the intrinsic units throughout this paper. The potentials are truncated at $r_c = 2.5\sigma$.

The bead-spring model is applied for flexible chain blends. In addition to the above LJ interaction between any pair of monomers, we use an anharmonic attractive interaction $V_{bond}(r)$ [12] for binding L_m “like” monomers within each chain, which is given by

$$V_{bond}(r) = \begin{cases} -0.5kR_0^2 \ln[1 - (r/R_0)^2] & \text{for } r < R_0, \\ \infty & \text{for } r \geq R_0, \end{cases} \quad (2)$$

where r is the distance between two successive monomers of the same chain, k is an energy parameter, and R_0 is a length parameter describing the extension of the flexible chain. The parameters R_0 and k are chosen as $R_0 = 1.5\sigma$ and $k = 30\epsilon/\sigma^2$, which prevent the chains from crossing each other under the temperature for the present study.

The simulations are performed in two spatial dimensions. Both systems consist of N_m monomers confined in a periodic cell of volume $V = L \times L$ with different volume fractions of the minority phase (e.g., *B* phase), defined as $\phi = N_m^B/N_m$. $L = 250\sigma$ is the system size. The density of the monomer $\rho = N_m/V$ is kept at $0.8\sigma^{-2}$ in all simulations. For the latter system, L_m “like” monomers are bonded to form $N_{chain} = N_m/L_m$ flexible chains.

To obtain the canonical ensemble correctly, we have supplemented the equations of motion using the generalized Gaussian moment thermostat proposed by Liu and Tuckerman [13]. The modified Hamiltonian of the system is described as

$$H = \sum_{i=1}^{N_m} \frac{\mathbf{p}_i^2}{2\mu} + V(\mathbf{r}) + \frac{p_{\eta_1}^2}{2Q_1} + \frac{p_{\eta_2}^2}{2Q_2} + N_f k_B T (\eta_1 + \eta_2), \quad (3)$$

where η_i and p_{η_i} are the thermostat variable and momentum, Q_i is the time scale parameter, and $N_f = 2(N_m - 1)$ is the total number of degrees of freedom. The $k_B T$ is the temperature of the system and is set to be 0.65ϵ in this study. Here, we apply the fourth-moment thermostat for the temperature control [Eq. (3)]. The corresponding Liouville operator is symmetrically factorized for building the symplectic and re-

versible integrator [14]. The integration time step is taken to be $\delta t = 0.005\tau$, where the time scale $\tau = \sqrt{\mu\sigma^2/\epsilon}$.

To prepare the initial configurations for the flexible chain system, we place the head monomer of each chain randomly in the simulation cell, and then generate the positions for the remaining monomers by a self-avoiding random walk under periodic boundary conditions. For a small molecular liquid system, only the above first step is performed. Then the MD simulation is conducted for enough steps to create an isotropic equilibrium state, where the purely repulsive Weeks-Chandler-Anderson (WCA) interaction [11] is applied between any pair of monomers. The quench process is produced by switching the WCA interaction to the above-described LJ interaction. We explore the phase-separation process by calculating the average domain size $R(t)$ as a function of the quench time t , where $R(t)$ is obtained from the first zero of the equal time pair-correlation function $g(r, t)$ [11]. In order to obtain the universal master curve, averages for each case are performed over 10–20 runs, with different initial uniform states. Such a measure is extensively applied and correctly reflects the competing contribution of various growth mechanisms to the domain growth. The main results are given in the following sections.

For small molecular liquid mixtures, the time span is of 8×10^5 steps for all runs. In the present quench simulations, phase separation is enhanced by the above two-component potentials, which correspond to strong segregation or deep quench. Figures 1(a) and 1(b) show the snapshots of phase-separating structures for the systems with $\phi = 0.30$ and 0.45 , respectively. Following the quench, after an initial transient, the well-defined domains of the coexisting phases are quickly established, and diffusive transport process of components through the bulk is hardly seen during the remaining process. Figure 1 shows that at early stages, droplets of the minority phase are circular for $\phi = 0.30$, in contrast to those with percolated structures for $\phi = 0.45$. As time elapses, diffusive coalescence of droplets is observed to determine the structural evolution. At late stages, droplets for $\phi = 0.45$ are obviously coarser than those for $\phi = 0.30$, which indicates the relative importance of hydrodynamic flows for different compositions of the mixture.

To get a quantitative view of the growth process, we calculate the averaged domain size $R(t)$ for various values of ϕ , and plot the results in Fig. 2 on a log-log scale. It is clearly seen in Fig. 2 that at early stages, the hydrodynamic contribution to the domain growth becomes increasingly important with approaching symmetric quench. On the other hand, for $\phi = 0.30$, the domain growth with $\alpha \approx 0.33$, which indicates no hydrodynamic coarsening, is observed to cross-over to a fast growth with $\alpha \approx 0.40$ at late stages. This is consistent with the scaling arguments [1] and a previous numerical study [15]. By increasing ϕ to the value of 0.42 , three distinct growth regimes are present (see Fig. 2). During the first regime, the hydrodynamic contribution to the domain growth gives $\alpha \approx 0.42$. By linearly fitting the data over the intermediate regime, we find that the effective growth exponent α is approximately equal to 0.25 , indicating that the diffusive coalescence of droplets becomes inefficient and phase separation starts being suppressed, i.e., the pinning effect. Afterwards, phase separation recovers to a fast growth with an exponent α similar to the case of $\phi = 0.30$. On the

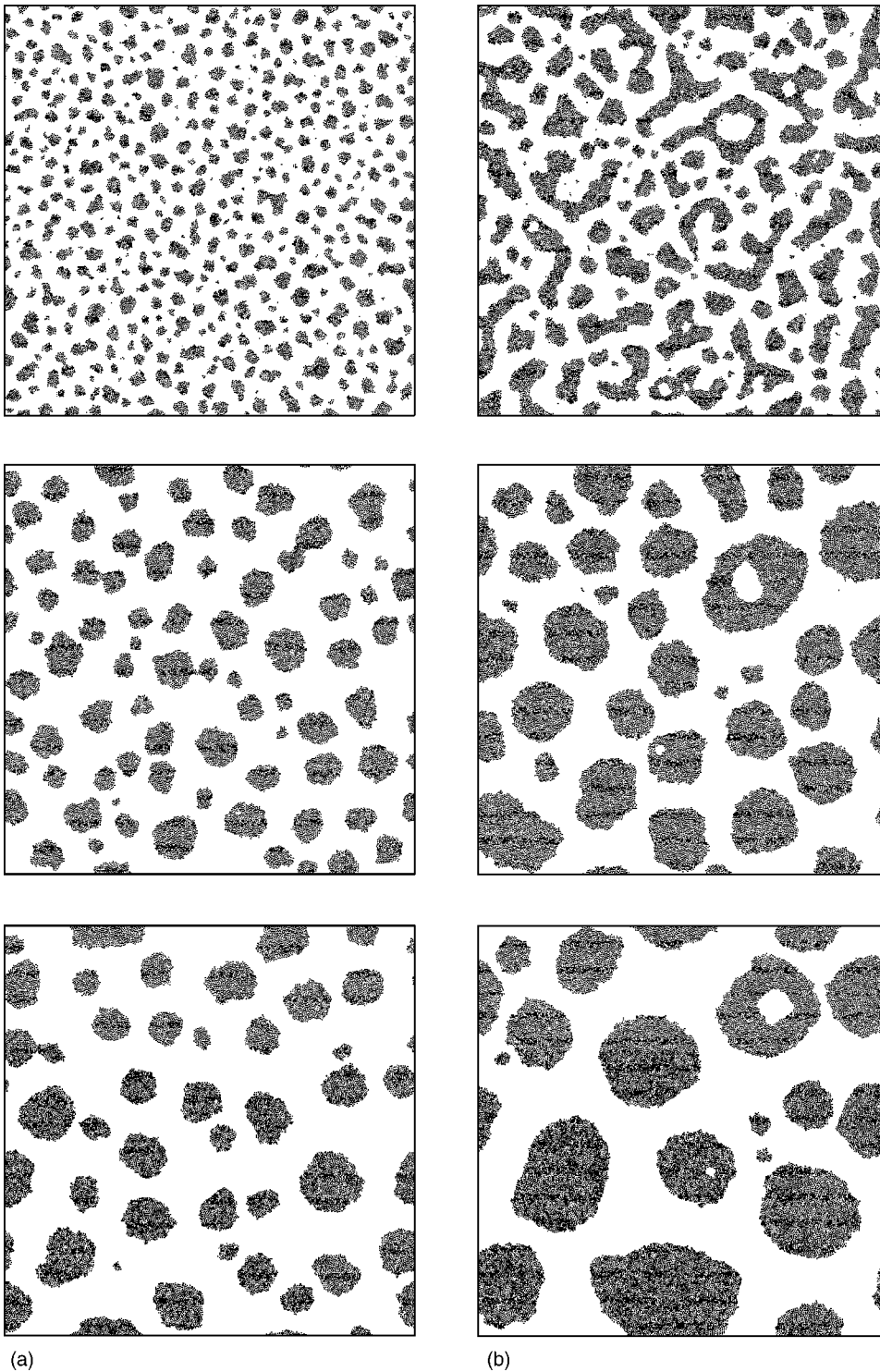


FIG. 1. Pattern evolution in small molecular liquid mixtures for (a) $\phi=0.30$ (left column) and (b) $\phi=0.45$ (right column). The minority phase is only shown and represented by the black region. Snapshots from top to bottom correspond to times $t=200\tau$, 2000τ , and 4000τ .

contrary, the domain growth for $\phi=0.45$ is gradually slowed down and no depinning effect is observed. In order to avoid that the slow growth at late stages is invalidated by finite size effects, we performed simulations on the large systems with $L \times L = 400\sigma \times 400\sigma$, and the significant slow growth is also observed at late stages during the same time span.

We next present the results on the flexible chain blends with $L_m = 10$. In such cases, the simulation time span is twice as long as in the first system, due to relatively long diffusion times of flexible chains. The time evolution of $R(t)$ is pre-

sented in Fig. 3 for $\phi=0.30, 0.42$, and 0.45 . In the present phase-separating systems, the domain growth curves for various ϕ show the behaviors compared with those of the first system (Fig. 2). However, the domain growth in the present system for $\phi=0.30$ becomes suppressed at late stages. On the other hand, for $\phi=0.42$, the growth process demonstrates the behavior similar to the first system, but the pinning herein is relatively strong with $\alpha \approx 0.16$. The time evolution of the pair correlation function is shown in Fig. 4, where each curve is sampled with the time interval of 800τ .

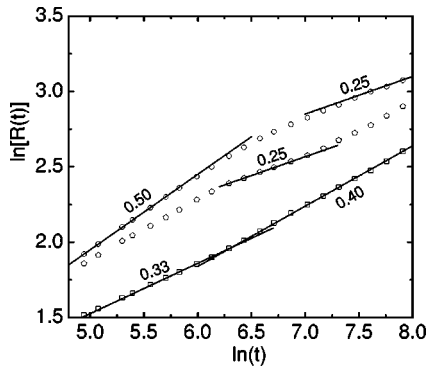


FIG. 2. Log-log plots of the average domain size $R(t)$ vs time t for small molecular liquid mixtures. Data lines from top to bottom correspond to $\phi=0.45$, 0.42 , and 0.30 , respectively. $R(t)$ is in units of σ and t is in units of τ .

A slow evolution can be seen at intermediate stage. For $\phi=0.45$, the domain growth is also gradually slowing down. Due to the large domain size, the results are also validated by performing simulations on the larger systems.

After presenting the main results, we now turn to the main purpose of the present work: the spontaneous pinning effect. As already mentioned, bulk diffusion is irrelevant for the domain growth at late stages due to the strong segregation. Diffusive coalescence of droplets is then expected to be responsible for the structural evolution and domain growth of phase separation. For $\phi=0.30$, two systems show some differences in the late-stage growth of domains. In the first phase-separating system, the coalescence of droplets still takes effect and the local hydrodynamic flows induced by coalescence make a considerable contribution to the domain growth. However, it starts being suppressed at late stages in the second system. One main reason for such a difference is due to the formation of larger distances between large droplets for the flexible polymer system (see Figs. 2 and 3). As we know, the mobility of isolated droplets decreases with the increase of their radii. This may be used to explain the spontaneous pinning phenomena in sufficiently asymmetric polymer blends wherein the hydrodynamic effects is believed to be trivial. Recently, Castellano and Corberi [16] have studied

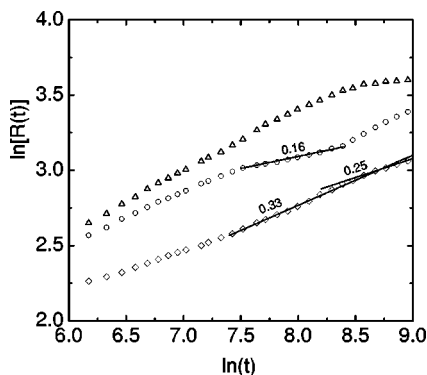


FIG. 3. Log-log plots of the average domain size $R(t)$ vs time t for flexible chain blends. Data lines from top to bottom correspond to $\phi=0.45$, 0.42 , and 0.30 , respectively. $R(t)$ is in units of σ and t is in units of τ .

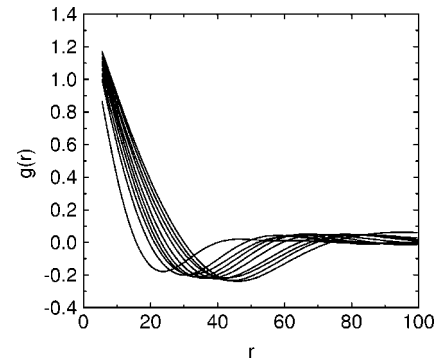


FIG. 4. Time evolution of the normalized pair correlation function for $\phi=0.42$ in the flexible chain blend. r is in units of σ .

phase separation of polymer blends without hydrodynamic effects and found the temporary pinning of the domain growth under the deep and sufficiently asymmetric quenches. However, the pinning observed by them is related to the fact that the asymptotic regime is not reached in their simulation time span. One can clearly see that the asymptotic regime is reached during our simulation time span; for earlier times the domain growth (Fig. 3) is similar to their results.

The intermittent pinning state observed for $\phi=0.42$, wherein the effective growth exponent has considerable deviation from the value of $1/3$, qualitatively supports the recent experimental observations by Takeno and Hashimoto [8] in a long time limit. While the quantitative understanding is difficult, this is very likely related to the correlated motion of droplets induced by the viscous-hydrodynamic response of the velocity field. In fact, many previous studies have presented such novel correlated motion of droplets. Tanaka [17] first observed the collision-induced collision between droplets, which still give the domain growth with the exponent of $1/3$ at early stages, while at late stages, the slow growth appears. Furukawa [18] has recently pointed out that the correlated motion between droplets will lead to the accumulation of isolated droplets under a symmetric quench and change the domain growth. In our present phase-separating cases, such a correlated motion can be observed, and may suppress the coalescence of droplets temporarily. After that, the influence disappears and *Brownian* motion of droplets is recovered. To further verify the above viewpoint, we have performed *Brownian* dynamics simulations for the present cases, wherein the hydrodynamic effects are screened out, and no pinning-depinning transition is found over the same simulation time span.

For $\phi=0.45$, we cannot confirm at present whether the pinning of domain growth is the intermittent or final stage. A study of much larger systems at much longer times is required in the future. However, considering the coarser droplets structure due to the prior hydrodynamic contribution, in the present cases phase separation may develop directly into the final slowing-down growth.

In summary, we have studied phase separation dynamics under asymmetric quenches by a continuous-space molecular dynamics model, which has an advantage over the usual phase-field model by avoiding the discretization of space [9].

Under the conditions of strong segregation and low thermal noise, the results show that the domain growth can be slowed down at late stages, which supports the spontaneous pinning effect observed experimentally in quenched polymer blends. In particular, the pinning-depinning transition of phase separation is first observed, which may be attributed to the correlated motion of droplets of the minority phase. Since the simulations are performed for two-dimensional systems, the detailed comparison with the experimental results is not possible. However, the major features may be suitably extended

to the three-dimensional systems. Moreover, we note that some experiments on polymer blend films [19] have also found the pinning of phase separation at late stages, which supports our results.

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