New Coarsening Mechanisms for Spinodal Decomposition Having Droplet Pattern in Binary Fluid Mixture: Collision-Induced Collisions

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The elementary process of droplet coarsening has been studied for phase-separating binary liquid mixtures. For a slightly asymmetric quench, we have found two new types of coarsening behavior: (i) *a multiple collision* caused by the coupling effect between the shape relaxation after binary collision and the geometrical configuration of neighboring droplets and (ii) *a collision-induced collision* likely caused by collision-diffusion coupling. For a nearly symmetric mixture the droplet density is so high that we probably need to consider new mechanisms of droplet coarsening unique to fluid systems, which originate from *the coupling between concentration and velocity fields.*

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In the late stage of spinodal decomposition, the morphology of phase-separated structure can be grouped into two types in terms of the composition symmetry [1]: an interconnected structure for a nearly symmetric quench and a droplet structure for an off-symmetric quench. The coarsening mechanisms proposed for droplet phase separation have so far been (i) evaporation-condensation mechanism [1,2] and (ii) collision and coalescence between droplets caused by the free, thermal diffusion of droplets without any interaction [1,3]. The former is known as the Lifshitz-Slyozov-Wagner (LSW) mechanism and the latter as the Binder-Stauffer (BS) mechanism. It is mainly dependent on the volume fraction of the droplet (minority) phase, Φ_d, which mechanism plays a dominant role. Both mechanisms give the power law of $R^3 = k(k_B T/5\pi\eta)t$ for the evolution of the mean droplet radius R in three dimensions (3D). Here k is a constant, T is the temperature, k_B is Boltzmann's constant, η is the viscosity, and t is the phase-separation time. For the LSW mechanism $k = 0.053$ and for the BS mechanism $k = 12\Phi_d$ [4]. These relations were experimentally confirmed for $\Phi_d < 0.15$ by Wong and Knobler [5] on the assumption $R \sim q_m^{-1}$ (q_m: peak wave number of scattering intensity). However, this assumption is questionable since it is inconsistent with the experimental relation $R > q_m^{-1}$ [6]. Thus k could be larger than $12\Phi_d$ [7]. For larger Φ_d, Wong and Knobler [5] found the increase of the time exponent from $\frac{1}{3}$ to 1 with an increase in the composition symmetry. This phenomenon was explained in terms of the intermittent cooperation between Brownian coagulation and hydrodynamic coarsening [4] by Furukawa [8].

So far little attention has been paid to the elementary process of droplet coalescence, partly because scattering techniques have been mainly used for experimental studies. From the theoretical viewpoints, deep considerations on the problem were given by Siggia [4], Furukawa [8], and Ohta [9]. In any studies, however, only the simple Brownian coagulation based on binary collisions without any interaction have been considered to account for the elementary process inducing droplet collisions. In this Letter, we demonstrate unusual elementary processes of droplet growth for near-symmetric fluid mixtures, which cannot be explained by the conventional theories.

The samples used were a mixture of styrene oligomer (OS) and ϵ-caprolactone oligomer (OCL). This mixture has an upper critical solution temperature (UCST)-type phase diagram. The critical, symmetric composition of the mixture was OCL/OS (2/8). The molecular weights of OS and OCL were 1000 and 5000, respectively [10]. The mixture studied had an off-symmetric composition of OCL/OS (35/65) and its phase-separation temperature was 150.0 °C. The mixture was sandwiched by two glass plates whose gap was several μm. Spinodal decomposition was triggered by a temperature quench.

Figure 1 shows the phase-separation behavior observed in a OCL/OS (35/65) mixture. For this mixture the OS-rich phase forms a droplet. The coarsening is dominated by direct collisions, and not by the evaporation-condensation mechanism. Figures 2(a) and 2(b) indicate the time evolution of the interface pattern for 131.0 °C and 119.8 °C, respectively. Here $\Phi_d = 0.27$ for 131.0 °C and $\Phi_d = 0.35$ for 119.8 °C. The interface pattern was extracted from the original images by a simple black and white operation of digital image analysis (DIA) [10,11]. It should be noted that there was little macroscopic flow. Figure 3 shows the temporal change in the droplet den-

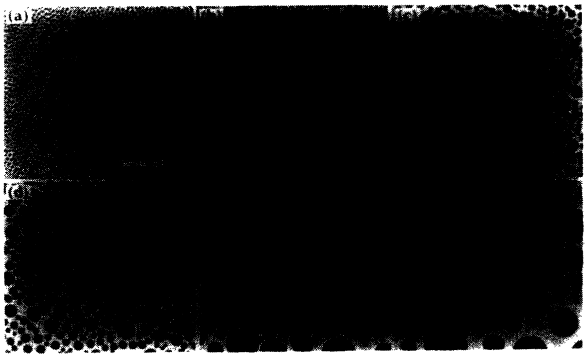

FIG. 1. Pattern evolution during spinodal decomposition in OCL/OS (35/65). (a) 2 s, (b) 9 s, (c) 60 s, (d) 120 s, (e) 1110 s, and (f) 3210 s after the quench from 151.0 to 131.0 °C. The bar corresponds to 40 μm.

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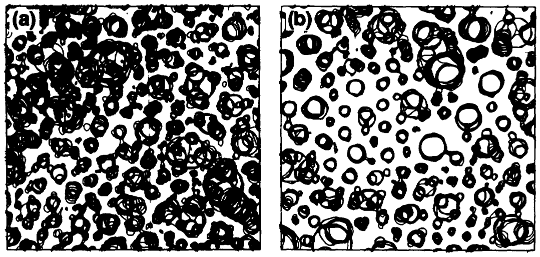

FIG. 2. Time evolution of interface pattern in OCL/OS (35/65) after the quench from 151.0 °C. The interface patterns are superimposed every 6 s from 60 to 180 s. (a) 131.0 °C, (b) 119.8 °C. The side length corresponds to 60 μm.

sity N and R. In regions I and II $R \sim t^{1/3}$, while in region III the coarsening rate slows down. It should be noted that in region I the relation $\frac{4}{3}\pi R^3 N = \text{const}$ does not hold, while it becomes constant in region III. This implies that the compositions of both droplets and matrix are still changing in region I, which is consistent with the following Fig. 5.

It is clearly demonstrated by both Figs. 2(a) and 2(b) that a droplet experiencing a collision has a much higher probability of a subsequent collision: Some droplets grow very rapidly by experiencing a number of collisions during the observation period, while the other droplets never collide with the neighboring droplets during the same period and do not grow in size. There is a striking difference in the coarsening rate between the droplets experiencing collisions and the droplets experiencing no collision. We call this unusual phenomenon *collision-induced collision* (CIC) [12]. The translational motion of the droplet can also be seen in Figs. 2(a) and 2(b). The motion is directional and much faster than that expected for the thermal diffusion of the droplet. The diffusion length L of a droplet of size R during a period of δt is $L \sim (D_R \delta t)^{1/2}$, where D_R is the diffusion constant of the droplet and $D_R = k_B T / 5\pi\eta R$. In our mixtures where $\eta \sim 1$ P around 120 °C, for example, $L \sim 1$ μm for $R \sim 1$ μm and $\delta t \sim 300$ s, which is consistent with the motion of small droplets experiencing no collisions in Figs. 2(a) and 2(b). The fact that large droplets ($R > 3$ μm) sometimes move directly toward their neighboring droplets over a few μm during $\delta t = 120$ s and collide with each other [see Figs. 2(a) and 2(b)] [13] can never be explained by the conventional BS mechanism, where collisions are assumed to be induced by the free, thermal Brownian motion of droplets. The large coarsening rate is also qualitatively consistent with the prediction of the intermittent cooperation of Brownian coagulation for droplet pattern and hydrodynamic coarsening for bicontinuous pattern [8]. However, the elementary coarsening behavior described above cannot be explained by the simple cooperation of the two mechanisms since this intermittency itself does not affect the droplet motion. For our mixtures ($\Phi_d = 0.2$–0.3), further, the intermittency plays few roles since we never see the coexistence of droplet and bicontinuous patterns (see Figs. 1 and 2).

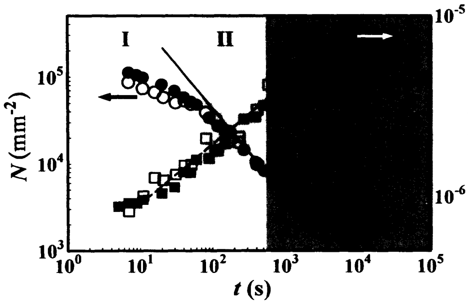

FIG. 3. Temporal change in N and R. Open and filled circles are N's at 119.8 and 131.0 °C. Open and filled squares are R's at 119.8 and 131.0 °C. The solid and dashed lines have slopes of -1 and $\frac{1}{3}$, respectively.

In addition to the above indirect CIC, we have also found another kind of CIC, which is more direct and apparent. Figure 4 shows such an example observed in OCL/OS(35/65). Two droplets coalesce by collision to form a new droplet and the droplet changes its shape with time. In this shape relaxation process, it collides with the neighboring droplet again simply because of the geometrical configuration. This is also an important process when the droplet density is very high. This clearly indicates that *the volume fraction of droplets is beyond the range where only binary collision can be assumed as in the conventional Brownian coagulation model.* Both types of CIC could seriously affect the coarsening dynamics. In the following we consider mainly the physical mechanism of the indirect CIC since the mechanism of the direct CIC is rather clear.

First we discuss the wetting effects on the interdroplet interaction since the system is in a quasi-2D configuration. When the minority phase is more wettable to glass, phase separation is strongly affected by wetting phenomena and the attractive interaction between droplets is induced via the wetting layers by capillary instability [14,15]. In our mixtures, however, the minority phase (OS-rich phase) is less wettable to glass. For such a case we have experimentally confirmed for both 1D and 2D

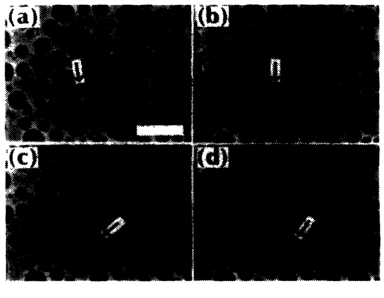

FIG. 4. Collision-induced collisions observed in OCL/OS (35/65). (a) 855.0 s, (b) 956.6 s, (c) 968.4 s, and (d) 991.4 s after the quench from 151.0 to 135.5 °C. The bar corresponds to 20 μm.

capillaries that there is no confinement effect other than a simple dimensional crossover [15]. The phenomenon cannot be explained by the van der Waals interaction, either, as estimated by Siggia [4]. Further, the phenomenon cannot be explained by the evaporation-condensation mechanism since this mechanism alone does not cause direct collisions [1].

We should also consider the effect of a hydrodynamic interaction between droplets. There is a hydrodynamic flow field around the droplet which is caused by the interface-tension driven shape relaxation after the collision. Since the lifetime of the velocity field is short, a subsequent collision can be regarded to occur after the complete decay of the hydrodynamic flow, which has been experimentally confirmed. Thus the phenomenon cannot be explained by the hydrodynamic flow induced by collision.

Thus none of the above mechanisms can account for the phenomenon. Before discussing a new mechanism, it is noteworthy pointing out the essential difference between solid and liquid systems: For a solid system the gross variable is only the composition ϕ, while for a fluid system they are ϕ and the velocity field v. Thus the kinetic equations for classical binary fluids are [1]

$$\frac{\partial\phi}{\partial t} = -\nabla\cdot(\phi\mathbf{v}) + L_0\nabla^2\frac{\delta F}{\delta\phi} + \theta, \qquad (1)$$

$$\rho\frac{\partial\mathbf{v}}{\partial t} = -\nabla\cdot\mathbf{\Pi} - \nabla p_1 + \eta\nabla^2\mathbf{v} + \zeta, \qquad (2)$$

$$F = \int d\mathbf{r}\left[-\frac{r}{2}\phi^2 + \frac{u}{4}\phi^4 + \frac{K}{2}(\nabla\phi)^2\right]. \qquad (3)$$

Here $\mathbf{\Pi}$ is the stress tensor caused by the fluctuation of ϕ. ρ is the density, p_1 is a part of the pressure, and η is the viscosity. θ and ζ are random forces. The characteristic feature of the fluid system is that the velocity field $\mathbf{v}(\mathbf{r},t)$ strongly affects the dynamics.

In the conventional theories of droplet phase separation, this important characteristic of fluid systems, which is known to play a significant role in bicontinuous pattern [1,4], has not been considered so far. On the basis of the above fluid model, the phenomenon of collision-induced collision could be explained as follows. The most important point is that the spatial variation (fluctuation) in ϕ causes the stress tensor $\mathbf{\Pi}$, or the force density F_ϕ against the fluid. Here $F_\phi = -\nabla\cdot\mathbf{\Pi} = -\phi\nabla[\frac{\delta F}{\delta\phi}] \sim -2r\phi\nabla\delta\phi$, where $\delta\phi$ is the deviation from the equilibrium concentration. For small Φ_d, the local equilibrium is likely established and $F_\phi = 0$ except at the interface of domains since the chemical potential is constant except at the interface, where the well-known Laplace law is satisfied. Thus there is no velocity field and the coarsening process is purely governed by diffusion mechanisms including BS and LSW mechanisms. This is consistent with the conventional understanding of the late-stage droplet phase separation. For large Φ_d, however, the overlap between the diffusion fields and the deviation from the local equilibrium could cause the concentration gradient $\nabla\delta\phi$ around a droplet. This situation is likely caused by an *interface quench effect* which is described later. Further, it should be stressed that for fluid systems such a situation could also be realized even for the evaporation-condensation mechanism for large Φ_d where the depletion layers could be overlapped with each other. For the latter case, we have the relation $\delta\phi_{\text{int}} \sim -\frac{\sigma}{4k_BTr\Delta\phi_b}(\frac{1}{R_1}+\frac{1}{R_2})$ near an interface from the Gibbs-Thomson relation. Here σ is the interface tension, $\Delta\phi_b[=(r/u)^{1/2}]$ is the final equilibrium concentration for an infinite domain size, and R_1 and R_2 are the principal curvatures. For both cases, the asymmetry in the spatial distribution of the neighboring droplets could cause for large Φ_d the imbalance of $\nabla\delta\phi$ (or flux) around the droplet and thus the imbalance of the force against the droplet, which likely leads to the translational hydrodynamic motion of the droplet and finally to the collision with a neighboring droplet. The inhomogeneous droplet distribution suggests the existence of the inhomogeneity in $\delta\phi$ of the matrix in a spatial scale beyond R. For a solid system an interface can move only by concentration diffusion, while *for a fluid system it can move by the translational motion of droplet.*

Finally we propose here a new effect unique to droplet phase separation of a fluid system, in relation to the above mechanism. In the conventional theories, the relaxation of the concentration field is assumed to be sufficiently fast so that the diffusion field can be approximated by a solution of the Laplace equation. This quasistationary approximation is valid only for a small dR/dt. Near the symmetric composition close to the percolation threshold, the droplet density is high enough to cause a direct, hard collision by Brownian motion in the early stage of phase separation. Since the shape relaxation after the collision is a hydrodynamic process and thus dR/dt is large, the quasistationary approximation could be violated severely. In this competitive regime, we probably need to consider *the coupling between the collision and the concentration diffusion.* Collision quickly reduces the local interface energy of the droplet since the local curvature of the droplet is rapidly decreased by coalescence. The interface reduction leads to the change in the local-equilibrium concentration difference between the two phases and the boundary condition. Thus there is a relaxation process of the local concentration field to follow this quick change in the local equilibrium caused by the droplet collision.

Next we estimate this coupling effect (*interface quench effect*). The local-equilibrium concentration $\Delta\phi_d^l$ for a domain size of R can be roughly estimated from the local energy minimum condition as follows, provided that the concentration profile can be approximated by the trapezoidal shape with an interface width of ξ in Eq. (3) and $R \gg \xi$:

$$\Delta\phi_d^l = \Delta\phi_b\left(\frac{1-(2d_p\xi/R)(1-\Phi_d)^{-1}}{1-\Phi_d+\Phi_d^3/(1-\Phi_d)^2}\right)^{1/2}, \qquad (4)$$

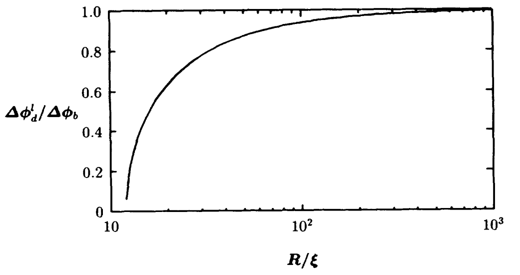

FIG. 5. Plot of $\Delta\phi_d^l/\Delta\phi_b$ against R/ξ based on Eq. (4) for $\Phi_d = \frac{1}{2}$.

where ξ is the correlation length, d_p is the spatial dimensionality of the domain, $\Delta\phi_d$ and $\Delta\phi_m$ are the concentrations of the droplet and the matrix phases measured from the average one, respectively ($\Delta\phi_m = -[\Phi_d/(1-\Phi_d)]\Delta\phi_d$). Here the relation $\xi^2 = K/2r$ is used. Figure 5 shows the plot of $\Delta\phi_d^l/\Delta\phi_b$ against R/ξ based on Eq. (4) for $\Phi_d = \frac{1}{2}$ for the sake of simplicity. In a phase-separation process, $\Delta\phi_d^l/\Delta\phi_b$ changes with $\tau = t/(\xi^2/D)$ through the dependence of R/ξ on τ. Here D is the diffusion constant and $D = k_BT/5\pi\eta\xi$. For LSW mechanism $(R/\xi)^3 = 0.053\tau$ [4], while for BS mechanism $(R/\xi)^3 = 12\Phi_d\tau$ [4]. In our case, however, collision induces the jump in R/ξ, which causes the jump in $\Delta\phi_d^l$ (see Fig. 5). Since the diffusion cannot follow this rapid hydrodynamic process, it is expected that the local equilibrium is violated by the *interface quench* due to collision. The same idea could be applied for the collision-induced change in $\delta\phi_{\text{int}}$.

To check the above possibility, we have to study whether the concentration diffusion can follow this quick collision-induced change in $\Delta\phi_d^l$ and $\delta\phi_{\text{int}}$ or not. The shape relaxation time for a domain of size R is estimated as $\tau_\sigma = c\eta R/\sigma$ (c: a constant), while its characteristic time of concentration diffusion is given by $\tau_D \sim R^2/D$. Thus $\tau_\sigma/\tau_D = cD\eta/\sigma R \sim c\xi/3R$ from $\sigma = 0.2k_BT/\xi^2$ [1]. For $\tau_\sigma < \tau_D$, the concentration deviates from its local equilibrium value by collisions and thus the *interface quench* effect is likely important. This condition ($\tau_\sigma < \tau_D$) can be easily satisfied for the so-called late stage. During this relaxation process characterized by τ_D which likely continues about $\tau_c \sim 5\tau_D$, there is a diffusion field around a droplet experiencing a collision. It should be noted that τ_c is very long for a semimacroscopic droplet. In our mixtures, for example, $\tau_c \sim 60$ s for $R = 2$ μm and $\xi = 10$ nm, while $\tau_\sigma < 1$ s [16].

The interaction strength is likely dependent on the strength of the diffusion flux. Thus the strength of the interaction decreases with time for *the interface quench effects* since $\Delta\phi_d^l/\Delta\phi_b$ and $\delta\phi_{\text{int}}$ become insensitive to the change in R with an increase in R (see Fig. 5). Thus the conventional BS and LSW mechanisms probably dominate the coarsening in the very late stage instead of the CIC mechanism, which could lead to the slowing down of the coarsening. The effective interaction range can be regarded as the droplet radius. This leads to the conclusion that CIC could be important for most *droplet spinodal composition* ($\frac{1}{6} < \Phi_d < \frac{1}{2}$).

In summary, we have found unusual droplet coarsening behavior, namely, *direct and indirect collision-induced collisions*, under a slightly, off-critical quench condition. Collisions between droplets during phase separation are not random, in contradiction to the conventional model. Droplets are likely interacted with each other via the coupling between diffusion fields around the droplets. *The local structure of droplet arrangement and the coupling between concentration and velocity fields* should be taken into account *for large* Φ_d. Since our experiments have been performed in quasi two dimensions, the effect of the dimensionality should be clarified. Further theoretical and experimental studies including the estimation of the coarsening rate for 3D are highly desirable to clarify the mechanisms of collision-induced collisions.

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[13] For a droplet of $R \sim 3$ μm, $\delta t \sim 6000$ s to move over a few μm by free Brownian motion in our mixtures.

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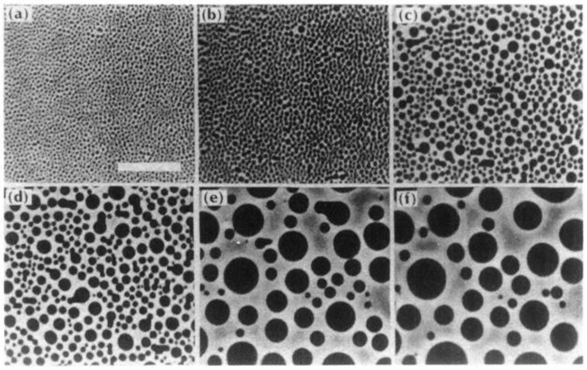
[16] This is supported by the fact that we rarely see the shape relaxation process of droplet in Figs. 2(a) and 2(b), where the interval is 6 s.



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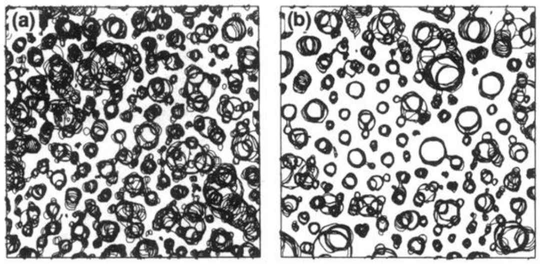

FIG. 2. Time evolution of interface pattern in OCL/OS (35/65) after the quench from 151.0 °C. The interface patterns are superimposed every 6 s from 60 to 180 s. (a) 131.0 °C, (b) 119.8 °C. The side length corresponds to 60 μm.

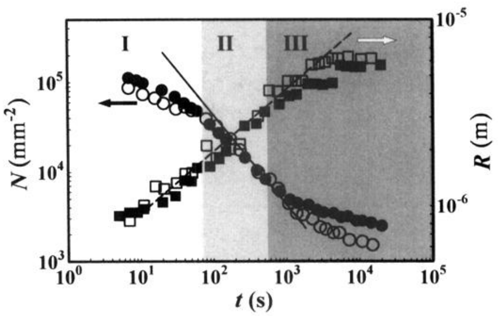

FIG. 3. Temporal change in N and R. Open and filled circles are N's at 119.8 and 131.0 °C. Open and filled squares are R's at 119.8 and 131.0 °C. The solid and dashed lines have slopes of -1 and $\frac{1}{3}$, respectively.

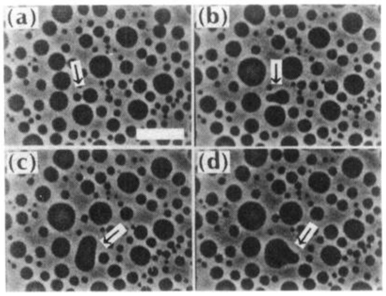

FIG. 4. Collision-induced collisions observed in OCL/OS (35/65). (a) 855.0 s, (b) 956.6 s, (c) 968.4 s, and (d) 991.4 s after the quench from 151.0 to 135.5 °C. The bar corresponds to 20 μm.