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Preservation of droplet collision history in phase separation of a binary fluid mixture

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Phase-separation phenomena are widely observed in various kinds of condensed matter. The common feature of these phenomena is the coarsening of a phase-separation pattern driven by the interfacial energy associated with the phase boundary. In contrast to the general phenomenology of liquid-liquid phase separation in which the memory of the structure is continuously lost with time upon coarsening, we have found an unusual phase-separation morphology that records the full history of pattern evolution for a liquid mixture. The collision history preserved in the trajectory pattern of each droplet demonstrates a strong spatial-temporal correlation in the structural development. [S1063-651X(96)50709-9]

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Ordering processes such as crystallization and phase separation [1] generally accompany pattern evolution. In a liquid-solid transition, or crystallization, the final structure is determined by the nucleation events of ordered crystals, and the nucleation process is memorized in the final pattern. This is because solidification prevents further deformation of crystallites. Thus we often see granular structures for melt-crystallized materials, and the volume is simply divided into small crystallites or spherulites. This pattern can be characterized by the nucleation location, the nucleation time sequence, and the growth rate of crystals. For the pattern generated by spherulitic growth characteristic of a dense branching morphology [2,3], we can reconstruct its full history of evolution from only the final morphology [4], since the growth rate of a spherulite is isotropic and generally constant with time under stable growth conditions [2,3].

On the other hand, in phase separation of liquid mixtures [1,5], including polymer mixtures [6,7], an initial structure appears that statistically reflects the thermal fluctuation of the order parameter (concentration), which then continuously coarsens to reduce the energy cost associated with the phase boundary. For phase separation with a low droplet density, the morphology is random and there is no interaction among droplets. For phase separation with a high droplet density, on the other hand, droplets have a more ordered spatial pattern with some regularity in their spatial configuration because of the conserved nature of the order parameter. Thus it is important to understand how these droplets coarsen with time under the influence of a strong spatial correlation, namely, the quasirandom nature of droplet configuration [8]. During the ordering process, the memory of the phase-separated structure is usually continuously lost and the final structure at $t \rightarrow \infty$ is believed to be independent of the initial one. Since the interface of a liquid droplet deforms flexibly to minimize the interfacial energy (leading to a spherical shape), the interface after collision has little correlation with the original interfaces. This is a natural consequence of the continuous decrease in the phase boundary for a fluid system. In this paper, we demonstrate the first example of a novel phase-separation behavior that preserves the entire history of the late-stage pattern evolution.

The binary mixture studied was a blend of oligomers of styrene (OS) and ϵ-caprolactone (OCL). The weight-average molecular weights of OS and OCL were 1000 and 2000, respectively. The polydispersity ratios M_w/M_n were 1.05 and 1.2 for OS and OCL, respectively. The critical composition ϕ_c of this mixture was about OCL:OS=33:67 and the critical temperature T_c was 135.5 °C. Figure 1 shows schematically the phase diagram of this system. It is known that OCL is more wettable to glass than OS because of its higher polarity. The mixture was sandwiched between two glass plates and the sample thickness d was controlled by monodisperse glass spheres with a diameter of ~ 7.1 μm as spacers. Samples were quenched to the desired temperatures by rapidly transferring them from a microscope hot stage (Mettler MP-500) whose temperature was above T_c to another hot stage (Linkam TH-600R) kept at the final temperature. The pattern evolution dynamics were studied using video microscopy.

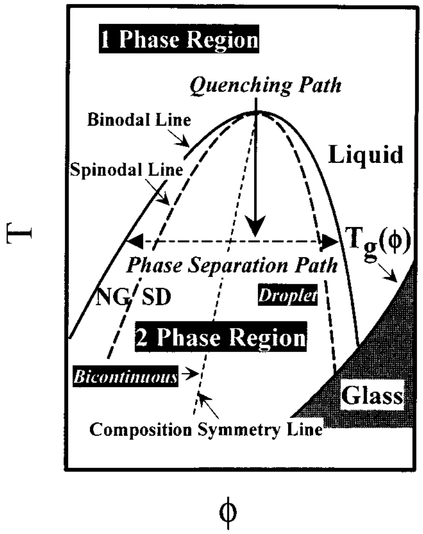

FIG. 1. Schematic phase diagram of OCL-OS mixtures (ϕ is the composition of OS). In the shaded area below the glass transition line [$T_g(\phi)$], the mixture is in a glassy state.

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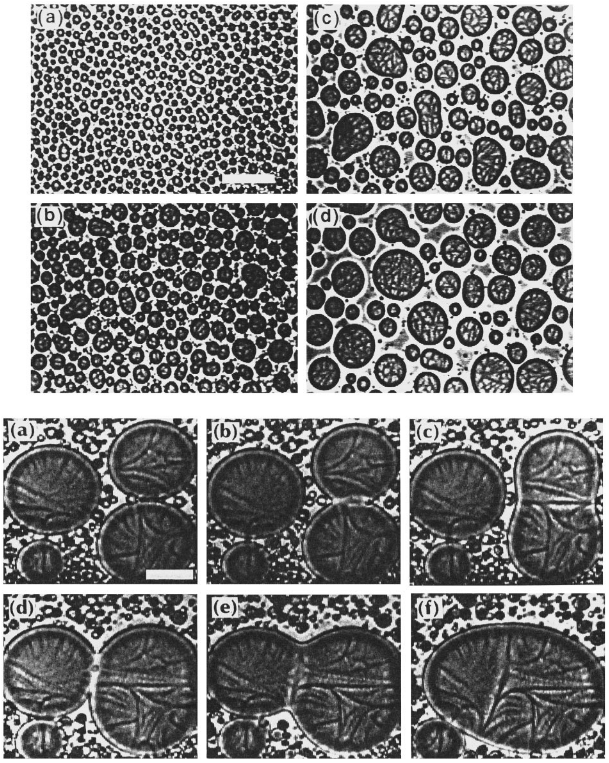

FIG. 2. Pattern evolution in OCL:OS (3:7) at $T=60\,^\circ\mathrm{C}$, observed by optical microscopy. (A) Overall coarsening process: (a) 15 s, (b) 120 s, (c) 300 s, and (d) 600 s after the quench. The bar corresponds to 50 μm. (B) Elementary process of droplet collisions: (a) 950 s, (b) 1010 s, (c) 1028 s, (d) 1113 s, (e) 1122 s, and (f) 1196 s. The bar corresponds to 30 μm.

Figure 2(A) shows the overall coarsening process observed in OCL:OS (3:7) at 60 °C. We notice that each droplet is compartmentalized into smaller ones. The pattern reflects the spatial distribution of fine subdroplets; the dark lines dividing the large droplets are the loci of contact lines. The fine subdroplets are likely formed by *a self-induced double phase separation*: Wetting to glass walls highly accelerates the initial process of coarsening [9] and the concentration diffusion cannot follow this quick hydrodynamic process. This leaves the system with macroscopic domains out of equilibrium and leads to secondary phase separation inside these domains [10]. A similar phenomenon can also be induced by a double temperature quench [11]. These small droplets are OS-rich and at this temperature they are likely very viscous or even elastic because of the slow dynamics associated with the glass transition of OS (which is around room temperature). Thus there is almost no coarsening in the fine droplets and their spatial distribution records the contact-point trajectory of colliding droplets: There are no fine droplets on the contact-point trajectory simply because of the absense of fine droplets on the interface. This makes the contact lines visible. The weak hydrodynamic interaction and the slow shape relaxation, both of which are associated with the large viscosity, prevent the fine droplets from being stirred.

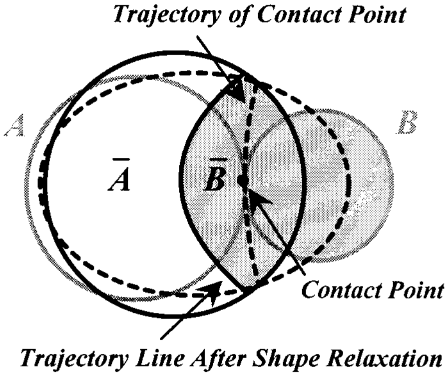

FIG. 3. Schematic diagram showing the locus of the contact point of colliding droplets. Two droplets A and B drawn by gray lines collide with each other and eventually form a new spherical droplet $A+B$ drawn by black solid lines through a transient state drawn by dashed line.

Figure 2(B) shows at higher magnification the elementary processes of droplet collision and how the trajectory of the contact interface between two colliding droplets is recorded inside the combined droplet formed by this collision. The numerous lines visible inside the large droplets reflect not only the contact-point trajectories at each collision but also the resulting shape relaxation of the interfacial boundary [13]. Thus *the entire history of successive collisions is recorded inside each domain*. The number of collisions to form a droplet and the order of the collisions contributing to its formation can be determined from the spatial-division patterns inside the droplet.

The elementary process of a binary collision is shown schematically in Fig. 3. The initial contact point results from collision between two droplets. The existence of the contact lines establishes and records the occurrence of interdroplet collisions, even if we do not observe the domain coarsening process and see only a pattern at a certain time of the late stage. This fact can be used as a fingerprint of droplet collisions and can be used to judge from *a single pattern* whether phase separation proceeds by the evaporation-condensation mechanism or by the Brownian-coagulation mechanism [1].

A feature peculiar to droplet coarsening for high droplet densities is discussed next [see Fig. 4(a)], based upon the contact-line patterns observed, namely, their confinement in virtual ''cage.'' The large droplets in each cell are found to be composed almost entirely of the smaller ones. This behavior can be qualitatively explained as follows: Since the volume fraction of droplets is high in our samples, there is an intrinsically strong correlation among droplets because of the conserved nature of the order parameter (concentration). The concentration changes almost periodically in space in all directions. Thus the droplets cannot travel freely without collisions and in this sense each droplet is confined within a small region of space surrounded by its neighbors. This leads naturally to the observed local spatial correlation among droplets. On this point, Furukawa [8] speculated that the inverse process of the coalescence is represented by successive divisions of droplets into many smaller droplets with self-similarity. This is quite consistent with the results of our observation summarized in Fig. 4(a). Based on the above idea, Furukawa obtained the general relation $S(k)\propto k^D$ for

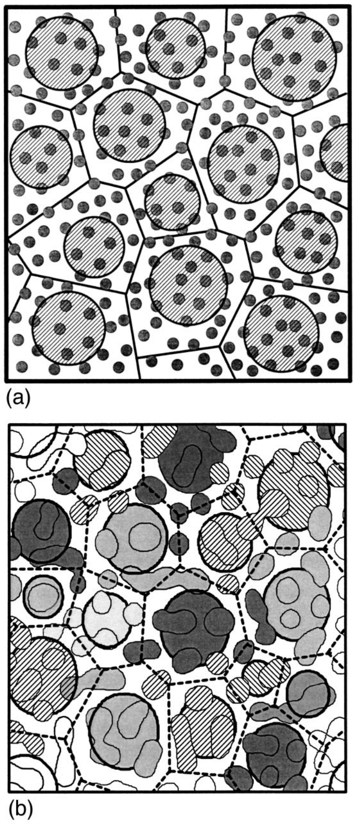

FIG. 4. (a) Spatial-temporal correlation among droplets for a high-droplet-density phase separation. This figure summarizes what is observed in our experiments. A pattern composed of the small gray droplets represents phase separation at a time t_1, while a pattern composed of shaded large droplets is that at a time t_2 ($\gg t_1$). The cell pattern at time t_2 is a Voronoi-like tessellation of space. (b) Droplet patterns obtained by superimposing two patterns of numerically simulated droplet spinodal decomposition at the reduced time of 48 (thin lines) and 400 (thick lines). Droplets of the same inner pattern later form a larger droplet of the same inner pattern. The droplet coarsening history in numerical simulation is followed precisely by checking every image by a time step of 4. The cell pattern drawn by dashed lines is a Voronoi-like tessellation of space at a time of 400.

small k, where k is the wave number, $S(k)$ is the structure factor, and D is the dimensionality of the system. Our pattern of contact-line features in Figs. 2(a) and 2(b) provides the first direct morphological evidence of this model.

To support the above rather speculative discussion, we performed numerical simulations of spinodal decomposition of a two-dimensional (2D) fluid mixture based on a Langevin fluid model. The kinetic equations used are [1]

$$\frac{\partial \phi}{\partial t} = -\vec{\nabla}\cdot(\phi\vec{v}) + L_0\nabla^2\frac{\delta\beta H}{\delta\phi} + \theta, \tag{1}$$

$$\rho\frac{\partial\vec{v}}{\partial t} = -\phi\vec{\nabla}\frac{\delta H}{\delta\phi} - \vec{\nabla}p_1 + \eta\nabla^2\vec{v} + \vec{\zeta}, \tag{2}$$

$$\beta H = \int d\vec{r}\left[-\frac{r}{2}\phi^2 + \frac{u}{4}\phi^4 + \frac{K}{2}(\vec{\nabla}\phi)^2\right]. \tag{3}$$

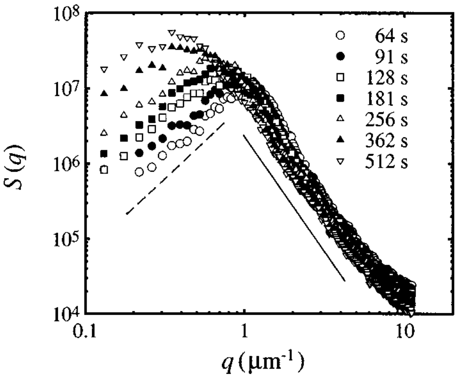

FIG. 5. The temporal change in the power spectrum $S(k)$ of a phase-separated pattern observed in OCL:OS (35:65) at 130 °C after the quench. The dashed line has a slope of 2, while the solid line has a slope of -3.

Here, ϕ is the local composition, L_0 is the bare kinetic coefficient, $\beta=1/k_BT$ (k_B:Boltzmann's constant), ρ is the density, p_1 is a part of the pressure, and η is the viscosity. θ and $\vec{\zeta}$ are random noises. The coupling between velocity and concentration fields is taken into account under an incompressibility condition, using the Oseen tensor [14,15]. Here we just summarize the morphological feature of off-symmetric spinodal decomposition and the details of simulation methods and results will be published elsewhere. The volume fraction of the minority phase (Φ_d) studied here was 0.4 and the simulation size was 128×128. The pattern evolution history is shown in Fig. 4(b). This result evidently supports our speculation that the geometrical confinement into a virtual cage strongly affects the coarsening history and leads to the strong spatial correlation between different times. This correlation originating from the cage effect plays a crucial role in the coarsening dynamics and the resulting pattern formation, especially for large Φ_d where the interdroplet gap is smaller than a droplet diameter. As can be seen in Fig. 4(b), the droplet coarsening is predominantly due to direct collision and coalescence between droplets. The evaporation-condensation mechanism plays no role in coarsening, which is supported by the fact that no droplets disappear by evaporation. This feature is quite consistent with our experimental observation and probably characteristic of droplet spinodal decomposition of a fluid mixture. Because of the rather high fluidity (small η) in our simulation, the spatial correlation in Fig. 4(b) is slightly weaker than that shown schematically in Fig. 4(a). However, it is still evident that *a droplet selectively interacts only with its neighbors*.

Figure 5 shows an example of the temporal change in $S(k)$ for the nearly symmetric mixture, OCL:OS(35:65), at 130 °C in the late stage of phase separation. Here, $\Phi_d \sim 0.2$. We obtained $S(k)$ from a real-space image by numerically calculating its power spectrum as described earlier [12]. At small k we obtain the power-law behavior $S(k) \propto k^{\alpha}$ ($\alpha \sim 2$). The high-wave-number part also obeys a power law, $S(k) \sim k^{-3}$. This relation is consistent with the prediction of the Porod law for two dimensions, which generally holds for two-phase systems having a sharp, smooth interface. The exponent $\alpha \sim 2$ at small k is consistent with the above argument of Furukawa [8] since in our case $D=2$ in the late stage. It should be noted that even for symmetric fluid mixtures, Shinozaki and Oono [16] and Alexander *et al.* [17] found $\alpha \sim 2$, respectively, in a Hele-Shaw cell and in a 2D fluid. Although there remains some ambiguity regarding the power-law behavior of the scattering function at small k, our real-space observation and numerical simulations suggest that the local spatial correlation among droplets is important for understanding the coarsening dynamics and the resulting pattern evolution, especially for droplet spinodal decomposition with high droplet density in quasi-2D configurations. This local correlation stems from the fact that a droplet cannot travel over its neighboring droplets and thus its motion is strongly restricted. Interdroplet collision is the only way to destroy the cage for a system of high droplet density. The coarsening process can be regarded as a renewal process of cages.

Here it should be noted that this local spatial correlation among droplets, or the regularity of the spatial arrangement of droplets [12], may explain the recent experimental findings [10,18,19] that droplet morphology is observed even for volume fractions larger than $\Phi_d = 1/6$, which is the percolation threshold theoretically predicted for 3D on the basis of random distribution of droplets [1].

In addition to the local spatial correlation, there is a strong temporal correlation originating from the local confinement of droplets. This is shown in Fig. 2(B), where droplets already having many space-division lines grow with time by sequential collisions with neighboring droplets. *The strong spatial correlation produces a consequent correlation between patterns at different times for the same area*. This can be easily understood from Fig. 4. There is no large-scale motion of a droplet, since it is bound by a transient cage of neighboring droplets and thus remains near its original nucleation site [see Fig. 4]. This strong correlation in both time and space originates from the local coarsening history and is probably caused by the conserved nature of the order parameter. Theoretical efforts have so far been devoted mainly to calculation of the temporal change in the correlation function $\langle \phi(\vec{r},t)\phi(0,0)\rangle$, where $\phi(\vec{r},t)$ is the order parameter (composition) and $\vec{r}$ is the position vector, with special emphasis on the statistical properties of the phase-separated pattern. In other words, the temporal change in the *averaged* spatial correlation has attracted much attention and in the averaging process important information on local correlation of droplet configuration and topological characteristics has been lost. Our results here provide a start toward the exploration of *nonaveraged* temporal and morphological aspects of such phase separations [20].

In conclusion, we have described here a case of liquid-liquid phase separation where the history of pattern evolution is fully preserved and recorded in the final morphology. This phenomenon is caused by the critical interplay between wetting-induced double phase separation [10] and very slow dynamics associated with the glass transition of one of the components. We need further studies to clarify the effects of wetting phenomena on the coarsening behavior. However, we point out that similar pattern evolution may be observed in viscous liquid mixtures containing very fine solid particles without the help of wetting phenomena. This experimental method will provide us with detailed information on the elementary process of interdroplet collisions, which cannot be obtained by other methods. The strong spatial-temporal correlation in the pattern of droplet phase separation has been clearly demonstrated by (i) the collision history preserved in the contact-line pattern of each droplet, (ii) the power-law behavior of the structure factor at low k, and (iii) numerical simulations of spinodal decomposition of a slightly off-symmetric fluid mixture based on a Langevin fluid model. The real-space characterization of the structural evolution has so far lagged behind in the study of phase separation, since most of the studies using scattering techniques (k-space measurements) probe the statistical properties of patterns rather than the understanding of the elementary coarsening process. The present study clearly indicates the additional benefits of studying the individual process of coarsening without an averaging operation.

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