

## Spontaneous Double Phase Separation Induced by Rapid Hydrodynamic Coarsening in Two-Dimensional Fluid Mixtures

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We demonstrate by numerical simulations that spinodal decomposition of fluid mixtures is strongly dependent upon their “fluidity,” which characterizes the relative importance of the two relevant transport mechanisms, hydrodynamic flow and diffusion. Thus, it may not be “universal,” at least in two dimensions. For a high fluidity, we find “spontaneous double phase separation.” We confirm that this unusual phenomenon is caused by the following mechanism: High fluidity causes rapid geometrical coarsening of domains due to a hydrodynamic process, which is too fast for diffusion to follow. This brings the system out of equilibrium and induces secondary phase separation. [S0031-9007(98)06528-4]

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Hydrodynamic effects on phase separation have been intensively studied from both the experimental and the theoretical viewpoints [1–3]. Late-stage coarsening dynamics of bicontinuous phase separation in three dimensions (3D), which is characterized by  $a \sim t$  ( $a$ : domain size;  $t$ : time), has been explained in terms of tube hydrodynamic instability proposed by Siggia [4]. This has been confirmed by both experiments [5] and simulations [6,7]. Hydrodynamic effects in two dimensions have also been studied extensively by numerical simulations [8]. The difficulty in the understanding of phase separation in fluid mixtures originates from the fact that there exist two relevant transport mechanisms for fluid mixtures, *diffusion* and *hydrodynamic flow*, and they are coupled with each other in a complicated manner. Only the former is responsible for the temporal increase in the order parameter (composition difference between two phases), and the latter just causes geometrical coarsening. Because of the complex nature of their nonlocal and nonlinear coupling, the hydrodynamic effects on phase separation have not been fully understood even for simple fluid mixtures. For example, there has been no analytical theory describing the late-stage phase-separation kinetics of 3D fluid mixtures. For critical 2D fluid mixtures, on the other hand, there have been a lot of arguments about the value of the scaling exponent  $\alpha$  of the domain coarsening ( $a \sim t^\alpha$ ), namely, whether  $\alpha$  should be 1/2 or 2/3 [8]. Further, the unusual fast-mode kinetics ( $a \sim t^{3/2}$ ) [9,10], which is much faster than hydrodynamic coarsening ( $a \sim t$ ), and double phase separation behavior [11] observed experimentally in the phase separation of 3D fluid mixtures under the influence of surface fields, are still very far from complete understanding. It is likely that both phenomena are deeply associated with the hydrodynamic effects on bicontinuous spinodal decomposition [11,12]. Thus, the deeper understanding of hydrodynamic effects is necessary for clarifying the physical mechanisms of these unusual phenomena.

In this Letter, we report a systematic numerical study on how “fluidity,” which characterizes the relative im-

portance of hydrodynamic flow to diffusion, affects the phase-separation kinetics of two-dimensional incompressible fluid mixtures. We also study the validity of the scaling concept and the universality of a fluid model known as “model  $H$ ” [1,2]. We demonstrate that, contrary to the common belief, even the so-called late stage of phase separation cannot be universally described by a single critical power law for 2D fluid mixtures and the phase-separation behavior even qualitatively depends upon the fluidity of a mixture; namely, the local-equilibrium assumption required for the scaling argument is severely violated for a case of high fluidity. As an extreme case, we find a phenomenon of “spontaneous double phase separation” under a high-fluidity condition. Our study indicates the breakdown of the concepts of “scaling” and “universality” for phase separation of 2D fluid mixtures.

The basic Langevin equations describing the dynamics of fluid phase separation (model  $H$ ) are [1,2]

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

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho (\vec{v} \cdot \vec{\nabla}) \vec{v} = \vec{F}_\phi - \nabla p_1 + \eta \nabla^2 \vec{v} + \vec{\zeta}, \quad (2)$$

where  $\phi$  is the composition,  $\vec{v}$  is the velocity,  $p_1$  is a part of pressure,  $\rho$  is the density,  $\eta$  is the viscosity, and  $L_\xi$  is the renormalized kinetic coefficient. Here  $H$  is the Ginzburg-Landau-type Hamiltonian, which is defined as

$$\beta H = -\frac{1}{2} r \phi^2 + \frac{1}{4} u \phi^4 + \frac{1}{2} K (\nabla \phi)^2, \quad (3)$$

where  $\beta = 1/k_B T$  ( $k_B$ : Boltzmann constant;  $T$ : temperature). In Eq. (2),  $\vec{F}_\phi$  is the thermodynamic force density acting on the fluid due to the fluctuations of the composition  $\phi$  and  $\vec{F}_\phi = -\phi \nabla \mu = -\nabla \pi + k_B T K \phi \nabla \nabla^2 \phi$  ( $\pi$ : osmotic pressure), where  $\mu = \delta H / \delta \phi$  is the chemical potential. Here  $\theta$  and  $\vec{\zeta}$  are Gaussian noises [1].

Here we scale length and time, respectively, by the correlation length of critical fluctuations,  $\xi = (K/r)^{1/2}$ , and their lifetime,  $\tau_\xi = \xi^2 / D_\xi$  ( $D_\xi = r L_\xi$ ). We define new

scaled variables as  $\vec{X} = \vec{x}/\xi$  ( $\vec{x}$ : a position vector),  $\tau = t/\tau_\xi$  ( $t$ : time), and  $\vec{V} = (\tau_\xi/\xi)\vec{v}$ . The composition is normalized as  $\Phi = \phi/\phi_e$ , where  $\phi_e = (r/u)^{1/2}$  is the final equilibrium composition. The scaled equation corresponding to Eq. (2) is  $\frac{D\vec{V}}{D\tau} = -\Gamma\vec{F}_\Phi - \nabla P_1 + \Xi\nabla^2\vec{V} + \vec{\Omega}$ , where  $D/D\tau$  is the Lagrange derivative,  $\vec{F}_\Phi$  is the scaled  $\vec{F}_\phi$ ,  $\Gamma = \frac{r\phi_e^2\tau_\xi^2}{\rho\beta\xi^2}$ ,  $P_1 = \frac{\tau_\xi^2}{\rho\xi^2}P_1$ ,  $\Xi = \frac{\eta\tau_\xi}{\rho\xi^2}$ , and  $\vec{\Omega} = \frac{\tau_\xi^2}{\rho\xi^2}\vec{\zeta}$ .

Then, the fluidity parameter  $R_d$  ( $d$ : the spatial dimensionality of a system) can be defined as

$$R_d = \frac{\Gamma}{\Xi} = \frac{r\phi_e^2\tau_\xi}{\eta\beta} = 6\pi r\phi_e^2\xi^3 = 18\pi\sigma\xi^2\beta, \quad (4)$$

which is the measure of the relative importance of the streaming term vs the diffusion term. Here  $\sigma$  is the interface tension and the relation  $\sigma/k_B T = \frac{1}{3}r\xi\phi_e^2$  is used. For 3D ( $d = 3$ ), we have the relation  $\sigma = A_\sigma k_B T/\xi^2$  ( $A_\sigma$  is the universal constant and  $A_\sigma = 0.1-0.2$ ), which can be derived from the two-scale-factor universality [1]. Thus,  $R_3 = 18\pi A_\sigma = 5-10$ . Hence, the fluidity is not a controllable parameter, but a rather universal constant in 3D [13]. In 2D, on the other hand,  $R_2$  has a critical anomaly of  $(T - T_c)^{-1}$ : Since  $r \sim (T - T_c)^\gamma$ ,  $\phi_e \sim (T - T_c)^\beta$ , and  $\xi \sim (T - T_c)^{-\nu}$ ,  $R_d \sim (T - T_c)^{\gamma+2\beta-3\nu}$ . Using the hyperscaling relation between exponents  $\gamma + 2\beta = d\nu$  [1], we get  $R_3 = 5-10$  and  $R_2 \sim (T - T_c)^{-\nu}$  ( $\nu = 1$  in 2D). Thus,  $R_2$  is not a universal constant in 2D and can be treated as a controllable parameter.

To study phase-separation kinetics of 2D critical fluid mixtures, we solve the scaled kinetic equations by the Euler method under periodic boundary conditions and the incompressibility condition  $\vec{\nabla} \cdot \vec{V} = 0$ . The system size was set to  $256 \times 256$ . We choose the grid size  $\Delta X = \Delta Y = 1$  and the time step  $\Delta\tau = 0.01$  to ensure the stability. We change the value of  $R_2$  to control the fluidity. The noise  $\Theta$  was introduced throughout the simulations to satisfy the fluctuation-dissipation relation. The velocity field  $\vec{V}$  in the wave number ( $q$ ) space,  $\vec{V}_q$ , is calculated from the relation  $\vec{V}_q = \mathbf{T}_q \cdot [-\Phi\nabla(-\Phi + \Phi^3 - \nabla^2\Phi)]_q$ , where  $\mathbf{T}_q$  is the so-called Oseen tensor in  $q$  space given by  $\mathbf{T}_q = \frac{R_q}{q^2}(\mathbf{I} - \frac{\vec{q}\vec{q}}{q^2})$ , where  $\mathbf{I}$  is the identity matrix and  $(\cdot\cdot\cdot)_q$  denotes the Fourier component of  $q$ .

First, we show one of the most extreme cases to demonstrate how strongly fluidity affects the pattern evolution. Figure 1 represents the overall pattern evolution during bi-continuous spinodal decomposition for a symmetric composition under a high-fluidity condition of  $R_2 = R = 120$ . It is evident that, even after the formation of a sharp interface, domains do not reach the final equilibrium composition and the temporal change in the darkness (composition) of domains can be seen. Note that it has so far been widely believed that there is no change in composition after the formation of a sharp interface. This local-equilibrium assumption is the heart of the scaling concept. This strong violation of the local equilibrium after the formation of a sharp interface is never seen for spinodal decomposition under a small fluidity condition, namely, for a small  $R$

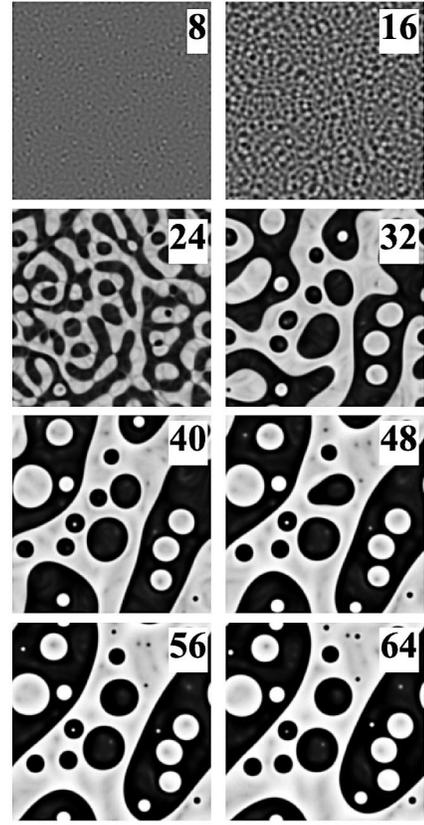


FIG. 1. 2D pattern evolution during spinodal decomposition for the fluidity parameter of  $R = 120$ .

( $R < 20$ ). In the late stage of phase separation, we even see spontaneous secondary phase separation of nucleation-growth type. For  $\tau > 40$ , we can clearly see the birth of small white and black droplets in the large black and white domains, respectively. This nucleation-growth probability is dependent upon the noise level of  $\Theta$  because the nucleation is an event overcoming the energy barrier by thermal noises. In Fig. 1,  $\Theta$  was set to  $10^{-3}$  in strength.

Figures 2(a) and 2(b) show the temporal change in the normalized concentration distribution function  $P(\phi)$  for  $R = 12$  and 120, respectively. For (b), which corresponds to the case of Fig. 1, the change in  $P(\phi)$  is significantly retarded from that expected from the rapid growth of the domain size: Even after the distribution function has distinct two peaks (namely, even after the formation of a sharp interface), the concentration does not reach the final equilibrium concentrations and has a broad distribution, in contrast to case (a) (see also Fig. 1). We even see the four peaks for the concentration distribution function, which is consistent with double phase separation seen in Fig. 1.

Next, we demonstrate how the exponent  $\alpha$  of the domain coarsening is affected by the fluidity. Figure 3 plots the characteristic wave number of the phase-separated structure  $\langle q \rangle$  against the reduced time  $\tau$ . Here  $\langle q \rangle$  is calculated as  $\langle q \rangle = \int d^2q [\vec{q}]S(\vec{q}) / \int d^2q S(\vec{q})$ , where  $S(\vec{q}) = \int d\vec{X} \exp(i\vec{X} \cdot \vec{q}) \langle \Phi(\vec{X})\Phi(0) \rangle$ . Figure 3 clearly indicates that the coarsening dynamics is crucially dependent upon

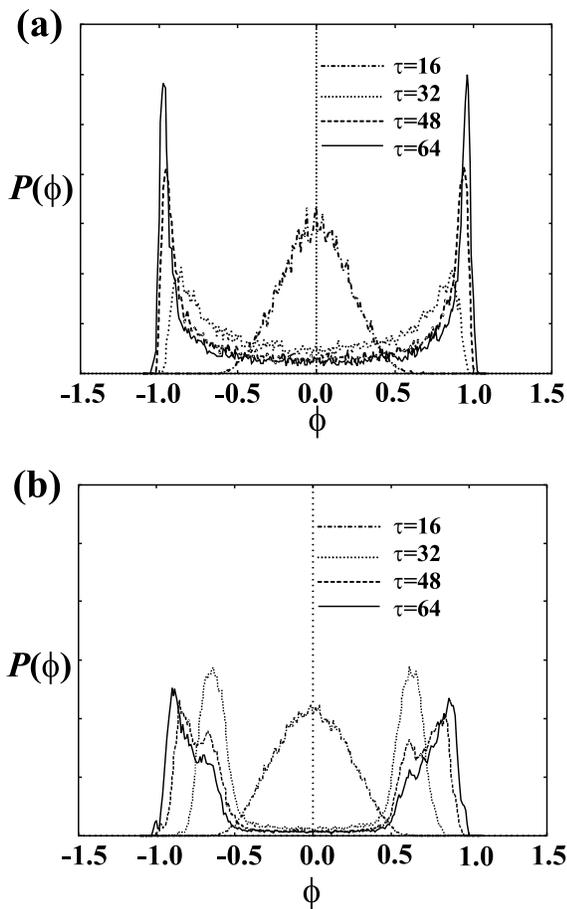


FIG. 2. Temporal change in  $P(\phi)$  for two fluidity parameters: (a)  $R = 12$  and (b)  $R = 120$ .

$R$ . With increasing  $R$  from 0.83 to 8.3, the exponent  $\alpha$  monotonically increases from  $\sim 2/3$  to  $\sim 1$ . This surprising result strongly indicates that the scaling exponent for the domain growth is “not” universal for 2D fluid mixtures at short times (at least for  $\tau < 100$ ), although the “true” long-time asymptotics might be universal. This may be related to the long-standing argument about the growth exponent of 2D fluid mixtures (see, e.g., Ref. [8]). This suggests that we need special care on the effects of the fluidity

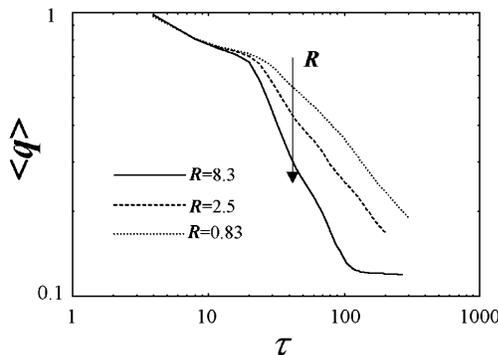


FIG. 3. Temporal change in  $\langle q \rangle$  for different  $R$ . The level off at large  $t$  for  $R = 8.3$  is due to a finite-size effect.

for the proper understanding of the universality of a fluid model (model  $H$ ) and the scaling law.

We now discuss the physical origin of the unusual phenomenon of spontaneous double phase separation shown in Fig. 1 [11]. In bicontinuous phase separation, the total interface area of the system is drastically reduced within a short time by the fast hydrodynamic coarsening driven by interface tension. Since the hydrodynamic interface motion is much faster than the concentration diffusion, *the hydrodynamic flow due to interface motion causes only the geometrical coarsening and does not accompany the concentration change*. That is, the hydrodynamic coarsening can be too quick for concentration diffusion to establish the local equilibrium. This should cause some kind of double quench effects, which we call *interface quench effects*. The effects lead to the following unusual situation: Macroscopic domains whose size is far beyond the interface thickness  $\xi$  are lying *within the coexisting curve*. Thus, these domains are metastable or unstable, and the secondary phase separation can be induced. In all previous studies [1,3], the local equilibrium has been assumed in the hydrodynamic regime, but it is probably not true when the phase-separation process is accelerated by (i) a high fluidity or (ii) wetting effects. This interface quench effect is a quite generic feature of hydrodynamic phase separation: It always exists in fluid spinodal decomposition as can be seen in Fig. 4. Whether or not it results in a drastic phenomenon of spontaneous double phase separation simply depends upon the strength of the effects.

To understand the strength of interface quench effects more quantitatively, we estimate the roles of hydrodynamic flow and diffusion on the local composition change separately. Figure 4 shows the temporal change in the average magnitudes per a lattice of the diffusion flux and the hydrodynamic flux. The timing when the hydrodynamic flux becomes more dominant than the diffusion flux in Eq. (1) becomes earlier and earlier with an increase in  $R$ . After the crossover, there is always the possibility that the diffusion process cannot catch up with the hydrodynamic geometrical growth of domains and the domains may become out of equilibrium. Whether the system really becomes out of

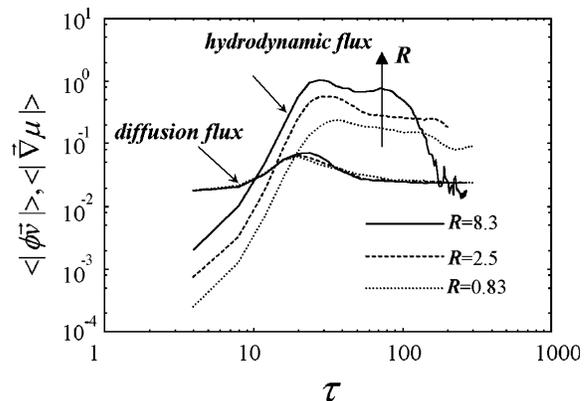


FIG. 4. Temporal change in the average hydrodynamic flux and the average diffusion flux per lattice.

equilibrium or not is crucially dependent upon whether at the crossover time the concentration in the domain already reaches the final equilibrium one or not.

The above behavior can be explained theoretically as follows. In the initial stage, the velocity field grows in a continuous manner, reflecting the increase in the composition difference between the two phases,  $\delta\phi$ . From Eq. (2), we have  $\eta\nabla^2\vec{v} \sim k_BTK\delta\phi\nabla^2\delta\phi$ . Since the only length scale is  $\xi$  in the initial stage, the velocity fields grow as  $v \sim (k_BTK/3\eta\xi)\delta\phi^2$ . Thus, we obtain the following simple relation to the scaled velocity  $V$ :  $V = v/(\xi/\tau\xi) \sim R_d(\delta\phi/2\phi_e)^2$ . In the late stage, on the other hand,  $\delta\phi$  approaches to  $2\phi_e$  with time. Since  $\sigma \sim k_BTK(2\phi_e)^2/3\xi$ , this expression of  $v$  reduces to the well-known relation  $v \sim \sigma/\eta$ , which gives the plateau value of  $v$  in the late stage for bicontinuous phase separation, namely,  $V \sim R_d$ . The proportionality between  $v$  and  $\delta\phi^2$  in the early stage can be confirmed in Fig. 5, where we plot the time evolution of  $v$  and the peak intensity of the structure factor  $S(q_{\max})$ . Note that  $S(q_{\max})$  is proportional to  $\delta\phi^2$  until the domain starts to grow in size. Since the temporal change of  $\delta\phi$  is purely dominated by diffusion (only diffusion can change the concentration distribution function) and not dependent upon  $R_d$ , the strength of velocity fields is simply proportional to  $R_d$  (see Fig. 4). On the other hand, the diffusion flux is dependent only upon the diffusion constant and not upon  $R_d$ . This explains the crossover behavior from a diffusion-dominated to a flow-dominated regime observed in Fig. 4 and further why this crossover occurs earlier with an increase in  $R_d$ .

Our numerical simulation unambiguously demonstrates that double phase separation can be induced in 2D fluid mixtures under a high-fluidity condition. In relation to this, we briefly discuss whether the similar phenomena can be observed in three dimensions or not. Such double phase separation was indeed observed experimentally in a confined geometry [11]. As discussed above, there is little room to control the fluidity parameter in three-dimensional fluid mixtures since it is a universal quantity that does not depend upon the material property such as viscosity [13]. Under the influence of a solid wall that

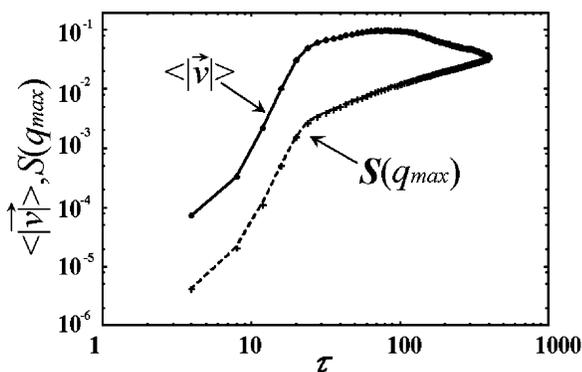


FIG. 5. Comparison of the growth of velocity fields  $\langle |\vec{v} \rangle$  with the growth of the peak scattering intensity  $S(q_{\max})$  for  $R = 0.24$ .

preferentially absorbs the  $A$ -rich phase of an  $A$ - $B$  mixture, it is known [9] that there is an enormous acceleration of the domain coarsening for phase separation of a critical fluid mixture; namely, domain sizes grow as  $a \sim t^{3/2}$ . The mechanism of this unusual fast growth of domains itself is not yet understood: Although Troian [14] proposed a model based on diffusion, we believe that it is caused by the hydrodynamic pumping mechanism due to the Rayleigh instability [12]. Even without understanding the mechanism, however, we can argue that double phase separation may be spontaneously induced solely by the fact that this fast growth ( $a \sim t^{3/2}$ ) is much faster than that in usual bulk phase separation ( $a \sim t$ ) [9].

In summary, we demonstrate by numerical simulations clear evidence that phase separation of fluid mixtures is strongly dependent upon the fluidity, and even the qualitative features are altered by the change in the fluidity. Contrary to common belief, it is thus not “universal” in two dimensions, at least at short times. We need further study to clarify whether this nonuniversal behavior is transient or truly asymptotic. Our study indicates that we cannot separate the early stage and the late stage in the conventional sense, since we cannot assume the establishment of the local equilibrium even after the formation of a sharp interface. This means the breakdown of the local-equilibrium assumption, which is the central concept behind the scaling behavior. Under a high-fluidity condition, the above unique features of 2D fluid mixtures even lead to a phenomenon of spontaneous double phase separation.

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