

Late-stage phase separation and sedimentation in a binary liquid mixture

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Visualization studies of the phase separation of the critical binary liquid mixture, aniline-cyclohexane, in the late stage of the gravity-dominated regime are reported. The sedimentation behavior, following the formation of the bulk interface, shows that the residual domains grow in size according to $a(t) = At^\phi$, with $\phi = 0.27 \pm 0.06$ and $A = (7 \pm 5) \times 10^{-7} \text{ m s}^{-\phi}$. Domain growth in the earlier stages of spinodal decomposition and nucleation mechanisms also yield similar growth exponents and prefactors. The differences are probably due to some hydrodynamic interactions during the sedimentation.

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The dynamics of phase-separation processes occurring in unstable binary liquid mixtures have been the subject of numerous investigations [1–7]. In such systems, domain growth of the new phases proceeds through a sequence of physically distinct mechanisms which ultimately lead to thermodynamic equilibrium. Typically, one observes a diffusive regime of domain coalescence at the beginning, followed by surface-tension-dominated growth, until gravity effects take over in the final stages.

While extensive studies of the diffusion- and surface-tension-controlled regimes exist [1–4], very few reports have systematically probed the consequences of gravity [5–7]. After a temperature quench in the miscibility gap of a binary liquid, domain sizes grow to reach the capillary length scale $l_c = (\sigma/g\Delta\rho)^{1/2}$, with σ the surface tension and $\Delta\rho$ the density difference between the two phases. From that point on, gravity becomes important. An ensuing instability occurs in which buoyancy first deforms, then tears the interconnected domain structures, yielding large-scale time-dependent flow patterns in the fluid [5,6]. Presumably, these irregular patterns originate from a balance of viscous forces and the sedimentation of nonspherical domains that do not necessarily settle in the direction of gravity [8]. Succeeding this convection activity, a quiescent period arises during which domain sizes were inferred to grow according to t^ϕ , with $\phi = 3 \pm 0.5$ [5]. A demixing zone subsequently appears, where droplets of opposing phases meet and lead to the formation of a bulk interface between the two macroscopic phases. Visualization studies of the demixing processes suggest that the droplet size is stabilized by the flow inside the mixing zone which resembles a porous medium [7]. After the emergence of the interface, the sedimentation of the residual domains continues to proceed until there remains two distinct and homogeneous phases. Finally, gravity induced concentration profiles are established in the fluid over long times [9].

In this work, we demonstrate, through visualization studies, the presence of domain growth during the sedimentation period following the appearance of the bulk interface. Coarsening in the critical aniline-cyclohexane mixture is seen to progress according to $a(t) = At^\phi$, where $a(t)$ is the typical domain size at time t , with $\phi = 0.27 \pm 0.06$ and $A = (7 \pm 5) \times 10^{-7} \text{ m s}^{-\phi}$. These are

systematic measurements of domain growth in this very late stage of the phase separation of a binary liquid mixture. Most of the previous experimental studies on the dynamics of phase separation of binary liquids [1,3,5,6] have been accomplished within mK from T_c to take advantage of the critical slowing down. Under such conditions, the processes in the gravity regime investigated in this work would occur over a period of 5–10 h due to the small density difference of the phases.

The equilibrium properties of the aniline-cyclohexane system are well established in the neighborhood of the consolute critical point [10–12]. In the temperature-composition plane, the coexistence curve displays an upper consolute temperature T_c of 29.84 °C at the critical composition C_c of 53% cyclohexane per weight. Spectroscopic grade aniline and cyclohexane from Anachemia were used throughout. The aniline was distilled in order to eliminate sulfur-containing impurities. Storage in the dark also prevented oxidative processes associated with potential residual impurities. The cyclohexane was used without further purification. The binary mixture was prepared at the critical composition using a Microliter # 701 microsyringe from Hamilton Co., Nevada. The final volume of 40 μl consisted of $16.1 \pm 0.1 \mu\text{l}$ of aniline and $23.9 \pm 0.1 \mu\text{l}$ of cyclohexane inserted into a 1.75-mm-i.d. high-precision ESR capillary tube.

The mixture was mechanically stirred in one phase at 45 °C, then stabilized at 32.0 ± 0.1 °C for 2 min. The capillary tube was then rapidly transferred and positioned vertically (in less than 2 s) into a water-cooled cell at 28.2 °C, whose temperature was controlled to ± 0.05 °C with a Haake F3 bath. From the thermal diffusivity of the binary mixture, as calculated from the thermal conductivities, the heat capacities, and the densities of the components, a thermal relaxation time of 8 s was estimated for the sample. Therefore, to achieve uniform sample temperature through diffusion should require about 30–40 s. These relaxation times were independently confirmed by measurements with an NMR method [13].

Spinodal decomposition proceeds rapidly through the diffusive and the surface-tension-driven mechanisms during this bath quench technique. Order-of-magnitude calculations, with the physical parameters of the binary mixture [10–12] and the coarsening rates for these mecha-

nisms [2,3], show that the capillary length scale $l_c = 250 \mu\text{m}$ is reached in about 10 s under the current experimental conditions. This corresponds roughly to the observed time after which the macroscopic flow begins.

About 15–20 s after the quench, sedimentation brings visible droplets (submillimeter size) and form a demixing zone midway in the sample [see Fig. 1(a)]. Through a complicated regime of rupturing and coalescence of droplets [7], the demixing zone evolves into the interface which separates the bulk phases. These processes lead to a quiescent interface nearly 100 s following the quench.

While the interface is well defined, both phases remain opalescent due to the presence of residual and settling domains [see Fig. 1(b)]. In time, each phase evolves into a clarified layer of equilibrium composition, and a suspension layer with the remaining domains, due to sedimentation [see Figs. 1(c)–1(e)]. A fairly sharp interface exists

between the clarified and suspension zones [see Figs. 1(b)–1(d)]. Diffusion eventually broadens slightly this interface [see Fig. 1(e)]. At later times, both macroscopic phases appear homogeneous with the exception of wetting droplets of opposing phases pinned to the glass surface [see Fig. 1(f)].

The sedimentation velocity of the residual domains can be conveniently measured with the opalescent fronts which migrate in their respective phases towards the interface. The position of the front in the upper phase, the cyclohexane-rich phase, was measured with a Starrett # 722 vernier (precision $\pm 5 \mu\text{m}$) every 80 s on average, between 300 and 2000 s after the quench. The position of the air-liquid meniscus was also measured ten times between 500 and 2000 s and its average provided a reference position. Typically, the error estimate (plus or minus one standard deviation) on the average position of the meniscus was $\pm 50 \mu\text{m}$. These measurements of the opalescent front and the meniscus, sample preparation, and quenching procedure were repeated in 28 independent experiments.

A solid sphere, of radius R , which settles in a quiescent fluid in the direction of a gravitational field, acquires an asymptotic sedimentation velocity given by [8]

$$V_s = (2g \Delta\rho R^2) / (9\eta), \quad (1)$$

where g is the acceleration due to gravity, $\Delta\rho$ the density difference between the sphere and the fluid, and η the dynamical viscosity of the fluid. The transient period, before the asymptotic regime, lasts approximately $(10\rho R^2) / (9\eta)$. Due to the opalescence in both phases (see Fig. 1), one infers the presence of micrometer-size domains. For these domains, and with ρ and η of the aniline-cyclohexane mixture [10,11], one estimates a transient period of about 10^{-7} s. To obtain a relaxation time on the order of seconds would require millimeter domain sizes. Therefore, the terminal sedimentation velocity (1) can be used to describe the settling of most domains following the appearance of the bulk interface during the experiment as shown in Fig. 1.

In the sedimentation stage of the phase separation, prior [1] and after the appearance of the bulk interface (see Fig. 1), the residual domains can be assumed spherical to a good approximation. Shape deformations are also neglected since $4\pi\sigma R^2 / k_B T \gg 1$ for micrometer-size domains in these experiments. The fusion time of domains with the bulk interface, $\tau_f \approx \eta R / \sigma$, is roughly 10^{-5} s for micrometer-size droplets of the aniline-cyclohexane mixture [10–12]; hence the lack of interference among the fusion and the slower settling processes. During the sedimentation, if the domain size is taken to grow according to $a(t) = At^\phi$, with ϕ the growth exponent and A the amplitude prefactor, then integration of Eq. (1) yields for the position of the sedimentation front x from a reference position x_0 as a function of time,

$$x - x_0 = (2g \Delta\rho A^2) t^{2\phi+1} / [9\eta(2\phi+1)]. \quad (2)$$

Therefore, the growth exponent can be retrieved from the slope in a plot of $\log_{10}(x - x_0)$ vs $\log_{10}(t)$, while the prefactor can be obtained from the intercept.

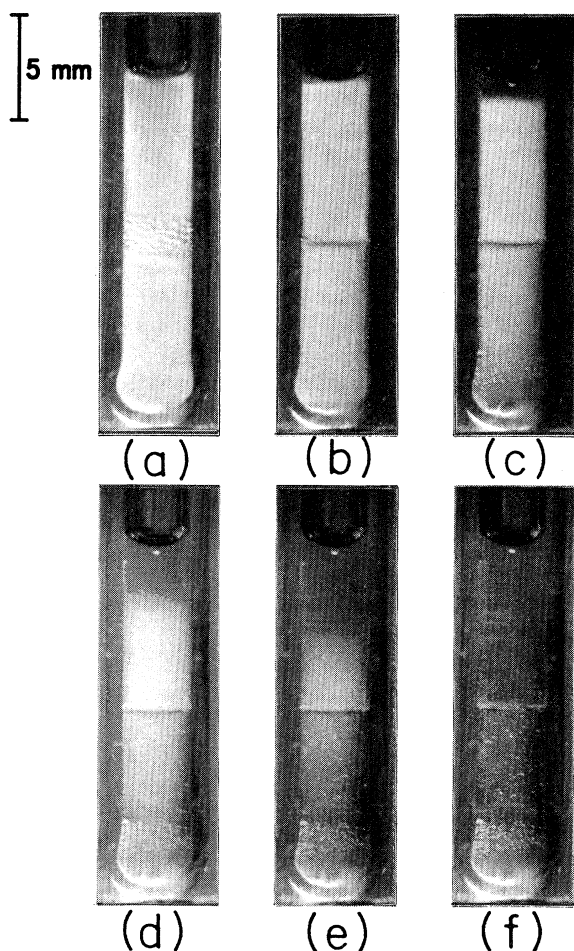


FIG. 1. Photographs of the critical aniline-cyclohexane mixture following a temperature quench from 32.0°C to 28.2°C . Time after the quench: (a) 60 s, (b) 180 s, (c) 600 s, (d) 1200 s, (e) 1800 s, (f) 3000 s. Note that the horizontal scale is deformed by 1.33 (the relative index of refraction of water/air) due to the refraction between the water coolant/curved glass cell/air.

Figure 2 shows the position of the sedimentation front of the opalescence in the upper phase of the critical aniline-cyclohexane mixture, as measured from the air-liquid meniscus, versus time, on doubly logarithmic scales. The slope of the linear least-squares regression of the 28 independent data sets (a total of 540 points) yields a growth exponent $\phi = 0.27 \pm 0.06$, where the error estimate corresponds to three standard deviations. The amplitude, obtained from the intercept, gives $A = (7 \pm 5) \times 10^{-7} \text{ m s}^{-\phi}$, with the error estimate also corresponding to three standard deviations.

To compare these results with the growth rate predicted by other theories [2,3], it proves convenient to express $a(t)$ and t in dimensionless form. In this case, the relevant length scale is $\xi(T_f)$, the correlation length of the critical fluctuations, and the relevant time scale is ξ^2/D , where $D = k_B T / 6\pi\eta\xi$. Hence the growth law $a(t) = At^\phi$ becomes $q_m = C\tau^{-\phi}$, where $q_m = \xi/a$, $\tau = tD/\xi^2$, and $C = (\xi/A)(\xi^2/D)^{-\phi}$. The experimental data (Fig. 2), the physical parameters of the aniline-cyclohexane mixture [10–12], and error analysis, yield $C = 0.33 \pm 0.49$, and $\phi = 0.27 \pm 0.06$, with the errors corresponding to three standard deviations. In an earlier stage of spinodal decomposition, droplet coalescence through diffusion leads to $q_m = 0.437v^{-1/3}\tau^{-1/3}$, with v the volume fraction [2,3]. Assuming v to be smaller than the three-dimensional (3D) continuum percolation threshold of 16%, one finds a dimensionless prefactor of 0.822. Similarly, nucleation in dilute mixtures yields, for the evaporation-condensation mechanism of Lifshitz-Slyozov [2,3], $q_m = 2.66\tau^{-1/3}$. Therefore, our data seem to support the diffusive droplet coalescence mechanism.

A posteriori, it should not be surprising to find such value for ϕ in the late sedimentation stage. Once the domain size exceeds the capillary length scale, gravitational stresses deform and rupture the interconnectivity

of the structures produced during the surface-tension-driven mechanism [2,3]. This instability engenders the sedimentation of the largest domains, irregular macroscopic flows, and ultimately the appearance of the bulk interface. As a consequence, in both macroscopic phases, the remaining and disconnected micrometer-size domains become subject to diffusion and therefore coalescence, in addition to sedimentation. Such a situation is akin to the earlier stages of spinodal decomposition, where domain coalescence also proceeds through diffusion [2,3]. If the composition of the residual domains is not at equilibrium and their volume fraction low, then growth according to the Lifshitz-Slyozov mechanism is also possible and reminiscent of the situation following nucleation.

The systematic deviation of $\phi = 0.27 \pm 0.06$ in the sedimentation growth regime from the ϕ observed in the diffusive droplet coalescence and the Lifshitz-Slyozov mechanisms is noteworthy. We searched, unsuccessfully, for systematic errors in the experiments. A potential source of error could arise from the sedimentation behavior of a polydisperse distribution of domain sizes. However, such a case normally leads to stratification with the formation of several distinct suspension zones separated by sharp interfaces or “shocks” [14]. In all the experiments, only one clarified zone and one suspension zone were observed in each phase. Another possible cause of error could be due to the sample preparation at the critical composition. Under the experimental conditions, deviations by at least 13% in volume fraction (i.e., $5 \mu\text{l}$) from criticality would be required to affect the surface-tension-dominated growth regime, which in turn would lead only to nucleation and growth [6].

Hydrodynamic effects could possibly account for the value of ϕ observed under sedimentation. Indeed, Eq. (1) corresponds to the settling of a single particle in a surrounding fluid with zero Reynolds number. The presence of many particles, hydrodynamic interactions between particles, and interparticle forces all combine to make the understanding of sedimentation more intricate [14]. For domain coalescence, Siggia [2] has considered some hydrodynamic effects on the growth rate. Using a simple model from lubrication theory, he showed how the displacement of fluid between a stationary domain and an approaching one leads to slower coalescence. Consideration of the induced circulation in the domains and possible surface deformations were also included as consequences of fluid displacement between domains. In a limiting case, where the fluid friction restrains the diffusion of the approaching domain closely to the fixed one prior to fusion, ϕ equals $\frac{1}{4}$ instead of $\frac{1}{3}$. Such effects could explain the observed value of ϕ during the sedimentation growth. However, other possible hydrodynamic effects such as back flow induced in the fluid by the sedimenting domains, screening by reorienting domains, and many-particle interactions also deserve to be examined. These issues represent some of the outstanding problems in sedimentation [14].

The interplay between diffusion and the relative motion due to gravity is characterized by the Peclet number, $\text{Pe} = 2V_s a / D$. With V_s from Eq. (1) and $D = k_B T / 6\pi\eta a$, $\text{Pe} = 8\pi a^4 g \Delta\rho / 3k_B T$. For $a < 1 \mu\text{m}$, diffusion dominates

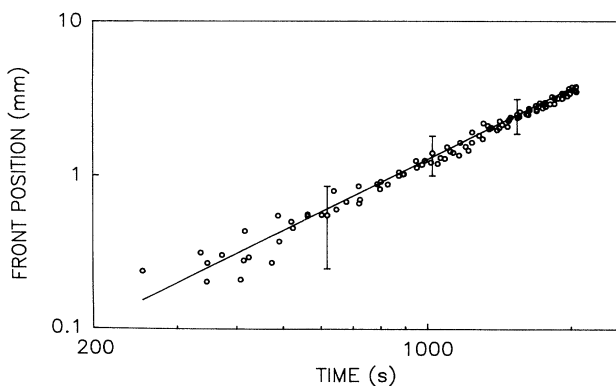


FIG. 2. Position of the sedimentation front in the upper phase, as measured from the air-liquid meniscus, vs time, on doubly logarithmic scales. The data points are from four typical and independent data sets. The solid line is the linear least-squares regression from 28 independent data sets (a total of 540 points), and the representative error bars correspond to plus or minus one standard deviation on the measurements of all the sets.

over sedimentation ($Pe \ll 1$), while for a $> 10 \mu\text{m}$, sedimentation becomes predominant ($Pe \gg 1$). In the experiments reported here, the typical domain size ranges between $1\text{--}5 \mu\text{m}$. Under these conditions, diffusion and sedimentation should contribute equally to the domain growth processes.

The Lifshitz-Slyozov mechanism was found robust against potential instabilities due to hydrodynamic effects [2]. This could possibly indicate the lack of nucleation and growth during the sedimentation regime, as ϕ should remain invariant, i.e., equal to $\frac{1}{3}$.

In summary, we have shown, through the sedimentation

behavior of the critical binary liquid mixture, aniline-cyclohexane, in the very late stage of phase separation, that domain growth proceeds according to $a(t) = At^\phi$, with $\phi = 0.27 \pm 0.06$ and $A = (7 \pm 5) \times 10^{-7} \text{ m s}^{-\phi}$. We speculated that the deviation of ϕ from the growth exponents of the mechanisms in the earlier stages of phase separation (droplet coalescence and Lifshitz-Slyozov) could be due to hydrodynamic effects in the sedimentation process.

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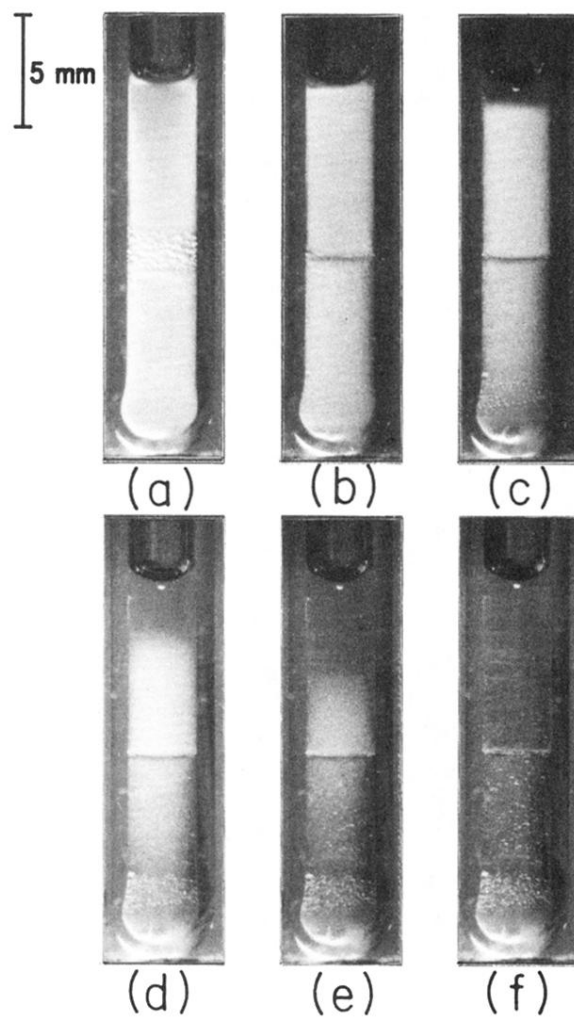


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