PHYSICAL REVIEW E VOLUME 50, NUMBER 2 AUGUST 1994

Dimple and nose coalescences in phase-separation processes

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(Received 10 January 1994)

Coalescence processes are investigated during phase separation in a density-matched liquid mixture (partially deuterated cyclohexane and methanol) under near-critical conditions. As a result of the interplay between capillary and lubrication forces, "nose" coalescence appears to be always associated with the slow growth of isolated droplets (exponent $\approx \frac{1}{3}$), whereas "dimple" coalescence corresponds to the fast growth of interconnected droplets (exponent ≈ 1). At each stage of growth, the distribution of droplets trapped during dimple coalescence is reminiscent of all of the previous coalescence events.

PACS number(s): 05.70.Jk, 64.60.Qb, 68.10.−m

The problem of coalescence between drops has already received considerable attention [1]. One of the important issues is the role of coalescence in the evolution of phase separation phenomena in liquid systems, whose influence is still poorly understood [2]. Two coalescence mechanisms were identified in experiments involving surfactant + water + oil [3] and in theory and numerical simulations [1] where these mechanisms have been defined as (i) "rim or dimple rupture" concerning deformable surfaces where dimpling occurs before the rupture of the surfaces, and (ii) "nose rupture" for drops with negligible deformation before rupture.

In order to investigate the role of coalescence in the phase separation process, we consider a density-matched binary liquid mixture near its critical point of miscibility. The interest in probing the features of coalescence processes in such a situation is guided by the following considerations. First, the system has negligible or very low sensitivity to gravity and coalescence can be attributed to the growth phenomenon only. Second, the scaling laws and universality are applicable, which makes the results generalizable to a wide range of systems and applications (microemulsions, polymers, monotectic alloys, etc.). In addition, the critical slowing down facilitates the observation of the evolution of the phase separation. Self-similarity of the growth also ensures that the processes observed at late times, where observation is easy, are also valid at earlier times.

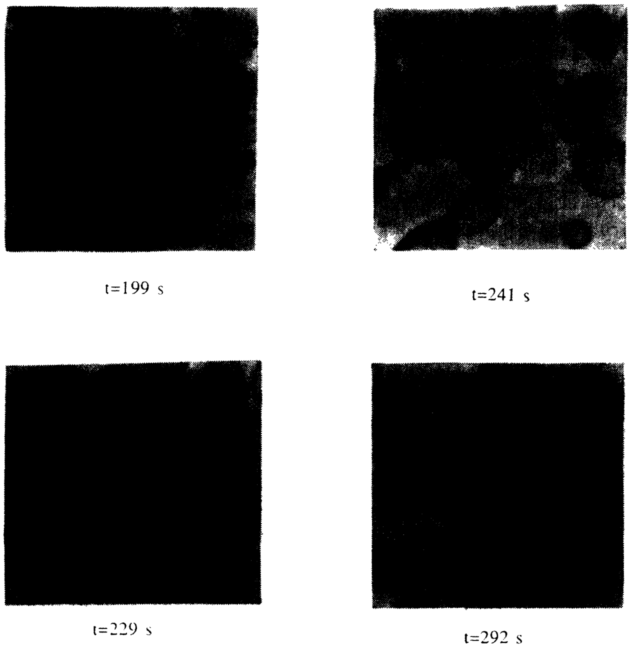
Different rates of growth can be monitored by changing the mixture concentration, and thus the volume fraction Φ_v of the new phases (Φ_v is the ratio of the volumes of the phases). At high volume fractions, a bicontinuous and interconnected pattern of domains is observed, with typical wavelength L_m growing linearly with time t, $L_m \propto t$ [4]. On the other hand, a much slower growth persists for low volume fractions where the droplets are compact but isolated. Here their average distance L_m varies as $L_m \propto t^{1/3}$ [5]. The change of growth rate with respect to concentration is abrupt and occurs in the zone $\Phi_v \approx 30\%$ as shown by recent experiments under a weak concentration gradient [6]. Siggia [4] has suggested that deformation of drops might occur prior to fusion very close to the critical point. The basic phenomenon is the balance between the lubrication forces of hydrodynamic origin [7], which tend to flatten the drops, and the capillary forces, which maintain the spherical shape of drops.

The object of this paper is to show that drop deformation is a common process during phase separation and that the mechanisms of coalescence, the morphology of the pattern of drops, and the growth laws are elements of the phase separation that cannot be separated. Coalescences of the dimple type are always associated with the linear, fast growth in the interconnected pattern of droplets. In contrast, coalescences of the nose type correspond to a slow growth in a pattern of isolated droplets. In addition, the dimple coalescences lead to a very curious phenomenon where a small droplet is trapped inside the dimple. This implies that, at each stage of the phase separation, a distribution of droplets is reminiscent of all of the earlier coalescence events.

OBSERVATIONS

The present investigation is performed in a density-matched mixture of partially deuterated cyclohexane and methanol [8]. Its critical concentration is $c_c = 0.709$ mass fraction of cyclohexane and the critical temperature $T_c = 319$ K. A typical experiment involves lowering the temperature at a rate as high as possible ("quench") from a temperature where the mixture is homogeneous (here $T_c + 5$ mK) to a temperature below the coexistence curve where it phase separates. The dynamics of phase separation is observed through direct visualization at different magnification ratios. Data are obtained for critical ($\Phi_v \approx \frac{1}{2}$) and off-critical ($\Phi_v \leq 0.3$) samples.

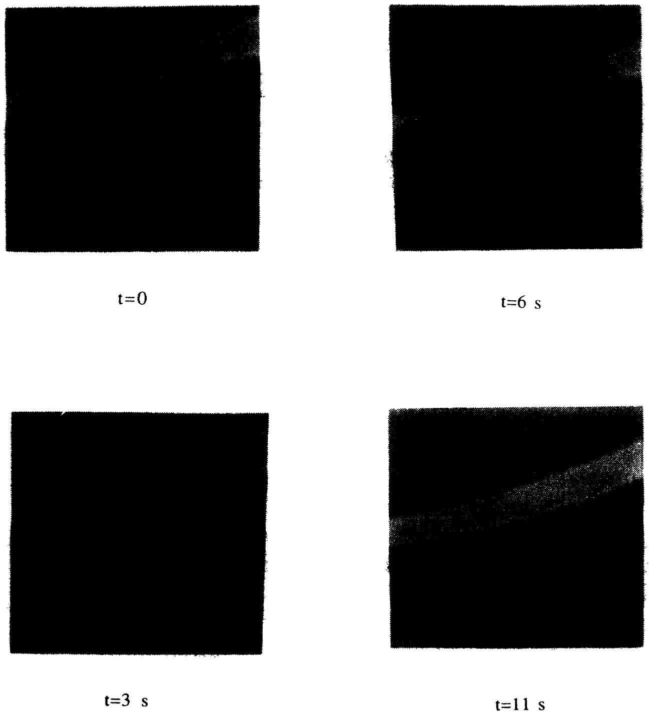
The mixture is prepared at the required concentration by weighing in an optical quartz cell (Hellma), sealed by a teflon screw cap. The cell is made of two optically flat circular windows separated by a spacer with a typical thickness of 3 mm. The cell is set in a water bath whose



t=199 s t=241 s

t=229 s t=292 s

FIG. 1. An example of dimple coalescence ($c=c_c$, $T=T_c-15$ mK). Time is counted with respect to the onset of phase separation. M^+ (M^-) corresponds to the two phases. The contrast has been magnified for the interfaces of interest. An arrow indicates the droplet that has been trapped during coalescence. The vertical dimension of the image corresponds to 4 mm.



t=0 t=6 s

t=3 s t=11 s

FIG. 2. Nose coalescence between two drops of different diameters (T_c-16 mK, $c=c_c-0.02\pm0.01$). M^+ (M^-) corresponds to the two phases. The contrast of the nose has been magnified at $t=0$ (arrow). The vertical dimension of the image corresponds to 7 mm.

temperature stability is within 1 mK. Temperature quenches are typically in the range 2.5–20 mK below T_c. The time that the sample takes to be at thermal equilibrium is typically 30 s and the studies covered a time range between 170 and 2000 s. The cell is illuminated by a parallel beam of white light. A plane with a thickness less than 0.1 mm is imaged on a CCD video camera. The signal is recorded for further analysis.

The sequence of photographs in Fig. 1 portrays the formation of a dimple between two approaching interfaces. These interfaces enclose the same phase with nearly the same radii of curvature R_1 and R_2 with an average radius $R_m=(R_1+R_2)/2$ which is related to the typical length scale L_m by $R_m \approx L_m/4$ since L_m is the pseudoperiod between the phases [8]. This phenomenon terminates in a small droplet (radius r_m) which represents the memory of this mode of coalescence. A key features of this observation is the presence of a distribution of droplets that signify the coalescence through the dimple rupture between the two approaching interfaces.

For off-critical quenches, the drops are not deformed before they fuse. Coalescence is initiated at a point (nose coalescence) as shown in Fig. 2 and proceeds through the flow of the smaller droplet, which has the highest capillary pressure, into the largest drop. Nose coalescence is always associated to the growth of a noninterconnected pattern of droplets.

DISCUSSION

The formation of a droplet which is the memory of a dimple coalescence is one of the most striking feature of the fast growth. In order to test the scaling properties of this distribution of droplets, the time dependence in scaled units of the ratio $\rho_m=r_m/2R_m=2r_m/L_m$ is reported in Fig. 3 for different quench depths. Scaled units of time are defined as $t^*=t/t_{\xi^-}$ where t_{ξ^-} is the lifetime of a fluctuation of correlation length ξ^- with $t_{\xi^-}=6\pi\eta(\xi^-)^3/k_BT_c$ and $\xi^-=\xi_0^-(1-T/T_c)^{-\nu}$; $\xi_0^-=1.65$ Å is the correlation length amplitude below T_c and $\nu=0.63$ is the universal exponent; k_B is the Boltzmann constant and $\eta \approx 7.5\times10^{-3}$ poise is the shear viscosity. Within the experimental uncertainties, the ratio is found constant: $\rho_m \approx 0.15$. In order to relate this ratio to the phase separation parameter, we approximate the approach of the two spherical surfaces of radius R_m, separated by a distance h, by the corresponding approach of a disk of radius $(r_m h)^{1/2}$ towards a plane at h. This is the Rayleigh approximation also used by Siggia [4]. The volume of the drop that results from the coalescence is the volume confined between the drops when the dimple forms. This corresponds approximately to the volume confined beneath the equivalent disk, i.e., $\pi R_m h^2$. Then the ratio ρ_m can be evaluated: $\rho_m \approx (3h^2/4R_m^2)^{1/3}$. The constancy of ρ_m throughout the growth is a test of scaling, and it supports that the minimum value of approach h is a fraction of R_m. The classical approximation [1,4] $h/R_m \approx 0.1$ gives $\rho_m \approx 0.2$, a value which compares well with the experimental value of 0.15 if one considers the crudeness of the above approximations.

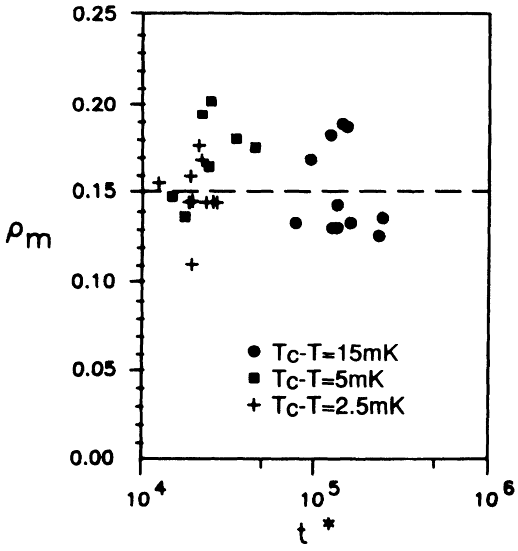


FIG. 3. The ratio ρ_m plotted versus the scaled time $t^*=t/t_{\xi^-}$.

The distribution law of droplet radii coming from dimple coalescence can be evaluated by means of a crude model. We assume that the size of each droplet is directly determined by the coalescence of two tubes. These tubes can be viewed as formed by percolating blobs of radius R_m. The number n_m of droplets of radius r_m which is created per unit time is given by the number of collisions between tubes,

$$\frac{dn_m}{dt}=\frac{dN}{dt}=-N^2\int_\Sigma p(r)\mathbf{V}\cdot\hat{\mathbf{n}}d\Sigma \ . \tag{1}$$

Here N is the number of tubes per unit volume, $p(r)$ is the pair distribution function of the tubes, $\mathbf{V}$ is the relative velocity of the tube interface, and $\hat{\mathbf{n}}$ is the outward unit normal to the surface of collision Σ. Here the surface of collision is not well defined when compared to binary collisions of spheres. We will then limit ourselves to scaling arguments. First, the relative velocity of the tubes is due to their growth and thus can be written as $V\propto\sigma/\eta$, where σ is the surface tension between the phases and η is the average viscosity of the two phases. Second, we apply scaling and consider L_m as the only relevant length scale. Assuming that p is a constant, the integral in (1) can be approximated by $\sigma L_m^2/\eta$ and we obtain

$$\frac{dN}{dt}\propto -N^2\sigma L_m 2/\eta \ . \tag{2}$$

We now make the crude assumption that each tube, formed of interconnected blobs, is of macroscopic length L_0. We neglect the volume of the droplets trapped during coalescence. Since the phase separation proceeds at constant volume fraction, the quantity $NL_0L_m^2$ is conserved during the growth and (2) becomes

$$\frac{dN}{dt}\propto L_m^{-2} \ . \tag{3}$$

Here L_m grows linearly with time and r_m remains proportional to L_m during the process. One thus obtains

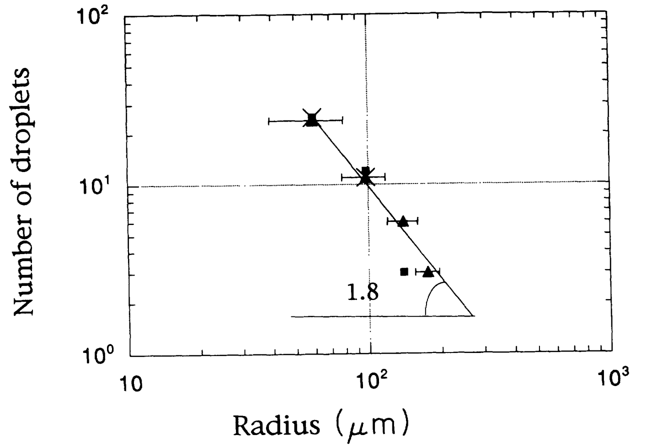


FIG. 4. Time evolution of the size distribution of the droplets issued from dimple coalescence at T_c-15 mK, 258 s (×), 317 s (■), and 376 s (▲) after the onset of phase separation.

$$\frac{dn(r_m)}{dr_m}\propto r_m^{-2} \ . \tag{4}$$

Our preliminary results obtained for a quench of 15 mK below T_c are displayed in Fig. 4. 120 droplets have been analyzed at three different times after the quench. At each time t a natural cutoff is the droplet radius of order $\rho_m R_m(t)$. It is interesting to note that the droplets do not coalesce with the "tubes" or other droplets as shown by the distribution of the smaller droplets which remains stable with time. The distribution develops by formation of largest droplets. The data at the largest times which correspond to the broader distribution relatively well fit to the power law $dn/dr_m=Ar_m^{-\theta}$ with an exponent $\theta=1.8$. The extreme values are between 1.5 and 2.9, with 2.2 as an intermediate value. This preliminary study seems therefore in reasonable agreement with the above theory.

We have thus obtained evidence regarding the unusual (and so far unobserved) coalescences processes of dimple and nose that accompany the phase separation process in liquid mixtures. The dimple coalescences give rise in the two separating phases to a broad distribution of isolated droplets which is the reminiscence or memory of all of the previous coalescence events. These observations should be relevant each time a phase separation is involved with a liquid phase as, e.g., liquid mixtures, microemulsion, polymers, and monotectic alloys. The relation of the pattern of droplets with the structure factor as observed in scattering experiments is still an open question.

ACKNOWLEDGMENTS

We thank H. Davis, F. Perrot, M. Robert, and K. Kawasaki for discussions. We thank L. Ratke for his organization and hospitality. The work has been partially supported by the Centre National d'Etudes Spatiales and the Indo-French Center for the Promotion of Advanced Research.

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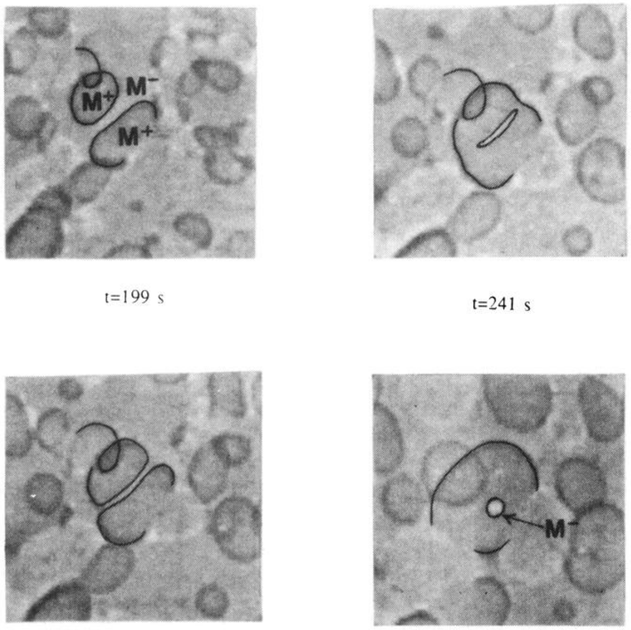

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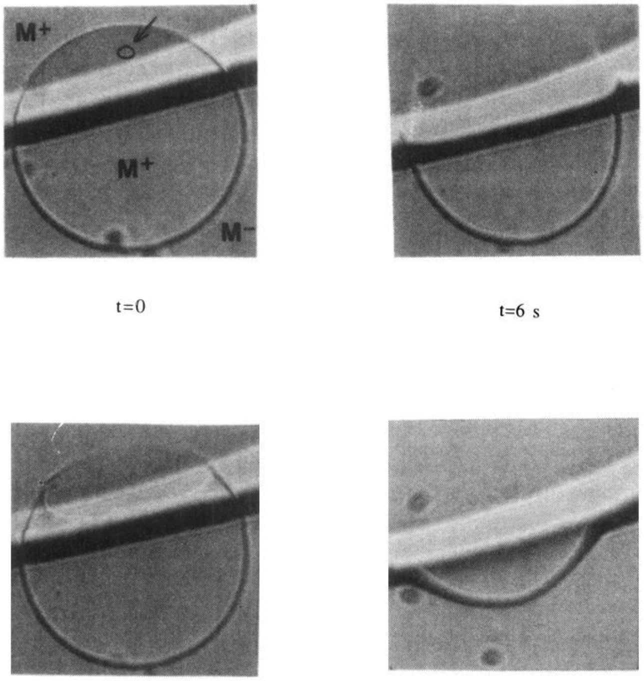

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