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Nucleation and Growth of Tightly Packed Droplets in Fluids

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Experiments of phase separation have been performed in a density-matched liquid mixture (partially deuterated cyclohexane-methanol at 1.4% below critical concentration) and in a pure fluid (SF_6 at 3.6% above critical density). The usual strong gravity-induced flows that accompany phase separation in pure fluids are suppressed by performing experiments under reduced gravity. Experiments under microgravity are compared with experiments on Earth. Phase separation under reduced gravity is characterized by a pattern of tightly packed droplets of the minority phase whose growth can be expressed over more than 7 decades in time by a single reduced power law with exponent $\frac{1}{3}$.

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Phase separation in fluids and liquid mixtures occurs when a sample is quenched from an initial state (temperature T_i) where it is homogeneous to another state (temperature T_f) where the one-phase state is no longer stable [1]. Domains nucleate and their size grows with time in order to ultimately reach two macroscopic equilibrium phases. As it was recently pointed out [2], the morphology of the two growing phases and the associated temporal growth laws are not fully predictable. We show in this Letter that this morphology cannot be understood only in terms of the equilibrium volume fraction ϕ of the minority phase (ϕ is the ratio minority phase volume/total volume). For instance, a simple criterion of percolation is not sufficient to deduce if the minority phase spans continuously over the experimental volume. Our report also clarifies how the growth laws of the domains vary when ϕ is systematically changed.

It is particularly interesting to perform such studies in the vicinity of a critical point (Fig. 1). Critical slowing down enables phase separation to be studied on an experimentally convenient time scale; in this region one also expects scaling to be relevant. Scaling by proper units of length and time—as defined hereafter—implies that all data from different experiments and different systems can be cast on the same universal master curve. The order parameter for liquid mixtures is the concentration difference $M = c - c_c$ (c_c is the critical concentration); at the consolute critical point, the osmotic compressibility diverges and the mutual diffusion coefficient vanishes. For pure fluids, M is the normalized density difference $(\rho - \rho_c)/\rho_c$, with ρ_c the critical density. At the gas-liquid critical point, the isothermal compressibility diverges and the thermal diffusivity goes to zero. The natural length scale is the correlation length ξ of the order parameter fluctuations, which varies with temperature T as $\xi = \xi_0(1 - T/T_c)^{-\nu}$, with ξ_0 a nonuniversal amplitude and $\nu = 0.63$ the universal critical exponent. The natural time scale is the relaxation time of the order parameter fluctuations of size ξ, given by $t_\xi = 6\pi\eta\xi^3/k_B T$, with η the shear viscosity and k_B the Boltzmann constant [3].

Late stages of growth cannot be observed without the suppression of gravitational flows due to the difference in density of the phases. In order to partially reduce these convective effects, which are a function of the parameter $\Delta\rho g_0$ (g_0 is the Earth gravity amplitude and $\Delta\rho$ is the density difference between the two phases that are forming), experiments have been carried out with a density-matched binary liquid of methanol and partially deuterated cyclohexane (CC*-Me) has been designed

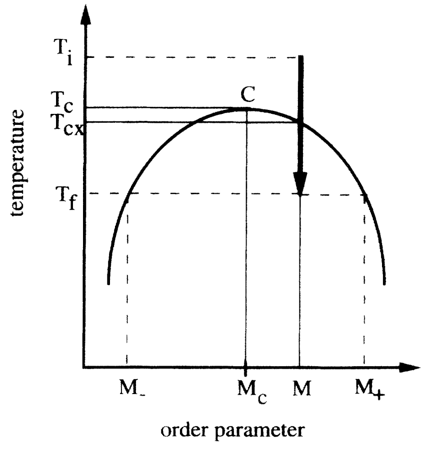

FIG. 1. Schematic of the phase diagram in the temperature T order parameter M plane (see text). The parameter $\phi = (M^+ - M)/(M^+ - M^-)$ is a function of the critical temperature T_c, the coexistence temperature T_{cx}, and the quench depth $\delta T = T_{cx} - T_f$. The coexistence curve expression, which delimits the phase separation domain, is given by $M = \pm B(1 - T/T_c)^\beta$, where $\beta = 0.325$ is a universal critical exponent and B is system dependent.

[4]. This stratagem obviously cannot be used with pure fluids [5,6].

Phase separation at $\phi = \frac{1}{2}$ has been extensively studied [7], and mainly with liquid mixtures. After a thermal quench at T_f into an unstable state, the two growing phases of equal volume form an interconnected pattern of domains that continuously coalesce. A number of experiments [8] under reduced gravity with the above density-matched mixture and pure fluid CO_2 have already been carried out. Results show that the influence of convective flows and sedimentation can be efficiently removed. A characteristic length L_m of the domains can be defined as the pseudoperiod between the phases. At late times, $L_m \sim t$. This linear growth in time can be viewed as the result of capillary flows [9]. When expressed in the scaled units, $K_m^* = 2\pi\xi(T_f)/L_m$ and $t^* = t/t_\xi$, all the results obtained with liquids and fluids and different quench depths can be cast on the same master curve, thus demonstrating that scaling and the notion of universality can be applied to the phase separation process.

Only a few experimental results are available when the volume fraction is very small ($\phi < 0.03$) [10–12], and gravity effects are negligible; the droplets do not coalesce and rather grow by a mechanism of diffusion through the majority phase. Experiments [12] show that, although the initial growth follows a power law with time whose exponent is $\frac{1}{2}$, the late stages are always characterized by a $\frac{1}{3}$ growth law exponent as described by Lifshitz and Slyozov [13].

Off-critical systems at large volume fraction have only been studied, to our knowledge, in a liquid mixture (water-isobutyric acid) by Wong and Knobler [10] who used light scattering techniques. For $\phi > 0.10$ a "slow" growth characterized by a $\frac{1}{3}$ growth law exponent is reported at early times and a faster growth at late times, with the growth exponent varying from $\frac{1}{3}$ to 1 as a function of ϕ. Since the densities of each component are closely similar, gravity effects were expected to be weak in these experiments. In this Letter, we show instead that the above crossover between fast and slow growth is due to the necessarily imperfect density matching. When experiments are performed under reduced gravity, no crossover is observed and two main results are obtained: (i) Droplets of the minority phase grow according to the simple power law $t^{1/3}$, and (ii) pure fluids and binary liquids follow the same scaled growth law over 7 decades in time, further supporting the application of universality to phase separation.

Experiments.—The first set of experiments (No. 1) was carried out on Earth, with the density-matched mixture (CC*-Me). Concentration in wt% cyclohexane is $c = c_c - 0.01$ ($c_c = 71.0$ wt% cyclohexane); the setup has been described in detail elsewhere [14]. The experimental procedure consists in quenching at various temperature depths and recording forward light scattering through the cell.

The set of experiments No. 2 was performed on Earth and under reduced gravity with the same mixture as above. The analysis was by direct imaging. The liquid was enclosed in a cell made of two cylindrical sapphire windows of 10 mm useful diameter separated by a 3.0 mm gold-coated brass spacer. In order to avoid heterogeneous nucleation on the cell walls, the cyclohexane-rich, nonwetting phase was chosen as the minority phase. Special care has been taken in order to reach a precision of $c = (c_c - 0.01) \pm 2 \times 10^{-3}$. During the flight experiment the temperature T_{cx} is verified after thorough homogenization by ultrasounds. We find $T_{cx} = 46.639\,°\mathrm{C}$, corresponding to a shift of 0.5 mK per month since the last ground testing 18 months earlier.

The set of experiments No. 3 was carried out in reduced gravity with pure fluid SF_6. The fluid was enclosed in a stainless steel cell of external rectangular shape with two windows. The internal volume is a cylinder (10.11 mm internal diameter, 2.43 mm thickness), with two natural silica glass windows (10 mm external diameter) epoxied along their cylindrical surface to the stainless steel wall. The cell was filled with an accuracy better than 0.1% with SF_6 (Air Liquide, of purity better than 99.98%) at a density of 764 $\mathrm{Kg\,m^{-3}}$. This density is larger by 3.6% than the critical density as checked by the variation of the meniscus height with temperature. Here also the nonwetting (vapor) minority phase is allowed to nucleate. The transition temperature of SF_6 was also checked after homogenization at $T_{cx} + 1$ K during the flight. The temperature which was found ($T_{cx} = 45.605\,°\mathrm{C}$) is the same as 18 months earlier.

Both cells enclosing the binary mixture and pure fluid (experiments No. 2 and No. 3) are set in high precision thermostats having a temperature stability better than 0.3 mK and a minimum temperature stepping of 1 mK. Temperature quenches are performed at a mean rate of 0.2 mK/s.

The cell is illuminated by a parallel white light beam. A plane (depth of field of order 0.1 mm fluid thickness) is imaged on a charge-coupled device video camera and a photo camera. The whole setup [15] is loaded in a spacecraft [16]. Remote control is used to command the experiment in real time from the ground. A directed acceleration of order $10^{-7}g_0$ originating from the friction with the high atmosphere and from the fact that the samples are not located at the center of mass of the spacecraft is permanently applied to the samples. Moreover, an acceleration (g jitter) which is randomly oriented is also present. It is generally lower than $10^{-4}g_0$, a value which can increase depending on the spacecraft activity. We did not notice any correlation between the residual accelerations and the phase separation process.

Results.—We first report on experiments that were performed on Earth with the density-matched mixture (sets No. 1 and No. 2). At early times, the scattering pattern is a ring shrinking with time which provides the structure factor of the growing domains. The wave vector K_m corresponding to the maximum intensity of the structure factor is related to the average spacing L_m between the droplets by $K_m = 2\pi/L_m$. At late times, we used only the data taken from photo images, of higher resolution than the video images (30 μm). We consider L_m in order to directly compare with the light scattering experiments. The spacing L_m is measured by hand on the picture by averaging over nearest-neighbor pairs of droplets. This procedure is repeated over many pairs located at different places in the cell (parameters needed to analyze the data are listed in Table I). The experimental results are shown in Fig. 2 for different quench depths. For quenches of 10 and 12 mK (respectively $\phi = 0.30 \pm 0.05$ and $\phi = 0.32 \pm 0.05$ according to Table I), the data show a crossover to a faster growth law after a time t_0^*. This crossover occurs for a larger time than the time obtained by Wong and Knobler. However, t_0^* should not be universal since it is geometry dependent.

In the set of experiments No. 2, with the density-matched liquid under reduced gravity, the sample was quenched from 5 mK above T_{cx} to 10 mK below T_{cx} and the phase separation was observed for about 7 h without showing any crossover. A pattern of monodisperse dense droplets was observed [Fig. 3(a)].

In the set of experiments No. 3 (SF_6 under reduced gravity), three quenches were performed from an initial temperature of 4 mK above T_{cx} to 5, 15, and 26 mK below T_{cx}. According to Table I, the volume fractions were, respectively, $\phi = 0.13$, 0.22, and 0.26. Phase separation was studied for about 1 h. Figures 3(b)–3(d) show the corresponding patterns, quite similar to that observed in the binary liquid. No significant wetting effects were observed near the walls. On the other hand, local heating due to the absorption of the laser light by the optical coating of the windows can become important. Such a temperature gradient should in turn create surface tension gradients at the gas-liquid interfaces, leading to Marangoni-induced movements and coalescences of droplets. This effect is visible on Fig. 2(c) where the laser was activated during the course of the phase separation.

The whole set of data obtained either on Earth (for $t < t_0^*$ only) or in reduced gravity can be put on a single master curve whose equation is $K_m^* = K_0 (t^*)^{-p}$. A linear regression fit gives $K_0 = 0.85 \pm 0.115$ and $p = 0.32 \pm 0.01$ (2 standard deviations). The data at small ϕ as obtained by Wong and Knobler [10] are in agreement with this fit.

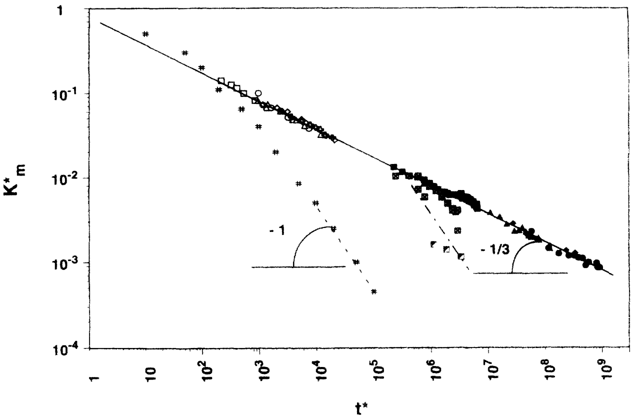

FIG. 2. Growth law at large volume fraction expressed in scaled units (see text). Open symbols are for a 10^{-2} off-critical CC*-Me mixture on Earth obtained by laser scattering after 2 mK (□), 4 mK (○), 5 mK (△), 8 mK (◇), and 10 mK (✥) quenches and by direct observation after 10 mk (⊠) and 12 mK (◩) quenchs. Full symbols are experiments under reduced gravity: with 10^{-2} off-critical CC*-Me mixture after a 10 mK quench (■); with 3.6% off-critical SF_6 after 5 mK (▲), 15 mK (◆), and 26 mK (●) quenches. For the sake of comparison, the critical data (#) corresponding to $\phi = 0.5$ are also plotted.

These results clearly show that pure fluids and liquid mixtures behave the same when gravity effects are suppressed. A striking result is the absence of crossover between fast and slow growth for large volume fractions ($\phi \approx 0.3$). This is in agreement with the data obtained in liquid mixtures under a weak concentration gradient [11], the change of growth occurring here for a volume fraction much larger than the 3D random percolation limit ($\phi \approx 0.15$) [9]. However, the comparison with percolation is, in our opinion, doubtful because it seems difficult to apply a criterion of static and random percolation to rather ordered structures which result from a dynamical process of coalescence.

The existence of a power law with exponent $\frac{1}{3}$ that lasts over 7 decades in t^* is striking. An extrapolation of these data to $t^* = 1$ gives $K_m^* \cong 0.85$ which is in reasonable agreement with the linear regime as proposed by Cahn [17] where the most unstable wave vector is $K_m^* \approx 0.7$.

For later times, two main models lead to a $\frac{1}{3}$ growth law. One is the asymptotic regime as described by Lifshitz and Slyozov [13] for very small ϕ and very low supersaturation. The first assumption is obviously

TABLE I. Useful parameters (see text). The definition of the coexistence curve amplitude is different for binary liquids where (a) $B = (c - c_c) t^{-\beta}$ and for pure fluids where (b) $B = (\rho/\rho_c^{-1}) t^{-\beta}$. (c) Reference [20]. (d) Reference [4]. The quantity $\Delta T = T_c - T_{cx}$ is calculated from the amplitude of the coexistence curve.

System	η (10^4 Pa s)	ξ_0^- (nm)	c_c	ρ_c (Kg m^{-3})	B^a	B^b	c	ρ (Kg m^{-3})	ΔT (mK)
SF_6^c	0.4	0.09		737		1.6		764	3
CC*-Me^d	7.5	0.165	0.71		0.752		0.70		0.5

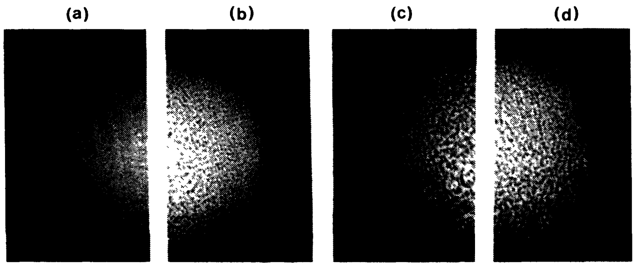

FIG. 3. Images of phase separation patterns in (a) a 10^{-2} off-critical CC*-Me mixture, 6 h 50 min after a quench of 10 mK below T_{cx} and (b)–(d) a 3.6% off-critical SF_6 fluid: (b) 1 h 33 min after a quench of 5 mK, (c) 1 h 24 min after a quench of 15 mK, and (d) 1 h 33 min after a quench of 26 mK. In (c) a laser beam was in the center of the sample. Note that the $\frac{1}{3}$ growth law has the surprising consequence of not showing any quench depth dependence in the droplet radius versus time for a given system [see images (b)–(d)].

not valid in our case and the second assumption is not verified either because the growing phases are at local equilibrium. This point can be checked by comparing the growth laws after (i) a thermal quench as above and (ii) a mixing induced by a shear flow. In the latter case, the initial stage of growth is made of droplets at the equilibrium concentration. After suppression of mixing, the phase separation in (ii) is found to be quite identical to that produced by a thermal quench as in (i) [18]. Finally, a key feature of the Lifshitz-Slyozov model is the disappearance of the smaller droplets on behalf of the bigger ones. This naturally causes a broad distribution in the sizes of droplets which is not observed here.

Another model which leads to a $\frac{1}{3}$ growth law exponent has been proposed by Binder and Stauffer [19] for a pattern of dense droplets. It is based on Brownian diffusion and the binary coalescence of the droplets. Since the diffusion constant is inversely proportional to the radius of the droplets, it is time dependent and allows the self-similarity of the pattern to be preserved. An approximate relation between L_m and the average droplet radius $\langle R \rangle$ can be written as $L_m \approx \langle R \rangle (4\pi/3\phi)^{1/3}$ and gives $K_m^* \approx 1.7t^{*1/3}$. Note that ϕ does not enter into this expression. The prefactor is larger by a factor of 2 than our experimental result.

It is difficult to admit that Brownian motion can be efficient for droplets whose radius is as large as 0.3 mm. However, one must note that the droplets are tightly packed. In order to coalesce, they have to move only over the scale of their interface thickness (a few correlation lengths). The characteristic time of this process is compatible with the time scale of the observed phase separation (some hours). If this mechanism were correct, one would get a striking demonstration of the influence of Brownian motion at the macroscopic scale.

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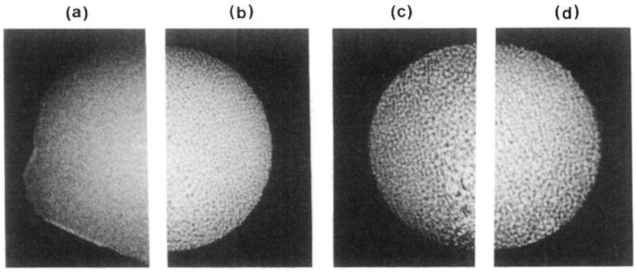

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