Spinodal decomposition between closely spaced plates

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We have studied the dynamics of phase separation in a binary liquid mixture contained between a pair of closely spaced quartz plates. The system behaves very differently from a bulk mixture undergoing spinodal decomposition. For example, the domains do not increase in size as a power of time, and in fact coarsening happens much faster than within a bulk mixture. This is because the process is dominated by the wetting of the plates by one of the two phases. One of the emerging phases, the one that wets the plates, forms an initially thick wetting layer on each quartz plate. Both layers are connected with a few isolated channels. As the time progresses, these layers thin, causing the channel radii to increase. We studied the growth of the channels in detail and found that there was a smallest radius r_{min}, such that channels with radius $r < r_{min}$ dissolved, while those with $r > r_{min}$ grew.

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When spinodal decomposition takes place in a metallic alloy, the domains, of characteristic size ℓ, grow as $\ell \sim t^a$, with $a = 1/3$ [1]. In fluid mixtures, on the other hand, domain growth is strongly influenced by flow, which arises as the domains seek to minimize the curvature of the interfaces. As a result, $a \simeq 1$ in the late stage of phase separation [1,2]. This flow adds considerably to the complexity of the problem, since one must now deal with two coupled equations: the diffusion equation and the Navier-Stokes (NS) equation.

In this experimental study we are interested in phase separation when the fluid mixture, of critical composition, is contained between two closely spaced plates and at a time when the domains are large in aerial size compared to the plate spacing. When this condition is satisfied, the dynamics of the process becomes simplified in certain respects. The NS equation can now be approximated by a modified form of Darcy's law [3]. In the Darcy flow limit, one expects from dimensional arguments that domains of fluid mixtures and binary alloys alike will grow as $\ell \sim t^{1/3}$ at very long times t after the quench. This prediction is indeed supported by an extensive computer simulation of the process [4]. The calculation referred to here ignores the role of wetting on domain growth, an effect which experimentally turns out to be exceedingly large in the systems we have studied. We find, in fact, that wetting completely dominates the morphology of the growing domains in the late stage of phase separation.

The system we have studied is a mixture of 2,6-lutidine and water (LW) of critical composition, contained between two circular quartz plates of radius $R_0 \simeq 7.5$ mm having a plate separation $2d$ of 50 and 100 μm. The mixture has an inverted coexistence curve, so that quenching it into the two-phase region requires an increase in temperature. In these experiments, the system was held for a long time at a temperature $T = T_i$, which was a few millikelvins below the critical temperature T_c and then "quenched" to a temperature of the order of 10 mK above

T_c. The value of T_c is 33.37 °C, and the critical concentration of the mixture is $c_c = 28.1$ wt. % lutidine [5]. The time for the system to reach its final temperature was $\simeq 25$ sec, so we were barred from studying the early stage of phase separation. This relatively long equilibration time was no limitation, however, because it took an even longer time than this for the domain size to become larger than the plate spacing. Phase separation was monitored for many hours following the quench, using a charge-coupled-device camera mounted on a microscope.

Before discussing the results in detail, we preview them in Fig. 1. Shown here is a set of microphotographs taken at times $t = 22, 39, 73,$ and 953 sec after the quench. The plate spacing of this cell here was 100 μm, and the quench depth $\delta T = T - T_c$ was 15 mK. We will discuss the microphotographs in detail below, but summarize our principal findings at the outset. The domains seen in Figs. 1(b)–1(d) are not droplets, as they appear. Rather, they are channels of water-rich phase connecting water-rich wetting layers that cover the plates. One mechanism for domain growth is the draining of the wetting phase into these channels. Throughout the process, the fractional volume of each phase is fixed at 1/2, since the system is of critical composition.

A notable feature of all of the measurements was the existence of a minimum size r_{min} of the channels. All channels which were smaller than r_{min} shrink until they disappear, while larger ones grow. This leads to a nonmonotonic change in the lateral area of the channels with time. The area fraction that the channels occupy, F_a, first decreases and then grows, reaching a minimum at a time we call t_{min}. Figure 1(c) is a photograph made at $t \simeq t_{min}$, 73 sec after the quench. We will argue below that this nonmonotonic behavior is a result of the surface energy of the system seeking a minimum.

The shape of the sample cell is shown as viewed from the top in Fig. 2(a) and from the side in Fig. 2(b). Except for the stem, seen on the right in Fig. 2(a), the quartz cell has circular symmetry when viewed from above. The LW
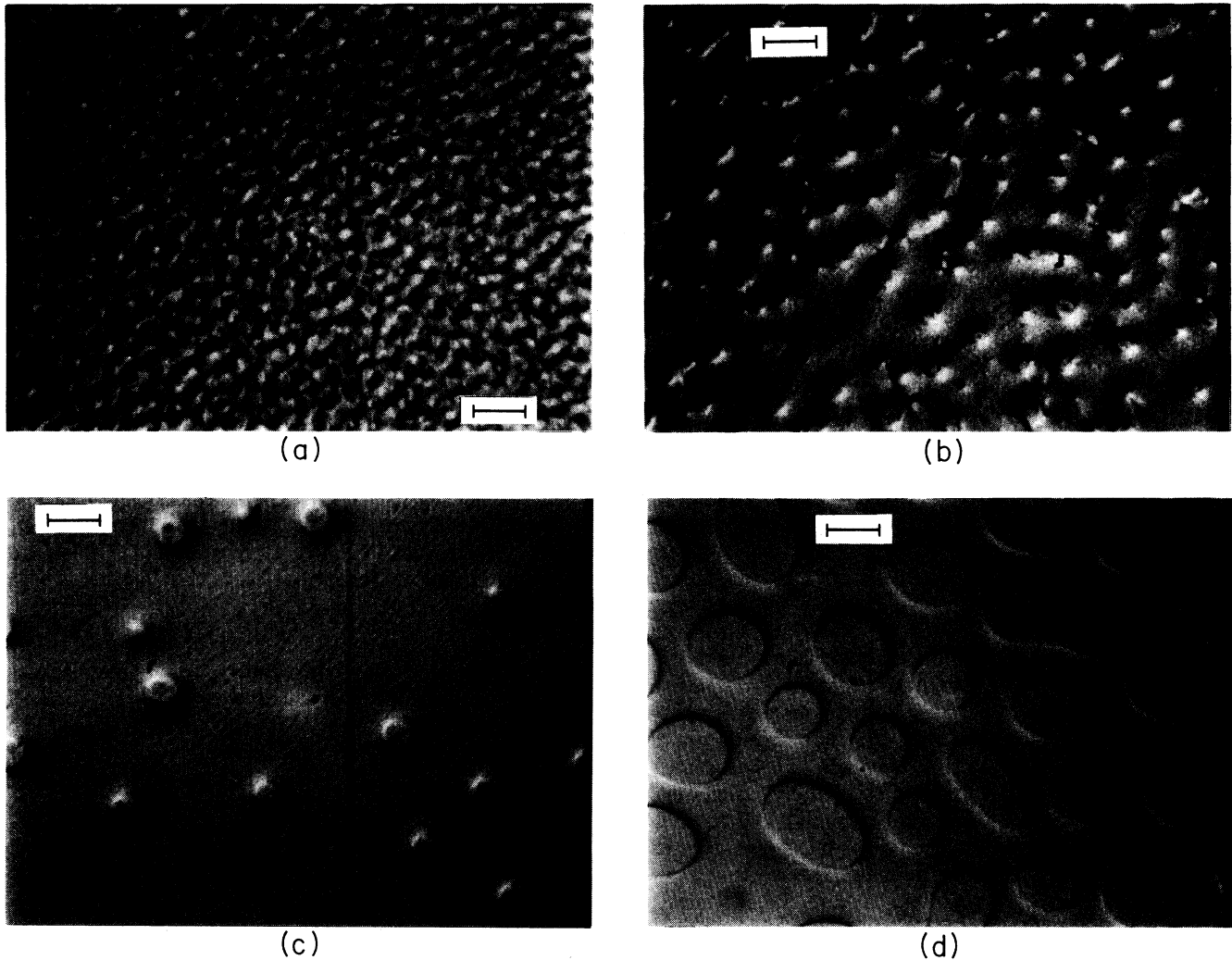
FIG. 1. Microphotographs of growing domains in a critical mixture of 2,6-lutidine + water contained between two quartz plates separated by $2d = 100$ μm. The measurements were recorded at (a) $t = 22$ sec, (b) 39 sec, (c) 73 sec, and (d) 953 sec after the quench. The quench depth $\Delta T = 15$ mK. The length of the solid bar is 100 micrometer in (a), (b), and (c), and is 200 μm in (d).

mixture fills the cell to the level indicated by the line LL. The cell was thoroughly cleaned and baked before it was filled, and the fluid in the cell was flooded with nitrogen before the cell was sealed. The filling was done at room temperature, where the mixture was in one phase.

Though the volume of the LW mixture between the plates is small, there was no difficulty in making a sample quite close to the critical composition. The reason is that the volume of fluid in the stem and in the annular region of the cell was conveniently large, so that one could easily measure out a precise amount of each component.

The cell was mounted horizontally in a stirred water bath with the circular plates facing upward. With this mounting, the fluid between the plates was isolated from the rest of the mixture in the stem and annular regions. Liquid-vapor surface tension kept the fluid from draining out of the plates and into the reservoir below. This ensured that the global composition of the mixture remained at its critical value through the entire phase sep-

aration process. This horizontal mounting also avoided the effect of gravity-induced coalescence of the channels on channels, an effect that was measurable when the cell was mounted so that plates of the cell were vertical.

The water bath was temperature controlled and had a short-term stability of ± 0.3 mK and a drift of approximately 1 mK/day. A video camera mounted on a microscope viewed the phase-separating fluid from above. The camera output went either into a VCR or directly into the computer. The sample was quenched by pouring a measured amount of hot water into the bath and then readjusting the temperature controller setting so that the system would quickly equilibrate at the new temperature setting.

We now consider the photographs in Fig. 1 in more detail. Shortly after the quench, i.e., $t < 1$ min [Fig. 1(a)], the typical size of a domain is much less than the spacing of the plates. This wormlike structure is typical of that seen in spinodal decomposition of fluids and metal-
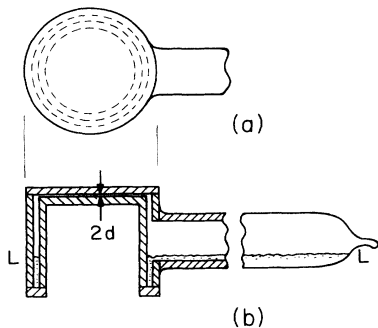
FIG. 2. Top and side views of the sample cell. The cell diameter was 1.8 cm.

lic alloys [1, 2]. Note that the two phases appear to be of roughly equal volume in this figure. However, in less than 1 min after the quench [Fig. 1(b)], the topology of the separating phases has changed entirely. It appears that the fractional area occupied by one of the phases has drastically decreased. As was already noted, this interpretation cannot be correct. Because the mixture is of critical composition and because the quench is very shallow ($\Delta T/T_c = 5 \times 10^{-5}$), the fractional volume of each phase is fixed at 1/2. One is therefore forced to the conclusion that a thick wetting layer of one of the phases (the water-rich phase, it turns out) has formed on the quartz plates shortly after the quench. The dropletlike structures in Figs. 1(b)–1(d) must actually be channels of the wetting phase. The total volume of these channels plus that of the wetting layers is fixed at half of the total fluid volume. As time goes on, the wetting layers on the two plates grow thinner, causing the channels of water-rich phase to increase in size. In the late stage of the process, the volume fraction of the channels returns to approximately 1/2, as may be seen in Fig. 1(d). All of our measurements in both sample cells show this same feature, namely the formation of a wetting layer, which thins as phase separation proceeds [6].

It was stated above that the wetting phase is the denser water-rich phase (the density of pure 2,6-lutidine is 0.92 g/cm^3). This was easily established by tilting the sample cell and noting that the circular regions drifted downward. This observation was confirmed by making a sample containing a 0.1% concentration of the dye, Sudan Red B, which accumulates in the lutidine-rich phase. Thus the channels were clear to the eye and the region between them was pink. Capillary rise experiments in well-cleaned glass and quartz capillaries also show that it is the water-rich phase of LW that wets these materials [7].

We have no direct evidence as to the relative thickness of the top and bottom wetting layers, though it is likely that they are equal in width. Though gravity could remove this symmetry, its effects should be small because this force is small compared to that of surface tension σ. A measure of the relative strength of gravity and surface tension is the ratio of the capillary length α to the plate spacing d, where $\alpha = \sqrt{\sigma/\Delta\rho g}$. Here g is the gravitational constant, $\Delta\rho$ is the difference in

density of the two phases, and σ is the surface tension. For LW, $\delta\rho = (0.08 \text{ g/cm}^3)(\Delta T/T_c)^\beta$, where $\beta = 0.328$ [2], and $\sigma = 0.1 k_B T_c/\xi^2$ [9]. The correlation length $\xi = \xi_{0-}(\Delta T/T_c)^{-\nu}$, where $\nu = 0.63$ [2]. The amplitude ξ_{0-} was measured to be 0.15 nm in LW [10]. Using these parameters, we estimate that $\alpha = 50$ μm at a quench depth $\Delta T = 10$ mK. At larger quench depths than this, α will exceed d, and gravitational effects will presumably become unimportant.

A simple argument, based on energy considerations, provides an explanation as to why there exists a minimum size of the channels. Assume first that there is only a single channel connecting the wetting layers on the upper and lower plates, as illustrated in Fig. 3(a). The symbol W labels the composition of the water-rich phase in the wetting layer and in the channel. In contact with these channels is the lutidine-rich phase, labeled L. The channels are assumed to be cylindrical, with radius r and vertical thickness $2h$. Here the thickness of each of the wetting layers is $d - h$. Thus the plate spacing is $2d$ and their radius is R_0, as already noted. The surface energy including the contribution of the channel is

$$E_s(r) = 2\pi\sigma[R_0^2 - r^2 + 2hr]. \tag{1}$$

There is also a volume contribution to the energy associated with the presence of the wetting layer. Since it varies as an inverse power of its thickness [11], and since these nonequilibrium wetting layers are macroscopically thick when $t \simeq t_{\min}$, we neglect this contribution to E_s.

Conservation of matter imposes a constraint on the parameters d, r, and R_0, namely

$$h = d\phi/(1 - r^2/R_0^2), \quad h < d \tag{2}$$

where ϕ is the volume fraction of the nonwetting lutidine phase. Equations (1) and (2) imply the existence of a critical channel radius $r = r^*$, at which $E_s(r)$ goes through a maximum. According to this model, when $r < r^*$, the channels will shrink and disappear, and when $r > r^*$, the channel is stable and will grow. Figure 3(b) shows the channel having grown at $t > t_{\min}, r > r_{\min}$. The corresponding thinning of the wetting layers is also indicated. If there are N channels (noninteracting) present instead of one, the second factor in the denominator of Eq. (2) is multiplied by $N = N(t)$, and Eq. (1)
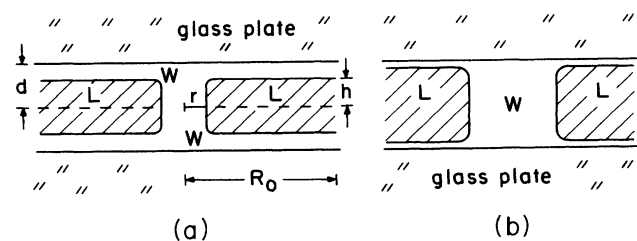

FIG. 3. Schematic view of a single channel connecting the water-rich wetting layers (W). Here L designates the lutidine-rich region, R_0 is the radius of the plates, and r is the radius of the channel. The (a) left and (b) right sketches show the channel growing at the expense of the wetting layer thickness.

gives the energy to create each channel.

Under the condition, $y(r) \equiv N(t)(r/R_0)^2 \ll 1$, which was well satisfied in this experiment [8], the above two equations give $r^* \simeq \phi d$, and the height of the energy barrier $\delta E \simeq (0.1\pi)k_B T(d/\xi)^2$ [12]. Here we have used the expression for σ given above [9]. We identify r^* with the minimum domain size $r_{\min}$. Since the magnitude of δE is very much greater than $k_B T$, there is a sharp borderline between channels which are growing and those which are shrinking. The generation of channels, however, is not thermally activated as in the usual nucleation of droplets in an off-critical system [13]. Rather, the channels are formed out of existing domains in the early stage, when $t < t_{\min}$. We regard this energy barrier issue as an interesting one, which we do not yet completely understand.

It is interesting to note that when $y(r^*) \ll 1$, as in this experiment, the denominator of (2) can be replaced by unity, and r^* will depend only on the volume fraction ϕ (1/2 in our experiments) and on the geometrical factor, d. Therefore r^* is independent of the quench depth ΔT as well as the properties of the fluid mixture, such as its surface tension. Since the above calculation ignores the interaction between channels, it should apply only near $t = t_{\min}$, when very few droplets are present. Using the values $d = 0.05$ mm, $\phi = 1/2$, one finds a critical radius $r^* = 25$ μm, which is consistent with our observations with the 100-μm cell. Repeated measurements of $r_{\min}$ made in the 50-μm cell also were in excellent agreement with the equation $r_{\min} = r^* = d/2$. In accord with the above predictions, we indeed observed that channels smaller than r^* dissolved while the larger ones grew.

Though most of our experiments were carried out in a critical LW mixture, a few measurements were made in this laboratory, using a critical mixture of isobutyric acid and water. The critical composition and critical temperature of this mixture are 38.6 wt. % and 26.08 °C, respectively [14]. The measurements, which were made using a cell of 100-μm plate spacing, also showed the channel radius to cross through a minimum, with r^* again being 25 μm.

Returning to the LW measurements there was one interesting exception to our finding that the water-rich phase was the one which formed a layer on the quartz plates. In that run, one out of six, it was observed that part of the gap area was wetted by the water-rich phase, whereas in another part of the gap, it was the lutidine-rich phase that formed the channels and the fluid layer on the plates.

For $t > t_{\min}$ the channels seen in Fig. 1 can grow either by receiving fluid from the water-rich wetting layers or by merging with each other. The first of these mechanisms will change both the mean aerial size of the channels as well as the area fraction that the channels occupy. We have measured both of these quantities as a function of time and designate them as A_m and F_a, respectively. In the photograph one sees channels that have merged in the recent past.

Figure 4 shows $A_m(t)$ (in mm^2) (open circles) and $F_a(t)$ (closed circles) on a log-log scale. The measurements were made in the 100-μm cell, with $\Delta T = 15$ mK. The error bars on the curve A_m vs t show the standard
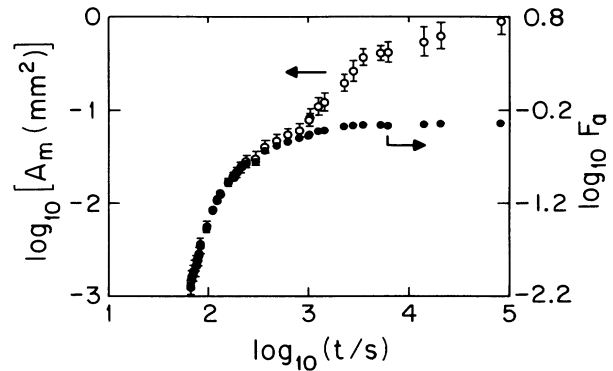

FIG. 4. The mean area of the water-rich channels as a function of time (left) and the volume fraction of mixture in the channels (right). The measurements were made in the cell of plate spacing, $2d = 100$ μm; the quench depth $\Delta T = 15$ mK.

deviation, which is seen to increase with time. Note that for $\log_{10}(t) > 3$, A_m grows approximately as $t^{1/3}$, in accordance with the dimensional arguments and computer simulations already mentioned. The finite size of the cell compared to the domains size blocks us being able to follow domain growth into this regime of very long times.

For the first 300 sec, the two sets of data points follow each other closely, implying that the growth of the channels is dominated by the draining of the wetting layers. In the later stage of coarsening, the wetting layers have become so thin that they contribute negligibly to the aerial growth of the channels, with the result that $F_a(t)$ then saturates at the global concentration value of 1/2. On the other hand, the merging process continues, but at an ever-decreasing rate. For $t > 10^4$ sec, the droplets have grown so large that the driving force for their subsequent growth has become very small. As a result, the channels virtually cease to change their morphology, and the pattern becomes static. Moreover the variance of the mean channel area has become comparable to the value of A_m itself. In this late stage pinning effects, produced by impurities on the plates, may become important.
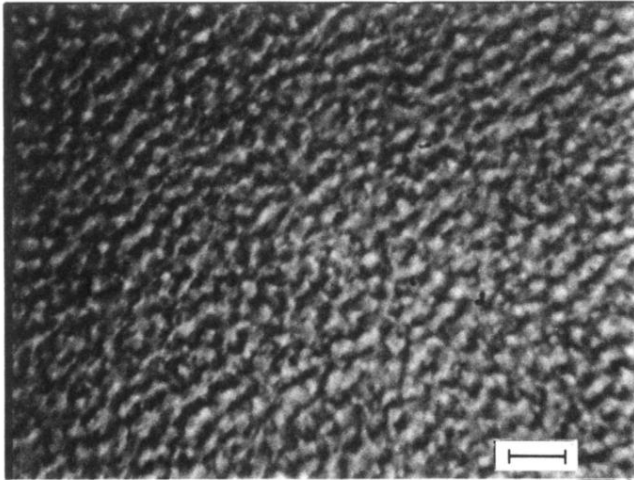
To summarize, we have seen that wetting forces can strongly influence phase separation of a fluid mixture confined between closely spaced plates. In the absence of wetting, the mean size of the domains is expected to grow much more slowly than in the bulk fluid [4]. In the system we have studied, a critical mixture of LW contained between quartz plates separated by 50 and 100 μm, wetting effects dominate. Very soon after the quench the wetting phase forms thick layers on the confining plates, but this layer is not directly seen. What is observed are channels of the same wetting phase that connect the two layers. There exists a minimum channel size $r_{\min}$ so that channels which are smaller than $r_{\min}$ were shrinking, while those with size larger than $r_{\min}$ were growing. The volume fraction occupied by the channels passes through a minimum and then increases with time. Unlike bulk spinodal decomposition, there is no significant interval of times over which the mean radius of these channels grows algebraically with time, at least in the experiments reported here. The complexity of the

phase separation process in this rather simple geometry indicates the importance of including wetting effects in phase separation of fluids in other confined geometries, such as in capillaries or in porous materials where the pores are macroscopic in size [15, 16].
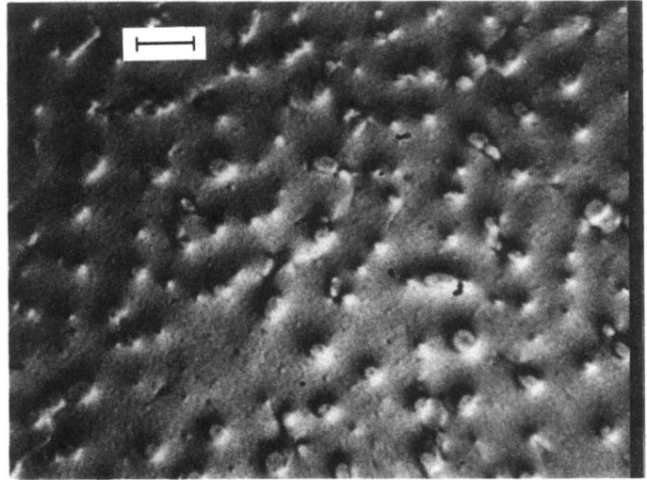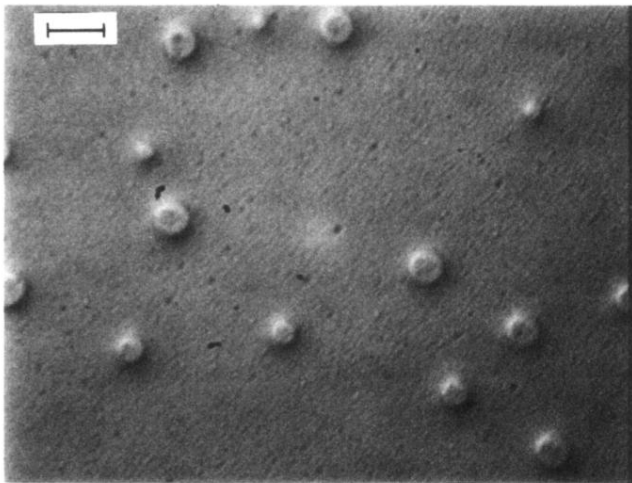
[1] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8; K. Binder, in *Condensed Matter Research Using Neutrons*, edited by S. W. Lovesey and K. Scherm (Plenum, New York, 1985); H. Furukawa, Adv. Phys. **34**, 703 (1985).

[2] W. I. Goldburg, in *Light Scattering Near Phase Transitions*, edited by H. Z. Cummins and A. P. Levanyuk (North-Holland, New York, 1983), p. 531.

[3] G. K. Batchelor, *An Introduction to Fluid Dynamics* (Cambridge University Press, Cambridge, 1967), Chap. 4.

[4] A. Shinozaki and Y. Oono, Phys. Rev. A **45**, R2161 (1992).

[5] E. Gulari, A. F. Collings, R. L. Schmidt, and C. J. Pings, J. Chem. Phys. **56**, 6169 (1972).

[6] In a computer simulation of spinodal decomposition in Hele-Shaw geometry and with wetting effects included, A. Shinozaki also sees the columnar structures we report on here [A. Shinozaki (private communication)].

[7] D. J. Durian, K. Abeysuriya, S. K. Watson, and C. Franck, Phys. Rev. A **42**, 4724 (1990).

[8] In the vicinity of r^*, which is where our interest in Eqs. (1) and (2) is centered, this condition is well satisfied since $(r^*/R_0)^2 \simeq 10^{-5}$ and N is less than 10^4.

[9] M. R. Moldover, Phys. Rev. A **31**, 1022 (1985).

[10] K. Y. Min (unpublished).

[11] A. J. Liu, D. J. Durian, E. Herbolzheimer, and S. A. Safran, Phys. Rev. Lett. **65**, 1897 (1990).

[12] If one assumes that the channels have the shape of the hole of a torus rather than a cylinder, and if one takes the radius of a cross section of the hole as h, one gets a value of r^* that is the same as we obtain within a factor of order unity.

[13] K. Binder, in *Statistical Physics*, edited by H. E. Stanley (North-Holland, New York, 1983).

[14] Y.-C. Chou, Ph.D. thesis, University of Pittsburgh, 1981 (unpublished).

[15] M. C. Goh, W. I. Goldburg, and C. M. Goldburg, Phys. Rev. Lett. **58**, 1008 (1987).

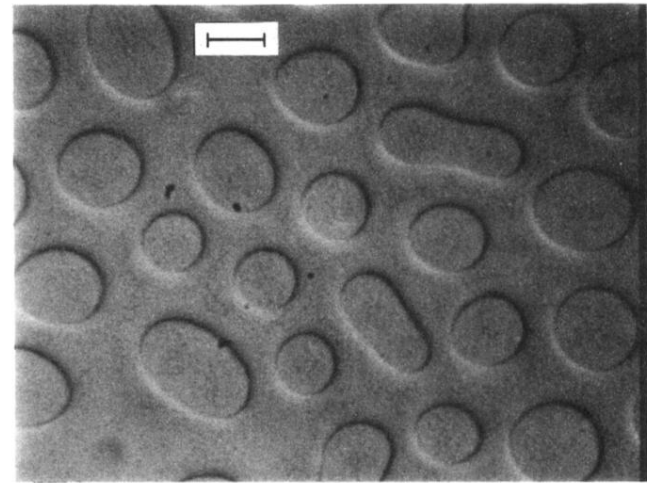[16] S. B. Dierker and P. Wiltzius, Phys. Rev. Lett. **58**, 1865 (1987).

FIG. 1. Microphotographs of growing domains in a critical mixture of 2,6-lutidine + water contained between two quartz plates separated by $2d = 100$ μm. The measurements were recorded at (a) $t = 22$ sec, (b) 39 sec, (c) 73 sec, and (d) 953 sec after the quench. The quench depth $\Delta T = 15$ mK. The length of the solid bar is 100 micrometer in (a), (b), and (c), and is 200 μm in (d).