Evidence for the Influence of Hydrodynamics in a Phase-Separating Fluid

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Light scattering and microscopic observation were used to study phase separation in a critical binary mixture of 2,6-lutidine and water. A crossover in the growth rate of nucleating regions occurred at a characteristic size $l \simeq 10\ \mu$m. We also observed the temporal fluctuations in the system. They give rise to a strongly non-Lorentzian power spectrum.

The early stage of phase separation in critical binary mixtures has been extensively studied in recent years.[1-4] We report here a continuation of these studies into late times. Our measurements in a critical mixture of 2,6-lutidine and water (LW) show an unexpected increase in the growth rate of the nucleating regions. We find that the growth rate of the characteristic length, l, changes from $l \propto t^{1/3}$ to $l \propto t^{a'}$ with $a' = 1.7 \pm 0.4$. The late-time droplet size was measured by direct visual microscopic observation. A second notable finding was that the temporal fluctuations in composition measured by light scattering at small angles give rise to a power spectrum which is strongly non-Lorentzian. In particular, the power sepctrum of the light-intensity fluctuations, $P(f)$, is of the approximate form $\ln P(f) \propto |f|^{\lambda}$ with $\lambda \simeq 1$. This non-Lorentzian behavior suggests that the fluctuation process is not diffusion dominated.[5] We conjecture that both the non-Lorentzian spectrum and the unexpectedly large value of a' are the result of coupling of hydrodynamic flow to the nucleating system. There is already evidence that such effects influence the phase separation process.[6] At still later times an additional instability is noted; a flow field of macroscopic vorticity develops in the mixture.

The sample cells were filled with a solution of near-critical composition c_c. Though cells of various optical path were used (0.1, 1, 5 mm), most of the measurements were made in the 1-mm cell. The setup allowed the simultaneous recording of visual measurements and power spectra. We describe the droplet growth experiments first.

The microscope was of large working distance (15 cm) to permit observations inside the water bath. Over the range of magnification used ($\times 12$–$\times 50$), the corresponding variation in depth of field was 2 mm to 20 μm.

Prior to the quench, the mixture was in the one-phase region at an initial temperature T_i roughly 2 mK below the critical temperature $T_c = 33.7°$C. Note that the LW system has a lower consolute point. As in the early-stage measurements, the coarsening rate showed no dependence on $\Delta T_i \equiv T_c - T_i$ but it rapidly increased with quench depth $\Delta T_f \equiv T_f - T_c$, where T_f is the final equilibrium temperature. The water bath and sample reached T_f in 10 sec or less. Both T_i and T_f were constant to within ± 0.1 mK over 1 h or more.

In the range 1 mK $\lesssim \Delta T_f \lesssim$ 5 mK the microscope showed the development of a granular interconnected structure that could first be resolved approximately 30 sec after the bath quench. The appearance of this structure was similar to that seen in glasses and metallic alloys undergoing spinodal decomposition.[7] In the first stage of phase separation, coarsening proceeded smoothly and without any apparent sedimentation of the nucleating regions. The estimates of grain size $l(t)$ were made by comparing with the diameter of 84-μm wires fastened to the front and back of the sample cells.

In the second stage a macroscopic vortex flow pattern quite suddenly developed in the fluid. This flow stretched the grains into twisted "strings" and prevented further measurements of $l(t)$. The slowest observable flow rates were of the order of 1 μm/sec. The vorticity developed after a time delay t_v which decreased smoothly with increasing ΔT_f. In the range 2 mK $\leq \Delta T_f \leq$ 11 mK, t_v decreased from 800 to 150 sec. (Here as elsewhere the origin of time is taken as the start of the quench.) A deliberate tenfold increase in the vertical temperature gradient in the bath produced little or no decrease in t_v. No such flow field was observed in the 0.1-mm cell, presumably because of pinning of the droplets by the walls. In the 5-mm cell where the composition differed measurably from the critical value, $t_v(\Delta T_f)$ was larger by a factor of 2 or 3 than the numbers quoted above.

In the third stage of phase separation, fluid flow slowed down, the interconnected grains broke up into near-spherical droplets, and a meniscus slowly formed. The remainder of this

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paper is almost exclusively concerned with measurements made in the first stage only, i.e., prior to the onset of macroscopic flow.

Figure 1 is a log-log plot of grain diameter l for four sets of measurements. There are two later-stage measurements (1-mm cell) at quench depths of 2.3 mK (open circles) and 3.3 mK (closed circles). The other two sets are early-time measurements[8] (0.1-mm cell) with similar quench depths of 2.5 mK (crosses) and 3.4 mK (diamonds). The early-time measurements show l increasing with an exponent $a' = 0.38 \pm 0.05$. Theoretical expectations agree with these early-time results.[9] When the grain size reaches $l \simeq 10$ μm, a' is seen to increase. An analysis of seventeen runs[10] in the range 1 mK $\leq \Delta T_f \leq$ 10 mK shows that following the crossover, $l = A(\Delta T_f) t^{1.7 \pm 0.4}$. The amplitude $A(\Delta T_f)$ is an increasing function of quench depth.[11]

We turn now to the temporal fluctuation measurements. The power spectra were derived from a computer-stored record of the fluctuating intensity I_k recorded by a photomultiplier located at a scattering angle θ. The photon momentum transfer k and the scattering angle are related through the equation $k = (4\pi n/\lambda_0) \sin(\theta/2)$, where λ_0 is the vacuum wavelength of the incident laser beam (6328 Å) and n is the refractive index of the scattering medium. For 2,6-lutidine–water we take $n = 1.33$.

In most runs the computer sample the intensity at a rate of 5 points/sec and collected the data for 2048 points. Figure 2 shows $I_k(t)$ for the first 102 sec (i.e., 512 data points) following the quench. The run was made with the 1-mm cell at $\Delta T_f = 2.1$ mK and $k = 8.7 \times 10^3$ cm^{-1}. In such thick samples, multiple scattering is known to affect intensity measurements as will be discussed below. When we look at the intensity fluctuations it is clear that low frequencies dominate. After the first 20 sec the rms intensity $[(I_k(t) - \langle I_k \rangle)^2]^{1/2}$ becomes comparable to $\langle I_k \rangle$ itself. During the remaining 306 sec the mean intensity changes slowly with time. We note that even the rapid fluctuations of smallest amplitude are larger than the instrumental noise; they also exceed the equilibrium-state spontaneous fluctuations.

Figure 3 is a semilog plot of $P(f)$ for the run displayed in Fig. 2. Here $P(f)$ is the discrete Fourier transform of $\langle I_k(t) I_k(t+\tau) \rangle$. The solid line was obtained by averaging the spectra of the first two consecutive 102-sec intervals. The dashed line is the spectrum for the fourth 102-sec interval. Each point on the graph is an average of five adjacent spectral components. Hence their frequency separation is $5/L$, where the record length is $L = 102$ sec. In addition, a window function was applied to the data.[12] Finally we have subtracted from $P(f)$ a nearly constant small background spectrum that was obtained by measuring $I_k(t)$ long after the system had reached two-phase equilibrium at $T_f - T_c = 2.1$ mK. From the figure it is seen that $P(f)$ initially decreases

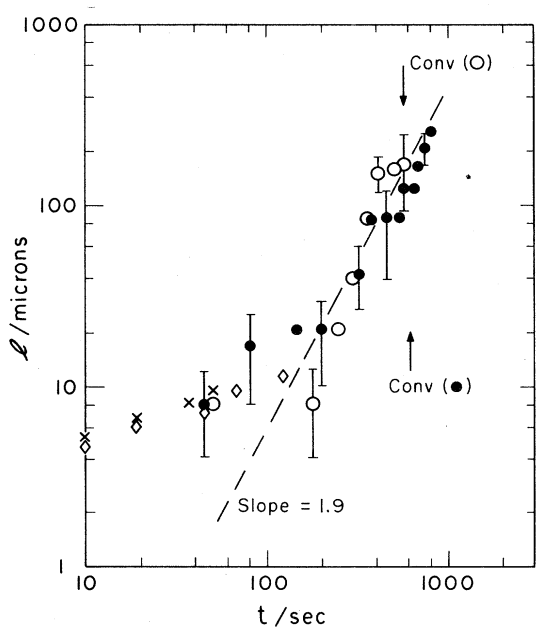

FIG. 1. Nucleate size vs time. The arrows show the time t_v when convection starts. Microscopic measurements: $\Delta T_f = 3.3$ mK (●); $\Delta T_f = 2.3$ mK (○). Early-time measurements: $\Delta T_f = 3.4$ mK (◇); $\Delta T_f = 2.5$ mK (×).

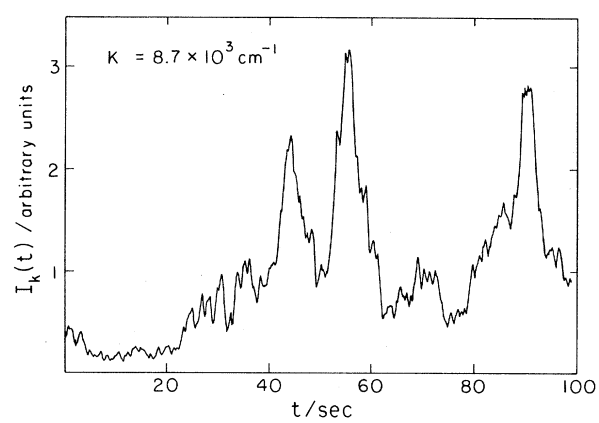

FIG. 2. Scattering light intensity, $I_k(t)$ for $\Delta T_f = 2.1$ mK.

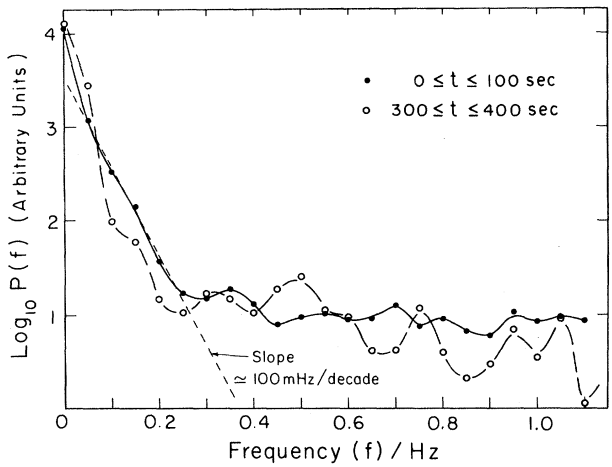

FIG. 3. Power spectrum for run of Fig. 2.

at a near-exponential rate.

It might be argued that the most meaningful parameter for characterizing the intensity fluctuations in this nonstationary process is $\langle I(t_1)I(t_2)\rangle$, where $t=0$ is the moment of quench, and the brackets designate the average of an ensemble of runs. Whereas this may be true in some sense, such an analysis would require a very large number of runs to form a statistically significant ensemble average and would not emphasize the almost stationary character of the observed fluctuation spectrum. In this initial and exploratory study it seemed sufficient to look at a smaller ensemble of runs, obtaining from each one a time (t) average of the Fourier transform of $I_k(t)I_k(t+\tau)$, i.e., $P(f)$. As will be seen below, the power spectra obtained from all such runs were similar.

In drawing conclusions from the power spectrum concerning the behavior of $c_k(t)$, there are interpretational difficulties of which the reader should be aware.

The primary problem is that nucleation is not a stationary random process, since the system obviously remembers the time of quench, $t=0$. Our justification for treating the process as stationary is that the mean lifetime of the fluctuations is short compared to each 100-sec Fourier-analysis interval, and that the calculated spectrum changed little from one time interval to another. Second, interpretation of the spectrum is difficult because the fluctuating intensity $I_k(t)$ may not be a Gaussian random variable. If in fact the origin of these fluctuations is the coherent growth or self-magnification of the sponge-like compositional structure, $I_k(t)$ need not be Gaussian, and there will be no simple relationship between $P(f)$ or $\langle I_k(t)I_k(t+\tau)\rangle$ and the composition Fourier components $c_k(t)$ themselves. On the other hand, if the fluctuations arise from many independent modes of oscillation of the "dilating sponge," then the Gaussian assumption may be approximately valid. In light of the latter possibility, it is interesting to examine the implication that the $c_k(t)$ are both Gaussian and stationary: For a Gaussian random process which is also Markovian, such as diffusion, $P(f)\propto(f^2+f_0^2)^{-1}$, which is contrary to our observations.

We draw attention to several notable features of these data that are shared by all the measurements we have taken.

(1) In the later stage of phase separation, oscillations develop in $P(f)$. These oscillations presumably reflect the appearance of the visually observed vorticity discussed above.

(2) Prior to the above instability, $P(f)$ is almost stationary in time. For example, the observed spectra in the first two 100-sec, intervals in Fig. 2 are virtually identical. The two spectra were averaged in Fig. 3 to improve statistical accuracy.

(3) In all runs $P(f)$ decreases for several decades at a near-exponential rate before leveling off. Assuming a spectrum of the form $P(f)\propto\exp(-|f|/f_0)$, we find that $f_0\lesssim 0.1$ Hz and is almost independent of k in the interval 3×10^3 cm$^{-1}\leq k_s\leq 20\times10^3$ cm^{-1}, where the measurements could conveniently be made. Also f_0 decreases with increasing quench depth. For example, in a series of seven runs in the range $\Delta T_f=2\pm1$ mK, $f_0=30\pm15$ mHz, while an average of four runs at $\Delta T_f=5\pm0.5$ mK gave $f_0=110\pm20$ mHz. The non-Lorentzian nature of $P(f)$ is evidence that the phase-separation process is dominated by a nondiffusive process such as the hydrodynamic coupling discussed above. In the absence of a theory to explain these power spectrum measurements we can only draw attention to an inverse time which is comparable to the characteristic decay rate of $P(f)$. A growing spherical droplet will produce an oscillatory variation[13] in I_k which is proportional to $[\sin kl(t)/kl(t)]^2$. On inserting the experimentally observed $l(t)$ into this expression, one obtains a dominant frequency of the order of 10^{-2} Hz at $k\simeq10^3$ cm^{-1}. In order of magnitude this is comparable to the frequencies f_0 which we observe. (If this Gaussian droplet or "dilating-sponge" picture is correct, the Gaussian approximation would be hard to

justify.) Note that this model implies that $I_k(t)$ is strongly dependent on k, contrary to our observations. This k dependence could be obscured by multiple scattering, which unfortunately was large (see Ref. 1).

(4) Varying the diameter of the incident laser beam did not change the form of $P(f)$, implying that the spectrum is not generated by fluctuations in the number of nucleating grains lying in the scattering volume V. This volume was usually much larger than the grain size.

In summary, these experiments reveal that in this system (a) the exponent a', which characterizes the droplet growth rate, increases by a factor of 5 or more at $l \simeq 10\ \mu$m, and (b) the power spectrum $P(f)$ is non-Lorentzian. Both observations suggest that hydrodynamic effects influence phase separation near the critical point in the LW system.

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[8]The parameter l was determined from the early-state scattering measurements using $l = 2\pi/k_m$, where k_m is proportional to the angle where the differential cross section has a maximum (see Ref. 1).

[9]See Ref. 1 for extensive references to the theoretical literature. Of special relevance are the following: K. Binder, Phys. Rev. B 15, 4425 (1977); J. S. Langer, M. Bar-on, and Harold D. Miller, Phys. Rev. A 11, 1417 (1975); J. Marro, A. B. Bortz, M. H. Kalos, and J. L. Lebowitz, Phys. Rev. B 12, 2000 (1975).

[10]Two previously reported measurements with a 5-mm cell (Ref. 2) yielded exponents which were consistent with $a' = \frac{1}{3}$. However, a more extensive series of measurements with this same slightly off-critical sample now show a crossover from slow coarsening (consistent with $a' = \frac{1}{3}$) to a more rapid growth rate corresponding to $a' = 2$. We have no explanation for the apparently anomalous absence of crossover in the 6-mK quench of Fig. 9 in this reference.

[11]It is possible that our measured a' may be larger than the true value by virtue of the microscope's finite depth of field, DF. Shortly after the quench when $l(t) = \mathrm{DF}$, this overlap could cause an apparent reduction in droplet size. We believe this effect to be small because the measured $l(t)$ was insensitive to the choice of magnification and hence to DF.

[12]R. K. Otnes and L. Enochson, *Digital Time Series Analysis* (Wiley-Interscience, New York, 1972). The calculated spectrum was insensitive to the choice of window function; both the Hanning and GEO windows were used.

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