Study of Phase Separation in a Critical Binary Liquid Mixture: Spinodal Decomposition*

John S. Huang, Walter I. Goldburg, and Allan W. Bjerkaas†
Department of Physics, University of Pittsburgh, Pittsburgh, Pennsylvania 15260
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Light scattering has been used to study phase separation near the critical point in a binary mixture of methanol and cyclohexane. The intensity measurements are in conformity with the spinodal decomposition theory of Cahn. Measurements were also made of the spectral width of the scattered light in the phase separation process.

We report here a light-scattering study of the dynamic behavior of a binary liquid mixture undergoing phase separation near the critical point. The parameters measured were the light intensity and the inverse lifetime of the concentration fluctuations. Our intensity measurements in the early stages of the phase separation process are in striking conformity with the linearized spinodal decomposition theory of Cahn.[1-4] To our knowledge, this is the first observation of spinodal decomposition (SD) in a fluid and also the first measurement of temporal fluctuations in the spinodal region. We have found that by working very near the critical point in a binary mixture, it is possible to achieve a sufficiently small value of the concentration diffusivity so that the SD process takes place over a time of the order of minutes. In the past, spinodal decomposition has been studied in glasses and metallic alloys.[3,4]

Our experiments were carried out in a critical mixture of methanol and cyclohexane sealed in a cylindrical glass tube. The beam of a 15-mW He-Ne laser was passed through the center of the sample, which was positioned in a water bath of temperature stability over a 15-min period better than 0.4 mK. In a typical run, the bath temperature was stabilized at a temperature $T \simeq T_c + 1$ mK and then quickly dropped to about 2 mK below its critical value $T_c = 45.14$°C. Photomultipliers placed on both sides of the transmitted beam at small scattering angles θ ($0.02 \lesssim \theta \lesssim 0.07$ rad) registered the scattered light intensity following this temperature drop. Alternatively the scattered light intensity was registered on photographic film. A typical measurement of the latter type is shown in Fig. 1. The dominant feature of this photograph is the presence of a ring of granular appearance. The dark spot at the center of the ring ($\theta = 0$) is produced by the unscattered laser beam. The radius of the ring corresponds to a scattering angle of $\theta = 0.05$ rad or photon momentum transfer $k \equiv 2k_0 \sin\theta/2 \simeq 7 \times 10^3$ cm^{-1}, where k_0 is the wave number of the laser beam in the mixture. This ring, which is the hallmark of spinodal decomposition, develops in roughly 1 min after the temperature drop and persists at its initial diameter for a time of the order of minutes before collapsing in diameter and finally disappearing at $\theta = 0$. Its persistence time decreases with increasing depth of quench. All of the above qualitative observations are in accord with the predictions of SD theory.[5] The lifetime τ_c of the granular intensity fluctuations of Fig. 1 was of the order of several seconds within the ring and a fraction of a second at both larger and smaller values of scattering angle.

In what follows we will be concerned with both the light intensity $I_k(t)$ at momentum transfer k, and its average over azimuthal angle (and hence over the size of the grains). This angular average, which we denote as $\langle I_k(t)\rangle$, may alternative-

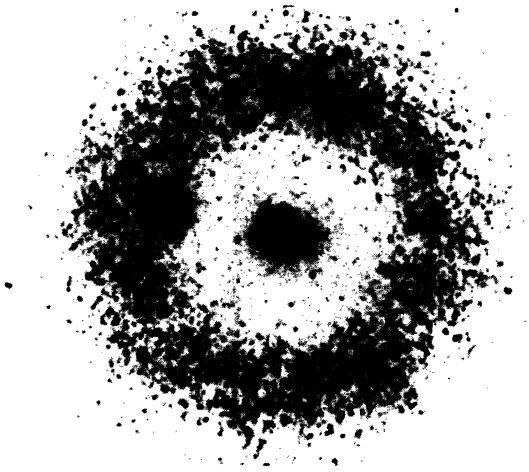

FIG. 1. Far-field scattering pattern from a binary liquid undergoing phase separation, presumably by spinodal decomposition. The diameter of the granular ring subtends an angle of approximately 0.1 rad. The central spot is the unscattered laser beam. The wavelength used was 6328 Å.

ly be viewed as a time average over intervals long compared to τ_c but short compared to the growth time of the ring. In the Born approximation $I_k(t) \propto |\delta c_k(t)|^2$, where δc_k is the kth component of concentration fluctuation in the system.

Cahn's theory in its linear form predicts that

$$\langle I_k(t)\rangle \propto \exp[2R(k)t], \quad (1)$$

where

$$R(k) = -Mk^2[(\partial^2 f/\partial c^2)_{P,T} + 2Kk^2]. \quad (2)$$

Here f is the free energy density in erg/cm^3, M is the mobility in erg^{-1} cm^{-1} sec^{-1}, and the number concentration c is in units of reciprocal volume. The parameter K is a measure of the surface energy of the system. In the Ginsburg-Landau theory it is expected to depend only weakly on temperature (the thermodynamic assumptions which enter Cahn's theory are identical to those of the Ginsburg-Landau theory). The concentration diffusivity of the mixture is $D = M(\partial^2 f/\partial c^2)_{P,T}$. In cyclohexane-methanol[6] along the line of critical composition in the one-phase region, $D = D_0\epsilon^{\nu}$, where $\epsilon \equiv (T_c - T)/T_c$, $\nu = 0.60 \pm 0.01$, and $D_0 = (1.91 \pm 0.2)\times 10^{-7}$ cm^2/sec. We will assume that the above relations hold within the spinodal region.

Equations (1) and (2) predict a maximum in $\langle I_k(t)\rangle$ at a value of k given by $k_m^2 = -(4K)^{-1}(\partial^2 f/\partial c^2)_{P,T}$. This parameter is related to the radius r_m of the ring in Fig. 1 by $k_m \simeq 4\pi/\lambda \sin(r_m/2L)$, where L is the distance from the sample to the photodetectors or the photographic plate. To estimate k_m we assume that f is of a modified Ginsburg-Landau form with $(\partial^2 f/\partial c^2)_{P,T} c_c^2/f_c = \epsilon^{\gamma}$, where c_c and f_c are the composition and free energy at the critical point, respectively. Using the value of K measured by Huang and Webb,[7] one has $Kc_c/f_c = 2$ Å (this parameter is expected to be of the order of an atomic length[3]) and $k_m = (3\text{ Å})^{-1}\epsilon^{\gamma/2}$, with the critical exponent γ expected to be approximately 1.3.[6,8,9] At $\Delta T = T - T_c = -2$ mK this corresponds to $k_m^{-1} \simeq 1.0$ μm. In these experiments, the reciprocal k value at $r = r_m$ was typically 1 to 1.3 μm, as predicted by the above theory.

Equations (1) and (2) predict that

$$\ln[\langle I_k(t)\rangle/\langle I_k(0)\rangle] = 2R(k)t = 2\{-Mk^2[(\partial^2 f/\partial c^2)_{P,T} + 2Kk^2]\}t,$$

where both M and $(\partial^2 f/\partial c^2)_{P,T}$ are functions of ΔT. Thus a plot of $\ln\langle I_k(t)\rangle$ versus t at fixed k should yield a straight line of slope $R(k)$. It was indeed found that in a time interval of about 1 min following the quench to $\Delta T \simeq -2$ mK, the scattered intensity (averaged over the fluctuation time τ_c) grew at an exponential rate. As already noted, the ring subsequently shrinks in diameter[5] and finally disappears, though a large amount of small-angle scattering remains. Extensive measurements were made of both the intensity and fluctuation time in this latter stage of phase separation; however, this work will not be discussed here.

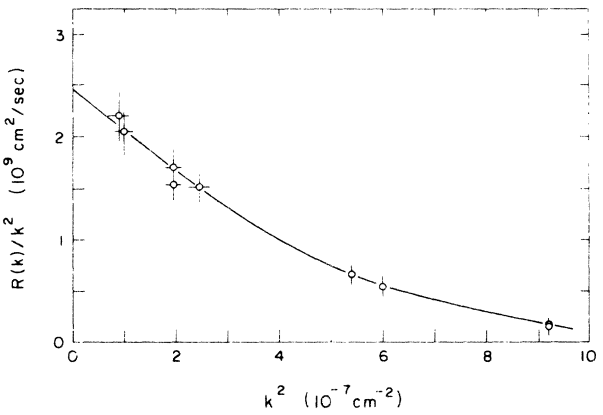

FIG. 2. The parameter $R(k)/k^2$ versus k^2 in the early stage of spinodal decomposition. Here $R(k)$ is the growth rate of the scattered light intensity at photon momentum transfer k. The value of $R(k)/k^2$ extrapolated to $k = 0$ yields the negative diffusion constant D.

According to Eq. (2), a plot of $R(k)/k^2$ versus k^2 should yield a straight line of negative slope and intercept $-M(\partial^2 f/\partial c^2)_{P,T} = -D$ at $k = 0$. We note that inside the spinodal, D is negative, since at points interior to the spinodal line, $(\partial^2 f/\partial c^2)_{P,T} < 0$, while M is always greater than zero.[3]

In Fig. 2, we have plotted $R(k)/k^2$ as a function of k^2 for scattering angles spanning the interval $10^{-2} < \theta < 10^{-1}$ rad. Equation (2) predicts a linear dependence of R/k^2 on k^2 whereas we observe a measurable bending of the line drawn by eye through the data points in this figure. Only an experiment carried out with better temperature control could determine whether this nonlinear behavior results from failure of Eq. (2) at large k. However, a similar bending has been observed in an x-ray study of SD in glass systems.[10,11]

It is interesting to compare the value of $|D|$ obtained from Fig. 2 [$|D| = \lim_{k\to 0} R(k)/k^2$] with the above-quoted value of D obtained from spectral-width measurements in the one-phase region at $\Delta T = 2$ mK. This latter value of D is 4.5×10^{-9} cm^2/sec, whereas the intensity measurements of

Fig. 2 yield $-D \simeq 2.5\times10^{-9}$ cm^2/sec. This agreement suggests that the relations $D = D_0|\epsilon|^{-\nu}$ and $|(\partial^2 f/\partial c^2)_{P,T}| \propto |\epsilon|^{-\gamma}$ have at least approximate validity inside the spinodal as well as on the coexistence curve.

A limit to the range of ΔT values (and hence ring diameters) which could be reached in these experiments was determined by the limiting rate (dT_b/dt) at which the bath temperature could be dropped and by the characteristic time (τ_s) for the sample subsequently to reach thermal equilibrium. The approximate values of these parameters were $dT_b/dt \lesssim \frac{1}{4}$ mK/sec and $\tau_s \lesssim 1$ min. It was impossible to produce SD at large values of ΔT because $R(k_m) \propto D \propto \Delta T^{\nu}$, so the process would occur at a rapid rate before the equilibrium bath temperature was reached. It is possible to estimate an upper limit on the accessible range of ΔT from a plot containing the two functions R^{-1} versus ΔT and the cooling rate of the sample. The result is that SD should be (and was) observed at $\Delta T \simeq -2$ mK. Before the temperature of the sample has fallen below this value of ΔT, the system has already passed through the early stages of SD. The absolute minimum attainable value of ΔT was established by the bath temperature stability.

We close with a few qualitative observations concerning the spectral width measurements. The photon correlation spectrometer used in this work provides a measurement of[12]

$$\langle I_k(t) I_k(t+\tau)\rangle \equiv G(\tau).$$

Since the random process being studied was not a stationary one, $G(\tau)$ also is a slowly varying function of time. At each $t \lesssim R^{-1}$, $G(\tau)$ was approximately exponential, though its form at somewhat larger t was markedly nonexponential. In the early state of SD, the characteristic decay time for $G(\tau)$ was of the order of the lifetime of critical fluctuations in the one-phase region at the same $|\Delta T|$. This latter lifetime is the inverse of $\Gamma(\Delta T) = Dk^2$. It was further found that $G(\tau)$ at $k \simeq k_m$, i.e., within the brightest region of the ring, had a damped oscillatory character.

Finally, it was observed that in the latter stages of phase separation, the correlation time of the intensity fluctuations grows to values which were an order of magnitude larger than the spontaneous concentration fluctuation lifetime at the equilibrium temperature of the system.

To summarize, we have studied phase separation in a critical binary liquid mixture and obtained results which are in accord with the linear form of spinodal decomposition theory. Also measured was the lifetime of fluctuations in the system. Cahn's theory makes no predictions concerning these fluctuations in the spinodal region.

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†Now at the Applied Physics Laboratory, Johns Hopkins University, Silver Spring, Md. 20910.

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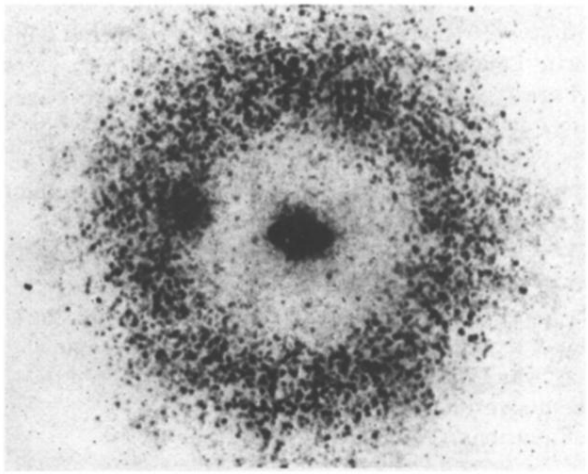

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