# Phase separation and coalescence in critically quenched isobutyric-acid-water and 2,6-lutidine-water mixtures

Y. C. Chou and Walter I. Goldburg

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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Light scattering was used to study phase separation in critically quenched mixtures of isobutyricacid-water and 2,6-lutidine-water. The measurements spanned the time interval  $10 \le t \le 10^3$  s and quench depths from 0.7 to 9 mK. The parameters measured were  $k_m(t)$ , i.e., the photon momentum transfer at the angle of maximum scattering, and the ring intensity  $I(k_m,t)$ . The early-stage measurements of  $k_m$  vs t are in very good agreement with the calculations of Kawasaki and Ohta and with the coalescence model of domain growth, which gives  $k_m \propto t^{-\varphi}$ , with  $\varphi = 1/3$ . In the late stage  $\varphi$  increases to unity in both systems. This implies that hydrodynamic effects control the rate of growth of the nucleating domains of size  $l \simeq k_m^{-1}$ . In both early and late stages, the intensity measurements are consistent with  $I(k_m,t) \propto l^3$ . The scattering experiments were supplemented by direct observation of domain growth with a microscope.

# I. INTRODUCTION

This paper is concerned with the dynamics of phase separation in critical solutions. Because the initial size of the nucleating grains can be as large as a micron near the critical point, the process is conveniently studied by light scattering and by direct microscopic observation, and we have used both of these experimental tools. Measurements were made on two mixtures: isobutyric acid and water (I-W) and 2, 6-lutidine and water (L-W). The present results confirm that hydrodynamic effects are important in the late stage of the process, an early conjecture of Cahn and Moldover.<sup>1</sup> Droplet growth is speeded up by fluid flow, which in turn is driven by the curvature of irregular surfaces which interpenetrate the nucleating fluid. To set the present study in perspective we review earlier related experiments, most of which were carried out on these same systems.

Using an ingenious pressure-jump technique to quench the system, Wong and Knobler<sup>2</sup> made extensive light scattering measurements of phase separation in isobutryic acid and water. When the critical mixture is quenched a few mK into the two-phase region it scatters light in the form of a ring which brightens, sharpens, and decreases in diameter as the system evolves toward its final equilibrium state. From elementary scattering theory one expects that the ring diameter  $\theta_m$ , or rather the corresponding photon momentum change  $k_m$ , is inversely proportional to the characteristic size l of the nucleating regions in the fluid. This ring has been associated with spinodal decomposition, a term introduced by Cahn.<sup>3</sup> Cahn was the first to consider and analyze the process of phase separation from an initially unstable state. Spinodal decomposition was first observed in metals but recently it has been studied in fluids.<sup>4</sup>

The parameters most readily measured in spinodal decomposition experiments are  $\theta_m$  vs t and the scattering intensity  $I(\theta_m, t)$ . In these so-called critical-quench experiments the fluid is driven through the critical temperature  $T_c$  from its initial one-phase temperature  $T_i$  to its final two-phase temperature  $T_f$ . The ring diameter is then measured as a function of time and temperature difference  $\Delta T_f \equiv |T_f - T_c|$ , there being only a weak dependence on  $\Delta T_i = |T_i - T_c|$ .

The most extensive spinodal decomposition measurements to date are those of Wong and Knobler<sup>2</sup> (W-K), and we will frequently refer to their work. Investigating the I-W system they measured  $k_m(t)$ , fitting their data to the form  $k_m(t) \propto t^{-\varphi}$ . The results were consistent with a time-independent  $\varphi$ , though this parameter did depend on quench depth  $\Delta T_{\epsilon}$ .

More recently Kim et al.<sup>5</sup> reported phase-separation measurements in L-W using a microscope to measure l(t) in the late stage (100 sec  $\leq t \leq 1000$ sec) and light scattering in the early stage (10 sec  $\leq t \leq 100$  sec). They observed a crossover from slow  $(\varphi \simeq \frac{1}{3})$  to rapid  $(\varphi \simeq 1.7)$  coarsening. The results were not fully satisfying, however, because neither experimental technique spanned both the slow and fast growth regimes. The present experiments were undertaken to remove this deficiency. A secondary goal was to verify that the light scattering results were sample independent and insensitive to both the quench technique and the quench rate. Because our light scattering measurements spanned a longer time interval than those of W-K, a speedup in the droplet growth rate was more clearly seen and  $\varphi$  was itself found to be time dependent.

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As a check on the above cited microscopic measurements of l(t) in L-W, we have used this same technique to measure domain growth in L-W and I-W, while simultaneously recording the ring diameter, i.e.,  $k_m(t)$ . Such experiments reveal whether  $k_m^{-1}(t)$  is roughly equal to the visually detected given size l and whether both parameters are characterized by the same exponent,  $\varphi(t)$ .

The remainder of the paper is organized as follows. Section II gives experimental details. In Sec. III our findings are presented along with a graphical comparison with the early-stage spinodal decomposition theories of Langer, Bar-on, and Miller, <sup>6</sup> and Kawasaki and Ohta.<sup>7</sup> Section IV is devoted to a discussion of the present results and a comparison with earlier experiments. Emphasis will be placed on analysis of the late stage of the process, due to Siggia.<sup>8</sup> Finally, the work is summarized in Sec. IV.

#### **II. EXPERIMENTAL**

#### A. Apparatus

The experimental arrangement is shown in Fig. 1. The sample (C) was located in a temperaturecontrolled, rapidly stirred water bath (B) identical to that used by Goldburg *et al.*<sup>9</sup> (This reference, which contains many relevant experimental details, will be subsequently referred to as I.) The bath temperature, which was monitored by quartz thermometer, was stable to within  $\pm 0.1$  mK over at least 1800 sec, which was the time span of the longest run. The incident laser beam, of vacuum wavelength  $\lambda_0 = 6328$  Å, went through an attenuator (A), was reflected by a mirror (M), and then went through a pinhole (S) before it reached the sample.



FIG. 1. Experimental arrangement, described in Sec. IIA.

The laser intensity did not exceed 0.3 mW and produced no observable local heating in the mixtures.

To monitor the intensity of the unscattered beam a microscope slide (G) reflected a small fraction of the beam into the photodiode D. Its output  $I_F$ provided a measure of the optical thickness of the sample and thereby the amount of multiple scattering from it.

The remaining unscattered intensity, as well as the scattered radiation  $I(\theta)$ , continued through the microscope slide and fell on the rotating mirror R. The mirror reflected the scattered light into the photomultipliers  $P_1$  and  $P_2$  (RCA Model 1P28). A stepping motor rotated the mirror so that its angular position  $\alpha(t)$  varied in a symmetrical sawtooth fashion. Its axis of rotation coincided with that of the incident laser beam. The amplitude of  $\alpha(t)$  was several degrees and its period T was 4 sec. The photomultiplier recorded  $I(\theta, t)$  only over a small fraction of T so that a complete angular distribution was recorded rapidly enough such that  $I(\theta, t)$  changed very little during a single sweep.

At the same instant in each mirror cycle a stepping-motor pulse triggered a minicomputer (PDP11/10),<sup>10</sup> which sampled the voltage outputs of  $P_1$  or  $P_2$ . These detectors were located at different distances from the mirror and therefore recorded the scattering over different angular ranges and with correspondingly different angular resolution  $\Delta \theta_{1,2}$ . The closer photomultplier,  $P_2$ , recorded  $I(\theta)$  during the first part of the run when the ring was relatively large and relatively weak and was, therefore, operated at greater sensitivity and lower angular resolution than  $P_1(\Delta \theta_2 = 2.5 \text{ mrad})$ .

When the scattered intensity exceeded the dynamic range of the computer input it was manually switched over to receive the signal from the more distant detector  $P_1$  whose angular resolution was  $\Delta \theta_1 = 1.5$  mrad. With these two detectors operated in tandem the scattered intensity could be recorded over four decades. This scheme requires that the relative gains of the two photomultipliers be accurately known. To minimize drift the gain ratios were remeasured after every run.

#### **B.** Sample preparation

Both samples were prepared from commercially available components, using multiply distilled water. They were of critical composition as evidenced by the volume equality of the two phases on cooling ~2 mK below  $T_c$ . The measured critical composition ( $c = c_c$ ) and critical temperatures

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determined in this way were close to the generally accepted values for I-W<sup>11</sup> and L-W.<sup>12,13</sup> These are I-W:  $c_{\sigma} = 38.6$  wt. % acid,  $T_{\sigma} = 26.08$  °C; L-W:  $c_{\sigma} = 28.16$  wt. %, 2, 6-lutidine  $T_{\sigma} = 33.37$  °C. The 2, 6-lutidine-water system has an inverted coexistence curve so this  $T_{\sigma}$  is a lower critical temperature. Whatever impurities were present in our samples are expected to have little effect other than to shift  $T_{\sigma}$  and perhaps  $c_{\sigma}$ .<sup>14,15</sup>

Except where otherwise specified, the sample cells were made of glass and were of the reentrant type. They accommodated roughly 1 ml of solution. The optical path was only 100  $\mu$  in order to minimize multiple scattering. To determine if our results were influenced by sample thickness, a one-mm cell was used in some of the microscope measurements. Both cells are sketched in Fig. 3 of I (the thick cell shown there contains two electrodes which were absent here). The samples were filled under atmospheric pressure.

L-W is reported to attack glass containers, producing a slow change in  $T_c$  with time.<sup>16</sup> Therefore,  $T_c$  was remeasured frequently. (In such remeasurements  $T_c$  was taken as the cloud-point temperature.) No drift in the critical temperature was detected.

#### C. Procedure

Prior to quenching, the samples were in equilibrium at the initial one-phase temperature  $T_i$ , which was typically several mK from  $T_c$ . For L-W  $T_i$  is less than  $T_c$ , hence a "quench" was an upward temperature jump. The heating was accomplished by applying a voltage pulse to a bare Nichrome heater immersed in the rapidly stirred water bath.

The I-W samples was quenched (cooled) by injecting a few ml of ice water into the bath with a syringe. With both quenching schemes the temperature changed by 95% of  $|T_f - T_i|$  in less than 3 sec. In a few more seconds the temperature bath stabilized at  $T = T_f$  so that the light scattering measurements could commence at  $t \simeq 10$  sec following the quench at t = 0. At that time the computer commenced its repetitive recording of  $I(\theta)$ while a chart recorder displayed  $I_F(t)$ . In the early stage of phase separation the angular scanning range ( $\theta$ ) at  $P_1$  was  $\pm 7.5^{\circ}$ , while at  $P_2$  it was  $\pm 4.5^{\circ}$ . This photomultiplier recorded the ring intensity at such small scattering angles that it became necessary to subtract spurious scattering arising from the walls of the water bath and the sample cell itself. This background contribution  $I_B(\theta)$  was measured at  $T = T_i$  prior to each run. Dividing  $I(\theta, t) = I_B(\theta)$  by  $I_F(t)$ , to correct for multiple scattering, gave the "corrected intensity"

$$\boldsymbol{g}(\boldsymbol{\theta}, t) \equiv \left[ I(\boldsymbol{\theta}, t) - I_{\boldsymbol{B}}(\boldsymbol{\theta}) \right] / I_{\boldsymbol{F}}(t) . \tag{1}$$

The background term  $I_B(\theta)$  contains a contribution from spontaneous composition fluctuations at  $T = T_i$ , but it was negligibly small compared to the scattering produced by the phase-separating mixture.

Of the wealth of data obtained from this experiment we present only our measurements of the time dependence of the ring diameter  $k_m(t)$  and ring intensity  $g_m(t) \equiv g(\theta_m, t)$ , where  $\theta_m$  is defined above. The momentum transfer at  $\theta = \theta_m$  is found from

$$k = (4\pi n / \lambda_0) \sin\frac{1}{2}\theta, \qquad (2)$$

where *n* is the refractive index of the critical mixture. For our systems, ideal-solution calculations give n(I-W) = 1.35 and n(L-W) = 1.38. These refractive indices differ insignificantly from that of pure water for which  $n_w = 1.33$ .

The microscope measurements utilized an instrument of large working distance so the sample could be viewed at the center of the water bath.<sup>5,9</sup> Most of the measurements were made at a magnification of 25.

#### III. RESULTS

#### A. $k_m$ vs t

Figures 2 and 3 show  $k_m$  vs t in I-W and L-W, respectively. The quench depths span the range 0.3 mK  $\leq \Delta T_f \leq 9$  mK and are shown in the figures. The runs were terminated at  $t \sim 10^3$  sec, when  $\theta_m(t)$  became too small to measure. The initial



FIG. 2. Ring diameter vs time in isobutyric acid-water at the indicated quench depths.  $\Delta T_f = T_f - T_c$ .



FIG. 3. Ring diameter vs time in 2, 6-lutidine-water.

conditions for I-W were similar to those of W-K (see their Fig. 5) except that our runs lasted several times longer.

In these two figures a solid line was drawn by eye through the data at  $\Delta T_f = 1.8 \text{ mK}$  (Fig. 2) and  $\Delta T_f = 0.6 \text{ mK}$  (Fig. 3) to draw attention to the curvature in  $k_m(t)$ . This curvature appears in the shallower quenches only. The measurements are consistent with a power-law variation of the coarsening rate,

$$k_m^{-1}(t) \propto t^{\varphi}, \tag{3}$$

with  $\varphi$  strongly dependent on  $\Delta T_f$  and slowly increasing with t. (The earlier experiments<sup>9</sup> established that  $\varphi$  is no more than weekly dependent on  $\Delta T_i$ .) At small quench depths the measurements at small t are consistent with  $\varphi = \frac{1}{3}$ , while at the largest t all the measurements are encompassed by  $\varphi = 0.95 \pm 0.15$ .

# B. $q_m vs \tau$

Figures 4 and 5 show the measurements of Figs. 2 and 3 in dimensionless units,

$$q_m = k_m(t)\,\xi(\Delta T_f)\,,\tag{4}$$

$$\tau = [D(\Delta T_{f})/\xi^{2}(\Delta T_{f})]t.$$
(5)

Here  $\xi$  is the correlation length in the critical mixture at a temperature  $|\Delta T \ ^{\circ}C|$  from the critical point in the *one-phase* region, and *D* is the composition diffusivity.<sup>17</sup> For I-W we used the data of Chu *et al.*<sup>12</sup>:

$$\xi = (3.57 \pm 0.07 \text{ Å})\epsilon^{-0.613 \pm 0.001}$$
(6a)

and

$$D = k_B T_c / 6\pi \eta^* \xi \ \mathrm{cm}^2 / \mathrm{sec} \,, \tag{6b}$$



FIG. 4. I-W data of Fig. 2 replotted in the dimensionless length and time units defined in the text.

where  $\epsilon = |T - T_c| / T_c$ , and the high-frequency kinematic viscosity  $\eta^* = 2.42 \times 10^{-2}$  P. The same parameters in L-W, as measured by Gulari *et al.*, <sup>13</sup> are

$$\xi = (2, 0 \pm 0, 2 \text{ Å}) \epsilon^{-0.60 \pm 0.08}$$
(6c)

and

$$D = (0, 29 \pm 0, 02) \times 10^{-5} \epsilon^{0.554 \pm 0.015} \text{ cm}^2/\text{sec}$$
. (6d)

The parameters in (6a)-(6d) were measured in the one-phase region.

The most important conclusion to be drawn from Figs. 4 and 5 is that the ring-diameter measurements exhibit the expected property of critical-point scaling, i.e., all the measurements collapse quite satisfactorily to form a single curved line. Furthermore, at each  $\tau$ ,  $q_m^{\text{L-W}} \simeq q_m^{\text{L-W}}$ , though the measured curve  $q_m^{\text{I-W}}(\tau)$  lies measurably below the corresponding curve for L-W.

If one extracts  $\varphi(\tau)$  from Figs. 4 and 5 it is seen that

 $\varphi_{\mathbf{I}} = 0.3 \pm 0.1, \quad 7 \le \tau \le 30,$ 

$$\varphi_{1-W}(\tau) = 1.1 \pm 0.1$$
,  $200 \le \tau \le 1000$ ,



FIG. 5. L-W data of Fig. 3 in dimensionless units.

and

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$$\varphi_{\text{L-W}}(\tau) = 0.4 \pm 0.1, \quad 10 \le \tau \le 40,$$

$$\varphi_{\text{L-W}}(\tau) = 0.95 \pm 0.1, \quad 300 \le \tau \le 1000.$$

Limited significance should be given to these numerical values since they are determined from less than a decade of data in both  $\tau$  and  $q_m$ .

The solid line in Fig. 4 summarizes the results of Wong and Knobler,<sup>2</sup> using Eqs. (4) and (6) to express their measurements of  $k_m$  vs t in reduced units. The excellent agreement between the W-K measurements and ours indicates a gratifying insensitivity to sample thickness and purity and to the quenching scheme.

The dashed lines labeled LBM and KO in Figs. 4 and 5 are the theoretical calculations of Langer, Bar-on, and Miller<sup>6</sup> (LBM) and Kawasaki and Ohta<sup>7</sup> (KO). They both use the same basic computational scheme (that of LBM); it avoids linearization assumptions and takes fluctuations into account. Kawasaki and Ohta, however, have included hydrodynamic effects. Both calculations share the fundamental assumption that the evolving system can be characterized by a single characteristic length. They should therefore not apply in the late stage  $[k_m^{-1}(t) \gg \xi(\Delta T_f)]$ , i.e., when the domain size is much greater than the interface thickness. Another of their assumptions-one which is relatively easily relaxed<sup>18</sup>—is that the system is quenched instantaneously from an initial state of complete disorder, i.e.,  $\Delta T_i = \infty$ . In the limited range over which the present results and the calculations should be compared, the agreement is very good, especially when the hydrodynamic interaction is included. Theoretically, flow effects should be unimportant at small  $\tau$  so that, as  $\tau \rightarrow 0$ , the LBM and KO theories should coincide.

#### C. Ring intensity versus time

Figures 6 and 7 show the relative ring intensity versus  $\tau$  in I-W and L-W, respectively. The quench depths  $\Delta T_f$  are as designated. The intensities have been expressed in reduced units, i.e., at each  $\Delta T_f$ ,  $I_m$  of Eq. (1) has been further divided by  $\epsilon^{-\gamma}$ , where  $\epsilon = |1 - T_f/T_c|$ . The factor contains the temperature dependence of the equilibrium composition susceptibility. The  $\gamma$  values used were the measured ones:  $\gamma$ (I-W) =1.24±0.05 (Ref. 11) and  $\gamma$ (L-W) = 1.26±0.02.<sup>13</sup>

The solid and broken lines labeled LBM and KO are the theoretical calculations of the scattering function  $S(q_m, \tau)$  (from which the previously discussed function  $q_m(\tau)$  was extracted). We have arbitrarily normalized the two theoretical curves to our measurements at  $\tau = 20$ .

In Figs. 6 and 7 the data lie on a relatively smooth



FIG. 6. Scaled ring intensity vs reduced time in I-W.

curve, as scaling agreements would suggest, but the slopes of lines drawn through the points differ at small  $\tau$ ; if we write  $g_m \propto \tau^{\theta(\tau)}$  then  $\theta_{I-W}(10) \simeq 0.6$ , whereas  $\theta_{L-W}(10) \simeq 0.9$ . However, at large  $\tau$ , the



FIG. 7. Scaled ring intensity vs reduced time in L-W.

slopes are almost equal, with  $\theta_{I-W} \simeq \theta_{L-W} \simeq 3$ . In the previous measurements of ring intensity in I-W and L-W, a similar increase of  $\theta$  with time was observed.<sup>9,19</sup>

In comparing our ring-intensity measurements with the calculations of LBM and KO it has been implicitly assumed that the  $I(\theta, t)$  is equal, within a multiplicative constant, to the scattering function S(k, t), which is the quantity of direct theoretical interest. The assumption is justified if (a) the attenuation of the transmitted beam is small and (b) the restrictions imposed by the first Born approximation are satisfied (these two conditions are not equivalent<sup>20</sup>). Here we discuss the beam attenuation problem and defer (b) to Sec. IV.

Our normalization of the scattering intensity by  $I_F(t)$  gives only an approximate correction for multiple scattering, which increases with increasing t.<sup>9</sup> A proper treatment would take into account the shape of the sample and the functional form of  $I(\theta, t)$ <sup>21</sup> which is not known. Let us assume that our multiple-scattering correction is adequate if, say, the forward beam attenuation is less than 10%. To determine the time interval over which our data are properly corrected we list in Table I the actual and dimensionless times  $t = t_u, \tau = \tau_u$ , beyond which  $I_F(t)/I_F(10) \le 0.9$ . Since the scattering is an increasing function of quench depth, a different entry appears for each  $\Delta T_f$  (see Figs. 6 and 7). Comparison of the entries in Table I and the scaled measurements of Figs. 6 and 7 suggest that the scattering correction is adequate out to  $\tau \simeq 200.$ 

# D. Visual observations

In the late stage of phase separation the nucleating domains can be seen with a low-power microscope.<sup>5</sup> The visual measurements described below are only semiquantitative, but they do provide

TABLE I. Multiple-scattering data. Actual and reduced times  $t_u$  and  $\tau_u$ , beyond which the unscattered intensity  $I_F(t)$  decreased by more than 10%.

Solution	$\Delta T_F \mathrm{mK}$	$t_u \sec$	τ <sub>u</sub>
I–W	0.7	>930	>120
	1.8	340	170
	3.4	110	180
	5.8	45	190
L-W	0.3	300	60
	0.6	140	100
	1.3	40	110
	1.5	40	140
	1.9	30	170

information that should not be overlooked when interpreting the scattering data.

During the I-W measurements a laser beam passed obliquely through the sample so that  $k_m(t)$ could be recorded at the same time. Runs were made at  $\Delta T_f = 0.5$ , 2.4, and 4.5 mK, and over the time interval 40 sec  $\leq t \leq 1000$  sec. With a 1-mm cell the nucleating fluid always exhibited a granular interconnected structure, i.e., isolated spherical drops were not seen. This interconnectedness is expected since the fractional amounts of both phases are equal. We were surprised, however, to find that the visually estimated l(t) grew at a faster rate than did  $k_m^{-1}(t)$  at all three guench depths. For example, in the interval 30 sec  $\leq t$  $\leq 100$  sec and at  $\Delta T_f = 2.4$  mK,  $l(t) \propto t^{\varphi_l}$ , with  $\varphi_1 = 1.3$ , whereas the ring diameter collapsed at a rate characterized by  $\varphi = 0.6$  in the range 100  $\sec \le t \le 500$  sec. Thus the two schemes for measuring grain size seemingly give different weights to the droplet-size distribution. Of course the visual measurements contain a subjective element that does not afflict the  $k_m$  data. It is likely, however, that more sophisticated statistical techniques of micrograph analysis would not remove this problem.

To examine the influence of sample thickness on visual grain size experiments on L-W were made with both thick (1 mm) and thin (0.1 mm) cells. In the thin cell the interconnected structure broke up into spherical droplets at  $l = 20-30 \ \mu$  but the simultaneously recorded  $k_m(t)$  showed no evidence of this morphological transition, which occurred at  $t \approx 200$  sec. The quench depth here was 1.4 mK. No such transition occurred in thick-cell measurements at the same quench depth. However, a hydrodynamic instability did intervene, causing macroscopic fluid flow, as discussed in detail in Ref. 5. In the thin cell this instability is presumably suppressed by the walls.

Finally, we note that in both systems the visual grain size is always much larger than  $k_m^{-1}(t)$ ; typically  $l(t)/k_m^{-1}(t)$  varies from 5 to 10. This result, however, is not surprising; in neutron scattering from liquid argon<sup>22</sup> the first diffraction peak occurs at  $k_m r_m \approx 7.5$ , where  $r_m$  is the maximum in the radial distribution function.

# IV. DISCUSSION

#### A. Domain growth

The present experiments confirm previous observations of a crossover from slow to rapid domain growth in critically quenched systems. In the early stage of phase separation, say,  $0.2 \le q_m \le 1$ , our results agree with the calculation of Kawasaki and Ohta,<sup>7</sup> who included hydrodynamic

effects in the underlying computational scheme of LBM. These authors assume that the system is quenched from an initially disordered state  $(\Delta T_i/T_c \gg 1)$ , whereas in the experiments  $\Delta T_i/T_c \approx 10^{-5}$ . One could, therefore, argue that this experimental test of the above results is not a conclusive one. On the other hand, earlier experiments<sup>9</sup> showed no initial-state effects.

As we will discuss below, our early-stage results also support the coalescence picture of domain growth,<sup>23</sup> which gives  $l = At^{1/3}$ .

To explain the accelerated rate of domain growth at large  $\tau$ , a different theoretical approach is required. Recently, Siggia<sup>8</sup> has carefully analyzed the problem of late-stage phase separation, taking into account both diffusion and hydrodynamic flow. To sort out various competing mechanisms it is useful to classify experiments as to whether the quenches are critical or off critical. In the offcritical experiments of W-K and Goldburg et al.<sup>24</sup> one expects spherical droplets of the minority phase to develop in the background of the mother phase. In the critical case two interpenetrating phases of near-equal volume should form. Siggia emphasizes that in this regime domain growth should proceed through three stages to which we will frequently refer: I, early stage (including coalescence),  $\xi \le l \le 5\xi (l = At^{1/3})$ ; II, flow stage (l = Bt),  $(k_B T/\sigma)^{1/2} \le l \le (\sigma/g\Delta\rho)^{1/2}$ ; and III, gravitational stage,  $l \ge (\sigma/g\Delta\rho)^{1/2}$ . To the left we have noted the mechanism which is responsible for domain growth, and to the right the range of grain sizes in which the corresponding mechanism dominates. Here  $\sigma$  is the surface tension (which approaches zero at the critical point),  $\Delta \rho$  is the density difference of the two phases, and g is the gravitational constant.

In stage I, theories of the LBM-KO type are appropriate. The coalescence picture<sup>23</sup> also applies, but only qualitatively because the coalescing regions do not yet have well-defined compositions and boundaries. With the same caveat one also can invoke the evaporation-condensation mechanism of Lifshitz and Slyozov.<sup>25</sup> Both mechanisms are diffusion controlled and give rise to a  $t^{1/3}$  growth rate.

In stage II, grain growth is controlled by fluid flow. This flow is driven by pressure gradients which arise from the curvature of the surfaces which interpenetrate the fluid. Cahn and Moldover<sup>1</sup> and Siggia<sup>8</sup> have independently observed that, from dimensional arguments alone, l should increase linearly with time in this regime. Finally, in III, the domains become so large that gravitational effects dominate and no simple power-law behavior is anticipated. The boundaries between the regimes are, of course, defined only very roughly. Siggia used a deformable spherical-drop approximation in his calculation of A and a tube approximation to estimate B. To compare his results with ours we take  $k_m^{-1} = l = a$ , where a is his drop radius. We thus ignore the difference in grain size as measured by scattering and by eye, as well as the nonspherical shape of the domains.

To estimate A and B, as well as the characteristic cross-over length  $l_{12} = (A^3/3B)^{1/2}$ , we follow Siggia in taking  $\sigma = 100\epsilon^{1.23}$  dynes/cm in both systems. Other needed parameters, also assumed to characterize both I-W and L-W, are  $\xi = \xi_0 \epsilon^{-0.62}$ (in the two-phase region),  $(c - c_c)/c_c = \epsilon^{1/3}$ ,  $\rho = 1$ g/cm<sup>3</sup>,  $\eta = 0.24$  P, and  $\Delta \rho = 0.1 \epsilon^{0.33}$  g/cm<sup>3</sup>.

For critically quenched systems Siggia estimates

$$a = \left(\frac{6}{5} k_B T / \pi \eta\right)^{1/3} t^{1/3} = A t^{1/3} \text{ in I}, \tag{7a}$$

$$a = (p\sigma/\eta)t = Bt \text{ in II}, \qquad (7b)$$

where p is a dimensionless constant and A turns out to be 10<sup>-4</sup> cm. The expression for A was obtained by Siggia using a coalescence argument. We have further assumed that a is much larger than the initial droplet size, which we might estimate to be several times  $\xi(\Delta T_f)$ . A more primitive estimate<sup>17 (c)</sup> of domain size in the coalescence regime<sup>23</sup> gave  $l \simeq (k_B T / 6\pi \eta)^{1/3} t^{1/3}$ .

Equation (7) can easily be written in dimensionless units  $q_m(\tau)$ , where  $q_m = \xi/a = k_m\xi$ , and  $\tau$  is defined in Eq. (5).<sup>26</sup> Approximating  $\sigma \simeq k_B T/\xi^2$  $= (k_B T/\xi_0^2)\epsilon^{2\nu}$ , Eq. (7) becomes

I 
$$q_m = (\frac{5}{36})^{1/3} \tau^{-1/3}, \quad \frac{1}{10} \le q_m \le 1,$$
 (8a)

II 
$$q_m = 1/6\pi\rho\tau$$
,  $q_{23} \le q_m \le \frac{1}{10}$ , (8b)

where  $q_{23} \equiv \xi g \Delta \rho / \sigma < 7 \times 10^{-3}$  for  $\Delta T_f > 1$  mK in both L-W and I-W. Since all of our measurements were at larger values of  $q_m$ , gravitational effects never come into play.

The above calculations will now be compared with our measurements. Consider first the early stage, where Eq. (8a) predicts that at, say,  $\tau = 10$ ,  $q_m = 0.24$ . At this time Figs. 4 and 5 shows that  $q_m^{I-W}(10) \simeq q_m^{I-W}(10) \simeq 0.5$ . The same level of agreement is seen in the unscaled data of Figs. 2 and 3. For example, in I-W at  $\Delta T_f = 1.8$  mK and L-W at  $\Delta T_f = 0.6$  mK,  $k_m^{-1}(100 \text{ sec}) \simeq 10^4$  cm<sup>-1</sup>. Equating  $a^{-1}$  with  $k_m$ , Eq. (7a) gives  $k_m(100 \text{ sec}) = 2.4 \times 10^3$ cm<sup>-1</sup>, whereas measurements give  $k_m(100 \text{ sec}) = 4 \times 10^3$  cm<sup>-1</sup> in both systems. Better agreement with such a simple calculation of domain growth would hardly be expected. The coalescence picture is also supported by the previously cited experiments of Refs. 2 and 17(c).

Next consider the measurements at large  $\tau$  where Eqs. (7b) and (8b) apply. Siggia's calculations give p = 0.1 but, as he notes, this greatly overestimates *a* as measured by WK. It is also an overestimate for the present measurements. To see this we insert the above estimates for  $\sigma$ ,  $\rho$ , and  $\eta$  into Eq. (8b) giving  $q_m(\tau) = 0.05/p\tau$ . To bring this equation into agreement with the latestage results in Figs. 4 and 5 at, say  $\tau = 400$ , requires that  $p \simeq 2 \times 10^{-3}$ . A more detailed theory is obviously required to calculate the numerical factor *B*.

# B. Ring intensity

Figures 6 and 7 compare the reduced ring intensity  $\mathcal{G}_m(\tau)$  with the theoretical calculations of the structure factors  $S(k_m, t)$  by LBM and KO. Implicit in this comparison is the assumed validity of the first Born approximation. This approximation should be applicable (i.e., the Born series converges and may be terminated at the first term) when the phase shift  $\alpha$  of light across a domain of size l (measured relative to the background fluid) is much less than  $2\pi$ .<sup>27</sup>

To determine when the Born condition is satisfied in these experiments we estimate  $\tilde{l}^{-1}(\Delta T_f)$ , where  $\tilde{l}$  is the domain size for which  $\alpha = 1$ . Near the critical point the phase shift is adequately approximated by  $\alpha = \Delta n \epsilon^{\beta} 2 \pi l(t) / \lambda_0$ , where  $\Delta n$  is the difference in refractive indices of the pure components and  $\beta$  is the critical exponent defining the coexistence curve. Taking  $\beta = 0.33$  (Ref. 28) and  $\Delta n(I-W) = 0.06$ ,<sup>29</sup>  $\Delta n(L-W) = 0.16$ ,<sup>27</sup> one finds  $\tilde{l}_{r-W}^{-1}(9 \text{ mK}) = 90 \text{ cm}^{-1}$  and  $\tilde{l}_{L-W}^{-1}(2 \text{ mK}) = 300 \text{ cm}^{-1}$ . Since all measurements were made at quench depths no larger than these, and since  $k_m(t)$  was always much larger than above values of  $\tilde{l}^{-1}$ , we feel justified in identifying the scattering intensity with  $S(k_m, t)$  over most of the measuring time interval.

Our finding that  $\mathscr{G}_m \propto t^3$  at large t can be accounted for by the following very crude model. The nucleating fluid is regarded as a random array of spheres, each of radius a(t). In this case the Born approximation (often called the Rayleigh-Gans approximation<sup>20</sup>) gives  $I(k_m, t) \propto a^3$ , since the radiated intensity from each sphere is proportional to  $a^6$ , and the number of spheres in the incident beam is proportional to  $a^{-3}$ . Assuming the  $a \propto t$  in the late stage gives  $I(k_m, t) \propto t^3$ , which agrees with our measurements.

The above argument implies that  $I(k_m, t)a^{-3} = I(k_m, t)k_m^3$  should be a constant over the full measuring interval, 10 sec  $\leq t \leq 1000$  sec. In reduced units  $[\mathscr{G}_m(\tau) =$  measured intensity  $\times \epsilon^{\gamma}$  and  $q_m = k_m \xi]$  this equation becomes  $\mathscr{G}_m(\tau)q_m^3(\tau) =$  const. independent of  $\tau$ . To obtain this result it is assumed that  $I(k_m, t)$  is proportional to  $\Delta c^2$ , where  $\Delta c(t)$  is the difference in composition between the background and nucleating phases, and that  $\Delta c(t)$  has reached



FIG. 8. Product of scaled ring intensity and  $q_m^3$  as a function of  $\tau$  for I-W ( $\bigcirc$ ) and L-W ( $\bigcirc$ ).

equilibrium value  $\Delta c(\infty) \sim \epsilon^{\beta}$ . Also we have invoked the scaling relation  $3\nu' - 2\beta - \gamma' = 0$ ,  $^{17(a)}$  where  $\nu'$ and  $\gamma'$  are, respectively, the correlation length and susceptibility exponents in the two-phase region.

In Fig. 8 the data in Figs. 3-6 are combined to form  $\mathfrak{G}_{mq_{m}^{3}}$  vs  $\tau$  for both I-W (open circles) and L-W (closed circles). Only a few representative data points are shown. As predicted, both sets of measurements lie roughly on a straight line of zero slope. Considering the crudeness of our arguments and the inadequacy of the multiple-scattering correction when  $\tau \ge 200$ , better agreement could hardly be expected.

# V. SUMMARY

Light scattering was used to study phase separation in critical binary mixtures of isobutyric acid-water and 2, 6-lutidine-water. The quantities measured were  $k_m(t)$  (ring diameter versus time) and the ring intensity  $I(k_m, t)$  vs t. The measurements, which exhibited critical-point scaling, were fitted to power-law form,  $k_m(t) \propto t^{\varphi(t)}$  and  $g(k_m, t) \propto t^{\theta(t)}$ . In the early stage of phase separation the results were in very good agreement with the calculations of Kawasaki and Ohta and with a coalescence picture, which gives  $\varphi = \frac{1}{3}$ . In the late stage  $\varphi = 1$ , as expected from dimensional and semiquantitative agreements which invoke hydrodynamic effects. However, the calculated grain size a(t) exceeds the measured values of  $k_m^{-1}(t)$  by roughly  $10^2$ .

The ring intensity exponent  $\theta$  increased more rapidly with time than expected from the early-

stage theories of LBM and KO. In both systems the measurements are consistent with  $\theta$  (large  $\tau$ ) = 3.

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- <sup>19</sup>A word of caution: not all authors have defined  $q_m$  and  $\tau$  identically. In this paper we use the same definitions as in I and KO, but this choice differs from that of LBM. While the numerical results of LBM are plotted correctly here, in I (and in KO) the curves labeled LBM should be shifted to the left by a factor of 2; see the erratum by Goldburg *et al.* in J. Chem. Phys. 69, 5214 (1978).
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