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4-1-1987

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### Recommended Citation

Rauseo, Steven N.; Easwar, Nalini; and Maher, James V., "Search for an Instability on a Quenched-Liquid Interface" (1987). Physics: Faculty Publications, Smith College, Northampton, MA.  
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## Search for an instability on a quenched-liquid interface

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(Received 9 December 1986)

We searched for signs of an instability on the interface between the two phases of a binary-liquid mixture, isobutyric acid and water, after the mixture was quenched further into the two-phase region. Such an instability would be the liquid-liquid analog of the Mullins-Sekerka instability seen in quenched alloys. Never is any dramatic growth observed, but under conditions of small dimensionless quench depth ( $\theta < 1.5 \times 10^{-3}$ ), the intensity of light scattered from the interface grows for small values of the momentum transfer  $k$ .

### I. INTRODUCTION

Since the Mullins-Sekerka instability<sup>1</sup> gives rise to dendritic growth in alloys, it has been extensively studied over many years.<sup>2</sup> Despite significant recent improvements in theoretical treatment,<sup>3</sup> computer simulation,<sup>4</sup> and laboratory experiment,<sup>5</sup> it is still difficult to make direct observations correspond sufficiently closely to calculational assumptions that meaning can be attached to comparing the two.

In this paper we report the results of an experiment in which we attempted to observe the Mullins-Sekerka instability in a particularly simple system (a binary-liquid mixture at critical composition) which corresponds quite closely to one of the earliest and simplest solidification models, the stationary symmetric model (SSM) of Langer and Turski.<sup>6</sup> If one could observe the instability in the binary-liquid system where there is no crystal-axis asymmetry, no net interfacial motion, and only composition diffusion, direct comparison of the observed dynamics with the SSM, as modified by Jasnow, Nicole, and Ohta<sup>7</sup> to account for hydrodynamic degrees of freedom, should be meaningful. As will be discussed below, we have used direct microscopic observation and both static and dynamic light scattering to search extensively for indications of the onset of the instability. We have not succeeded in observing it. Only under a very restricted set of circumstances do we observe any departure from equilibrium interfacial behavior, in which case the departure does not increase after very early times.

### II. THE MODEL

The SSM is the first and simplest model discussed by Langer and Turski in their series of articles on interfacial instabilities;<sup>6</sup> it uses a simple two-component system (single-order parameter) capable of displaying a Mullins-Sekerka type instability.<sup>1</sup> Langer and Turski performed a linear stability analysis for the interface and derived the dispersion relation, thus predicting which are the unstable modes of the interface when the system is subjected to a concentration flux across the interface. Such a flux can arise in a binary system subjected to a temperature quench. A typical system phase diagram is shown in Fig.

1; two components ( $A$  and  $B$ ) are miscible above  $T_c$ , and separate into two phases below  $T_c$ . (Call the upper phase 1 and the lower 2.) Choose the order parameter to be  $C$ , the volume fraction of  $A$ . The miscibility gap is given by  $\Delta C = B|\epsilon|^\beta$ , where  $\epsilon$  is the reduced temperature  $T/T_c - 1$ . The system is further characterized by the correlation length of the concentration fluctuations,  $\xi = \xi_0\epsilon^{-\nu}$ , the diffusion constant  $D = D_0\epsilon^\nu$  and the surface tension of the interface  $\sigma = \sigma_0\epsilon^\mu$ , where  $\nu \approx 0.6$ ,  $\beta \approx \frac{1}{3}$ , and  $\mu \approx 2\nu$ . These are the only variables needed to characterize the system at equilibrium in the original model. In later work, Jasnow, Nicole, and Ohta<sup>7</sup> and Kawasaki and Ohta<sup>8</sup> included the effects of hydrodynamics and gravity on the dispersion relation. Their results further extended the range of stable wave numbers for disturbances of the interface, but still predicted an unstable region.

In an attempt at a close experimental realization of this model, we have searched for an instability on the interface between the two phases of a binary-liquid mixture in its two-phase region as we quenched the system further from its consolute point. The interface between the two phases

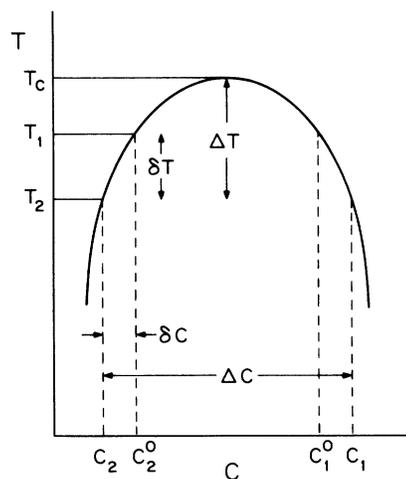


FIG. 1. Coexistence curve for a typical binary-liquid mixture.

is expected to become unstable when the system is quenched deeper into the two-phase region. We characterize the depth of a quench by the ratio  $d = \delta T / \Delta T$ , the dimensionless temperature drop, where the system was originally at  $T_1 = T_c - \Delta T + \delta T$  and is quenched to  $T_2 = T_c - \Delta T$ . The quench can also be characterized by the dimensionless concentration change,  $\theta = \delta C / \Delta C = [(1 + \delta T / \Delta T)^\beta - 1] / 2 \approx (\beta / 2)(\delta T / \Delta T) \approx \frac{1}{6}(\delta T / \Delta T)$ , where the approximate equality holds for small values of  $d$ . Immediately after the quench, within a correlation length of the interface, the concentration is assumed<sup>9</sup> to take its new values and a concentration gradient is established as shown in Fig. 2. This gradient is the driving force of the instability in the SSM; in the Langer and Turski analysis,<sup>6</sup> for a given quench depth, a planar interface is unstable against any disturbances of wave number  $k < k_c$ , where

$$k_c = (\Delta C)^{1/2} [\xi (dC/dz)_\infty]^{1/2} \approx \theta^{1/2} / \xi, \quad (1)$$

the  $z$  direction being perpendicular to the interface. In the linear regime, the disturbances grow as  $e^{i\omega t}$ . If  $\kappa = k / k_c \ll 1$ , then the dispersion relation simplifies to

$$i\omega \approx 4(Dk_c^2)(k_c \xi)^2 (1 - \kappa^2)^2. \quad (2)$$

With the addition of velocity fields and viscous damping by Jasnow *et al.* the range of unstable wave numbers is reduced, though not dramatically. Near the critical point, where the diffusion constant is small, only disturbances of the interface of wave number  $k \leq 0.49k_c$  are unstable at the nominal quench<sup>10</sup>  $\theta \sim 0.1$ . Kawasaki and Ohta further modify the dispersion relation, by including the effects of gravity.<sup>8</sup> In this case, wave numbers near zero are also stabilized.

Following a preliminary report that our experiments failed to show any clear sign of an instability on the interface,<sup>11</sup> several authors began calculations to investigate possible stabilizing effects. Immediately after a quench,

the concentration gradient should begin to relax, and thus remove the driving force of the instability. Calculations by Onuki *et al.*<sup>2</sup> suggest that this extends the time needed to see an instability on the interface to very late times. Ohta<sup>13</sup> has also worked to simplify the full dispersion relation of Kawasaki and Ohta, throwing out all non-Markovian terms. His results imply that for an interfacial instability to be seen, the quench must be quite large ( $\delta T \approx \frac{1}{2} \Delta T$ ); at such large quench depths bulk nucleation is almost instantaneous.

### III. THE EXPERIMENT

For our experiments, we used the binary-liquid mixture isobutyric acid and water (IBW) at near critical composition (62.1 vol. % water).<sup>14</sup> We made use of the property of IBW that the critical temperature responds strongly to changes in pressure, thus allowing the system to be forced more rapidly into the two-phase region by a pressure change (which propagates through the system at the speed of sound) than could be attained by a temperature quench. IBW responds to a pressure quench<sup>15</sup> with  $dT_c/dP \approx -55$  mK/atm, while the local heating<sup>16</sup> is only  $dT/dP \approx 5$  mK/atm.

$T_c$  for IBW is 26.12°C (Ref. 17); a commercially available temperature controller was used to hold the temperature fluctuations within  $\pm 0.3$  mK for periods of hours,  $\pm 1$  mK over 24 h. The pressure could be controlled to about 0.01 atm, and thus quenches as small as 0.5 mK were obtained. Typically our data were taken with  $\Delta T$  ranging from 20 mK to 1.2 K (beyond  $\Delta T \approx 1.3$  K corrections to scaling are required). Quench depths ranged from  $\theta = 1.2 \times 10^{-3}$  to over  $2 \times 10^{-2}$ .

One complicating factor in our search for the interfacial instability is that the bulk system may well nucleate before there is an opportunity to observe any growth on the interface. The rate of nucleation<sup>18</sup> is exponentially dependent on quench depth; except for the work of Onuki *et al.*,<sup>12</sup> available theory is silent on the question of the time scale for the interfacial instability to become macroscopic.

We sought evidence of an instability in several ways. First, the system was observed using a Wild microscope at magnification  $50\times$ . Structures down to 3 microns could be distinguished. For quenches ranging from  $\theta = 1.7 \times 10^{-3}$  to  $2.2 \times 10^{-2}$  we photographed the interface with the microscope.

After microscopy failed to detect any evidence of an instability, we turned to light scattering as a probe which should be more sensitive to the earliest stages of the unstable growth. As is well known, at equilibrium, the interface is always being disturbed by thermal fluctuations, with the energy distributed among the various modes. The equilibrium power spectrum<sup>19,20</sup> for the ripples on the interface is the following:

$$P_k(\omega) \approx -k(k_B T / \pi \omega \rho) \text{Im}[1/D(i\omega\tau_0)], \quad (3)$$

where  $D(S)=0$  is the equilibrium dispersion relation  $\tau_0 = \rho / 2\eta k^2$  and  $\eta$  is the viscosity.

For  $\rho_1 = \rho_2$

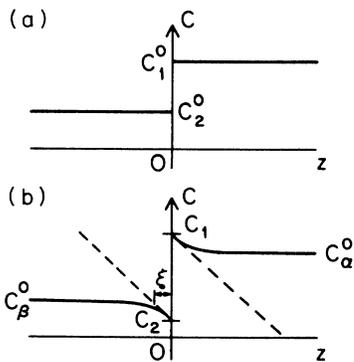


FIG. 2. Concentration vs height above the interface before and after a quench. The gradient at the interface is estimated by  $\delta C / \xi$ .

TABLE I. Predicted growth times from Eq. (2), all for  $k \ll k_c$  (any  $k$  in the ranges observed in our experiment).

$\Delta T = 1.25$ K	$1/i\omega$
$\theta = 0.001$	0.42 sec
$\theta = 0.1$	0.0042 sec
$\Delta T = 0.50$ k	$1/i\omega$
$\theta = 0.002$	450 sec
$\theta = 0.01$	20 sec
$\Delta T = 0.10$ K	$1/i\omega$
$\theta = 0.004$	18 h
$\theta = 0.015$	1.5 h

$$D(S) = y + S^2 + S[1 + (1 + 2S)_+^{1/2}], \quad (4)$$

where  $y = \sigma\rho/8\eta^2k$ .

This power spectrum has been confirmed by measurements of several systems;<sup>19–21</sup> dramatic departures by the interface from this known equilibrium behavior would be an observable feature of the onset of instability. We searched for an instability after quenching by observing the autocorrelation function

$$G_k(\tau) = \int d\omega e^{i\omega\tau} P_k(\omega),$$

at a given angle, looking for a change in the shape of  $G_k(\tau)$  (from decay with time to growth) as a signature of the growth of that mode. We used  $1/i\omega$  from the dispersion relation of Langer and Turski<sup>6</sup> as a rough estimate of the interesting range of correlation times. Table I gives  $1/i\omega$  from the dispersion relation for different values of the parameters ( $\theta, \Delta T$ ) over the range of the experiment for typical values of  $k$ . Our measured  $k$  values were always much less than  $k_c$  and should probe the region of expected instability.<sup>10</sup> For  $\Delta T = 1$  K and  $\theta = 1.0 \times 10^{-3}$ ,  $k_c = 2.2 \times 10^5 \text{ cm}^{-1}$ . Our autocorrelation data were taken for values of  $k$  ranging from  $k = 30$ – $1000 \text{ cm}^{-1}$ ,  $\theta$  ranging from  $5 \times 10^{-3}$  to  $2 \times 10^{-2}$ , and  $\Delta T$  ranging from 100 mK to 1.2 K.

Also, and often at the same time, we sought to see an increase in the intensity of the light scattered from the interface over a range of values of angle  $\alpha$  (for fixed  $\alpha_0$ ). Angles are as defined in Fig. 3. The expected equilibrium intensity<sup>29,21</sup> as a function of wave number and scattering angle is the following:

$$I = 4(k_B T / \lambda^2 \sigma k^2) \cos\alpha [\Phi(\alpha_1, \alpha)]^2 d\Omega, \quad (5)$$

where  $d\Omega$  is the solid angle subtended by the detector and

$$\Phi = [\pi \cos\alpha_1 \sin(\gamma_1 - \alpha_1)] / [\sin\gamma_1 \cos\alpha + \sin\alpha_1 \cos\gamma],$$

for  $\phi = 0$ . The wave number  $k$  is not as simple a function of scattering angle as it is in the case of scattering from the bulk. Here

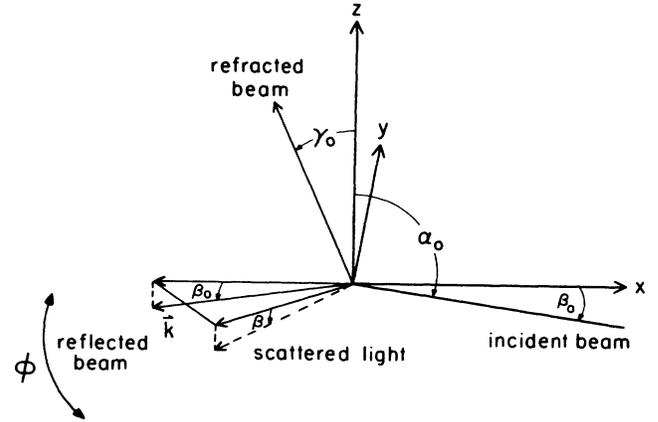


FIG. 3. Light-scattering configuration. The rest position of the interface defines the  $x$ - $y$  plane. The incident, reflected, and refracted beams define the  $x$ - $z$  plane.  $\beta_0 = \alpha_0 - \pi/2$  ( $\beta = \alpha - \pi/2$ ).  $\gamma_0$  is the angle to which the incoming beam is refracted [i.e.,  $n_1 \sin(\pi/2 - \gamma_0) = n_2 \sin(\alpha_0 - \pi/2)$ , where  $n_1$  and  $n_2$  are the indices of refraction of the upper and lower phases, respectively].  $\gamma$  is defined analogously [i.e.,  $n_1 \sin(\pi/2 - \gamma) = n_2 \sin(\alpha - \pi/2)$ ].  $\phi$  is the azimuthal angle measured between the reflected beam and the scattered light.

$$k = Q_0 (\sin^2\alpha + \sin^2\alpha_0 - 2 \sin\alpha \sin\alpha_0 \cos\phi)^{1/2}.$$

( $Q_0 = 2\pi n / \lambda$ , where  $n$  is equal to the index of refraction of the fluid and  $\lambda$  is equal to the wavelength of the incident light.) When  $\phi = 0$ ,  $k = Q_0 |\sin\alpha - \sin\alpha_0| = Q_0 |\cos\beta - \cos\beta_0|$ .

From Fig. 3, one can see that this difference of cosines implies that the light scattering from the interface probes only  $k$  vectors in the plane of the interface; thus, when  $\phi = 0$ , only rather low wave numbers are accessible (from 30–600  $\text{cm}^{-1}$ ) since, for small values of  $\beta$  and  $\beta_0$ ,  $|\cos\beta - \cos\beta_0| \approx |\beta^2 - \beta_0^2|$ . An oscillating mirror was used to allow us to scan this range of values of the scattering angle. Set in the scattering plane ( $\phi = 0$ ), the mirror allowed a very precise setting of  $(\beta_0 - \beta)$  in increments of  $\frac{1}{12}^\circ$ . We observed the intensity for  $k$  values as low as 30  $\text{cm}^{-1}$ , but the geometry of this setup did not allow for measurements of  $k > 600 \text{ cm}^{-1}$ ; higher wave numbers (up to about 4000  $\text{cm}^{-1}$ ) were obtained for measurements not using the mirror. In the higher wave number measurements the count rates were too low to measure autocorrelation functions; intensity measurements were only possible by keeping the photomultiplier dark current below 50 counts/sec. In the oscillating mirror measurements, we observed the full angular range in an interval of 2.25 sec and then repeated the measurement every 9 sec until bulk nucleation set in (which ranged from 5–120 min depending on  $\Delta T$  and the depth of the quench). We then constructed average intensities for various time intervals, comparing them with the equilibrium data.

Like many other nonequilibrium experiments (e.g., Maher, Easwar, Goldberg, and Joshua<sup>22</sup>), our system had to be far more carefully prepared than an experiment to

be conducted at equilibrium in order for results to be reproducible. It is still not clear what aspects of stirring the sample and allowing it to come to equilibrium were most sensitive in reaching a reasonable equilibrium, or what effect impurities on the interface may have had on the ripplon spectrum. However, the sample was carefully filtered and was exceptionally clean; our stirring was far more vigorous and our temperature control far more careful overnight (as the sample came to equilibrium) than that needed for equilibrium experiments on the bulk fluids.

#### IV. DATA ANALYSIS AND RESULTS

As mentioned above, in all our observations with the microscope, no growth was seen on the interface in the time before nucleation in the bulk obscured the view. This time was for some cases only a few minutes and for others more than one hour. The driving force for the interfacial instability is of course related to the energetics of nucleation, and so the time scales for the two could well change in the same way with quench depth. Quenches by temperature change (as opposed to changing  $T_c$  with a pressure change) were also observed and never exhibited any visible interfacial roughening.

Much as for the results from our microscope investigation, the light-scattering data showed little change in the time before the onset of bulk nucleation. Whenever changes were observed in the correlation function of the light scattered from the interface to a specific angle, changes of the same time scale could also be seen when we observed light scattered from a beam directed through only one of the phases (avoiding the interface) (see Fig. 4).

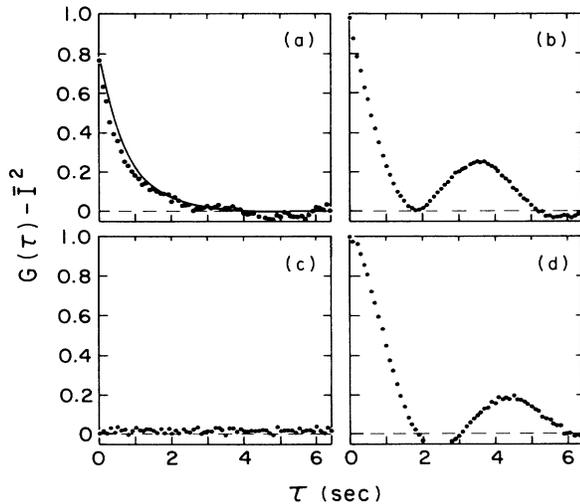


FIG. 4. Correlation functions before and 45 min after a quench for the following. (a) Scattering from the interface at equilibrium ( $\Delta\beta=1.1^\circ$ ,  $k=250\text{ cm}^{-1}$ ). The prediction of  $G(\tau)$  from theory (see Ref. 19) is included. (b) Scattering from the interface, after a quench,  $\theta=1.3\times 10^{-3}$ . (c) Scattering from the bulk at equilibrium,  $1.1^\circ$  from transmitted beam. (d) Scattering from the bulk, after a quench,  $\theta=1.2\times 10^{-3}$ .

The characteristic time for the growth of these intensity-intensity autocorrelation functions was always compatible with that expected from previous reports of nucleation.<sup>23</sup> Autocorrelation functions measured at equilibrium and those measured before the onset of nucleation were in good agreement with Eq. (5) above.

Similarly, the intensity measurements at large wave number ( $100\leq k\leq 4000\text{ cm}^{-1}$ ) showed no change from before to after the quench for any quench depth. As was mentioned above, the photon counting rate at these wave numbers was very low (typically 200–400 counts/sec superimposed on a dark current background of 40–50 counts/sec), so an intensity change of less than 20% would not be observable in this measurement.

Only the intensity data scanned over small- $k$  values for small values of  $\theta$  showed any consistent changes not attributable to nucleation. Typical changes are shown in Fig. 5 where an equilibrium intensity pattern [in good agreement with Eq. (5)] is compared with a pattern observed after the quench. In these cases, the intensity at low- $k$  values *decreased*, while at high  $k$ , it *increased*. These changes were not seen developing with time, but appeared as soon as the interface had settled from the pressure jump ( $\leq 9$  sec). The intensity profiles then maintained about the same shape from that time until nucleation set in. Consistent results were seen when a temperature

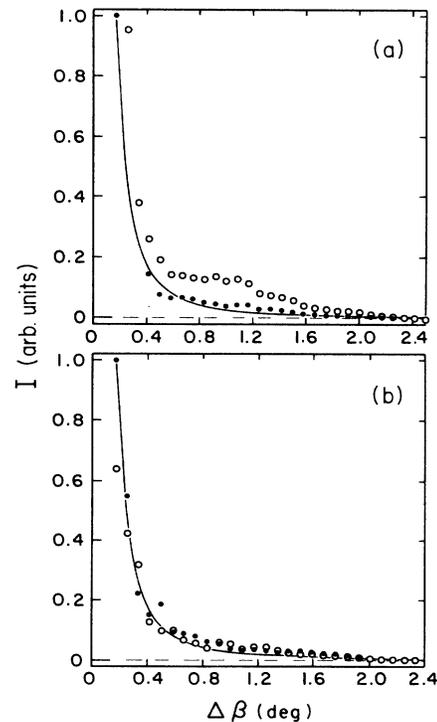


FIG. 5. (a) Scan data showing the change in the intensity profile for a quench of  $\theta=1.1\times 10^{-3}$  and  $\Delta T=1.2\text{ K}$ . (b) Scan data showing the lack of any change in the intensity profile for a quench of  $\theta=2.3\times 10^{-3}$  and  $\Delta T=1.1\text{ K}$ .

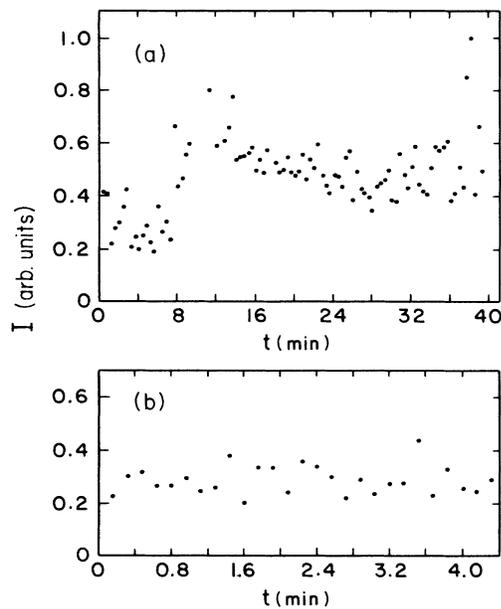


FIG. 6. Intensity vs time for two different runs at  $k=250 \text{ cm}^{-1}$ . (a) At  $t=8 \text{ min}$  the system was quenched with  $\theta=1.1 \times 10^{-3}$ . (b) At  $t=2 \text{ min}$  the system was quenched with  $\theta=2.3 \times 10^{-3}$ .

quench of small  $\theta$  was substituted for the pressure quench.

When the quench depth  $\theta$  was larger than  $1.5 \times 10^{-3}$  this intensity change was never observed; Fig. 6 shows the time development of a typical intensity measurement from before to after a quench for small  $k$  and large and small  $\theta$ . If this effect, seen at small  $\theta$  and not when  $\theta$  is increased, is to be attributed to the early stages of instability, a critical wave number must be moving through our observable range. In the SSM,  $k_c$  and the fastest growing wave number  $k_M$  ( $\sim k_c/\sqrt{3}$  for  $k_c\xi \ll 1$ ) decrease when  $\theta$

and  $\Delta T$  decrease. Our observed critical wave number is much smaller than the SSM model expectation and appears to have instability above and not below. Thus it would have to be a lower critical wave number, such as that predicted by Ohta<sup>13</sup> to arise from gravity stabilizing the small wave numbers, although Ohta's lower cutoff has no  $\theta$  dependence. When the power in a given mode does grow after a shallow quench, its failure to continue to grow during the time of observation presumably indicates that a relaxation mechanism is damping the instability and preventing it from growing very far.

Thus while this critical binary-liquid mixture would seem to have the advantage of being a close realization of an SSM system which one can observe as it goes unstable, viscous effects, which are absent from the corresponding solidification problem, and the effects of the driving force decaying, or both, work to prevent any instability on the interface from becoming visible.

Also worth reporting are those effects seen when a "reverse quench" was applied (moving the system closer to the critical point). The bulk fluids are stable; no nucleation occurs. Within five minutes after the pressure is applied or the temperature is raised, however, the light reflected off the interface is deformed, with flares, rings, or spots appearing for several seconds and then disappearing. These effects continue for tens of minutes to hours. These effects were only noted and photographed and not measured quantitatively. Their origin is not understood, since all available theories predict that the interface should be stable.

#### ACKNOWLEDGMENTS

We gratefully acknowledge helpful discussions with W. I. Goldberg, D. Jasnow, T. Ohta, and A. Onuki. We also appreciate R. Tobin's fabricating our glass sample holder. This experiment was supported by the U. S. Department of Energy under Grant No. DE-FG02-84ER45131.

<sup>1</sup>W. W. Mullins and R. F. Sekerka, *J. Appl. Phys.* **34**, 323 (1963).

<sup>2</sup>J. S. Langer, *Rev. Mod. Phys.* **52**, 1 (1980).

<sup>3</sup>E. Ben-Jacob, N. Goldenfeld, J. S. Langer, and G. Schon, *Phys. Rev. Lett.* **51**, 1930 (1983); D. A. Kessler, J. Koplik, and H. Levine, *Phys. Rev. A* **30**, 28 20 (1984); D. L. Meiron, *Phys. Rev. A* **33**, 2704 (1986).

<sup>4</sup>T. A. Witten and L. M. Sander, *Phys. Rev. Lett.* **47**, 1400 (1981); *Phys. Rev. B* **27**, 5685 (1983); D. Bensimon, L. P. Kadanoff, S. Liang, B. Schraiman, and C. Tang (unpublished); T. Vicsek, *Phys. Rev. Lett.* **53**, 2281 (1984); L. A. Turkevich and H. Scher, *ibid.* **55**, 1026 (1985); L. P. Kadanoff, *J. Stat. Phys.* **39**, 267 (1985); S. K. Sarkar and M. H. Jensen (unpublished); H. Guo and D. Jasnow (unpublished), E. Ben-Jacob, N. D. Goldenfeld, J. Koplik, H. Levine, T. Mueller, and L. M. Sander, *Phys. Rev. Lett.* **55**, 1315 (1985).

<sup>5</sup>F. Heslot and A. Libchaber, *Phys. Scr. T* **9**, 126 (1985); M. E. Glicksman and N. B. Singh, *American Society for Testing and Materials, Special Technical Publication* 890, edited by M.

E. Fine and E. A. Stark (ASTM, Philadelphia, 1986).

<sup>6</sup>J. S. Langer and L. A. Turski, *Acta Metall.* **25**, 1113 (1977).

<sup>7</sup>D. Jasnow, D. A. Nicole, and T. Ohta, *Phys. Rev. A* **23**, 3192 (1981).

<sup>8</sup>K. Kawasaki and T. Ohta, *Physica* **118A**, 175 (1963).

<sup>9</sup>The assumption that diffusion will immediately carry the interface to the new equilibrium is not obvious for solids (see, e.g., P. G. Sherron, *Trans. Met. Soc. AIME* **233**, 736 (1965) but is probably reasonable for this liquid system with its large correlation length and qualitatively reasonable rate of growth of nucleated droplets (see, e.g., Ref. 22).

<sup>10</sup>The work of Ref. 7 suggests more generally that the maximum wave number for instability decreases as  $\theta^{1/2}$ .

<sup>11</sup>S. N. Rauseo and J. V. Maher, *Bull. Am. Phys. Soc.* **32**, 556 (1985).

<sup>12</sup>A. Onuki, K. Sekimoto, and D. Jasnow, *Prog. Theor. Phys.* **74**, 685 (1985).

<sup>13</sup>T. Ohta (private communication).

<sup>14</sup>S. C. Greer, *Phys. Rev. A* **14**, 1770 (1976).

- <sup>15</sup>N.-C. Wong and C. M. Knobler, *J. Chem. Phys.* **66**, 4707 (1977).
- <sup>16</sup>G. Morrison and C. M. Knobler, *J. Chem. Phys.* **65**, 5507 (1976).
- <sup>17</sup>B. Chu, F. J. Schoenes, and W. I. Kao, *J. Am. Chem. Soc.* **90**, 3042 (1968).
- <sup>18</sup>E. D. Siebert and C. M. Knobler, *Phys. Rev. Lett.* **52**, 1133 (1984).
- <sup>19</sup>E. S. Wu, Ph.D. thesis, Cornell University, 1973 (unpublished).
- <sup>20</sup>M. A. Bouchiat and J. Meunier, *J. Phys. (Paris) Colloq.* **33**, C1-141 (1972).
- <sup>21</sup>John S. Huang, Ph.D. thesis, Cornell University, 1969 (unpublished).
- <sup>22</sup>J. V. Maher, N. Easwar, W. I. Goldberg, and M. Joshua, *Phys. Rev. Lett.* **49**, 1850 (1984).
- <sup>23</sup>S. Krishnamurthy and W. I. Goldberg, *Phys. Rev. A* **22**, 2147 (1980).