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Evidence for Coupling of Velocity and Composition Fluctuations in a Binary Liquid Mixture

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A critical mixture of isobutyric acid and water was quenched from the one-phase region into the two-phase region and, after the spinodal ring was well developed, a reverse quench returned the system to the one-phase region. Light-scattering measurements for this process exhibit a clearly nondiffusive relaxation which, at least for early times after the quench reversal, is in good agreement with Ruiz's scheme for the coupling of velocity and composition fluctuations.

In a recent series of papers Ruiz and Nelson[1,2] have discussed the properties of "active" turbulent mixing of two fluids; i.e., mixing which is observably affected by coupling between velocity and composition fluctuations. As a simple special case of velocity-composition coupling, Ruiz[3] has performed an approximate calculation for the behavior of the relaxation of very large composition fluctuations under conditions where the mass diffusion coefficient, D, becomes sufficiently small that active coupling to the velocity field can compete with diffusive relaxation.

In this Letter we report the results of an experiment designed to look for active coupling effects near the critical point in a binary fluid mixture. In each measurement a critical mixture of isobutyric acid and water, initially at equilibrium at temperature T_1 in the one-phase region, was quenched to temperature T_2 in the two-phase region (at time $t = -t_0$), allowed to remain at T_2 until the spinodal light scattering maximum reached a wave number $k_m \sim 2000$ cm^{-1}, and then abruptly returned to T_1 (at time $t = 0$). Under these circumstances, Ruiz's primary prediction[3] is that

$$\ln k_m(t) = \tfrac{1}{2}\ln\frac{A}{2D} + \frac{\alpha}{2D\nu}C_{\text{tot}}(t), \qquad (1)$$

where $k_m(t)$ is the time-dependent wave number of the maximum in the light-scattering angular distribution, A is a constant of the motion, $t = 0$ is the time of return to the one-phase region, ν is the kinematic viscosity, and α is the coefficient of the composition-gradient-squared term in the Landau-Ginzburg Hamiltonian. $C_{\text{tot}}(t)$ is the global strength of the concentration fluctuations, $\psi_{\vec{k}}(t)$; i.e.,

$$C_{\text{tot}}(t) \equiv \frac{1}{2}\int\frac{d^3k}{(2\pi)^3}\langle|\psi_{\vec{k}}(t)|^2\rangle.$$

A quantitative test of Ruiz's prediction requires a good estimate of the parameter $R \equiv \alpha C_{\text{tot}}(t = 0)/2D\nu$. One renormalization-group calculation,[4] which uses an Ornstein-Zernike form for the susceptibility of the order parameter, gives $R = B(\epsilon_2/\epsilon_1)^{2\beta}$ where B is of order unity, $\epsilon_2 = (T_c - T_2)/T_c$, $\epsilon_1 = (T_1 - T_c)/T_c$, and $\beta \simeq \tfrac{2}{3}$. This result is readily obtained on use of $\alpha = \epsilon^2/\chi\rho$, where ρ is the mass density and χ is the order-parameter susceptibility. Taking $\chi \simeq \epsilon^{-\gamma}/k_B T$, $D(T_1) = k_B T/6\pi\nu\rho\,\xi(T_1)$ [where the correlation length $\xi(T) = (3.57\text{ Å})\epsilon^{-0.613}$ for isobutyric acid + water],[5] $C_{\text{tot}}(t = 0) \simeq \epsilon_2^{2\beta}$, and $\nu = 2\beta$ gives $B = 3\pi$. An alternative renormalization-group calculation[6] of R yields a result which is similar in temperature dependence and in order of magnitude,

viz., $R \approx 5\sigma(T_2)\xi(T_2)\xi(T_1)/k_B T_c$ where the surface tension is $\sigma \simeq k_B T/\xi^2$. Using the latter estimate of R we can recast Eq. (1) as

$$\ln\frac{k_m(0)}{k_m(t)} = a\left(\frac{\epsilon_2}{\epsilon_1}\right)^{2\beta}\left[1 - \frac{C_{tot}(t)}{C_{tot}(0)}\right], \qquad (2)$$

where $a = 2.8$.

The measurements were performed by directing a laser beam ($\lambda = 6328$ Å) through a reentrant cell of thickness 1 mm and reflecting the emerging light from a mirror into a photomultiplier. The mirror was rotated through an angular range of ±10° about the orientation which directed the central beam into the photomultiplier. In this way the photomultiplier was used to measure angular distributions. Each angular distribution measurement required 1 sec and successive measurements were separated by integral multiples of 4 sec. The laser output and the turbidity were continuously measured by directing the small fractions of the beam reflected from thin glass slides (fixed at the input and output points of the cell's temperature bath) onto a laser intensity meter and a photodiode, respectively. The quenches and their reversals were accomplished not by changing temperature from T_1 to T_2 and back but rather by abruptly varying the pressure applied to the liquid mixture. Since it is known[7] that changes in pressure in isobutyric acid-water mixtures change the critical temperature T_c by ~57 mK/atm and T hardly at all, these pressure changes are equivalent to changing the temperature. In the discussion below we shall consistently use the temperature notation defined above. Signals from the photomultiplier and photodiode were digitized and used to construct angular distributions proportional to the structure function $S(k,t) \equiv \langle |\psi_{\vec{k}}(t)|^2 \rangle$.

The temperature control on the sample's water bath kept temperature fluctuations within ± 0.2 mK over periods of hours. Compromise was necessary to keep fractional temperature uncertainties as small as possible and yet stay close enough to T_c to keep D very small ($D = 2.51 \times 10^{-6} \times \epsilon^{0.6}$ cm²/sec).[8] We have chosen to make measurements with $T_1 - T_c = 2$, 4 and 6 mK; thus in the one-phase region, the equilibrium toward which our reverse-quenched systems relax is characterized by $\epsilon_1 \sim 10^{-5}$ and $D \sim 5\times10^{-9}$ cm²/sec.

The behavior of the system was investigated for quench depths $T_c - T_2 = 2$, 4, 6, and 8 mK. The time scales for spinodal decomposition are known to be quite different for such different quench depths; in each case we measured angular dis-

tributions as the spinodal light-scattering ring developed and reversed the quench when k_m decreased to $\simeq 2000$ cm^{-1}. Up to the reversal of quench, the system always showed the behavior previously reported for spinodal decomposition in this system.[9] In particular the structure factor was of the scaling form $S(k,t) = k_m^{-3}(t)F(k/k_m(t))$, where $F(x)$ is independent of time and quench depth.

To achieve reproducible results in this experiment, it was necessary to stir the mixture thoroughly and then wait for a prolonged interval prior to the quench. The requisite minimum equilibration time was ~25 min, which is much longer than the viscous damping time, τ_d (taking the viscosity of the mixture to be ~10^{-2} poise, we estimate τ_d to be 2 min) and also much longer than the equilibration time required for normal spinodal decomposition experiments. In determining that our results do not depend on this time, we have found that results obtained with our stirring procedure agree well with results obtained after stirring the system 20 mK above T_c, and then leaving the system at T_1 for hours before quenching. It would be very desirable to understand why sloppier stirring methods are inadequate for the present experiment when they were perfectly adequate for spinodal decomposition studies.

The results of the present experiment are in good agreement with the only previously available measurements,[7] in which Wong and Knobler reported that, after reversal of quench, the dimensionless wave number for maximum scattering, $q_m = k_m\xi(\epsilon)$, and the dimensionless time, $\tau = D/\xi^2 t$, were related by $q_m \sim \tau^{-0.1}$. We find a slight concavity to a plot of $\ln q_m$ vs $\ln\tau$ but the concave curves are never far from a straight line of slope ~-0.15.

Our main experimental result is shown in Fig. 1 where $\ln[k_m(0)/k_m(t)]$ is plotted against

$$F \equiv (\epsilon_2/\epsilon_1)^{2\beta}[1 - C_{tot}(t)/C_{tot}(0)];$$

we have approximated $C_{tot}(t)$ with the product of $k_m(t)$ and the turbidity, $T(t)$. For the early stages $[T(t) \gtrsim 0.3T(0)]$, all measurements fall on a straight line of slope ~0.2. At late times each curve shows a dramatic departure from linearity; note that increasing time corresponds to increasing F. We have not found an empirical relation to make both early- and late-time data fall on the same curve.

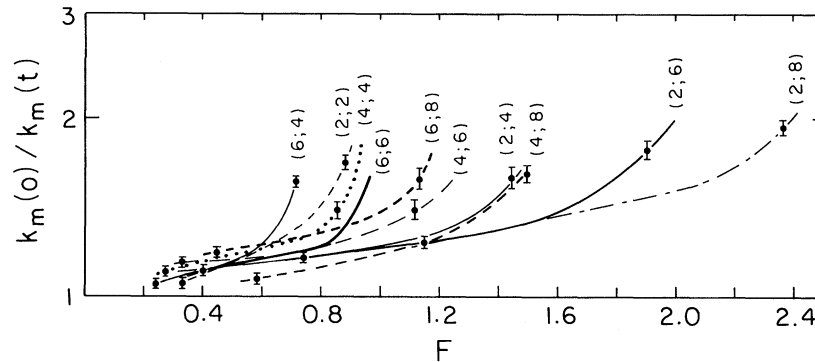The early-time data appear to support Ruiz's

FIG. 1. Each curve represents the result of a set of measurements at the indicated combination $(T_1 - T_c;\ T_c -T_2)$. The error bars show typical standard deviations. F is defined in the text.

predictions[3] strongly. The empirical slope R $\simeq 0.2$ is slightly more than an order of magnitude smaller than the renormalization-group prediction of 2.8, but this is not at all a shocking disagreement. The discrepancy may arise from Ruiz's dropping factors of order unity in his analysis.[3] The departures from scaling at late times are more difficult to assess. It is clear that Eq. (2) was never intended to be used at very late times; no noise term is included in Ruiz's driving force so that at the very least his results cannot be applied near equilibrium where thermal fluctuations are important. On the other hand, with the empirical value $R = 0.2$, Eq. (2) places very severe limits on the ratio $q_m(0)/q_m(t)$; i.e., this ratio, which clearly must diverge at very late times since $q_m(\infty) \to 0$, is not allowed by Eq. (2) to exceed ~1.2 if $\epsilon_1/\epsilon_2 \sim 1.0$. The departures from Eq. (2) tend to appear when the turbidity has dropped to ~30% of its value at $t = 0$. This occurs at dimensionless times $\tau = 50$–200 depending on ϵ_1. Values of the slope R for short-time data and values of the dimensionless time, τ, and the turbidity ratio, $T(\tau)/T(0)$, measured at the break from Eq. (2) are listed in Table I for various values of ϵ_1 and ϵ_2. While there is a significant time interval within which Eq. (2) is successful, the dramatic "late-time" departures occur long before the system approaches equilibrium even though the crucial dimensionless ratio is $\nu/D \gtrsim 10^6$.

An alternative way to view the results of the present experiment is shown in Fig. 2 where several light-scattering angular distributions are displayed for the case $T_1 - T_c = 2$ mK, $T_c - T_2 = 6$ mK. It is instructive to compare the measurements in Fig. 2 with calculations based on the assumption that the composition fluctuations built up before $t = 0$ will relax diffusively. Such calcu-

lations are shown along with the measured angular distributions. In this simple diffusion model the $t = 0$ angular distribution is accepted as an initial condition and the scattering at each wave number is assumed to decrease as $\exp(-2Dk^2 t)$ where D was adjusted to fit the data from 1000 to 2000 cm^{-1} in an ensemble of similar measurements. The data show clear departures from the simple diffusion picture. While these departures are not unexpected, the calculation allows one to classify the observed phenomena. First, the decay at wave numbers in the range $0.6\,k_m(0) \lesssim k \lesssim k_m(0)$ is roughly exponential but sufficiently slow that the diffusion constant used in the calculation had to be adjusted to 40% of the accepted[8] equilibrium value. Second, the decay at smaller wave numbers $[\simeq 0.4\,k_m(0)]$ is initially much faster than would be predicted by the accepted equilibrium value while later the scattering at these wave numbers almost entirely ceases to change.

TABLE I. For each combination of $T_1 - T_c$ and $T_c -T_2$, column 3 lists the empirical values of the slope, a, extracted by fitting the short-time data by Eq. (2). Columns 4 and 5 list the dimensionless time and the turbidity ratio when the data depart from linearity.

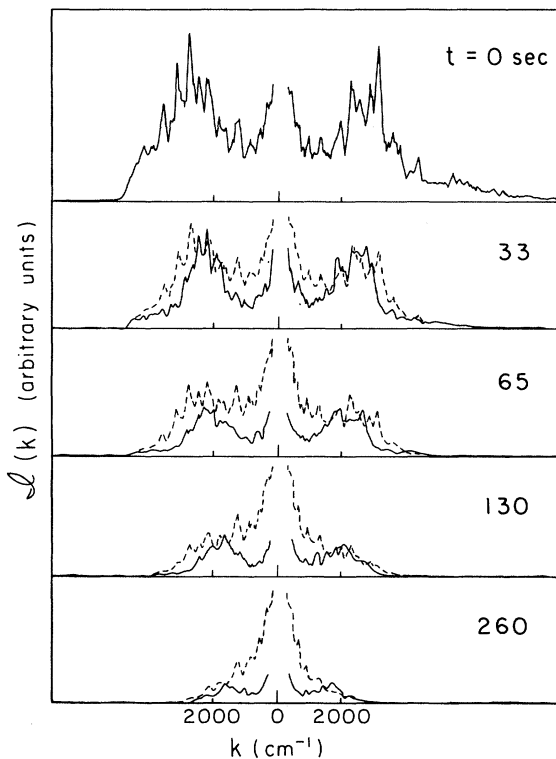| $T_1 - T_c$ mK	$T_c - T_2$ mK	Slope, a	τ	$T(\tau)/T(0)$
2	2	0.41 ± 0.05	~55	0.39
2	4	0.23 ± 0.03	50	0.27
2	6	0.15 ± 0.04	60	0.38
2	8	0.20 ± 0.03	40	0.27
4	4	0.24 ± 0.06	140	0.26
4	6	0.17 ± 0.04	120	0.31
4	8	0.18 ± 0.05	140	0.26
6	2	0.29 ± 0.04	200	0.31
6	4	0.18 ± 0.05	220	0.22
6	8	0.21 ± 0.05	200	0.33

FIG. 2. Angular distributions for light scattering just as the quench is reversed and for several later times. Solid curves represent measured data while the dashed curves result from the diffusion calculations described in the text. In the range of k where the forward beam saturates the photomultiplier, the data are not shown.

The rapid early decay and subsequent stability at these small wave numbers keeps the spinodal ring from disappearing at late times as can be seen from Fig. 2.

In summary, it is clear that the experiment presented herein departs significantly from the expectations of simple diffusion models and thereby shows evidence for an importance of hydrodynamic effects in the relaxation of large composition fluctuations. These observed effects appear to be substantially in agreement with the predictions of Ruiz[3] until the diameter of the light-scattering ring has shrunk to ~80% of its initial ($t = 0$) value and the turbidity is ~30% of its initial value.

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Interference Phenomena in the Theory of Daumas-Hérold Domain Walls

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A theoretical study of dislocations in intercalation compounds reveals that the local deformation of the host near an intercalant island exhibits damped spatial oscillations, resulting in strong interference effects in the elastic energy of Daumas-Hérold domain walls. Explicit calculations for stage 2 predict that a large energy barrier must be overcome before two domains with matching intercalant layers can merge, while staggered domains should bind to each other. Experimental implications are discussed.

There has been for many years a widespread interest in polycrystalline systems and domain structures of every sort because of their pervasiveness in nature and their practical importance, and because of their fundamental appeal as a relatively well defined example of metastability. Yet the list of cases for which both tractable and realistic models of domain boundaries could be