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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.

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In a recent series of papers Ruiz and Nelson\(^1\) 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\(^2\) has performed an approximate calculation for 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 \(k_m \approx 2000\) cm\(^{-1}\), and then abruptly returned to \(T_1\) (at time \(t = 0\)). Under these circumstances, Ruiz's primary prediction\(^3\) is that

\[
\ln k_m(t) = \frac{1}{2} \ln \frac{A}{2D} + \frac{\alpha}{2Dv} C_{\text{tot}}(t),
\]

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, \(\nu\) is the kinematic viscosity, and \(\alpha\) 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, \(\psi^2(t)\); i.e.,

\[
C_{\text{tot}}(t) = \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \langle |\psi^2(t)|^2 \rangle.
\]

A quantitative test of Ruiz's prediction requires a good estimate of the parameter \(R = \frac{\alpha C_{\text{tot}}(t = 0)}{2Dv}\). One renormalization-group calculation,\(^4\) which uses an Ornstein-Zernike form for the susceptibility of the order parameter, gives \(R = B(\epsilon_c/\epsilon_3)\) where \(B\) is of order unity, \(\epsilon_c = (T_c - T_2)/T_2\), \(\epsilon_3 = (T_1 - T_2)/T_2\), and \(\beta = \frac{\alpha/2}{4}\). This result is readily obtained on use of \(\alpha = \epsilon^2/\chi \rho\), where \(\rho\) is the mass density and \(\chi\) is the order-parameter susceptibility. Taking \(\chi = \epsilon^{-7}/k_B T\),

\[
D(T_c) = k_B T/6\pi \rho \xi(T_c) [\text{where the correlation length} \xi(T) = (3.5\text{ Å}) \epsilon^{-6.63} \text{ for isobutyric acid + water}]\]

\(C_{\text{tot}}(t = 0) \approx \epsilon_2^{1/2}\), and \(\nu = 2B\) gives \(B = 3\pi\). An alternative renormalization-group calculation\(^5\) of \(R\) yields a result which is similar in temperature dependence and in order of magnitude,
\[ R = 50(T_1)'(T_1)/k_bT_c \]

where the surface tension is \( \sigma = k_bT/\ell^2 \). Using the latter estimate of \( R \) we can recast Eq. (1) as

\[ \ln \kappa_m(t) = a \left( \frac{\epsilon_1}{\epsilon_2} \right)^{\frac{2.8}{2}} \left[ 1 - \frac{C_{10}(t)}{C_{10}(0)} \right], \]

where \( a = 2.8 \).

The measurements were performed by directing a laser beam (\( \lambda = 6328 \text{ Å} \)) through a reentrant cell of thickness 1 mm and reflecting the emerging light from a mirror into a photomultiplier. The mirror was rotated through a range of \( \pm 10^\circ \) 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 fragments 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 \( \sim 57 \) 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

\[ S(k, t) = \langle |\mathbf{q} + \mathbf{z}(t)|^2 \rangle. \]

The temperature control on the sample’s water bath kept temperature fluctuations within \( \pm 0.2 \) 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 (\( D = 2.51 \times 10^{-6} \times \epsilon_{10.6} \) cm\(^2\)/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 \( \epsilon_1 = 10^{-5} \) and \( D = 5 \times 10^{-9} \) cm\(^2\)/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-

\[ \lim_{t \to \infty} \frac{\kappa_m(t)}{k_m(t)} = \lim_{t \to \infty} \frac{C_1(t)}{C_0(t)} \]

and obtained the following results:

\[ F = \frac{(\epsilon_1/\epsilon_2)^{2.8}}{1 - \frac{C_{10}(t)}{C_{10}(0)}}; \]

we have approximated \( C_{10}(t) \) with the product of \( \kappa_m(t) \) and the turbidity, \( T(t) \). For the early stages \( T(t) \approx 0.3T(0) \), 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
predictions\textsuperscript{3} strongly. The empirical slope $R \approx 0.2$ 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.\textsuperscript{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 $\approx 1.2$ if $\epsilon_\iota/\epsilon_\vee \approx 1.0$. The departures from Eq. (2) tend to appear when the turbidity has dropped to $\approx 30\%$ of its value at $t = 0$. This occurs at dimensionless times $\tau = 50 - 200$ depending on $\epsilon_\iota$. Values of the slope $R$ for short-time data and values of the dimensionless time, $\tau$, and the turbidity ratio, $T(\tau)/T(0)$, measured at the break from Eq. (2) are listed in Table I for various values of $\epsilon_\iota$ and $\epsilon_\vee$. 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 $\nu/D \approx 10^9$.

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 calculations 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 $\exp(-2Dk^2t)$ 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 equilibrium value. Second, the decay at smaller wave numbers [$\approx 0.4 k_m(0)$] 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.

![Graph](https://via.placeholder.com/150)

**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.

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

**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.
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\(^1\) 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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\(^3\)R. Ruiz, to be published (two papers).
\(^4\)R. Petschek, private communication.
\(^6\)T. Ohta, private communication.

Interference Phenomena in the Theory of Daumas-Hérod 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-Hérod 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.

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There has been for many years a widespread interest in polycrystalline systems and domain structures of every sort because of their pervasive 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