Spinodal Decomposition in a Binary Fluid

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(Received 21 December 1992)

Light scattering has been used to study a mixture of 3-methylpentane and nitroethane undergoing spinodal decomposition. The scattered intensity has been measured in absolute units allowing the first test of theory with no adjustable parameters. The measured structure factor does not evolve according to theory even when the initial fluctuations are taken into account. We believe the reason is that the evolving concentration field causes the sample temperature to change continuously throughout the decomposition process.

PACS numbers: 64.75.+g, 05.70.Jk, 64.60.Ht

Spinodal decomposition is the process whereby a fluid, fluid mixture, or alloy suddenly quenched into the unstable region lying within the system's two-phase region undergoes phase separation. This process has been the subject of intensive theoretical [1-7] and experimental [8-12] effort for over 30 years and has served as a testing ground for the development of the most fundamental ideas regarding the behavior of systems far from equilibrium. Theory predicts the temporal evolution of the scaled structure factor $\tilde{S}(q,\tau)$ as a function of the scaled wave vector, $q \equiv k\xi_-$, and dimensionless time, $\tau \equiv (k_BT/6\pi\eta\xi_-^3)t$, following such a quench [4]. Here k is the actual scattering wave vector, ξ_- is the equilibrium correlation length and η the viscosity, both at the final temperature, and t is the time after the quench. The structure factor is scaled by the $k=0$ limit of its equilibrium value at the final temperature. Comparison of experiment with theory, thus, demands not only accurate control of temperature but also accurate knowledge of the relevant system parameters as functions of temperature. To our knowledge, no such comparison, free of adjustable parameters, has been made to date.

We have measured the angular distribution and intensities of scattered light in absolute units for a series of quenches performed on a mixture of 3-methylpentane and nitroethane (3MP+NE) at the critical concentration. Quench depths ranging from 116 μK to 20.6 mK below the critical temperature, $T_c \simeq 26.85\,°\mathrm{C}$, have been studied for reduced times in the range $0.2 \le \tau \le 100$. We have compared the results for $\tilde{S}(q,\tau)$ with the best currently available theory, a self-consistent version [13] of the treatment of Kawasaki and Ohta [4]. We find that $\tilde{S}(q,\tau)$ evolves much more rapidly than theory predicts; for example, by the time $\tau=10$ the peak in the data is about 3 times as large as predicted. We believe this is primarily the result of assuming that the decomposition process is isothermal [2], but, because the time for thermal diffusion to occur throughout the sample is long compared to that for mass diffusion to occur over a correlation length, it is actually adiabatic. As the sample decomposes, heat of mixing is released, and the sample temperature evolves back toward the critical temperature [7]. Consequently, the very earliest stages of decomposition occur at a temperature further below T_c than the final temperature, which results in the process being more rapid than expected.

Figure 1 is a schematic of the apparatus. The sample was contained in the central region (dotted) of diameter 3.33 cm and length 2.00 cm, between two thin (0.23 mm) flexible glass windows. The two chambers adjacent to the sample were filled with *o*-xylene which has almost exactly the same value of $(\partial T/\partial P)_S$ as the sample. Its pressure and, thus, that of the sample, was controlled by a feedback control system involving a solenoid activated piston, which could change the pressure by 0.07 MPa in 5 ms. Quenches were performed by suddenly lowering the pressure, which decreased both T_c and the temperature of the sample and the *o*-xylene, with a net effect of $d(T-T_c)/dP \simeq 150$ mK/MPa.

Light scattered at angle θ was imaged into a ring of diameter $f\tan\theta$ in the focal plane of the lens of focal length

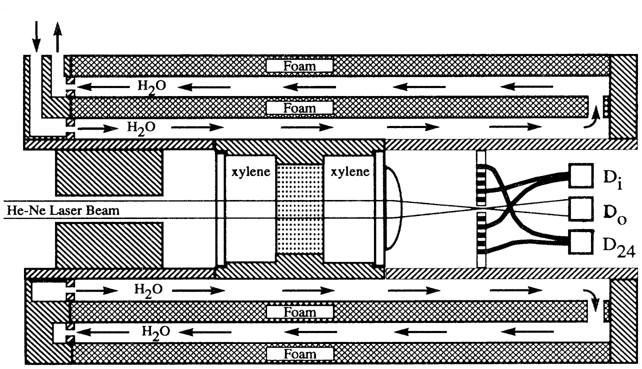

FIG. 1. Cross-sectional view of the cylindrical apparatus. The 3MP+NE sample is contained in the dotted region. The arrows indicate the flow direction of the water used to control sample temperature. The sample is bounded by 0.23 mm thick flexible windows in the axial direction, and both the sample and the *o*-xylene in the adjacent chambers are quenched together to minimize axial heat flow. The lens maps light scattered at a given angle into a circle in a plane containing concentric rings of optical fibers leading to detectors D_1-D_{24}.

f. An array of 24 concentric rings composed of 0.5 mm diam optical fibers was placed in the focal plane and centered on the focused transmitted beam, which passed through a 1.0 mm diam hole in the center of the array and fell on silicon photodiode, D_0. Identical detectors, D_1–D_{24}, were used to measure the scattered optical power collected by each of the rings of fibers. The range of scattering angles was $0.7° \leq \theta \leq 13°$, corresponding to $1720\ \text{cm}^{-1} \leq k \leq 30600\ \text{cm}^{-1}$. Each ring had a spread in θ of ±0.14°. The entire detector array could be sampled at a rate as great as once every 1.0 ms to determine $S(k,t)$.

The sample temperature was controlled by a circulating water bath, as shown in Fig. 1, and was stable to $\pm 15\ \mu\text{K}$(rms) per 24 h. Measurements of $S(k)$ made as a function of temperature in the one-phase region served to calibrate the apparatus and determine the system parameters including T_c, which varied linearly with time at a rate of 11 μK/h due to diffusion of xylene through the gaskets used to seal the thin windows. Simultaneous measurement of the turbidity served to determine the absolute scattering amplitude or susceptibility to ±1%. The susceptibility χ_+ and correlation length ξ_+ in the one-phase region were very consistent with the best known values [14] for the exponents γ and ν and their amplitudes Γ_0^+ and $\xi_0^+ = 2.207$ Å, together with the width of the coexistence curve, B, agreed with the theoretical value [15] for the ratio $\xi_0^3\Gamma_0/B^2$ to within 1%. We related χ_+ and ξ_+ to the values below T_c, χ_- and ξ_-, using the universal amplitude ratios [15], $\Gamma_0^+/\Gamma_0^- = 4.95$ and $\xi_0^+/\xi_0^- = 1.96$. We took values for $\eta(T)$ from Clerke *et al.* [16].

Preceding each subcritical quench a supercritical quench to $T \simeq T_c + 0.5$ mK was performed. The scattered light served as an extremely sensitive ($\sim 4\ \mu$K) measure of the actual value of $T - T_c$ achieved in this quench. We then numerically integrated the equation

$$\Delta P = \int_{(T-T_c)_s}^{(T-T_c)_f} \frac{d(T-T_c)}{(\partial T/\partial P)_S - dT_c/DP}$$

to determine how much *additional* pressure change would be required to reach the desired value of $T - T_c$, $(T - T_c)_f$, given the value $(T - T_c)_s$ achieved by the supercritical quench. Without this procedure a 1% error in $d(T - T_c)/dP$ would result in an uncertainty in final quench depth of $\gtrsim 100\ \mu$K for quenches originating at $T - T_c \simeq 10$ mK. The value of dT_c/dP was determined to be 34.97 ± 0.06 mK/MPa by direct measurement. Since $(\partial T/\partial P)_S$ depends (weakly) on $T - T_c$ it was necessary to parametrize it. This was done using the thermodynamic relation $(\partial T/\partial P)_S = \alpha T/\rho c_p$, where α is the thermal expansion coefficient, and ρc_p is the specific heat per unit volume. Both α and c_p include a background and a weakly singular portion. The singular amplitude A_0^+ of c_p was determined using the universal amplitude ratio $(\xi_0^+)^3 \rho_c A_0^+/k_B = 0.01865$. The singular amplitude of α, α_0^+, was then determined using the identity $\alpha_0^+ = \rho_c A_0^+ (dT_c/dP)/T_c$, and the background contribution to α was obtained from the density data. We then used the results of supercritical quenches from $T - T_c \simeq 10$ mK to $T - T_c \simeq 0.5$ mK to fix the only remaining unknown parameter, the background heat capacity. We estimate the overall uncertainty in quench depths to be about $10\ \mu\text{K} + 0.01(T - T_c)_f$. The reader should note that $(T - T_c)_f$ determined in this manner is the temperature the system would ultimately reach in equilibrium following an adiabatic quench. We have scaled our data in terms of equilibrium system parameters at this value of $(T - T_c)_f$ for each quench.

Despite choosing nearly indexed matched components, this system does exhibit some multiple scattering, both in the one-phase region very near T_c ($\leq 7\%$ at $T - T_c = 100$ μK) and especially at larger reduced times ($\leq 15\%$ in the vicinity of the peak for $\tau = 100$), when the turbidity attained values as great as 0.21 cm^{-1}. We were able to correct the data for this effect to all orders by a direct simulation of the scattering process in our sample geometry [17]. We have also tested this method in a more traditional geometry and find it works very well even under conditions where more than $\frac{2}{3}$ of the light emerging from the cell has been scattered more than once. Thus, we are quite confident of its accuracy in the present case.

Figure 2 shows the results of a sensitive test of the repeatability of quenches into the spinodal region. Two quenches were performed from 10 mK above to 116 μK below. The quenches were performed after independent calibrations and measurements of the critical temperature 5 d apart. The data are graphed at the same actual time

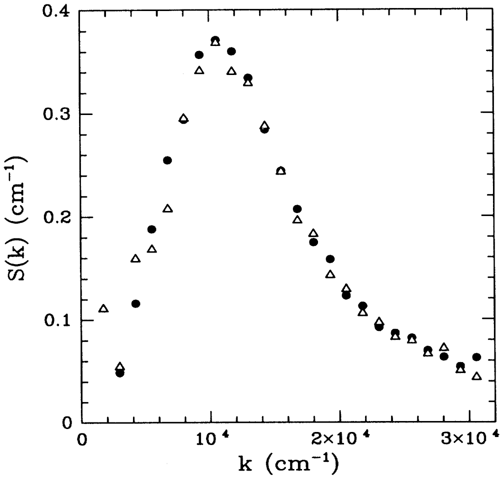

FIG. 2. Data for $S(k, t = 2\ \text{s})$ for two quenches from 10 mK above T_c to 116 μK below showing the reproducibility of the results. (△) after one calibration, (●) after a different calibration 5 d later. A quench depth difference of 20 μK would be easily discernible.

after the quench.

The data resulting from quenches into the two-phase region will be compared to the theory by Kawasaki and Ohta modified so as to be self-consistent [13]. These authors equated the parameter μ appearing in Eq. (2.14) of Ref. [4] to the equivalent parameter computed by Langer, Bar-on, and Miller [3]. The latter theory does not include hydrodynamic effects, and since μ is determined from the structure factor, which is strongly influenced by hydrodynamics, it should be calculated self-consistently. We also included the effect of the initial fluctuations present before the quench in calculating $\tilde{S}(q,\tau)$ by including their value as the initial condition. This causes the calculated result for $\tilde{S}(q,\tau)$ to depend on final quench depth, even for the same set of initial fluctuations.

The evolution of $\tilde{S}(q,\tau)$ over a large range in reduced time is shown in Fig. 3. The eight quenches shown cover a range in quench depth from 116 μK to 20.617 mK, and were all made from 10 mK above T_c. The uppermost solid curve is the self-consistent theoretical result for the deepest quench, while the lower is for the shallowest. To demonstrate the substantial difference between the original theory and the self-consistent one, the dashed lines show the original theory of Kawasaki and Ohta with the same initial conditions. The theory does not extend beyond $q=1$, due to an intrinsic cutoff. The data seem to scale. This is unexpected since inclusion of the initial conditions destroys scaling for the theoretical curves.

There is one unfortunate experimental complication which we have not yet discussed. The apparatus design keeps the sample reasonably, but not perfectly, adiabatic. Radial heat diffusing from the walls of the cell raises the temperature in the volume probed by the beam by no more than 1.0 μK during the first 120 s following a quench. The *o*-xylene temperature follows that of the sample quite well, minimizing axial heat flow; however, the temperature of the thin windows does not vary in response to pressure. Consequently, they remain at the initial temperature during a pressure change, and heat diffuses out of them into both the sample and the *o*-xylene during the decomposition process. We have made what should be a worst case estimate of the effect of this heat flow on the measured value $\tilde{S}(q,\tau)$. We find that it influences the peak height but not position. We estimate that at the latest time for which data from each quench appears in Fig. 3, the measured peak heights may be too small by as much as 30% for the three shallowest quenches (116, 210, and 538 μK), decreasing to 18%, 9%, and 3% for the next three deeper quenches (1.036, 2.079, and 5.156 mK), respectively. At earlier times the errors are smaller. We stress that this represents a worst case estimate and that the effect artificially decreases the measured peak heights, bringing them closer to the theory. The effect is evident at $\tau=5$ when the 116 μK quench has fallen ~20% below the other data. Given a reliable theory for the scattering during an arbitrary temperature history, we will be able to correct the data reliably to account for this effect, by combining such a theory with the solution of the heat flow equation.

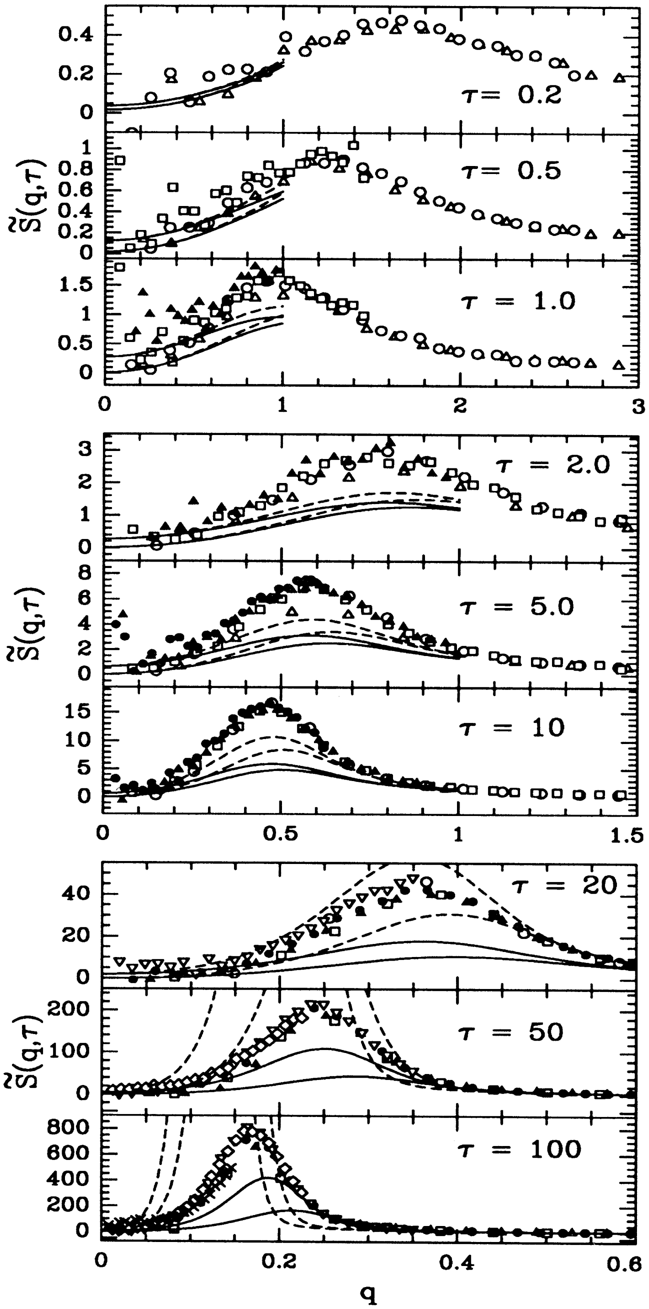

FIG. 3. Evolution of the scaled structure factor $\tilde{S}(q,\tau)$ as a function of dimensionless wave vector q up to a reduced time of $\tau=100$. All quenches were initiated from 10 mK above T_c. Final temperatures were (△) 0.116 mK, (○) 0.210 mK, (□) 0.538 mK, (▲) 1.036 mK, (●) 2.079 mK, (▽) 5.156 mK, (◇) 10.370 mK, and (×) 20.617 mK below the critical point. The dashed curves are the original theory of Kawasaki and Ohta, and the solid curves show the same theory calculated self-consistently.

As may be seen from Fig. 3, the theory is simply not applicable to our data. We have been able to identify two effects which are present in the experiment, but which are not incorporated in the theory. First, as mentioned previously, the experiment is adiabatic, while the theory assumes the system is held uniformly at the final value of $T-T_c$ throughout the decomposition process. Instead, as decomposition proceeds, heat is released, and the sample temperature, insofar as it can be defined during this process, must increase with time. We have scaled our data using parameters appropriate to the final value to which $T-T_c$ will ultimately evolve. In reality the sample will be further below T_c than this throughout the entire decomposition process and will, thus, evolve more rapidly and on a somewhat different spatial scale than expected theoretically. Second, during the actual quench process the long wavelength concentration modes are essentially frozen in amplitude. Since the nonanalytic portions of the specific heat and thermal expansion coefficient are related to these modes, this means that $(\partial T/\partial P)_S$ should be effectively frozen at or near its background value during the quench. This effect would also result in $T-T_c$ overshooting its final value during the initial stages of decomposition.

Previous experiments [9] using the isobutyric acid/water system would likely not have seen these effects because the ratio of the singular part of the heat capacity to the background is 15 times smaller in this mixture [18,19] than it is in 3MP+NE, and this results in much less of a temperature change due to the heat of mixing.

A new theoretical treatment incorporating the effects discovered above in a self-consistent manner has been carried out by James Donley and will be published separately. We used this theory in estimating the effects of the heat flow from the thin windows. We are indebted to Dr. Donley for providing us with computer code which we used for this purpose. We would also like to acknowledge helpful discussions with James Langer and James Donley. This research was supported by NSF Grant No. DMR-90-18089.

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