Periodic Spinodal Decomposition: Light Scattering in the Phase-Separating and Disordered Regimes

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If a fluid mixture is periodically driven through its critical point, two distinct regimes are observed by light scattering. In one, the system ultimately approaches a meniscus-free state, and in the other, phase separation finally occurs. We focus attention on differing scaling forms of the structure factor in these two regimes and on the unexpectedly strong concentration fluctuations which are present in the disordered-phase state. Mean-field behavior is seen in this system.

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Two competing effects occur when a fluid mixture is periodically quenched through its critical point.[1] In the low-temperature portion of the quench period, domains of the separating phases grow in composition difference and in size while on the high-temperature half period, they tend to dissolve. If the average temperature $\bar{T}$ is low enough, phase separation prevails. In this regime local domains develop and, as phase separation advances, the two phases become distinct, with a sharp interface between them. On the other hand if $\bar{T}$ is greater than a certain critical value (which we found to be greater than T_c for the range of parameters considered), the mixture remains in a disordered phase, and after many quench periods seems to approach a (period-averaged) steady state. This transition occurs at some average temperature $\bar{T}=T^*$ whose numerical value depends on the quench amplitude T_1 and on the period t_p of the temperature oscillations.

We have studied this new type of phase transition with light scattering and herein summarize our findings. Our most unexpected observations were in the disordered-phase regime, $\bar{T}>T^*$. After the periodic state is approached, the scattering intensity becomes very large, implying correspondingly large spatial variations in composition, even though the system is visually homogeneous in each portion of the temperature cycle. Down to wave numbers at least of order 10^3 cm^{-1} the scattering is, in fact, greater than if the system were in thermal equilibrium and at its critical temperature. The structure factor $S(k,t)$ for this disordered-phase system approaches a strongly enhanced limiting intensity which is almost stationary at short wavelengths. As the system evolves toward its steady state, a ring of scattered light develops, intensifies, and shrinks in diameter. In this respect its behavior is as in normal spinodal decomposition (NSD). However $S(k,t)$ has a somewhat different scaling form.

In the phase-separating regime of periodic spinodal decomposition (PSD), $\bar{T}<T^*$ $S(k,t)$ also has the same angular dependence as in NSD but with a different dependence on quench depth that suggests mean-field rather than Ising behavior.

The experiments were performed on an isobutyric-acid–water (I-W) mixture of critical composition. The setup is the same as in Ref. 1, but with one exception: To improve the signal-to-noise ratio, a conical lens[2] collected the light over all azimuthal angles and focused it on a traveling photodiode which thus recorded the scattered intensities as a function of scattering angle θ and t. Here, as in Ref. 1, it was the pressure over the mixture rather than the temperature which was periodically varied. We will assume the two modulation schemes to be equivalent and will designate quench depths in temperature units.

The quench scheme is diagrammed in the inset of Fig. 1. Prior to the initial quench, at $t=0$, the mixture is in thermal equilibrium at the one-phase temperature $T=\bar{T}+T_1$. In NSD, characteristic phase separation times are of the order of seconds to minutes,[3] while in the present experiments the collapse time could be prolonged to an hour.[1] The light source was a He-Ne laser ($\lambda_0=633$ nm) and the angular range of the mea-

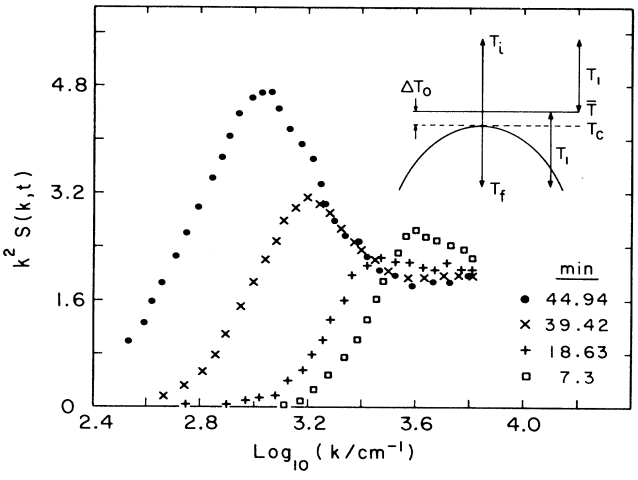

FIG. 1. Weighted angular distribution of scattering at various times for $\sigma>\sigma^*$ (disordered-phase regime). The quench period is 1.0 sec. Inset shows the coexistence curve in the temperature-composition plane and defines quench parameters. This diagram corresponds to $\sigma=(\bar{T}-T_c)/T_1>0$.

surements was $0.3° \leq \theta \leq 3.0°$. In I-W the refractive index is $n = 1.36$, so that the corresponding wave-number interval is $0.7 \times 10^3 \leq k \leq 6.8 \times 10^3$ cm^{-1}, where $k = (4\pi n/\lambda_0)\sin(\theta/2)$. Other relevant parameters for this mixture are $T_c = 26.1$ °C, viscosity $\eta = 0.024$ P, $\xi(T) = \xi_0 \epsilon^{-\nu}$, where $\nu = 0.613$, $\epsilon = (T - T_c)/T_c$ $(T > T_c)$, and $\xi_0(T > T_c) = 0.357$ nm. The quench amplitude T_1 spanned the interval 3 mK $\leq T_1 \leq 10$ mK and 2 mK $\geq (\bar{T} - T_c) \geq -2.7$ mK. The data were corrected for multiple scattering by dividing the measured intensity by the forward intensity $I_F(t)$. The time variation of I_F also identified the two regimes $\bar{T}$ greater or less than T^*, as discussed below. With the exception of the data in Fig. 3 the quench period was fixed at $t_p = 1.0$ sec in the measurements discussed here.

When existing theories of NSD are extended to cover PSD[4,5] three new parameters appear, the reduced quench depth σ, characteristic length $\xi_c(T_1)$, and scaled time interval μ: (a) $\sigma \equiv (\bar{T} - T_c)/T_1$, (b) $\xi_c(T_1) \equiv \xi_0(T_1/T_c)^{-\nu}$, (c) $\mu \equiv [k_B T/12\pi\eta\xi_c^3(T_1)]t_p \propto t_p T_1^{3\nu}$.

The phase transition identified in these experiments may equivalently be designated by the temperature T^* or by a critical value of $\sigma^*(\mu) = (T^* - T_c)/T_1$. Experimentally σ^* is positive and increases (weakly) with increasing μ.

As noted above, the light scattering takes the form of a collapsing halo of growing intensity for both σ greater and less than σ^*. But the forward intensity I_F exhibits a different time dependence in these two regimes. For $\sigma < \sigma^*$, i.e., in the regime where a meniscus forms after many quench periods, $I_F(t)$ continues to decrease with time, as the spinodal ring collapses, just as in NSD. As σ is increased above a certain value of σ (σ^*), $I_F(t)$ behaves very differently, namely, $I_F(t)$ quickly reaches its final value and remains there even though a spinodal ring is intensifying and collapsing.

When $\sigma > \sigma^*$ the composition fluctuations become stronger than at thermal equilibrium where the structure factor satisfies well the Ornstein-Zernike (OZ) equation $S_{eq}(k,t) = A/(k^2 + \xi^{-1})$, where A is a constant. Rather than plotting $S(k,t)$ vs k, we show in Fig. 1 $H(k,t) \equiv k^2 S(k,t)$ vs log$k$. The measurements are at $t = 7.30$, 18.63, 39.42, and 44.94 min with $\mu = 3.5$ and $\sigma = 0.25$, where σ^* lies between the values 0.16 and 0.20. Were these curves of OZ form, one would have $H(k,t) = k^2 S(k,t) = A/[1 + (k\xi)^{-2}] < A$. However, the data in Fig. 1 show a maximum which is greater than A and a shifting to smaller k as t increases. The intensity maxima appear to tend to a limiting value greater than A/k^2 down to the lower limit of the measurable wave-number region. It follows that the small-k composition fluctuations are stronger than if the system were in thermal equilibrium and at its critical temperature. When the data of Fig. 1 are replotted to show $1/S(k,t)$ vs k^2, they fit a straight line (down to a small value of k) in accordance with the OZ theory but with ξ^2 roughly zero or even negative. The measurements conform to this modified OZ form at late times only ($t \gtrsim 30$ min for the parameters of Fig. 1). While stronger-than-critical scattering is to be expected from a phase-separating mixture, as in NSD, it was not anticipated in this driven, disordered-phase system.[4,5]

The peaks in Fig. 1 do not imply the existence of a ring. In fact the ring has completely collapsed by 44.94 min for the run of Fig. 1. Roughly 10 min after the collapse of the ring the scattering always develops azimuthal asymmetry, with a maximum in the horizontal direction. This suggests that gravity is stretching the composition fluctuations in the vertical direction. Visual observation of the scattering pattern after many hours (in some cases a day) reveals little further change in $S(k,t)$.

While we observe notable differences between PSD and NSD when $\sigma < \sigma^*$, a common feature is the development of a collapsing ring. The ring size, $k_m(t)$, has the same functional form as in NSD, and in fact the two sets of measurements can be mapped onto each other. To do so one rescales t and k as $q_m = k_m \xi$ and $\tau = (k_B T/6\pi\eta\xi^3)t$ but with ξ replaced by a new length, ξ_{eff}. In Fig. 2 we plot $[\xi_c(T_1)/\xi_{eff}]^2$ vs σ. The data points lie on a straight line, implying that $\xi_{eff} \propto (\sigma^* - \sigma)^{-\nu_{eff}}$ with $\nu_{eff} \simeq \frac{1}{2}$, but we cannot determine ν_{eff} with precision. For each μ, ξ_{eff}^{-2} decreases until it reaches zero at the extrapolated value $\sigma = \sigma^*$. The set of values $\sigma^*(\mu)$ deduced from this extrapolation are, within error, equal to those obtained from the forward intensity data referred to above.

As in NSD,[6,7] the domains, which appear and grow when $\sigma < \sigma^*$, have a self-similar form.[8] This self-

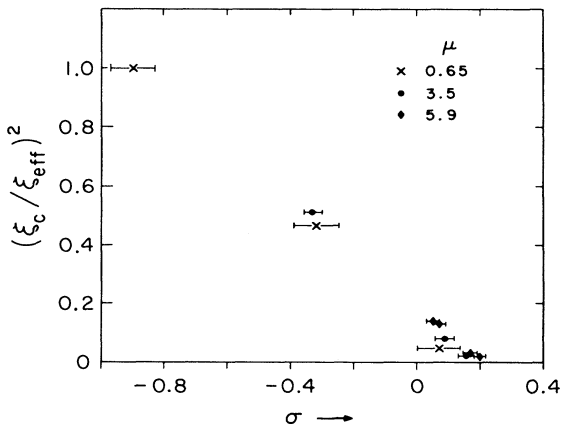

FIG. 2. The values of ξ_{eff} in this figure are obtained by mapping the normal and periodic ($\sigma < \sigma^*$) spinodal decomposition data onto each other. The quantities when plotted in this fashion are expected to be independent of μ.

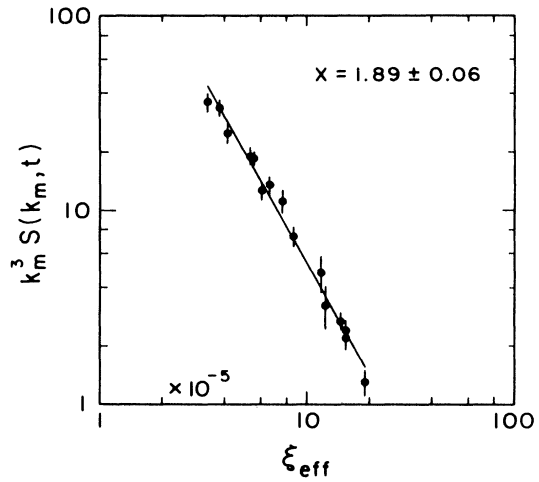

FIG. 3. The scaling function $k_m^3 S(k_m,t)$ vs the effective correlation length ξ_{eff}. The solid line is a least-squares fit to the data points and yields the exponent X defined in the text.

similarity is revealed in a rescaling of $S(k,t)$ and k itself. As in NSD, the k dependence of $S(k,t)$ implies that the scattering is dominated by the interfaces between growing domains.[9] The signature of interface scattering is the relation $S(k,t) \propto 1/k^4$ at large k. This dependence is found here when $\sigma < \sigma^*$ as well as in computer simulations and laboratory studies of NSD.[9] Even when $\sigma > \sigma^*$ a rescaling of $S(k,t)$ and k reveals a self-similarity of the domains. Now, however, $S(k,t) \propto 1/k^{\phi}$ at large k with $\phi \simeq 2.6$. Presumably $\phi < 4$ because the (transient) domains never develop sharp boundaries in the disordered-phase regime.

Another type of rescaling is indicative of a mean-field aspect to PSD when $\sigma < \sigma^*$. In NSD the quantity $J_{\text{NSD}} \equiv k_m^3 S(k_m,t)/(T_c - T)^{2\beta}$ (with $\beta = 0.31$) is independent of time and $T_c - T$.[10] Equivalently $k_m^3 S(k(m),t) \propto (T_c - T)^{2\beta} \propto (T_c - T)^{\nu} \propto \xi^{-1}$. Analogously we find that $k_m^3 S(k_m,t)/T_1(\sigma^* - \sigma)^{\theta}$ is a constant independent of time, T, t_p, and σ if $\theta \simeq 1.0$. This suggests that the system supports fluctuations of a mean-field type. To confirm this we fitted the measurements with the form $k_m^3 S(k_m,t) \propto \xi_{\text{eff}}^{-X}$. Our data points in Fig. 3 were obtained from individual runs for which the range for t_1 and $\bar{T}$ is the same as that given earlier. In some runs $t_p = 2.0$ sec instead of 1.0 sec. This figure reveals that $X = 1.89 \pm 0.06$. A value of $X = 2.0$ is expected from mean-field theory, which predicts $\xi_{\text{eff}}^{-2} = \xi_0(\Delta T_{\text{eff}}/T_c)$. This leads to $k_m^3 \times S(k_m,t) \propto \xi^{-2}$ $(X = 2)$ rather than the NSD result $X = 1$. Such mean-field behavior is predicted and observed in systems far from equilibrium.[11]

In summary, we have verified a theoretical prediction[4,5] of a phase transition in spinodal decomposition: When the average temperature exceeds some critical value, $\bar{T} = T^*$, the fluid mixture evolves to a disordered phase state, and when $\bar{T}$ is below T^*, phase separation occurs. The transition temperature T^* is a function of the amplitude (and the period) of the temperature oscillations. When $\bar{T} > T^*$, very large composition fluctuations are observed—so large, in fact, that the fluctuation-dissipation theorem may not hold in this new disordered phase. Thus it would be very interesting to examine the renormalization effect of these fluctuations on, say, the concentration decay rate at long wavelengths. In both regimes the structure factor has a self-similar form but at large k it shows a distinctly different power-law behavior.

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