Observation of Periodic Spinodal Decomposition

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Periodic spinodal decomposition has been observed in a critical binary mixture of isobutyric acid and water. As predicted by Onuki, phase separation can be dramatically slowed down by a periodic quench of appropriately chosen mean value and amplitude of the temperature variations. Depending on details of the quench conditions, two steady-state conditions can be achieved, in one of which the system has completely separated.

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Phase separation (nucleation or spinodal decomposition) is typically studied in experiments of the transient type; one quenches the fluid mixture or molten alloy into the two-phase region of the phase diagram and follows its temporal approach to thermal equilibrium.[1] An alternative method[2] is to quench the system periodically about some mean value while observing its evolution toward a steady, nonequilibrium state as $t\to\infty$. We report here light scattering measurements of this second type in a binary mixture of critical composition.

As pointed out by Onuki[2,3] new effects can be expected to appear under periodic quench. If the system's critical temperature, T_c, lies between the extremes of the temperature cycle, the steady-state behavior of the system is determined by a competition between two processes, spinodal decomposition when $T<T_c$ and dissolution of the spinodally decomposed clusters when T rises above T_c. On lowering the mean temperature of the sample (its amplitude and period of oscillation held constant) one should approach a particular value such that the evolution of the system toward the steady state should be greatly retarded. By observing the system under these "slow motion" conditions there is hope of extracting detailed information from light scattering experiments that is not available in normal spinodal decomposition (NSD) experiments.

We indeed observe the above phenomena, described and analyzed by Onuki, but in some important respects our results are at odds with his findings. Most notably, we observe that the time evolution of the structure factor $S(k, t)$ is very insensitive to a naturally occurring dimensionless parameter, μ, which is the ratio of the characteristic growth rate of clusters to the frequency of the temperature oscillation. Before discussing these results and presenting experimental details, we define various dimensionless parameters which enter Onuki's theory and our experiments.

Referring to the inset in Fig. 1, we imagine the temperature to be cycled with amplitude T_1 about an average temperature $T_{\text{ave}}=T_c+\Delta T_0$ and with period t_p. Onuki's dimensionless squared wave number for growth $r(t)$ undergoes a stepwise oscillation given by $r(t)=r_1[\sigma+F(t/t_p)]$, where $F(x)$ is a periodic function of mean value zero and amplitude 1. It can be shown that $\sigma=a(\Delta T_0/T_1)^{2\nu}$, where a is positive (negative) when $T_{\text{ave}}>T_c$ ($T_{\text{ave}}<T_c$). In the analysis of our data, the magnitude of a will be taken as unity.

Onuki casts his results in terms of a characteristic length $\xi_c\propto r_1^{-1/2}$ and the above mentioned parameters μ and σ. He finds that the wavelength above which fluctuations will grow during the periodic quench is $\xi_c=\xi_0(T_1/T_c)^{-\nu}$, where ξ_0 is the amplitude of the correlation length (we use its known value in one phase, $T>T_c$). He also finds $\mu=k_BTt_p/12\pi\eta\xi_c^3$, with η the viscosity of the critical mixture. As noted above, Onuki's main prediction is that for each

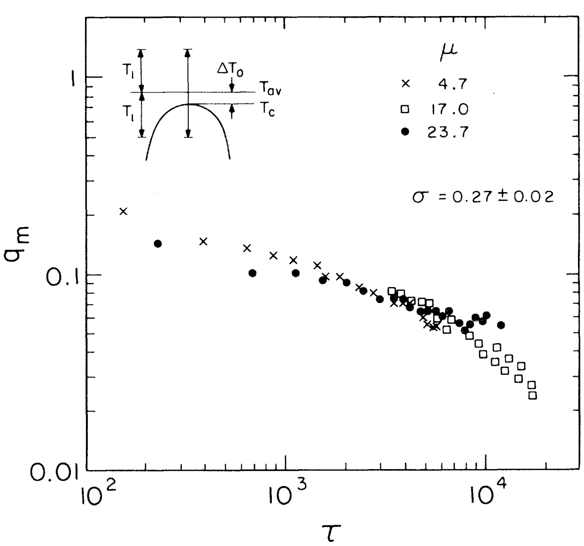

FIG. 1. Scaled ring diameter vs reduced time for a value of σ lying above the transition ($\sigma>\sigma_c$).

value of μ there is a critical value of σ (σ_c) such that when $\sigma < \sigma_c$ the system eventually phase separates and when $\sigma > \sigma_c$ the system tends to a periodic state with no progression toward complete phase separation.

In this experiment we have used a square-wave variation of period $t_p = 1$ sec to study periodic spinodal decomposition in a critical sample of isobutyric acid and water over a range of parameters $4.4 \leq \mu \leq 23.7$ and $-0.66 \leq \sigma \leq 0.33$. For these measurements the periodic quench was actually accomplished by cycling the pressure to force T_c through the (fixed) system temperature,[4] but we shall use the equivalent temperature variation language throughout our discussion. Both angular distributions and turbidity were measured for 6328-Å laser light passing through the reentrant cell containing the sample, thus allowing us to construct the time-dependent structure factor $S(k, t)$.

As the sample is periodically quenched, it scatters light into a ring whose diameter is characteristic of the mean size of the clusters of the two different phases; this ring appears as a maximum in $S(k, t)$ at wave number $k_m = (4\pi n/\lambda_0) \times \sin(\theta_m/2)$, where θ_m is the angle of the maximum scattering intensity and n is the average index of refraction of the sample.[1] Whereas in normal spinodal decomposition this ring collapses in a few minutes or less, we have succeeded in prolonging the collapse through 1.5 h by periodically quenching the system. This slowing down of the ring collapse is a strong function of σ. Indeed, we have observed a phase transition of the sort predicted by Onuki: In runs with $\sigma \gtrsim 0.27$ the system tends to a periodic state with no visible meniscus even after as much as 30 h of periodic quenching while in runs with $\sigma \lesssim 0.06$ the system completely phase separates in 10 h or less. For values of σ between 0.06 and 0.27 complete phase separation takes much longer than 10 h if it occurs at all. Because of the long times involved it is difficult to avoid small temperature drifts to which the data are nevertheless sensitive, but data taken at $\sigma = 0.20$ resemble the $\sigma = 0.27$ results reasonably closely while those at $\sigma = 0.15$ resemble those at $\sigma = 0.06$. For this reason we place σ_c in the range 0.15–0.20. At both short and long times and regardless of whether or not the system undergoes complete phase separation, a cloudiness is visible to the eye in the sample during half of each 1-sec quench period. This cloudiness, however, makes no important mark on a typical measured angular distribution; the individual angular distributions are indistinguishable from those measured in NSD.

To present the data we use ξ_c to define a dimensionless wave number and a dimensionless time:

$$q_m = \xi_c k_m \text{ and } \tau = (k_B T_c / 6\pi\eta\xi_c^3)t ,$$

where we take ξ_0 and η to be 3.57 Å and 2.42×10^{-2} P, respectively. These dimensionless units do not correspond exactly to those used in NSD analyses, but they are similar and they proceed naturally from the physics of the periodic quench. Where possible we fitted the data by the forms

$$q_m \propto \tau^{-\varphi}, \quad I_m \propto \tau^{\theta}, \quad k_m^3 I_m \propto \tau^{-x} ,$$

where $I_m = I(k_m)$ is the maximum light scattering intensity. The product $k_m^3 I_m$ has been found to be independent of time and quench depth in NSD experiments,[5,6] in computer simulations,[7] and in some theoretical calculations.[8] Typical examples of our data are shown in Figs. 1–3. The exponent φ is found to be approximately independent of both μ and σ with a value $\sim\frac{1}{3}$ for early times ($\tau \lesssim 10^3$) and ~ 1 for later times. This behavior can be seen in Fig. 1 for cases with a

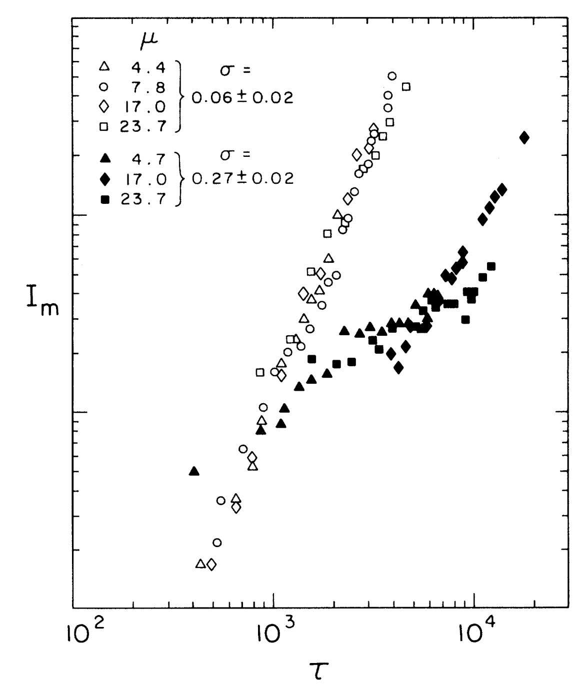

FIG. 2. Scaled ring intensity vs reduced time for two different σ values lying on either side of the transition ($\sigma > \sigma_c$ and $\sigma < \sigma_c$).

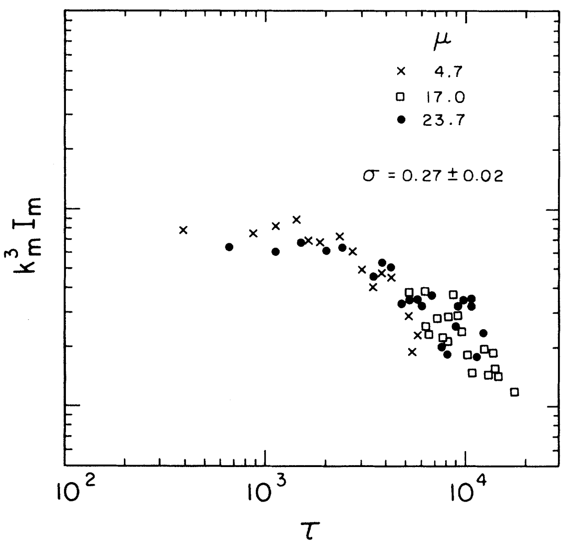

FIG. 3. $k_m{}^3 I_m$ vs reduced time for a value of σ lying above the transition.

large value of σ. Several cases, each with both large and small values of σ, are shown in Fig. 2, where it can be seen that θ is significantly different for large values of σ (θ changes with time from 0.7 to 1.5 when $\sigma = 0.27$) than for small values ($\theta \sim 2.5$ when $\sigma = 0.06$). For small values of σ, $k_m{}^3 I_m$ is independent of τ, i.e., $x = 0$, just as is the case for NSD.[9] Figure 3 shows that this product loses its time independence for large values of σ at late times ($\tau \gtrsim 3 \times 10^3$); at $\sigma = 0.27$, $x \simeq 1$. As σ is increased beyond 0.3, one no longer sees the development of a spinodal ring.

Several striking results have emerged from this analysis: (1) There appears to be no dependence on μ. Several very different μ values are shown to fall on the same curve for each value of σ, in each of the figures. We have thus far varied μ only by varying T_1. We plan to vary μ by varying t_p but in Onuki's formalism this should not matter as long as t_p is much less than the collapse time for NSD; our $t_p = 1$ sec easily meets this requirement. (2) θ and x are significantly different above and below $\sigma_c \simeq 0.15$, but there is no appreciable difference in φ. This same trend appears in Onuki's published calculations for $\mu = 5$. (3) The crossover in NSD from slow early-time to rapid later-time domain growth ($\varphi \sim \frac{1}{3} \rightarrow \varphi \sim 1$) is difficult to observe.[6,9] This is also true for the periodic case with low values of σ, but as we increase σ we observe more and more of the $\varphi \sim \frac{1}{3}$ region. Figure 1 shows that, for runs with $\sigma = 0.27$, the $\varphi = \frac{1}{3}$ region extends to $\tau = 4 \times 10^3$ while for NSD this region ends at $\tau \simeq 30$. (4) The well-known NSD scaling law $x = 0$ ($k_m{}^3 I_m = \text{const}$) holds only for $\sigma < \sigma_c$. Above the transition the scaling law fails dramatically as can be seen in Fig. 3.

In summary, we have seen the phase transition which Onuki predicts as we hold μ constant and lower σ. The critical value, σ_c, for this transition does not depend on μ. Using this periodic spinodal decomposition we have been able to follow the collapse of the spinodal ring over many orders of magnitude more both in actual time and in dimensionless time than has been possible in normal spinodal decomposition experiments.

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