Steady-State Nucleation in a Binary Mixture: The Effect of Stirring

K. Y. Min, J. Stavans, [a] R. Piazza, [b] and W. I. Goldburg

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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Using light scattering, we have studied the effect of shear on nucleation in the binary fluid mixture 2,6-lutidine plus water. The experimental method differs from traditional ones in that the measurements were made in the steady state: Droplets which formed in the quenched mixture were constantly being ruptured by the continuous shear. The shear was produced by the spinning of a stirrer magnet inside the sample. It was found that when the stirring frequency f exceeds, by a very small amount, some critical value f_c (for a fixed quench depth δT), the scattering changes by orders of magnitude. Our results are compared with a simple theory of Onuki and Takesue.

Nucleation is usually viewed as a transient phenomenon. One typically quenches or supersaturates a system and records the growth of droplets of the minority phase.[1] In the present experiment we study nucleation under steady-state conditions. The system under study is a binary fluid mixture. Initially the system is driven into the two-phase state, where droplets are formed. The fluid is then vigorously stirred, producing local shear $S(r,t)$, which ruptures those droplets which have grown to sufficient size.[2] Droplets grow and are broken, with the droplet size distribution eventually reaching a steady state. As the mean value of the shear S is increased, droplets of increasingly smaller size are fragmented. Eventually a value of S is reached, at which point droplets even as small as the critical radius are ruptured. At this value, $S = S_c$, nucleation is therefore inhibited, and light scattered from the stirred mixture will abruptly decrease. At every value of S the width of the droplet size distribution should be narrow.

The above scenario is the core of a theory of Onuki and Takesue[3] (OT). This theory is consistent with our observations made in a series of off-critical samples of the mixture 2,6-lutidine and water (LW). This system has an inverted coexistence curve, so that it is "quenched" into the two-phase region by raising its temperature.

Our steady-state observations show no evidence of the hysteresis that is seen in normal (transient) nucleation experiments; holding the shear constant, the scattered intensity I increases when the quench depth δT is increased above some critical value, and it decreases precipitously on cooling through this same value of δT. If the theory of OT is correct, our experimental technique may provide a method of measuring the critical radius r_c of nucleated droplets, since only droplets of this size will be present when S is very close to the frequency S_c.

The critical temperature T_c of LW is 33.3 °C,[4] and the critical water concentration c_c is 71.3 wt.%. Our measurements were made in three off-critical, water-rich sealed samples. Their concentrations c were $c = 76.3$,

77.6, and 79.1 wt.%. The temperatures $T_{cx}(c)$ at which the samples phase separated in the absence of stirring were accurately measured. The procedure was to bring the sample into the one-phase region, near T_{cx}, and then heat it in steps of 1–2 mK, while gently stirring it continuously. The temperature at which a meniscus appeared after a lapsed time of 20 h was taken as T_{cx}.

The crucial sample parameters in this experiment were $\Delta T(c) = T_{cx}(c) - T_c$ and the "quench depth" $\delta T = T - T_{cx}(c)$. We first determined $\Delta T(c)$ from the measurement of $T_{cx}(c)$ in the sample of interest and from a similar measurement of T_c in a critical sample. However, to avoid errors that arise from utilizing measurements on two different samples, we finally used the alternative method of extracting ΔT from a measurement of the decay rate, Γ, of composition fluctuations, as measured by photon correlation spectroscopy.[5] These measurement were made within a few mK of $T_{cx}(c)$. The appropriate equation is $\Gamma = Dk^2$, where k is the photon scattering vector, and the composition diffusivity[6] $D = k_B T/6\pi\eta \times \xi(\Delta T)$. In this equation $\xi = \xi_0 \epsilon^{-\nu}$, where $\epsilon = |\Delta T(c)|/T_c$. The critical exponent ν was taken to be the Ising value of 0.625,[5] and the viscosity was $\eta = 0.025$ P.[4] In our three samples, the measured values of $\xi(\Delta T)$ were 16 nm (110 mK), 10.5 nm (220 mK), and 7.2 nm (400 mK), in order of increasing concentration, c. The standard deviations in ξ and ΔT were 6% and 1%, respectively.

The sample cells were sealed Pyrex cylinders 3 cm in diameter and 4.5 cm high. The height was chosen to avoid stagnant regions in the flow at the top of the cell. The cells were immersed in a stirred water bath whose temperature was kept constant with a precision of ± 0.5 mK/day. The phase separation temperature was periodically remeasured to correct for the small drift in T_c. The samples were prepared on the water-rich side of the critical concentration so as to avoid heterogeneous nucleation induced by the wetting of Pyrex by water. Simple capillary-rise experiments show that, while Pyrex is wetted by the water-rich phase, quartz is wetted by the

lutidine-rich phase.

Stirring was produced by a magnetic stirring bar contained within the cells. The stirring frequency f was stabilized to within ± 0.1 Hz. The stirring raised the temperature of the LW samples relative to that of the surrounding temperature-controlled water bath by an amount that was directly measurable by a thermistor in thermal contact with the sample within the cell. All quoted temperatures have been corrected for this shear-induced heating, which was as large as 30 mK at $f = 15$ Hz. The theory of OT, to which we compare our measurements, is couched in terms of the local shear $S(\mathbf{r}, t)$. With our geometry, the local shear is not exactly known. For simplicity we assumed that the stirrer generated uniform Couette-type flow in the cell, so that the velocity a distance ρ from its axis is $\rho \omega$, making the shear uniform with the value $S = 2\pi f$. The assumption that the flow was approximately laminar appears to be a good one, in spite of the turbulent appearance of the stirred mixture. We concluded this from a measurement of the sample heating as a function of f. If the flow is laminar, the temperature rise in the sample, relative to that of the surrounding water bath, should be proportional to f^2. Over most of the frequency interval, 2 Hz $< f <$ 16 Hz, we observed this quadratic dependence.

Though all the light scattering measurements were made on the axis of the cell, it is important to know if the temperature of the stirred mixture was reasonably uniform throughout its volume. We determined that it was in a separate experiment on a cell of identical shape that was filled with water and which contained two thermistors. One thermistor was located at the center of the cell and the other barely protruded through the wall. Using a bridge with these two resistive elements in their arms, it was established that the 1-sec time-averaged temperature gradient did not exceed 0.2 mK at all stirring frequencies.

A He-Ne laser was the light source (vacuum wavelength of 633 nm). The scattered light was detected by a photomultiplier, and a photodiode recorded the transmitted light intensity, from which the turbidity of the sample could be determined. The experiment proceeded as follows: With the stirrer turned off, the sample was quenched deeply enough so that it became strongly and uniformly turbid. The time required to reach the strongly turbid state was of the order of a few min. The system was left in this state for about 20 min, so that it can reach a condition of late-stage droplet growth, where subsequent growth of the droplets proceeds relatively slowly. The bath temperature was then reduced to a predetermined value δT above T_{cx}.

Then the stirrer was turned on and f was progressively and slowly increased to a value f_c where the turbidity abruptly decreased. Because stirring raised the sample temperature significantly, it was necessary to readjust the bath temperature every time f was changed, in order

to keep the sample temperature (and thus δT) at a fixed value. The scattered intensity, recorded at a stirring frequency slightly greater than f_c, was equal to its value when the stirrer was off and the mixture was in one phase at temperature $T = T_{cx}$. From this observation, it is concluded that all droplets are destroyed by stirring at $f \ge f_c$; the scattering that remains when f exceeds f_c presumably comes from spontaneous composition fluctuations alone. From other experiments[7] there is reason to expect, however, that stirring decreases the *lifetime* of the composition fluctuations when the system is driven into the one-phase state.

A preferred procedure for measuring the abrupt destruction of droplets by stirring was to hold the frequency constant and to adjust the quench depth δT to a value at which the scattered intensity abruptly dropped. Both procedures gave the same values of δT as a function of f. A series of such measurements yields the same function, f_c vs δT.

It is useful to review the theory of OT before discussing the data. The critical radius is given by $r_c \approx \xi/\phi$, where the volume fraction of the minority phase, ϕ, is related to the quench depth δT and ΔT throughout the equation,[1]

$$\phi \approx \tfrac{1}{2} - \tfrac{1}{2}\{1/(1+\delta T/\Delta T)\}^\beta \approx \beta \delta T/2\Delta T,$$

with the latter approximation holding when $\delta T/\Delta T$ is small, as in these experiments. The coexistence-curve exponent β has the value 0.31.[5]

For a given shear rate S, the maximum droplet size $r_{\max}$ which can exist in a sheared fluid is given approximately by $r_{\max} = C\sigma/\eta S$, where η is the viscosity of the mixture, σ is the surface tension, and C is a constant that is weakly dependent on the type of flow.[8] Near the critical point[9] $\sigma = 0.1 k_B T/\xi^2$, where k_B is Boltzmann's constant. Setting $r_{\max} = r_c$ at $f = f_c$, one obtains

$$f_c = C\sigma\phi/2\pi\xi\eta \approx 0.1 C k_B T\beta\delta T/4\pi\xi^3\eta\Delta T. \quad (1)$$

Expressing f_c in units of the inverse lifetime Γ_ξ of a composition fluctuation, $\Gamma_\xi = k_B T/6\pi\eta\xi^3$, Eq. (1) becomes

$$F_c = f_c/\Gamma_\xi = 0.15 C\beta\delta T/\Delta T. \quad (2)$$

It is this equation with which we compare our measurements in Fig. 1. In this plot of $\delta T/\Delta T$ vs F_c, data are shown for all three samples. To a fair approximation the data points fall on a single straight line (a result which is consistent with laminar flow rather than turbulent shear in the cell). A least-squares fit of the data in Fig. 1 by a straight line shows that $\delta T/\Delta T = \text{const} \times f^\omega$, with $\omega = 0.90 \pm 0.02$. The straight line in Fig. 1 was drawn with a slope, $\omega = 1$, so as to obtain an approximate value for C in Eq. (2). The data correspond to $C = 0.16 \pm 0.05$, in good agreement with published values.[8] To give a feeling for the numerical values of the control parameters in this experiment, we note that for the sample
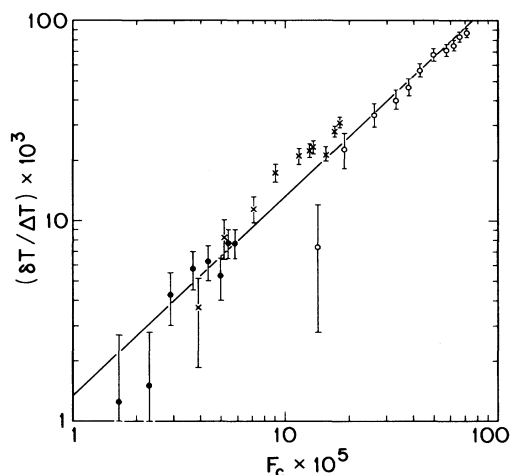
FIG. 1. Log-log plot of nondimensional quench depth as a function of reduced critical frequency. Data are shown for samples of three different compositions: $c = 79.1\%$ (closed circles), $c = 77.6\%$ (crosses), and $c = 76.3\%$ (open circles). The straight line, of slope unity, is a least-squares fit to the data.
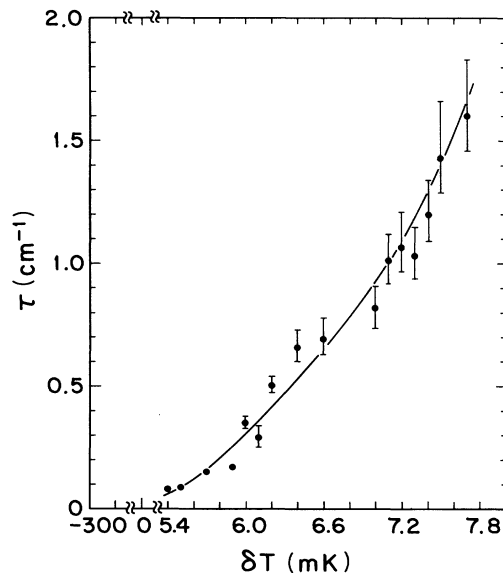

FIG. 2. Turbidity as a function of quench depth $\delta T = T - T_{cx}(c)$ for the sample of composition $c = 76.3$ wt.%. The stirring frequency is 13 Hz. Note the two breaks in the temperature scale. The solid line is a guide to the eye.

of intermediate composition, $c = 77.6$ wt.% (for which $\Delta T = 220$ mK), f_c ranged from 3.0 Hz at $\delta T = 0.8 \pm 0.4$ mK to 14.0 Hz at $\delta T = 6.8 \pm 0.4$ mK.

We also analyzed the data in Fig. 1 under the assumption that the stirred mixture was fully turbulent, so that the time average of $S(\mathbf{r},t) = S(\mathbf{r})$ could be estimated from the theory of Kolmogorov. Since $S(r)$ increases with decreasing eddy size r, the shear that should be most effective in rupturing the droplets is presumably that value of S associated with eddies of minimal size, $r = r_d$. At this value of r the Kolmogorov theory gives $S_c \sim f_c^{3/2}$. In this case then, δT should be proportional to $f^{3/2}$, which is contrary to the observed linear variation of δT with f_c seen in Fig. 1. This calculation supports our assumption of laminar flow, with $S = 2\pi f$.

Figure 2 shows the extreme sensitivity of I to small variations in δT near the threshold, $f = f_c$. This is a plot of the turbidity versus quench depth δT for a sample of composition $c = 76.3$ wt.%. The stirring frequency $f = 13 \pm 0.1$ Hz. We take the turbidity τ to be $\tau = (1/d)\ln[I_0/I_T]$, where d is the diameter of the sample ($d = 3.0$ cm) and I_0 should be the intensity of the incident beam. To avoid errors connected with loss of incident beam intensity from reflections at glass surface, we have taken I_0 to be the transmitted intensity at a sample temperature 300 mK below T_c. Here the fluid mixture is in one phase and the scattering from composition fluctuations is negligibly weak.

The transmitted intensity I_T is measured as a function of T, commencing at $T - T_{cx} = \delta T = 5.4$ mK. Note that τ changes steeply from 0.08 cm^{-1} at $\delta T = 5.4$ mK to 1.5 cm^{-1} as the temperature is increased by merely 2 mK. Increasing δT appreciably beyond 7.7 mK increased the

turbidity so much that it could no longer be reliably measured. In the sense conveyed by this graph, a sharp transition has occurred at a well-defined value of δT, for a fixed value of f, which we have called f_c. The transition may have been even sharper if the fluctuations in stirring frequency could have been further reduced. The same value of f_c vs δT was obtained on either cooling or heating through the transition. This behavior differs from a first-order phase transition in a normal, unstirred mixture, in that no hysteresis is observed in our stirring experiments.

Our samples were prepared with great care so as to avoid introducing dirt particles on which droplets could nucleate. However, we also have made measurements on "dirty" samples which contained small fibers. These fibers induced heterogeneous nucleation at a value of δT which was smaller than in the clean samples. Nevertheless we also observed a knee in $I(T)$ vs δT at fixed stirring frequency. Assuming that the transition occurs at a value of f_c for which the radius of ruptured droplets is the critical radius, these experiments in a dirty mixture suggest that one can deduce the critical radius r_c even under heterogeneous nucleation conditions.

An alternative interpretation of our experiments is that the measured δT results from a shear-dependent upward shift in the coexistence curve. One might expect this, since it is known that the shearing of a near-critical fluid mixture will depress its critical temperature if the coexistence curve is a normal one. In our system, with its inverted coexistence curve, the disordering effect of shear should raise $T_{cx}(c)$, in accord with our observa-

tions. This explanation would appear to be ruled out by the fact that our values of ΔT are sufficiently large (and Γ_ξ sufficiently small) that we are in the weak-shear regime ($S/\Gamma_\xi \ll 1$) at all stirring frequencies. In this case no such shear-induced shift in the coexistence curve should occur.

[a]Present address: Department of Electronics, Weizmann Institute of Science, Rehovot, Israel.

[b]Present address: Department of Electronics, University of Pavia, Via Abbiategrasso 209, 27100 Pavia, Italy.

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