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Turbulent Suppression of Spinodal Decomposition

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Light scattering experiments reveal a strong suppression of phase separation near the critical point of a vigorously stirred binary liquid mixture. For stirring Reynolds numbers R ranging from 6.0×10^3 to 4.5×10^4, the apparent critical temperature is depressed by ~1 mK to ~50 mK. This temperature depression $\Delta T_c'$ can be fitted to a power law $\Delta T_c' \sim R^{\lambda}$ where $\lambda\sim2$. The magnitude of $\Delta T_c'$ is consistent with simple models which attribute the effect to the suppression of composition fluctuations by shear; however, these models predict $\lambda\simeq0.80$ in contrast to the observed value of ~2. Below the apparent critical temperature the turbidity τ changes significantly throughout a temperature range of tens of millikelvin following a power law $\tau\propto(T_c-T)^{\zeta}$ where ζ increases from ~1 to ~6 as R is increased.

I. INTRODUCTION

Interesting new phenomena are expected to appear when binary liquid mixtures are vigorously stirred near the consolute point.[1,2] We report one such effect, a strong suppression of phase separation produced by continuous stirring. This stirring causes a dramatic depression of the temperature at which 632.8-nm laser light scattering begins to show effects from phase separation. The depression was seen in a critical mixture of 3-methylpentane and nitroethane (3MP-NE) in two types of experiments: (1) measurements of the attenuation of a laser beam passing through the binary mixture and (2) measurements of laser radiation at 90°.

Two recent calculations address the phenomena expected of a binary mixture under the influence of a strong shearing force in very different limits. Onuki and Kawasaki[1] (OK) are concerned with the behavior of a critical mixture exposed to a uniform shear. They find that shear flow suppresses composition fluctuations near the critical point and thus renormalizes the critical temperature T_c, shifting it downward. Velocity fluctuations, for the case of uniform shear, are scarcely affected at length scales relevant to critical phenomena.

Ruiz and Nelson[2] (RN) consider the velocity composition coupling in a very different limit, where a binary mixture is so strongly stirred as to be fully turbulent. The well-known scaling arguments of Kolmogorov[3] are invoked to describe the velocity spectrum imposed by stirring. Although RN are primarily concerned with turbulent mixing of a binary mixture just *above* T_c in the one-phase region, their calculations suggest that an interesting steady state should develop *below* T_c in a phase-separating fluid which is vigorously stirred at long wavelengths.

The results reported here will be discussed qualitatively, drawing on ideas from the calculations of OK and RN. A discussion of our data follows a description of the experiment.

II. EXPERIMENTAL PROCEDURES AND DATA PRESENTATION

Two sample cells were used for the measurements. The cells were ~10-cm-long Pyrex tubes oriented vertically, having 3.3-cm inner diameters and capillary filling stems on top. Each cell was filled with an equimolar (critical) mixture of 3-methylpentane and nitroethane, then frozen and sealed *in vacuo*. The measured critical temperatures were within 30 mK of the accepted value, 26.4 °C.[4] A glass stirring propeller of diameter ~2.5 cm, containing within it a small bar magnet, was mounted between glass bushings near the bottom of one of the cells. In the other cell a 0.5×2.5 cm^2 stirrer formed from nickel wire rested on the bottom of the cell. Rotation frequencies fell in the range $4\lesssim f\lesssim30$ Hz. At each stirring frequency a Reynolds number R was determined using $R=2\pi fr^2/\nu$ where r, the radius of the stirrer, has been set equal to 12 mm and ν, the kinematic viscosity, is taken to be 0.006 cm^2/sec (we neglect the weak temperature dependence of ν).[5]

Each sample was located in a water bath whose temperature was controlled to within 0.2 mK. Sample temperatures (T), however, were elevated by viscous losses due to stirring. The temperature rise was several mK at $f\simeq20$ Hz. This internal temperature rise was measured at all rotation speeds and has been corrected for in the data presented below.

The light source was a He-Ne laser (632.8 nm) which was attenuated to less than 1 mW to minimize heating. The laser beam passed horizontally through the cell near the midpoint of its height. The steady-state unscattered laser intensity $I_F(R,T)$ was measured by a photodiode; the steady-state scattered intensity at 90°, $I_\perp(R,T)$, was measured by a photomultiplier (FW130) operating in the photon-counting mode.

In addition to measuring the mean forward intensity, we also measured the amplitude $\sigma_F(R,T)$ of the RMS

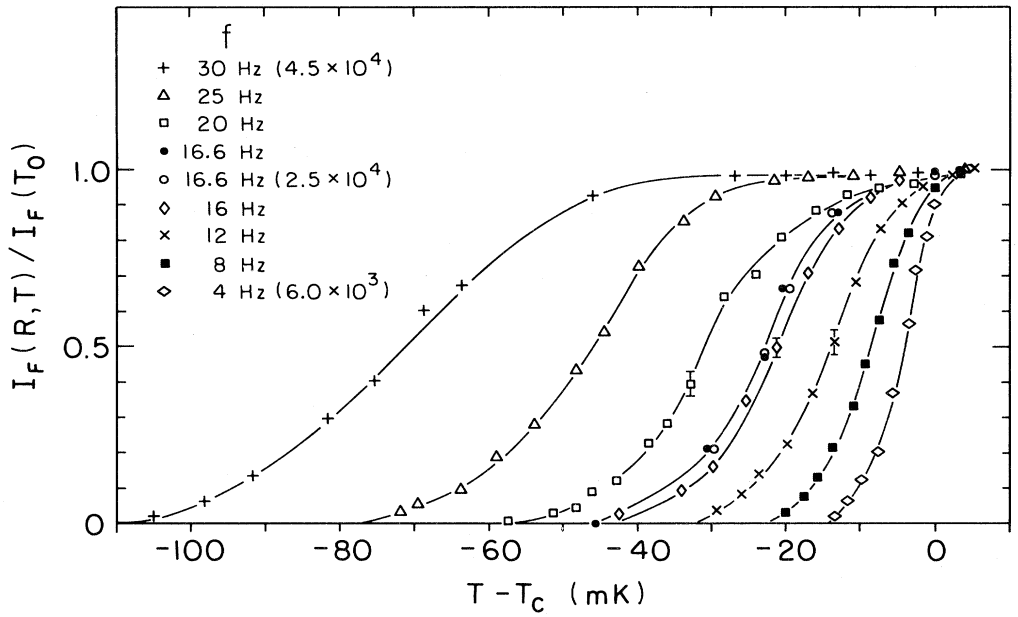

FIG. 1. Normalized mean forward intensity $I_F(R,T)/I_F(T_0)$ vs $T-T_c$ for different stirring frequencies f. Corresponding Reynolds numbers are given in parentheses for selected frequencies. The reference temperature T_0 was taken to be 5 mK above T_c. Lines have been drawn through the data points to guide the eye.

temporal fluctuations in $I_F(R,T)$ in the steady state. We define

$$\sigma_F^2(R,T)\equiv\frac{\langle[I_F(R,T,t)-\langle I_F(R,T,t)\rangle]^2\rangle}{\langle I_F(R,T,t)\rangle^2},$$

where the average, designated by angular brackets, was over a 10-sec interval and t denotes time.

Figure 1 shows the normalized mean forward intensity $I_F(R,T)/I_F(T_0)$ vs $T-T_c$ for several different stirring frequencies f. The forward intensity at the reference temperature, $T_0=T_c+5$ mK, was measured in the absence of stirring. At each stirring speed the sample temperature was lowered in roughly 5-mK steps and was held constant (with stirrer running) roughly 5 min before I_F was recorded. This time interval was ample to assure that the steady state had been reached. At a stirring frequency of 16.6 Hz measurements were made in both cooling (solid circles in Fig. 1) and heating (open circles) runs. No hysteresis is evident; apparently the steady-state ratio of intensities does not depend on the initial conditions.

It is clear from Fig. 1 that the stirring induces a steady state dramatically different from any behavior of the unstirred system. Once quenched below T_c, an unstirred system at first shows the strong light scattering associated with spinodal decomposition and then later settles into a two-phase equilibrium with only weak light scattering.[6] In the stirred system, the steady state for temperatures slightly less than T_c exhibits very little light scattering, suggesting that any phase separation which may have taken place has been confined to the formation of droplets which are small compared to the wavelength of light. Then at a Reynolds-number-dependent temperature $T_c'(R)$, a steady state is reached at which the transmitted light beam is noticeably attenuated. As the temperature is reduced still further, this attenuation becomes progressively more marked until a temperature is reached, tens of mK below $T_c'(R)$, where the steady state allows essentially no transmission of light through the sample.

In light of the above observations, let us associate phase separation with the onset of the precipitous drop in $I_F(R,T)/I_F(T_0)$ and define an apparent depression of the critical temperature, $\Delta T_c'(R)=T_c-T_c'(R)$. We identify the phase-separation temperature $T_c'(R)$ with the temperature at which the forward intensity has clearly dropped below its value in the one-phase region. Operationally we have taken this to be a drop of 15%, i.e., $I_F(R,T)/I(T_0)=0.85$ (see Sec. III). Using this definition, $\Delta T_c'(R)=12$ mK at $f=16$ Hz or $R=2.4\times10^4$.

Figure 2 shows a plot of $\log_{10}\sigma_F(R,T)$ versus temperature at a stirring frequency of 16 Hz ($R=2.4\times10^4$). Note the knee in $\sigma_F(R,T)$ occurring at approximately 7 mK below the equilibrium T_c. Associating this knee with phase separation we get $\Delta T_c'=T_c-T_c'(R)\simeq7\pm3$ mK. This value compares favorably with the value of 12 ± 2 mK obtained from measurements of $I_F(R,T)$ itself at $f=16$ Hz ($R=2.4\times10^4$).

Figure 3(a) shows double-logarithmic plots of ΔT_c versus frequency for both samples. The measurements can be fitted rather well by a power law $\Delta T_c\propto R^\lambda$ (recall that $f\propto R$). For measurements made with the glass stirrer, $\lambda\simeq2.1$. This plot would acquire a gentle concave-upward character, and the average value of λ would be diminished if ΔT_c were defined by letting I_F/I_0 be less than 0.85 (e.g., $\lambda\sim1.4$ for $I_F/I_0=0.5$). Measurements made with the nickel wire stirrer give $\lambda\sim1.4$. Therefore, in each of our two stirring cells measurements made at the same frequency, and thus the same stirring Reynolds number, give

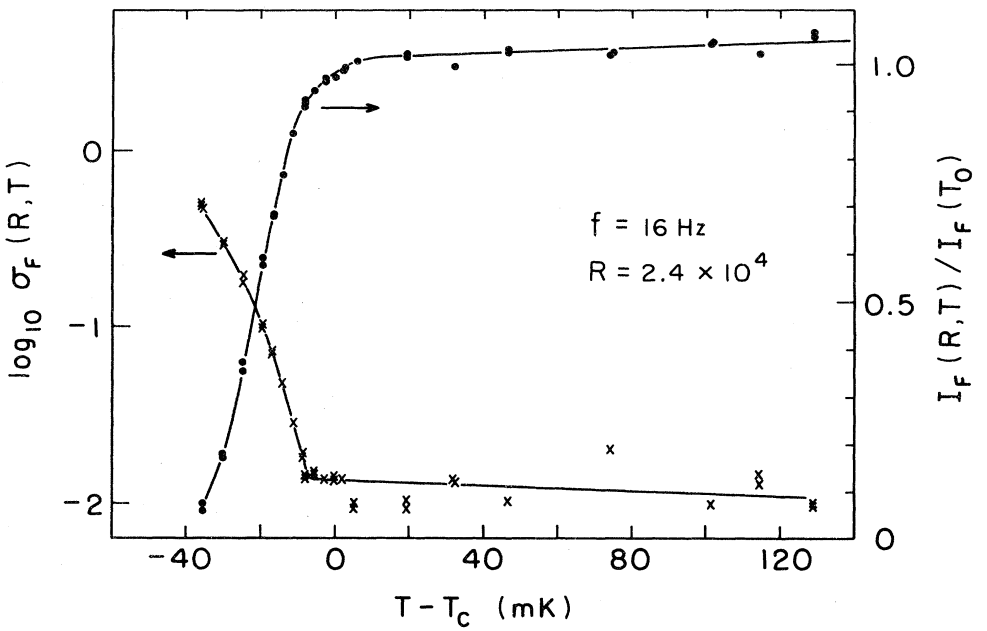

FIG. 2. $\mathrm{Log}_{10}\sigma_F(R,T)$ vs $T-T_c$ for stirring frequency $=16$ Hz ($R=2.4\times10^4$). Corresponding $I_F(R,T)/I_F(T_0)$ measurements are superposed for comparison. Lines have been drawn through the data points to guide the eye.

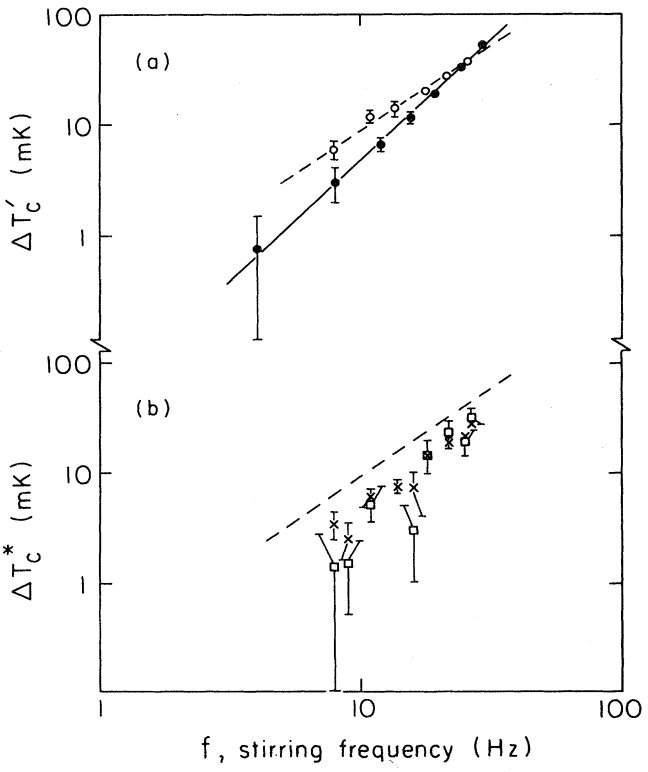

FIG. 3. ΔT_c vs stirring frequency f. (a) $\Delta T_c'$ determined by I_F measurements using the cells with the glass stirring rod (solid circles) and the nickel stirring wire (open circles). (b) ΔT_c^* determined by σ_F (crosses) and $I_\perp$ (squares) using the cell with the nickel stirring wire. Dotted line is from I_F determination of $\Delta T_c'$ using nickel wire stirrer [transcribed from (a)].

slightly different results for ΔT_c (as may be seen in the figure).

We have also measured $I_\perp(R,T)$, the average 90° light scattering intensity, as a function of temperature and frequency. For temperatures above T_c, the measurements show $I_\perp$ vs T to be independent of R and exhibit the same temperature dependence observed by Chang *et al.*[4] in their equilibrium measurements. Below T_c, $I_\perp$ increases significantly over the equilibrium value as the stirring frequency increases. For nonzero frequency the peak in $I_\perp(R,T)$, which is usually associated with the critical temperature, occurs below T_c at temperature $T_c^*(R)$. An example of $I_\perp(R,T)$ is shown for $f=16$ Hz in Fig. 4; the corresponding forward intensity measurement is also shown for comparison. While the peak in $I_\perp$ is broad on a millikelvin scale, making the position of the maximum more uncertain than is the 0.85 point in $I_F(R,T)/I_F(T_0)$, the two can be seen to agree qualitatively. Both $\Delta T_c^*(R)=T_c-T_c^*(R)$ and the apparent suppression of the critical temperature extracted from the variance of I_F are in reasonably close agreement with the $\Delta T_c'(R)$ defined above. There is a tendency for $\Delta T_c'$ to exceed ΔT_c^* by a few millikelvin. This can be seen in Fig. 3(b) which shows all three of these quantities as measured using the cell containing the nickel stirring wire.

It is interesting to note that at each frequency, $I_\perp(T)$ can be qualitatively fit with an Ornstein-Zernike function using $T_c^*(R)$ as a critical temperature. That is, $I_\perp(R,T)\simeq A/(k^2+\xi^{-2})$, where A is a normalization constant, k is the momentum transfer of the scattered radiation, and $\xi^{\pm}=\xi_0^{\pm}\,|\,1-T/T_c^*(R)\,|^{-\bar{\nu}}$. Plotting $(A/I-k^2)^{1/2\bar{\nu}}$ vs T results in a V-shaped curve with the point of the V occurring at $T_c^*(R)$. From such a plot the amplitudes $\xi_0^{\pm}$ below and above $T_c^*(R)$ were obtained by measuring the slopes of the two branches of the V. These

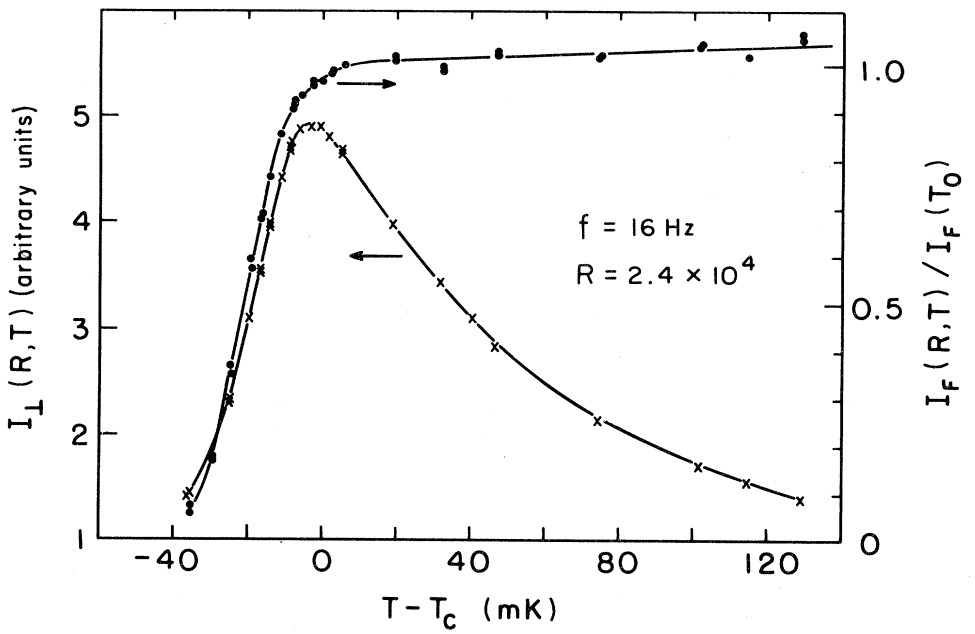

FIG. 4. Average 90° light scattering intensity $I_\perp(R,T)$ vs $T-T_c$ at $f=16$ Hz. Corresponding $I_F(R,T)/I_F(T_0)$ measurements are superposed for comparison. Lines have been drawn through the data points to guide the eye.

amplitudes are presented in Table I. The values of ξ_0^+ are in good agreement with the equilibrium measurements of Chang *et al.*[4] However, the ratios of the amplitudes ξ_0^+/ξ_0^-, also presented in Table I, are somewhat larger than predicted from a renormalization group (RG) calculation for a binary mixture in equilibrium.[7] Surprisingly, ξ_0^+/ξ_0^- decreases towards the RG value as R increases.

In addition to the results reported above, we also measured the spectral width of the stirred fluid using self-beating light spectroscopy. However, we were unable to separate out the effects of composition fluctuations from the less interesting spectral width arising from velocity gradients across the diameter of the laser beam.

III. DISCUSSION

Based on present knowledge, we can only offer a crude and somewhat speculative discussion of our data. Consider first the apparent depression of T_c. We expect that the shear produced by vigorously stirring the binary mixture will inhibit the growth of nucleating domains normally seen in spinodal decomposition experiments when a mixture is quenched to temperature $T<T_c$. We suggest that phase separation will occur only when the binary mixture is quenched deeply enough that the maximum characteristic rate for domain growth $\Gamma(k)$ just exceeds the rate of shear $S(k)$. We use this assumption to estimate the shift in critical temperature $\Delta T_c'(R)$, produced by stirring at Reynolds number R.

TABLE I. Correlation length amplitudes extracted from $I_\perp$ measurements as described in the text.

f (Hz)	ξ_0^+ (Å)[a]	ξ_0^- (Å)[a]	ξ_0^+/ξ_0^-[a]
4	2.3	0.80	2.9
9	2.4	0.79	3.0
16	2.3	0.89	2.6
25	2.7	1.20	2.3
0	2.28[b]		
0			1.91[c]

[a]Uncertainties in our experimental values are approximately ±10%.
[b]Equilibrium measurement for NE-3MP from Ref. 4.
[c]Renormalization-group calculation correct to order ϵ^2 for a binary mixture (Ref. 7).

In the spirit of Cahn's linear theory of spinodal decomposition,[8] $\Gamma(k)$ is taken as positive for k less than a critical wave number k_m, with a peak value Γ_{pk} of the order of $\Gamma(k_m)\simeq D(k_m)k_m^2$. The composition diffusivity D is roughly given by $D\simeq k_BT/6\pi\eta\xi(T)$, where η is the viscosity (we ignore its weak temperature dependence).[5] Since k_m also is of order $\xi^{-1}(T)$,[9] $\Gamma_{pk}\propto\xi^{-3}(T)\propto|T-T_c|^{3\bar{\nu}}$. As the temperature of the mixture is lowered below T_c at a fixed R, Γ_{pk} increases until at some temperature it exceeds the shear rate at k_m. This temperature is identified as $T_c'(R)$. Next we estimate $S(k_m)$ and find $\Delta T_C'(R)$.

According to generally accepted scaling ideas about turbulent mixing,[2] S loses its k dependence for k much greater than Kolomogorov's viscous cutoff wave number (k_d) and is roughly given by $S(k)\sim\nu k_0^2R^{3/2}$, where ν is the kinematic viscosity and k_0^{-1} is the size of the largest eddies (~1 cm in our case). In the present experiments $k_d\sim10^3$ cm$^{-1}\ll\xi^{-1}(T)$, so that the above value of S is set equal to Γ_{pk} to find $T_c'(R)$. The result is

$$t'\equiv\Delta T_c'(R)/T_c\sim R^{1/2\bar{\nu}}(6\pi\eta\xi_0^3\nu k_0^2/k_BT)^{1/3\bar{\nu}}\,.$$

Taking $\bar{\nu}=\frac{5}{8}$, $\xi_0=2.28$ Å, and $\eta\simeq0.005$ poise,[4] we find $\Delta T_C'(R)=0.1$ K for a stirring frequency of 16 Hz. This is

an order of magnitude larger than we observe, but not too bad in view of the crudeness of our calculation.

Onuki and Kawasaki[1] have made a very careful calculation of the effects of *uniform* (i.e., nonturbulent) shear on binary liquid mixtures near the consolute point. They calculate[10] a depression in T_c given by $t' = 0.0832(16\eta\xi_0^3 S/k_B T)^{1/3\bar{\nu}}$. Apart from a numerical factor of 0.077, this is the same result we obtained above in our crude argument if we estimate the shear rate by $S = \nu k_0^2 R^{3/2}$ as we did before. Using the estimate of OK for t', we obtain a depression ~ 8 mK for a stirring frequency of 16 Hz. This value is very close to the observed depression in T_c of ~ 12 mK at $f = 16$ Hz.

Although our crude theory and the calculation of OK give reasonable estimates of the magnitude of the depression of T_c, both predict that $\lambda = 1/2\bar{\nu} = 0.80$ in contrast to the measured value, $\lambda \sim 2$ (Fig. 3). Thus we observe a much *stronger* dependence of the critical-temperature depression on the Reynolds number than the above models predict. With respect to this discrepancy we note that our dimensional argument ignores a possible shift in the critical composition arising from stirring. Perhaps more importantly, the dimensional argument takes no account of the fact that fluctuations at wave number $k \sim k_m$ can increase by a turbulent cascade from lower to higher wave numbers as well as by the thermodynamic instability discussed above.[11]

We now turn our attention to the temperature dependence of the light scattering at fixed stirring frequency. In the presentation of our data we identified phase separation with a drop in I_F/I_0 by 15%. This choice is consistent with the sharp rise in the normalized RMS amplitude $\sigma_F(R,T)$ of the temporal fluctuations in I_F (Fig. 2). It is also consistent with precise equilibrium turbidity measurements by Chang *et al.* which reveal that I_F/I_0 drops by less than 10% unless the temperature is within ~ 1 mK of T_c.[4] Significantly larger reductions in equilibrium values of I_F/I_0 occur only at temperatures much nearer T_c. [This relatively small attenuation of I_F near T_c is due to the extremely small difference ($< 1\%$) of the indices of refraction of 3MP and NE.[4]] In contrast with measurements in unstirred binary mixtures, we observe a rapidly changing I_F over a temperature range of 10 to 50 mK (Fig. 1). Clearly our steady state is far from equilibrium and thus the usual thermally driven fluctuations in the dielectric constant are not sufficiently large to explain the functional form of I_F which we observe.

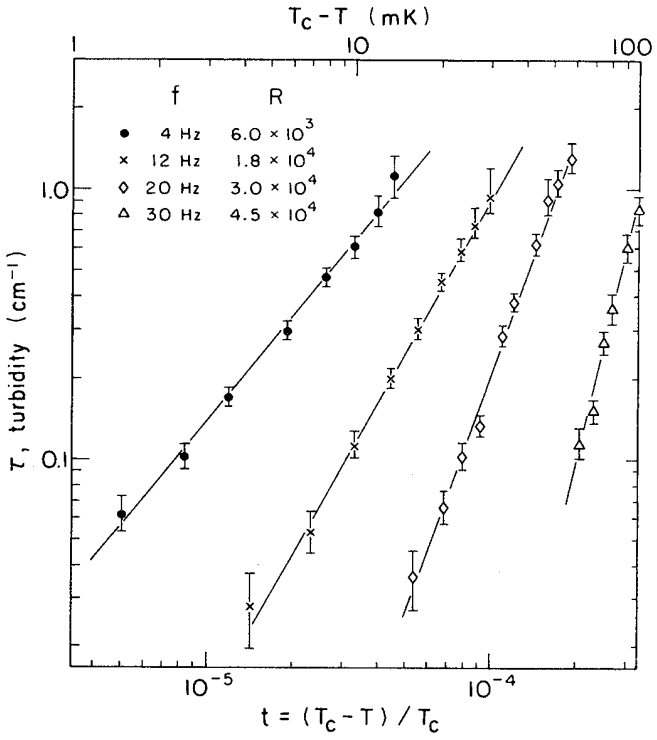

FIG. 5. Double-logarithmic plot of the turbidity vs the reduced temperature $t = (T_c - T)/T_c$ for different stirring frequencies. Corresponding Reynolds numbers R are labeled.

Suppose instead that the steady state below $T_c'(R)$ is that of a binary mixture undergoing phase separation but impeded from progressing to large length scales by the effect of turbulence. Using dimensional and scaling arguments from the theory of spinodal decomposition,[12] the intensity of scattered light from the phase-separating mixture is approximately $I(k) \simeq \langle \Delta c \rangle^2 k_m^{-3} F(k/k_m)$, where $F(x)$ is a sharply peaked function around $x = 1$ and $\langle \Delta c \rangle \sim |t|^{\beta} \sim |t|^{1/3}$ is the composition difference between phases. Taking $Dk_m^2 \approx S(k_m) \approx \nu k_0^2 R^{3/2}$ as before, and approximating $F(k/k_m)$ by a δ function at $k = k_m$, integration over scattering angle yields a turbidity τ near and below T_c' which is proportional to $|t|^{\zeta} R^{-3/4}$, where $\zeta \approx 2\beta + \bar{\nu}/2 \approx 1.0$. (In making this estimate, we have assumed that the important scattering takes place at small angles where polarization variations are negligible.) This functional dependence yields no more than qualitative agreement with our observations: for fixed Reynolds number, $\log\tau \propto 1.0 \log t$ where τ is the turbidity. Several of the curves from Fig. 1 are shown in Fig. 5 as $\log\tau$ vs $\log(t)$. These are all very close to straight lines and show slopes ζ which vary from ~ 1 to ~ 6 with ζ monotonically increasing with stirring frequency.

Consistent with the preceding model, the sharp increase in $\sigma_F(R,T)$ below T_c' might be viewed as arising from small domains of fluid at opposite ends of the two-phase miscibility gap being rapidly stretched and transported through the laser beam. Apparently, these fluctuating domains are not small enough (i.e., $\lesssim 500$ Å) to appreciably affect the scattering of light at 90° for $T < T_c'$.

IV. SUMMARY AND CONCLUSION

In summary, we have observed a large depression in the apparent critical temperature T_c of a stirred binary liquid mixture. Although the magnitude of the depression $\Delta T_c'(R)$ in T_c is consistent with models which attribute a depression in T_c to the suppression of composition fluctuations by shear, these models do not account for the observed functional dependence of $\Delta T_c'$ on the Reynolds number. Below the apparent critical temperature, the turbidity τ changes significantly throughout a temperature range of tens of millikelvin following a power law $\tau \propto (T_c - T)^{\zeta}$ where $1 < \zeta < 6$. Within this temperature range the system appears to exhibit incomplete phase

separation brought about by stirring a phase-separating mixture at long wavelengths.

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[11]We are grateful to D. R. Nelson for an enlightening discussion of this point.

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