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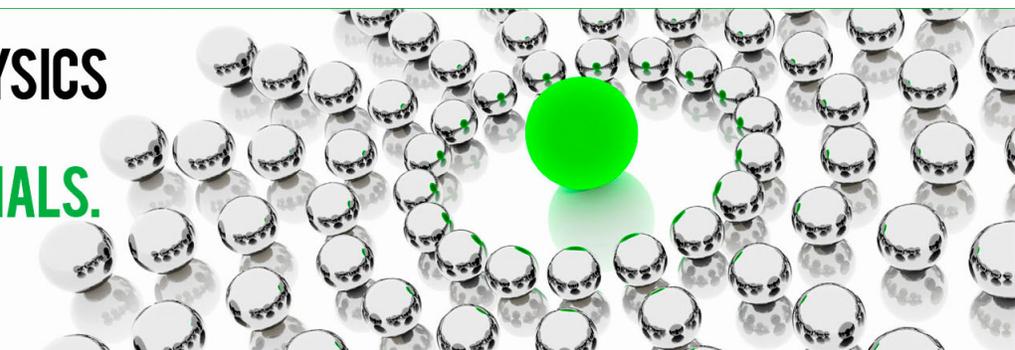
Rayleigh linewidth and turbidity measurements near a multicomponent fluid tricritical point*

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(Received 17 February 1976)

Rayleigh linewidth measurements have been performed near the tricritical point of an ethanol–water–benzene–ammonium sulfate mixture. We approached the tricritical temperature T_t along various paths of constant composition using several different samples. The linewidth always varies linearly with temperature in both two phase and three phase regions near T_t (but in the hydrodynamic regime). Since the linewidth is inversely proportional to the correlation length ξ in this regime, we find an exponent $\nu = 1.0$ in both two and three phase regions, as expected from mean field theory for thermodynamic paths of constant composition. Because of the strong temperature dependence of ξ, the hydrodynamic regime extends only to $T - T_t \simeq 1$ K. Measurements of the turbidity τ indicate that the product $\Gamma \tau^{1/2}$ is constant within our experimental uncertainties, from which we infer that the susceptibility exponent $\gamma \approx 2$ along paths of constant composition near the tricritical point.

I. INTRODUCTION AND THEORY

The only fluid tricritical point that has been extensively investigated is that which occurs in ^{3}He–^{4}He mixtures.[1] Griffiths and Widom[2,3] have pointed out that tricritical points of a different type occur in certain fluid mixtures containing three or more components. In contrast to the ^{3}He–^{4}He case which is known as a symmetric tricritical point, the multicomponent mixtures do not have a symmetry operation that relates two of the coexisting phases near the tricritical point. Recently, Lang and Widom[4] have studied the phase diagram of one particular system (benzene–ethanol–water–ammonium sulfate) and have determined its tricritical composition and temperature. In addition, they estimated the tricritical exponents associated with the vanishing of the three phase region in composition space as the tricritical temperature is approached. However, none of the other tricritical exponents have been measured for this system. In this paper we present the results of measurements made by laser light scattering techniques, from which the tricritical behavior of the correlation length and concentration susceptibility has been determined.

The static tricritical exponents are expected to assume classical or mean-field values, as indicated by the application of renormalizationgroup techniques to models of the ^{3}He–^{4}He system by Riedel and Wegner.[5] Griffiths has presented[6] a phenomenological model of the classical Landau type which is applicable to quaternary fluid mixtures. Many of its predictions for the shape of the three phase region in composition space have in fact been confirmed by Lang and Widom.[4]

In this paper we are concerned with the tricritical exponents ν and γ which characterize, respectively, the correlation length ξ for concentration fluctuations and the susceptibility $\partial \psi / \partial \zeta$. Here ψ is the order parameter and ζ is its thermodynamic conjugate field. For a multicomponent mixture, ψ is a linear combination of the mole fractions of the various components, and ζ is linearly related to their chemical potentials.

It is necessary to distinguish between several values of the exponents which depend on the thermodynamic path of approach to the tricritical point, and we shall use Griffith's notation[7] in doing this. In the mean field approximation, $\gamma_t = 1$ and $\eta_t = 0$.[5,8] If the scaling relation $\gamma_t = (2 - \eta_t)\nu_t$ applies as expected, then $\nu_t = \frac{1}{2}$. These exponents are expected to be correct provided the path of approach to the tricritical point is one along which the field ζ is constant. However, in our experiments we follow paths of constant composition instead. In this case it seems plausible that the exponents γ_t and ν_t will be increased by a factor of ϕ (the crossover exponent[7] which in the mean-field approximation is 2), or equivalently in the case at hand, by a factor of $(1 - \alpha_t)^{-1}$, with the specific heat exponent α_t equal to[5] $\frac{1}{2}$ (see the discussion in Refs. 7 and 9). This leads us to expect observed exponents of $\nu = 1$ and $\gamma = 2$.

The property probed by Rayleigh linewidth measurements is the decay rate of concentration fluctuations, which is a dynamic property. However, the dynamics of multicomponent fluid tricritical points have not been investigated theoretically, with the exception of a study by Kawasaki[10] to which we shall return later. Our results can be understood nevertheless by utilizing the fact that the linewidth is inversely proportional to the correlation length ξ in the so-called hydrodynamic regime, defined by the inequality $q\xi \ll 1$, where q is the wavenumber of the fluctuation. Assuming that background contributions are negligible, as has always been found to be the case for fluid mixtures, the precise relationship predicted by mode–mode coupling theory and confirmed by many experiments is[11]

$$\Gamma = 1.052(k_B T / 6\pi \eta_s \xi)q^2 , \quad (1)$$

where η_s is the macroscopic shear viscosity. Now η_s has a critical part that typically exhibits a weak logarithmic divergence given by[11]

$$\eta_s = (8\bar{\eta}_s / 15\pi^2) \ln(q_D \xi) + \eta_s^B , \quad (2)$$

where q_D and $\bar{\eta}_s$ are constants characteristic of the system and η_s^B is the background shear viscosity. Regard-

less of the exact behavior of η_s in this system, it is clear that its divergence, if any, will be quite weak. In this case, previous work[11] indicates that Eq. (1) always fits the linewidth data within a few percent in the hydrodynamic regime, if the measured shear viscosity is replaced by an adjusted parameter. Qualitatively, Eq. (1) is the linewidth of light scattered by a collection of spherical scatterers of radius ξ. There is no reason to expect that the proximity of a tricritical point would change the relationship between Γ and ξ. Consequently, we use this relationship to determine the exponent ν describing the tricritical behavior of ξ.

The susceptibility exponent γ can be determined from the temperature dependence of the turbidity, as discussed by Puglielli and Ford.[12] Assuming that the correlation function for the order parameter is of the Ornstein–Zernike type (i.e., $\eta = 0$), the turbidity is of the form

$$\tau = B\chi f(\alpha) , \tag{3}$$

where χ is the susceptibility and B is a prefactor that depends on the concentration dependence of the dielectric constant. The argument of the function $f(\alpha)$ is $\alpha \equiv 2(k_0 \xi)^2$, where k_0 is the wave vector of the incident light in the fluid. Sufficiently far from T_t, α is small and $f(\alpha)$ approaches a constant, independent of α. Thus in this regime, the turbidity is a direct measure of the susceptibility and can be used to estimate the exponent γ.

II. SAMPLES AND APPARATUS

We present results for two samples which were prepared (in different laboratories) from spectroscopic grade components without special treatment other than centrifugation to remove dust. Sample A, whose composition is given in Table I, was prepared by weight to match the tricritical composition determined by Lang and Widom. Sample B has a slightly different composition and is discussed here in order to demonstrate that the central results are not significantly dependent on the exact sample composition. However, the domain in temperature of three phase coexistence is quite different for these samples, a result which is not surprising given the characteristics of the phase diagram determined by Lang and Widom.[4] If the overall composition of the sample is represented by a point in a composition tetrahedron, then the region of three phase coexistence is a solid figure bounded by a smooth space curve. This figure adjoins both two and one phase regions. As the temperature is increased toward the tricritical temperature T_t, the three phase region shrinks continuously toward a point outside itself. The qualita-
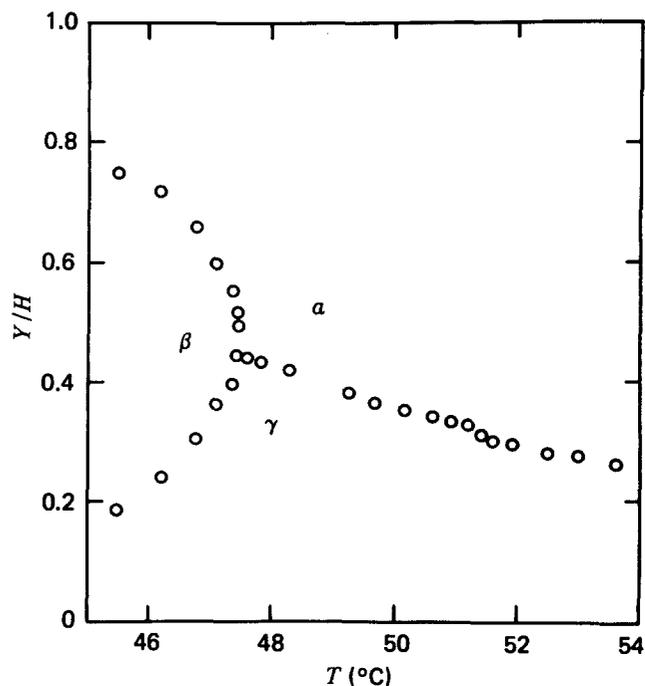
TABLE I. Sample composition by mass fraction.

	Sample A	Sample B
Benzene	0.181	0.199
Ethanol	0.450	0.427
Water	0.351	0.351
Ammonium sulfate	0.0175	0.0222
Three phase region	$47.7 < T < 48.5\,°C$	$T < 47.4\,°C$

FIG. 1. Meniscus heights Y (normalized to the sample height H) as a function of temperature for sample B. There are three phases below $47.4\,°C$, but only two phases (α and γ) above this temperature.

tive behavior observed for any given sample will then be extremely sensitive to its exact composition.

Sample B is located in the three phase region for temperatures below $47.4\,°C$, as shown in Fig. 1, which gives the meniscus heights as a function of temperature for this sample. The three phases are denoted by the letters α, β, γ beginning at the top of the sample. As the temperature is increased, the middle (β) phase continuously shrinks to zero, leaving only the α and γ phases. The remaining meniscus moves only gradually as the temperature is further increased to $60\,°C$. In terms of the phase diagram in composition space, this sample enters the two phase region at a temperature $T < T_t$, while the three phase region is still of finite size. The sample is not exactly at the tricritical composition, and hence nothing striking occurs at T_t. If viewed in the space of thermodynamic fields (chemical potentials and temperature) the system passes near the tricritical point and then moves away from it as the temperature is increased.

Sample A, which has nominally the tricritical composition, exhibits quite different behavior. At temperatures below $47.7\,°C$, only the α and β phases are present, with β predominating. As the temperature is increased, the γ phase appears at the bottom of the sample at $47.7\,°C$. At $48.5\,°C$, the meniscus separating α and β reaches the top of the sample, leaving only β and γ phases at higher temperatures. Again, this sample passes near the tricritical point in the field space, but not exactly through it. Many other samples have been prepared in order to approach the tricritical point more closely, but without much success. The precision required is much better than 1% in each component, as
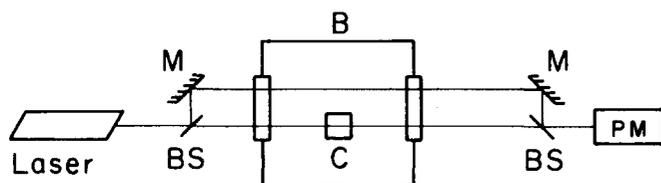
FIG. 2. Optical arrangement used to measure the turbidity showing the sample cell (C), temperature-controlled bath (B), and the two optical paths.

minute variations significantly affect the location of the phase boundaries. Fortunately, the critical behavior does *not* seem to be strongly dependent on the precise composition. Both of the samples discussed here are sufficiently close to the tricritical composition to exhibit tricritical behavior.

The light scattering measurements (homodyne spectroscopy) were performed in different laboratories using standard techniques. For sample A, a digital correlator was used to measure the linewidth of scattered light from a helium—neon laser at 33.4° from the forward direction. The sample temperature was controlled to within 10^{-3} °C, but this precision was not actually required because the sample composition was not exactly at the tricritical value. For sample B, a real time spectrum analyzer was used to measure the spectrum of scattered light at 4880 Å and a scattering angle of 90°. After subtraction of the shot noise background (determined using a light bulb supplying the same photocurrent), the linewidths were obtained by nonlinear least squares fitting. Temperature control was good to about 0.005 °C, which was adequate for the present experiments.

In addition, turbidity measurements were performed for sample A using the optical arrangment shown in Fig. 2. A split beam technique was used to compensate for laser intensity variations. The intensity of each beam was about 0.015 mW, and they were detected alternately by a photomultiplier that was known to be linear to better than 1% over the relevant intensity range. The turbidity τ was obtained from the relation

$$\tau = C - (L^{-1})\ln(R/R_0) , \qquad (4)$$

where R and R_0 are the counting rates obtained from the sample and reference beams, L is the path length, and C is a constant determined by assuming that the attenuation is negligible far from T_t. The turbidity is such a strong function of temperature that this is a good assumption.

III. RESULTS

The temperature dependence of the Rayleigh linewidth Γ for the β phase of sample A is shown in Fig. 3 as Γ/q^2, where $q = (4\pi n/\lambda_0)\sin\frac{1}{2}\theta$ is the scattering vector. Here θ is the scattering angle, λ_0 is the vacuum wavelength, and n is the index of refraction. We use the mass-weighted average 1.38 as an estimate of n even though the actual value differs slightly in the different phases. We find experimentally that the linewidth is in fact proportional to q^2, although a search for small

deviations from this q dependence has not been undertaken.

The central feature of Fig. 3 is that the linewidth is accurately linear in temperature, although its slope changes abruptly when the number of phases changes by one. The minimum value of Γ is attained at 48.5 °C, the upper limit of three phase coexistence.

Similar behavior is found for sample B, whose composition is slightly different, as shown in Fig. 4. In this case, we present measurements over a larger temperature range and in several of the coexisting phases. In the two phase region at high temperatures, we again find a linear temperature dependence, especially in the strongly scattering α phase. A nonlinear least squares fit of a single power law $A[(T - T^*)/T^*]^\nu$ to the α phase data above 47.4 °C was performed, with A, T^*, and ν as adjustable parameters. The exponent was $\nu = 0.96 \pm 0.05$, where the quoted uncertainty reflects the correlations between all three adjusted parameters. A log–log plot of the resulting best fit is shown in Fig. 5. The significance of the parameter T^* will be discussed in the next section.

The γ phase linewidth in the two phase region above 47.4 °C is essentially the same as that of the α phase, except for small deviations above 50 °C. This small departure from linearity of the γ phase linewidth could be an experimental artifact, since the scattering is extremely weak in that phase above 50 °C, and heterodyning with stray light would tend to reduce the linewidth.

Linewidth data for the three phase region below 47.4 °C is also shown in Fig. 4. While the variation is approximately linear, the data are not extensive enough to draw quantitative conclusions for this sample.

Finally, in Fig. 6 we present turbidity data on the β phase of sample A. The turbidity is much more strongly temperature dependent than the linewidth, and is difficult to measure below 46 °C. It increases as the line width decreases, again showing slope discontinuities at 47.7 and 48.5 °C. Motivated by the considerations of Sec. I, we have plotted in Fig. 6 the product $\Gamma\tau^{1/2}$ vs T. It can be seen that this product is approximately independent of temperature.
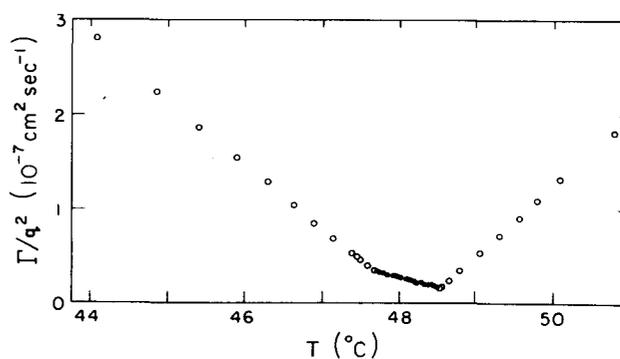

FIG. 3. Rayleigh linewidth as a function of temperature for the β phase of sample A. There are three phases in the region indicated by solid points (see text).
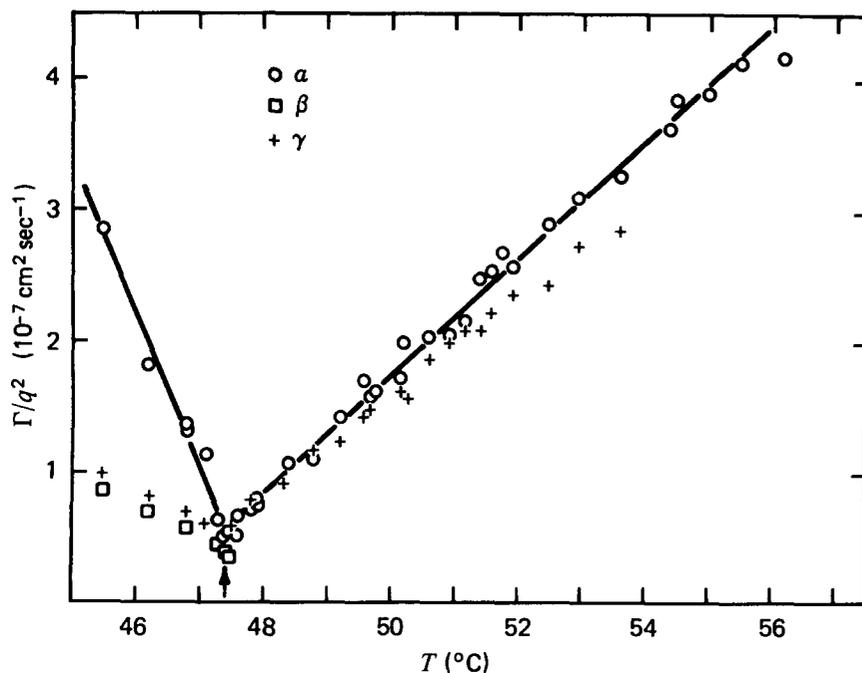
FIG. 4. Rayleigh linewidth as a function of temperature for all phases of sample B. The β phase exists only to the left of the arrow. The solid lines are drawn through the α phase data.

IV. DISCUSSION AND CONCLUSIONS

In order to interpret these measurements in terms of tricritical exponents, it is first necessary to consider the fact that our samples do not have exactly the tricritical composition. This situation is of course inevitable, given the number of composition variables to be adjusted. Sample A is probably quite close to the tricritical composition, as indicated by the fact that the linewidth in the three phase temperature range

FIG. 5. Least squares fit of the α phase data of Fig. 4 to a power law. The slope is 0.96 ± 0.05.

would extrapolate to zero at $49.2 \pm 0.1\,°C$, which almost coincides with the estimated tricritical temperature.[4]

In the case of ordinary critical points in binary mixtures, samples which are not at the critical composition show apparent divergences at temperatures other than the critical temperature, when a path within a one phase region is followed.[13,14] However, the critical exponents characterizing these divergences are unchanged. Similar behavior has been observed[1,15] for the exponent describing the concentration susceptibility in ^3He-^4He mixtures near the tricritical point. Thus, the fact that our samples are not exactly at the tricritical composition does not necessarily prevent us from observing tricritical behavior. We must also expect that the correlation length and concentration susceptibility will appear to diverge at temperatures other than the tricritical temperature. The linewidth data of Figs. 3 and 4 do in fact show this behavior. Each of the
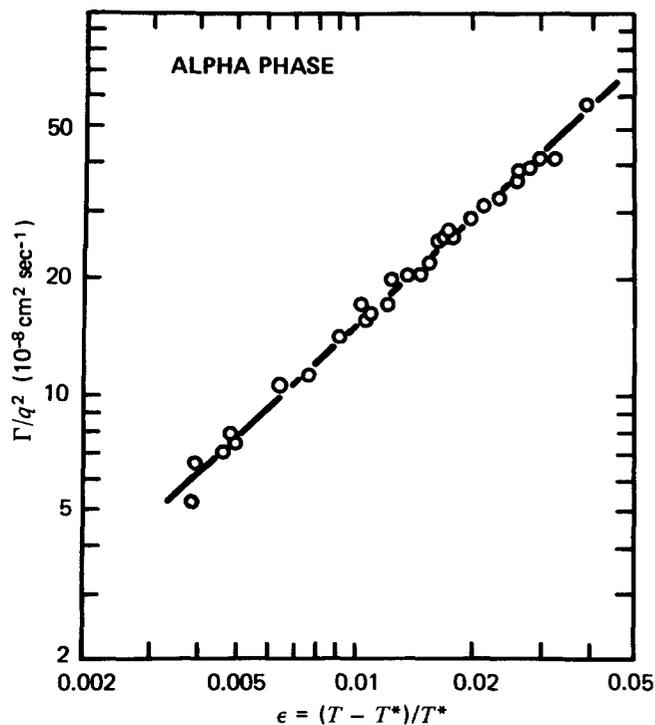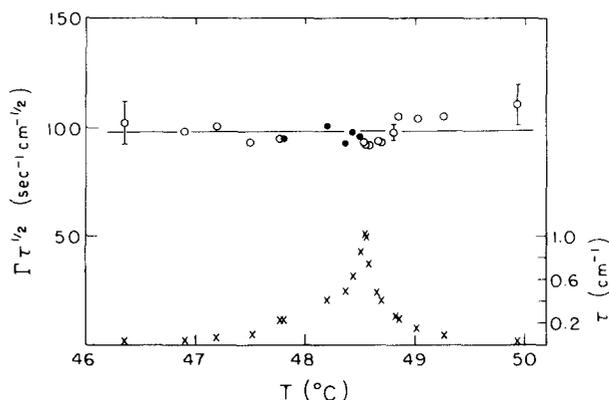

FIG. 6. Turbidity as a function of temperature for sample A. Discontinuities occur when the number of phases changes. The horizontal line indicates that the product $\Gamma\tau^{1/2}$ is approximately constant. The solid points lie in the three phase region.

straight line segments in these figures extrapolates to zero at a different temperature T^*. However, the exponent ν characterizing the inverse of the linewidth or the correlation length is the same on each segment, namely unity. This behavior is consistent with the expected classical value, as discussed in Sec. I.

Kawasaki[10] has predicted the existence of two critical modes with decay rates proportional to $\xi^{-3}f(q\xi)$, where $f(q\xi)$ is a scaling function that behaves as $(q\xi)^2$ when $q\xi \ll 1$. This leads one to expect a linewidth proportional to $q^2\xi^{-1}$, a result that strengthens our interpretation of the data. Papoular[16] has recently noted that a van Hove theory of the dynamics, which would predict an order parameter decay rate that behaves asymptotically as ϵ^2 in the three phase region, is not substantiated by our observations.

Light scattering measurements in ^{3}He–^{4}He mixtures by Leiderer et al.[17,18] also show mean field behavior. However, their exponents apply to the "subsidiary order parameter"[7] and not to the superfluid order parameter. For example, they found $\gamma = \nu = \eta = 1$ in the superfluid phase below T_t. Our experiments in the quaternary system would be analogous to the behavior of the superfluid order parameter, whose fluctuations cannot be studied by light scattering.

The absolute value of the correlation length cannot be obtained accurately without viscosity measurements. However, we can obtain a rough estimate by using the viscosity of ethanol–water mixtures at 49 °C in conjunction with Eq. (1) and the data of Fig. 3. Along the middle segment of Fig. 3 we estimate that $\xi \approx (3 \times 10^{-10}) \times \epsilon^{-1} m$, where $\epsilon = (T_t - T)/T_t$ and $T_t = 49.2\,°$C. The numerical coefficient could be substantially in error but it is reasonable. The important qualitative point is that the temperature dependence is much stronger than is the case near an ordinary critical point. Consequently, ξ becomes comparable to the reciprocal of the scattering vector q relatively far from T_t. Even though we can approach no closer than 0.8 °C to T_t while preserving three phases, we are probably barely within the hydrodynamic regime. The linewidth data show no deviations from hydrodynamic behavior, however. Near an ordinary critical point the hydrodynamic regime extends at least a factor of 100 closer to the critical point.

If the exponent γ is in fact 2, as suggested in Sec. I, and if the turbidity is proportional to the susceptibility, then the product $\Gamma\tau^{1/2}$ should be constant. The data of Fig. 6 indicate that this product is in fact constant to within 10%, so that $\gamma \approx 2$. However, if our measurements are not accurately within the hydrodynamic regime, as suggested by the estimated size of ξ, then the turbidity would have to be corrected by the function $f(\alpha)$ of Eq. (3). The exponent γ would then be somewhat increased. Consequently, our approximate result $\gamma \approx 2$ is actually a lower limit. We cannot carry out

these corrections because the absolute magnitude of ξ is not accurately known.

Because of the large number of degrees of freedom of this system, one cannot approach the tricritical point as closely as one can approach the critical point of a binary system. This limitation stands in the way of measurements extending over many decades in ϵ. However, the linewidth and turbidity measurements presented here support the applicability of mean field tricritical exponents in this quaternary fluid system. Measurements of the angular dependence of the intensity of scattered light would be desirable in order to verify these conclusions. Further theoretical work on the relaxation of concentration fluctuations in multicomponent systems would facilitate a more direct interpretation of our linewidth measurements.

ACKNOWLEDGMENTS

*Work supported by the Research Corporation and the National Science Foundation.

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