Light-Scattering Study of the Critical Behavior of a Three-Component Liquid Mixture*

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Light scattering measurements were made in the ternary system bromobenzene-water-acetone, with the acetone playing the role of an impurity. Because of the long range of the concentration fluctuations exhibited by this system, it was possible to explore with relative ease the nonhydrodynamic as well as the hydrodynamic regimes. Measurements of both the intensity and spectral width of the scattered light yielded a number of parameters which could be compared with several forms of theory.

Recently reported light scattering measurements[1] revealed that the addition of roughly 6% H_3PO_2 to a critical binary mixture of phenol and water produced virtually no change in the critical exponents γ and γ^*. These exponents characterize, respectively, the divergence of the scattered light intensity (I) and the inverse spectral width (Γ^{-1}) as the critical temperature, T_c, is approached. The aim of the present experiment was to examine critical behavior of a system in which the fraction of impurity present was very large. We chose for this study a critical mixture of bromobenzene (18.8 wt%), water (23.6 wt%), and acetone (57.6 wt%), with the acetone playing the role of the impurity.[2-4]

The experimental techniques for measuring I and Γ have been described in Ref. 1. The primary light source was the 6328-Å line from a 15-mW He-Ne laser. Sample preparation was facilitated by the fact that bromobenzene-water-acetone (henceforth referred to as BWA) has a very symmetric binodal curve in a wt% representation.[5] Except where otherwise noted, the experiments were carried out above T_c, which was 28.39°C. The intensity and spectral width measurements spanned the intervals $1°C \lesssim \Delta T \lesssim 8°C$ and $0.025°C \lesssim \Delta T \lesssim 6°C$, respectively, where $\Delta T \equiv T - T_c$.

Probably the most striking property of BWA is the long range of the critical fluctuations which this system (and perhaps a large class of ternary systems[6]) exhibits. For example, at a scattering angle θ of 144° we observe that the product of the photon momentum transfer K and the correlation length ξ_Γ is unity when $\Delta T = 0.3°C$. As usual $K = (4\pi/\lambda)\sin\frac{1}{2}\theta$, where λ is the wavelength of light in the mixture. In contrast, observations at the same scattering angle in the pure binary mixture

cyclohexane-aniline give $K\xi_\Gamma = 1$ when $\Delta T \lesssim 0.03°$ C.[7]

By making measurements at several scattering angles and covering a wide temperature range, it was possible to span both the hydrodynamic ($K\xi \ll 1$) and nonhydrodynamic ($K\xi \gg 1$) regimes.[8] In addition to yielding values of γ and γ^*, the data also provided a determination of the exponents ν and ν_Γ. The exponents ν, ν_Γ, γ, and γ^* are defined by the equations

$$\xi = \xi_0 \epsilon^{-\nu}, \quad \xi_\Gamma = \xi_{0\Gamma}\epsilon^{-\nu_\Gamma}, \tag{1}$$

$$\lim_{K\to 0} I^{-1} \propto \epsilon^\gamma, \tag{2}$$

and

$$\lim_{K\to 0} \Gamma \propto K^2 \epsilon^{\gamma^*}, \tag{3}$$

where $\epsilon \equiv \Delta T/T_c$. Here ξ and ξ_Γ are the correlation lengths obtained from intensity and spectral width measurements, respectively. By measuring both I and Γ in the transition region, $K\xi \lesssim 1$, the exponents ν and ν_Γ could be obtained from the following equations:

$$I^{-1} \propto \epsilon^\gamma(1 + K^2\xi^2), \tag{4}$$

$$\Gamma \propto K^2 \epsilon^{\gamma^*}(1 + K^2\xi_\Gamma^2) \equiv DK^2(1 + K^2\xi_\Gamma^2), \tag{5}$$

where the parameter D is a concentration diffusivity.

From the scattered light intensity measurements, it was found that

$$\gamma = 1.50 \pm 0.08, \quad 2\nu = 1.50 \pm 0.08, \tag{6}$$

and from the spectral width data

$$\gamma^* = 0.78 \pm 0.06, \quad 2\nu_\Gamma = 1.54 \pm 0.10. \tag{7}$$

The static scaling <u>Ansatz</u> leads to the relation $\gamma = 2\nu$ if one takes the exponent η to be zero.[9] Also, it is expected from the theoretical work of

Kawasaki,[10] Kadanoff,[11] and Swift[12] that $\gamma^* = \nu = \nu_\Gamma$. These predicted equalities are consistent with our observations as well as those of others.[13]

All of the results quoted in (6) and (7) lead to a value of γ which is larger than the values (1.2-1.4) obtained in most pure binary systems and simple fluids.[13] It thus appears that our ternary mixture is exhibiting the critical-exponent renormalization discussed in Refs. 3 and 4 and by Fisher.[14] Using rather general thermodynamic arguments, Fisher has shown that the exponent γ in an impure system is related to γ and the heat capacity exponent α in the pure system as follows:

$$\gamma_0 < \gamma_x < \gamma_0/(1-\alpha_0), \tag{8}$$

where the subscripts x and zero refer to the impure and pure systems, respectively. Only at temperatures sufficiently close to T_c and for sufficiently large impurity concentrations does one expect to observe γ_x close to the "fully renormalized" $\gamma_x{}^F \equiv \gamma_0/(1-\alpha_0)$. The assumption that $\gamma_0 = 1.3$ and that α_0 has its Ising model value of $\frac{1}{8}$ in the pure binary bromobenzene-water mixture leads to a value $\gamma_x{}^F = 1.5$. From Eq. (6), this is seen to be very close to the observed value. It should be noted here that bromobenzene and water are essentially immiscible and therefore that the critical temperature of the binary mixture is so high that in fact the single-phase state may not exist except, perhaps, at elevated pressures. It is the extreme immiscibility of these

fluids that could well account for the fact that the critical exponents in (6) and (7) show appreciable renormalization.[15] This explanation is suggested by recent work of Fisher and Scesney,[16] who have calculated γ_x using a mobile-electron Ising model in which the absence of electrons plays the role of an impurity. They find that for values of $|\epsilon|$ in the interval 10^{-2} to 10^{-4} and for very large impurity concentrations, $\gamma_x \simeq 1.4$.[17] This is midway between γ_0 and our experimental value.

It has already been noted that the nonhydrodynamic region is readily accessible to study in BWA because the range of the fluctuations is so large. This fact is apparent in Fig. 1, which shows a plot of $\log\Gamma$ vs $\log\Delta T$ for two scattering angles. At $\theta = 28.6°$, $\log\Gamma \propto \log\Delta T$, in agreement with Eq. (3). Curve A is a straight-line fit to the data points. The measurements at this small scattering angle (for which $K\xi_\Gamma \ll 1$) provide an evaluation of both γ^* as well as the amplitude of D. The upper set of points corresponds to the scattering angle $\theta = 144.4°$. The straight line B in Fig. 1 is a line parallel to A but shifted upward by the factor $K^2(\theta = 144.4°)/K^2(\theta = 28.6°)$. As expected, the measured values of Γ at the larger angle lie on this line in the asymptotic region $K\xi \ll 1$, i.e., at the larger values of ΔT. By fitting the upper set of data points with Eqs. (1) and (5) in the interval $0.3°C \lesssim T \lesssim 1°$ ($K\xi_\Gamma \lesssim 1$), it was possible to evaluate $\xi_{0\Gamma}$ as well as the exponent ν_Γ. This fit is shown as the curved line C in Fig. 1. Equation (5) is clearly seen to fail for
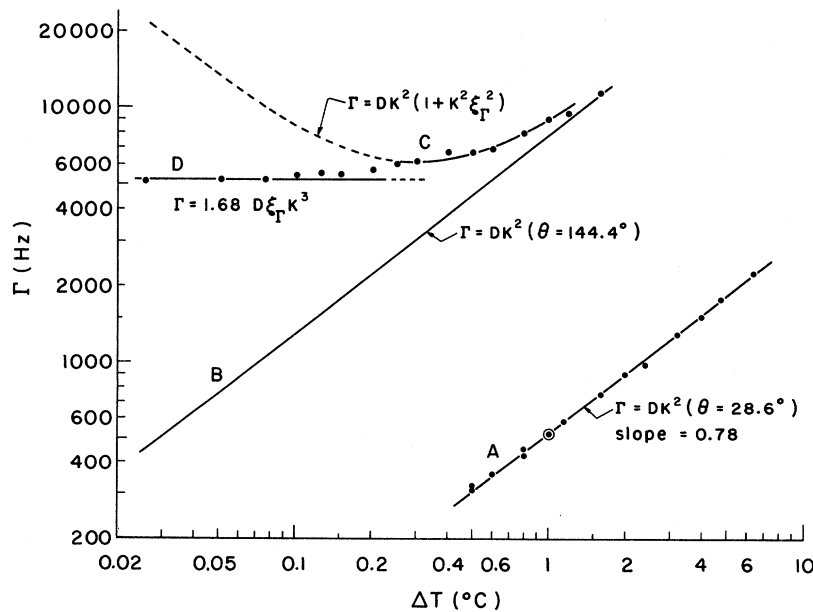

FIG. 1. Temperature dependence of the decay rate Γ of the concentration fluctuations in the bromobenzene-water-acetone system. The lines in figure represent a fit of the data by various equations given in the text.

$\Delta T \lesssim 0.2$ (dashed portion of curve).

Of special interest is the temperature interval $0.02°C \lesssim \Delta T \lesssim 0.1°C$, which corresponds to the non-hydrodynamic region. Here Γ is seen to become temperature independent. By measuring Γ at various values of K over this interval, it was found that $\Gamma \propto K^{3.0 \pm 0.2}$. This observation is in agreement with the predictions of dynamic scaling[8] and with the recent work of Kawasaki.[10] Kawasaki's analysis of mode-mode coupling in the decay of concentration fluctuations in a binary system yields the relation[18]

$$\Gamma = 1.52 D \xi_\Gamma K^3, \quad K \xi_\Gamma \gg 1. \tag{9}$$

The horizontal line D in Fig. 1 corresponds to $\Gamma = 1.68 D \xi K^3$, which is in agreement with (9) when experimental errors are taken into account and also with the results of the previously mentioned study of the cyclohexane-aniline system.[7] Also, it was observed that in BWA, $\xi_{0\Gamma}^2/\xi_0^2 = 0.3 ^{+0.2}_{-0.1}$. For a binary mixture Fawasaki predicts this ratio to be 0.6.[10]

Finally, from preliminary measurements carried out below the critical temperature and in the hydrodynamic regime, we have measured the ratio

$$R_I \equiv I(\Delta T)/I(-\Delta T), \quad K\xi \ll 1. \tag{10}$$

In (10) the functional dependence of I on ΔT has been explicitly designated. Both $I(\Delta T)$ and $I(-\Delta T)$ refer to the same scattering angle, which in our case was 50°. At $|\Delta T| = 2.6°$ and in the high-density phase, it was found that $R_I = 1.41 \pm 0.1$.[19] This result obviously suggests strong renormalization, since it is not only smaller than the Ising-model value, $R_I \simeq 5$, but also than the mean-field prediction, $R_I = 2$. In the few one- and two-component systems which have so far been studied, R_I is observed to be approximately 5.[1,20]

Recently, Fisher and Scesney have evaluated R_I using the mobile-electron Ising model mentioned above.[21] They find that for a system which, in the absence of impurities, has $R_I = 5$ and $\gamma_0 = 1.25$, the renormalized value of R_I is 1.2 in the limit of high impurity concentration and small $|\epsilon|$. This is in good agreement with our measurement.

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[6]A ternary system possesses a line of critical points (or plait points) lying on the coexistence surface. At each temperature, the critical point is characterized by a critical composition. Varying the temperature at fixed sample composition takes one further away from one critical point but still leaves one close to an infinity of others if the coexistence surface is steep. This may account for the apparently large value of ξ_Γ exhibited by BWA. (We are indebted to Professor B. Widom for this observation.)

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[17]To obtain this value of γ_x from Ref. 16 it is assumed that $\alpha_0 = \frac{1}{8}$ and $\gamma_0 = 1.3$.

[18]The right side of (9) is temperature independent because $D \propto \epsilon^\nu$ and $\xi \propto \epsilon^{-\nu}$ (see Refs. 9-12).

[19]This ratio is of interest only insofar as R_I is independent of $|\Delta T|$, i.e., if γ has the same value above and below T_c. In these preliminary experiments the two exponents were found to differ by approximately twice the experimental error.

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