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OBSERVATION OF TIME-DEPENDENT CONCENTRATION FLUCTUATIONS IN CRITICAL MIXTURES*

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Frequency spectra of time-dependent fluctuations for systems near the critical point have been studied using a He-Ne laser with heterodyne[1,2] and "self-beating"[3] techniques. Although preliminary experiments show essential agreement with the Landau-Placzek theory,[4] Fixman and Botch,[5] and more recently Felderhof,[6] have proposed a modified linewidth formula which takes into account the effects of correlation. An estimate on the magnitude of departures from the Landau prediction has also been made.[7] In view of the additional difficulties which one encounters in critical opalescence studies of one-component systems due to the effects of isothermal compressibility and gravity,[8] we have chosen a critical mixture with a very large Debye molecular interaction parameter[9] (l) for our experiments. This Letter presents recent measurements on the angular dependence of the spectral distribution of quasielastically scattered light from a binary fluid mixture, isobutyric acid and water, near its critical mixing point. We will report subsequently the results of a detailed experimental study of the temperature as well as the angular dependence of the spectral width of the isobutyric acid-water system in the very immediate neighborhood of its critical mixing point.

For binary fluid mixtures, Debye[10] considered the diffusion broadening as reflection from standing concentration waves in which each wave with a wavelength Λ is one of the Fourier components of the fluctuation pattern and obeys the Bragg relation

$$K = ks, \tag{1}$$

where $K = 2\pi/\Lambda$, $k = 2\pi/\lambda$, and $s = 2\sin\frac{1}{2}\theta$, with λ the wavelength in the medium and θ the scattering angle. If the nonpropagating concentration fluctuations decay exponentially with time, the power spectrum, $I(\vec{K}, \omega)$, is a Lorentzian-shaped line with a half-width Γ which determines the decay rates of concentration fluctuations. The shape of $I(\vec{K}, \omega)$ provides information on the time-dependent correlation function even if $I(\vec{K}, \omega)$ does not obey the Landau-type theory. With a "self-beating" technique, the power spectrum $I_S(\vec{K}, \omega)$ of the current fluctuations entering the General Radio 1900-A wave analyzer, as a function of frequency ω and at constant $\vec{K}$, is directly proportional to $2\Gamma/[\omega^2 + (2\Gamma)^2]$ which is also a Lorentzian-shaped line centered at $\omega = 0$ with a width equal to 2Γ. The Debye theory predicts that, in the absence of correlation,

$$\Gamma = aK^2, \tag{2}$$

where a is proportional to the change of osmotic pressure with respect to concentration $(\partial\pi/\partial c)$. A logical extension of the theory for systems near the critical point would be Fixman's modification[5] which predicts that

$$\Gamma = (a + bK^2)K^2, \tag{3}$$

where $a/b = \kappa^2$, κ being related to the inverse correlation length of Ornstein and Zernike: $G(r) \propto e^{-\kappa r}/r$.

We have selected the isobutyric acid-water system for the following reasons: (1) Both components could be purified. (2) Both components are stable since the phase separation temperature in several sealed samples remains constant to within 0.001° over periods of many months. (3) The system is weakly opalescent. (4) The system has the largest known Debye

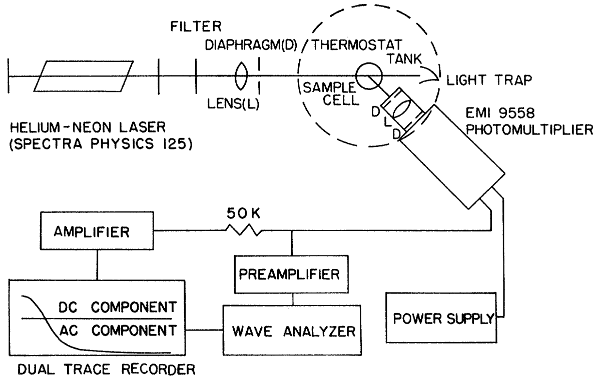

FIG. 1. Block diagram of a light-scattering photometer in combination with a "self-beating" spectral analysis system.

molecular interaction parameter (l) for binary fluid mixtures. This would imply relatively large values of b/a. Our method of detection was essentially that of Benedek. A block diagram of our light scattering photometer in combination with the spectral analysis system is shown in Fig. 1. A centrifuged colloidal silica (LUDOX) sample in a cylindrical cell of 10 mm i.d. was used as a standard for final optical alignment of the photometer. The observed intensity after scattering volume corrections ($\sin\theta$) is a constant to within about 2% over an angular range from 30° to 130°. The temperature of the insulated tank bath was controlled to ±0.000 35° over periods of several hours using an ac bridge and phase-sensitive detector.[11] The critical mixing point was determined in a separate experiment.[12]

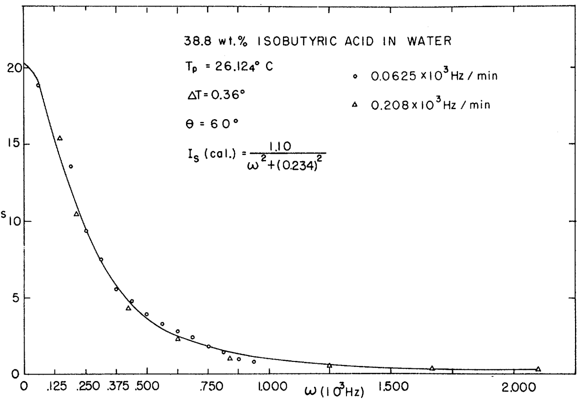

FIG. 2. A plot of I_s vs ω.

In Fig. 2, we show a plot of I_s vs ω at $T-T_c = 0.36°$ and $\theta = 60°$ for a two-component system of 38.8 wt% isobutyric acid in water. The experimental points have been checked using two scanning speeds (62.5 and 208 Hz/min) and corrected for background. A dual-trace recorder was used to monitor simultaneously both the ac and the dc components of the signal so that any variation in the incident intensity during the course of a run could be compensated. The agreement between the calculated Lorentzian-shaped line and the experimental points in Fig. 2 is indeed remarkable. However, we have been unable to fit with certainty the calculated curve to the measured spectrum to 20 linewidths, as was the case for sulfur hexafluoride near its critical point,[3] because of fluctuations in our scattering data. At $\theta = 60°$ and $T-T_c = 0.36°$, 2Γ was estimated to be about 2.3×10^2 Hz. It should be noted that although we were able to fit our scattering curves with Lorentzians to about 10 or more linewidths (2Γ) from the center, the values of 2Γ could only be attained to within about 10%. In Fig. 3, we show a plot of Γ versus $\sin^2\frac{1}{2}\theta$. Here we have picked a fixed temperature distance of 0.36° from the critical solution temperature partly because we want to avoid any quibble on the possibility of multiple scattering, and partly because we have been able to establish the scattered intensity at $\omega = 0$ only by extrapolation. We have thus also avoided measurements at small temperature distances where the linewidths would be very narrow. Yet at $\Delta T = 0.36°$, an estimated deviation of 20% from

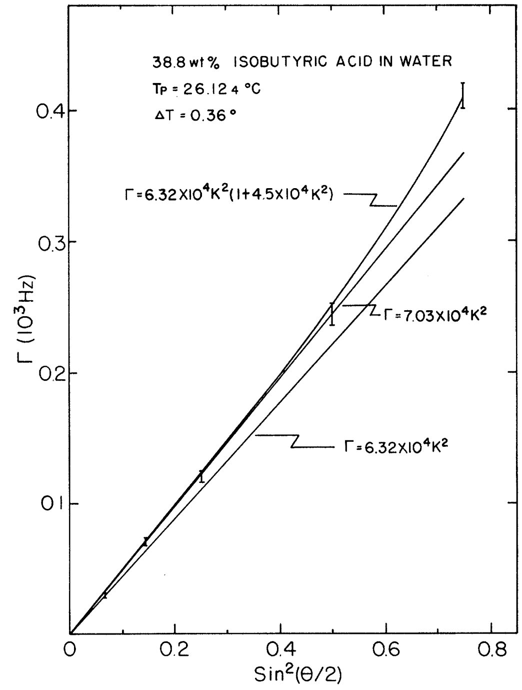

FIG. 3. A plot of Γ versus $\sin^2\frac{1}{2}\theta$.

the K^2 dependence still exists at $\theta = 120°$. Within the limits of error of our experiments, we see that the linewidth appears to be proportional to K^2 up to $\theta = 90°$. However, on closer examination, we note that the point at $\theta = 120°$ lies above the empirical equation $\Gamma = 7.03 \times 10^4 K^2$ with K expressed in $\mathrm{Å}^{-1}$. We now make use of our scattering data from angular dissymmetry measurements.[12] If we take $l^2 = 324\ \mathrm{Å}^2$, $\lambda = 4744\ \mathrm{Å}$, $\tau - 1 = (T - T_c)/T_c = 1.20 \times 10^{-3}$, we find

$$\Gamma = aK^2[1 + (b/a)K^2] = 6.32 \times 10^4 K^2 (1 + 4.5 \times 10^4 K^2), \tag{4}$$

where $b/a = l^2/6(\tau - 1)$. Γ and K are expressed in kHz and $\mathrm{Å}^{-1}$, respectively. Equation (4) clearly fits our scattering data. Further work is definitely indicated since we have only one half-width at $\theta = 120°$ showing a measureable deviation from the K^2 dependence. On the other hand, we are certain that Eq. (2), $\Gamma = aK^2$, holds whenever the magnitude of correlation is small and Γ approaches zero as K approaches zero. At intermediate temperature distances, where the effects of correlation may have to be taken into account, we have some evidence to show that Eq. (3) indeed agrees with experiments.

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CONDENSATE TURBULENCE IN A WEAKLY COUPLED BOSON GAS*

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The ring-model approximation is applied to thermal equilibrium below the λ-point, to the relaxation of a chaotic condensate into the zero-momentum state, and to turbulent counterflow of condensate and normal fluid.

This note reports some applications of quantum-field correlation equations whose classical-field limit constitutes a statistical approximation, along the lines of current turbulence theory, for chaotic solutions of the Gross-Pitaevskii equation.[1] The quantum effects prevent an ultraviolet catastrophe.

Assume the standard second-quantized Hamiltonian

$$H = \sum_k k^2 q_k^\dagger q_k + \tfrac{1}{2} \sum_{krs} V_{k-s} q_k^\dagger q_p^\dagger q_r q_s \tag{1}$$

$$(k + p = r + s),$$

with $V_k = |V_k|$ and $\hbar = 2m = 1$. The correlation equations, called the ring-model approximation[2] (RMA), predict the evolution of $Q_k(t, t') = \langle q_k^\dagger(t') q_k(t) \rangle$ from an initial time. Here $q_k(t)$ is the Heisenberg destruction operator and $\langle\ \rangle$ denotes trace over a Gaussian initial-state ensemble, which can be far from thermal equilibrium. The structure of the approximation is best exhibited by considering statistically steady states and using the spectrum function $Q_k(\omega) = (2\pi)^{-1} \int Q_k(t, t') e^{i\omega(t-t')} d(t-t')$. [All integrations will be over $(-\infty, \infty)$.] After Fourier transformation and some algebraic manipula-