

scattering regime, $(dP/d\Omega)$ does not fall off with energy. Thus, if the spectrometer resolution can be maintained at higher energies, explicit contact with multiple-scattering calculations such as those reported here may prove more fruitful than attempts to interpret data taken at very low energies, especially in the absence of a more complete treatment of the dipole-scattering term.

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Nonexponential Decay of Critical Concentration Fluctuations in a Binary Liquid

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By use of light scattering techniques a careful investigation has been made of the time dependence of the concentration fluctuations near the critical point of a binary liquid mixture. The experiments reveal deviations from exponential decay of these fluctuations at temperatures within 20 mdeg from the critical temperature. The observed deviations from exponential decay are in agreement with a recent theoretical prediction of Bhattacharjee and Ferrell.

This Letter is concerned with the time dependence of the order-parameter fluctuations in fluids close to the critical point. An early experimental study, made by Volochine, Bergé, and Lagues,¹ indicated that the relaxation of the concentration fluctuations of a binary liquid remained exponential even at temperatures within 3 mK from the critical temperature.¹ However, when it was established that the magnitude of the decay rate of the fluctuations was measurably affected by the critical viscosity anomaly,² Perl and Ferrell predicted that the memory effects in the viscosity should also induce a non-Lorentzian distortion of the Rayleigh line.³ A possible frequency dependence of the decay rate of the order-parameter fluctuations has also been mentioned by Kawasaki and co-workers.^{4,5}

A first attempt to measure the effect was made by Bendjaballah.⁶ He concluded that any nonexponential decay due to the frequency dependence of the viscosity was quite small and within the

resolution of his experiments. A similar conclusion was obtained by Wonica, Swinney, and Cummins⁷ and, more recently, by Sorensen, Mockler, and O'Sullivan.⁸ These authors were motivated by the large departure from exponential decay predicted by the dynamic droplet model, but which was not observed. The question remains whether smaller departures from exponential decay due to the frequency dependence of the viscosity can be detected experimentally.

By modifying a light scattering facility, previously constructed for an accurate determination of the static critical correlation function,⁹ and cross-correlating the scattered light intensity as registered by two different photomultiplier tubes, we have *indeed* detected the presence of departures from exponential decay in the time-dependent correlation function of the concentration fluctuations close to the critical point of a binary liquid. The experimental results differ qualitatively and quantitatively from the effect

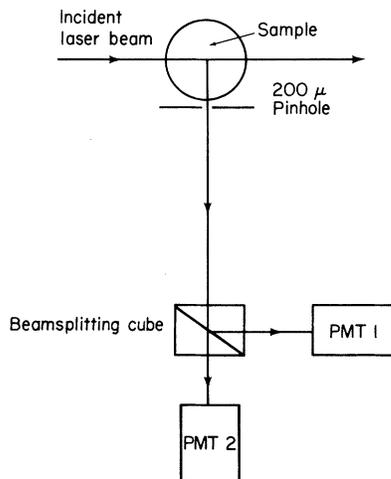


FIG. 1. Schematic representation of the arrangement for detecting the scattered light.

predicted by Ohta and Kawasaki,⁵ but can be explained as arising from the frequency dependence of the critical viscosity as recently proposed by Bhattacharjee and Ferrell.¹⁰

The experiment was conducted in the binary liquid 3-methylpentane-nitroethane with the same sample in which the static critical correlation function was determined previously.⁹ The incident laser light, after passing through an intensity stabilizer consisting of a variable attenuator, and a servo loop, was focused at the center of the sample by a lens with a focal length of 7.5 cm. The light scattered at 90° was directed to two different photomultiplier tubes with the aid of a beam splitter as indicated in Fig. 1. The outputs of the two channeltrons were cross-correlated by use of a clipped correlator with 128 channels and a time base of 2 μs per channel. This procedure eliminated to first order the effects upon the measurement of after-pulsing in the photomultiplier tubes.

The actual quantity measured experimentally is the intensity correlation function $G^{(2)}(\tau)$. Since the scattering volume $V \approx 10^{-2} \text{ mm}^3$ satisfies the condition $V \gg \xi^3$, where $\xi \leq 420 \text{ nm}$ is the correlation length, the electric field correlation function squared, $|G^{(1)}(\tau)|^2$, is proportional to $G^{(2)}(\tau)$ minus the base line.¹¹ It is imperative that the base line be determined accurately, since an error in the base line would introduce an apparent deviation from exponential decay. One can determine the base line experimentally in two ways. The first way is to measure the intensity correlation function at $\tau \rightarrow \infty$; in practice we deter-

TABLE I. Observed normalized second cumulant k_2 for the correlation function near the critical point.

$\Delta T = T - T_c$ (mK)	k_2
1.8	0.033 ± 0.008
2.7	0.031 ± 0.010
3.8	0.045 ± 0.010
5.5	0.022 ± 0.008
11.7	0.016 ± 0.007
20.3	0.003 ± 0.010

mined the base line from the number of counts in the 128th channel which has a delay time corresponding to 10 decay constants. The second method is to deduce the base line from the total number of incident counts, the total number of clipped counts, and the time of an experimental run. The two determinations of the base line agreed within their statistical uncertainty of 0.054%, the second method being slightly more accurate.

Near the critical point of the binary liquid under consideration, the electric field correlation function is proportional to the concentration correlation function.⁹ Preliminary autocorrelation function measurements using one photomultiplier tube indicated deviations from exponential decay when the critical temperature was approached to within 20 mK. Therefore, the cross-correlation experiments were conducted at temperatures within this range of 20 mK from the critical temperature T_c . A test experiment with thermal light confirmed the absence of any undesirable effects such as after-pulsing in our cross-correlation scheme.

The data are analyzed by considering the function $\kappa(\tau) \equiv [B^{-1}G^{(2)}(\tau) - 1]^{1/2} = \beta |g^{(1)}(\tau)|$, where B is the base line and $g^{(1)}(\tau)$ the normalized electric field correlation. An expansion of $\kappa(\tau)$ to second order in τ

$$\ln \kappa(\tau) = c - K_1 \tau + \frac{1}{2} K_2 \tau^2 \quad (1)$$

yields a normalized second cumulant $k_2 = K_2/K_1^2$ which is a measure of the deviation from exponential of the correlation function,¹² while $c = \ln \beta$ is an instrumental constant related to the coherence area of the scattered light. The normalized second cumulants obtained from our experimental data are listed in Table I as a function of temperature; the uncertainties quoted represent *two* standard deviations. The experiments were performed with an illuminating laser power of 1 mW. It was verified that the same results were ob-

tained with larger laser powers up to 7 mW, provided a temperature correction was made for local heating effects.⁹ From the data in Table I it is seen that k_2 starts to deviate from zero at $\Delta T = T - T_c = 20$ mK, increasing to a level of about 0.03 at a few millidegrees from T_c .

Before interpreting the experimental data a number of instrumental sources that possibly could lead to apparent deviations from exponential decay need to be considered. Upon approaching the critical point the scattered light intensity increases rapidly and multiple scattering is also known to cause deviations from exponential decay.¹³ For our experiment the effect was analyzed by Ferrell and Bhattacharjee.¹⁴ Because of the small cross section for light scattering of the 3-methylpentane-nitroethane mixture,⁹ it was found that for our light scattering geometry multiple scattering contributes a maximum amount of 0.004 to k_2 at $T = T_c$.

In principle, light may be scattered not only from the incident beam, but also from a beam reflected at the cell wall causing another distortion of the observed line shape. This effect vanishes at a 90° scattering angle; allowing for the instrumental uncertainties in the alignment, this effect upon k_2 was less than 8×10^{-4} . Other possible sources of distortion are heterodyning between the scattered and reflected beams and second-order after-pulsing effects not eliminated by the cross-correlating procedure. Again these effects could be estimated and were found to contribute at most 0.005 to k_2 . The data quoted in Table I have been corrected for the aforementioned effects, while any errors due to an uncertainty in the base line are within ± 0.005 . We conclude that the observed effects indeed represent a departure from exponential decay of the concentration correlation function.

Ohta and Kawasaki considered the Fourier transform of the order-parameter correlation function $g^{(1)}(\omega) \propto [i\omega + \Gamma + Q(\omega)]^{-1}$ and derived an expression for the limiting frequency-dependent contribution $Q(\omega)$ to the decay rate.⁵ Evaluating their expression, with the known physical proper-

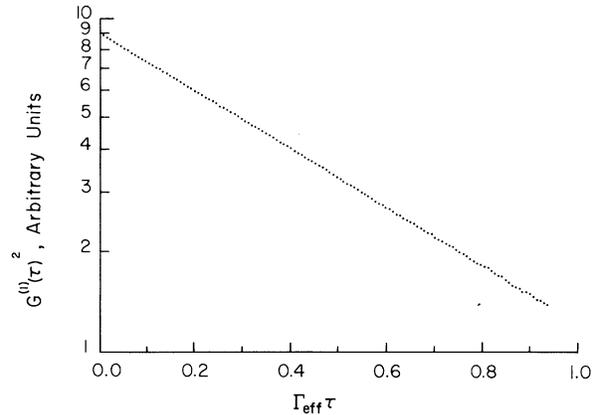


FIG. 2. Experimental data for $[G^{(1)}(\tau)]^2$ as a function of $\Gamma_{\text{eff}} \tau$ ($\Gamma_{\text{eff}} = 3682 \text{ s}^{-1}$) with $\Delta T = 1.8$ mK.

ties of our mixture, inverting $g^{(1)}(\omega)$ to obtain $g^{(1)}(\tau)$, and performing a cumulant analysis on the calculated values for $g^{-1}(\tau)$, we obtain $k_2 = -0.006$. This result is smaller than the observed value $k = 0.03$ and has even the opposite sign.

The theory was therefore reconsidered by Bhattacharjee and Ferrell who made an analysis of the effect of the frequency dependence of the viscosity on the correlation function.¹⁰ Introducing the deviation function

$$\Delta \ln g^{(1)}(\tau) = \ln \kappa(\tau) - c + \Gamma \tau, \quad (2)$$

where Γ is the decay rate in the absence of any memory effects, they predict

$$\Delta \ln g^{(1)}(t) = \frac{1}{3} x_\eta \left\{ H(t) + [\gamma + \pi/\sqrt{3}] \Gamma \left(\frac{2}{3} \right) - \frac{13}{4} \right\} t + C_r(t) \quad (3)$$

in terms of the dimensionless variable $t = \Gamma \tau$. Here x_η is the critical exponent for the viscosity,¹⁵ while $\gamma = 0.577$ is Euler's constant. The function $H(t)$ is given by

$$H(t) = t \ln t + \frac{9}{4} \left\{ 1 + (q\xi)^{-2} \right\}^{1/3} (t - t^{4/3}), \quad (3a)$$

where q is the wave number. The function $C_r(t)$ can be expanded in powers of t yielding [the function $C_r(t)$ is related to the function $B_r(t)$ of Bhattacharjee and Ferrell¹⁰ by $B_r(t) = d^2 C_r(t)/dt^2$]:

$$C_r(t) = 0.221t + (1 + \frac{1}{2}s_0) \frac{1}{2}t^2 + (1 + s_0 - \frac{1}{5}s_0^2) \frac{1}{12}t^3 + (\frac{1}{3} + \frac{1}{2}s_0 - \frac{1}{5}s_0^2 + \frac{1}{24}s_0^3) \frac{1}{24}t^4 - t^{1/3} \left[\frac{9}{28}t^2 + \frac{9}{140}t^3 + \frac{3}{260}t^4 \right] \quad (3b)$$

with $s_0 = \Gamma(\frac{2}{3})^{-3} = 0.403$.

Since the theory is concerned with the time dependence of the correlation function asymptotically close to the critical point, we focus here our attention on the experimental data obtained at ΔT

= 1.8 mK which is the temperature closest to T_c at which the experiment was performed. In Fig. 2 we show $[G^{(1)}(\tau)]^2$ determined experimentally as a function of $\Gamma_{\text{eff}} \tau$, where $\Gamma_{\text{eff}} = 3682 \text{ s}^{-1}$ is the

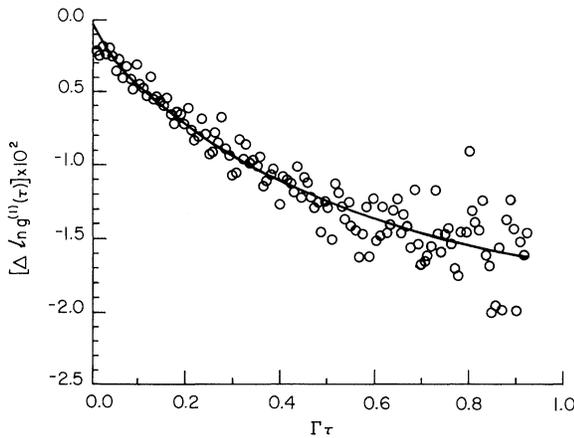


FIG. 3. Deviations $\Delta \ln g^{(1)}$ as a function of $t = \Gamma\tau$ with $\Delta T = 1.8$ mK. The circles represent the experimental data and the curve represents the deviations predicted by the theory of Bhattacharjee and Ferrell.

mean effective decay rate. This correlation function was obtained from seven runs yielding 7 million counts in the first channel of which about $\frac{2}{3}$ belonged to the base line.

In order to compare the experimentally observed time dependence with (3), we took $x_\eta = 0.065$ as calculated from the dynamic renormalization group theory,¹⁵ as well as from the mode-coupling theory,¹⁶ to second order in ϵ . This value is in good agreement with the values 0.062 and 0.063 which we deduced from the experimental viscosity data of Stein, Allegra, and Allen¹⁷ and Tsai and McIntyre,¹⁸ as earlier noted by other investigators.^{19,20} We emphasize that Eq. (3) allows us to calculate $\Delta \ln g^{(1)}(t)$ without any adjustable constants. The quantities to be deduced from the experiment are the decay rate Γ in the absence of any memory effects and c . For this purpose we took as an initial guess $\Gamma = \Gamma_{\text{eff}}$, deducted the deviations predicted by (3) from the experimental data, and fit the remainder to an exponential decay law. The procedure, when iterated, converged rapidly, yielding $\Gamma = 3629 \text{ s}^{-1}$. In Fig. 3 we show the experimental deviations $\Delta \ln g^{(1)}(\tau)$ as defined by (2). The curve in this figure represents the theory, Eq. (3). If we approximate this theoretical formula over the time interval of our experiment by a cumulant expansion, we obtain $k_2 \approx 0.030$ in good agreement with the value $k_2 = 0.033 \pm 0.008$ observed experimentally. We conclude that the measured departures

from exponential decay can indeed be attributed to the memory effects predicted by Bhattacharjee and Ferrell.¹⁰

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