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Time dependence of critical concentration fluctuations in a binary liquid

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Accurate measurements of the time dependence of the order-parameter fluctuations in the binary liquid mixture 3-methylpentane and nitroethane very close to the critical temperature are reported. The experiments were performed by cross correlating the scattered light received by two different photomultiplier tubes to eliminate distortions of the observed correlation function due to afterpulsing. The measurements reveal the presence of small but noticeable deviations from exponential decay of the critical concentration fluctuations. The observed phenomenon can be attributed to the effect of a frequency-dependent critical viscosity as predicted by Ferrell and co-workers.

I. INTRODUCTION

A system near a critical point exhibits large thermal fluctuations of the order parameter associated with the phase transition. In general, it is to be expected that the decay rate of these order-parameter fluctuations not only will depend on the wave number, but also on the frequency of the fluctuations.[1] However, early experimental work indicated that the relaxation of the order-parameter fluctuations in a binary liquid near the critical mixing point, which in this case is to be identified with the relaxation of concentration fluctuations, remained exponential even very close to the critical temperature.[2] The theory of dynamic critical phenomena, summarized in several review articles,[1,3,4] shows that the decay rate of the order-parameter fluctuations in classical fluids is related to the shear viscosity of the fluid. The viscosity of a fluid displays an enhancement near the critical point which does depend on frequency.[5-7] Hence when the critical viscosity enhancement was found to have a noticeable effect on the observed decay rate of the order-parameter fluctuations,[8] it was predicted by Perl and Ferrell[5] that the frequency dependence of the critical viscosity enhancement should not only affect the magnitude of the decay rate of the order-parameter fluctuations,[5,9,10] but that it should also cause a non-Lorentzian line shape of the order-parameter fluctuation spectrum.

A first attempt to measure this effect was made by Bendjaballah in our laboratory.[11] He concluded that any deviations of the order-parameter fluctuations from a simple exponential decay law, if present at all, are quite small and within the experimental resolution attainable at the time. A similarly negative conclusion was reported by Chu and co-workers.[12] Subsequently, Ackerson *et al.* raised the possibility of substantial deviations of the relaxation of the order-parameter fluctuations from exponential decay on the basis of a dynamic droplet model[13] which were, however, not found experimentally.[14,15] However, the question of whether smaller departures from exponential decay due to the frequency dependence of the viscosity can be detected experimentally remained unresolved.

As we shall see the effect is indeed quite small and can only be observed very close to the critical temperature, where the interpretation of light scattering in most fluids is complicated by multiple scattering contributions.[16] During the past decade we have made some detailed experimental studies of the concentration fluctuations in the binary liquid 3-methylpentane and nitroethane near the critical point.[8,17,18] As originally suggested by McIntyre and co-workers,[19] the coupling between concentration fluctuations and refractive index fluctuations in this system is sufficiently small so that multiple scattering contributions remain small even very close to the critical temperature, while the coupling is still sufficiently large so that the observed Rayleigh scattering near the critical point can be attributed to the fluctuations in the concentration which is the order parameter of the transition.[18] Hence the 3-methylpentane and nitroethane system would appear to be an ideal system to investigate possible deviations of the critical concentration fluctuations from exponential decay. Nevertheless, the work of Bendjaballah[11] had shown that even for the system 3-methylpentane and nitroethane the experimental resolution would have to be improved substantially over the resolution previously attainable in our laboratory. Recently, we reported experimental studies of the decay rate of the concentration fluctuations in

3-methylpentane and nitroethane near the critical point with an accuracy significantly better than that of the decay rate data obtained originally.[20] In these experiments we consistently encountered small but noticeable deviations from exponential decay in the measured light scattering intensity autocorrelation function very close to the critical temperature. Since one can imagine several experimental artifacts that could cause a distortion of the measured autocorrelation function,[21–23] we decided to perform some special experiments to investigate whether we were observing a real physical phenomenon.

Some of our results were announced in an earlier letter.[24] In this paper we describe the experiment and evaluate various possible experimental errors that could effect the observed time dependence of the critical concentration fluctuations. In addition, we present a detailed analysis of the temperature dependence of the effect.

II. EXPERIMENTAL METHOD

In the experiment we determine the autocorrelation function of the intensity of light scattered by a sample of 3-methylpentane and nitroethane with photon correlation spectroscopy. The optical arrangement of the experiment is indicated schematically in Fig. 1. Light from a 6.4-mW He-Ne laser source passes through a variable attenuator and intensity stabilizer as described previously.[18,20] With the stabilizer any changes of the incident light intensity were within a few tenths of a percent over a period of 20 h. Stabilization of the light intensity was important because of the duration, 4 to 5 h for each single run, necessary to acquire adequate statistics. The variable attenuation enabled us to fix the incident light intensity at a given level. The experimental data reported in this paper were obtained with an incident light intensity of 1 mW. This incident beam is focused at the center of the sample cell by a lens with a focal length of 7.5 cm. The binary liquid sample, the thermostat, and the system for regulating and measuring the temperature were the same as described in our previous paper.[20] The composition of the liquid sample is equal to the critical composition to within 0.6%. The critical temperature of the mixture is $T_c = 299.545$ K.

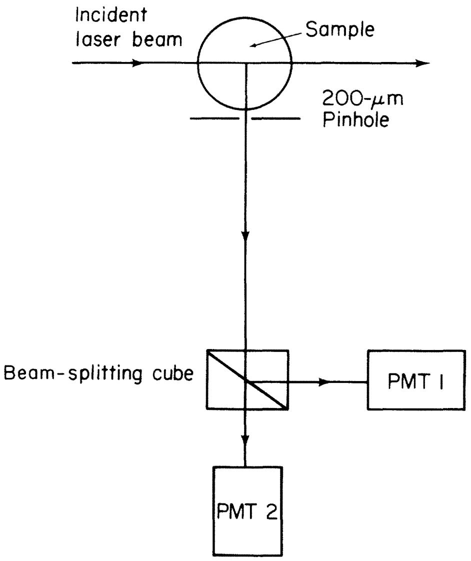

FIG. 1. Schematic representation of optical arrangement as seen from above.

The major difference between our previous experiments and the experiments reported in this paper concerns the method by which the correlation function of the scattered light intensity is measured. In our previous experiments this correlation function was determined by registering and processing the signals from the scattered light received by a single photomultiplier. In the present experiment we measure this autocorrelation function by cross correlating the signals as received by two separate photomultipliers located at equal optical path lengths from the center of the scattering cell. This cross correlating scheme, originally suggested to us by Bendjaballah,[11] eliminates distortions of the correlation function due to afterpulsing processes in the photomultiplier tubes[22,23,25] as will be further discussed below. For this purpose the scattered light is divided by a beam-splitting cube and diverted to the two photomultiplier detectors. Ideally, the scattered light intensity should have been divided equally; in practice, the ratio turned out to be closer to 3:2. This difference may be due either to an asymmetry in the beam-splitting cube or to differences in the gain and sensitivity of the two photomultiplier tubes. In any case, this difference in sensitivity between the two detectors is not important. The observed scattering volume is specified by a pinhole with a diameter of 200 μm located just outside the sample cell and the diameter of 1 mm of the two optically conjugate photocathodes of the photomultiplier tubes. The distance between the pinhole and the photocathodes also determines the spatial coherence of the detected radiation. As discussed previously[20] the observed scattered intensity correlation function may deviate from simple exponential behavior as a result of mixing between light scattered from the incident beam and light scattered from a beam reflected off the wall of the scattering cell. To avoid this effect all experiments were done with a scattering angle of 90°.

In Fig. 2 we give a schematic representation of the signal processing system. The pulses detected by each photomultiplier tube were standardized in am-

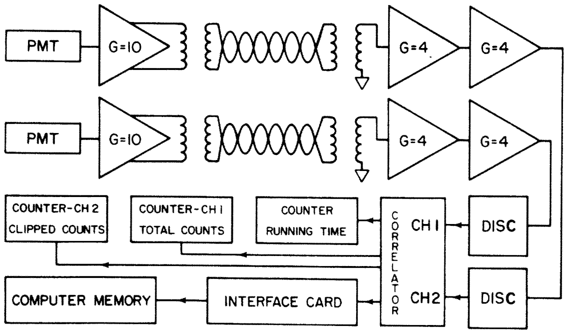

FIG. 2. Schematic representation of signal processing system.

plitude and duration with discriminators. The widths of the output pulses were set at 30 ns with a dead time following each pulse of also 30 ns. The count rate on either photomultiplier tube did not exceed 5000 counts/s. The outputs thus obtained from the two photomultiplier circuits were then cross correlated with the same single-clipped digital autocorrelator used in our previous experiments.[20] The correlator has two input circuits. The output of the photomultiplier with the lower count rate was directed to the clipper, while the output of the other multiplier was used to supply the unclipped signal. A detailed description of the home-built correlator is contained in a separate report.[26] The correlator has 128 channels. For all experiments reported in this paper the delay time between two successive channels was set at 2 μs.

The clipped-count rate $n_k(t)$ at time t is defined such that $n_k(t)=0$ if $n(t,\delta t)\leq k$ and $n_k(t)=1$ if $n(t,\delta t)>k$, where $n(t,\delta t)$ is the number of counts at time t during a time interval δt and where k is the clipping level. In our experiments the time window δt was 2 μs, equal to the delay time between two successive channels, and the clipping level k was zero. In principle, clipping could distort nonexponential correlation functions,[27] if $n>1$. This is not a problem here, first, since the observed deviations from exponential decay are very small, and secondly, since the probability of registering more than one count is negligibly small. The probability of finding n counts in the time interval δt may be estimated from the Poisson distribution

$$P(n,\bar{n})=e^{-\bar{n}}(\bar{n})^n/n!\ ,$$

where $\bar{n}$ is the average number of counts. Typically, this average number of counts $\bar{n}$ registered in a sample interval δt was 0.011, and we conclude that the probability of finding n counts larger than unity is less than 6×10^{-5}.

The experimentally observed photoelectron-count autocorrelation function is to be identified with the light intensity autocorrelation function

$$G^{(2)}(t)=\langle I(t)I(0)\rangle\ .$$

It can be related to the electric field autocorrelation function

$$G^{(1)}(t)=\langle E^*(t)E(0)\rangle\ ,$$

if the electric field is assumed to be a Gaussian random variable[27]

$$G^{(2)}(t)=\langle I\rangle^2+\beta\,|\,G^{(1)}(t)\,|^2\ . \tag{2.1}$$

The coefficient β depends on such factors as the spatial coherence of the scattered light at the detectors, count rate, clipping level, and sample time. In our experiments the coefficient β was treated as an unknown constant in the fitting procedure; it was found to be between 0.56 and 0.58. The intensity autocorrelation function was measured at various temperatures T above the critical temperature T_c down to a minimum temperature difference

$$\Delta T=T-T_c=1.8\text{ mK}\ .$$

At this temperature the correlation length ξ is about 420 nm. Hence a typical cluster size $\xi^3\simeq7\times10^{-20}$ m^3 associated with the critical fluctuations is still small compared to the scattering volume

$$V\simeq10^{-2}\text{ mm}^3=10^{-11}\text{ m}^3\ ,$$

and the assumption of Gaussian statistics remains justified. Introducing normalized autocorrelation functions

$$g^{(2)}(t)=G^{(2)}(t)/\langle I\rangle^2$$

and

$$g^{(1)}(t)=G^{(1)}(t)/\langle I\rangle\ ,$$

one obtains

$$G^{(2)}(t)/B=g^{(2)}(t)=1+\beta\,|\,g^{(1)}(t)\,|^2\ , \tag{2.2}$$

where in the sequel we refer to $B=\langle I\rangle^2$ as the "base line."

An error in the base line will cause an apparent deviation from exponential decay of the observed correlation function $G^{(2)}(t)-B$. Therefore special attention was paid to an accurate determination of the base line. The base line can be determined experimentally in two ways. The first way is to measure the intensity correlation function at $t\rightarrow\infty$. In practice, this is done by observing the number of counts in the 128th channel of the correlator which is constructed so that the delay between the 127th and the 128th channel is equivalent to 1208 sample intervals. The shift rate of 2 μs per channel was chosen so that the first 127 channels cover approximately a time interval of two relaxation times of the intensity autocorrelation function. Hence the 128th channel yields the value of this correlation function at a time corresponding to twenty relaxation times. The random error associated with this method of determining the base line may be estimated as

$$\lim_{t\to\infty} (G^{(2)}(t))^{1/2} ,$$

since the count rate is low.[28] Each individual run for measuring $G^{(2)}(t)$ yielded a base line of approximately 6.7×10^5 counts with an estimated random error of 0.12%. A determination of $G^{(2)}(t)$ at a given temperature was always based on 5 to 7 runs, so that the final expected error in the base line determined by this method would be about 0.05%.

The second method of determining the base line takes advantage of the fact that the base line is equivalent to the accidental coincidence rate. Thus by recording the total number N of pulses received by the correlator, the total number of clipped events N_k, and the total running time t_{tot} in units of the sample interval, the base line can be deduced from the relation

$$B = NN_k/t_{\text{tot}} . \tag{2.3}$$

Each individual run yielded approximately $N_1 \simeq 9\times10^7$ and $N_2 \simeq 6\times10^7$, so that $N_1N_2 \simeq 5\times10^{15}(1\pm0.0002)$, while any errors in the time measurements were negligibly small. Averaging over 5 to 7 runs thus yields an error in the base line of about 0.007%. While this random error is almost an order of magnitude smaller than that obtained with the first method, the second method will lead to systematic errors if during the course of a run the laser intensity would shift or if the sensitivity of the photomultiplier tubes would change. A simple example of such a case was pointed out by Oliver.[21] If the average count rate for one half of the run is $\bar{n}$ and for the other half $\bar{n}(1+\Delta)$, then the method leads to a loss of $\Delta^2/4$ in the accuracy of the base line. The first method does not suffer from this deficiency, since in that case the coincidence rate is monitored continuously. Hence in order to judge the actual accuracy obtained with the second method we must consider the stability of the average count rate. At any given temperature the normalized correlation function

$$g^{(2)}(t) = G^{(2)}(t)/B$$

was determined by concatenating 5 to 7 individual runs. Each run lasted 4 to 5 h and we circumvented part of the problem by normalizing the correlation function from each run individually. Furthermore, the stability of the average count rate could be checked by comparing the results from the different runs at the same temperature, and it was found that the variations in the count rate were typically ±1%. Except for the measurements at

$$\Delta T = T - T_c = 3.8 \text{ mK} ,$$

the difference in the average count rate between any two runs at the same temperature never exceeded 2.65%. As a consequence, any systematic errors in the base line calculated from the accidental coincidence rate due to variations in light level and gain or sensitivity of the photomultipliers are typically 0.0025% and never exceed 0.018%. The measurements at $\Delta T = 3.8$ mK are somewhat anomalous in that the maximum difference between the average count rates of two different runs is 4.1%; however, even in this atypical case the error in the base line would be less than 0.042%. We conclude that the method of calculating the base line from the accidental coincidence rate has the higher accuracy, and this was the method adopted in deducing the normalized intensity autocorrelation function $g^{(2)}(t)$ from the observed photoelectron-count correlation function $G^{(2)}(t)$. In retrospect, we had noted that our earlier decay rate measurements[20] also became more reproducible when this method of determining the base line was employed in the reduction of the data.

Correlated afterpulsing, arising from feedback mechanisms in a photomultiplier tube, will cause a distortion of the measured correlation function at small times.[21,22,25] In our previous experiments performed with a single photomultiplier tube[20] a correction for afterpulsing effects was made by calibrating the afterpulsing probability of the photomultiplier tube.[25] In the measurements reported here the intensity correlation function was determined by

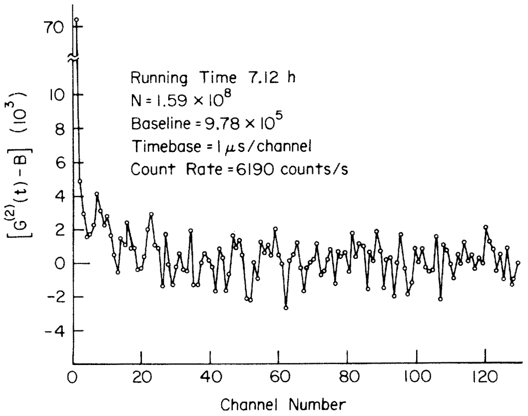

FIG. 3. Experimental correlation function $G^{(2)}(t)-B$ of a thermal light source as observed from autocorrelation with a single photomultiplier tube. The size in the early channels indicates afterpulsing effects.

cross correlating the output of two photomultiplier tubes. Given an uncorrelated light source, which is our lowest-order assumption, an initiating event cannot cause a correlated afterpulse in the other tube. Hence in the cross-correlation experiments this lowest-order afterpulsing contribution to the intensity correlation function must be absent. In Fig. 3 we show the correlation function $G^{(2)}(t)-B$ observed with a single photomultiplier tube for Gaussian white light produced by a light bulb driven with a constant current source[25]; the sharp rise in the early channels is a measure of the afterpulsing probability. In Fig. 4 we show the correlation function $G^{(2)}(t)-B$ of the same Gaussian white light, but now observed by using the two photomultiplier tubes configured for cross correlation. The actual quantity displayed is $[G^{(2)}(t)-B]/\sigma$, where σ is the standard deviation; the base line is as flat as can be expected from statistics. The base line may be estimated by averaging over all the bins; the base line so derived agrees to within statistical accuracy with the value obtained from the count rates in each channel and the running time. A comparison between Figs. 3 and 4 demonstrates the efficacy of cross correlation in the removal of afterpulsing effects to lowest order.

III. EXPERIMENTAL CORRELATION FUNCTION DATA AND CUMULANTS

Our preliminary measurements indicated that any deviations of the concentration correlation function from exponential decay, if present at all, only occur at temperatures within 20 mK of the critical temperature. In this temperature range we determined the correlation function at six different temperatures corresponding to $\Delta T=20.3$, 11.7, 5.5, 3.8, and 1.8 mK. The experimental data obtained for $[G^{(1)}(t)]^2$ are shown in Fig. 5 as a function of the channel number of the correlator; as mentioned earlier the distances between two successive channels corresponds to 2 μs. The data at each temperature were obtained as the sum of 5 to 7 different runs, each run lasting 4 to 5 h. The experiment yields $[G^{(1)}(t)]^2$ in arbitrary units. For convenience, the data were normalized so that the value at the first channel was unity. The data were then multiplied by $10^{0.2(i-1)}$, where $i=1,2,\ldots,6$ is a number assigned to each temperature, so as to display the correlation function data at all temperatures in one single figure. The experimental correlation function data were corrected for multiple scattering and second-order afterpulsing effects as described in Secs. IV A and IV B. The original experimental data, together with the small corrections applied to the data, are documented in a separate report.[29]

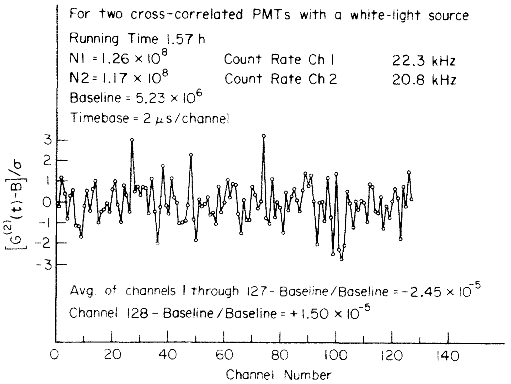

FIG. 4. Experimental correlation function $G^{(2)}(t)-B$ of a thermal light source as observed from cross correlation with two photomultiplier tubes. The data are plotted in units of the standard deviation σ and the observed correlation function is flat within statistical accuracy.

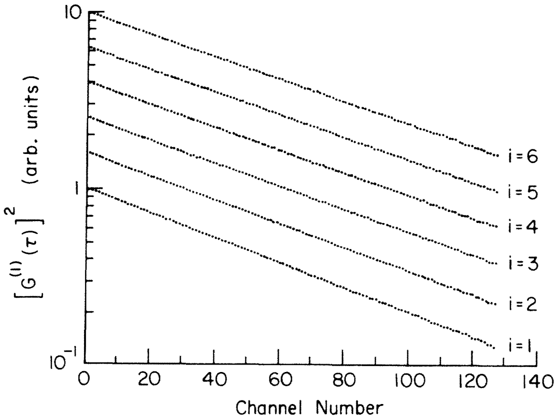

FIG. 5. Experimental data obtained for $[G^{(1)}(t)]^2 \propto G^{(2)}(t)-B$ as a function of channel number (time base: 2 μs). The data correspond to $\Delta T=20.3$ mK ($i=1$), 11.7 mK ($i=2$), 5.5 mK ($i=3$), 3.8 mK ($i=4$), 2.7 mK ($i=5$), and 1.8 mK ($i=6$).

To analyze the data we consider the function

$$\kappa(t)=[B^{-1}G^{(2)}(t)-1]^{1/2} , \qquad (3.1)$$

so that

$$\ln\kappa(t)=c+\ln g^{(1)}(t) , \qquad (3.2)$$

where c is related to the instrumental constant β introduced in Eqs. (2.1) and (2.2) by $c=\frac{1}{2}\ln\beta$. As noted earlier, β is approximately constant; it decreased by only 4% as we approached the critical point from $\Delta T=20.3$ to 1.8 mK. If the scattered light is Lorentzian, $g^{(1)}(t)$ has the form of an exponential function with a single decay rate Γ

$$g^{(1)}(t)=\exp(-\Gamma t) . \qquad (3.3)$$

To investigate whether actual experimental correlation function data decay exponentially, one often in-

TABLE I. Decay rates deduced from the experimental data.

$\Delta T = T - T_c$ (mK)	$K_1 \pm 2\sigma_{K_1}$ (s^{-1})	$\Gamma_{\text{eff}} \pm 2\sigma_\Gamma$ (s^{-1})
1.8	3739±14	3673±5
2.7	3749±18	3688±5
3.8	3763±18	3690±6
5.5	3769±15	3724±4
11.7	3876±14	3839±4
20.3	4047±22	4034±6

troduces a cumulant expansion truncated after the second term[30]

$$\ln g^{(1)}(t) = -K_1 t + \tfrac{1}{2} K_2 t^2 \,. \tag{3.4}$$

If $g^{(1)}(t)$ has the exponential form, then $K_1 = \Gamma$ and $K_2 = 0$. In practice K_1, the initial slope, is the best estimate for the decay rate determining the time scale, while the normalized second cumulant

$$k_2 = K_2 / K_1^2 \tag{3.5}$$

is typically used to characterize the magnitude of any deviations from exponential decay.

As a first step we thus fit the experimental data at each temperature to the quadratic polynomial

$$\ln\kappa(t) = c - K_1 t + \tfrac{1}{2} K_2 t^2 \,. \tag{3.6}$$

In Table I we present the values obtained for the first cumulant K_1 which provides an estimate of the decay rate; the quoted errors are *two* standard deviations. For comparison, we also give in Table I the values of an effective decay rate Γ_{eff}, when the data are fitted to a straight line

$$\ln\kappa(t) = c' - \Gamma_{\text{eff}} t \,. \tag{3.7}$$

It is worth noting that the values obtained for Γ_{eff} reproduce our earlier set of data[20] to within 1%. The agreement becomes almost perfect if account is made of the fact that the present data correspond to a laser light intensity of 1 mW, while the decay rates published earlier correspond to zero light intensity level.

Of more interest to us in the present paper are deviations from exponential decay as indicated by the normalized second cumulant k_2. The values obtained for this normalized second cumulant are presented in Table II. At $\Delta T = 20$ mK the deviations from exponential decay are still within experimental error, but closer to the critical temperature k_2 increases to $k_2 = 0.038 \pm 0.014$ at $\Delta T = 1.8$ mK. The minor differences with the values quoted in the earlier publication[24] are due to small corrections applied to the experimental data. In Table II we also give an estimated random error, identified with *two* standard deviations, when the data are fit to (3.6), and an estimated maximum systematic error due to uncertainties in the base line and heterodyning effects as discussed in Secs. IV C and IV E.

It should be noted that use of the cumulant expansion presupposes that $\ln g^{(1)}(t)$ is an analytic function of the time t. As we shall see, this assumption is in fact not valid. As a consequence, the values obtained for k_2 will depend on the number of terms retained in the cumulant expansion and on the time interval covered by the correlation function data. We therefore present the values of the cumulants deduced from the experimental data only as a phenomenological indication that the experimental correlation function data do indeed deviate from exponential decay. A more detailed discussion of the time dependence of the correlation function will be presented in Sec. V.

IV. CORRECTIONS AND ERROR ANALYSIS

Since the observed deviations from exponential decay are small, it is important to ascertain that these deviations are indeed to be attributed to the concentration fluctuations in the liquid sample and

TABLE II. Normalized second cumulant k_2 for the correlation function near the critical temperature.

	Experiment			
$\Delta T = T - T_c$ (mK)	k_2	Estimated random error ($2\sigma_{k_2}$)	Estimated maximum systematic error	Theory k_2
1.8	0.038	0.008	0.006	0.027±0.002
2.7	0.035	0.010	0.006	0.026±0.002
3.8	0.042	0.010	0.006	0.025±0.002
5.5	0.025	0.008	0.006	0.023±0.001
11.7	0.020	0.007	0.006	0.016±0.001
20.3	0.006	0.010	0.006	0.009±0.001

not to any artifacts associated with the measurement procedure.[21–23] In particular we have investigated the possible effects due to multiple scattering, afterpulsing, uncertainties in the base line, mixing of light scattered from the incident beam and a reflected beam in the sample, heterodyning, local heating, and convection.

A. Multiple scattering

Light scattering measurements in fluids very close to the critical point are commonly affected by multiple scattering contributions. Since multiple scattering contributions will cause deviations from exponential decay in the scattered intensity correlation function,[16,31] it is important to evaluate the effect. For the 3-methylpentane and nitroethane system the multiple scattering contributions are known to be small,[18] and it is sufficient to consider doubly scattered contributions only.

For our experimental arrangement the theory was formulated by Ferrell and Bhattacharjee.[32] They expand $\ln g^{(1)}(t)$ in a power series in terms of $\tau=\Gamma t$, where Γ is the decay rate associated with the correlation function of the singly scattered light. Truncating the expansion after the term quadratic in τ, one obtains

$$\ln g^{(1)}(\tau)=-\tau+\tilde{\epsilon}\sum_{m=1}^{2}(-1)^m C_m \tau^m \,, \tag{4.1}$$

where $\tilde{\epsilon}$ is a small parameter proportional to the scattering strength of the liquid sample. At the critical temperature $\Delta T=0$, the coefficients C_1 and C_2 are given by[32]

$$C_1(\Delta T=0)=-0.17\gamma_0^{-1}(\ln\gamma_0-2.2)\,, \tag{4.2a}$$

$$C_2(\Delta T=0)=+1.12\gamma_0^{-1}(\ln\gamma_0+0.13)\,, \tag{4.2b}$$

in terms of a parameter $\gamma_0=2r_0/h$, where r_0 is the radius of the scattering cell and h the height of the observed scattering volume. For our experimental configuration $\tilde{\epsilon}=0.021$ and $\gamma_0\simeq 50$ as determined in a previous paper.[20] The first term $m=1$ in the expansion (4.1) represents a correction to the decay rate as a result of double scattering. From (4.2a) it follows that $\tilde{\epsilon}C_1\simeq 0.01\%$, and we conclude that this correction to the decay rate is completely negligible. The second term $m=2$ in the expansion (4.1) represents a contribution to the curvature. From (4.2b) we find $\tilde{\epsilon}C_2\simeq 1.9\times 10^{-3}$, which is equivalent to a second normalized cumulant value $k_2\simeq 0.004$. On comparing with the normalized second cumulant values presented in Table II we conclude that double scattering cannot be responsible for the observed deviations from exponential decay, but a correction for this effect is obviously desirable. The coefficient C_2 may be estimated as a function of temperature from[32]

$$C_2(\tilde{\alpha})=C_2(0)/(1+\tilde{\alpha}+\tfrac{9}{8}\tilde{\alpha}^2)\,, \tag{4.3}$$

where $C_2(0)$ is the value of C_2 at the critical temperature quoted in (4.2b). The parameter $\tilde{\alpha}$ is defined as $\tilde{\alpha}=(q_0\xi)^{-1}$, where ξ is the correlation length and $q_0=1.37\times 10^5\ \text{cm}^{-1}$ is the wave number of the incident light in the liquid medium. The correlation length can be represented by the power law

$$\xi=\xi_0(\Delta T^*)^{-\nu}\,, \tag{4.4}$$

where $\Delta T^*=(T-T_c)/T_c$ and where

$$\xi_0=0.228\ \text{nm},\quad \nu=0.625 \tag{4.5}$$

as determined previously.[18] With C_2 thus determined we subtracted the calculated double-scattering contribution $\tilde{\epsilon}C_2\tau^2$ from the experimental data for $\ln\kappa(t)$ prior to the analysis of the experimental data.

B. Afterpulsing

As demonstrated in Sec. II, our cross-correlation method eliminates afterpulsing effects to the extent that an initiating pulse in one photomultiplier tube cannot cause a correlated afterpulse in the other tube given an uncorrelated light source. However, it is possible for an afterpulse in one tube to be causally related to a pulse occurring in the other tube, when the incident photons are temporally correlated.

In order to evaluate the effect we relate the actually measured count rate $\tilde{n}(t)$ to the true count rate $n(t)$ by

$$\begin{aligned}\tilde{n}(t)&=n(t)+\int_{-\infty}^{t}\alpha(t-t')n(t')dt'\\ &=n(t)+\int_{0}^{\infty}\alpha(t')n(t-t')dt'\,,\end{aligned} \tag{4.6}$$

where $\alpha(t')$ is the probability of finding a correlated afterpulse after a time interval t'. The average apparent count rate $\langle\tilde{n}\rangle$ is related to the average true count rate $\langle n\rangle$ by

$$\langle\tilde{n}\rangle=\langle n\rangle(1+\alpha)\,, \tag{4.7}$$

where α is the total integrated afterpulsing probability of the photomultiplier tube

$$\alpha=\int_0^{\infty}\alpha(t')dt'\,. \tag{4.8}$$

Let $n_i(t)$ and $\tilde{n}_i(t)$ be the count rates received and processed by photomultiplier tube i and $\alpha_i(t)$ the afterpulsing probability of photomultiplier tube i

($i=1,2$). From (4.6) it follows that the observed intensity correlation function

$$\tilde{G}^{(2)}(t)=\langle \tilde{n}_1(t)\tilde{n}_2(0)\rangle$$

is related to the true intensity correlation function

$$G^{(2)}(t)=\langle n_1(t)n_2(0)\rangle$$

by

$$\begin{aligned}\langle \tilde{n}_1(t)\tilde{n}_2(0)\rangle=\langle n_1(t)n_2(0)\rangle &+\int_0^\infty \alpha_1(t_1')\langle n_1(t-t_1')n_2(0)\rangle dt_1'\\ &+\int_0^\infty \alpha_2(t_2')\langle n_1(t+t_2')n_2(0)\rangle dt_2'\\ &+\int_0^\infty\int_0^\infty \alpha_1(t_1')\alpha_2(t_2')\langle n_1(t-t_1'+t_2')n_2(0)\rangle dt_1'dt_2' ,\end{aligned} \tag{4.9}$$

if the output of photomultiplier tube 1 is used to supply the delayed unclipped signal to the correlator. Since a single photon cannot generate photoelectrons in the two photomultiplier tubes simultaneously, it is desirable to decompose (4.9) into

$$\begin{aligned}\langle \tilde{n}_1(t)\tilde{n}_2(0)\rangle=\langle n_1(t)n_2(0)\rangle &+\alpha_1(t)\langle n_1\rangle\delta_{12}\\ &+\lim_{\epsilon\to 0}\int_0^{t-\epsilon} \alpha_1(t_1')\langle n_1(t-t_1')n_2(0)\rangle dt_1'\\ &+\lim_{\epsilon\to 0}\int_{t+\epsilon}^\infty \alpha_1(t_1')\langle n_1(t-t_1')n_2(0)\rangle dt_2'\\ &+\int_0^\infty \alpha_2(t_2')\langle n_1(t+t_2')n_2(0)\rangle dt_2' ,\end{aligned} \tag{4.10}$$

where δ_{12} is a delta function such that $\delta_{ij}=1$ if $i=j$, and where we have neglected the last term in (4.9) which is quadratic in the afterpulsing probability. We assume that the true intensity correlation function decays as[27]

$$G^{(2)}(t)=\langle n_1(t)n_2(0)\rangle=\langle n_1\rangle\langle n_2\rangle[1+\beta\exp(-2\Gamma\,|\,t\,|\,)] , \tag{4.11}$$

where Γ is the decay rate of the electric field correlation function. Substitution of (4.11) into (4.10) yields

$$\begin{aligned}\langle \tilde{n}_1(t)\tilde{n}_2(0)\rangle=\langle n_1\rangle\langle n_2\rangle(1+\alpha_1+\alpha_2)+\alpha_1(t)\langle n_1\rangle\delta_{12}+\beta\langle n_1\rangle\langle n_2\rangle e^{-2\Gamma t}\\ \times\left[1+\int_0^t\alpha_1(t_1')e^{+2\Gamma t_1'}dt_1'+e^{+4\Gamma t}\int_t^\infty \alpha_1(t_1')e^{-2\Gamma t_1'}dt_1'\right.\\ \left.+\int_0^\infty \alpha_1(t_2')e^{-2\Gamma t_2'}dt_2'\right] .\end{aligned} \tag{4.12}$$

The first term in (4.12) represents the observed base line

$$\tilde{B}=\langle \tilde{n}_1\rangle\langle \tilde{n}_2\rangle\simeq\langle n_1\rangle\langle n_2\rangle(1+\alpha_1+\alpha_2) . \tag{4.13}$$

The second term in (4.12) is eliminated by the cross-correlation method. However, to assess the effects of afterpulsing completely we also need to consider the remaining contributions in (4.12).

To estimate the effects we assume that the afterpulsing probabilities $\alpha_i(t')$ can be characterized by a function of the form

$$\alpha_i(t')=2\alpha_i\gamma_i e^{-2\gamma_i t'} , \tag{4.14}$$

where the amplitude is normalized so as to satisfy condition (4.8). An examination of Fig. 3 suggests that this is a reasonable assumption. A comparison between Figs. 3 and 5 also indicates that $\gamma_i \gg \Gamma$. Substitution of (4.14) into (4.12) yields

$$\begin{aligned}\langle \tilde{n}_1(t)\tilde{n}_2(0)\rangle=\langle n_1\rangle\langle n_2\rangle(1+\alpha_1+\alpha_2)+\alpha_1(t)\langle n_1\rangle\delta_{12}+\beta\langle n_1\rangle\langle n_2\rangle e^{-2\Gamma t}\\ \times\left[1+\frac{\alpha_1\gamma_1}{\gamma_1-\Gamma}+\frac{\alpha_2\gamma_2}{\gamma_2+\Gamma}+\left[\frac{\alpha_1\gamma_1}{\gamma_1+\Gamma}-\frac{\alpha_1\gamma_1}{\gamma_1-\Gamma}\right]e^{-2(\gamma_1-\Gamma)t}\right] .\end{aligned} \tag{4.15}$$

Since $\Gamma \ll \gamma_i$, we expand (4.15) in terms of Γ/γ_1 and Γ/γ_2. If we retain only terms linear in α_i and Γ/γ_i, we obtain for the observed normalized correlation function $\tilde{g}^{(2)}(t)=\tilde{G}^{(2)}(t)/\tilde{B}$

$$\tilde{g}^{(2)}(t)=1+\alpha_1(t)\langle n_1\rangle\delta_{12}+\beta\left[1+\frac{\alpha_1\Gamma}{\gamma_1}-\frac{\alpha_2\Gamma}{\gamma_2}\right]e^{-2\Gamma t}-2\beta\frac{\alpha_1\Gamma}{\gamma_1}e^{-2\gamma_1 t} . \tag{4.16}$$

The third term simply modifies the instrumental constant β, but the last term in (4.16) represents a small correction to be applied to the data.

From a calibration of photomultiplier tube 1 we find $\alpha_1 \simeq 0.8\times 10^{-3}$ and $\gamma_1 \simeq 0.55\times 10^{5}\ \mathrm{s}^{-1}$. On comparing γ_1 with the values quoted in Table I we conclude $\Gamma/\gamma_1 \simeq 0.07$. An inspection of the output of photomultiplier tube 2 indicates that α_2 and γ_2 will be of the same order of magnitude as α_1 and γ_1. We conclude that the effect of the correction term

$$-2\beta\alpha_1(\Gamma/\gamma_1)e^{-2\gamma_1 t} = -\beta\alpha_1(t)\Gamma/\gamma_1^2\ ,$$

which was taken into account, is very small; contributions from terms of order $\alpha_i^2\Gamma/\gamma_i$ or $\alpha_i(\Gamma/\gamma_i)^2$ are obviously negligible.

C. Uncertainty in the base line

The normalized electric field correlation function $g^{(1)}(t)$ is related to the intensity correlation function $G^{(2)}(t)$ by

$$\beta[g^{(1)}(t)]^2 = [G^{(2)}(t) - B]/B\ . \tag{4.17}$$

Let us assume that the observed base line $\tilde{B}$ differs from the true base line by a relative error δ_B

$$\tilde{B} = B(1+\delta_B)\ . \tag{4.18}$$

The experimentally observed apparent electric field correlation function $\tilde{g}^{(1)}(t)$, such that

$$\beta[\tilde{g}^{(1)}(t)]^2 = [G^{(2)}(t) - \tilde{B}]/\tilde{B}$$

is then related to the true electric field correlation function $g^{(1)}(t)$ by

$$\tilde{g}^{(1)}(t) = g^{(1)}(t) \times \left[1 - \frac{\delta_B}{\beta}\,\frac{1+\beta[g^{(1)}(t)]^2}{g^{(1)}(t)}\right]^{1/2}, \tag{4.19}$$

where we have only retained the first-order correction term in δ_B. After taking the logarithm and expanding the exponential function

$$[g^{(1)}(t)]^2 = \exp(-2\Gamma t)\ ,$$

we obtain

$$\ln\tilde{g}^{(1)}(t) = \ln g^{(1)}(t) - \frac{\delta_B(1+\beta)}{\beta} - \frac{\delta_B}{\beta}\Gamma t - \frac{\delta_B}{\beta}\Gamma^2 t^2 + \cdots\ . \tag{4.20}$$

The first correction term in (4.20) modifies the instrumental constant c in (3.2). The effect of the second correction term is to modify the decay rate Γ by a factor $(1+\delta_B/\beta)$. The third correction term contributes an amount $2\delta_B/\beta \simeq 4\delta_B$ to the normalized second cumulant k_2. Estimates for the errors δ_B in the determination of the base line were presented in Sec. II. For a typical error $\delta_B \simeq 0.0025\%$ the contribution $4\delta_B$ to k_2 is only 1×10^{-4} and thus negligibly small. Even for the largest error $\delta_B = 0.042\%$ at $\Delta T = 3.8$ mK the contribution to k_2 is only 1.7×10^{-3}. We conclude that the observed deviations from exponential decay cannot be attributed to uncertainties in the base line, but we do include the estimate $4\delta_B$ in the quoted systematic error for k_2.

D. Scattering from multiple beams in the sample

As demonstrated in a previous paper,[20] part of the incident light will be reflected at the glass-air interface upon exiting the optical cell. As a consequence, the observed scattered light intensity contains not only light scattered from the incident beam, but also a contribution due to light scattered from the reflected beam. Mixing of these two types of scattered light will cause apparent deviations from a simple exponential decay with a single relaxation rate, if the scattering angles θ_1 and θ_2 and hence the wave numbers

$$q_1 = 2q_0\sin(\theta_1/2)$$

and

$$q_2 = 2q_0\sin(\theta_2/2)$$

associated with the light scattered from the incident beam and with the light scattered from the reflected beam, respectively, are in fact different. If the laser and sample are aligned in such a manner that the incident and reflected beams are colinear and if the scattering angle is 90°, then $\theta_1 = \theta_2$ and no distortion will be present in the observed correlation function. We now consider the effect of small deviations from this ideal optical configuration.

As argued in a previous paper,[20] the observed intensity correlation function $\tilde{G}^{(2)}(t)$ minus the base line becomes

$$\tilde{G}^{(2)}(t) - B = I_1^2 e^{-2\Gamma_1 t} + I_2^2 e^{-2\Gamma_2 t} + 2I_1 I_2 e^{-(\Gamma_1+\Gamma_2)t}\ , \tag{4.21}$$

where I_i is the intensity of the light scattered from the fluctuations with wave number q_i and where Γ_i is the decay rate of the corresponding electric field correlation function. The apparent electric field correlation function $\tilde{g}^{(1)}(t)$ is thus related to the true electric field correlation function $g^{(1)}(t)$ by

$$\tilde{g}^{(1)}(t)=g^{(1)}(t)\left[1+\frac{I_2^2}{I_1^2}\exp[-2(\Gamma_2-\Gamma_1)t]+\frac{2I_2}{I_1}\exp[-(\Gamma_2-\Gamma_1)t]\right]^{1/2} . \tag{4.22}$$

The intensity I_i of light scattered from fluctuations with wave number q_i is inversely proportional to $(1+q_i^2\xi^2)$ in the Ornstein-Zernike approximation. We thus estimate the strength I_2 of the light scattered from the reflected beam relative to the strength I_1 of the light scattered from the incident beam as

$$\frac{I_2}{I_1}=R\left[\frac{1+q_1^2\xi^2}{1+q_2^2\xi^2}\right] , \tag{4.23}$$

where $R \simeq 0.04$ is the reflection coefficient of the glass-air interface. The decay rates Γ_2 and Γ_1 are related by

$$\frac{\Gamma_2}{\Gamma_1}=\left[\frac{q_2}{q_1}\right]^{z_{\text{eff}}} , \tag{4.24}$$

where z_{eff} is an effective dynamic scaling exponent introduced in previous papers,[20,33] and which, for the temperatures of the present experiments, is close to 3. Since $I_2/I_1 \simeq 0.04 \ll 1$ and $|\Gamma_2-\Gamma_1|t \ll 1$, we obtain from (4.22) after expanding the exponential functions

$$\ln\tilde{g}^{(1)}(t)=\ln g^{(1)}(t)+\frac{I_2}{I_1}\left[1+\frac{I_2}{2I_1}\right]-\frac{I_2}{I_1}\left[1+\frac{I_2}{I_1}\right](\Gamma_2-\Gamma_1)t+\frac{I_2}{I_1}\left[1+\frac{2I_2}{I_1}\right](\Gamma_2-\Gamma_1)^2\frac{t^2}{2}+\cdots . \tag{4.25}$$

The first correction term again affects the instrumental constant c in (3.6), the second correction term modifies the first cumulant K_1 by a negligibly small amount, and the third correction term yields a small contribution δk_2 to the normalized second cumulant k_2

$$\delta k_2 \simeq \frac{I_2}{I_1}\left[1+\frac{2I_2}{I_1}\right]\left[\frac{\Gamma_2-\Gamma_1}{\Gamma_1}\right]^2 . \tag{4.26}$$

If we assume a liberal estimate of a 5° difference between the two scattering angles, i.e., if we assume the scattering angles to be 87.5° and 92.5°, we find that $(\Gamma_2-\Gamma_1)/\Gamma_1 \simeq 0.14$, so that $\delta k_2 \simeq 8.5\times 10^{-4}$. We conclude that the effect is very small; it is included in the error estimates assigned to the experimental values of k_2 in Table II.

E. Heterodyning

In principle, the observed correlation function can be affected by heterodyning effects if the scattered light detected by the photomultiplier has also a contribution from local oscillators such as from dust and glints in the sample. If we assume coherent mixing, the observed intensity correlation function $\tilde{G}^{(2)}(t)$ minus the base line would become[27]

$$\tilde{G}^{(2)}(t)-B=I_1^2e^{-2\Gamma t}+2I_1I_2e^{-\Gamma t} , \tag{4.27}$$

where I_1 is the intensity of the light scattered by the fluid and I_2 the intensity of the local oscillator. If the wave fronts of the light scattered by the fluid and the local oscillator are not parallel over the detector surface, the heterodyning will be less than indicated in (4.27). Hence for given intensity I_2, Eq. (4.27) represents an upper estimate of the effect. Assuming $I_2/I_1 \ll 1$, we obtain from (4.27)

$$\ln\tilde{g}^{(1)}(t)=\ln g^{(1)}(t)-\frac{I_2^2}{2I_1^2}+\frac{I_2}{I_1}e^{\Gamma t} . \tag{4.28}$$

The last term $(I_2/I_1)e^{\Gamma t}$ causes a deviation from the assumed linear behavior, $-\Gamma t$, of $\ln g^{(1)}(t)$.

A detailed study of the intensity of the light scattered from the same sample at 90° was made earlier in collaboration with Chang.[18] To obtain an estimate for the intensity ratio I_2/I_1 we examined the intensity of the scattered light at a temperature $\Delta T=T-T_c=10\,^{\circ}\mathrm{C}$ far away from the critical temperature. The intensity of the scattered light by the fluid can also be estimated theoretically from an analysis of the thermodynamic properties of the 3-methylpentane and nitroethane mixture as discussed earlier.[18] Such an estimate appeared to account for at least half of the scattered intensity at this temperature. If we attribute the other half to spurious contributions from local oscillators, we conclude that for the temperatures considered here $I_2/I_1 \leq 0.0025$. An analysis of (4.28) with the values for Γ observed experimentally indicates that the correction would lead to a shift δk_2 of the normalized second cumulant k_2 of not more than 0.002. Since this is a maximum estimate, we do not apply any corrections for heterodyning effects to the experimental data, but we do include an amount 0.002 in the estimated systematic errors assigned to k_2.

F. Local heating and convection

In principle, the temperature of the scattering volume will differ from the temperature of the surrounding fluid in the optical cell due to local heating by the incident laser light. We assume that the temperature rise δT is proportional to the incident power per unit area that is proportional to the power U of the laser light and inversely proportional to the square of the focusing length l:

$$\delta T = DU/l^2 \ . \tag{4.29}$$

In our previous experiments[18,20] the coefficient D was found to be $D = 0.0056$ K m^2/W which for the focusing length used in our present experiments implies a temperature rise of about 1.05 mK/mW. In our previous investigation of the decay rate of the concentration fluctuations[20] the measurements were obtained at various laser power levels down to levels as small as 45 μW. Since at a given power level and at a given count rate the cross-correlation method quadruples the time required to make a measurement, the measurements reported here were performed at a laser power level of 1 mW so as to avoid excessively long experimental runs. Since the critical temperature T_c was determined under the same conditions, the estimated local heating of about 1 mK should not affect the values measured for $\Delta T = T - T_c$.

However, if the laser is heating a portion of the fluid sample it is possible for thermal convections to develop. Convection currents could induce in the scattered light a Doppler shift proportional to $\vec{q}\cdot\vec{v}$, where $\vec{v}$ is the local fluid velocity which in turn could cause apparent distortions in the spectrum of the scattered light. Starting from the nominal temperature corresponding to $\Delta T = T - T_c = 5$ mK, we made a series of measurements in which the laser power level was increased from 1 to 7 mW. The data were again subjected to a cumulant analysis, and the normalized second cumulant k_2 was determined as a function of the laser power level. The results are shown in Fig. 6. The circles represent the values of k_2 previously obtained from the measurements with a power level of 1 mW; the error bands correspond to the sum of the random and systematic errors quoted in Table II. The squares represent the new values of k_2 obtained with higher power levels; they are displayed at the estimated equivalent temperatures $\Delta T = [0.5 + (U - 1)1.05]$ mK. Although the resolution of these additional power level dependent measurements is not as good, the results definitely indicate that k_2 *decreases* with increasing power level by amounts comparable to what one would expect from the dependence of k_2 on temperature. On the other hand, if Doppler effects due to convection were important, we would expect the observed deviations from exponential decay to *increase* with the power level. We conclude that there are no detectable contributions from convection currents to the observed time dependence of the scattered light intensity.

V. COMPARISON WITH THEORY

Although Perl and Ferrell had predicted the presence of deviations from exponential decay of the order-parameter correlation function in fluids very close to the critical point,[5] their theory was not sufficiently developed to enable us to make a quantitative comparison with our experimental results. As an alternative we considered a paper of Ohta and Kawasaki[34] which seemed to give an expression for a frequency-dependent decay rate. However, the effect predicted by Ohta and Kawasaki appeared to be much smaller than the deviations observed experimentally and also implied the opposite sign for the curvature of $\ln g^{(1)}(t)$ as a function of time.[24,35] Motivated by our experimental results, the theory was further developed by Bhattacharjee and Ferrell[36] and by Ohta.[37] Both theories lead to essentially the same curvature of $\ln g^{(1)}(t)$ at the critical point.[36] We consider here the more detailed theoretical analysis of Bhattacharjee and Ferrell which includes an estimate of the temperature dependence of the effect.

A theoretical description can be based on either the mode-coupling theory of dynamic critical phenomena as developed by Kawasaki[3,38] or on the decoupled-mode version of critical dynamics as formulated by Ferrell.[39] According to these theories, which are equivalent in the Ornstein-Zernike ap-

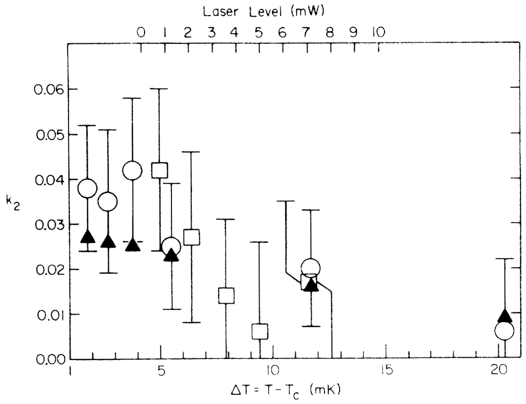

FIG. 6. Normalized second cumulant k_2 as a function of $\Delta T = T - T_c$. The circles represent the values deduced from the measurements with a laser power of 1 mW. The squares represent the values deduced from some check measurements with higher laser power levels. The triangles represent values of k_2 estimated from the theory as discussed in Sec. V.

proximation for the static order-parameter correlation function, the decay of the order-parameter fluctuations in fluids is coupled to the decay of the shear modes. A theory for the frequency dependence of the shear viscosity was developed by Perl and Ferrell[5] and by Bhattacharjee and Ferrell.[40] The effect of the frequency dependence of the shear viscosity on the decay of the order-parameter fluctuations is twofold. First, it modifies the decay rate Γ at zero frequency. This effect was not evaluated by Bhattacharjee and Ferrell,[36] but has been considered by Perl and Ferrell[5] and by Garisto and Kapral.[10] Secondly, it causes an explicit dependence of the decay rate Γ on the frequency which in our experiments is seen as a deviation from exponential decay of the critical concentration fluctuations. Here we focus our attention on these deviations from exponential decay as revealed by the curvature of $\ln g^{(1)}(t)$ as a function of t.

Bhattacharjee and Ferrell[36] consider the decay rate Γ as a function of wave number, temperature, and frequency and introduce a dimensionless time τ such that

$$\tau=\Gamma_0 t \; , \tag{5.1}$$

where Γ_0 is the decay rate Γ at zero frequency. To specify the deviations from exponential decay of the correlation function $g^{(1)}(t)$ they define a deviation function by writing $\ln g^{(1)}(t)$ as

$$\ln g^{(1)}(t)=-\tau+e^{\tau}\Delta G=-\tau+\frac{z}{3}e^{\tau}\Delta\widetilde{G} \; , \tag{5.2}$$

where z is a dynamic scaling exponent, whose theoretical value $z \simeq 3.06$ was previously found to be in good agreement with experiment.[20,33] They then show that the deviation function $e^{\tau}\Delta\widetilde{G}$ is given by

$$e^{\tau}\Delta\widetilde{G}=\int_{s_0}^{\infty} ds \frac{f(s)[e^{-(s-1)\tau}-1]}{(s-1)^2} + \int_{s_0}^{\infty} ds \frac{f(s)}{s(s-1)} \; , \tag{5.3}$$

where $f(s)$ is a spectral function such that $f(s)=0$ for $s<s_0$. This spectral function can be approximated by

$$f(s)=1-\frac{a}{s^{1/3}}-\frac{b}{s} \; , \tag{5.4}$$

TABLE III. Parameters for the comparison with the theory of Bhattacharjee and Ferrell.

$\Delta T=T-T_c$ (mK)	s_0	$\Gamma_0 \pm 2\sigma_{\Gamma_0}$ (s^{-1})
1.8	0.72	3667±4
2.7	0.77	3683±4
3.8	0.84	3686±5
5.5	0.95	3723±4
11.7	1.47	3841±3
20.3	2.74	4040±5

while s_0 is identified with the root of the equation

$$f(s)=0 \; . \tag{5.5}$$

The coefficients a and b in (5.4) are given by[41]

$$a=\left[\frac{1+q^2\xi^2}{q^2\xi^2}\right]a_0 \; , \tag{5.6a}$$

$$b=\left[\frac{1+q^2\xi^2}{q^2\xi^2}\right]\left\{b_0+\left[\frac{4}{3\pi q\xi}\right]^2 \times\left[\frac{8.104}{A}-\left[1+\frac{1}{A}\right]\right]\right\} , \tag{5.6b}$$

where $q=1.93\times10^5\ \mathrm{cm}^{-1}$ is the wave number and where A is a constant that characterizes the frequency dependence of the viscosity at the critical point

$$A=6\ln2+6-3\pi\simeq0.734 \; . \tag{5.7}$$

At the critical temperature ($q\xi\to\infty$) the coefficients a and b assume the values a_0 and b_0, respectively. The best estimates, proposed by Bhattacharjee and Ferrell for a_0 and b_0, are[42]

$$a_0=0.68, \quad b_0=0.14 \; . \tag{5.8}$$

The value of the threshold s_0 is determined by substituting (5.6) into (5.4) and solving (5.5) numerically. The values thus obtained for s_0 as a function of temperature are presented in Table III.

Substitution of (5.4) into (5.3) yields for the deviation function

$$e^{\tau}\Delta\widetilde{G}=(1-b)\left[\tau Ei[(1-s_0)\tau]+\tau\ln\left|\frac{s_0}{1-s_0}\right|-\frac{[e^{(1-s_0)\tau}-1]}{1-s_0}\right] +b\left[e^{\tau}Ei(-s_0\tau)-Ei[(1-s_0)\tau]-\ln\left|\frac{s_0}{1-s_0}\right|+\frac{\tau}{s_0}\right]+aX \; , \tag{5.9}$$

with

$$X=-\int_{s_0}^{\infty}\frac{ds}{s^{1/3}}\frac{[e^{-(s-1)\tau}-1]}{(s-1)^2}-\int_{s_0}^{\infty}\frac{ds}{s^{4/3}}\frac{1}{(s-1)}\,, \tag{5.10}$$

and where $Ei(u)$ is the integral exponential function

$$Ei(x)=P\int_{-\infty}^{x}\frac{e^y dy}{y}\,. \tag{5.11}$$

The first integral in (5.10) cannot be evaluated in closed form. Following the advice of Bhattacharjee and Ferrell[36] we approximate X by a series expansion

$$X=\frac{3\tau}{s_0^{1/3}}-\Gamma(\tfrac{2}{3})\sum_{n=0}^{\infty}\frac{\tau^{n+(4/3)}}{(n+\frac{4}{3})(n+\frac{1}{3})n!}+s_0^{2/3}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-1)^n s_0^n \tau^{m+n+2}}{(m+n+2)(m+n+1)m!n!(n+\frac{2}{3})}\,, \tag{5.12}$$

where $\Gamma(\frac{2}{3})\simeq 1.354$. Equation (5.9) is not in a form suitable for numerical analysis; some individual terms diverge as $s_0 \rightarrow 1$, while the sum must remain finite. We must therefore rewrite the equation so as to cancel the diverging contributions explicitly. This goal is achieved by introducing the series expansion for the integral exponential function

$$Ei(x)=\gamma+\ln x+\sum_{n=1}^{\infty}\frac{x^n}{nn!}\,, \tag{5.13}$$

where $\gamma=0.577$ is Euler's constant. By substituting (5.12) and (5.13) into (5.9) and rearranging terms we obtain

$$\begin{aligned} e^{\tau}\Delta\widetilde{G}=&[(1-b)\tau-b]\left[\gamma+\sum_{n=1}^{\infty}\frac{[(1-s_0)\tau]^n}{nn!}\right]-(1-b)\left[\frac{e^{(1-s_0)\tau}-1}{1-s_0}\right]\\ &-[b-be^{\tau}-(1-b)\tau]\ln(s_0\tau)+be^{\tau}\left[\gamma+\sum_{n=1}^{\infty}\frac{(-s_0\tau)^n}{nn!}\right]+\left[\frac{3a}{s_0^{1/3}}+\frac{b}{s_0}\right]\tau\\ &-a\Gamma(\tfrac{2}{3})\sum_{n=0}^{\infty}\frac{\tau^{n+(4/3)}}{(n+\frac{4}{3})(n+\frac{1}{3})n!}+as_0^{2/3}\tau^2\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-s_0)^n\tau^{m+n}}{(m+n+2)(m+n+1)m!n!}\,. \end{aligned} \tag{5.14}$$

In order to evaluate the theoretical expression for the deviation function we need to determine the decay rate Γ_0. Taking $\Gamma_0=\Gamma_{\text{eff}}$ as quoted in Table I as a first guess, we subtract the deviation function $e^{\tau}\Delta G$ from the data for $\ln g^{(1)}(t)$ and fit the results to a linear function of t so as to obtain a new estimate for Γ_0. The procedure is repeated until convergence is obtained. The values thus obtained for Γ_0 are included in Table III. Upon comparison with the effective decay rates in Table I we note that the

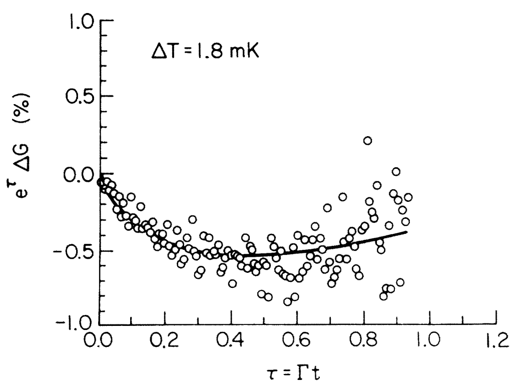

FIG. 7. Deviation $e^{\tau}\Delta G=\ln g^{(1)}(t)+\tau$ as a function of τ at $\Delta T=1.8$ mK. The circles represent the experimental data and the curve the function calculated from the theory.

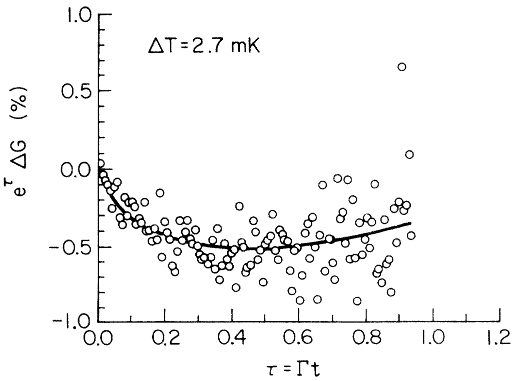

FIG. 8. Deviation $e^{\tau}\Delta G=\ln g^{(1)}(\tau)+\tau$ as a function of τ at $\Delta T=2.7$ mK. The circles represent the experimental data and the curve the function calculated from the theory.

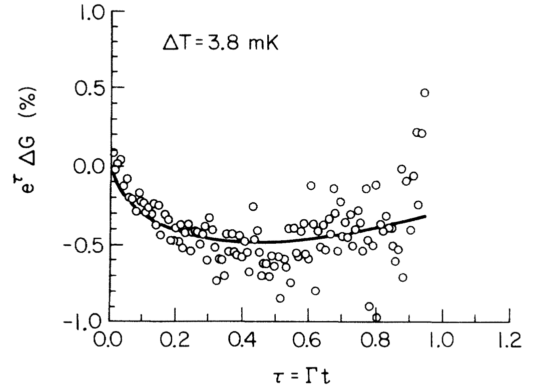

FIG. 9. Deviation $e^{\tau}\Delta G = \ln g^{(1)}(\tau)+\tau$ as a function of τ at $\Delta T = 3.8$ mK. The circles represent the experimental data and the curve the function calculated from the theory.

shift in the decay rate is negligibly small. This result does not necessarily mean that the effect of the frequency dependence on the viscosity is negligibly small. Calculations of Garisto and Kapral[10] indicate that the frequency correction could be as much as 2%. When in our previous work the effective decay rate data were compared with the mode-coupling equations without including any frequency corrections, deviations of a few percent were also noted. However, the result does mean that the effect of the curvature of $\ln g^{(1)}(t)$ upon the determination of the decay rate is very small.

To compare the observed deviation from exponential decay with the theoretical predictions, we can proceed in two ways. An indirect procedure is to evaluate the predicted values of the deviation function

$$e^{\tau}\Delta G = (z/3)e^{\tau}\Delta\tilde{G}$$

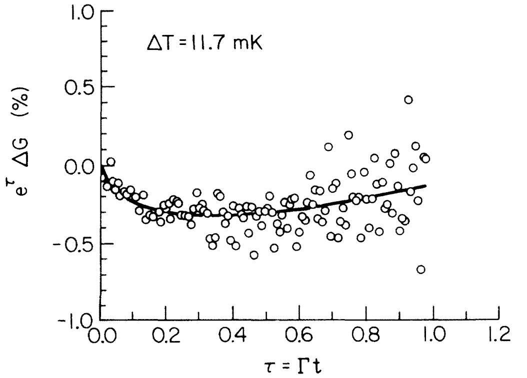

FIG. 11. Deviation $e^{\tau}\Delta G = \ln g^{(1)}(\tau)+\tau$ as a function of τ at $\Delta T = 11.7$ mK. The circles represent the experimental data and the curve the function calculated from the theory.

at the experimental values of τ and to subject the theoretical data to the same cumulant analysis as was done with the experimental data. The theoretical estimates thus obtained for the normalized second cumulant k_2 are given in the last column of Table II. The agreement between the experimental and theoretical values of k_2 is satisfactory.

However, as is evident from (5.14) the actual curvature of $\ln g^{(1)}(t)$ cannot be represented by a quadratic function of τ. A more direct and accurate method is to determine the experimental deviations as $\ln g^{(1)}(t)+\tau$ and compare these experimental deviations as a function of τ with the theoretical values for $e^{\tau}\Delta G$ directly. The results of this procedure are shown in Figs. 7—12. The figures clearly illustrate that the theory reproduces the experimentally observed curvatures well within experimental error at all temperatures.

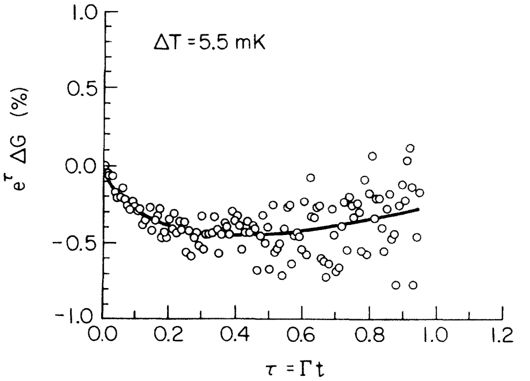

FIG. 10. Deviation $e^{\tau}\Delta G = \ln g^{(1)}(\tau)+\tau$ as a function of τ at $\Delta T = 5.5$ mK. The circles represent the experimental data and the curve the function calculated from the theory.

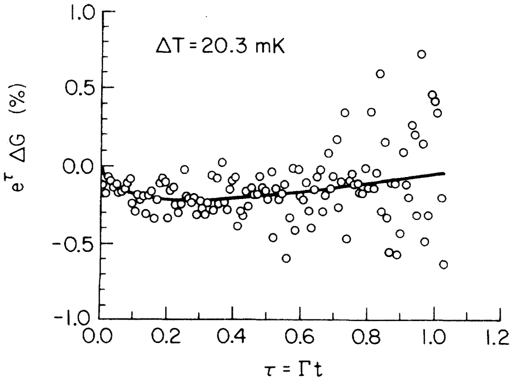

FIG. 12. Deviation $e^{\tau}\Delta G = \ln g^{(1)}(\tau)+\tau$ as a function of τ at $\Delta T = 20.3$ mK. The circles represent the experimental data and the curve the function calculated from the theory.

VI. CONCLUSION

We have observed deviations from exponential decay of the critical concentration fluctuations in a binary liquid mixture and have demonstrated that the effect can be attributed to the coupling with a frequency-dependent critical viscosity as estimated by Ferrell and co-workers.

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[41] See Eqs. (4.2), (4.3), (4.4), (A3), (A22), and (E3) in Ref. 36.

[42] See Eq. (5.1) in Ref. 36.