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# Decay rate of critical concentration fluctuations in a binary liquid

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We report a detailed experimental study of the decay rate of the order-parameter fluctuations in the binary liquid 3-methylpentane and nitroethane near the critical mixing point. This system has the advantage that the decay rate can be measured close to the critical temperature without multiple-scattering corrections. The data cover a range $0.1 < q\xi < 27$, where $q$ is the wave number of the fluctuations and $\xi$ the correlation length. From the data we conclude that the decay rate $\Gamma$ varies at the critical temperature as $\Gamma \propto q^z$ with $z = 3.06 \pm 0.02$. The observed variation of the decay rate as a function of temperature and wave number is consistent with the behavior predicted by the mode-coupling theory of critical dynamics, but an accurate analysis of the data is limited by the lack of a systematic theoretical procedure for dealing with the short-wavelength contributions to the transport coefficients. The paper concludes with a discussion of the Stokes-Einstein relation between the diffusion coefficient and the viscosity coefficient near the critical point.

## I. INTRODUCTION

A system near a critical point exhibits large fluctuations in the order parameter associated with the phase transition. The static order-parameter correlation function close to the critical point is expected to satisfy a scaling law with universal critical exponent values. These critical exponents have been calculated theoretically, originally from temperature series for the three-dimensional Ising model and subsequently for systems with a Landau-Ginzburg Hamiltonian by applying renormalization-group techniques.[1] Detailed predictions of the time dependence of the order-parameter correlation function of fluids near a critical point have been made from the mode-coupling theory of critical dynamics and, more recently, by extending renormalization-group techniques to the treatment of dynamic critical phenomena. For a review of the theory of dynamic critical phenomena the reader is referred to the articles of Hohenberg and Halperin[2] and of Gunton.[3]

Critical fluctuations in fluids are investigated experimentally most conveniently by light-scattering techniques. We have made such a study of the concentration fluctuations in the binary liquid 3-methylpentane and nitroethane near the critical mixing point. This system has the advantage that the refractive indices of the two liquid components are sufficiently close so that the effect of multiple scattering remains small even at temperatures within a millidegree off the critical temperature. At the same time the difference between the refractive indices is sufficiently large so that the observed dielectric constant fluctuations may be attributed to the fluctuations of the concentration which is the order parameter for this transition.[4]

In a previous paper we reported an experimental study of the static correlation function of this mixture near the critical point. The experimental correlation-function data appeared to be in a good agreement with the behavior predicted theoretically for the universality class of three-dimensional systems with short-range forces and a scalar order parameter.[4] In this paper we report a comprehensive experimental study of the decay rate of the concentration fluctuations of the same system. The data were obtained by measuring the autocorrelation function of the scattered light intensity using a digital photon-correlation technique.[5] Combining these results with our earlier data for the static correlation function and with viscosity data obtained by other investigators,[6,7] we investigate several predictions of the theory of critical dynamics in considerable detail.

## II. EXPERIMENTAL METHOD

### A. Sample and temperature measurement

The experiments were performed with the same binary-liquid sample for which we previously determined the static correlation function.[4] The liquid sample, under its own vapor pressure, is contained in a 6-cm long Pyrex cylindrical tube with an internal and external diameter of 1.0 and 1.3 cm, respectively. The critical temperature $T_c$ of the sample is $(299.545 \pm 0.002)$ K. To verify whether the composition of the sample corresponds to the critical concentration we determined the position of the meniscus below $T_c$ as a function of temperature. After analyzing the data with the aid of the coexistence curve data of Wims *et al.*[8] and the density data of Greer and Hocken[9] and of Reeder *et al.*,[10] we concluded that the actual concentration differed from the critical concentration by only 0.6% (corresponding to 0.003-mole fraction units), our sample being slightly richer in nitroethane.[11]

The sample cell is located in an oven and thermostat as indicated in Fig. 1. A heating wire of 10 kΩ is tightly wound noninductively around the copper cylinder surrounding the sample cell. The temperature is controlled to within about 0.3 mK with the aid of a thermistor attached to the surface of this cylinder. The thermostat, as well as the optical arrangement to be discussed below, is located in an air bath whose temperature was kept stable within about 0.02 K. The actual temperature of the sample was determined by measuring the frequency of a quartz oscillator embedded in the copper cylinder at a location close to where the laser beam passes through the sample. We measured this frequency with an electronic counter using a rubidium clock frequency standard with a long-term stability within $1 \times 10^{-10}$ per month. In a previous paper, we showed that the effect of possible concentration gradients induced by gravity can be neglected when the data are taken at a level corresponding to that of the appearance of the meniscus after passing through the critical temperature.[4]

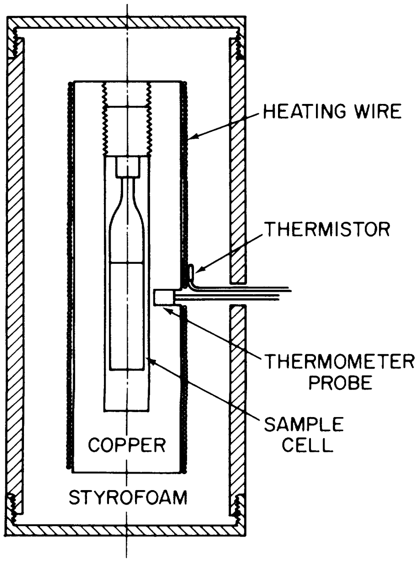

FIG. 1. Sample cell and surrounding thermostat.

In each experimental run we started at a temperature $T$ well above the critical temperature $T_c$, then lowered the temperature in small steps. In order to obtain the light-scattering data as a function of $T - T_c$, the frequency $f_c$ corresponding to the critical temperature, was redetermined after each experimental run. To determine the critical temperature we observed the characteristics of the transmitted laser beam. Upon passing through the critical temperature it was noted that streaming occurs when material is exchanged between the upper and lower parts of the sample due to the density differences between the two phases. In our sample this streaming is clearly seen because of the low turbidity of the mixture. The fact that this streaming indeed indicated transition through the critical point was confirmed by the observation that after a long waiting period of 12 hours or so invariably a splitting of the laser beam was observed indicating the presence of a meniscus. In practice we set the laser intensity at a low level between 50 and 100 $\mu$W to avoid local heating effects as discussed in Sec. III. The transmitted beam was allowed to pass through a thin glass plate producing interference when projected on a screen. When the sample passes through the critical temperature, these interference fringes begin to move within about 20 min due to the phase delays caused by the density variations associated with the streaming. We found this test to be convenient and very sensitive allowing us to determine the critical temperature to within 0.3 mK.

### B. Optical arrangement

The optical arrangement for investigating light scattered by the sample is schematically indicated in Fig. 2. The light source is a 6.4-mW He-Ne laser whose polarization is perpendicular to the plane determined by the incident beam and the direction in which the scattered light is observed. After passing through an intensity stabilizer, the incident beam is focused at the center of the sample cell by a lens with a focal length of 7.5 cm.

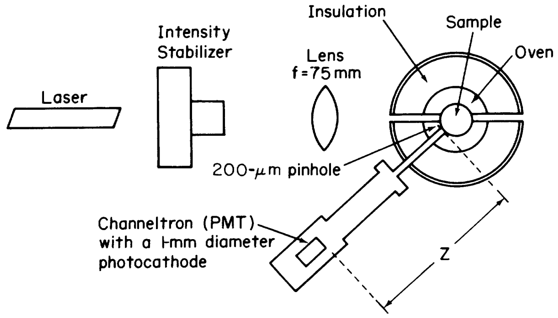

FIG. 2. Top view of optical arrangement.

The intensity stabilizer is a variable attenuator consisting of two neutral density (ND) plates; the attenuation factor can be adjusted by moving both plates along their lengths. This ND filter serves two purposes. First, the incident light intensity is kept constant by splitting off a part of the light exiting from the attenuator and monitoring it with a photodiode whose output is compared with a reference voltage; the amplified and integrated error signal then drives a servo motor which adjusts the optical density of the attenuator. In this way the baseline of the measured correlation function is stabilized against long-term drifts. Secondly, the attenuator enables us to vary the incident light intensity in a controlled manner and to study the decay rate as a function of the incident light intensity.

In our experiment the scattered light was investigated at scattering angles of about 30°, 90°, and 147°. The geometrical dimensions of the scattering volume and the scattered beam are specified by a pinhole with a diameter of 200 $\mu$m located just outside the sample cell and the diameter of 1 mm of the photocathode of the multiplier located a distance $Z$ from the pinhole. In our experiment the scattering volume was of the order of $10^{-2}$ mm$^3$.

The normalized time-dependent intensity correlation function $g^{(2)}(\tau) \equiv \langle I(\tau)I(0)\rangle / \langle I \rangle^2$ is related to the normalized electric-field correlation function $g^{(1)}(\tau) \equiv \langle E^*(\tau)E(0)\rangle / \langle I \rangle$ by

$$g^{(2)}(\tau) = 1 + f(A)\,|\,g^{(1)}(\tau)\,|^2 , \qquad (2.1)$$

where $f(A)$ is a function of the coherence area $A$ at the position of the cathode of the photomultiplier.[12,13] To obtain a satisfactory signal to baseline ratio, $f(A)$ should be close to unity. This function $f(A)$ depends on the separation $Z$ and can be estimated as indicated by Jakeman.[12] The separation $Z$ used in our experiments at the scattering angles of 30°, 90°, and 147° was 40, 30, and 27 cm, respectively, corresponding to the estimated values of $f(A) = 0.70$, 0.65, and 0.55, respectively. In the actual experiments, the coefficient $f(A)$ is treated as an unknown parameter.

The thermostat is mounted coaxially with the turntable. The pinhole and the photomultiplier are mounted on the turntable so as to be colinear with the laser beam in the absence of the focusing lens and the sample cell. At this juncture the lens is reinserted and adjusted so that the light illuminates the photocathode. The turntable is then rotated to bring the collection optics to the desired scattering angle. The sample is then inserted and the oven and beam paths sealed. Insertion of the sample causes a slight deviation of the transmitted beam due to the fact that the sample cell is not exactly concentric with the oven. This deviation is recorded. At the end of an experimental run, after the sample cell is rotated 90°, the deviation is remeasured. In this way we are able to determine the precise location of the center of the sample cell relative to the center of the oven leading to a maximum correction of 0.25° to the scattering angle as measured with the turntable. If we assume that the uncertainty in the scattering angle is of the magnitude of the correction, we conclude that the resulting error in the decay rate is negligibly small, except for the data obtained at a scattering angle of 30° where the corresponding uncertainty in $\Gamma$ becomes of the order of 2%.

### C. Photon-correlation method

The autocorrelation function of the scattered light intensity was determined by a home-built clipped correlator with 128 channels which was connected to the memory of a minicomputer. A block diagram of the electronic detection system is shown in Fig. 3. The scattered light is registered by a Channeltron located in a photomultiplier tube housing. The pulses emanating from the Channeltron are first passed through a preamplifier with a gain of 10, placed close to the anode of the phototube. The output of the preamplifier is transmitted over a balanced twisted pair line and then coupled via a transformer to a two-stage amplifier possessing a total gain of 16. Transformer coupling allows us to reject common mode noise, while also enabling us to eliminate a ground loop. The amplifiers are followed by a discriminator which generates a standardized output pulse provided that the input exceeds a specified threshold; a discrim-

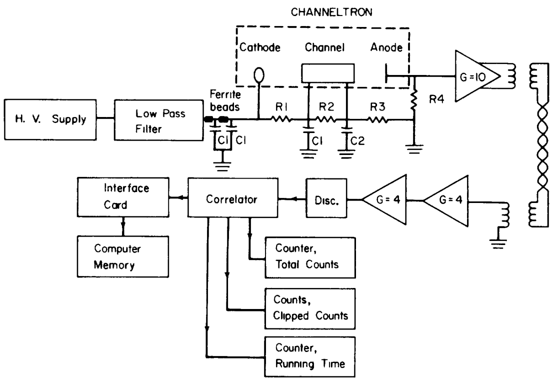

FIG. 3. Block diagram of electronic detection system.

ination level of 175 mV was found to be adequate. It is estimated that the number of pulses rejected by the discriminator is less than 1%. The width of the output pulse from the discriminator was set at 30 ns with a deadtime following each pulse of also 30 ns. The standardized signal is finally transmitted to the correlator. The count rates observed in our experiments never exceeded $10^4$ counts/s and were usually much smaller. A count rate as high as $2\times10^4$ is near the damage threshold of the channel-multiplier tube used. The operating conditions imply that the amplifier will be driven into saturation by a significant number of incoming pulses. Since the deadtime after the pulses generated by the discriminator is much longer than the recovery times of the amplifiers, this has no detrimental effect; rather, by using the amplifiers under these conditions, the dynamic range of the electronics is effectively increased. The advantage of this method has been recognized by previous investigators.[14]

The experimentally observed photoelectron-count autocorrelation function $G^{(2)}(\tau)$ is related to the electric-field correlation function $g^{(1)}(\tau)$ by

$$\begin{aligned} G^{(2)}(\tau) &= B + |G^{(1)}(\tau)|^2 \\ &= B[1 + C|g^{(1)}(\tau)|^2] , \end{aligned} \tag{2.2}$$

where $B$ is the baseline and $C$ an instrument constant related to the coherence area of the scattered light as discussed above. The baseline can be determined by observing the accidental coincidence rate. That is, from the total number $N$ of pulses in the experimental run, the number of clipped events $N_k$, and the total running time $\tau_{\text{tot}}$, measured in units of the sample interval, the baseline can be identified as $B = NN_k/\tau_{\text{tot}}$. It can also be determined by observing the count rate at the 128th channel which followed the preceding channel by a delay line corresponding to 1208 channels. The two methods for determining the baseline usually agreed to within their standard deviations, typically within 0.1%. In a few cases where this condition was not satisfied the run was rejected as unreliable.

The time dependence of the correlation function $G^{(1)}(\tau)$ thus obtained can be affected by the occurrence of afterpulsing from feedback mechanisms in the photomultiplier tube. These effects were accounted for by calibrating the afterpulsing probability of the photomultiplier tube as described elsewhere.[15] For futher details concerning the experimental method the reader is referred to a separate report.[11]

To examine the effect of possible local heating of the fluid by the laser beam we made a preliminary analysis of the decay rate as a function of the incident light intensity by varying the laser power from 1 to 7 mW. The decay rate was found to increase linearly with the laser power. From the known temperature dependence of the decay rate the effect could be interpreted as corresponding to a temperature rise $\delta T = 1.0$ mK/mW. If we assume that this rise is proportional to the incident power per unit area, i.e., proportional to $U$, and inversely proportional to the square of the focusing length $l$,

$$\delta T = DU/l^2 , \tag{2.3}$$

the effect implies $D = 0.0056$ K m$^2$/W. A similar heating effect in 3-methylpentane and nitroethane was noted by Sorensen *et al.*[16] In our previous light-scattering-intensity measurements the effect was accounted for by applying a correction to the measured temperature. In the experiments reported in this paper a different approach was adopted. First, the power level was reduced substantially and all data were taken at power levels between 45 $\mu$W and 3.4 mW. Second, at each temperature the decay rates were measured with at least two different power levels and then extrapolated to a decay rate corresponding to zero laser power. Except for a few data points far away from the critical temperature, the power levels were always chosen so that the correction due to this extrapolation was less than 0.2%.

## III. EXPERIMENTAL DECAY RATES

The autocorrelation function $G^{(2)}(\tau)$ of the scattered light intensity was measured at three different scattering angles, namely, $\theta=29.8°$, 89.5°, and 146.8° which, with a refractive index value of 1.377, correspond to the wave numbers $q=0.704\times10^5$, $1.92\times10^5$, and $2.62\times10^5$ cm$^{-1}$, respectively. A representative example of the experimental results obtained for $(G^{(1)}(\tau))^2=G^{(2)}(\tau)-B$ is shown in Fig. 4. The correlation function shown in this figure was obtained at the scattering angle $\theta=89.5°$ and at a temperature for which $T-T_c=32.2$ mK. We identify the decay rate $\Gamma$ of the order-parameter correlation function with the decay rate of $G^{(1)}(\tau)$:

$$G^{(1)}(\tau)\propto \exp(-\Gamma\tau) \ . \tag{3.1}$$

Hence, $2\Gamma$ is deduced from the experimental data by fitting $\ln(G^{(1)}(\tau))^2$ to a straight line, taking into account the statistical errors in $G^{(2)}(\tau)$ and the baseline $B$. The correlation function $(G^{(1)}(\tau))^2$ is plotted in Fig. 4 as a function of the dimensionless time $\Gamma\tau$. At each temperature the time base of the correlator was adjusted so that the autocorrelation function was measured over a time interval corresponding to one decay time, i.e., $\Gamma\tau\simeq1$. In all experimental runs this condition was satisfied to within 20%.

The experimental correlation function data obtained at 29.8° and 89.5° could be represented by an exponential decay law within experimental precision except for the data at temperatures within 20 mK from the critical temperature, where small but definite deviations from exponential decay were observed.[17] At these temperatures we continue to define $\Gamma$ as the effective decay rate when the data are fit to an exponential decay law over the experimental time interval which corresponds approximately to one relaxation time.

The experimental correlation-function data obtained at 146.8° showed systematic deviations outside the experimental error when fitted to an exponential decay law with one relaxation rate. To explain this effect it should be noted that the observed scattered light intensity contains, in principle, contributions not only from light scattered from the incident beam but also from light scattered from the beam reflected by the wall of the optical cell. The data obtained at 90° all correspond to the same wave number $q$ because of the symmetry of the situation. For the data obtained at 30° the effect is negligibly small, since the ratio of the intensity of light scattered in the forward direction to the intensity of light scattered in the backward direction diverges as the critical point is approached. However, the effect becomes significant at the scattering angle of 146.8°. To account for this effect we note that the intensity autocorrelation function is given by

$$\langle I(\tau)I(0)\rangle=\langle E^*(\tau)E(\tau)E^*(0)E(0)\rangle=\langle E^*(\tau)E(\tau)\rangle\langle E^*(0)E(0)\rangle+\langle E^*(\tau)E(0)\rangle\langle E^*(0)E(\tau)\rangle \ , \tag{3.2}$$

where we have again assumed that the electric field $E$ is a Gaussian random variable.[13] The electric field is now decomposed as

$$E=E_{q_1}+E_{q_2} \ , \tag{3.3}$$

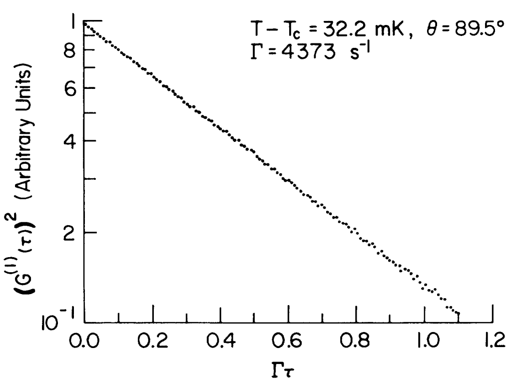

FIG. 4. Experimental data obtained for $G^{(1)}(\tau)^2$ as a function of $\Gamma\tau$ at $T-T_c$ = 32.2 mK.

where $q_1$ and $q_2$ are the two wave numbers of the fluctuations probed by light scattered from the incident beam and from the reflected beam. If we assume $E_{q_1}$ and $E_{q_2}$ to be uncorrelated, we obtain

$$\langle I(\tau)I(0)\rangle=(I_1+I_2)^2+I_1^2e^{-2\Gamma_1\tau}+I_2^2e^{-2\Gamma_2\tau}+2I_1I_2e^{-(\Gamma_1+\Gamma_2)\tau} \ , \tag{3.4}$$

where $I_i$ is the intensity and $\Gamma_i$ the decay rate of the electric-field correlation function with wave number $q_i$. The decoupling approximation is consistent with the assumption that three-point correlation functions can be ignored relative to certain four-point correlation functions, as was shown by Oxtoby and Gelbart for the static case.[18] We then conclude that the data should be analyzed as

$$G^{(2)}(\tau)=B+N_1^2e^{-2\Gamma_1\tau}+N_2^2e^{-2\Gamma_2\tau}+2N_1N_2e^{-(\Gamma_1+\Gamma_2)\tau} \ . \tag{3.5}$$

Since $N_1$, $N_2$, $\Gamma_1$, and $\Gamma_2$ are not known *a priori*, Eq. (3.5) as it stands is not suitable for an accurate analysis; the equation contains too many free parameters and the minimum in $\chi^2$ under these conditions is too shallow to obtain a reliable fit. The number of free parameters can be reduced by noting that in the Ornstein-Zernike approximation the intensity ratio $N_2/N_1$ has the form

$$N_2/N_1=\alpha_R G_0(1+q_1^2\xi^2)/(1+q_2^2\xi^2)\ . \tag{3.6}$$

Here $\alpha_R$ is a reflection coefficient which is assumed to be 0.04 and $G_0$ a factor which takes into account any error in the estimate of $\alpha_R$ and any geometrical effects. The factor $G_0$ should be slightly less than unity and it should be independent of temperature; i.e., all fits for data at a specific scattering angle should contain the same value of $G_0$. As further discussed in Sec. VI, we note that a zeroth-order solution of the mode-coupling equations indicates that the decay rate $\Gamma$ at a given temperature and scattering angle should be proportional to $q^2\Omega_0(q\xi)$, where

$$\Omega_0(x)=\frac{3}{4x^2}[1+x^2+(x^3-x^{-1})\arctan x]\ . \tag{3.7}$$

The function $\Omega_0(x)$ (with or without the prefactor $3/4x^2$) is commonly referred to as the Kawasaki function.[19] It thus follows that the decay rates $\Gamma_1$ and $\Gamma_2$ are related by

$$\frac{\Gamma_1}{\Gamma_2}=\frac{x_1^2\Omega_0(x_1)}{x_2^2\Omega_0(x_2)}\ , \tag{3.8}$$

where $x_i=q_i\xi$.

The experimental data obtained at 146.8° were fit to (3.5), subject to the constraints (3.6) and (3.8) with $N_1$, $G_0$, and $\Gamma_1$ as the only adjustable parameters. We carried out the same procedure for the data obtained at the scattering angle of 29.8°. In this case the procedure yielded corrections less than 0.5% which are of little statistic significance as expected.

The experimental decay-rate data obtained as a function of $\Delta T=T-T_c$ are presented in Tables I, II, and III. The data obtained at the scattering angle of 90° appear to have the higher precision because of the simplified geometrical configuration at this scattering angle. At this scattering angle we therefore made a comprehensive analysis of the temperature dependence of $\Gamma$ taking 54 correlation-function data in a temperature range corresponding to the range 0.3 mK $\leq \Delta T \leq$ 1.3 K, while the data taken at the scattering angles of 29.8° and 146.8° yield supplemental information concerning the wave-number dependence of the decay rate. The decay rates $\Gamma$ as determined from the statistical analysis had typically a standard deviation of fractions of a percent. However, the accuracy of the decay-rate data as judged from the spread of the data at different temperatures and scattering angles is of the order of 2%. For the results obtained at $\theta=146.8°$ and presented in Table III, we give both the effective decay rate $\Gamma_{\text{eff}}$ when the correlation-function data are forced to be represented by an exponential decay law with a single decay rate, as well as the decay rate $\Gamma$ after correcting for a contribution due to scattering from the reflected beam as discussed above. It can be readily verified that any errors due to the approximate nature of Eqs. (3.6) and (3.8) in determining these corrections are well within experimental accuracy.

In the tables we also quote the corresponding values of the scaling variable $x=q\xi$. For our mix-

TABLE I. Experimental decay rates at $q=0.704\times10^5$ cm$^{-1}$ ($\theta=29.8°$).

| $T-T_c$ (K) | $x=q\xi$ | $\Gamma$ (s$^{-1}$) |
|---|---|---|
| 0.4000 | 0.100 | 1824 |
| 0.3173 | 0.116 | 1490 |
| 0.2525 | 0.134 | 1332 |
| 0.2014 | 0.154 | 1151 |
| 0.1599 | 0.178 | 963.6 |
| 0.1284 | 0.204 | 820.1 |
| 0.1010 | 0.238 | 716.7 |
| 0.0818 | 0.271 | 640.6 |
| 0.0644 | 0.315 | 557.4 |
| 0.0512 | 0.363 | 484.5 |
| 0.0424 | 0.409 | 432.0 |
| 0.0326 | 0.481 | 369.3 |
| 0.0265 | 0.548 | 335.4 |
| 0.0215 | 0.624 | 303.7 |
| 0.0174 | 0.714 | 282.5 |
| 0.0140 | 0.818 | 259.8 |
| 0.0101 | 1.00 | 234.7 |
| 0.0084 | 1.12 | 221.2 |
| 0.0074 | 1.22 | 217.4 |
| 0.0062 | 1.37 | 206.7 |
| 0.0054 | 1.48 | 202.7 |
| 0.0043 | 1.71 | 192.2 |
| 0.0033 | 2.01 | 184.8 |
| 0.0024 | 2.46 | 182.0 |
| $0.0012^5$ | 3.70 | 175.8 |
| $0.0004^5$ | 7.00 | 172.8 |

TABLE II. Experimental decay rates at $q=1.92\times10^5\ \mathrm{cm}^{-1}$ ($\theta=89.5^\circ$).

| $T-T_c$ (K) | $x=q\xi$ | $\Gamma$ ($\mathrm{s}^{-1}$) |
|---|---|---|
| 1.2650 | 0.134 | 29918 |
| 1.0036 | 0.155 | 25216 |
| 0.7955 | 0.179 | 21654 |
| 0.6381 | 0.205 | 18671 |
| 0.5042 | 0.238 | 16080 |
| 0.3995 | 0.275 | 13845 |
| 0.3177 | 0.317 | 11998 |
| 0.2547 | 0.364 | 10521 |
| 0.2000 | 0.424 | 9127 |
| 0.1600 | 0.487 | 8096 |
| 0.1291 | 0.557 | 7211 |
| 0.1015 | 0.647 | 6427 |
| 0.0806 | 0.748 | 5820 |
| 0.0655 | 0.851 | 5357 |
| 0.0549 | 0.950 | 5039 |
| 0.0464 | 1.06 | 4523 |
| 0.0379 | 1.20 | 4781 |
| 0.0322 | 1.33 | 4358 |
| 0.0284 | 1.44 | 4252 |
| 0.0245 | 1.57 | 4153 |
| 0.0221 | 1.68 | 4084 |
| 0.0199 | 1.79 | 4012 |
| 0.0182 | 1.89 | 3979 |
| 0.0166 | 2.01 | 3916 |
| 0.0157 | 2.08 | 3915 |
| 0.0145 | 2.18 | 3872 |
| 0.0137 | 2.27 | 3839 |
| 0.0130 | 2.34 | 3849 |
| 0.0124 | 2.41 | 3812 |
| 0.0119 | 2.48 | 3822 |
| 0.0113 | 2.55 | 3819 |
| 0.0108 | 2.62 | 3799 |
| 0.0104 | 2.68 | 3785 |
| 0.0099 | 2.77 | 3780 |
| 0.0094 | 2.86 | 3769 |
| 0.0090 | 2.95 | 3758 |
| 0.0085 | 3.05 | 3766 |
| 0.0080 | 3.17 | 3737 |
| 0.0075 | 3.30 | 3739 |
| 0.0069 | 3.48 | 3706 |
| 0.0065 | 3.61 | 3708 |
| 0.0060 | 3.80 | 3698 |
| 0.0055 | 4.02 | 3696 |
| 0.0050 | 4.27 | 3675 |
| 0.0045 | 4.56 | 3680 |
| 0.0039 | 5.00 | 3698 |
| 0.0034 | 5.36 | 3663 |
| 0.0030 | 5.80 | 3668 |
| 0.0026 | 6.34 | 3663 |
| 0.0022 | 7.14 | 3644 |
| 0.0016 | 8.59 | 3655 |
| 0.0012 | 10.3 | 3644 |
| 0.0007 | 14.4 | 3661 |
| 0.0003 | 24.5 | 3651 |

ture the correlation length $\xi$ is represented by[4]

$$\xi=\xi_0(\Delta T^*)^{-\nu}\ , \tag{3.9}$$

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

$$\xi_0=0.228\ \mathrm{nm},\quad \nu=0.625\ . \tag{3.10}$$

The errors in the parameters $\xi_0$ and $\nu$ are strongly correlated when deduced from the light-scattering data[4] and the question arises what accuracy can be attributed to the calculated correlation-length values. When our previous light-scattering measurements for the static correlation function were analyzed with a fixed exponent value $\nu$, we obtained a two-standard-deviation error in $\xi_0$ of about 2%.[4] Furthermore, a comparison can be made with an earlier determination of $\xi$ by Chang *et al.* with a different optical-detection method.[20] While these earlier data were represented with a different exponent value $\nu$, it appears that the actual $\xi$ values from the two experiments agree to within 1% in the overlapping experimental temperature range. We are thus confident that (3.9) and (3.10) do represent the correlation length to within a few percent.

The experimental correlation-function data could, in principle, be affected by double-scattering contributions.[21,22] For our experiment the effect was analyzed by Ferrell and Bhattacharjee.[23] To estimate the effect it is again sufficient to use the Ornstein-Zernike approximation for the scattered light intensity $I(\theta,\phi)$[24]

$$I(\theta,\phi)=B_0\sin^2\phi\Big/\left[(q_0\xi)^{-2}+\left[2\sin\frac{\theta}{2}\right]\right]\ . \tag{3.11}$$

Here $q_0$ is the wave number of the incident light, $\phi$ the angle between the initial direction of polarization and the direction of scattering, and $B_0$ a constant which can be extracted from turbidity data.[4] To estimate the double-scattering contribution to the time-dependent correlation function Ferrell and Bhattacharjee expand the electric-field autocorrelation function $\langle E(\tau)E(0)\rangle$ as

$$\ln\langle E(\tau)E(0)\rangle=\ln I_s-\Gamma_s +\tilde{\epsilon}\sum_{n=0}^{\infty}(-L)^n C_n(\Gamma_s\tau)^n\ , \tag{3.12}$$

where $I_s$ is the singly scattered light intensity and $\Gamma_s$ the associated decay rate of the singly scattered light. The parameters $\tilde{\epsilon}$ is defined as

TABLE III. Experimental decay rates at $q=2.62\times10^{5}$ cm$^{-1}$ ($\theta=146.8°$).

| $T-T_c$ (K) | $x=q\xi$ | $\Gamma_{\text{eff}}$ ($\text{s}^{-1}$) | $\Gamma$ ($\text{s}^{-1}$) |
|---|---|---|---|
| 0.7951 | 0.243 | 40714 | 42185 |
| 0.6325 | 0.281 | 34871 | 35406 |
| 0.5046 | 0.323 | 29485 | 30622 |
| 0.3997 | 0.374 | 25738 | 26412 |
| 0.3178 | 0.432 | 23077 | 23777 |
| 0.2544 | 0.496 | 20389 | 20760 |
| 0.1994 | 0.578 | 18064 | 18160 |
| 0.1594 | 0.665 | 16122 | 16330 |
| 0.1317 | 0.749 | 14900 | 15389 |
| 0.1018 | 0.879 | 13482 | 13595 |
| 0.0795 | 1.03 | 12184 | 12212 |
| 0.0614 | 1.21 | 11474 | 11386 |
| 0.0543 | 1.30 | 11133 | 10942 |
| 0.0465 | 1.44 | 10764 | 10911 |
| 0.0379 | 1.63 | 10300 | 10348 |
| 0.0321 | 1.81 | 10118 | 10395 |
| 0.0279 | 1.98 | 9906 | 10188 |
| 0.0240 | 2.17 | 9706 | 9983 |
| 0.0215 | 2.32 | 9622 | 9894 |
| 0.0172 | 2.67 | 9383 | 9822 |
| 0.0157 | 2.83 | 9327 | 9801 |
| 0.0142 | 3.01 | 9381 | 9742 |
| 0.0133 | 3.14 | 9270 | 9629 |
| 0.0116 | 3.42 | 9174 | 9448 |
| 0.0096 | 3.86 | 9043 | 9575 |
| 0.0089 | 4.04 | 9064 | 9660 |
| 0.0084 | 4.19 | 8970 | 9519 |
| 0.0071 | 4.65 | 8890 | 9704 |
| 0.0064 | 4.98 | 8860 | 9463 |
| 0.0054 | 5.53 | 8831 | 9482 |
| 0.0045 | 6.21 | 8694 | 9289 |
| 0.0034 | 7.39 | 8595 | 9586 |
| 0.0027 | 8.53 | 8286 | 9400 |
| 0.0020 | 10.2 | 8389 | 9491 |
| 0.0012 | 14.0 | 8470 | 9599 |
| 0.0004 | 27.8 | 8610 | 9637 |

$$\tilde{\epsilon}=4\pi r_0 B_0 \ , \tag{3.13}$$

where $r_0$ is the radius of the scattering cell ($r_0=0.5$ cm). The analysis of Bhattacharjee and Ferrell indicates that at the critical temperature

$$\tilde{\epsilon}C_1=-0.17\tilde{\epsilon}\gamma_0^{-1}\ln(\gamma_0-2.2) \ , \tag{3.14}$$

where $\gamma_0=2r_0/h$, $h$ being the height of the observed volume. For our experiment $\tilde{\epsilon}=2.1\times10^{-2}$, $\gamma_0\simeq50$, and thus $\tilde{\epsilon}C_1\simeq1.2\times10^{-4}$. We conclude that $\Gamma_s$ may be identified with the coefficient in (3.12) that is linear in $\tau$. The same authors showed that the effective decay rate when the data are represented by an exponential decay law with a single relaxation rate, becomes

$$\gamma_{\text{eff}}=[1-1.16\tilde{\epsilon}\gamma_0^{-1}(\ln\gamma_0-0.11)]\Gamma_s \ . \tag{3.15}$$

From the above expression we conclude that at the critical point $\Gamma_{\text{eff}}$ can still be identified with $\Gamma_s$ to within 0.3%.

The experimental decay-rate data are shown in Fig. 5 as a function of $\Delta T=T\text{-}T_c$. The data taken

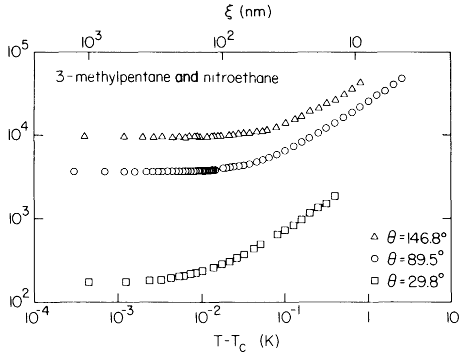

FIG. 5. Experimental decay-rate data as a function of $T=T-T_c$.

at $\Delta T > 0.1$ K correspond to the hydrodynamic regime $q\xi < 1$, where the decay rate decreases upon approaching the critical point. The data taken at $\Delta T < 0.01$ K correspond to the critical regime $q\xi > 1$, where the decay rate approaches a value which is almost independent of the temperature. This qualitative behavior of the decay rate in the critical region has been observed by many previous investigators as reviewed by Swinney and Henry.[25]

## IV. VISCOSITY

In order to compare the decay-rate data with theoretical predictions one also needs information concerning the shear viscosity $\eta_s$ of the fluid. For 3-methylpentane and nitroethane the viscosity was measured by Stein *et al.*[6] and by Tsai and McIntyre.[7] The measurements of Tsai and McIntyre have a very high precision, but Stein and coworkers paid more attention to the calibration of the viscosity on an absolute basis.[26] As argued in a previous publication[27] we accept as the most accurate values the data of Tsai and McIntyre, but shifted by $(3.1 \pm 0.7)\%$ so as to conform to the calibration of Stein *et al.*

The viscosity diverges weakly at the critical point and it is currently often represented by a power-law divergence of the form[28–31]

$$\frac{\eta_s}{\bar{\eta}_s}=(Q_0\xi)^{x_\eta}\ , \tag{4.1}$$

where $x_\eta$ is a critical exponent further discussed in Sec. V and $Q_0$ a system-dependent amplitude. The coefficient $\bar{\eta}_s$ is interpreted as a background or bare viscosity coefficient, i.e., a viscosity in the absence of critical fluctuations. In practice, it is identified with the viscosity values obtained by extrapolating data away from the critical point. For liquids it is often represented by an Arrhenius equation of the form

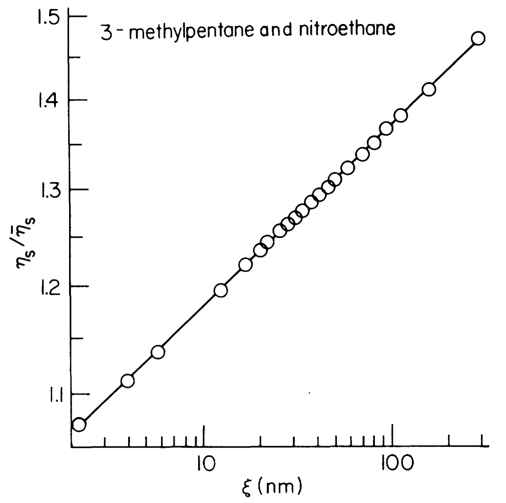

FIG. 6. Log-log plot of the viscosity ratio $\eta_s/\bar{\eta}_s$ of 3-methylpentane and nitroethane at the critical concentration as deduced from the measurements of Tsai and McIntyre (Ref. 7) as a function of the correlation length $\xi$.

$$\bar{\eta}_s = A_\eta \exp(B_\eta/k_BT)\ , \tag{4.2}$$

where $k_B$ is Boltzmann's constant. Tsai and McIntyre deduced estimated values for the background viscosity $\bar{\eta}_s$ of 3-methylpentane and nitroethane as well, by interpolating between the viscosity data at low and high concentrations at various temperatures[7]; these values for $\bar{\eta}_s$ can be represented by (4.2) with the parameters $A = 2.431 \times 10^{-3}$ Pa s and $B_\eta = 1.133 \times 10^{-20}$ J. The values thus deduced for $\eta_s/\bar{\eta}_s$ are plotted in Fig. 6 on a double-logarithmic scale. If we substitute (3.9) and (4.2) into (4.1) and fit the resulting equation to the viscosity data at the critical concentration, we obtain

$$Q_0 = (1.35 \pm 0.18)\ \text{nm}^{-1}\ ,$$
$$x_\eta = 0.0635 \pm 0.0004, \tag{4.3}$$

where the quoted errors represent two standard deviations. The statistical error in $x_\eta$ is small due to the smoothness of the data. If we analyze the data of Stein *et al.*[6] by the same procedure we obtain $Q_0 = (1.2 \pm 0.8)\ \text{nm}^{-1}$ and $x_\eta = 0.062 \pm 0.002$. If we consider the differences in $x_\eta$ deduced from the two data sets as an estimate for the accuracy, we conclude

$$x_\eta = 0.063 \pm 0.001 \ , \tag{4.4}$$

not counting, however, any possible bias due to the extrapolation procedure in determining $\bar{\eta}_s$.

To our knowledge, use of Eqs. (4.1) and (4.2) to represent the viscosity of liquid mixtures near the consolute point was first proposed by Debye and coworkers,[32,33] and an early fit of these equations to the viscosity data for 3-methylpentane and nitroethane is, among other possible representations, already found in the original thesis of Tsai.[34]

## V. DYNAMIC-SCALING EXPONENT

The principle of dynamic scaling, originally formulated by Ferrell *et al.*[35] and by Halperin and Hohenberg[36] as a phenomenological postulate and subsequently confirmed by the renormalization-group theory of critical dynamics,[2,37] asserts that at temperatures sufficiently close to $T_c$ and at wave numbers sufficiently large, the decay rate $\Gamma$ of the order-parameter fluctuations should approach a scaled behavior of the form

$$\Gamma = q^z \bar{\Omega}(q\xi) \ . \tag{5.1}$$

In addition it is predicted that the shear viscosity $\eta_s$ will diverge as

$$\eta_s \propto \xi^{x_\eta} \ . \tag{5.2}$$

The dynamic-scaling function $\Omega(y)$ satisfies the boundary conditions

$$\lim_{y \to 0} \bar{\Omega}(y) = C_0 y^{-(1+x_\eta)} \ , \tag{5.3a}$$

$$\lim_{y \to \infty} \bar{\Omega}(y) = C_\infty \ , \tag{5.3b}$$

where $C_0$ and $C_\infty$ are constants. The dynamic critical exponent $z$ and the viscosity exponent $x_\eta$ should satisfy the relation

$$z = 3 + x_\eta \ . \tag{5.4}$$

At a given temperature, i.e., at a given value of $\xi$, $\Gamma$ will vary as $q^2$ for $q\xi << 1$ in agreement with the laws of hydrodynamics, while in the critical regime $q\xi >> 1$, $\Gamma$ will vary as $q^z$.

The exponents $x_\eta$ and $z$ should be the same for all systems belonging to the dynamic universality class of fluid systems. The scaling function $\bar{\Omega}(y)$ should also be universal after being properly normalized as discussed later. A simple analysis of the mode-coupling equations yields as a first approximation[38] $x_\eta = 8/15\pi^2 \simeq 0.054$. More detailed theoretical calculations have produced slightly larger values of this exponent.[37,39] The best theoretical values currently available are

$$x_\eta = 0.065, \ \ z = 3.065, \tag{5.5}$$

obtained both from the renormalization-group theory[37] and the mode-coupling theory of critical dynamics[3] up to second order of a perturbation solution in terms of $\epsilon = 4 - d$, where $d$ is the dimensionality of the system. The scaling function $\bar{\Omega}(y)$ is not known very accurately.

It is now well established[40] that the thermodynamic properties of fluids approach a simple asymptotic power-law behavior with universal exponent values provided that the critical temperature is approached to within $10^{-3}$. Hence, one must expect *a priori* that the validity of the asymptotic dynamic behavior is restricted to a similarly small range in temperature. However, it appears that the restrictions in dealing with dynamic critical phenomena are even more severe. In deriving the asymptotic equations one assumes implicitly that the critical point is approached sufficiently closely so that the singular contribution to the shear viscosity is large compared with the normal shear viscosity $\bar{\eta}_s$.[2,38] In fact, the mode-coupling equations do indicate small deviations from the scaled behavior (5.1) even in a temperature range where the static correlation function assumes its asymptotic critical behavior.[41]

In the case of the viscosity it is usually assumed that the anomaly is multiplicative,[28] i.e., the ratio $\eta_s/\bar{\eta}_s$ is assumed to diverge as $\xi^{x_\eta}$ as given by (5.1). Taking into account the temperature dependence of $\bar{\eta}_s$ we do find a value $x = 0.063$ as quoted in (4.4) in good agreement with the theoretical prediction.

Several investigators have attempted to measure the dynamic-scaling exponent from light-scattering data and a value for $z$ close to 3 is usually found.[20,42–44] However, the literature data do not allow us to discriminate between 3.00 and 3.06. In fact, the value recently reported for 3-methylpentane and nitroethane by Sorensen *et al.*[16] is $z = 2.992 \pm 0.014$ in good agreement with an earlier determination by Chang *et al.*,[20] but in disagreement with the theoretical prediction (5.5). Because of the small difference between 3.00 and 3.06 we do not want to determine the exponent $z$ by fitting the data to (5.1) with an approximate expression for the scaling function $\bar{\Omega}(y)$ of unknown accuracy. Instead we prefer to make an asymptotic analysis following a procedure previously considered by Chang *et al.*[20] and by Chu and Lin.[43]

For this purpose we fit the decay-rate data $\Gamma(T)$ at each temperature to a power law of the form

$$\Gamma(T)\propto q^{z_{\mathrm{eff}}(T)} . \qquad (5.6)$$

From the boundary conditions (5.3) it follows that $z_{\mathrm{eff}}(T)$ should approach the value of 2 away from $T_c$, while it should approach the dynamic-scaling exponent value $z$ in the limit $T\rightarrow T_c$. The values obtained for $z_{\mathrm{eff}}$ as a function of temperature are presented in Fig. 7. The data clearly show the transition from the hydrodynamic regime to the critical regime. In Fig. 8 we show the values obtained for $z_{\mathrm{eff}}$, together with their standard deviations, over the last ten millidegrees from the critical temperature. Extrapolating these data linearly to $T_c$ we obtain as the limiting value

$$z=\lim_{T\rightarrow T_c} z_{\mathrm{eff}}(T)=3.063\pm0.024, \qquad (5.7)$$

where the quoted error represents two standard deviations. This result is in excellent agreement with the theoretical prediction (5.5), as well as with the value $x_\eta=0.063\pm0.001$ deduced from the viscosity data for this mixture, as announced in an earlier letter.[45]

## VI. COMPARISON WITH THE MODE-COUPLING THEORY

In the mode-coupling theory of the critical behavior of the viscosity $\bar\eta_s$ and the decay rate $\Gamma$ a distinction is made between anomalous contributions $\Delta\eta_s$ and $\Delta\Gamma$ due to the long-wavelength fluctuations and so-called bare or background contributions due to the short-wavelength fluctuations[19]

$$\eta_s=\Delta\eta_s+\bar\eta_s , \qquad (6.1a)$$

$$\Gamma=\Delta\Gamma+\bar\Gamma . \qquad (6.1b)$$

Unfortunately no systematic theoretical treatment for dealing with the bare contributions is currently available. In practice, the background contributions are treated empirically by extrapolating experimental information for the transport properties away from the critical region smoothly into the critical region.[33] The contributions from the long-wavelength fluctuations are treated with the methods of generalized hydrodynamics. Retaining only bilinear coupling contributions one obtains[19]

$$\Delta\eta_s(\vec{q})=\frac{1}{(2\pi)^3}\frac{k_BT}{2q^2}\int dk\,k^4\int_0^\pi d\vartheta\,\sin^3\vartheta\int_0^{2\pi} d\phi\,\sin^2\phi\left[\frac{1}{\chi(\vec{k})}-\frac{1}{\chi(\vec{q}-\vec{k})}\right]^2\frac{\chi(\vec{k})\chi(\vec{q}-\vec{k})}{[\Gamma(\vec{k})+\Gamma(\vec{q}-\vec{k})]} , \qquad (6.2)$$

$$\Delta\Gamma(\vec{q})=\frac{k_BT}{(2\pi)^3}q^2\int dk\,k^2\int_0^\pi d\vartheta\,\sin^3\vartheta\int_0^{2\pi} d\phi\,\frac{\chi(\vec{q}-\vec{k})}{\chi(\vec{q})}\left[\frac{1}{k^2\eta_s(\vec{k})+\rho\Gamma(\vec{q}-\vec{k})}\right] , \qquad (6.3)$$

where $\chi(\vec{q})$ is the Fourier transform of the static order-parameter correlation function, $\rho$ is the density and where $\vartheta$ and $\phi$ are the polar and azimuthal angles of $\vec{k}$ in a coordinate system with the polar axis in the direction of $\vec{q}$. Equation (6.2) implies[38] that the viscosity $\Delta\eta$ in the hydrodynamic limit $q\rightarrow0$ will diverge as $x_\eta\ln(Q_0\xi)$ with

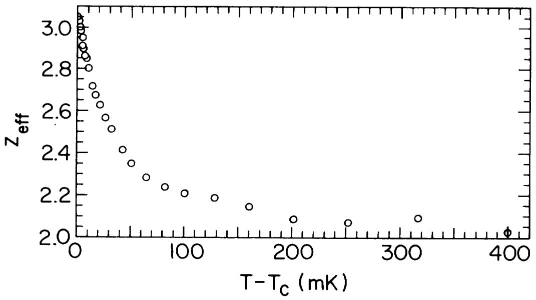

FIG. 7. Values of the effective exponent $z_{\mathrm{eff}}$ as a function of $T-T_c$.

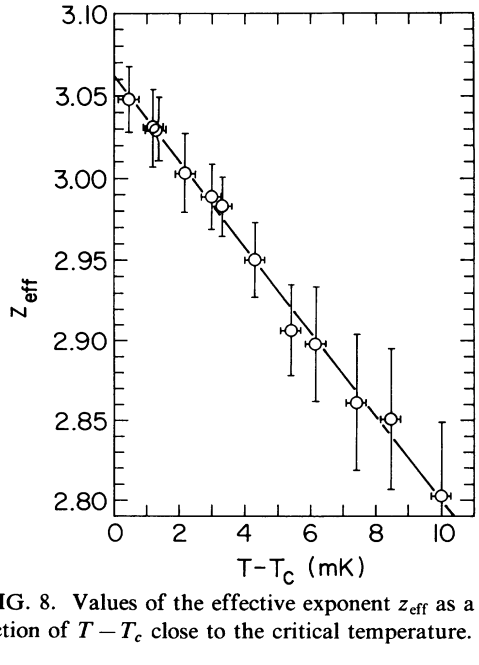

FIG. 8. Values of the effective exponent $z_{\mathrm{eff}}$ as a function of $T-T_c$ close to the critical temperature.

$x_\eta = 8/15\pi^2$. To a good approximation $x_\eta$ may be identified with the critical exponent in the power law (4.1) for the viscosity. However, it is known that vertex corrections lead to a slightly larger value $x_\eta \simeq 0.065$.[2,39,46] It is difficult to evaluate the vertex corrections, but we account for them approximately by multiplying the right-hand side of (6.2) with a factor

$$X_0 = \frac{15\pi^2}{8} x_\eta \; , \tag{6.4}$$

where $x_\eta$ will be taken as $x = 0.063$ as quoted in (4.4). This correction factor ensures that the mode-coupling integrals in this approximation will be consistent with the observed asymptotic critical behavior of the viscosity. The Fourier transform $\chi(\vec{q})$ of the static correlation function can be represented as $(\Delta T^*)^{-\gamma} g(q\xi)$, where $g(q\xi)$ is a correlation scaling function.[4] We thus obtain

$$\Delta\eta_s(q) = \frac{X_0 k_B T}{16\pi^2 q^2} \int dk\, k^4 \int_0^\pi d\vartheta \sin^3\vartheta \left[ \frac{1}{g(k\xi)} - \frac{1}{g(|\vec{q}-\vec{k}|\xi)} \right]^2 \frac{g(k\xi) g(|\vec{q}-\vec{k}|\xi)}{\Gamma(k) + \Gamma(|\vec{q}-\vec{k}|)} \; , \tag{6.5}$$

$$\Delta\Gamma(q) = \frac{k_B T q^2}{4\pi^2} \int dk\, k^2 \int_0^\pi d\vartheta \sin^3\vartheta \frac{g(|\vec{q}-\vec{k}|\xi)}{g(q\xi)} \left[ \frac{1}{k^2 \eta_s(k) + \rho\Gamma(|\vec{q}-\vec{k}|)} \right] , \tag{6.6}$$

where we have integrated over the azimuthal angle $\phi$.

The correlation scaling function $g(x)$ was determined previously from light-scattering-intensity measurements and it was shown that the data could be represented by various approximants.[4] Among those approximants we find the Fisher-Burford approximant[47] the easiest to use in practice and we adopt

$$g(x) = \frac{(1+\psi^2 x^2)^{\eta/2}}{1 + (1+\psi^2\eta/2) x^2} \; , \tag{6.7}$$

with $\eta = 0.024$ and $\psi = 0.014$.[4]

An equation for the background viscosity $\bar{\eta}_s$ of our mixture was presented in Sec. IV. In the case of fluids near the gas-liquid critical point one can calculate the background decay rate $\bar{\Gamma}$ from the thermal conductivity and the specific heat at constant pressure.[33,48] In the case of mixtures near the critical mixing point it is related to the background contribution $\bar{L}$ to the Onsager coefficient associated with the diffusion equation[20]

$$\bar{\Gamma} = \frac{\bar{L}}{\chi(q)} \; . \tag{6.8}$$

This background contribution has often been neglected in the analysis of experimental decay-rate data in binary liquids,[48] but arguments indicating its presence were given by Chang and co-workers[20] and by Oxtoby and Gelbart.[41] Introducing the Ornstein-Zernike approximation for $\chi(q)$, we prefer to write $\bar{\Gamma}$ in a form analogous to a form proposed by Bhattacharjee and coworkers[49]:

$$\bar{\Gamma} = \frac{k_B T q^2}{6\pi\bar{\eta}_s \xi} \left[ \frac{1+q^2\xi^2}{q_C \xi} \right] , \tag{6.9}$$

where, in the small temperature range under consideration, $q_C$ may be treated as a constant with the dimension of a wave number. Since the background contributions to $\Gamma$ turn out to be small, this approximate expression is adequate for our purpose.

In the absence of experimental information for the coefficient $\bar{L}$, and hence, for $q_C$, Oxtoby and Gelbart[41] proposed that it be estimated from the experimental viscosity data by inverting (6.5), given an approximate solution for $\Delta\Gamma$ from (6.6). In our terminology their procedure yields

$$q_C = u Q_0 \; , \tag{6.10}$$

where $Q_0$ is the amplitude of the power law (4.1) for the viscosity. The estimate of Oxtoby and Gelbart implies[41]

$$u \simeq \frac{4}{3C} \simeq 1.5 \; , \tag{6.11}$$

which may be compared with the estimate $u \simeq 4e^{4/3}/3\pi \simeq 1.6$ used by Bhattacharjee *et al.*[49] Using this procedure with $Q_0 = 1.35\ \mathrm{nm}^{-1}$ as quoted in (4.3) we estimated the background contribution $\bar{\Gamma}$ for the data obtained at the three scattering angles. The resulting corrections relative to the experimental decay rate $\Gamma$ are represented by the full curves in Fig. 9. The background contribution is completely negligible for $q\xi \geq 1$. For small $q\xi$ the contribution increases up to 5.1% at

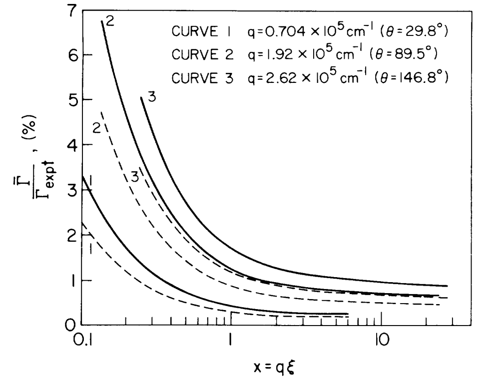

FIG. 9. The relative background contribution $\bar{\Gamma}/\Gamma$ as estimated from the viscosity data. The full curves correspond to the assumption $q_D^{-1}=0$ and the dashed curves to the assumption $q_D^{-1} = 0.14$ nm.

$\theta = 147°$, up to 6.3% at $\theta=90°$ and up to 3.3% at $\theta=30°$.

The mode-coupling integrals are usually solved by an iterative procedure. That is, a zeroth-order solution for the decay rate $\Gamma$ is substituted into (6.5) to yield the viscosity which in turn is substituted into the integral (6.6) for the decay rate. As a suitable zeroth-order solution we propose an equation of the form

$$\Gamma_0=\frac{k_BTq^2}{6\pi\eta_s\xi}\Omega(q\xi)+\bar{\Gamma}\ , \tag{6.12}$$

with

$$\Omega(x)=\Omega_0(x)C(x)(1+p^2x^2)^{x_\eta/2}\ . \tag{6.13}$$

The function $\Omega(x)$ in (6.12) reduces to the Kawasaki function $\Omega_0(x)$, defined by (3.7), when $g(x)$ in (6.6) is approximated by the Ornstein-Zernike form $g(x)=(1+x^2)^{-1}$, when the viscosity $\eta_s(k)$ is treated as a constant independent of $k$ and when the term $\rho\Gamma$ in the intergrand of (6.6) is neglected.[19,41] The function $C(x)$ is a correction factor which accounts for the difference between the Ornstein-Zernike function and the Fisher-Burford approximant for $g(x)$ in evaluating the decay rate from (6.6). We calculated $C(x)$ numerically and found it to be close to unity ranging from 1.003 at $x=0$ to 1.012 at $x=100$ and beyond, in good agreement with the results reported by Swinney and Saleh[50] when adjusted for our exponent value $\eta = 0.024$. This factor, therefore, can be neglected, but in practice we retained the correction. It is our experience that the iteration procedure does not converge rapidly when $\Omega(x)$ in (6.12) is identified with the Kawasaki function $\Omega_0(x)$ and two or three iterations are then needed to obtain results consistent at the 1% level. The reason is that the Kawasaki function implies that $\Gamma$ in the limit $x\to\infty$ will vary as $q^3$ in contrast to the theoretical and observed variation as $q^{3+x_\eta}$. We therefore impose the correct asymptotic behavior by introducing a factor $(1+p^2x^2)^{x_\eta/2}$. In Fig. 10 we compare the experimental decay rates $\Gamma$ with the zeroth-order representation $\Gamma_0$ as defined by (6.12) and (6.13) with $p=\frac{1}{2}$. We conclude that $\Gamma_0$ is a reasonable empirical approximation of the experimental data. With this zeroth-order approximation no successive interactions are needed in solving the mode-coupling integrals.

To investigate whether our decay-rate data are consistent with the experimental viscosity data we substitute the zeroth-order approximation (6.12) into the integral (6.5) for the viscosity taking the hydrodynamic limit $q\to0$:

$$\Delta\eta_s(0)=\frac{X_0k_BT}{120\pi^2}\int dk\,\frac{k^6\xi^4}{\Gamma_0(k)}\left[\frac{2+\psi^2\eta}{1+(1+\psi^2\eta/2)k^2\xi^2}-\frac{\psi^2\eta}{1+\psi^2k^2\xi^2}\right]^2\simeq\frac{X_0k_BT}{30\pi^2}\int dk\,\frac{k^6\xi^4}{(1+k^2\xi^2)^2\Gamma_0(k)}\ . \tag{6.14}$$

We calculated this integral numerically. The differences between the values thus calculated for the viscosity $\eta_s=\Delta\eta_s+\bar{\eta}_s$ and the experimental viscosity data as represented by (4.1) with (4.2) and (4.3) are indicated by the curve labeled $q_D^{-1}=0$ in Fig. 11. It is seen that the integral reproduces the experimental viscosity data within about 2%.

Having verified that our decay-rate data are consistent with the available information for the viscosity, we now substitute $\Gamma_0$ into (6.5) to calculate $\Delta\eta_s(q)$ as a function of $q$ at each temperature and substitute the results into the integral (6.6) for the decay rate $\Delta\Gamma(q)$. The two-dimensional integrals were evaluated numerically with Gaussian quadrature. For completeness we also retained the term $\rho\Gamma(\,|\vec{q}-\vec{k}\,|\,)\simeq\rho\Gamma_0(\,|\vec{q}-\vec{k}\,|\,)$ in the integrand of (6.6), but its effect was found to be small and never contributed more than 1.5% in the calculated decay rate. In Fig. 12 we compare the experimental critical decay rates, defined as

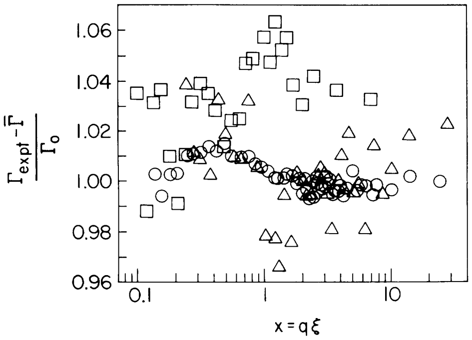

FIG. 10. Comparison between the experimental decay rate $\Gamma$ and the zeroth-order approximation $\Gamma_0$ defined by (6.11) and (6.12). The background contribution $\bar{\Gamma}$ was estimated with the assumption $q_D^{-1}=0$. The symbols are the same as in Fig. 5.

$\Delta\Gamma_{expt}=\Gamma_{expt}-\bar{\Gamma}$, with the values $\Delta\Gamma_{calc}$ thus calculated from the mode-coupling integrals. We first consider the experimental data obtained at a scattering angle of 90° which have the highest precision. Most of the data at 90° are reproduced by the mode-coupling integrals to within 1%. Very close to the critical temperature at $x \simeq 10$ a small increase of a few percent can be noticed. However, in the analysis of the mode-coupling equations we have neglected any frequency dependence of the decay rate which indeed was observed in the last 10 *m* deg.[17] The calculations of Garisto and Kapral[51] and of Lo and Kawasaki[52] indicate that frequency corrections may indeed increase the effective decay rate by a few percent. We conclude that the data at 90° are consistent with the mode-coupling integrals to within 2%. The data obtained at 147° exhibit larger deviations which may be due to the fact that a correction had to be made for scattering from the reflected beam. The data obtained at 30° have a tendency to be slightly larger than those obtained at 90° except far away from the critical temperature. This could in part be due to an error in the determination of the scattering angle which is most serious at this smaller scattering angle as discussed in Sec. II C. On the whole, the data are consistent with the mode-coupling integrals within about 4%.

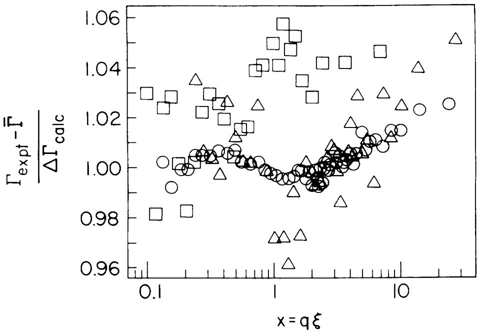

FIG. 12. Comparison between the experimental critical-decay-rate data $\Delta\Gamma_{expt}=\Gamma_{expt}-\bar{\Gamma}$ and the values calculated from the mode-coupling integrals with $q_D^{-1}=0$. The symbols are the same as in Fig. 5.

In Fig. 13 we compare the critical decay rate $\Delta\Gamma_{calc}$ as calculated from the mode-coupling intergrals with the critical decay rate $\Delta\Gamma_0=\Gamma_0-\bar{\Gamma}$ as implied by the proposed zeroth-order solution (6.2). The ratio $\Gamma=\Delta\Gamma_{calc}/\Delta\Gamma_0$ is indeed close to unity. The behavior of this ratio in the limit $x \to 0$ may be affected due to the difficulties in obtaining an accurate estimate of the background contribution $\bar{\Gamma}$.

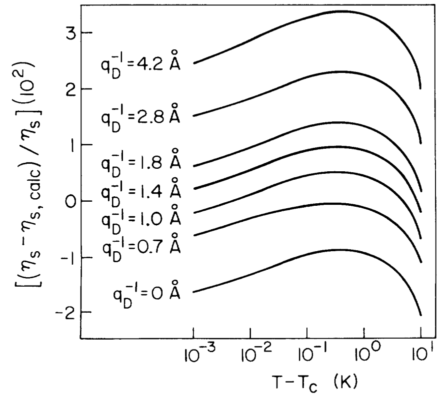

FIG. 11. Comparison between the viscosity calculated from the mode-coupling integral (6.13) and the experimental viscosity data for various values of $q_D^{-1}$.

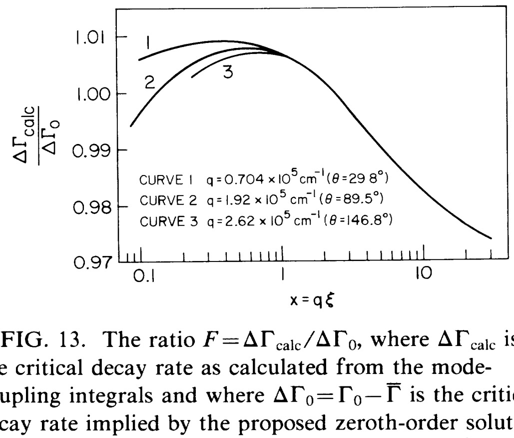

FIG. 13. The ratio $F=\Delta\Gamma_{calc}/\Delta\Gamma_0$, where $\Delta\Gamma_{calc}$ is the critical decay rate as calculated from the mode-coupling integrals and where $\Delta\Gamma_0=\Gamma_0-\bar{\Gamma}$ is the critical decay rate implied by the proposed zeroth-order solution (6.12). In making this plot we have assumed $q_D^{-1}=0$.

The quantities $\Delta\eta_s$ and $\Delta\Gamma$ are supposed to represent the long-wavelength contributions to the viscosity and the decay rate, i.e., contributions from wavelengths larger than the average intermolecular distances. In comparing the data with the theoretical predictions we have, like most other investigators, integrated the mode-coupling integrals over all values of the wave number $k$. This procedure is justified if the contributions to the mode-coupling integrals for large values of $k$ are negligibly small. Bhattacharjee and co-workers recently pointed out that this assumption is, in fact, not valid.[49] For instance, instead of (6.14) where the integral is taken over all wave numbers, they proposed that the viscosity $\Delta\eta_s(0)$ be evaluated from

$$\Delta\eta_s(0)=\frac{X_0 k_B T}{30\pi^2}\int_0^{q_D} dk \frac{k^6\xi^4}{(1+k^2\xi^2)^2\Gamma_0(k)} , \tag{6.15}$$

where $q_D$ is a maximum cutoff wave number. Unfortunately, the value of the cutoff wave number is not known. To investigate which values of $q_D$ would be compatible with the experimental data for 3-methlypentane and nitroethane, we evaluated (6.15) for various values of $q_D$ using for $\Gamma_0(k)$ the zeroth-order representation (6.12) earlier adopted for our experimental decay rate data. The differences between the values thus calculated for the viscosity $\eta_s=\Delta\eta_s+\eta_s$ and the experimental viscosity data as represented by (4.1) are indicated by the various curves in Fig. 11. It is seen that the integral (6.15) reproduces the experimental data within 1% for 0.07 nm $\leq q_D^{-1}\leq$ 0.14 nm. The maximum possible value of $q_D^{-1}$ = 0.14 nm is surprisingly small, and much smaller than the values adopted by Bhattacharjee *et al.* from an analysis of viscosity data of fluids near the gas-liquid critical point. We do not know why this is so. One problem is the lack of a precise theoretical definition of the bare viscosity $\bar{\eta}_s$. Since the viscosity anomaly is very weak, different values adopted for $\bar{\eta}_s$ will seriously affect the amplitude $Q_0$ in the power law (4.1) for the viscosity and, hence, in the value found for $q_D^{-1}$. In any case, we reevaluated the mode-coupling integrals introducing in both (6.5) and (6.6) a cutoff $q_D^{-1}$ = 0.14 nm. Introduction of a cutoff wave number into the mode-coupling integrals also affects the relationship between the parameter $q_C$ in the expression (6.9) for the background decay rate $\bar{\Gamma}$ and the amplitude $Q_0$ of the power law for the viscosity. From the work of Bhattacharjee *et al.*[49] we conclude that (6.10) is to be replaced with

$$\frac{1}{Q_0}=u\left[\frac{1}{q_C}+\frac{1}{2q_D}\right] . \tag{6.16}$$

The relative background decay-rate contributions obtained with $q_D^{-1}$ = 0.14 nm are indicated by the dashed curves in Fig. 9. In Fig. 14 we compare the critical decay rates $\Delta\Gamma$ deduced from the experimental data with the values calculated from the mode-coupling integrals. The data in this figure are to be compared with whose in Fig. 12 for $q_D^{-1}=0$. The pattern is the same as in Fig. 12 and the agreement between experimental and calculated values is comparable. We conclude that the data are consistent with the mode-coupling equations with or without a cutoff parameter, but the procedure is clearly hampered by a lack of knowledge of how to separate the short-wavelength from the long-wavelength contributions.

## VII. DYNAMIC-AMPLITUDE RATIO

The theory of critical dynamics predicts that sufficiently close to the critical point the diffusion coefficient $D$ should satisfy a Stokes-Einstein relation of the form

$$D=\frac{Rk_BT}{6\pi\eta_s\xi} , \tag{7.1}$$

where $R$ is a universal constant.[2] This diffusion coefficient is related to the critical part of the decay rate by

$$D=\lim_{q\to 0}\Delta\Gamma(q)/q^2 . \tag{7.2}$$

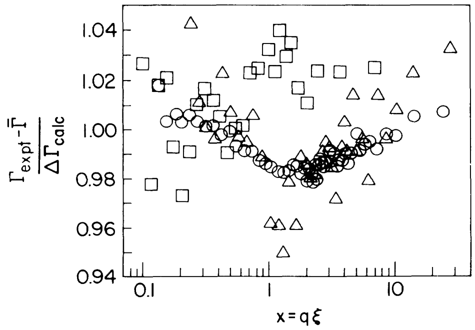

FIG. 14. Comparison between the experimental critical-decay-rate data $\Delta\Gamma_{\text{expt}}=\Gamma_{\text{expt}}-\bar{\Gamma}$ and the values calculated from the mode-coupling integrals with $q_D^{-1}$ = 0.14 nm. The symbols are the same as in Fig. 5.

The mode-coupling integrals to the approximation considered here imply a value of $R$ close to unity as further discussed below. Siggia and co-workers evaluated $R$ to first order in $\epsilon=4-d$ from a renormalization-group treatment of critical dynamics; they obtained two estimates $R=$ 0.79 and 1.20, and judged the latter value to be more reliable.[37]

Any experimental value of $R$ is affected by the combined errors in $\xi$, $\eta_s$, and $D$, or $\Delta\Gamma$, and it appears to be difficult to determine $R$ accurately. Experimental arguments in favor of a value $R\simeq$ 1.20 have been reported by Chen *et al.*[53] for the mixture *n*-hexane and nitrobenzene, and by Sorensen *et al.*,[16] for the same system considered in this paper. The result has been interpreted[53] as implying $R/6\pi\simeq1/5\pi$, which corresponds to Stokes's law for a spherical droplet moving in a medium with the same viscosity as that of the liquid in the droplet.[54] It has led Beysens *et al.*[55] to assume $R/6\pi=1/5\pi$ and then use (7.1) and (7.2) for determining the correlation length $\xi$ from experimental decay-rate data[55]. On the other hand, we deduced[27] from our light-scattering data for 3-methylpentane and nitroethane $R\simeq1.02$, a value confirmed by Güttinger and Cannell from light-scattering data for xenon near the gas-liquid critical point.[56] Subsequently, Beysens[57] has reported a revised value $R\simeq1.16$. Because of the controversies surrounding the experimental determination of the dynamic-amplitude ratio $R$ we discuss the issue here in some further detail.

In our previous approach we introduced a quantity $R(x)$ defined as[27]

$$R(x)\equiv\frac{\Delta\Gamma}{q^2\Omega_0(x)}\frac{6\pi\eta_s\xi}{k_BT}\ , \tag{7.3}$$

where $\Omega_0(x)$ is again the Kawasaki function defined by (3.7). Since $\lim_{x\to0}\Omega_0(x)=1$, we identified $R$ with

$$R=\lim_{x\to0}R(x)\ . \tag{7.4}$$

The values deduced for $R(x)$ from the experimental data are plotted in Fig. 15 over the range $0.1\le x\le0.7$. We note that in this range $R(x)$ is independent of $x$ within the experimental accuracy and we conclude $R=1.020\pm0.028$, where the quoted error represents two standard deviations. In deducing $\Delta\Gamma$ from the decay-rate we estimated the background contribution $\overline{\Gamma}$ from (6.9) by the procedure discussed in Sect. VI and assuming $q_D^{-1}=0$.

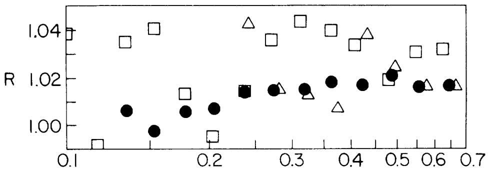

FIG. 15. The coefficient $R(x)$ as a function of $x$ for small values of $x=q\xi$, deduced from the light-scattering measurements at 30° (squares), 90° (circles), and 147° (triangles). The background decay rate $\overline{\Gamma}$ was estimated with the assumption $q_D^{-1}=0$.

For completeness, we repeated the analysis by estimating $\overline{\Gamma}$ with the assumption $q_D^{-1}=0.14$ nm. The results thus obtained are shown in Fig. 16 and we arrive at the average value $R=1.029\pm0.026$. Allowing for a 2% error in the correlation length and a 1.5% error in the viscosity data,[27] we conclude

$$R=1.03\pm0.06\ . \tag{7.5}$$

In order to interpret this result we note that the decay rate $\Gamma$ exhibits a strongly singular behavior and the viscosity $\eta_s$ a weakly singular behavior. Hence, in taking the limit $q\to0$ we can make a distinction between a regime of temperatures where $\Delta\eta_s<<\overline{\eta}_s$ and a fully asymptotic regime where $\Delta\eta_s>>\overline{\eta}_s$. The value for $R$ quoted above was determined in a regime where $\Delta\eta_s<<\overline{\eta}_s$. The value calculated theoretically by Siggia *et al.*[37] corresponds to the fully asymptotic regime. The values of $R$ will not be necessarily the same in the two regimes.

In the previous section we concluded that the experimental decay-rate data are consistent with the mode-coupling integral (6.6). This integral implies a value for $R$ close to unity at all temperatures. When $\Delta\eta_s<<\overline{\eta}_s$, the viscosity $\eta_s$ in

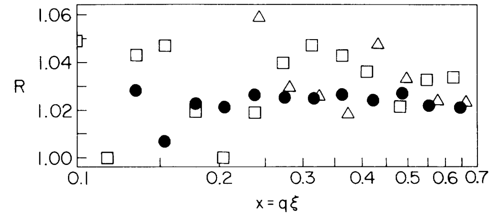

FIG. 16. The coefficient $R(x)$ as a function of $x$ for small values of $x=q\xi$, deduced from the light-scattering measurements at 30° (squares), 90° (circles), and 147° (triangles). The background decay rate $\overline{\Gamma}$ was estimated with the assumption $q_D^{-1}=0.14$ nm.

the integrand of (6.6) is essentially independent of $k$, while the term $\rho\Gamma$ is negligibly small, and we recover the zeroth-order solution (6.12) with $R=1$. In the fully asymptotic regime the viscosity will satisfy a scaling law of the form

$$\Delta\eta_s(q) \simeq \eta_s(q) \simeq \eta_s(0)/(1+a^2q^2\xi^2)^{x_\eta}/2 \,, \tag{7.6}$$

so that $\lim_{q\xi\to\infty}\eta_s(q)=(Q_0/aq)^{x_\eta}$, where $a$ is a constant.[39,58] It thus follows from (6.6), that in the fully asymptotic regime,

$$R \simeq \frac{2}{\pi}\int_0^\infty dx \frac{(1+a^2x^2)^{x_\eta/2}}{1+x^2}$$
$$= \frac{a^{x_\eta}}{\pi} \frac{\Gamma\left[\frac{1}{2}-\frac{x_\eta}{2}\right]\Gamma(\frac{1}{2})}{\Gamma\left[1-\frac{x_\eta}{2}\right]}$$
$$\times F\left[-\frac{x_\eta}{2},\frac{1}{2}-\frac{x_\eta}{2};1-\frac{x_\eta}{2};\frac{a^2-1}{a^2}\right], \tag{7.7}$$

where $F$ is an hypergeometric function.[59,60] An approximate analysis of the nonlocal viscosity by Perl and Ferrell[58] suggest $a \simeq 0.5$, so that (7.7) implies $R \simeq 1.02$. To the extent that our data are consistent with (6.6) we recover a value of $R$ close to unity at all intermediate temperatures of our experimental data. However, we cannot justifiably extrapolate the mode-coupling integrals (6.5) and (6.6) to the fully asymptotic regime where $\Delta\eta_s/\bar{\eta}_s >> 1$, because of the approximate nature of the treatment of the vertex corrections and because of the neglect of any frequency dependence, the importance of which has been emphasized by Ferrell *et al.*[58,61] Our data points closest to the critical temperature ($\Delta T^* \simeq 10^{-6}$) correspond to $x=7$ at $\theta=30°$ and $x=28$ at $\theta=147°$ as can be seen from the information in Tables I and III. An extrapolation of the power law (4.1) for the viscosity suggests that even at $\Delta T^* \simeq 10^{-8}$ or $10^{-9}$, the background viscosity $\bar{n}_s$ is still of the same order of magnitude as $\Delta\eta_s$. Hence, we are unable to probe experimentally the fully asymptotic regime where $x << 1$ and $\Delta\eta_s/\bar{\eta} >> 1$.

## VIII. CONCLUSIONS

We have determined the decay rate $\Gamma$ of the order-parameter fluctuations in the binary liquid 3-methylpentane and nitroethane near the critical mixing point as a function of temperature and wave number. From the data we conclude that the decay rate varies at the critical temperature as $\Gamma \propto q^z$ with $z=3.06 \pm 0.02$ in good agreement with the theoretical predictions. The observed dependence of the decay rate on temperature and wave number is consistent with the predictions of the mode-coupling theory of critical dynamics, but a complication arises due to the lack of detailed theoretical predictions for the short-wavelength contributions to the transport coefficients. A dynamic-amplitude ratio $R$ may be defined as $\lim_{q\to 0} 6\pi\eta_s\xi\Delta\Gamma/q^2k_BT$. From the data we conclude $R=1.03 \pm 0.06$ at temperatures where $\Delta\eta_s/\bar{\eta}_s << 1$, but we are unable to determine $R$ in the fully asymptotic regime where $\Delta\eta_s/\bar{\eta} >> 1$.

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