Autocorrelation spectroscopy studies of single and multiple scattered light from a critical fluid mixture*

C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan
Department of Physics and Astrophysics, University of Colorado, Boulder, Colorado 80309
(Received 9 February 1977)

We describe photon autocorrelation studies of both the depolarized and polarized components of light scattered from the critical binary mixture methanol-cyclohexane, carried out to $k\xi \cong 80$, in an effort to differentiate between the Rayleigh linewidth predictions of the mode theories and the dynamic droplet model, and to assess the validity of our treatment of the autocorrelation function of light which undergoes double scattering from a critical fluid. (Here k is the scattering wave number and ξ the Orstein-Zernike correlation length.) We achieved sample temperature control of ± 15 μ°C for periods of 24 hours and reduced sample temperature gradients to $\lesssim \pm 40$ μ°C/cm. We developed a technique for measuring the effects of laser heating upon the temperature of the fluid within the scattering volume. These latter measurements enabled us to determine the critical temperature of our system to an accuracy of ± 60 μ°C. We find agreement between the predictions of our theory of the double-scattered autocorrelation function and the measured depolarized intensity autocorrelation function. The double-scattered contribution becomes significant for the methanol-cyclohexane system at $k\xi \cong 0.6$, and higher than second-order scattering becomes important for $k\xi \gtrsim 1$. Despite the large multiple-scattered component in the light scattered from the fluid in the nonhydrodynamic regime, the Rayleigh linewidth is affected only slightly. We show how to estimate the amount of multiple scattered light from depolarization-ratio measurements, and make qualitative assessments of the modifications of the Rayleigh linewidth due to higher-order scattering. Despite the small effect of multiple scattering upon the Rayleigh linewidth at large values of $k\xi$, the uncertainty introduced is large enough to obscure the differences between the fits of the mode theories and the dynamic droplet model to our experimental results.

I. INTRODUCTION

Light-beating spectroscopy as applied to critical fluid systems has proved to be a powerful technique for probing the dynamical response of such systems.[1] In particular, measurements of the Rayleigh linewidth of light scattered by a fluid near its critical point provide data from which the dynamical behavior of the order parameter fluctuations can be inferred. In recent years, several theories have been developed to predict this linewidth, namely, the mode-mode,[2,3] decoupled mode,[4] and dynamic droplet[5] theories of critical fluid light scattering. Each of these theories successfully describes the Rayleigh linewidth data for the region $k\xi \lesssim 10$, where k is the scattering wave number and ξ is the Ornstein-Zernike correlation length. However, the three theoretical models predict slightly different results in the nonhydrodynamic regime, where $k\xi \gtrsim 1$, with the discrepancies increasing as $k\xi$ increases.

To date, the Rayleigh linewidth data for critical fluid systems have been limited to the region $k\xi \lesssim 20$, and due to the large experimental errors, it has not been possible to determine which of the theories best describes the data in the nonhydrodynamic regime.[1] It is clearly important to take improved Rayleigh linewidth data in the regime of large $k\xi$ values in order to provide experimental results which can be used to test the available theories. However, there are very serious difficulties associated with any attempt to extract Rayleigh linewidth data which can be used for this purpose. In particular, we shall consider two experimental problems that are imposed by the requirements for meaningful Rayleigh linewidth measurements very near the critical point of a fluid system, and a theoretical problem, multiple scattering, which has been ignored in previous measurements.

First, the performance of a Rayleigh linewidth measurement on a critical fluid near its transition temperature requires that we control our sample temperature within very narrow limits, and that we are able to measure our temperature precisely. In general, temperature control of *better* than ± 0.1 m°C is required. In addition to the necessity for state-of-the-art temperature *control*, there is a second major experimental difficulty that has been given little attention, namely the problem of precisely determining the temperature of the fluid within the scattering volume. This remaining unknown is due to the effect of local heating of the fluid due to the incident laser beam. Despite the low incident power ($\cong 1$ mW) used in a typical measurement of this type, it is *essential* that the possible effects of laser heating be known.

We must also address the questions of the possible modifications of the observed photocount autocorrelation function by double- and higher-order-

scattered components, and of the size of such components in the scattered light. Although previous light-scattering measurements on critical fluids have attempted to detect the effect of multiple scattering in the Rayleigh linewidth,[6,7] with negative results, there have not even been satisfactory qualitative explanations for the apparent absence of such effects. Recently, we presented a technique by which the decay time of the correlation function of light which is double-scattered from a critical fluid system can be calculated.[8,9] We showed that in the far nonhydrodynamic regime for a critical fluid, the single- and double-scattered Rayleigh linewidths are nearly equal, and thus provided the first explanation of the lack of an observable effect due to double scattering in earlier work.

There has been considerable theoretical interest in the problem of multiple scattering.[10-13] This work has been concerned with the intensity of the multiple-scattered component. For our purposes here, the major result of this work has been to show that the depolarized-scattered light is due mostly to multiple scattering from *independent* scattering events. Very recently, Beysens and Zalczer[14] have used this result to calculate the double-scattered spectrum in a critical fluid and have compared their calculation successfully to experiment for a particular scattering geometry.

The purpose of this paper is to report the results of Rayleigh scattering measurements on a critical mixture of the binary fluid system methanol-cyclohexane which we have carried out to $k\xi \cong 80$, in an attempt to differentiate between the competing theoretical descriptions. To perform such measurements, we developed a two-stage temperature control system and sample configuration with which we have achieved temperature control of $\pm 15\ \mu°C$ for periods of 24 hours. Thermal gradients were measured and shown to be less than $\pm 40\ \mu°C/cm$. As a result, the critical temperature T_c could be determined to a precision of $\pm 60\ \mu°C$. A technique has been developed to measure the temperature shifts of the fluid within the scattering volume due to laser heating, and to incorporate our knowledge of such laser heating effects into the determination of $T - T_c$. Thus we were able to extend our measurements to $T - T_c$ values as small as $155 \pm 70\ \mu°C$ $[(T - T_c)/T_c = t \cong 5 \times 10^{-7}]$.

In an effort to use our theory of the double-scattered correlation function to infer the true single-scattered Rayleigh linewidth, we studied the intensity autocorrelation function of the depolarized scattered light as well as that of the total-scattered light field. We establish the validity of our theoretical results by demonstrating the agreement between the double scattering theory and the experimental depolarized scattering results. We use an effective second-order theory, with which the relative magnitudes of the double- and single-scattered intensities can be inferred from measured values of the depolarization ratio. We show that double scattering becomes significant for our system at $k_0\xi \cong 0.6$, and that an analysis based upon single plus double scattering is valid to $k_0\xi \cong 1$. However, for $k_0\xi > 1$ higher-order scattering effects must be considered. Thus, we show that for our system, which is typical of critical fluids studied previously, the scattered light, even for $k\xi$ values around unity, contains a significant multiple-scattered component, which increases to major proportions as $k\xi$ increases. We make *qualitative* arguments, based upon our knowledge of the double-scattered correlation function, to estimate the effects of multiple scattering upon the Rayleigh linewidth. We conclude that, while the effects are small, they introduce enough uncertainty to militate against a definitive choice being made among the Rayleigh linewidth descriptions provided by the mode theories and the dynamic droplet model.

II. REVIEW OF THEORY

A. Critical fluid light-scattering theories

The critical part of the single-scattered Rayleigh linewidth predicted by the Kawasaki mode-mode theory is given by[2]

$$\Gamma_c = \frac{k_B T}{6\pi\eta_s \xi^3} K_0(k\xi) H(k\xi), \tag{1}$$

where k_B is Boltzmann's constant, T is the temperature, η_s is the shear viscosity,

$$K_0(x) = \tfrac{3}{4}[1 + x^2 + (x^3 - x^{-1})]\tan^{-1}x, \tag{2}$$

and

$$H(x) = R(x)V(x). \tag{3}$$

$R(x)$ represents viscosity corrections and $V(x)$ is the vertex correction. This expression is rather complex and many of the terms can only be evaluated numerically. Therefore, we concern ourselves only with the predictions of the mode-mode theory and plot the results in Fig. 1 as curve *a*.

The other mode theory is the decoupled-mode theory of Perl and Ferrell.[4] They find a form very similar to that given by the mode-mode theory,

$$\Gamma_c = \frac{k_B T}{6\pi\eta_{\text{eff}} \xi^3} K_0(k\xi). \tag{4}$$

Here $K_0(x)$ has the same form as Eq. (2) and η_{eff} is a complex function of the viscosity and $k\xi$ (see Swinney and Henry[1]). We plot the decoupled-mode

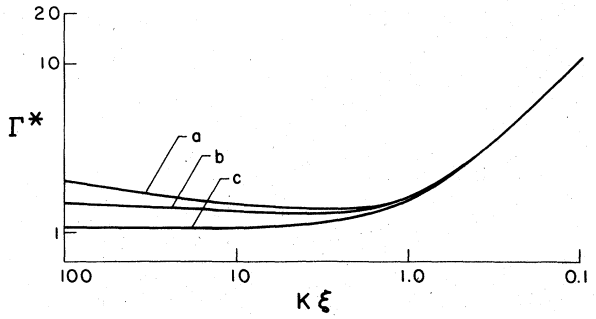

FIG. 1. Scaled linewidth versus k for the mode-mode theory, curve a; the decoupled-mode theory, curve b; and the dynamic droplet model, curve c.

theory results in Fig. 1 as curve b.

The dynamic droplet model[5] predicts a form,

$$\Gamma_c = \gamma^{-1} \frac{k_B T}{6\pi\eta_b \xi} k^3 (1 + k^2\xi^2)^{1/2}, \tag{5}$$

where η_b is the background shear viscosity. The factor γ^{-1} is of order unity and depends on the fitting procedure used to determine the decay rate of the predicted nonexponential light-scattered correlation function. If Γ_c is represented by the first cumulant of the decay, $\gamma^{-1} = (2/\pi)^{1/2}$. We have found, and recent work by others has also shown,[15] that the correlation function is exponential, contrary to the prediction of the droplet model. Thus, the droplet model fails in this area and must be improved. Nevertheless, because of its experimentally correct linewidth prediction [Eq. (5)] and its physical simplicity, the model is still quite viable. In any event, the meaning of the factor γ must be left inexact until a successful exponential droplet model is formulated. We shall use γ as a variable factor in fitting the data, and may consider the product $\gamma\eta_b$ as some sort of noncritical effective viscosity, similar to that in the decoupled mode theory result, Eq. (4).

We plot the droplet model linewidth in Fig. 1 as curve c with $\gamma = 0.997$ to normalize it to the mode theory results. All three theoretical results in Fig. 1 are plotted as the scaled linewidth[1] defined as

$$\Gamma^* = \frac{6\pi\eta_s}{k_B T} \frac{\Gamma_c}{k^3}. \tag{6}$$

Using this form, the data from different fluids should all lie on the same curve. Inspection of Fig. 1 shows that the results of the three theories begin to deviate significantly for $k\xi > 1$. Swinney and Henry[1] have indicated that the mode-mode prediction for $k\xi > 10$ may be too large (see Theil *et al.*,[6] also Lai and Chen[16]) but the data are scarce in this region. We also point out that if in the droplet model a critical viscosity having a logarithmic divergence were used instead of the background viscosity, the results of the droplet model and the decoupled-mode theory would be nearly identical for all $k\xi$.[8]

B. Double scattering from critical fluid systems

We have successfully predicted the correlation function and decay time of light double-scattered from systems of noninteracting particles undergoing Brownian diffusion.[17] The results of our theoretical treatment indicated that the double-scattering process could be viewed as two independent single-scattering processes in succession.

We applied these results to a critical fluid system to predict the double-scattered spectrum and intensity.[9] We found that in the region $k_0\xi \gtrsim 8$ the single- and double-scattered correlation times (determined from the first cumulant[18] of the intensity autocorrelation function) were nearly equal, especially at a scattering angle of 90°. This result provided the first explanation of why double-scattering effects had never been detected in dynamical light-scattering experiments on critical fluid systems.[6,7]

Any problem concerning multiple scattering is dependent upon the geometry of the scattering volume. In the above work, the results were found for a spherical scattering geometry in which the second scatterers are distributed in spherical symmetry about the first. This geometry can be satisfied by observing the scattered light from a region in a rather wide incident beam. If the incident beam is narrowed, the spherical scattering geometry assumption breaks down and one observes deviations of as much as 20% in the correlation time from the spherical geometry calculation.[17] However, we have also found that this geometry can be satisfied using a narrow incident beam and a wide acceptance region about that beam for the photodetector.[8] Thus, we feel that the spherical scattering geometry may be the most general scattering geometry, and our results pertain to this geometry.

We now wish to present further results of our double-scattering calculations for critical fluids. For further discussion of the procedures used to determine these results, we refer the reader to our other work.[9]

We have calculated the double-scattered correlation function as a function of time for both the polarized and depolarized components of the double-scattered light. We assume the usual scattering geometry where the incident polarization is perpendicular to the scattering plane. Then, "polarized" refers to that light scattered with polarization parallel to the incident polarization, and

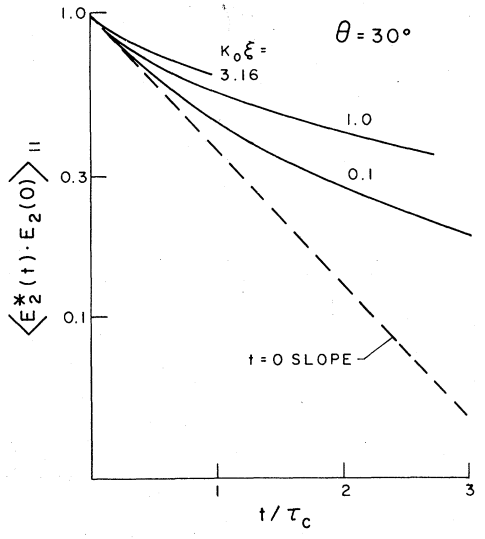

FIG. 2. *Polarized* correlation function of light double scattered from a critical fluid system. $\theta_{scat} = 30°$.

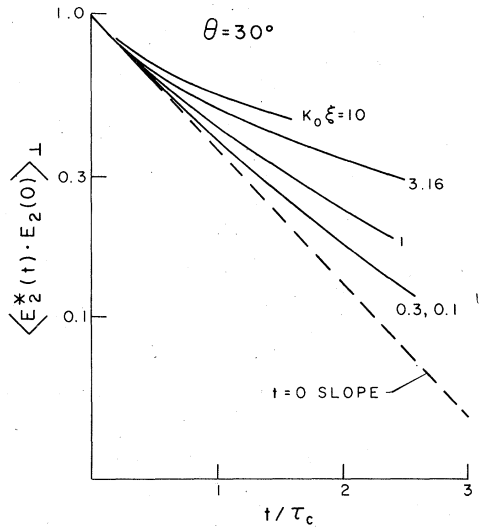

FIG. 4. *Depolarized* correlation function of light double scattered from a critical fluid system. $\theta_{scat} = 30°$.

"depolarized" refers to that light scattered with polarization perpendicular to the incident polarization. We present the polarized result for scattering angles of 30° and 90° in Figs. 2 and 3, respectively, and the depolarized result for scattering angles of 30° and 90° in Figs. 4 and 5, respectively. The figures are parametrized on $k_0\xi$, and each $k_0\xi$ curve is normalized to the same $t=0$ slope or first cumulant. We stress that k_0 is the *incident wave vector*. Usually such results are plotted versus $k\xi$ where k is the *scattering wave vector*. We deviate from this practice for double-scattering because a change in scattering angle is not equivalent to a change in wavelength in the double-scattered spectrum. The correlation functions for both the polarized and depolarized components at a scattering angle of 90°, while not exponential, are well characterized by the first cumulant. However, at 30° for each polarization, the first cumulant becomes progressively insufficient to describe the correlation function as $k_0\xi$ increases, the spectra for large $k_0\xi$ being very nonexponential.

This behavior will lead to difficulties in analyzing our data in terms of the theory. We have seen for noninteracting Brownian particle systems that the

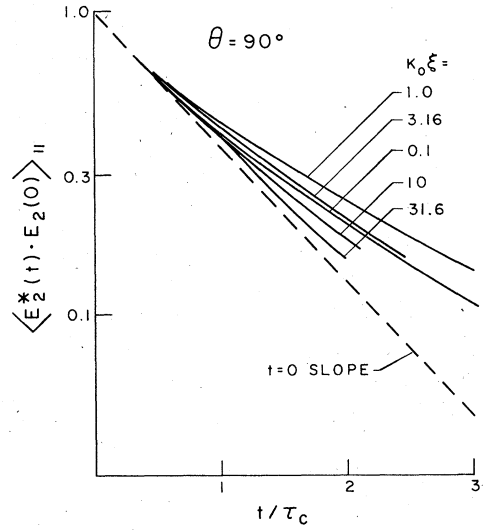

FIG. 3. *Polarized* correlation function of light double scattered from a critical fluid system. $\theta_{scat} = 90°$.

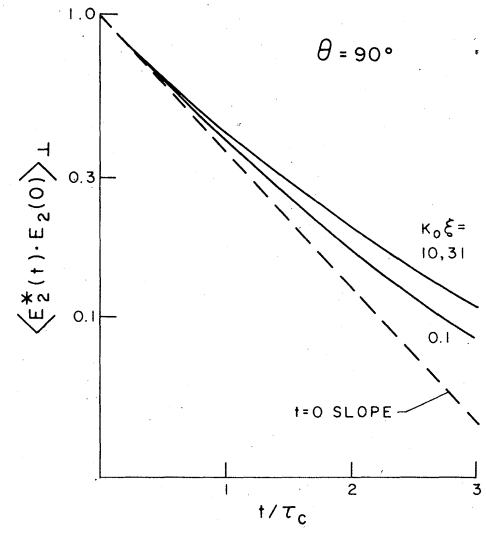

FIG. 5. *Depolarized* correlation function of light double scattered from a critical fluid system. $\theta_{scat} = 90°$.

first cumulant could be extracted from the data, and successfully compared to the first-cumulant calculations of our double-scattering theory. This was possible because the spectra were only slightly nonexponential ($K_2/K_1^2 \sim 0.07$ where K_1 and K_2 are the first and second cumulant[18]). Thus, we might expect the same sort of results when dealing with critical fluid double-scattering at a scattering angle of 90°, for all $k_0\xi$, and at a scattering angle of 30° for $k_0\xi < 1$. However, at $\theta = 30°$ and $k_0\xi > 1$ we probably will not be successful in extracting the first cumulant from the data due to the excessive nonexponentiality, and so the decay time will appear longer (thus, the linewidth will appear shorter) than the theoretically determined first-cumulant prediction.

Since we are concerned with the effects of multiple scattering on the correlation time of the scattered light, we need a parameter other than the first cumulant with which to characterize the decay rate of the double-scattered correlation function. We shall make the choice of defining the correlation time as that time at which the correlation function is $1/e$ times its $t = 0$ value. This is reasonable, since for an exponential decay this is the decay time. Furthermore, such a definition will reflect the apparent lengthening of the correlation time due to the nonexponentiality. We emphasize that this is only a means of describing the general behavior of the correlation time that might be observed in a light-scattering experiment.

We may now repeat our comparison of the double- and single-scattered correlation times while recognizing that the nonexponentiality of the double-scattered correlation functions may make the correlation time appear longer than indicated by the first cumulant. In Figs. 6 and 7 we compare the

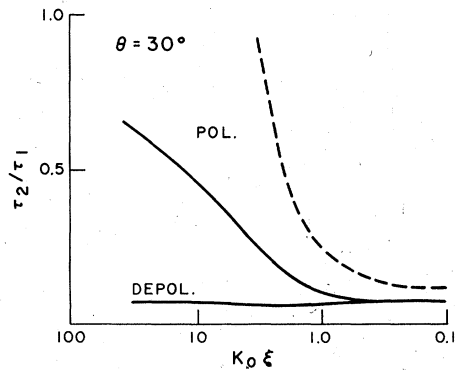

FIG. 6. Ratio of the double- to single-scattered correlation times of light scattered from a critical fluid system. Solid lines are for the first cumulant values, dashed line is for the polarized $1/e$ value. $\theta_{scat} = 30°$.

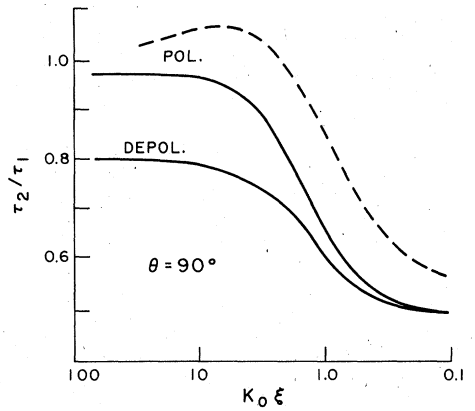

FIG. 7. Ratio of the double- to single-scattered correlation times of light scattered from a critical fluid system. Solid lines are for the first cumulant values, dashed line is for the polarized $1/e$ value. $\theta_{scat} = 90°$.

single- and double-scattered correlation times for scattering angles of 30° and 90°, respectively. To do this, we plot the ratio τ_2/τ_1 versus $k_0\xi$. The solid line represents the first-cumulant value for τ_2 as was presented before.[9] The dashed line represents the $1/e$ correlation time for the polarized component of the double-scattered light. This component is always much more intense than the double-scattered depolarized component (see Fig. 8). We see that by taking into account the apparent lengthening of the correlation time due to the nonexponentiality, we strengthen our former conclusion that double scattering which is dominated by the polarized component should have little observable effect on the single-scattered spectrum in the $k_0\xi \gtrsim 5$ region.[9] This is evinced by Figs. 6 and 7 where we see that the ratio τ_2/τ_1 for the very intense polarized component of the double-scattered light is qualitatively equal to unity.

A measure of the total amount of double scattering from an isotropic system can be obtained from a measurement of the *total* depolarized to polarized light-scattering intensities, the depolarization ratio R. For instance, if there is only single scattering, all the scattered light will be polarized and $R = 0$. As higher-order scattering increases, R increases. However, as we have shown,[9] an accurate estimate of the amount of higher-order scattering can only be obtained by interpreting the depolarization ratio properly. We write the depolarization ratio to *second*-order as

$$R = \frac{I_\perp}{I_\parallel} \simeq \frac{I_{2\perp}}{I_1 + I_{2\parallel}}, \tag{7}$$

where $\perp$ and $\parallel$ imply polarized and depolarized, respectively, and $I_{1\perp} = 0$.

We wish to find the ratio I_2/I_1, where $I_2 = I_{2\perp} + I_{2\parallel}$.

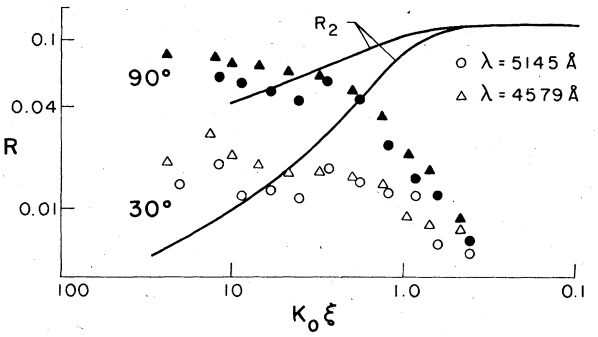

FIG. 8. Solid lines are the theoretically determined values of $R_2 = I_{2\perp}/I_{2\parallel}$. Also plotted are the experimental values of the depolarization ratio R found for our fluid system in the wide-beam geometry.

To do so we use our double-scattering theory to evaluate the relative intensities of the depolarized to polarized double-scattered light. We call this relative intensity $R_2 = I_{2\perp}/I_{2\parallel}$ and plot our theoretical results as the solid curves in Fig. 8. We may show that

$$\frac{I_2}{I_1} = \frac{R(1+R_2)}{R_2 - R} . \tag{8}$$

Thus, we can use our depolarization-ratio measurements along with Fig. 8 and Eq. (8) to evaluate the ratio of the double- to single-scattered light intensities when higher-order scattering is small. This condition is met when $I_2/I_1 \ll 1$ or, equivalently, when $R \ll R_2$.

C. Multiple scattering

The extension of our double-scattering theory to higher orders is quite straightforward. We use our assumption of independent scattering events described by the single-scattering process and apply this to n scattering events. The nth-order scattered field is then found by averaging over the $n-1$ relative positions of the n scattering regions. This averaging procedure appears to be prohibitively difficult for $n \geq 3$, however; so it has not been performed.

We may, however, approach the problem on a nonanalytic level and come up with some qualitative predictions concerning higher-order scattered light. We have shown[17] that for pointlike particles undergoing Brownian diffusion the double-scattered spectrum was independent of the scattering angle and had a correlation time equal to the single-scattered correlation time at 180° scattering angle. This is equal to one-half the single-scattered correlation time at 90°. We may visualize that each scattering event might have a scattering angle anywhere from 0–180°. For pointlike particles the scattering is isotropic. Thus, there is no preferred direction, and we might expect an average scattering angle of 90° for each event. On the average each event contributes a correlation time equal to that for single-scattering at 90°. Two such events would give half this time; the spectrum that is indeed predicted and observed. This argument is easily generalized to n scattering events to find that the nth-order correlation time will be $\tau_n = \tau_1(90°)/n$. This argument has been successfully applied to scattering from Brownian motion systems.[8]

We now apply this reasoning to scattering from a critical fluid system. Since each order of scattered light will have a correlation time smaller than the preceding order, the multiple-scattered light, which is the sum of all orders for which $n \geq 2$, will have a correlation time smaller than the double-scattered component alone. Equivalently, the linewidth will be greater.

The extent to which each scattering event reduces the correlation time is indicated by the extent of reduction from single- to double-scattering. Thus, as seen in Figs. 6 and 7 a larger reduction in the correlation time is experienced for small $k_0\xi$ than for large $k_0\xi$. In the region $k_0\xi \gtrsim 8$, the reduction is relatively small (~4–40%). Thus, in this region the reduction in the correlation time from n- to $(n+1)$-order scattering can also be expected to be small. The multiple-scattered field will then have a correlation time smaller than that of the double-scattered field but probably not much smaller in this region of $k_0\xi$.

The method for determining the ratio I_2/I_1 described at the end of the last section can be extended to higher orders of scattering if the ratios $R_n = I_{n\perp}/I_{n\parallel}$ for all n are known. Such a technique uses the assumption that the scattering process is a random process described by the Poisson distribution and has already been applied to systems of Brownian particle light scatterers.[8] However calculation of R_n for $n \geq 3$ for critical fluid systems appears to be quite difficult and has not been done. We may, however, use the second-order theory above as an indication of when higher-order-scattering intensities are large, by observing when the condition $I_2/I_1 \ll 1$ breaks down. Thus, as $I_2 \to I_1$, or equivalently $R \to R_2$, higher-order intensities must also be growing large. We shall use this breakdown of Eq. (8) to indicate when we must qualitatively consider higher-order scattering.

III. EXPERIMENTAL

A. Binary fluid mixture

We use the binary fluid mixture methanol and cyclohexane. A binary fluid mixture is of the same

universality class as a simple fluid system,[19] and therefore will give results of a general nature for this class of systems. This particular system was chosen because of its convenient critical temperature, 45 °C, the commercial availability of the fluids in high purity, their nearly equal mass densities which ensures small gravity effects and because we had used this system in other critical phenomena studies in our laboratory.[20]

The difference in the indices of refraction of these two fluids is $\Delta n = 0.0978$. This is a measure of the light-scattering cross section of the system. Other systems with a better index match are available and would be preferable in order to reduce multiple-scattering effects. However, since we wished to test our double-scattering theory, a fluid system which would double scatter somewhat was desirable.

Freshly opened bottles of Fisher spectrographic grade reagents were mixed under a dry nitrogen atmosphere. The resulting concentration was 29.03% by weight methanol, in good agreement with the critical concentration of 29.0%.[20,21] The mixture was doubly sealed in a glass tube which was then placed in our temperature control apparatus.

As seen by Eqs. (1), (4), and (5), a knowledge of the shear viscosity of the fluid system is necessary for analysis of the Rayleigh linewidth data. We have measured the shear viscosity of our fluid system at the critical concentration at various temperatures above T_c in a Poiseuille flow viscometer. We have determined both the background viscosity, necessary for the dynamic droplet model, and the full macroscopic critical viscosity, necessary for the mode theories, from our data. The background viscosity obeys the form

$$\log_{10}\eta_b = A + B/T\,, \tag{9}$$

where experimentally $A = -2.667$ and $B = 775$ °K. The full macroscopic viscosity obeys the form

$$\eta_s = \eta_b - 0.0306(2.74 + \nu \ln t)\,. \tag{10}$$

B. Temperature control and laser heating

Our temperature control cell consisted of four coaxial cylindrical "cans" in vacuum. The temperature control system consisted of a two-stage device. The first stage controlled temperature to ±5 m°C, creating an environment for the inner can which holds the fluid sample. The second stage controlled the temperature of this inner can. We achieved a temperature control of ±15 μ°C/day with this system. Also, no thermal gradients were found to <40 μ°C/cm. The details of this system are given elsewhere.[8]

We measured, for the first time, the heating effect of the laser beam incident on a critical fluid system. We consider the Ornstein-Zernike formula for the light-scattering intensity from a critical fluid

$$I = A/(k^2 + \xi^{-2})\,, \tag{11}$$

where A is not strongly dependent on temperature. We differentiate Eq. (11) with respect to the temperature, using $\xi = \xi_0 t^{-\nu}$, where $t = (T - T_c)/T_c$, to find

$$\frac{dI}{I} = \frac{-2\nu}{1 + k^2\xi^2}\,\frac{dT}{T - T_c}\,. \tag{12}$$

Equation (12) indicates by how much the scattered intensity decreases for a given increase in the temperature of the fluid system. Equation (12) also indicates that the change in scattering intensity is largest for small k, which corresponds to forward scattering angles. For our smallest scattering angle of 30° we have calculated dI/I as a function of $T - T_c$ using Eq. (12) and typical values of $\nu = 0.64$, $\xi_0 = 2.5$ Å, and $\lambda = 5145$ Å, for $dT = 1$ m°C. We find that the scattered intensity changes by as much as 2.6% in the region $T - T_c \simeq 10$ m°C. This effect should be easily measured.

Our technique is to direct the beam of a laser into the critical fluid system and measure the decrease in scattered intensity due to the heating effect of the beam. For this technique to be successful, we must assume that there is little fluid mixing in and out of the illuminated scattering volume. This is reasonable if the fluid is not disturbed. We expect convection effects due to density changes to be small because we expect heating of the order of only a few millidegrees. Even if there is some mixing, we shall take the measured heating as an average involving the mixing.

To measure the laser heating effect in our fluid system, we directed the beam of an argon ion laser operating at either $\lambda = 5145$ Å or 4579 Å through a focusing lens, and into our fluid system. Once the beam was allowed to enter the fluids, the incident and scattered intensities ($\theta = 30°$) were monitored with strip chart recorders operating off the output of two power meters.

We found the scattered intensity decreased exponentially to another constant value in about an hour, indicating the extent of the laser heating. For a given incident beam configuration, various incident powers were used and dI/I was measured. Equation (12) was then used to determine dT, the temperature increment due to laser heating. The temperature change was linear with the incident power, except at large values of incident power (~5 mW) where the heating effect no longer increased as rapidly. When the beam was focused to a diameter of ~1.5 mm, we found a heating effect of 1.5 m°C/mW for $\lambda = 5145$ Å and 2.0 m°C/mW

for $\lambda = 4579$ Å. For an unfocused incident beam of diameter ~5.5 mm, heating effects of 0.36 m°C/mW for $\lambda = 5145$ Å, and 0.50 m°C/mW for $\lambda = 4579$ Å were measured.[22] The errors in these measurements are estimated at approximately ±25%.

The above values, especially for the narrower beam, are unexpectedly large. Since we have no reason to believe the system methanol and cyclohexane is atypical with regard to its energy absorption properties, we infer that light-scattering experiments reported heretofore might have been affected by laser heating. Notice that an incident power of less than 1 mW can cause a 1 m°C heating effect which, very close to the critical point, could cause large errors in the determination of $T - T_c$.

In the experiments to be reported here, we used our knowledge of the laser heating effect, either to adjust our incident power so that the heating would be very small, or to determine the magnitude of the heating, and account for it in our $T - T_c$ determination. This technique coupled with our excellent temperature control allowed us to perform light-scattering experiments very close to T_c.

C. The light-scattering experiments

We have performed two different light-scattering experiments. First, to test our double-scattering predictions we have measured the relative intensity and correlation time of the depolarized light scattered from our critical fluid system. We shall refer to this as the *depolarized-scattering experiment.* Second, we have measured the correlation time of *all* the light scattered from our critical fluid. This experiment was designed to be similar to prior measurements performed by others[1] to determine the Rayleigh linewidth of the scattered light. We shall call this experiment the *Rayleigh linewidth experiment.*

In the depolarized-scattering experiment, the incident beam from an argon ion laser first passed through a Glan-Thompson polarizing prism of extinction ratio 5×10^{-5}. This prism ensured a vertical polarization of the light incident on the critical fluid system. The scattered light passed through another similar polarizing prism before being detected by the photomultiplier tube. This detection polarizing prism could be adjusted so as to pass either the polarized or depolarized component of the scattered light. Details of the techniques used to ensure accurate adjustment of this polarizer are given elsewhere.[17]

In our theory of the double-scattered contribution to the Rayleigh linewidth, we assumed the relative spatial distribution of first- and second-scattering regions to be spherically symmetric. In addition, we demonstrated that a *wide-beam* configuration, in which the incident laser beam is either expanded of left unfocused, provides experimental conditions which are consistent with the assumption of spherical symmetry.[9] Thus, in these measurements the laser beam was not focused and had a diameter of ~5.5 mm (visual).[22] We shall refer to this incident beam arrangement as the *wide-beam geometry.*

In the Rayleigh linewidth measurement, the light was first focused by a 33.3-cm focal-length lens 24 cm distant from the fluids, which caused a beam width of ~1.5 mm (visual)[22] in the fluids. This *narrow-beam geometry* simulated the scattering configuration used in previous experiments of this type, and, because the scattering volume is smaller, helped cut down the relative magnitude of the higher-order scattered light. To further simulate the conditions of earlier measurements, the detection polarizer was not used in this experiment. Also, since the depolarized scattered intensity was never more than ~8% of the polarized intensity (see Fig. 8), removal of the depolarized scattered component would not have significantly affected the spectral measurements.

As we have mentioned earlier in this paper, we expect that while the spherical-scattering geometry assumption may not hold precisely for such a narrow-beam geometry, it should not lead to any qualitative errors in our analysis to follow.

Before any measurements on the critical fluid system were performed, a monodisperse system of Brownian diffusing particles was placed in the sample cell and temperature control system, and its light-scattering spectrum was measured. We found that the decay time of the scattered-light correlation function accurately reproduced that measured when this system was not in the temperature control cell to better than 1%. We also found that the correlation function when measured from inside the cell was quite exponential ($K_2/K_1^2 \lesssim 0.03$) as expected for a monodisperse system.[18]

IV. RESULTS

A. Depolarized scattering measurements

In Fig. 8 along with our theoretical prediction of the ratio $R_2 = I_{2\perp}/I_{2\parallel}$ we plot our depolarization ratio data, $R = I_\perp/I_\parallel$, for the *wide-beam geometry.* Scattering angles of 30° and 90° were used at incident beam wavelengths of $\lambda = 4579$ Å and 5145 Å. Inspection of the data shows that the depolarization ratio, and thus the multiple scattering, increases with $k_0\xi$ until $k_0\xi \gtrsim 4$ where it levels off. This behavior is expected from the Ornstein-Zernike form [Eq. (11)] for the total scattering cross section which also increases with $k_0\xi$ and then levels off for large $k_0\xi$ at finite angles.

To avoid confusion we stress that two different results are plotted in Fig. 8. The theoretical values of R_2 and the measured values of depolarization ratio R. As R approaches R_2 in Fig. 8, the second-order theory embodied in Eq. (8) breaks down indicating yet higher-order scattering processes.

In the region where $R \ll R_2$ we may use Eq. (8) to determine I_2/I_1. We find that double scattering is significant ($I_2/I_1 \sim 15\%$) even for $k_0\xi \simeq 0.6$ or $T - T_c \simeq 150$ m°C. For $k_0\xi \gtrsim 0.8$, I_2/I_1 is no longer much less than unity, and so we expect Eq. (8) to break down, implying that multiple-scattering effects become important. This analysis, then, indicates the regions of approximately solely single, single plus double, and multiple scattering as $k_0\xi \lesssim 0.6$, $0.6 < k_0\xi < 0.8$, and $k_0\xi \gtrsim 0.8$, respectively.

In Figs. 9 and 10, we plot the depolarized light-scattering linewidth results against our double-scattering theory, for scattering angles of 30° and 90°, respectively. Here we plot the double-scattered scaled linewidth which is similar to that for single scattering given in Eq. (6),

$$\Gamma_2^* = \frac{6\pi\eta_s}{k_B T}\,\frac{\Gamma_2}{k_0^3}\,. \tag{13}$$

The solid lines in Figs. 9 and 10 represent the first cumulant values. For the viscosity in Eq. (13) we used the background viscosity given in Eq. (9) to be consistent with our use of the droplet model form Eq. (5) in our double-scattering theory.[9]

The 30° data agree quite well with the theory except in the region $k_0\xi \lesssim 0.8$, while the 90° data are ~20% too large except in the region $k_0\xi \lesssim 0.8$. We must remember, however, that the theory represents the first cumulant values of the correlation functions. We discussed above how the 90° double-scattered correlation functions were reasonably

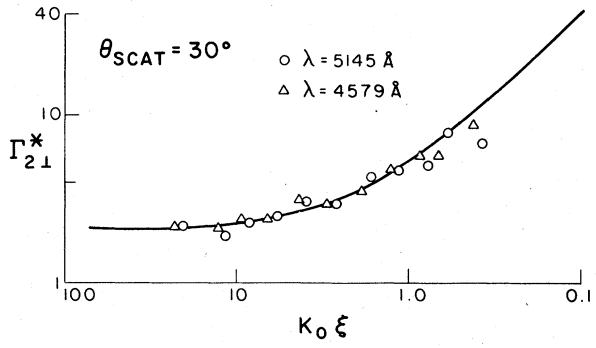

FIG. 9. Depolarized scaled linewidth of light scattered from the critical fluid system methanol and cyclohexane. Solid line represents the theoretical double-scattered first cumulant prediction. $\theta_{scat} = 30°$.

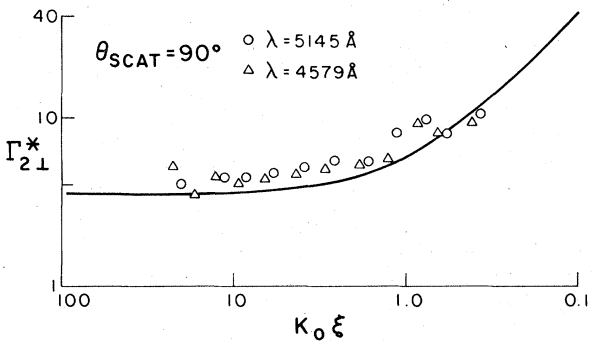

FIG. 10. Depolarized scaled linewidth of light scattered from the critical fluid system methanol and cyclohexane. Solid line represents the theoretical double-scattered first cumulant prediction. $\theta_{scat} = 90°$.

exponential and well described by the first cumulant. Thus, we feel that the data in Fig. 10 represent the first cumulant of the experimentally observed correlation functions and the discrepancy between theory and experiment is real. The experimental 90° depolarized correlation functions were nonexponential, but not to the degree where the first cumulant could not be determined. On the other hand, we found that for $k_0\xi > 1$, at a scattering angle of 30°, the theoretically determined double-scattered correlation functions were highly nonexponential. This was found to be true in our experiments also. Thus, the first cumulant was not determined accurately from the data, having a systematic error which made the decay times appear at least 20% too large, and therefore, making the first cumulant or linewidth appear 20% *too small*. Thus, we conclude that the fit of theory and experiment in the 30° case is erroneous; the data being at least 20% too low. If this were taken into account, Fig. 9 would corroborate Fig. 10.

Our depolarized data are only qualitatively described by our double-scattering theory in the region $k_0\xi > 0.8$. Our depolarization ratio measurements have indicated that, for this region, scattering of higher-order than double is significant. Thus, we cannot expect the double-scattering theory to hold in this region. We have discussed above, however, that in the large $k_0\xi$ region we expect the correlation time of the multiple-scattered field to be slightly shorter than the double-scattered correlation time. This is indeed what we observe, as best seen in Fig. 10, where the data have linewidths (remember $\Gamma \propto 1/\tau$) ~20% larger than the double-scattering prediction.

We conclude that these data are in agreement with the predictions of our theory of double scattering, once the effects of multiple scattering are qualitatively accounted for.

B. Rayleigh linewidth measurements

In this section we describe our Rayleigh linewidth measurements. Here we use the term Rayleigh linewidth for the linewidth or decay time of *all* the light scattered from our critical fluid system; not just the single-scattered component. We do this because previous Rayleigh linewidth measurements (see Ref. 1 and references therein) have assumed strictly single scattering, and few efforts were made to account for the double- and higher-order scattered fields. Thus, in these experiments the linewidth of all the light scattered was taken to be the Rayleigh linewidth. We wish, in effect, to repeat these measurements in order to illustrate that the single-scattering theories may still, albeit fortuitously, describe the data even when multiple scattering is present. It is also for this reason that we have used the narrow-beam geometry as opposed to the wide-beam geometry used in the depolarized-scattering experiment.

Our first measurements were concerned with the degree of exponentiality of the scattered-light correlation time. We found for the range 8 m°C $< T - T_c <$ 6 °C that the spectra were quite exponential with a second cumulant of $K_2/K_1^2 \lesssim 0.03$. This is in conflict with the dynamic-droplet-model prediction of nonexponential spectra with a predicted $K_2/K_1^2 = 0.15$ for all T. This result corroborates the result of Wonica, Swinney, and Cummins[15] who also found an exponential correlation function for light scattered from xenon 18 m°C above the critical temperature. The correlation function for $T - T_c \lesssim 8$ m°C became increasingly nonexponential. However, as we shall see multiple scattering should be quite large in this region, and is undoubtedly the cause of this observed nonexponentiality.

The Rayleigh linewidth of our fluid system was measured in the range 0.155 ±0.07 m°C to 6.3 °C at scattering angles of 30°, 60°, and 90° and for incident wavelengths of 4579 Å and 5145 Å. For $T - T_c \leq 8$ m°C, where the correlation function was slightly nonexponential, the first cumulant was still used as the Rayleigh linewidth.

We fitted our data by the dynamic-droplet-model prediction, Eq. (5), with Eq. (6) for the scaled linewidth using a least-squares routine. We used the background viscosity determined from our viscosity measurements and given in Eq. (9). Allowing ξ_0, ν, and γ to vary, we found a best fit to 100 data points, for $\xi_0 = 2.38$ Å, $\nu = 0.654$, and $\gamma = 1.037$. The value of ξ_0 and ν are quite reasonable, and γ is near unity as expected.

We have shown in the depolarization ratio measurements discussed above that for the wide-beam (diameter $\simeq 5.5$ mm) geometry multiple scattering became important for $k_0\xi > 0.8$. In our Rayleigh linewidth measurements, we have used a narrower beam-geometry (diameter $\simeq 1.5$ mm) and do not expect multiple-scattering to become important until $k_0\xi$ is larger. This is because the relative magnitude of the multiple scattering decreases with the size of the scattering volume.[17] We have made depolarization-ratio measurements for this geometry. Using Eq. (8) and the values of R_2 given in Fig. 8, we find that the double-scattered intensity becomes 15% to 20% of the single-scattered intensity for $k_0\xi \simeq 1.0$. Thus, $k_0\xi = 1.0$ represents the division between the region of purely single scattering, $k_0\xi \leq 1.0$, and the region of multiple scattering where $k_0\xi > 1.0$. This is a severe restriction, for the most interesting region is the $k\xi > 1$ region. Also, since we have modeled our experiment to simulate the experiments of others, we expect that a similar, though undetected, division existed for other systems.

Because of this, we also fitted the single-scattering result of the droplet model to the data for which $k\xi < 1$, the single-scattering region. There are 33 such points. A least-squares fit to these points yields values of $\xi_0 = 2.41$ Å and $\nu = 0.652$ for a fixed γ of 1.037. The parameter γ was held fixed because it is most sensitive to the data for $k\xi > 1$ which were excluded in this fit. The values of ξ_0 and ν corroborate very well with those obtained from the fit to all 100 data points. This fit is plotted in Fig. 11. The quality of the fit to all the data is remarkable in light of the known large amount of multiple scattering in the region $k\xi > 1$. This result illustrates the fact that multiple scattering has apparently little observable effect on Rayleigh linewidth measurements.

We also fitted our data by the mode-mode and decoupled-mode theories. These two theories give nearly identical results for $k\xi < 1$. Thus, we may fit the theories to the data points in this region,

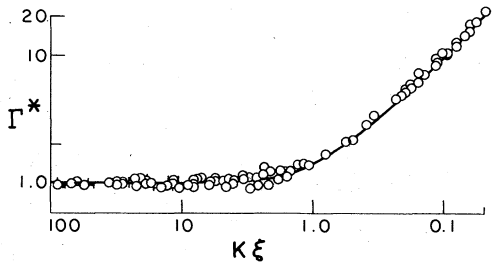

FIG. 11. Scaled Rayleigh linewidth of all the light scattered from the critical fluid system methanol and cyclohexane. Solid line represents the best fit to the dynamic droplet model of 33 data points for which $k\xi < 1$ and for which multiple scattering is small. Values of $\xi_0 = 2.41$ Å and $\nu = 0.652$ were found for $\gamma = 1.037$.

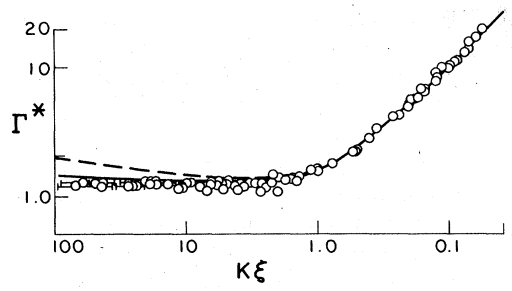

FIG. 12. Scaled Rayleigh linewidth of all the light scattered from the critical fluid system methanol and cyclohexane. Solid line represents the best fit to the mode theories of the first 33 data points for which $k\xi < 1$ and for which multiple scattering is small. Values of $\xi_0 = 2.85$ Å and $\nu = 0.627$ were found.

which we have shown to be essentially single-scattering points, and compare theory and experiment. We again use the scaled linewidth in Eq. (6) where we now use the macroscopic critical viscosity as determined in our viscosity measurements and given in Eq. (10).

Comparison of theory and experiment is given in Fig. 12. We see that both theories deviate from the data by predicting linewidths that are too large in the region $k\xi \gtrsim 10$. This is especially true for the mode-mode result. The least-squares fit yielded values of $\xi_0 = 2.85$ Å and $\nu = 0.627$, both reasonable values, but slightly different than those found for the droplet model.

To be fair in our comparison of the theories to the data, we must remember that the droplet model had a third fitting parameter γ not allowed in the mode theories. We have fit the decoupled-mode theory result to the data including the parameter γ. A good fit of data and theory is found for $\gamma = 1.085$, $\xi_0 = 2.77$ Å, and $\nu = 0.616$. We find that, given an equal number of fitting variables the decoupled mode theory and the droplet model give comparable fits to the data.

V. DISCUSSION

Our wide-beam depolarized spectrum data indicate the success of our double-scattering theory. The deviation of the data from the double-scattering prediction in Fig. 10 is due to the presence of higher-order scattered fields which, we have argued, would have linewidths larger than the double-scattered field. The presence of these higher-order fields was also indicated by our depolarization-ratio data analysis. Indeed, the fact that $R > R_2$ as seen in Fig. 8 indicates the extreme breakdown of the second-order Eq. (8), suggesting that the higher-order-scattered fields are very intense. Despite this, the deviation of the depolarized linewidth data from the double-scattering prediction in Fig. 10 is small, roughly 20%. We have made qualitative arguments, however, that in the large-$k_0\xi$ region we do not expect the linewidths of each succeeding higher-order term to be significantly different. Thus, we conclude that this qualitative argument is borne out by the data.

Since the depolarized light characterizes the double-scattered light, this experimental success reaffirms our theoretical results given in Figs. 6 and 7 for *both* polarizations. We see qualitatively that, if the effects of multiple scattering are included, the ratios $\tau_2/\tau_2(=\Gamma_1/\Gamma_2)$ will be slightly smaller than indicated in Figs. 6 and 7. The data for our system indicate these ratios are ~20% smaller. We can conclude that *multiple scattering* will have very little effect on correlation time or linewidth measurements on critical fluids in the region $k_0\xi \gtrsim 5$. Of course for very small $k_0\xi$, the multiple-scattered field should have a significantly different linewidth than the single-scattered field (see Figs. 6 and 7), but in this region its intensity will be small and will probably not affect the spectrum. It also appears that any effect the multiple scattering would have, would be to make the linewidth appear slightly larger than the single-scattered linewidth.

Some experiments have been performed to detect the effects of multiple scattering on Rayleigh linewidth measurements in the critical region ($k\xi > 1$).[6,7] The methods used consisted of adjusting the size of the scattering volume in order to vary the amount of multiple scattering. No changes in the Rayleigh linewidth were observed. Our results explain why this negative result was found.

In our Rayleigh linewidth measurements, we have purposely performed an experiment which we consider to be typical of other Rayleigh linewidth experiments on critical fluid systems. We have found that the single-scattering theories, in particular the dynamic-droplet and decoupled-mode theories, give excellent fits to the data to values of $k\xi \simeq 80$. Our depolarization ratio measurements for the narrow-beam geometry, however, indicate that the intensities of double and higher-order scattering are large in the region $k\xi > 1$. This experiment reaffirms our conclusions regarding Figs. 6 and 7. It also represents an explicit example that for a relatively typical scattering geometry and absolute scattering cross section ($\Delta n = 0.0978$) the linewidth data appear to give quantitative verification of the single-scattering theories even in the large-$k\xi$ region where the multiple-scattered intensity has been shown to be large. We would suggest that the value $k\xi > 1$ for the multiple-scattered intensity to become relatively large is a rather typical value for most previous Rayleigh

linewidth experiments and assume that similar nonobservable effects of multiple scattering may have been present in these experiments.

We have seen that our Rayleigh linewidth data are fit best by the dynamic-droplet-model prediction, or by the decoupled-mode theory in which γ is allowed to vary. The mode-mode prediction seems to describe the data least effectively. However, in our work on double scattering from Brownian diffusing particles[17] we have seen that one of the effects of double scattering was to drastically reduce any dependence upon the scattering wave vector k. Thus, we might expect that the slightly different k dependences of the three theories in the large-$k\xi$ region might be washed out by multiple scattering.

We conclude that Figs. 9 and 10 cannot be taken as a definitive test of the theories in the large-$k\xi$ region, because of the large multiple-scattered intensity. Efforts to account for the multiple-scattering effects are difficult because the corrections to the linewidth are small, and, because of the nonexponentiality of the correlation functions, difficult to characterize in a quantitative way.

Lai and Chen[16] reported measurements of the Rayleigh linewidth to $k\xi \sim 50$ which purport to support the mode-mode theory results. Their system was the binary fluid mixture n-hexane and nitrobenzene. These fluids have a very large index of refraction mismatch of $\Delta n = 0.18$. By way of comparison, our fluid system has a mismatch of 0.098. Thus, we could expect twice as much multiple scattering in their system as ours for a given scattering geometry. They took no precautions against the effects of multiple scattering, probably because these effects have always been neglected or underestimated. Furthermore, they claimed measurements to $T - T_c = 0.3$ m°C, but they did not know the extent of the incident laser beam heating of the fluids. We have seen that for reasonable beam powers of 1 mW heating effects of 0.3–1 m°C may result. Certainly, we can see the need for more and careful work in this large-$k\xi$ region.

Finally, we would suggest that a careful Rayleigh linewidth study on a fluid system that does not have a large scattering cross section would be most interesting. With the techniques developed here one should be able, both to approach the critical temperature very precisely, and to measure the magnitude of the double scattering, to ensure that it is small. Thus a measurement of the purely single-scattered Rayleigh linewidth should be possible, deep into the critical region. We are currently planning such an experiment.

---

*Work supported in part by the U. S. Energy Research and Development Administration under Contract No. E(11-1)-2203.

[1]H. L. Swinney and D. L. Henry, Phys. Rev. A 8, 2586 (1973).
[2]K. Kawasaki, Ann. Phys. (N.Y.) 61, 1 (1970); K. Kawasaki and S. M. Lo, Phys. Rev. Lett. 29, 48 (1972); S. M. Lo and K. Kawasaki, Phys. Rev. A 8, 2176 (1973).
[3]L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968).
[4]R. Perl and R. A. Ferrell, Phys. Rev. Lett. 29, 51 (1972); R. Perl and R. A. Ferrell, Phys. Rev. A 6, 2358 (1972).
[5]B. J. Ackerson, C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 34, 1371 (1975); C. M. Sorensen, B. J. Ackerson, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. A 13, 1593 (1976).
[6]D. Theil, B. Chu, A. Stein, and G. Allen, J. Chem. Phys. 62, 3689 (1975).
[7]B. Volochine and P. Berge, J. Phys. (Paris) 31, 819 (1970).
[8]C. M. Sorensen, Ph.D. thesis (University of Colorado, 1976) (unpublished).
[9]C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Opt. Commun. 20, 140 (1977).
[10]D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. 60, 3359 (1974).
[11]H. M. J. Boots, D. Bedeaux, and P. Mazur, Physica 84A, 217 (1976).
[12]L. A. Reith and H. L. Swinney, Phys. Rev. A 12, 1094 (1975).
[13]A. J. Bray and R. F. Chang, Phys. Rev. A 12, 2594 (1975).
[14]D. Beysens and G. Zalczer, Phys. Rev. A 15, 765 (1977).
[15]D. Wonica, H. L. Swinney, and H. Z. Cummins, Phys. Rev. Lett. 37, 66 (1976).
[16]C. C. Lai and S. H. Chen, Phys. Rev. Lett. 29, 401 (1972).
[17]C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. A 14, 1520 (1976).
[18]D. E. Koppel, J. Chem. Phys. 57, 4814 (1972).
[19]R. F. Chang, H. Bustyn, J. V. Sengers, and A. J. Bray, Phys. Rev. Lett. 37, 1481 (1976).
[20]C. L. Hartley, D. T. Jacobs, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 33, 1129 (1974); D. T. Jacobs, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 37, 1471 (1976).
[21]J. S. Huang and W. W. Webb, J. Chem. Phys. 50, 3677 (1969).
[22]The beam width is interpreted as the diameter of the visually observed spot-size when the beam strikes a smooth surface.