

(1965).

⁷K. Kawasaki, *Phys. Rev. A* **1**, 1750 (1970).

⁸H. Z. Cummins and H. L. Swinney, *Phys. Rev. Letters* **25**, 1165 (1970).

⁹A preliminary report of our results appeared in: G. D'Arrigo, D. Sette, and P. Tartaglia, *Phys. Letters* **35A**, 133 (1971).

¹⁰G. D'Arrigo, D. Sette, and P. Tartaglia, in *Proceedings of the Seventh International Congress on Acoustics*, Budapest, 1971, Vol. 4, p. 17 (unpublished).

¹¹L. Mistura and P. Tartaglia, *Phys. Letters* **36A**, 345 (1971).

¹²G. D'Arrigo, L. Mistura, and P. Tartaglia, *Phys. Rev. A* **1**, 286 (1970).

¹³J. Swift, *Phys. Rev.* **173**, 257 (1968).

¹⁴R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A* **2**, 1047 (1970).

¹⁵G. D'Arrigo and D. Sette, *J. Chem. Phys.* **48**, 691 (1968).

¹⁶J. S. Rowlinson, *Liquids and Liquid Mixtures*, 2nd ed. (Plenum, New York, 1969).

¹⁷J. Timmermans, *J. Chem. Phys.* **20**, 491 (1923).

¹⁸S. H. Chen and N. Polonsky, *J. Phys. Soc. Japan Suppl.* **26**, 179 (1969).

¹⁹S. S. Aliev and P. K. Khabibullaev, *Sov. Phys. Acoust.* **16**, 108 (1970).

²⁰H. J. McSkimmin, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1964), Vol. I, Part A, p. 271.

²¹P. Drapler, *Bull. Acad. Sci. Beige* **1**, 621 (1911).

Viscosity and Light Scattering in Critical Mixtures

S. Ballaro¹, G. Maisano, P. Migliardo, and F. Wanderlingh

Istituto di Fisica dell'Universita, Messina, Italy

and Gruppo Nazionale Struttura della Materia del Consiglio Nazionale delle Ricerche, Messina, Italy

(Received 3 January 1972)

Simultaneous measurements of both viscosity and light scattering are performed on two critical mixtures. The first one is a triethylamine-water solution, which exhibits a lower consolute point, the second one a methanol-cyclohexane mixture with an upper consolute point. It is found that the singular behavior of viscosity cannot be fitted by a simple power law, nor by a logarithmic one, in the entire range of temperature. The asymptotic behavior, however, tends to become logarithmic as the critical temperature is approached. The simultaneous observation of scattered light allows one to exclude the intervention of spurious processes, like a breaking of correlations because of impurities. In addition, it is shown that the correlation length seems to depend mainly on the reduced temperature, irrespective of the system under examination.

I. INTRODUCTION

In the present paper we report a series of measurements of viscosity and light scattering, performed simultaneously on a critical binary mixture. There are, in the literature, many measurements on viscosity, the majority of which seem to indicate that, near the critical point, this physical property can exhibit, at most, a logarithmic divergence.¹ However, certain results seem to indicate a stronger divergence, at least at those temperatures not too close to the critical temperature.² Now Kawasaki³ has recently shown that a logical inconsistency would derive from a divergence of viscosity stronger than a logarithmic one, as a consequence of the application of the scaling laws in the frame of the mode-mode coupling theory. Therefore, a divergence in the viscosity stronger than a logarithmic one would indicate that the scaling laws do not apply in that range. As suggested by Tsai,⁴ one can postulate the existence of two critical regions. The first one, classical in character, takes place relatively far from the

critical point. In such a region the viscosity can diverge strongly. Close to the critical point, however, there is a second critical region, in which scaling laws would apply, and therefore the viscosity can diverge at most logarithmically.

Alternatively, Barber and Champion² suggest that impurities of various kinds present in the system prevent the correlation length from becoming larger and larger as the critical point is approached. In such a case the strong divergence of viscosity, observed relatively far from the critical point, would be the effective behavior, while the weak divergence observed near the critical point is simply due to the impurity effect of breaking the critical correlations.

The experiments we report in the present paper are performed in order to discriminate between the two points of view sketched above. For this purpose we perform, on the same sample and at the same time, measurements of both the viscosity and the scattered-light intensity.

We use a vibrating-wire viscometer which allows a good thermostatisation by immersing the viscome-

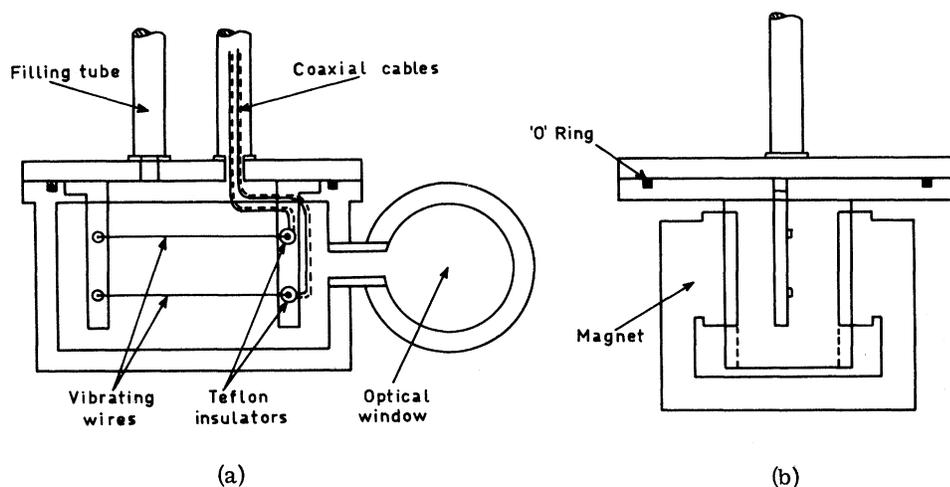


FIG. 1. Schematic view of viscometer: (a) front view; (b) side view.

ter, in which the sample is maintained at rest, in a large thermostatic bath. The optical arrangement we use is not a refined one because our main interest is simply the observation of the approach to the critical point as measured by the increasing correlation length. As explained in Sec. II, we detect a light beam that is due to both a direct beam and a scattered beam. The two beams have different intensities. As the critical point is approached, we expect a decrease in the intensity of the direct beam, and an increase of the scattered one. In such a way, the measured light intensity would exhibit a nonmonotonic behavior, as a function of the temperature, so that information concerning the correlation length can be related to the existence of maxima or minima in the intensity measurements, rather than in the absolute value.

We performed measurements on two entirely different systems. The first one was a mixture of triethylamine-water, which exhibits a lower critical consolute temperature. The second one was a mixture of methanol-cyclohexane, which exhibits an upper critical consolute point.

In Sec. II we describe in some detail the experimental equipment and the procedure followed in the measurements. Sections III and IV are dedicated to the experimental results obtained in the two mixtures, respectively. In Sec. V we discuss the results obtained in the viscosity measurements while the measurements of scattered light are discussed in Sec. VI.

II. EXPERIMENTAL SETUP AND PROCEDURE

The apparatus consists essentially of a vibrating-wire viscometer.⁵ The viscosity of the fluid under examination was tested through the damping exerted on the motion of a vibrating wire. The latter is a metallic wire in a magnetic field, and therefore can be driven by a suitable electric current. A

general view of the viscometer is shown in Fig. 1. It can be seen that we employ two wires. With this arrangement a viscosity measurement is possible either below or above the critical consolute point; i. e., the viscosity of the two components can be measured, after the phase separation occurs, giving two distinct values, so that the critical temperature can easily be determined.

Such a viscometer can be used in several ways. One can drive the wire with a pulse of dc current in order to observe the subsequent damped oscillations (see Fig. 2). A logarithmic plot of the successive pulse amplitudes then provides the damping constant of the wire which, in turn, is related to the viscosity of the medium. The kinematic viscosity of the fluid under examination can be obtained either by a calculation of the dynamics of the wire or by a calibration of the viscometer with fluids of well-known viscosity (e. g., glycerol-water solutions). We use the second alternative. For further details on this method see Ref. 5 and our previous work.⁶ In the present work such a method was used in the methanol-cyclohexane measurements.

Alternatively, one can drive the wire with an ac current of angular frequency ω ; then the amplitude of the vibrations of the wire can be recorded as a function of ω , and the resonance peak will give information on the losses suffered by the vibrating wire which are again related to the viscosity of the medium. A block diagram of the electronic equipment used in this arrangement is shown in Fig. 3. The information on the viscosity can be obtained in two ways. The Q of the vibrating system can be calculated from the shape of the resonance peak or, alternatively, the impedance of the system can be measured by the ratio between the driving current and the peak amplitude.

It is to be noted that we are interested in the mechanical impedance of the wire. The voltage

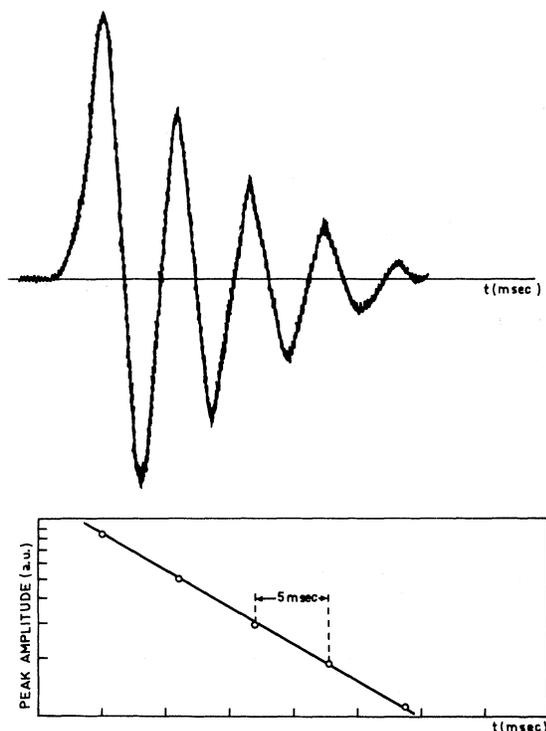


FIG. 2. Damped oscillations of vibrating wire. Insert: semilogarithmic plot of peak amplitude vs time.

peak measures the amplitude of mechanical vibrations, while the current is related to the driving force. From this point of view the electrical resistivity of the wire gives a contribution that will be detected far from the resonant frequency and then subtracted. For this reason we use, in such an arrangement, a silver wire rather than a tungsten one in order to minimize the electrical resistivity. Test measurements have shown that both the Q determination and the peak-amplitude measurement give consistent results. The second method, however, appears to be more sensitive. In addition, the system under examination can be followed continuously when the temperature of the mixture is changed, giving information about the approach to the state of thermodynamic equilibrium.

A straightforward calculation can be carried out in order to examine the dynamics of the wire.⁵ However, in such a case it is better to calibrate the viscometer using a fluid of known viscosity, and we follow this procedure. From test measurements we can assert that, in the range of interest, the kinematic viscosity of the medium and the reciprocal peak amplitude (at constant driving-current amplitude) are linearly related to each other.

However, an absolute evaluation of viscosity requires a more careful stability control in the elec-

tronic apparatus (mainly in the zero suppression of the constant Ohmic part of the signal). In the following we therefore prefer to report the viscosity measurements in arbitrary units. In addition to the viscosity measurements we perform, on the same sample and at the same time, light scattering measurements. Such measurements can give useful information concerning the proximity of the state of the system to the critical point. It is found⁷ that light scattered at small angles first increases as the system approaches its critical point and then suddenly drops very near to the critical point.

The purpose of our measurements is simply to achieve a very sensitive control on the approach to the critical point. The apparatus we use does not allow accurate measurements of critical scattering. However, in addition to the mentioned control function, our measurements reveal a peculiar behavior that we shall discuss later.

A schematic view of the optical disposition is shown in Fig. 4. The over-all optical geometry is such that the light scattered between the angles of 0.34° and 1.76° is detected. In addition to light scattered by the medium, however, there is spurious scattering which originates in the optical components we use (mirrors, windows, etc.). Such a contribution decreases as the system goes to the critical point, being scattered out of the angles of detection.

As far as temperature control and measurements are concerned, we use a Leeds and Northrup thermostatic bath, which ensures a temperature control better than 10^{-3}°K . The thermostat, in turn, was placed in a closed room in which the temperature was roughly controlled and maintained a few degrees above the thermostatic bath temperature. The electronic equipment for the experimental measurement was located in another room. The particular choice of viscometer allows its immersion in the thermostatic bath, thus ensuring a very careful control and stability of temperature.

Temperature measurements are carried out by

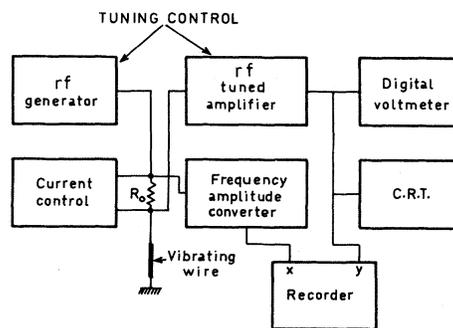


FIG. 3. Block diagram of electronic equipment.

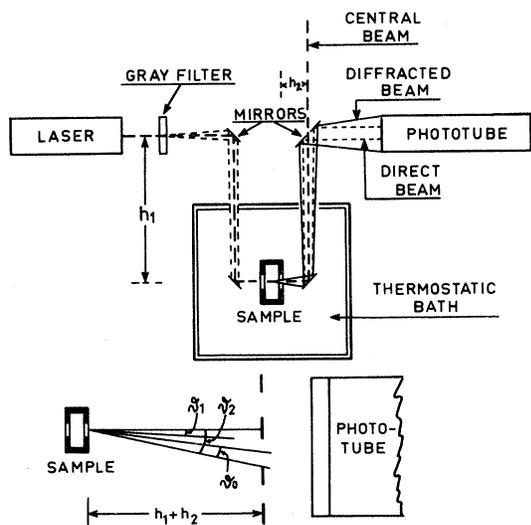


FIG. 4. Schematic view of optical arrangement. In the lower part are sketched the angles of interest (see text).

three sensitive probes. The first one is incorporated in the thermostat as part of the control and regulation device. The second one is a mercury capillary thermometer with a sensitivity of 10^{-2}°C . This thermometer measures the bath temperature. The third probe consists of a four-wire NTC resistor placed inside the viscometer and mounted as an arm of a Müller bridge. This probe allows temperature measurements of better than 10^{-3}°C .

In the experiments on the triethylamine-water

critical system, we use also a less refined thermostat for preliminary measurements, as will be discussed in Sec. III.

III. EXPERIMENTAL RESULTS IN TRIETHYLAMINE-WATER MIXTURE

The triethylamine-water mixture exhibits a lower critical consolute point; i. e., the system can exist in a single homogeneous phase only below the critical temperature. For the critical composition and an evaluation of the critical temperature we refer to Refs. 8 and 9.

The procedure we followed in the present experiments was, as discussed in Sec. II to detect the resonance-peak amplitude of the vibrating silver wire. The experimental results are shown in Figs. 5 and 6. The circles in Fig. 5 refer to measurements of the viscosity as a function of the temperature in the range between 14 and 19°C (the critical temperature being approximately in the neighborhood of 18°C), performed with an auxiliary thermostat with transparent walls, where the temperature control was about $2 \times 10^{-2}^{\circ}\text{C}$. The purpose of such preliminary experiments was to detect the critical temperature to better than 0.5°C in order to concentrate the successive measurements, in the main thermostat and with a careful temperature control, in the range of interest. The location of the critical temperature was visually detected through the onset of the critical opalescence and the subsequent formation of the meniscus.

Preliminary test measurements had shown that the critical temperature remained constant, with an accuracy of 10^{-1}°C , for a given sample in the

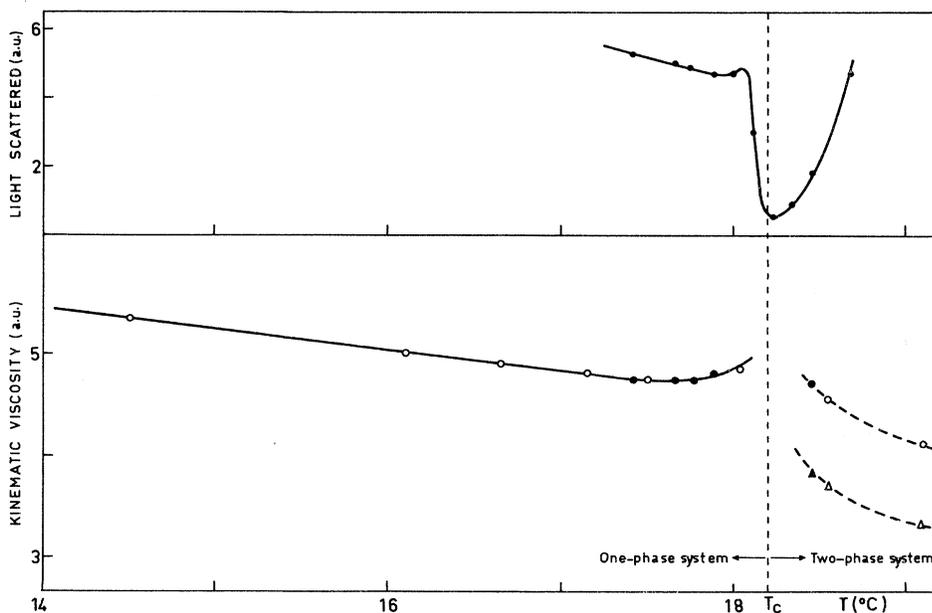


FIG. 5. Triethylamine-water solution. Lower curves refer to viscosity; upper curves refer to light-scattering measurements. The critical temperature was later found to be at 18.200°C .

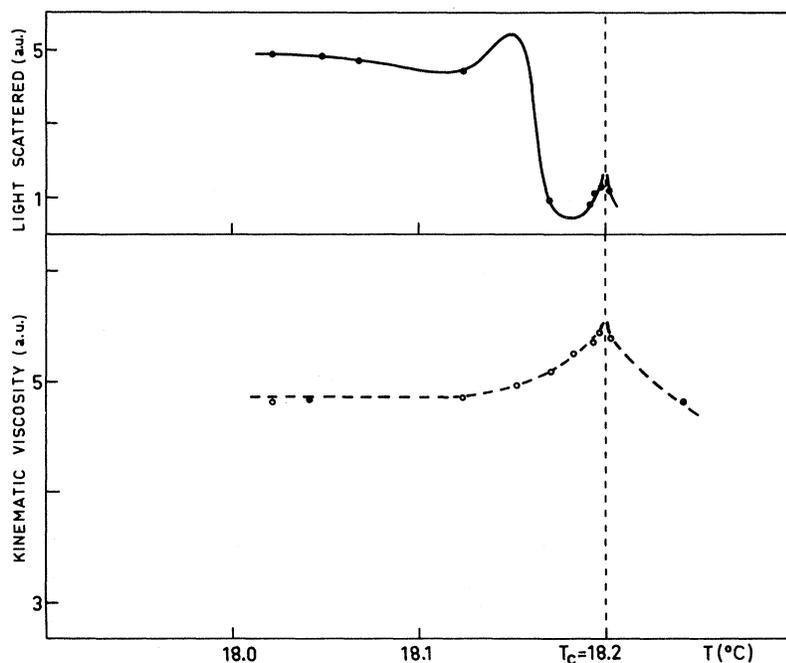


FIG. 6. Measurements near the critical point on the triethylamine-water solution. The meaning of the curves is the same as in Fig. 5.

viscometer, during several days, and after several passages above and below the critical point. In Fig. 5 and to the right of the critical temperature, the lower points refer to the triethylamine-rich phase, while the upper points refer to the water-rich phase. The full circles in Fig. 5 refer to measurements performed in the main thermostat, in the range between 17 and 19 °C, with an accuracy of 10^{-3} °C. During these measurements the light scattering was also determined. The line in the upper part of the figure refers to the light-scattering measurements. We should emphasize that we observe, near the critical point, that each change in the bath temperature was followed by an increase in the scattered-light intensity. This increase disappeared when the system reached the new equilibrium state and is in fact a good test for the reaching of the equilibrium. The deep minimum of the scattered-light intensity allows us to locate with reasonable accuracy the critical temperature in the neighborhood of 18.2 °C. Further details and a discussion of the light-scattering experiment are reported in Sec. VI.

Figure 6 refers to successive accurate measurements at intervals of about 10^{-3} °C in the immediate neighborhood of the critical point, and precisely between 18 and 18.2 °C. At the same time, the scattered light was also detected. In order to perform the last set of measurements we first cooled the thermostatic bath well below the critical temperature, in order to be sure that the system had gone into the homogeneous phase state, and then we gently warmed it until the temperature of 18 °C was

reached. At this point we started with measurement steps. In Fig. 6 we also report, as before, light-scattering data. The meaning of the point to the right of the critical temperature and of the upper line is the same as in Fig. 5. Full circles in Fig. 6 represent measurements carried out in the previous sets, which fall into the temperature interval spanned in the last one.

IV. EXPERIMENTAL RESULTS IN METHANOL-CYCLOHEXANE MIXTURE

As can be seen from Fig. 6, the behavior of the scattered-light intensity becomes very peculiar near the critical point. In fact, after the drop of intensity due to intense critical opalescence,⁷ a sharp peak appears at a few millidegrees from the critical point. We discuss such behavior in Sec. VI.

In order to test this phenomenon we have performed a set of measurements of the same kind on a different critical system, and precisely on a methanol-cyclohexane critical mixture. Such a system exhibits an upper consolute point. Estimates of critical concentration and critical temperature are found in the literature.¹⁰ We performed measurements only in the immediate neighborhood of the critical point, using the main thermostatic bath, with a temperature control better than 10^{-3} °C. The method we used consists of the recording of damped oscillations of a tungsten wire (see Sec. II and Ref. 6).

The results we obtained are summarized in Fig. 7. As a result of the narrowness of the tempera-

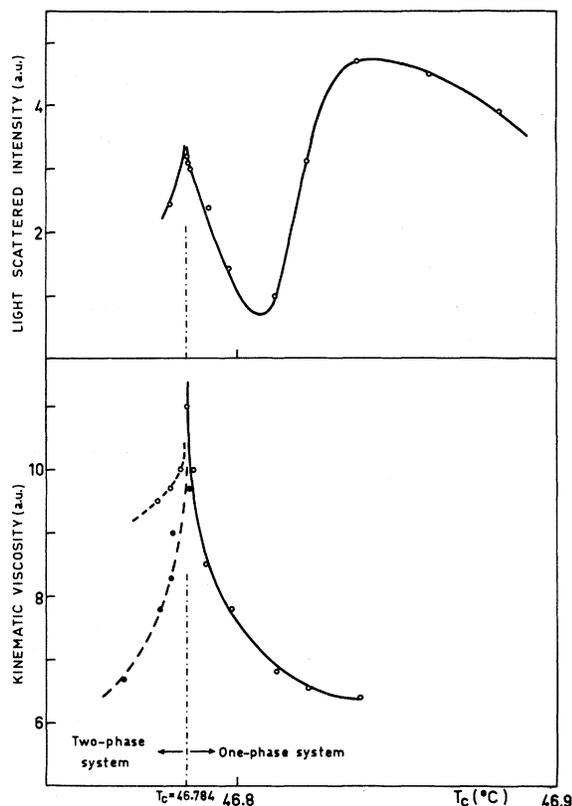


FIG. 7. Measurement near the critical point on the methanol-cyclohexane solution. The meaning of the curves is the same as in Fig. 5.

ture range spanned by our measurements, it is not possible, in such a case, to extrapolate a "normal" behavior for the viscosity. However, we believe that in such a limited range a linear dependence of "normal" viscosity versus temperature can be assumed. It can be shown that anomalous behavior of the scattered-light intensity was also reproduced in such a system. It is to be noted that, because the methanol-cyclohexane mixture exhibits an upper consolute temperature while the triethylamine-water system exhibits a lower one, the curve of Fig. 7 presents a reversed behavior as compared with the curve in Fig. 6.

V. DISCUSSION OF EXPERIMENTAL RESULTS ON VISCOSITY

In recent years much attention has been paid to the observation of the anomalous behavior of viscosity near the critical point, both from a theoretical and an experimental point of view. In the following, we limit ourselves to a discussion mainly concerned with the critical mixture.

The oldest theory seems to be the one attributed to Fixman¹¹ that predicts a rather strong anomaly due to an increase in entropy production near the

critical point. Then Kawasaki¹² obtained the same results from a more rigorous standpoint. His prediction can be put in the form

$$D \Delta\eta \sim \xi^{-1}, \quad (1)$$

where D is the diffusion coefficient, $\Delta\eta$ the anomalous part of the viscosity, and ξ the correlation length among fluctuations of concentration.

It is well known that, near the critical point, ξ diverges as

$$\xi \sim \epsilon^{-\nu}, \quad (2)$$

where $\epsilon = (T - T_c)/T_c$ and several theoretical and experimental works assign to the critical index ν the value¹³

$$\nu = \frac{2}{3}. \quad (3)$$

Now, depending on the behavior of the diffusion constant D , the excess viscosity $\Delta\eta$ can either diverge or stay finite at the critical point. In the earlier approach^{11,12} a power law of the kind

$$D \sim \xi^{-2} \quad (4)$$

was indicated. In such a case, a strong divergence results for $\Delta\eta$. The prediction (4) is based mainly on the assumption that the Onsager kinetic coefficient α , defined by

$$D = \alpha \left(\frac{\partial \mu}{\partial \rho} \right)_T, \quad (5)$$

is well behaved near the critical point.¹⁴ Now some experimental results exist which indicate that this is not the case. Chu and Schoenes¹⁵ find a power law for D :

$$D \sim \epsilon^{2/3}. \quad (6)$$

As a consequence, the critical exponent characterizing the behavior of the viscosity would be zero, indicating a divergence that is logarithmic at most, and may reduce to a strong cusp.

More recent theories confirm such results. Kadanoff and Swift¹⁶ and Swift¹⁷ derive, on the basis of the scaling-laws hypothesis, a theory which predicts, at most, logarithmic divergence. More recently Kawasaki³ shows that even a very weak divergence of the excess viscosity is inconsistent with the mode-mode coupling theory of transport processes.

On the other hand, it is well known that the scaling laws have only an asymptotic validity. A pre-critical region in which scaling does not apply can be theoretically predicted.¹⁸ From the experimental point of view, there are a large number of investigations with rather scattered results.¹⁹ An interesting feature of some results consists of a nonmonotonic behavior of the excess viscosity near the critical point. An indication in this direction was first given by Leister *et al.*⁴ on a 3-methyl-

pentane-nitroethane mixture. They found a strong divergence of the excess viscosity in the range 13.5–0.08 °C from the critical temperature with a critical exponent of 0.34, while in the immediate neighborhood of the critical point the divergence became less dramatic and, in fact, tended to a logarithmic (at most) behavior.

More recently, Barber and Champion² obtained a similar result on an isobutyric acid–water mixture. They found a power-law divergence with an exponent of 0.35 in the range 1–0.1 °C, while closer to the critical point the excess viscosity seems to round off to a constant value, indicating the existence of only a strong cusp. Analogous results are obtained by Tsai.⁴ Barber and Champion suggest that such a rounding off may be due to the effect of impurities which prevent the range of correlations from increasing indefinitely. In the absence of this effect the power law would be the correct description for the excess viscosity. On the contrary, Leister *et al.*⁴ explain their results with the hypothesis of two critical regions, the first one classical in character, in which a strong divergence would be expected, and the second one, close to the critical point, in which a scaling hypothesis would apply, with a consequent logarithmic divergence at most.

In a later paper Stein *et al.*²⁰ have gotten contradictory data on the basis of more careful measurements. However, from their experimental results, whose behavior is still analogous to that of the data reported in Fig. 9, it is quite evident that a single (logarithmic or power) law cannot easily be fitted to all the data points. In particular, as a consequence of such a fitting procedure, the differences between calculated and measured values exhibit a systematic behavior and become negative and larger as ϵ goes to zero. Allegra *et al.* explain such behavior with the hypothesis of a breaking of correlations due to impurities.²¹

On the whole, from the body of experimental results now available, it seems that a critical exponent describing the divergence of viscosity would be very small and practically zero, thus indicating a logarithmic divergence, at most, very near the critical point. The data concerning the existence of a classical critical region, relatively far from the critical point where the scaling hypothesis would no longer apply, as suggested by Tsai,⁴ are not sufficient.

The results of our experiment stress the fact that a single power law cannot be valid over the entire range of the measurements.

The most crucial step in the elaboration of the experimental data consists in evaluating the "ideal" part of the viscosity η_{id} , from which the anomalous part $\Delta\eta$ can be obtained:

$$\Delta\eta = \eta - \eta_{id} \quad (7)$$

The usual procedure consists in extrapolating an Arrhenius law from data far from the critical point. A criticism of this procedure is that it is not clear how far from the critical point one has to go to be sure that anomalous behavior is no longer present.

We proceed in a different manner. Because the ideal Arrhenius dependence is expressed by an exponential law

$$\eta(T) = \eta_0 e^{A/T} \quad (8)$$

a plot of the quantity $T \ln \eta$ vs T would give a straight line until Eq. (8) applies. A deviation from linearity could easily appear and would indicate the onset of anomalous behavior. In Fig. 8 we report such a plot for the triethylamine–water mixture. It can be seen that a sudden and rather drastic deviation from the linear behavior takes place at a temperature of about 17.4 °C, i. e., at 0.8 °C from the critical temperature (18.2 °C).

The indication that the critical behavior appears only this close to the critical point is in contrast

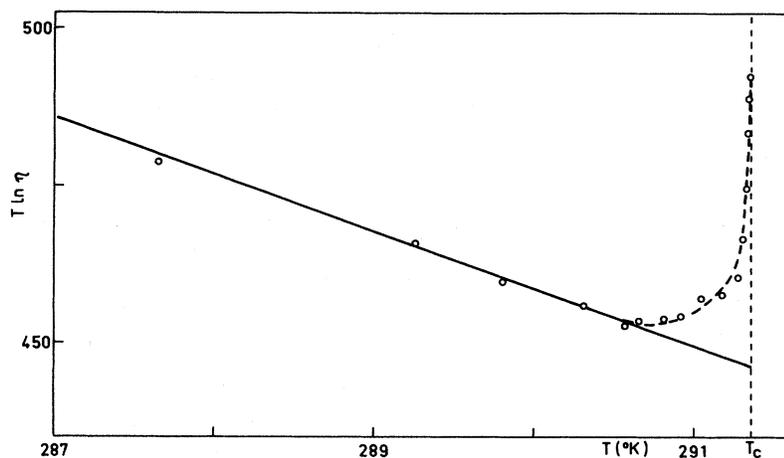


FIG. 8. $T \ln \eta$ vs T in triethylamine–water solution. The straight line corresponds to an Arrhenius-type law.

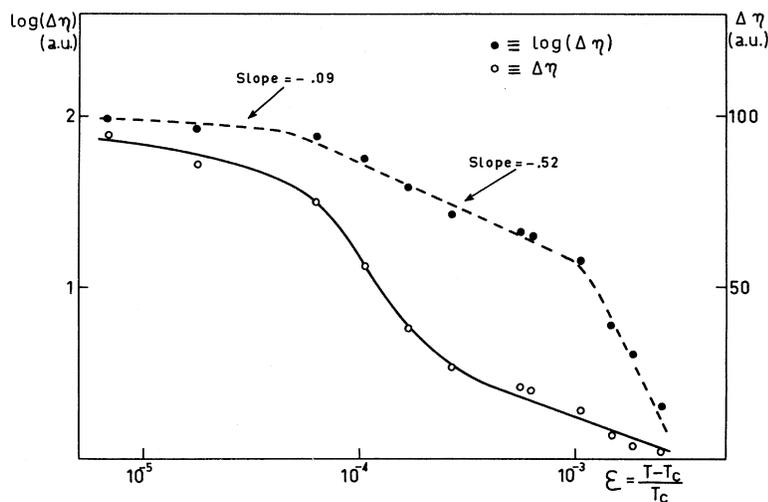


FIG. 9. $\Delta\eta$ and $\ln\Delta\eta$ vs reduced temperature plot for triethylamine-water system.

with the majority of experimental results obtained by other authors. Here we point out that this is a common feature of our experiments.⁶ We have carefully tested such circumstances, carrying out several sets of measurements of viscosity as a function of temperature, at intervals of about 0.5 °C both on the triethylamine-water mixture and in the other mixtures, such as aniline-cyclohexane or methanol-cyclohexane. In all cases, an anomalous behavior of the viscosity appears closer to the critical point than indicated by other authors. In particular, the value of 17.4 °C found for the onset of the anomaly in the triethylamine-water system was systematically obtained, irrespective of the experimental procedure that we followed (see Sec. II).

Such peculiarity should thus be attributed to the particular choice of viscometer. Unfortunately, at present, the data available are not sufficient to make a definitive comparison between the capillary-flow viscometer usually used and other kinds of viscometers, such as those in which a rotating disk or an oscillating cylinder are used. There is a system for which two entirely different kinds of measurements have been carried out (the 3-methylpentane-nitroethane mixture). Leister and co-workers^{4,20} use a Cannon-Fenske capillary viscometer, while Tsai⁴ uses a rotating-cylinder viscometer (closed viscometer). There is some indication that in Tsai's measurements, the critical behavior appeared somewhat closer to the critical point than in the measurements of Leister *et al.* In addition, the numerical values of the critical parameters in the two investigations are quite different. It is interesting to note that our values are very close to those obtained by Tsai, as we shall see later.

It is commonly accepted¹ that capillary-flow measurements are affected by several uncertain-

ties. In particular, it seems that thermodynamic equilibrium is not well assured. On the other hand, we can follow continuously the behavior of viscosity when the temperature is changed, as explained in Sec. II. A general feature of our results is that the viscosity shows an apparent increase during the time spent by the system in reaching a new equilibrium state upon the change in the bath temperature, while the viscosity gradually drops to a lower value when the equilibrium is attained. Analogous indications are provided by the light-scattering measurements.

We can tentatively conclude that the better thermodynamic equilibrium that we are able to ensure through the use of a closed viscometer is the cause of the delayed appearance of critical behavior.

From the plot of Fig. 8 the ideal viscosity can be extrapolated up to the critical point, and then the excess viscosity $\Delta\eta$ can be obtained. We plot both $\Delta\eta$ and $\ln\Delta\eta$ as a function of $\ln\epsilon$ in Fig. 9. It can be noted that the critical behavior of the viscosity is observed in a range of about four decades, namely, up to $\epsilon \approx 10^{-6}$.

It is evident that our results are in good qualitative agreement with those obtained by Leister *et al.*,⁴ Tsai,⁴ and Barber and Champion.² In particular, the quantity $\ln\Delta\eta$ tends to become constant when $\epsilon \rightarrow 0$. In this respect our results confirm that the anomalous behavior of the excess viscosity can be described by at most a logarithmic law.

The data of Fig. 9, together with similar results quoted above, show that the anomalous behavior of the excess viscosity cannot simply be described by a single (power or logarithmic) law. It is to be stressed that from our results on light scattering, we are sure that no impurity effects are present.

On the other hand, the very definition of critical

index refers to an asymptotic behavior rather than to an actual one. We believe that in such a case a fitting procedure throughout the entire set of data points would be less appropriate. From data such as those of Fig. 9, one can argue that the asymptotic behavior is, in fact, a logarithmic one. However, relatively far from the critical point the excess viscosity seems to diverge more strongly. It is a matter of convenience whether one draws a rounded line through the experimental points or a certain number of straight lines with different slopes. The second procedure can be used in order to have information concerning the strength of the divergence at various distances from the critical temperature.

For the sake of comparison, from the data of Fig. 9 we obtain a value of 0.52 for the exponent with which $\Delta\eta$ diverges in the range $\sim 10^{-4} < \epsilon < 10^{-3}$. This value is to be compared with the value 0.34 found by Leister *et al.* and the value 0.35 found by Barber and Champion with the use of the open viscometer, and with the value 0.523 found by Tsai with the use of a closed viscometer.

For the slope near the critical point, we obtain a value of 0.09. Again one can compare such value with the value 0.04 of Barber and Champion and the value 0.107 of Tsai.

In conclusion, from our results it seems evident that the excess viscosity exhibits, when the temperature approaches the critical value, a divergence, which becomes less and less strong as ϵ goes to zero.

An asymptotic behavior finally takes place for small ϵ , indicating, at most, a logarithmic divergence. A tentative explanation of such behavior can be given if one supposes that different transport coefficients do not become singular in the same range of values of ϵ . If, in particular, the Onsager kinetic coefficient α becomes singular only very near the critical point, a behavior such as that of Fig. 9 for the excess viscosity can be expected.

Alternatively, one can explain the experimental results by making the hypothesis that the excess viscosity stays finite at the critical point. A strong cusp in the viscosity, centered at the critical temperature, will also give results like those of Fig. 9.

VI. DISCUSSION OF EXPERIMENTAL RESULTS ON LIGHT SCATTERING

The observation of scattered light was primarily performed in order to have a sensitive probe indicating the reaching of a thermodynamic equilibrium state and to have a clear indication of the closeness to the critical temperature. It is in fact well known that the intensity of scattered light suddenly drops near the critical point⁷ owing to the greatly enhanced turbidity of the system (or, equivalently,

to the intervention of multiple-scattering processes²²).

In addition the simultaneous measurement of light intensity and viscosity allows one to relate directly the latter to the increase in the correlation length, and thus to exclude any effect due to impurities.²³

However, since the experiment performed on the triethylamine-water system showed a very peculiar behavior very near the critical point, we repeated the same experiment on a different system: a methanol-cyclohexane mixture. The results are very similar to those obtained in the former system, and we shall briefly discuss them in the following.

As explained in Sec. I, our measured light intensity is the sum of a direct beam due to spurious scattering and a beam of light scattered by the sample. The intensities of the two beams change with temperature, the first one being lowered by scattering processes in the sample, the second one being increased by the same processes. In addition, very near to the critical point multiple-scattering processes become important.

The observed experimental behavior of the light intensity shows an initial decrease due to the first contribution, then an increase when the second contribution becomes predominant, and finally a drastic drop near the critical temperature due to multiple scattering. Very near the critical point, however, we observe again a sharp increase, probably due to the marked forward character of the scattering.

In Fig. 10 we report on the same curve the data obtained for the two systems examined. It can be seen that in both cases the same behavior was observed, and loci of maxima or minima occur for the two systems at the same values of the reduced temperature ϵ .

In spite of the simplicity of our optical apparatus, two conclusions can be drawn, in our opinion, from the experimental results. The first one is that, in fact, the correlation length continues to increase as one approaches the critical point. A breaking of correlations would instead lead to a nearly constant behavior of the measured light intensity. The second one is that the correlation length ξ seems to depend on the reduced temperature ϵ essentially in the same way for the two systems under examination.

VII. CONCLUSIONS

We have observed, on the same sample and at the same time, the critical behavior of two physical quantities, namely, the viscosity and the light scattering, in critical mixtures.

The simultaneity of the measurements allows us to correlate the behavior of viscosity with the in-

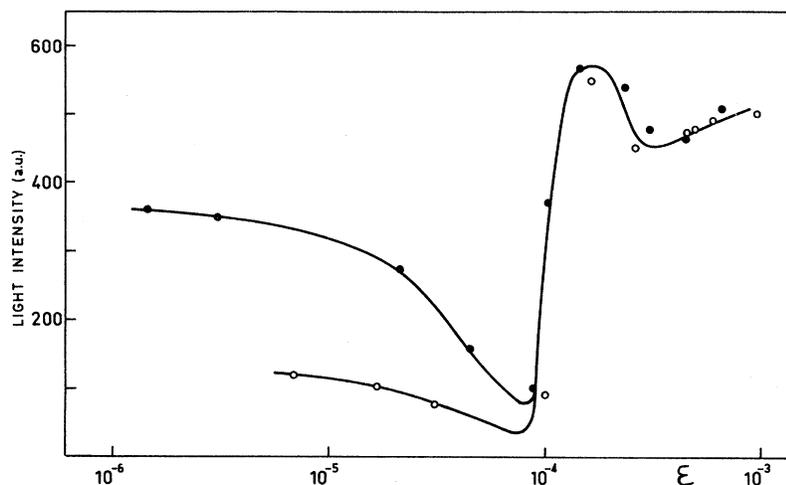


FIG. 10. Light intensity vs reduced temperature. The circles refer to the triethylamine-water solution, the solid circles to the methanol-cyclohexane solution.

creasing correlation length. The critical behavior of viscosity cannot be explained by a single power law, nor by a logarithmic one. Relatively far from the critical temperature ($5 \times 10^{-5} < \epsilon < 10^{-3}$) the viscosity shows a stronger divergence consistent with a power law whose exponent is of the order of 0.5, while very near the critical point ($\epsilon < 5 \times 10^{-5}$) such a divergence becomes less drastic and, in fact, tends to a logarithmic one (critical exponent less than 0.09). On the other hand, from the simultaneous light-scattering measurements we can exclude that such behavior is due to the effect of impurities that break down the critical correlation, as Barber and Champion² and Allegra *et al.*²¹ suggest. In fact we can see that in the same range of temperature the correlation length again increases when the reduced temperature ϵ goes to zero. We then conclude that our experiments indicate that the logarithmic divergence in the excess viscosity takes place only asymptotically. Relatively far from the critical point there is a range of temperature in which the viscosity diverges more strongly than logarithmically.

Since Kawasaki³ has shown that a strong divergence in the viscosity would imply a logical incon-

sistency in the frame of the scaling laws, one can deduce that either the critical behavior of a transport coefficient must set in before the scaling laws become effective or the excess viscosity stays finite at the critical point, exhibiting only a strong cusp. In addition, we observe the same behavior of scattered light in two entirely different critical mixtures, the first one with an upper critical consolute point and the other with a lower one. Such a result well agrees with the idea of universality, showing that the correlation length of the critical fluctuation seems to be a function of reduced temperature only, irrespective of the particular system under examination.

Research is in progress in order to improve the viscosity and light measurements. In particular we hope that a direct comparison between the excess viscosity and the light-scattering intensity could be helpful in assessing the actual behavior of the viscosity close to the critical point.

ACKNOWLEDGMENT

The authors wish to thank Professor M. Tosi for stimulating and helpful discussions and for reviewing the manuscript.

¹J. V. Sengers, in Lectures, International School of Physics, Enrico Fermi, Course LI, Critical Phenomena, 1970, University of Maryland Technical Report No. 7107, 1970 (unpublished), and references cited therein.

²T. R. Barber and J. V. Champion, *Phys. Letters* **29A**, 622 (1969).

³K. Kawasaki, *Ann. Phys. (N.Y.)* **61**, 1 (1970).

⁴B. Tsai, master thesis as reported by Sengers (Ref. 1); see also H. M. Leister, J. C. Allegra, and G. F. Allen, *J. Chem. Phys.* **51**, 3701 (1969).

⁵J. T. Tough, W. D. McCormick, and J. C. Dash, *Rev. Sci. Instr.* **35**, 1345 (1964).

⁶S. Ballaro', P. Migliardo, and F. Wanderlingh,

Nuovo Cimento Letters **1**, 129 (1971).

⁷See, e.g., W. P. Kao and B. Chu, *J. Chem. Phys.* **50**, 3986 (1969).

⁸F. Kohler and O. K. Rice, *J. Chem. Phys.* **26**, 1614 (1957).

⁹V. K. Semchenko and E. L. Zorina, *Dokl. Akad. Nauk SSSR* **80**, 903 (1951).

¹⁰J. Brunet and K. E. Gubbins, *Trans. Faraday Soc.* **65**, 1255 (1969), as reported by J. Sengers (Ref. 1).

¹¹M. Fixman, *J. Chem. Phys.* **36**, 310 (1962).

¹²K. Kawasaki, *Phys. Rev.* **150**, 291 (1966).

¹³For a classification and evaluation of critical index see, e.g., L. P. Kadanoff, in Report of the Proceedings

of the International School of Physics, Enrico Fermi, Course LI, Critical Phenomena, 1970 (unpublished); and also Fisher, Rept. Progr. Phys. **30**, 615 (1967).

¹⁴G. Arcovito, C. Faloci, M. Roberti, and L. Mistura, Phys. Rev. Letters **22**, 1040 (1969).

¹⁵B. Chu and F. J. Schoenes, Phys. Rev. Letters **21**, 6 (1968).

¹⁶L. P. Kadanoff and J. Swift, Phys. Rev. **166**, 89 (1968).

¹⁷J. Swift, Phys. Rev. **173**, 257 (1968).

¹⁸C. Di Castro, Nuovo Cimento **1**, 199 (1971), and references cited therein.

ences cited therein.

¹⁹For a comprehensive review on this argument see Ref. 1.

²⁰A. Stein, J. C. Allegra, and G. F. Allen, J. Chem. Phys. **55**, 4265 (1971).

²¹J. C. Allegra, A. Stein, and G. F. Allen, J. Chem. Phys. **55**, 1716 (1971).

²²P. N. Pusey and W. I. Goldberg, Phys. Rev. A **3**, 766 (1971).

²³See also P. Gluck and M. Luban, Phys. Letters **28A**, 607 (1969).

PHYSICAL REVIEW A

VOLUME 6, NUMBER 4

OCTOBER 1972

Statistics of the Radiation from Astronomical Masers

N. J. Evans II*

Department of Physics, University of California, Berkeley 94720

and

R. E. Hills†

Radio Astronomy Laboratory, University of California, Berkeley 94720

and

O. E. H. Rydbeck and E. Kollberg‡

*Onsala Space Observatory and Research Laboratory of Electronics,
Chalmers University of Technology, Gothenberg, Sweden*

(Received 15 May 1972)

The results of an experimental determination of the statistical properties of radiation from OH maser sources are reported and interpreted. The radiation is found to have Gaussian statistics with no deviations greater than 1%.

Radiation from astronomical objects is generally assumed to arise through processes in which the individual particles radiate independently. The resulting radiation fields are Gaussian; a complete description of such fields requires only the evaluation of quantities which are of second order in the field strength.¹ Consequently, astronomical measurements are normally limited to estimating the power spectrum and the angular distribution of intensity, which correspond to the second-order temporal and spatial correlation functions of the radiation field. In maser systems, stimulated emission is dominant so that the radiating particles no longer act independently. This may produce a non-Gaussian radiation field if the system has nonlinear properties. In the case where a maser amplifier provides linear amplification of initially random signals, such as radiation from a background source or from spontaneous emission within the amplifying region, no departures from Gaussian statistics will develop. However, if saturation occurs, reducing the gain for high intensities, large amplitudes will appear less frequently in the output than in a Gaussian field of the same mean intensity.

Conversely, if the gain increases for large signals, the probability density will show an excess of large amplitudes. The latter type of nonlinearity might be produced through the interaction of beams traveling in slightly different directions through a medium with population inversion. In such media, the stronger beam may rob energy from the weaker beam.² In any case, both the coherence of the individual radiators and the nonlinear gain characteristic are necessary to disturb the Gaussian nature of the original field.

The extreme brightness of many OH and H₂O emission sources,^{3,4} usually associated with regions of ionized hydrogen or with cool giant stars, can be best explained by maser amplification. In some cases the shapes of the emission lines in the power spectra indicate saturation of the maser process.⁵ Because these conditions bear considerable resemblance to laboratory systems which produce non-Gaussian radiation fields,⁶⁻⁸ we have carried out a search for departures from Gaussian statistics in the radiation from astronomical masers.

In this experiment we investigated the statistical