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Comparative measurements of viscosity near the critical point

G. Carini, Jr., G. Maisano, P. Migliardo, and F. Wanderlingh
Istituto di Fisica and Gruppo Nazionale Struttura della Materia del Consiglio Nazionale delle Ricerche, Messina, Italy

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The viscosity of the critical mixture isobutyric acid-water was measured by three different methods used simultaneously. The comparison of the results obtained in this way allows better insight into the anomalous behavior of the viscosity, and also into the question of the "ideal viscosity." One of the most important results consists in the experimental observation of the relaxation of the coupling between viscous and diffusive modes, as predicted by Kadanoff. Also, measurements of the Rayleigh linewidth were performed so that the question of the "high-frequency" viscosity could be discussed. It is shown that each kind of measurement involves a characteristic frequency and wave number, which should be compared with the frequencies characteristic of the critical system. In such a way, as the critical point is approached and consequently all the frequencies changed, a number of modifications can occur in the behavior of the viscosity. In particular there is a decrease in the viscosity, measured at nonzero frequency and a relaxation at the Kadanoff cutoff frequency. Very close to the critical point the viscosity rounds off revealing a cusplike behavior, unless a dependence on the shear gradient is allowed.

I. INTRODUCTION

Theoretical predictions for the shear viscosity in critical systems show that a weak anomaly is to be expected, consisting at most of a logarithmic divergence or, perhaps, of a cusplike behavior.[1]

However, from an experimental point of view it is to be noted that experimental results obtained by various authors with different techniques in many cases do not agree with each other. Actually, while an asymptotic logarithmic behavior was generally found, the relative amount of singularity, the distance from the critical point at which the anomalous behavior begins, and the behavior of the singularity not too close to the critical point are often very different from author to author.

In addition, a systematic deviation is found in the analysis of light-scattering experiments. In fact, when the Rayleigh linewidth Γ is analyzed in terms of the Kawasaki theory, the asymptotic value of the coefficient $k_B T/16\eta$ gives always for η a value lower than that directly measured.[2,3]

In discussing the critical behavior of the viscosity, some questions are to be taken into account. Mainly, (i) the way in which the nonsingular part of the viscosity is subtracted can sensibly alter the results. This is seen, for example, in the work of Gulari *et al.*,[4] and also in the present measurements. (ii) The way in which the data are analyzed can also affect the result. For example, as pointed out in Ref. 5 a strong cusp in the excess viscosity centered about the critical temperature, can generate data suggesting a "classical region." For similar remarks, see also Ref. 6.

Apart from this consideration, however, the intrinsic behavior of the anomalous viscosity can depend in a crucial way on the type of viscometer used. There are some theoretical considerations that give support to this idea.

First of all a dependence of viscosity on the shear rate can take place.[7] Also, nonlocality can sensibly affect the measurements.[8,9] Finally, the mode-mode coupling theory foresees a relaxation of the coupling between viscous and diffusive modes.[10]

Because the parameters determining the magnitude of such effects depend on the method used to measure the viscosity, one can expect that, while different viscometers give the same results far from the critical point, their indication could become different as the critical point is approached. On the other hand a direct comparison between results obtained by various authors by using different methods in different systems, although indicative, is rather questionable.

In order to give some clarifying insight on the various questions sketched above, we planned an experiment in which the viscosity is measured on the same critical system by various methods, simultaneously. In such a way the role played by the particular viscometer used can be unambiguously shown.

II. EXPERIMENTAL SETUP AND PROCEDURE

We measure the viscosity, in a critical mixture of isobutyric acid in water, by three entirely different methods, namely: By means of (i) a vibrating-wire viscometer; (ii) a falling ball of 0.4-mm radius; and (iii) the observation of Brownian motion of microspheres (~1-μm radius) by means of light scattering.

In Figs. 1(a) and 1(b), we sketch the structure of the cell and its accessories. *T*-*T* are the walls of the thermostat in which the cell is merged; *C* is an optically polished cylinder of fused silica that ensures the optical accessibility to the sample without disturbing its thermostatation. A light beam *L* can be sent into the sample and reflected back by the plane mirror *M* that forms the bottom of the cell. *W* is the vibrating wire, acted upon by the magnet *H*. The use of the vibrating-wire viscometer has been described elsewhere.[5, 11] However, we will stress that in the present measurements the autofrequency at which the wire oscillates is higher (1300 Hz) than that used in previous measurements. In addition an improved single-shot technique is used, as we shall see later. *R* is a magnetic ring that can be turned by means of the same magnet *H*. The ring drags a small sphere *S* from the lower to the upper side and then the sphere falls down. Measurements of the stationary velocity of the falling ball allow the evaluation of the viscosity by the Stokes law. The sphere is built up of a plastic material whose density slightly exceedes that of the liquid. The radius of the sphere (0.4 mm) and the viscosity of the liquid ($1.4 < \eta < 3$ cP) ensure that the stationary velocity is attained with a time constant less than 20 msec, during which the sphere falls less than a few millimeters. The stationary velocity is then measured by detecting the time interval between the passage of the falling ball through two levels h_1, h_2 [see Fig. 1(b)]. The detection is made by an electronic counter and a photocell system. The measured values (larger than 300 msec) compared with the above-mentioned time constant confirm that, in fact, stationary motion is fully established. This method is not used close to the critical point because the turbidity of the medium prevents a precise optical observation of the falling ball. The measurement of viscosity by the observation of the Brownian motion is performed by putting in the liquid sample a small quantity of Teflon microspheres of 1.15-μm radius. A focused light beam from a 5-mW He-Ne laser is sent into the sample and reflected back by the mirror *M*. An optical system consisting of lenses and slits allows both the choice of a small scattering volume *V* and of an exactly scattering angle of 26°. We detect the linewidth Λ of the scattered light by using a usual homodyne light beating spectroscopy, and a correlation technique. In our system, values of Λ in the range $1 < \Lambda < 250$ sec^{-1} are detectable.

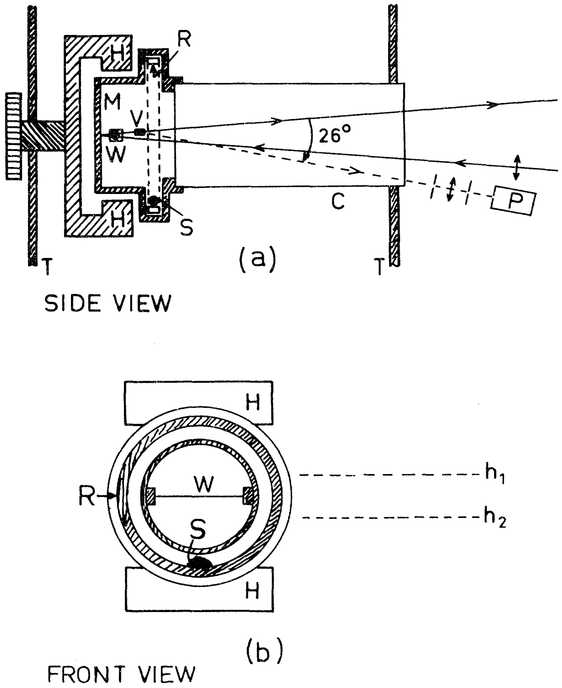

FIG. 1. Schematic view of the cell and its accessories. (a) Side view; (b) front view.

It is to be noted that, as the critical point is approached, the intensity of the critical scattering becomes larger and larger, masking the scattering due to the microsphere, so that measurements become useless for $\epsilon < 2\times10^{-3}$. Very close to the critical point, however, critical scattering dominates and the experimental correlation function of the scattered light can be used to obtain the Rayleigh linewidth Γ.

As mentioned above, we performed the measurements on a critical mixture of isobutyric acid in water. Both the components are doubly distilled from high purity (C.ERBA Research grade materials) before the preparation of the mixture. We use the concentration of 38% by weight of isobutyric acid. The thermostatic control is obtained by using a proportional feedback circuitry and it is better than 10^{-3} °K. The temperature is monitored by a negative temperature coefficient (NTC) sensor, that acts as a four-wire thermometer, sealed into the cell. Such a thermometer was previously calibrated by a platinum thermometer standardized by the N.B.S.

The procedure of measurements is as follows:

(i) After a change of the temperature the system is allowed to reach the equilibrium; the required time increases as the critical point is approached and becomes of the order of 10 h. The reaching of equilibrium can also be controlled by displaying the above-mentioned correlation function which reveals the existence of even very small inhomogeneities or convection currents.

(ii) The sample is stirred by rotating the magnetic ring R. In such a way a standard concentration of microspheres is restored. After stirring, a waiting time of about 2 h is allowed.

(iii) The first measurement concerns Brownian motion, because such a method does not disturb the sample.

(iv) The viscosity is then measured by the vibrating wire. A single short pulse of current is sent into the wire and the subsequent damped oscillations are photographically detected by an oscilloscope.

(v) The viscosity is then measured by means of the falling sphere and after the temperature of the thermostat is changed for the successive measurements.

The over-all precision of our viscosity measurements can be estimated to be of the order of 0.5%.

III. EXPERIMENTAL RESULTS AND DATA HANDLING

Before starting with measurements in the critical mixture, a careful standardization of the three methods was performed by using a water–ethyl-alcohol mixture (40% by weight of alcohol) whose viscosity changes from 2.9 to 1.5 cP as the temperature changes from 20 to 40 °C. However, as it is known, the results obtained by the procedures described above do not depend in the same way on the density ρ and on the viscosity η. In fact the damping α of the oscillations of the vibrating wire is related to the kinematic viscosity η/ρ. The linewidth Λ of the light scattered by the Brownian particles depends on the viscosity η, through the well-known Einstein-Stokes equation

$$\Lambda^{-1} = (6\pi\eta r/k_B T)\, k^{-2} \quad , \tag{1}$$

and the time t expended by the falling ball to cross the two levels h_1, h_2 depends both on the viscosity η and on the difference between the density ρ' of the sphere and that of the liquid as

$$t = \frac{9}{2}\,\frac{h_2 - h_1}{g r^2}\,\frac{\eta}{\rho' - \rho} \quad . \tag{2}$$

In the range of interest, from the standardization measurements, it was found, in fact, that α, Λ^{-1}, and t are linearly related to η/ρ, η, and $\eta/(\rho' - \rho)$; then we normalize our data by putting

$$\alpha' = \alpha\rho \propto \eta, \quad \Lambda^{-1} \propto \eta, \quad t' = (\rho' - \rho)\, t \propto \eta \, . \tag{3}$$

Such a procedure requires the knowledge of the density of the critical mixture in the range of temperature of interest. We performed this measurement in a separate experiment up to 0.05 °C from the critical temperature, and extrapolated the results up to the critical point. It is clear, however, that if the density had an anomalous behavior close to the critical point, an asymptotic difference in the results obtained by means of the three viscometers would arise.[2]

As it is well known, a crucial step in the data handling is the evaluation of the "ideal" part of the viscosity. In our opinion, however, the entire argument of the "ideal" viscosity is questionable. The singular part of the viscosity due to the critical behavior is calculated by the various authors on the ground of specified processes. However, their calculations do not exclude that other processes, more or less related to the critical phenomena, might take place: As a matter of fact we can mention the anomalous behavior of the noncritical water-alcohol mixture. In order to compare experimental data with a theory, the "ideal" viscosity would be determined as the viscosity in the absence of the processes involved in the theory: Such a quantity is clearly unobservable. One can believe, at most, that the "ideal" viscosity will be an analytic function of the temperature, so that in a range of a temperature sufficiently small very near the critical point its contribution could be considered as a constant. It is, in fact, true that the asymptotic behavior of the viscosity is quite unaffected by the choice of the "ideal" viscosity, while over an extended range of temperature the results crucially depend on that choice.[4] Our present measurements confirm this point of view. In addition, as we shall see in the following, the comparison between the data given by the different methods allows a calculation in which the "ideal" viscosity does not enter at all.

It is only for the sake of comparison that we calculate an "ideal" viscosity by using both an Arrhenius-type law,

$$\eta^{AR} = \eta_0 e^{A/T} \tag{4}$$

and an equation due to Bingham,[12]

$$T = A/\eta_B + C + B\eta^B \, . \tag{5}$$

Equation (5) was tested over 87 substances, giving a difference of less than 0.17%. The parameters entering the Eqs. (4) and (5) have been evaluated by using the data taken at temperatures far (>11 °C) from the critical point. For the critical temperature, by observing visually the formation of the meniscus, we found a value of 26.246 ±0.002 °C which agrees with the values obtained by other authors.

In Fig. 2 the data points are plotted. The inset shows an enlarged part of the curves near the critical point. It can be seen that while the results given by the falling ball and by the Brownian motion are in quantitative agreement the results given by the vibrating-wire viscometer become completely different as the critical point is approached. We

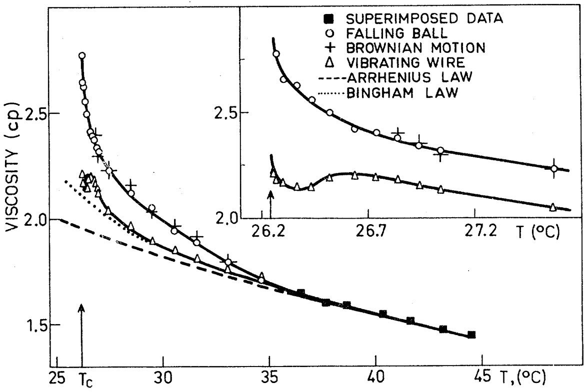

FIG. 2. Viscosity as a function of the temperature. Dashed line: ideal Arrhenius viscosity; dotted line: ideal Bingham viscosity. In the inset the data close to the critical point.

emphasize that the use of the three methods in noncritical systems always gives the same results, as we have carefully tested.

The following peculiar features can be stressed:

(i) The anomalous increase of the viscosity begins relatively far from the critical point as far as the falling ball and the Brownian motion are concerned. The data obtained by such methods are in close agreement with data obtained by other authors.[13,14] On the contrary, the results given by the vibrating wire show an anomalous behavior only near to the critical point. Such peculiarity is more pronounced if the Bingham law is assumed for the "ideal" viscosity, but holds also in the hypothesis of an Arrhenius-type behavior. This circumstance seems to be characteristic of the vibrating-wire viscometer, as previously reported.[5]

(ii) Near the critical point the viscosity, as measured by the vibrating-wire, shows a nonmonotonic behavior, well above the experimental uncertainty.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

In Fig. 3 we report, as a function of the logarithm of the reduced temperature $\epsilon = (T - T_c)/T_c$, the excess viscosity obtained either by subtracting an Arrhenius ideal viscosity or a Bingham one. As far as the falling ball and the Brownian motion measurements are concerned, the behavior is the same in the two cases. Generally speaking, there is an initial sharp increase in the excess viscosity, whose slope becomes smaller and smaller as the critical point is approached. A straight line fits the data in the range $3 \times 10^{-4} < \epsilon < 10^{-2}$, showing a logarithmic divergence. The whole data set, however, cannot be fitted by a single power or logarithmic law. Such a circumstance, elsewhere mentioned[5] and shown by a number of similar works, was recently stressed by Sengers,[2] and suggests a cusplike behavior for the excess viscosity.

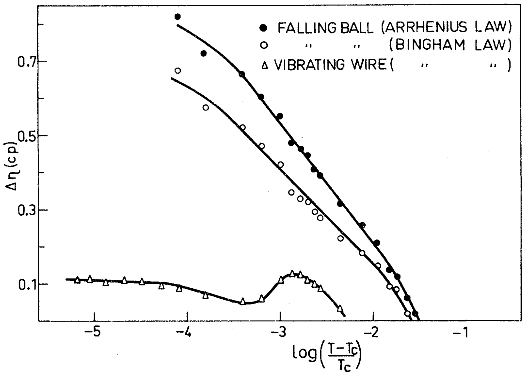

FIG. 3. Excess viscosity as a function of the reduced temperature.

On the contrary the results obtained by the vibrating-wire viscometer are quite different. Apart from any detailed consideration we would remark that different viscometers, while giving the same results far from the critical point, behave quite differently as the critical temperature is approached.

This shows unambiguously, in our opinion, that the concept of viscosity, in critical region, needs a more careful operative definition from the experimental point of view. We will see in the following that the discrepancies observed between the behavior of the vibrating-wire viscometer and the other methods can be explained by taking into account nonlocality and frequency dependence of viscosity. Also the shear-rate dependence seems to play a role, although a definite answer to such a question is not at the present possible.

As a general rule, to each method used for the viscosity measurements is associated a characteristic length or, equivalently, wave vector q, and a characteristic frequency ω. In the case of the falling ball (and in the usual capillary-flow measurements) ω is zero, and q is very small because of the macroscopic dimension of the probe. In the case of Brownian motion, q is related to the size of the particles, while for the frequency concerned one deals with a distribution associated to the Fourier transform of the velocities distribution.

In the case of vibrating wire (or oscillating disk and similar devices) the wave vector q could be associated with the spatial distribution of velocity introduced by the device. As order of magnitude the inverse penetration depth could be assumed, by taking[15] $q = (\rho\omega/\eta)^{1/2}$. The frequency ω, of course, is the well-defined frequency at which the probe operates.

As far as the nonlocality is concerned, a treatment given by Perl and Ferrell[8,9] gives the following equation:

$$[\eta(\gamma)-\eta(0)]/\eta(0)=(8/15\pi)\sigma(\gamma)\ , \qquad (6)$$

where $\eta(0)$ is the zero-frequency viscosity and

$$\gamma=(\omega/Dq^2)^{1/3} \qquad (7)$$

measures the frequency in units of the critical diffusive linewidth evaluated at wave number q. The function $\sigma(\gamma)$ is given in Ref. 9. It is zero for $\gamma=0$ and, becomes increasingly negative for $\gamma>0$. Any correction for nonlocality is therefore to be expected for the falling-ball measurements. In the case of Brownian motion, ω can be evaluated by means of the measurements of the linewidth Λ, and a value of a few hertz arises. Taking also into account the values of D given in the literature[16] and the size of the particles, one obtains a value of γ which is lower than 10^{-1}, so that the corresponding correction for nonlocality is practically undetectable.

On the contrary, in the case of the vibrating wire, ω is about 8×10^3 sec^{-1}, and q (the inverse penetration depth) is of the order of 10^3 cm^{-1}, so that one gets a value of $\gamma\simeq30$. Then $\sigma(\gamma)$ can be evaluated from the asymptotic formula given in Ref. 9, as

$$\sigma(\gamma)=0.169-\ln\gamma-0.479\gamma^{-2}\ . \qquad (8)$$

Thus it turns out that the frequency-dependent viscosity would be about 15% less than its zero-frequency value. Such a difference increases when the critical point is approached. This is in fair agreement with our data (see Fig. 2), and justifies the "less sensitive" behavior of the vibrating-wire viscometer.

Let us now discuss the nonmonotonic behavior shown by the viscosity as measured by the vibrating wire viscometer. Within the framework of the mode-mode coupling theory as developed by Kadanoff and Swift,[10,17] three regions of increasing frequency can be distinguished. Each of them is characterized by a cutoff frequency such that at higher frequencies one mode relaxes and its contribution to the anomalous behavior of the transport coefficients becomes vanishing. As far as the shear viscosity in critical mixtures is concerned, there are two contributions to be considered. The first one is due to the coupling among viscous and acoustic modes[17] and it is present in the three regions and relaxes at a characteristic frequency

$$\Omega_S=V\xi^{-1}\ , \qquad (9)$$

where V is the sound velocity; i.e., the relaxation occurs when the correlation length becomes comparable with the acoustic wavelength associated with the frequency involved in the measurement. This characteristic frequency Ω is rather high, also very near the critical point ($\epsilon<10^{-5}$), being of the order of 10^8 sec^{-1}.

The second contribution arises from the coupling between viscous and mass diffusive modes, and relaxes at a frequency

$$\Omega_D=D\xi^{-2}\ , \qquad (10)$$

D being the mass-diffusion coefficient. A numerical evaluation of such an inverse relaxation time can be made, for the isobutyric acid-water system, by using the data of Chu *et al.*[16] The results are shown in Fig. 4. As foreseen by the theory, Ω_D behaves roughly like ϵ^2. In the case of our vibrating-wire viscometer the angular frequency is 8168 sec^{-1}, so that the diffusive mode contribution would relax for a reduced temperature ϵ less than 1.112×10^{-3}. In Fig. 5 we report the experimental data in the region of interest on an enlarged scale. It can be noted that the nonmonotonic behavior of the viscosity measured by the vibrating wire takes place, actually, at the above-mentioned temperature. We therefore suggest with confidence that such behavior is explained as experimental evidence for the relaxation of the coupling between viscous and diffusive modes.

In order to test such a hypothesis, we write the viscosity as the sum of a term η^*, that contains both the "ideal" viscosity and the contribution due to the coupling with acoustic modes, plus a contribution of magnitude A that relaxes just at

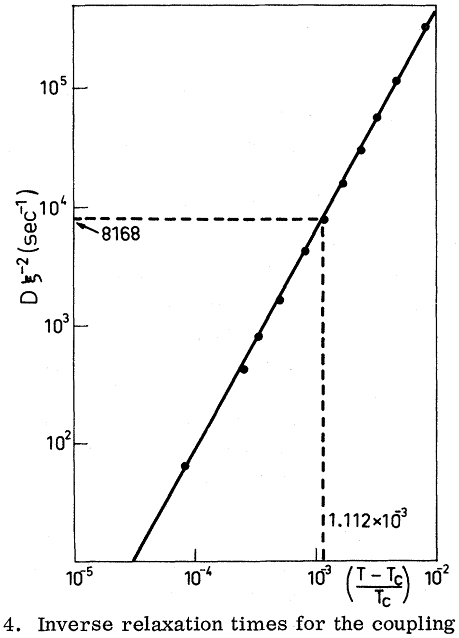

FIG. 4. Inverse relaxation times for the coupling between viscous and diffusive modes.

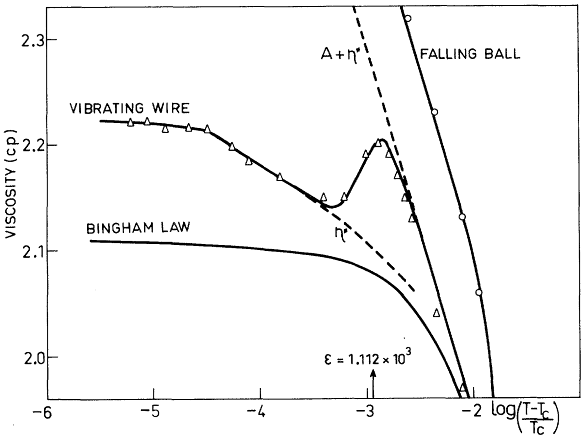

FIG. 5. Viscosity experimental data in the neighborhood of the relaxation temperature.

the frequency Ω_D:

$$\eta = \eta^* + A\left[1 + (\omega/\Omega_D)^2\right]^{-1}. \tag{11}$$

The unrelaxed value $\eta^* + A$ can be evaluated by the extrapolation of the experimental data obtained for $\epsilon > 1.112\times10^{-3}$ towards small ϵ values; analogously the relaxed value η^* can be obtained extrapolating the data obtained for $\epsilon < 1.112\times10^{-3}$ towards large ϵ value (dashed lines in Fig. 5). Then one can evaluate the left-hand side of the equation

$$(\eta - \eta^*)/A = \left[1 + (\omega/\Omega_D)^2\right]^{-1} \tag{12}$$

and compare the obtained values with the right-hand side as calculated from the D and ξ data of Chu *et al.*[16] (circles and dashed lines in Fig. 6). The agreement is surprisingly good, so that we believe that we actually observe the relaxation of the contribution due to the coupling with diffusive modes, predicted by Kadanoff, and that in the relaxation region the viscosity can be adequately described in Eq. (11). To our knowledge such experimental evidence has not been observed until now. In addition, in the preceding procedure the magnitude of the "ideal" viscosity does not enter explicitly.

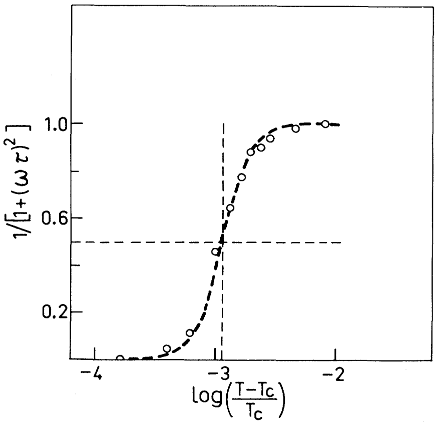

FIG. 6. Theoretical (dashed line) and experimental (circle) data concerning the relaxation of the coupling with diffusive modes.

Another indirect comparison can be obtained by plotting the relative excess viscosity $\Delta\eta/\eta$ as a function of $\log_{10}\epsilon$. On the ground of current theories one expects a straight line with a negative slope of 0.033.[2] In Fig. 7 we report such a plot. The results obtained by the falling ball (and by the Brownian motion) give a good agreement as far as the Bingham equation is used to subtract the "ideal" viscosity.

This could be an indication that such an equation describes the viscosity of our system better than the Arrhenius law. As far as the vibrating-wire viscometer is concerned, according to the above considerations, one can plot the quantity $A/(A+\eta^*)$, i.e., the relative anomalous contribution given by the coupling with diffusive modes. Again there is a good agreement, the slope being -0.0337.

Some remark should be made about the "rounding off" of the viscosity very near to the critical point. Also this feature appears to be relevant in connection with the vibrating-wire viscometer, although in the literature other examples are available.[2] As mentioned above such a peculiarity could indicate a cusplike behavior in the anomalous viscosity. On the other hand, also a shear-rate dependence of the viscosity[7] could explain the rounding off, especially taking into account both the rather high values of the velocity gradient introduced by the vibrating wire and the closeness to the critical point at which the rounding off becomes evident At the present, however, we cannot decide between these two possibilities.

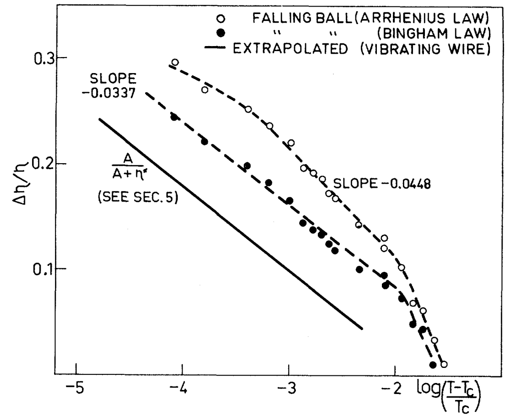

FIG. 7. Relative increase of the viscosity as a function of the reduced temperature.

V. HIGH-FREQUENCY VISCOSITY

As mentioned in Secs. II and III we use the light scattering experimental setup to detect the Rayleigh linewidth for temperatures close to the critical point, enough that the critical scattering dominates. The obtained data are analyzed in terms of the Kawasaki prediction and are plotted in Fig. 8. There is good agreement between our data and that obtained by Chu *et al.*[16] In particular, our figure for the asymptotic constant value

$$\Gamma/k^3 = 1.00\times10^{-13}\ \mathrm{cm}^3/\mathrm{sec}$$

favorably compares with the value 1.06×10^{-13} cm^3/sec obtained by Chu. On the right-hand side of Fig. 8 we have indicated the quantity $k_BT/16\eta$, i.e., the expected asymptotic value of Γ/k^3, calculated by using the Arrhenius viscosity η^{AR}, the Bingham viscosity η^B, the relaxed value of the viscosity η^* given by the vibrating-wire viscometer, and the "hydrodynamic" value η^{HD} given by the falling ball measurements. We can also compare our data with the data obtained by Chang *et al.* on a 3-methylpentane nitroethane mixture.[3] Their asymptotic value of Γ/k^3 corresponds to a viscosity of 0.49 cP. The "ideal" viscosity in their system is 0.38 cP, while the measured viscosity increases up to about 0.540 cP. It follows that the "hydrodynamic" viscosity is about 10% larger than the "high-frequency" viscosity calculated from the Γ/k^3 value, while "ideal" viscosity is about 22% lower.

In our case a similar situation arises. Our "hydrodynamic" viscosity, even if taken relatively far from the critical point, is about 13% larger, and the "ideal" Bingham viscosity is about 15% lower than the value $\eta = 2.47$ calculated from the asymptotic Γ/k^3 value. Also, the relaxed value is still 10% lower.

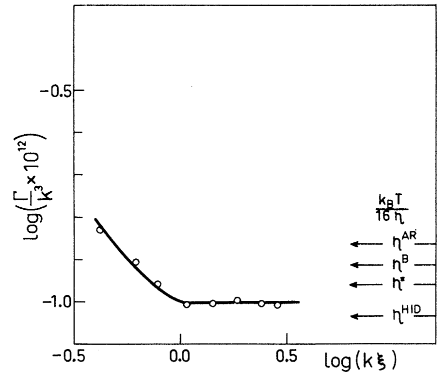

FIG. 8. Rayleigh linewidth measurement (dots) and Kawasaki plot (full line). On the right-hand side the arrows indicate the asymptotic Γ/k^3 values obtained with different viscosities (see text).

On the other hand, according to the consideration mentioned in Sec. IV, the viscosity implied in the light-scattering experiment has to be considered as measured with a probe fixed by the dynamics of the concentration fluctuations.

The wave vector q associated to such a probe is given by the scattering wave vector k, and the frequency ω can be measured by the Rayleigh linewidth $\Gamma = Dk^2$. It follows that (i) the parameter γ associated with nonlocality correction remains constant throughout the measurement and equal to 1. (From Ref. 9 this implies a decrease of about 5% in the viscosity with respect to the zero-frequency value). (ii) The ratio ω/Ω_D becomes equal to $(k\xi)^2$, so that in the asymptotic region $k\xi > 1$ one is concerned with a viscosity in which the contribution due to the coupling with diffusive modes is relaxed.

As a consequence the "hydrodynamic" viscosity is larger than the "high-frequency" viscosity computed from the asymptotic Γ/k^3 value, because the former is a nonrelaxed one. On the contrary, the relaxed viscosity, as measured by the vibrating wire (apart from considerations of a hypothetical shear rate dependence), is lower because of the larger nonlocality effects. Such considerations are quite consistent with our experimental data, as shown in Fig. 8.

VI. CONCLUDING REMARKS

From the discussion developed so far it appears that the mechanisms appealed to in order to explain the critical behavior of the viscosity at least lead to a comparison between two characteristic frequencies. The magnitude of these frequencies can be very different although they show a common origin.

Having in mind the coupling between viscous and diffusive modes, the diffusion coefficient $\boldsymbol{D}$ gives rise to two frequencies characteristic of the critical system one examines. The first one is the cutoff frequency $\boldsymbol{\Omega}_D$, as given by Kadanoff[10] [see Eq. (10)], which measures the time for mass diffusion to cross a correlation length. The second one, $\Omega_q = Dq^2$, measures the time for mass diffusion to cross the characteristic length q^{-1}.

As the temperature changes, and the critical point is approached, the following behavior occurs: (i) ω remains practically constant, or changes slowly (as in the case of Brownian motion, as a result of the increase in viscosity); (ii) $\boldsymbol{\Omega}_D$ changes quickly as ϵ^2; (iii) Ω_q changes roughly, as $\epsilon^{2/3}$, because the diffusion coefficient changes. Also, q can change slowly, as is the case if q^{-1} represents the inverse penetration depth that depends on the kinematic viscosity.

The following comments are pertinent:

(a) The ratio between ω and Ω_q enters the correction for the frequency dependence of the viscosity, as shown by Perl and Ferrell.[8,9] In the case of the vibrating-wire viscometer such a correction is as high as 15% and increases up to 20 to 25% as the critical point is approached, because of the decrease in Ω_q. As far as the Brownian motion is concerned, Ω_q is 10^2 times larger because of the small dimensions of Brownian particles. An estimate of ω, on the basis of the linewidth Λ measurements, obtains an order of magnitude of only a few hertz. As a consequence, in such a case the correction would be less than 1% and cannot be detected in our measurements. Finally, the zero frequency connected with the falling ball prevents any effect.

(b) The ratio between ω and Ω_D enters the relaxation of the coupling between viscous and diffusive modes, as shown by Kadanoff. In the case of the vibrating-wire viscometer such a relaxation takes place at $\epsilon = 1.112\times10^{-3}$ and it has been experimentally observed. In the case of the Brownian motion its low frequency prevents the effect, unless ϵ is lowered to about 10^{-5}. The zero frequency connected with the falling ball excludes this phenomenon.

When we consider the "high-frequency" viscosity in connection with Rayleigh-linewidth Γ measurements, a rather peculiar situation takes place. Actually, in such a case, both the frequency ω (to which the viscosity measurements are concerned) and Ω_q become equal to Dk^2, k being the wave number involved in the light-scattering measurements. The ratio ω/Ω_D becomes the ratio $\Omega_q/\Omega_D = (k\xi)^2$, so that the condition $k\xi = 1$ marks the temperature at which the relaxation of the coupling with diffusive modes takes place.

In conclusion we have shown that the results obtained in the viscosity measurements depend on the method used. The vibrating-wire viscometer allows the experimental observation of the relaxation of the coupling with diffusive modes. The behavior of the viscosity very near the critical point rounds off, revealing a cusplike behavior, unless a dependence of the viscosity on the shear gradient is allowed. Further work is in progress in order to extend the measurements to a larger range of frequencies and substances.

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[1] For a comprehensive review on this argument, see *Critical Phenomena, Proceedings of the International School "Enrico Fermi", Course LI,* edited by M. S. Green (Academic, New York, 1971).

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