

## Light-Scattering Investigation of Brownian Motion in a Critical Mixture\*

Kenneth B. Lyons, Richard C. Mockler, and William J. O'Sullivan

*Department of Physics and Astrophysics, University of Colorado, Boulder, Colorado 80302*

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The diffusion coefficient of Brownian particles in the binary mixture nitroethane-iso-octane close to the critical phase transition has been measured using autocorrelation spectroscopy. The results support a logarithmic divergence in the shear viscosity.

To date the only published investigation of Brownian motion in a binary liquid near the critical point has been performed by Bal'tsevich, Martynets, and Matizen<sup>1,2</sup> (BMM) who applied microphotography to follow individual particles. In this Letter we present results of a study of Brownian motion in a critical mixture using autocorrelation spectroscopy. These data represent a statistical improvement over the earlier results since the light-scattering process effectively averages over a large particle population.

The theoretical and experimental results relative to the anomalous viscosity near a critical mixing point have recently been reviewed by Sengers.<sup>3</sup> It seems well established that a power-law divergence does not exist and, while the exact mathematical form is not understood, a logarithmic divergence is indicated. This has been supported by further recent work.<sup>4</sup>

The Brownian motion of particles in a critical mixture should reflect the anomalous viscosity<sup>1,2</sup> without involving a macroscopic disturbance during measurement. The effective viscosity  $\eta$  is obtained from the diffusion coefficient  $D$  by the equation due to Einstein:

$$D = k_B T / 3\pi d \eta, \quad (1)$$

where  $d$  is the diameter of the particles,  $k_B$  is Boltzmann's constant, and  $T$  is the temperature.

The use of autocorrelation spectroscopy to investigate Brownian motion has been discussed by Clark, Lunacek, and Benedek.<sup>5</sup> If the particles are monodisperse, the correlation function is given by

$$g(\tau, d) = A \exp(-\tau/\tau_c) + B, \quad (2)$$

where  $\tau_c$  is a function of particle diameter  $d$ ,

$$\tau_c(d) = (DK^2)^{-1} = 3\pi d \eta / k_B T K^2, \quad (3)$$

with  $K$  the scattering momentum transfer, and  $A$  and  $B$  are constants determined by factors such as count rate and scattering geometry. If one has a distribution of particle sizes specified by a distribution function  $f(d)$ , then the spectrum

takes the form

$$g(\tau) = \int_0^\infty dx f(x) g(\tau, x) / \int_0^\infty dx f(x). \quad (4)$$

In this work we assumed a Gaussian distribution of inverse particle size (i.e., a Gaussian distribution of  $\tau_c$ ) of the form

$$f(d) = D_0 \exp[-(d^{-1} - d_0^{-1})^2 w^2] \quad (5)$$

and performed a least-squares analysis with  $w$  and  $d_0$  as adjustable parameters.  $D_0$  is a normalization constant. Using this technique we were able to fit the spectrum typically to within 0.2% out to  $\tau \sim 5\tau_c(d_0)$ , where  $\tau_c(d_0)$  is given by Eq. (3).

The system chosen for this investigation was nitroethane-iso-octane (2, 2, 4-trimethylpentane)<sup>6-8</sup> which opalesces only weakly at the transition, because of the near perfect match of the refractive indices of the components. This choice was made to prevent the critical opalescence from masking the Brownian scattering. The critical parameters of this system were located by observation of the meniscus position as a function of temperature and concentration in a series of samples. We determined the critical concentration to be  $C_c = 47.8 \pm 0.4$  wt% nitroethane, and the critical temperature to be  $T_c = 30.8 \pm 0.4^\circ\text{C}$ . The location of these parameters by visual observations is difficult since the meniscus is very hard to see, hence the rather large uncertainties. The values of  $T_c$  and  $C_c$  agree with previous investigations.<sup>6-8</sup> The particles used were Teflon microspheres manufactured by the Dupont Company, and fractionated centrifugally in our laboratory. The Stokes diameter of the particles was measured by introducing them into pure nitroethane and performing the autocorrelation spectroscopy. Using available data<sup>9</sup> on the viscosity of nitroethane we found the mean particle size, from Eq. (5), to be  $d_0 = 0.31 \mu\text{m}$ , and the fractional width determined from the least squares ( $w/d_0$ ) to be 17%. The measurements in pure nitroethane and in the mixture were performed at the same scattering angle, which was  $59.7^\circ \pm 1^\circ$ .

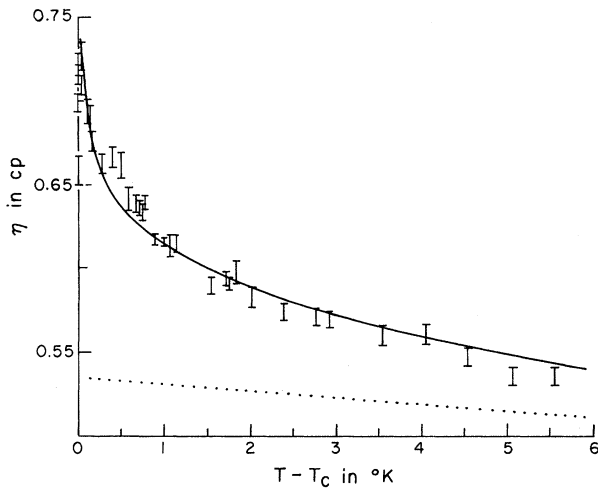


FIG. 1. Plot of the viscosity, in centipoise, versus temperature. The solid line is a logarithmic fit to the data,  $\Delta\eta/\eta_0 = 0.134 \log_{10}[0.083(T - T_c)]$ . The dotted line is an extrapolation of the background viscosity from temperatures greater than  $T - T_c = 7^\circ\text{C}$ ,  $\log_{10}\eta_0 = -1.175 + 286/T$ .

The  $0.31\text{-}\mu\text{m}$  particles had a slow settling rate, but it was significant enough to require that the sample be agitated approximately every two days to keep the particle distribution at the scattering volume from changing. It was then necessary to wait at least 7 h to allow larger, extraneous dust to settle out. We waited more than 10 h before beginning any measurements, and they were then very reproducible for a period of 2 days, with no evidence of significant coagulation during this period. The sample was agitated in this manner eight times during taking of the data shown in Fig. 1.

The temperatures were measured differentially by an uncalibrated platinum sensor and an ac Kelvin double bridge. Resolution was  $\pm 0.0001^\circ\text{C}$  and stability at each point was held to  $\pm 0.003^\circ\text{C}$ . The absolute temperature was known only to  $0.3^\circ\text{K}$ . The temperature gradient along the entire sample, of length 2 cm, including laser heating, is estimated to be less than  $0.005^\circ\text{C}$ .

The results are displayed in Fig. 1, graphed as absolute viscosity, with relative errors bars as determined by standard techniques from the least-squares procedure. As the transition is approached from above, the observed viscosity shows a logarithmic divergence (see Fig. 2), which seems to round off for  $T - T_c \lesssim 0.01^\circ\text{C}$ , but remains valid for  $0.01 < T - T_c < 7^\circ\text{C}$ . Below the transition it falls very sharply, probably as

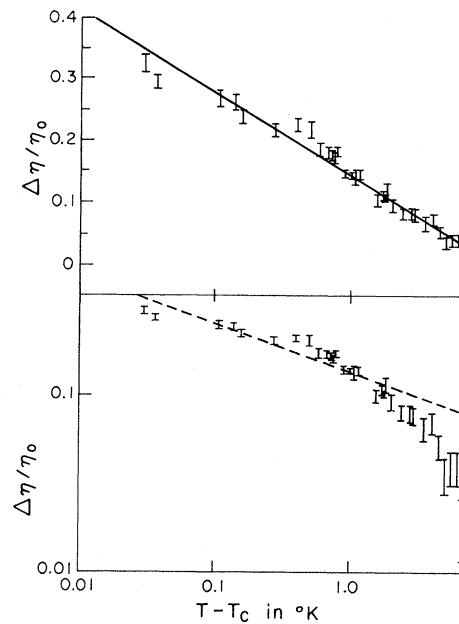


FIG. 2. Top, plot of the fractional anomalous viscosity  $(\eta - \eta_0)/\eta_0$ ; bottom, its log versus  $\log(T - T_c)$ . The semilog fit and the background viscosity are as in Fig. 1, and the log-log fit is  $\Delta\eta/\eta_0 = (T - T_c)^{-0.28}/6.86$ .

a result of the rapidly changing concentration of the phases. (The scattering volume is in the iso-octane-rich phase.) In the region  $T - T_c \lesssim 0.01^\circ\text{C}$  it is hard to say whether the rounding effect is real, indicating a nondivergent viscosity, or possibly caused by impurities, by temperature gradients, or by an error in the critical concentration. The latter is a distinct possibility since the critical concentration has been reported only to one-figure accuracy,<sup>6-8</sup> and there is considerable room for error in our determination.

As mentioned, BMM observed a drastic reduction in the mobility of their particles near the critical point.<sup>1,2</sup> In their study of the phenol-water system,<sup>2</sup> where the Brownian particles were "incidental dust particles," they observed the diffusion constant to decrease by a factor of 4. In later work<sup>1</sup> on the methanol-cyclohexane system they used fractionated glass-dust particles with  $d \approx 0.23 \mu\text{m}$  and found that the diffusion constant dropped by a factor of 2 at the transition. In both cases the observed change in "effective viscosity" was several times that found by more standard viscometric techniques, with the discrepancy still evident as far as  $0.1^\circ\text{C}$  from the transition. In marked contrast to these results, our data show a decrease in mobility of only

26% at the transition.

The results in the two systems investigated by BMM led Giterman, Likht, and Steinberg<sup>10</sup> to postulate a theory of "trapping" and "entrainment" of the particles by concentration fluctuations. In both of these systems, as well as the system treated in this work, it is possible to assume that the particles might interact more favorably with one component than with the other, resulting in an energy "well" at appropriate concentration fluctuations. The Teflon particles could interact more favorably with the polar nitroethane molecules; glass particles might interact more with methanol than with cyclohexane; and "incidental dust" particles might do anything. However, the large "anomalous mobility" observed by BMM<sup>1,2</sup> was significant for  $T - T_c$  as large as  $0.1^\circ\text{C}$ , where  $\xi \sim 0.1d$ , in which case it seems unreasonable that any actual entrapment could be occurring. Indeed, the result of the theory gives  $D \sim (T - T_c)^{1.33}$  while their data gave  $D \sim (T - T_c)^{0.2}$ . The explanation advanced by BMM, on the other hand, supposed the existence of a correlated layer of fluid at the surface of the ball, of thickness approximately  $\xi$ . They calculate the extra diameter needed to explain their results, and find it compares well with  $\xi(T)$ . Therefore, this explanation seems more plausible.

It should be the case, however, that such a "correlated layer" could be important only if the composition were substantially altered near the surface of the particle. This implies a strong interaction with the fluid components, and therefore should be specific to the system studied. It is significant in this regard that the more polar system<sup>2</sup> (phenol-water) showed a much larger effect, even though the particles used in that investigation were several times larger than in methanol-cyclohexane. We see, then, that our data need not be viewed as a contradiction of the results of BMM. Rather, it would seem that in our system the effects of a correlated layer, if present, are small, since we observed only a 35% increase in the viscosity, similar to that obtained by more standard viscometric methods in various binary liquid systems near the critical point.<sup>3</sup> Further evidence for this viewpoint is given by the logarithmic dependence of our data, as seen in Fig. 2, in agreement with a recent theory of the anomalous shear viscosity due to Perl and Ferrell.<sup>11</sup> That theory predicts

$$\Delta\eta/\eta_0 = A \ln Q_D \xi, \quad (6)$$

where  $\xi$  is the correlation length,  $Q_D$  is a Debye cutoff parameter, and  $A = 0.054$ . If we assume that  $\xi \sim (T - T_c)^{-5/8}$ , the results shown in Fig. 2, for the data in the range  $0.01 < T - T_c < 7^\circ\text{C}$ , give  $A = 0.093 \pm 0.004$ . On the other hand, if we fit the data for  $0.01 < T - T_c < 0.5^\circ\text{C}$ , we obtain  $A = 0.057 \pm 0.003$ , in good agreement with the theory.<sup>11</sup> The agreement with the theory for the shear viscosity in the critical region definitely lends credence to the view that the anomaly we have observed includes little if any effect of a surface layer. The data of BMM showed a definite power-law dependence, and so, since we observed a logarithmic dependence, it seems reasonable that the mechanisms could be different.

We plan to continue this investigation to obtain data on the dependence of the effect on the size of the particles. If the correlation length is causing significant errors in the measured viscosity, those errors should be greatly magnified for smaller particles. This should allow a more definite conclusion as to the problems outlined above. We also plan investigation of the effect of small changes in concentration, with a view to defining the critical parameters more precisely. The role of impurities is unknown at this point and will bear investigation. Data at higher temperatures are needed to improve the extrapolation of the background, since an extrapolation from  $T - T_c > 7^\circ\text{C}$  is not considered entirely satisfactory.<sup>12</sup>

With these reservations we conclude that our data support a logarithmic divergence in the shear viscosity, in agreement with the experimental results reviewed by Sengers.<sup>3</sup> We have ignored the wave-vector and frequency dependence of  $\eta$  since, for the *bulk* of the data used, the condition  $K\xi \ll 1$  is satisfied, as well as the condition  $DK^2 \ll S^*$ , where  $S^*$  is the linewidth for a concentration fluctuation of wave number  $\xi^{-1}$ . We further conclude that the "anomalous mobility" observed by earlier workers was not important in our work. The technique shows promise of further elucidating critical phenomena.

*Note added in proof.*—After submission of this paper it was brought to the authors' attention that Polonski and Chen have conducted a similar investigation at the Massachusetts Institute of Technology. This work is reported in N. Polonski, dissertation, University of Paris, 1970 (unpublished).

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## Electron Cyclotron Drift Instability Experiment\*

B. H. Ripin and R. L. Stenzel

*University of California, Los Angeles, California 90024*

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The electron cyclotron drift instability has been observed in a controlled, steady-state experiment. Enhanced noise bands are seen in the first two Bernstein wave dispersion branches. Dispersion, noise frequency dependence upon magnetic field and ion beam velocity, and saturation are demonstrated.

Recently, considerable theoretical attention has been focused on high-frequency microinstabilities which arise when an energetic ion beam traverses a plasma perpendicular to a magnetic field.<sup>1-6</sup> The interest is largely due to the fact that this situation occurs in fusion devices such as magnetic pinches,<sup>7</sup> in injection and heating schemes for fusion devices such as ion or neutral beam injection,<sup>8</sup> and may also occur naturally in space or in the ionosphere.<sup>9</sup> In this Letter we report the first laboratory experiment on an important instability of this type, the electron cyclotron drift instability.

The electron cyclotron drift instability is caused by the interaction of a fast ion beam with electron Bernstein waves when the beam velocity  $v_b$  approximately equals the wave phase velocity,  $v_p$ . We observe high-frequency noise spontaneously growing up to 45 dB above background noise in a band of frequencies above the electron cyclotron frequency  $f_{ce}$ , and peaking below the intersection of the beam velocity with the Bernstein wave dispersion relation. A second, though weaker, noise band is seen in the next higher branch of the dispersion relation ( $2 < f/f_{ce} < 3$ ). The frequency of

the enhanced noise band exhibits consistent behavior with magnetic field and beam velocity. The noise consists of plasma waves with phase velocities parallel to the beam, group velocity opposite to the beam ( $v_p \approx v_b$ ,  $v_g \approx -v_p$ ), and dispersion following closely the Bernstein wave dispersion relation. Test Bernstein waves are seen to grow against the beam. We see a spatial growth and saturation of the noise along the beam.

The experimental apparatus is shown in Fig. 1. A large plasma device (1 m diam  $\times$  2 m long) contains a steady-state ion source which projects a low-divergence ( $\theta \approx 1^\circ$ ) hydrogen ion beam, with cross section 5 cm perpendicular to  $\vec{B}_0$  and 10 cm parallel to  $\vec{B}_0$ , across a background plasma perpendicular to the magnetic field  $\vec{B}_0$ . The background plasma is produced by a dc discharge and/or ionization by the ion beam in hydrogen at  $p \approx 1$  mTorr ( $n_e \approx 10^8$  cm<sup>-3</sup>,  $kT_e \approx 0.6$  eV). The magnetic field is generated by a pair of internally mounted Helmholtz coils ( $B_0 \approx 150$  G, 24 cm diam) which preserves the quiescence of the background plasma ( $\delta n_i/n_e \approx 10^{-4}$ ) in the absence of the beam. The ion source contains a dc discharge with multipole containment<sup>10</sup> and electro-