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# ONSET OF LONG-RANGE ORDER IN A CRITICAL SOLUTION OF MACROMOLECULES*

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(Received 4 March 1966)

Diffusion broadening has been observed in the inelastic scattering of monochromatic light off a binary fluid, cyclohexane-polystyrene, near its critical point for mixing. The broadening a few tenths of a degree above the critical temperature is an order of magnitude less than in a binary mixture of small molecules (cyclohexane-aniline)[1] and two orders of magnitude less than in a pure fluid ($SF_6$).[2] The dependence of the broadening on scattering angle agrees with that found for the other fluids,[1, 2] and with expectation[3]; but its increase with rising temperature is less rapid than for these fluids, being less than linear in $\Delta T$.

The method used was substantially that of Benedek.[4, 2] A 12-mm diameter cylindrical sample of cyclohexane containing 6.5% by volume National Bureau of Standards standard 705 polystyrene, with narrow molecular-weight distribution,[5] was irradiated with monochromatic light at 6328 Å from a He:Ne laser. Light scattered at an angle $\theta$ with respect to the incident direction was detected at a photomultiplier, where interference between the different frequency components in the scattered light produced a fluctuating photoemission. The noise spectrum of the amplified photocurrent, with dc component suppressed, was analyzed into its frequency components using a spectrum analyzer (Nelson-Ross type 011) with a resolution of 10 Hz.

Photographs of typical spectra are displayed in Fig. 1. Each photograph shows the digitized average of the noise amplitudes obtained in about 100 sweeps through the spectrum, each of 8 sec duration. An ND-800 Enhancetron

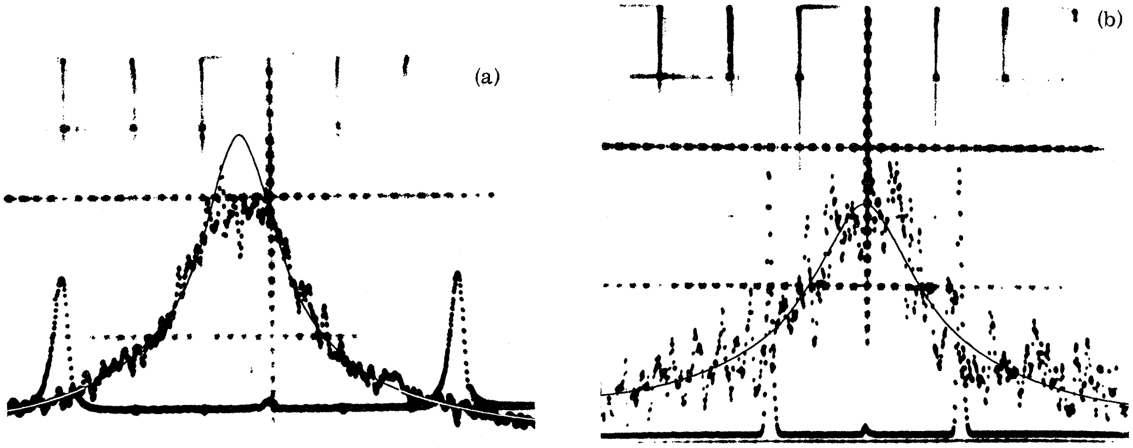

FIG. 1. Oscilloscope traces of digitized and time-averaged spectra of noise currents produced by the inelastically scattered light. (a) $\theta = 40°$, $T - T_S = 0.3°C$, marker pips at ±150 Hz. (b) $\theta = 80°$, $T - T_S = 4.0°C$, marker pips at ±1000 Hz. The solid curves are square-root Lorentzians fitted to the data. Suppression of low-frequency components and some drift of the heterodyne frequency of the spectrum analyzer account for the depression in the center of the narrower spectrum [part (a)]. Spectra obtained at $\theta = 20°$ and $\Delta T < 2°C$ are about as clean as that in (a), though narrower for small $\Delta T$ and therefore more susceptible to drift.

was used to perform the average.

The noise spectra have approximately square-root Lorentzian shape, as found for a pure fluid by Benedek and Ford,[2] and as required[2] for a Lorentzian spectrum of optical frequencies in the scattered light. The observed shape is consistent with exponential relaxation[3] of the fluctuations in concentration responsible for the inelastic scattering.

Assuming the scattered light has Lorentzian profile, its spectral width, or the reciprocal of the relaxation time multiplied by $\pi$, is equal to the half-width at half-amplitude of the detected noise current, divided by $\sqrt{3}$. (The noise current is proportional to the square root of the noise energy; the spectrum of the latter is Lorentzian, with half-width equal to the full width of the spectrum of the scattered light.[2]) The spectral widths deduced in this way from the observed noise amplitudes are displayed in Fig. 2. The data are for scattering angles of 20°, 40°, 80°, and for temperatures 0.05 to 30°C above the temperature $T_S = 24.28$°C $\approx T_{\text{crit}}$ at which the phases separated. The data may be represented approximately, as indicated by the solid lines in Fig. 2, by the semiempirical equation

$$\Delta\nu = 2.6[(2\pi/\lambda)\sin(\theta/2)]^2(T-T_S)^{0.6}\ \text{Hz}, \qquad (1)$$

in which $\lambda = 0.44$ is the wavelength of the light in the fluid, expressed in microns. In this equation the angular dependence is that expected theoretically for isotropic diffusion[3]; the coefficient 2.6 and the exponent in the temperature factor have been chosen arbitrarily. (They best fit the data for $\theta = 20°$ and $T-T_S < 16$°C.)

Although the agreement is not perfect, it is evident that the observed broadening conforms at least approximately to the $\sin^2(\theta/2)$ dependence expected theoretically. The observed dependence of the broadening on temperature, however, is not even approximately represented by linearity in $T-T_{\text{crit}}$, as expected on classical theory for small molecules[3] and shown by the dotted line in Fig. 2; rather, the breadth of the scattered line increases significantly less rapidly than linearly, the proportionality being more nearly to the square root of $T-T_S$.

No striking deviation from linearity in $T-T_S$ was observed for the intensity (dc component) of the scattered light. Within the range 0.1-2°C above $T_S$ the reciprocal intensity was found to vary approximately (within ~10%) as $2+17(T-T_S)$, $3.5+24(T-T_S)$, $5+20(T-T_S)$, in arbitrary units, at $\theta = 20°, 40°, 80°$, respectively.[6] The over-all dependence,

$$I^{-1}(\theta, T) = C(\theta)[0.38\sin^2(\theta/2) + (T-T_S+0.1)], \qquad (2)$$

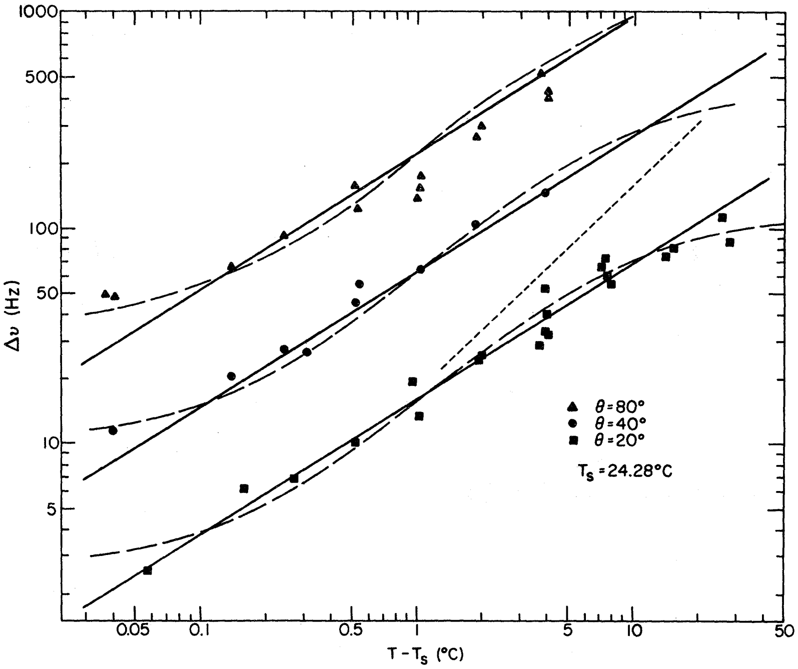

FIG. 2. Spectral width of the scattered light as a function of temperature and scattering angle. Dotted line indicates linearity in $T-T_S$. Solid lines are given in Eq. (2), dashed curves by Eq. (3).

agrees with that predicted by Debye[7] for a critical mixture with critical temperature $T_{\text{crit}} = T_S - 0.1°\text{C}$.[8]

Some decrease in the rate of growth of the spectral width of the scattered light can be expected at high temperatures, owing to the limit on disorder imposed by the finite extent of individual polymer molecules. These molecules, of average molecular weight $M = 180\,000$,[5] at infinite dilution have an end-end extension given by the empirical relation $L^2 \approx 0.47M$ ($\text{Å}^2$),[9] or radius of gyration $r = L/\sqrt{6} \approx 120$ Å. From the observations of Cummins, Knable, and Yeh[10] of the broadening for somewhat larger latex spheres suspended in dilute solution in water, the limiting breadth due to Brownian diffusion of spheres of this radius in cyclohexane (with viscosity 0.6 that of water) is found on extrapolation to be ~250 Hz for $\theta = 20°$, and larger in proportion to $\sin^2(\theta/2)$ for the other angles. The value thus estimated is considerably larger at $\theta = 20°$ than the ~100 Hz which seems to be approached experimentally at this angle at high $T$. The estimate is a crude one, however, and probably gives too large a value for the Brownian diffusion, and hence for the linewidth, as it neglects interactions between the polymer molecules. Such interactions are certainly significant in the nondilute solution used in our investigations.[11]

It is tempting, in view of the possible offset of $T_{\text{crit}}$ from $T_S$ and approach to a limiting $\Delta\nu$ at high $T$, to try to reanalyze the data in Fig. 2 assuming that the breadth at first increases linearly with $T - T_{\text{crit}}$, $T_{\text{crit}} \neq T_S$, then, far from $T_{\text{crit}}$, approaches a constant limiting value. If these features are combined by modifying Eq. (1) to read as follows:

$$\Delta\nu = 2.6\left(\frac{2\pi}{\lambda}\sin\frac{\theta}{2}\right)^2 \frac{T - T_c}{1 + 0.13(T - T_c)}\ \text{Hz}, \tag{3}$$

with $T_c = T_S - 0.15$, then as good a fit to the data is obtained (dashed curves in Fig. 2) as with Eq. (1). The offset assumed here, $T_S - T_{\text{crit}} = 0.15°\text{C}$, is consistent with that used in Eq. (2). The limiting breadth,

$$\Delta\nu \to 20\left(\frac{2\pi}{\lambda}\sin\frac{\theta}{2}\right)^2\ \text{Hz},$$

is not much greater than the breadth found experimentally at $T = 50°\text{C}$.[12]

In conclusion, the authors wish to thank Dr. D. McIntyre of the National Bureau of Standards for lending them the sample of polystyrene used in this experiment,[6] and Dr. C. O. Alley, Jr., of the University of Maryland for the opportunity to do this work in his quantum electronics laboratory.

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*Work supported in part under Advanced Research Projects Agency Contract No. SD-101 and National Aeronautics and Space Administration Grant No. NGR 21-002-022.

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[12] Equation (3) should not be assumed to apply for temperatures much above those used in our experiments.

For example, over large intervals of temperature noncompensating changes in viscosity and molecular extension might cause discernable changes in the Brownian diffusion and hence require the use of a "limiting breadth" which itself is a function of temperature.

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# QUANTUM RESONANCES IN THE AMPLIFICATION OF ULTRASOUND IN BISMUTH

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(Received 28 December 1965)

In this Letter experimental evidence is presented of ultrasonic amplification in bismuth subjected simultaneously to an electric and a magnetic field. Recently, an increase of 14 dB/cm in the amplitude of a 15-Mc/sec shear wave in bismuth with application of an electric drift field was reported.[1] However, it was not evident whether this figure represents a net gain in the electronic part of the ultrasonic interaction. In what follows, we have proven the existence of ultrasonic gain by observing "inverted" giant quantum oscillations, i.e., the maxima of ultrasonic attenuation[2] are converted into minima by the application of a suitable electric field. Estimated values of the de-attenuation caused by the electric drift field range around 85 dB/cm, the "net" gain referred to the attenuation at zero magnetic field being 18 dB/cm, at 223 Mc/sec.

The present experiment was carried out at 4.2°K with a single crystal of pure bismuth (resistance ratio $\rho_{300°\mathrm{K}}/\rho_{4.2°\mathrm{K}}=140$). The sample dimensions are $1.407\times0.389\times0.680$ cm$^3$, along the respective edge directions $\hat{\xi}$, $\hat{\eta}$, $\hat{\zeta}$ as given in Table I. The electric field $\vec{E}$ is applied along $\hat{\xi}$, the wave normal $\hat{q}$ of the ultrasound along $\hat{\zeta}$, and the magnetic field $\vec{B}$ can be rotated in the $\hat{\xi}$-$\hat{\eta}$ plane. Ultrasonic waves were generated and received by $Y$-cut quartz transducers (fundamental frequency 20 Mc/sec) with the direction of polarization along $\hat{\xi}$. We observed a longitudinal wave $L$ and two shear waves $S_1$, $S_2$ with apparent velocities of (2.14, 0.96, and 0.83)$\times10^5$ cm/sec, respectively, whereas the values calculated from the elastic constants[3] are (2.12, 1.37, and 1.04)$\times10^5$ cm/sec, respectively. The strong discrepancy of the shear wave velocities may be due to boundary reflections caused by the large deviations (≈34°) between wave normal and direction of energy flux.[4] The mode $L$ shows virtually no magnetoacoustic electronic interaction; $S_1$ is slightly and $S_2$ very strongly affected. The measurements described below refer to mode $S_2$ with $\sphericalangle(\vec{E},\vec{B})=\Theta=56°$.

Table I. Components of the unit edge vectors $\hat{\xi},\hat{\eta},\hat{\zeta}$ in the crystallographic coordinate system: $x$ = binary axis, $y$ = bisectrix, $z$ = trigonal axis.

| | $\hat{\xi}$ | $\hat{\eta}$ | $\hat{\zeta}$ |
|---|---|---|---|
| $x$ | −0.492 | −0.848 | +0.180 |
| $y$ | −0.636 | +0.495 | +0.580 |
| $z$ | +0.592 | −0.195 | +0.794 |

Figure 1 shows the received amplitude of $S_2$ at 188 Mc/sec as a function of the magnetic field strength. In curve $b$ no electric drift field

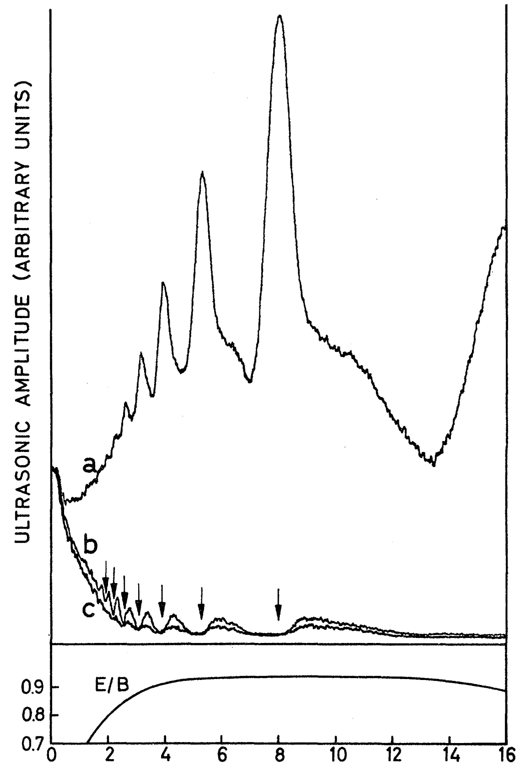

FIG. 1. Received amplitude of shear wave $S_2$ at 188 Mc/sec in bismuth as a function of magnetic field strength. $a$, $\vec{B}$ "normal," drift field applied; $b$, $\vec{B}$ "normal," without drift field; $c$, $\vec{B}$ "reverse," drift field applied. Lower curve: $E/B$ in units of $10^5$ cm/sec.