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BRILLOUIN LINEWIDTHS IN CO_2 NEAR THE CRITICAL POINT*

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We have measured the linewidth of light Brillouin scattered from CO_2 for $0.015 \leq T-T_c \leq 15°C$. As T_c is approached from high temperature, the linewidth increases rapidly but then saturates at $T-T_c \approx 1°C$ and remains roughly constant to $T-T_c = 0.015°C$. These results are discussed in the light of the dynamic scaling laws.

We report here measurements of Brillouin scattering from CO_2 near its critical point over the temperature range $0.015 \leq T-T_c \leq 15°C$ along the critical isochore. From these measurements we obtain the sound velocity, Brillouin linewidth, and ratio of the integrated intensity of the Rayleigh line to that of the Brillouin line. The new features we have found are the following: (1) The linewidth increases rapidly from $T-T_c = 15°$ to $T-T_c = 1°$ but then remains constant to $T-T_c = 0.015°$. (2) The sound velocity decreases to a constant value of 190 ± 3.6 m/sec as T approaches T_c at scattering wave vector $q = 2.18\times10^5$ cm^{-1}, a value about 5% larger than that found by Gammon, Swinney, and Cummins[1] at $q = 1.54 \times 10^5$ cm^{-1}. (3) The intensity ratio diverges as $(T-T_c)^{1.02\pm0.03}$ over the entire temperature range. The data for $(T-T_c) < 1°$ were obtained using a technique which is described here for the first time.

Several authors have reported observations of Brillouin scattering near the critical point in both one-component[1,2] and binary-liquid systems.[3] Measurements in the one-component systems have been limited to the temperature range $T-T_c > 2°C$ because the instrumental wings of the very intense Rayleigh component of the scattered light obscure the Brillouin components as the critical point is approached. In order to overcome this difficulty we have developed apparatus utilizing a Michelson interferometer with unequal optical path lengths to filter out the unwanted light. Using a path difference of 23 cm, the Brillouin component is transmitted with neligible loss while the Rayleigh component is attenuated by a factor of 60 or more.

Light from a stabilized, single-frequency, 6328-Å, He-Ne laser (Spectra Physics model 119) was scattered from a sample of Matheson research-grade CO_2 containing impurities of 2.5 ppm nitrogen and 0.6 ppm oxygen. The sample was held in a copper-jacketed stainless steel cell fitted with glass windows sealed to the cell by gold-plated stainless steel V rings. The oil bath surrounding the cell was temperature stabilized to ±0.001°C. The critical temperature was determined by observing the vanishing of the meniscus; $T-T_c$ measurements were made to an accuracy of ±0.003°C using a Leeds and Northrup platinum resistance thermometer. The cell was filled to the critical density by first over-filling and then allowing some CO_2 to escape so that the meniscus vanished at the critical temperature within 3 mm of the cell center. We measured the width of the Rayleigh line at several temperatures obtaining good numerical agreement with the results of Swinney and Cummins,[4] indicating that our density was the same as theirs. Light scattered through 166° was collimated by a conical window, filtered by the Michelson interferometer (at $T-T_c < 1.0$°C only), and analyzed by a piezoelectrically scanned Fabry-Perot interferometer with a free spectral range of 1970 MHz and an average finesse of 40.

The Fabry-Perot was swept once each second through a range large enough to include one Brillouin line and one Rayleigh line. Pulses from a cooled RCA 7265 photomultiplier were counted into the memory of a computer of average transients (TMC model 4606), whose addresses were swept in synchronism with the Fabry-Perot. Readout of the data accumulated in the computer memory on each sweep displayed the Brillouin line with a signal-to-noise ratio that increased as the square root of the number of sweeps. Except at $T-T_c = 0.015$°C, where the Brillouin component was significantly reduced by multiple scattering, an adequate signal-to-noise ratio was reached in 20 to 50 min. The narrow Rayleigh line gave an average instrumental line shape that was used in analyzing the Brillouin lines; furthermore, the Rayleigh line was intense enough to be observed directly on an oscilloscope, permitting the continuous monitoring of both interferometers. The spectra for several values of $T-T_c$ are shown in Fig. 1.

The ratio of the integrated intensity of the Rayleigh component to that of the Brillouin components is plotted as a function of $T-T_c$ in Fig. 2. Far from T_c the Michelson interferometer was not required, and the intensities of both lines were obtained from data collected during a single run. When the Michelson interferometer was used, two separate runs were made—one of about 3000 sweeps with the Michelson transmitting the Brillouin line, and a second of 25 sweeps with the Michelson transmitting the Rayleigh line and the laser intensity attenuated 10 to 100 times to avoid saturating the detection system. It can be shown[5] that the integrated intensity of a spectral line transmitted through the Michelson set with the maximum transmission at the center

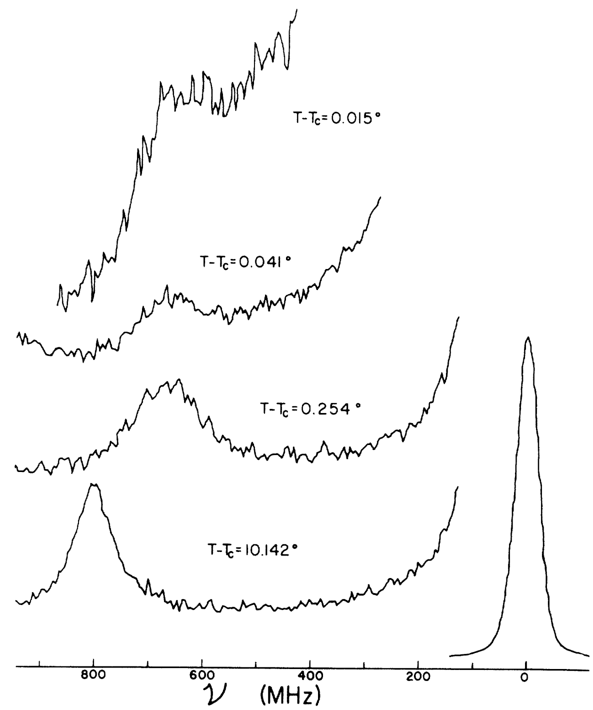

FIG. 1. Brillouin spectra of CO_2 near the critical point showing the Rayleigh line at reduced gain on the right. Data at the three lowest temperatures were obtained using a Michelson interferometer as a filter. Peak intensity of the Brillouin line is about 100 counts/sec.

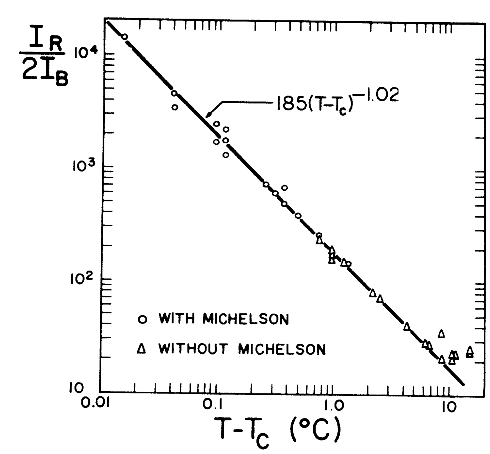

FIG. 2. Ratio of the integrated intensity of the Rayleigh component to that of the Brillouin components along the critical isochore.

frequency of the line is proportional to $\frac{1}{2}[1+\exp(-\Delta\omega_{1/2}\tau)]$, where $\Delta\omega_{1/2}$ is the half-width at half-maximum of the line and τ is the time required for light to travel the difference in path length between the two arms. To correct for this effect the measured ratios for data taken using the Michelson were reduced by 9.6%. At temperatures near T_c the intense scattering of light greatly increases the probability of multiple scattering which might be expected to influence the intensity-ratio data. Geometrical considerations show, however, that the collection efficiency of the conical collimating lens is more than 10^3 times as great for light scattered within 0.013 cm of the lens axis than for light scattered further from the axis. Since the laser beam was focused in the scattering region, we expect multiply scattered light to contribute negligibly to the measured intensity ratios. At high temperatures we expect the data to be less reliable because stray light may make up as much as 50% of the light scattered at the incident frequency, causing the Rayleigh peak to appear larger than it really is.

The natural width of the Brillouin component and the sound velocity are shown as functions of $T-T_c$ in Fig. 3. Linewidths were obtained by subtracting the instrumental width from that of the Brillouin line, an accurate procedure for lines fitted well by a Lorentzian shape. Linewidths obtained in this way should contain a negligible contribution due to either a finite acceptance angle or multiple scattering. The half acceptance angle of the detector is limited by the Fabry-Perot to 2.5×10^{-4} rad; the definition of the scattering angle was limited by alignment of the optical axes to 4×10^{-3} rad. These effects contribute an estimated 200 kHz to the measured Brillouin linewidth, far below the limits of resolution. Multiple scattering is not expected to influence the measured linewidths because of the low collection efficiency for light scattered off axis. The sound velocities were calculated from the frequency shift of the Brillouin line using $n=1.1077$ obtained from Straub's[6] results for the index of refraction of CO_2 at the critical density. The sound velocity for small $T-T_c$ shows very little temperature dependence; a linear least-squares fit to these data gives, for $T-T_c<1°C$,

$$c=190-1.6(T-T_c)\pm3.6 \text{ m/sec}. \qquad (1)$$

Recently, Kadanoff and Swift[7] have made predictions of the behavior of the transport coefficients near T_c using the scaling-law idea. We consider our results in the light of their predictions, assuming the divergences in C_p, C_v, and the order parameter ξ to be proportional to $\epsilon^{-\gamma}$, $\epsilon^{-\alpha}$, and $\epsilon^{-\nu}$, respectively, with $\epsilon=|(T-T_c)/T_c|$. Before discussing the transport coefficients we estimate these exponents from our intensity data and earlier experiments.

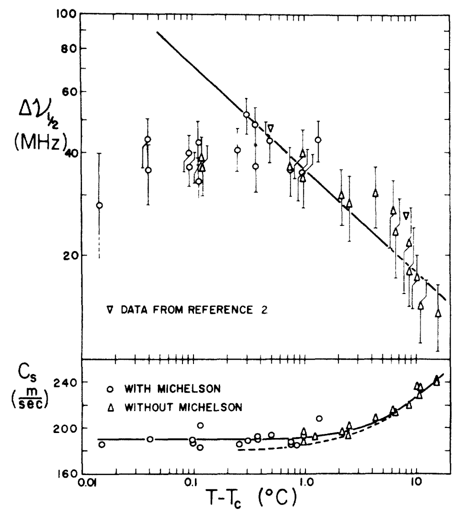

FIG. 3. Upper: Brillouin-line half-width at half-maximum. The solid line of slope −0.29 represents the contribution of λ/C_v in Eq. (2). Lower: Sound velocity calculated from Brillouin scattering at 166° using index of refraction data from Ref. 6. The dashed curve is taken from Brillouin scattering data at 88.6° from Ref. 1.

Standard treatment of the light-scattering problem[8] predicts that the ratio of the Rayleigh to Brillouin intensities is given by $I_R/2I_B=(C_p/C_v)-1$; this is strictly correct only if the sound velocity measured at the Brillouin frequency is equal to the sound velocity at zero frequency,[9,1] a condition that is not satisfied in our experiment. We can conclude only that the slope of the intensity ratio must lie between γ and $\gamma-\alpha$, $1.02\pm0.03\leq\gamma\leq1.02\pm0.03+\alpha$, in agreement with the value 0.95 ± 0.15 in Ref. 1. Combining this result with Swinney and Cummins's measurement of the thermal diffusivity, $\lambda/(\rho C_p)\propto\epsilon^{0.73\pm0.02}$, we find for the low-frequency divergence of the thermal conductivity λ $0.29\pm0.04\leq\theta\leq0.29\pm0.04+\alpha$ where $\lambda(0)\propto\epsilon^{-\theta}$. The prediction of Kadanoff and Swift for $\lambda(0)$ depends on whether the shear viscosity, η, is weakly divergent or strongly cusped at high frequency. They expect $\lambda(0)\sim\epsilon^{-\nu-\frac{1}{2}\alpha}$ if η diverges, and $\lambda(0)\sim\epsilon^{-\gamma+\nu}$ if η is cusped. If we assume that η does diverge, this yields 0.29

$\pm 0.04-\frac{1}{2}\alpha \leq \nu \leq 0.29 \pm 0.04+\frac{1}{2}\alpha$, which is quite low in view of the currently accepted value $\nu \approx \frac{2}{3}$. On the other hand, if η is cusped we have $\lambda \sim \epsilon^{-\gamma+\nu}$, and the thermal diffusivity, $\lambda/(\rho C_p)$, is proportional to ϵ^{ν}; measurements of thermal diffusivity in Ref. 5 give directly that $\nu = 0.73 \pm 0.02$, closer to the accepted value. We take this as evidence that η is cusped and not divergent at high frequency.

The standard hydrodynamic result for the Brillouin half-width at half-maximum is[7,8]

$$\Delta\omega_{1/2} = \frac{q^2}{2\rho}\left[\frac{4}{3}\eta(\omega) + \zeta(\omega) + \left(\frac{\lambda(\omega)}{C_v} - \frac{\lambda(\omega)}{C_p}\right)\right], \quad (2)$$

where ρ is the density and η and ζ are the shear and bulk viscosities evaluated at the frequency of the Brillouin line. Kadanoff and Swift define low-, intermediate-, and high-frequency regions separated by temperature-dependent boundaries. As they have summarized in Sec. IV of Ref. 7, $\lambda(\omega)$ is expected to diverge at low and intermediate frequencies as discussed above and to be at most weakly divergent at high frequencies; $\eta(\omega)$ is weakly divergent or strongly cusped at all frequencies, although the behavior may be different in the low- and intermediate- or high-frequency regions; and $\zeta(\omega)$ is expected to diverge strongly as $\epsilon^{\alpha-3\nu}$ at low frequency and $\epsilon^{-\nu+\frac{1}{2}\alpha}$ at intermediate and high frequencies. Using rough estimates of ζ and assuming that $\eta(\omega)$ is not too different from its low-frequency value, we expect to cross from the low- to intermediate-frequency regions at $T-T_c \approx 3°C$ and from the intermediate- to high-frequency regions at $T-T_c \approx 0.5°C$. Applying these results to Eq. (2) and neglecting the effect of η, at temperatures above $T-T_c \approx 3°$ we would expect to observe a divergence of the linewidth roughly proportional to $\epsilon^{-0.29}$ if the dominant contribution is from the $\lambda(\omega)/C_v$ term; if the $\zeta(\omega)$ term dominates, the divergence is much stronger, roughly ϵ^{-2}. Below $T-T_c = 0.5°$, the only divergence arises from $\zeta(\omega) \sim \epsilon^{-\nu+\frac{1}{2}\alpha}$. We do not observe the predicted high-frequency (low-temperature) divergence in the linewidth, possibly because the contribution from ζ, although divergent, is not large at $T-T_c \leq 0.015°C$. Taking this as an indication that the larger contribution is from λ/C_v, we would expect a slope of -0.29 at the higher temperatures as shown by the solid line in Fig. 3. A steeper slope is not ruled out, indicating that a strongly divergent low-frequency ζ contribution may be present.

From Eq. (1) at $T-T_c = 0.2°$, corresponding to a sound-wave frequency $\nu = 650$ MHz, we find the sound velocity $c(650\text{ MHz}) = 189 \pm 3.6$ m/sec. This value is to be compared with the Brillouin scattering results of Ref. 1 at the same temperature but at a different angle and hence a different frequency: $c(440\text{ MHz}) = 180 \pm 1.5$ m/sec. The difference between the two results, $c(650\text{ MHz}) - c(440\text{ MHz}) = 9 \pm 3.9$ m/sec, may be attributed to an internal relaxation frequency ν_R according to the relation

$$c(\nu) = c_\infty \frac{(c_\infty - c_0)}{1 + (\nu/\nu_R)^2}.$$

We find $\nu_R \approx 200$ MHz, much too large for molecular relaxation processes but lying approximately on the boundary separating the intermediate- and high-frequency regions of Ref. 7. The fact that this velocity dispersion apparently vanishes far from T_c provides additional evidence that it is not molecular relaxation but rather is characteristic of the critical region as has been suggested by Gammon, Swinney, and Cummins[1] for the larger dispersion between ultrasonic data and their hypersonic data.

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