BRILLOUIN SCATTERING IN CARBON DIOXIDE IN THE CRITICAL REGION*

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The velocity and attenuation of sound in fluids near the critical point have been studied extensively by traditional ultrasonic techniques.[1] The availability of stable single-frequency cw lasers now permits extension of these measurements to the hypersonic region by light-scattering experiments.[2]

In this Letter we report observations of the Brillouin scattering spectrum of CO_2 over a range of 0.2 to 6.0°C above T_c (the critical temperature) on the critical isochore and 0.1 to 8.0°C below T_c in the coexisting gas and liquid phases. The hypersonic velocities derived from the measured Brillouin shifts are compared with both observed and calculated low-frequency velocities. In addition, the observed relative intensities of the Rayleigh and Brillouin components provide new information on the critical divergence of the isothermal compressibility κ_T.

Experimental.—The spectra were obtained using a single-frequency 6328-Å He-Ne laser (either a 230-μW Perkin-Elmer model 5800 or a 130-μW Spectra-Physics model 119). The carbon dioxide sample cell was formed from thick-walled Pyrex tubing with a square inside cross section. It was filled within 0.8% of the critical density from a cylinder with less than 50 ppm impurities. The sample cell was suspended in an oil bath which was index-matched to the glass and temperature-controlled to ±0.01°C. Light scattered at an angle of 88.6° was analyzed with a pressure-scanned Fabry-Perot with a 10-cm etalon which gave a working resolution of 40 to 60 MHz. An ITT FW130 photomultiplier followed by photon-counting equipment formed the detection system.

Velocities.—Spectra of the liquid and vapor at $T_c - T = 1.12$°C are shown in Fig. 1. The vapor and liquid spectra were in all cases obtained at heights of +4.5 and −4.5 mm with respect to the meniscus. No variation in the spectrum was observed when the height was varied in a given phase. Note in Fig. 1 that the intensity of the Rayleigh component was approximately the same in the liquid and the vapor; this was always observed.

The closest approaches to the critical temperature were 0.1°C below T_c and 0.2°C above T_c, sufficiently far from T_c that density gradients were not a problem.[3] The absence of depolarized scattered light indicated that multiple scattering was not significant. Also, at 0.1°C above T_c a beam power more than 10 times that used in the data collection was required in order to see any sample-heating effect. As the critical temperature was approached, the intensity of the Rayleigh (central) component increased rapidly. As a result, the Brillouin components were ultimately lost in the instrumental wings of the Rayleigh component, even though the Brillouin shift was found to approach a nonzero value as $T \to T_c$. The high contrast of our Fabry-Perot (which has 98% reflecting $\lambda/100$ plates) enabled us to obtain spectra very near T_c as noted above.

The measured Brillouin shifts were converted to sound velocities using Straub's refractive-index data.[4] Our velocities are plotted in Fig. 2 along with those obtained in ultrasonic experiments.[5-8] We have also included theoretical values for the low-frequency sound velocity above T_c computed from thermodynamic data[9] using

$$v^2 = (c_p/c_v)(\partial p/\partial \rho)_T. \quad (1)$$

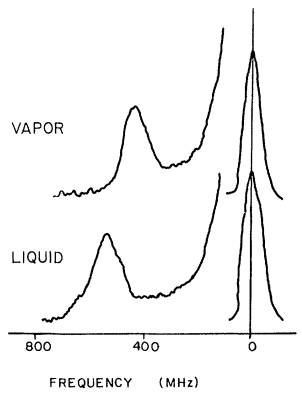

FIG. 1. Brillouin spectra on the liquid and vapor sides of the coexistence curve of carbon dioxide at $T_c - T = 1.12$°C. The Rayleigh components are on the right, and the Brillouin components are on the left at 100 times higher gain. The Brillouin component intensities were about 300 counts/sec. The scattering angle was 88.6°.

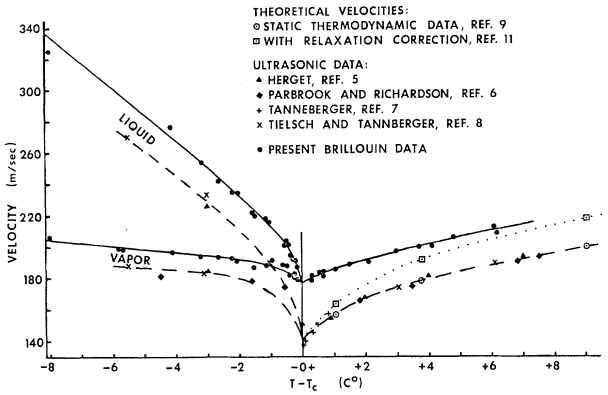

FIG. 2. The velocity of sound in carbon dioxide along the liquid and gas sides of the coexistence curve below T_c, and along the critical isochore above T_c. The dotted line in the region above T_c represents theoretical sound values including corrections for vibrational relaxation.

The theoretical values are seen to agree with the ultrasonic measurements.

The difference between the ultrasonic and light-scattering results is due, in part, to vibrational relaxation effects which have been studied by Henderson and co-workers.[10] The ultrasonic data were obtained at frequencies between 0.26 and 2.0 MHz, well below the 4- to 10-MHz relaxation frequency for densities near ρ_c. The Brillouin velocities, however, correspond to frequencies between 425 and 840 MHz, well above the vibrational relaxation frequencies. Thus, although Eq. (1) with static values of the parameters correctly predicts the ultrasonic velocities, predictions of the high-frequency velocities measured in Brillouin scattering require that c_p and c_v be corrected for the effect of vibrational relaxation. The ratio c_p/c_v must be replaced by $(c_p-c')/(c_v-c')$, where $c'=2.4$ cal/mole deg is the vibrational contribution to the low-frequency specific heat.[11] With this modification, Eq. (1) gives the dotted curve shown in Fig. 2.

For temperatures far from T_c the dotted curve approaches the extrapolated Brillouin observations, and the difference between ultrasonic and light-scattering results in this domain can thus be attributed to vibrational relaxation. As $T \to T_c$, both c_p and c_v diverge, and the effect of the essentially constant vibrational contribution c' becomes less and less important. The dotted curve thus approaches the ultrasonic curve as $T \to T_c$. Therefore, if the vibrational relaxation were the only difference between the ultrasonic and light-scattering experiments, our data should follow the dotted curve and merge with the ultrasonic data near T_c. The difference between our data and the dotted curve is presumably due to a structural relaxation arising from the relatively slow cluster formation associated with critical fluctuations. A closely related ultrasonic experiment by Chynoweth and Schneider revealed a similar but smaller velocity dispersion with frequency in xenon.[12] Our observations fit in with their phenomenological description of structure fluctuations with distributed relaxation times. Moreover, a structural relaxation in the critical region can also account for the large maximum in ultrasonic attenuation at T_c observed in ultrasonic experiments.[5,12,13]

Linewidths.—The Brillouin components were observed to have widths from $1\frac{1}{2}$ to 2 times the instrumental width which was given by the instrumental response to the very narrow Rayleigh line. The excess width, which was independent of temperature within the experimental resolution, was approximately 35 MHz in the vapor phases above and below T_c. Although some of this excess width was presumably due to attenuation associated with the observed velocity dispersion, an unknown fraction of it was produced by "smearing" of the Brillouin components due to the finite collection aperture. Thus our data only permit us to set an upper limit of about 35 MHz for the true full width at half-maximum. A higher precision experiment should, in principle, show a maximum in linewidth at or near T_c. In each spectrum the liquid linewidths were found to exceed the gas linewidths (see Fig. 1). At 0.5°C below T_c, where the liquid and gas Brillouin shifts are nearly equal, the difference which was 25 ± 5 MHz must be due to attenuation in the liquid.

Intensities.—The integrated intensity of the Rayleigh component, I_R, is proportional to $\kappa_T-\kappa_S$ (or c_p-c_v), and the integrated intensity of the two Brillouin components, $2I_B$, is proportional to κ_S (or c_v).[14] Further, the ratio $L_R/2I_B$, the Landau-Placzek ratio, is theoretically equal to $(c_p-c_v)/c_v$.[14] Since the Rayleigh component is produced by slow fluctuations and since $c_p \gg c_v$ in the critical region, L_R should vary as the static specific heat c_p, i.e., $L_R \propto |T-T_c|^{-\gamma}$ as $T \to T_c$. On the other hand, the Brillouin intensity must be evaluated at the frequency of the Brillouin shift and

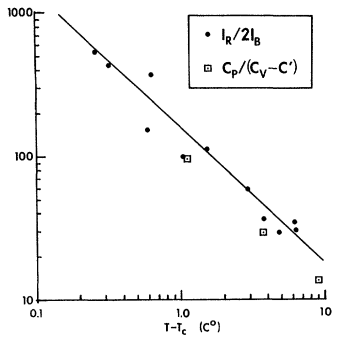

FIG. 3. Experimental values of $I_R/2I_B$ and thermodynamic data for $c_p/(c_v-c')$ vs $T-T_c$ on the critical isochore above T_c. The source of c_p and c_v is explained in Ref. 9; c' is from Ref. 11.

hence is proportional to the hypersonic specific heat c_v^{hs} (or κ_S^{hs}). Far from the critical point, $c_v^{hs}=c_v-c'$, where c' is the contribution from vibration. As $T\to T_c$, however, $\kappa_S^{hs}=1/\rho v_{hs}^2$ does not diverge since our data show that v_{hs} approaches a nonzero limit. This means that the divergence in the static c_v (or κ_S), which is proportional to $|T-T_c|^{-\alpha}$, affects the Brillouin intensity far from T_c but gradually relaxes out as $T\to T_c$. Thus we predict that $I_R/2I_B$ should diverge as $|T-T_c|^{-\varphi}$ with $\gamma-\alpha<\varphi\leq\gamma$.

Our observed values of $I_R/2I_B$ on the critical isochore above T_c, obtained by integrating the spectra, are plotted in Fig. 3 along with the ratio $c_p/(c_v-c')$ calculated from thermodynamic data.[9,11] The solid line is a least-squares fit to our data. The observed slope of 0.95 ± 0.15 is in agreement with the classical prediction $\gamma=1$, $\alpha=0$, and with recent density-gradient measurements in xenon by Wilcox and Balzarini.[15] Our result is in apparent disagreement with the value $\gamma=1.4$ found by Green, Vicentini-Missoni, and Levelt Sengers[16] in view of the currently accepted bounds for α of $0\leq\alpha\leq0.2$.

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