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LOW-FREQUENCY SOUND VELOCITY IN CO_2 NEAR THE CRITICAL POINT*

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We have used a standing wave technique to measure the velocity of ≈1-kHz sound waves in CO_2 near its critical point along critical and near-critical isochores. The measurements indicate the existence of a logarithmic divergence over several decades in $T-T_c$ for the adiabatic compressibility and the specific heat at constant volume along the critical isochore.

In recent years, calorimetric measurements by Bagatskii, Voronel', and Gusak,[1] Voronel' et al.,[2,3] Edwards, Lipa, and Buckingham,[4] and Moldover and Little[5] have revealed approximately logarithmic singularities in the specific heat at constant volume C_V at the critical points of Ar, O_2, Xe, and He. Such nonclassical behavior was first predicted by the exact solution to the two-dimensional Ising model[6] and is consistent with recent scaling-law equations of state.[7-9]

Related data on C_V near the critical point may also be obtained from sound-velocity measurements. For a single-phase system the low-frequency sound velocity u and the adiabatic compressibility κ_S are related by

$$\kappa_S=\rho^{-1}u^{-2}, \tag{1}$$

where ρ is the mass density of the fluid. The specific heat at constant volume C_V can then be calculated from κ_S using

$$C_V=T(\partial P/\partial T)_V{}^2[\kappa_S{}^{-1}V^{-1}+(\partial P/\partial V)_T]^{-1}, \tag{2}$$

where V is the specific volume, P is the pressure, and T is the temperature. As the critical point is approached along the critical isochore, $(\partial P/\partial V)_T$ becomes vanishingly small and

$$\lim(T\to T_c)\ C_V\to T(\partial P/\partial T)_V{}^2V\kappa_S. \tag{3}$$

Therefore, a logarithmic singularity in C_V at the critical point implies a similar singularity[10] in κ_S and vice versa. Logarithmic singularities in κ_S have been reported by Williamson and Chase[11] in He and by Van Dael, Van Itterbeck, and Theon[12] in Ar. We report here similar results in CO_2, for which previous sound-velocity measurements[13-16] as well as calorimetric measurements[17] of C_V do not allow definite conclusions concerning the critical exponents of κ_S and C_V.

To obtain accurate values for κ_S and C_V from sound velocity measurements in the critical region we took the following precautions: (1) Measurements were made over a reasonably large range of $T-T_c$. (2) The test cell was made as short as possible to reduce the effect of gravitationally induced density gradients. (3) Low frequencies were employed to avoid velocity dispersion due to relaxation effects. (4) Measurements were made at constant density to facilitate a slow and reproducible approach to the critical point (or the coexistence curve). The test cell, the sound-wave generating and receiving system, the pressure control and measurement system, and the temperature control and measurement apparatus, all of which were designed with the above criteria in mind, are described in detail by Feke.[18] The test cell consists of a 4.26-cm-high cylindrical cavity terminated at each end by a 0.5-in.-diam capacitor microphone. In the resonance technique used here requirements (2) and (3) above are, of course, in conflict. The desired low frequencies dictate the minimum height of the required cavity. The sound velocity u at a frequency f is obtained from a measurement of the fundamental longitudinal resonance frequency f of the cavity using

$$u(f)=2df, \tag{4}$$

where d is the acoustic length of the cell. In the region of critical density the resonance frequency of this cell fell from 2400 Hz at $T-T_c=10°C$ to a minimum of about 1200 Hz at the critical point. Such frequencies are well below the vibrational relaxation frequencies[19,20] of CO_2. Whether or not the velocities measured at these low frequencies are affected by other relaxation effects remains an open question.

When the critical point is approached along an isotherm, one tries to change the density by small amounts by varying the pressure. This is very difficult because of the extremely large isothermal compressibility of a fluid near its critical point. The advantage of approaching the critical point isochorically is that one may work with a closed cell which is not distrubed mechanically as the temperature is lowered by incremental cooling. In our measurements we filled the cell at 40°C (9°C above the critical temperature) to the desired density (±0.001 g/cm^3) using a commercial high-precision pressure gauge to measure the filling pressure. The corresponding density was calculated from PVT data.[21] The cell was then sealed and sound-velocity measurements were carried out at the desired temperatures. The absolute temperature was measured to ±0.001°C using a platinum resistance thermometer. In addition, a commercial quartz thermometer was used to enable us to measure relative temperature changes of the order of a few ten-thousandths of a degree.

With average filling densities between 0.45 and 0.48 g/cm^3, minima in velocity ranging between 107 and 114 m/sec have been observed at temperatures between 31.04 and 31.12°C. These results are shown in Table I. The actual velocity versus temperature behavior for a density of 0.467 g/cm^3 is shown in Fig. 1. Using this and similar velocity data we have plotted in Fig. 2 the temperature dependence of κ_S calculated from the measured sound velocity at densities of 0.467 and 0.469 g/cm^3 (two independent runs at essentially critical density; $\rho_c = 0.468$ g/cm^3) and at 0.482 g/cm^3. For the purpose of these plots T_c was taken to be, in each case, the temperature at which the minimum velocity was observed. The graph in Fig. 2 indicates the existence of a logarithmic singularity in κ_S as the critical point is approached along the critical isochore. This logarithmic behavior seems to extend from $T-T_c \sim 20$°C to $T-T_c \sim 0.02$°C. The behavior for a density of 0.482 g/cm^3 seems to be logarithmic over a much smaller temperature range.

Table I. Measured velocity minima in CO_2.

Average density (g/cm^3)	Velocity minimum (m/sec)	Temperature (°C)
0.45[a]	109	31.04
0.467	110	31.11
0.469	111	31.06
0.469	112	31.08
0.47[a]	107	31.11
0.47[a]	114	31.09
0.470	110	31.08
0.472	114	31.04
0.482	108	31.12

[a] These results were obtained with commercial grade CO_2; the other runs were obtained with research grade CO_2.

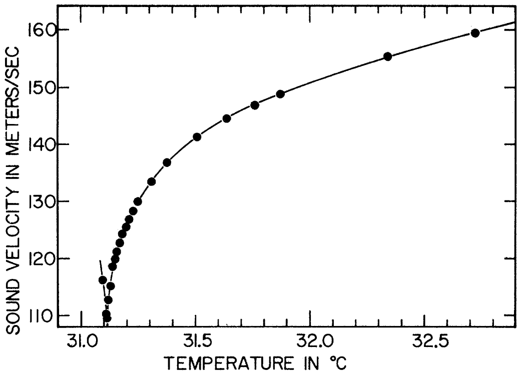

FIG. 1. The velocity of sound in CO_2 at a density of 0.467 ± 0.001 g/cm^3 as a function of temperature in the one-phase region.

The solid line in Fig. 2 represents a least-squares fit to the experimental compressibility at critical density between $T-T_c = 20$°C and $T-T_c = 0.02$°C. The equation of this line is

$$\kappa_S = -0.5518 - 1.715 \ln[(T-T_c)/T_c], \qquad (5)$$

where $T_c = 304.20$ K (the generally accepted value) and κ_S is in units of 10^{-9} cm^2/dyn. In the lower part of Fig. 2 are presented the values of C_V

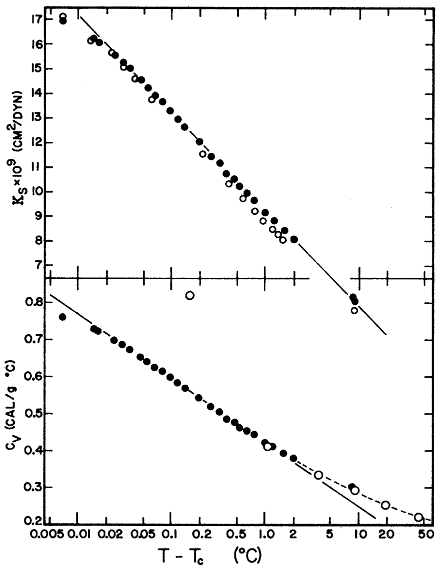

FIG. 2. The adiabatic compressibility κ_S and the specific heat at constant volume C_V of CO_2 as a function of $T-T_c$. The solid circles represent the values calculated from our velocity measurements at critical density (two separate runs at 0.467 and at 0.469 g/cm^3). The small open circles represent the compressibility for a density of 0.482 g/cm^3. The large open circles indicate the calorimetric specific-heat measurements of Michels and Strijland. The solid lines show the logarithmic behavior of κ_S and C_V discussed in the text.

calculated from Eq. (2) using our measured velocities on the critical isochore and the data for $(\partial P/\partial T)_V$ and $(\partial P/\partial V)_T$ from Ref. 21. As indicated, these calculated values of C_V are in excellent agreement with the experimental measurements of C_V of Michels and Strijland.[17] Their anomalously high C_V measured at $T-T_c=0.16°\mathrm{C}$ is probably due to the relatively large temperature increments used in their calorimetric technique. The graph indicates logarithmic behavior of C_V for $0.02°\mathrm{C}<T-T_c<1°\mathrm{C}$. The solid line in the lower part of Fig. 2 represents the least-squares fit to the calculated C_V data in the above temperature range:

$$C_V=-0.005\,014-0.075\,10\ln[(T-T_c)/T_c] \qquad (6)$$

with C_V in units of cal/g °C. The behavior for $1°\mathrm{C}<T-T_c<50°\mathrm{C}$ is of the form $(T-T_c)^{-0.16}$.

Figure 2 indicates that the experimental points begin to deviate from logarithmic behavior for $T-T_c$ less than 0.02°C. In this region, the measured velocities were higher than one would expect from a continuation of logarithmic behavior. This can be understood in terms of gravitationally induced density gradients.[12] From visual observations in CO_2 by Lorentzen[22] and by Schmidt[23] we conclude that close to the critical temperature the density may vary by 10% over the height of our test cell. Since our technique effectively yields the acoustic travel time through the cell, each of the velocity minima listed in Table I represents an averaged value of the velocity which is necessarily higher than the true velocity for small values of $T-T_c$.

From our velocity measurements we conclude that in CO_2, κ_S shows a logarithmic singularity for $\epsilon=(T-T_c)/T_c<3\times10^{-2}$ and for $T>T_c$ along the critical isochore. Furthermore, from these velocity measurements and thermodynamic data we deduce that C_V behaves logarithmically as a function of $T-T_c$ for $\epsilon<3\times10^{-3}$, although behavior of the form $C_V\sim(T-T_c)^{-\alpha}$, with α small but not zero, cannot be ruled out if the region $\epsilon<2\times10^{-4}$ is considered separately. We also suggest that low-frequency velocity measurements provide a way of obtaining meaningful values of C_V in the vicinity of the critical point where precise calorimetric measurements are ruled out because they involve measuring an average C_V over some temperature interval.

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SURFACE MODES OF VIBRATION IN MONATOMIC CRYSTALS*

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In computer-experimental studies of surface vibrations in monatomic crystals, surface modes of a new type have been found near the Brillouin zone boundary in gaps between bands of different kinds of bulk modes (e.g., longitudinal and transverse). Other surface modes, including Rayleigh waves and extra high- or low-frequency modes when adsorbed films are present, have also been found and investigated.

There have been many studies of surface vibrational modes in elastic continua and simple one-, two-, and three-dimensional crystal models. Three basic types of surface modes have been obtained in these calculations: Rayleigh modes,[1] optical surface modes in diatomic systems, and extra high- or low-frequency surface modes produced by adsorbed atoms or by a macroscopic layer of one material lying on a substrate of another material.

Here we report what are thought to be the first studies of surface modes in realistic monatomic model crystals.[2] In addition to Rayleigh modes, which are present for wave vectors throughout the two-dimensional Brillouin zone associated with the surface, other surface modes have been found which exist only for wave vectors in parts of the zone, near the zone boundary. These modes may have frequencies below those of all the bulk modes (in that part of the Brillouin zone), or they may fall in a gap[3] between bands of different kinds of bulk modes (e.g., transverse and longitudinal modes). To our knowledge, no such modes have been obtained in previous calculations.[4]

The present study is part of a program to investigate surface vibrations in model crystals whose atoms interact through realistic pair potentials. The method of calculation has been described previously[5] and detailed results of the present study will be published elsewhere. Here we describe only the most interesting qualitative results for the (111) surface of an fcc crystal.

In Fig. 1(a) the frequency versus wave-vector relations are shown for two symmetry directions and the edge of the Brillouin zone. The labeling of the symmetry points is shown in Fig. 1(b). It can be seen in Fig. 1(a) that the three bulk bands, which correspond roughly to one longitudinal and two transverse modes, show gaps in some parts of the Brillouin zone, near the zone boundary. In these gaps it is possible for surface modes to exist, and in fact, such modes are present. There is one surface mode[6] (for a given two-dimensional wave vector) in the large gap on the left and another, which is limited to a very small region near the $\bar{K}$ point, in the smaller gap on the right. That these modes are in fact localized near the surface has been determined by examining the associated eigenvectors. The eigenvectors also show that these modes correspond to vibrations primarily parallel to the surface, whereas the Rayleigh modes are associated with vibrations primarily perpendicular to the surface. The results shown in Fig. 1(a) are for a crystal with surfaces which is 11 layers thick. In Fig. 1(c) the curves along the zone boundary are given for a crystal 21 layers thick; it can be seen that the only important effect of increasing the thickness of the crystal is to populate the bulk bands more densely, and that the surface modes are virtually unchanged.

In addition to the surface modes in the "band gaps" mentioned above, there are Rayleigh modes throughout the Brillouin zone with frequencies lying beneath all three of the bulk bands, as can be seen in Figs. 1(a) and 1(c). In a crystal with two surfaces, there are two such modes which are nearly degenerate near the edge of the zone but which split near the origin.[6]

The case of an adsorbed monolayer of light or heavy atoms has also been studied. The results in the case of a very light layer (1:5 mass ratio) are shown in Fig. 1(d). There are no low-frequency Rayleigh modes at the zone boundary, but three extra high-frequency surface modes are