Low-frequency sound velocity near the critical point of xenon*

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(Received 4 February 1974)

By measuring the resonant frequency of an azimuthal mode in a horizontal annular resonator, it was possible to determine the sound velocity in xenon at ~1 kHz without difficulties caused by gravity-induced density gradients near the critical point. It was shown that the resulting velocity data along the critical isochore above T_c and in the coexisting vapor below T_c correspond to the thermodynamic (zero-frequency limiting) values. The experimental data were fitted with a theoretical curve based on the linear-model parametric equation of state, and the resulting value of 0.08 for the critical exponent α is in good agreement with the value determined previously from specific-heat data.

I. INTRODUCTION

Low-frequency sound-velocity data in the critical region provide direct and important information about the critical behavior of the thermodynamic properties.[1] The "static" velocity $u(0)$, which corresponds to the zero-frequency limit of measurements made at sufficiently low frequencies, is given by

$$u^2(0)=\frac{1}{\rho\kappa_S}=\frac{1}{\rho\kappa_T}+\frac{T(\partial P/\partial T)_v^2}{\rho^2 C_v}. \qquad (1)$$

Since the isothermal compressibility κ_T diverges much more strongly (like $\epsilon^{-\gamma}$) than the adiabatic value κ_S, the behavior of $u^2(0)$ near the critical point is dominated by the variation in the constant-volume specific heat C_v. Thus the analysis of velocity data along the critical isochore as a function of the reduced temperature $\epsilon=(T-T_c)/T_c$ can provide a value of the critical exponent α. Indeed, this exponent can be determined more easily from acoustic than from traditional calorimetric measurements.

A knowledge of the static velocity is also crucial for acoustic investigations of the dynamics of critical fluctuations. At higher frequencies there is considerable velocity dispersion $[u(\omega)-u(0)]$ and critical attenuation.[2-5] Analysis of such results in terms of the mode-mode coupling theories[6] of Kawasaki and Mistura requires accurate values of $u(0)$. For further details, see the preceding paper.[5]

Previous measurements,[7] utilizing the longitudinal modes of a cylindrical resonant cavity, were limited to frequencies above ~7 kHz since a short cell was needed to minimize gravity effects. In addition, it was not possible to obtain data in the individual coexisting phases below T_c since the meniscus formed in the center of the cavity. These difficulties have been overcome with a new cell design which employs the azimuthal resonant mode in a horizontal annular resonator.

This new resonator has been used at ~1 kHz to obtain data along a near-critical isochore and in the coexisting vapor. The results are compared with well-established 1-MHz velocity data and with theoretical predictions based on a linear-model parametric equation of state.

II. EXPERIMENTAL DESIGN AND RESULTS

The experimental cell, consisting of an annular acoustic resonator mounted in a brass pressure vessel, is shown in Fig. 1. This resonator is a modified version of the resonator first used by Kojima to study persistent currents in liquid helium.[8] The use of azimuthal modes in an annular resonator for low-frequency velocity measurements has several advantages in comparison with longitudinal modes in a cylindrical plane-wave resonator. Long acoustic path lengths (and thus low frequencies) can be achieved with short vertical heights; this allows one to minimize both the effects of dispersion and gravity-induced density gradients near the critical point. For example, in comparison with the resonator of Kline and Carome,[7] our resonator provides a pathlength which is 11 times longer with a vertical height which is 40% less. Furthermore, it is not necessary to make cavity end corrections when an azimuthal mode is used, and the geometry is such that this mode is well separated from other resonant modes of the annulus. Finally, it is possible to investigate each of the coexisting phases below T_c. In our design, small drainage holes were drilled in the bottom of the annulus (not shown in Fig. 1). This allowed liquid to drain out of the resonator, and measurements were made on the coexisting vapor phase down to 14.7°C. By inverting the cell one could have studied the coexisting liquid, but this was not done in the present investigation. (A few isolated points in the liquid

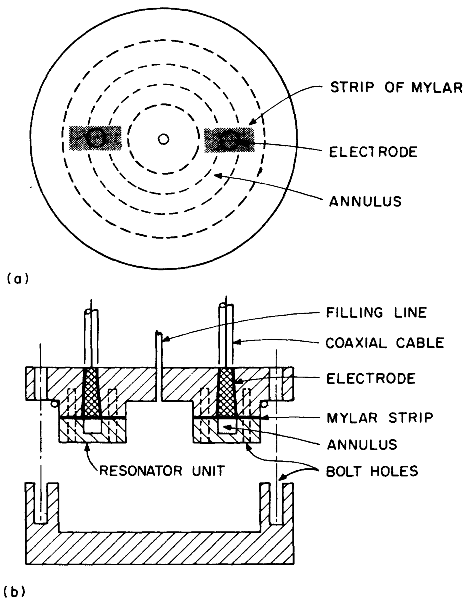

FIG. 1. Schematic diagram of the experimental cell. (a) Top view with bolt holes and electrical connections omitted; (b) cross-sectional view.

phase were obtained by adding xenon just below T_c so as to almost fill the cell with liquid.)

The resonator unit was made of copper and had an annulus with an i.d. of 4.03 cm, an o.d. of 5.03 cm, and a height of 0.37 cm. The cover of the pressure vessel contained two 5-mm-diam copper electrodes located 180° apart. These tapered electrodes were mounted in the cover with Stycast epoxy cement which provided both electrical insulation and a pressure seal. The transmitter and receiver transducers were identical solid dielectric capacitors and could be interchanged. Each transducer consisted of a 6-mm-wide strip of 0.0005-in.-thick Mylar film which was metallized with a gold coating on one side. A Mylar film was placed over each electrode button, and the resonantor was then bolted into position on the bottom of the cover plate. The electrode surface and the gold coating form a parallel-plate capacitor with the Mylar as the dielectric medium. The surface of the electrode was not highly polished; indeed it was purposely roughened with 60-grit sandpaper. This surface roughness is important at high pressures in obtaining the proper motion of the Mylar film in response to either an applied ac voltage (driver) or an acoustic pressure wave (receiver). In operation, the transducers were biased with a dc voltage in the range 100–250 V; the optimal value was ~180 V. Such a bias voltage is required to charge the receiving capacitive transducer so that a change in voltage will occur when the sound wave causes a variation in the Mylar-electrode spacing. For the drive transducer, a bias voltage is not necessary but was desirable in our case (where direct electrical pickup was low). The mechanical force developed at the driver is proportional to the square of the applied voltage. Thus for an applied electrical signal $V_0 + V_1 \sin\omega t$, where $V_0 > V_1$, the principal mechanical oscillation is at frequency ω. The weaker mechanical component at 2ω is filtered out by the receiving electronics.

When the cover was bolted to the body of the pressure vessel (using a lead O-ring to make the seal), there was a small gap just below the resonator unit so that the annulus was freely connected, via the drainage holes, to the "well" in the center of the cell. The filling line with shut-off valve connected directly to this well. The pressure vessel and valve were immersed in a large, well-regulated oil bath. This bath, the gas-handling apparatus, the xenon sample itself, and the temperature control and measurement procedures were all the same as those used in Ref. 5. The pressure cell used in this experiment was considerably less massive than the one used in Ref. 5 and was therefore more susceptible to short-term temperature cycling of the bath. The temperature stability during a measurement was approximately ±2 mK.

The electronic components used for the acoustic measurements were a GR 1900A wave analyzer, a Krohn-Hite DCA-10R power amplifier for the drive transducer, a PAR CR-4 preamplifier for the received signal, and a GR 1192B frequency counter. The resonant frequencies of the azimuthal (or circumferential) modes were related to the sound velocity u by

$$u = \lambda f = 2\pi \bar{r} f / m , \tag{2}$$

where $\bar{r}$ is the average radius of the annulus and m is an integer which indexes the modes ($m = 1$ is the fundamental, $m = 2$ is the second harmonic, etc.). For our resonator $2\pi\bar{r} = 14.23$ cm, and a negligible error was introduced by using Eq. (2) rather than the much more complicated exact solution for a track of finite width.[9] The resonant frequency can be measured with an accuracy of 0.2% far from T_c and 1% near T_c, and the observed f values are reproducible within those limits over a period of about 15 min. At several temperatures above T_c, measurements were carried out for modes with $m = 1$, 2, 3, and 4. The velocity values obtained from frequencies associated with different m values agreed with each other within the limits of experimental error, and there was no systematic trend to the variation of u with m. Thus there was no experimental indication of dispersion over the range from ~600 Hz to ~3 kHz. The strongest signals and best signal-to-noise ratios were obtained with the second harmonic. Therefore all the final data on the variation of u with temperature were obtained with the $m=2$ mode. The frequency of this mode varied from ~1 kHz near T_c to ~1.7 kHz at $T-T_c=+2.7°$ and $-1.8°$.

The results of two independent runs are shown in Fig. 2, where the velocity along the critical isochore above T_c and in the coexisting vapor below T_c is given as a function of $T-T_c$. Each run was obtained on a separate filling of the cell. The filling procedure was to maintain the cell temperature at about 17 °C (i.e., $\Delta T \simeq 0.3°$) and adjust the amount of xenon to obtain a minimum velocity. Then the cell was heated to about 20 °C and allowed to equilibrate for several hours. The velocity was measured and compared with an interpolated 1-MHz value[4,5] along the critical isochore at that temperature. If the values were in good agreement, as they should be that far from T_c, it was assumed that a critical filling density had been achieved[10] and a run was made by monotonically lowering the temperature. After each change in the bath temperature (usually less than 0.1° far from T_c and often less than 0.02° near T_c) the cell was allowed to equilibrate for at least 15 min far from T_c and for 30–60 min near T_c before measurements were made. The temperature corresponding to the minimum in the sound velocity (i.e., the critical temperature) was 16.70 °C for each of these runs. This value should be compared with $T_c=16.64$ °C obtained from the dielectric data in Ref. 5 and values of T_{min} between 16.67 and 16.79 °C reported by Kline and Carome.[7]

III. DISCUSSION

On the basis of the mode-mode coupling theory and the experimental dispersion results reported in Ref. 5, it can be demonstrated that the velocity data shown in Fig. 2 correspond to the zero-frequency limiting values $u(0)$. The experimental resonance frequency of ~1.1 kHz near T_c leads to a reduced frequency $\omega^*=\omega/\omega_D$ of 1.1 and 0.05 at $\Delta T=10$ and 50 mdeg, respectively (see Ref. 5). Thus the dispersion $\Delta u = u(1.1\text{ kHz}) - u(0)$ will be 2.8 m sec^{-1} at $\Delta T=10$ mdeg and 0.2 m sec^{-1} at $\Delta T=50$ mdeg. The latter value is comparable with the experimental uncertainty in the u values.

As indicated in Fig. 2, the kilohertz velocities sufficiently far from T_c are in very good agreement with the well-established velocities at 1 MHz.[4,5] This agreement extends to higher temperatures than those shown in the figure; for example, at $\Delta T=4.78°$, $u(1\text{ MHz})=128.95\pm0.15$ m sec^{-1} and $u(1.8\text{ kHz})=129.0\pm0.1$ m sec^{-1}. It is obviously necessary that the 1-MHz values used in such comparisons should themselves be free from critical dispersion. As an example, $\omega^*\simeq 0.03$ for the 1-MHz point at $\Delta T=1.78°$ and the dispersion $u(1\text{ MHz})-u(0)$ is only 0.1 m sec^{-1}. Naturally, 1-MHz data closer to T_c will show appreciable dispersion (see Fig. 6 of Ref. 5).

Although it is not indicated in Fig. 2, our data

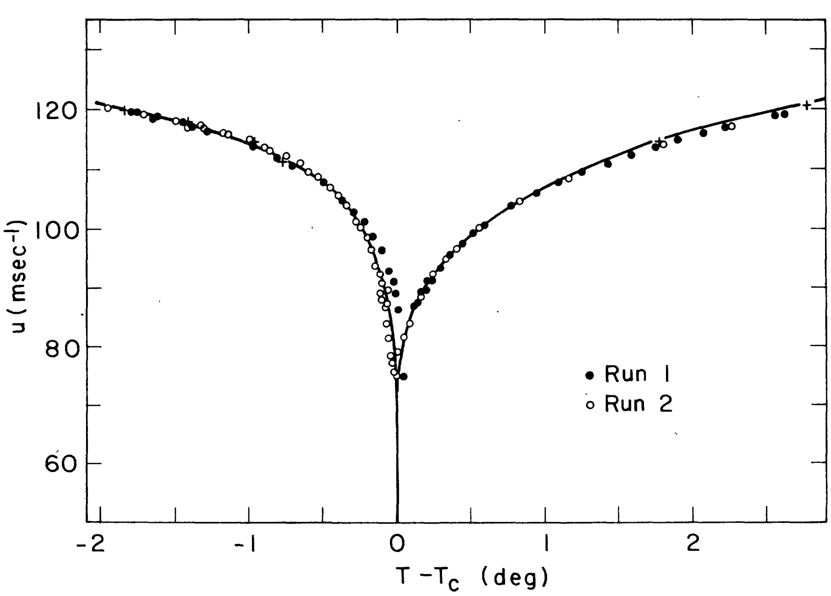

FIG. 2. Low-frequency sound velocity in xenon. Open and filled circles represent data obtained at ~1 kHz for two runs in the annular resonator. Crosses represent data obtained at 1 MHz in Refs. 4 and 5. Data above T_c are for the critical isochore, and data below T_c are for the coexisting vapor. The line represents a least-squares fit to these data using a theoretical expression derived from a linear-model parametric equation of state.

above T_c are also consistent with the ~8-kHz velocity values of Kline and Carome[7] if the latter are systematically corrected. It is shown in Ref. 4 that the Kline-Carome velocities over the range $\Delta T = 3°$ to $8°$ are high by the approximately constant amount of 1.4 m sec^{-1}. This is presumably due to the fact that no corrections were made for cavity end effects in their plane-wave resonator. (Kline and Carome state that their absolute velocity could easily be in error by 1%.) In the range $\Delta T = 0°$ to $2.5°$, the Kline-Carome u values lie parallel to our present values but high. Correction by either subtracting 1.4 m sec^{-1} or multiplying their values by 0.985 will produce good agreement. Thus the basic shape of the temperature variation in $u(0)$ is the same in both experiments.

It should be noted with regard to Fig. 2 that there is a considerable difference between the data points from runs 1 and 2 just below T_c. Data in the range $-0.2° \leq \Delta T \leq 0°$ are less reliable than elsewhere; equilibration is very slow in this region and adequate time may not have been allowed. However, below $\Delta T = -0.2°$ the internal agreement is good and there is no doubt that the sound velocities correspond to the coexisting vapor. For $\Delta T < -1°$ there are substantial differences between the velocities in the vapor and liquid phases (see Fig. 6 of Ref. 5), and a few isolated data points obtained with the cell completely filled with liquid gave good agreement with the 1-MHz data in the coexisting liquid.

The linear-model parametric equation of state[11] has been used by Hohenberg and Barmatz[12] to examine gravity effects in fluids near their critical point. The resulting analysis for a cell 0.5 cm high indicates that appreciable gravity effects are important above T_c only when $\epsilon \leq 2\times10^{-4}$, which corresponds to $\Delta T \leq 60$ mdeg in xenon. Very few of our data points are that close to T_c, and no attempt has been made to apply a gravity correction. The effect of gravity is somewhat greater below T_c, and density gradients may have been responsible for the greater uncertainty in the data just below T_c.

In conclusion, we shall analyze these new experimental $u(0)$ values in terms of behavior expected from the linear-model parametric equation of state and shall determine the critical heat-capacity exponent α. The details of this calculation, including the manner in which numerical values were obtained for the various adjustable parameters, are given in Ref. 5 and will not be repeated here. In essence, the free energy per unit volume is represented by

$$A(\rho, T) = A_s(\rho, T) + \mu_0(\rho_c, T)\rho + A_0(T), \qquad (3)$$

where the *singular* part A_s can be written in terms of the parametric variables r and θ (with r being essentially the radial distance from the critical point and θ describing the angular position in the ρ, T plane). The term A_s leads to the singluar heat-capacity term C_v^{sing} which diverges like $r^{-\alpha}$. The nonsingular free energy terms $\mu_0\rho$ and A_0 are represented by Taylor series expansions in the reduced temperature ϵ, and these terms contribute to the background heat capacity C_v^{back}. The total heat capacity, which is needed in Eq. (1), is given by $C_v^{\text{sing}} + C_v^{\text{back}}$.

The smooth curve shown in Fig. 2 was obtained using the parameters listed in Table III of Ref. 5. Several of these parameters were adjusted to achieve a best fit to the static sound velocity (see Ref. 5), so the good agreement between the points and the curve is in effect a test of the ability of the theory to represent the experiment with physically reasonable parameters. The fit far from T_c is essentially determined by the expansion parameters used for μ_0 and A_0. It is likely that the Taylor series expansion is not a perfect representation since the curve is slightly above the points near $\Delta T = 2°$ but slightly below the 1-MHz velocity points near $\Delta T = 5°$. In the region near T_c, say $-1° < \Delta T < 1°$, the fit is much less dependent on the background term and is quite sensitive to the value of the critical exponent α. The least-squares value of α is 0.08 (with an estimated uncertainty[13] of ±0.02), in very good agreement with the value obtained from an analysis of gravity-corrected specific-heat data.[14]

IV. SUMMARY

A new acoustic cell design, which makes it possible to measure the azimuthal resonant mode in a horizontal annulus, has been used to measure the "static" sound velocity in xenon near its critical point. Velocity data along the critical isochore above T_c and in the coexisting vapor below T_c can be well represented by theoretical curves based on the linear-model parametric equation of state. The critical exponent α for the constant-volume specific heat found from these sound velocity data is 0.08.

*Work supported in part by the National Science Foundation.

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[9]See P. M. Morse and K. U. Ingard, *Theoretical Acoustics* (McGraw-Hill, New York, 1968), pp. 603 and 604. It is possible to estimate that the u values calculated with Eq. (2) are systematically high by 0.1%. However, the accuracy of the calculation of u from the exact solution is only ±0.1% owing to limitations in the accuracy of tabulated values of Bessel functions of the second kind. Since random errors are the limiting factor in this experiment, we have not undertaken a more accurate evaluation of this systematic error.

[10]Although the filling density ρ was not directly determined, we estimate on the basis of acoustic data in Refs. 4 and 5 that $0.995\rho_c < \rho < 1.005\,\rho_c$.

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