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# ULTRASONIC PROPAGATION NEAR THE CRITICAL POINT IN HELIUM

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A logarithmic singularity in the specific heat at constant volume $C_v$ at the critical point has recently been reported to occur in argon[1] and oxygen.[2] Such a result is in direct contradiction to standard theory,[3,4] according to which $C_v$ must remain finite at the critical point. Reconsideration of the theory in view of these data leads us to new inferences about the critical point. Among these is the prediction that the sound velocity exhibits anomalous behavior, which we have indeed observed.

The situation can be concisely discussed in terms of the stiffness matrix which, starting from the fundamental equation $U=U(S,V)$, can be written[4]

$$\begin{bmatrix} \left(\frac{\partial T}{\partial S}\right)_v & \left(\frac{\partial T}{\partial V}\right)_s \\ -\left(\frac{\partial P}{\partial S}\right)_v & -\left(\frac{\partial P}{\partial V}\right)_s \end{bmatrix} = \begin{bmatrix} \frac{T}{C_v} & \frac{T}{C_v}\left(\frac{\partial P}{\partial T}\right)_v \\ \frac{T}{C_v}\left(\frac{\partial P}{\partial T}\right)_v & \frac{1}{V\kappa_s} \end{bmatrix}. \tag{1}$$

Here $\kappa_S$ is the adiabatic compressibility. This matrix can be diagonalized by a nonsingular linear transformation of the variables, yielding the diagonal elements

$$\lambda_1 = T/C_v, \quad \lambda_2 = 1/V\kappa_T. \tag{2}$$

According to standard theory, $\lambda_2 = 0$ and $\lambda_1 \neq 0$ at the critical point, ensuring that $C_p$, the coefficient of thermal expansion $\alpha$, and the isothermal compressibility $\kappa_T$ become infinite there.[4] The observation that $C_v \to \infty$ implies, on the other hand, that at $T_c$

$$\lambda_1 = \lambda_2 = 0. \tag{3}$$

Note that $\lambda_1$ and $\lambda_2$ are not eigenvalues, and inverting the order of the variables $U=U(V,S)$ we arrive at

$$\lambda_1' = 1/V\kappa_s, \quad \lambda_2' = T/C_p. \tag{4}$$

Now according to a well-known rule,[5] the number of positive, negative, and vanishing terms in the diagonalized form must be independent of the particular transformation used. Hence, Eq. (3) implies $\lambda_1' = \lambda_2' = 0$, so that $\kappa_S$ must have a singularity at the critical point and the sound velocity $u = (\rho\kappa_S)^{-1/2}$ must vanish. Strictly speaking, the sound velocity should be regarded as complex in order to take dissipation into account. The quantity $\lambda_1'$, however, is connected only with the real part, and as the critical point is approached the imaginary part will eventually become dominant. Hence the signal will be expected to fade out as the phenomenon of sound propagation becomes purely dissipative. High attenuation has in fact been previously observed in the critical region, e.g., in xenon.[6]

Besides potentially confirming the observed behavior of $C_v$, sound velocity measurements have several other advantages. The available resolution (≈0.01 %) is much greater than in specific-heat measurements, and each observation is made at a fixed temperature instead of over a temperature interval. By making measurements along a suitable line in the phase diagram, e.g., an isotherm or an isobar, it is possible to remain in a homogeneous phase at all times, whereas measurements of $C_v$ along an isopycnal are necessarily carried out in the mixed phase below $T_c$. In the latter circumstances small departures of $\rho$ from the critical value may lead to large contributions from the latent heat close to $T_c$. We have accordingly undertaken a study of the sound velocity at 1 Mc/sec in the critical region of helium ($T_c = 5.1994$°K, $P_c = 1718$ mm Hg). Similar measurements have previously been made in xenon,[6] but with insufficient resolution to detect the presence of a singularity in the compressibility.

Changes in sound velocity were measured by a phase-sensitive method[7] which provided a resolution of about 0.01 % with the 0.396-cm path length used in the experiment. The absolute value of the velocity was chosen to agree with earlier measurements along the vapor-pressure curve.[8] The ultrasonic chamber was contained in a vacuum-jacketed pressure vessel, the temperature of which was controlled within $\pm 10^{-4}$ °K by an automatic regulator.[9] This vessel was initially filled with liquid helium from the bath through a needle valve; subsequent changes in density were effected by removing gas or adding it from a room-temperature reservoir. The pressure was controlled manually, and was measured with a resolution of ±0.1 mm Hg on a Wallace and Tiernan gauge calibrated against a mercury manometer. Absolute values are believed to be accurate to within ±1 mm Hg. All pressures refer to mercury at 0°C, and temperatures are given on the 1958 scale.[10]

The following precautions were taken to promote equilibrium: (1) The pressure vessel was made of copper; (2) the fluid was stirred continuously during the course of the experiments; (3) the velocity was observed during the establishment of equilibrium, and measurements were made only after it was essentially steady (this required from 5 minutes to about half an hour close to the critical point); (4) measurements were made with both increasing and decreasing pressure or temperature as a check of reproducibility. Although at no time did we wait several hours for equilibrium (as was done in references 1 and 2), we believe that the above precautions, especially (4), are sufficient to ensure the reliability of the data.

Results of measurements along the isobar $P = 1718 \pm 1$ mm Hg and the isotherm $T = 5.200 \pm 0.002$°K are shown in Fig. 1. The observed rapid fall in sound velocity $u$ as the critical point is approached from any direction is in agreement with expectation. Because, as anticipated, the attenuation is high in the critical region, measurements are impossible with the present apparatus over a region of width about $2\times10^{-3}$ °K or 2.5 mm Hg; nevertheless, the drop outside this region is so rapid that the vanishing of $u$ at the critical point does not appear unreasonable.

The behavior of the adiabatic compressibility $\kappa_S$ is more revealing, but its evaluation from $u$ requires knowledge of the density. We have estimated $\rho(P, T)$ from the expansion given by Edwards and Woodbury,[11]

$$P = -Atv - \tfrac{1}{3}Bv^3 - \tfrac{1}{2}Ctv^2 - Dt^2v + f(t), \qquad (5)$$

where $t = T - T_c$, $v = V - V_c$, and $A$, $B$, $C$, and $D$ are given in reference 11. In order to carry out

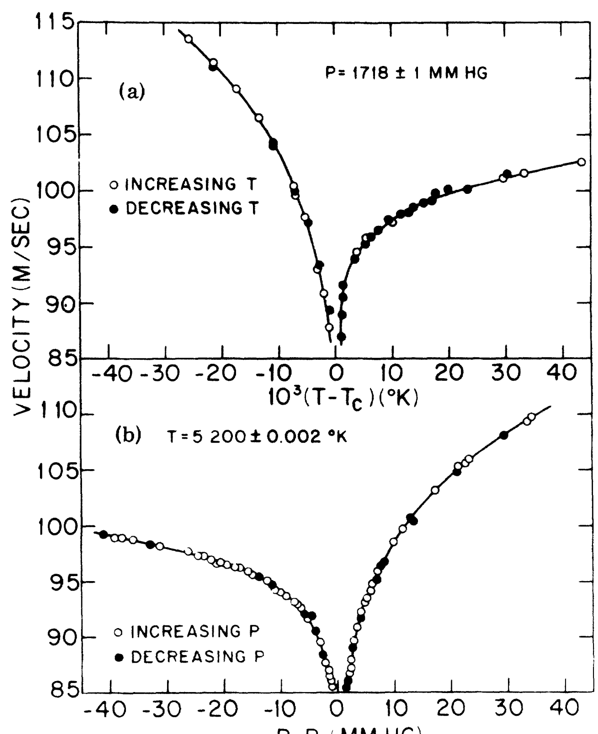


FIG. 1. Sound velocity as a function of temperature (a) and pressure (b) in the critical region.

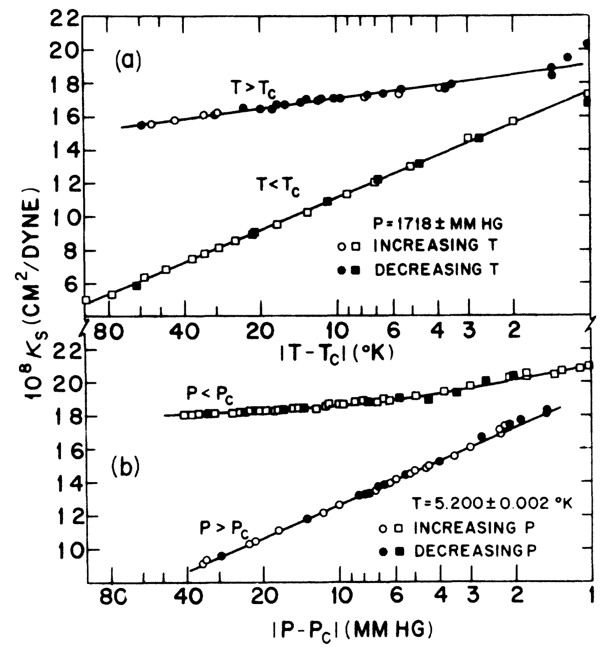


FIG. 2. Adiabatic compressibility (a) as a function of $\log|T-T_c|$ and (b) as a function of $\log|P-P_c|$ in the critical region.

this calculation, $f(t)$ was chosen to give Edward and Woodbury's density values along the vapor-pressure curve, and for $T>T_c$ was adjusted (somewhat arbitrarily) so that the maximum in $(\partial V/\partial P)_T$ falls on the extrapolated vapor-pressure curve. The errors involved in this procedure are difficult to estimate, but it is unlikely that they can be so large as to change the qualitative nature of the singularity in $\kappa_S$.

Figure 2 shows $\kappa_S$ along the above isobar and isotherm plotted against $\log|T-T_c|$ or $\log|P-P_c|$. The presence of a logarithmic singularity over $1\frac{1}{2}$ to 2 decades in the liquidlike phase ($T<T_c$ or $P>P_c$) is clearly indicated. In the gaslike phase the slope is much smaller, but a singularity is still evident. Indeed, along the isotherm the singularity may even be stronger than logarithmic. Although the shape of these curves near the critical point is very sensitive to the precise values chosen for $P_c$ and $T_c$, no reasonable assignment of these quantities would suggest that $\kappa_S$ is leveling off to a finite value. We therefore conclude that $\kappa_S$ exhibits just such a singularity at the critical point as would be expected on the basis of the reported behavior of $C_v$.

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