We have considered here the three-dimensional case. Unfortunately, this consideration cannot be applied to the one-dimensional case since the collision term of Balescu-Lenard type goes to zero and the triple interactions have to be taken into account. Therefore we can have only qualitative correspondence between our consideration and the numerical results of the paper.[2]

Our arguments can equally well be applied to stellar systems with some modification of "particle" trajectories. They show that the approach to equilibrium in such systems should be much faster than predicted by binary interactions.

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Brillouin Spectrum of Xenon Near Its Critical Point*

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We have accurately measured the Brillouin spectrum of pure xenon along the critical isochore using two high-resolution spherical Fabry-Perot interferometers in tandem. The spectrum, which contained an extra diffusive mode, is analyzed in terms of a hydrodynamic model employing a relaxing bulk viscosity. We obtain the temperature dependence of the relaxation time, the bulk viscosity, the specific heat ratio C_p/C_v at finite k and ω, the correlation range, and the $k=0$, $\omega=0$ values for the compressibility and C_p-C_v.

This Letter reports accurate measurements of the Brillouin portion of the spectrum of light scattered by a pure fluid, xenon, near its critical point. The measurements were made along the critical isochore at temperatures ranging from 20°C above the critical temperature T_c to within 0.10°C of T_c. The spectral measurements were made using two high-resolution spherical Fabry-Perot interferometers in tandem. This technique enabled us to resolve clearly the weak Brillouin portion of the spectrum despite the presence of the extremely intense Rayleigh component. In addition to the normal Rayleigh and Brillouin components the spectrum contained an additional diffusive mode centered at the frequency of the incident light. The intensity of this extra mode increased as the critical point was approached, and for the lowest temperature studied, $T_c+0.10$°C, its integrated intensity was at least twice the integrated intensity of one Brillouin component. The general appearance of the spectrum as well as its dependence upon temperature is shown in Fig. 1.

The experimental setup consisted of a single-mode, frequency-stabilized, helium-neon laser; a high-pressure cell having two optical-quality glass windows; an axiconical collecting lens; a spectrometer consisting of two high-resolution spherical Fabry-Perot interferometers which were pressure swept in tandem; a photomultiplier tube; and a strip-chart recorder. The cell was carefully cleaned and filled to within 0.1% of the critical density with xenon containing less than 18 ppm of impurities. The cell temperature was controlled to within ±0.001°C, and was measured using a platinum resistance thermometer. The meniscus was observed to disappear at a temperature of (16.597±0.01)°C, which was taken as the critical temperature, in good agreement with the accepted value of 16.590°C. Light scattered at an angle of 170°, corresponding to a scattering wave vector $k=2.25\times10^5$ cm^{-1}, was collected by an axiconical lens and spectrally analyzed using the tandem interferometer. The extremely high contrast of the interferometer, and its narrow instrumental width of 20

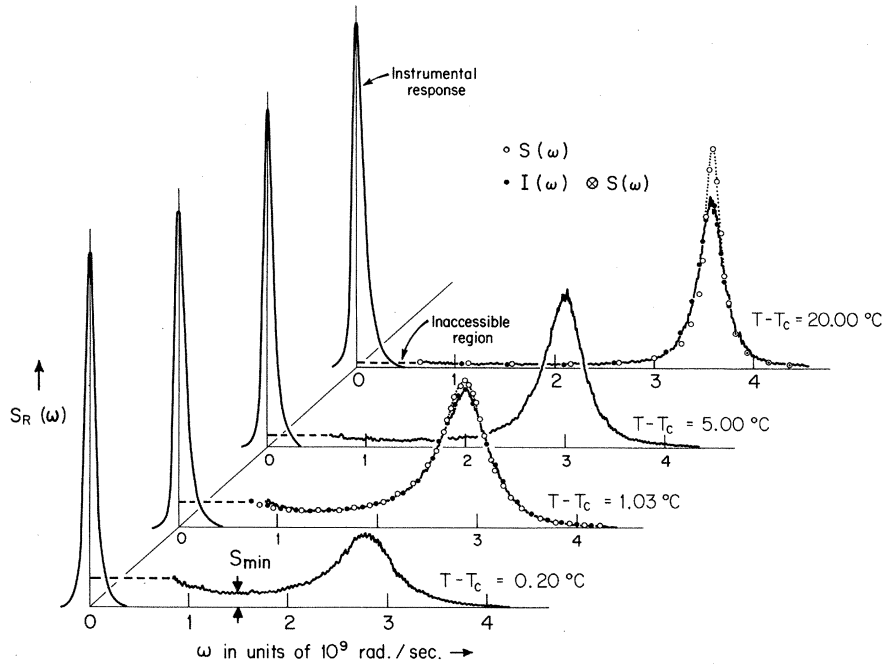

FIG. 1. The Brillouin spectrum of xenon for four temperatures along the critical isochore. The experimental traces are shown as solid curves. The open circles represent the spectrum $S_\tau(\omega)$ calculated from our hydrodynamic model without including the effects of the instrument. The closed circles are the convolution of $S_\tau(\omega)$ with the instrumental response function $I(\omega)$, and these agree accurately with the experimental spectra. The increase of spectral power between $\omega = 0$ and the Brillouin component clearly shows the growth of the diffusive mode as $T - T_c$ goes to zero.

MHz, permitted us to measure accurately the weak Brillouin portion of the spectrum to within 125 MHz of the extremely intense Rayleight line, and to discover a previously undetected[1-3] diffusive mode whose amplitude midway between the Rayleigh and Brillouin components is denoted as $S_{\min}$ in Fig. 1. The instrument response function $I(\omega)$ was determined independently for each spectrum recorded by measuring the folding of $I(\omega)$ with the very narrow Rayleigh line.[4] This also determined the relative intensities of the Rayleigh and Brillouin components.

The recorded spectrum $S_R(\omega)$ is the convolution of $I(\omega)$, measured as described above, with the true spectrum $S(\omega)$:

$$S_R(\omega) = \int_{-\infty}^{\infty} I(\omega-\omega')S(\omega')d\omega' \equiv I(\omega) \otimes S(\omega).$$

For each spectrum, an analytic function $S_\tau(\omega)$ was generated, which, when numerically convolved with the instrumental response function $I(\omega)$, yielded a good fit to the recorded spectrum $S_R(\omega)$. The physical model used for $S_\tau(\omega)$ was that of the spectrum of a fluid whose bulk viscosity relaxes with a single relaxation time. Such a spectrum has the form of a normal Rayleigh-Brillouin spectrum with an additional Lorentzian mode centered at the origin,[5] as is needed to explain our spectra as shown in Fig. 1. This physical model provides the simplest mathematical description which includes the possibility of a critical relaxation in the transport coefficients, as is expected from the mode-mode coupling schemes. The entire spectrum is completely determined by specifying the values of six parameters appearing in the expression for the spectrum. The six parameters involved are the low-frequency sound speed C_0, the infinite-frequency sound speed C_∞, the relaxation time for the bulk viscosity τ, the specific-heat ratio C_p/C_v, the ratio $\Lambda/\rho_0 C_v$, where Λ is the thermal conductivity and ρ_0 the average density, and the nonrelaxing viscosity term $\zeta_0 = (\frac{4}{3}\eta_s + \eta_{v0})/\rho_0$, where η_s is the shear viscosity and η_{v0} the nonrelaxing part of the bulk viscosity. The exact form for $S_\tau(\omega)$ which we employed is

$$S_\tau(\omega) = \mathrm{Re}[(F(s)/G(s))_{s=i\omega}], \tag{1}$$

where

$$F(s) = s^2 + [a + b(s)]k^2 s + ab(s)k^4 + C_0^2 k^2(1 - 1/\gamma) \tag{2}$$

and

$$G(s) = s^3 + [a + b(s)]k^2 s^2 + [C_0^2 k^2 + ab(s)k^4]s + aC_0^2 k^4/\gamma. \quad (3)$$

Following Mountain we have used the notation $a = \Lambda/\rho_0 C_v$ and $b(s) = \zeta_0 + \eta_v(s)/\rho_0$, where

$$\eta_v(s) = \rho_0(C_\infty^2 - C_0^2)\tau/(1 + s\tau).$$

The actual deconvolution of a recorded spectrum was accomplished in the following manner: Values for the six parameters were estimated and the resulting $S_\tau(\omega)$ was numerically convolved with the instrumental response function $I(\omega)$, using the discrete fast Fourier transform.[6] The convolved spectrum was then compared with the recorded spectrum and a better estimate of the parameters made. This procedure was repeated until satisfactory agreement between $S_\tau(\omega) \otimes I(\omega)$ and $S_R(\omega)$ was obtained, thereby providing, at all temperatures, an accurate analytic representation of the true deconvolved spectrum $S(\omega)$. It is important to recognize that the values of the six parameters were not uniquely established by this procedure because it was not possible to measure the Brillouin spectrum within 125 MHz of the Rayleigh component. In fact, the experimental data effectively permitted the determination of five of the six parameters. In order to select physically meaningful values of all six parameters which enter into this single relaxation hydrodynamic model, one of the parameters must be independently specified. The two possible choices for specification are the low-frequency sound speed C_0 and the nonrelaxing viscosity term $\zeta_0 = (\frac{4}{3}\eta_s + \eta_{v0})/\rho_0$. The ultrasonic sound speed has been measured[7,8] and the nonrelaxing viscosity term can be reasonably estimated by assuming that $\eta_{v0} \approx \eta_s$[9] and using measured values for η_s.[10] It was assumed that η_s is independent of the temperature, as has been experimentally observed for the case of CO_2.[11] The estimated value of ζ_0 was 1.2×10^{-7} m^2/sec independent of temperature

In our analysis we considered each of the following possibilities. First, following Mountain,[12] we set ζ_0 equal to 1.2×10^{-7} m^2/sec and used the ultrasonic values of the sound speed for C_0. This proved to be an overspecification of the parameters as no possible choice of the remaining parameters resulted in agreement with the deconvolved spectra. The second possibility consisted of using the ultrasonic sound speed for C_0 and allowing ζ_0 to vary freely. In this case, although excellent agreement with the deconvolved spectra could be obtained, the resulting values for ζ_0 were ~4 times larger than the value estimated above. Furthermore, the value obtained for τ, the relaxation time, was $\sim 2 \times 10^{-9}$ sec and was independent of the temperature. This corresponds to a relaxation frequency of ~80 MHz. While this choice of parameters accounts for all of the dispersion between the ultrasonic values for C_0 and the hypersonic (~500 MHz) sound speed[13] as determined by this experiment, it fails to account for the fact that dispersion in the sound speed is observed at frequencies as low as 250kHz.[7,8] The third approach which was tried, and which we propose to adopt for our analysis, was that of estimating ζ_0 as mentioned above and allowing C_0 to vary freely. For this purpose ζ_0 was set equal to 1.2×10^{-7} m^2/sec and assumed to be temperature independent. Again good fits were obtained, but in this case, at each temperature, C_0 had to be assigned a value well above the ultrasonic sound speed as shown in Table I. This table also shows the temperature dependence of C_∞, the infinite-frequency sound speed predicted by this fit, as well as the measured ultrasonic (0.55 MHz) sound velocity,[8] and the hypersonic (~500 MHz) velocity measured in this experiment. The difference between the ultrasonic sound speed and the values of C_0 necessary to fit the Brillouin data could be accounted for by a second relaxation in the bulk viscosity, one having a relaxation frequency well below 500 MHz. For our spectra obtained in the frequency regime of 500 MHz, the lower-frequency relaxation would have the effect of raising the values of C_0 necessary to describe the spectra. The existence of two relaxations would explain both our observed spectra and the observations of dispersion in the ultrasonic speed at low frequencies. The possibility of two relaxations in the bulk viscosity is supported by the theoretical work of Kadanoff and Swift.[14] Of course it is also possible that a continuous distribution of relaxation times may be necessary to account for the full frequency dependence of the sound speed and attenuation. In a separate Letter Garland, Eden, and Mistura analyze the existing Brillouin and ultrasonic absorption data using theories of Fixman[15] and Kawasaki[16] which contain such a distribution of relaxation times.

Table I also shows for each temperature the values of the three remaining parameters, τ, C_p/C_v, and $\Lambda/\rho_0 C_v$, needed to fit the deconvolved

Table I. Values of the parameters C_0, C_∞, τ, C_p/C_v, and $\Lambda/\rho_0 C_v$ used in the hydrodynamic model, for each temperature studied. The measured ultrasonic sound velocity V_{ult} (see Ref. 9) and the hypersonic sound velocity V_{hyp} measured by this experiment are also given

$T - T_c$ °C	C_0 m/sec	V_{ult} m/sec	V_{hyp} m/sec	C_∞ m/sec	τ 10^{-9} sec	C_p/C_v	$\Lambda/\rho_0 C_v$ 10^{-7} m^2/sec
0.10	111.0	94.8	123.7	127.5	.54	1983	3.4
0.20	114.9	97.0	124.3	130.8	.38	951	2.7
0.30	116.6	98.8	127.3	133.1	.41	656	2.5
0.40	115.4	100.6	124.5	131.0	.37	497	2.4
0.50	116.5	102.2	126.8	132.4	.41	391	2.2
0.70	116.2	104.9	124.3	131.6	.34	279	2.1
1.03	118.2	108.4	126.8	134.0	.35	183	1.8
2.24	122.7	117.0	128.9	136.5	.29	82	1.5
3.00	127.9	121.8	132.7	141.6	.23	59	1.3
5.00	130.8	129.6	134.3	143.0	.20	35	1.1
7.50	138.6	136.7	140.5	150.4	.13	23	1.0
10.00	143.8	142.4	146.7	150.7	.24	18	1.0
15.00	150.0	151.8	152.4	155.4	.25	12	0.9
20.00	160.4	159.4	162.4	164.6	.25	10	0.9

spectra. As a final check the spectrum predicted by this model was numerically convolved with the instrumental response function and compared with the observed spectrum for all temperatures studied. As can be seen from Fig. 1, excellent agreement was obtained. Aside from a possible Botch-Fixman[17] correction to the Rayleigh linewidth, the spectrum predicted by this model reproduces for each temperature all of the known features of the Rayleigh-Brillouin spectrum.

The values of C_p/C_v listed above correspond to finite k and ω. It is possible to connect this quantity with the $k=0$, $\omega=0$ susceptibilities as follows. We apply the Ornstein-Zernike model to account for the k dependence and the hydrodynamic relaxation model to account for the frequency dependence. This gives

$$\frac{C_p}{C_v}=\frac{C_p(k,\omega)}{C_v(k,\omega)}(1+k^2\xi^2)\frac{C_{00}^2}{C_0^2}, \tag{4}$$

where C_{00} is the true zero-frequency sound speed, and ξ is the Ornstein-Zernike correlation range. Since C_{00} has not been measured and ξ is not known along the critical isochore, we eliminate the quantity $C_p/C_vC_{00}^2$, using the thermodynamic identity $\rho_0 K_T = C_p/C_vC_{00}^2$ where K_T is the isothermal compressibility. Since $K_T/K_I=\xi^2/R^2$, where $K_I=1/nk_BT$ is the isothermal compressibility of an ideal gas of number density n and R is the direct correlation range, we find

$$\frac{\xi^2}{R^2}=\frac{C_p(k,\omega)}{C_v(k,\omega)}\frac{(1+k^2\xi^2)}{\rho_0 C_0^2}nk_BT. \tag{5}$$

This equation can be solved, using our experimental data, to give ξ^2 along the critical isochore. We used a value for R of 5.6 Å.[18] Using these values of ξ we then calculate $(\partial\rho/\partial\mu)_T = \rho_c^2 K_T$, where μ is the chemical potential. Finally, from K_T we obtain

$$C_p - C_v = \frac{T}{\rho_0}\left(\frac{\partial p}{\partial T}\right)_\rho^2 KT,$$

using a value[19] of 1.176 atm/°K for $(\partial p/\partial T)_\rho$ independent of the temperature. We find the following results for ξ, $(\partial\rho/\partial\mu)_T$, and C_p-C_v along the critical isochore:

$$\xi = 3.02\epsilon^{-0.60}\ \text{Å},$$

$$(\partial\rho/\partial\mu)_T = 1.63\epsilon^{-1.21}\times10^{-9}\ \text{g}^2/\text{erg cm}^3,$$

$$C_p - C_v = 1.70\epsilon^{-1.20}\ \text{cal/mole °K}.$$

Here $\epsilon = (T - T_c)/T_c$ is the reduced temperature. Our values for $C_p - C_v$ are in excellent agreement with those obtained from analysis of PVT data.[20] The numerical values of the relaxation time τ are comparable with the time necessary for a sound wave to travel one correlation length, as would be expected from the mode-mode coupling theory.[14] However, the temperature dependence of τ ($\tau \sim 10^{-10}\epsilon^{-0.2}$ sec) is very weak compared with the temperature dependence of the correlation range.

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Critical Sound Absorption in Xenon*

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Ultrasonic attenuation in Xe has been measured along a near-critical isochore at frequencies in the range 0.4–5 MHz and at temperatures above T_c. Hypersonic attenuation values obtained from Brillouin linewidths are also cited. It is shown that the critical attenuation per wavelength depends on temperature and frequency through a single reduced variable $\omega^* = \omega/\omega_D$, where the characteristic frequency $\omega_D = (2\Lambda/\rho C_p)\xi^{-2}$. The experimental results are compared with numerical calculations based on a recent theoretical formulation by Kawasaki.

In this Letter we wish to report and interpret recent measurements of the sound absorption in Xe near its critical point. Data obtained as a function of frequency and temperature for $\rho \simeq \rho_c$ and $T > T_c$ will be discussed. Following a brief description of the experimental procedures, a modified version of the pertinent theory will be outlined and the results will be discussed in terms of this theory. The essential result of both theory and experiment is that the critical attenuation per wavelength depends only on a single reduced variable $\omega^* = \omega/\omega_D$.

Previous ultrasonic investigations have clearly indicated that α_λ, the attenuation per wavelength, shows an anomalous behavior near the critical point.[1] However, none of these investigations presented sufficient data to allow a quantitative comparison with the predictions of recent theoretical studies.[2-6] With this in mind, a modification of the traditional pulse interferometer has