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 been developed[7] in which the received signal is compared with a continuous coherent reference signal. Phase-sensitive detection and signal averaging provided an output which is sensitive to small delay changes and has a very high signal-to-noise ratio. Signals attenuated by more than 80 dB can be easily detected, and very accurate α_λ values are directly obtained from differential path measurements (the path can be continuously varied between 0.1 and 2 cm). Thus, this method is ideally suited for the measurement of ultrasonic velocity and attenuation in fluids near their critical point.

Both sound velocity and attenuation measurements have been carried out in high-purity xenon using X-cut 1-MHz quartz transducers. Data were obtained in the critical region along several isotherms and isochores at frequencies of 0.4, 0.55, 1, 3, and 5 MHz. A complete account of this experimental work will be presented elsewhere[8] and will include a comparison with the previous ultrasonic results of Chynoweth and Schneider.[9] In this Letter, we report only the attenuation data obtained along a single near-critical isochore at temperatures from 0.08 to 20°C above T_c.[10,11] The 0.55-MHz velocity data obtained along this isochore are cited in a separate Letter on critical light scattering in xenon.[12] Additional ultrasonic velocity data will be cited in an independent analysis of velocity dispersion.[13]

Our ultrasonic attenuation results are shown in Fig. 1 where the critical absorption per wavelength is plotted versus the reduced frequency $\omega^* = \omega/\omega_D$. Also shown are hypersonic attenuation values obtained from Brillouin linewidths.[12] The characteristic frequency ω_D is defined by

$$\omega_D \equiv (2\Lambda/\rho C_p)\xi^{-2}, \tag{1}$$

where Λ is the coefficient of thermal conductivity, C_p is the specific heat (i.e., the heat capacity per gram), and ξ is the correlation length. The critical attenuation is defined as the difference between the observed total attenuation and the so-called classical contribution $\alpha_\lambda(\text{class}) = \pi\omega u^{-2}[(\frac{4}{3}\eta + \zeta)/\rho + \Lambda(C_v^{-1} - C_p^{-1})/\rho]$, where ζ denotes the normal ("nonrelaxing") bulk viscosity. The value of $\Lambda(C_v^{-1} - C_p^{-1})/\rho$ is known as a function of temperature along the critical isochore,[12] and $(\frac{4}{3}\eta + \zeta)/\rho$ is assumed to have a temperature-independent value of 1.2×10^{-3} cm^2 sec^{-1} (see Ref. 12). At ultrasonic frequencies, $\alpha_\lambda(\text{class})$ is quite small and makes a significant contribution only when the total attenuation is very low (i.e., far from the critical point). At hypersonic frequencies, $\alpha_\lambda(\text{class})$ makes a sizable contribution throughout the critical region.

The most striking feature of Fig. 1 is that all the points, taken over a wide range of temperature and frequency, fall on a single curve. This is a new result, and the rest of this Letter is devoted to explaining to what extent the observed behavior is to be expected on theoretical grounds.

Some time ago, Fixman[2] and Botch and Fixman[3] proposed that energy transfer between

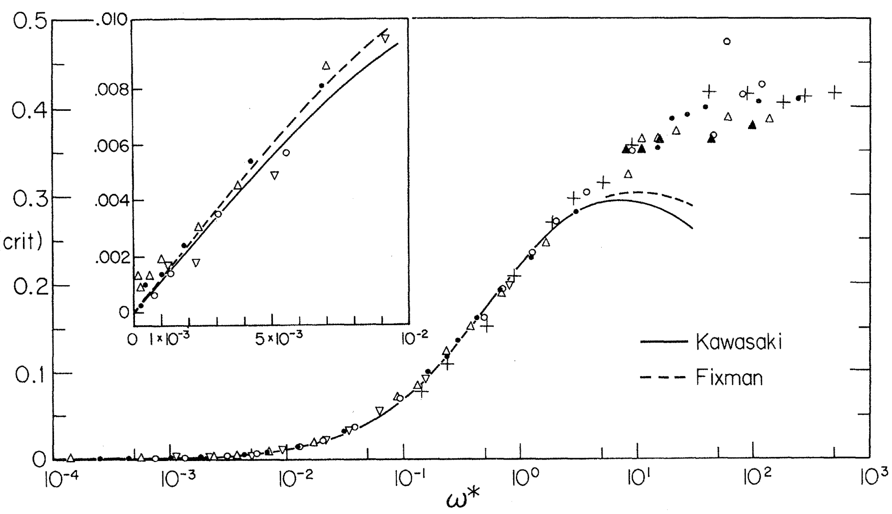

FIG. 1. Critical sound attenuation per wavelength in Xe as a function of the reduced frequency $\omega^* = \omega/\omega_D$. Ultrasonic data are shown at 0.4 (solid triangle), 0.55 (open triangle), 1 (solid dot), 3 (open dot), and 5 (inverted triangle) MHz. Hypersonic values at ~500 MHz (pulses) were obtained from Brillouin linewidths. All data were obtained along the critical isochore at temperatures above T_c. The theoretical curves represent Eq. (6) with the value of B chosen empirically so as to obtain the best fit for $\omega^* < 1$.

sound waves and density fluctuations might explain the anomalous acoustic behavior in the critical region. We shall show that a modified version of Fixman's theory will give results identical to those obtained recently by Kawasaki[6] on the basis of an analysis of anomalous contributions to the bulk viscosity. Let $\sigma(\vec{q}, t)$ be an order-parameter fluctuation with wave vector $\vec{q}$ at time t. In our case $\sigma(\vec{q}, t)$ will be the Fourier transform of $\rho(\vec{r}, t)-\rho_c$. Following Mistura and Sette,[14] we shall assume that the energy of the system associated with the density fluctuations which interact with the sound wave has the form

$$\delta U(t) \equiv U(t)-\langle U\rangle = \frac{1}{2V}\sum_{\vec{q}} b(q)|\sigma(\vec{q}, t)|^2 + \cdots, \tag{2}$$

where $b(q)=-V\langle|\sigma(q)|^2\rangle^{-1}\partial\ln\langle|\sigma(q)|^2\rangle/\partial\beta$ and $\beta=1/k_BT$. This expression is based on the assumption that fluctuations with different wave numbers q are statistically independent and Gaussian variables.[14] Let us now define a complex, frequency-dependent excess specific heat $\Delta(\omega)$ in terms of a time-dependent correlation function:

$$\Delta(\omega)=\frac{i\omega}{k_BT^2\rho V}\int_0^\infty dt\, e^{i\omega t}\langle\delta U(0)\delta U(t)\rangle. \tag{3}$$

Furthermore, we shall assume that the order-parameter fluctuations decay according to the diffusion equation $\dot{\sigma}(\vec{q}, t)=-\tau^{-1}(q)\sigma(\vec{q}, t)$.[15] This assumption, together with Eq. (2), allows us to write Eq. (3) in the form

$$\Delta(\omega)=\frac{i\omega}{k_BT^2\rho}\frac{1}{(2\pi)^3}\int d^3q[\partial\ln\langle|\sigma(q)|^2\rangle/\partial\beta]^2\frac{1}{2\tau^{-1}(q)-i\omega}. \tag{4}$$

For the static behavior of the fluctuations at small values of q, we assume the Ornstein-Zernike form, as modified by the small Fisher correction: $\langle|\sigma(q)|^2\rangle=A(q^2+\kappa^2)^{-1+\eta/2}$, where $\kappa\equiv\xi^{-1}$ is the inverse correlation length. A recent investigation of the Ising model[16] indicates that this form should be valid up to $x\equiv q\xi\lesssim 2$. The situation is less clear with respect to the decay rate. As $q\to 0$ hydrodynamics must become valid and we therefore have $\tau^{-1}(q)\to(\Lambda/\rho C_p)q^2$. If one accepts dynamic scaling ideas,[17] a more general expression can be written in the form $\tau^{-1}(q)=(\omega_D/2)K(x)$, where ω_D is the characteristic frequency defined in Eq. (1), and the function $K(x)$ must have the following properties:

$$\lim_{x\to 0}K(x)\propto x^2,\quad \lim_{x\to 0}K(x)\propto x^3.$$

Since the critical absorption per wavelength is directly related to the imaginary part of $\Delta(\omega)$,[2] we obtain

$$\alpha_\lambda(\text{crit})=\frac{k_BT^3}{\pi\rho^3}\left(1-\frac{\eta}{2}\right)^2\frac{1}{u^2C_V^2}\left(\frac{\partial P}{\partial T}\right)_V^2\kappa\left(\frac{\partial\kappa}{\partial T}\right)^2\int_0^\infty\frac{x^2dx}{(1+x^2)^2}\frac{\omega^*K(x)}{K^2(x)+\omega^{*2}}. \tag{5}$$

This result is essentially identical to an expression obtained by Kawasaki[6] from a very similar analysis of the complex bulk viscosity. However, our use of the reduced variable ω^* simplifies the result in an important way. On the basis of scaling-law predictions of u, C_V, and κ, the quantity which appears in front of the integral in Eq. (5) should be, at most, a very slowing varying function of temperature. Indeed, our ultrasonic data indicate that this quantity (call it B) is a constant. Thus,

$$\alpha_\lambda(\text{crit})=BI(\omega^*), \tag{6}$$

where the integral $I(\omega^*)$ defined in Eq. (5) depends on temperature and frequency through the single variable ω^*. The conclusion that B is independent of temperature is greatly strengthened by the excellent agreement between our data and the high-frequency Brillouin results. Since the hypersonic and ultrasonic frequencies differ by several orders of magnitude, a given ω^* value corresponds to quite different temperatures in each case.

Before discussing Fig. 1 in more detail, it must be stressed that the feasibility of fitting the data with a unique curve is rather sensitive to the temperature dependence chosen for ω_D. Assuming power-law divergences for ξ, C_p, and Λ which are characterized by the critical exponents ν, γ, and ψ, respectively, we find from Eq. (1) that $\omega_D=a\epsilon^{2\nu+\gamma-\psi}$, where $\epsilon\equiv(T-T_c)/T_c$. On the basis of mode-mode coupling results,[4] we have taken $2\nu+\gamma-\psi=3\nu=2.0$. From the available thermal diffusivity data[18] and correlation lengths[19] we can then determine the value 5.38×10^{12} sec^{-1} for the coefficient a.

Let us first comment on the hydrodynamic region which must occur at sufficiently low values of ω^*. According to the mode-mode coupling prediction of Kadanoff and Swift,[4] $\alpha_\lambda(\mathrm{crit}) \sim \omega\epsilon^{-2} \sim \omega^*$ in this region. The inset in Fig. 1 shows that our data conform to this limiting theoretical behavior for $\omega^* \lesssim 5\times 10^{-3}$.

In order to compare theory and experiment at higher values of ω^*, the function $K(x)$ must be specified and the integral $I(\omega^*)$ evaluated numerically. Kawasaki[5,6] has recently proposed an explicit form for $K(x)$ which has the correct limiting behavior at low and high x values: $K(x) = \frac{3}{4}[1+x^2(x^3+1/x)\tan^{-1}x]$. It should be noted that for small values of x this Kawasaki form reduces to $K(x) = x^2(1+\frac{3}{5}x^2)$, which is a modification of the form originally proposed by Fixman[3]: $K(x) = x^2(1+x^2)$. For comparison, we have calculated $I(\omega^*)$ for ω^* values up to 30 using both the Kawasaki form and Fixman form of $K(x)$. As mentioned in connection with our choice of $\langle|\sigma(q)|^2\rangle$, the theoretical expression given in Eq. (5) should be correct as long as the major contributions to the integral come from the interval $x<2$. Table I shows that this condition is satisfied when $\omega^* \lesssim 2$. In order to obtain the best visual fit of $BI(\omega^*)$ to the experimental $\alpha_\lambda(\mathrm{crit})$ points in the range $\omega^* \lesssim 2$, we have adopted the empirical value of 2.3 for B in the case of the Fixman calculation and 1.9 for B in the case of the Kawasaki calculation. Such empirical B values can be compared with the "experimental" value of 1.6 ± 0.2 obtained in the range $\epsilon = (2\text{-}6)\times10^{-4}$ from our present sound velocity data and available data for C_V,[20] $(\partial P/\partial T)_V$,[10] and κ.[19] This comparison suggests that the Kawasaki form of $K(x)$ is to be preferred over the Fixman form. However, it must be pointed out that although the value used for a in $\omega_D = a\epsilon^2$ does not influence the shape of the semilog plot shown in Fig. 1 it will influence the B values. In summary, the experimental $\alpha_\lambda(\mathrm{crit})$ values for $\omega^* \lesssim 2$ can be well represented by Eq. (5) but they do not provide a very sensitive test of the form of $K(x)$.

Table I. Values of $I(\omega^*)$ and the contributions to this integral from the regions $x=0$ to 1 and $x=0$ to 2 for the choice of the Fixman (F) and the Kawasaki (K) form of $K(x)$.

ω^*		$I(\omega^*)=\int_0^\infty$	$\int_0^1$ (%)	$\int_0^2$ (%)
0.02	F	0.0088	90	99
	K	0.0100	86	98
0.2	F	0.0472	81.4	98.5
	K	0.0562	74.8	96.6
2	F	0.1135	38.3	93.3
	K	0.1384	28.4	86.6
20	F	0.1282	4.6	53.9
	K	0.1448	3.3	33.6

At still higher reduced frequencies ($\omega^* \gtrsim 2$), Eq. (5) is no longer in agreement with the experimental data. Table I shows that x values greater than 2 begin to contribute significantly to $I(\omega^*)$, and it is reasonable to expect a breakdown in the theory due to the inadequacy of the Ornstein-Zernike form for $\langle|\sigma(q)|^2\rangle$. On the basis of rather general assumptions about the form of $\langle|\sigma(q)|^2\rangle$ for large values of q, Kawasaki[6] has recently estimated that the absorption per wavelength in a sufficiently high-frequency region must be practically independent of both temperature and frequency. This prediction is confirmed by our experimental data for $\omega^* > 30$. Although an analysis of the possible contributions from higher-order processes has not yet been carried out, this qualitative agreement between theory and experiment supports the idea that the relaxation process first proposed by Fixman may be the only process responsible for the excess absorption in the critical region.

In conclusion, we have demonstrated experimentally that the critical attenuation per wavelength depends essentially on a single variable —the reduced frequency $\omega^* = \omega/\omega_D \sim \omega\epsilon^{-2}$. In the range $0 \leqslant \omega^* < 2$, experiment is in good agreement with existing theory. At very low frequencies ($\omega^* \leqslant 5\times10^{-3}$) we find hydrodynamic behavior with a temperature dependence in agreement with the Kadanoff and Swift prediction.[4] At intermediate frequencies ($\omega^* \leqslant 2$), we have shown that Eq. (5) can provide a good representation of the experimental data. Although these data are not extremely sensitive to the choice of $K(x)$, it would appear that the Kawasaki form is somewhat preferable to the Fixman form. For higher frequencies ($\omega^* > 2$) we have observed deviations of the experimental points from the values predicted by Eq. (5) and we have given a possible explanation for these deviations within the framework of a single relaxation mechanism with a continuous distribution of relaxation times. Finally, we have shown that the existing experimental data support the recent estimate by Kawasaki[6] of the limiting attenuation behavior at very high frequencies ($\omega^* \gtrsim 30$).

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Dispersion of the Velocity of Sound in Xenon in the Critical Region*

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The sound velocity in xenon on the critical isochore was determined in Brillouin scattering measurements at scattering angles of 40° and 90°. The sound dispersion calculated from our data, ultrasonic data, and other Brillouin data agrees with the Kawasaki theory for a particular choice of parameters, but the dispersion in the Brillouin velocities is 2 to 3 times smaller than the theory predicts when values obtained for the parameters from other experiments are used.

The spectrum of light scattered by a fluid contains a pair of inelastic (Brillouin) components shifted symmetrically from the incident frequency by $\Delta\nu_B = vq/2\pi$, where $q = 2K_0 \sin\frac{1}{2}\theta$ (K_0 is the wave vector of the incident light in the medium and θ is the scattering angle). Near the critical point the sound velocity in the low-frequency limit, v_0, should approach zero as $(T-T_c)^{\alpha/2}$, where α is the exponent which describes the critical divergence in the specific heat c_v. For nonzero frequencies, however, the velocity may approach a nonzero limiting value as $T \to T_c$ due to dispersion associated with the coupling of sound waves to the critical density fluctuations, as first proposed by Fixman.[1]

The presence of a dispersion in the sound velocity of a simple fluid near the critical point was first reported many years ago by Chynoweth and Schneider,[2] whose measurements in xenon revealed a small but definite dispersion in the frequency range 0.25 to 1.25 MHz for $(T-T_c) \lesssim 2$°C. A large dispersion in the sound velocity was observed in recent Brillouin scattering experiments[3] in CO_2 (in the frequency range 420 to 800 MHz), and the temperature at which this dispersion occurred agreed qualitatively with the theory of Kadanoff and Swift,[4] which predicts a strongly temperature-dependent dispersion at a frequency $\omega_R = \chi\xi^{-2}$, where χ is the thermal diffusivity ($\chi \equiv \lambda/\rho c_p$, where λ, ρ, and c_p are the thermal conductivity, density, and constant-pressure specific heat, respectively) and ξ is the correlation length. The comparison of the observed dispersion with the Kadanoff-Swift prediction was made using