Rayleigh Linewidth in Xenon Near the Critical Point*

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The Rayleigh linewidth Γ of xenon was measured on the critical isochore between 0.003 and 5.0°C above T_c. In the hydrodynamic region ($q\xi \leq 0.2$) we find $\Gamma = q^2\chi_0[(T-T_c)/T_c]^{\gamma-\psi}$ with $\chi_0 = (6.94 \pm 0.21) \times 10^{-4}$ cm^2/sec, and $\gamma - \psi = 0.751 \pm 0.004$. Our data over the entire region $0.009 \leq q\xi \leq 6.7$ agree quite well with the recent Kawasaki extended mode-mode coupling theory. However, the Kadanoff-Swift-Kawasaki result $\gamma - \psi = \nu$ does not appear to be valid.

During the past five years there have been several determinations of the spectrum of laser light quasielastically scattered by single-component fluids and binary liquid mixtures in the vicinity of the critical point. The Rayleigh linewidths for the two single-component fluids studied so far (SF_6 by Saxman and Benedak,[1] and CO_2 by Swinney and Cummins[2]) were found to have markedly different temperature dependences, contrary to the expected "universality" of critical phenomena. Since it was possible that the critical behavior of CO_2 and SF_6 was influenced by the internal degrees of freedom of the molecules, we have undertaken a study of the Rayleigh linewidth in a monatomic system, xenon.[3]

Measurements were made along the critical isochore at temperatures between 0.003 and 5.0°C above T_c, for scattering angles $42° \leq \theta \leq 138°$, so that $0.8 \times 10^5 \leq q \leq 2.1 \times 10^5$ cm^{-1}. ($q = 2nK_0 \sin\frac{1}{2}\theta$, where n is the refractive index and K_0 is the magnitude of the wave vector in vacuum of the incident light.)

The 30-mm-long sample cell was formed from thick-walled Pyrex tubing with a 6.0×6.0-mm-square inside cross section. After the cell was pumped to a high vacuum, it was loaded by cryogenic transfer from a cylinder of Matheson research grade xenon containing less than 50 ppm inpurities and then sealed off. The sample density, determined by observing the height of the meniscus over a range of several degrees below T_c, was 0.3% below the critical density. The cell was immersed in a vigorously stirred oil bath which was index matched to the glass and which was stable to ±0.002°C over several hours.

Temperatures were measured with a relative accuracy of better than ±0.001°C with a calibrated thermistor suspended near the sample cell in the thermostat. The critical temperature, taken to be the temperature at which the meniscus first appeared as the temperature was lowered from above T_c, was 16.606±0.020°C for our xenon sample, which is in good agreement with the value 16.59°C observed by Habgood and Schneider.[4]

The Rayleigh linewidth was measured by the optical homodyne technique. Light from a Spectra-Physics model 125 He-Ne laser was attenuated to avoid heating of the sample and was then focused to a diameter less than 0.2 mm in the fluid. The scattered light was detected by a photomultiplier mounted on an optical bench which could be rotated about a vertical axis passing through the sample cell. The spectrum of the photocurrent was analyzed with two Singer spectrum analyzers, the model SB-15a for linewidths between 5 and 200 kHz and the model LP1a between 0.02 and 5 kHz. The spectrum analyzer output was squared and the resultant spectra were computer fitted with a Lorentzian line shape.

Near the critical point, the divergence in the compressibility of a simple fluid leads to a large gravitationally produced density gradient; therefore, at temperatures close to the critical temperature, the linewidth was measured as a function of height as well as scattering angle. Near T_c the linewidth as a function of height exhibits a minimum at a density essentially equal to the critical density,[2] and at temperatures a few millidegrees above T_c the minimum becomes quite sharp. (For example, at $T-T_c = 0.008$°C, the linewidth for a beam height 0.5 mm different from the height corresponding to the minimum linewidth was 24% greater than the minimum value, and linewidth differences larger than the measurement uncertainty were observed for height changes of only 0.1 mm.) Very near the critical temperature it was difficult to determine the linewidth minimum because the height corresponding to the minimum linewidth occasionally drifted 0.1 mm even when the thermostat was stable to ±0.001°C during the measurements.

After selecting those data points believed to correspond to the critical density, we had 155 values of Γ to compare with various theoretical predictions. Before describing the comparison, we briefly review the current theory.

Theory.—(a) Landau-Placzek: The range of correlations in a fluid is represented by the correlation length ξ which diverges as the critical point is approached: $\xi = \xi_0 \epsilon^{-\nu}$, where $\epsilon \equiv (T - T_c)/T_c$. In the hydrodynamic region ($q\xi \ll 1$) the dynamics of density fluctuations are described by the linearized equations of hydrodynamics which predict a Lorentzian Rayleigh line of half-width[5]

$$\Gamma = \chi q^2, \tag{1}$$

where $\chi \equiv \lambda/\rho c_p$ is the thermal diffusivity (λ, ρ, and c_p are the thermal conductivity, density, and specific heat at constant pressure, respectively). Near the critical point λ and c_p diverge as $\epsilon^{-\psi}$ and $\epsilon^{-\gamma}$, respectively; therefore, we can write $\chi = \chi_0 \epsilon^{\gamma - \psi}$.

(b) Fixman-Botch: As the critical point is approached, the increasing range of correlations destroys the strictly local nature of the hydrodynamics. Fixman first suggested that the hydrodynamic equations could be properly modified by the addition of a nonlocal pressure term.[6] Solution of the modified hydrodynamic equations leads to a modified Rayleigh linewidth[7]

$$\Gamma = \chi q^2 (1 + b q^2 \xi^2), \tag{2}$$

with $b = 1$. Far from the critical point, $q\xi \ll 1$ and the Landau-Placzek result (1) is recovered.

(c) Dynamical scaling: Halperin and Hohenberg have proposed that the Rayleigh linewidth $\Gamma(q, \xi^{-1})$ is a homogeneous function of q and ξ^{-1}, and this assumption, together with the known form of Γ in the hydrodynamic limit, Eq. (1), leads to the expression[8]

$$\Gamma = q^z \Omega(q\xi), \tag{3}$$

where $z = 2 + (\gamma - \psi)/\nu$. In the limit $q\xi \ll 1$, Eq. (3) becomes (by assumption) equal to Eq. (1), and in the critical limit $q\xi \gg 1$, Eq. (3) becomes

$$\Gamma = B q^z, \tag{4}$$

where B is a temperature-independent constant. For intermediate values of $q\xi$, $\Omega(q\xi)$ is unspecified, as is the exponent z.

(d) Kadanoff-Swift: These authors carried out a mode-mode coupling analysis of transport coefficients in the critical region and found that $\gamma - \psi = \nu$.[9] This result, when combined with the dynamical scaling arguments above, implies that z [in Eqs. (3) and (4)] is equal to 3.

(e) Kawasaki: Recently Kawasaki has carried out a detailed mode-mode coupling analysis of density fluctuations in fluids and has derived the following closed expression for the Rayleigh linewidth which applies to all values of $q\xi$ [10]:

$$\Gamma = (k_B T / 8\pi\eta\xi^3) \times [1 + q^2\xi^2 + (q^3\xi^3 - q^{-1}\xi^{-1}) \arctan q\xi], \tag{5}$$

where k_B is the Boltzmann constant and η is the high-frequency part of the shear viscosity. [An alternative derivation of (5) has been given by Ferrell.[11]] In the limit $q\xi \ll 1$, Eq. (5) again reduces to the hydrodynamic result (1), with the thermal diffusivity given by $\chi = k_B T / 6\pi\eta\xi$. Since η has no critical anomaly in the Kawasaki theory, the thermal diffusivity is proportional to ξ^{-1} as in Kadanoff-Swift. For $q\xi \lesssim 1$, Eq. (5) becomes

$$\Gamma = \chi q^2 [1 + (\tfrac{3}{5}) q^2 \xi^2], \tag{6}$$

which differs from the Fixman-Botch result (2) only in that $b = \frac{3}{5}$ rather than unity. In the limit $q\xi \gg 1$, Eq. (5) becomes

$$\Gamma = A q^3, \tag{7}$$

where A is given by

$$A \equiv (k_B T / 16\eta) = (3\pi/8)\chi\xi. \tag{8}$$

A temperature-dependent linewidth of the form predicted by Kawasaki was first observed in the binary mixture aniline-cyclohexane by Bergé et al.[12]

Experimental Results.—(a) Hydrodynamic region ($q\xi << 1$): Our 53 data points for which $q\xi \leq 0.2$ (as determined by the analysis in the following paragraphs) accurately obey the q^2 angle dependence predicted by Eq. (1). A least-squares analysis of a log-log plot of those data, which is a straight line within the experimental uncertainty, yields $\chi_0 = (6.94 \pm 0.21) \times 10^{-4}$ cm^2/sec and $\gamma - \psi = 0.751 \pm 0.004$.

(b) Nonlocal hydrodynamic region ($q\xi \leq 1$): As the critical temperature is approached we find that small deviations from the hydrodynamic behavior are accurately described by the Fixman type of equation. Our values for the correlation length, obtained by fitting the linewidth data for $q\xi \leq 1$ by Eq. (2), can be compared with the correlation lengths obtained by Giglio and Benedek[13] from measurements of the angular dependence of the scattering intensity. The latter measurements were made along an unknown density path which approached the critical density as T was increased above T_c; therefore, only the values of ξ for which $T - T_c > 0.120$°C are included in this comparison. The value of the constant b

that brings our correlation lengths into coincidence with those from intensity measurements is $b = 0.55 \pm 0.12$, in agreement with Kawasaki's result $b = \frac{3}{5}$. (Chu, Kuwahara, and Fenby have recently examined linewidth and intensity data for several simple fluids and binary mixtures and have also concluded that $b = \frac{3}{5}$ within the experimental uncertainty.[14]) The temperature range over which Eq. (2) is applicable to our data is too small to deduce the correlation length exponent ν from the data, but if we impose the constraints $\nu = \gamma - \psi = 0.751$ and $b = \frac{3}{5}$, then $\xi_0 = 0.51 \pm 0.06$ Å.

Our values for the correlation length are about 12 times smaller than the values obtained by Yeh (for the same ϵ) in linewidth measurements on xenon, but Yeh has reanalyzed his data, including an aperture correction formerly omitted, and has obtained correlation length values comparable with ours.[15]

(c) Critical region ($q\xi \gg 1$): We find that very near the critical point the Rayleigh linewidth exhibits the predicted temperature-independent q^3 behavior [Eq. (7)]. A least-squares analysis of the data for which $q\xi > 1$, using the complete Kawasaki expression (5) with the values of χ_0 and $\gamma - \psi$ obtained from the hydrodynamic region, yields $A = (4.7 \pm 0.2) \times 10^{-12}$ cm^3/sec; since $\xi_0 = 8A/3\pi\chi_0$, we have $\xi_0 = 0.58 \pm 0.03$ Å. The Kawasaki equation with these values for the parameters is shown in Fig. 1 along with the experimental data. The data in the region $1 < q\xi < 0.2$ show a small systematic departure from the Kawasaki theory with an rms error of 7%, compared with 5% for the region $q\xi > 1$ and 3% for $q\xi < 0.2$. Although this deviation from the theory may be explained at least partially by the difficulty we had in finding the minimum linewidth as a function of height, Bergé *et al.* also observed a systematic departure from the Kawasaki theory for $q\xi \sim 1$ in their linewidth measurements on aniline-cyclohexane.[12]

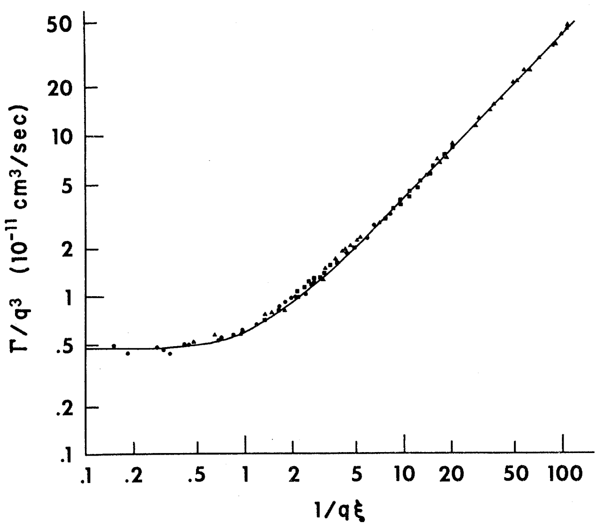

FIG. 1. Γ/q^3 vs $1/q\xi$ for xenon on the critical isochore between 0.003 and 5.0°C above T_c. Solid triangles, $\theta = 42°$; solid squares, $42° < \theta < 138°$; solid circles, $\theta = 138°$. The solid line is a plot of the Kawasaki linewidth equation (5) for the parameters $\chi_0 = 5.94 \times 10^{-4}$ cm^2/sec, $\nu = 0.751$, and $\xi_0 = 0.58$ Å.

An alternative to the above procedure of obtaining χ_0 and $\gamma - \psi$ from the linewidths in the hydrodynamic region and ξ_0 from the linewidths in the critical region is to fit simultaneously the data for all values of $q\xi$ with the Kawasaki equation. Since there are 87 data points for $0.2 < q\xi < 1$ and only 15 points for $q\xi > 1$, this latter procedure gives undue weight to the intermediate-$q\xi$ region, and the resultant value of A, $A = (5.1 \pm 0.2) \times 10^{-12}$ cm^3/sec, is clearly greater than the value of Γ/q^3 in the limit $q\xi \gg 1$.

Attempts were also made to fit the linewidth data with the more general scaling function of Halperin and Hohenberg, Eq. (3). With $\gamma - \psi$ fixed at the value measured in the hydrodynamic region and with values of ν as low as 0.5, the scatter in the data using the generalized function appears qualitatively no worse than in Fig. 1.

Discussion. – Our results for $\gamma - \psi$ for xenon are shown in Table I along with results from linewidth measurements on other simple fluids[1,2,16] and on binary mixtures[12,17-19] (in a mix-

Table I. Results of Rayleigh linewidth determinations of the exponent $\gamma - \psi$ which describes the critical behavior of the thermal diffusivity χ for one-component fluids at the critical density and the diffusion constant D for binary mixtures at the critical concentrations: $\chi \sim D \sim \epsilon^{\gamma-\psi}$, where $\epsilon \equiv (T - T_c)/T_c$ and $T > T_c$.

System	Author	Ref.	$\gamma - \psi$
Xe	Henry	This	0.751 ± 0.004
SF_6	Benedek	1	1.26 ± 0.02
SF_6	Braun	16	0.89 ± 0.07
CO_2	Swinney	2	0.73 ± 0.02
Isobutyric acid + water	Chu	17	0.68 ± 0.04
n-hexane + nitrobenzene	Chen	18	0.66 ± 0.02
Aniline + cyclohexane	Bergé	12	0.59 ± 0.06
Phenol + water	Pusey	19	0.68 ± 0.03

ture the binary diffusion constant plays the same role that χ plays in a one-component fluid). The exponents for Xe and CO_2 are seen to be in reasonable agreement, but somewhat higher than the exponents observed for the mixtures. In contrast to these results for CO_2, Xe, and four binary mixtures, the result $\gamma-\psi=1.26\pm0.02$ has been obtained for SF_6 by Benedek and collaborators[1] in a series of very careful experiments over the past five years; however, Braun et al.[16] have recently reported $\gamma-\psi=0.89\pm0.07$, so the problem of SF_6 remains unresolved.

Our results for $\gamma-\psi$ can be combined with the results for γ from other experiments to deduce a value for ψ. Vicentini-Missoni, Levelt Sengers, and Green have fit the Habgood and Schneider *PVT* data for xenon with their scaling-law equation of state obtaining $\gamma=1.26$.[20] The compressibility exponent for xenon below T_c has been determined directly from measurements of the scattering intensity by Giglio and Benedek,[13] who found $\gamma_{\text{liquid}}'=1.228\pm0.028$ and $\gamma_{\text{vapor}}'=1.244\pm0.017$, and according to the scaling laws of Widom and Kadanoff, $\gamma'=\gamma$.[21] Hence we take $\gamma=1.25\pm0.02$ and conclude that $\psi=0.05\pm0.03$. Direct measurements of the thermal conductivity in the critical region are extremely difficult, and the only fluid which has been studied extensively enough to determine the exponent ψ is CO_2, for which Murthy and Simon have recently reported $\psi=0.674\pm0.002$.[22]

Our results for xenon and the similar recent results of Bergé et al.[12] for aniline-cyclohexane indicate that the Kawasaki function, Eq. (5), is a very good representation of the experimental data. In particular, the predicted temperature-independent limiting linewidth, $\Gamma=(k_BT/16\eta)q^3$, has been found to be in good agreement with independent viscosity data for aniline-cyclohexane[12] and CO_2.[23] Our value for the limiting linewidth in the critical region is also in good agreement with independent viscosity data for xenon extrapolated to the critical point.[24]

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