tain $R=(\theta_2/\theta_1)^{-1/4}$. Thus fission is predicted to occur when the soliton goes from a region of higher temperature into a region of lower temperature ($\theta_2<\theta_1$), but the effect is much weaker (thresholds are higher) than shoal-induced fission of water waves.

A fission process qualitatively similar to that discussed here is expected to occur also for envelope solitions described by the nonlinear parabolic equation,[19] but that requires a separate investigation.

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Rayleigh Linewidth in SF_6 Near the Critical Point*

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In two entirely independent experiments we have measured the Rayleight linewidth for SF_6 on the critical isochore and the results are found to be in strong disagreement with previously reported measurements. Our linewidth data, after subtraction of background terms, exhibit the same critical behavior observed in other fluid systems ($\varphi=0.61 \pm 0.04$). Within the experimental uncertainty our results agree with linewidths calculated from the Kawasaki theory with no adjustable parameters.

The fundamental question to be answered by Rayleigh linewidth measurements on fluids near the critical point is whether or not a dynamic property such as the linewidth (the decay rate for fluctuations in the order parameter for the phase transition) behaves similarly for different systems in the same sense that the static properties are known to exhibit a similarity in critical behavior for different systems. In an effort to answer this question, there have been numerous measurements in the past six years of the Rayleigh linewidth for pure fluids and mixtures near the critical point. In the hydrodynamic region the linewidth is given by $\Gamma = \chi q^2$ for a pure fluid and $\Gamma = Dq^2$ for a binary mixture, where χ is the thermal diffusivity, D is the binary diffusion coefficient, and q is the magnitude of the scattering vector. ($\chi \equiv \lambda/\rho c_p$, where λ, ρ, and c_p are the thermal conductivity, density, and specific heat, respectively.)

The results of linewidth measurements of the thermal diffusivity (on the critical isochore) and the binary diffusion coefficient (at the critical concentration) were in most cases fitted by an expression of the form $\chi = \chi_0 \epsilon^{\varphi}$ (with $\epsilon \equiv |T - T_c|/T_c$) in analogy with the simple exponential laws known to describe the behavior of static properties of fluids. The values of the exponent φ obtained for the four binary mixtures studied ranged[1] from 0.59 to 0.68, while for CO_2 $\varphi = 0.73$,[2] for xenon $\varphi = 0.75$,[3] and for SF_6 $\varphi = 1.26$.[4] The markedly different exponent for SF_6, supported by additional measurements on six near-critical isochores, is contrary to the expected "universality" of critical phenomena and consequently has been a puzzle for several years.

Recently it has become clear[5] that there is a large nonsingular background contribution to the thermal conductivity, and the contribution of this nonanomalous background should be subtracted before the thermal diffusivity data are fitted by a simple exponential law. Sengers and Keyes[5] have reanalyzed the CO_2 linewidth data, taking the background thermal conductivity into account, and found that the correct exponent φ is 0.62 rather than 0.73. A similar analysis[6] of the xenon data was found to reduce φ from 0.75 to 0.64. For SF_6, however, Throdorakopoulos[7] found that the inclusion of the background thermal conductivity did not bring the SF_6 exponent into accord with the results for other fluids. Braun *et al.*[8] have recently presented new SF_6 linewidth data for which $\varphi = 0.89$, but as with the earlier SF_6 data, the background correction does not bring these data into agreement with the results for other fluids.

We report here the results of two additional SF_6 linewidth experiments undertaken completely independently at the University of Massachusetts (by K.H.L. and T.A.K., whose preliminary results have been reported[9]) and at Johns Hopkins University (by T.K.L. and H.L.S.). Within the experimental uncertainty, the two results are identical and, in contrast to the previously reported SF_6 linewidth measurements, our data agree with the results for other fluids and with the Kadanoff-Swift-Kawasaki mode-mode coupling theory.

The linewidth measurements at Johns Hopkins utilized the same optical beating spectrometer and apparatus previously used in studying carbon dioxide and xenon.[2,3] For SF_6, 196 data points were obtained along the critical ioschore over the temperature range $0.001 \leq T - T_c \leq 3.5$°C, for scattering angles 29.7°, 59.6°, 90°, 120.4°, and 150.3°. Most of the data (151 points), including all the data for $T - T_c < 0.3$°C, were obtained for $\theta = 90°$, which corresponds to a scattering vector $q = 1.5307 \times 10^5$ cm^{-1}. The sample, containing less than 50 ppm impurities, was 0.8% below ρ_c; T_c, measured with a precision of 0.0005°C, was (45.586 ± 0.020)°C.

The University of Massachusetts experiment utilized the same collection optics, sample cell, temperature control, and filling procedure as described elsewhere.[9,10] Light scattered from roughly a single coherence region at $\theta = 45.3°$ is detected by a photomiltiplier, and the photoelectron pulses are applied to the input of a digital autocorrelation computer.[10] Pulses arriving during a time increment are counted in a three-bit register and the multiplications are carried out in real time. Since the average number of pulses per increment is much less than 1, the correlator operates essentially as an unclipped "ideal" correlator.[11] Over twenty linewidths were extracted from the exponential part of the intensity (photocount) correlation function in the temperature range $0.009 \leq T - T_c \leq 4.02$°C.

Our results for Γ/q^2 on the critical isochore are plotted in Fig. 1 along with the data of Saxman and Benedek[4] and Braun *et al.*[8] Our $\theta = 90°$ data for $T - T_c \lesssim 0.2$°C and $\theta = 45°$ data for $T - T_c \lesssim 0.1$°C extend into the region very near T_c where the correlation range ξ ($\xi = \xi_0 \epsilon^{-\nu}$) is so large that hydrodynamics must be supplanted by a more general dynamical theory, as we shall discuss later. However, the remainder of the data are in the hydrodynamic region ($q\xi \ll 1$) where the data from all four experiments should fall on a single curve describing the thermal diffusivity, $\chi = \Gamma/q^2$. Note that in the hydrodynamic region a few tenths of a degree above T_c our results differ from previous experiments by as much as a factor of 3 or more. Before comparing our results with the theoretical predictions, we briefly review the theory.[6]

We assume that any physical property of a system near the critical point can be written as the sum of two terms: (1) the regular part, which is

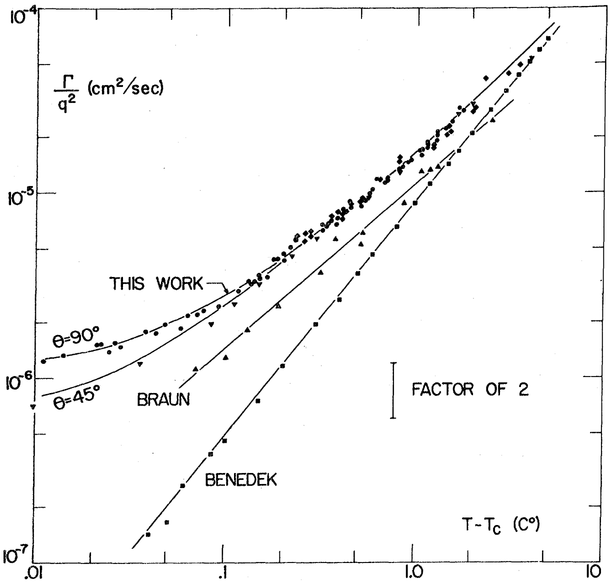

FIG. 1. Γ/q^2 vs $T-T_c$ for SF_6 on the critical isochore. Previous experiments: Braun *et al.* (Ref. 8), $\theta=7.5°$ (triangles); Benedek (Ref. 4), $\theta=13.9°$ (squares). Present experiments: Johns Hopkins, $\theta=90°$ (circles), $\theta=29.7°$, 59.6°, 120.4°, and 150.3° (diamonds); University of Massachusetts, $\theta=45.3°$ (inverted triangles). Curves through our data are given by Eq. (2) using the set of best-fit parameters.

the value the property would have in the absence of any critical anomaly, and (2) the singular part, which in the hydrodynamic region ($q\xi \ll 1$) diverges to infinity or converges to zero as the critical point is approached. Thus, for example, for the thermal conductivity we can write $\lambda_q=\lambda^r+\lambda_q{}^s$, where the subscripts q indicate the possible q dependence of the singular part of the thermal conductivity very near T_c.

Generalizing the hydrodynamic result $\Gamma=(\lambda/\rho c_p)q^2$ to include a q dependence in λ and c_p, and separating λ and c_p into regular and singular parts, we have

$$\Gamma=[\lambda^r/\rho(c_p)_q]+\Gamma_q{}^s[(c_p)_q{}^s/(c_p)_q], \qquad (1)$$

where $\Gamma_q{}^s \equiv [\lambda_q{}^s/\rho(c_p)_q{}^s]q^2$ is the singular part of the linewidth. If the Ornstein-Zernike form is assumed for the q dependence of $(c_p)_q{}^s$ and $(c_p)_q$, $(c_p)_q=c_p(q=0)/(1+q^2\xi^2)$, then (1) becomes

$$\Gamma=(\lambda^r/\rho c_p)q^2(1+q^2\xi^2)+\Gamma_q{}^s[(c_p)^s/c_p], \qquad (2)$$

where the absence of a subscript q on c_p indicates the $q=0$ (thermodynamic) quantity. For our SF_6 data the ratio $(c_p)^s/c_p$ differs from 1 by not more than 6%; we shall refer to the first term on the right-hand side of (2) as the "background" part of the linewidth, and the second term as the "singular" part.

In 1968 Kadanoff and Swift[12] developed a mode-mode coupling theory for the critical behavior of transport coefficients, which Kawasaki[13] has extended to derive an expression for the singular part of the linewidth that is applicable over the entire domain from the hydrodynamic region to the critical point:

$$\Gamma_q{}^s=(k_BT/6\pi\eta^*\xi^3)K(q\xi), \qquad (3)$$

where $K(x)\equiv\frac{3}{4}[1+x^2+(x^3-x^{-1})\tan^{-1}x]$ and k_B and η^* are the Boltzmann constant and the high-frequency shear viscosity, respectively. In the hydrodynamic limit, $q\xi \ll 1$, Eq. (3) becomes $\Gamma_q{}^s=(k_BT/6\pi\eta^*\xi)q^2$; hence the Kadanoff-Swift-Kawasaki theory predicts that the exponent φ that describes the critical behavior of the singular part of the thermal diffusivity should be equal to the correlation-length exponent ν, a prediction which is supported by the agreement between the measured values of ν and the values of φ obtained for binary mixtures and (after background corrections) for CO_2 and xenon.

We have analyzed our linewidth data using (2) with the Kawasaki form (3) for $\Gamma_q{}^s$, a procedure which requires independent data for λ^r, c_p, ξ, and η^*. From the data of Lis and Kellard[14] and Venart[14] we found $\lambda^r(\rho_c,T)=(3.31+1.8\epsilon)\times10^3$ erg/cm sec °C. The relation $\rho c_p=\rho c_v+T(\partial P/\partial T)_\rho{}^2\kappa_T$ was used to determine c_p, where c_v was obtained from the data of Fritsch and Carome,[15] and several experiments were analyzed to obtain[16] $(\partial P/\partial T)_\rho=0.854$ atm/°C and[16,17] $\kappa_T=(1.44\times10^{-3})\epsilon^{-1.225}$ atm^{-1}.

Puglielli and Ford[17] have measured the correlation length for SF_6, obtaining $\xi=1.5\epsilon^{-0.67}$ Å, but there have been no direct measurements of the viscosity of SF_6 in the critical region; however, Henry[18] has examined the viscosity data that have been reported for other fluids near the critical point (xenon, CO_2, argon, krypton, nitrogen, oxygen, ethane, methane, and propane) and has established a relation for the corresponding states, $\eta^r(\rho_c,T_c)/\eta(0,T_c)=2.24\pm0.06$. Combining the latter result with the low-density SF_6 viscosity data[19] yields $\eta^r(\rho_c,T_c)=347$ μP, which is the value we will assume for η^*.[20]

As a first test of the theory, the temperature dependence of the singular part of the linewidth in the hydrodynamic region can be compared with the predicted exponent relation $\varphi=\nu$. The data, after the background is subtracted, are fitted by a power law with $\varphi=0.61\pm0.04$, in good agree-

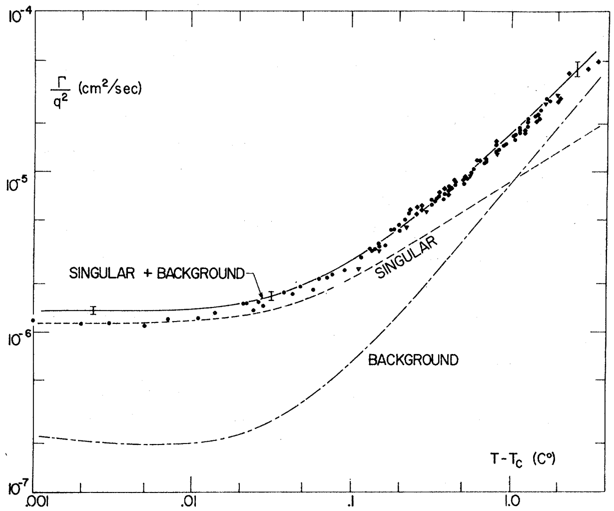

FIG. 2. Comparison of present linewidth with theory. The theoretical linewidth (solid curve) is the sum of a singular term derived by Kawasaki (dashed curve) and a background term (dot-dashed curve). The curves are drawn for $\theta = 90°$ and the error bars represent the estimated combined uncertainty in the measured parameters used. University of Massachusetts data: $\theta = 45.3°$ (inverted triangles; data below $T - T_c = 0.1°C$ are omitted for clarity). Johns Hopkins data: $\theta = 90°$ (circles); $\theta = 29.7°$, 59.6°, 120.4°, and 150.3° (diamonds).

ment with the theory and with the results for other fluids. The uncertainty in φ arises primarily from the uncertainty in the background (15%); our data (after averaging) have an uncertainty of 6%.

A more crucial test of the theory is a direct comparison of the magnitude as well as the temperature dependence of the linewidth data with the theory. Such a comparison is shown in Fig. 2, where the solid line is the theoretical curve obtained by susbtituting the parameter values quoted above into Eq. (2), with the Kawasaki form for the singular part of the linewidth. The singular and background parts of the linewidth, which sum to give the theoretical linewidth, are shown for $\theta = 90°$ in Fig. 2 by the dashed and dot-dashed curves, respectively. The rms deviation of the data for all angles from the theory is only 8%, which is no larger than the estimated uncertainty in the theoretical linewidths (indicated by the error bars).[21]

We have also fitted our data by the theory using a nonlinear least-squares fitting routine with η^*, ξ_0, and ν as free parameters, obtaining $\eta^* = 400 \pm 30$ μP, $\xi_0 = 2.16 \pm 0.50$ Å, and $\nu = 0.61 \pm 0.04$. With the viscosity fixed at $\eta^* = 374$ μP, the best-fit parameters are $\xi_0 = 2.3 \pm 0.3$ Å and $\nu = 0.61 \pm 0.04$. The stated uncertainties arise primarily from the rather large uncertainty in the background.

We have shown that, contrary to earlier reports, the Rayleigh linewidth for SF_6 exhibits the same critical behavior observed for other fluids, and furthermore there is remarkably good agreement between the linewidth data and the theoretical linewidth calculated by adding the background contribution to Kawasaki's result for the singular part of the linewidth.

It is gratifying to find that the present data of Benedek and co-workers (see the following Letter) are consistent with the results we have discussed here and with those reported by Mohr and Langley.[9]

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[21]If the Wu and Webb (Ref. 20) viscosity is used, the rms deviation of the data from the theory (with ξ from Ref. 17) is 20%; the deviation is especially large (32%) near T_c.

Spectrum and Intensity of Light Scattered from Sulfur Hexafluoride along the Critical Isochore*

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We have measured the thermal diffusivity (D), the isothermal compressibility (κ_T), and the pressure (P) along the critical isochore of sulfur hexafluoride over the temperature range $0.048°\mathrm{K} < (T - T_c) < 2.4°\mathrm{K}$. We find that $\kappa_T = 1.26 \times 10^{-9}(T/T_c - 1)^{-1.235 \pm 0.015}$ cm^2/dyne and that $(\partial P/\partial T)_V = [7.91 + 0.18(T - T_c) \pm 0.1] \times 10^5$ dyne/cm^2 deg. We discuss our measurements of D in terms of the Kadanoff-Swift-Kawasaki mode-mode coupling theory.

Using the techniques of optical mixing spectroscopy,[1] we have measured the spectrum of light scattered quasielastically from thermal entropy fluctuations in sulfur hexafluoride at critical density over the temperature range $0.048°\mathrm{K} < T - T_c < 2.4°\mathrm{K}$. From these measurements we have deduced the magnitude and temperature dependence of the thermal diffusivity (D) along the critical isochore. From the intensity of the scattered light we have deduced the temperature dependence of the isothermal compressibility (κ_T) along the same path. Finally, we have measured the pressure (P) as a function of temperature and have obtained accurate values for $(\partial P/\partial T)_V$ on the critical isochore.

In our experiment, light from an intensity-stabilized He-Ne laser enters a high pressure optical cell at an incidence angle of 2.42° to the normal of the entrance window. A focusing lens near the exit window of the cell images the scattering region on the entrance aperture of a photomultiplier tube. A second aperture, located in the focal plane of this lens, selects (with angular spread $\Delta\theta/\theta = 0.1$) the scattering angle ($\theta$) and thereby determines the wave vector ($\vec{K}$) of the entropy fluctuation whose scattering is observed. The alignment procedure is such that the scattered rays accepted by the collection optics make the same angle with the window normal as does the transmitted beam. This procedure ensures first that the scattering vector $\vec{K}$ is independent of the index of refraction of the fluid and second that the ratio of the intensity of the scattered light collected to the intensity of the transmitted beam is independent of optical attenuation in the sample. In our experiment, $K = 8380$ cm^{-1}.

The sample cell was filled to within 0.1% of critical density with sulfur hexafluoride of impurity content <20 ppm. Temperatures were measured with a platinum resistance thermometer in accordance with the 1948 International Practical Temperature Scale, and the critical temperature (T_c) was determined to be 318.707 $\pm 0.002°\mathrm{K}$ by direct observation of the disappear-