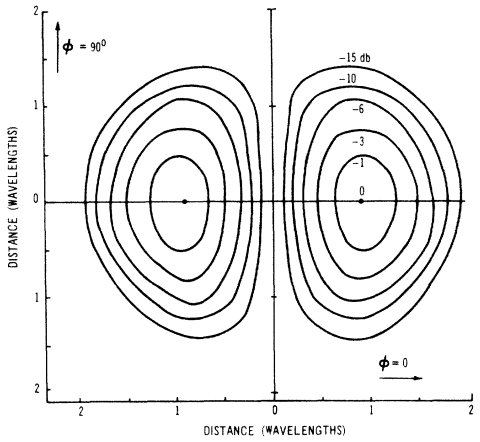

FIG. 2. Contours of the longitudinal field intensity, I_L, in the focal plane.

for a wider aperture system, and the experimental measurements will undoubtedly show some errors arising from field perturbations caused by the receiver.

The results of Fig. 1(b) show the increasing complexity in the variation of I_L on moving away from the focus. The small asymmetries with respect to the axis are caused by the scanning direction being slightly off parallel with the $\varphi = 0$ direction. The patterns are not symmetric with respect to the focal plane since, at the microwave frequency used, the focus is only 31 wavelengths from the lens and motions of several wavelengths along the axis are not negligible.

In addition to the results shown in Figs. 1 and 2, some measurements have been made with sources having nonuniform amplitude distribution across the lens. Since microwave beams can be "shaped" rather conveniently, measurements at microwave frequencies could be used to obtain information on the longitudinal field distribution for focused laser beams having more complex amplitude distribution.

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OBSERVATION OF THE SPECTRUM OF LIGHT SCATTERED FROM A PURE FLUID NEAR ITS CRITICAL POINT*

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This Letter presents recent measurements of the spectral distribution of light scattered quasielastically from a pure fluid (SF_6) near its critical point. We present data on the half-width of the spectrum of the light scattered 14° away from the incident direction: (a) along an isochore very close to the critical isochore over a temperature range $1\times10^{-5} \leq (T-T_c)/T_c \leq 6\times10^{-3}$, and (b) along the gaseous portion of the coexistence line over a temperature range $-6\times10^{-4} \leq (T-T_c)/T_c < 1\times10^{-5}$.

The scattering is produced by entropy fluctuations which decay very slowly in the critical region. As a result, the spectrum of the scattered light is extremely narrow (~$10-10^4$ cps). To observe such narrow spectral lines we have developed a novel "square-law" or "self-beating" spectrometer.[1] Figure 1 is a schematic diagram of this spectrometer. It consists of three parts: (1) the light source, (2) the scattering cell and light-collecting optics, and (3) an electronic system for spectral analysis. We used a Spectra-Physics model 115 helium-neon laser with ~5-mW output power as the light source. While the spectral output of this laser consists of about six longitudinal modes spaced 250 Mc/sec apart near 6328 Å, the feature limiting the resolution of this spectrometer is the intrinsic spectral width of the light in each mode. This is less than ~2 cps. The laser beam passes through the scattering cell where the temperature is controlled to ±0.003°K with a servo-stabilized bath. Temperature was measured with a platinum resis-

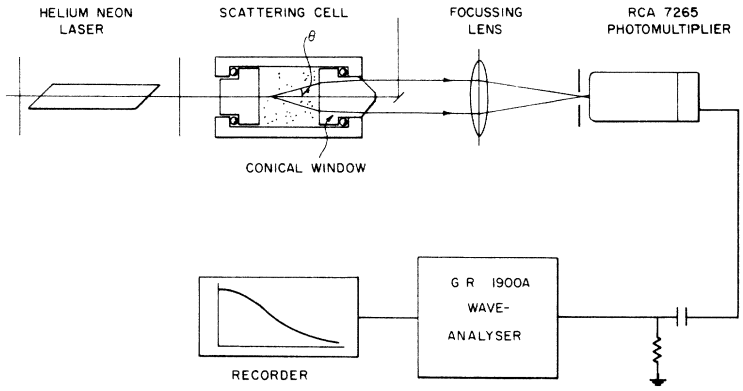

FIG. 1. Block diagram of "self-beating" or "square-law" spectrometer showing laser light source, scattering cell with conical optics, and the spectral analysis system.

tance thermometer. Light scattered through an angle θ is collected over an azimuth of 2π by a conical lens and emerges parallel to the cone axis. It then meets a spherical lens and is brought to a focus at the center of a pin-hole aperture before the face of an RCA 7265 photomultiplier tube. Those rays which do not come out of the cell nearly parallel to the axis cannot pass through the pin hole. These optics enable very efficient collection of light and a delicate control on the range $\delta\theta$ of scattering angles accepted by the spectrometer. In our system $\delta\theta$ was 0.6°.

The power spectrum $I_1(\omega)$ of the light falling on the surface of the photomultiplier can be obtained by carrying out a spectral analysis of the fluctuations in the photocurrent. The fluctuations in the photocurrent are proportional to the square of the fluctuations in the incident field, and the spectrum of these fluctuations $I_2(\omega)$ is analyzed by the G. R. 1900-*A* whose output $[I_2(\omega)]_{\text{out}}$ is, in fact, the square root of $I_2(\omega)$. The connection between $[I_2(\omega)]_{\text{out}}$ and the desired quantity $I_1(\omega)$ can be obtained as follows.[1] The electric field of the light wave reaching the phototube surface has a time dependence of the form $\delta E(t)e^{-i\omega_0 t}$, where ω_0 is the angular frequency of the incident light wave. The amplitude $\delta E(t)$ is a random variable directly proportional to the fluctuations in the dielectric constant of the scattering medium.[1-4] The power spectrum $I_1(\omega)$ of the scattered light is closely related to the correlation function $R_1(\tau)$ for the fluctuations in the scattered field. This quantity is given by

$$R_1(\tau) = \langle E(t+\tau)\cdot E^*(t)\rangle = \langle \delta E(t+\tau)\delta E^*(t)\rangle e^{-i\omega_0\tau}. \quad (1)$$

$R_1(\tau)$ is related to the spectrum through[5]

$$I_1(\omega) = \frac{1}{2\pi R_1(0)}\int_{-\infty}^{\infty} R_1(\tau)e^{i\omega\tau}d\tau. \quad (2)$$

The spectrum is normalized to unity via

$$\int_{-\infty}^{\infty} I_1(\omega)d\omega = 1.$$

The photocurrent is proportional to the square of the incident electric field. More exactly, since the photocurrent does not contain fluctuations as rapid as the light frequency, the photocurrent is proportional simply to $|E(t)|^2 = |\delta E(t)|^2$. This quantity contains both a dc part which is blocked before spectral analysis by an *R-C* network (see Fig. 1), and a fluctuating part whose correlation function $R_2(\tau)$ is simply[1] the square of the correlation function for $\delta E(t)$, i.e.,

$$R_2(\tau) = \langle |\delta E(t+\tau)|^2 |\delta E(t)|^2\rangle, = |\langle \delta E(t+\tau)\delta E^*(t)\rangle|^2 = |R_1(\tau)|^2. \quad (3)$$

The spectrum $I_2(\omega)$ of the fluctuations in $|\delta E(t)|^2$ is thus related to the square of the correlation function for the scattered field:

$$I_2(\omega) = \frac{1}{2\pi |R_1(0)|^2}\int_{-\infty}^{\infty} |R_1(\tau)|^2 e^{i\omega\tau}d\tau. \quad (4)$$

The power spectrum of the fluctuations in the photocurrent is directly proportional to $I_2(\omega)$; hence the designation "square-law" spectrometer. $I_2(\omega)$ can be connected more directly to $I_1(\omega)$ by expressing $R_1(\tau)$ in terms of $I_1(\omega)$ with Eq. (2). This gives

$$I_2(\omega) = \int_{-\infty}^{\infty} I_1(\omega')I_1(\omega'-\omega)d\omega'. \quad (5)$$

The spectral density at ω is the sum total of all the beat notes between spectral components

separated an amount ω apart. Hence, the term "self-beating" spectrometer. The G. R. 1900-A wave analyzer decomposes the fluctuations in the photocurrent into their spectral components. However, as its rectifier is a linear full-wave detector, it provides the square root of the power spectrum of these fluctuations. The output $[I_2(\omega)]_{out}$ of this spectrum analysis is thus proportional to $[I_2(\omega)]^{1/2}$.

If the correlation function for the scattered field dies off exponentially with a decay rate Γ like

$$R_1(\tau) = \langle |\delta E(t)|^2 \rangle e^{-i\omega_0\tau} e^{-\Gamma\tau}, \qquad (6)$$

then the power spectrum $I_1(\omega)$ is a Lorentzian-shaped line centered at ω_0 with a width Γ. The spectrum $I_2(\omega)$ is also a Lorentzian-shaped line centered at $\omega = 0$ with a width equal to 2Γ. The spectral output of the wave analyzer $[I_2(\omega)]_{out}$, which appears on the recorder, would then have the form of a square root of a Lorentzian, viz:

$$[I_2(\omega)]_{out} \propto [I_2(\omega)]^{1/2} = \left(\frac{2\Gamma/\pi}{\omega^2 + (2\Gamma)^2}\right)^{1/2}. \qquad (7)$$

If the decay is not exponential, by unfolding the spectrum using Eq. (4) or (5) we can determine the form of the temporal behavior of correlation function $|R_1(\tau)|$. In Fig. 2 we show the output spectrum of the wave analyzer for light scattered at $(T-T_c) = 0.318°K$ very near the critical isochore. The frequency $\Delta\nu$ at which the spectral intensity falls to $1/\sqrt{2}$ of its maximum value was 780 cps. This corresponds to $\Gamma = \pi\Delta\nu = 2450$ rad/sec. As we see from the figure, the shape is very precisely a square-root Lorentzian even for frequencies as far as twenty linewidths from the center. The band width of the wave analyzer was only 10 cps. Thus, the resolving power of the system is about 5×10^{13}. This is many orders of magnitude greater than the best optical spectrometers.

In Figure 3 we show measurements of the correlation rate Γ as a function of the temperature. Extreme care was taken at each point to insure the establishment of thermal equilibrium. An average equilibration time was ~20 hours. The line with positive slope represents measurements above the transition temperature along an isochore for which the fluid density was less than ρ_c by $(\rho_c-\rho)/\rho_c \sim 0.02$. For this isochore the minimum value of Γ was 640 rad/sec. For $0 < (T-T_c) < 1.5°K$, Γ is approximately linear in T with a slope $d\Gamma/dT = (5.9 \pm 0.25)\times10^3$ rad/sec°K. Below T_c, Γ rises quite rapidly as we move along the gas portion of the coexistence line. The results in this

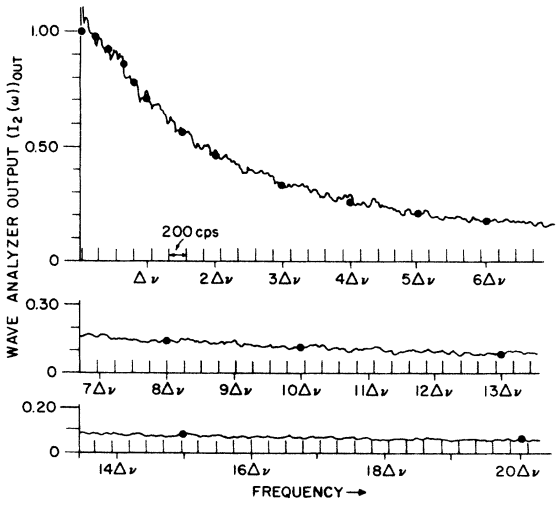

FIG. 2. The output spectrum of the spectrum analyzer at $T-T_c = 0.318°K$. The heavy black dots are the values calculated for a square root of a Lorentzian, i.e., $[I_2(\omega)]_{out} = (1+x^2)^{-1/2}$. This calculated line shape fits the spectrum for frequencies as far as 20 linewidths ($\Delta\nu$) from the center. At this temperature, $\Delta\nu = 780$ cps.

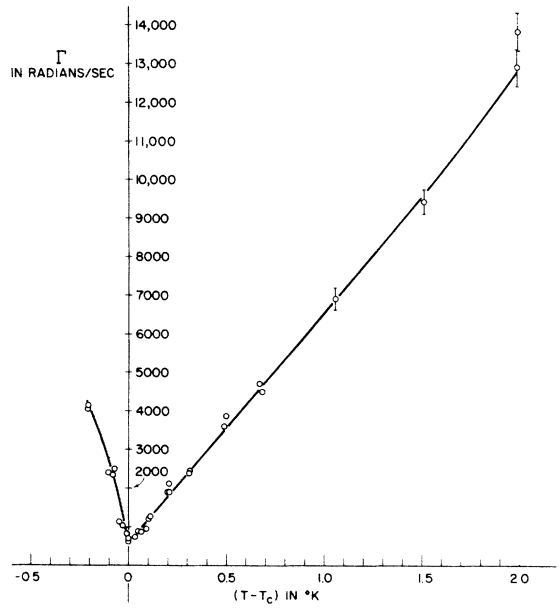

FIG. 3. Measurements of the correlation rate Γ for the entropy fluctuations in SF_6 as a function of the temperature. Above T_c, the data are taken along an isochore whose density ρ is $(\rho_c-\rho)/\rho_c \simeq 0.02$. Below T_c the data are taken along the gaseous portion of the coexistence line.

temperature region are insufficient to establish accurately the form of the temperature dependence of Γ.

A theory of the spectrum of the quasielastic scattering of light has been given by Landau and Placzek,[1,3,4] and the subject has been reviewed by Mountain.[6] According to this theory, the scattering is a reflection off a fluctuation in the dielectric constant produced by a nonpropagating fluctuation in the entropy having a wave vector $\vec{K}$ which satisfies the Bragg reflection conditions, $\vec{K}=\vec{k}-\vec{k}_0$. $\vec{k}$ and $\vec{k}_0$ are the wave vectors of the scattered and incident light waves. The entropy fluctuations are presumed to die away at a rate determined by the Fourier heat-flow equation. As a result,[1,4,6] the correlation rate Γ is given by

$$\Gamma=(\Lambda/C_p{}^*)K^2, \tag{8}$$

where Λ is the thermal conductivity; $C_p{}^*$ is the specific heat at constant pressure per unit volume; and the scattering vector $|K| = (4\pi n/\lambda_0)\sin\theta/2$, where n is the index of refraction of the scattering medium, θ the scattering angle, and λ_0 the incident light wavelength. By measuring Γ for different scattering angles, we have semiquantitatively substantiated[1] the K^2 dependence in Eq. (8). The extreme narrowness of the spectrum results from the fact that as $T-T_c$ the specific heat C_p diverges very strongly.

We now examine quantitatively whether the Landau-Placzek theory applies. The wave vector K is fixed by the index of refraction (n) and the apex angle of the conical lens. In the liquid state[7] $n=1.170$ for $\rho=1.37$ g/cc. Using the Lorentz-Lorenz relation, we obtain $n=1.09\pm0.01$ for $\rho=\rho_c=0.730$ g/cc. This gives $K=2.64\times10^4$ cm^{-1}. The thermal conductivity Λ has been measured in the critical region with satisfactory accuracy only for a single gas: CO_2.[8,9] These measurements indicate that Λ diverges like $C_v{}^*$, where $C_v{}^*$ is the specific heat at constant volume per unit volume of the fluid. If one takes[8] the proportionality factor linking $C_v{}^*$ and Λ as $\epsilon\eta/\rho$ where η is the viscosity and ρ the mass density, then for CO_2 the coefficient ϵ is close to the Eucken factor[10] for the dilute gas. Applying these observations to sulfur hexafluoride, we expect that $\Lambda/C_p{}^*=(\epsilon\eta/\rho)(C_v{}^*/C_p{}^*)$; i.e., the linewidth approaches zero as C_v/C_p. To estimate ϵ for SF_6, we chose again the dilute-gas value, $\epsilon=1.20$. η has been measured[11] for SF_6 at $T=T_c$ only in the regime of low densities ($\rho\sim0$). Its value is $\eta(0,T_c)=1.66\times10^{-4}$ g/cm sec. An analysis[12] of measurements on noble gases shown that the ratio $\eta(\rho,T)/\eta(0,T)$ obeys a law of corresponding states. This implies that $\eta(\rho_c,T_c)/\eta(0,T_c)$ is independent of the gas, and in fact this ratio has the value 2.19 for the noble gases. Applying this observation to SF_6 we have $\eta(\rho_cT_c)=3.6\times10^{-4}$ g/cm sec. The temperature dependence of $\eta(\rho\ T)$ near the critical point is negligible.

In the critical region neither C_v nor C_p has been directly measured for SF_6. Nevertheless we can estimate both of these in the critical region as follows. It is well known[13] that those fluids whose equations of state obey a law of corresponding states have the property that their configurational specific heats C_{v_c} are all the same when expressed as functions of (T/T_c) and (ρ/ρ_c). ($C_{v_c}\equiv C_v-C_{v_0}$ where C_{v_0} is the specific heat at constant volume for the dilute gas.) Similarly, C_p-C_v is a corresponding-state function for all such gases. Now, C_{v_0} has been measured[14] as a function of temperature for SF_6, and C_{v_c} and C_p-C_v are known quite accurately for xenon in the critical region. In fact, the C_{v_c} data on xenon are in very good agreement with recent measurements[16] on argon. From the xenon data on C_{v_c} and the SF_6 data on $C_{v_0}(T)$, we can compute C_v for SF_6. Combining this with the C_p-C_v data of xenon we can obtain C_p for SF_6. The temperature dependence of C_p for SF_6 obtained in this way is in satisfactory agreement with values of C_p obtained from experimental pressure-volume-temperature data[17] on SF_6.

By this method we have computed the expected temperature dependence of Γ, $\Gamma_{th}\equiv(\epsilon\eta/\rho)\times(C_v/C_p)K^2$, along the critical isochore. The values so obtained are given for several temperatures in Table I. To compare these with the experimental data, we must keep in mind

Table I. The temperature dependence of the correlation rate Γ as obtained theoretically and experimentally.

$T-T_c$ (°K)	Γ_{th} theory (rad/sec)	$(\Gamma-\Gamma_{min})$ expt. (rad/sec)
0.0	0	0
0.5	2420	2900
1.0	5650	5800
1.5	9800	8900
2.0	14 700	12 700

that the measurements were made along an isochore slightly displaced from the critical one. Hence, Γ_{min}, the minimum value of Γ, is not zero. The relevant comparison is to be made between the changes $(\Gamma-\Gamma_{min})$ and the changes in Γ_{th}. In column 3 of Table I we give $\Gamma-\Gamma_{min}$ for several temperatures. It should be noticed that theoretically Γ_{th} is not a linear function of the temperature. Nevertheless the change $\Gamma-\Gamma_{min}$ is correctly predicted by the theory for each point to within ~15%. We believe this to be a satisfactory confirmation of the Landau-Placzek theory in view of the uncertainties involved in estimating Λ and C_p.

This experiment represents the first measurements of the spectral distribution of light quasielastically scattered from a pure fluid. The first announcement of this work was made at the Conference on Critical Phenomena at the National Bureau of Standards, Washington, April 1965).[1] Subsequently and independently, Alpert and his co-workers[18] have reported the observation of the spectral profile of light scattered from CO_2 using a heterodyne form of laser spectrometer.

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