Thermal Diffusivity of CO_2 in the Critical Region*

H. L. SWINNEY AND HERMAN Z. CUMMINS
Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218
(Received 26 February 1968)

We have measured the Rayleigh linewidth in CO_2 in the critical region using a self-beat spectrometer. The linewidth was measured as a function of both temperature and cell height. The thermal diffusivity χ calculated using the Landau-Placzek equation is in excellent agreement with the values that have been obtained by thermodynamic measurements at three temperatures within the temperature range we investigated ($T-T_c=-1.04$, $+1.06$, and $+3.8$C°). Thus the Landau-Placzek equation is directly verified in the critical region, at least for temperatures not too close to T_c. However, we find that very near T_c [for $\epsilon\equiv(T-T_c)/T_c\lesssim 10^{-4}$], the correlation length in CO_2 is of sufficiently long range ($\sim$250 Å at $\epsilon=10^{-4}$) to require that the Fixman-modified linewidth equation be used in order to correctly describe the linewidth behavior. The thermal diffusivity was obtained along the critical isochore for the temperature range $0.02\leq(T-T_c)\leq 5.3$C° and along both the gas and liquid sides of the coexistence line for $0.02\leq(T_c-T)\leq 2.3$C°. The results are (in units of cm²/sec): along the critical isochore, $\chi=(18.1\pm0.5)\times10^{-6}(T-T_c)^{0.73\pm0.02}$; along the gas coexistence line, $\chi=(36.0\pm3.0)\times10^{-6}(T_c-T)^{0.66\pm0.05}$; and along the liquid coexistence line, $\chi=(34.8\pm2.5)\times10^{-6}(T_c-T)^{0.72\pm0.05}$. These exponents are in reasonable quantitative agreement with the prediction of Kadanoff and Swift that $\chi\sim|\epsilon|^{-\nu}(\nu\approx\frac{2}{3})$. Our exponents are also in accord with the thermal-conductivity divergence $\lambda\sim\epsilon^{-1/2}$ predicted by Fixman and by Mountain and Zwanzig, if the isothermal compressibility diverges as $\epsilon^{-5/4}$, as predicted by the Ising model. Thus both theory and experiment indicate a stronger divergence in the thermal conductivity than has heretofore been assumed. Our subcritical exponents are also in agreement with the linewidth measurements by Saxman and Benedek in SF_6; however, above the critical temperature they obtained an exponent of 1.27, in definite disagreement with our result.

I. INTRODUCTION

A. Historical Background

In recent years it has become increasingly apparent that such diverse systems as simple fluids, binary mixtures, ferromagnets, antiferromagnets, and binary metallic alloys exhibit marked similarities in their behavior near critical points.[1] Much of the new information has come from detailed studies of the asymptotic behavior of the thermodynamic properties of these systems as they approach critical points. New experimental techniques and refinements of older ones have revealed the presence of some striking anomalies in these properties which in turn have stimulated the development of the theory of critical phenomena for which the accurate determinations of the asymptotic behavior of the thermodynamic properties serve as crucial tests.[2–4]

It has been recognized for over 50 years that light-scattering measurements can provide information on the critical point in fluids and binary mixtures through the observation of critical opalescence.[5] Although light-scattering measurements were until quite recently limited to observation of the total scattered intensity, it was recognized that the spectrum of the scattered light contains independently useful information.

According to Landau and Placzek, the central (quasi-elastic) component of the Rayleigh-scattered light should be a Lorentzian whose half-width at half-maximum $\Gamma\equiv\Delta\omega_{1/2}$ is given for pure fluids by[6]

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

where $\boldsymbol{K}$, the momentum-transfer vector, is given by $|\boldsymbol{K}|=2nK_0(\sin\frac{1}{2}\theta)$, and n, K_0, and θ are the refractive index, the magnitude of the wave vector of the incident light in vacuum, and the scattering angle, respectively. χ, the thermal diffusivity, equals $\lambda/\rho c_p$, where λ, ρ, and c_p are the thermal conductivity, the density, and the specific heat at constant pressure, respectively. The specific heat c_p diverges in the same way as the isothermal compressibility, which is known to be strongly divergent at the critical point, whereas λ is expected to be only weakly divergent. Hence the Rayleigh linewidth should go to zero at the critical point. Thus measurements of the Rayleigh linewidth can be used to study the detailed temperature and density dependence of χ in the critical region.

Until quite recently measurements of the Rayleigh linewidth in the critical region were not possible since the linewidths (typically several kHz) are far too small to be measured with conventional spectroscopic techniques. With the advent of the laser, however, it was recognized that the technique of light-beating spectroscopy could be used to measure the widths of ex-

* This research was supported by the Advanced Research Projects Agency (Project DEFENDER) and was monitored by the U. S. Army Research Office (Durham) under Contract No. DA-31-124-ARO-D-400.

[1] *Critical Phenomena, Proceedings of a Conference, Washington, D. C., 1965,* edited by M. S. Green and J. V. Sengers, Natl. Bur. Std. (U. S.) Misc. Publ. No. 273 (1966).

[2] L. P. Kadanoff, W. Götze, D. Hamblen, R. Hecht, E. A. S. Lewis, V. V. Palciauskas, M. Rayl, and J. Swift, Rev. Mod. Phys. 39, 395 (1967).

[3] M. E. Fisher, Rept. Progr. Phys. 30, 615 (1967).

[4] P. Heller, Rept. Progr. Phys. 30, 731 (1967).

[5] See the review by O. K. Rice, in *Thermodynamics and Physics of Matter*, edited by F. D. Rossini (Princeton University Press, Princeton, N. J., 1955), p. 419.

[6] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley Publishing Co., Reading, Mass., 1960), p. 392; L. Landau and G. Placzek, Physik Z. Sowjetunion 5, 172 (1934). The linewidth resulting from concentration fluctuations was derived earlier by M. Leontowitsch, Z. Physik 72, 247 (1931).

TABLE I. Critical parameters.

Physical quantity	Temperature dependence[a]	Value of exponent[b] Theory	Experiment
$c_p \sim \kappa_T$	$T>T_c$ $\epsilon^{-\gamma}$	Classical, 1.00[b] Ising model, 1.250±0.001[b]	Green *et al.* data analysis, 1.4[g] Wilcox and Balzarini, 1.0[h]
	$T<T_c$ $(-\epsilon)^{-\gamma'}$	Classical, 1.00[b] Ising model, 1.31±0.05[b]	Green *et al.* data analysis, 1.4[g]
λ (thermal conductivity)	$T>T_c$ $\epsilon^{-\psi}$	Kadanoff and Swift, $\gamma-\nu$[c] Fixman[d] and Mountain and Zwanzig,[e] 0.5	Sengers, $\lambda \sim c_v$[i]; thus $\psi=0.1\pm0.1$
	$T<T_c$ $(-\epsilon)^{-\psi'}$	Kadanoff and Swift, $\gamma'-'\nu$[c]	?
$\chi \equiv \lambda/\rho c_p$ (thermal diffusivity)	$T>T_c$ $\epsilon^{\gamma-\psi}$	Kadanoff and Swift, ν[c] Fixman[d] and Mountain and Zwanzig,[e] $\gamma-0.5$	Thermodynamic experiments, 0.78[j] Present experiment, 0.73±0.02 Saxman and Benedek, 1.27[k]
	$T<T_c$ $(-\epsilon)^{\gamma'-\psi'}$	Kadanoff and Swift, ν'[c]	Present experiment: gas, 0.66±0.05: liquid, 0.72±0.05 Saxman and Benedek, 0.64[k]
ξ (correlation length)	$T>T_c$ $\epsilon^{-\nu}$	Classical, 0.50[b] Ising model, 0.643±0.003[b]	Ferromagnets and antiferromagnets, 0.65±0.03[b]
	$T<T_c$ $(-\epsilon)^{-\nu'}$	Classical, 0.50[b] Scaling law result, $\nu'=\nu$[b] Ising model, 0.675±0.03[f]	?

[a] $\epsilon \equiv (T-T_c)/T_c$. The indicated temperature dependence is along the critical isochore for $T>T_c$ and along the coexistence line for $T<T_c$.
[b] Reference 2.
[c] Reference 44.
[d] Reference 41.
[e] Reference 40.
[f] Reference 3.
[g] Reference 19.
[h] Reference 35.
[i] References 27 and 36.
[j] Reference 25.
[k] Reference 34.

tremely narrow spectral lines.[7] A laser heterodyne spectrometer was first used to study the linewidth of light scattered from a polymer solution,[8] and was subsequently employed by Alpert *et al.* to study the binary mixture aniline-cyclohexane in the critical region.[9]

The first measurements of the Rayleigh linewidth of a pure fluid were reported by Ford and Benedek for sulphur hexafluoride,[10] and shortly afterwards Alpert *et al.* reported linewidth measurements for carbon dioxide.[11] These experiments showed that the Rayleigh linewidth along the critical isochore approaches zero approximately linearly with $|T-T_c|$ and also follows the $\sin^2(\frac{1}{2}\theta)$ dependence predicted by the Landau-Placzek equation [Eq. (1)]. Similar behavior was found in the experiments with binary mixtures where the diffusion coefficient D (which plays the role that χ plays for pure fluids) also goes to zero at the critical point.[9,12]

Although these experiments agreed qualitatively with the Landau-Placzek prediction, quantitative verification of Eq. (1) was not possible since direct thermodynamic determinations of the thermal diffusivity χ (or the binary diffusion coefficient D) do not exist in the critical region covered by the light-scattering experiments. However, Lastovka and Benedek[13] measured the Rayleigh linewidth in toluene far from the critical region and found that χ deduced from their linewidths using Eq. (1) agrees within the experimental uncertainty with the value obtained by conventional thermodynamic measurements.

B. Critical Exponents

Many of the thermodynamic properties of systems in the critical region are found to exhibit simple power-law dependences on the reduced differential temperature $\epsilon \equiv (T-T_c)/T_c$. Predictions of the numerical values for the exponents deduced from "classical" theories (e.g., the van der Waals fluid and the Weiss ferromagnet) have been available for many years, and recently numerical approximation techniques have produced predictions for the exponents for the three-dimensional Ising model (and hence for the mathematically identical lattice gas). Some of these predictions along with the experimental values for some of the exponents of interest are shown in Table I. (See the recent review articles for a complete compilation.[2-4])

Above the critical temperature on the critical isochore the specific heat at constant pressure c_p (which diverges in the same way as the isothermal compressibility κ_T) is proportional to $\epsilon^{-\gamma}$, while the thermal conductivity λ is proportional to $\epsilon^{-\psi}$. Therefore χ is proportional to $\epsilon^{\gamma-\psi}$. Similarly, below the critical temperature on the coexistence curve, χ is proportional to $(-\epsilon)^{\gamma'-\psi'}$.

The exponent γ is 1.00 for "classical" models and is

[7] A. T. Forrester, R. A. Gudmundsen, and P. O. Johnson, Phys. Rev. **99**, 1691 (1955); A. T. Forrester, J. Opt. Soc. Am. **51**, 253 (1961).
[8] H. Z. Cummins, N. Knable, and Y. Yeh, Phys. Rev. Letters **12**, 150 (1964).
[9] S. S. Alpert, Y. Yeh, and E. Lipworth, Phys. Rev. Letters **14**, 486 (1965); S. S. Alpert, Ref. 1, p. 157.
[10] N. C. Ford, Jr. and G. B. Benedek, Ref. 1, p. 150; Phys. Rev. Letters **15**, 649 (1965).
[11] S. S. Alpert, D. Balzarini, R. Novick, L. Seigel, and Y. Yeh, in *Physics of Quantum Electronics, Conference Proceedings, 1965*, edited by P. L. Kelly, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Co., New York, 1966), p. 253.
[12] P. Debye, Phys. Rev. Letters **14**, 783 (1965).
[13] J. B. Lastovka and G. B. Benedek, Phys. Rev. Letters **17**, 1039 (1966).

predicted by the Ising model to be 1.25. Direct experimental determination of γ in the critical region of fluids is extremely difficult since the divergent compressibility leads to large gravitationally produced density gradients.[14] The only detailed direct study of the divergence in λ was for CO_2 by Sengers and collaborators; the singularity was thought to be weak, like the singularity in c_v which is proportional to $\epsilon^{0.1\pm0.1}$.[15]

Linewidth determinations of the thermal diffusivity appeared to offer a simple way of choosing between the classical and Ising models since $\gamma-\psi$ would be approximately 0.9 for the former and approximately 1.2 for the latter. By using a beam of very small diameter, linewidth measurements can be performed at essentially a unique density, even when there are large density gradients in the sample. Moreover, unlike thermodynamic determinations of λ which require a temperature gradient in the sample, linewidth measurements can be carried out for an isothermal sample.

While the early experiments demonstrated the usefulness of Rayleigh linewidth measurements, the result $\gamma-\psi=1$ had a large uncertainty for several reasons. First, the mean density was not precisely known. Secondly, the linewidth was not investigated as a function of height in the region near T_c where density gradients are significant. [In plots of the linewidths versus $(T-T_c)$ in the experiments cited, the extrapolated linewidth at $T=T_c$ was nonzero in every case by an amount considerably larger than the instrumental resolution.] And thirdly, the temperature ranges over which the measurements were performed were not sufficiently large to yield accurate exponents.

II. DESCRIPTION OF PRESENT EXPERIMENT

We have measured the Rayleigh linewidth for carbon dioxide along the critical isochore for the temperature range $0.018\leq T-T_c\leq 5.27$C° and along both the gas and liquid sides of the coexistence line for $-0.019\leq T-T_c\leq -2.31$C°.[16] The linewidth was measured both as a function of the beam height in the sample cell and as a function of temperature. Measurements were made over more than two orders of magnitude in $T-T_c$, both above and below T_c, a sufficiently large range in temperature to yield fairly accurate values for the exponents $\gamma-\psi$ and $\gamma'-\psi'$.

The 77-mm-long sample cell was formed from thick-walled Pyrex tubing with a 6.0×6.0 mm square inside cross section. The all-glass sample cell avoids the problem of contamination sometimes encountered when a critical fluid sample is in contact with valves or O rings, and the square walls avoid the problem of the focusing effect of round tubing. After pumping to high vacuum, the cell was loaded by cryogenic transfer from a cylinder of Matheson research grade CO_2 containing less than 50 ppm impurities and then sealed off. The loading was checked by observing the movement of the meniscus over several degrees below T_c. By employing the predictions of the law of corresponding states[17] the density was then determined to exceed the critical density ρ_c by approximately 0.3%.

The cell was suspended in an oil bath which was matched in refractive index (at the critical temperature and the laser wavelength) to the Pyrex. The temperature of the oil bath was stable within one millidegree for several hours and within several millidegrees per day. The bath was vigorously stirred to minimize temperature gradients; its temperature was measured with a calibrated thermistor and a dc Wheatstone bridge with a relative accuracy of ±0.0002C°. The critical temperature of the carbon dioxide was 31.080±0.015°C.

The problem of density gradients in the critical region was mentioned in Sec. I. Not only is the density a function of height in the sample at a fixed temperature, but also the density at *any* fixed height in the sample varies with temperature. In our spectrometer the diameter of the focused laser beam was 0.2 mm, so that each linewidth measurement corresponded to a density averaged over a height of only 0.2 mm. The sample cell was suspended from a micrometer so that its height in the thermostat could be varied. Thus the linewidth could be measured as a function of height as well as temperature.

We used the self-beat spectrometer technique of Ford and Benedek[10] to measure the linewidth, since the self-beat or homodyne spectrometer is simpler to set up and easier to align than the heterodyne spectrometer used by Cummins *et al.*[8] and by Alpert, Yeh, and collaborators.[9,11] The 75-mW output from a He-Ne laser was attenuated up to 30 dB to avoid heating of the sample. Spectra were obtained at scattering angles (θ) of 90°, 22°, 16°, and 15°, with an acceptance aperture of 0.3° in all cases. The scattered light was focused onto an RCA 7326 photomultiplier and the photocurrent was Fourier-analyzed with a Panoramic spectrum analyzer (Models SB-15a and LP-1a). The output of the spectrum analyzer was electronically squared and the resultant spectra were computer fit to a Lorentzian lineshape.

As a consequence of the critical opalescence, multiple scattering can be a serious problem in the critical region, leading to spurious results. At $T-T_c=0.026$C°, the "photon mean free path" in our sample was 40 mm, many times longer than the 1.5-mm length of the scattering volume. At that temperature and $\theta=90°$ we varied the size of the scattering volume, examined different scattering volumes within the sample cell, and

[14] See discussion by B. Chu and J. A. Duisman, J. Chem. Phys. 46, 3267 (1967).

[15] J. V. Sengers, Ref. 1, p. 165; Proceedings of the Fourth Technical Meeting of the Society of Engineering Science, 1967 (to be published).

[16] Preliminary results of this experiment were reported by H. L. Swinney and H. Z. Cummins, Bull. Am. Phys. Soc. 12, 588 (1967); see also a related investigation of the Brillouin components, R. W. Gammon, H. L. Swinney and H. Z. Cummins, Phys. Rev. Letters 19, 1467 (1967).

[17] E. A. Guggenheim, J. Chem. Phys. 13, 253 (1945).

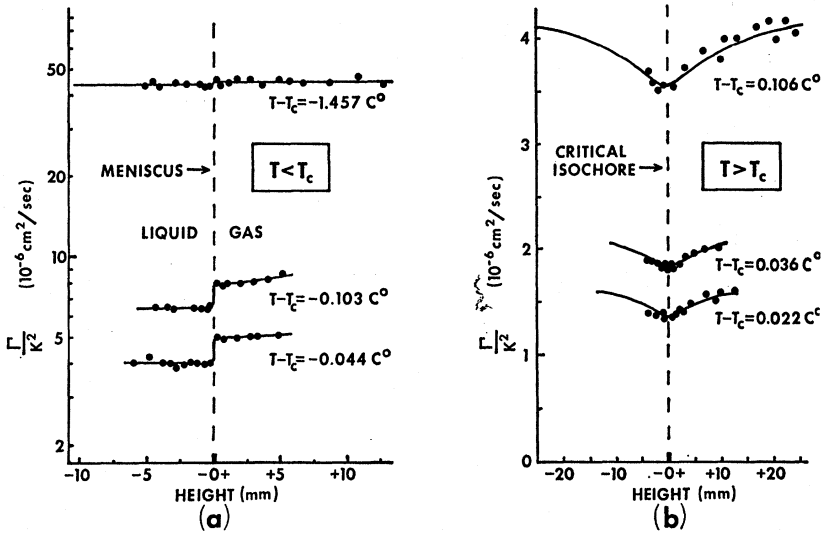

FIG. 1. Γ/K^2 as a function of beam height in the sample cell. The height resolution is equal to the diameter of the focused beam, 0.2 mm. (a) For three temperatures below T_c (height is measured relative to the meniscus height). (b) For three temperatures above T_c (height is measured relative to the height which corresponds to the minimum in Γ/K^2).

measured the depolarization of the scattered light; these tests indicated that multiple scattering effects were not significant in our experiment.

III. EXPERIMENTAL RESULTS

In general, any departure of the spectra from the Lorentzian lineshape was less than our experimental uncertainty. For most of the spectra, the experimental amplitude at any frequency differed from the amplitude of the computer-fit Lorentzian by an amount not greater than 2%, which is approximately equal to the experimental uncertainty. At no temperature or angle were spectra *consistently* obtained with a departure from the Lorentzian shape which was larger than the experimental error; hence the occasional non-Lorentzian spectra were discarded.

The linewidth- (Γ) versus-height data were converted into Γ/K^2-versus-height graphs. [If Eq. (1) is assumed to be valid, $\Gamma/K^2=\chi$.] This required knowledge of the refractive index as a function of height, which was obtained from density-versus-height curves using the Lorentz-Lorenz relation. (Density-versus-height curves were obtained from Straub[18] for a few temperatures and were computed from Fig. 1 of Green, Vicentini-Missoni, and Sengers[19] for other temperatures.)

Figure 1(a) is a graph of Γ/K^2 versus height for three temperatures less than T_c. Figure 1(b) shows Γ/K^2 versus height for three temperatures greater than T_c. Above T_c measurements were not made for heights less than 6 mm below h_c, the height which corresponds to the critical density, because the cell holder blocked the beam. For densities near the critical density, however, $|\rho-\rho_c|$ versus h is symmetrical about h_c,[18,19] and since $\chi_T(\rho-\rho_c)$ has a minimum very near $\rho=\rho_c$, as will be explained later, $\chi_T(\rho-\rho_c)$ is symmetrical about $\rho=\rho_c$ and hence about $h=h_c$. This is indicated in Fig. 1(b) by the extension of the curves to the left beyond the data points. Note that there is a distinct minimum in Γ/K^2 even as far as 0.106C° above T_c. As the critical temperature is approached, the magnitude of the density gradient increases and the minimum in Γ/K^2 as a function of height becomes sharper. At a fixed temperature below T_c the density varies only slightly with height within each phase (e.g., at $T-T_c=-0.049$C°, the density varies only 0.5% for a height variation of 10 mm within each phase above or below the meniscus).[18] Thus Γ/K^2 varies only slightly as a function of height within each subcritical phase. The values of Γ/K^2 on the gas and liquid sides of the coexistence line are given by the limiting value of Γ/K^2 as $h\rightarrow h_{\text{meniscus}}$ within each phase.

IV. FIXMAN'S MODIFICATION

Before attempting to extract the temperature dependence of χ from our Γ/K^2 data, we must consider the validity of Eq. (1) in the critical region.

Fixman has shown that in the immediate neighborhood of the critical temperature the linearized hydrodynamic equations must be modified slightly in order to include the effects of long-range density correlations.[20] Botch has incorporated Fixman's modification in a derivation of the Rayleigh linewidth, and has obtained for the linewidth[21]

$$\Gamma=\chi K^2(1+\xi^2K^2), \qquad (2)$$

where ξ is the two-body correlation length. On the critical isochore, $\xi\sim\epsilon^{-\nu}$ as $\epsilon\rightarrow+0$. On the coexistence

[18] J. Straub, Chem. Ingr. Tech. 5/6, 291 (1967); thesis, Technische Hochschule, München, Germany, 1965 (unpublished).

[19] M. S. Green, M. Vicentini-Missoni, and J. M. H. Levelt Sengers, Phys. Rev. Letters 18, 1113 (1967). *Note added in proof:* The authors find in a more thorough analysis of the carbon dioxide data alone that $\gamma\approx1.24$ (private communication).

[20] M. Fixman, J. Chem. Phys. 33, 1357, 1363 (1960); W. D. Botch and M. Fixman, *ibid.* 42, 199 (1965).

[21] W. D. Botch, Ph.D. dissertation, University of Oregon, 1963, p. 63 (unpublished); see also the discussion and references in Ref. 23.

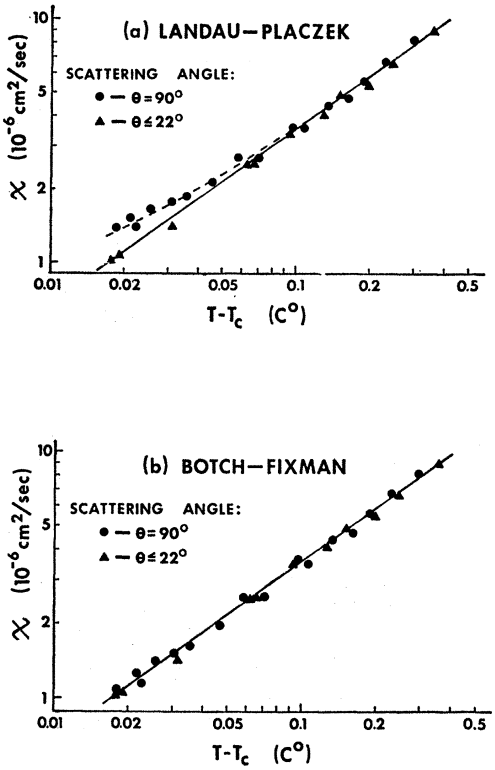

FIG. 2. χ versus $(T-T_c)$ for T above T_c from (a) the Landau-Placzek equation, $\chi=\Gamma/K^2$, and (b) the Botch-Fixman equation, $\chi=(\Gamma/K^2)/(1+\xi^2K^2)$.

line, $\xi\sim(-\epsilon)^{-\nu'}$ as $\epsilon\rightarrow-0$.[2] Thus Eq. (1) is applicable for $K\xi\ll1$, that is, for sufficiently small $\epsilon^{-\nu}[\sin(\frac{1}{2}\theta)]$ for $T>T_c$, and for sufficiently small $(-\epsilon)^{-\nu'}[\sin(\frac{1}{2}\theta)]$ for $T<T_c$.

In order to explore the possible existence of a Fixman modification term in CO_2, we plotted Γ/K^2 versus $(T-T_c)$ for $\theta=90°$, 22°, and 15° (for $T-T_c\leq0.4$C°), as shown in Fig. 2(a). Fixman's modification predicts that $\Gamma/K^2=\chi(1+\xi^2K^2)$, so that the Γ/K^2 data will be dependent on the scattering angle. Figure 2(a) exhibits just this effect, since the 90° data curve upward as T approaches T_c.

The temperature range for which we observed a significant Fixman correction was insufficient to deduce ν from our data. For ferromagnets $\nu=\frac{2}{3}$, and for the Ising model $\nu=0.643\pm0.003$.[2,3] With the assumption that $\nu=\frac{2}{3}$ we were able to bring our data into agreement with Fixman's equation by taking $\xi=(0.53\pm0.11)\epsilon^{-2/3}$ Å [$\xi=(150\pm30)$Å at $\epsilon=2\times10^{-4}$]. The result $(\Gamma/K^2)/(1+\xi^2K^2)=\chi$ is plotted in Fig. 2(b). Notice that the correction term becomes unimportant for temperatures over 0.1C° above T_c, where the Landau-Placzek and Fixman equations become essentially equal.

The value of ξ that we have obtained for CO_2 is approximately three times smaller than the value 520 Å obtained by Chu[22] for an isobutyric acid–water mixture at $\epsilon=2\times10^{-4}$; this is qualitatively what one would expect on the basis of angular scattering intensity measurements.[23] However, our ξ is approximately 15 times smaller than the surprisingly large result reported by Yeh for xenon.[24]

V. TEMPERATURE DEPENDENCE OF χ

Following the application of the Fixman modification to the Γ/K^2 data, the resultant values for the thermal diffusivity were plotted as a function of temperature. Values of χ obtained from the limiting values of Γ/K^2 as $h\rightarrow h_{\text{meniscus}}$ [Fig. 1(a)] from either side in the coexistence region (i.e., along the liquid and vapor sides of the coexistence curve) are plotted versus $(T-T_c)$ in Fig. 3. Values obtained from the minima in the Γ/K^2-versus-h curves in the $T>T_c$ region [Fig. 1(b)] are plotted in Fig. 4. The data of Seigel and Wilcox shown in Fig. 4 will be discussed in Sec. VI.

Our data points shown in Figs. 3 and 4 are representative rather than exhaustive; at most temperatures more than one run was made, and on the scale of Figs. 3 and 4 many of those points would superpose.

Note that within the temperature range of our data, there are three thermodynamic data points: At $T-T_c=-1.04$ (on the liquid side of the coexistence line), $T-T_c=1.06$, and $T-T_c=3.76$C°.[25] For those three points the average difference between our values for χ obtained using Eq. (1) and the values for χ measured by classical thermodynamic experiments is 7%. Thus

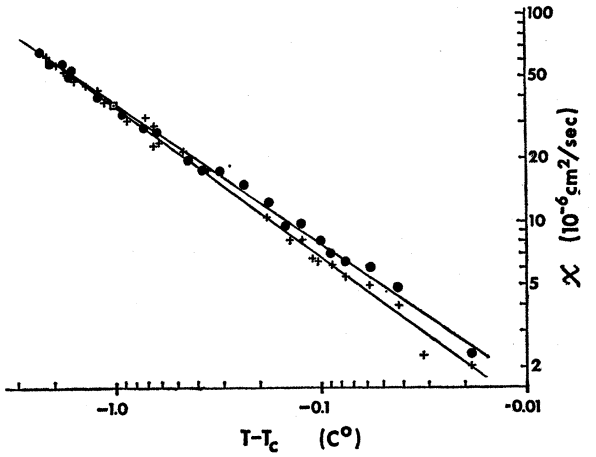

FIG. 3. χ versus $(T-T_c)$ for $T<T_c$. ⊡, thermodynamic data; present experiment: ●, gas; +, liquid. The slope of the lower line, which is for the liquid side of the coexistence curve, is 0.72±0.05; the slope of the upper line, for the gas, is 0.66±0.05. The source of the thermodynamic datum, which is on the liquid side of the coexistence curve, is given in Ref. 25.

[22] B. Chu, Phys. Rev. Letters 18, 200 (1967); J. Chem. Phys. 47, 3816 (1967).

[23] H. Z. Cummins and H. L. Swinney, J. Chem. Phys. 45, 4438 (1966).

[24] Y. Yeh, Phys. Rev. Letters 18, 1043 (1967).

[25] The thermodynamic data used in this paper were compiled by Dr. J. V. Sengers from experiments of the van der Waals Laboratory. The sources of the data for this compilation were given in Refs. 45–51 of R. D. Mountain, Rev. Mod. Phys. 38, 205 (1966).

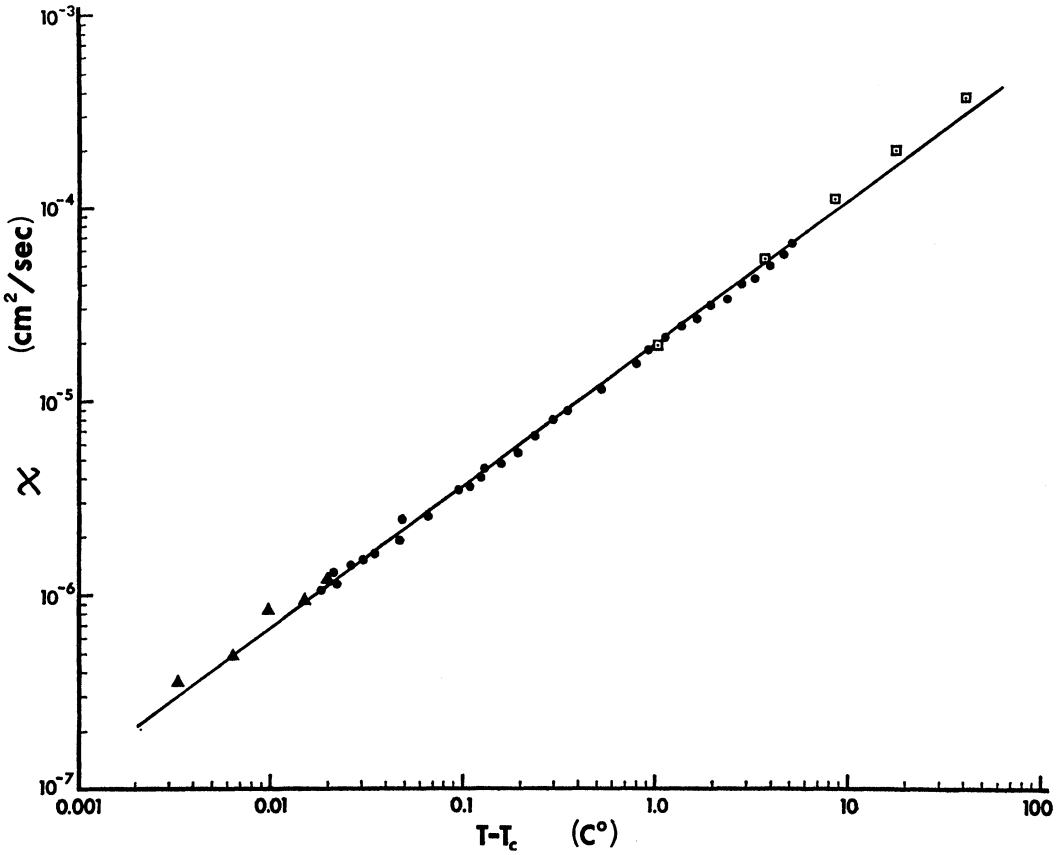

FIG. 4. The thermal diffusivity along the critical isochore versus the difference temperature $T-T_c$. ●, present experiment; ⊡, thermodynamic data; ▲, Seigel and Wilcox. The source of the thermodynamic data is given in Ref. 25; the data of Seigel and Wilcox are from Ref. 28. From a least squares fit of the data from the present experiment to a straight line, the slope is 0.73±0.02. The slope given by combining the three independent sets of data is also 0.73±0.02.

the Landau-Placzek equation [Eq. (1)] appears valid in the critical region, at least for temperatures not too close to T_c.

The exponents for the dependence of χ on $|\epsilon|$ along the critical isochore and along the two sides of the coexistence line are given by the magnitudes of the slopes of the curves in Figs. 3 and 4. Using as the critical temperature the temperature at which the meniscus appeared as the temperature was lowered, a least-squares analysis of our data yields for the thermal diffusivity on the critical isochore, $\chi=(18.1\pm0.5)\times10^{-6}(T-T_c)^{0.73\pm0.02}$ cm^2/sec. The results along the liquid and gas sides of the coexistence line are $\chi_L=(34.8\pm2.5)\times10^{-6}(T_c-T)^{0.72\pm0.05}$ cm^2/sec and $\chi_G=(36.0\pm3.0)\times10^{-6}(T_c-T)^{0.66\pm0.05}$ cm^2/sec. The value for T_c was varied in an attempt to improve the least-squares fit of the data, but no improvement was obtained by using a critical temperature different from that at which the meniscus appeared.

We will now give some justification for our assertion that the minima in our χ-versus-h graphs correspond to χ at densities very near $\rho=\rho_c$. The maximum in the isothermal compressibility as a function of density does not occur at $\rho=\rho_c$ (see discussion by Widom[26]); however, near T_c, the difference between the critical density and the density corresponding to the maximum in κ_T is very small. Also, near T_c the isotherms are so flat that the maximum compressibility and the compressibility at $\rho=\rho_c$ are essentially equal. Our interest is only for the range $T-T_c\lesssim0.2$C°, since only this near T_c do our χ-versus-h data exhibit discernible minima. From the above comments on κ_T and from Sengers's thermodynamic data for λ versus ρ,[27] we conclude that for $T-T_c\lesssim0.2$ the minima in $\lambda/\kappa_T\sim\chi$ occur at densities within 0.4% of the critical density.

VI. COMPARISON WITH OTHER RESULTS

A. Comparison with Other Experiments

The classical thermodynamic measurements of the thermal diffusivity of CO_2 yield, in a least-squares fit,

[26] B. Widom, J. Chem. Phys. 43, 3898 (1965).

[27] See Ref. 15 and J. V. Sengers, thesis, van der Waals Laboratory, Amsterdam, 1962 (unpublished); A. Michels, J. V. Sengers, and P. S. van der Gulik, Physica 28, 1201, 1216 (1962); A. Michels and J. V. Sengers, *ibid.* 28, 1238 (1962); J. V. Sengers, J. Heat Mass Transfer 8, 1103 (1965).

the exponent $\gamma-\psi=0.78$ for the temperature range $1.06\leq T-T_c\leq 44\text{C}°$.[25] Linewidth determinations of χ for CO_2 reported by Seigel and Wilcox give $\gamma-\psi=0.7\pm0.1$ for $0.0033\leq T-T_c\leq 0.020\text{C}°$.[28] (Using our ξ we compute that for the angles and temperatures they investigated, the Landau-Placzek equation is accurate within a few percent.) Recent linewidth measurements by Osmundson and White have also given $\gamma-\psi=\frac{2}{3}$ for CO_2.[29] Combining our thermal diffusivity data with the thermodynamic data and the Seigel and Wilcox data, we have $\gamma-\psi=0.73\pm0.02$ for $0.0033\leq T-T_c\leq 44\text{C}°$, a range of four orders of magnitude in the difference temperature (see Fig. 4).

Three recent experiments in binary mixtures have also given an exponent of less than one for the dependence of the linewidth upon $T-T_c$. Chu[30] found an exponent of 0.67 for the mixture isobutyric acid and water; in an aniline-cyclohexane mixture Berge and Volochine[31] have obtained an exponent of 0.55 ± 0.05; and Chen and Polonsky[32] obtained an exponent of 0.65 ± 0.05 for the mixture *n*-hexane and nitrobenzene. In measurements of the relaxation time for the concentration fluctuations in the critical mixture nitrobenzene in iso-octane, Gravatt has also obtained an exponent of less than 1 (0.90 ± 0.05) for the dependence of the reciprocal relaxation time upon $T-T_c$.[33] In contrast to these results for four binary mixtures and for carbon dioxide, Saxman and Benedek have found $\gamma-\psi=1.27$ for sulphur hexafluoride.[34] However, for $T<T_c$, Saxman and Benedek obtained $\gamma'-\psi'=0.64$, in agreement with our result for carbon dioxide.

We will now discuss the data for γ and ψ obtained in separate experiments in order to compare our result for $\gamma-\psi$ with the expected temperature dependence of the thermal diffusivity. Green, Vicentini-Missoni, and Sengers have concluded from an analysis of the data from experiments for a variety of gases that $\gamma=\gamma'=1.4$.[19] Heller has analyzed the data from several experiments on carbon dioxide and has concluded that $\gamma=1.35\pm0.15$ and $\gamma'=1.1\pm0.4$.[4,35]

The question of whether or not the thermal conductivity has an anomaly in the critical region was a subject of controversy for thirty years, but the controversy was resolved by some very careful thermodynamic experiments by Sengers, Michels, and van der Gulik.[27] They found that the thermal conductivity does indeed exhibit a pronounced anomaly in the critical region. The nature of the singularity in λ has been investigated by Sengers, who compared λ and c_v data and concluded that, to a first approximation, λ diverges as c_v on the critical isochore.[15,36] That is, $0\leq\psi\leq0.2$.

Combining the data for γ and ψ from the experiments cited, we can now compare the resultant $\gamma-\psi$ with our value for $\gamma-\psi$ (the subcritical thermodynamic data are insufficient to permit a comparison with our data). It appears likely that $\gamma=1.3\pm0.1$ and that c_v has a weak singularity (logarithmic to 0.1); thus the assumption that λ behaves as c_v leads to a lower bound of 1.1 for $\gamma-\psi$, far larger than our $\gamma-\psi=0.73$.[37] We are led to the conclusion that the singularity in the thermal conductivity is even greater than that indicated by thermodynamic experiments. For $\gamma=1.3\pm0.1$ our data require that $\psi=0.57\pm0.12$. Possibly $\gamma=\frac{5}{4}$, $\psi=\frac{1}{2}$, and $\gamma-\psi=\frac{3}{4}$. Within three times our experimental error our data also allow $\gamma=\frac{4}{3}$, $\psi=\frac{2}{3}$, and $\gamma-\psi=\frac{2}{3}$.

B. Comparison with Theory

Theoretical investigations of systems near the critical point have very recently been extended to the dynamical properties. Kawasaki, Mountain, Zwanzig, Deutch, and Fixman have applied correlation function techniques to predict the behavior of transport coefficients in the critical region.[38–41] Several investigators, Ferrell *et al.*, Halperin and Hohenberg, and Kadanoff and Swift, have extended scaling-law techniques to dynamic phenomena.[42–44]

Kadanoff and Swift predict that $\lambda\sim\rho c_p\xi^{-1}$, so that $\chi=\lambda/\rho c_p\sim\xi^{-1}$.[44] Thus, measurements of $\chi(\rho,T)$ yield the behavior of ξ^{-1} as a function of density and temperature. Hence our graphs of χ_T versus height, as in Fig. 1, can

---

[28] L. Seigel and L. R. Wilcox, Bull. Am. Phys. Soc. **12**, 525 (1967).

[29] J. S. Osmundson and J. A. White, Bull. Am. Phys. Soc. **13**, 183 (1968); B. Maccabee and J. A. White, *ibid.* **13**, 182 (1968).

[30] B. Chu (private communication); see also Ref. 22.

[31] P. Berge and B. Volochine, Phys. Letters **26A**, 267 (1968).

[32] S. H. Chen and N. Polonsky (private communication); see also Bull. Am. Phys. Soc. **13**, 183 (1968).

[33] C. C. Gravatt, Phys. Rev. Letters **18**, 948 (1967); see also P. Debye, C. C. Gravatt, and M. Ieda, J. Chem. Phys. **46**, 2352 (1967).

[34] G. B. Benedek, in *Brandeis University Summer Institute in Theoretical Physics, 1966 Lectures*, edited by M. Chretien, S. Deser, and E. P. Gross (Gordon and Breach Science Publishers, Inc., New York, 1968), Vol. 2; A. C. Saxman and G. B. Benedek (to be published).

[35] L. R. Wilcox and D. Balzarini have recently obtained the result $\gamma=1.0$ for xenon and carbon dioxide by using a novel forward-scattering optical interference technique: for xenon, J. Chem. Phys. **48**, 753 (1968); for carbon dioxide, the result is preliminary (private communication). However, see Bull. Am. Phys. Soc. **13**, 579 (1968).

[36] The thermodynamic specific-heat data used in that analysis are not sufficiently accurate to make a reliable conclusion concerning the critical exponent. J. V. Sengers (private communication).

[37] If $\gamma=1.0$ as found by Wilcox and Balzarini (Ref. 35), and $\psi=0.2$, then $\gamma-\psi=0.8$, in fair agreement with our data.

[38] K. Kawasaki, Phys. Rev. **145**, 224 (1966); **148**, 375 (1966); **150**, 291 (1966). In the last of these three references it is shown that the thermal conductivity is not anomalous in the critical region, but Kadanoff and Swift (Ref. 44) have pointed out that Kawasaki's proof fails when sound waves are allowed.

[39] J. M. Deutch and R. Zwanzig, J. Chem. Phys. **46**, 1612 (1967).

[40] R. D. Mountain and R. Zwanzig, J. Chem. Phys. **48**, 1451 (1968).

[41] M. Fixman, J. Chem. Phys. **47**, 2808 (1967). Fixman's estimate for λ_0 for $CO_2(\lambda_0\approx\frac{1}{2}\lambda$ at $T-T_c=3.8\text{C}°)$ appears high, for our data accurately follow a straight line on log-log plot throughout the temperature range investigated, $0.018\leq T-T_c\leq 5.3\text{C}°$.

[42] R. A. Ferrell *et al.*, Phys. Letters **24A**, 493 (1967); Phys. Rev. Letters **18**, 891 (1967).

[43] B. I. Halperin and P. C. Hohenberg, Phys. Rev. Letters **19**, 700 (1967).

[44] L. P. Kadanoff and J. Swift, Phys. Rev. **165**, 310 (1968); **166**, 89 (1968).

be viewed as isotherms of the reciprocal correlation length. Further, since $\chi \sim \xi^{-1}$, the exponent for the divergence of the thermal diffusivity on the critical isochore, $\gamma - \psi$, equals ν. Our result is then $\nu = 0.73 \pm 0.02$, somewhat higher than either the Ising model $\nu = 0.643 \pm 0.003$ or the experimental result for ferromagnets and antiferromagnets, $\nu = 0.65 \pm 0.03$.[2] There exist no data for ν in pure fluids; however, measurements of either the Rayleigh linewidth or the scattering intensity as a function of angle at various temperatures will yield $\xi(T)$ and hence ν. In our experiment the $K\xi$ term in Eq. (2) was not measurable over a sufficient temperature range to deduce ν from the data, but such measurements are quite feasible.

According to the Kadanoff and Swift prediction, $\chi \sim \xi^{-1}$, the exponent that we have determined along the coexistence line is ν'. There exist practically no experimental data for ν' with which we could compare our results $\nu_G' = 0.66 \pm 0.05$ and $\nu_L' = 0.72 \pm 0.05$. While the scatter in our data dictate the uncertainty ± 0.05, it is clear that the data indicate $\nu_L' > \nu_G'$ if ν' is the exponent for the dependence of the total thermal diffusivity on $T - T_c$. This inequality in the gas and liquid exponents can be understood from Fig. 1(a), where very near T_c, $\chi_L < \chi_G$, while further from T_c ($T - T_c \approx -2C°$), $\chi_L = \chi_G$. However, if $\chi = \chi_0 + \chi'$, where χ_0 is temperature-independent (and χ_0 may have different values in the gas and liquid), and χ' is the anomalous part of the thermal diffusivity, then it is possible that the scaling-law result $\nu_L' = \nu_G' = \nu$ and our thermal-diffusivity data are both correct. For then a log-log plot of the total thermal diffusivity versus $(T - T_c)$, such as our Fig. 3, could yield $\nu_L' \neq \nu_G'$ very near T_c, even if χ_L' and χ_G' behaved in the same way. Our result $\nu_L' (= \gamma_L' - \psi_L') > \nu_G' (= \gamma_G' - \psi_G')$ is in the same direction as the difference observed by Roach for γ' in the gas and liquid along the coexistence line of He^4: $\gamma_L' = 1.22$ and $\gamma_G' = 1.07$.[45]

Using time-dependent correlation functions obtained by assuming that the free energy depends quadratically on the density gradient, Fixman calculates that on the critical isochore, $\lambda' \sim \epsilon^{-1/2}$, where $\lambda = \lambda_0 + \lambda'$, and λ_0 and λ' are, respectively, the temperature-independent and anomalous parts of the thermal conductivity.[41] For temperatures sufficiently near T_c, $\lambda' \gg \lambda_0$, and then Fixman's prediction becomes $\psi = 0.5$. Mountain and Zwanzig have also obtained $\psi = 0.5$ in a calculation of the thermal conductivity for a van der Waals gas using the time correlation function method.[40] If we combine the prediction $\psi = 0.5$ with the Ising model γ, we have $\gamma - \psi = 0.75$, in agreement with our result.[46]

[45] P. R. Roach, Phys. Rev. **170**, 213 (1968).

[46] The result $\psi = 0.5$ was obtained by Mountain and Zwanzig for a van der Waals gas, so their result should properly be combined with the classical $\gamma = 1.00$, which yields $\gamma - \psi = 0.5$. On the other hand, the exponents given by the Ising model, for which there is no result for ψ, are in better agreement with experiment than the classical exponents. Hence we have combined the Ising $\gamma = 1.25$ with the prediction $\psi = 0.5$.

Swift[47] has predicted that the diffusion coefficient D for a binary mixture should behave in the critical region as $D \sim \xi^{-1}$, which is the same critical behavior that Kadanoff and Swift obtained for the thermal diffusivity of a pure fluid. Since the Rayleigh linewidth in a binary mixture is given by Eq. (2) with χ replaced by D, the temperature dependence of the linewidth in mixtures and pure fluids should be described by the same exponent. The agreement between the exponents obtained for binary mixtures[30–32] and for carbon dioxide support Swift's prediction.

In conclusion, our results are in reasonable agreement with the behavior that Kadanoff and Swift have predicted for the thermal diffusivity, $\chi \sim \xi^{-1}$. Our data are also in accord with the $\lambda \sim \epsilon^{-1/2}$ behavior predicted by Fixman and by Mountain and Zwanzig, if this prediction is combined with the Ising model γ. Thus the predictions of a strong critical point singularity in the thermal conductivity are substantiated by our data.

VII. SUMMARY

The Landau-Placzek equation for the linewidth is accurately obeyed in the critical region for temperatures not too close to T_c, but for $\epsilon \lesssim 10^{-4}$, the correlation length in carbon dioxide is sufficiently long-range to require that the Botch-Fixman equation be used in order to describe correctly the linewidth behavior. The magnitude of the Fixman correction that we observe in carbon dioxide is far smaller than seen by Chu in isobutyric acid and water or by Yeh in xenon.

From our data the exponent for the dependence of χ upon ϵ along the critical isochore is 0.73 ± 0.02 for a range of more than two orders of magnitude in ϵ; our data combined with the thermodynamic data and the data of Seigel and Wilcox yields an exponent 0.73 ± 0.02 for four orders of magnitude: $1.1 \times 10^{-5} \leq \epsilon \leq 1.5 \times 10^{-1}$. Below T_c, our exponent for the gas side of the coexistence line is 0.66 ± 0.05, and for the liquid, 0.72 ± 0.05.

Our exponents both above and below T_c are in reasonable accord with the recent prediction by Kadanoff and Swift that $\chi \sim \xi^{-1}$. Our data are also in agreement with the divergence in the thermal conductivity predicted by Fixman and by Mountain and Zwanzig, if the compressibility diverges with an exponent $\gamma \approx 1.25$.

Our results give further verification of the anomalous behavior of the thermal conductivity in the critical region, as observed by Sengers *et al.* In addition, our results indicate a stronger singularity in the thermal conductivity than has been assumed heretofore. The exponent for the divergence is likely in the range $0.5 \leq \psi \leq 0.7$.

Measurements of the scattered light intensity as a function of ρ and T along with linewidth measurements such as those reported here would yield both γ and $\gamma - \psi$ and thus ψ. Further, the exponent ν could be

[47] J. Swift (to be published).

obtained from measurements of the linewidth or intensity as a function of θ and T very near T_c. Although carbon dioxide was in a sense a fortunate choice for this experiment since it has been studied more thoroughly than any other gas near its critical point, it will be interesting to have these results for a monatomic gas, for then there will be no possibility that the results will be influenced by the internal degrees of freedom.

ACKNOWLEDGMENTS

We are grateful to Donald L. Henry for assistance in the data collection. We wish to thank Dr. J. V. Sengers and Dr. R. D. Mountain for some helpful discussions, and Dr. Sengers for the compilation of thermodynamic data for carbon dioxide used in this paper. We also wish to acknowledge helpful conversations with L. Seigel, D. Balzarini, and Professor L. R. Wilcox.

PHYSICAL REVIEW VOLUME 171, NUMBER 1 5 JULY 1968

Investigation of Rayleigh Wings and Brillouin-Stimulated Scattering in Liquids*

MARGUERITE DENARIEZ†
Laboratoire de Photophysique Moléculaire Faculté des Sciences, Orsay, France

AND

GEORGES BRET‡
C.S.F., C.E.P.C.A., Orsay, France

(Received 27 November 1967‡; revised manuscript received 7 February 1968)

Measurements of the spatial gain associated with stimulated Brillouin and Rayleigh-wing scattering are presented. These results are obtained by amplifying a signal in a short cell. This technique enables us to obtain reliable data even in liquids where self-focusing has a very low threshold. Comparison of measured and calculated gains in different liquids demonstrates the steady-state character of the gain at the Brillouin frequency for larger-linewidth liquids and the transient effect in liquids with sharper linewidths. We give values for the gain at the Stokes frequencies on the Rayleigh wings of nitrobenzene and toluene, and compare them with the calculated values using simple models for the scattering cross section.

I. INTRODUCTION

THE scattering of light by density and entropy fluctuations,[1–3] random motion of anisotropic molecules,[4–8] and other molecular degrees of freedom[9,10] in matter has been known for a long time. These scattering effects can give a great deal of information about the matter itself and have been the subject of investigation over a period of many years. To each of these scatterings the general quantum formulation of the interaction between light and matter associates a stimulated emission. When scattering occurs with frequency change, the stimulated effect gives rise to amplification or absorption of light at the scattering frequencies with a variety of spatial and time behaviors depending upon the ratio of different time constants. When several intense waves are present, interactions are more complex.[11–14] All these effects have only recently been carefully analyzed theoretically, because of the interest generated by the advent of powerful Q-switched lasers.[15–19]

Because of the relatively large linewidth of Raman lines compared with laser linewidths, the stimulated

* Some of the results discussed in the present paper have been reported in a very condensed form [Compt. Rend. **264**, 1815 (1967); **265**, 144 (1967)]. This paper was presented at the Symposium on Nonlinear Optics. Erevan, USSR, October 1967.

† Work performed in partial fulfillment of the requirements for the degree of Doctor-ès-Sciences at the Université de Paris, thesis No. A.O. 1912.

‡ Present address: Institut d'Optique, Bât. 503, Faculté des Sciences, 91—Orsay, France.

[1] A. Einstein, Ann. Physik **33**, 1275 (1910).
[2] L. Brillouin, Ann. Phys. (Paris) **17**, 88 (1922).
[3] M. Leontovich and Mandelstam, Z. Physik **75**, 350 (1932).
[4] Lord Rayleigh, Phil. Mag. **44**, 28 (1897); **35**, 373 (1918).
[5] J. Cabannes, Ann. Phys. (Paris), **15**, 5 (1921).
[6] J. Cabannes and P. Daure, Compt. Rend. **186**, 1533 (1928).
[7] L. D. Landau and G. Plackzek, Phys. Z. Soviet Union **5**, 172 (1934).
[8] M. A. Leontovich, J. Phys. Radium **4**, 499 (1961).
[9] C. V. Raman, Ind. J. Phys. **2**, 3 (1928); **2**, 87 (1928).
[10] G. Landsberg and L. Mandelstam, Naturwiss. **16**, 557 (1928); **16**, 772 (1928).
[11] B. P. Stoïcheff, Phys. Letters **7**, 186 (1963).
[12] E. Garmire, Pandarese, and C. H. Townes, Phys. Rev. Letters **11**, 160 (1963).
[13] N. Bloembergen and Y. R. Shen, Phys. Rev. **137**, 1787 (1965).
[14] N. Bloembergen and P. Lallemand, Phys. Rev. Letters **16**, 81 (1966).
[15] R. W. Hellwarth, Phys. Rev. **130**, 1850 (1963).
[16] R. Y. Chiao, E. Garmire, and C. H. Townes, in *Proceedings of the International School of Physics "Enrico Fermi"* (Academic Press Inc., New York, 1963).
[17] D. I. Mash, V. V. Morozov, V. S. Starunov, and I. L. Fabelinskii, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **2**, 41 (1965) [English transl.: Soviet Phys.—JETP Letters **2**, 25 (1965)].
[18] N. Bloembergen and Y. R. Shen, Phys. Rev. **133**, A37 (1964); see also N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965).
[19] V. M. Faĭn and E. G. Yashchin, Zh. Eksperim. i Teor. Fiz. **46**, 695 (1964) [English transl.: Soviet Phys.—JETP **19**, 474 (1964)].