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Spectral Distribution of Scattered Light in a Simple Fluid

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The spectral distribution of light scattered by density fluctuations in a dense, monatomic, one-component fluid is calculated from the time dependence of the density fluctuations predicted by the linearized hydrodynamic equations of irreversible thermodynamics. The results of Landau and Placzek are verified and a procedure for deriving correction terms is discussed with the dispersion in the velocity of thermal sound waves obtained as an illustration. Particular attention is paid to the critical region. The properties of carbon dioxide are used to estimate the spectral distribution of critical opalescence. A comparison is made between light-scattering and sound-propagation experiments. Space dispersion near the critical point in the pressure and the thermal conductivity is examined briefly. Finally, some of the experimental problems involved in measuring the spectral distribution of the scattered light are discussed.

I. INTRODUCTION

When a beam of monochromatic light is passed through a dense, transparent medium, some of the light is scattered since the density is not uniform. There would be no shift in frequency of the scattered light if the density nonuniformities were static. As frozen-in nonuniformities are not possible in a fluid, density fluctuations in a fluid are time-dependent. This means that the frequency of light scattered by density fluctuations in a dense fluid exhibits a spectrum characteristic of the time dependence of the density fluctuations.[1]

In the past it has not been possible to study experimentally, in any detail, the spectral distribution of the scattered light.[2–12] The changes in frequency are very small, too small to be resolved fully by the optical detection systems which were available. This situation is changing. The gas laser has made possible the development of optical heterodyne systems which are capable of detecting exceedingly small changes in frequency.[13] Laser research has inspired the development of very high resolution interferometers.[14] These developments have increased the interest in the spectrum of light scattered by density fluctuations.

This article describes the type of information which can be obtained by determining the spectrum of the light scattered by density fluctuations in a dense fluid. To accomplish this we calculate the spectrum of light scattered by density fluctuations in a dense, one component, classical fluid of spherically symmetric molecules. The linearized hydrodynamic equations of irreversible thermodynamics are used to compute the relaxation in time of the spontaneous density fluctuations in the fluid.[15] This phenomenological theory is valid for low frequencies and long wavelengths. Although the frequencies we consider are much higher than those usually encountered in hydrodynamics, it is hoped that the results will be of use in understanding the properties of fluids.

This approach is essentially that of Landau and Placzek.[16] The lowest order solutions of these equations are well known in the sense that they are quoted in the literature. We also obtain higher order terms in the solutions which are of interest to anyone trying to interpret light-scattering experiments of this type.

This study was undertaken with the hope that the spectrum of critical opalescence would contain useful information about the critical point of the liquid–vapor transition. Sections 5 and 7 are concerned with the spectrum of critical opalescence.

Section 6 is devoted to a comparison of what can be learned from a light-scattering experiment as opposed to a sound-propagation and absorption experiment. As is shown, the two types of measurements are not identical.

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[15] F. V. Hunt in *AIP Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1957), Chap. 3c, p. 3-33.

[16] L. Landau and G. Placzek, Physik Z. Sowjetunion **5**, 172 (1934). This note suggests the method used in this article. No calculations are presented in support of their conclusions.

In the final section, we summarize the information one could expect to obtain from the spectrum of the scattered light. We also discuss the experimental problem of resolution and the detectors one might use in such light-scattering experiments.

2. THERMODYNAMIC APPROACH

A qualitative picture of the scattering of light by density fluctuations can be obtained by separating density fluctuations into two types, those relieved by mechanical processes and those relieved by thermal processes. This separation occurs naturally in the thermodynamic theory of fluctuations where density fluctuations can be described in terms of pressure fluctuations and temperature or entropy fluctuations. Brillouin has suggested that light is scattered by thermal sound waves in the fluid.[17] These waves are analogous to Debye waves in a crystal. Because sound propagation is an adiabatic process, density fluctuations should be decomposed into pressure fluctuations at constant entropy and entropy fluctuations at constant pressure. This decomposition is discussed in detail by Frenkel.[18] We quote his conclusions only.

The frequency of the light scattered by the fluctuations at constant entropy (thermal sound waves or phonons) is shifted by an amount proportional to the velocity of the phonons. Energy and momentum considerations require that the proportionality constant be the magnitude of the change in the wave vector of the scattered light. Two lines are observed because scattering can occur from waves traveling in opposite directions but at the same speed. These lines are broadened somewhat because of the dissipative processes which damp out the waves. These lines are known as the Mandelshtam–Brillouin doublet or more simply as the Brillouin lines.

The light scattered by the fluctuations at constant pressure is not shifted in frequency although it is broadened somewhat due to the thermal dissipative processes which damp out these fluctuations.

We see that the fine structure of the scattered light consists of three lines. The ratio of the intensity of the central line I_0 to that of the two shifted lines $2I_1$ is determined by thermodynamic fluctuation theory to be

$$I_0/2I_1=(c_p-c_v)/c_v, \tag{1}$$

where c_p and c_v are the specific heats at constant pressure and constant volume. Landau and Placzek have observed that the widths of these lines are determined by the lifetimes of the density fluctuations described by the linearized hydrodynamic equations of irreversible thermodynamics.[16]

There have been numerous attempts to observe the spectrum of the light scattered by density fluctuations.[2–12] It has been possible to detect the presence of the Brillouin lines in liquids using the conventional techniques of high resolution spectroscopy. The details such as line widths and shapes have not been measured with any precision.[19] Only one study of the spectrum of the central line has been reported.[20]

In the next few sections the Landau–Placzek theory is developed in detail. First we point out the relationship between the fluctuations in the density and the intensity of scattered light. Then we obtain the time dependence of the kth Fourier component of the density fluctuation. Finally, we determine the fine structure implied by this time dependence.

3. HYDRODYNAMIC THEORY OF FLUCTUATIONS

Komarov and Fisher[21] have shown, by adapting Van Hove's[22] neutron-scattering results to light scattering, that the intensity I' of light scattered from a fluid is

$$I'(\mathbf{R},\omega)=(\alpha^2\Omega^4N/2\pi c^4R^2)I_0\sin^2\phi\,\mathcal{S}(\mathbf{k},\omega). \tag{2}$$

The light, scattered at the origin, is observed at $\mathbf{R}$. The angular frequency of the scattered light is Ω, ω is the *shift* in the angular frequency and $\mathbf{k}$ is the *change* in the wave vector of the scattered light from that of the incident light in the medium, $\mathbf{k}_1$;

$$k=k_1 2\sin(\theta/2), \tag{3}$$

where θ is the scattering angle. There are N spherically symmetric molecules of polarizability α in the scattering volume. The incident light is assumed to be in the form of a plane, polarized, monochromatic wave.

The angle between $\mathbf{R}$ and the electric vector of the incident wave is denoted by ϕ. The polarization of the scattered light depends only on ϕ because the molecules are isotropic. The intensity of the incident light is I_0. R. Pecora has derived an equation equivalent to Eq. (2).[23]

The information about the density fluctuations is contained in the generalized structure factor $\mathcal{S}(\mathbf{k},\omega)$, which is the space and time Fourier transform of the two-body correlation function of the medium. It is defined by Van Hove[22] to be

$$G(\mathbf{r},t)=N^{-1}\langle\sum_{l,j=1}^{N}\int d\mathbf{r}'\delta[\mathbf{r}+\mathbf{r}_l(0)-\mathbf{r}']\delta[\mathbf{r}'-\mathbf{r}_j(t)]\rangle, \tag{4}$$

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[17] Leon Brillouin, Ann. Phys. (Paris) **17**, 88 (1922).

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[19] The first measurements of the width of Brillouin lines in liquids were reported recently by D. I. Mash, V. S. Starunov, and I. L. Fabelinskiĭ, Zh. Eksperim. i Teor. Fiz. **47**, 783 (1964) [English transl.: Soviet Phys.—JETP **20**, 523 (1965)].

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[21] L. I. Komarov and I. Z. Fisher, Zh. Eksperim. i Teor. Fiz. **43**, 1927 (1962) [English transl.: Soviet Phys.—JETP **16**, 1358 (1963)].

[22] Leon Van Hove, Phys. Rev. **95**, 249 (1954).

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where the sums are carried out over all molecules in the system. The angular brackets $\langle \cdots \rangle$ indicate an ensemble average over the initial states of the system. For long times and sufficiently large r, the form of $G(\mathbf{r}, t)$ reduces to the autocorrelated density

$$G(\mathbf{r}, t)=N^{-1}\int d\mathbf{r}' \langle \rho[\mathbf{r}'-\mathbf{r}, 0]\rho(\mathbf{r}', t) \rangle. \tag{5}$$

Here we consider only this latter form of $G(\mathbf{r}, t)$.

Our main concern is with the frequency dependence of $\mathcal{S}(\mathbf{k}, \omega)$. We determine this by implementing the Landau–Placzek observation that the decay in time of density fluctuations is described by the linearized hydrodynamic equations of irreversible thermodynamics. First we obtain the time dependence of the kth Fourier component of the density. From this, we construct the time-dependent density–density correlation function and the generalized structure factor.

This way of constructing $\mathcal{S}(\mathbf{k}, \omega)$ has been discussed by Van Hove and shown to be a long-time approximation. As defined, $\mathcal{S}(\mathbf{k}, \omega)$ is the transform of a density–density correlation function. Since we are making a long-time approximation, our results are valid only at "low" frequencies. This should not lead to any difficulties, because the time constants involved in the hydrodynamic small-oscillation problem are long compared to the time intervals characteristic of molecular scattering processes. This method has been quite useful in describing the magnetic scattering of neutrons near the Curie point in iron.[24–26]

The linearized hydrodynamic equations[15] are: the continuity equation

$$\partial\rho_1/\partial t+\rho_0 \operatorname{div} \mathbf{v}=0; \tag{6}$$

the Navier–Stokes equation

$$\rho_0\frac{\partial \mathbf{v}}{\partial t}+\frac{C_0^2}{\gamma} \operatorname{grad} \rho_1+\frac{C_0^2\beta\rho_0}{\gamma} \operatorname{grad} T_1 -(\tfrac{4}{3}\eta_s+\eta_B) \operatorname{grad} \operatorname{div} \mathbf{v}=0; \tag{7}$$

and the energy-transport equation

$$\rho_0 c_v\frac{\partial T_1}{\partial t}-\frac{c_v(\gamma-1)}{\beta}\frac{\partial \rho_1}{\partial t}-\lambda\nabla^2 T_1=0. \tag{8}$$

In these equations, $\rho=\rho_0+\rho_1$ is the number density, $T=T_0+T_1$ is the temperature; ρ_0 and T_0 being the equilibrium values. The ratio of the specific heat at constant pressure to the specific heat at constant volume is denoted by $\gamma=c_p/c_v$. The shear and bulk viscosities are η_s and η_B, λ is the thermal conductivity, β is the thermal expansion coefficient, and C_0 is the low-frequency limit of the sound velocity.

In this linearized theory of small oscillations about equilibrium, the transverse part of the velocity is not coupled to the density. For this reason we neglect the transverse part of the Navier–Stokes equation in our considerations. This limits the applicability of this theory to fluids in which angular correlations between the molecules are not important. Also, we made use of the concept of local thermodynamic equilibrium when we replaced the pressure and entropy deviations which usually appear in the Navier–Stokes and energy equations by the corresponding density and temperature deviations. Thermodynamic relationships were used to to this. The choice of density and temperature over entropy and pressure as independent variables is an arbitrary one. The final expression for the density–density correlation function is, of course, independent of this choice as long as local thermodynamic equilibrium obtains. The labor involved is less when the density is an independent variable.

The procedure used is to first eliminate the velocity by taking the divergence of each term in Eq. (7) and then substitute for div $\mathbf{v}$ from Eq. (6). Next we obtain the Fourier (space) and Laplace (time) transforms of these equations. Then we solve the resulting equations for $n(\mathbf{k}, s)$, the Fourier–Laplace transform of the density. The inverse Laplace transform of $n(\mathbf{k}, s)$ is the time-dependent, kth Fourier component of the density, $n(\mathbf{k}, t)$:

$$n(\mathbf{k}, s)=\int_v d\mathbf{r}\int_0^\infty dt \exp(-i\mathbf{k}\cdot\mathbf{r}) \exp(-st)\rho_1(\mathbf{r}, t),$$

$$T(\mathbf{k}, s)=\int_v d\mathbf{r}\int_0^\infty dt \exp(-i\mathbf{k}\cdot\mathbf{r}) \exp(-st) T_1(\mathbf{r}, t). \tag{9}$$

The elimination of the velocity (longitudinal component) and the transformation of the density and temperature leads to two simultaneous linear equations for $n(\mathbf{k}, s)$ and $T(\mathbf{k}, s)$ in terms of the initial values

$$n(\mathbf{k})=\int_v d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r})\rho_1(\mathbf{r}, 0)$$

and

$$T(\mathbf{k})=\int_v d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r}) T_1(\mathbf{r}, 0). \tag{10}$$

These equations are

$$n(\mathbf{k}, s)[s^2+C_0^2k^2/\gamma+(\tfrac{4}{3}\eta_s+\eta_B)k^2s/\rho_0] +(C_0^2\beta\rho_0k^2/\gamma)T(\mathbf{k}, s)=n(\mathbf{k})[s+(\tfrac{4}{3}\eta_s+\eta_B)k^2/\rho_0] \tag{11}$$

and

$$n(\mathbf{k}, s)[-sc_v(\gamma-1)/\beta]+T(\mathbf{k}, s)[\rho_0c_vs+\lambda k^2] =-n(\mathbf{k})c_v(\gamma-1)/\beta+\rho_0c_vT(\mathbf{k}). \tag{12}$$

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[24] Leon Van Hove, Phys. Rev. **95**, 1374 (1954).

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Only the magnitude of **k** is important so the vector notation is no longer used. Because the density and temperature are thermodynamically independent, it is unnecessary to include terms involving $T(k)$ in the solution for $n(k, s)$.

The solution of Eqs. (11) and (12) for $n(k, s)$ is

$$n(k,s)=n(k)\frac{s^2+(a+b)k^2s+abk^4+C_0^2(1-1/\gamma)k^2}{s^3+(a+b)k^2s^2+(C_0^2k^2+abk^4)s+aC_0^2k^4/\gamma}. \tag{13}$$

We have introduced the notation

$$a=\lambda/\rho_0c_v$$

and

$$b=(\tfrac{4}{3}\eta_s+\eta_B)/\rho_0. \tag{14}$$

The next step is to compute the inverse Laplace transform of $n(k, s)$. This inversion requires that we find the roots of the denominator of Eq. (13) set equal to zero,

$$s^3+(a+b)k^2s^2+(C_0^2k^2+abk^4)s+aC_0^2k^4/\gamma=0. \tag{15}$$

While an exact algebraic solution of a cubic equation is always possible, it is not particularly useful in this case because of its algebraic complexity.

It is more convenient to develop a convergent scheme for approximating the solutions to the dispersion equation, Eq. (15), in a power series of the coefficients. To do this, we first note that $k=10^5$ cm^{-1} is typical of the changes in the wave vector which occur in light scattering. (This corresponds to a scattering angle of approximately 60° when a 6328-Å He–Ne laser is used as the light source). With $k=10^5$ cm^{-1}, the ratio of ak^2 to C_0k and of bk^2 to C_0k is commonly on the order of $\frac{1}{100}$. The parameters to use are ak^2/C_0k and bk^2/C_0k.

The solutions to Eq. (15) to lowest order in ak^2 and bk^2 are

$$\begin{aligned} s&=\pm iCk_0-\tfrac{1}{2}(a+b-a/\gamma)k^2,\\ s&=-(a/\gamma)k^2; \end{aligned} \tag{16}$$

or, in terms of the original parameters,

$$\begin{aligned} s&=\pm iC_0k-\tfrac{1}{2}\left[\frac{\frac{4}{3}\eta_s+\eta_B}{\rho_0}+\frac{1}{\rho_0}\left(\frac{\lambda}{c_v}-\frac{\lambda}{c_p}\right)\right]k^2\\ s&=-\lambda k^2/\rho_0c_p. \end{aligned} \tag{17}$$

These are the predictions of the Landau–Placzek theory. The real part of the first two solutions is effectively the low-frequency sound-absorption coefficient. In the rest of this paper, it is denoted by Γk^2; i.e.,

$$\frac{1}{2}\left[\frac{\frac{4}{3}\eta_s+\eta_B}{\rho_0}+\frac{1}{\rho_0}\left(\frac{\lambda}{c_v}-\frac{\lambda}{c_p}\right)\right]k^2=\Gamma k^2. \tag{18}$$

Higher order corrections to the usual solutions, Eq. (17), can be generated by the same procedure. The first correction to the low-frequency sound velocity is found to be quadratic in k:

$$s=\pm i(C_0k+C_2k^3)-\Gamma k^2, \tag{19}$$

where

$$C_2=[3\Gamma^2+ab-2\Gamma(a+b)]/2C_0. \tag{20}$$

The velocity of a thermal sound wave, v_{th}, exhibits dispersion when k is large enough;

$$v_{\text{th}}=C_0\left[1+\frac{3\Gamma^2+ab-2\Gamma(a+b)}{2C_0^2}k^2+\cdots\right]. \tag{21}$$

The significance of this dispersion and its relationship to the sound propagation problem are discussed in Sec. 6.

Using the first-order solutions, Eq. (17), the lowest order terms of the inverse Laplace transform of $n(k, s)$ are

$$n(k,t)=n(k)\left\{\frac{c_p-c_v}{c_p}\exp\left[-(\lambda k^2/\rho_0c_p)t\right]+\frac{c_v}{c_p}\exp\left(-\Gamma k^2t\right)\cos C_0kt\right\}. \tag{22}$$

The kth component of the density–density correlation function $F(k, t)$ is

$$\begin{aligned} F(k,t)&=\langle n(-k)n(k,t)\rangle\\ &=\langle n(-k)n(k)\rangle\left\{\frac{c_p-c_v}{c_p}\exp\left[-(\lambda k^2/\rho_0c_p)t\right]+\frac{c_v}{c_p}\exp\left(-\Gamma k^2t\right)\cos C_0kt\right\}. \end{aligned} \tag{23}$$

The angular brackets $\langle\cdots\rangle$ indicate an ensemble average over the initial values of the variables.

The quantity which is of direct interest in a light-scattering experiment is the generalized structure factor $\mathcal{S}(k, \omega)$;

$$\mathcal{S}(k,\omega)=2\,\mathrm{Re}\int_0^\infty dt\exp(i\omega t)F(k,t). \tag{24}$$

It follows from Eq. (23) that

$$\mathcal{S}(k,\omega)=S(k)\sigma(k,\omega), \tag{25}$$

where

$$S(k)=\langle n(-k)n(k)\rangle \tag{26}$$

is the ordinary structure factor and

$$\sigma(k,\omega)=\frac{c_p-c_v}{c_p}\frac{2\lambda k^2/\rho_0c_p}{(\lambda k^2/\rho_0c_p)^2+\omega^2}+\frac{c_v}{c_p}\left[\frac{\Gamma k^2}{(\Gamma k^2)^2+(\omega+C_0k)^2}+\frac{\Gamma k^2}{(\Gamma k^2)^2+(\omega-C_0k)^2}\right]. \tag{27}$$

This way of constructing the density–density correlation function, Eq. (23), is essentially a convolution approximation. It is not the same as the "convolution approximation" introduced by Vineyard[27] in the analysis of neutron-scattering experiments. This distinction has been discussed by Singwi and Sjölander.[28]

The method used to obtain Eq. (23) is the same as that used by Kadanoff and Martin.[29] Their results differ in that they used the density and the heat energy density as the independent variables. Because the heat energy density is linear in the density, it is difficult to obtain a direct evaluation of the generalized structure factor from their equations. Leontovich[30,31] and Rytov[32] also have used this approach to study time-dependent fluctuations.

Away from the critical point, the structure factor

$$S(k)=\langle n(-k)n(k)\rangle$$

is proportional to the compressibility and is independent of k. As the critical point is approached, k dependence develops reflecting the long range of the correlation between two particles. The Ornstein–Zernicke[33] expression for the two-body, time-independent correlation function is

$$g(r)-1=A\exp(-\kappa r)/r, \tag{28}$$

where κ^{-1} is the two-body correlation length. The quantity A has been shown by Fixman to be on the order of the range of intermolecular forces.[34] The structure factor associated with Eq. (28) is

$$S(k)=A/(k^2+\kappa^2). \tag{29}$$

Equation (29) is commonly used to describe scattering of light and x rays in the critical region.[35,36] The appropriateness of Eq. (29) has been questioned by some authors.[37–39] Since the exact form of $S(k)$ is not really important for this discussion, we do not examine these interesting questions. The recent review by M. E. Fisher is particularly recommended for that purpose.[40]

4. ACCURACY OF THE APPROXIMATE SOLUTIONS

The approximation procedure used to solve Eq. (15) is valid when ak^2 and bk^2 are sufficiently small in comparison with C_0k. To obtain some idea of the usefulness of the approximate solutions, Eq. (17), we solve the dispersion equation numerically, Eq. (15), when the parameters a, b, C_0, and γ are given numerical values appropriate to water at 22.9°C and 1 atm pressure.[41] Under these conditions $a=1.46\times10^{-3}$ cm^2/sec, $b=4.47\times10^{-2}$ cm^2/sec, $C_0=1.49\times10^5$ cm/sec,[42] and $\gamma=1.009$. With $k=10^5$ cm^{-1}, the dispersion equation is

$$s^3+(4.62\times10^8)s^2+(2.22\times10^{20}+9.92\times10^{15})s+3.14\times10^{27}=0. \tag{30}$$

The roots of Eq. (30) obtained numerically are

$$s=-1.46\times10^7/\text{sec}$$

$$s=-2.24\times10^8\pm1.49\times10^{10}i/\text{sec}.$$

The approximate solutions, Eqs. (16) and (17), yield the same results to three significant figures. Increasing k to 10^6 cm^{-1} does not alter the agreement significantly.

The value of the bulk viscosity used to compute b was inferred from ultrasonic absorption data and found to be about three times as large as the shear viscosity.[43] Recent measurements of Brillouin scattering in water[11,12] have found a small amount (on the order of three percent) of negative dispersion in the phonon velocity. In order to have Eq. (21) account for this shift in the phonon velocity it is necessary that the absorption coefficient, Γ, be about one order of magnitude larger than required by the ultrasonic measurements. The approximate solutions give good estimates even if bk^2/C_0 is as large as $\frac{1}{10}$. If larger values of this ratio occur it probably would be worthwhile to solve the dispersion equation by a procedure which takes the large value of b into account.

5. CRITICAL OPALESCENCE

As stated earlier, a primary reason for this review was an interest in critical opalescence. In this section we examine the structure predicted by $\sigma(k,\omega)$, Eq. (27), of the light scattered in the supercritical region of carbon dioxide.

Figures 1, 2, and 3 contain most of the relevant parameters for carbon dioxide in the supercritical region. [$T_c=31.04$°C, $P_c=72.85$ atm, $\rho_c=236$ amagat. (For

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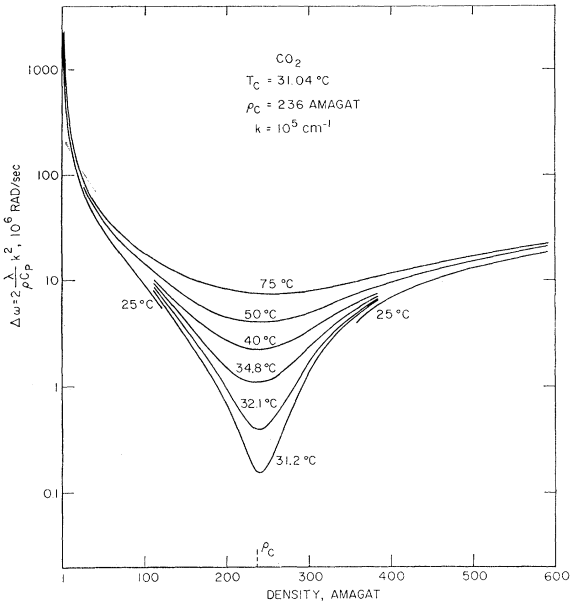

FIG. 1. The half-width of the undisplaced line in the supercritical region of carbon dioxide for $k=10^5$ cm^{-1}.

carbon dioxide, 1 amagat$=0.0019764$ g/cm^3.)][44–51] Figure 1 is the width of the central line; twice the thermal diffusivity times $k^2=10^{10}$ cm^{-2}. The shift of the Brillouin lines, C_0k with $k=10^5$ cm^{-1}, is shown in Fig. 2. The fraction of the light contained in the central line, $(1-\gamma^{-1})$, is indicated in Fig. 3.

Estimates of the width of the Brillouin lines, $2\Gamma k^2$, are not reliable near the critical point of carbon dioxide because the bulk viscosity, η_B, is not known as a function of density and temperature. There is reason to believe that Γk^2 is on the order of $C_0k/10$. This is based on the large sound absorption observed near the critical point.[52] In any case the Brillouin lines are much broader than the central lines. If $\Gamma k^2/C_0k\sim\frac{1}{10}$, there is also a small ($\sim$1%) amount of negative dispersion in the phonon velocity. This would result in a corresponding decrease in the separation of the Brillouin lines. This small effect has not been included in Fig. 2.

Figure 4 gives the relative intensity per unit solid angle of the scattered light for a 1-cm^3 scattering volume as predicted by Eq. (29) of Ref. 21. No attempt has been made to correct for the angular dissymmetry indicated by Eq. (29). Estimates of this effect based on the available *PVT* data and Fixman's[34] expression for κ^{-1}, the correlation length, indicate that the anisotropy is less than 10 percent for the indicated isotherms. These estimates are in agreement with the measurements of Skripov and Kopalakov.[53]

In Fig. 5, $\sigma(k,\omega)$ defined by Eq. (27) is plotted as a function of frequency, ω, for carbon dioxide at $T=32.1$°C, $\rho=230$ amagat, and $k=10^5$ cm^{-1}. Near the critical point, the central line of $\sigma(k,\omega)$ is dominant because of the large value of the ratio of the specific heats, γ. As the scattering angle is decreased, the width of the central line is strongly reduced since k is proportional to $\sin\theta/2$, where θ is the scattering angle.

In Fig. 6, $\sigma(k,\omega)$ is plotted for the same density and wave vector but for $T=75$°C. While the spacing between the lines is not to scale, the lines themselves are. The width of the Brillouin lines was computed under the unverified assumption that the shear and bulk viscosities are equal.

Fixman[34] has modified the basic equations, Eqs. (6), (7), and (8), slightly by including a term which describes the effects of the long-range density correlations on the pressure. If this term were included in Eq. (7), the term

$$(\partial p/\partial\rho)_T \operatorname{grad} \rho_1 \tag{31}$$

would be replaced by

$$(\partial p/\partial\rho)_T \operatorname{grad} [\rho_1-\kappa^{-2}\nabla^2\rho_1], \tag{32}$$

where κ^{-1} is the Ornstein–Zernicke[33] two-body corre-

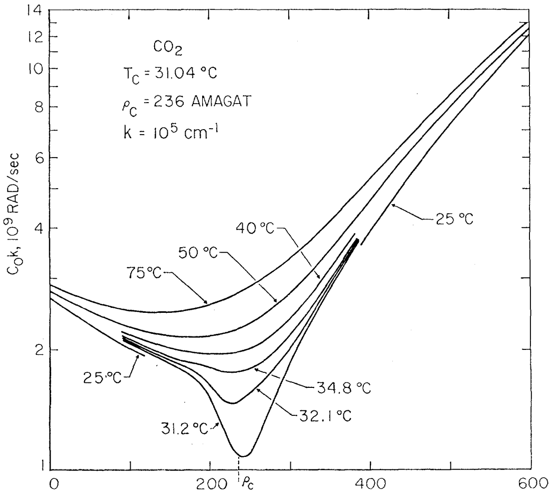

FIG. 2. The frequency shift of the Brillouin lines in the supercritical region of carbon dioxide for $k=10^5$ cm^{-1}.

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[44] Figures 1–4 have been constructed from a compilation of the properties of carbon dioxide prepared by J. V. Sengers. The author wishes to thank Dr. Sengers for his aid and encouragement in preparing this section. References 45–51 are the sources of the data.

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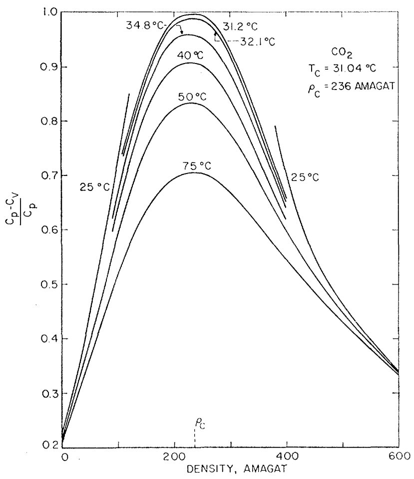

FIG. 3. The fraction of the scattered light contained in the undisplaced line for carbon dioxide in the supercritical regon.

lation length. The argument used to introduce this term is somewhat involved and the reader is referred to Fixman's papers for the details. We shall examine the significance of this term after we examine the consequences of the term.

The dispersion equation is changed by the inclusion of Fixman's term in Eq. (7). This new dispersion equation can be solved using the method of Sec. III.

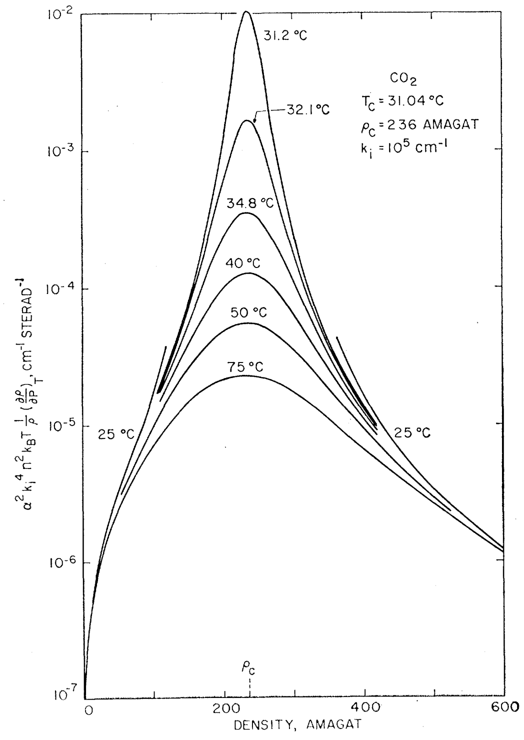

FIG. 4. The relative intensity per unit solid angle of the scattered light for a 1-cm^3 sample of carbon dioxide in the supercritical region. The number density is indicated by n.

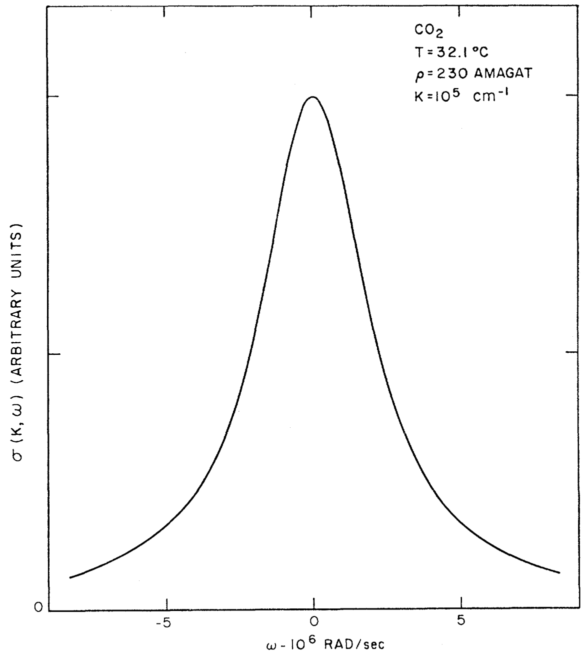

FIG. 5. The distribution in frequency of the scattered light near the critical point. The Brillouin doublet does not show up on this scale.

As expected, there are no important changes unless the two-body correlation length of Eq. (25), κ^{-1}, is of the order of k^{-1} or larger. The half-width of the central line is changed from

$$2\lambda k^2/\rho_0 C_p.$$

to

$$\frac{2\lambda k^2}{\rho_0 C_p}\left(\frac{1+k^2/\kappa^2}{1+k^2/\gamma\kappa^2}\right). \qquad (33)$$

The velocity of the low-frequency phonons is

$$C_0(1+k^2/\gamma\kappa^2)^{\frac{1}{2}}, \qquad (34)$$

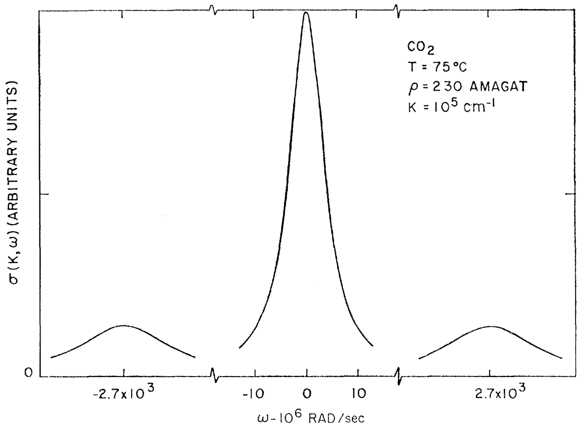

FIG. 6. The distribution in frequency of the scattered light away from the critical point.

and the absorption coefficient Γ becomes

$$\frac{1}{2}\left[\frac{\frac{4}{3}\eta_s+\eta_B}{\rho_0}+\frac{\lambda}{\rho_0 c_v}-\frac{\lambda}{\rho_0 c_p}\left(\frac{1+k^2/\kappa^2}{1+k^2/\gamma\kappa^2}\right)\right]. \tag{35}$$

These results have been obtained by Botch in his published thesis.[54]

The term (32), introduced into the hydrodynamics by Fixman[34] to account for the long range of the two-body correlation function, can be discussed best in terms of its Fourier transform. The term (32) implies k dependence between the pressure and the density of the form

$$p(k)=(\partial p/\partial\rho)_T[1+k^2/\kappa^2]n(k). \tag{36}$$

A reasonable extension of Eq. (36) is to suggest that Eq. (36) contains the first two terms of an expansion of the transform of the nonlocal expression

$$\delta p(\mathbf{r})=\int Q(|\mathbf{r}-\mathbf{r}'|)\,\delta\rho(\mathbf{r}')\,d\mathbf{r}', \tag{37}$$

where δp and $\delta\rho$ are the deviations from equilibrium. Some of the consequences of Eq. (37) for both light scattering and sound propagation have been investigated by Giterman and Kontorovich.[55] Because the functional form of $Q(r)$ is not known, their results are formal.

Some of the transport coefficients also may be nonlocal near the critical point. In the "derivation" of hydrodynamics, the transport coefficients appear as integrals of current–current correlation functions.[56,57] The macroscopic coefficients are the $k\rightarrow0$ and $\omega\rightarrow0$ limits of these integrals. In Mori's Markoffian, nonlocal theory of fluctuations, the "transport coefficients" may be k-dependent; i.e., the $k\rightarrow0$ limit need not be taken.[57]

Near the critical point, the current–current correlation functions *may* have a range which is comparable with the reciprocal of the change in the wave vector of the scattered light. This is suggested by the long range of the two-body correlation function.

If the thermal conductivity were a nonlocal quantity which is spherically symmetric, the term $\lambda\nabla^2T(r)$ in Eq. (6) would be replaced by

$$\int\lambda(|\mathbf{r}-\mathbf{r}'|)\,\nabla'^2T(r')\,d\mathbf{r}'. \tag{38}$$

The Fourier transform of Eq. (38) is $-k^2\lambda(k)\,T(k)$. When the range of $\lambda(r)$ is much less than k^{-1} and when $\nabla^2T(r)$ is effectively constant over this range, ∇^2T may be taken outside of the integral so that

$$\int\lambda(|\mathbf{r}-\mathbf{r}'|)\,\nabla'^2T(r')\,d\mathbf{r}'=\lambda\nabla^2T(r) \tag{39}$$

and

$$\int\exp\,(i\mathbf{k}\cdot\mathbf{r})\int\lambda(|\mathbf{r}-\mathbf{r}'|)\,\nabla^2T(r')\,d\mathbf{r}'=-k^2\lambda T(k). \tag{40}$$

Nonlocality has the effect of making the transport coefficients k-dependent.

In principle, it should be possible to detect nonlocality, if it is present, by measuring the variation of the line width as k changes. In practice, this would be possible only if the $k=0$ values of the transport coefficients and the values of the thermodynamic functions are known quite accurately. To illustrate this, we discuss the effect of a k-dependent thermal conductivity on the width of the central line.

If the thermal conductivity is k-dependent, care must be exercised in using the solution to the dispersion equation which produces the unshifted line, Eq. (17). If $\lambda(r)$ is always nonnegative, there is no problem because $\lambda(k)\leq\lambda$ for all values of k and the approximation scheme we have used will converge rapidly. However, if $\lambda(r)<0$ for some range of values of r, it is possible that $\lambda(k)$ may be appreciably greater than λ for some values of k and the first-order solution, Eq. (17), with λ replaced by $\lambda(k)$, may not be adequate. To this question there is no definite theoretical answer at present. Should the experimental results indicate that the first-order solution is not sufficient, there is no problem in generating the higher order terms in the diffusive solution.

There would be a problem in distinguishing nonlocality in the thermal conductivity from nonlocality in the pressure. This, in principle, could be overcome by first determining the pressure term from measurements of the shift of the Brillouin lines.

Nonlocal effects do not change the basic shape of the lines; their shapes are still Lorentzian, but their widths no longer have such a simple dependence on k. The problem of classifying lines would be even more complicated if the transport coefficients were to depend on the frequency.[32] It is not our purpose to discuss this possibility.[58] If more than three lines were observed, or if the line shapes were not Lorentzian, then frequency-dependent transport coefficients might be necessary to account for such effects.

This discussion assumes that the range of any nonlocal terms remains microscopic. If the range should become infinite (macroscopic), then the phenomenological equations would not be capable of describing the behavior of the small-scale density fluctuations.

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The resolution needed to measure the frequency spectrum of the scattered light is much higher than the resolution available with conventional optical techniques. An optical resolving power $\omega/\Delta\omega \approx 10^9$ is needed to resolve the central line. Light modulation systems are in principle capable of providing the necessary resolution, although the experimental difficulties are increased due to the relatively wide spread in the frequency of scattered light.[13]

Light-scattering experiments are particularly appealing near the critical point where experiments are notoriously difficult, because in a light-scattering experiment no gradients are imposed on the system. This makes it much easier to maintain thermal equilibrium during the experiment. In fact, it is possible to determine optically whether or not true equilibrium has been achieved.[59] Density measurements can be made precisely if optical methods are used.[60,61] (It may be that only optical methods are suitable for accurate density determinations near the critical point.)

Light-scattering experiments are also of value in probing the very high frequency properties of materials. In the next section, we compare the information obtained by light-scattering and the information obtained by sound-propagation and absorption measurements.

It is important to keep in mind that *light-scattering experiments are only as good as the PVT data used to specify the thermodynamic state of the scattering system.* In this respect, light-scattering measurements are no different from conventional determinations of transport properties.

6. RELATIONSHIP OF LIGHT SCATTERING TO SOUND PROPAGATION

When we solved the dispersion equation, Eq. (15), for the "frequency" s as a function of the wave vector k, we assumed that k was a real, positive quantity. The result was a complex frequency. This is in keeping with the representation of thermal sound waves (phonons) damped in time, but not in space.

The propagation of driven sound waves involves waves of a fixed frequency, $s = 2\pi i\nu$, where ν is a real quantity. The dispersion equation is then solved for the complex wave vector k. This corresponds to a stationary wave train which is spatially damped. The distinction between the two types of waves has been recognized for may years.[43,62]

The point of this discussion is that the dispersion in the phase velocity measured by the light-scattering experiment is predicted to be negative by Eq. (21). The phase velocity of driven sound waves can only have positive dispersion when Eqs. (6), (7), and (8) are valid.[63] The reason for this difference is that the dispersion equation, Eq. (15), contains four unknowns, the real and imaginary parts of the frequency and of the wave vector. Two of these quantities are specified by the experiment and then the other two are obtained in terms of the specified quantities.

This situation can be worked out exactly for the case of zero thermal conductivity.[30] Then $a = 0$ and Eq. (15) becomes

$$s[s^2 + bk^2 s + C_0^2 k^2] = 0. \tag{41}$$

We ignore the $s = 0$ root as it has no physical meaning.

First, the light-scattering problem requires that k be real. The solution of Eq. (41) is

$$s = -\tfrac{1}{2}bk^2 \pm iC_0 k[1 - b^2k^2/4C_0^2]^{\frac{1}{2}}. \tag{42}$$

The phase velocity is

$$v_{\mathrm{th}} = \pm C_0[1 - b^2k^2/4C_0^2]^{\frac{1}{2}}, \tag{43}$$

which decreases as k increases; the dispersion is negative.

The sound problem requires that $s = i\omega$, where ω is the angular frequency (real) of the sound generator. The dispersion equation is

$$k^2(C_0^2 + ib\omega) - \omega^2 = 0$$

$$k^2 = [\omega^2(C_0^2 - ib\omega)]/(C_0^4 + b^2\omega^2). \tag{44}$$

The phase velocity for the driven sound wave is

$$\begin{aligned} v_s &= \omega/Rek \\ &= \frac{\pm\sqrt{2}C_0(1 + b^2\omega^2/C_0^4)^{\frac{1}{2}}}{[1 + (1 + b^2\omega^2/C_0^4)^{\frac{1}{2}}]^{\frac{1}{2}}}. \end{aligned} \tag{45}$$

This phase velocity is an increasing function of frequency; the dispersion is positive. A discussion of why the two-phase velocities are different may be found in Sec. 10 of Ref. 43.

From this example, it is clear that the information contained in light-scattering experiments is not to be interpreted in the same way as the information obtained in sound-propagation experiments. This does not seem to have been appreciated widely.

Positive dispersion in the phase velocity of the thermal wave has been observed in some liquids.[1] This means that for those liquids, the theory we have used is not adequate to describe the density fluctuations. A reasonable modification might be the inclusion of angular correlations between the molecules which modify the propagation of waves in the fluid.[64] We do not discuss this aspect of the problem further.

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7. SUMMARY

A measurement of the spectrum of the light scattered by density fluctuations contains four pieces of information. The Brillouin doublet contains two of these. The separation of the doublets is determined by the speed of the *thermal* sound wave while the width of these lines is proportional to Γ, the sound absorption coefficient. By measuring the speed and lifetime of the phonons, it is possible to examine the high-frequency properties of the fluid. A precise measurement of Γ would be very useful in inferring the value of the bulk viscosity, η_B. Direct measurement of η_B has not been possible, and sound absorption measurements, which also measure Γ, are often difficult to make with sufficient precision to determine accurately the bulk viscosity.

The width of the central line is proportional to the thermal diffusivity, $\lambda/\rho_0 c_p$. Interest in this quantity is greatest near the critical point where conventional measurements of the thermal conductivity are difficult.[50]

Finally, the ratio of the intensity of the central line to that of the doublet lines is

$$I_0/2I_1=(c_p-c_v)/c_v. \tag{1}$$

The integrated intensity of each of the lines can be used to determine γ, the ratio of the specific heats. The intensity of the central line, I_0, increases rapidly as the critical point is approached. The intensity of the doublet, $2I_1$, remains more or less constant because their total intensity is proportional to the isothermal compressibility divided by c_p, the specific heat at constant pressure. This ratio is not varying rapidly in the critical region. Of course, to utilize this information as efficiently as possible, measurements should be made for several values of k (scattering angle).

So far, we have examined only the theoretical side of the problem. What is possible experimentally? As in all scattering problems, what is possible depends on the intensity of the scattered light and the resolving power of the detector. To date, only the intensity of the three lines and the position of the Brillouin lines have been measured in liquids.[19,20]

A resolving power on the order of 10^8 is needed to measure the widths of the Brillouin lines. Resolving powers as large as 3×10^8 have been obtained, using a spherical-mirror interferometer of the type invented by Connes.[14,65,66] It may be quite difficult to detect the Brillouin lines in the critical region. These lines are broad and, in comparison with the central line, very weak.

The central line is much narrower than the doublets and probably will require another type of detector. Optical heterodyne detection techniques have been used to obtain extremely large resolving powers.[13] It should be possible for this technique to operate in the range of frequencies appropriate to the width of the central line. However, because this system requires a large amount of scattered light in order to work, its usefulness may be limited to the scattering in the critical region. Since this is the region where the central line is most interesting, this is not a serious limitation.

In conclusion, it is now possible to study the spectral distribution of light scattered by density fluctuations. Such experiments are of interest because they provide a means of probing the dynamical behavior of a fluid on a scale which is not available by other means. Also, they are a way to measure transport properties of the fluid without imposing some sort of gradient on the system. This is particularly desirable near the critical point. The inference of the bulk viscosity from the width of the Brillouin lines and the possibility of studying nonlocal effects near the critical point are two examples of what can be examined in this way.

ACKNOWLEDGMENTS

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