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Thermal Relaxation and Brillouin Scattering in Liquids

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Weak coupling of internal degrees of freedom of molecules to the translational degrees of freedom of a fluid results in additional modes of motion for density fluctuations. These new modes affect the spectral distribution of light scattered by density fluctuations so that the Landau-Placzek ratio is not satisfied. The case of thermal relaxation with a single relaxation time is worked out in detail. Formulas for the spectral distribution of the scattered light, for the ratio of the intensities of the central (Rayleigh) to the Brillouin components and for the phonon velocity are derived and applied to carbon disulfide and carbon tetrachloride. The data for carbon tetrachloride are shown to be inconsistent with the single relaxation time model for thermal relaxation.

Key Words: Brillouin scattering, density fluctuations in liquids, light scattering in liquids, Rayleigh scattering, spectral distribution of scattered light, thermal relaxation, volume viscosity.

1. Introduction

In this paper we are concerned with density fluctuations in a fluid in which internal degrees of freedom of the molecules are weakly coupled to the translational degrees of freedom of the fluid. Thermal relaxation is an example of the type of processes we have in mind. Problems of this type are of interest because it is now possible to experimentally probe the frequency spectrum of density fluctuations with light scattering experiments using a laser as the light source [1].[1] The coupling of internal degrees of freedom to the translational motion means that the decay of density fluctuations will proceed by more ways than the three "normal modes" usually considered. This is reflected in the spectral distribution of light scattered by density fluctuations. In this paper we investigate a relatively simple case involving thermal relaxation with a single relaxation time. The existence of the additional mode is shown and the effect of this mode on the spectrum of the scattered light is examined in detail.

Light scattering experiments provide a Fourier analysis of the density variations in a fluid. The variation of the intensity of the scattered light with the scattering angle θ (and therefore with the *change* in the wave vector of the scattered light) Fourier decompose the spatial dependence of the fluctuations while the *shifts* in the frequency of the scattered light decompose the time dependence of the fluctuations [2]. Such experiments enable us to study collective motions in the fluid without seriously disturbing the fluid. On the other hand, it is also possible to use light scattering measurements in conjunction with a model for the fluctuations to measure several of the bulk properties of the fluid. For example, the sound velocity and the sound absorption coefficient can be obtained by measuring the shift in frequency and the width of the Brillouin lines.

In some circumstances it is possible to obtain from light scattering experiments information about the structure of the correlation functions whose time integrals are the transport coefficients [3]. An example of this type provides the basis for the calculations we present.

This paper consists of three parts. In the first part we review the relationship between density fluctuations and light scattering. The phenomenological approach of Einstein and Smoluchow-

[1] Figures in brackets indicate the literature references at the end of this paper.

ski [4] is discussed and compared with the formulation of scattering problems of Van Hove [5]. The generalized structure factor $\mathcal{S}(k, \omega)$ is introduced and some of its properties are described.

The second part of the paper consists of a detailed analysis of the frequency spectrum of density fluctuations in a fluid in which thermal relaxation of vibrational degrees of freedom can occur. Particular emphasis is placed on single relaxation time processes. The results for single relaxation time processes are summarized at the end so that readers not wishing to go through the details of the calculation will not lose heart.

The third part of the paper consists of a comparison of available experimental data with the analysis of the density fluctuations. The primary example is concerned with CS_2, a substance whose internal degrees of freedom relax with a single relaxation time. We also demonstrate that the data for CCl_4 are not in agreement with the predictions for a single relaxation time.

2. Light Scattering Formalism

2.1. Phenomenological Theory of Einstein-Smoluchowski

The random thermal motion of molecules in a fluid produces fluctuations in the density and also in the orientation of molecules in volumes small compared to the wavelength of the incident light. These fluctuations result in local variations in the dielectric constant and therefore scatter light. We are concerned in this paper only with fluctuations in the density. Orientation fluctuations result in the depolarization of the scattered light making it possible to experimentally separate the scattering by density fluctuations, which is fully polarized, from the scattering by orientation fluctuations [6].

The intensity of the scattered light is

$$I(\mathbf{R}, \omega) = I_0 \left[\frac{Nk_i^4}{16\pi^2 R^2}\right] \sin^2 \varphi \langle [\epsilon(k, \omega)]^2 \rangle. \tag{1}$$

In eq (1) incident plane polarized light of intensity I_0 and wave vector $\mathbf{k}_i$ is scattered at the origin and is observed at $\mathbf{R}$. There are N molecules in the scattering volume. The angle between the electric vector of the incident wave and $\mathbf{R}$ is φ; $\epsilon(k, \omega)$ is the Fourier component of the fluctuation in the dielectric constant. The *shift* in the angular frequency of the scattered light is ω and the *change* in the wave vector in the medium of the scattered light is $\mathbf{k}$; since only the direction of $\mathbf{k}$ changes

$$k = 2nk_i \sin \theta/2. \tag{2}$$

The index of refraction of the scattering fluid is n and the scattering angle is θ. The angular brackets $\langle . . . \rangle$ indicate an ensemble average over the initial states of the system.

Direct calculation of $\epsilon(k, \omega)$ is avoided by assuming that fluctuations in the dielectric constant are due to fluctuations in the density and the temperature;

$$\Delta\epsilon = (\partial\epsilon/\partial\rho)_T \Delta\rho + (\partial\epsilon/\partial T)_\rho \Delta T. \tag{3}$$

The contribution of the temperature fluctuations is ignored; we assume that $(\partial\epsilon/\partial\rho)_T \gg (\partial\epsilon/\partial T)\rho$. Equation (1) is now reduced to

$$I(\mathbf{R}, \omega) = I_0 \left[\frac{Nk_i^4}{16\pi^2 R^2}\right] \sin^2 \varphi (\partial\epsilon/\partial\rho)_T^2 \langle [\rho(k, \omega)]^2 \rangle \tag{4}$$

where $\rho(k, \omega)$ is a Fourier component of the density fluctuation. The problem is now one of

calculating $\rho(k, \omega)$ from the appropriate kinetic model of the fluid. For dense fluids the appropriate model is described by the linearized hydrodynamic equations of irreversible thermodynamics.

We should note that $(\partial\epsilon/\partial\rho)_T$ has been assumed to be independent of the *shift* in the frequency of the scattered light, ω. If this is not the case it is probably also true that the separation of $\Delta\epsilon$ into a thermodynamic derivative times a fluctuation term is not a meaningful procedure. Of course the value of $(\partial\epsilon/\partial\rho)_T$ may vary somewhat as the frequency of the incident light changes, reflecting the frequency dependence of the dielectric constant.

2.2. Molecular Theory

Before we undertake the calculation of $\rho(k, \omega)$ we review the light scattering formalism obtained by adapting Van Hove's neutron scattering paper [5] to light scattering. Komarov and Fisher [7] have shown that the intensity of light scattered from a fluid of N molecules of effective polarizability α is

$$I(\mathbf{R}, \omega) = I_0 \left[\frac{N\alpha^2 k_i^4}{2\pi R^2}\right] \sin^2 \varphi\, \mathcal{S}(k, \omega). \tag{5}$$

The important change from eq (4) is to replace the mean square fluctuation $\langle [\rho(k, \omega)]^2 \rangle$ by the generalized structure factor $\mathcal{S}(k, \omega)$ which is the space and time Fourier transform of the two-body correlation function. The correlation function is defined by Van Hove to be

$$G(\mathbf{r}, t) = N^{-1} \left\langle \sum_{i,j=1}^{N} \int d\mathbf{r}' \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}'] \delta[\mathbf{r}' - \mathbf{r}_j(t)] \right\rangle. \tag{6}$$

For long times and sufficiently large r, $G(\mathbf{r}, t)$ reduces to the autocorrelated density

$$G(r, t) = N^{-1} \int d\mathbf{r}' \langle \rho[\mathbf{r}' - \mathbf{r}(0), 0] \rho(\mathbf{r}', t) \rangle. \tag{7}$$

Equation (7) is appropriate to light scattering in fluids [8]. Care must be taken to use

$$\mathcal{S}(k, \omega) = \int d\mathbf{r} \int dt e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\omega t} G(r, t) \tag{8}$$

only to describe the fully polarized part of the scattered light. The inclusion of angular correlations, which result in depolarization, is a more complicated problem than the one we consider here [9].

In this paper we are concerned with $\mathcal{S}(k, \omega)$ as defined by eqs (7) and (8);

$$\mathcal{S}(k, \omega) = \langle \rho(k, \omega) \rho(-k) \rangle. \tag{9}$$

Thus eqs (4) and (5) predict the same frequency distribution for light scattered by density fluctuations. A useful property of $\mathcal{S}(k, \omega)$ is the sum rule

$$S(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, \mathcal{S}(k, \omega) = \langle \rho(k) \rho(-k) \rangle. \tag{10}$$

$S(k)$ is the ordinary structure factor. Finally, we note that $\mathcal{S}(k, \omega)$ is an even function of ω at high temperatures; that is $\hbar\omega/k_B T \ll 1$ where k_B is Boltzman's constant and T is the absolute temperature. In this paper we assume that the inequality is satisfied.

3. Density Fluctuations When the Internal Modes Decay With a Single Relaxation Time

We are concerned with the calculation of $\mathcal{S}(k, \omega)$ for a fluid whose molecules possess internal degrees of freedom which are weakly coupled to the translational modes of the fluid. Further we shall suppose that the transfer of energy from the internal degrees to the translational degrees of freedom is described by a single relaxation time process [10, 11].

The procedure to be used is to solve the linearized hydrodynamic equations for $\rho(k, \omega)$ in terms of an initial fluctuation $\rho(k)$ [5]. The use of initial values facilitates calculation of the average over initial states indicated by $\langle . . . \rangle$.

An equivalent procedure is the hydrodynamic fluctuation theory of Landau and Lifshitz [12]. This method has been used by Rytov to discuss fluctuations in a viscoelastic medium [13].

The linearized hydrodynamic equations for the system are the continuity equation

$$\partial\rho_1/\partial t + \rho_0 \operatorname{div} \mathbf{v} = 0, \tag{11}$$

the longitudinal part of the Navier-Stokes equation (suitably modified to allow for a frequency dependent bulk viscosity)

$$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = -\left(\frac{c_0^2}{\gamma}\right) \operatorname{grad} \rho_1 - \left(\frac{c_0^2 \beta \rho_0}{\gamma}\right) \operatorname{grad} T_1 + \left(\frac{4}{3}\eta_s + \eta_v\right) \operatorname{grad} \operatorname{div} \mathbf{v} + \int_0^t \eta'(t-t') \operatorname{grad} \operatorname{div} \mathbf{v}(t') dt', \tag{12}$$

and the energy transport equation.

$$\rho_0 c_v (\partial T_1/\partial t) - [c_v(\gamma-1)/\beta](\partial\rho_1/\partial t) - \lambda \nabla^2 T_1 = 0. \tag{13}$$

Here $\rho = \rho_0 + \rho_1$ is the number density, $T = T_0 + T_1$ is the temperature; ρ_0 and T_0 being the equilibrium values. The shear viscosity is η_s, the bulk or volume viscosity consists of a frequency independent part η_v and frequency dependent part which is the Fourier transform of $\eta'(t)$. The low frequency (adiabatic) sound speed is c_0, the thermal expansion coefficient is β, the thermal conductivity is λ and the ratio of the specific heat at constant pressure c_p to the specific heat at constant volume c_v is denoted by γ.

The analysis proceeds as in reference 8. First the Fourier (space) and Laplace (time) transforms are taken of eqs (11), (12), and (13). Then we solve for

$$\rho(k, s) = \int_v d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \int_0^\infty dt e^{-st} \rho_1(r, t) \tag{14}$$

in terms of the initial value

$$\rho(k) = \int_v d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \rho(r, 0) \tag{15}$$

The result is

$$\frac{\rho(k, s)}{\rho(k)} = \frac{F(s)}{G(s)} \tag{16}$$

where

$$F(s)=s^2+s[ak^2+b_0k^2+b'(s)k^2]+ab_0k^4+ab'(s)k^4+c_0^2k^2(1-1/\gamma) \tag{17}$$

and

$$G(s)=s^3+s^2[ak^2+b_0k^2+b'(s)k^2]+s[c_0^2k^2+ab_0k^4+ab'(s)k^4]+c_0^2ak^4/\gamma. \tag{18}$$

The quantities

$$\begin{aligned} a&=\lambda/\rho_0c_v \\ b&=(4/3\eta_s+\eta_n)/\rho_0 \\ b'(s)&=\frac{1}{\rho_0}\int_0^\infty e^{-st}\eta'(t)dt \end{aligned} \tag{19}$$

have been introduced to simplify the notation. Equation 19 for $b'(s)$ applies to any frequency dependent bulk viscosity. We will be concerned with $b'(s)$ for a single relaxation time process;

$$b'(s)=b_1/(1+s\tau) \tag{20}$$

where τ is the relaxation time.

The dispersion equation is

$$G(s)=0 \tag{21}$$

and is used in ultrasonics with s replaced by $i\omega$. It is known from ultrasonics [10] that

$$b_1=(c_\infty^2-c_0^2)\tau \tag{22}$$

where c_∞ is the infinite frequency sound speed. In thermal relaxation [11]

$$b_1=\left[\frac{(c_p-c_v)c_I}{(c_v-c_I)c_p}\right]c_0^2\tau,$$

where c_I is the specific heat of the vibrational degrees of freedom.

To compute $\mathcal{S}(k,\omega)$ we first observe that

$$\rho(k,\omega)=2\ \mathrm{Re}\int_0^\infty dte^{-i\omega t}\rho(k,t) \tag{23}$$

where $\rho(k,t)$ is the inverse Laplace transform of $\rho(k,s)$. It follows that

$$\begin{aligned} \mathcal{S}(k,\omega)&=\langle\rho(k)\rho(-k)\rangle\ \{2\ \mathrm{Re}\ F(i\omega)/G(i\omega)\} \\ &=\langle\rho(k)\rho(-k)\rangle\sigma(k,\omega). \end{aligned} \tag{24}$$

An exact expression for $\sigma(k,\omega)$ may be readily obtained by replacing s by $i\omega$ in eq (16) and taking twice the real part. The resulting expression is quite involved; direct substitution leads to

$$\sigma(k,\omega)=2[N_1D_1+N_2D_2]/[D_1^2+D_2^2] \tag{25}$$

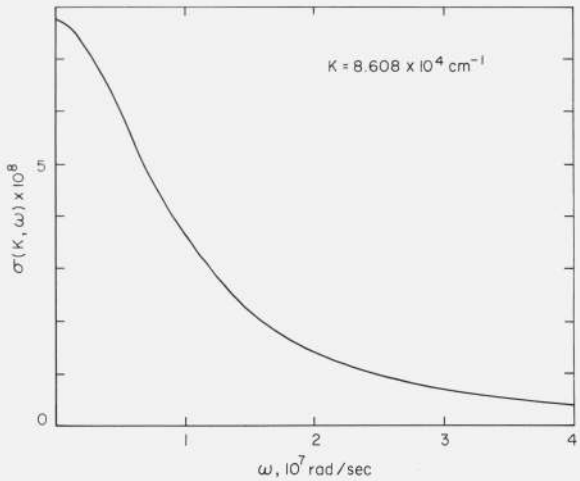

FIGURE 1. *The central component of* $\sigma(k, \omega)$ *for scattering in* CS_2 *at 20 °C as a function of* ω.
When a He-Ne laser is the source, $k=8.608\times10^4$ cm^{-1} corresponds to scattering at 30°

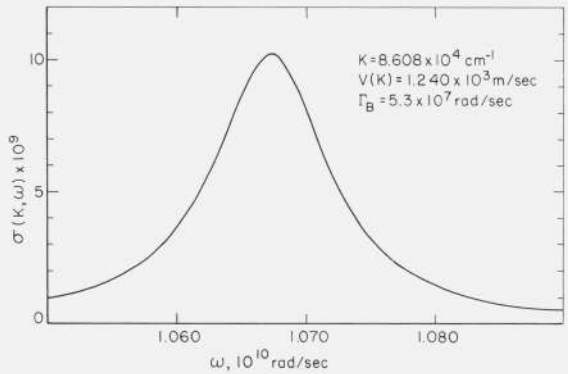

FIGURE 2. *The phonon component of* $\sigma(k, \omega)$ *for scattering in* CS_2 *at 20 °C as a function of* ω.
When a He-Ne laser is the source $k=8.608\times10^4$ cm^{-1} corresponds to scattering at 30°

where

$$N_1 = -\omega^2 + ab_0k^4 + c_0^2k^2(1-1/\gamma) + (ab_1k^4 + b_1k^2\omega^2\tau)/(1+\omega^2\tau^2),$$

$$N_2 = \omega[ak^2 + b_0k^2 + (b_1k^2 - ab_1k^4\tau)/(1+\omega^2\tau^2)],$$

$$D_1 = -\omega^2(ak^2 + b_0k^2) + c_0^2ak^4/\gamma + (ab_1k^4\omega^2\tau - \omega^2b_1k^2)/(1+\omega^2\tau^2) \tag{26}$$

and

$$D_2 = \omega[-\omega^2 + c_0^2k^2 + ab_0k^4 + (b_1k^2\omega^2\tau + ab_1k^4)/(1+\omega^2\tau^2)]. \tag{27}$$

Now we have an exact expression for the frequency distribution of the scattered light. If we wish to be able to interpret this in terms of the properties of the material, we must develop a way to pick out the significant portions of $\sigma(k, \omega)$ for different values of ω. We have evaluated $\sigma(k, \omega)$ for a representative set of material parameters and $k=8.608\times10^4$; the results are shown in figure 1 and figure 2. This corresponds to $\theta=30°$ for scattering in CS_2 using a He-Ne laser. To obtain as much useful information as possible from such a pattern it is necessary to write eq (25) as a sum of terms which are individually important only over a restricted range of frequencies ω. The denominator does not obviously factor so an indirect approach is needed. One method is to pick out the important terms, say for small ω and to discard the rest. Another approach, one used profitably in reference 8, is to approximately compute the inverse Laplace transform of $\rho(k, s)$ and then to compute $\rho(k, \omega)$ by means of eq (23). The virtue of this method is that algebraic expressions for the modes of motion of the density fluctuations are obtained. The difficulty of course is to obtain good approximate solutions to the dispersion equation, eq (21). We shall make use of both approaches to investigate the properties of $\sigma(k, \omega)$.

4. Properties of $\sigma(k, \omega)$

In this section we are concerned with the construction of a good approximation to $\sigma(k, \omega)$ which will permit interpretation of spectral distribution curves in terms of the properties of the

scattering fluid. The results of this section are contained in eqs (43), (45), and (46), and are listed, for convenience, in subsection 4.6.

4.1. Approximate Solution of the Dispersion Equation

When $b'(s)$ is given by eq (20), the transform for the density, eq (16), is

$$\frac{\rho(k, s)}{\rho(k)} = \frac{F_1(s)}{G_1(s)}$$

where

$$F_1(s) = (1+s\tau)s^2 + s[(1+s\tau)(ak^2+b_0k^2)+b_1k^2] + (1+s\tau)[ab_0k^4 + c_0^2k^2(1-1/\gamma)] + ab_1k^4 \tag{28}$$

and

$$G_1(s) = \tau s^4 + s^3[1+\tau(ak^2+bk^2)] + s^2[ak^2+b_0k^2+b_1k^2+\tau(c_0^2k^2+ab_0k^4)]$$
$$+ s[c_0^2k^2+ab_0k^4+ab_1k^4+\tau(c_0^2ak^4/\gamma)] + c_0^2ak^4/\gamma. \tag{29}$$

The first step in computing $\rho(k, t)$ is to obtain approximate roots of

$$G_1(s) = 0. \tag{30}$$

It is convenient to introduce the dimensionless quantities

$$\begin{aligned} Y &= s/c_0k \\ \alpha &= ak^2/c_0k \\ \beta_0 &= b_0k^2/c_0k \\ \beta_1 &= b_1k^2/c_0k \\ D &= c_0k\tau \end{aligned} \tag{31}$$

into eq (30) with the result

$$DY^4 + Y^3[1+D(\alpha+\beta_0)] + Y^2[\alpha+\beta_0+\beta_1+D(1+\alpha\beta_0)] + Y[1+\alpha\beta_0+\alpha\beta_1+D\alpha/\gamma] + \alpha/\gamma = 0. \tag{32}$$

For interesting values of the change in the wave vector, k,

$$D \approx 1, \qquad \beta_1 \approx 1$$

while

$$\alpha \ll 1, \qquad \beta_0 \ll 1.$$

First we look for solutions of eq (31) which are of order unity. The relevant parts of eq (31) are

$$DY^4+Y^3+(D+\beta_1)Y^2+Y\simeq 0; \tag{33}$$

we have neglected terms of order α and α^2. One root of eq (33) is zero so we also must examine eq (32) for solutions of order α. The dominant terms are then

$$Y+\alpha/\gamma\simeq 0. \tag{34}$$

Here terms of order α^2 and smaller have been dropped. The solution to eq (34) is

$$Y=-\alpha/\gamma \tag{35}$$

or

$$s=-\lambda k^2/\rho_0 c_p$$

which also appears in classical theory.

When the $Y=0$ term is removed from eq (33) we have

$$Y^3+Y^2/D+\left[\frac{D+\beta_1}{D}\right]Y+\frac{1}{D}=0. \tag{36}$$

The formal factoring of eq (36) is

$$(Y+A)(Y^2+BY+C)=0. \tag{37}$$

Two solutions are

$$Y=-B/2\pm iC^{1/2}[1-B^2/4C]^{1/2} \tag{38}$$

which correspond to the phonon modes. The third solution,

$$Y=-A$$

yields a second nonpropagating mode. In order that damping occur, it is necessary that $A>0$ be satisfied. For phonons to exist it is necessary that $B^2/4C\ll 1$ so

$$Y\simeq -B/2\pm iC^{1/2}. \tag{38'}$$

Comparison of eqs (36) and (37) shows that

$$AC=1/D$$

therefore

$$Y=-1/CD. \tag{39'}$$

Now multiply eqs (38′) and (39′) by c_0k to obtain

$$s=\Gamma_B\pm ivk;\ vk=c_0kC^{1/2} \tag{40}$$

and

$$s = -c_0^2/v^2\tau.$$

The lifetime of the phonons is $(\Gamma_B)^{-1}$ and their speed is v. These are as yet unspecified quantities to be extracted from the exact expression of $\sigma(k, \omega)$. Before we do this we shall obtain an approximate formula for $\sigma(k, \omega)$.

4.2. Calculation of $\sigma(k, \omega)$

We take $G_1(s)$ to be

$$G_1(s) = \tau(s + ak^2/\gamma)(s + \Gamma_B - ivk)(s + \Gamma_B + ivk)(s + c_0^2/v^2\tau). \tag{41}$$

Combining eqs (28) and (41) it is a straight forward process to obtain the inverse Laplace transform of $\rho(k, s)$. Ignoring small terms, we obtain

$$\frac{\rho(k, t)}{\rho(k)} = (1 - 1/\gamma)e^{-\lambda k^2 t}/\rho_0 c_p + \left[\frac{(c_\infty^2 - c_0^2)k^2 - (v^2/c_0^2 - 1)(c_0^4/v^4\tau^2 + c_0^2k^2(1 - 1/\gamma))}{c_0^4/v^4\tau^2 + v^2k^2}\right] e - c_0^2 t/v^2\tau$$

$$+ \left[\frac{[1 - c_0^2/v^2(1 - 1/\gamma)](v^2k^2 + c_0^2/v^2\tau^2) - (c_\infty^2 - c_0^2)k^2}{v^2k^2 + c_0^4/v^4\tau^2}\right] \times e^{-\Gamma_B t}\cos(vkt). \tag{42}$$

Next we apply the operation indicated in eqs (23) and (24) to obtain

$$\sigma'(k, \omega) \simeq (1 - 1/\gamma)\left[\frac{2\lambda k^2/\rho_0 c_p}{(\lambda k^2/\rho_0 c_p)^2 + \omega^2}\right]$$

$$+ \left[\frac{(c_\infty^2 - c_0^2)k^2 - (v^2/c_0^2 - 1)(c_0^4/v^4\tau^2 + c_0^2k^2(1 - 1/\gamma))}{c_0^4/v^4\tau^2 + v^2k^2}\right]\left[\frac{2c_0^2/v^2\tau}{c_0^4/v^4\tau^2 + \omega^2}\right]$$

$$+ \left[\frac{[1 - c_0^2/v^2(1 - 1/\gamma)][v^2k^2 + c_0^2/v^2\tau^2] - (c_\infty^2 - c_0^2)k^2}{c_0^4/v^4\tau^2 + v^2k^2}\right]$$

$$\times \left[\frac{\Gamma_B}{\Gamma_B^2 + (\omega - vk)^2} + \frac{\Gamma_B}{\Gamma_B^2 + (\omega + vk)^2}\right]. \tag{43}$$

The prime means that σ' is an approximation to $\sigma(k, \omega)$, which is given by eq (25).

The first term in eq (43) corresponds to decay of a fluctuation by a thermal diffusion process. We refer to it as the thermal mode. The second term also represents a nonpropagating type of decay which is coupled to the internal degrees of freedom of the molecules. The last term represents the phonon modes. Equation (43) is derived on the assumption that $(ak^2/\gamma)\tau$ is much less than one. If this is not the case, eq (43) is a poor representation of the nonpropagating modes.

4.3. Determination of $v(k)$ and Γ_B

Thus far the phonon speed v and width Γ_B are undetermined quantities. In this subsection we remedy this by comparing the phonon terms of eq (43) with the significant parts of $\sigma(k, \omega)$, eq (25), when $\omega \sim vk$.

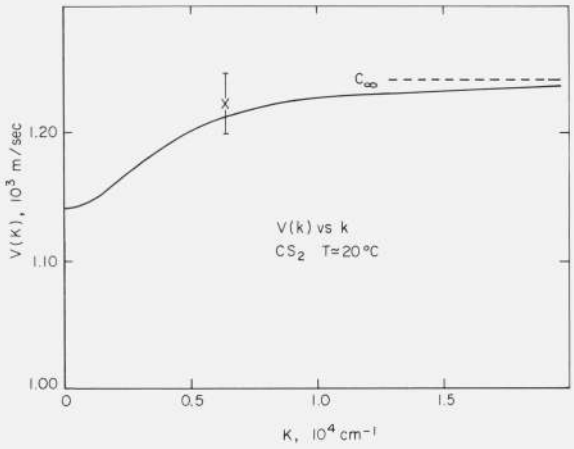

FIGURE 3. *The phonon velocity* v(k) *as a function of the wave vector* k *for* CS_2 *at 20°C.*
The experimental point (x) is taken from reference 18. Equation (45) and parameters from table 1 were used to construct this curve.

The direct evaluation of $\sigma(k, \omega)$ shows that the phonon peak coincides with the vanishing of the imaginary part of the dispersion relation,

$$D_2(\omega)=0. \tag{44}$$

The positive root of eq (44) determines the phonon frequency $v(k)k$. Neglecting the term involving the thermal diffusivity, a, eq (44) is

$$-\omega^2+c_0^2k^2+b_1k^2\omega^2\tau/(1+\omega^2\tau^2)=0.$$

The solution is

$$(\omega\tau)^2=(v(k)k\tau)^2=1/2[(c_\infty k\tau)^2-1]+1/2[(1-c_\infty^2k^2\tau^2)^2+4c_0^2k^2\tau^2]^{1/2}. \tag{45}$$

From eq (45) we see that as $k\rightarrow 0$, $v(k)\rightarrow c_0$ and as $k\rightarrow\infty$, $v(k)\rightarrow c_\infty$. The variation of $v(k)$ with k is indicated in figure 3

The width Γ_B is obtained by observing that if $D_2(v(k)k)=0$, $D_1(v(k)k)=-2[v(k)k]^2\Gamma_B$. The minus sign is necessary so that $\Gamma_B>0$ be satisfied. Direct substitution in eq (26) yields

$$2\Gamma_B=ak^2+b_0k^2-\left(\frac{c_0^2}{v^2}\right)\left(\frac{ak^2}{\gamma}\right)+\left[\frac{b_1k^2}{1+v^2k^2\tau^2}\right](1-ak^2\tau). \tag{46}$$

It should be noted that the width due to the relaxation is not simply added to the classical absorption term $ak^2(1-1/\gamma)+b_0k^2$. In practice this difference may not be significant, although for CS_2 it amounts to about 5 percent of Γ_B.

The method used to obtain $v(k)$ and Γ_B should be applicable to more complicated situations although it would be advisable to examine $D_1(\omega)$ and $D_2(\omega)$ numerically and to verify that $D_2(v(k)k)=0$ for each new situation.

4.4. Comparison With the Exact Expression

The approximate frequency distribution contained in eq (43) has been compared numerically with the exact expression, eq (25). This is illustrated in figure 4 where the percent deviation of the approximate expression from the exact one is shown as a function of frequency. The parameters are the ones used to obtain figure 1. The deviation in the central components is probably due to a small error in the width of the thermal diffusion mode. A decrease of 1 percent in that width would eliminate most of the difference between $\sigma(k, \omega)$ and $\sigma'(k, \omega)$. The deviation in the phonon

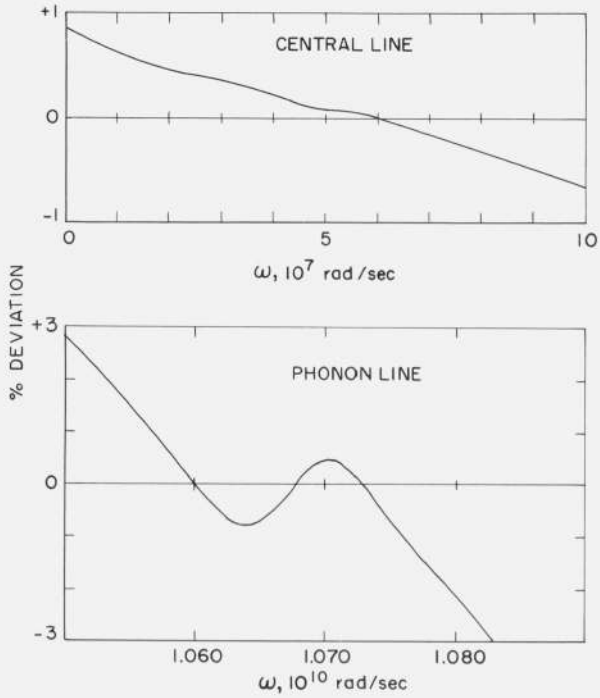

FIGURE 4. *The percent deviation* $[(\sigma-\sigma')/\sigma]$ *100 of the approximate frequency distribution,* $\sigma'(k, \omega)$, *from the exact distribution,* $\sigma(k, \omega)$, *is shown as a function of frequency* ω.

The parameters are those of CS_2 at 20 °C and $k=8.608\times10^4$ cm^{-1}.

component indicates that the maxima of the exact and approximate expressions do not quite coincide. This results in the oscillating deviation shown in figure 4. Deviations greater than 1 percent occur when the magnitude of $\sigma'(k, \omega)$ has fallen to less than 1 percent of its maximum value $\sigma'(k, 0)$. The sum rule, eq (10), is satisfied by the approximate expression $\sigma'(k, \omega)$ to within 1 percent using this set of parameters.

It is, of course, possible to improve the accuracy of $\sigma'(k, \omega)$ by obtaining more accurate solutions to the dispersion equation. This would involve using the solutions we have found, eqs (35) and (40), as the starting point of an iteration of the dispersion equation. The resulting formula for $\sigma'(k, \omega)$ would be much more complicated than eq (43).

4.5. Intensity Ratio

The ratio of the intensity of the unshifted (central) components of the scattered light to the intensity of the Brillouin components is a quantity which is readily obtained experimentally. This ratio, $\mathscr{I}=I_c/2I_B$, is easily obtained from eq (43) by integrating the individual terms:

$$\mathscr{I}=\frac{(1-1/\gamma)+\dfrac{(c_\infty^2-c_0^2)k^2-(v^2/c_0^2-1)[(c_0^4/v^4\tau^2)+c_0^2k^2(1-1/\gamma)]}{c_0^4/v^4\tau^2+v^2k^2}}{\dfrac{[1-c_0^2/v^2(1-1/\gamma)]\,[v^2k^2+c_0^2/v^2\tau^2]-(c_\infty^2-c_0^2)k^2}{c_0^4/v^4\tau^2+v^2k^2}}. \tag{47}$$

At low phonon frequencies $vk\tau \ll 1$ this reduces to the Landau-Placzek result

$$\mathscr{I}=\gamma-1. \tag{48}$$

At large phonon frequencies ($vk\tau \gg 1$) a more involved expression than eq (48) is obtained;

$$\mathscr{I}=(\gamma-1)[1+\{\gamma/(\gamma-1)\}\,\{(c_\infty^2-c_0^2)/c_0^2\}]. \tag{49}$$

The high frequency limit, eq (49) was obtained earlier by Rytov [13].

The ratio of intensities $\mathscr{I}$, given by eq (47) agrees within 1 percent of $\mathscr{I}$ obtained by numerical integration of the exact expression for $\sigma(k, \omega)$. From an experimental point of view, eq (47) should be taken to be an upper bound on $\mathscr{I}$. This is because it may be difficult to detect all of the light scattered by the second nonpropagating mode; the difficulty arises from the large width of this component.

4.6. Summary of the Properties of $\sigma(k, \omega)$

In the previous paragraphs we have shown that $\sigma(k, \omega)$, the frequency distribution function, may be approximately represented as a sum of four Lorentzian curves;

$$\sigma'(k, \omega) = (1-1/\gamma)\left[\frac{2\lambda k^2/\rho_0 c_p}{(\lambda k^2/\rho_0 c_p)^2+\omega^2}\right] + \left[\frac{(c_\infty^2-c_0^2)k^2-(v^2/c_0^2-1)(c_0^4/v^4\tau^2+c_0^2k^2(1-1/\gamma))}{c_0^4/v^4\tau^2+v^2k^2}\right]\times\left[\frac{2c_0^2/v^2\tau}{(c_0^2/v^2\tau)^2+\omega^2}\right] \tag{43}$$

$$+\left[\frac{[1-c_0^2/v^2(1-1/\gamma)][v^2k^2+c_0^2/v^2\tau^2]-(c_\infty^2-c_0^2)k^2}{c_0^4/v^4\tau^2+v^2k^2}\right] \times\left[\frac{\Gamma_B}{\Gamma_B^2+(\omega-vk)^2}+\frac{\Gamma_B}{\Gamma_B^2+(\omega+vk)^2}\right] \tag{44}$$

where the phonon speed $v(k)$ satisfies

$$[v(k)k\tau]^2 = 1/2[(c_\infty k\tau)^2-1]+1/2[(1-c_\infty^2k^2\tau^2)^2+4c_0^2k^2\tau^2]^{1/2} \tag{45}$$

and the phonon width is

$$2\Gamma_B = ak^2+b_0k^2-\left(\frac{c_0^2}{v^2}\right)\left(\frac{ak^2}{\gamma}\right)+\left(\frac{b_1k^2}{1+[v(k)k\tau)]^2}\right)(1-ak^2\tau). \tag{46}$$

The ratio of the central components to that of the Brillouin lines is, in the high frequency limit $(v(k)\rightarrow c_\infty)$

$$\mathscr{I} = (\gamma-1)[1+\{\gamma/(\gamma-1)\}\{(c_\infty^2-c_0^2)/c_0^2\}]. \tag{49}$$

5. Comparison With Experiment

5.1. CS_2

In the previous sections, various points have been illustrated by using parameters appropriate to carbon disulfide (CS_2). For example, Figures 1, 2, and 3 show $\sigma(k, \omega)$ and $v(k)$ for CS_2 as predicted by egs (25) and (45). Comparison with experiment is limited to the phonon speed and to $\mathscr{I}$, the ratio of the intensities of the central and Brillouin components.

The parameters for CS_2 at approximately 20 °C are listed in table 1. Several measurements of the phonon speed are listed in table 2. To within the precision with which τ and k are known, eq (45) predicts that $v(k)$ lies within the experimental uncertainty in each case.

TABLE 1. *Material parameters:* CS_2 *at 20 °C*

Parameter	Value	Reference
a	1.95×10^{-3} cm²/sec	6
b_0	3.84×10^{-3} cm²/sec	14
b_1	4.76 cm²/sec	10
c_0	1.142×10^5 cm/sec	10
τ	2.04×10^{-9} sec	10
n	1.675	6
ρ_0	1.262 gm/cm³	6
γ	1.55	10

TABLE 2. *Phonon velocity and intensity ratio;* CS_2

Reference	Experimental		Calculated	
	Velocity	$\mathscr{I}$	Velocity	$\mathscr{I}$
	m/sec		*m/sec*	
15	1235	–	1241	0.83
16	1241	0.77	1241	.83
17	1250	.71	1241	.83
6	1265	.93	1241	.83
18	1223	–	1212	.69

The experimental velocities have been reduced to 20 °C using $dv/dT = -3.2$ m/sec-deg [6]. The velocities were calculated using eq (45). $\mathscr{I}$ values were calculated using eq (47). The material parameters were taken from table 1 and **k**, the wave vector, was determined from information in the references.

Three of the references contain measurements of $\mathscr{I}$. Here the agreement is not as close. The value of $\mathscr{I}$ predicted by eq (49) is 0.83. That the agreement with the phonon velocity is better than the agreement with $\mathscr{I}$ is not surprising. The limited sensitivity of the detectors used in these measurements makes it difficult to obtain accurate determinations of $\mathscr{I}$. The presence of the "second" nonpropagating mode aggravates the situation; unless the detector is quite sensitive, much of the light in that mode would be lost in the noise of the detector.

5.2. CCl_4

Sufficient data exist for carbon tetrachloride (CCl_4) to warrant comparison with the prediction of the single relaxation time theory. This comparison indicates that only a part of the energy of the internal degrees of freedom relaxes with a time on the order of $10^{-10} - 10^{-11}$ sec. Presumably the remainder of the energy relaxes more rapidly than can be detected by light scattering experiments.

The parameters for CCl_4 at approximately 20 °C are listed in table 3. Four measurements of the phonon speed obtained from Brillouin scattering measurements and one acoustic measurement of the speed of sound in CCl_4 are listed in table 4. The calculated velocities in table 4 are based on the assumption that only 75 percent of the internal specific heat is involved in the relaxation process and that $\tau = 5.12 \times 10^{-11}$ sec. This value for τ is consistent with the acoustic measurement. The agreement between the measured and calculated values of $\mathscr{I}$ is poor. This is not unexpected if another relaxation time exists for CCl_4. This would imply the existence of another nonpropagating mode which would make $\mathscr{I}$ larger than the prediction of eq (47).

Also, for CCl_4, there is a measurement of the width of the Brillouin line. Experimentally $\Gamma_B \approx 4 \times 10^9$ rad/sec while eq (46) predicts $\Gamma_B \approx 5 \times 10^9$ rad/sec if 3/4 of the internal specific heat is involved in the relaxation process.

TABLE 3. *Material parameters:* CCl_4 *at 20 °C*

Parameter	Value	Reference
a	1.78×10^{-3} cm²/sec	6
b_0	5.98×10^{-3} cm²/sec	14
b_1	3.59×10^{-2} cm²/sec	10
c_0	9.20×10^4 cm/sec	10
τ	5.12×10^{-11} sec	
n	1.472	6
ρ_0	1.594 gm/cm³	6
γ	1.46	10

The relaxation time τ was estimated from acoustic measurements [19].

TABLE 4. *Phonon velocity and intensity ratio;* CCl_4

Reference	Experimental		Calculated	
	Velocity	$\mathscr{I}$	Velocity	$\mathscr{I}$
	m/sec		*m/sec*	
6	1040	1.10	1024	0.77
16	988	0.75	990	.62
17	1000	.72	990	.62
20	1002	–	990	.62
19	972 – acoustic measurement			

The experimental velocities have been reduced to 20 °C using $dv/dT = -3.1$ m/sec – deg [6]. The velocities were calculated using eq (45). $\mathscr{I}$ values were calculated using eq (47). The material parameters were taken from table 3 and **k**, the wave vector, was determined from information in the references.

In a previous publication [21] we stated that more than one relaxation time exists in CCl_4 and therefore the single relaxation time theory did not apply. Although the available data are insufficient to fully verify this statement, the phonon speed comparison suggests that this statement is correct.

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