

SOME RESULTS OF THE EXPERIMENTAL STUDY OF THE FINE STRUCTURE OF RAYLEIGH SCATTERING LINES IN LIQUIDS OF VARIOUS VISCOSITIES\*

I. L. FABELINSKIĬ

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THE main reason for my choice of this topic for my report is that an experimental search for fine structure in the scattering of light was the first collaborative research done by G. S. Landsberg and L. I. Mandel'shtam; it was begun in 1925, and has now developed into a fruitful field of molecular optics and acoustics.

The idea that there must exist a fine structure of the Rayleigh line was put forward by Mandel'shtam as early as 1918.<sup>[1,2]</sup> This idea of his is one of the major sources of experimental and theoretical researches on the problem of the molecular scattering of light.

Here we must make some historical remarks bearing on the subject of this report.

First of all it must be noted that after Mandel'shtam<sup>[3]</sup> pointed out (1907) that the mechanism which Rayleigh<sup>[4]</sup> took as the basis for his theory of light scattering should actually not lead to any scattering, Smoluchowski<sup>[15]</sup> found (1908) the correct cause of the scattering of light. This cause is fluctuations of density, which reach such magnitudes at the critical temperature that critical opalescence is the result.

Einstein<sup>[6]</sup> (1910) made use of this idea of fluctuations and developed a theory of the scattering of light in pure liquids and solutions, which gave a formula expressing the intensity of the scattered light as a function of the wavelength and parameters characteristic of the scattering medium. To calculate the intensity of the scattered light Einstein<sup>[6]</sup> used the method of expansion of the density fluctuations in a series of spatial plane waves. It must be emphasized that this expansion of the density fluctuations in terms of plane waves was a purely formal step in Einstein's theory. In his work this expansion was simply a computational device. Einstein's "formal" waves were static in time.

Debye<sup>[7]</sup> (1912) perfected the Einstein theory of specific heats of solids and expressed the energy of thermal motions in terms of the energies of elastic plane waves. In this paper Debye says nothing about the molecular scattering of light, just as in his paper on the scattering of light Einstein gave no attention to the problem of specific heats. Six years after Debye's work Mandel'shtam (1918) came to the conclusion that Einstein's "formal" waves and Debye's thermal waves are really the same thing<sup>[8]</sup>; thus dynamics was

brought into the "formal" waves, and they were changed from a computational device to a physical phenomenon. This was an important forward step, which has led to major advances in molecular optics.

From this new point of view the scattering of light can now be regarded as the diffraction of the light by the elastic thermal waves.<sup>[9,11]</sup> The great diversity of frequencies and directions of propagation of the elastic thermal waves leads to scattering of light in all directions.

At first glance it seems difficult to pick out one particular elastic wave and study the diffraction of light by it. One can, however, realize such an experiment in practice. In fact, if one directs a parallel beam of monochromatic light at the scattering volume, the light diffracted (scattered) in a direction  $k'$  at an angle  $\theta$  with the direction of propagation  $k$  of the original beam will have maximum intensity when the relation (Fig. 1)

$$k' - k - q = 0 \tag{1}$$

holds between the wave vectors  $k$ ,  $k'$ , and  $q$  of the exciting light, the scattered light, and the elastic wave.

Equation (1) is the well known Bragg condition, which can also be written (when the small difference of the absolute values  $|k'|$  and  $|k|$  is neglected) in the form

$$2n\Lambda \sin \frac{\theta}{2} = \lambda, \tag{2}$$

where  $n$  is the index of refraction of the scattering medium,  $\Lambda$  is the wavelength of the elastic wave, and  $\lambda$  is the wavelength in vacuum of the exciting light.

It is not hard to see that the frequencies of the elastic waves responsible for the scattering in various directions are given by the formula

$$f = \frac{2nV \sin \frac{\theta}{2}}{\lambda} \tag{3}$$

If as a concrete example we consider a crystal of

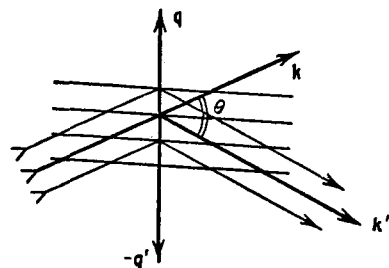


FIG. 1. Illustrating the diffraction of light by an elastic thermal wave.

\*Report at session of the Scientific Council, Physics Institute of the Academy of Sciences of the U.S.S.R., held February 12, 1962, in memory of G. S. Landsberg.

quartz and scattering excited by the mercury resonance line  $\lambda 2537 \text{ \AA}$  at angle  $\theta = 180^\circ$ , and assume  $V = 6 \times 10^5 \text{ cm/sec}$  and  $n = 1.6$ , we get from Eq. (3)  $f \approx 7 \times 10^{10} \text{ cps}$ . Under the chosen conditions all the other waves will play no part in the observed molecular scattering of the light in the quartz. The elastic waves propagated in various directions in a crystal of finite dimensions form standing waves, and the variation with time of the density in these waves leads to a modulation of the scattered light.<sup>[9-11]</sup> Thus at the angle  $\theta$  (in the direction  $k'$ ) one will observe a doublet

$$\nu \pm f,$$

where  $\nu$  is the frequency of the exciting light waves; the fractional frequency change in this modulation is

$$\pm \frac{f}{\nu} = \pm \frac{\Delta\nu}{\nu} = 2n \frac{v}{c} \sin \frac{\theta}{2}. \quad (4)$$

Thus the maximum fractional frequency for quartz (at  $\theta = 180^\circ$ ) is  $\Delta\nu/\nu \approx 6 \times 10^{-5}$ . For scattering angle  $\theta = 90^\circ$  the value is even smaller. Equation (4) was obtained by Mandel'shtam<sup>[9]</sup>; the same result was also found by Brillouin.<sup>[12]</sup> The fine-structure components of a scattered-light line are now called Mandel'shtam-Brillouin components.

Mandel'shtam further showed<sup>[9]</sup> that the scattering by isobaric density fluctuations, which are not included in the Debye treatment, leads to the appearance of an undisplaced line in the scattered light. Consequently, if the excitation is by a monochromatic line, a triplet must appear in the scattered light.\*

The pattern of the phenomenon in question was thus determined, and one could go on to the experimental study of the spectral composition of the scattered light.

Landsberg and Mandel'shtam chose to work with a crystal, since in a crystal the damping of the elastic waves is smaller than in a liquid, and  $\Delta\nu/\nu$  is much larger. The best results were to be expected with a quartz crystal, since there are large natural specimens of quartz and the optical purity is greater than that of other crystals. The natural source of quartz in our country in 1925 was the antique shops where it existed in the form of seals belonging to formerly prominent Russian families. Landsberg became a frequenter of antique shops and a buyer of quartz seals. As a rule the quartz crystals in the seals were not of good enough quality. They abounded in foreign inclusions and other inhomogeneities, which led to the appearance of a large amount of parasitic light which had nothing in common with the light from molecular scattering.

\*In a crystal, owing to the anisotropy of the velocity of the elastic waves, the existence of a longitudinal and two quasi-transverse waves, and effects of various states of polarization of the light, there must be 25 components in the general case.<sup>[13,14]</sup> In a liquid there must be only three components, and in an amorphous solid, five components.

Only after Landsberg<sup>[2]</sup> had established an objective criterion for distinguishing the molecular-scattering light from the parasitic light was it possible to select the best of the quartz crystals and make a quantitative study of the total molecular scattering of a quartz crystal. Landsberg and his pupils<sup>[2,15]</sup> succeeded in studying the scattering of light in quartz in detail and finding the main laws of the phenomenon. These researches on the total molecular scattering in quartz and other crystals, begun by Landsberg, are still continuing and constantly giving interesting new results.\*

After the main laws of the total molecular scattering in quartz had been established, one could turn to the original problem of the spectral study of the fine structure of the scattered line. It must be remarked that in the Physics Department of the Moscow State University, where this work was done, the best spectrograph at that time was a Fuess quartz spectrograph with a Lummer-Gehrcke plate, which was scarcely adequate for the problem; but there was no choice, and the work began.

In the very first experiments lines of altered frequencies were found in the spectrum of the scattered light, but the changes of frequency were so large, and the number and locations of the lines so different from expectations that these observed lines could not be lines of the fine structure. Soon, however, everything was explained and understood. In this way the combination (Raman) scattering of light was discovered.

The study of the new phenomenon took Landsberg and Mandel'shtam away from the original problem for almost two years. When they resumed it, they had the same apparatus, from which it was hard to expect completely good results, but nevertheless the work was continued. The wish to get results with spectroscopic instruments really suitable for the problem obliged Landsberg and Mandel'shtam to turn to D. S. Rozhdestvenskiĭ in Leningrad, who had available spectroscopes of high resolving power. Rozhdestvenskiĭ at once understood the importance of the problem and provided for the joint research a spectroscope of high resolving power (a Michelson echelon) and a collaborator, E. F. Gross. The work continued in the two places. In 1930 the phenomenon was observed both in Moscow and in Leningrad.

The fine structure of the Rayleigh line in quartz was found by Landsberg and Mandel'shtam<sup>[2]</sup> and by Gross<sup>[16]</sup> in crystalline quartz; Gross<sup>[17]</sup> also observed the fine structure of the scattered line in liquids. The main laws of the phenomenon as predicted by Mandel'shtam were confirmed experimentally.

In a careful analysis of the problem of the fine structure of the scattering of light in liquids M. A. Leontovich<sup>[18,19]</sup> and Mandel'shtam<sup>[19]</sup> called atten-

\*See also the report by V. L. Ginzburg on page 649.

tion to a difficulty in principle: as has already been said, the displaced Mandel'shtam-Brillouin lines are shifted from the undisplaced line by the amount  $\Delta\nu$  given by Eq. (4). If the medium absorbs sound, then it is clear that the Mandel'shtam-Brillouin components will be characterized by a finite width.<sup>[20,21]</sup> The half-width of each component will be given by

$$\delta\nu = \frac{\alpha\nu}{\pi}, \quad (5)$$

where  $\alpha$  is the amplitude absorption coefficient per unit length, which according to the hydrodynamical theory\* is given by

$$\alpha = \alpha_\eta + \alpha_{\eta'} = \frac{\Omega^2}{2V_0^3\rho} \left\{ \frac{4}{3} \eta + \eta' \right\}. \quad (6)$$

Here  $\Omega = 2\pi f$ ,  $\eta$  and  $\eta'$  are the shear and bulk viscosities, respectively, and  $\rho$  is the density of the liquid. If we set  $\delta\nu = \Delta\nu$ , it is clear that in this case the discrete lines of the fine structure cannot be observed. When we compare the corresponding values for  $\Delta\nu$  and  $\delta\nu$  from Eqs. (4) and (5) and use Eq. (2), we easily find that the condition for the absence of discrete fine structure is

$$\alpha\Lambda = \pi \simeq 1,$$

and that the structure is also absent if

$$\alpha\Lambda \gg 1. \quad (6')$$

Consequently, to observe the discrete lines of the structure we must have

$$\alpha\Lambda \ll 1. \quad (7)$$

If we take  $\alpha$  from ultrasonic measurements at a definite frequency and extrapolate with a quadratic law, in accordance with the hydrodynamical formula (6), to the frequency which gives the scattering of light at a prescribed angle  $\theta$ , we get values of  $\alpha$  from which [using also Eq. (2)] we can calculate the quantity  $\alpha\Lambda$ . For carbon tetrachloride, benzol, and carbon disulfide, for example, the respective values of  $\alpha\Lambda$  are 5, 11, and 70. Consequently, for these liquids the hydrodynamical theory forbids a fine structure of the scattered line.

Nevertheless quite distinct fine-structure lines are observed with these liquids. This is the difficulty in principle encountered by the hydrodynamical theory of sound absorption.

We must call attention to the fact that roughly speaking one can divide liquids into those for which the shear viscosity is small and the bulk viscosity is large (these include the liquids mentioned above), and those for which the shear viscosity is large, or even extremely large, and the bulk viscosity is relatively small.

\*In this formula we have neglected a term which depends on the thermal conductivity. In the cases considered it is of no practical importance.

So far we have been speaking of liquids for which  $\eta' > \eta$ . In considering the difficulty with the conclusions of the hydrodynamical theory, which forbids fine structure for liquids for which  $\eta' > \eta$ , Mandel'shtam and Leontovich concluded that within the framework of the hydrodynamical theory there is no escape from the contradiction.

Mandel'shtam and Leontovich found a way out of this difficulty in the relaxation theory of the propagation of sound in liquids, which they developed.<sup>[19]</sup>

In this theory it is assumed that there is relaxation only of the bulk viscosity; the expressions found for the absorption and the speed of sound  $V$ , caused by relaxation of the bulk viscosity, are

$$\alpha_{\eta'} = \frac{\Omega^2\tau \left[ \left( \frac{V_\infty}{V_0} \right)^2 - 1 \right]}{2V_0(1 + \Omega^2\tau^2)},$$

$$\frac{V_0}{V} - 1 = -\frac{1}{2} \frac{\Omega^2\tau^2 \left[ \left( \frac{V_\infty}{V_0} \right)^2 - 1 \right]}{1 + \Omega^2\tau^2}, \quad (8)$$

where  $\tau$  is the relaxation time  $V_\infty$  and  $V_0$  are the speeds of sound at frequencies  $\Omega \rightarrow \infty$  and  $\Omega \rightarrow 0$ . The formulas (8) of the relaxation theory clearly show that the quadratic frequency dependence of  $\alpha_{\eta'}$  holds only at low frequencies, for which  $\Omega\tau \ll 1$ , whereas when the frequency is so high that  $\Omega\tau \gg 1$ , there is no frequency dependence of  $\alpha_{\eta'}$  and  $V$  at all. Thus it is quite understandable that at a frequency  $\sim 10^{10}$  cps  $\alpha\Lambda$  can be much smaller than unity, although the hydrodynamical theory gives  $\alpha\Lambda \gg 1$ ; consequently the relaxation theory easily disposes of the contradiction. A glance at the relaxation-theory formula (8) is enough to see that this theory assumes the existence of a dispersion of the speed of sound, i.e., a difference between  $V_\infty$  and  $V_0$ , and that it is supposed that  $V_\infty > V_0$ . If it should turn out that  $V_\infty = V_0$ , this would mean that the mechanism is not that assumed by the relaxation theory, and the theory can give nothing; in particular, it also cannot explain the contradiction whose solution gave rise to it.

The dispersion of the speed of sound is an important physical phenomenon, which had also been of interest independently of the relaxation theory. But all attempts to detect a dispersion of the speed of sound in the sonic and ultrasonic ranges had been unsuccessful.

The Mandel'shtam-Leontovich relaxation theory appeared before any dispersion of the speed of sound had been found. The search for dispersion of the speed of sound continued after the development of the relaxation theory. Finally it was found by Shpakovskii<sup>[22]</sup> in acetic acid, amounting to  $\sim 1$  percent in the ultrasonic frequency range. No dispersion was found in other liquids, as long as ultrasonic technique was incapable of significantly increasing the range of working frequencies. It was already clear at that time, however, that the study of the fine structure can give valuable

information about the speed of sound at extremely high frequencies of  $\sim 10^{10}$  cps, which were then inaccessible to ultrasonic technique. Even now such frequencies of artificially generated sound are not studied in liquids because of the large absorption. R. Rao<sup>[23]</sup> was the first to use the fine structure to determine the speed of hypersound (sound at frequencies above  $10^9$  cps). Rao concluded from his experiments that in carbon tetrachloride there is a positive dispersion of sound of  $\sim 20$  percent, and in acetone there is a negative dispersion of roughly the same size.

The explanation of the negative dispersion given by Rao (cf. [24]) is clearly unsatisfactory, although generally speaking a negative dispersion is possible.<sup>[24,25]</sup> After Rao's work his compatriot Venkateswaran<sup>[26]</sup> made thorough experiments to determine the speed of hypersound from the fine structure for a broad class of liquids and concluded that there is no dispersion of the speed of sound for any of the seventeen substances he studied, including acetone, carbon tetrachloride, benzol, and chloroform. Venkateswaran ascribes Rao's results to experimental errors, and indicates that the error of his own measurements was at worst  $\pm 25$  m/sec (less than 2 percent). Consequently if we suppose that Venkateswaran's experiments are correct, we have the definite conclusion that the relaxation theory of the propagation of sound in liquids is erroneous.

In fact, the relaxation theory enables us to get a criterion for estimating the amount of dispersion of the speed of sound. This criterion is as follows:

$$\frac{\Delta V}{V} = \frac{\eta'}{2V^2\alpha\tau} = \frac{\alpha_\eta}{f^2} \frac{V \left( \frac{\alpha}{\alpha_\eta} - 1 \right)}{4\pi^2\tau}, \quad (9)$$

where  $\Delta V = V_\infty - V_0$ ,  $V = \frac{1}{2}(V_\infty + V_0)$ ,  $\alpha$  is the experimentally measured value of the absorption coefficient, and  $\alpha_\eta$  is the absorption coefficient caused by the shear viscosity and calculated from Eq. (6) when we set  $\eta' = 0$ . Equation (9) makes it possible to estimate the expected dispersion, or more exactly, the total fractional change of the speed. If a fine structure is observed in cases for which according to the classical theory  $\alpha\Lambda \approx 10$ , then we can say that the corre-

sponding speed of the elastic waves which modulate the scattered light actually lies beyond the relaxation region, and consequently  $\Delta V$  is practically determined by the total change of speed.

Using Eq. (9) and data on  $\alpha$ ,  $\alpha_\eta$ , and assuming that  $\tau < 1/2\pi f'$  (where  $f'$  is the frequency up to which the frequency dependence of the absorption is quadratic), one can estimate the quantity  $\Delta V/V$  for various liquids.

This estimate shows that in benzol  $\Delta V/V$  should exceed 5 percent, and that it is 9 percent for carbon disulfide; the situation is similar for carbon tetrachloride, chloroform, and a number of other liquids. Consequently the question arises, are the relaxation theory and the absorption measurements on which this estimate is based erroneous, or is the error in the experiments on the determination of the speed of sound from the fine structure of the Rayleigh line?

To settle this question the author of the present report and his collaborators O. A. Shustin, V. A. Molchanov, and M. S. Pesin, working in Landsberg's laboratory, undertook<sup>[29,30,28]</sup> a new determination of the speed of hypersound from the Mandel'shtam-Brillouin components, primarily for the liquids for which Eq. (9) predicted the existence of an appreciable dispersion of the speed of sound.

We were able to construct an interference apparatus of comparatively large effective aperture, which enabled us to study the phenomenon for various states of polarization and over a broad range of temperatures.

The speed of hypersound was determined from the relation

$$V = c\Lambda\Delta\nu, \quad (10)$$

where  $c$  is the speed of light,  $\Lambda$  is determined from Eq. (2) and is expressed in cm, and  $\Delta\nu$  is the displacement of the maximum of the Mandel'shtam-Brillouin component from that of the undisplaced line and is expressed in  $\text{cm}^{-1}$ . The speeds of hypersound determined in this way are shown in Table I.

Table I shows that in six liquids a positive dispersion of the speed of sound is reliably observed, namely in the cases for which the relaxation theory [the criterion (9)] predicts that an appreciable dispersion is

Table I. Speeds of hypersound and ultrasound, and dispersion of sound, in various liquids

| Substance            | Temperature<br>$t, ^\circ\text{C}$ | Speed of<br>hypersound,<br>$V, \text{m/sec}$ | Speed of<br>ultrasound,<br>$V, \text{m/sec}$ | Dispersion<br>of the speed,<br>$\frac{\Delta V}{V} \cdot 10^2$ |
|----------------------|------------------------------------|--|--|--|
| Benzene              | 20                                 | $1470 \pm 20$                                | 1324   | 10   |
| Carbon disulfide     | 20                                 | $1265 \pm 22$                                | 1158   | 9  |
| Carbon tetrachloride | 20                                 | $1040 \pm 27$                                | 920  | 12   |
| Toluene              | 20                                 | $1314 \pm 34$                                | 1324   | 0  |
| Acetone              | 20                                 | $1190 \pm 40$                                | 1190   | 0  |
| Methylene chloride   | 20                                 | $1245 \pm 36$                                | 1092   | 13   |
| Methylene bromide    | 24                                 | $1099 \pm 30$                                | 971  | 12   |
| Acetic acid          | 20                                 | $1140 \pm 35$                                | 1144   | 0  |
| Chloroform           | 20                                 | $1211 \pm 43$                                | 1005   | 17   |
| Water                | 20                                 | $1480 \pm 20$                                | 1490   | 0  |

to be expected. In the cases for which the relaxation theory offers no hope for a large dispersion, we indeed did not find it. Obviously this cannot all be regarded as accidental.

Zeros have been entered in the last column of Table I for these latter cases, but it must be emphasized that we do not assert that there is no dispersion at all in these cases; we only state that the accuracy of our method is not enough to detect it, and consequently in these cases the dispersion does not exceed 2 or 3 percent; it may be much smaller.

On the basis of the relaxation-theory formula (8), measurements of the absorption at low sound frequencies, and our measurements of the dispersion, we can determine  $\tau$ , and thus calculate  $\alpha_{\eta}/f^2$  as a function of the frequency. The results of such a calculation are shown by the solid curve in Fig. 2. At the time when we had some of the data presented above there appeared a paper by Lamb and Andraea,<sup>[31]</sup> who found a strong relaxation change of  $\alpha_{\eta}/f^2$  as function of  $f$  in carbon disulfide up to frequencies  $f = 2 \times 10^8$  cps. Their data are shown in Fig. 2 as black circles.

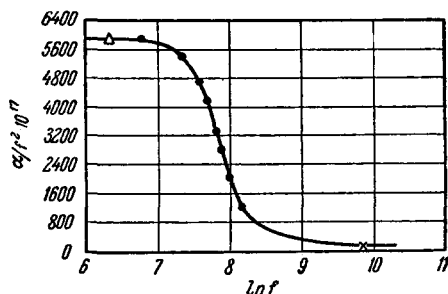


FIG. 2. Dependence of  $\alpha/f^2$  on  $f$  for carbon disulfide.  $\Delta$  is the acoustical and  $\times$  the hypersonic value of  $\alpha/f^2$ , from which the solid curve was constructed; points  $\bullet$  are the experimental data of<sup>[31]</sup>.

There is very good agreement between the ultrasonic data and the hypersonic data and the relaxation theory with a single relaxation time.

In the case of methylene chloride, which has been studied in the ultrasonic region,<sup>[32]</sup> the agreement is not so good (Fig. 3). Evidently, as we have already pointed out,<sup>[28]</sup> this is explained by the fact that the type of relaxation theory with a single relaxation time does not give a quantitative description of the phenomenon. For the other liquids in which we have found a dispersion of the speed of sound the comparison cannot yet be made, since the necessary ultrasonic measurements are not available.

Recently there has been much attention given to the interpretation of absorption and dispersion of sound from the point of view of simplified molecular ideas. In particular it is supposed that there exists a whole group of liquids (the so-called Kneser liquids) in which absorption and dispersion of sound are caused by thermal relaxation with the same mechanism as in vapors and gases.

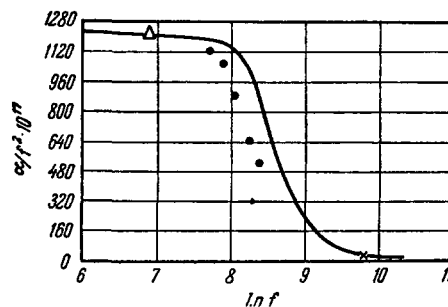


FIG. 3. Dependence of  $\alpha/f^2$  on  $f$  for methylene chloride.  $\Delta$  is the acoustical and  $\times$  the hypersonic value of  $\alpha/f^2$  from which the solid curve was constructed; points  $\bullet$  are the experimental data of<sup>[32]</sup>.

These liquids also include those in which we found dispersion of the speed of sound. From the stated assumption it is a natural conclusion that the volume viscosity is due only to exchange of energy between internal and external degrees of freedom. In this case one gets from the general relaxation theory of Mandel'shtam and Leontovich formulas<sup>[33]</sup> which have also been obtained by Herzfeld<sup>[34]</sup> in a different way. In particular, the theory gives

$$\frac{\Delta V}{V_0} = \frac{1}{2} \frac{\sum_i c'_i (c_p - c_v)}{c_p (c_v - \sum_i c'_i)}, \quad (11)$$

where  $c_p$  and  $c_v$  are the specific heats at constant pressure and at constant volume, and  $c'_i$  is the specific heat of the  $i$ -th vibrational degree of freedom:

$$c'_i = g_i \frac{R x^2}{e^x (1 - e^{-x})^2}. \quad (12)$$

Here  $x = h\nu_i/RT$  and  $g_i$  is the degree of degeneracy of the frequency  $\nu_i$ . The summation in Eq. (11) is taken over all characteristic frequencies of the molecule.

For carbon disulfide the dispersion calculated from Eqs. (11) and (12) is in good agreement with the hypersonic and ultrasonic data. Recently Pesin<sup>[33]</sup> has found that roughly speaking the other liquids that show dispersion (Table I) fall into two groups. Methylene chloride, chloroform, and methylene bromide have about twice as much dispersion as indicated by Eq. (11). Benzol and carbon tetrachloride have about half as much dispersion as predicted by Eq. (11).

In calculating the dispersion for the second group of liquids one can use not all of the vibrational frequencies, but only particular groups, basing the choice on symmetry arguments or on the Fermi resonance. In each individual case one can arrange the calculation so as to agree with experiment, but there is no general method, and it is as yet impossible to say beforehand what sort of dispersion is to be expected in any new case.

The situation is no better for the first group of liquids; here one cannot explain the observed dispersion at all with the complete vibrational specific heat.

The point is evidently that the assumption that in regard to the absorption and dispersion of sound liquids can behave like gases or vapors has no physical basis, and this moreover follows rather clearly from [19].

It is a matter of great interest to study the fine structure of a line of the scattered light in viscous liquids (with increasing viscosity) right up to the glassy state.

The relaxation theory of the propagation of sound in liquids developed by Mandel'shtam and Leontovich [19] referred to the bulk viscosity coefficient.

On the basis of the Maxwell scheme of viscosity M. A. Isakovich [35] extended the theory also to cases in which there is relaxation of both the volume and the shear viscosities.

In accordance with this theory we would be correct in thinking that at very high viscosities and in glasses we should expect a distinct fine structure, since at frequencies  $\sim 10^{10}$  cps the large shear viscosity should be much diminished or even disappear; because of the relaxation the phenomenon should be mainly determined by the elastic constants of the amorphous medium.

In the initial period of the study of the fine structure in viscous liquids and glasses the situation was in a certain sense the reverse of that which arose in the initial period of the study of liquids of small viscosity. In fact, in liquids with small  $\eta$  and with large bulk viscosity  $\eta'$  there was a distinct fine structure, although the hydrodynamical theory forbade it. The relaxation theory had to be developed to explain the presence of the fine structure.

In the study of liquids with large shear viscosities and of glasses the already existing relaxation theory allowed one to expect a fine structure, but it could not be observed in the experiments.

Many attempts were made to find a fine structure in viscous liquids and glasses (we refer for example only to some of them, [16,37]) but they invariably gave negative results. This unanimity led some authors [37] to the idea that there should in general be no fine structure in extremely viscous liquids and in glasses.

Their arguments were about as follows: the half-widths of the Mandel'shtam-Brillouin lines are given by the relations (5) and (6). Glasses are media at the high-viscosity limit, and therefore in such media  $\delta\nu \gg \Delta\nu$ ; consequently, there can be no discrete structure. In [37] this point of view was supported with experiments which, as has been shown, [38] actually could not serve as any confirmation of that opinion.

Landsberg repeatedly pointed out the untenability of this point of view, which fails completely to take account of the relaxation theory and the conclusions which follow from it. In a paper by Krishnan [39] which then appeared it was stated that a fine structure of the Rayleigh line had been observed in fused quartz; it seemed that the question of the fine structure in amorphous substances was settled.

Soon, however, there appeared a note [40] by compatriots of Krishnan, which pointed out the fallacy in the method used in [39], where a resonance filter was used. According to the view expressed in [40] it was not the fine structure that was observed, but an entirely different phenomenon associated with the passage of light through the resonance filter. Thus the question was again an open one.

Numerous attempts to find a fine structure in highly viscous media which were undertaken in Landsberg's laboratory remained unsuccessful for a rather long time. A very intense central component was observed in highly viscous liquids, but there were no fine-structure components.

As has been indicated, it was not at once understood what the reason was for this experimental result. One of the reasons for the absence of fine structure in this case could be the following: on the basis of the ideas of the relaxation theory one might suppose that in cases in which there is relaxation of a large quantity  $\eta$  it is quite possible that  $\Delta V/V$  is also large, i.e., for high frequencies the liquid will behave like a solid. Let us now suppose that  $\Delta V/V \approx 1$ ; this means that as we go from small to large viscosities the speed of hypersound is doubled. If this were so, it would lead to extremely important consequences, mainly of an experimental nature. In fact, for observation at the angle  $\theta = 90^\circ$  the integrated scattering coefficient for both Mandel'shtam-Brillouin components [24,27] is given by

$$R_{90^\circ} = \frac{\pi^2}{2\lambda^4} \left( e \frac{\partial e}{\partial Q} \right)_s^2 \beta_s kT,$$

where, as is well known, the adiabatic compressibility is

$$\beta_s = \frac{1}{QV^2}.$$

If it is assumed that  $V$  has been doubled, then  $\beta_s$ , and thus also  $R_{90^\circ}$ , is diminished by a factor four. When we take into account also the direct dependence of  $R_{90^\circ}$  on  $T$ , the decrease of the intensity is even greater. Now this means that instead of the usual exposure of 10–12 h the exposure goes up to 50–60 h. Such an increase of the exposure puts much higher requirements on the temperature and pressure controls of the interference apparatus. A change of pressure by 4–5 mm Hg or of temperature by  $0.5^\circ$  during the exposure time is inadmissible. Therefore one must either complicate the apparatus or secure a great increase of the effective aperture at the expense of other optical qualities.

The author of this report and M. S. Pesin followed the latter course. The aperture of the apparatus was increased by almost an order of magnitude, and the long-expected results were obtained with it. [41,42] The fine structure was detected over the entire range of variation of viscosity from fractions of a poise to  $10^8$  poise, right up to the glassy state, in glycerine and triacetin. The speed of hypersound determined from the

**Table II.** Temperature dependence of the speed of hypersound in glycerine

|                  |      |      |      |      |      |                     |                   |                 |
|------------------|------|------|------|------|------|---------------------|-------------------|-----------------|
| <i>t</i> , °C    | 150  | 50   | 45   | 35   | 22   | -27                 | -45               | -70             |
| <i>η</i> , poise | 0,05 | 1    | 1,8  | 3,2  | 9    | 3.9·10 <sup>3</sup> | 2·10 <sup>5</sup> | 10 <sup>8</sup> |
| <i>V</i> , m/sec | 1580 | 1690 | 2420 | 2800 | 2900 | 3290                | 3520              | 3665            |

**Table III.** Temperature dependence of the speed of hypersound in triacetin\*

|                  |      |      |      |      |                   |                   |
|------------------|------|------|------|------|-------------------|-------------------|
| <i>t</i> , °C    | 72   | 20   | 0    | -15  | -40               | -60               |
| <i>η</i> , poise | 0.02 | 0.23 | 0.70 | 4.68 | 2·10 <sup>3</sup> | 3·10 <sup>6</sup> |
| <i>V</i> , m/sec | 1246 | 1616 | 2065 | 2386 | 2537              | 2718              |

\*The error in the determination of the speed of hypersound at various temperatures fluctuates from 5 percent to 8 percent, the inaccuracy in the determination of the speed being smaller at low temperatures than at high temperatures.

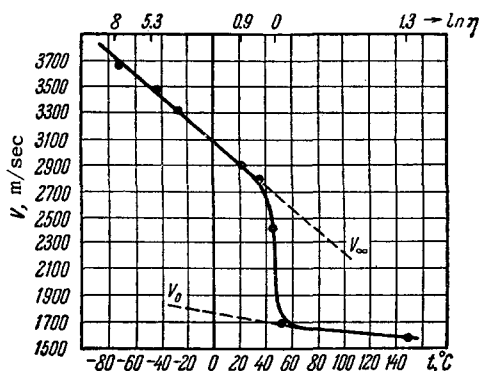


FIG. 4. Dependence of the speed of hypersound in glycerine on the temperature and viscosity.<sup>[41]</sup>

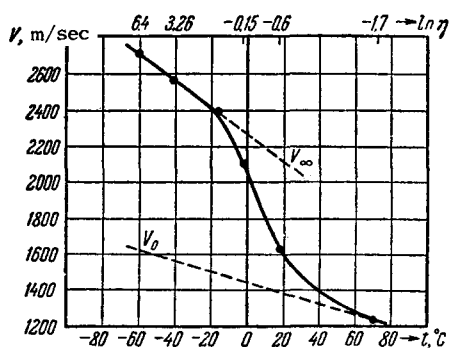


FIG. 5. Dependence of the speed of hypersound in triacetin on the temperature and viscosity.<sup>[42]</sup>

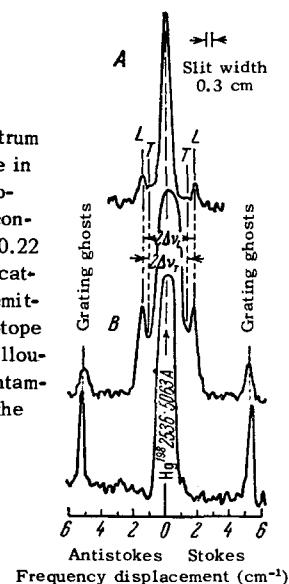
fine-structure spectra is shown in Tables II and III and plotted in the curves of Figs. 4 and 5. Figure 6 gives an idea of the distinctness of the fine-structure lines.

It can be seen from Figs. 4 and 5 and Tables II and III that even at comparatively moderate viscosities

FIG. 6. Microphotogram of the spectrum of the fine structure of the scattered line in glycerine<sup>[33]</sup> at -27° C. Longitudinal doublet. L - Mandel'shtam-Brillouin components; Φ - background of photographic plate in the neighborhood of the lines.



FIG. 7. Microphotograms of the spectrum of the fine structure of the scattered line in specimens A and B of fused quartz. Obtained with a spectrograph with a 35-ft concave diffraction grating with dispersion 0.22 Å/mm. Resolving power 300,000. The scattering was excited by the line λ2537 Å emitted by a lamp containing the mercury isotope <sup>199</sup>Hg. L - longitudinal Mandel'shtam-Brillouin components; T - transverse Mandel'shtam-Brillouin components. The spectrum of the exciting line is shown below.



the speed of hypersound reaches an almost doubled value, and consequently that at frequencies  $\sim 10^{10}$  cps such a liquid behaves like a solid.

Interesting results have recently been obtained in a study of the fine structure of the Rayleigh line in fused quartz.<sup>[43]</sup>

In these experiments Canadian scientists<sup>[43]</sup> have found not only the Mandel'shtam-Brillouin lines caused by the longitudinal wave, but also two satellites caused by the transverse elastic wave. The results are shown in Fig. 7. The numerical results for two specimens are as follows: for the longitudinal wave  $V_L = (5.99 \pm 0.08) \times 10^5$  cm/sec and  $(5.84 \pm 0.04) \times 10^5$  cm/sec; for the transverse wave  $V_T = (3.72 \pm 1.08) \times 10^5$  cm/sec and  $(3.97 \pm 0.2) \times 10^5$  cm/sec. Quite recently considerable material has been obtained from studies of

the absorption and speed of ultrasound in viscous liquids,<sup>[34]</sup> which is in qualitative agreement with the results of [41] and [42].

Attempts to describe the results obtained in the ultrasonic and hypersonic frequency ranges by means of the relaxation theory show that one can so far count only on a qualitative agreement. Quantitative comparisons give unsatisfactory results. Therefore there is need for continuation of the experimental and particularly the theoretical investigations. But the fundamental question which had previously been unsettled—the observation of the fine structure in extremely viscous liquids and in glasses—can now be regarded as settled.

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