INTERFEROMETRIC STUDIES OF LIGHT SCATTERING IN VISCOUS LIQUIDS AND GLASSES*

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1. Introduction

AN earlier paper appearing in the present issue of the *Proceedings* dealt with the case of mobile liquids and contained a discussion, based on the data for such liquids, of the origin of the central or undisplaced spectral component in the interferometer patterns of the light scattered by them. It emerged very clearly from these studies that the viscosity of the liquid plays a fundamental role in the appearance of this component and is the factor which principally determines its intensity relatively to the outer displaced or Brillouin components and also its state of polarisation. Accordingly, it becomes of interest to extend the study to liquids of high viscosity and to investigate how the results obtained with them are influenced by variation of temperature. The case of phenol already dealt with gives us some indication of what to expect in such cases. But the extension to liquids of great viscosity considered in the present paper has led to results which are of a somewhat unexpected character and therefore of exceptional interest.

2. Experimental Arrangements

The liquids studied are glycerine, castor oil, cyclohexanol and glycol as well as glucose. One of the chief difficulties in the investigations on light scattering by viscous liquids is that the ordinary method of distillation is inapplicable for rendering them free from dust and fluorescence. In the case of glycerine it is also of the utmost importance to remove all traces of water, as the presence of the latter lowers the viscosity considerably. A modified method which was found to work satisfactorily for glycerine, cyclohexanol and glycol is illustrated in Fig. 1. The liquid was first freed from water and other impurities by distilling in a reflexer and taking the middle

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* A preliminary report on the results of this investigation was made in two short notes in *Nature* (Raman and Venkateswaran, 1938, 1939).
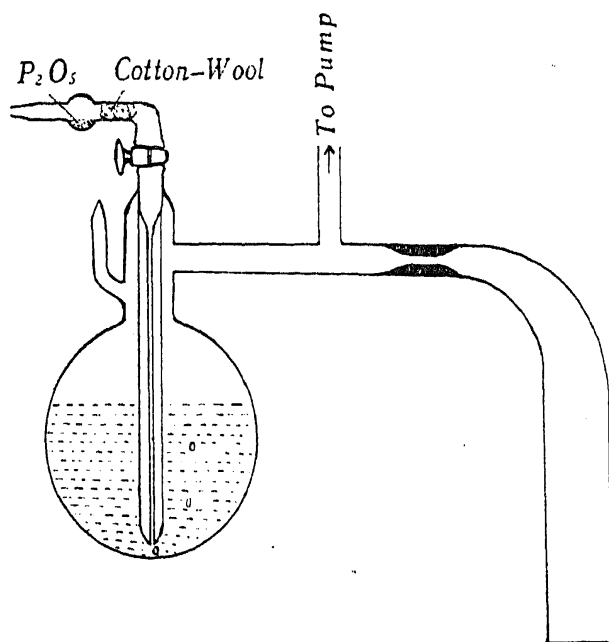
P₂Oₛ   Cotton-Wool   To Pump

FIG. 1. Distillation Apparatus for Glycerine

fraction which distils over at a constant boiling point.   The liquid was trans-
ferred through a side tube to a bulb of 500 c.c. capacity, which was connected
to a Wood's tube and to a vacuum pump through a plug of cotton-wool.
A small stream of air was let in through a capillary tube dipping into the
liquid, which helped to avoid bumping. The liquid was heated by a carefully
regulated electric heater and the first fraction of the distillate was removed
by a side trap (not shown in the figure). The distillation was repeated
several times and the Wood's tube filled with the liquid was finally sealed off.
In the case of castor oil and glucose the substances supplied by the dealers
were transferred to the tube without further purification and the air bubbles
locked in the fluids removed by warming, while being connected to a pump-
ing system. The experimental arrangement was the same as that used in
the previous communications, a zinc-mercury amalgam lamp being the source
of illumination. For investigating glycerine at 0° C., the tube was mounted
within a metal lined wooden box, with the illumination end alone
coming out through a side hole. In the case of liquids, the observations
were made of the light scattered backwards; glasses were studied in the trans-
verse setting. The plate distance for the Fabry-Perot plates was 5 mm.
except in the case of the optical glass for which a 3-mm. separation was used,
as the sound velocity in it is as high as 5,000 metres per second.

3. *Experimental Results*

The interference patterns obtained with the 4810 A.U. radiations of
the zinc arc for all liquids included in the present investigation and
for styrol glass, are given in Plate XIV. In both the organic and

inorganic glasses, in spite of the fact that the interference rings are very intense, no displaced components could be observed; but a weak background overlapping the pattern is detectable. Glucose is the most viscous of the liquids studied, and no trace of the Brillouin components has been observed for it. Glycerine has been investigated at 0°, 26°, 42°, and 110° C. For all the four temperatures the spectra of glycerine are nearly of the same intensity as revealed by the intensity of the Raman line at 3,000 cm.$^{-1}$ due to the C–H group, which appears in the neighbourhood of the zinc lines. At 0° C., the Brillouin components are extremely weak. The central component is very intense; but for this temperature, it is possible that part of its intensity is due to parasitic light. At 26° C. the displaced components brighten up, though the central component still remains intense. For 4810 A.U., the positive and negative components overlap; they are just separated out in the 4622 A.U. radiations. At 42° C., they are more intense and at 110° C. their intensity is comparable to that of the central component. The Brillouin shift at 110° C. is also considerably less than at the room temperature. These changes in glycerine are analogous to those already reported for phenol, though more pronounced as we should expect from the great viscosity of the former. In castor oil, the components can be clearly seen, though they are extremely weak and difficult of reproduction in Plate XIV. With 7·5 mm. separation for the Fabry-Perot plates, the two components were found to overlap each other. In the case of glycerine, castor oil and phenol at the room temperature, the Brillouin components could not be identified in the mercury radiations, as they are overwhelmed by the hyperfine structure satellites. The negative result reported by Raman and Rao (1938) for glycerine and phenol using mercury radiations is thus not surprising. In glycol and cyclohexanol which are comparatively less viscous, the Brillouin components are very intense. Another feature which deserves special mention is that in all these liquids, the displaced components are as sharp as the incident radiation. The main features of the patterns are described in Table I. From the frequency shift $\delta \nu$ of the Brillouin components for 4722 A.U. the velocity of the thermal sound waves in these liquids is calculated using the relation $\delta \nu =$ $2 \nu \cdot \dfrac{v}{c} \mu \sin \theta/2$, where ν is the frequency of the incident radiation, v and μ are the velocity of sound and the refractive index of the medium and c the velocity of light. These velocities are given in Table I along with the supersonic velocity, the temperature of observation, the viscosity and the refractive index of the liquid. The measurements for phenol are also given in the table.

TABLE I

Liquid	Temp. °C.	η in Poises	Refractive Index	Hypersonics			Ultrasonics		
				Intensity*	$\delta\nu$ in cm.$^{-1}$	Velocity m./sec.	Velocity m./sec.	Temp. °C.	Author
Glycerine ..	0	120·4	..	v.w.	..	≈2500	..	..	..
	26	9·54	1·473	w.	·51	2500	1957	28·5	Bhagavantam & Rao[1]
	42	..	1·469	med.	·50	2412	1926	40	do.
	110	..	1·456	st.	·39	1898	1840	70	do.
Castor oil ..	28	6·04	1·453	v.w.	·33	1626	1508	18	Zachoval[3]
Cyclohexanol ..	35	·203	1·465	st.	·29	1403	1442	35	Bhagavantam & Rao[1]
Ethylene glycol ..	30	·170	1·427	st.	·33	1670	1721	24	Parthasarathy[2]
Phenol ..	26	·09	1·564	v.w.	·346	1568	..	..	..
	42	·047	1·532	w.	·290	1343	..	..	..
	82	·016	1·501	med.	·265	1251	..	..	..

* v.w.= very weak, w.= weak, med.= medium intensity, st.= strong.

[1] Bhagavantam and Joga Rao, *Proc. Ind. Acad. Sci.*, A, 1939, **9**, 312.
[2] Parthasarathy, *ibid.*, 1935, **2**, 497.
[3] Zachoval, *Compt. Rend.*, 1939, **208**, 265.

4. Significance of the Results

The appearance of clear and well-defined Brillouin components arising from standing material waves in highly viscous liquids is very significant. According to the principles of classical hydrodynamics, plane sound waves propagated through a viscous liquid suffer a diminution of amplitude in the ratio of $\frac{1}{e}$ in traversing a number of wavelengths given by $\frac{3v\lambda}{8\pi^2\eta}$, where v is the velocity and λ the wavelength of sound, and η is the viscosity of the liquid (Lamb, *Hydrodynamics*). For 4722 A.U. radiations and at room temperature, this factor has been calculated for various liquids and entered in column six of Table II. It will be seen that except in the case of phenol, carbon tetrachloride and ether, the amplitude of the wave will be reduced to less than half its value before traversing one wavelength. In the case of glycerine and castor oil, this damping due to viscous forces is so great that we should expect that the waves would not have any physical existence. The corresponding Brillouin components should, therefore, be unobservable at room temperature. The appearance of these components thus signifies that the thermal sound waves are propagated as if the kinematic viscosity has little or no influence on them. The only effect of increased liquid viscosity is to decrease the intensity of the coherent modified scattering and enhance that of the central component. This is well illustrated by the temperature studies with phenol and glycerine.

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TABLE II
$$\lambda = 4722 \ \text{A.U.}$$

Liquid	Temp. °C.	Density	Viscosity C.G.S. Units	Sound Velocity $\times 10^{-2}$ cm./sec.	$\frac{1}{e}$	$\frac{4}{3}\pi\eta/\rho\lambda$ $\times 10^{-2}$	Half-breadth in cm.$^{-1}$
Glycerine ..	26	1·26	9·54	2500	·025	13430	..
Castor oil ..	28	·96	6·04	1626	·024	11160	..
Cyclohexanol ..	35	·962	·203	1403	·640	471	·046
Glycol ..	30	1·116	·170	1670	·90	270	·027
Phenol ..	26	1·072	·090	1568	1·6	149	·016
	42	1·058	·047	1343	2·6	79	·009
	82	1·025	·016	1251	7·0	28	·003
Carbon tetrachloride	25	1·595	·008	938	10·0	·9	·001
Ethyl ether ..	30	·7135	·002	943	38·0	·5	·0005

Another point of view regarding the spectral character of scattered light has been developed by Leontowitsch (1931) by applying the method of Fourier analysis to the kinetics of fluctuations in a liquid medium. From the expression for intensity given by him it follows that two displaced components of the Brillouin type would appear in the scattered light if $v > \frac{4}{3}\frac{\pi\eta}{\rho\lambda}$, where v and λ are the sound velocity and wavelength and η and ρ are viscosity and density of the liquid respectively. The half-breadth Δw of the components is given by $\frac{\Delta w}{w_1} = \frac{2}{3}\frac{\pi\eta}{\rho v\lambda}$, where w_1 is the frequency shift of the component. According to this theory, the displaced components would be sharper for liquids of lower viscosity and if the viscosity is so great that $v < \frac{4}{3}\frac{\pi\eta}{\rho\lambda}$, there will be no displaced components, but only a broadening of the central component. Leontowitsch himself has suggested that glycerine would provide a rigorous test of the theory. The values of $\frac{4}{3}\frac{\pi\eta}{\rho\lambda}$ as well as the half-breadth of the components are calculated for glycerine, castor oil, cyclohexanol, glycol, phenol, carbon tetrachloride and ethyl ether and given in Table II. It will be noticed that $v < \frac{4}{3}\frac{\pi\eta}{\rho\lambda}$ in the case of glycerine and castor oil and therefore the appearance of the Brillouin components and of a sharp undisplaced line in these liquids contradicts one of the main predictions of the theory. It will be seen also that the experimental observations, namely that the Brillouin components are broader for mobile liquids than for the viscous ones like glycol, cyclohexanol and phenol and that in the case of the latter, they become broader at higher temperatures are directly contrary to the conclusions indicated by the half-breadth values given in Table II.

We are thus obliged to reject the theory of light scattering put forward by Leontowitsch.

5. The Rigidity of Liquids

One of the striking facts of observation appearing from the present investigation is that the velocity of thermal sound waves in glycerine and castor oil at the room temperature calculated from the frequency shift of the Brillouin components is considerably higher than the ultrasonic velocity as determined for these liquids at the same temperature for longitudinal waves of frequency in the neighbourhood of 10^7 sec.$^{-1}$ generated by a piezo-electric oscillator. In the case of less viscous liquids included in Table I and several others which are dealt with in another paper appearing in these *Proceedings*, these two velocities are observed to be nearly equal. The unexpected appearance of the Brillouin components and the enhanced velocity of the thermal waves responsible for them together provide the clue for an understanding of the nature of the liquid state and liquid viscosity. According to Clerk Maxwell, the behaviour of amorphous bodies under the influence of a shearing strain is given by the equation

$\frac{ds}{dt} = \frac{1}{n}\frac{dF}{dt} + \frac{1}{\eta}$ F, where s is the shearing strain; F, the corresponding

stress; t, the time; n the rigidity modulus, and η the coefficient of viscosity.

If the deformation is constant, $\frac{ds}{dt} = 0$ and the solution of the above equation

gives $F = F_0\, e^{-\frac{t}{\tau}}$, where $\tau = \frac{\eta}{n}$ is the relaxation time, that is, the time at which

the stress decreases in the ratio $e:1$. In the case of periodic processes, when the period t of the external force is greater than τ, the relaxation time, the Maxwell's equation reduces to the well-known law of viscous flow for

liquids, *viz.*, $\frac{ds}{dt} = \frac{F}{\eta}$. If $t \ll \tau$ it reduces to the Hooke's law, $s_2 = \frac{F}{n}$;

in other words, for mechanical disturbances of sufficiently high frequency, the medium would behave practically as a rigid solid.

It is clear that if a liquid possesses the properties of a solid, the velocity of propagation of the elastic longitudinal waves would be given by

$v_{solid} = \sqrt{\frac{k + \frac{4}{3}n}{\rho}}$, instead of $v_{liquid} = \sqrt{\frac{k}{\rho}}$ for an ordinary liquid, where

k and ρ are the bulk modulus and the density of the medium respectively. From the fact that the velocity for ultrasonic waves of frequency of the order of 10^7 cycles per second is the same as that calculated from the adiabatic compressibility determined by static method for several liquids, we may conclude that the time of relaxation is less than 10^{-7} sec. and the fugitive

rigidity of the liquid does not enter into the expression for velocity. In the case of thermal waves, the modulation frequency is given by $2\mu \frac{v}{\lambda}$ for backward scattering, where μ is the refractive index of the medium and λ, the wavelength of the incident light. The frequency of these waves varies from 6×10^9 per second in CCl_4 to 10×10^9 in castor oil and $15 \cdot 6 \times 10^{10}$ in glycerine, the corresponding time-periods being $1 \cdot 7 \times 10^{-10}$, $1 \cdot 10^{-10}$ and $\cdot 64 \times 10^{-10}$ second respectively. Since in the case of mobile liquids, e.g., CCl_4, ether, etc., there is no increase in the sound velocity as we go from the ultrasonic to this *hypersonic* region, we have to assume that the time of relaxation is less than the time-period of the operative thermal waves. In glycerine at 26° C., the hypersonic velocity is nearly one-third as much more as the supersonic velocity and in castor oil also it is distinctly higher than the latter. This large increase in the velocity may be explained only by assuming that for very high frequencies, the rigidity of the liquid comes into play.

Taking the two expressions $v_{sol.} = \sqrt{\dfrac{k + \frac{4}{3} n}{\rho}}$ and $v_{liq.} = \sqrt{\dfrac{k}{\rho}}$ as giving the velocities of sound in the hypersonic and ultrasonic ranges of frequencies respectively, the bulk modulus and the rigidity modulus are calculated and given in Table III. The adiabatic compressibility, $\frac{1}{k}$, given by

TABLE III

Liquid	η in Poises	Ultra-sonic Velocity	Hyper-sonic Velocity	$k \times 10^{-10}$	$n \times 10^{-10}$
Glycerine	9·54	1957·	2500	4·83	2·28
Castor oil	6·04	1508	1626	2·18	·18

Liquid	τ Time of Relaxation	Time-Period of Hypersonic Waves	Calculated Adiabatic Compressibility	Adiabatic Compressibility (Observed)
Glycerine	$4 \cdot 2 \times 10^{-10}$	$\cdot 64 \times 10^{-10}$	$20 \cdot 7 \times 10^{-6}$	21×10^{-6}
Castor oil	33×10^{-10}	1×10^{-10}	$45 \cdot 9 \times 10^{-6}$	47×10^{-6}

the former agrees well with the directly observed value. The time of relaxation calculated from the viscosity and the rigidity, making use of the Maxwell's formula $\eta = n\tau$ is entered in column seven of the table, and the corresponding

time-period of the hypersonic waves in column eight. In both the liquids, the time of relaxation is much larger than the actual value of the time-period of the Debye waves in the medium. With rising temperature, the divergence between the 'hypersonic' and 'ultrasonic' velocities in glycerine diminishes (see Table I), as is to be expected from the rapidly falling viscosity and the consequent fall of the relaxation time. These observations thus provide for the first time an experimental proof of the thesis that for periodic processes of very high frequencies, a liquid behaves essentially as a solid.

The question now arises whether the solid state thus revealed is crystalline or amorphous in character. In the case of crystals, the entire light scattering exhibits itself as modified components as was shown by Raman and Venkateswaran (1938) in a Note to *Nature* on their observations with gypsum. On account of the extreme difficulty of obtaining crystals free from inclusions and imperfections and in view of the fact that the phenomenon is very weak in solids, it has not been possible to obtain successful results with other crystals. That crystals, in general, give well-defined Brillouin components which are very intense compared to the central component is also shown by the observations of Sibaiya (1938) with rochelle-salt, and Gross (1940) with quartz. In the case of liquids, however, with increase of viscosity, the displaced components tend to disappear while the central component progressively gains in intensity, the patterns being then very similar to those observed for glasses. The liquid state is thus more akin to a glass than to a crystal.

The above conclusions are also supported by the observations that the rotational wings on either side of the Rayleigh line appearing in the spectra of light scattered by liquids are very weak in highly viscous liquids. In Fig. 2, Plate XIV, the spectra of a series of seven liquids taken with a narrow slit and a high dispersion spectrograph are reproduced. It will be seen that in spite of the fact that ρ, the depolarisation of glycerine, is as high as $\cdot 33$, the 'wings' are almost completely absent as in the case of glasses, while they are a prominent feature of mobile liquids, *e.g.*, chloroform, toluene and benzene. In formic acid ($\rho = \cdot 53$) for which the viscosity lies between these two extremes, the wing possesses only a moderate intensity.

In conclusion, the author desires to place on record his heartfelt thanks to Prof. Sir C. V. Raman for his keen interest in the work.

Summary

In an interferometric study of light scattering by highly viscous liquids, sharp and well-defined Brillouin components have been recorded for glycerine and castor oil. The intensity of these components in glycerine shows a

progressive increase as the temperature is raised from 0° to 110° C., the central undisplaced component indicating a corresponding diminution in intensity. The Brillouin components appear with great intensity in cyclohexanol and glycol which are relatively less viscous. On the other hand, no displaced components are observed in glucose and in styrol and optical glasses. While the velocity of the thermal sound waves calculated from the Brillouin displacement agrees well with the supersonic velocity in cyclohexanol and glycol, it is considerably higher than the latter in glycerine and castor oil. The divergence between the 'hypersonic' and the 'ultrasonic' velocities diminishes as the temperature of glycerine is raised to 110° C. The appearance of well-defined Brillouin components in these highly viscous liquids indicates that the ordinary laws of hydrodynamics are not valid for the propagation of these high frequency waves in the medium. The results are also shown to be in contradiction to the predictions made by the theory of light scattering in liquids put forward by Leontowitsch. From the ultrasonic and hypersonic velocities in glycerine and castor oil, the bulk modulus, k, and the rigidity modulus, n, have been determined. The time of relaxation τ calculated using the Maxwell's formula $\eta = n\tau$ where η is the viscosity, is in both cases greater than the time-period of the thermal sound waves, thereby furnishing an experimental proof of the thesis that the liquid behaves essentially as an amorphous solid at sufficiently high frequencies. These conclusions are also supported by observations on the dependence of the intensity of the rotational 'wing' on the viscosity of the liquid.

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