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OF THE

INDIAN ASSOCIATION

FOR THE CULTIVATION OF SCIENCE.

Vol. VIII, Part II.

Conducted by
Prof. C. V. RAMAN, M.A., D.Sc.

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VII. Investigations on the Acoustics of the Pianoforte : I

BY

SUSHIL KRISHNA DATTA, M.Sc.,

Palit Research Scholar in the University of Calcutta.

(Received for publication on 1st May, 1923.)

1. Introduction.

In a paper published in the Proceedings of the Indian Association for the Cultivation of Science, Vol. VII, parts I and II, Mr. Panchanan Das has given an equation for the pressure exerted by the pianoforte hammer for the case when the hammer is rigid. He obtained the solution by the functional method of Kaufmann¹ considering the discontinuous changes in the pressure of the hammer due to the successive reflections of the impulse from the ends of the string. Prof. C. V. Raman and B. Banerji² obtained the solution of the same problem in a different manner by regarding the motion during impact as that of a loaded string. Mr. Das proceeded on a line similar to that given by Prof. Love³ for the longitudinal vibrations of a rod struck at the end.

The equation obtained by Mr. Das for the pressure exerted by the hammer is

$$F = 2\rho v_0 c \left[e^{-\frac{1}{2}ct} + e^{-\frac{1}{2}k(ct-2a)} \left\{ 1 - k(ct-2a) \right\} + e^{-\frac{1}{2}k(ct-4a)} \left\{ 1 - 2k(ct-4a) + \frac{k^2}{2!} (ct-4a)^2 \right\} \dots \right] \dots \quad (1)$$

¹ Ann. der Physik, Vol. 54 (1895).

² Proc. Roy. Soc. A, Vol. 97 (1920).

³ Love's "Theory of Elasticity," p. 411, Art. 281 (2nd Edn.)

where

ρ = the linear density of the string

m = the mass of the hammer

$h = 2\rho/m$

c = velocity of propagation of transverse wave on the string

v_0 = the initial velocity of the hammer

a = the distance of the striking point from the nearer end

t = variable time

He considered the total duration of contact of the hammer as divided up into a series of epochs determined by $0 < ct < 2a$, $2a < ct < 4a$, $4a < ct < 6a$ and so on, so that each of these epochs corresponds to the time taken by a pulse starting from the striking point in returning to the striking point after reflection from the nearer end.¹ Thus the pressures in the successive epochs are :—

$$\left. \begin{aligned} F_1 &= 2\rho v_0 c e^{-hct} \\ F_2 &= 2\rho v_0 c \left[e^{-hct} + e^{-h(ct-2a)} \left\{ 1 - h(ct-2a) \right\} \right] \\ F_3 &= 2\rho v_0 c \left[e^{-hct} + e^{-h(ct-2a)} \left\{ 1 - h(ct-2a) \right\} \right. \\ &\quad \left. + e^{-h(ct-4a)} \left\{ 1 - 2h(ct-4a) + \frac{h^2}{2!} (ct-4a)^2 \right\} \right] \end{aligned} \right\} (2)$$

It will thus be seen, that at the end of every epoch, the pressure increases by a sudden jump of magnitude $2\rho v_0 c$. Now we can determine the amplitudes of the different harmonics if we know the nature of the force acting on the string. For if F be the force acting on the string at a point distant a from one end, then using the notation adopted in Art. 130 of Lord Rayleigh's 'Theory of Sound,' Vol. 1, we find

¹ In his work Mr. Das considered reflection from the nearer end only, as the hammer leaves the string before the reflected pulse from the farther end reaches it—a supposition which is valid only for striking points near the ends.

that the amplitudes of the different harmonics are given by

$$\phi_n = \frac{2}{\pi c p} \sin \frac{\pi n a}{l} \int_0^l F \sin n(t-t') dt' \quad \dots (3)$$

where the integration is to be made over the whole duration of contact. Thus we can proceed to calculate the amplitudes of the different harmonics by substituting for F the value given by the equation. In the present paper it will be shown that the amplitudes of the different harmonics as calculated from the equation agree with those found experimentally.

2. *The calculation of the amplitudes of the different harmonics.*

In order to calculate the amplitudes of the different harmonics we have to integrate the pressure equation over the whole of the duration of contact of the hammer with the string. But as the actual integration of the equation involves considerable mathematical labour, a mechanical and graphical method was employed in the integration of equation (3) given above, which considerably simplified the calculation. The method followed is that given below.

The pressures at successive epochs given by equation (2) are plotted against time, thus giving the variation of pressure of the hammer with time throughout the whole of the duration of contact of the hammer—(the point where the curve cuts the axis of time gives the duration of contact). Now since the magnitude of the discontinuous change in the pressure exerted by the hammer is the same at the end of each epoch, the plotting of the pressure-time curve is much simplified by calculating the initial discontinuity and the pressures at the end of every epoch at which the pressure suffers a sudden discontinuous change, and joining the intermediate portions for which the pressure decreases continuously by a continuous

straight line. The error committed in this way is very small as the actual curve differs very little from a straight line. Thus, at the time $t=0$, the pressure suddenly increases to $2\rho v_0 c$, and then continuously decreases until the reflected pulse from the end arrives at the hammer which takes place at the time $ct=2a$, when the pressure again increases suddenly by the same amount, *viz.*, $2\rho v_0 c$. Just at the end of the first epoch, *i.e.*, at the time $ct=2a$, the pressure is $F_1 = 2\rho v_0 c e^{-kt}$ and then suddenly increases by an amount equal to $2\rho v_0 c$, and again falls off continuously until the second reflected pulse reaches it, which takes place at the end of the time $ct=4a$, when it again increases discontinuously by the same amount, and again falls off continuously until the third reflected pulse reaches it, and so on, till the impact ceases. Having obtained the pressure time curve between the time $t=0$ to the time when the curve cuts the axis of time, we proceed to calculate the value of the expression.

$$\phi_s = \frac{2}{\pi c \rho} \sin \frac{\pi a}{l} \int_0^t F \sin n(t-t') dt'$$

Now the expression inside the integral sign can be broken up into two expressions

$$\int_0^t F \sin n(t-t') dt' = \int_0^t F \sin nt \cos nt' dt' - \int_0^t F \cos nt \sin nt' dt'$$

and taking $\sin nt$ and $\cos nt$ outside the integral sign, the expression for ϕ_s becomes

$$\phi_s = \frac{2}{\pi c \rho} \sin \frac{\pi a}{l} \left[\sin nt \int_0^t F \cos nt' dt' - \cos nt \int_0^t F \sin nt' dt' \right] \dots \quad (4)$$

Thus to calculate the values of ϕ , we multiply each ordinate of the pressure-time graph by $\cos nt'$ and $\sin nt'$ respectively and obtain two new curves with these values as ordinates. The areas of these curves between the origin and the point where they cut the axis of time give the values of the two integrals in equation (4). The areas of these curves were measured by means of a planimeter and the amplitudes of the different harmonics were obtained by putting $s=1, 2, 3$, etc., respectively. In the numerical computation, those values of ρ, v_0, c and k were used which were afterwards employed in the experimental determination described below. The calculated values of the amplitudes up to the tenth harmonic are given in Tables I and II for two different striking points, *viz.*, $l/10$ and $l/9$.

3. *Experimental determination of the amplitudes of the different harmonics.*

An experimental verification of the above results was attempted in the following way. A steel wire 150 cm. long was stretched over the bridges fixed on the table. The linear density of the wire was .081 gm. per centimetre. A mechanical hammering arrangement was made by mounting a small solid brass cylinder at the end of a light pivoted shaft, which could be caused to impinge transversely on the wire. The effective mass of the hammer used was 20.5 grammes. The amplitudes of the different harmonics were measured by means of an observing microscope. For measuring the amplitude of the fundamental, the microscope was focussed on the middle of the string and the hammer was caused to strike at the points for which the calculations were made, *viz.*, $l/10$ and $l/9$ respectively. To measure the amplitude of the octave, the microscope was focussed at $l/4$, and the string was damped at the middle immediately after the impact so as to stop the fundamental. Similarly, for other harmonics the string was damped at the corresponding node immediately *after* impact,

and observed at an antinode. The different amplitudes as measured by the microscope were then corrected for the amplitudes of other harmonics for which the point of observation is also an antinode. Thus from the measured amplitude of the fundamental were subtracted those of the 3rd, 5th and so on; similarly for others. In the following tables are given the observed values of the amplitudes of the different harmonics along with those calculated from the equation for two different striking points, *viz.*, $l/10$ and $l/9$. The measurements were made up to the tenth harmonic for both the striking points.

TABLE I.

Striking point at $l/10$.

Harmonics	Observed amplitudes.	Calculated amplitudes.
Fundamental	·3700 cm.	·3975 cm.
Octave	·0588 "	·0593 "
Third	·0433 "	·0433 "
Fourth	·0130 "	·0131 "
Fifth	·0078 "	·0079 "
Sixth	·0100 "	·0147 "
Seventh	·0020 "	·0022 "
Eighth	·0157 "	·0173 "
Ninth	·00112 "	·00128 "
Tenth	·0 "	·0 "

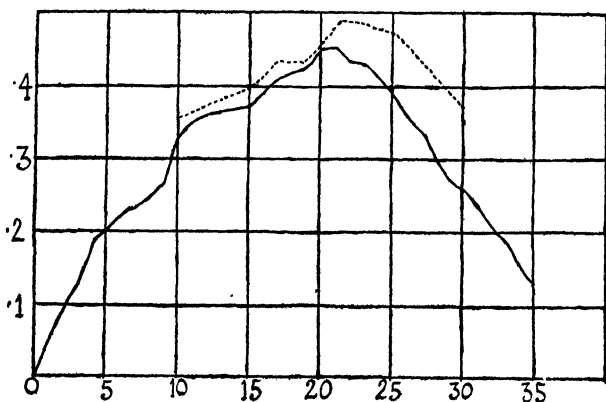
TABLE II.
Striking point 1/9.

Harmonics.			Observed amplitudes.	Calculated amplitudes.
Fundamental	·4240 cm.	·4322 cm.
Octave	·0345 „	·0365 „
Third	·0167 „	·0173 „
Fourth	·0217 „	·0240 „
Fifth	·0046 „	·0043 „
Sixth	·0029 „	·0027 „
Seventh	·0071 „	·0068 „
Eighth	·0020 „	·0023 „
Ninth	0 „	0 „
Tenth	·0022 „	·0025 „

4. *Variation of the amplitudes of the different harmonics with the striking point.*

In order to test the equation more fully, the amplitudes of the fundamental were determined for different striking points along the string both from the equation as well as experimentally. Theoretical calculations were made for seven different striking points along the string, *viz.*, $1/15$, $1/10$, $1/9$, $1/8$, $1/7$, $1/6$ and $1/5$. Beyond the point $1/5$ the equation does not hold good, as the reflected pulses from the other end arrive at the hammer before it leaves the string, of which no account is taken in Mr. Das's equation. Experimental determination was made up to the point $1/5$ of the string at an interval of 1 cm. The result is shown graphically in Fig. 1.

Fig. I



The dotted curve gives the theoretical results whilst the continuous curve represents the experimental values. In Figs. II and III are given the curves showing the amplitudes of the octave and the third harmonic for different striking points along the string up to the middle point obtained experimentally. The ordinates are the amplitudes, and the abscissæ are the distances of the striking point from the end.

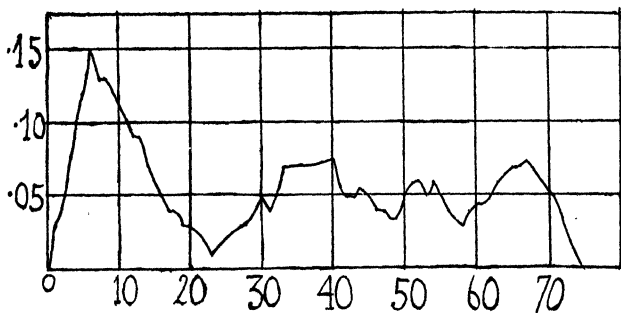


Fig. II

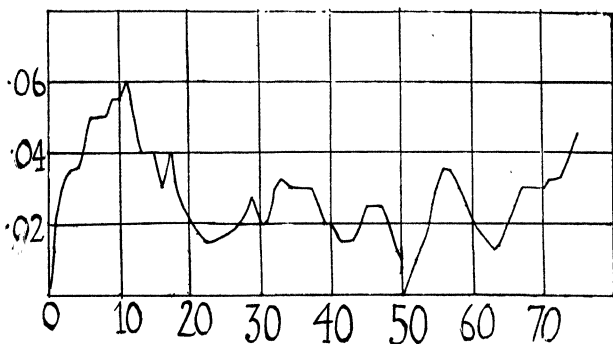


Fig. III

5. Conclusion.

The very close agreement between the observed and the calculated values as seen from the above tables is a very good confirmation of the equation. It is also seen from the above tables that the observed amplitudes are always less than the calculated ones, a fact which follows from theoretical considerations. For, some amount of dissipation of energy takes place in the system of which no account is taken in Mr. Das's theory. Moreover some allowance must be made for the fact that a certain time elapses, however small that may be, between the striking of the hammer and the measurement by the microscope, the effect of which is to lower the observed values.

It is seen from the curve showing the variation of amplitudes of the fundamental with striking point, that near about the point $l/7$ the amplitude of the fundamental is a maximum. Now in an actual pianoforte the choice of striking point is generally made at about the same point, *viz.* $l/7$. This may be due to the fact that the amplitude is a maximum at this point. The reason for this fact is that beyond this point the $\sin nt'$ and $\cos nt'$ terms in the integrals

change sign and so a part of the curve comes on the negative side of the time axis. At this point the value of the duration of contact becomes nearly $\frac{3}{4}$ th of the period of the string. The position of the striking point for which the amplitude of the fundamental is a maximum also depends on the mass of the hammer. As the weight of the hammer increases the point of maximum is shifted towards the end.

The rapid recovery of the amplitude of a harmonic as the striking point is moved away from one of its nodes is markedly shown in the results of the investigation.

The calculations have been made up to the point $l/5$, for beyond this we have to take into account the reflections from both ends which I hope to do in a later paper.

Further investigations as to the duration of contact and the effect of elasticity of the hammer are now in progress and will be given in a later paper.

The investigation here described was carried out in the Palit Laboratory at the University College of Science at the suggestion of Prof. C. V. Raman, Palit Professor of Physics, and the author is indebted to him for the unfailing interest he has taken during the progress of the work.

UNIVERSITY COLLEGE OF SCIENCE,
DEPARTMENT OF PHYSICS,
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1st May, 1923.

VIII. On the Temperature Variation of the Electrical Conductivity of Copper and Iron fused with Mica.

BY

K. R. RAMANATHAN, M.A.,

Assistant Lecturer in Physics, University College, Rangoon.

Three years ago, there was published in the Philosophical Magazine¹ a paper by A. L. Williams and Miss Mackey containing the results of some experiments on the electrical conductivity of mixtures of copper and iron with mica. The most remarkable feature about them was the very large variation of conductivity with temperature.

In Part B of the above paper are given the resistances of two samples each of copper-mica and iron-mica mixtures as measured by Miss Mackey. In all these, I find that the variation of resistance with temperature is expressed over the whole range of the experiment with a fair degree of accuracy by means of either of the formulæ

$$R = PT^{-1} e^{Q/T} \quad \dots (1)$$

or

$$R = P_1 T^{-1/2} e^{Q_1/T} \quad \dots (2)$$

where R = resistance of the sample

T = temperature measured on the absolute centigrade scale and P, Q, P₁, Q₁, are constants.

¹ Phil. Mag., Vol. XL, 1920, p. 281.

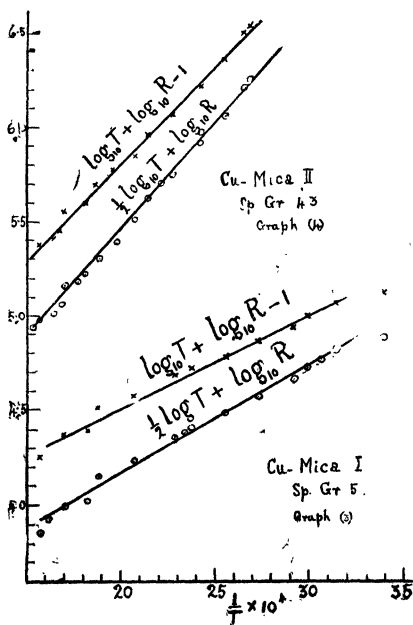
Taking logarithms,

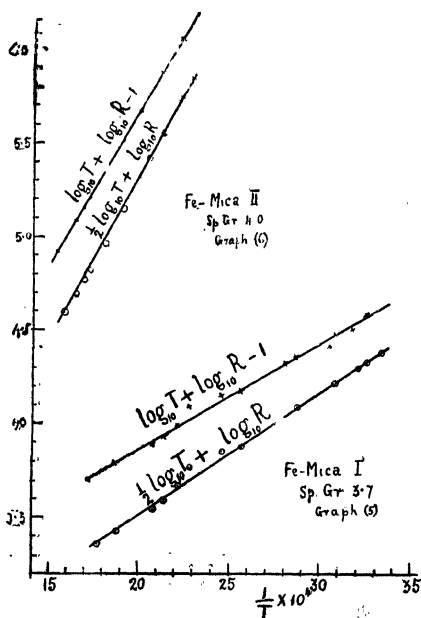
$$\log_{10} R + \log_{10} T = \log_{10} P + \frac{Q}{2 \cdot 303T}$$

and

$$\log_{10} R + \frac{1}{2} \log_{10} T = \log_{10} P_1 + \frac{Q_1}{2 \cdot 303T}$$

The quantities $\log_{10} R + \log_{10} T$ and $\log_{10} R + \frac{1}{2} \log_{10} T$ are plotted against T^{-1} in graphs 3 to 6, and the graphs are straight lines.





(The graphs have been given the same numbers as in Miss Mackey's paper.)

Since the samples used were irregular, their specific resistances could not be determined and there is no significance in calculating the values of P and P_1 . In the following table are given the values of Q and Q_1 for the different specimens :

Specimens.	sp. gr.	Q	Q_1
Cu-mica I	5.1	1.27×10^3	1.13×10^3
Cu-mica II	4.3	2.68×10^3	2.36×10^3
Fe-mica I	3.7	1.50×10^3	1.30×10^3
Fe-mica II	4.0	4.01×10^3	3.78×10^3

It will be noted that Q and Q_1 show a decrease with increasing metal content in Cu-mica and an increase with increasing metal content in Fe-mica.

Theoretical.

The expression $R = PT^{-1} e^{Q/T}$ can be put into the form $\sigma = P^{-1} T e^{-Q/T}$ where σ is the conductivity of the sample. This is of the same form as the expression for the variation of the number of thermions in equilibrium with a metal in a vacuum enclosure

$$n = A T^\lambda e^{-b/T} \quad \dots (1)$$

where λ is a constant which may be given any value between 0 and $\frac{1}{2}$ without appreciable difference (O. W. Richardson: Emission of Electricity from Hot Bodies, Chap. III). Assuming the concentration of free electrons in the mixture to vary in a similar manner with temperature, we can calculate the variation of conductivity with temperature. On the electron theory of metallic conduction,

$$\sigma \propto \frac{n e^2 l v}{T}$$

where

n = number of free electrons per unit volume

v = root-mean square of the velocity of electrons

l = mean free path of the electron

and

e = electronic charge

Since

$$v \propto T^{1/2}$$

$$\sigma \propto n e^2 l / T^{3/2}$$

If we assume that l is independent of temperature, and n varies with temperature according to equation (3)

$$\sigma \propto T^{\lambda - \frac{1}{2}} e^{-b/T}$$

If $\lambda = 3/2$

$$\sigma \propto T e^{-b/T}$$

and if $\lambda = 1$.

$$\sigma \propto T^{\frac{1}{2}} e^{-b/T}$$

Since writing the above note, there has appeared in the Journal of the Franklin Institute a paper on the "Resistivity of vitreous materials" by L. L. Holladay where the author has put forward the same type of formula to explain the variation of the resistivity of a number of specimens of glass with temperature. It is of interest to compare the values of Q for the glasses and the metal-mica mixtures. The values calculated by Holladay for the glasses range for different specimens from 9.37×10^3 to 1.30×10^4 and are thus of the same order of quantities as those calculated for the metal-mica mixtures.

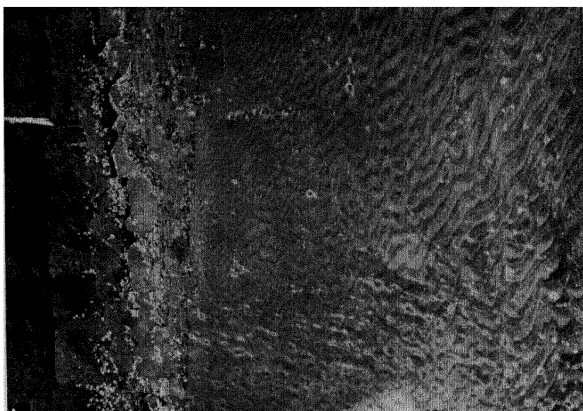


Fig. II

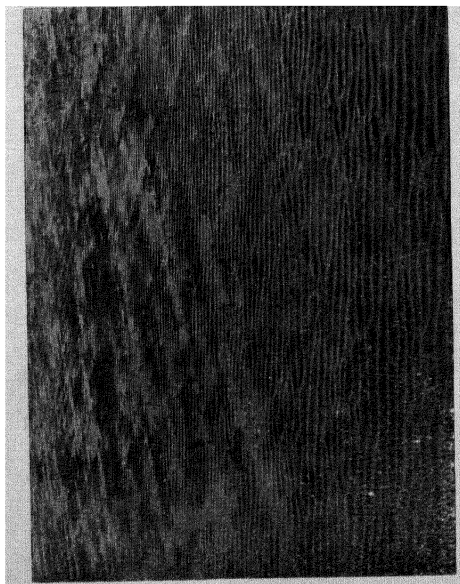


Fig. I

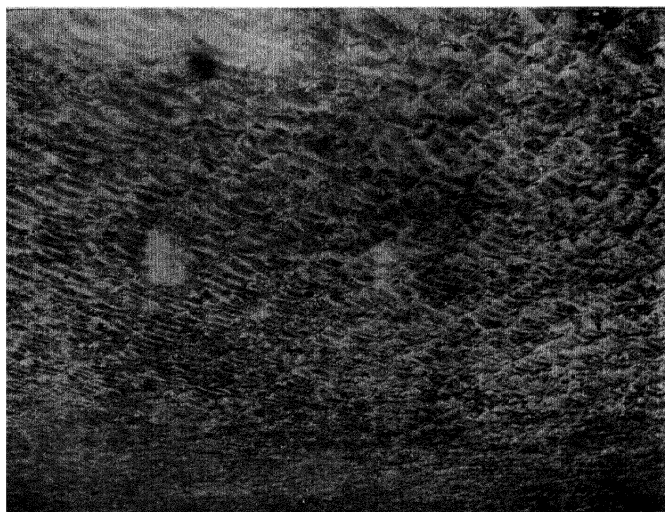
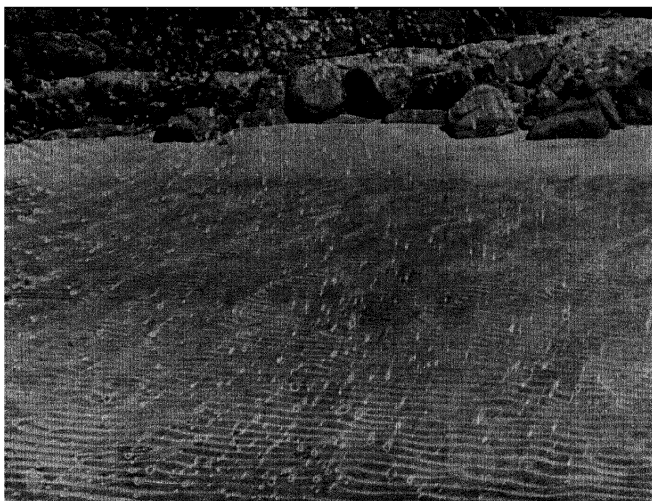


Fig. II

IX. Effect of Barriers on Ripple-Mark

By

S. K. BANERJI, D.Sc.,

Director, Bombay and Alibag Observatories.

[Plates III and IV.]

I had on many previous occasions examined theoretically the effect of various types of barriers on a set of plane waves. But little did I expect then to see the effects of barriers on wave motion manifested on such a magnificent scale as I have recently done during my stay at Alibag. The sea beach in front of the magnetic observatory at Alibag has a very little slope hardly more than 7° . The sand is of such a fine quality that it easily catches impressions of waves. The impressions are in the forms of ridges and hollows all regularly arranged parallel to the wave-fronts. They are formed during high tides and are left behind when the sea retires.

In front of the beach at Alibag there is an old fort which acts as a barrier to the advancing sea-waves during high tides. The effective length of the fort acting as a barrier is



nearly 300 yards and during high tide an equivalent length behind the fort is covered with water, this length of course varying according to the day of the lunar month and the order of the tide. But when the sea retires, nothing but a set of impressions of the waves is left behind the fort on the fine sand with perhaps a small quantity of water here and there clogged in the hollows between the ridges.

A certain minimum head of water appears to be necessary in order that the sand may catch impressions of waves. As a consequence of this a certain portion of the beach measured from the highest point wetted by the water remains almost a plane without any impression. But beyond this the whole of the beach exposed during ebb-tide (and it is quite possible that a portion of the beach still beneath water) is marked by a conspicuous set of ridges and hollows. In the open beach these arrange themselves parallel to the wave front in a perfectly regular manner. A photograph of the impressions on the open beach is given in Fig. I, Pl. III.

The effect of the barrier on the waves is however the most interesting. The sets of parallel ridges on the open beach curve round as we come behind the barrier, and as we approach it they become deformed and curly in appearance and meet the edge of the barrier inclined at definite angles to it. This edge-effect is shown in Fig. II, Pl. III. In the central region just behind the barrier, the ridges again arrange themselves in a regular manner parallel to the barrier. The wave systems in this region approach the barrier almost normally to it and are reflected as such. This is clearly shown in Fig. I, Pl. IV. As we move from the barrier towards the shore, the ridges gradually lose their regularity and a well-defined region of very complex impressions is easily recognised. These complex impressions appear to be produced by the meeting of the succession of waves coming from either side. A sample of the complex impressions is shown in Fig. II, Pl. IV.

It should be remembered that a set of tidal waves approaching a sloping beach usually breaks and moves forward as a 'rolling' wave. If we conceive of a set of waves approaching a sloping beach in succession, then we can easily picture to ourselves that by the time the second wave arrives, the first will have gone up the beach to the maximum extent and begun to retrace its steps and met the second half-way, giving a backward push to the lower portion of this wave, while the crest will still maintain its forward velocity. In consequence, it will break and appear to move as a rolling wave. It is not usually the second wave that breaks, but breaking may take place at a much earlier stage on account of the continuous downward flow of water during the return journey maintained by the succession of advancing waves. Owing to this complexity no mathematical form can be assumed for these waves. But if the slope of the beach is neglected and the advancing waves be assumed to have their elevation varying as simple harmonic function of the time the general features of the sand impressions formed behind the barrier at Alibag are easily explained from theoretical considerations.

A rough drawing of the impressions formed on the sand has been made after a careful examination of them as they were actually found. This is reproduced above in the text.

X. The Diffraction of X-rays in Liquids, Liquid Mixtures, Solutions, Fluid Crystals and Amorphous Solids.

BY

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AND

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Assistant Lecturer in Physics, University College, Rangoon.¹

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6. Calculation of the intensity of X-ray scattering.
7. Comparison with observations.
8. Liquid crystals.
9. Amorphous solids.
10. Summary and conclusion.

1. Introduction.

When a narrow pencil of homogeneous X-rays passes through a thin layer of liquid and is received on a photographic plate, it is found that with a sufficient exposure, besides the central spot given by the undeviated pencil, there appears on the plate also a circular diffraction halo surrounding the

¹ A preliminary note in which the theory developed in this paper was indicated appeared in "Nature," Feb. 10, 1923, p. 185.

centre and separated from it by a relatively clear space. This somewhat surprising observation was made by Debye and Scherrer¹ in the course of their work on X-ray diffraction. The same result has also been obtained in some recent X-ray studies by Hewlett² in which the ionization method was employed. Keesom and Smedt³ have also studied the phenomenon in the case of several liquids by the photographic method and find that in some cases there is a weak second halo outside the first and even the suspicion of a third.

The behaviour in this respect of the special class of substances known as liquid crystals and studied by Lehmann and others is obviously of much interest. At the suggestion of Prof. Debye, observations were made by Hückel⁴ with several of these substances, particularly with p-azoxyanisol and cholesteryl-propionate which were studied in (1) the solid crystalline, (2) the liquid crystalline, and (3) the liquid isotropic conditions. In the solid crystalline state, several sharp rings similar to those of other crystal powders were obtained, but remarkably enough, there was no notable difference shown by the photographs obtained with the isotropic and crystalline liquid states. In both cases a single diffraction halo appeared as in the case of ordinary liquids. It may also be mentioned that observations by Freidrich⁵ on the scattering of X-rays by wax and other amorphous solids and by Jauncey⁶ on the scattering by glass similarly show a maximum at a considerable angular distance from the undeviated pencil. It thus appears that in the three cases of an isotropic liquid, of a liquid crystal, and of an amorphous solid, we have essentially similar phenomena exhibited.

¹ Nachrichten Gottingen, 1916.

² C. W. Hewlett: Physical Review, XX, 1922, p. 688.

³ Keesom and Smedt: Proc. Roy. Soc. Amsterdam, XXV, 1922, p. 118, and XXVI, 1923, p. 112.

⁴ Hückel, Phys. Zeit, 1921, p. 561.

⁵ Freidrich: Phys. Zeit. 14, 1913, p. 317.

⁶ Jauncey: Phys. Review, XX, 1922, p. 405.

From the survey of the literature, it would appear that no satisfactory explanation of the appearance of the diffraction halo in these cases has so far been put forward. One view that has been suggested¹ is that the halo might be a diffraction-effect arising from the finite size of the molecule or the co-operation of the different atoms in it. This suggestion however must be negatived in view of Keesom and Smedt's observation that a liquid like argon which presumably has monatomic molecules shows the phenomenon in much the same degree as substances with more complex molecules. Another view that has been put forward by Hewlett² is that ordinary liquids possess something resembling crystal structure. The idea that in a liquid there are large groups of regularly arranged atoms is also put forward by A. H. Compton³ in his recent report on X-ray scattering, when referring to observations by Hewlett and Duane. These hypotheses by Hewlett and Compton appear to us to be somewhat artificial; they have obviously been introduced in order to explain the observed effects, but lack independent justification. Keesom and Smedt have attempted to interpret their results as due to the interference of the effects of two neighbouring molecules, using for this purpose a formula proposed by Ehrenfest. Their theory, however, appears to us inadequate. The essential features of the phenomenon are the region of the relatively very small intensity of scattering surrounding the central spot, and beyond this a moderately sharp diffraction-halo, having a much greater intensity than the scattering at large angles. Neither of these features is indicated by Ehrenfest's formula. To make the point clear we give below in Fig. 1C the curve of intensity for benzene reproduced from Hewlett's paper, and in Fig. 1A for comparison with it a graph of the intensity calculated from Ehrenfest's formula. It will be seen that

¹ Debye : referred to by Hückel.

² *Loc. cit.*

³ Bulletin, National Research Council, U. S. A., No. 20, p. 14.

there is little in common between them. Finally we should mention an attempt which has been made by L. Brillouin¹ to explain the phenomena of X-ray diffraction in liquids and amorphous solids on the basis of the quantum theory of specific heats. We give in Fig. 1B a graph of the intensity in different directions drawn from his final formula. It will be seen that it bears no resemblance whatever to the observed result given in Fig. 1C.

We propose in this paper to approach the problem from an entirely different standpoint. In a series of publications² that have appeared in the course of the last two years, the authors and their co-workers have discussed the optical problem of the scattering of light in liquids under various conditions and shown that the experimental evidence amply confirms the

¹ *Annales de Physique*, Jan-Feb. 1922, pp. 88-122.

² 1. Notes by C. V. Raman in *Nature*, November 10, 1921, and several subsequent issues.

2. "Molecular Diffraction of Light" by C. V. Raman, Calcutta University Press, February, 1922.

3. "The Molecular Scattering of Light in Water and the Colour of the Sea" by C. V. Raman, *Proc. Roy. Soc.*, April 1922, pp. 64-80.

4. "The Molecular Scattering of Light in Vapours and in Liquids and its Relation to the Opalescence observed in the Critical State" by K. R. Ramanathan, *Proc. Roy. Soc.*, Vol. 102, 1922, pp. 151-161.

5. "The Molecular Scattering of Light in N-pentane" by R. Venkateswaran, *Trans Chem. Soc.*, Vol. 121, 1922, p. 2655.

6. "The Molecular Scattering of Light in Liquid Mixtures" by C. V. Raman and K. R. Ramanathan, *Phil. Mag.*, Jan. 1923, pp. 213-224.

7. "The Molecular Scattering and Extinction of Light in Liquids and the Determination of the Avogadro Constant" by C. V. Raman and K. S. Rao, *Phil. Mag.*, March 1922, pp. 635-640.

8. "Electromagnetic Theory of Scattering of Light in Fluids" by K. R. Ramanathan, *Proc. Ind. Assn. for the Cultivation of Science*, Vol. VIII, Part I, pp. 1-22.

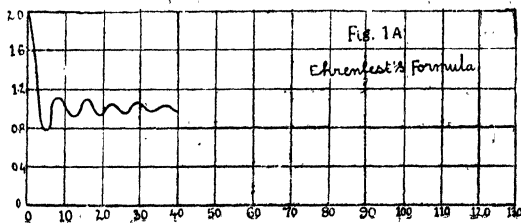
9. "The Visual and Photographic Albedo of the Earth," by K. R. Ramanathan, *Astrophysical Journal*, April, 1923.

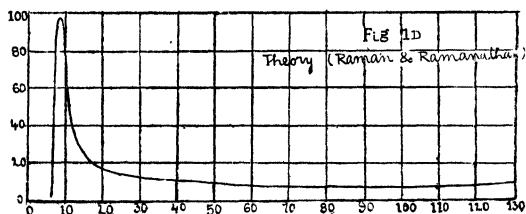
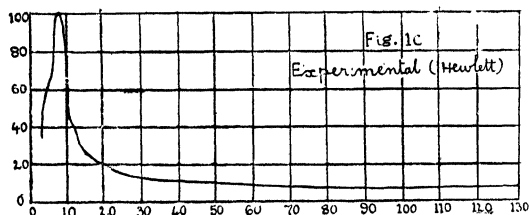
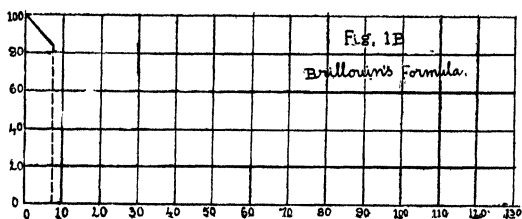
10. "The Molecular Scattering of Light in Benzene Liquid and Vapour" by K. R. Ramanathan, appearing in the *Physical Review*, 1923.

11. "The Molecular Scattering of Light in Liquid Mixtures" by J. C. Kameswarar, appearing in the *Physical Review*, 1923.

And other forthcoming papers.

statistical-thermodynamical theory of light-scattering developed by Smoluchowski and Einstein. The essential idea of the Einstein-Smoluchowski method is to treat a fluid as a continuous substance subject to local changes of density determined by thermodynamical considerations. Leaving out of account the effects due to the anisotropy of the molecules, the theory leads in the optical case to precisely the same results as those given by a more explicitly molecular treatment. This is due to the circumstance that the length of light waves is vastly greater than the scale of molecular dimensions, and hence the assumption involved in treating the substance as a structureless continuum does not lead to any appreciable error. The case is different however when we deal with the problem of diffraction of X-rays. The wave-length here is less than the average distance apart of the molecules, and in applying the statistical-thermodynamical considerations developed by Smoluchowski and Einstein, we have explicitly to take into account the fact that the medium is not continuous, but consists of a finite number of discrete particles. When this is done, the experimental results are explained quantitatively in a satisfactory manner. Fig. 1D gives the graph of intensity calculated from the formula we have developed in this paper. When account is taken of the imperfect homogeneity of the X-rays used by Hewlett, it will be seen that his experimental curve reproduces with remarkable fidelity the indications of theory.

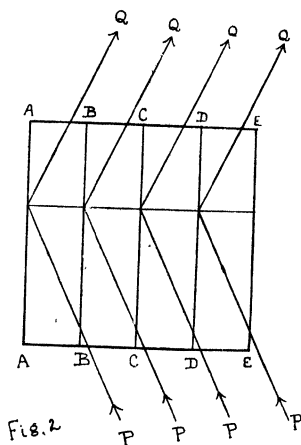




2. Comparison with the optical scattering problem.

In order more clearly to appreciate the relations between the optical and X-ray problems, it is desirable here to give a brief outline of the theory of the former case. In Fig. 2, let ABCDE represent a unit volume of fluid (supposed of refractive index only slightly differing from unity) on which a parallel pencil of light is incident. Let n be the total number of molecules in it and let PPPP represent the in-falling rays and QQQQ the scattered rays in the particular direction under consideration. The volume ABCDE

may be divided into a very large number of slices by a series of equidistant planes perpendicular to the plane of the paper and equally inclined to the incident and scattered rays. It is assumed that each slice is thick enough to be several molecules deep and yet very thin compared with the wave length of the incident light. It is obvious that with these assumptions the scattered waves arising from the molecules in each slice may be taken to be all in identical phases. Let, A, B, C, D, etc. be successive



planes which are situated at such intervals that the path differences of the scattered rays arising from layers adjacent to them differ by one wave-length. Each of the slabs AB, BC, etc., thus contains a considerable number, say r of the thin slices into which the medium was supposed to be divided. Then $AB = BC = CD = DE = \lambda/2 \sin \frac{1}{2} \theta$ where θ is the angle of scattering and λ is the wave-length of the incident radiation. Since the effects of all the molecules in a given slice, say the p th, of any one slab are taken to be in the same phase, they also agree in phase with those from the p th slice of every

other slab. The amplitudes of the scattered waves arising from all the molecules lying in the p^{th} slices of all the slabs may then be added up; and their resultant amplitude is proportional to the total number of molecules contained in the slices thus added together; denote this by n_p . The whole scattering may then be found by summing up the effects proportional to $n_1, n_2, \dots, n_p, \dots, n_r$, due regard being had to their respective phases, which are distributed at regular intervals from 0 to 2π . If $n_1 = n_2 = \dots = n_p = \dots = n_r$, the effects of the different slices would completely extinguish each other by interference. This corresponds to the case of a completely homogeneous medium, that is, a crystal at the absolute zero of temperature for waves of length great compared with its grating constant. In every other case, n_1, n_2 etc. would show fluctuations in value, and part of the incident energy would appear as scattered or internally reflected radiation. We know that $n_1 + n_2 + \dots + n_p + \dots = n$ and hence, denoting $n_1 - n/r = \Delta n_1, n_2 - n/r = \Delta n_2$ so on, the resulting effect would simply arise from the quantities $\Delta n_1, \Delta n_2$ etc. which represent the fluctuations from the mean density, the part due to the mean density itself disappearing by interference.

We can now consider the magnitude of the fluctuations $\Delta n_1, \Delta n_2$, etc. in different cases. We take first the case of an ideal gas which has been discussed by H. A. Lorentz.¹ Here the distribution of the molecules is a purely random one, and the average expectation of magnitude of the fluctuations $\Delta n_1, \Delta n_2$, etc. can be very simply shewn from probability considerations to be $\sqrt{n/r}$. If further, we make the assumption which is *a priori* justifiable in the case of an ideal gas—that the quantities $\Delta n_1, \Delta n_2$, etc. are as often positive as negative and vary quite independently of each other, then to find their aggregate effect, we add up *not* their amplitudes in their respective phases, but their intensities without regard to phase.

¹ Proc. Roy. Soc. Amsterdam, Vol. 13, 1910, p. 92.

The total scattering will thus be proportional to $r(\sqrt{n/r})$, or simply n , that is, to the total number of molecules in the fluid per unit of volume. This is the well-known Rayleigh law of scattering.

We next consider the case of a gas not obeying Boyle's law in which the distribution of molecules is no longer a random one. Here, applying Boltzmann's principle of entropy-probability, we find the mean value of Δn_1 to be, $n \sqrt{R\beta T/Nr}$ where R and N are respectively the gas constant and Avogadro constant for a gram-molecule, T is the absolute temperature and β is the isothermal compressibility of the fluid. Assuming as in the case of an ideal gas that $\Delta n_1, \Delta n_2$, may be as often positive as negative, and that their values are quite independent of each other, we get the total scattering by squaring and adding their intensities. The net result is thus proportional to

$$n^2 RT\beta/N \quad \dots (1)$$

and is thus proportional to the compressibility and to the absolute temperature and to the *square* of the density. For a gas obeying Boyle's law, β is the reciprocal of the pressure and it is easily seen that the expression reduces to n , which is the Rayleigh law of scattering.

For a liquid or very dense vapour of which the refractive index is sensibly greater than unity, the discussion proceeds on exactly the same lines as above, except that the local electromagnetic field due to the molecules themselves cannot be neglected in comparison with the field due to the incident wave and must be taken into account as in Lorentz's theory of dispersion. This increases the intensity of the scattered light without affecting its state of polarisation as shown in the paper (8) by Ramanathan quoted above. The scattering due to a unit volume is now proportional to

$$\left(\frac{\mu^2 + 2}{3}\right)^2 n^2 RT\beta/N \quad \dots (2)$$

where μ is the refractive index of the fluid. When μ is sufficiently nearly equal to unity, (2) reduces to (1).

3. X-ray scattering at very small angles with the primary beam.

It will be seen that the simple treatment given above depends essentially on the possibility of dividing up the medium into slabs of thickness $\lambda/2\sin\frac{1}{2}\theta$ which can be further subdivided into several slices, each of which is many molecules thick, so that the fluctuations of density in any slice can be assumed to be independent of those in neighbouring ones. This, in general, is obviously possible only when λ is large, which is true in the optical case. When λ is comparable with molecular dimensions, and θ has any moderate value, each slab of thickness $\lambda/2\sin\frac{1}{2}\theta$ would be only a few molecules thick, and it would no longer be possible to assume that when it is sub-divided into thinner slices, the fluctuations in the different slices are uncorrelated, *i.e.*, independent of each other. In fact, it is easy to see that when the volume of the liquid is divided into very thin slices each only a molecule or so in thickness, any excess of density in one slice necessarily involves a deficiency in the adjoining slices and *vice-versâ*. The simple summation of the intensities of the scattered waves due to the density-fluctuations in the different slices, thus ceases to be admissible.

In one case, however, the Einstein-Smoluchowski theory may be applied as it stands to the problem of X-ray scattering. This is when the angle of scattering θ is very small. The thickness $\lambda/2\sin\frac{1}{2}\theta$ of the slabs AB, BC, CD, is then appreciable and may be made as large as we please by sufficiently decreasing θ . For instance if $\lambda = 0.71$ A. U., and $\theta = 10'$ of arc, $\lambda/2\sin\frac{1}{2}\theta = 239$ A. U. and each of the slabs AB, BC, etc., would, if we take the case of benzene liquid, be about 50 molecules thick. This thickness should be ample to enable the Einstein-

Smoluchowski theory to be applied. The isothermal compressibility β being 90×10^{-12} dynes per cm^2 for benzene, it is easily shown by calculation that the scattering given by formula (1) is $1/40$ times smaller than in proportion to the number of molecules per unit volume. The scattering of X-rays at these small angles by liquids is thus almost negligible. Even for an angle of scattering of 2 degrees, a layer $\lambda/2\sin\frac{1}{2}\theta$ thick would be about 5 molecules deep, and though the Einstein-Smoluchowski theory would not be strictly valid, it could still be applied as a rough approximation, and the result indicated, *viz.*, that the scattering is very small would hold good.

It is thus seen to be a simple consequence of thermodynamics that in respect of scattering of X-rays through small angles, ordinary liquids stand in a position not very dissimilar to that of a complete crystal or of a crystal powder. The principal point of difference is that, in crystals, the compressibility is even smaller than in liquids and the scattering at small angles is therefore practically evanescent.

4. *Explanation of the X-ray diffraction-halo of liquids.*

As the angle of scattering θ is gradually increased, a stage is arrived at when the slab $\lambda/2\sin\frac{1}{2}\theta$ is only one or two molecules thick, and it is clear that the thermodynamical theory based on the idea that the fluid is a structureless continuum must then be modified. The essentially new feature that must be taken into account is that the fluctuations of density in neighbouring slices are no longer uncorrelated. Without going very deeply into the mathematical theory, it is easy to understand in a general way the nature of the results to be expected. For simplicity, we shall consider the case of a liquid which has only a very small compressibility, and in which consequently the thermal fluctuations of density are very small; this means again that the molecules tend to be distributed in space in a manner approaching uniformity.

and not chaotically as in a gas. If, as before, there be n molecules per unit of volume, it is convenient to regard as the mean molecular distance a length λ_0 given by the formula

$$\lambda_0 = kn^{-1/3}$$

where k is a number of the order of magnitude of unity; regarding the exact value of k , we shall have more to say hereafter. Further, let the angle of scattering θ be such that $\lambda = 2\lambda_0 \sin \frac{1}{2}\theta$. Then each of the slabs AB, BC, etc., would on the average be just one molecule thick. It is obvious that in such a case, as has already been remarked, the supposition that when each slab is further subdivided into a number of slices, the effects of the molecules contained in the different slices would practically cut each other out by interference, would be entirely wide of the mark. In the first place, the number of the molecules in the different slices, would show fluctuations of *relatively* considerable magnitude. Further, instead of these fluctuations of density being entirely uncorrelated, they would be almost completely correlated in the direction of amplifying the total observed effect. For assuming that out of the r slices into which the slab AB is divided, the middle slice contains at any instant an excess number of molecules, the chance that at the same instant the slices near the face A or B contain a corresponding deficiency in molecules is very large. Since the scattered waves due to molecules in the middle and the outer faces of the slab differ in path by $\lambda/2$, the effects due to the excess in one slice and the deficiency in the others, would have *identical* phases, and their amplitudes would thus add up. Thus a very large scattering may be expected in the direction referred to, in fact many times greater than if the different molecules were regarded as scattering centres in random distribution of phase.

Theory thus leads us to expect a very large scattering in the direction θ where $\lambda = 2\lambda_0 \sin \frac{1}{2}\theta$, λ_0 being the mean molecular distance. Since as we have seen, the scattering is almost

nothing at small angles, it follows it should increase rather abruptly as θ increases and approaches the value $2 \sin^{-1} \lambda/2\lambda_0$. On the other hand, when θ reaches and passes this special value, we should expect a fall of intensity which is somewhat less rapid. For, as the angle of scattering is increased, the quantity $2\lambda_0 \sin \frac{1}{2}\theta$ becomes greater than λ , and hence the fluctuations of density in the different slices begin to neutralise each other's effects by interference, but not perfectly, owing to the want of correlation. At large angles, a considerable effect would be left over as the result of this incomplete correlation, and this may be expected to be still much greater than the Einstein scattering obtained in directions nearly parallel to the primary beam.

The theory thus clearly indicates that the diffraction-halo should be fairly sharp at its inner edge, and rather diffuse at its outer margin. These features are well shown in Hewlett's ionisation curves and Huckel's photographs already cited.

5. Analysis of molecular positions in a liquid and in mixtures and solutions.

In order to present the theory of the X-ray diffraction-halo exhibited by liquids as outlined above in a more complete mathematical form, we have to see how the theory of density-fluctuations which is based on the idea that a fluid may be regarded as a continuum should be modified so as to take into account its actual coarse-grained structure. From general thermodynamical considerations, it is clear that the distribution of the molecules in any small volume of liquid can neither be absolutely uniform and geometrically regular and periodic as in a perfect crystal, or absolutely chaotic as in an ideal gas. The character of the distribution as influenced by the thermal agitation and other factors must in fact be intermediate between these two extreme types. The density of matter present must fluctuate

from place to place and these fluctuations of density may be viewed in two rather different aspects. The first way of regarding them is that adopted by Einstein and Smoluchowski, that is, to ignore the independent existence of discrete molecules and confine attention to the total quantity of matter present in volumes which are small enough to be beyond the limit of microscopic observation, but large enough to contain a great number of molecules. This is quite sufficient for the purpose of dealing with the optical problem and also the X-ray scattering at very small angles. The second way of regarding the matter is to take cognisance of the individual molecules and of their movements in order to discuss and analyse the fine structure of the liquid, and this is necessary when we discuss the scattering of X-rays at larger angles. When we consider the fluctuations of density from the first point of view, their magnitude may be predicted completely from a knowledge of the compressibility of the matter in bulk, and it is unnecessary to know either the weight of the molecules or their size and shape. The fine structure of the liquid on the other hand can only be fully determined if we know the properties of the individual molecules. The thermal agitation is *one* of the factors that must be considered in carrying out this analysis of the positions of the molecules in any state of aggregation of matter, but that it is not the only factor is a fairly obvious proposition. To realise this, we have only to recall the extreme case of a crystal at the absolute zero of temperature. Here we have no "thermal" fluctuations of density, but the structure exhibits complex periodic fluctuations of density that do not vary with time.

As a preliminary to the more complete analysis of positions of molecules in a liquid, we shall first set out clearly the theory of density-fluctuations in a liquid in the simpler form sufficient for the optical problem.

Thermal fluctuations of density: Let us assume that the fluid is enclosed in a cube of edge-length L each way in the

fluid, the co-ordinates of any point within this volume lying between the limits

$$0 < x < L$$

$$0 < y < L$$

$$0 < z < L.$$

Let the density of the liquid in any small region be denoted by

$$\rho, \text{ where } \rho = \rho_0 + \Delta$$

ρ_0 being the average density, and Δ the fluctuation. The work done in compressing the fluid contained in any small volume V so that its density is increased by Δ is

$$\frac{1}{2} \cdot \frac{1}{\beta} \left(\frac{\Delta}{\rho_0} \right)^2 V$$

and putting this equal to

$$\frac{1}{2} R T/N,$$

we get at once for the mean square of the fluctuation

$$\Delta^2 = \rho_0^2 \cdot R T \beta / NV.$$

The same result may also be derived by assuming that the medium is traversed by plane sound-waves of different wavelengths, whose energy is distributed in accordance with the equipartition principle. Following Einstein,¹ we may write

$$\Delta = \sum_l \sum_m \sum_n B_{lmn} \cos 2\pi l \frac{x}{2L} \cos 2\pi m \frac{y}{2L} \cos 2\pi n \frac{z}{2L}$$

where l, m, n , are positive integers. The potential energy in the sound-wave whose amplitude is B_{lmn} when integrated over the volume L^3 is easily shown to be

$$\frac{L^3}{16} \frac{B_{lmn}^2}{\rho_0^2} \cdot \frac{1}{\beta}$$

¹ *Annalen der Physik*, 1910, Band 33, p. 1283.

The law of distribution of each B_{lmn} is thus

$$C \exp. \left\{ \frac{-N L^3}{RT} \cdot \frac{B_{lmn}^*}{\rho_0^*} \right\} d B_{lmn}$$

where C is a constant, and it follows that the mean value

$$\frac{1}{N} \overline{B_{lmn}^*} = \rho_0^* \cdot RT\beta/NL^3$$

which is identical with that given above, since

$$\overline{\Delta^2} = \frac{1}{N} \overline{B_{lmn}^{*2}}$$

This method of analysing the irregular distribution of molecules in a fluid into a system of sound-waves in a continuous medium is of course merely a convenient mathematical artifice. Einstein adopts it in his paper and shows that for each given direction, it is sound-waves of a particular wave-length that are chiefly responsible for the scattering of light; this wave-length λ_1 is connected with the angle of scattering θ and the wave-length of the light λ inside the fluid by the formula

$$\lambda = 2 \lambda_1 \sin \frac{1}{2} \theta$$

The wave-length of the sound waves which are chiefly effective is thus, except for very small angles of scattering, of the same order of magnitude as the wave-length of the incident radiation.

In order that the thermal energy of the fluid may be identified with the energy of propagation of sound waves in it, it must, as is well-known, be assumed that the sound-wave spectrum is limited on the short wave-length side, the smallest permissible wave-length λ_2 being given by the expression

$$\lambda_2 = n^{-\frac{1}{2}} \cdot \sqrt{\frac{4\pi}{9}} = 1.118 \cdot n^{-\frac{1}{2}}$$

It is thus clear *prima facie* that Einstein's method of considering the problem of scattering must fail when the wave-length of the incident radiation and the direction of observation considered are such that the sound-waves chiefly responsible

for the scattering have a wave-length equal to or less than this limiting wave-length which is determined by the structure of the medium. We have already shown however, that even before this limit is reached, the influence of the discrete structure begins to be felt and the conception of sound-waves in a continuous medium ceases to be appropriate as a method of dealing with the scattering problem.

Analysis of Fine Structure of Liquids : In the foregoing application of the Fourier analysis to the determination of the thermal fluctuations of density, it was tacitly assumed that apart from these fluctuations, the fluid itself could be regarded as a uniform continuum. This limitation must now be dispensed with, and the Fourier analysis applied to the determination of the actual distribution of matter in the fluid. The result of the analysis would depend on the manner in which the molecules, or rather the electrons in them responsible for the scattering of X-rays, are dispersed in space. If they formed a regular space-lattice—(this contingency cannot of course arise in any actual liquid)—the analysis would indicate a definite periodicity in the distribution of matter with wave-length equal to the grating constant of the lattice. Actually, of course, we cannot expect such sharply-defined periodicities or “structural line-spectra” in a liquid. We should rather expect to get as the result of the analysis, a “continuous structural spectrum” having its chief peak of intensity at a wave-length equal to or comparable with the mean distance between neighbouring molecules. We have to find a formula which will indicate the distribution of intensity in the “structural spectrum.” This cannot of course be done completely without a knowledge of the special characteristics of the molecules under discussion. But, by considering only the essential features of the case, it would appear that the problem can, at least approximately, be solved with a knowledge of only the general thermodynamic properties of the fluid.

Let us imagine a cube in the fluid, which is normally of edge-length λ_0 distended or compressed into a cube of edge-length λ_1 ; the work done in the process is given by the expression

$$\frac{1}{2} \cdot \frac{1}{\beta} \cdot \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2$$

where β is the isothermal compressibility of the fluid. Actually as the result of thermal agitation, the cube might change shape as well as volume. If we take the cube to remain always a rectangular parallelepiped, the three edge-lengths may each be either greater or less than λ_0 . It is only one chance in eight that all the edge-lengths would be *greater* (or less as the case may be) than λ_0 . The average work corresponding to a change of one of the edge-lengths from λ_0 to λ_1 may thus be taken to be

$$\frac{1}{16} \cdot \frac{1}{\beta} \cdot \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2$$

and its thermodynamic probability may in accordance with Boltzmann's principle be written as

$$A \cdot \exp - \left\{ \frac{1}{16} \cdot \frac{N}{RT\beta} \cdot \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\} \cdot d\lambda_1,$$

where A is a constant. If λ_1 be taken to represent a wave-length in the Fourier analysis of the distribution of matter in the fluid, the expression just written is the formula for "the distribution of intensity in the structural spectrum." The expression gives a peak at the wave-length $\lambda_1 = \lambda_0$ with intensity falling off more or less rapidly on either side of the peak. It will be understood that here we are dealing with real periodicities in the distribution of matter, and not merely with fictitious mathematical periodicities as in the discussion of the thermal fluctuations of density. Further, these structural waves pass through the fluid in all directions, and

we may more appropriately write as the expression for the intensity in the structural-spectrum,

$$B \cdot \exp. - \left\{ \frac{1}{16} \cdot \frac{N}{RT\beta} \cdot \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\} d\lambda_1 d\Omega$$

where B is another constant, and $d\Omega$ is the elementary solid angle.

The problem is now to determine the wave-length λ_0 of the peak in the "structural spectrum." *Prima facie*, we shall not be appreciably in error if we take λ_0 to be identical with the mean distance between neighbouring molecules in the fluid. The evaluation of this mean distance is a very important problem in kinetic theory which does not appear as yet to have been adequately discussed. For an ideal gas, Hertz¹ has shown the mean distance between neighbouring molecules to be $0.554 n^{-\frac{1}{3}}$ where n is the number of molecules per unit of volume. For a regular cubical arrangement of molecules, λ_0 is evidently equal to $1 \cdot n^{-\frac{1}{3}}$, and for the closest² possible packing $\lambda_0 = 2^{\frac{1}{6}} \cdot n^{-\frac{1}{3}} = 1.123n^{-\frac{1}{3}}$. In a liquid, the arrangement of the molecules is intermediate in type between the absolutely chaotic distribution characteristic of an ideal gas and the regular arrangement characteristic of a crystal. Gans³ has attempted to take into account the finite volume of the molecules in the calculation of the mean molecular distance, and found that with increasing density of the fluid, λ_0 increases from $0.554 n^{-\frac{1}{3}}$ to $n^{-\frac{1}{3}}$ and even more. His treatment is however open to certain criticisms, and the numerical values given by him cannot be accepted as correct. The problem is considered afresh in a separate paper by one of us, and the general result emerges that for a liquid, λ_0 is

¹ Math. Annalen 67, 387, 1909.

² Jean's Dynamical Theory of Gases, 3rd Edition, p. 330.

³ Phys. Zeit., XXIII, 1922, p. 109.

$k, n^{-\frac{1}{2}}$ where k is a fraction ranging from about 0.8 to 1.0 according to the nature of the liquid and its condition as to temperature, pressure, etc. λ_0 may also be expressed in terms of the mean linear dimension or diameter σ of the molecule under consideration. The theoretical discussion indicates that in liquids under ordinary conditions λ_0 is of the same order of quantities as σ but may be some 10% to 20% greater.

Liquid Mixtures and Solutions: As we have just seen, the "structural spectrum" of a liquid consisting of only one substance is determined principally by the mean distance between neighbouring molecules and by its compressibility. Passing on to the case of mixtures and solutions, it is not difficult to see that the structural spectrum should, like many other physical characters, be at least roughly an additive property. For, to a first approximation, the volume of a mixture is the sum of the volumes of its components, and hence it is legitimate to assume that the mean distance between two molecules of the same kind in a mixture does not differ notably from what it is in the pure components. Thus if we have a succession of at least three molecules of one kind

A A A

or three molecules of the other kind

B B B

in a line, we have periodicities which are the same as those in the pure components. On the other hand, if we have at least four molecules forming a chain in which the two kinds of molecules alternate,

A B A B

or

B A B A

we would have wave-lengths corresponding to the sum of the two just considered. In the conditions subsisting in a fluid,

the formation of periodic arrays of four or more molecules of this special type is relatively an improbable event, and hence we are justified in assuming that the "structural spectrum" of a mixture or solution would contain principally only those wave-lengths which occur in the pure components. The same reasoning indicates that the distribution of "intensity" in the structural spectrum in the neighbourhood of these principal wave-lengths would be much the same as in the pure components. Hence we may as a first approximation take the structural spectrum of a mixture to be determined by simple addition of the structural spectra of the pure components taken in the proper proportions.

A more exact discussion of the case of mixtures and solutions would involve a consideration of the changes of density and of compressibility which occur when the two substances are mixed, and the influence on the structural spectrum of the local spontaneous fluctuations of density and composition; the precise magnitude of these fluctuations may be determined thermodynamically from the data for the compressibility and partial vapour-pressures of the mixture. *Primá facie*, the local fluctuations of *composition* of the mixture would have very little influence on the structural spectrum. For, we are only concerned with the average effect corresponding to the mean composition of the whole liquid. If the two components make up the structural spectrum in proportion to their respective concentrations, the average effect would be the same as if the liquid was uniform throughout and exhibited no fluctuations of composition. The fluctuations of *density* on the other hand are all-important, as in the case of a pure liquid. The *compressibility* of the mixture therefore enters in a fundamental way in the problem and where this shows marked deviations from the additive rule,¹ the distribution of

¹ For data regarding the compressibility of mixtures and solutions, see Cohen and Schüt's *Piezo-Chemie*, Leipzig, 1919, pp. 118-142.

intensity in the structural spectrum would differ from that given by a simple superposition of the spectra of the two components. Any notable change of volume on mixture may also be expected to result in a shift of the positions of the peaks in the spectra.

6. *Calculation of the Intensity of X-ray Scattering.*

Having analysed the distribution of matter in the fluid into a "Structural spectrum," in other words, into a number of superposed periodic distributions of different wave-lengths, we proceed to determine the X-ray scattering at different angles by this structure. We ignore the periodicities of larger wave-length which may be identified with sound-waves traversing the medium and which, as we have seen, are only of importance when we discuss the scattering in directions nearly identical with the primary beam. For larger angles of scattering, the periodicities of shorter wave-lengths which arise from the discrete structure of the medium are the only ones that need be considered. It is obvious that each of the periodic distributions of matter into which we have analysed the structure of the fluid would cause an internal reflection or enhanced scattering of the incident X-radiation in the direction given by the Bragg formula

$$2 \lambda_1 \sin \frac{1}{2} \theta = \lambda$$

where λ is the wave-length of the incident X-radiation and λ_1 is the wave-length under consideration in the structural spectrum. Since the structural waves traverse the fluid in all directions, the enhanced scattering or internal reflection corresponding to the wave-length λ_1 would occur in all directions coinciding with the generators of the cone of semi-vertical angle θ . Since λ_0 is the wave-length giving the peak of intensity in the structural spectrum, the special value of θ given by the relation

$$2 \lambda_0 \sin \frac{1}{2} \theta = \lambda$$

gives the cone of greatest intensity of the scattered X-rays, and the scattering would be considerably less both for larger and smaller value of θ . The formation of a fairly well-defined circular diffraction-halo in the X-ray scattering by liquids is thus clearly explained on the conception of the structural spectrum.

From the standpoint of the electromagnetic theory, the problem of determining the effect of the periodic distributions of the matter forming the structural spectrum on the propagation of radiation through the substance is very similar to that solved by Einstein in his paper on light-scattering in fluids except that the law of distribution of intensity in the "Structural spectrum" is different from that in the "Sound-wave spectrum." In fact, we can obtain an expression for the scattering due to the "Structural spectrum" merely by a slight modification of Einstein's treatment for the "Sound-wave spectrum." In the optical problem, we have light-scattering of the same intensity in all azimuths when the incident wave is assumed to have its electrical vector perpendicular to the plane of observation. This is due to the fact that the sound-waves of different wave-lengths which, as explained above, are each separately responsible for the scattering in different directions, are all, in accordance with the equipartition principle, of the *same intensity*. In the "Structural spectrum," on the other hand, the periodic distributions of matter of different wave-lengths follow the special exponential law of intensity

$$A \exp. \left\{ -\frac{1}{16} \frac{N}{RT\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\} d\lambda_1$$

Observing, as before, that each periodic distribution of wave-length λ_1 , is responsible for scattering in a specific direction, the distribution of intensity in the diffraction-halo should obviously follow the law of the structural spectrum very

closely. We may therefore write the intensity of the scattered radiation in any direction θ to be simply

$$C_1 \exp. \left\{ -\frac{1}{16} \frac{N}{RT\beta} \cdot \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\}$$

where λ_1 is given by the Bragg formula

$$\lambda = 2 \lambda_1 \sin \frac{1}{2} \theta$$

and C_1 is a numerical factor.

A useful verification of the formula is obtained by considering the case of a fluid of great compressibility, *e.g.*, a gas. In such a case, β is very large and the formula indicates, as is otherwise to be expected, that the scattering is of equal intensity in all directions perpendicular to the direction of the electric vector in the incident rays. If the incident X-rays are unpolarised, we should multiply the numerical factor C_1 by $(1 + \cos \theta)$ exactly as in the ordinary theory of light-scattering.

The numerical factor C_1 may be evaluated in the following way. In experiments on X-ray scattering, the wavelength λ is generally much smaller than the mean distance between neighbouring molecules. The concentration of the scattered radiation in the form of a diffraction-halo is due to the arrangement of the molecules not being a random one, and hence there existing a correlation of the phases of the waves scattered by neighbouring molecules,—agreement of phase and increased intensity in certain directions, disagreement of phase and diminished intensity in others. The problem is analogous to that of the diffraction of light by a large number of fine holes arranged in a roughly uniform manner in an opaque screen. We know that in such a case, the integrated intensity of the diffracted light in all directions

together is simply equal to the energy transmitted by any one aperture multiplied by the number of apertures. Exactly the same way, C_1 may be found by integrating the energy of the scattered radiation in all directions and putting it equal to the scattering by one molecule multiplied by the number of molecules in the volume under consideration.

7. Comparison with Observations.

In order to test the indications of the foregoing theory by comparison with experiments on the scattering of monochromatic X-radiation by liquids, we require to know the compressibility β of the liquid and the mean distance λ_0 between neighbouring molecules in the liquid. The latter quantity may be roughly estimated from the known molecular mass M and the density d of the liquid; the best way of finding it is however from the X-ray scattering itself. As is evident, the formula

$$C_1 \text{ exp. } \left\{ -\frac{1}{16} \frac{N}{RT\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\}$$

when graphed gives a strongly pronounced maximum at the wave-length $\lambda_1 = \lambda_0$, and the general shape of the curve reproduces with striking accuracy, the experimental curves obtained by Hewlett by the ionisation method. (See Fig. 1C and Fig. 1D above, in comparing which allowance should be made for the imperfect monochromatism of the X-ray pencil used by Hewlett). From the known wave-length of the X-rays used and from the angle of scattering θ_0 for maximum intensity, λ_0 may be found by using the Bragg formula

$$\lambda = 2\lambda_0 \sin \frac{1}{2}\theta_0$$

That λ_0 thus determined is of the same order of quantities

as the value of the mean molecular distance otherwise found is seen from the following table :

TABLE.

SUBSTANCE.	λ	θ_0	λ_0	$\sqrt{\frac{3}{d}M} = n^{-\frac{1}{2}}$	$\lambda_0 \cdot n^{\frac{1}{2}}$
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Results of Hewlett.

Benzene712A	8.5°	4.80A	5.27A	0.911
Octane	„	8.1°	5.04A	6.45A	0.781
Mesitylene	„	6.5°	6.28A	6.13A	1.024

Results of Keesom and Smedt—First paper.

Oxygen	1.54A	27°	3.30A	3.59A	0.919
Argon	„	27°	3.30A	3.61A	0.914
Benzene	„	18°	4.92A	5.27A	0.934
Water	„	29°	3.08A	3.09A	0.997
Aethyl alcohol	„	22°	4.04A	4.57A	0.884
Aethyl aether	„	19°	4.67A	5.55A	0.841
Formic acid	„	24°	3.70A	3.96A	0.934

Results of Keesom and Smedt—Second paper.

Oxygen712A	12.5	3.27A	3.59A	0.911
Argon	„	13.0	3.15A	3.61A	0.873
Water	„	13.44	3.04A	3.09A	0.984
Nitrogen	„	11.34	3.60A	3.85A	0.935
Carbon disulphide	„	13.23	3.09A †	4.63A †	0.667

The mean distance λ_0 between neighbouring molecules found from the X-ray data is in every case of the same order of magnitude as $n^{-\frac{1}{3}}$ where n is the number of molecules per unit of volume. The last column gives the value of k where $\lambda_0 = k.n^{-\frac{1}{3}}$. It is seen that k is generally about 0.8 or 0.9 as is indicated by theory. It is noteworthy that of the 5 common liquids reported upon by Keesom and Smedt in their first paper, water which has the smallest compressibility has a value of k which is practically unity, while for ether which is highly compressible, k has the relatively low value 0.841.

The compressibilities of the three liquids for which Hewlett has given scattering curves are respectively as follows:—

Benzene	...	90×10^{-12}	dyne/cm ²
Octane	...	120×10^{-12}	„
Mesitylene	...	75×10^{-12}	„

The differences between these are distinctly too small to produce any notable variation in the sharpness of the halo according to the formula. Strictly speaking, however, the halo for octane may be expected to be slightly less sharp than that for benzene or mesitylene. Hewlett's curves seem to indicate that this is actually the case, though owing to the width of the slit used and other complications, the data cannot be regarded as sufficiently precise on the point. Accurate data are as yet not available for any other liquid. It would be of interest to find experimentally whether liquids of high compressibility, *e.g.*, ether, exhibit a more diffuse halo than others, and whether any effect is produced by raising the temperature of the liquid towards the critical point; with rise of temperature and consequently increase of both T and β , the halo may be expected to broaden, and since λ_0 would increase with rise of temperature, the halo should also approach more closely the direction of the primary rays. The scattering at small angles should also increase in accordance with the Einstein-Smoluchowski formula. These indications of theory remain to be tested by observation.

The preceding calculations are based on the analysis of the fine structure of the liquid into a continuous "structural spectrum" having the mean distance λ_0 between neighbouring molecules as its dominant wave-length. While this analysis no doubt correctly represents the facts in broad outline, it leaves out of account the special features arising from the structural peculiarities of the individual molecules and their influence on the distribution of matter in a closely packed assemblage. Other periods, particularly those with wave-lengths much smaller than λ_0 , may conceivably become prominent when a dense aggregation of matter is analysed. In such a case, fainter diffuse haloes may arise outside the principal one. Then again, anomalies may arise in the case of highly asymmetrical molecules in which, instead of a single value of λ_0 , we may have two or even three separate values of the mean distance depending on the special relative configuration of neighbouring molecules. The principal halo would then itself exhibit a complicated structure which might become better defined at lower temperatures when the thermal agitation and its diffusing influence are minimised.

A convenient way of visualizing the complications that may arise in individual cases is to consider the powder diffraction-haloes obtained by the Debye-Scherrer method with the same substance in the solid crystalline state. It is well-known that with the finest powders in which the individual particles are microscopic or ultra-microscopic crystals, the diffraction-rings obtained by this method are relatively diffuse.¹ If we imagine the process of subdivision of the individual crystals continued gradually, a stage would be reached when the outer rings would practically all have merged into a diffuse general blackening of the photographic film and even the first few intense rings would have broadened out

¹ See, Szigmondy's *Kolloid-Chemie*, Appendix on the X-ray analysis of colloids, by Scherrer.

and merged into a single halo. If we imagine all the crystals broken up into individual molecules, we should still get a halo, because, as we have already seen, thermodynamic considerations ensure a certain degree of uniformity in the spacing of the molecules. In view of this analogy, it may be expected that some of the less prominent details of the powder-halo may also survive and find their counterpart in the liquid-halo, though diffused and modified by the expansion or contraction which takes place on melting.

The considerations indicated above suggest that it would be of great interest to compare the diffraction-halo shown in the liquid state with that shown by the same substance in the state of crystalline powder below its melting temperature. Unfortunately, as yet, sufficient experimental material is not to hand for making such a comparison. In two cases, however, that of water and benzene respectively, the necessary data are available. X-ray powder-photographs of ice have been obtained by Dennison¹ and the results have been discussed theoretically by Sir W. H. Bragg,² who has pointed out a defect in the experimental technique of Dennison's work. The spacings observed in A.U. are chiefly, 3.92, 3.67, 3.44, 2.68, 2.26, 2.07, 1.95, 1.92, 1.53, 1.37, 1.30, 1.17. The first four roughly group about a mean 3.42 A.U. and the next four which are nearly coincident give a strong halo at 2.05 A.U. Allowing for the contraction and re-arrangement which takes place on melting, these spacings are in general agreement with the first and second diffraction haloes found for liquid water by Keesom and Smedt. The X-ray powder photograph of solid crystalline benzene taken by Broome³ shows extremely strong haloes corresponding to spacings of 4.90 and 4.46 A.U., a second prominent group of haloes corresponding respectively to spacings of 3.71,

¹ Physical Review, Jun. 1921.

² Physical Society's Proceedings. 1922, p. 101.

³ Phys. Zeits., March 1923, Plate VI.

3.44 and 3.11 A.U. and a third group corresponding to a spacing of about 2.00 A.U. The first prominent halo of liquid benzene corresponds to a spacing of 4.80 A.U., while Hewlett's curves also show distinct bumps corresponding to spacings of 3.40 A.U. and 2.04 A.U. The agreement appears significant.

Finally, it may be remarked that observations on the X-ray diffraction by liquids consisting of molecules with extended chains of CH_2 groups and the like, *e.g.*, the fatty acids, would be of interest. No data appear to be available regarding these.

Leaving now the case of pure liquids, we may refer in passing to the case of liquid mixtures and of solutions. Wyckoff¹ has studied mixtures of benzene and carbon tetrachloride, water and glycerol, methylene iodide and carbon tetrachloride, and also aqueous solutions of potassium chloride and of alum. The X-ray diffraction-effects shown by the liquid mixtures tried were found by him to be more or less merely superpositions of the effects shown by the components separately. Those due to the aqueous solutions were practically similar to that of pure water. The results for mixtures are in agreement with the approximate theory already indicated. In the case of aqueous solutions, the dissolved material was probably insufficient in quantity to appreciably influence the observed results. Wyckoff has not studied the case of partially miscible liquids. It would be of interest to examine some cases of this kind, special attention being paid to the phenomena observed in the immediate vicinity of the critical solution temperature and for small angles of scattering.

8. *Liquid Crystals.*

Hückel's result, already cited in the introduction, that no notable difference is observable between the diffraction haloes

¹ American Journal of Science, Vol. V, 1923, p. 455.

shown by "turbid" and "clear" anisotropic liquids readily receives explanation in the light of the foregoing theory and of the ideas regarding the constitution of these bodies put forward by Oseen in two recent memoirs.¹ Oseen considers separately two types of interaction between the molecules, (*a*) forces tending to alter the relative positions of their centres of gravity, and (*b*) couples tending to alter their relative orientation. The equation of state of the fluid is derived by statistical-thermodynamical considerations on the basis of the assumed laws of interaction between the molecules. Both theory and observation indicate that in the turbid anisotropic liquids, there are regions whose dimensions include many wave-lengths of visible light over which the molecules are (at least approximately) similarly oriented. Similarity of orientation does not however necessarily involve any special regularity of spacing² beyond what may be expected on known thermo-dynamical principles from the compressibility of the liquid. It is probable also that the orientations are not exactly identical but that there is only a mean direction about which they oscillate. The absence of rigidity clearly shows that the definite space-lattices characteristic of solid crystals do not exist in the "turbid" fluids. Since the X-ray pattern is determined by the spacing of the molecules, and since what is observed in the experiments is the aggregate effect of groups oriented in all possible directions, it is clear that the diffraction-halo of a turbid

¹ Stockholm Academy, Handlingar, Band 61, No. 16 and Band 63, No. 1, 1921.

² In this connection, it is of interest to refer to the experiments of Barker (Jour. Chem. Soc., 1906, Vol. 89, p. 1120) and Beilby on the influence of a set of regularly arranged molecules on the crystal formation of an isomorphous substance. Barker found that if a thin film of NaNO_3 be allowed to dry on a polished surface of calcite, the crystals of NaNO_3 had their edges parallel to those of calcite. Beilby has shown that even when there are intervening films of foreign material, the orienting influence was exerted through the films provided they were sufficiently thin. Therefore the existence of an orienting influence does not necessarily connote a definiteness of spacing. (Beilby—Aggregation and Flow in Solids, p. 102.)

anisotropic liquid would differ little from that of the clear liquid.¹ The observations of Hückel are thus readily understood.

A detailed comparison of the X-ray photographs for the solid crystalline, anisotropic liquid, and isotropic fluid states for p-azoxyanisol and cholesterylpropionate reproduced with Hückel's paper is instructive. For both substances, the diameter of the liquid halo is approximately the same as that of the most intense group of rings in the crystal-powder photograph. Further, the haloes for the anisotropic and of isotropic liquids state, though very similar, are not absolutely identical and show slight differences in detail. This is not surprising in view of the fact that the compressibility, and other physical properties depending on the molecular arrangement are not identical for the two states. Further studies in regard to this would be well worth undertaking.

The recent studies of Friedel and Royer² and of Friedel³ on anisotropic liquids with equidistant planes are of great interest in this connection. Friedel characterises as the 'smectic' state an arrangement in which the molecules besides having a common direction are in addition arranged in equidistant parallel layers, and which is thus intermediate between the amorphous and crystalline states of matter. To use the phraseology of our present investigation, the "smectic" state is a state of aggregation for which the "structural spectrum" for a particular direction is similar to that of a crystal, but for perpendicular directions is similar to that of a liquid. The X-ray diffraction by the "smectic" state of matter would thus simultaneously exhibit the characters of a crystal and of a liquid in different

¹ The X-ray method of observation is thus in a sense less powerful than the optical one in this particular field. Detailed studies of the scattering of ordinary light by "turbid" anisotropic fluids in different directions and at different temperatures would be of interest in relation to the varying size of the molecular groups.

² Comptes Rendus, Dec. 1921, June, 1922.

³ Annales de Physique, November, 1922.

directions. The observations of De Broglie and Friedel¹ on the X-ray diffraction by oleate films, and of Piper² and Grindley on the X-ray diffraction by soap-curds may be explained on this basis.

9. *Amorphous Solids.*

It is well-known that many liquids and liquid mixtures when freed from dust may be cooled much below the ordinary melting temperature without crystallization occurring, and that they then pass into a highly viscous or glassy condition.³ The view has therefore gained general acceptance that vitreous or amorphous solids are really super-cooled liquids, the softening temperature being higher than that of observation. We have already seen that even in liquids, the positions of the molecules are not distributed at random but with a certain degree of regularity depending on the compressibility of the substance. Since, by lowering of temperature, the compressibility of a liquid generally diminishes, it follows that when the substance reaches the highly viscous condition, the molecules are arranged with not less than the degree of regularity characteristic of the ordinary fluid condition. The statement frequently made that in an amorphous solid, the molecules are disposed at "random" is therefore certainly erroneous. It is true we do not have that complete regularity of spacing and orientation characteristic of a crystal. Since an amorphous solid is optically isotropic, it follows that the orientation of the molecules does not lie in any particular direction. But the spacing of the molecules has a considerable degree of regularity. The "structural spectrum" of an amorphous solid is therefore very similar to that of a liquid.

¹ Comptes Rendus, March 12, 1913.

² Phys. Soc. of London, Proceedings, August 1923, p. 269.

³ See for instance, G. Tammann. "Aggregat Zustand" Leopold Voss, Leipzig, 1922.

A valuable confirmation of the views expressed above is furnished by observations on the scattering of light in amorphous solids such as optical glass and in supercooled liquids. Observations with liquids such as salol (phenyl salicylate) which may be converted into glassy solids by sufficiently cooling them show that the light-scattering power in the glassy condition remains of the same order of quantities as in the fluid state. The fact that the optical behaviour of an amorphous solid is very similar to that of a liquid is a justification for inferring that in regard to X-ray diffraction as well, they should behave similarly. The observations of Jauncey by the ionisation method referred to in the introduction, and of Wyckoff (*1C*) show in fact that ordinary glass gives a diffraction-halo very similar to that of a liquid. This does not, as has sometimes been suggested, indicate that glass possesses a rudimentary crystalline structure. The diffraction-halo observed is truly characteristic of the amorphous or non-crystalline condition. The sharpness of the halo is a measure of the regularity in the spacing of the molecules. An extensive series of observations of the X-ray diffraction-halo given by liquids which are supercooled and made to pass into the vitreous condition would be of interest in order further to elucidate the nature of the amorphous condition, and particularly to determine whether, when the temperature is taken below the softening point, any further re-arrangement of the molecules takes place or not.

Incidentally, it may be remarked that the conception of the "structural spectrum" may also be usefully extended to the case of solids and of solid solutions which are not truly amorphous but consist of microscopic or ultra-microscopic crystals packed together. The smaller the crystals, the more diffuse and weaker would be the lines of the "structural spectrum" and the more nearly would the X-ray scattering approximate to that characteristic of a truly amorphous body.

10. Summary and Conclusion.

The paper considers the explanation of the diffraction-haloes observed when a pencil of monochromatic X-radiation passes through a film of liquid and is received on a photographic plate. Explanations previously suggested are discussed and are shown to be inadequate.

(1) The explanation of the phenomenon is shown to depend on the consideration that the positions of the molecules in liquids are not at random but possess a certain degree of regularity which can be estimated thermodynamically from the compressibility of the fluid.

(2) The Smoluchowski-Einstein theory of light-scattering in fluids cannot be applied as it stands to the problem of the X-ray scattering owing to the fact that it practically treats the fluid as a continuum, an assumption which is justifiable in the optical case but not in the X-ray problem where the wave-length is much smaller; it is essential here to take into account the discrete structure of the medium.

(3) For very small angles of scattering, however, the Einstein-Smoluchowski theory is applicable even in the X-ray problem, and an explanation is readily forthcoming why liquids scatter very little at such angles.

(4) For larger angles of scattering, the discrete structure of the medium is taken into account by analysing the distribution of matter in the fluid into a continuous "structural spectrum" which has its peak of intensity at a wave-length equal to the mean distance λ_0 between neighbouring molecules. The law of the "structural spectrum" is exponential and is given by

$$A \exp. \left\{ -\frac{1}{16} \frac{N}{RT\beta} \cdot \lambda_0^3 \left(1 - \frac{\lambda_1^2}{\lambda_0^2} \right)^2 \right\} d\lambda_1$$

(5) The X-ray scattering in different directions is obtained very simply by combining the law of the structural

spectrum with the Bragg formula,

$$\lambda = 2\lambda_1 \sin \frac{1}{2}\theta$$

and this gives a diffraction-halo with its maximum intensity in the directions for which $\lambda_1 = \lambda_0$. The curve of intensity of the scattering in different directions agrees well with the experimental results of Hewlett, and the mean molecular distance λ_0 with the value deduced from kinetic theory.

(6) A discussion of the case of liquid mixtures indicates that the X-ray diffraction-halo should be practically a simple superposition of the haloes due to the separate components, as has been observed by Wyckoff.

(7) Diffraction by anisotropic liquids is discussed and the experimental results obtained by Hückel, and by De Broglie and Friedel are explained.

(8) Very similar arguments explain the X-ray diffraction-halo shown by amorphous solids.

(9) Some of the finer details of the halo observed in the experiments are also discussed and are shown to be intelligible in the light of the theory set out.

Annual Report for the year 1922.

1. The Committee of Management beg to submit the following report showing the work done by the Association during the year under review.

2. The Physical Laboratory of the Association continued as usual to be a centre of active research in various branches of the science, and attracted workers from different parts of India and Burma. The following list of papers which were contributed from the Laboratory of the Association or published in its Proceedings during the year 1922 may serve as an indication of the volume of the research work in which the Association has co-operated.

Proceedings of the Association, Vol. VII, Pts. III & IV.

1. Quetelet's Rings in Mica. By Nihal Karan Sethi, D.Sc., Professor of Physics and C. M. Sogani, M.Sc., Asstt. Professor of Physics, Benares Hindu University.
2. On the Colours of Tempered Steel and Other Tarnished Metal Surfaces. By Brojendra Nath Chuckerbutti, D.Sc., Asstt. Professor of Physics, Calcutta University.
3. Thunderstorms in Trivandrum, By K. R. Ramathan, M.A., Director, Trivandrum Observatory.
4. An Optical Study of Free and Forced Convection from Thin Heated Wires in Air. By Satish Chandra Pramanik, M.Sc., Research Scholar, Indian Association for the Cultivation of Science.
5. On Laminar Diffraction and the Theory of Microscopic Vision. By Nalini Kanta Sur, M.Sc., Lecturer in Physics, Ewing Christian College, Allahabad.
6. On the Theory and Some Applications of Sub-synchronous Pendulums. By Durgadas Banerjee, M.Sc.,

Demonstrator of Physics, University College of Science, Calcutta.

7. On Whispering Galleries. By C. V. Raman, M. A., D.Sc., Palit Professor of Physics, Calcutta University.

Proceedings of the Royal Society, 1922.

1. On the Molecular Scattering of Light in Water and the Colour of the Sea. By Prof. C. V. Raman.
2. On the Molecular Scattering of Light in Vapours and in Liquids and its Relation to the Opalescence Observed in the Critical State. By K. R. Ramathan, M.A.

Philosophical Magazine, 1922.

1. On the Phenomenon of the Radiant Spectrum. By Prof. C. V. Raman.
2. On the Convection of Light in Moving Gases. By Prof. C. V. Raman and Dr. N. K. Sethi.
3. On a New Optical Property of Biaxial Crystals. By Prof. C. V. Raman and V. S. Tamma.

Astrophysical Journal, 1922.

1. Einstein's Aberration Experiment. By Prof. C. V. Raman.

Journal of the Calcutta Mathematical Society, 1922.

1. On the Disturbed Electron Orbits in an Electromagnetic Field. By Panchanon Das, M.Sc.
2. Caustics formed by Diffraction. By P. Das, M.Sc.
3. On the Spectra of Isotopes. By P. Das, M.Sc.
4. Ripples of Finite Amplitude on a Viscous Liquid. By J. C. Kameswar Ray, M.Sc.

Nature.

1. Optical Observation of the Thermal Agitation of the Atoms in Crystals. By Prof. C. V. Raman.
2. Anisotropy of Molecules. By C. V. Raman.
3. The Colours of Tempered Steel. By Prof. C. V. Raman.
4. Molecular Structure of Amorphous Solids. By Prof. C. V. Raman.
5. The Radiant Spectrum. By C. V. Raman.
6. Diffraction by Molecular Clusters and the Quantum Structure of Light. By C. V. Raman.
7. Einstein's Aberration Expt. By Prof. C. V. Raman.
8. Molecular Aelotropy in Liquids. By Prof. C. V. Raman.
9. Opalescence Phenomena in Liquid Mixtures. By Prof. C. V. Raman.
10. Transparency of Liquids and the Colour of the Sea. By Prof. C. V. Raman.
11. The Spectrum of Neutral Helium. By. C. V. Raman.

Early in the year under report, your Honorary Secretary accepted an invitation from the University of Madras and delivered a special course of 6 lectures illustrated by experiments on "Recent Developments in Physics" which were attended by crowded audiences from all parts of that Presidency. He also attended the Science Congress at Madras as Honorary General Secretary of that organisation. Later in the year, your Secretary visited the old Government Granary at Bankipur in Patna with a view to study the whispering gallery effect and conducted experiments at the Victoria Memorial and at the General Post Office, Calcutta, with the result that he discovered two new whispering galleries which had remained unsuspected hitherto. Three special lectures were delivered by him at Benares at the invitation of the Vice-Chancellor of the Hindu University during the year

under review. He also visited Vizianagram at the invitation of H. H. The Maharaja to deliver an address to the College Science Association.

Mr. K. R. Ramanathan was deputed by the Madras University with a research scholarship to work at the Laboratory of this Association. He continued his work on the determination of molecular scattering of light in liquids and gases at different temperatures and high pressures up to 100 atmospheres.

Mr. K. Seshagiri Rao was also awarded a special research scholarship by the Madras University to continue his work in our Laboratory on the scattering of light in liquids and gases.

Babu Satish Chandra Pramanik held a research scholarship from the Association during a part of the year under report.

Mr. V. S. Tamma, Professor of Physics, Meerut College, worked here in the Laboratory for about six months on conical refraction in crystals and on the scattering of light in mixtures of phenol and water.

Mr. Lalji Srivastava, Professor of Physics, Government College, Ajmere, worked nearly ten months in the Laboratory on the effect of temperature on the scattering of light in quartz and on the double refraction of rock salt.

Mr. N. C. Krishna Iyer, Professor of Physics, Government College, Rangoon, worked in this Laboratory for nearly three months on the vibrations of strings.

Mr. Nalini Kanta Sur, Lecturer in Physics, Ewing Christian College, Allahabad, worked here for about three months on the scattering of light in smoky quartz.

Mr. D. B. Deodhar, Reader in Physics, Lucknow University, worked here about a month on the scattering of light in gaseous mixtures.

Mr. L. A. Ramdas was working in this Laboratory on the colours of Labradorite and of potassium chlorate crystals.

Mr. S. Bidwai, Lecturer in Physics, Meerut College, worked in this Laboratory for about two months on the colours of haematite crystals.

Mr. R. S. Deoras of the College of Science, Nagpur, also worked in this Laboratory for some time.

Mr. S. Ramakrishna Iyer, Assistant Professor of Physics, Maharajah's College, Trivandrum, worked for about 2 months on electrical discharge in gases at low pressures and on the absorption of light in liquids.

Applied Electricity Class.

During the latter part of the year under report, Mr. S. K. Dutt, M.A., Dipl. Ing (Charlottenburg), came forward to deliver a course of lectures on Applied Electricity. We convey our thanks to Mr. Dutt for his taking interest in the Association by delivering such useful lectures. Some 150 students took admission in the above class and about 20 lectures were delivered on the subject.

Department of Chemistry.

During the year under report the general lectures in Chemistry were discontinued as there was no response to the announcement made in the papers and the notices sent to different colleges.

The Commercial Analysis class went on as usual with five students of whom two will appear at the final examination in June 1923.

Mr. R. Venkateswaran of the Burma Educational Service worked at the Laboratory of the Association and contributed an important paper on the 'Molecular Scattering' of light in n-pentane to the Transactions of the Chemical Society of London for December 1922. Prof. Y. Venkataramiah, sometime Vizianagram Scholar of the Association, worked on ultra-violet scattering and absorption in benzene. It is hoped that

the Chemical Laboratory of the Association will soon develop into an active centre of research in Physical Chemistry.

Botany Department.

The required number of lectures in Botany for I.A. and I.Sc. students were delivered by Profs. Joytish Chandra Pal and Raj Kumar Sen and the practical classes were held by these professors with the assistance of a demonstrator.

The test examination of the 2nd year Botany class was held in due time. The first three students will be awarded prizes. Their names are given in order of merit:—

1. Pramatha Nath Dutta.
2. Ramendra Nath Ghosh.
3. Harendra Nath Seal.

Library.

The following special additions to the Library were made during the year:—

1. One set of Annalen der Physik for 20 years.
2. One set of Encyklopadie der Mathematischen Wissenschaften.
3. One set of Winkelmann's Handbuch der Physik.
4. Kaiser and Runge's Handbuch Der Spektroskopie.

The following publications were also subscribed for as usual:—

1. Scientific American Monthly.
2. Nature.
3. Science Abstracts, A & B.
4. American Journal of Science.
5. Philosophical Magazine.
6. Botanical Gazette.
7. Annals of Botany.
8. Astrophysical Journal.
9. Chemical News.

10. Proceedings of the Royal Society, A & B.
11. Transactions of the Royal Society, A & B.
12. Physical Review.
13. Annalen der Physik.
14. Physikalische Berichte.
15. Zeitschrift fur Physik.
13. Physikalische Zeitschrift.
17. Encyklopadie der Mathematischen Wissenschaften.
18. Collegian.

The Committee have to acknowledge with thanks the presentation of Journals and Periodicals in exchange from the following Societies :—

1. The Smithsonian Institution.
2. Cambridge Philosophical Society.
3. Physico-Mathematical Society, Tokyo, Japan.
4. Manchester Literary and Philosophical Society.
5. American Philosophical Society.
6. University of Illinois.
7. Faraday Society.
8. Franklin Institution.
9. American Geographical Society.
10. South African Association for the Advancement of Science.
11. Sitzungsberichte of the Prussian Academy of Sciences, Berlin.
12. Sitzungsberichte of the Academy of Sciences, Vienna, Austria.
13. University of Pennsylvania, Philadelphia.
14. Museum Journal of the University of Philadelphia.
15. Journal de Physique and Radium of the Physical Society of France.
16. Publications of the Royal Canadian Institute.
17. Technological and Scientific papers and Circulars of the Bureau of Standards.
18. University of Iowa.

19. University of Calcutta.
20. Calcutta Mathematical Society.
21. Government of India.
22. Government of Bengal.
23. Government of Mysore.
24. University of Bombay.
25. Government of Bombay.
26. University of Allahabad.
27. University of Punjab.
28. Agricultural Research Institute, Pusa.
29. Asiatic Society of Bengal.
30. Indian Institute of Science, Bangalore.
31. Editor, Indian Engineering.

The Committee of Management express their grateful thanks to Rai Chunilal Bose Bahadur, C.I.E., I.S.O., M.B., F.C.S., etc., who has kindly expressed his willingness to present the Journal of the Chemical Society, London, to our Association. Several numbers have already been received by the Association.

The thanks of the Association are due to the Editors of *the Englishman* and *the Indian Daily News* for gratuitously supplying to the library of the Association their widely circulated daily newspapers and publishing in their columns the daily Meteorological reports of this Institution.

Workshop.

During the year under review a large Universal Cincinnati-Milling Machine and a 4 H. P. motor have been purchased for the equipment of the Workshop. The mechanics turned out the following apparatus during the year :—

1. Iron cross tubes for scattering experiments.
2. Brass caps to fit the ends of the cross tube, air-tight with glass windows.
3. Gunmetal-casting cube for scattering of gas at high pressure.

4. Eagle-mounting for 13 ft. radius concave grating.
5. 2nd iron cross tubes of 3" diameter with brass nozzles for glass windows.
6. One divided circle for fitting up nicol and double image prism.
7. One lead-sheet covered box for X-ray tube with slit and windows.
8. Four aluminium triangles for chemical work.
9. Two rheostats for use with accumulators.
10. One iron screw cap with nozzle for piezometer.
11. Fitting up one constant deviation spectroscope from different parts purchased.
12. Making and fitting a constant deviation drum for the above.
13. One conical brass tube for Balopticon projector.
14. Fitting up one polarimeter from different parts purchased.
15. Finishing and fitting up of four pieces of brass screws in iron chairs for adjustable stools.
16. Two galvanised iron buckets for garden.
17. One brass tube for liquid air experiments.
18. Making and fitting up of five cross tubes of different angles with zinc nozzles for glass windows for scattering experiments.

Purchase of Instruments.

The following instruments were purchased during the year :—

1. One big quartz spectrograph.
2. One infra-red spectrometer with thermopile and rock-salt prism.
3. One 13 ft. radius concave grating.
4. One big electromagnet for obtaining fields up to 40,000 Gauss.
5. Three 10" induction coils.

6. Three mercury interrupters, Butt's standard type.
7. One Nutting photometer.
8. One Pulfrich refractometer.
9. One constant deviation spectroscope.
10. One Rayleigh refractometer.
11. One polarimeter.
12. One pointolite with resistance and extra lamps.
13. 2 doz. X-Ray tubes with accessories and rectifiers.
14. One portable resistance with switchboard and ammeter for X-ray coils.
15. One oxygen cylinder with reducing valve and pressure gauge.
16. One CO₂ cylinder with reducing valve and pressure gauge.
17. Microscopical accessories for the Botanical Laboratory.

Financial Position.

On the 31st December 1922 the Association had in the custody of the Imperial Bank of India, Government securities of the value of Rs. 2,30,400-0-0 for the general fund, Rs. 6,000-0-0 for the Ripon Professorship fund, Rs. 500-0-0 for the Nikunja Garabini Medal fund, a floating balance in the bank of Rs. 3,349-5-6, and cash balance in the office of Rs. 241-4-6, amounting in all to Rs. 2,40,490-10-0.

The assets of the Association as shown in its balance sheet on the 31st December, 23, amounted to Rs. 3,83,408-2-4, on account of the general fund and Rs. 68,601-5-0 on account of special funds totalling to Rs. 4,52,009-7-4.

On the 31st December 1921 the Association had in custody of Imperial Bank of India, Government securities of the value of Rs. 2,30,400-0-0 for the general fund, Rs. 6,000-0-0 for the Ripon Professorship fund, Rs. 500-0-0 for the Nikunja Garabini Medal fund, a floating balance in the bank of Rs. 7,274-5-6, and a cash balance in the office of Rs. 180-14-0,

amounting in all Rs. 2,44,355-3-6: The floating balance in the bank on 31st December 1921 included the special donations of Rs. 3,000 and Rs. 2,000 respectively earmarked for purchase of instruments and equipment, received in 1921 and expended in the following year.

The assets of the Association as shown in its balance sheet on the 31st December 1921 amounted to Rs. 3,77,079-1-7 on account of general fund, and Rs. 65,837-14-1 on account of special funds, totalling to Rs. 4,42,917-15-8.

The increased assets during the year under report were mainly under the following heads :—

	Rs.	A.	P.
1. Scientific Instruments ...	4,314	15	9
2. Botanical Instruments ...	1,203	1	9
3. Books and Journals for Library ...	1,815	3	0
4. Addition to Workshop Equipment ...	4,700	15	9

$3\frac{1}{2}\%$ Government securities for Rs. 2,000 were also purchased for the Association early in December 1922. The transaction however appeared in the Bank's accounts for January 1923, and will therefore be included in the report for 1923.

The thanks of the Association are due to His Highness the Maharaja of Cooh-Bihar, G.C.I.E., etc., for his generous contribution of Rs. 100 per month in aid of the establishment of a permanent professorship and also to the following members who are kind enough to continue their annual subscriptions.

1. Raja Peary Mohan Mukerjee, C.S.I., M.A., B.L.
2. Babu Nirmal Chandra Chander, M.A., B.L.

A special donation of Rs. 1,000 was received from the Vizianagram Samsthanam for equipping the laboratory, etc., for which the Committee of Management offers its grateful acknowledgment.

Acknowledgment.

The thanks of the Association are due to their Honorary Engineers Rai Krishna Chandra Banerji, and Babu Bhabadev

Chatterjee, to their Honorary Legal Advisers Babus Jatindra Chandra Bose and Nirmal Chandra Chander, to their Honorary Auditor, Babu Ishan Chandra Bose, to their Honorary Librarian Dr. Rasik Lal Datta, to their Honorary Secretary, Prof. C. V. Raman, and to their Honorary Assistant Secretaries Babus Jyotish Chandra Pal and Ashutosh Dey for their gratuitous services.

Obituary.

During the year under report the Association has to mourn the loss by death of two of its members who took a lively interest in its cause; Mr. E. W. Vredenburg, who was a member and took an active part in its scientific meetings and Rai Radha Churn Pal Bahadur who was a Trustee and a member of the Committee of Management for the last 16 years.

Though not occurring in the year under review the Committee have recorded their deepest sense of sorrow at the great loss they have sustained by the death of our President Raja Peary Mohan Mookerjee Bahadur who was one of our life members, president and a trustee. He took real interest for the welfare of the Association and substantially helped it with a subscription of Rs. 300 per annum. His loss will be severely felt for many years to come. The Association has recorded in a special general meeting its deep debt of gratitude to the revered memory of the late Raja Peary Mohan Mookerjee and a copy of the resolution was sent to his son Kumar Bhupendra Nath Mookerjee to convey their condolence to the bereaved family.

BALANCE SHEET AS ON THE 31ST DECEMBER 1922.

Dr.

Balance Sheet as on

	Rs.	A.	P.
To Government Securities $3\frac{1}{2}$ per cent. General fund	2,30,400	0	0
" " Ripon Professorship fund	6,000	0	0
" " Nikunja Garabini fund	500	0	0
Value of land and old building	31,680	11	9
Lecture Hall and Gallery	23,465	5	3
Vizianagram Laboratory	40,900	14	0
Range of shops (East side)	2,516	10	9
Range of shops (West side)	2,308	5	0
Durwan's Room	303	13	9
Servants' quarters	1,024	0	0
Observatory	3,116	3	3
Bonus, Provident fund	1,922	0	0
Contribution to Provident fund account	1,803	3	1
Scientific Instrument account General fund	41,640	13	8
" " K. K. Tagore fund	25,000	0	0
Botanical Instrument account	2,329	6	0
Library account	23,508	8	4
Tools and Implements account	161	12	3
Workshop Instrument account	9,592	2	3
Sir Richard Temple Prize account	245	0	0
Floating Balance in the Imperial Bank on the 31st December 1922	3,349	5	6
Cash in Office, on the 31st December 1922	241	4	6

 4,52,009 7 4

Certified that the accounts for the year 1922 have been audited and found correct.

(Sd.) I. C. BOSE,
Honorary Auditor.

the 31st December 1922.

Cr.

	Rs.	A.	P.
General fund	3,83,408	2	4
Ripon Professorship fund	10,830	0	0
H. H. The Maharaja of Cooch-Bihar Professorship fund	21,210	0	0
Hare Professorship fund	1,025	0	0
Victoria Professorship fund	1,000	0	0
Dr. Sircar Memorial fund	9,621	0	3
Deposit account	646	14	0
Vizianagram fund account	940	0	0
Provident fund account	2,956	2	4
Medal fund, Woodburn	500	0	0
" " Dr. Mahendralal Sircar	3,000	0	0
" " Joykissen Mukerji	9,339	0	0
" " Nikunja Garabini	500	0	0
" " Jatindra Chandra	550	0	0
Interest account Dr. M. L. Sircar Medal fund	420	0	0
" " Ripon Professorship fund	5,718	0	3
" " Nikunja Garabini fund	178	13	2
" " Wood-burn Medal fund	89	0	0
" " Jatindra Chandra Prize fund	77	7	0

 4,52,009 7 4

(Sd.) C. V. RAMAN,
Honorary Secretary.

Dr

Receipt and Expenditure during the

	Rs.	A.	P.
To Subscription account	598	0	0
Rent from shops	3,660	0	0
H. H. The Maharaja of Cooch-Bihar Professorship fund	1,200	0	0
Miscellaneous account	238	11	3
Interest account, General fund	7,909	7	4
" Ripon Prof. fund	190	0	0
" Nikunja Garabini fund	17	8	0
" Jatindra Chandra Prize fund	19	4	0
" Woodburn fund	17	8	0
" Dr. Sircar Research Medal fund	105	0	0
Fees from students	16,192	0	0
Scientific Instrument (Transferred Entry)	3,005	0	0
Bulletins sold account	31	9	0
Provident fund account	707	15	6
Old Material sold account	22	0	0
Dr. Sircar Memorial fund	613	0	0
Deposit from students	295	0	0
Vizianagram fund account	1,000	0	0
Suspense account	739	5	3
Floating Balance in the Imperial Bank on 31st December 1921	7,274	5	6
Cash in Office, on 31st December 1922	180	14	0

 44,016 7 10

Certified that the accounts for the year 1922, have been audited and found correct.

(Sd.) I. C. BOSE,
Honorary Auditor.

year ending 31st December 1922.

Cr.

	Rs.	A.	P.
By Commission account General fund	21	3	0
" Ripon Prof. fund	1	6	0
" Nikunja Garabini fund	0	3	0
Contribution of Provident fund	220	11	0
Building Repairs account	135	9	6
Cooch-Bihar Prof. fund account	600	0	0
Physics Research Scholarship account	550	0	0
Chemistry Research Scholarship account	150	0	0
Scientific Instrument account General fund	5,851	5	9
Municipal Tax account	1,757	6	0
Gas account	582	1	6
Electric account	828	1	6
Provident fund account	250	0	0
Workshop Petty charges account	151	4	0
Postage stamp account	178	12	9
Printing charges	1,342	4	9
Laboratory charges account	3,279	15	9
Library account	2,050	8	0
Furniture account	864	11	0
Electric Installation account	52	8	0
Deposit account	160	0	0
Charges General account	672	10	6
Botany Class account	2,495	0	3
Establishment account	9,023	1	6
Workshop Instrument account	7,764	15	9
Botany Instrument account	1,203	1	9
Miscellaneous account	5	4	7
Suspense account	59	0	0
Vizianagram fund account	60	0	0
Woodburn fund Interest account	105	0	0
Observatory account	9	12	0
Floating Balance in the Imperial Bank on 31st December 1922	3,349	5	6
Cash in Office on the 31st December 1922	241	4	6
	44,016	7	10

(Sd.) C. V. RAMAN,
Honorary Secretary.

