The diffraction of X-rays in liquids, liquid mixtures, solutions, fluid crystals and amorphous solids

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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 centre and separated from it by a relatively clear space. This somewhat surprising observation was made by Debye and Scherrer\(^1\) in the course of their work on X-ray diffraction. The same result has also been obtained in some recent X-ray studies by Hewlett\(^2\) in which the ionisation method was employed. Keesom and Smedt\(^3\) have also

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\(^*\)A preliminary note in which the theory developed in this paper was indicated appeared in *Nature (London)* Feb. 10, 1923, 185.

\(^1\)Nachrichten Göttingen 1916.


\(^3\)Keesom and Smedt: *Proc. Roy. Soc.* (Amsterdam) 1922 XXV, 118 and 1923 XXVI 112.
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 Huckel 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 Freidrich on the scattering of X-rays by wax and other amorphous solids and by Jauncey 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.

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 suggested is that the halo might be a diffraction-effect arising from the finite size of the molecule or the cooperation 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 Hewlett 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 Compton 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,

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†Freidrich: Z. Phys. 1913 14 317.
‡Jauncey: Phys. Rev. 1922 XX 405.
§Debye: referred to by Hückel.
Loc. cit.
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 figure 1C the curve of intensity for benzene reproduced from Hewlett's paper, and in figure 1A for comparison with it a graph of the intensity calculated from Ehrenfest's formula. It will be seen that there is little in common between them. Finally we should mention an attempt which has been made by L Brillouin* 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 figure 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 figure 1C.

We propose in this paper to approach the problem from an entirely different standpoint. In a series of publications† 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 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

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†1. Notes by C V Raman in Nature (London) November 10, 1921, and several subsequent issues.
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 wavelength 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. Figure 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 figure 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 wavelength 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
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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 wavelength. 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 $AB = BC = CD = DE = \lambda/2 \sin 1/2 \theta$ where $\theta$ is the angle of scattering and $\lambda$ is the wavelength 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 $n_1, n_2, \ldots n_p, \ldots n$, of the successive slices, due regard being had to their respective phases, which are distributed at regular intervals from 0 to $2\pi$. If $n_1 = n_2 = \ldots n_p = \ldots n$, 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 $n_1 + n_2 + \ldots n_p + n = n$ 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.* 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 shown 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. The total scattering will thus be proportional to $r(\sqrt{n/r})^2$ 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 $\Delta n_1$ to be, $n\sqrt{R\beta T/Nr}$

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where $R$ and $N$ are respectively the gas constant and Avogadro constant for a gram-molecule, $T$ is the absolute temperature and $\beta$ is the isothermal compressibility of the fluid. Assuming as in the case of an ideal gas that $\Delta n_1, \Delta n_2, \ldots$, 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

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

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, $\beta$ 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 electro-magnetic 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

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

where $\mu$ is the refractive index of the fluid. When $\mu$ 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 $\lambda$ is large, which is true in the optical case. When $\lambda$ is comparable with molecular dimensions, and $\theta$ 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 subdivided 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-versa. 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 $\theta$ 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 $\theta$. 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 $\beta$ being $90 \times 10^{-12}$ 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 $\theta$ 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 $\lambda_0$ 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 $\theta$ 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 \( \theta \) where \( \lambda = 2\lambda_0 \sin \frac{1}{2} \theta, \lambda_0 \) 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 \( \theta \) increases and approaches the value \( 2\sin^{-1}\frac{1}{2}\lambda/2\lambda_0 \). On the other hand, when \( \theta \) 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 \( \lambda \), 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

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

$\rho_0$ being the average density and $\Delta$ the fluctuation. The work done in compressing
the fluid contained in any small volume $V$ so that its density is increased by $\Delta$ is

$$\frac{1}{2} \beta \left( \frac{\Delta}{\rho_0} \right)^2 V$$
and putting this equal to

\[ \frac{1}{2}RT/N, \]

we get at once for the mean square of the fluctuation

\[ \Delta^2 = \rho_0^2 \cdot RT \beta / NV. \]

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,* we may write

\[ \Delta = \sum_{l} \sum_{m} \sum_{n} B_{l m n} \cos 2\pi l \frac{x}{2L} \cos 2\pi m \frac{y}{2L} \cos 2\pi n \frac{z}{2L} \]

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

\[ \frac{L^3 B_{l m n}^2}{16 \rho_0^2 \cdot \beta}. \]

The law of distribution of each \( B_{l m n} \) is thus

\[ C \exp \left\{ -\frac{N}{RT} \frac{L^3 B_{l m n}^2}{16 \rho_0^2} \right\} dB_{l m n} \]

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

\[ \frac{1}{2} B_{l m n}^2 = \rho_0^2 \cdot RT \beta / NL^3 \]

which is identical with that given above, since

\[ \Delta^2 = \frac{1}{2} B_{l m n}^2. \]

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 wavelength that are chiefly responsible for the scattering of light; this wavelength \( \lambda_1 \) is connected with the angle of scattering \( \theta \) and the wavelength of the light \( \lambda \) inside the fluid by the formula

\[ \lambda = 2\lambda_1 \sin \frac{1}{2} \theta. \]

The wavelength 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 wavelength of the incident radiation.

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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 wavelength side, the smallest permissible wavelength \( \lambda_2 \) being given by the expression

\[
\lambda_2 = n^{-1/3} \sqrt[3]{\frac{4\pi}{9}} = 1.118 \cdot n^{-1/3}.
\]

It is thus clear *prima facie* that Einstein’s method of considering the problem of scattering must fail when the wavelength of the incident radiation and the direction of observation considered are such that the sound-waves chiefly responsible for the scattering have a wavelength equal to or less than this limiting wavelength 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 wavelength 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 wavelength 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 \( \lambda_0 \) distended or compressed into a cube of edge-length \( \lambda_1 \); the work done in the process is given by the expression

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

where \( \beta \) 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 \( \lambda_0 \). It is only one chance in eight that all the edge-lengths would be greater (or less as the case may be) than \( \lambda_0 \). The average work corresponding to a change of one of the edge-lengths from \( \lambda_0 \) to \( \lambda_1 \) may thus be taken to be

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

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

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

where \( A \) is a constant. If \( \lambda_1 \) be taken to represent a wavelength 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 wavelength \( \lambda_1 = \lambda_0 \) 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,

\[
B \exp \left\{ \frac{1}{16} \frac{N}{RT \beta} \lambda_0^3 \left( 1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\} d\lambda_1 \, d\Omega
\]

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

The problem is now to determine the wavelength \( \lambda_0 \) of the peak in the "structural spectrum." Prima facie, we shall not be appreciably in error if we take \( \lambda_0 \) 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, Hertz\(^*\) has shown the mean distance between neighbouring molecules to be \( 0.554 n^{-1/3} \) where \( n \) is the number of molecules per unit of volume. For a regular cubical arrangement of molecules, \( \lambda_0 \) is evidently equal to \( n^{-1/3} \), and for the closest\(^*\) possible packing \( \lambda_0 = 2^{1/6} n^{-1/3} = 1.123 n^{-1/3} \). 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. Gans* 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, $\lambda_0$ increases from $0.554 n^{-1/3}$ to $n^{-1/3}$ 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, $\lambda$ is $k, n^{-1/3}$ 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. $\lambda_0$ may also be expressed in terms of the mean linear dimension or diameter $\sigma$ of the molecule under consideration. The theoretical discussion indicates that in liquids under ordinary conditions $\lambda_0$ is of the same order of quantities as $\sigma$ 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 charcteristics, 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 wavelengths 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

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solution would contain principally only those wavelengths 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 wavelengths 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. Prima 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,* the distribution of 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 wavelengths, we proceed to determine the X-ray scattering at different angles by this structure. We ignore the periodicities of larger wavelength 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 wavelengths 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

*For data regarding the compressibility of mixtures and solutions, see Cohen and Schut's Piezo-Chemie, Leipzig, 1919, pp. 113–142.
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 \( \lambda \) is the wavelength of the incident X-radiation and \( \lambda_1 \) is the wavelength 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 wavelength \( \lambda_1 \) would occur in all directions coinciding with the generators of the cone of semi-vertical angle \( \theta \). Since \( \lambda_0 \) is the wavelength giving the peak of intensity in the structural spectrum, the special value of \( \theta \) 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 values of \( \theta \). 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 wavelengths 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 wavelengths follow the special exponential law of intensity

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

Observing, as before, that each periodic distribution of wavelength \( \lambda_1 \), 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 $\theta$ to be simply

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

where $\lambda_1$ 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, $\beta$ 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 $\lambda$ 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 $\beta$ of the liquid and the mean distance $\lambda_0$
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

\[ C_1 \exp \left\{ -\frac{1}{16RT\beta} \lambda_0^3 \left( 1 - \frac{\lambda_0^3}{\lambda_1^3} \right)^2 \right\} \]

when graphed gives a strongly pronounced maximum at the wavelength \( \lambda_1 = \lambda_0 \), and the general shape of the curve reproduces with striking accuracy, the experimental curves obtained by Hewlett by the ionisation method. (See figure 1C and figure 1D above, in comparing which allowance should be made for the imperfect monochromatism of the X-ray pencil used by Hewlett). From the known wavelength of the X-rays used and from the angle of scattering \( \theta_0 \) for maximum intensity, \( \lambda_0 \) may be found by using the Bragg formula

\[ \lambda = 2\lambda_0 \sin \frac{\theta}{2}. \]

That \( \lambda_0 \) 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>
<thead>
<tr>
<th>Substance</th>
<th>( \lambda )</th>
<th>( \theta_0 )</th>
<th>( \lambda_0 )</th>
<th>( \sqrt{\frac{M}{d}} = n^{1/3} )</th>
<th>( \lambda_0 \cdot n^{1/3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.712A</td>
<td>8.5°</td>
<td>4.80A</td>
<td>5.27A</td>
<td>0.911</td>
</tr>
<tr>
<td>Octane</td>
<td>&quot;</td>
<td>8.1°</td>
<td>5.04A</td>
<td>6.45A</td>
<td>0.781</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>&quot;</td>
<td>6.5°</td>
<td>6.28A</td>
<td>6.13A</td>
<td>1.024</td>
</tr>
</tbody>
</table>

Results of Hewlett

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \lambda )</th>
<th>( \theta_0 )</th>
<th>( \lambda_0 )</th>
<th>( \sqrt{\frac{M}{d}} = n^{1/3} )</th>
<th>( \lambda_0 \cdot n^{1/3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>1.54A</td>
<td>27°</td>
<td>3.30A</td>
<td>3.59A</td>
<td>0.919</td>
</tr>
<tr>
<td>Argon</td>
<td>&quot;</td>
<td>27°</td>
<td>3.30A</td>
<td>3.61A</td>
<td>0.914</td>
</tr>
<tr>
<td>Benzene</td>
<td>&quot;</td>
<td>18°</td>
<td>4.92A</td>
<td>5.27A</td>
<td>0.934</td>
</tr>
<tr>
<td>Water</td>
<td>&quot;</td>
<td>29°</td>
<td>3.08A</td>
<td>3.09A</td>
<td>0.997</td>
</tr>
<tr>
<td>Aethyl alcohol</td>
<td>&quot;</td>
<td>22°</td>
<td>4.04A</td>
<td>4.57A</td>
<td>0.884</td>
</tr>
<tr>
<td>Aethyl aether</td>
<td>&quot;</td>
<td>19°</td>
<td>4.67A</td>
<td>5.55A</td>
<td>0.841</td>
</tr>
<tr>
<td>Formic acid</td>
<td>&quot;</td>
<td>24°</td>
<td>3.70A</td>
<td>3.96A</td>
<td>0.934</td>
</tr>
</tbody>
</table>

Results of Keesom and Smedt—First paper

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \lambda )</th>
<th>( \theta_0 )</th>
<th>( \lambda_0 )</th>
<th>( \sqrt{\frac{M}{d}} = n^{1/3} )</th>
<th>( \lambda_0 \cdot n^{1/3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>0.712A</td>
<td>12.5</td>
<td>3.27A</td>
<td>3.59A</td>
<td>0.911</td>
</tr>
<tr>
<td>Argon</td>
<td>&quot;</td>
<td>13.0</td>
<td>3.15A</td>
<td>3.61A</td>
<td>0.873</td>
</tr>
<tr>
<td>Water</td>
<td>&quot;</td>
<td>13.44</td>
<td>3.04A</td>
<td>3.09A</td>
<td>0.984</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>&quot;</td>
<td>11.34</td>
<td>3.60A</td>
<td>3.85A</td>
<td>0.935</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>&quot;</td>
<td>13.23</td>
<td>3.09A</td>
<td>4.63A?</td>
<td>0.667</td>
</tr>
</tbody>
</table>

Results of Keesom and Smedt—Second paper
The mean distance \( \lambda_0 \) between neighbouring molecules found from the X-ray data is in every case of the same order of magnitude as \( n^{-1/3} \) where \( n \) is the number of molecules per unit of volume. The last column gives the value of \( k \) where \( \lambda_0 = k \cdot n^{-1/3} \). 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:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Compressibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>( 90 \times 10^{-12} ) dyne/cm(^2)</td>
</tr>
<tr>
<td>Octane</td>
<td>( 120 \times 10^{-12} ) &quot;</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>( 75 \times 10^{-12} ) &quot;</td>
</tr>
</tbody>
</table>

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 \( \beta \), the halo may be expected to broaden, and since \( \lambda_0 \) 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 \( \lambda_0 \) between neighbouring molecules as its dominant wavelength. 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 wavelengths much smaller than \( \lambda_0 \), 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 \( \lambda_0 \), we may have two or even three separate values of the mean distance depending on the special relative configur-
Diffraction of X-rays in Liquids

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. 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 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 Dennison and the results have been discussed theoretically by Sir W H Bragg, 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, 1·96, 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 Broome 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, 3·44 and 3·11 A.U. and a third group corresponding to a spacing of about 2·00 A.U.

*See, Szegmondy’s Kolloid Chemie, Appendix on the X-ray analysis of colloids by Scherrer.
§Z. Phys. March 1923, Plate VI.
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 CH₂ 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. Wyckoff* 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 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.† 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 wavelengths of visible light over which the molecules are (at least approximately) similarly oriented. Similarity of orientation does not however necessarily

†Stockholm Academy, Handlingar, Band 61, No. 16 and Band 63, No. 1, 1921.
DIFFRACTION OF X-RAYS IN LIQUIDS

involve any special regularity of spacing* beyond what may be expected on known
thermodynamical 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 anisotropic
liquid would differ little from that of the clear liquid.† The observations of Hückel
are thus readily understood.

A detailed comparison of the X-ray photographs for the solid crystalline,
anisotropic liquid, the isotropic fluid states for p-azoxyanisol and cholesteryl-
propionate 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 Royer‡ and of Friedel§ 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

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*In this connection, it is of interest to refer to the experiments of Barker (J. Chem. Soc. 1906 89 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 NaNO₃ be allowed to dry on a polished surface of calcite, the crystals of NaNO₃ 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).

†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.

‡Comptes Rendus Dec. 1921, June 1922.

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 directions. The observations of De Broglie and Friedel* on the X-ray diffraction by oleate films, and of Piper† 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. 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.

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,

*Comptes Rendus, March 12, 1913.
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 rearrangement 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 wavelength 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 wavelength equal to the mean distance $\lambda_0$ between neighbouring molecules. The law of the \"structural
spectrum" is exponential and is given by

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

(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 \( \lambda_0 \) 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.