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# X-RAY DIFFRACTION IN LIQUIDS

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WHAT is the cause of halos formed by x-rays passing through supposedly amorphous substances such as liquids?[1] Surely the liquid does not contain minute crystals, and if not, what causes the effects obtained? These queries were not satisfactorily answered three years ago. Today it is agreed, at least by the most active investigators and by all who are publishing opinions, that the diffraction effects with liquids do indicate spatial orderly arrangements of molecules. This view may seem at first a surprising admission, but, upon careful consideration, it becomes most reasonable. The purpose of this paper is to elaborate this view and to give the outline of the experimental results which substantiate it. The status of the study of x-ray diffraction in liquids is briefly this: (1) the phenomenon is understood qualitatively in the same sense that we understand crystal diffraction; (2) theoretical analysis has not given great assistance because of the complexity in liquids and the corresponding necessary crude approximations; (3) the value of x-rays in the study of the nature of liquids, of solutions and of molecular structure has been demonstrated.

X-ray diffraction has proved to be a powerful means for the study of crystal structure. The diffraction law of Bragg, $\lambda = 2d \sin \theta/2$, has won full confidence by the consistent results obtained through its use. But its correctness has been actually proved. For the values of the wave-length, $\lambda$, as determined from measurements with crystals, have been verified by experiments with ruled line gratings. It is the periodicity of the crystal planes, separated by the distance $d$ that gives the diffraction maxima at angles $\theta/2$, where $\theta$ is the deviation of the x-rays, and this is the view of both the electromagnetic and quantum theories. Throughout this paper, however, the language will be in terms of the electromagnetic theory. In the crystal the periodicity is not that of diffraction centers located in actual planes, for the x-rays are scattered by the electrons which are distributed throughout the atoms and consequently cannot all lie in planes. If the density of distribution varies periodically with depth in a crystal, then theory shows that there will be regular reflection of x-rays in accord with Bragg's formula if $d$ is the distance of separation of recurring densities. If the distribution concentrates the

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[1] This article does not refer to liquid crystals but to optically isotropic liquids. The connection of our discussion with the condition called "liquid crystals" is quite definite and is chiefly one of magnitude of the individual molecular groups. But the discussion of this point is beyond the scope of this article. The discussion is confined to what are ordinarily regarded as "amorphous" liquids. It is also the policy of this article to omit the details of the argument favoring its interpretation of the present status, emphasizing rather the nature and diversity of results.

electrons in planes, then the intensity of the diffraction at the angle $\theta/2$ is large. As, however, the distribution of electrons approaches a uniform one between these planes, the regular reflection approaches a zero value. Any distribution that is roughly periodic in space would give an intensity maximum for the $\lambda$ and $\theta$ of Bragg's formula.

From these considerations it is obvious that if there is a sufficiently marked space periodicity in the structure of liquids, there would be found an x-ray diffraction effect. Debye and Scherrer[2] were the first observers of the diffraction halo in liquids. The term "halo" is used because the experiments were performed with a circular beam of x-rays and the diffraction ring thus formed is much broader and more diffuse than would be formed with a powdered crystal. It is agreed by all that this halo demonstrates a periodicity in the liquid, but its nature has been the cause of discussion.

Is the effective periodicity located within the atom, (electron distribution in the atom), within the molecule (atomic distribution), or intermolecular (molecular distribution)? The answer is to be found through experiment. Even then the three possibilities can be reduced to two or one only in a qualitative sense, for all the effects may exist although not necessarily detectable. Doubtless the halo found in monatomic substances[3] should be accounted for by the first cause. When complex molecules are used, the third cause is the predominating one, since the chief diffraction maxima are accounted for by a periodicity in the distribution of molecules. (Of course it is understood that the ultimate diffraction centers are electrons, and that, with the correct regard for phase differences those of one atom may be considered as grouped at atomic "centers" and that, again by a similar process, the electrons of all the atoms in a molecule may be regarded as grouped at a molecular "center." Thus three interference effects, between electrons in the atom, between atoms and between molecules, are based upon the scattering of x-rays by electrons.)

All three types of distribution of diffraction centers are of interest, for we desire to secure information leading to any evidence as to arrangements of electrons in atoms, of atoms in the molecule, and molecules in any group of molecules. But with liquids in general, experiment shows that the interest must rest chiefly in the last named, for the results thus far obtained are not capable of giving a considerable amount of finer detail.

What can cause a molecular grouping that is perfect enough to lead to diffraction halos? The reply which might come to mind at once is that the "shape" of the molecules, if sufficiently asymmetrical, might cause such an arrangement. Thus if the molecules were cigar shaped, the probability of parallel grouping of the molecules would be greater than that of any other. But shape has no meaning other than the space apparently occupied by the molecules and the molecular grouping would depend upon the nature of the

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[2] Debye and Scherrer, Nachr. Göttingen, 1916.

[3] Keesom and de Smedt, Versl. Akad. Amsterdam **31,** 87 (1922) and **32,** 72 (1923), used argon.

molecular forces. In the crystal, the forces are electrostatic and electrodynamic, and the atoms (or molecules) are in stable configuration in mean positions representing minimum potential energy. If then in a liquid, molecules, oblong in shape, have a high probability of parallelism, it is because of the nature of the molecular forces. And it is not at all surprising if oblong molecules are thus frequently found parallel. The kinetic energy possessed by the molecules because of specific heat will not necessarily disturb the parallelism to a serious extent. For this kinetic energy is represented by the acoustic waves which travel throughout the liquid, permitting the relative velocities of two adjacent molecules to be small in comparison with the actual velocity of either.

If the x-rays give evidence of periodic molecular grouping, it must not be supposed that these groups are large or that the molecules in any one well defined group remain permanently members of that group. At any one instant these small orderly molecular groups might exist at numerous points in the liquid, the regions between them being not so orderly. The percentage of the volume occupied by fairly orderly groups might be large in some liquids and not so large in others. The evidence today strongly favors this orderly arrangement in groups which has been called[4] the "cybotactic" condition. This view will be discussed at greater length in the latter part of the article.

With the foregoing introductory remarks concerning the nature of the phenomena involved, an account will now be given of some of the results obtained. Reference will not be made to all the literature, for the endeavor of this article will be to give to the reader the present status of experimental results without burdening him with all the material now in print.[5] For a partial list of the literature up to 1928, the reader is advised to consult Drucker's article.[6]

*The diameters of chain molecules.* In the diffraction rings of chain molecules, such as n-alcohols, n-fatty acids, and n-paraffins there is always a major intensity maximum which is located at approximately the same angular deviation. It indicates the separation of planes $d$, by approximately 4.6 Å.u. The interpretation made by the investigators[7] is that $d$ is the effective "diameter" of these chain molecules. The square of this value, 4.6 Å.u., is the area of cross section occupied by the chain. This agrees with the well-known surface film experiments of Adam. It should be emphasized at this point, however, that the measurements of observers who have used different x-ray beams for examination must of necessity be expected to differ slightly in computed results. For, unless the radiation is strictly monochromatic.

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[4] Stewart and Morrow, Phys. Rev. **30**, p. 232 (1927).

[5] There have been published approximately sixty papers containing data on x-ray diffraction in about two hundred fifty different liquids.

[6] Drucker, Phys. Zeits. **29**, p. 273 (1928).

[7] Sogani, Ind. Jl. Physics **1**, p. 357 (1927); Katz, Zeits. f. Physik **45**, p. 97 (1927); Vaiyanathan, Ind. Jl. Physics **3**, p. 391 (1928); Stewart and Morrow, Phys. Rev. **30**, p. 232 (1927); Morrow, Phys. Rev. **31**, p. 10 (1928); Stewart, Phys. Rev. **32**, p. 153 (1928).

the diffraction angle of maximum intensity may not correspond exactly to the wave-length used in computations. For this reason it will be the policy of this paper to ignore these minor differences in distances measured by the workers in this field. Just now the experimental work is largely of a scouting nature. At a later time, more accurate measurements will be made where needed. Then details of disagreements in results will be in point.

*Effect of branches upon the diameter of chain molecules.* Isomers of the n-alcohols and of n-paraffins have been examined[8] and the branches increase the effective diameters of the chains. The details contain certain information in regard to the structure of molecules, but not sufficiently definite for this resumé.

*Existence of double molecules in polar compounds.* In polar compounds, especially in n-alcohols, n-fatty acids, and benzene and cyclohexane derivatives, there is frequently a second intensity maximum in the x-ray diffraction, which, using Bragg's law, gives a $d$ greater than the length of one molecule, in some cases equal to twice the molecular length and in others less than twice this length. There seems to be no objection to the conclusion that this measurement indicates the grouping of two polar molecules by the attraction of the two polar groups. With the chain molecules this means an arrangement of the two attracting polar molecules end to end in a line and parallel to similar neighbors. With the chain molecules and an OH group, if the latter is attached in a branch, the end to end arrangement is replaced by a parallel side by side arrangement of molecules, provided the attachment is elsewhere than next to the end carbon atom.

*Nature of the carbon chains.* Experiments[9] with the n-paraffins, the assumption of the parallel arrangement of the molecules and the best values of the densities, lead to the conclusion that the carbon atom occupies a distance of 1.24 Å. u. along the chain. This is in agreement with results with alcohols when the length of single molecules are measured. This distance along the chain compared with separation in the diamond, 1.54 Å. u. and the diameter of the chain 4.6 Å. u. leads one to favor a nonlinear arrangement of the carbon atoms in the chains. There is found other corroborative evidence such as a decrease in molecular diameter with decrease in the number of carbon atoms in case there are only from one to five in the chain.

*Simultaneous measurement of more than one diameter of a chain.* This has been accomplished in two cases, 2-methyl hexane[10] and di-n-propyl carbinol.[11] The measurements were 5.25 Å.u. and 4.84 Å.u. for the former and 4.85 and 4.5 Å.u. for the latter. In the latter there was also a third intensity maximum from which the length of a single molecule was obtained. Such evidence, and there is much of it, shows that the diffraction intensities in-

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[8] Chiefly by Stewart and Skinner, Phys. Rev. **31**, p. 1 (1928); Stewart, Phys. Rev. **32**, p. 153 (1928).

[9] Stewart, Phys. Rev. **31**, p. 174 (1928).

[10] Stewart, Phys. Rev. **31**, p. 174 (1928).

[11] Stewart, Phys. Rev. **31**, p. 1 (1928).

dicate actual molecular arrangement. One could not get three such mean or average values for one liquid.

*Benzene, cyclohexane and their derivates.* The benzene and cyclohexane "rings" give unusually sharp diffraction intensity variations. There is at present a difference of interpretation of the measurements on these compounds and their derivatives. Krishnamurti[12] interprets his work as indicating the thickness of the ring for benzene to be about 3 Å.u. The author,[13] with a larger range of material, favors the view that benzene and cyclohexane have a thickness of 4.7 Å.u. and 5.1 Å.u. respectively, and corresponding areas perpendicular to the thickness of 31.4 Å.u. and 35.2 Å.u. The area of the former thickness agrees with crystalline determinations, but its thickness is much greater, 4.7 Å.u. as contrasted with 3.0 Å.u. in the crystal.[14]

The *o*−, *m*−, and *p*− drivatives of benzene and cyclohexane have decreasing thicknesses, the para compound beng the least. This has been shown only for five series of compounds. (See reference (12) ). The data are too meager for generalization.

*Solutions.* Krishnamurti[15] has investigated the cases of ammonium nitrate and acetamide in water, different kinds of sugar solutions, aqueous solutions of phenol, trimethyl carbinol, piperidine, glycerine, ethyl alcohol, lactic acid, pyridine and butyric acids. Hertlein[16] used aqueous solutions of butyl and amyl alcohol. Prins[17] studied the effect of heavy atoms dissolved in liquid. Banerje[18] investigated x-ray diffraction in liquid alloys of sodium and potassium. The results of all these observations lead us to understand that the investigations by means of x-ray diffraction emphasize differences in the nature of solutions. With one class of solutions, the diffraction maximum intensities do not correspond to those of the component liquids taken separately, but the solution seems to be a *new* space arrangement. Such liquids really hold each other in an intimate manner. Another class of solutions exist in which each of the two components shows its own intensity maximum, indicating an independent space grouping, each with its own kind. Then there are solutions which can be put in neither class. It is increasingly evident that the x-ray experiments do shed light upon the nature of solutions and will become an interesting method of their study. It has already shown that with some solutions the nature of the binding forces between the two components is similar to those existing in the crystalline structure of solid solutions.

*Effect of temperature.* So far as experiments have proceeded, the effect of increasing the temperature is very similar to that in the case of the crystal.

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[12] Krishnamurti, Ind. Phys. **3**, p. 275 (1929).

[13] Stewart, Phys. Rev. **33**, 889 (1929).

[14] There is no reason to doubt the measurements with either crystals or liquids. The effective diameter may be greater in the liquid and the differences of method may also cause a difference.

[15] Krishnamurti, Ind. Jl., Phys. **2**, p. 501 (1928) and **3**, p. 209 (1928) and **3**, p. 331 (1928).

[16] Hertlein, Zeits. f. Physik **54**, p. 341 (1929).

[17] Prins, Nature, p. 84, Jan. 19, 1929.

[18] Banerje, Ind. Jl. of Phys. **3**, p. 399 (1929).

There is a displacement of the intensity maximum, a diminution of the magnitude of this maximum and a broadening of the maximum peak in an intensity diffraction curve. This similarity to effects in a crystal adds weight to the conception of the cybotactic condition.

*Theory of x-ray diffraction in liquids.* There are two ways of approach to an adequate theory of x-ray diffraction in liquids. One is by assuming ideal systems, such as molecules each of which occupies a spherical space. The other approach is by the consideration of molecules that have asymetrical forces and occupy spaces not spherical. The former leads more easily to a mathematical expression. The latter is more descriptive of the actual case. Three theoretical contributions of the former type will be mentioned. Ehrenfest[19] considered the scattering produced by pairs of electrons separated by a distance $a$, and assumed the pairs to be independent. Thus his theory was applicable to gases only. Debye[20] considered the scattering in gases both with single scattering particles and pairs. He considered the results with the molecules vanishingly small and with them occupying a considerable portion of the total volume. Raman and Ramanathan[21] discussed liquids and the effect of thermal fluctuations of density and applied probability considerations to the liquid as a continuum. They assumed symmetrical molecules. Their theory is the one most applicable to a liquid and is in agreement with observations in several respects.

But the most direct approach to an understanding is the descriptive rather than the analytical theory and is presented in the introductory remarks. The foregoing results of computation from x-ray diffraction, varied in nature, seem clearly to give confidence in the assumption of the cybotactic condition in liquids in general and in the validity of the use of Bragg's formula.[22] There is undoubtedly a spatial arrangement of molecules so general that throughout the liquid at any instant can be found frequent, well ordered groups. Quantitative measurements, not here described, indicate that most of the liquid is effective in producing marked diffraction effects. In fact, the liquid will produce coherent diffraction practically as intense as the powdered crystal of the same material. This description is what one would always have naturally supposed, were it not for the kinetic heat energy. The equivalence of a continuum and acoustic waves is, however, a satisfactory assumption. We are to regard the cybotactic condition as a common one, and the forces involved more asymmetrical then even the shape of the space occupied by

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[19] Ehrenfest, Proc. Akad. Wet. Amsterdam **27**, p. 1184 (1915).

[20] Debye, Jl. of Mathematics and Physics **4**, p. 133 (1925) and in German in Phys. Zeits. **28**, p. 135 (1927).

[21] Raman and Ramanathan, Proc. Ind. Assoc. for Culti. Sci. **8**, p. 127 (1923).

[22] In using Bragg's Law with the foregoing determinations of effective diameters we are making two assumptions which must be borne in mind, though, for present purposes, they are nearly enough correct. We choose to regard the $d$, computed for the maximum in the diffraction intensity-angle curve, as the separation of diffraction centers, when the curve is really a statistical result. Also we have assumed a very simple picture of molecular arrangement in interpreting a given $d$ as the effective molecular diameter.

a molecule would lead one to believe. The theory from a descriptive view point, is then satisfactorily established.[23] On the analytical side, however, there is much room for improvement. In the meantime experiment in the field will add to our knowledge of molecular structure and the nature of solutions.

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[23] Krishnamurti, (in a very recent paper published in reprint form May 1, 1929, and to appear in Ind. Jl. of Physics, **3** 1929) goes a little further and indicates that the spatial arrangement is similar to that in crystals, in fact that "the planes containing the maximum number of molecules per unit area . . . . occur in the liquid approximately as they do in a crystal."