XRay Studies of the Molecular Arrangement in Liquids

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X-Ray Studies of the Molecular Arrangement in Liquids[1]

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An improved technique has been developed for taking x-ray diffraction photographs of weakly absorbing liquids. Photographs of water, heptane, decane, benzene and cyclohexane have been taken and several hitherto unobserved details have been discovered. The photographs of water have been mathematically investigated by the method of Zernike and Prins, and it was concluded that nearly every molecule has four others around it. No evidence was found either for the definite "quartz-like" arrangement or for the extensive degree of close packing which are postulated by Bernal and Fowler. With the organic compounds there was apparent in every case a striking resemblance of the outer parts of the photographs to electron diffraction photographs of the corresponding vapors. This is in agreement with Debye's prediction and argues for a relatively low degree of periodicity in the liquid structure. It has been shown further that the two outer bands which occur in the photographs of the normal hydrocarbons should appear whenever the molecules of the liquid consist largely of lengths of straight saturated hydrocarbon chain. Some discussion of the structure of the organic liquids has been given. In particular, a theory on the structure of liquid benzene has been postulated and found, using the method of Zernike and Prins, to predict with satisfactory accuracy the observed photograph. The viewpoint which has been found useful in the present discussions is that, to a predominating extent, adjacent molecules in the liquid are held together in very nearly the same manner as in the crystal, while, except for this, the arrangement is random.

INTRODUCTION

IN the interpretation of the x-ray scattering from liquids, different investigators have shown preference for different theories. Without at this place attempting a discussion of their relative merits, it may be pointed out that the physical pictures upon which they are based are not necessarily mutually exclusive. Their relative values must depend on the *quantitative* descriptions of these basic pictures. It appears that there is much to be gained by efforts toward a more quantitative interpretation of the x-ray diffraction photographs.

It is a great pity that much of the technique employed by investigators in the field has been so inferior to what is attainable as to fail to show all but the strongest, innermost bands, and, in some of the earlier work, even to introduce false effects. The outer detail of a picture may be weak merely because of the rapid decrease of the atomic scattering factor and the increasing contribution of the incoherently scattered radiation. For example, when the water picture is corrected for these, the second and third bands are comparable to the first (compare Fig. 3 with Fig. 4).

There are usually two important sources of error in making diffraction studies of liquids:

(a) Scattering from the glass tube or other container is superimposed on that from the liquid itself.
(b) The x-ray beam is not strictly monochromatic, but has a background of continuous radiation, the scattering of which is superimposed on that of the monochromatic rays.

In the present work they have been avoided by

(a) using a flowing cylindrical jet of the liquid, and
(b) using a rocksalt crystal monochromator.

APPARATUS AND TECHNIQUE

A vertical section of the camera (effective film diameter = 57.3 mm) and circulating system is shown in Fig. 1. A motor with reducing gear by compressing and releasing the rubber bulb A alternately fills the glass bulb B through the lower valve and empties it through the upper valve. The float valve serves to regulate the flow, always keeping a certain minimum amount of liquid around it. In order to make pictures of liquids at other than room temperature, these parts were made small enough to be enclosed completely in a 1-quart Dewar vessel, and the remainder of the circulating system was made with Dewar insulation (double walled, silvered and evacuated). As little as 20 cc of liquid can be circulated in this system. The liquid jet is 0.66 mm in diameter.

[1] Adapted from the dissertation submitted by the author to the Board of University Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
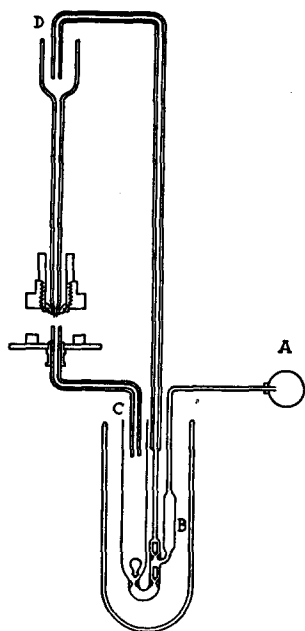
FIG. 1.

The film holder is a brass collar which can be strapped on to the camera, a rubber edging on the collar serving to make the joint air- and light-tight. Aluminum foil, 0.025 mm thick was always used over the film.

Copper $K\alpha$ radiation was used, obtained from a Seemann hot-filament x-ray tube[2] operating at 20 m.a. and 45 kv peak. In order to get effectively monochromatic radiation, the very compact Seemann monochromator-slit system was used, which contains a small excellent rocksalt crystal set for the (200) reflection. It was later found that the intensity of the reflections could be about doubled, without causing appreciable broadening, by polishing the crystal face,[3] so a polished crystal was used in all subsequent work.

A special design for the filament in the x-ray tube was used in this work in order to secure a uniformly intense beam through the slit. This is a problem which becomes important when a crystal monochromator is used, for, if the part of the focus which serves as the source of x-rays is not uniform, the sample will be exposed to a beam of corresponding non-uniformity. If

there is appreciable absorption in the sample, this can cause considerable error in the relative intensities at different parts of the photograph; Möller and Reis's absorption corrections,[4] which were used in this work, are based on the assumption of a uniform, parallel beam. The filament is shown in Fig. 2. It is made by winding the
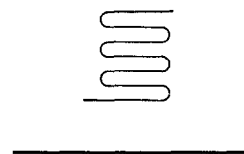

FIG. 2.

tungsten wire between the teeth of a small comb, specially made for the purpose, of small strips of thin sheet iron. In mounting the filament there was placed over the focusing tube a flat metal disk having a small rectangular hole into which the filament protruded. The effect is that of a flat surface, a small rectangular section of which emits electrons. The electrons move perpendicular to this surface, producing a small rectangular focal spot, which appears like a diffuse projection of the filament itself. Pinhole photographs showed very excellent spots, and films placed where the sample should be showed that the beam coming through the slit was very uniform.

It was found that the darkening which occurs on the films in the region of very small angular deviation could be avoided, for the most part, by replacing the air in the camera by a gas of less scattering power. A slow stream of helium was passed through the camera for this purpose, hydrogen not being used since it appeared to fog the films due to its reducing properties. For taking photographs of liquids at low temperatures, it was found necessary to dry the gas with phosphorus pentoxide and to close off C and D in order to avoid the condensation of ice on the liquid. For liquids near the boiling point it was found necessary to increase the rate of flow of the helium in order to sweep out the vapors. Even so, these pictures of hot liquids showed considerable darkening at small angles, and it is not certain whether this is purely the tempera-

[2] Purchased from the Seemann Laboratory, Freiburg i. Br.

[3] Others have observed similar effects. An example is given in Bragg and Bragg, X-Rays and Crystal Structure, p. 219, 1924. (London, G. Bell and Sons, Ltd.)

[4] H. Möller and A. Reis, Zeits. f. physik. Chemie A139, 425 (1929).

ture effect or whether an appreciable part of it was due to scattering by the vapor surrounding the jet. Considerable evaporation from the jet occurred in these cases, sometimes amounting to as much as 20 cc of liquid per hour. In order to conserve the substance, traps were inserted in the outgoing gas line.

The time of exposure was variable, depending on the purpose of the exposure. Ten hours sufficed for the weak, outer parts of the photographs. A set of comparison spots, made by exposing small sections of a strip of film for measured lengths of time, was made for every photograph and developed simultaneously with it. The films were photometered with a Moll microphotometer. As a rule, for all but the inner part of the film, a 5-mm horizontal strip of the film was photometered, in five 1-mm sections, the five curves being superimposed on the same piece of sensitized paper. For the inner part of the film, where the bands have appreciable curvature, a 3-mm strip was taken. This method of minimizing the effect of grain irregularities is simpler than the method of Richtmyer and Hirsch[5] (in which the film is constantly oscillated) and quite as effective.

MATERIALS

The liquids studied in this work were water, benzene, cyclohexane, normal heptane and normal decane. Some of the cyclohexane which was used was obtained from the Eastman Kodak Company, and some was made by the author by the catalytic hydrogenation of benzene. The two samples had the same refractive index and gave identical pictures. Both the heptane and the decane, which were of over 99 percent purity, were very kindly supplied by the American Petroleum Institute from their supplies at the Bureau of Standards.

STUDY OF WATER

In the case of water it was possible to check some of the results against a very similar, careful piece of work by Meyer,[6] who, also using a free jet and a crystal monochromator, took photo-
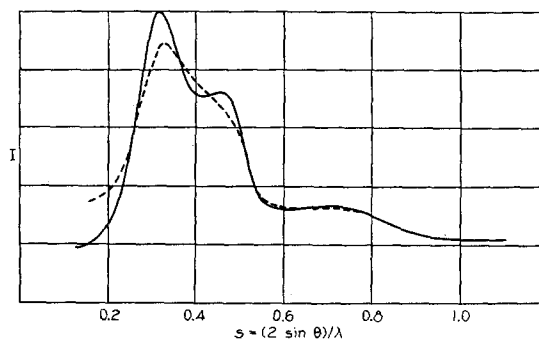

FIG. 3. Intensity curves for water at 3° (full line) and at 90° (dotted line). Corrected for absorption and polarization.

graphs of water between 3° and 40°. Amaldi[7] has also tried a crystal monochromator but, although he reports little advantage over the use of low voltage, filtered radiation, his published intensity curves differ somewhat from those of Meyer or of the present writer.

Pictures of water were taken at various temperatures between 3° and 90°. The intensity curves for the two extremes are given in Fig. 3.

Existing discussions of the water photograph

There are to be found in the literature a number of interpretations of the x-ray diffraction from water. First, it has been frequently pointed out that the position of the first band is in agreement with the hypothesis of a rough close packing of spherical molecules, the Keesom[8] relation being applied. Meyer, who first observed the second band, explained its appearance by pointing to the prevailing conception of water as an associated liquid. The disappearance of the second band with rise in temperature (which can be better described as a decrease in the intensity of both maxima and an increase in intensity between them) was correspondingly interpreted as due to the decrease in association. This interpretation was substantiated by the fact that the addition of salts, which should also break up association, had the same effect. Stewart, suggesting that "cybotaxis" should replace "association," explained the bands by postulating the existence of rough "planes," pointing out that the two strongest lines in the picture of powdered ice were not far from

[5] F. K. Richtmyer and F. R. Hirsch, Jr., Rev. Sci. Inst. 4, 353 (1933).
[6] H. H. Meyer, Ann. d. Physik 5, 701 (1930).
[7] E. Amaldi, Phys. Zeits. 32, 914 (1931).
[8] W. H. Keesom, Physica 2, 718 (1922).

the first two bands in the picture of water. The change in the photograph which occurs with rise in temperature he correspondingly explained as follows: "With temperature increase, the nature of the group changes, one set of planes becoming more poorly defined because of more slippage and less orderly arrangement. The alteration in grouping is also shown by the decrease in distance between planes."[9] This last sentence refers to the anomalous *outward* movement of the first band with rise in temperature.

There is, finally, the paper by Bernal and Fowler[10] which appeared about the time the present calculations were begun. As a starting point, they use the formula given by Zernike and Prins[11] for coherent x-ray scattering by an atomic liquid:

$$I(x) = KPF^2(x)\left\{1 + \mu \int_0^\infty 4\pi r^2[\rho(r) - 1] \right.$$
$$\left. \times (\sin xr/xr)dr\right\} \quad (1)$$

where r is the distance, in Angstroms, from the center of an atom.

$\rho(r)$ is the average density of atomic centers at distance r from the center of an atom. It is in arbitrary units; $\rho = 1$ corresponds to the average density throughout the liquid.

μ is the reciprocal of the atomic volume of the liquid, in atoms per cubic Angstrom.

$x = (4\pi \sin \theta)/\lambda$, where λ is the wave-length of the x-rays, in Angstroms, and θ is half the scattering angle.

$F(x)$ is the atomic scattering factor for the given value of x.

$I(x)$ is the contribution of the coherently scattered radiation to the total intensity for the given value of x.

P is the polarization factor $(1 + \cos^2 2\theta)/2$ when unpolarized x-rays are used, or $(1 + 0.723 \cos^2 2\theta)/2$ when using Cu $K\alpha$ x-rays reflected from a rocksalt crystal.

K is a constant.

By postulating a water structure somewhat analogous to the structure of quartz, and modified by some close packing, they synthesized a density function $\rho(r)$ which led, using this formula, to an intensity distribution curve resembling that of Fig. 3 except that the second maximum was much too weak. It may be pointed out that an examination of the density functions (p. 520 of their article) by which they represent the "quartz-like" structure and the "close packed" structure shows a great deal of arbitrariness in the selection of these functions. It is felt, therefore, that their choice of wording was perhaps unfortunate in its emphasis of the analogy to the crystalline structures.

The calculations to be presented here are more direct. Zernike and Prins[11] showed that, by a simple application of the Fourier integral theorem, the above equation could be solved for $\rho(r)$:

$$[\rho(r) - 1] = \frac{1}{2\mu\pi^2} \int_0^\infty x^2[E(x) - 1]\frac{\sin rx}{rx}dx, \quad (2)$$

where

$$E(x) = I(x)/KPF^2(x).$$

The absolute value of I is not known in these experiments. E, however, is determined by placing it equal to unity for large values of x, since the value of the integral in (1) approaches zero with increasing x. Debye and Menke[12] have already applied this formula to obtain the ρ-function for liquid mercury and liquid gallium. Amaldi[7] actually tried it for water but, upon getting a geometrically impossible ρ-function, concluded that there is too much "relative orientation" of the molecules in water for the method to be applicable.

Sources of inaccuracy

There are, indeed, several reasons why it is much more difficult to apply in the case of water than in the case of mercury or of gallium, the trouble lying in the accurate determination of the E-function. To begin with, the contribution of the incoherently scattered radiation to the total intensity is far more important in the case of a light compound like water than in the case

[9] G. W. Stewart, Phys. Rev. **35**, 1426 (1930).
[10] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933). The author wishes to acknowledge the influence of this paper in the following discussion.
[11] F. Zernike and J. A. Prins, Zeits. f. Physik **41**, 184 (1927).

[12] P. Debye and H. Menke, Phys. Zeits. **31**, 797 (1930); H. Menke, Phys. Zeits. **33**, 593 (1932).

of these heavy metals. Thus, for water, the incoherent scattering is about half the total at about $x=5$. There is, in addition, the fact that the F-curves for the lighter elements fall off so rapidly with x that small inaccuracies in the I-curve are much magnified in the E-curve. It might be pointed out further, in this connection, that the F-curves are less accurately known for the light elements than for the heavy ones. There is also the fact that the experimental intensity curve extends to only a finite value of x whereas the integral must be extended to infinity. Meyer used molybdenum radiation in addition to copper radiation, making available for these calculations a part of the curve somewhat past that shown in the figure. The remainder of the curve must be considered, for the purpose of these calculations, to be flat. There is, finally, the difficulty to which Amaldi referred, namely, that in using the factor F_{H_2O} it is assumed that the liquid consists of H_2O units in which the electron distribution has spherical symmetry. Accordingly, the formula is not so correctly applicable in the case of water as in the cases which Menke investigated. Nevertheless, it is felt that the lack of rigor introduced by this is not more important than the practically unavoidable difficulties mentioned above. For, firstly, if the structure of water resembles that described in the work of Stewart, Bernal and Fowler, or the present writer, the structural unit may be considered, in place of a bent H_2O molecule, as an oxygen atom approximately tetrahedrally surrounded by four half-hydrogens, the electron distribution of which is much more nearly spherical. Moreover, the effect of the dissymmetry due to the hydrogens would be small except at small angles.

It would appear, then, that the accuracy of the E-curve, as worked out purely from experimental data, leaves much to be desired. There exists, however, an important criterion for the correctness of an E-curve, namely, that the ρ-function calculated from it must be zero for all values of r less than the atomic diameter. The problem, accordingly, consists of finding an E-curve which (a) leads to a ρ-function which is approximately zero for $r<2.5A$, and (b) within the limits of uncertainty explained above, corresponds to the experimental intensity curve.
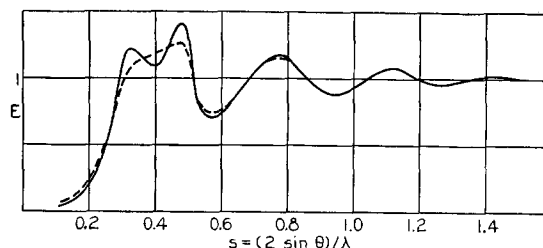

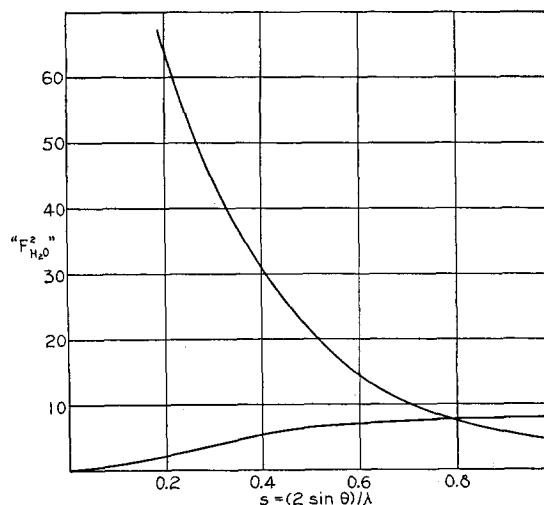FIG. 4. E-curves for water at 3° (full line) and at 90° (dotted line).

FIG. 5. Coherent and incoherent scattering by water. Incoherent scattering calculated for $\lambda=1.54A$.

Fig. 4 shows the curve adopted. It fulfills the first condition quite satisfactorily—ρ does not differ from zero by more than 0.25 near $r=0.5A$ and by more than 0.05 near $r=2A$. This is approximately the tolerance allowed in Menke's work also. Concerning the second, it corresponds to Fig. 3 when using the curves for incoherent and coherent scattering shown in Fig. 5. The curve for incoherent scattering was calculated by applying the modified Wentzel formula[13] to the f-values for H and O given by James and Brindley.[14] The curve for $F^2_{H_2O}$ is almost exactly the same as that of James and Brindley for $O^=$.

We have, of course, no way of proving that the curve which was adopted is the correct one, or the only possible one; it seemed, however, during the course of the trials which led to it, that any curve which satisfies the two conditions

[13] E. O. Wollan, Rev. Mod. Phys. 4, 206 (1932).
[14] R. W. James and G. W. Brindley, Phil. Mag. 12, 81 (1931).

stated above must differ but slightly from the curve adopted.

TECHNIQUE OF THE CALCULATIONS

The integrations were performed graphically, using a thin graph paper. A set of $\sin rx/rx$ curves was prepared, each on a separate sheet, for values of r differing by 0.2A. On another sheet was constructed the $x^2[E(x)-1]$ curve. By placing one sheet on the other, with a third sheet above, taking care to have the rulings coincide, and placing upon a glass plate illuminated from below, corresponding ordinates of the two curves could be readily picked out and their products plotted directly on the upper sheet. The area under this third curve is proportional to the desired integral. Where a harmonic analyzer is available, the work can be performed in much less time and with much less tedium.

THE STRUCTURE OF WATER

The ρ-function for water at 3°, calculated in the manner described above, is plotted in Fig. 6. The first peak occurs at about $r=2.9$A and the following maximum is at $r=4.5$A. The first two minima are at $r=3.4$A and at $r=5.7$A. The value of $\int 4\pi r^2 \rho(r)dr$ extended under the first peak (as far as 3.4A) corresponds veiy nearly to four units; i.e., *each oxygen atom has, on the average, about four nearest neighboring oxygens.*

It is, of course, to be realized, in seeking to visualize a structure of water which is in agreement with the ρ-curve, that the information given by the curve is of a rather indefinite nature. For example, it does not tell whether every oxygen has four nearest neighbors, or whether some have three while others have five, nor does it tell the relative orientations of these oxygens. It is apparent, however, that it is possible to describe in a rough way a simple and reasonable structure which seems in agreement with the curve. For if, in water, each oxygen is surrounded by four others, not in a tridymite-like (tetrahedral), or quartz-like, or, indeed, in any very regular manner, the corresponding ρ-curve would have the characteristics of that which has been calculated, and the density of water would be very close to that which is ob-
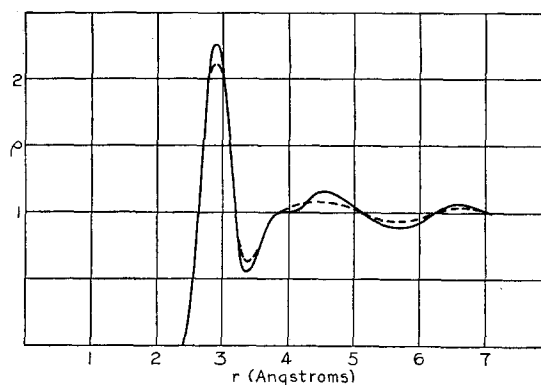

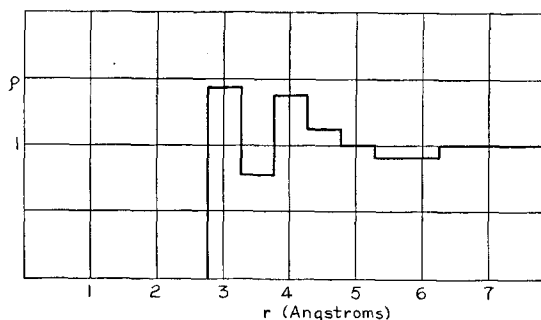FIG. 6. ρ-curves for water at 3° (full line) and at 90° (dotted line).

FIG. 7. Bernal and Fowler's ρ-curve for water at 3°.

served. (Fig. 7 shows approximately the ρ-curve of Bernal and Fowler. There is only a suggestion in the present results of the strong maximum at $r=4$A which is due to their postulated quartz-like structure.)

What has been described here is, in the most general terms, merely a broken down ice structure. In ice it appears that each oxygen is tetrahedrally surrounded by four others, with the hydrogens on or near the center lines between adjacent pairs of oxygens.[15] If water had a structure in which each oxygen were tetrahedrally surrounded by four equidistant hydrogens and each hydrogen were on the center line between a pair of oxygens, but in which there were otherwise random orientation about the hydrogen bonds (comparable to vitreous silica), the ρ-curve would have a very strong peak at $r=4.5$A and would be very low in the region

[15] Peculiarities in the crystallography of ice and in the dielectric properties are probably to be ascribed to the anomalous properties of the hydrogen bond between oxygens rather than to an essential error in this picture.

between the two peaks. Now, although the ρ-curve has a maximum at $r = 4.5$A, it is not nearly so sharp nor so strong as it would be for the above case, and between the two peaks it has only a narrow minimum instead of being nearly zero over the whole range. The most obvious modification of the above picture in order to account for the differences in the ρ-curve and also to account for the density is to suppose that the O–H–O angle is not necessarily 180° but can have any value between 180° and, say, 150°. (Or, since the scattering of x-rays by hydrogen is neglected, an equivalent supposition is that the H–O–H angles are now no longer the tetrahedral angle (109.5°). Both effects probably exist.)

In this development, for simplicity of the visualization, the hydrogens were considered as equally held between pairs of oxygens. If, as seems more nearly true, definite H_2O units exist, the description must be given as follows: The molecule may be considered as a tetrahedron, the oxygens being at the center, positive charges (hydrogens) at two of the vertices, and concentrations of negative charge (electrons) at the other two vertices.[10] Then the liquid is considered to have a continuous structure, in which each hydrogen of a molecule is in close proximity to one of the concentrations of negative charge in another molecule, while, except for this, there is no very distinctive relative orientation of the molecules.

A ρ-function corresponding to the x-ray photograph of hot water (90°) was separately worked out (Fig. 6). The essential difference between it and the one for cold water is that the outer details are about half as pronounced. The size of the first peak is not noticeably different. Thus, the predominating feature of the arrangement at 90° is still the four-coordination, although the randomness is otherwise greater than at 3°.

The decrease in the density of water on approaching the freezing point may be due to some peculiar arrangement which exists to too small an extent to show on the photographs. It seems more reasonable, however, to suppose that it is due merely to the increasing tendency for the O–H–O angles to approach 180° as the heat motion becomes less violent.

It is of some interest to inquire whether the ρ-curves of Fig. 6 and the above interpretations

support, or are compatible with the theory of cybotaxis. The question would appear difficult to answer in view of the difficulty in constructing and examining three-dimensional models which would correspond to the curves. To the present author, however, it appears likely, in view of the lack of sharpness of the maxima and minima in the ρ-curves beyond the first, that cybotactic planes can have no very clear existence in the arrangement. It is believed that there is little, if any, distinct periodicity, and, in any case, it should be considered as incidental; the characteristic of the structure which is mainly to be stressed is the relative arrangement of nearest neighbors.

STUDY OF n-HEPTANE AND n-DECANE

Photographs were taken of normal heptane at $-50°$ and at 80°. A comparison of the intensity curves (Fig. 8) illustrates the typical temperature effects—inward displacement and broadening of the strong band and increase in intensity at small angles. The first band is well known, appearing in nearly the same position for all the liquid normal paraffins and higher alcohols. The two outer maxima, at $s = 0.46$ and at $s = 0.81$ had not been observed before for n-heptane, so it became a matter of great interest to determine whether, like the first maximum, these were also to be found with the other liquid normal paraffins. Accordingly, some n-decane was procured and a picture taken, at room temperature, the picture turning out to be practically identical with that of n-heptane. It appears, however, that this observation is not altogether a new one. When Stewart reported the x-ray scattering from the normal paraffins, he mentioned the appearance of both of these outer bands in the cases only of tetradecane and pentadecane, but seemed uncertain as to whether the accuracy of the experiments warranted their recognition. More recently, electron diffraction work[16] has shown that these two outer maxima also occur in the pictures of various oils.

The first band has already been thoroughly discussed in the literature. It is characteristic of closely packed parallel hydrocarbon chains. Concerning the third maximum, at $s = 0.81$,

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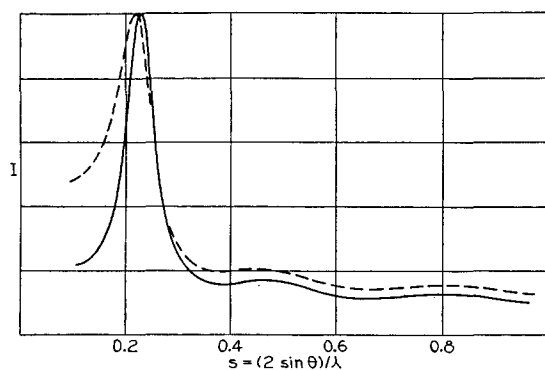[16] L. R. Maxwell, Phys. Rev. **44**, 73 (1933).

FIG. 8. Intensity curves for *n*-heptane at $-50°$ (full line) and at $65°$ (dotted line). Corrected for absorption and polarization.
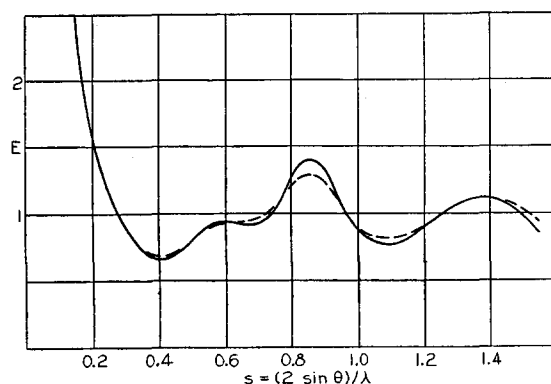

FIG. 9. Calculated *E*-curves for gaseous $C_{14}H_{30}$ (full line) and C_5H_{12} (dotted line).

Stewart has noticed that the corresponding interplanar distance, as calculated from Bragg's law, is about equal to the periodicity of the carbon atoms in the direction of the hydrocarbon chain axis, so he has correspondingly suggested that the molecules are arranged in such a manner as to form planes of carbon atoms perpendicular to the direction of the molecule axis.

There is, however, a matter of great importance not mentioned in the above, namely, that the two outer maxima are in the same positions as the maxima observed by Wierl[17] in his electron diffraction pictures of gaseous normal paraffins. Wierl took pictures only of *n*-pentane and *n*-hexane, but it is apparent from the theory of x-ray scattering by gases that the higher ones would have the same characteristics. (Fig. 9

shows calculated *E*-curves for plane zigzag chains of five and fourteen carbons, where the C–C distance is 1.54A and the angles are 109.5°; the two curves are almost identical.) In fact, these maxima would appear whenever we have molecules consisting largely of lengths of saturated hydrocarbon chains, as in the case of the oils which Maxwell investigated. This recalls Debye's conclusions that only the inner bands are to be ascribed to intermolecular arrangement, while the outer details are the same as those of the gas.[18] Accordingly, the facts would seem to suggest that, except for the parallel orientation of the molecules, there is extensive disarrangement in the liquid. The recent calculations of Warren are fully in accord with this view.[19]

STUDY OF BENZENE

Photographs of benzene were taken at 8° and at 65°. The typical temperature effect is again apparent in the comparison of the two intensity curves (Fig. 10). All of the bands in the benzene picture have been observed before without the use of a crystal monochromator, although not all, apparently, by any one observer.

There is in the literature some discussion of the benzene picture. Stewart[20] supposes that in liquid benzene the structure is characterized by the parallel orientation of flat benzene rings, and the distance between the rough planes so formed is given, using Bragg's law, by the position of the first, strong band. This gives the interplanar distance, or the thickness of the ring, as 4.7A. Katz[21] is more concerned with the weak band just outside the strong one and calculates from it, also assuming parallel orientation of the rings, the thickness of the rings to be about 3.6A. The first band is, then, to be explained by using Keesom's equation, assuming that the packing is mainly a random one. Eastman[22] has been tempted to compare the x-ray picture of the powdered solid with that of the liquid. The agreement is not good. The

[17] R. Wierl, Ann. d. Physik 8, 521 (1930).

[18] P. Debye, M. I. T. J. Math. and Physics 4 (1925).
[19] B. E. Warren, Phys. Rev. 44, 969 (1933). In fact, from the point of view of his calculations, had he not neglected the inner details when subtracting the $4\pi r^2\rho$ curve from the *g*-curve (p. 971 of his article) he would have been in position to predict the two outer bands.
[20] G. W. Stewart, Phys. Rev. 33, 889 (1929).
[21] J. R. Katz, Zeits. f. angew. Chemie 41, 329 (1929).
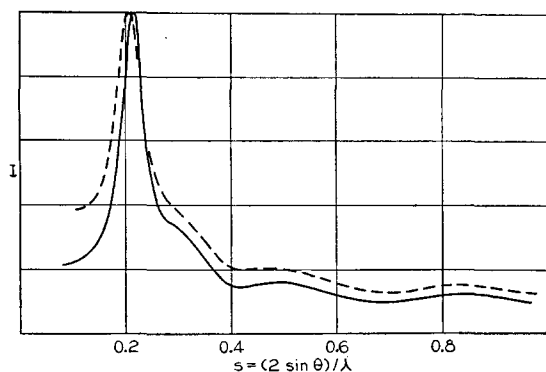[22] E. D. Eastman, J. Am. Chem. Soc. 46, 917 (1924).

FIG. 10. Intensity curves for benzene at 8° (full line) and at 65° (dotted line). Corrected for absorption and polarization.
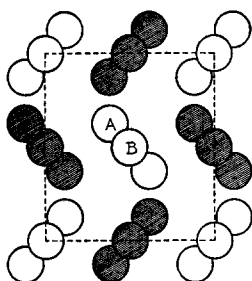

FIG. 11. The unit cell of benzene (orthorhombic); $a = 7.44A$, $b = 9.65A$, $c = 6.81A$. The hatched molecules are half the b distance below the plane of the others.

FIG. 12. ρ-curve for benzene.

FIG. 13. E-curve for benzene as calculated from the ρ-curve of Fig. 12.

position of the strong band in the liquid picture differs from that of the strongest powder line by about five percent, the powder line corresponding to the *larger* spacing, whereas the implied looseness of the liquid structure should require the opposite. There is no striking resemblance at all between the remainders of the photographs.

The calculation of the ρ-function from the x-ray diffraction photograph by means of Eq. (2) is subject to the same difficulties which were discussed for the case of water and which, in fact, enter here to an even greater extent. It was accordingly thought more desirable to proceed from the opposite direction; i.e., by hypothesizing that the influences which determine the crystal structure still exist in the liquid extensively enough to determine roughly the relative arrangement of adjacent molecules (the idea here being similar to that with water), to prepare a ρ-function and see if it led, by Eq. (1) to an E-curve in agreement with the experimental curve. In Fig. 11 is shown the unit cell
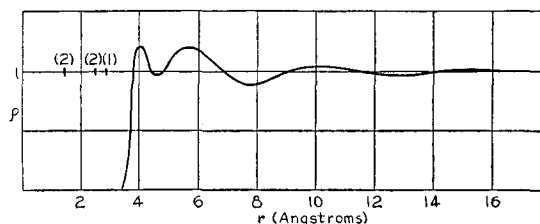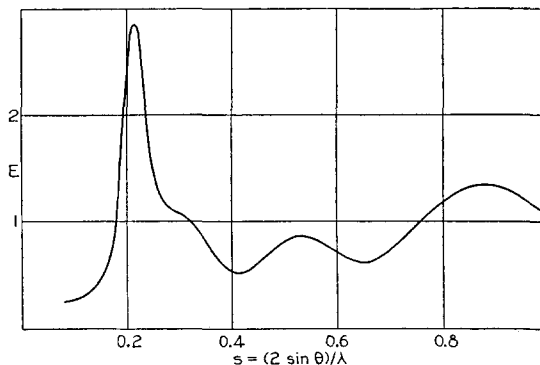
of crystalline benzene, as determined by Cox.[23] It is admittedly not in thorough agreement with the observed intensities of reflections and, in addition, suffers from the defect common to many organic crystal structure determinations, that the positions of the hydrogens, which are of major importance in the molecular arrangement, are mainly to be inferred from the positions of the carbons. An examination of this structure shows that carbon atoms like "A" have six neighbors at a distance of 3.85A, four at 4.10A, and four at 4.35A, while atoms like "B" have four at 3.85A, four at 3.95A, two at 4.20A, and two at 4.35A. The prominence of C–C distances of about 3.9A is very striking. Without proposing a detailed theory of the liquid structure, one may suppose that the crystal forces still exist in the liquid extensively enough to preserve this prominence of the smallest C–C distance.

It was remarkable that the first ρ-curve which was tried gave essentially the desired result. Fig. 12 shows the finally adopted curve, which differs only in minor details from that which was first tried. The peak at $r = 4A$ corresponds to an

[23] E. G. Cox, Proc. Roy. Soc. A135, 491 (1932).

average concentration of about eight atoms at this distance. The value of r (5.5A) for the position of the next peak was taken as the average distance between other than adjacent carbons of neighboring molecules (adjacent carbons being already represented in the first peak). In Fig. 13 is shown the E-curve which was calculated from this, and which corresponds (using James and Brindley's table for F_C) with the experimental intensity curve.

Incidental items of the calculations

While recognizing that relations between the ρ- and E-curves exist, in a rigorous sense, only between their wholes, it became apparent, during the calculations with benzene, that the following relations between certain of their characteristics could be more or less definitely identified:

(a) The first, strong peak of the E-curve is associated mainly with the strong maximum in ρ at $r=5.5A$, the minimum which follows it, and the minimum between $r=3A$ and $r=4A$. A similar sequence of nearly equally spaced maxima and minima would be characteristic of any liquid having small molecules relatively widely separated. This is apparently the foundation for Keesom's relation.

(b) The bulge at the bottom of the first strong peak of the intensity curve is due to the sharp rise in ρ at $r=4A$. It could appear in approximately this position whenever there exists in the liquid a predominance of interatomic distances of about 4A. One can, accordingly, explain the fact that Katz has observed it in the photographs of many simple benzene derivatives by suggesting that there is a tendency for this feature to be preserved in any arrangement of benzene rings.

(c) The two outermost maxima are due to the atoms at $r=1.42A$, 2.48A, and 2.84A, the interatomic distances within the molecule itself. The second of these maxima is in the same position as the one found by Wierl for the gas.[17] The first, however, is at a slightly larger value of s than is the corresponding maximum of the gas picture. It became clear, however, during the above calculations, that this shift is an effect of the remainder of the ρ-curve; this value of s is not so large that the intermolecular arrangement is negligible. It may be noticed, however, that in

the higher temperature picture, the minimum which precedes it is weaker and there is a corresponding shift of this maximum toward that of the gas.

Rumpf[24] has also observed the outermost maximum, in the same position (although his curve shows a much narrower and sharper peak than does the one here given). He has calculated from its position that the C–C distance in benzene is 1.36A. The question here is mainly what F-curve to use. The calculations were repeated, using James and Brindley's more recent curve, which falls off much less rapidly in this region than does the curve used by Rumpf, and also taking into account the slowly rising curve for the incoherent scattering. A distance of 1.42A was found to be in closest agreement with the observed position of the maximum.

STUDY OF CYCLOHEXANE

Diffraction photographs were taken of liquid cyclohexane at 8° and at 65°. The intensity curves are given in Fig. 14. The first band seems to be the only one as yet mentioned in the literature. Because of its sharpness, the effect of the finite width of the jet on its shape was investigated. The effect was, however, found to be small, the correction being, for the low temperature picture, an increase in peak intensity of about five percent and the same decrease in width. The third and fourth maxima are in approximately the same positions as those found by Wierl in the electron diffraction from the gas.
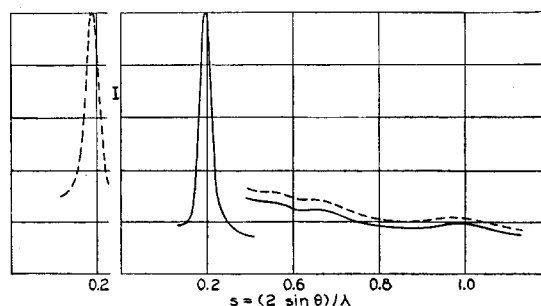

FIG. 14. Intensity curves for cyclohexane at 8° (full line) and at 65° (dotted line). Corrected for absorption and polarization. The ordinate scale for the outer parts of the curves is doubled.

$s = (2 \sin \theta)/\lambda$

[24] E. Rumpf, Ann. d. Physik 9, 704 (1931).

The crystal structure of cyclohexane is not known. Hassel and Kringstad[25] have, however, shown it to be cubic ($a_0 = 8.41A$, four molecules in the unit cell) and have shown its space group to be probably T_h^2 or O_h^4. This is of some interest in view of the general belief that the liquid structure is characterized by parallel orientation of the rings, the thickness of the ring being, from the position of the strong band, about 5.1A. Since the arrangement cannot be of such a type in the crystal, since it is cubic, it is very probable that there is no great tendency for parallel orientation in the liquid either.

THE SOLUTION OF CYCLOHEXANE AND BENZENE

Ward[26] has found that in the x-ray scattering from a solution of cyclohexane and benzene, the two main peaks for the pure components were both present. The simplest explanation, which he presented, is that we have here, not a random distribution of the two kinds of molecules, but

an emulsion of one liquid in the other. It may be pointed out that, even if we accept an explanation of this nature, it is unnecessary to assume the existence of aggregates so large that "emulsion" is more applicable than "association." If we should assume the existence in the solution of aggregates of only a few (hardly more than ten) cyclohexane molecules, arranged as in pure cyclohexane, calculations such as have been presented in this paper would undoubtedly be in accord with the experimental observation. The carbon atoms in the interior of the group would be surrounded very nearly as in the pure liquid; the atoms at the surface of the group would be less nearly so surrounded; it appears not at all unreasonable to suppose that the average ρ-function for the carbon atoms of such a small aggregate would sufficiently resemble the ρ-function for pure cyclohexane to account for the appearance of an intensity maximum in approximately the same position as the strong band of the pure liquid.

The author acknowledges with pleasure his debt of gratitude to Dr. Emil Ott for suggesting this work and for his aid during its progress.

[25] O. Hassel and H. Kringstad, Tidsskrift f. Kjemi og Bergvesen 10, 128 (1930); C. A. 25, 1500 (1931).
[26] H. K. Ward, J. Chem. Phys. 2, 153 (1934).

The Ultraviolet Absorption of Methane

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The absorption spectrum of methane from 1450A to 850A is found to be entirely continuous and all excited states up to the first ionization potential are repulsive.

THE absorption spectrum of methane in the Schumann region was photographed first by Leifson[1] using a small vacuum grating spectrograph and an uncondensed discharge in hydrogen as a continuous source. He found six bands at low pressures all below 1558A. Rose,[2] using the same source and a small prism instru-

ment, was unable to find these bands, and suggested that Leifson's bands were merely gaps in the band spectrum of hydrogen, which appears with great intensity in such a source. The object of the present work was to photograph the spectrum under greater dispersion and resolving power, using a source which gave a true continuum in the region in question and to extend the spectrum to shorter wave-lengths, below the Schumann region.

[1] S. Leifson, Astrophys. J. 63, 87 (1926).
[2] A. Rose, Zeits. f. Physik 81, 758 (1933).