STRUCTURE OF LIQUIDS AND SOLUTIONS

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As we focus our attention on the liquid state and on solutions, I shall make a few comments on the relation of the liquid state to the gaseous and solid states of matter. The space in a system constituting a gas is sparsely occupied. Owing to their thermal energy, the molecules of a gas are in continual motion and collide occasionally with one another and with the walls of their container but rebound without loss of energy to the system. Because of the near-independence of the particles of a gas, a gas can expand to an unlimited volume. Thus, the distinctive feature of the gaseous state is that its particles (atoms or molecules) are substantially independent of each other except for occasional collisions.

A primary property of a liquid is that it occupies a certain amount of space; it has a definite density at a given temperature and pressure. The particles of a liquid are close enough to be in contact with one another. In contrast to the gas, the attraction of one molecule to its immediate neighbor is high and, when a liquid is poured, it maintains a constant volume. Furthermore, the molecules in a liquid do not have particular partners as they do in solids, and this irregularity allows a greater degree of tolerance in molecular arrangement. Thus, the liquid state is characterized by its irregularity or indefiniteness in molecular arrangement.

If one could use an experimental technique which would be on an observational time-scale small enough, the measured properties of a liquid would likely match those of a solid. One experimental observation which supports this prediction is that ultrasonic waves of a sufficiently high frequency can set up shear waves in liquids as they do in solids. Also, it has been shown by neutron beam diffraction that a molecule in a liquid has time to vibrate 10 to 100 times before the structure changes. In this short time-scale the structure of the liquid is physically but not geometrically like that of a crystal.

If the thermal agitation of a liquid is reduced to a point where it is insufficient to break the attractive forces between molecules, then at temperatures below this, bonds between molecules are permanently maintained and collections of molecules take on a rigidity, thus giving the system a bridgework of bonds. The pattern of such a framework may be random or ordered; the ordered arrangement is the one of lesser energy and, therefore, tends to develop. The ordered arrangement is, of course, the crystalline state. Thus, the dominant feature of the crystalline state, in contrast to the gaesous and the liquid states, is the bonding forces between its molecules that give this state its orderly arrangement. Thermal agitation tends to disturb this order in the solid so that, when the temperature is high enough and the average thermal energy of a molecule exceeds its bonding energy, the molecules escape from one another's influence and the solid melts.

Another interesting difference between solids and liquids is that the melting point of a pure solid, which does not show liquid crystallinity, is sharp; however,

a liquid cooled through the freezing point with appropriate precautions does not solidify, nor do its properties change greatly in passing through the temperature at which it normally freezes. A conclusion one might draw here is that the solid and liquid are alternative ways of arranging molecules. When a crystal is heated short of the melting point, the atoms increase their vibration and move farther apart but do not change partners. On the other hand, a liquid upon being heated shows a change in identity and number of neighbors about a reference molecule. Thus, a liquid may be described as a continuous series of phases, each "stable" at a particular temperature.

From these few remarks about the properties of liquids and solids one might conclude that a liquid near its freezing point has a structure which is not very different from that of a solid. At this point there must be about the same number of molecules surrounding a reference molecule in the liquid state as there are when the material is in the solid state. In characterizing the three states of matter, one can say that crystalline solids have regular and coherent structure; liquids have irregular and coherent structure; and gases have irregular and incoherent structure.

In much of the vast literature on the liquid state there has been an effort to explain the thermal, mechanical, and other properties of liquids. The results of these studies have brought little success in accounting for the structural character of the liquid state when one considers, in a relative way, the successes of the molecular theory of gases and of the lattice theory of crystalline solids. This lack of success evidently lies in the fact that it is extremely difficult to construct a model of the liquid state which corresponds to its structure and at the same time to have a model which yields itself to mathematical computation.

A number of theories of liquids have been proposed. These are the kinetic multiple contact theory of Kirkwood (1935, 1939, 1946) and of Born and Green (1946); the cell theory of Lennard-Jones and Devonshire (1937, 1938); the cybotactic hypothesis of Stewart (1930); and the hole theories of Frenkel (1946), of Eyring (1936), Eyring and Hirschfelder (1937), and of Furth and his coworkers (1939, 1941). The last three theories assume that a large part of the liquid has a crystalline arrangement, which is in contradiction with the experimental facts that liquids lack a long-range order.

None of the theories mentioned above have made much use of the experimental evidence that has accumulated, or is accumulating, on the actual molecular structure of liquids and solutions. The first papers on the structure of liquids by x-ray methods are the classical studies of Prins (1935), of Stewart (1930) and of Morgan and Warren (1938). These early papers have been followed by a number of others on the structure of liquids, such as, neutron diffraction of liquids (Thewlis, 1950), structure of solutions (Brady, 1958a, b; Brady and Krause, 1957; Strauss, 1960; Ritter, personal communication), and the structure of formamide (Brown and DeSando, unpublished) by the x-ray method and by the microwave technique (Costain and Dowling, 1960). All data show liquids and solutions possess short-range order. This short-range order is practically limited to molecules in the first, second, and third spheres around a given molecule; i.e., beyond two or three molecular diameters the arrangement in one place in the liquid has no effect on that in another.

Many attempts have been made to explain the structure of ionic solutions. Some of the big advances in recent years in our knowledge of these systems come from classical papers such as those by Debye and Hückel (1923a, b) and by Mayer (1950). Much of the early evidence relative to the structure of solutions is based on such measurements as conductance, viscosity, boiling point, and freezing point. The use of x-rays to study the structure of solutions is relatively new. Stewart (1939) made some attempt to use x-rays in the study of the structure of ionic solutions and concluded that the electrostatic field of the ions broke down

the tetrahedral structure of water. Prins (1935) made some observations on how the x-ray diffraction patterns of solutions could be correlated with various structural elements of the solution. He assumed that the x-ray scattering in a solution was due to (1) the water structure, (2) the water-ion structure and (3) the ions alone. Bernal and Fowler (1933) concluded the effect of ions in solution was to either increase or decrease the structural regularity of the solution depending on whether the ions were solvated or unsolvated. Several workers have carried out radial distribution functions for a number of solutions including sodium hydroxide, hydrochloric acid, and phosphoric acid (Finbak and Bastiansen, 1943; Devik et al., 1944; Bastiansen and Finbak, 1944). Apparently the resolution of the distribution functions was not good enough for them to attempt to draw any quantitative results from their data. Brady has studied the structure of lithium chloride (1958a), potassium chloride (Brady and Krause, 1957), potassium hydroxide (1958a), and iron(III) chloride (1958b) solutions. Ritter (personal communication) has studied the structure of barium iodide solutions.

Since my students and I have used x-ray methods in some of our studies, I shall focus our attention on the knowledge of the structure of liquids and solutions which can be gained from the experimental and theoretical procedures of x-ray diffraction. Occasionally, other experimental methods will be mentioned to supplement the evidence from this method.

This paper is a general review, written for an audience representing different scientific disciplines, and the details of the theoretical aspects of the x-ray method have been omitted; only the results of the findings are discussed. The interested reader may find the theory described in many of the references cited at the end of this article.

Instrumentation

Let us take a very brief look at the experimental practices of x-ray methods. Details of the equipment used for x-ray studies may be found in many standard textbooks and monographs on the subject. It will suffice here to say that there are two common types of instrumentation available for x-ray diffraction studies. The simplest and least expensive type is to record the x-ray diffraction pattern on photographic film, using a powder camera. A more elaborate method is to detect the diffracted radiation by means of a quantum counter, such as a Geiger or scintillation counter. The latter instrumentation is the better of the two for the study of liquids and solutions because one can get better curve fitting and, thus, better peak resolution in the radial distribution curve.

Diffracting Power of Atoms

When an atom is exposed to electromagnetic radiation, the electrons are accelerated, and they radiate at the frequency of the incident radiation. At optical frequencies the superposition of the waves scattered by individual atoms results in ordinary optical refraction. When x-rays strike an atom they are diffracted by the cloud of electrons forming the outer part of the atom. A schematic representation of the scattering of x-rays by atoms is given in figure 1. The diffracting power of an atom is determined by the number of electrons in the atom. Atoms such as iodine and lead, which have high atomic numbers, are higher in diffracting power than atoms such as carbon and oxygen, which have low atomic numbers. Therefore, in studying any material one can expect better diffraction patterns from large atoms than from small ones. If one is working with liquids or solutions in which there is short-range order, the choice of a system with large atoms, or at least some large atoms, will result in a better diffraction pattern than would be obtained from a system composed of only small atoms.

Periodic Repetition of Atoms

A pure chemical substance has the fundamental feature that all of its atoms or molecules are duplicates of all other atoms or molecules in the substance. From the viewpoint of geometry each atom or molecule is a copy of some arbitrarily selected reference atom or molecule of the mass. When this reference unit is repeated systematically, a periodic pattern exists. In nature this periodic repetition is found in one, two, or three dimensions. A systematic study of repetitive patterns shows that there are two types of purely one-dimensional patterns, 17 types of purely two-dimensional patterns, and 230 types of purely three-dimensional patterns.

The crystalline solid with its periodic repetition in three dimensions reveals its structure very easily through the use of x-ray. The x-rays, whose wavelength is comparable to the lattice spacing of the atoms in a crystal, will be diffracted under certain conditions. W. L. Bragg explained the characteristics of the diffracted beam by a simple model in which he assumed that the x-rays are reflected from the atoms which are periodically arranged in the crystal. The diffracted beam is found only in those special situations where the reflections from atoms arranged
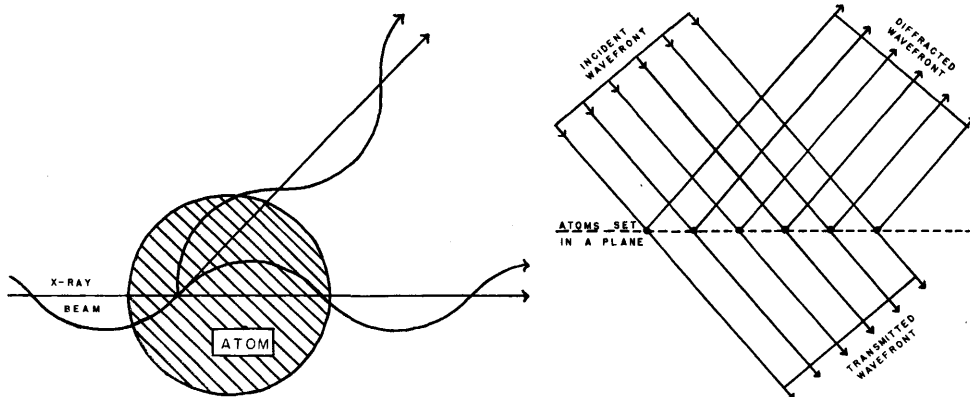

FIGURE 1. (Left) Scattering of x-rays by an atom.
FIGURE 2. (Right) Schematic diagram to show reflection and transmission of x-rays by atoms set in a plane.

in parallel planes interfere constructively. If a train of x-rays whose wave front is perpendicular to the direction of propagation is scattered by an array of atoms, the scattered x-rays interfere with each other except when they are in phase, i.e., when the difference between the wavelength of the scattered rays by different atoms is zero or a whole number of wavelengths.

Because of the great penetrating power of x-rays, a single atom cannot reflect a large fraction of the incident x-rays; many of the rays are transmitted through a single atom. This statement can be illustrated schematically as shown in figure 2. As can be seen in this diagram, the distance from the original wave front to an atom and on to a new wave front is the same for all atomic locations for the atoms set in a given plane. The directions of the wave fronts are either a continuation of the beam (transmitted beam) or a reflection of the beam (diffracted beam). In order to get the resultant reflection, the partial reflection from many atoms, periodically arranged, must be added. In order for these reflections to be constructive, each reflecting layer of atoms must be an integral number of wavelengths longer than the one immediately above it. This is illustrated in figure 3, where A'B'C' is an integral number of wavelengths longer than ABC and, therefore,

constructive interference of x-rays results. The difference in the lengths of the paths followed by these two rays is $n\lambda$.

So much for the crystalline solid which, by its periodic arrangement of atoms, gives a series of sharp rings in its diffraction pattern. A diffraction pattern of sodium chloride crystals is shown in figure 4(A).
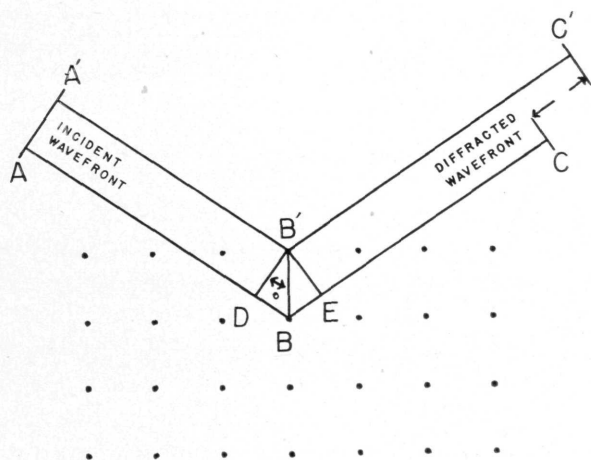

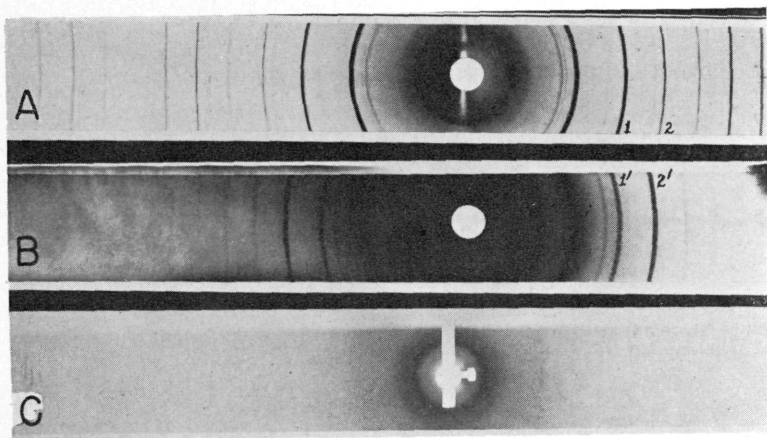FIGURE 3.   Illustration of constructive reflections of x-rays from periodic arrangement of atoms.

FIGURE 4.   Diffraction patterns of A, sodium chloride; B, metallic sodium in a propylene polymer; and C, a 12.4 molal solution of lithium iodide in water. Note the change in the breadth of the rings (1 and 1', 2 and 2') as the particle size decreases.

Non-Crystalline Materials

There is no sharp dividing line between crystalline and non-crystalline materials. With decreasing crystallite size, the widths of the lines composing the powder pattern of a solid increase, and the stronger lines in the pattern assume a diffuse design characteristic of non-crystalline materials. This kind of pattern is illustrated in figure 4(B), where a dispersion of metallic sodium in a propylene polymer is shown. Ring broadening takes place when the crystallite size falls below ap-

proximately 10^{-5} cm.   This effect is analogous to the imperfect resolution of an optical grating containing only a few lines.   As the particle size of the crystallite becomes increasingly smaller, the x-ray reflections become increasingly diffuse until at the limit of 10^{-7} to 10^{-8} cm, which is the region of atomic dimensions, a precise, repetitive pattern ceases to exist.   The repetitive order found in liquids is obviously somewhere between that of the solid and the region of atomic dimensions.

The x-ray diffraction pattern of a liquid or a solution consists of diffuse halos, usually no more than two or three in number.   This kind of pattern shows that the molecules of a liquid have short-range order.   Beyond two or three molecular diameters the structure in one part of the liquid has no effect on that in another part.   However, the existence of halos in the x-ray pattern shows that there is some short-range order in the liquid and solution to give a "smeared-out" ring. A diffraction pattern of a 12 molal solution of lithium iodide in water is shown in
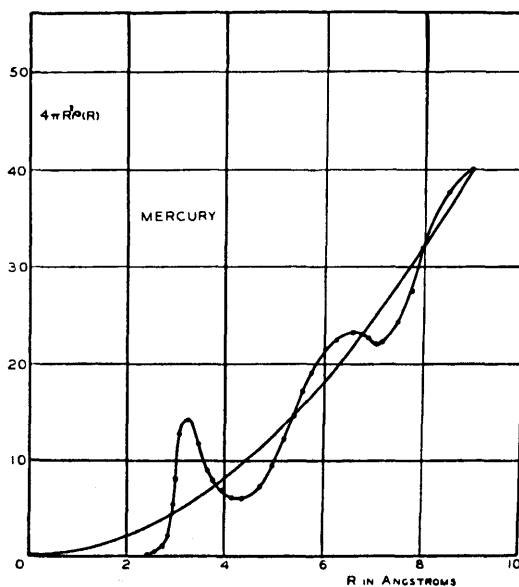

FIGURE 5.   Radial distribution curve for mercury. (Reproduced with permission from Gingrich, N. S. 1943.   Revs. Modern Phys. 15: 106).

figure 4(C).   The marked difference between this pattern and that of a crystalline solid is obvious.   It can be seen that a crystalline material gives a rich diffraction pattern with an orderly arrangement of a large number of images in the three dimensions of reciprocal space.   These patterns can be used to obtain accurate data on the arrangement of atoms.   The diffuse patterns from non-crystalline materials, liquids, and solutions reflect only the statistical approximate order in these systems.   These patterns can likewise be interpreted to obtain an arrangement of atoms in the structure.

As one studies the diffraction pattern of a non-crystalline material, he finds that the possibilities of interpretation become more restrictive than in solids. However, there are two ways that one can proceed to interpret the x-ray diffraction patterns of liquids and solutions.   First, one can postulate particular arrangements of atoms, the intensity patterns at different angles can be calculated, and these calculated values compared with the actual diffraction pattern of the specimen.

Another method, and the one described herein, is to convert the experimental diffraction pattern by the Fourier Series method into a vector diagram. If there is only one type of atom present in the species, this diagram will represent the radial distribution of atoms around any particular atom in the specimen. If there is more than one type of atom present, all the vectors in the specimen are superposed in all directions; the vector diagram must be interpreted in terms of atomic arrangements.

To understand the radial distribution function, let us suppose that we pick a molecule (considered as a point) at random in the liquid and draw a series of spheres around it with their volumes regularly increasing. These spheres shall be drawn so that the volume interval between two neighboring spheres is always the same. The radial-distribution function is then the average of the number of atoms or electrons between such neighboring spheres as a function of the radial distance from the central atom or electron. In other words, the distribution function is a measure of the average density of the liquid as a function of inter-molecular distance.

As expected, the function is zero at very small distances since atoms and molecules occupy a finite space and cannot be closer together than their diameters. The value of the radial distribution function jumps to a high maximum at the distance of nearest neighbors to the reference molecule; it falls off and then peaks again less sharply for the next nearest neighbors; and it peaks still less sharply for the third nearest neighbors. Eventually the function smears out to a uniform value. The radial distribution curve of mercury as determined by Gingrich (1943) is given in figure 5. The curve gives the average distribution of neighboring atoms (electron density) as a function of the distance from the center of a reference mercury atom. Also, from the radial distribution curve one gets directly the concentration of atoms at distances from a given atom and, since the work is quantitative, the areas under the peaks give directly the number of atoms in that range of distances.

Structure of Water and Formamide

The x-ray structure of water was first worked out by Morgan and Warren (1938) and the results of their study are shown in figure 6. The first peak in this curve, which represents the distance between closest neighbors, is at 2.90 Å at a temperature of 1.5°C and at 3.05 Å at a temperature of 83°C. This peak represents the distance between oxygen atoms in neighboring water molecules and compares favorably with the value of 2.76 Å in ice. The intermolecular distance in water is, therefore, slightly greater than in ice and increases with temperature. The area under the first peak in the radial distribution curve gives a value of approximately four nearest neighbors. At the temperatures of 1.5°, 13° and 30°C, a marked concentration of neighbors at a distance of approximately 4.5 Å is clearly indicated on the distribution curve.

From the value of the distance between the nearest neighbors, the number of nearest neighbors, and the presence of neighbors at a distance of 4.5 Å, the structure of water can be established. As one sets out to establish the structure of water, one of the logical structures that might come to mind at first is a close-packed arrangement of the molecules. In the close-packed arrangement one would expect to find a number of nearest neighbors approximately equal to twelve (assume the molecules are essentially spherical). From the experimental data of Morgan and Warren, it is clear that water does not even approximate a close-packed liquid. Another line of reasoning one might follow in arriving at the structure of water is to relate the structure of water to that of ice. Figure 7 gives a diagrammatic representation of the structure of ice. It can be seen from this diagram that, in ice, each water molecule is surrounded by four neighboring molecules in tetrachedral arrangement. From the value of the distance between

closest neighbors, the number of nearest neighbors, and the broad peak at 4.5 Å, all obtained from the radial distribution curve, it is evident that the water structure approximates that of ice. The disappearance of the peak at 4.5 Å as the temperature rises indicates that the tetrahedral bonding in water becomes less sharply defined or less prevalent. Therefore, in a brief summary of the work of Morgan and Warren, one can say that x-ray results show an essentially tetrahedral structure for water, but that this structure cannot be interpreted uniquely in terms of a definite number of neighbors at a certain distance. The structure undoubtedly involves a continual change in neighbors in the tetrahedral unit. The structure of water has been verified by other workers (Brady and Romanow, 1960; Strauss, 1960).
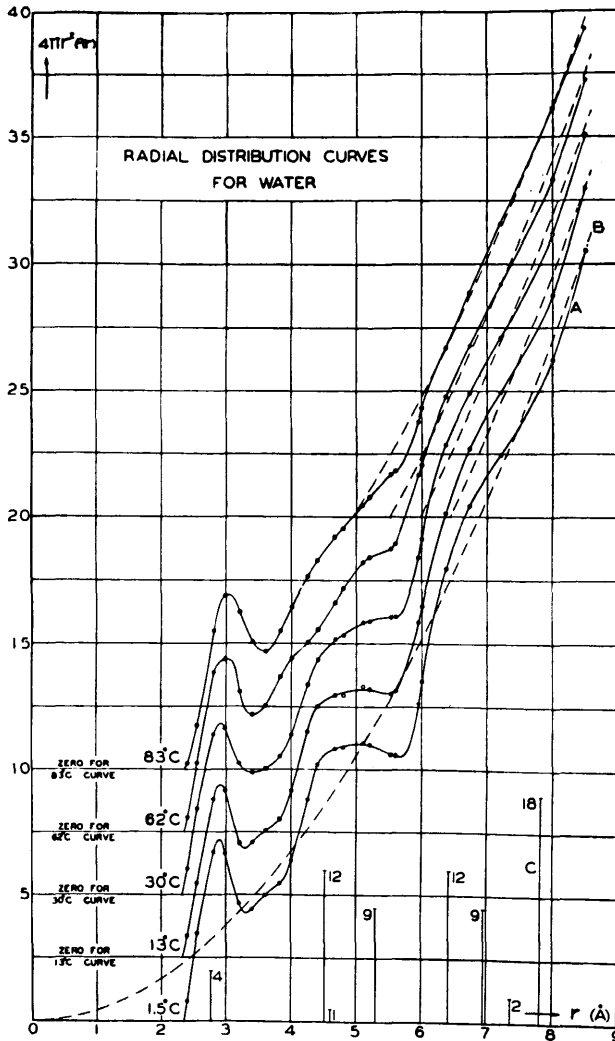
FIGURE 6. Radial distribution curves for water for various temperatures. (Reproduced with permission from Morgan, J. and B. E. Warren. 1938. J. Chem. Phys. 6: 670).

The structure of the formamide molecule was worked out by Costain and Dowling (1960) using microwave spectroscopy. A picture of their structure of the molecule is given in figure 8. Costain and Dowling concluded that the H_2N—C group forms a shallow pyramid while the N'—CHO group is planar. The dihedral angle between the $H'NC$ plane and the NCO plane is $7° \pm 5°$ and between the $H''NC$ plane and the NCH plane is $12° \pm 5°$. The C—N distance in the moleclue is 1.38 Å. X-ray methods are not very definitive in unraveling the structure of formamide. The radial distribution curve in figure 9 shows a peak at 4.0 Å and one at 4.9 Å. The 4.0 Å distance is the combination of atomic distances across the formamide dimer, i.e., carbon-carbon, oxygen-oxygen, nitrogen-nitrogen, etc.
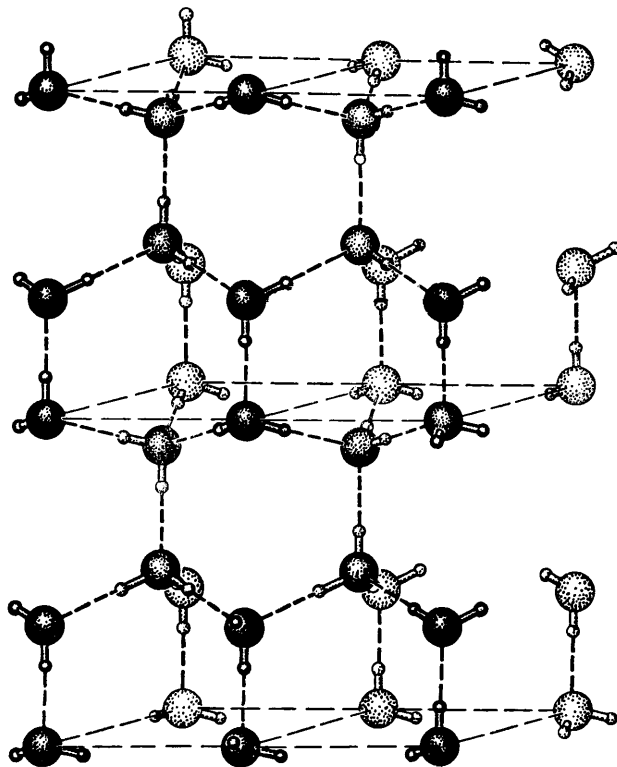

FIGURE 7. Diagrammatic representation of the structure of ice. (Reproduced with permission from Pauling, L. 1960. The Nature of the Chemical Bond. Cornell University Press. 465 pp.).

distance, while the 4.9 Å distance is most likely the distance between dimers. The peak at approximately 1.5 Å indicates the presence of the C—N bond. The complete analysis of the x-ray structure of formamide will be published elsewhere.

Before leaving the consideration of pure liquids, I should call attention to a recent proposal by Bernal (1959) on the geometry of liquids. He has proposed that liquids show fivefold axial symmetry which is quite in contrast with solids which can have only twofold, threefold, fourfold, or sixfold axial symmetry. An arrangement of fivefold symmetry in a two-dimensional pattern, representing Bernal's ideas, is shown in figure 10. Alongside this pattern is one representing sixfold symmetry which leads to a two-dimensional hexagonal pattern. The
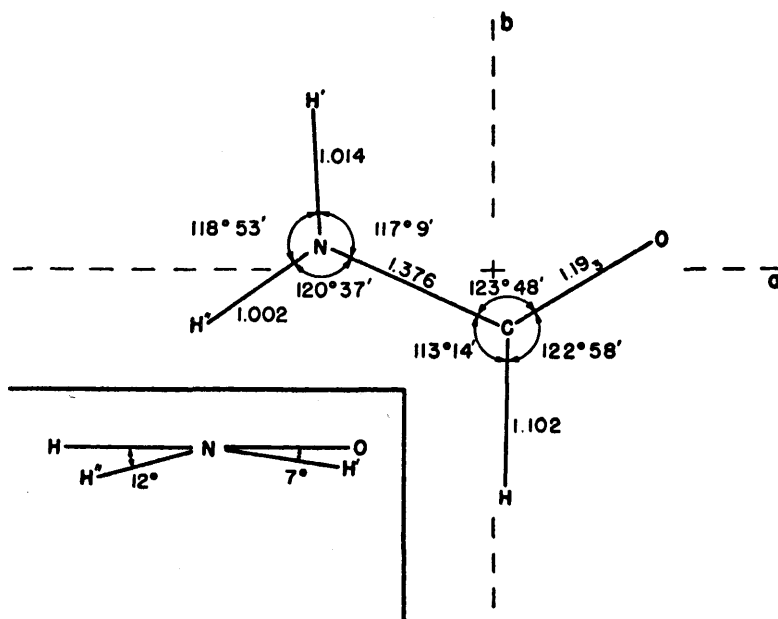
FIGURE 8. Probable structure for the formamide molecule. Insert shows molecule viewed along N—C bond with the N—CHO plane perpendicular to the plane of the drawing. (Reproduced with permission from Costain, C. C. and J. M. Dowling. 1960. J. Chem. Phys. 32: 165).
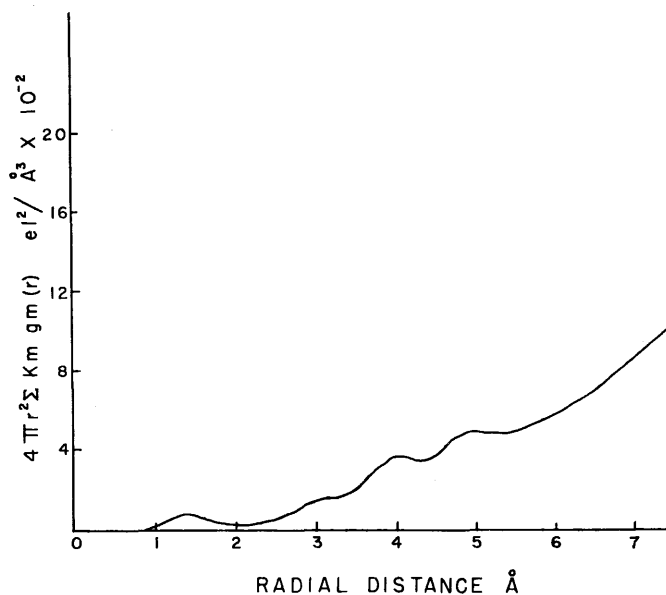

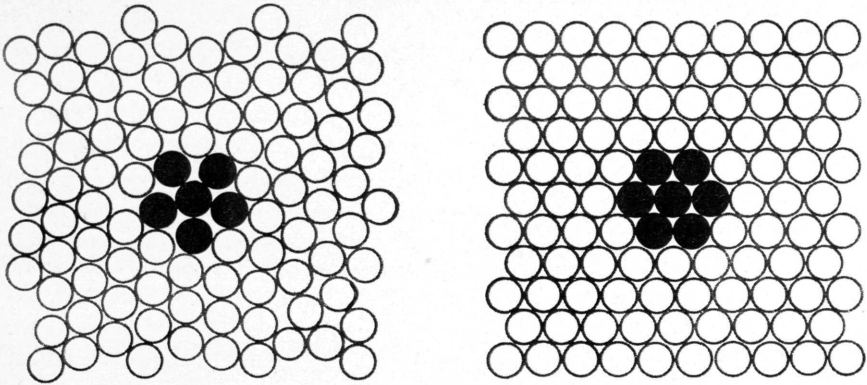FIGURE 9. Radial distribution curve for formamide.

FIGURE 10.   Figure on left represents fivefold symmetry in two dimensions. Figure on right represents sixfold symmetry in two dimensions. (Reproduced by permission from Bernal, J. D. 1960. Sci. Am. 203: 130).
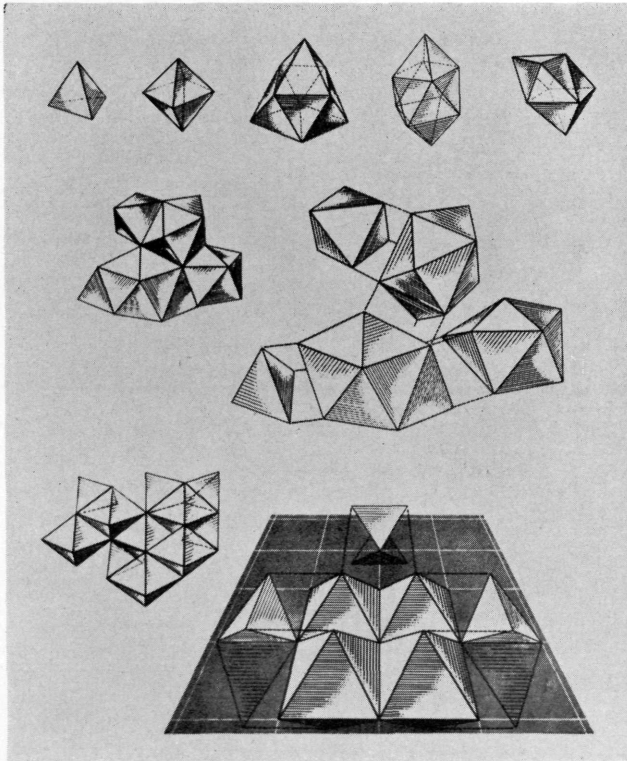

FIGURE 11.   Diagram representing polyhedral "holes" in liquid structure. From left to right at the top are: regular tetrahedron, regular octahedron, and three semiregular solids with 14, 16, and 12 faces, resp. (Reproduced with permission from Bernal, J. D. 1960. Sci. Am. 203: 124).

first of these patterns shows irregularity over an extended area while the second shows regularity. Bernal concludes that the fivefold axial symmetry which gives irregularity over an extended volume is the basic structure of liquids.

If one takes a reference point in a liquid that is not a molecule and surrounds this point with molecules, the positions of these molecules may be thought of as defining a hole in the shape of a polyhedron (formed if the centers of the atoms are connected with straight lines). Furthermore, if one considers relatively dense packing and an ideal structure in which all the molecules are the same distance apart, mention need be made only of the polyhedra with equal edges, namely, the tetrahedron, octahedron, and three semiregular figures (see upper portion of figure 11). If these polyhedra represent the geometry of "holes" in a liquid, then these polyhedra may be used to build the structure of a liquid. In the middle and lower portions of figure 11 there are two possible patterns of arrangements. The arrangements in each case are nested at the left and exploded at the right. The lower pattern is composed only of tetrahedra and octahedra in the ratio of two to one and shows regular arrangement which results in a repeating pattern. The upper pattern is a typical irregular pattern composed of one each of the different polyhedra represented at the top of the figure. This pattern, if extended, would not give a repeating arrangement. Thus, using Bernal's ideas, this sort of an arrangement results in an example of a possible network of "holes" to form a liquid structure.
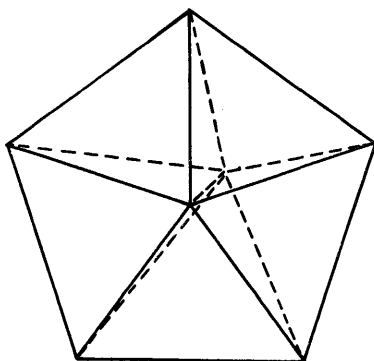

FIGURE 12.   Model of the packing of five tetrahedral "holes" sharing a common edge. This pattern shows fivefold symmetry.

There are a large number of arrangements of "holes" that might correspond to the short-range order of a liquid. Assuming the tetrahedra represent "holes" in the liquid around which molecular spacings take place, another likely arrangement is the packing of the five tetrahedra in such a fashion that they have an edge in common. This arrangement, shown in figure 12, gives a cross-sectional view in which are seen five molecules arranged at the apices of the tetrahedra. Such a pattern shows fivefold axial symmetry and cannot grow indefinitely since it closes in on itself.

This brief resumé of Bernal's geometry of liquids cannot do justice to a very interesting idea. The interested reader is referred to the original paper (Bernal, 1959).

Structure of Solutions

A number of measured properties of solutions, such as conductance and viscosity, show abnormal behavior in the concentrated regions. For example, it has been known for some time that the electrical conductance of most 1:1

electrolytes in water rises as the concentration of the solute rises, passes through a maximum, and then decreases. Theoretically one would expect the conductance to increase as the concentration of solute increases. X-ray structure studies of solutions show that this decrease in conductance can be attributed to ionic aggregates in the system. Several of these studies will be cited in the paragraphs which follow.

I shall consider first two different solutions which have been studied in my research. A detailed report on the complete analysis and interpretation of the structure of these two solutions, along with others of the same solutes at different concentrations, will be published elsewhere. The first of these solutions is a 12.4 molal solution of lithium iodide in water. The radial distribution curve for this system is shown in figure 13. This curve has been corrected for the contribution of water. The peaks below 2 Å are considered to result from spurious effects, characteristic of Fourier inversion and are, therefore, not significant in the analysis of the structure. The first important peak is the one at 3.7 Å, which represents
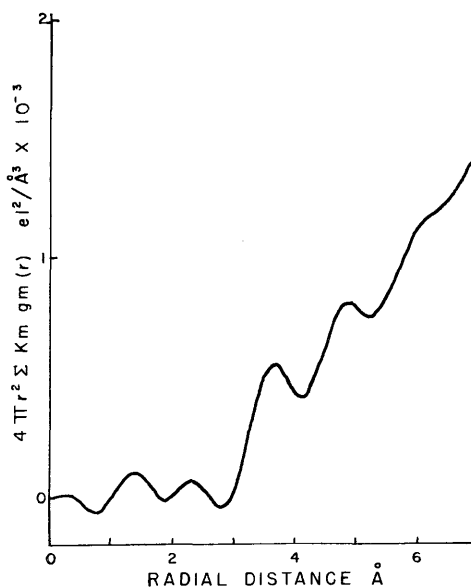

FIGURE 13. Radial distribution curve for a 12.4 molal solution of lithium iodide in water.

an iodide ion-water interaction while the peak at 4.95 Å represents an iodide ion-iodide ion interaction. The area under the first peak is 7.9 and under the second peak it is approximately two. The details by which one arrives at these peak assignments and areas will be described elsewhere, and for the present consideration it will be sufficient to accept the assignments. With these peak assignments and the areas under the peaks, one must set out to assign a structure to the system using any available information at one's disposal. The first logical information to seek is whether the structure of crystalline lithium iodide trihydrate has been determined. Fortunately, the structure of the crystal has been worked out by West (1934), who proposed a hexagonal symmetry. It will be remembered that from the radial distribution curve is obtained the distance of nearest neighbors, next nearest neighbors, second nearest neighbors, and, from areas under the peaks, the number of atoms in that range of distances. If one has this knowledge of the crystalline structure of lithium iodide trihydrate and uses the data from the

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radial distribution curve, he can construct a model of the ionic aggregate such as that shown in figure 14. In this structure there is a centrally located lithium ion surrounded by six molecules of water at a distance of 2.4 Å and six iodide ions at a distance of 4.5 Å. The lithium ion, water molecule, and iodide ion are represented in figure 14 by an increase in the diameter of the circle, respectively. It should be noted that the lithium ion is not only in the center of a regular octahedron whose apical positions are occupied by water molecules, but it is also located in the center of a flattened octahedron formed by iodide ions.
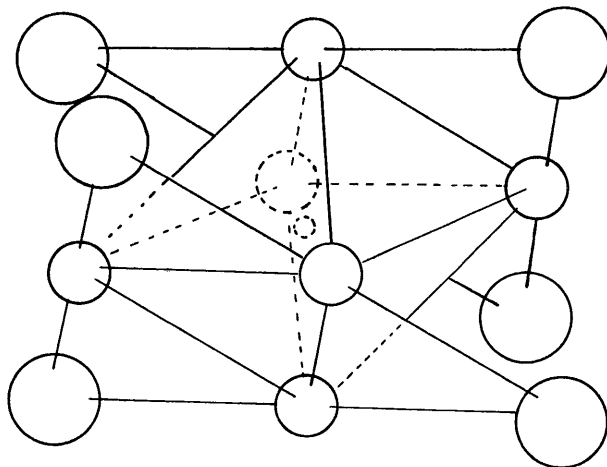

FIGURE 14.   Proposed model of the aggregate of lithium and iodide ions and water molecules in a 12.4 molal solution of lithium iodide. Lithium ion is represented by smallest circle, water by next smallest, and iodide ion by the largest circle.
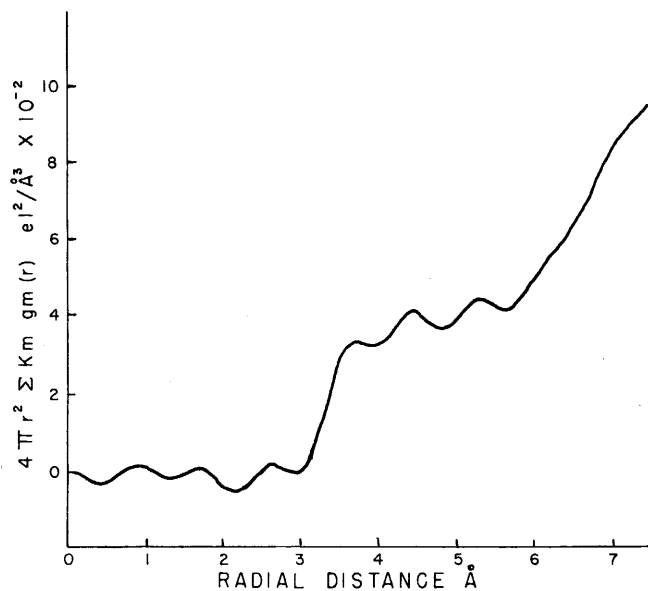

FIGURE 15.   Radial distribution curve for a 4.02 molal solution of potasssium iodide in formamide.

The aggregate shown in figure 14 can be extended in all directions to accomodate twenty-one extra molecules of water and additional lithium ions to preserve electrical neutrality in the "lattice" of the 12.4 molal solution. Therefore, the structure sketched in figure 14 represents the predominate species in the aqueous solution of 12.4 molal lithium iodide.

Next, let us consider a solution of potassium iodide in formamide. Formamide has a large dielectric constant (109 at 20°C) compared to water with a value of 78.5 at 25°C. Because of the large dielectric constant of formamide, one might expect less association of ions in this solvent than in water. Let us look at the radial distribution curve for a 4.02 molal solution of potassium iodide in formamide to see what kind of ion aggregate, if any, exists in such a solution. Figure 15 represents the radial distribution curve of such a solution.
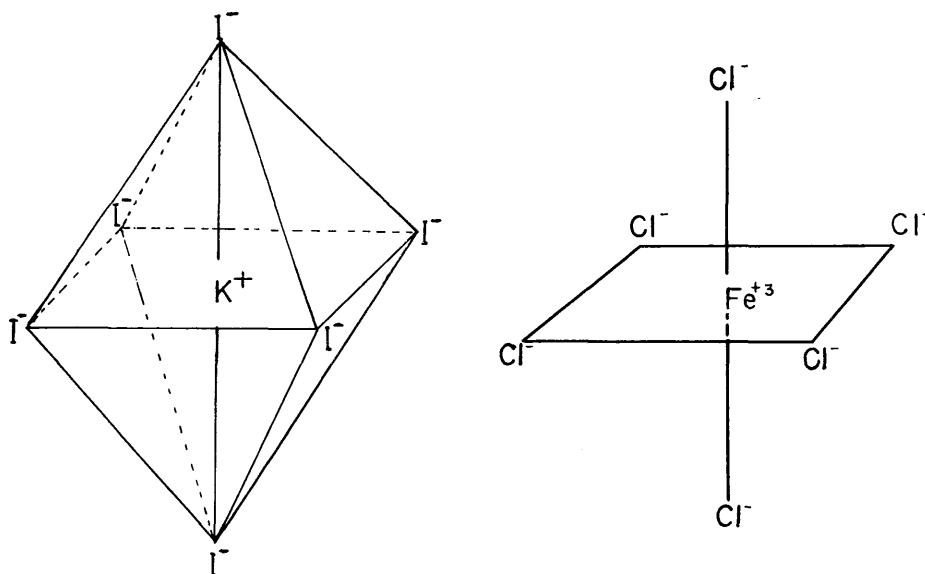

FIGURE 16. (Left) Proposed model of the aggregate of potassium and iodide ions in a 4.02 molal solution of potassium iodide in formamide.

FIGURE 17. (Right) Proposed model of the aggregate of iron (III) and chloride ions in a concentrated solution of iron(III) chloride.

The two peaks I wish to consider first in this curve are at 3.70 Å and 5.25 Å. The first of these distances is a potassium ion—iodide ion interaction and the second an iodide ion—iodide ion interaction. Using these distances and what one knows about comparable distances in crystalline potassium iodide, one can construct a model like that in figure 16. The area under the potassium ion—iodide ion peak gives a coordination number of 6.7. The model proposed in figure 16 fits the nearest and next nearest neighbor spacings quite well, i.e., potassium ion—iodide ion distance and iodide ion—iodide ion distance. The structural unit in this solution is a $K_5I_6^{-1}$ anion and electrical neutrality is obtained by a potassium cation. A likely location for four of the potassium ions is in four of the faces of the octahedral structure for the KI_6^{-5} unit (fig. 16). The peak at 4.4 Å represents a potassium ion—iodide ion distance, with the potassium ion on the negative end of the formamide dipole and the iodide ion on the positive end of the same dipole. Details of the interpretation of the structure of the 4.02 molal solution of potassium iodide in formamide and of other solutions of the same salt in formamide will be published later.

A few studies of solutions by other research workers will be cited.   Brady (1958a) has interpreted the structure of solutions of lithium chloride (0.11 LiCl:0.89 H_2O) in water.   He based his structure on a tetrahedrally arranged sphere of water molecules coordinated to a centrally located lithium ion.   He then postulated that some of the molecules of water in the sphere of hydration around the lithium ion are shared by two chloride ions per water molecule.   This assignment of locations of chloride ions results in two distances representing chloride ion—chloride ion interaction, i.e., a distance between two chloride ions
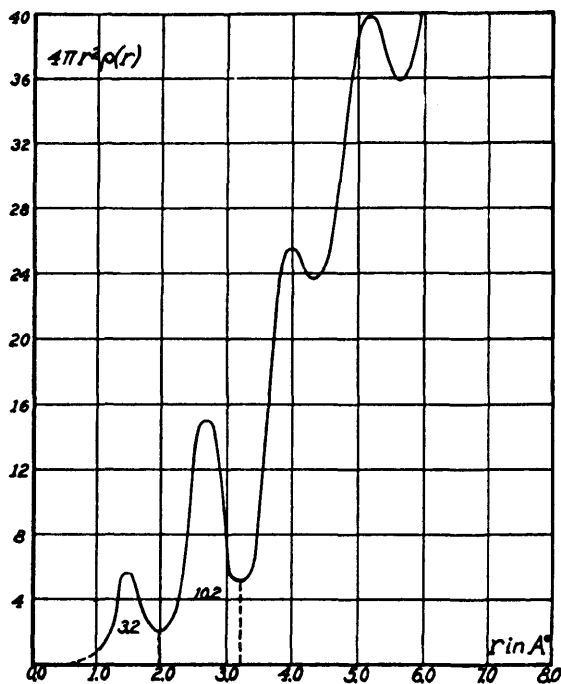

FIGURE 18.   Radial distribution curve for carbon black.   (Reproduced with permission from Warren, B. E.   1934.   J. Chem. Phys. 2: 553).

TABLE 1

Number of neighbors and distances in a single graphite layer (Warren, 1934)

Average Distance (Å)	Distance (Å)	Number of Neighbors
	1.42	3
2.6	2.46	6
	2.84	3
4.0	3.75	6
	4.25	6
5.0	4.92	6
	5.11	6

sharing the same molecule of water located at the apices of the tetrahedron and a distance between chloride ions which are associated with two different molecules of water located at two different apices of the same tetrahedron.

In solutions of iron(III) chloride in water Brady (1958b) found that as the concentration of iron(III) chloride increases, the extent of higher order complexing increases and in a nearly saturated solution, the octahedral ion, $(FeCl_6)^{-3}$, is the predominant form present. This ion is shown in figure 17.

Other Applications of X-ray Analysis of Non-Crystalline Materials

A number of studies of non-crystalline materials, other than those already cited, have been made; only a few will be mentioned here. The structure of carbon black was worked out a number of years ago by Warren (1934). The radial distribution curve shown in figure 18 agrees with the existence of single graphite layers. The data from Warren are summarized in table 1.

Figure 19 shows the arrangement of neighbors about a reference atom in a single graphite layer. The circles in the background on the drawing outline the number of neighbors and the distances from the reference atom starting at 1.42 Å and going to a 5.11 Å distance.
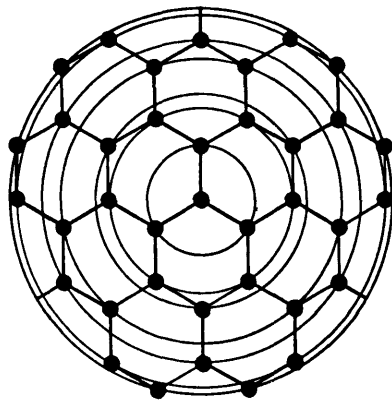

FIGURE 19.   Arrangement of neighbors about a reference atom in a single graphite layer. (Reproduced with permission from Warren, B. E. 1934. J. Chem. Phys. 2: 554).

From this study of carbon black it is clear that it is not a truly amorphous form of carbon. The existence of single layers of graphite is clearly established, and the diffraction data indicate a heterogeneous mixture containing particles which range from single graphite layers to graphite crystals of larger size.

I shall mention one more interesting study of a non-crystalline material. Klug and Alexander (1954) report a study of the structure of polyisoprene. The isoprene unit has a stoichiometric composition of C_5H_8 and has the name, 2-methyl-1,3-butadiene. The radial distribution curve for this non-crystalline system is given in figure 20. The first peak indicates two nearest neighbors at about 1.5 Å, and the second peak shows approximately three second neighbors at 2.55 Å. The positions and areas of the first two peaks in the polyisoprene curve show that the polysiosprene structure consists of coiled or folded long-chain methyl-1,3-butadiene. The radial distribution curve for this non-crystalline of 109° and a single-double bond angle of approximately 125°. The data, however, do not allow one to make a definite choice between the several possible ways in which addition takes place in the polymerization of the isoprene.

Figure 21 shows the relationship between the radial distribution curves of

polyisoprene and natural rubber. It is clear that the structures of polyisoprene and natural rubber are very much alike. The first two peaks are very similiar while the indefiniteness of the third peak results from rotational freedom about the single bond in the polymer. This structural relationship between polyisoprene and natural rubber is one of the most convincing evidences in our knowledge that natural rubber has isoprene as its building unit.

The examples of the radial distribution procedure cited in this paper point up its importance. The method yields itself to many other uses such as structure of polymers, of molten salts, of elements such as sulfur when melted, and of molten alloys.
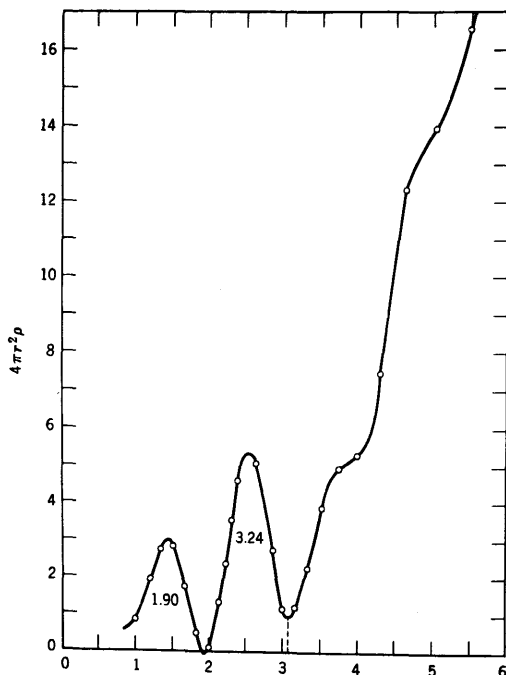

FIGURE 20. Radial distribution function of synthetic polyisoprene. (Reproduced with permission from Klug, H. P. and L. E. Alexander. 1954. X-Ray Diffraction Procedures. John Wiley & Sons, Inc. 716 pp.).
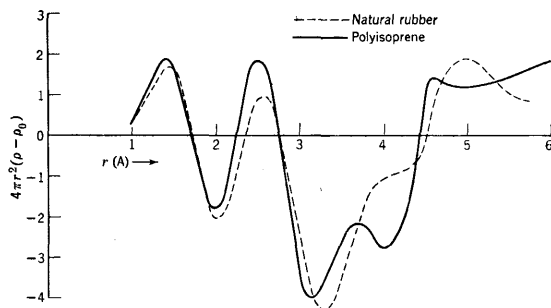

FIGURE 21. Radial distribution curves from polyisoprene and natural rubber. (Reproduced with permission from Klug, H. P. and L. E. Alexander. 1954. X-Ray Diffraction Procedures. John Wiley & Sons, Inc. 716 pp.).

In this brief review of the structure of liquids and solutions I have attempted to acquaint you with the end results of the x-ray method without burdening you with the theory involved. Adequate references have been given to guide an interested person into a deeper understanding of the subject. It is safe to say that the studies of the structures of liquids and solutions will result in some interesting new developments in the future. Workers have only begun to look into the mysteries of the structures of these systems.

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