DIFFRACTION STUDIES OF THE STRUCTURE OF LIQUIDS[1]

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I. INTRODUCTION

Relating the structure of matter to its properties relies greatly on the various experimental methods of "seeing" atoms. One of these, diffraction, has provided the majority of what is now known of atom sizes and arrangements in the solid and gaseous states; and it provides useful, but much less detailed, descriptions of the liquid state, which is still only imperfectly under-

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stood. In this review are discussed the structural descriptions of liquids as given by diffraction experiments. Liquids are classified as monatomic and polyatomic,[2] and there is also a section on glasses since the same diffraction techniques apply. Although the sections on liquids are supposed to be complete through 1960, there is only a selection of illustrative references for glasses. Small angle scattering and studies on colloidal and liquid crystal systems are not included, nor has any attempt been made to summarize theories of the liquid state. Neither has there been included a discussion of the recent applications (42, 170, 176, 381, 382, 383) of van Hove's formalism (175) for the determination of momentum distributions, which promises to yield important information about atomic motions in liquids. We begin with a brief description of the methods of determining average spatial distributions of atoms in liquids.

II. THE RADIAL DISTRIBUTION FUNCTION

In most diffraction and certain theoretical investigations of liquids, knowledge of structure is sought, and such knowledge is frequently displayed as a distribution function giving the probability of finding a pair of atoms in a given configuration. The pair distribution function may be represented as $P(\mathbf{r}_1, \mathbf{r}_2)$, which gives the probability of simultaneously finding atom 1 in a unit volume located at $\mathbf{r}_1$ and atom 2 in a unit volume at $\mathbf{r}_2$. By placing the coördinate system's origin on an atom and integrating over the space accessible to that kind of atom, a distribution function $P(\mathbf{r}_2 - \mathbf{r}_1)$ is obtained. In a crystal, for example, the occurrence of maxima in this function is periodic, and the period is determined by the direction of the position vector, $\mathbf{r}_2 - \mathbf{r}_1$; but in a gas the probability $P(\mathbf{r}_2 - \mathbf{r}_1)$ of finding an atom in a unit volume separated from another atom by $\mathbf{r}_2 - \mathbf{r}_1$ is essentially (exactly, for an ideal gas) $1/V$, which is independent of both the length and direction of the position vector (V being the volume). This result follows from the complete lack of correlation between the motions of individual atoms in a gas, and from the equivalence of all directions in space.

In a liquid, or very dense gas, all directions are again equivalent so that the distribution function still depends only on the magnitude of $\mathbf{r}_2 - \mathbf{r}_1$, namely, r. Here atomic motions are not independent of one another, and our ignorance regarding the relative motion of atom pairs may be incorporated into a correlation function $g(r)$, with the distribution function written, using the same form as for a gas, as $g(r)/V$. Since there is no correlation for large separations, $g(r)$ approaches 1 for large r; and because of finite atom size $g(r)$ is zero up to about an atomic diameter. Integration over the angular variables in spherical coördinates gives a radial distribution function, $4\pi r^2 g(r)/V$. Multiplying this function by N, the number of atoms in the system, expresses the radial distribution function in terms of the number density, $\rho(r) = g(r)N/V$. The measurement of the diffracted intensity and the bulk density leads to the determination of the usual radial distribution function $4\pi r^2 \rho(r)$, which gives the number of atoms in a spherical shell of radius r and unit thickness centered on an atom arbitrarily selected as the origin.

The radial distribution function furnishes, through the location and area of its maxima, the mean, if not the most likely, interatomic distances in the liquid as well as an indication of the number of neighbors at various distances. If the liquid were completely uniform then $\rho(r)$ would be $\rho_0 = N/V$, but in an actual liquid the derived function $\rho(r)$ shows how the density is redistributed within the vicinity of an atom in the liquid. Typical distribution functions are shown in Figure 3. The function $\rho(r)$ differs appreciably from ρ_0 only for small values of r, and the disappearance of positional correlation results in the convergence of ρ to ρ_0 for large r, that is, $g(r)$ approaches 1. It is commonly said that a liquid has short-range, but not long-range, order; but such expressions may be misleading since such order does not have the same implication as ordering in a solid. In this connection, it should also be emphasized that the radial distribution function is an average in time and space over many configurations.

Once the radial distribution function has been found, it is tempting to furnish a detailed structural model which accounts for the "popular" distances within the liquid as well as the coördination geometry. But the wary critic may see the ambiguity in such a procedure: The derived information is one-dimensional, but proposed structures are three-dimensional. To the extent that we understand the rules of atomic architecture, we are as well off in deducing a structure from these data as the carpenter who must rebuild a house given only the frequency with which each size of lumber is to be used. Even though we demand that a proposed model be consistent with the distribution function, such consistency does not guarantee the correctness of the model. Fortunately, one can frequently complement diffraction data with results of spectral, thermodynamic, or, nowadays, magnetic resonance studies to furnish more detail and greater certainty about structure.

Beside the obvious ambiguity in the interpretation of diffraction experiments, there are complications having to do with experimental conditions and also with the way in which the intensity information is converted into the distribution function, and these are discussed in subsequent sections. In spite of the obstacles to obtaining atom arrangements in liquids, the diffraction method, when carefully applied and conservatively

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[2] These terms are used to designate liquids containing only one kind of atom (elements) and those containing more than one kind of atom.

interpreted, has provided a substantial understanding of the structure of liquids as well as important information for testing and constructing theories of the liquid state.

A. THE MONATOMIC LIQUID

The determination of the radial distribution function for a liquid requires measuring the intensity of its coherent scattering as a function of angular displacement from the incident radiation. In this section we review the relationship between the observed intensity and the radial distribution function, and in the next we describe some of the ways used for recording intensities and the problems arising in deriving structural information from them.

For N atoms the intensity observed at an angle 2θ from the incident beam is (71, 124, 139, 179)

$$I(\theta) = N(I_{\text{coh}}(\theta) + I_{\text{inc}}(\theta))P(\theta)A(\theta)G(\theta)$$

where $P(\theta)$ is a polarization correction $^1/_2(1 + \cos^2 2\theta)$, $A(\theta)$ is an absorption correction determined by the sample shape and experimental geometry, and $G(\theta)$ is a geometrical factor whose value is 1 in the cylindrical symmetry usually used in recording intensities. We have ignored the possible contribution of fluorescent radiation excited in the sample, which may be important for X-rays. It is the coherent intensity, I_{coh}, which is needed for structure determination, and, in the X-ray case, the incoherent intensity, I_{inc}, is due to the Compton scattering and has been given approximately by Heisenberg (157) and Bewilogua (22). More recently, Freeman (126, 127, 128, 129, 130), using self-consistent field wave functions, has provided more accurate values for the Compton scattering of a number of atoms.

In obtaining Debye's expression (92) for the coherent intensity an averaging is carried out (387, 389, 404) with the assumption of equal probabilities for all orientations of any given interatomic vector.[3] In this averaging the spherical symmetry of the atomic form factor or scattering factor, f, leads to

$$I_{\text{coh}} = N^{-1} \sum\sum f_m f_n \frac{\sin sr_{mn}}{sr_{mn}} = N^{-1} f^2 \sum\sum \frac{\sin sr_{mn}}{sr_{mn}}$$

in which r_{mn} is the separation between the pair of atoms m and n, and $s = 4\pi\lambda^{-1} \sin\theta$ (λ is the wave length of the radiation).[4] For neutrons the form factor is independent of s (except for very light atoms or for magnetic interactions); but for X-rays f is very nearly equal to the number of electrons per atom at $s = 0$ and decreases rapidly for increasing s.

Since every atom is at zero distance from itself we can separate the self-scattering or the independent scattering, which is associated only with phase differences arising from within an atom. This gives

$$I_{\text{coh}} = f^2 + N^{-1} f^2 \sum_{m \neq n}\sum \frac{\sin sr_{mn}}{sr_{mn}}$$

For a liquid we assume that the probability of finding a given value of r is a continuous function of r and introduce the number of atoms, $4\pi r^2 \rho(r)dr$, separated from a given atom by a distance lying between r and $r + dr$. The number of such pairs is then $N \cdot 4\pi r^2 \rho(r)dr$. This permits the conversion of the double sum to an integral so that

$$i(s) \equiv \frac{I_{\text{coh}} - f^2}{f^2} = \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin sr}{sr}\, dr$$

or

$$si(s) = \int_0^\infty 4\pi r \rho(r) \sin sr\, dr$$

This integral does not converge, but Warren and Gingrich (389) have shown that one can add and subtract the integral $\int 4\pi r \rho_0 \sin sr\, dr$ to give one which does

$$si(s) = \int_0^\infty 4\pi r[\rho(r) - \rho_0] \sin sr\, dr$$

in which the additive term has been dropped because its value is practically zero for all but the smallest values of s.

Since the intensity function $si(s)$ is the Fourier sine transform of $4\pi r(\rho - \rho_0)$ we can write the inverse relationship

$$4\pi r(\rho - \rho_0) = (2/\pi) \int_0^\infty si(s) \sin sr\, ds$$

which gives the distribution function from a measurement of scattered intensity.

At this point we can show the corresponding treatment of a molecular liquid, again under the assumption of spherical orientational symmetry. We have

$$I_{\text{coh}} = \overline{F^2} + N^{-1} \bar{F}^2 \sum\sum \frac{\sin sr_{mn}}{sr_{mn}}$$

where F is the form factor for the molecule, N is the number of molecules, and r is the intermolecular separation. The indicated averages are (assuming centrosymmetry)

$$\overline{F^2} = \sum\sum f_i f_j \frac{\sin sr_{ij}}{sr_{ij}}$$

and

$$\bar{F} = \sum f_i \frac{\sin sr_i}{sr_i}$$

in which i and j go over all atoms in the molecule, r_{ij}

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[3] It has been shown (237) that the zeroth approximation in a statistical mechanical averaging over configurations in a free volume liquid gives the same result and that a higher approximation gives a negligible correction except near the critical temperature.

[4] A more exact analysis, taking account of the finite sample size, but still giving the same result, has been given by Fournet (124).

is the distance between atoms i and j, and r_i is the distance from the inversion center. Use of the corresponding Fourier integrals requires that structure of the molecule itself be known, and the distribution of molecule centers is then determined. Since it is usually more desirable to get the distribution of atom centers, the *a priori* knowledge that molecules exist has rarely been utilized in this way.

Before going on to the polyatomic liquid it will be useful to point out that instead of finding the Fourier transform of $si(s) = s(I - f^2)f^{-2}$ it is possible to find the Fourier transform of $s(I - f^2)$. Extensive use has been made of this transform in X-ray studies by Finbak (113, 116), and the meaning of such a transform is easily given. We still get a density function, ρ_e, which, however, describes the electron, rather than the atom, density. As one might expect, this function has maxima at the same places, but they are extremely smeary. Inclusion of the factor f^{-2} has the mathematical effect of sharpening the distribution function (and changing its dimension as well), and we can see that inclusion of this rapidly increasing function of s serves to weight or emphasize the contribution of intensity at large s. In terms of diffraction theory, its inclusion essentially corrects the intensity to that expected for point scatterers. Unfortunately, in the case of X-rays, it becomes more and more difficult to determine $(I - f^2)$ with precision at the larger values of s, and Finbak believed that use of the factor f^{-2} gives unjustified emphasis to this part of the data.

In the neutron case, where f is constant with angle, the question of dual density functions does not arise, and the data are automatically sharpened. A more detailed discussion of sharpening is included in Section V.

B. THE POLYATOMIC LIQUID

Returning to Debye's expression and proceeding as before, we introduce functions $4\pi r^2\rho_{ij}dr$ which give the number of atoms of type j at a distance between r and $r + dr$ from an atom of type i, and we have, after separating the self scattering

$$I_{coh} = N^{-1} \sum N_i f_i^2 + N^{-1} \sum N_i \sum \int_0^\infty f_i f_j \, 4\pi r^2 \rho_{ij} \frac{\sin sr}{sr} \, dr$$

It is convenient to think of the structurally sensitive part of the intensity, that is $I_{coh} - \Sigma x_i f_i^2$, as a sum of components each of which is dependent on the interactions of a particular type of atom pair. Thus we may write $I_{coh} - \Sigma x_i f_i^2 \equiv \Sigma\Sigma i_{ij}(s)$ as well as $\rho(r) \equiv \Sigma x_i \cdot \Sigma A_{ij}\rho_{ij}$, where A_{ij} is the contribution of a single pair i, j. But in this form we cannot carry out the Fourier inversion in the X-ray case because each integral in the sum depends on s in a different way. An approximate solution to this problem was provided by Warren, Krutter, and Morningstar (390), who took advantage of the close agreement between reduced scattering factors f/K (K is the number of electrons in the scatterer) for atoms of nearly the same atomic number. Thus an f_e such that $f_i = K_i f_e$ can be adopted, and the integrals can be factored to give

$$s(I_{coh} - \sum x_i f_i^2) f_e^{-2} = \sum x_i \sum K_i K_j \int_0^\infty 4\pi r \rho_{ij} \sin sr \, dr$$

As before, we include a term containing ρ_0, the bulk density, and the inversion of the intensity function gives

$$4\pi r\left(\sum x_i \sum K_i K_j \rho_{ij} - \sum x_i \sum Z_i Z_j x_j \rho_0\right) =$$
$$(2/\pi) \int_0^\infty s(I_{coh} - \sum x_i f_i^2) f_e^{-2} \sin sr \, ds$$

The first term on the left is $4\pi r\rho_e$ where ρ_e is usually written as $\Sigma x_i K_i \rho_i$ with $\rho_i = \Sigma K_j \rho_{ij}$ (note that ρ_e is an electron density function), and the second term is just $\rho_0(\Sigma x_i Z_i)^2$ where Z is the atomic number. Since this treatment is approximate, various techniques have been used for interpreting the area under the curve of $4\pi r^2\rho_e$ and for estimating the appropriate values of the K's, but it can be seen that the contribution of a pair i, j is essentially $2x_i K_i K_j$. This results from the equality of $x_i\rho_{ij}$ and $x_j\rho_{ji}$ when all atoms of a given type are structurally equivalent. If a certain area, A, is supposed to be due to i, j pairs then the quotient $A/2x_i K_i K_j$ gives the number of i, j pairs per atom of type i, that is the number of atoms of type j lying within the indicated distance from an atom of type i. The analysis is the same for like atoms, except that the factor of 2 does not appear.

A more satisfactory analysis of the polyatomic case employs a powerful Fourier formalism set forth by Waser and Schomaker (391), who, in their famous paper, show how to predict the exact effect of the atomic scattering factor on the peak shape and area contributed to ρ_e by a given atom pair. This method also allows one to predict the effect of other factors on ρ_e and is discussed in Section V.

III. EXPERIMENTAL TECHNIQUES

In any diffraction experiment a sample is exposed to collimated radiation, and the spatial distribution of diffracted intensity is recorded. If the directions of the incident and diffracted beams are represented by the vectors $\mathbf{S}_0$ and $\mathbf{S}$, then the behavior of a crystal and a liquid may be contrasted by saying that the crystal's diffracted intensity is a discontinuous function of $\mathbf{S} - \mathbf{S}_0$, being non-zero only for a Bragg reflection. The intensity diffracted by a liquid, however, is a continuous function of the magnitude of $\mathbf{S} - \mathbf{S}_0$, which is usually taken to be $2\lambda^{-1} \sin \theta$. Thus, for a liquid, we need only to record the scattering along any azimuth from $\mathbf{S}_0$.

There have been two ways of detecting the scattering, the one using photographic film, and the other a radiation detector such as a counter or ionization chamber. Each method has certain advantages, but the use of a counter is increasingly favored (and the only one practical for neutrons). Gingrich (139) has discussed in detail some of the experimental features of X-ray diffraction studies of liquids.

In addition to a detector, a source of radiation and a method of monochromatization are necessary. The latter is needed because, once the intensity record is made, the diffraction due to one wave length cannot be separated easily from that of the others. Some of the factors upon which the selection of an appropriate wave length is based are:

(a) In a transmission method the radiation must be sufficiently penetrating so that not too great a fraction is lost before reaching the detector. Optimum sample thickness is of the order of μ^{-1}, the reciprocal of the linear absorption coefficient for the wave length used.

(b) For a reflection technique, it is desirable to avoid deep penetration so that the scattering volume is localized near the sample surface. This simplifies the absorption correction.

(c) Because the intensity is a function of $\lambda^{-1} \sin \theta$ (or s, which is $4\pi\lambda^{-1} \sin \theta$) the wave length acts as a scale factor. The smaller the wave length, the greater is the value of s to which measurements may extend ($s_{\max} = 4\pi/\lambda$), but a wave length that is too short crowds the intensity at small s too close to the incident beam to be measured conveniently. This difficulty is sometimes avoided by using a long wave length for low angles and a shorter one for the rest of the range.

(d) For X-rays a wave length that corresponds to an absorption edge in the sample is avoided since it excites fluorescent X-rays which add an undesirable background. If the diffracted beam is monochromatized, this ceases to be a limitation on the composition of either the sample or X-ray target.

One characteristic of the radiation that is of no concern in the photographic method is the stability of its source, since the entire angular range is recorded at once. In a counter method, however, there should be an extremely stable source or some method of monitoring intensity so that data from each angular region may be normalized to the same incident intensity.

Several methods have been used for monochromatization:

(*a*) *Crystal Monochromatization*—This is the usual method for neutrons and the most selective one for X-rays. Variations (217) include placing the monochromator between the radiation source and the sample or, less frequently, in the diffracted beam. The latter arrangement is advantageous in discriminating against fluorescent X-rays but it can only be used conveniently when a counter is the detector. With slightly divergent collimation the bent and ground Du Mond–Johansson (98, 181, 182, 183) focusing monochromator guards against undue intensity loss, and the Fankuchen cut (110, 111) frequently is used with parallel collimation.

(*b*) *Balanced or Ross Filters* (314, 340).—In this technique two intensity records are made for two different absorbers whose absorption edges bracket the desired wave length. When the absorptions have been matched properly or balanced a nearly monochromatic window is obtained, and the necessary intensity data are given by the difference in the two records.

(*c*) *Partial Monochromatization* has been achieved in a counter method by using an absorber for the $K\beta$ radiation and then selecting the response of a scintillation detector in the $K\alpha$ range by means of a pulse height analyzer. Since, for the low energies of X-ray range, the resolution of a scintillator is rather poor, a proportional counter is much to be preferred in this method. Even with crystal monochromatization a pulse height analyzer is useful because background counting rates can be reduced to as little as 2 counts/min., and it also permits one to operate an X-ray tube at the high voltage needed for efficient X-ray production and, at the same time, reject pulses due to the shorter wave lengths passed in higher orders by the monochromator.

IV. TREATMENT OF DATA

We can now outline the procedure that leads to the determination of a radial distribution function.

(*a*) *Correction for Background and Fluorescent Radiation.*—Both of these are nearly constant quantities subtracted over the entire angular range. In the neutron case a constant correction for multiple scattering is usually applied.

(*b*) *The Absorption Correction.*—This correction has been tabulated for a number of sample shapes (317). Corrections have been worked out (311) for the absorption of a cylindrical sample holder, and an absorption correction for parafocusing geometry is available (231, 246). Even though, for the last case, the correction has been held to be independent of angle, this is true only for highly absorbing samples, and the correction may be substantial otherwise.

(*c*) *The Polarization Correction.*—If a monochromator is used this becomes $(1 + \cos^2 2\alpha \cos^2 2\theta)/(1 + \cos^2 2\alpha)$ where α is the Bragg angle for the crystal.

(*d*) At this stage the intensity is in arbitrary units and it must be scaled to the units of f^2. Scaling depends on the fact that at large values of s the observed corrected intensity approaches that of independent atoms, that is, $\Sigma x_i f_i^2 + I_{\text{inc}}$. In the neutron case, the fact that I_{inc} is usually isotropic and the constancy of the neutron form factors makes it easy to calculate the value of I_∞ about which the observed intensity oscillates and to which it finally converges at large s. Comparison of the value of the arbitrarily scaled corrected intensity with I_∞ furnishes the necessary scale factor.

In the case of X-rays one calculates $\Sigma x_i f_i^2 + I_{inc}$ with tabulated values of form factors and incoherent scattering. The former may be corrected for dispersion (90, 369). The arbitrarily scaled intensity may be fitted approximately by eye, but analytical tests for correctness of fit have been proposed (177, 213, 255), and these may be used for calculating the scale factor.

(*e*) Having scaled the intensity one can then subtract the incoherent contribution and tabulate the intensity function $s(I_{coh} - \Sigma x_i f_i^2)$ in preparation for the Fourier inversion. Where values of form factors are available from several sources, differences between them lead to noticeable differences in the radial distribution functions.

(*f*) The inversion of the intensity function may be carried out either by graphical or numerical integration. For graphical integration a curve must be drawn for each value of r, but this can be speeded by making a series of measuring strips giving the positions of selected values of $\sin sr$ on the s scale for each value of r, and by making use of the fact that the curves $\pm s(I_{coh} - \Sigma x_i f_i^2)$ form the envelope of all integrands.

In numerical methods a linear or quadratic interpolation is usually used, but one must guard against taking too large an interval in s. This problem becomes more acute with increasing r so that, for example, with an interval of 0.1Å.$^{-1}$ in s there are only about 5 panels per half-cycle of $\sin sr$ for $r = 6.0$ Å. (period in $s = 2\pi/r$), and considering the oscillation of the intensity function itself, it is clear that serious errors may develop unless the interval in s is sufficiently small (see Fig. 1). The use of Filon's method (112) helps to avoid this difficulty.

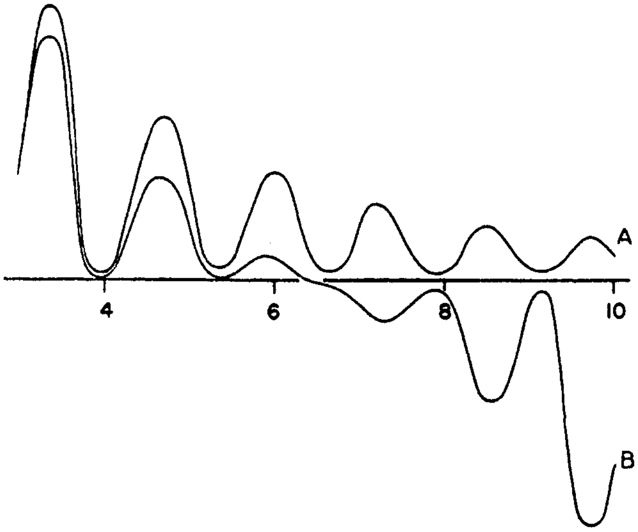

FIG. 1.—An arbitrary function was inverted by numerical integration to give the curves shown above. For A the increment in s is 0.05, whereas it is 0.5 for B. In the former case the increment is small compared to period in $\sin sr$ (namely, $2\pi/r$). When the period in $\sin sr$, however, becomes comparable with the increment, as it does for r approaching 2π in B, the error becomes enormous.

V. INTERPRETATION OF THE RADIAL DISTRIBUTION FUNCTION

Structure determinations based on radial distribution data fall into two main categories. In the first, the radial distribution function yields the mean distribution of interatomic distances for those liquids in which there are no permanent aggregates of atoms, either molecules or complex ions. Examples include the inert gases, metals, and certain molten salts. In such cases it is impossible to characterize the liquid in terms of fixed coördination, and attempts to confirm lattice or microcrystalline arrangements have not been convincing. Indeed such ordering is inconsistent with the properties of the liquid state, and it is presumptuous to interpret the radial distribution function in terms of specific geometrical models. The most that can be said of such a function is that it is consistent with a particular statistical distribution, and indeed such experimentally determined distribution functions have been used extensively in the testing of statistical mechanical theories of the liquid state.

Representative of the second category are the determinations of the structures of molecules or complex ions in liquids. The deduction of the intramolecular arrangements is strongly suggestive of the procedures used for electron diffraction by gases. Thus the first maximum in the radial distribution function for carbon tetrachloride is easily ascribed to carbon–chlorine pairs, and the second (at a distance $\sqrt{8/3}$ times that of the first) to the chlorine–chlorine pairs within the molecule. Special success has been achieved with strongly scattering molecules or complex ions dispersed in a solvent of low scattering power, although corrections must be made for solvent–solvent and solvent–solute interactions. Obviously it is extremely difficult, if not impossible, to unravel structures where more than one solute species is present, as in the cases of certain solutions of transition metal ions.

That experimental findings should fall into these two broad categories was fully anticipated by the progenitors of the radial distribution method in diffraction, Zernike and Prins (404). In either category, deductions about structure are based on the peak positions and areas in the radial distribution function, but even assuming that a careful determination has been made, the positions of maxima may not have unique structural significance. This comes from the possibility that a given maximum may be a superposition of maxima spanning the apparent distance at which the observed maximum occurs.

The determination of the area of a peak provides mean coördination numbers, but unless the maximum is discrete the assignment of area is not unique. Discrete maxima occur occasionally (in the radial distribution for chlorine, Cl_2, for example, the first maximum is discrete), and this usually is taken as an indication of the existence of a permanent species. Methods for assigning area in cases where the peaks are not discrete include:

(a) For a first maximum the right-hand side of the peak is drawn to be symmetrical with the left-hand side, or the left side of the second maximum may be extrapolated to the r axis, and the difference between the extrapolation and radial distribution function is taken.

(b) A vertical line is dropped to the r scale at the minima on either side of the maximum (on the right only, if the first maximum). The indicated area gives the mean number of neighbors within that range.

(c) Synthetic peaks are calculated and fitted to that part of the maximum which seems reasonably free of interference from neighboring maxima.

The arbitrariness of making the assignment of area leads to considerable variance for different treatments of a given distribution function, and this may produce uncertainties of as much as 1, or even more, in the coördination number.

As we proceed with the discussion of areas, only the treatment of X-ray intensity data will be indicated. If the function $s(I_{\mathrm{coh}} - f^2)f^{-2}$ has been inverted, then the distribution function will be in terms of atom density, and the area gives the number of neighbors directly. If, however, an electron density is obtained, as in the polyatomic case, then the area is in units of f^2, that is electron², and for a given maximum is very nearly proportional to Z_1Z_2n, where n is the coördination number sought. Here the determination of the number of nearest neighbors for an atom requires assessing the contribution of a single pair, and this was discussed for the method of Warren, Krutter, and Morningstar in Section IIB.

In place of this approximate method Waser and Schomaker (391) have shown how form factors may be used exactly in determining the area contributed by a single pair. For the electron distribution function obtained by inverting $s(I_{\mathrm{coh}} - \Sigma\, x_i f_i^2)$, a single pair i, j gives a peak whose shape is $T_{ij}(u) = \pi^{-1}\int_0^\infty f_i f_j \cos us\, \mathrm{d}s$ where u is the distance from the center of the peak.

As we mentioned before, however, such an inversion of $s(I_{\mathrm{coh}} - \Sigma\, x_i f_i^2)$ gives a distribution function with extremely broad and smeary maxima. This difficulty can be overcome, to a great extent, by a sharpening procedure. The smeariness in the unsharpened distribution is due largely to intra-atomic diffraction, which is also responsible for the diminishing of intensity with increasing angle. The sharpening procedure may be used to compensate for any arbitrary share of this diminution of intensity.

In the monatomic case, division of $s(I_{\mathrm{coh}} - f^2)$ by f^2 compensates completely for the diminution, and the resultant distribution is much sharper than the corresponding electron distribution function. In the treatment of Warren, Krutter, and Morningstar, division by f_e^2 compensates in a similar way. This type of sharpening was what Finbak (116) objected to on the grounds that any error at large s is magnified and might give spurious maxima in the distribution function. Therefore a comparison between sharpened and unsharpened distribution functions has been used as a test for false peaks.

Attempts to meet at least part of Finbak's criticism have involved the simultaneous application of an exponential function, or artificial temperature factor, $\exp\,(-bs^2)$, along with the sharpening function. Although counting techniques now permit arbitrary improvement of the precision of the intensity determination at large s, there still exists a practical need for a compromise that utilizes the data at large s to give sufficient detail, but yet does not create false detail. It is characteristic of the Fourier method that the resolution obtainable in the distribution function depends on s_0, the upper limit to which measurement extends. Terminating the inversion at smaller values of s has much in common with the application of an artificial temperature factor, which attaches decreasing weight to the high angle data. We see, however, that any differences in the distribution functions obtained with and without an artificial temperature factor can as well be laid to the failure of the damped function to resolve the density as to the cutoff error itself. The effect of the finite upper limit, as well as that of any arbitrary modification of the intensity function, has been described by Waser and Schomaker (391), and we briefly summarize their treatment of these effects.

The intensity function $s(I_{\mathrm{coh}} - \Sigma x_i f_i^2)$ may be considered as a sum of contributions, $s\Sigma\Sigma i_{ij}(s)$, from the various kinds of atom pairs. Each contribution is given by

$$si_{ij}(s) = \int f_i f_j 4\pi r(\rho_{ij} - x_j\rho_0) \sin sr\, \mathrm{d}r$$

or

$$si_{ij}(s)(f_i f_j)^{-1} = \int 4\pi r(\rho_{ij} - x_j\rho_0) \sin sr\, \mathrm{d}r$$

Now if we consider $4\pi r(\rho - \rho_0)$ to be given by a corresponding sum of contributions $\Sigma\Sigma x_i 4\pi r(\rho_{ij} - x_j\rho_0)$, it is clear that, in order to obtain this sum, we should have to invert not $s\Sigma\Sigma i_{ij}(s)$ but $s\Sigma\Sigma i_{ij}(s)(f_i f_j)^{-1}$. This is, of course, impossible since there is no way to decompose the intensity into separate contributions weighted by the appropriate $(f_i f_j)^{-1}$.

In actual practice $s(I_{\mathrm{coh}} - \Sigma x_i f_i^2)M_1(s)M_2(s)M_3(s)$ is inverted so that the contribution by i, j pairs is

$$si_{ij}(s)(f_i f_j)^{-1}M_{ij}(s)M_1(s)M_2(s)M_3(s)$$

where

$M_{ij}(s) = f_i f_j$
$M_1(s) = \exp(-bs^2)$
$M_2(s)$ = a sharpening function such as f_e^2 or $(\Sigma x_1 f_1(0)/\Sigma x_1 f_1(s))^2$ or some other convenient function,
$M_3(s)$ = a step function which is unity up to s_0 and zero beyond.

The resulting density contribution from i, j pairs is the convolution of ρ_{ij} with $T(r)$, the cosine transform of $M_{ij}M_1M_2M_3$. Dropping subscripts, we may write the relationship between the density contribution actually obtained for i, j pairs (electron density) and the corresponding atom density as

$$r\rho_e(r) = (\pi/2)\int_{-\infty}^{\infty} u\rho(u)T(u-r)\,du$$

$T(r)$ may be considered as the ideal peak contributed by a single pair so that, regardless of what treatment of data is required, there is a means of predicting its effect on peak areas. This procedure may be used successfully to assign area where there is reason to believe that a particular well-resolved peak is associated with a particular pair. The ideal peak shape is given by

$$T(r) = \pi^{-1}\int_0^{\infty} M_{ij}(s)M_1(s)M_2(s)M_3(s)\cos sr\,ds = \pi^{-1}\int_0^{s_0} M_{ij}(s)M_1(s)M_2(s)\cos sr\,ds$$

Where applicable, this proves to be a highly effective way of assigning areas and of determining the number of pairs contributing to a particular peak. The number of i, j pairs per atom of i is given by dividing the associated area by $x_i\,\delta\int_{-\infty}^{\infty} T_{ij}(r)dr$, where δ is 1 for i = j and 2 for i$\neq$j.

For a given $M_3(s)$ the amount of sharpening provided may be adjusted by varying b, and some typical peak shapes are shown in Figure 2. It can be seen that undesirable ripple is created by oversharpening, and the peaks themselves undershoot. Tompson and Gingrich (374) have called attention to the need for including the negative as well as the positive areas to obtain more reliable total areas in such cases. The ripple behaves like $(s_0r)^{-1}\sin s_0r$, and this fact can be useful in diagnosing ripple suspected to be due to the finite upper limit.

Bienenstock (23) discusses one aspect of data treatment which may not be handled by these methods, namely, scaling errors, and he shows that if the fractional error in the scaling is α then, to a first approximation, α is the fractional error in peak area. In addition, there is an oscillatory component introduced which can account for ripples in the distribution function at small r and can also distort peaks in both area and position.

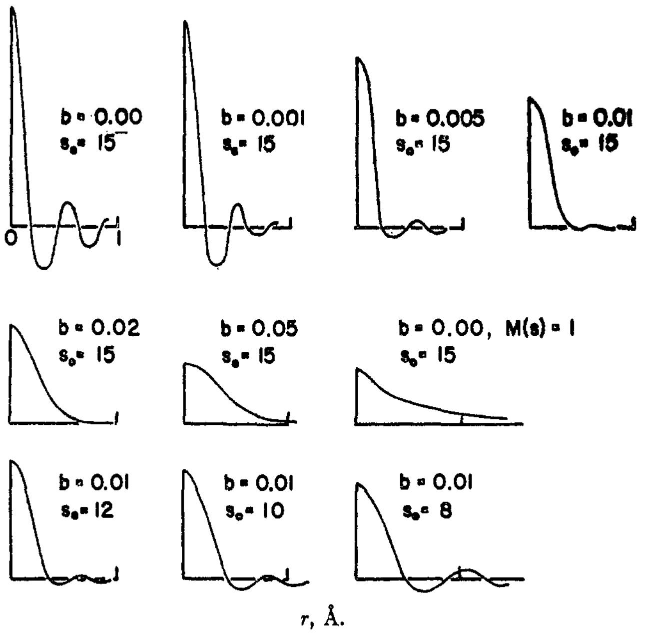

FIG. 2.—The effect of data treatment is shown for a single interaction. Each curve is calculated according to

$$T(r) = \pi^{-1}\int_0^{s_0} f_i f_j \exp(-bs^2)M(s)\cos rs\,ds.$$

In all cases but the one indicated $M(s) = f_e^{-2}$. Both the effect of artificial damping and of termination may be seen. The enormous sharpening effect of f_e^{-2} is seen in comparing the two curves for b = 0.00. The undesirable ripple may be almost completely removed by damping, without too serious a loss in resolution. In the sequence for b = 0.01 the termination ripple has its first maximum at $7.725/s_0$.

To summarize, the radial distribution function provides meaningful information about the mean number of nearest neighbors and their mean distance of approach; and in certain cases intramolecular configurations may be deduced. Although in the latter case confirmation of structure is afforded by agreement between observed intensity and that calculated on the basis of the model (as for electron diffraction by gases), such a procedure is not generally applicable since the radial distribution function rarely gives enough information to permit identification of all of the interactions needed to get good agreement between calculated and observed intensities.

VI. THE ELEMENTS

Only a few of the elements are liquid under ordinary conditions, and much of the experimental effort in studying the liquid elements goes into maintaining the sample at a low or high temperature as required. Previous reviews of experimental work present data for some of the elements (74, 75, 87, 132, 133, 143, 196, 228, 283, 285, 286, 318, 320, 378), and the last comprehensive review of the elements is that of Gingrich (139).

Of the elements perhaps the inert gases have received the most attention as a result of their relative simplicity as liquids. The same simplicity has made them popular subjects for theoretical descriptions, and the aptness of many a theory of the liquid state has been demonstrated by its ability to produce a radial distribution function agreeing with that observed for an inert gas. There is an enormous literature on the theory of liquids, and we may mention a few representative works. Among them are the celebrated methods of Born-Green-Yvon (29, 397) and of Kirkwood (195) in which the radial distribution function is obtained by the solution of integro-differential equations. Other methods of obtaining the distribution function are based on cell models (11, 65, 72, 149, 172, 229, 294), free volume models (109, 197), smeared crystal models (258, 315), the highly instructive statistical geometrical model of Bernal (18, 19, 20), and the elegant Monte Carlo techniques originally employed in this work at the Los Alamos Laboratories (1, 2, 240, 313). A review of most of these methods may be found in the reference work by Hirschfelder, Curtiss, and Bird (173).

Although the radial distribution function is, of course, sensitive to the geometry selected for a cell model, it does not seem to be greatly affected by the choice of potential function in the Born-Green-Yvon or Kirkwood treatments. Results (199) based on a Lennard-Jones 6:12 potential are little different from those (198, 200) in which a model of hard, non-interacting spheres is assumed. The main difference is that in the latter case the first peak in the distribution function rises sharply to a maximum at one atomic diameter, whereas in the former the maximum is rounded and shifted to 1.1-1.2 atomic diameters.

The result for hard spheres had been anticipated in mechanical experiments by Debye and Menke (93, 94) and by Morrell and Hildebrand (251), who determined optically the distribution of colored gelatine balls in a medium of the same density and refractive index. In these cases the agreement between the calculated distribution functions and those observed for, say, argon is quite acceptable. Radchenko (284) tried to determine the effect of interatomic forces by placing weak magnets in plastic balls, and he concluded that entirely different arrangements might have similar distribution functions.

Before proceeding to the diffraction results for the inert gases we should point out that, for most liquids, the diffraction experiment has been unable to furnish proof of coincidence between liquid structures and structures in the corresponding solids (except for occasional agreement in number of nearest neighbors and their mean separation). Moreover, it is practically impossible to deduce the average geometrical disposition of nearest neighbors, much less remote neighbors, even in those hopeful attempts made at or near the freezing point. Indeed, experimental evidence supports the notion of complete discontinuity between liquid and solid. The late Professor Kirkwood summarizes by saying, "We believe that liquid structure cannot be adequately described in terms of a lattice blurred by thermal motion, but that the local order in liquids manifested in the radial distribution function is of an essentially different nature from the long range order in crystals (198)."

A. THE INERT GASES

1. *Helium*

In spite of the difficulty of making diffraction measurements on liquid helium, there has been great interest in comparing its scattering above and below the lambda transition. Early observation (192) showed no difference in scattering for HeI and HeII, and later work (15, 146, 168, 178, 291, 292, 293) seems to confirm this even to the extent of showing (377) no anomaly in the low angle scattering at the transition temperature. Nevertheless, because of very small intensity differences, Henshaw (165, 166) suggested that there is some indication of less spatial order below the lambda point than above. Although others (147) also find the first maximum in intensity to be from 4 to 6% greater above the lambda transition, and even though this temperature effect is in the opposite direction from that exhibited by ordinary liquids, the exact structural implication, if any, is not made clear. The distribution functions obtained at 1.06° and 2.29°K. under saturation vapor pressure are practically superimposable and differ in height by only about 2% at the first maximum.

Henshaw's results, obtained over a wide range of conditions, show a distance of closest approach (that is, where the distribution function becomes essentially zero) that remains practically constant at about 2.3 Å., but the first maximum in the distribution function, as well as the mean number of nearest neighbors, changes with temperature and pressure. In going from a density of 0.166 g./cm.^{3} at 2.05°K. and 14.9 atm. to 0.184 g./cm.^{3} at 4.2°K. and 51.3 atm. there is also a shift in the main maximum in intensity to higher angles, and it becomes sharper. The maxima in the distribution function also become more sharply defined and indicate smaller mean separations. Some of the results are given in Table I.

TABLE I

RADIAL DISTRIBUTION DATA FOR HELIUM

T, °K.	Pressure	Mean separation of nearest neighbors, Å.	Mean number of nearest neighbors	Ref.
1.06 2.29 2.46	VP	3.80	8.5–9.7	(165)
5.04	VP	3.94	5.8–7.0	(166)
4.2	51.3 atm.	3.55	8.9–10.2	(166)
1.4	VP	4.00	10.4	(147)
2.4	VP	3.85	10.5	(147)
4.2	VP	3.87	10.6	(147)
2.06	VP	3.15 and 4.24	4 + 6	(292)

Henshaw records positions of second nearest neighbors at about 5 Å. The second maximum in the radial distribution, however, actually occurs around 7 Å., and the former value is near a minimum, having been inferred by subtracting a symmetrical first maximum from the distribution function. This resolution is one of subjective judgment, and his further suggestion that close packing may be deduced from the fact that the ratio of separations between first and second neighbors is approximately $\sqrt{2}$ seems somewhat beyond actual experimental verification. Even so, it is reasonably certain that there is little or no demonstrable structural change at the lambda point, and other indications are that changes in the momentum may be more significant in explaining the transition (144, 164, 170, 220).

2. Neon

In a neutron diffraction study of liquid neon at 26°K., Henshaw (163) has made intensity measurements to about $s = 6$ Å.$^{-1}$. The distribution function's first maximum is at 3.17 Å. and corresponds to 8.8 nearest neighbors. Comparison with the density changes upon melting shows that more than a mere dilation of the solid structure is involved. These results are in excellent agreement with those obtained in an extensive X-ray study by Stirpe and Tompson (356) over a wide range of conditions. At 24.7°K. they report 8.4–8.5 nearest neighbors centered at 3.18 Å. Their measurements are along the saturation vapor pressure curve and show a decrease to about 4 nearest neighbors at the critical temperature. The maxima in the intensity and in the radial distribution function broaden with increasing temperature, in keeping with the intuitive notion that increased thermal motion reduces preferential ordering. In a qualitative study of the low angle scattering they show that large scale inhomogeneities become significant as the critical region is approached and that, at equal densities, the low angle scattering is much the same for the gas and liquid.

Henshaw considers the possibility that the repulsive energy in the pair potential function rises more sharply than r^{-12} and that the potential bowl may be broader than that in the Lennard-Jones 6:12 potential. This he bases on the fact that the ratio between the distances at which the density cutoff and first density maximum are observed is less (0.79) than the expected value (0.89) for a Lennard-Jones potential. Even though the small incoherent correction has little influence on this ratio, it must be remembered that the finite upper limit of intensity measurement and other experimental factors broaden all maxima in the distribution function (391). Thus the value of 0.79 must be viewed as a lower limit.

3. Argon

Liquid argon is perhaps the most accessible of the inert gases in terms of boiling point and commercial availability, and it has received much attention (105, 106, 107, 138, 162, 169, 190, 219).

TABLE II

RADIAL DISTRIBUTION DATA FOR ARGON

T, °K.	Pressure, atm.	Mean separation of nearest neighbors, Å.	Mean number of nearest neighbors	Ref.
86.3	VP	3.9	8.2	(169)
89	1.2	3.8	9.6–10.3	(219)
84	VP	3.81	8.2	(162)
90	4.5	3.90	7	(106)
84.4	0.8	3.79	10.2–10.9	(107)
91.8	1.8	3.79	6.8–7.2	(107)
126.7	18.3	3.8	5.9–6.2	(107)
144.1	37.7	3.8	3.9–4.6	(107)
149.3	46.8	4.5	6	(107)

In a now classic study (107) of argon, which includes measurements at ten points along the vapor pressure curve and at fifteen other conditions, there is demonstrated spectacularly the effect of both temperature and pressure on the observed intensity and the distribution functions. The measurements extend to about $s = 8.5$ Å.$^{-1}$ and are some of the first to be made with a counter as detector.

In proceeding from 84.4°K. and 0.8 atm. to 149.3°K. and 46.8 atm. (see Table II) the number and sharpness of oscillations in the intensity decrease markedly, and the intensity at small angles becomes noticeable. As expected, there is a corresponding broadening of the maxima in the distribution function at the higher temperatures. The behavior of the distribution function at small values of r is not shown, but considerable undershoot (to negative values) is suggested. Thus, unless this is taken into account, the number of nearest neighbors may be slightly overestimated.

An interesting sequence spanning the critical temperature above the critical pressure shows the change from the intensity expected for a liquid to that of a gas; and in another series the intensity scattered by the vapor is shown to change from a practically smooth curve at low pressure to one with a pronounced maximum at high pressure.

The results show that samples with the same specific volume scatter similarly and that there is no abrupt change in passing through the critical region. Detail persists in the diffraction pattern even at volumes 10–20% greater than the critical volume.

4. Krypton

The only study of liquid krypton is one by neutron diffraction recently completed by Clayton and Heaton (67, 68) at the Argonne National Laboratory. Their findings (Table III) are similar to those for the other inert gases except for scale, but they also studied the effects of data treatment in considerable detail. Moderate shifts in the scale factor and in the isotropic

TABLE III

RADIAL DISTRIBUTION DATA FOR KRYPTON AT SATURATION VAPOR PRESSURE (68)

T, °K.	Mean separation of nearest neighbors, Å.	Mean number of nearest neighbors
117	4.02	8.5
133	4.04	8.0
153	4.08	7.0
183	4.10	6.5
210	4.20	4.0

background correction had little effect on the radial distribution function. Much more dramatic, however, is the effect on the radial distribution function produced by terminating the intensity data at selected values of s. The intensity curve for 117°K. is shown in Figure 4, and the distribution functions obtained by termination of the Fourier transform at the points indicated are shown in Figure 5. The most evident trend, aside from the loss of detail, is in the appearance of a small maximum between the first and second main maxima. Although it might be thought that this is a result of the improved resolution afforded by the higher upper limit, its behavior is exactly that expected for termination error. Stirpe and Tompson (356) came to a similar conclusion about a small intervening peak for neon. This phenomenon occurs in many determinations, and it usually can be accounted for in this way.

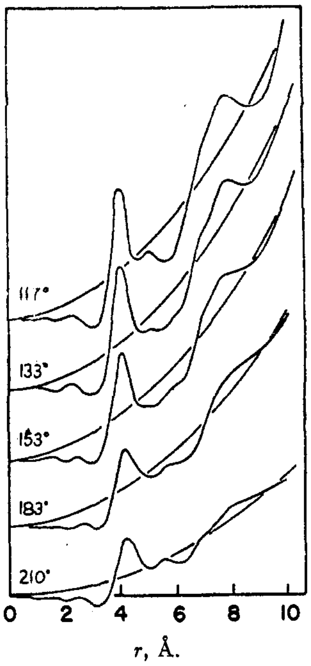

FIG. 3.—Radial distribution curves for liquid krypton (67). The parabolas are given by $4\pi r^2\rho_0$. (Reproduced by permission.)

Finbak (117) recognized this and other types of errors as the source of small spurious maxima in the radial distribution function. His statement still applies to current work on the inert gases and many metals: "When the small extra maxima are removed, all these distribution curves become astonishingly similar and extremely simple."

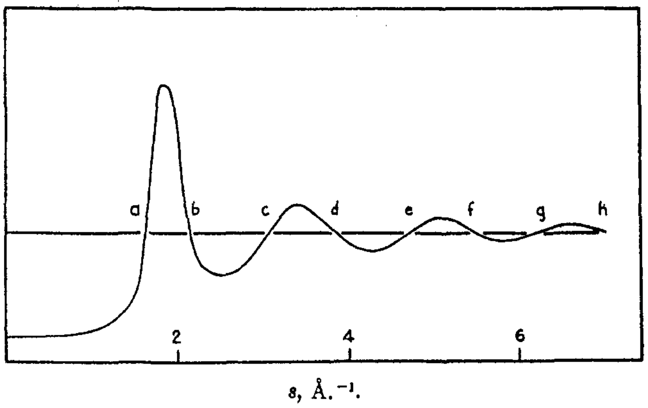

FIG. 4.—Intensity for liquid krypton at 117°K (67). (Reproduced by permission.)

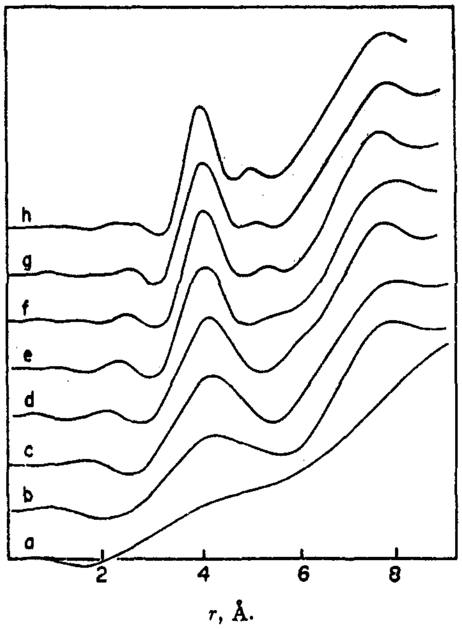

FIG. 5.—The effect of termination is examined in this sequence where the Fourier inversion of intensity for liquid krypton at 117°K. was carried, in each case, to the corresponding limit indicated in Fig. 4. The behavior of the small maxima flanking the first maximum is approximately that expected from the termination effect (67). (Reproduced by permission.)

In addition, Clayton and Heaton show how peak positions and area shift with termination (see Table IV). Table IV also includes the ratio between r_0, the

TABLE IV

EFFECT OF TERMINATION OF INTENSITY DATA, 117°K. (68)

s_0, Å.$^{-1}$	r_0/r_m	r_m, Å.	Mean number of nearest neighbors
2.14	0.59	4.46	12.0
3.10	0.70	4.30	11.5
3.90	0.74	4.20	11.0
4.76	0.79	4.14	10.0
5.54	0.81	4.08	9.5
6.35	0.82	4.05	9.0
7.30	0.84	4.02	8.5

value of r at which the distribution function falls to zero, and r_m, the value of r at the first maximum, and it seems to approach that value suggested by the Lennard-Jones potential.

5. Xenon

That the radial distribution function depends largely on volume is once again demonstrated in the work of Campbell and Hildebrand (55). The function for 160°K. and 1 atm. is practically superimposable on that of 183°K. and 130 atm, where the density is the same. The results are much the same as those for the other inert gases, and there is a small, but prominent, maximum in the distribution function between the first two main maxima. Since the behavior of the distribution function is not shown from $r = 0$ out to the first maximum it is more difficult to tell whether it is caused by the finite intensity limit, but the minor peak is in the correct location for attribution as such. The number of nearest neighbors ranges from 8.3 to 10.1 depending on the conditions and the way of assigning areas, and their mean separation ranges from 4.43 to 4.50 Å.

B. THE NON-METALS

1. Oxygen

From early observations (188, 189, 359) it was deduced that the internuclear distance in the oxygen molecule is about 1.3 Å. More recent diffraction measurements agree on this point, but uncertainty still remains about the structure of liquid oxygen. Sharrah and Gingrich (326, 327) obtained maxima in the radial distribution function at 1.3, 2.2, and 3.4 Å. at 89°K. and 1.25, 2.15, and 3.2 at 62°K. Since the area of the first peak was for slightly more (1.18 at 62° and 1.08 at 89°) than one near neighbor, and because of the discrete peak at 2.15 Å. they suggested, with some hesitancy, the possible existence of ozone, O_3, molecules in the liquid. It has been shown (28, 184, 358), however, that the peak at 2.15 Å. probably is due to termination error.

When this work was first repeated by neutron diffraction (169) the maximum at 2.2 Å. did not occur in the distribution function. At the same time 1.5 nearest neighbors at 1.25 Å. were found and tetrahedral O_4 molecules, present in about 25% by weight, were presumed responsible for the excess beyond the value of 1 expected for a diatomic molecule.

A question about the significance of unusual low angle intensity for the neutron case evidently provoked a re-examination of this system, and in measurements at 54.7, 62.4, 69.0, and 90.7°K., Henshaw (167) proposes an angularly dependent magnetic contribution to the scattering to explain this anomaly. After subtracting a correction based on the assumption of independent magnetic moments and a magnetic scattering cross section of 4.58 barns, good agreement is obtained between the corrected neutron intensity and the X-ray intensity. It is good enough, considering the spread of the corrected neutron data, that the author's suggestion of magnetic coupling must be viewed with reservation.

The radial distribution functions in this study are highly oscillatory, and the peak at 2.2 Å. reappears. A serious systematic error is probable, and, if the locations of main peaks are taken from the least oscillatory curve at 54.7°K. the subsidiary maxima in the other curves are reasonably well accounted for by a termination error due to the cutoff at $s = 7.6$ Å.$^{-1}$.

Although Henshaw indicates that the first maximum (at 1.26 Å.) contains an area of 1.26 atoms and that this could be explained by 12% by weight of O_4, he adds that the experiments may not be precise enough to warrant attaching significance to the deviation of the value 1.26 from unity. The second maximum in the distribution function at about 4 Å. gives 16–20 second nearest atom neighbors or 8–10 molecules per atom of oxygen.

The available diffraction data do not provide a very satisfactory picture of the structure of liquid oxygen, but it seems quite unlikely that significant amounts of molecules other than the diatomic O_2 might be found upon careful re-examination.

2. Nitrogen

Twenty years after the first measurements on liquid nitrogen (191), Sharrah (325) repeated the observations, finding intensity maxima at different locations, and he obtained a radial distribution function with a discrete maximum at 1.3 Å. containing 1.03 atoms. The separation is about 0.2 Å. greater than that found for gaseous nitrogen molecules, and is greater than that shown in the radial distribution function obtained from neutron diffraction (169), namely, 1.1 Å. In both functions there is a gap in atom density between the first and second main maxima, the latter occurring at about 4.4 Å. in the neutron study and at about 4.0 Å. in the X-ray case. Although Sharrah's radial distribution function shows a small intervening bump, the distance of closest approach for the second nearest atom neighbors is approximately 3 Å. In the neutron study, 23.6 atom neighbors or 11.8 molecule neighbors per nitrogen atom are assigned to the second maximum. Although these studies agree on the expected diatomic molecule indicated by the first maximum, the over-all agreement of the distribution functions is not satisfactory. The explanation for this is more likely to be found in intensity and scaling errors than in the difference in upper limits for intensity data (6.3 Å.$^{-1}$ for X-rays and 7.4 Å.$^{-1}$ for neutrons).

3. Chlorine

The main feature in the radial distribution function (134, 135, 136) is the discrete first maximum at 2.01 Å., which corresponds to 1 atom neighbor per chlorine atom. The second main peak, at 4.0 Å., appears to contain only 6–8 atoms.

4. Phosphorus

In liquid yellow phosphorus the tetrahedral molecule P_4 apparently exists, as the first peak, at 2.25 Å., is discrete, and corresponds to 3 nearest neighbors (372). The existence of the molecule is supported by the constancy of the peak's position with temperature, although it does become slightly broader at higher temperature. Even though the higher melting amorphous red and black forms of phosphorus also show 3 nearest neighbors at 2.28 Å., the remaining features of their radial distribution functions are different from those of yellow phosphorus, and it is likely that they have disordered structures related to the puckered layering in crystalline black phosphorus (177).

5. Sulfur

Liquid sulfur was the subject of several observations (27, 88, 89, 274, 276, 277, 278, 282) of the way in which positions of maxima in the intensity change with temperature. In an attempt to resolve conflicting findings Gingrich (137) had made photographic measurements over the range 124–300°, and found an apparent shift near 160°, the temperature above which sudden cooling yields plastic or amorphous sulfur. On re-examination, however, with improved collimation and counting techniques, he and Tompson (374) discovered that this effect was due actually to the varying relative contributions of two maxima (at s = 1.23 and 1.72 Å.$^{-1}$), the positions of which are insensitive to temperature.

At 300° the two maxima are of comparable intensity, but below 200° the maximum at 1.72 Å.$^{-1}$ predominates. Except for this feature the curves are remarkably similar at the several temperatures. At each temperature the number of nearest neighbors (at 2.07 Å.) is essentially 2. There are additional maxima in the radial distribution function which occur at distances appropriate (3.4 and 4.5 Å.) to a ring-like S_8 molecule, and although the first maximum remains unaffected, the third maximum, especially, undergoes drastic broadening with increasing temperature. It is attractive to think that the S_8 molecule does exist in liquid sulfur and that extensive reorganization involving both ring scission and chain formation may account for these observations.

Tompson and Gingrich found that their X-ray intensity agreed well with that they obtained by neutron diffraction, but not as well with that obtained earlier by Chamberlain (66). In addition they completed an interesting demonstration of the effect of the high angle intensity limit on the radial distribution function. Seven distribution functions, obtained by terminating the Fourier transform at values of s ranging from 5.76 to 15 Å.$^{-1}$, show the improvement of resolution at the higher cutoff values.

This careful study, carried to high s values with Ag radiation, appears to be representative of the best analyses that are currently being made with X-rays.

6. Selenium and Tellurium

When Prins had completed his early study (279) of selenium, the difficulties he had encountered were put aside, and his interest in "cette oeuvre laborieuse" was bequeathed to Lark-Horovitz. Under the direction of the latter, radial distribution functions for liquid selenium and tellurium eventually were obtained (50, 51, 53). There is good evidence for the retention of connectivity of atoms as found in the solids. but whether the atom chains form closed rings in the liquid is not firmly established, although it is strongly suggested. At 235 and 310° liquid selenium has 2 (observed value 2.3) nearest neighbors at 2.36 Å.; and at 465 and 610° liquid tellurium has 2 (observed 2.3) nearest neighbors at 2.9 Å. The values for liquid selenium agree well with those found (50, 131, 151, 204, 205, 297, 306, 307, 308) for amorphous selenium at room temperature, although there is lack of agreement on the further details of the radial distribution functions.

C. METALS

1. Alkali Metals

Gingrich and Heaton (140) recently have completed a neutron study of the alkali metals. There seems to be good agreement between their findings and those given in the earlier literature (see Table V). The use of neutrons was considered to be an improvement over X-rays

TABLE V

RADIAL DISTRIBUTION DATA FOR THE ALKALI METALS

	Temperature, °C.	Mean number of nearest neighbors	Mean separation of nearest neighbors, Å.	Ref.
Li	180	9.5	3.15	(140)
	200	9.8	3.24	(136)
Na	100	9.0	3.82	(140)
	100	7–8	3.83	(375, 376)
	103	9–10	4.0	(362)
	115	...	3.83	(141)
	400	7–8	3.90	(375, 376)
K	65	9.0	4.64	(140)
	70	9.0	4.7	(371)
	100	10	4.7	(221)
	115	...	4.62	(141)
	300	9	4.7	(221)
	395	9.2	4.76	(371)
Rb	40	9.5	4.97	(140)
Cs	30	9.0	5.31	(140)

in the cases of lithium, for which the incoherent scattering is a large part of the X-ray intensity, and of rubidium and cesium, for which large absorption coefficients make transmission measurements by X-ray difficult.

As might be expected, the number of nearest neighbors seems to be constant, between 9 and 10, for all members of the series, and, in fact, a normalization of the distribution curves to a common density and size shows little difference among the members. For instance, the ratio of the positions of the first and second maxima in the radial distribution functions is 1.9 for each metal.

A rather unusual feature of the study of rubidium is the splitting of the first maximum in the distribution function above 160°. At 240° this is manifested as a shoulder at about 5.8 Å., but at 360° there are two maxima, one at 5.0 and the other at 5.8 Å., of about equal height. Attempts to eliminate this effect by application of an artificial temperature factor were unsuccessful, so that one cannot easily blame the extra peak on termination error. Such behavior does not seem to occur for liquid cesium, although a small bump between the first and second maxima appears in the radial distribution function at 300°, which, however, is not present at 30° and 575°.

2. Mercury

Mercury has been studied more than any other metal, and the literature contains some lively controversy about the results, especially for the intensity. With the exception of Debye and Menke's (93, 94) pioneering work in deriving a radial distribution function for mercury, the early investigations (81, 270, 288, 289, 321, 322, 370, 392, 393, 396) displayed only intensities, to which Bragg's law occasionally was applied to estimate the separation of near neighbors.

In 1935 Boyd and Wakeham (32) made photographic measurements from −36 to 250°. Molybdenum Kα X-radiation was incident at a grazing angle, and the Kβ radiation was filtered with zirconium oxide. A large inner maximum (at s values of 1.4–1.7 Å.$^{-1}$, depending on temperature) became the subject of reinvestigation when Gregg and Gingrich (148) suggested that it might have arisen from incomplete monochromatization. The work was repeated in the same laboratory by Campbell and Hildebrand (54) using a crystal monochromator. They, too, found a strong inner maximum although at s = 1.25 Å.$^{-1}$. Subsequent determinations (80, 159, 180, 235, 236, 262, 335, 337, 380), as well as the other ealier ones, failed to confirm the presence of the large inner maximum, and since the same camera was used for both experiments in which it appeared, we conclude that it was a function of the apparatus. This, however, does not satisfactorily explain why the intensity of the inner maximum varied with temperature.

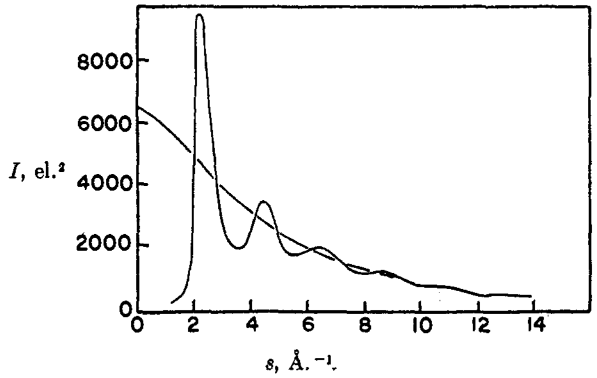

FIG. 6.—X-Ray intensity for liquid mercury at room temperature; the smooth curve is $f^2 + I_{inc.}$

Data from the radial distribution functions are assembled in Table VI. Most of the functions show assorted small maxima or ripples between the first and the second main maxima, and in some cases these are quite pronounced (32, 54, 159, 335). Since they are so irregular and irreproducible it is probable that they arise from a combination of termination error and incomplete compensation for absorption.

TABLE VI

RADIAL DISTRIBUTION DATA FOR MERCURY

Radiation, neutron or X-ray	Mean separation of nearest neighbors, Å.	Mean number of nearest neighbors	Ref.
X	3.23	10	(93)
X	3.0 + 3.47	6 + 4	(159)
X	3.0 (30°)	6	(32)
X	2.87 (−36°)	6	(32)
X	3.00	4.4-7	(54)
n	3.0	8	(380)
X	3.12	8	(335)
X	3.15	8	(262)
X	3.1	8.2	(337)
X	. . .	8.6	(180)

3. Lead and Bismuth

These metals frequently have been considered together as their melting points are relatively low, and since they are completely miscible in each other they are a convenient binary system to study. Many experiments on lead (81, 82, 83, 290, 295, 321) and bismuth (81, 82, 83, 266, 274, 290) dealt only with the positions of maxima in the intensity, but more recent investigations of lead (66, 86, 158, 328, 329) and bismuth (47, 48, 49, 66, 86, 158, 203, 309, 328, 329, 360) include the radial distribution function. A summary is shown in Table VII.

The mean separation for lead is somewhat shorter than that in the crystal at room temperature, namely, 3.49 Å., while the separation for bismuth lies between 3.11 and 3.47 Å., the distances to the three nearest and three next nearest neighbors in the crystal. Because it appears that the mean coördination number of lead is nearly 12 and the mean interatomic distance is shorter

TABLE VII

RADIAL DISTRIBUTION DATA FOR LEAD AND BISMUTH

	Radiation, electron neutron or X-ray	T, °C.	Mean separation of nearest neighbors, Å.	Mean number of nearest neighbors	Ref.
Pb	X	375	3.40	9 + 4	(158)
	n	390	3.4	12	(66)
	X	...	3.4	11	(86)
	n	350	3.40	9.4	(329)
	X	331	3.39	12.1	(328)
	n	350	3.38	11.7	(328)
Bi	X	285	3.35	7.6	(328)
	n	300	3.36	7.8	(328)
	n	300	3.35	7.7	(329)
	X	...	3.2	7–7.5	(86)
	n	310	3.2	8 to 4 Å.	(66)
	X	340	3.32	7–8	(158)
	e	280	3.55	8.6	(49)
	e	...	3.32	7	(309)

than in the crystal, the lower density of the liquid indicates empty regions comparable in size with atomic dimensions. Although we cannot further describe these regions, the liquid may not be viewed as being produced by a dilation of the solid; rather the destruction of long-range order prevents efficient packing and leaves a greater proportion of unfilled space. The decrease in density (4%) upon melting, however, is less than that expected (10%) for a "perfectly disordered" (19) arrangement, but perhaps the closer approach of atoms accounts for this.

That the density of liquid bismuth is greater than that of the solid is to be expected upon melting of the open solid structure and the accompanying increase in coördination number. Why the arrangements in liquid bismuth and liquid lead are so very different remains a baffling structural question.

4. *Miscellaneous*

Of the remaining metals, mainly those with low melting points have been studied: aluminum (47, 49, 136, 266), tin (46, 48, 49, 86, 136, 158, 266, 274, 309, 321), thallium (158, 321, 370), indium (49, 136, 158, 194, 295, 309), gold (158), gallium (158, 295, 340), germanium (158), zinc (136, 295), cadmium (136), antimony (160, 161), and silver (310). Radial distribution data are given in Table VIII. As is to be expected from the previous discussion, there is considerable variation in results of different workers, some due to undetected errors in intensity and scaling, some to termination error, and some to the subjective assignment of peak areas. Estimated probable errors for most studies of liquid metals are: mean number of nearest neighbors 0.5–1; mean separation of nearest neighbors, 0.1 Å. Some of the studies (158, 309, 310) in Table VIII show the enigmatic small maximum lying between the first and second main maxima of the distribution function. Experience suggests that this is due to experimental rather than to a structural effect.

TABLE VIII

RADIAL DISTRIBUTION DATA FOR METALS

	Radiation, electron or X-ray	T, °C.	Mean separation of nearest neighbors, Å.	Mean number of nearest neighbors	Ref.
Ag	e	...	2.86	...	(310)
Al	X	700	2.96	10.6	(136)
	e	720	2.94	10	(49)
Au	X	1100	2.86	11	(158)
Cd	X	350	3.06	8.3	(136)
Ga	e	...	2.79	9.0	(295)
	X	20	2.77	11	(158)
	X	34	2.81	10.5	(340)
Ge	X	1000	2.70	8	(158)
In	X	160	3.30	8.5	(136)
	X	390	3.36	8.4	(136)
	X	165	3.17	8	(158)
	e	170	3.40	11	(49)
	e	...	3.32	10.1	(295)
	X	176	3.32	8.5	(340)
Sb	X	665	3.12	6	(160, 161)
Sn	X	...	3.3	10	(86)
	X	280	3.2	10	(158)
	e	...	3.38	10.9	(309)
	X	250	3.38	10	(136)
	X	390	3.36	8.9	(136)
	e	300	3.6	11.5	(46, 48, 49)
	e	350	3.4	10	(46, 48)
	e	390	3.4	8.9	(46, 48)
Tl	X	375	3.30	8	(158)
Zn	X	460	2.94	10.8	(136)

D. AMORPHOUS ELEMENTS

Richter and his colleagues have studied the noncrystalline solid phases of selenium (131, 151, 297, 306, 307, 308), antimony (296, 298, 300, 302), arsenic (299, 304, 305), germanium (301, 303), silicon (301), and bismuth (310), which are produced by rapid cooling of either vapor or liquid. Although their diffraction patterns resemble those obtained from liquids, the accompanying distribution functions are highly oscillatory and contain regions of negative density. The behavior of the distribution function to the left of the first maximum is almost never shown, and the fact that in most cases the left side of the first maximum plunges steeply toward negative densities suggests a common irregularity either in the data or in the way it is processed. The authors of these reports give highly detailed interpretations in terms of layer formation and coördination polyhedra, but these have been criticized by Krebs (202), who offers an explanation for the spurious maxima based on error in the intensity scale (205). Table IX shows some of the results.

VII. POLYATOMIC LIQUIDS

A. COMPOUNDS

In this section we discuss compounds, but intermetallic ones are to be found under alloys, and a subsequent section deals with glassy compounds.

1. *Organic Compounds*

Historically this class of liquids has consumed more attention and has been the subject of more publications

TABLE IX

RADIAL DISTRIBUTION DATA FOR AMORPHOUS ELEMENTS

	Mean separation of nearest neighbors, Å.	Mean number of nearest neighbors	Ref.
As	...	3.1	(204, 205)
	...	3.2	(204, 205)
	2.25	2	(304)
	2.51	2.3–3	(305)
	2.46–2.50	3	(299)
Ge	2.5	4	(301)
	2.36	4	(303)
Si	2.4	4.2	(301)
Sb	2.8	4	(368)
	...	3	(298)
	2.87	...	(296, 300)
	2.86	3	(298)
Bi	3.3	6.8	(310)

(by scores of pages) than any other. Indeed, one of the first diffraction experiments in this field was that of Debye and Scherrer (95) on paraffin. The growth of interest in studying the diffraction of organic liquids paralleled the development of theories of chemical binding, and it was fitting, although not always rewarding, to apply a then new technique to the problems suggested by these theories. Diffraction by gases and crystals was ultimately to furnish the detailed description of molecular configurations and bond lengths that the chemist needs, but in retrospect it seems that concern with organic liquids at a time when the theory and the limitations of the diffraction method had not been perfected supplied little structural information. Some of the early studies of these complex liquids led inevitably to notions about the structure of liquids which are no longer felt to apply.

From studies reaching over almost twenty years Stewart developed a picture of liquid structure involving cybotaxis (344). This was the term he applied to molecular ordering sufficient to cause X-ray diffraction effects, and it was suggested that a liquid behaved as if composed of very small and imperfect crystals or ordered regions (perhaps 10–20. Å across) which were without sharp boundaries and constantly in motion.

In sequences of hydrocarbons, alcohols, and acids an intensity maximum that remains unchanged in position with increasing chain length was interpreted to yield diameters of transverse cross sections, while the maximum that changes position was supposed to give chain lengths. Warren (386) was able to rationalize the observed intensity patterns on the assumption of approximate parallelism of extended carbon skeletons, but it was not necessary to assume the organization required by the postulate of cybotaxis. In his many papers, Stewart felt that such organization justified the application of Bragg's law[5] to determine "spacings," and he did not determine radial distribution functions, even though worthwhile results were obtained by others (142, 399) who inverted his reliable intensity data. There are several reviews of his pioneering work (344, 346, 348, 350, 354), and a selection of other qualitative, and rather inconclusive, studies includes such compounds as fatty acids, pyridine, piperidine, and quinoline (338, 339); normal paraffins (206, 343); hexamethylbenzene (209); hexamethylenetetramine (210); naphthalene (59, 61, 62); benzene (58, 60); and hexyl alcohol (265). Cybotaxis, in the meantime, seems likely to suffer the fate of phlogiston.

a. Carbon Tetrachloride

Eisenstein (104) obtained intensities by photographic and counter methods to $s = 12$ Å.$^{-1}$ using crystal monochromatization. Applying the method of Warren, Krutter, and Morningstar (390) he found 4.6 chlorine neighbors per carbon (775 el.^{2} observed *vs.* 648 el.^{2} for 4 neighbors) at 1.85 Å. and 3.4 chlorine neighbors per chlorine (4129 el.^{2} observed *vs.* 3610 calculated for 3 neighbors) at 2.95 Å. The ratio of these two distances is 1.60, within 2% of the value 1.63 expected for tetrahedral geometry. Peaks at 3.9 and 6.2 Å. are assigned to intermolecular pairs.

Since the structure of the carbon tetrachloride molecule was well established by this and other means, Eisenstein calculated the intensity based on the tetrahedral configuration. A density function was used in which only the intramolecular atom pairs appeared. Beyond 3.6 Å. the density was taken to be that of the bulk liquid, and exceptionally good agreement with observed intensity was found for $s > 4$ Å.$^{-1}$. Below this value, contributions of intermolecular pairs give added detail which cannot, of course, be reproduced easily.

Bray and Gingrich (40) repeated this work at 25 and $-20°$. The intramolecular distances are 1.74 and 2.92 Å., and the corresponding maxima in the radial distribution function are discrete at both temperatures.

b. Hydrocarbons

Katzoff (187) carefully measured the intensities from normal heptane and decane, benzene, and cyclohexane. Although he did not carry out a distribution analysis, his suggestion that benzene molecules might be oriented as in the solid led to fair agreement between calculated and observed intensities. Pierce (264), however, upon inverting these data, was not convinced of the correctness of the suggestion. Pierce showed that at high angles the experimental intensity could be fitted with that due to independent molecules, and that benzene molecules are probably roughly parallel in the liquid with a mean distance of 4.3 Å. between molecular planes. He also tried to interpret Katzoff's data for normal heptane, but was unable to reach any definite conclusion about mutual orien-

[5] Bragg's law does provide a crude estimate of distances at which density maxima occur, but a translational identity period, as in a crystal, is not required. For diatomic molecules with an internuclear separation a, the first maximum in intensity would be observed at s such that $sa = 7.72$ (the value of x for the second maximum in $x^{-1} \sin x$) so that $\lambda = 0.814(2a \sin \theta)$.

tation of molecules (263). The first two maxima in his radial distribution function, at 1.4 and 2.5 Å. if interpreted as due to the first and second carbon neighbors, give 120° for the C–C–C angle. The first distance probably is in error, and Zachariasen (399) finds 1.54 and 2.50 Å. for these distances in nonyl alcohol, giving an angle of about 109°.

Skrishevskii and Mamedov (336) were able to distinguish between benzene and toluene, since the distribution function for the latter contained a peak at 1.65 Å. which they attributed to the interaction of the ring and methyl carbons. Subsequently Mamedov (238) compared the intensities for the xylene isomers.

c. Methanol and Ethanol

Harvey (155, 156) investigated these alcohols at room temperature and at −75°. The greater detail in intensity and the accompanying increase in resolution in the radial distribution function at low temperature simplify interpretation. Harvey's intensities agree well with those of others (45, 99, 384), and his interpretation parallels that of Prietzschk (268) and of Zachariasen (399), which was deduced from somewhat cruder data (355). The first maximum for methanol is at 1.6 Å., which is somewhat large, but it undoubtedly is due to carbon–oxygen pairs. The second, at 2.7 Å., is hardly noticeable at room temperature and is astonishingly well resolved at −75°. Its area corresponds to 2 oxygen neighbors per oxygen. Since it readily suggests hydrogen-bonded oxygen pairs, there must be a significant amount of chain formation in the liquid.

Ethanol gives similar results, with a spectacular temperature dependence. The first maximum in the distribution function is at 1.50 Å., which is consistent with the superposition of carbon–oxygen pairs (1.43 Å.) and carbon–carbon pairs (1.54 Å.). The third maximum, at 2.9 Å., again suggests 2 oxygen neighbors per oxygen. A second maximum, due to the terminal carbon–oxygen distance, is at 2.4 Å.

Propanol and butanol have also been studied (145), but with inconclusive results.

d. Miscellaneous

The carbon–chlorine distance in *o*-dichlorobenzene and *p*-dichlorobenzene has been estimated to be 1.7 Å. (84, 331), and the iodine–iodine distance in *p,p'*-diiodophenylmethane to be 10.5 Å. (201). A brief report on 1,3-(trimethyltin)-propane appeared recently (239).

2. Water

Bernal and Fowler's famous review (21) of hydration phenomena relied heavily on their interpretation of diffraction data (6, 243, 345, 347) for water. They proposed a continuous transition, with relative amounts changing with increasing temperature, from a tridymite or ice-like structure, through a quartz-like one, to a close-packed structure resembling that of solid ammonia. The models giving best agreement between calculated and observed intensities involve 4 nearest neighbors centered at 3.0 Å. These are nearly the values found by Morgan and Warren (250), whose definitive work over a range of temperature provides the best available radial distribution data.

Their intensity and radial distribution functions both show a loss of detail with increasing temperature, and the first maximum in the latter shifts from 2.90 Å. at 1.5° to 3.05 Å. at 83°. Accompanying this shift is a gradual increase in the apparent number of nearest neighbors from 4.4 to 4.9. For complete tetrahedral alignment a significant maximum at about $3.0 \times \sqrt{8/3}$ Å. is expected, but is not nicely resolved. On the basis of this and the density change on melting, Morgan and Warren suggested that the structure be described more aptly as a broken down ice structure. The remarkable (because the contact distance in the crystal is 2.76 Å.) density increase accompanying melting is supposed to be due to the filling in of neighbors between the first and second coördination shells in the crystal rather than to the closer approach of second nearest neighbors. Much of this description had been surmised by Katzoff (187), who first obtained a radial distribution function from X-ray data.

Incidentally, Stewart (349) compared the scattering from heavy water (D_2O) and normal water, finding virtually no difference at 25°. The slightly sharper peaks for heavy water are attributed to the fact that the heavy water is closer to its freezing point.

Following Morgan and Warren's careful study, Simons (330) and Finbak and Viervoll (121) made determinations with similar results. The former found 4 nearest neighbors lying between 2.75 and 3.25 Å., and the distribution function we construct from the latter's data gives about 4.5 nearest neighbors centered at 2.9 Å. This distribution function practically coincides with that of Morgan and Warren, although its second maximum, corresponding to the tetrahedron's edge, is more clearly indicated.

A more recent determination (100, 102) of the distribution function is rather dubious, agreeing only poorly with the earlier findings. Moreover, a rather unusual octahedral coördination is proposed without checking its consistency with area in the distribution function. To resolve what to them appeared to be a conflict, Brady and Romanow (39) report having obtained essentially the same radial distribution function as Morgan and Warren, although there is no indication that application of a significant absorption correction (231, 246) was made.

Future reconsideration requires careful attention to the incoherent correction (which is only approximately known), the absorption correction (especially in the usual parafocusing geometry), and the independent coherent scattering. For the last, the form factor of Banyard and March (10) should be valuable. At the moment, X-ray measurements on liquid water are only able to confirm our intuitive notions, which are based largely on the well-known structures of ice and the solid hydrates of some of the permanent gases (125, 257, 259). Measurements of the incoherent neutron scattering have shown distinct momentum components and a duration of configurations for about 10^{-12} sec. (42, 176).

3. Molten Salts

a. Alkali Halides

The alkali halides are perhaps the simplest systems in which to learn something of molten salt structures, and they have been studied in great detail at the Oak Ridge National Laboratory (230). The interpretation is similar to the one which Zarzycki (402) deduces from the decrease of both the mean number of nearest neighbors and their distance of closest approach upon melting. He has suggested that, taken together with the decrease in density, these observations show the existence of lacunae or hollow places in the liquid, that is, unoccupied space surrounded by ions in close contact. This is a rather vague picture, and the average description given by the distribution function includes no further detail. It is apparent, however, that the reduced efficiency of filling space permits a wider range of interionic distances than in the crystal, and that these separations are centered, for unlike ions, at values smaller than those the crystals have even at room temperature (see Table X). Distances between like ions seem to be larger, however. Coördination numbers for the liquids are significantly less than 6, the usual value for the solids, although Zarzycki (400) does find nearly 6 halide neighbors per cation in molten barium chloride and calcium fluoride.

TABLE X

RADIAL DISTRIBUTION DATA FOR ALKALI HALIDES

	Radiation	Mean separation of anion–cation, Å.	Anion–cation separation in crystal at room temperature, Å.	Mean number of nearest neighbors	Ref.
LiF	X	2.0	2.00	3.7	(402)
LiCl	X	2.47	2.57	4.0	(230)
	X	2.6		4.1	(400)
	n	...		3.5	(230)
LiBr	X	2.68	2.75	5.2	(230)
LiI	X	2.85	3.00	5.6	(230)
NaF	X	2.4	2.31	4.1	(402)
NaCl	X	2.8	2.81	4.7	(400)
NaI	X	3.15	3.23	4.0	(230)
KF	X	2.8	2.66	4.9	(402)
KCl	X	3.10	3.14	3.7	(230)
	X	3.2		5.2	(400)
	X	...		4.5	(230)
	X	3.14		5.8	(248)
	n	3.10		3.5	(230)
CsCl	X	3.53	3.57	4.6	(230)
CsBr	X	3.55	3.71	4.6	(230)
	n	3.55		4.7	(230)
CsI	X	3.85	3.95	4.5	(230)

The studies at Oak Ridge show the utmost precaution at every stage, and both neutrons and X-rays were used, with the spectrometer for the latter of rather sophisticated design. The negative neutron cross section for Li^7 permits unequivocal assignment of the lithium–chloride interaction, as it produces a minimum in the radial distribution function. In making assignments of peak areas the formalism of Waser and Schomaker (391) was used.

With reference to other investigations of alkali halides (218, 248, 400, 403), mention should be made of Zarzycki's ingenious apparatus (400). The molten salt is held by surface tension in a slotted platinum ribbon. Heating is controlled by passage of large currents through the ribbon, and X-ray measurements are made by transmission.

b. Low-melting Metal Halides

Ritter, Wood, and Harris have investigated aluminum chloride (154), indium trichloride (394), tin tetraiodide (395), and cadmium iodide (312), and molecule formation is adduced in each case but the last. Aluminum chloride is an unusual salt because it suffers a 45% decrease in density on melting, and its electrical resistivity increases enormously. The positions of the maxima in the radial distribution function lead to the proposal of a molecule Al_2Cl_6 in which two tetrahedra of chlorines share a common edge. The tetrahedral coördination of aluminum is borne out by the corresponding area in the first maximum, lying at 2.20 Å. As expected the second maximum falls at $2.20 \times \sqrt{8/3} = 3.60$ Å.

For indium iodide the results are less satisfying. The behavior of the distribution function is not shown for $r < 2$ Å., and only two principal maxima occur, at 2.70 and 4.52 Å. If one takes the area of the first maximum to give 4 iodines per indium (4.7 observed) then a model similar to that for aluminum chloride seems likely. In all, however, this proposal is more speculative.

Tin tetraiodide appears to be tetrahedral with a tin–iodine distance of 2.66 Å., and an iodine–iodine distance of 4.35 Å.

The interpretation of the distribution function for cadmium iodide is almost completely subjective. Although the area of the first maximum at 2.90 Å. gives 6 iodine neighbors per cadmium, the authors rule out regular octahedral coördination because the requisite maxima at $2.90 \times \sqrt{2}$ and 2.90×2 Å. do not appear to be resolved. They contend, moreover, that such an arrangement would have too high a density and then go on to propose that the liquid is formed by a dilation of the solid in order that they might account for the position of the second maximum.

That the agreement with the maximum required by the octahedron is lacking does not seem surprising nor serious inasmuch as the second maximum is surely a superposition of several interactions, and it spans a range of 2 Å. As for the density, each cadmium could well have six octahedral neighbors, and yet the liquid could manage a sufficiently low density through inefficient packing. If the octahedral interactions are viewed as smeared together with others in the second maximum, then the awkwardness can be avoided of having to account for an inconsistency in the cadmium–iodide distance required by dilation and of having to suggest preferential interaction to form some CdI_2 molecules.

In liquid bismuth(I) tetrachloroaluminate good evidence has been found for the existence of a triangular trimer, Bi_3^{+++} (233). A bismuth–bismuth distance of 3.0 Å. is reported, but the further details of the structure are to appear later.

c. Oxy-salts

These include only potassium nitrate (79), sodium nitrate (79, 216, 361), and sodium nitrite (361). It seems reasonable to suppose that the anions are intact in the melts, as 3 (2.6 observed) and 2 (1.7 observed) oxygen neighbors per nitrogen are found for the nitrate and nitrite. The mean nitrogen–oxygen distance is about 1.2 Å. in each case. The second maximum in the distribution function suffers from overlap of oxygen–oxygen and cation–oxygen interactions, but the mean separations are estimated to be 2.20 A. for the former and 2.45 and 2.95 Å. for sodium–oxygen and potassium–oxygen. The third maximum, at 4.3 Å. is quite large and probably contains interactions of ions of like charge.

4. Miscellaneous

Data for nitric oxide are consistent with a diatomic molecule of mean internuclear separation 1.3 Å. For nitrous oxide the first maximum in the distribution function is at 1.2 Å., and its area, 225 $el.^2$, is that expected for a linear (as opposed to a triangular) molecule (325).

Krogh-Moe's study (212) of carbon disulfide provides carbon–sulfur and sulfur–sulfur distances of 1.55 and 3.1 Å.. respectively, while Bastiansen and Finbak inferred a sulfur–oxygen distance of 1.46 Å. and an O–S–O angle of 124° in sulfur dioxide (13).

B. ALLOYS

The search for novel structural effects in alloys has been rather disappointing. Among the elusive effects for which diffraction evidence has been sought are compound formation, segregation into regions of essentially pure components, specific interactions in eutectic melts, and retention of crystalline arrangements. One of the earliest such studies was that of Banerjee (9), who attempted to show the formation of Na_2K molecules in the molten alloy. Later examination (141, 256) gives no such evidence and indicates a smooth variation in radial distribution with changing composition. It is shown that, for the first maximum, a sum of distribution functions for the pure components (weighted according to composition) can be made to coincide with the observed distribution function. Such coincidence, which omits explicit account of pairs of unlike atoms, should not be taken in the misleading sense that such pairs do not occur nor that the liquid is segregated into regions of pure components.

The coincidence of $x_1\rho_1 + x_2\rho_2$ with the observed distribution function merely implies that

$$A_{12} = (n_{12} + n_{21})^{-1}(n_{11}A_{11} + n_{22}A_{22})$$

where $x_j n_{ij}$ is the number of atoms of type j around one of type i, and the A's are the areas that single atom pairs contribute to the first maximum in the radial distribution function. If the n's have comparable values, then A_{12} becomes essentially the arithmetic mean of A_{11} and A_{22}, although the geometric mean is likely to be nearer to the value that should then be used. There will not be too much difference in these means for atoms of about the same atomic number, so that agreement of a distribution function so calculated with the one observed is a good indication of the random participation of atoms in a common distribution.

This type of variation of distribution function with composition also has been found for the mercury–indium (193) and tin–cadmium (3) systems. In the lead–bismuth (76, 223), lead–tin (334), tin–bismuth (227), lead–zinc (234), tin–zinc, and aluminum–silver (226) systems correspondence between observed intensity for the eutectic melts and a calculated sum of contributions from the pure liquids has been taken as evidence of segregation. The preceding analysis shows that such need not be the case.

Heterogeneity also has been suggested (158) for the molten compound AuSn, but on the basis of an unusual splitting in the first intensity maximum. The splitting has been confirmed (225, 260), but it can be accounted for by a fortuitous synthesis of $(sr)^{-1} \sin sr$ components. The radial distribution functions for all of these systems show no indication of irregularities. That for AuSn has only two pronounced maxima, one at 3.0 Å. and the other at 4 Å., while the function changes smoothly with composition in the lead–bismuth system (328), and it is unlikely that the supposed segregation into pure components exists in any of these systems.

In the aluminum–iron system it has been proposed (26) that iron in the liquid retains the coördination polyhedron of aluminums existing in the solid.

Only in electron diffraction studies of very thin metal films does the distribution function support the hypothesis that segregation of components occurs. For both aluminum–tin and aluminum–indium (49) there are two large maxima in the vicinity of 2.7 and 3.5 Å. which have been assigned to aluminum–aluminum and tin–tin (or indium–indium) pairs. As the temperature is raised, however, an intervening maximum at 3.1 Å. becomes especially prominent. It is possible that in the film there is preferential accumulation of one component in the surface phase which becomes washed out with increasing temperature.

One of the best demonstrations of the persistence of crystal forces in the liquids is that by Smallman and Frost (337), who studied the mercury–thallium system in the vicinity of the compound Hg_5Tl_2. These atoms have essentially the same scattering power so that the variation of scattered intensity with composition can be taken as a qualitative index of relative ordering of nearest neighbors. In a series at constant temperature they found that the lower the melting point of the alloy the smaller is the intensity of the first maximum; the intensity actually follows the melting point and is a maximum for Hg_5Tl_2. Although these workers go on to propose an approach to the crystalline arrangement for the melt, the precision of the distances used in the argument does not seem sufficient to confirm the conclusion. They do not suggest, however, that the solutions are not homogeneous, as true solutions are indicated in zinc and cadmium amalgams as well (185, 186).

There have been several studies (50, 52, 203, 367) of molten semiconductors with no unusual features to report. In both InSb and GaSe each atom is surrounded by 6 neighbors, at 3.13 Å. in the former and 2.40 Å. in the latter. The molten compounds In_2Bi and InBi do not seem to retain the specific interactions found in the solids (5).

C. SOLUTIONS OF NON-ELECTROLYTES

Our inability to describe most of these solutions as perfect extends to X-ray diffraction. Almost without exception the many studies in this area have been qualitative and productive of little understanding of structure. Upon occasion, the enthusiasm for a preconceived model has sought justification in what later proved to be erroneous results, but the justification was found, nevertheless. So Ward's (385) suggestion of the existence of emulsoid behavior in the cyclohexane–benzene system was found lacking by Murray and Warren (253). This did not deter Bell and Davey (17) from an assault upon the system seven years later, but their extensive discourse on molecular ordering was found to be "without experimental foundation" (108).

The qualitative studies are mostly in water solution and do not result in radial distribution data. Rather the dependence of intensity on concentration has been of concern, and Bragg's law is still applied empirically. In this category are aqueous solutions of sugar (56, 207), formaldehyde (356), dioxane (63), methanol (287), ethanol (63, 208, 373), acetone (85), and phenol (208, 249). Other systems include toluene–ethanol (25), benzene–ethanol (57), cyclohexane–carbon tetrachloride (64), ethanol–carbon tetrachloride (64), benzene–nitrobenzene, benzene–acetone, dioxane–ethanol (366), and such complicated ones as 1-butanol–1,2-dimethylcyclohexane (241, 242).

Rumpf (316) was able to find a bromine–bromine distance (3.53 Å.) for carbon tetrabromide in benzene, and Grjotheim and Krogh-Moe (152) have given evidence of sulfur chains for sulfur dissolved in carbon disulfide.

Holleman (174) tried to study the interaction between terminal iodine atoms in a series of di-iodoalkanes dissolved in decane. This involved compensating for all other interactions by subtracting from the distribution function a distribution due to mono-iodohexane. It appears that the uncertainty in the distribution functions probably is greater than the effect to be detected, and the interpretation is rather dubious. An iodine–iodine distance of 3.6 Å. is indicated for methylene iodide.

D. IONIC SOLUTIONS

Because of its importance in theories of ion–ion and ion–solvent interaction, knowledge of coördination or solvation numbers and of spatial configuration is in great demand. The diffraction method provides necessary information for theoretical purposes, but, as we have seen, it is often insufficient in detail, and subjective judgment must be applied to identifying even the first maximum in the radial distribution function. As it is in the case of solutions of non-electrolytes, most of the study of ionic solutions has been qualitative, and radial distribution functions are not included. Again, many of the observations are limited to the way in which intensity depends on concentration, and they have generated speculation over alterations in solvent structure, degree of ionization, or extent of solvation. Such studies include sulfuric acid (30, 211), sulfates (323, 324, 363, 364), halides (16, 243, 271, 272, 351, 352, 353), and a rather comprehensive attempt to classify the scattering patterns of salt solutions (273, 275, 280, 281). Studies of aqueous ammonium nitrate (244) and perchloric acid (245) were uninformative.

1. Solvation Studies

Attempts to get more detail about ion–solvent interactions have relied on radial distribution functions, but in most cases these only suggest structural possibilities, and limited, but not unequivocal, confirmation of proposed structures is provided. Thus Finbak, for example, concluded that, in concentrated sulfuric acid (115, 120, 122), there is hydrogen bonding between oxygens of adjacent sulfate ions. This he believed to follow from the fact that the distribution maximum at 2.85 Å. decreases upon dilution. Also he and his colleagues obtained these interatomic distances: S–O in sulfate, 1.51 Å.; P–O in phosphate, 1.56 Å.; N–O in nitrate, 1.2 A.; O–O in nitrate, 3.7 Å.; and Cl–H_2O in hydrochloric acid, 3.3 Å. (12, 13, 119). Although at first (97) it appeared that each sodium in concentrated sodium hydroxide is surrounded by 4 waters at 2.03 Å., a later experiment on 25% solution gave 6 waters at 2.33 Å. Much of this work confirmed the enhancement of hydrogen-bonding in acids and bases, and further discussion of the applicability of diffraction methods is given in a review by Samoilov (319).

In an effort to understand the effect of dissolved ions on the structure of water, Brady and Krause (38) have investigated solutions of potassium hydroxide, both of whose ions are of about the same size as a water molecule, and also potassium chloride. The distribution functions for the hydroxide solutions are very much like that for water, and this suggests that the ions enter substitutionally into the water arrangement. Although this presumes coördination numbers of about 4 for the ions, the insensitivity of the calculated peak area to the water–hydroxide contribution makes values as high as 6 a possibility for the hydration number of hydroxide. There is clearly an infinite number of ways in which the first maximum might be fitted with the three pairs of interactions falling in this range, but this choice is made in view of its consistency with accepted notions concerning solvation.

For the potassium chloride solution the first maximum (at 3.2 Å.) is ascribed largely to chlorine–water pairs, and the water–water interaction appears as a shoulder at 2.8 Å. The overlapping of water–water, chlorine–water, and potassium–water interactions makes accounting for the area especially difficult. The problem seems to be that there is too much area unless a greater number of water–water pairs is accepted. It is suggested that this may be made possible through the disrupting of the usual water arrangement by the large chloride ions.

Brady (35) later examined a more concentrated solution of potassium hydroxide (approximately $KOH \cdot 3H_2O$) and also one of lithium chloride (approximately $LiCl \cdot 8H_2O$) as part of this study. The former solution was used to decide between 4 and 6 for the hydration number of hydroxide ion. In its distribution function a small peak appears at about 3.9 Å., and, since this is about $2.8 \times \sqrt{2}$, it was assumed that it is due to an octahedron of waters around each hydroxide. This may be so, but the supposition can hardly be substantiated, as suggested, by the agreement between calculated and observed areas for the first maximum when the choice between 4 and 6 involves only 3% of the area.

For the lithium chloride solution there is little evidence for the water–water interaction that occurs at 2.8–2.9 A. for pure water and in dilute solutions. The first maximum in the distribution function occurs at a chlorine–water distance, but accounting for its area requires considerable juggling of overlapping interactions, and it is possible to do this in a way that pleases intuition. A hydration number of 4 was assumed for lithium, and associated water–water interactions have been subtracted. Chlorines then were assumed to have 8–9 water neighbors and the interactions of these waters were subtracted leaving an area consistent with a hydration by 8–9 waters. In this analysis the interactions of water between the two hydrated ions were ignored, and it is likely that the hydration number of the chloride ion is somewhat smaller. To correct for this and try to extract the desired information appears to be futile, because one's expectation is virtually the only guide in choosing from the wide spectrum of possible coördination numbers. It is clear, however, and significant that lithium chloride produces an extensive rearrangement of water molecules upon solution.

Lithium iodide also produces a marked change in water's structure, and a hydration number of 8 has been suggested for the iodide ion (357).

Most recently Brady (37) describes measurements on erbium chloride and iodide solutions, showing nicely the octahedral coördination of the erbium ion by water molecules. An accounting is given of the likely deposition of halide ions near the solvated cation, and there is a discussion of the ordering effect that the tight solvation sheath has upon neighboring water molecules. There appears to be an error in the calculation of the expected erbium–iodine and erbium–chlorine distance based on the radii given. We calculate 4.8 and 4.4 Å., and, although the values 5.2 and 4.6 Å. are used in the interpretation, the main features of the structural description seem to agree with what one expects.

2. Halide Complexes

At times the failure to obtain meaningful information from the distribution data has resulted from poor resolution, disturbance by diffraction errors, or lack of its complete utilization. Thus in an inconclusive study (269) of 1.05 and 2.98 *F* barium iodide solutions, the only positive result is that there is a barium–iodine interaction at 3.8 Å. Again, only the distances in the radial distribution functions were used to make structural deductions for aqueous solutions of mercury halide complexes (100, 103) and for calcium and potassium chloride solutions (101). The functions themselves are questionable, however, because a proportionate amount for pure water has been subtracted from them. This is to assume that the water distribution is unaltered upon addition of solute, a rather unlikely surmise. Even though assignments of various interactions are not checked against peak areas, and though coördination numbers given are those assumed *a priori*, it is probable that tetrahedral halide complexes, HgX_4^{--}, exist in the solutions studied. Tetrahedral iodide complexes for both mercury(II) and zinc(II) had been suggested by earlier work (77, 78).

Nilsson has examined iodide, thiocyanate, and thiosulfate complexes of silver(I) in aqueous solution (254). He, too, tried to make a solvent correction by subtracting a distribution function for a lithium iodide solution containing the same concentration of iodide as estimated to be free in the solution of complex. For the iodide this has little effect, however, on any but the most dilute solutions (maximum silver ion concentration is 3.7 *F*). The first maximum (at 2.9 Å.) is attributed entirely to silver–iodine interactions, and a coordination number of 4 is obtained. The iodine–iodine interaction expected for a tetrahedron is apparent in the maximum at 4.8 Å. Nilsson supposed that polynuclear species must exist to give four-coördination because the I/Ag ratio in the solution is only 2.9, but the nature of the species cannot be deduced. A previous study (73) of silver iodide complexes in acetone gave a similar distribution function, but molecular weight considerations led to curious proposals of a non-linear AgI_2^- and an ion $Ag_4I_6^{--}$, depending on the conditions (which are not given).

For the thiocyanate and thiosulfate complexes it proved impossible to determine coördination numbers of silver, even though it is reasonably certain that the sulfur is attached to silver in both cases.

Debot's study (91) of zinc and cadmium chloride solutions is based on the unlikely assumption that linear molecules of $ZnCl_2$ and $CdCl_2$ exist in solution, and the resulting distribution function is supposed to give the distribution of these molecules. In another study (215) 3 chlorine neighbors at 2.28 Å. and one water neighbor at 2.05 are assigned to each zinc in 27.5 molal zinc chloride solution, which is virtually molten $ZnCl_2 \cdot 2H_2O$.

To see whether the extent of complex ion formation could be determined by diffraction, Brady (36) measured the X-ray scattering from ferric chloride solution and decided that half of the iron in 5.1 molal solution is complexed as octahedral $FeCl_6^{---}$ ions. He appears, however, to have ignored the fact that any reasonable coördination of the remaining half of the iron (say, by water) would make a substantial contribution to the area of the first maximum, and the example of a literal mono-coördinate $FeCl^{++}$, with which he dismisses the remaining half, is unrealistic.

In a repetition of this work and in experiments with added chloride ion (as hydrochloric acid), it seems that a more reasonable interpretation can be made in terms of $FeCl_4^-$ complex ions (342). Both studies suggest minimal coördination of iron by water, but the latter interpretation is more acceptable in terms of spectral and extraction measurements (60).

3. *Polynuclear Complexes*

In a unique application of the methods of treating electron diffraction data, the structures of several heavy metal halide complex ions have been given (358). Although it has been objected (14) that interaction between solvent (water) and the ion has been ignored, the credibility of the results justifies the assumption that the short-range interactions between the heavy scatterers dominate the intensity. Octahedral coördination of metal by halide is found for the hexachloro- and hexabromoplatinate(IV) ions. The metal–halogen and halogen–halogen distances are 2.37, 3.35 Å., and 2.43, 3.41 Å. In a solution of $Nb_6Cl_{14} \cdot 7H_2O$ good evidence exists for the $Nb_6Cl_{12}^{++}$ ion. The niobiums are at the corners of an octahedron of edge 2.9 Å., and the chlorines are on radial lines bisecting the octahedron's edges so that the niobium–chlorine distance is 2.4 Å. Similar structures are found for $Ta_6Br_{12}^{++}$ and $Ta_6Cl_{12}^{++}$.

Equally complex structures have been unravelled for the silicotungstate ion, $SiW_{12}O_{40}^{----}$ (232), the $Bi_6(OH)_{12}^{6+}$ ion (233), the $Mo_6Cl_8^{4+}$ ion in ethanol (45), and the $Hf_4(OH)_8Cl_8$ molecule (252). In the first two cases the correctness of the proposed structures is confirmed by the beautiful agreement (to $s = 16$ Å.$^{-1}$) between calculated and observed intensities. The structure of the silicotungstate ion in solution is essentially the same as that found for the crystal, and the same probably is true of the phosphotungstate ion (7, 8). The structure of the bismuth hydroxide complex is like that of the niobium chloride complex, with an octahedron edge of 3.70 Å. and a bismuth–oxygen distance of 2.33 Å.

The analysis of the molybdenum chloride data is not as persuasive, but similarity with the crystal configuration (43, 44) is likely. In this, the corners of an octahedron of molybdenums point toward the faces of a cube defined by eight chlorines. The molybdenum–molybdenum distance is 2.6 Å., and that for molybdenum–chlorine is 2.5 Å.

Using data to $s = 10$ Å.$^{-1}$, Muha and Vaughan (252) have shown the correspondence between solution and crystal structures (69) for the $(Hf_4(OH)_8 \cdot 16H_2O)^{8+}$ ion and the similar ion for zirconium. When the oxyhalides are dissolved it appears that the two halogens per hafnium are incorporated with this complex cation to give a neutral molecule.

E. GLASSES

In 1940 Warren (388) reviewed the X-ray work on glasses which, at that time, applied (with the exception of beryllium fluoride) only to silicates and borates. It was then quite well established that the tetrahedral coördination of silicon by oxygen was the rule in glassy silica as well as in modified glasses. Addition of alkali metal oxides as modifiers apparently breaks Si–O–Si bonds and gives singly bonded oxygens. Continued addition results in structural units small enough to orient more easily and eventually to form crystalline material, and devitrification occurs.

For boric oxide the picture of planar trigonal coördination of boron is accepted, and when alkali metal oxide is added, not only are singly bonded oxygens produced, but a point is reached where there is enough oxygen for tetrahedral coördination to take place.

Since the time of Warren's review there has been little structural work on glasses other than borates and silicates, and for these the findings reflect the features he described. Zarzycki (401) looked at both silicon dioxide and germanium dioxide glasses, finding the expected four-coördination in both the solid glasses and the melts at temperatures well above 1000°.

In a clever neutron study of silica (41), a velocity selector was used to scan *s* at constant angle, and the radial distribution found is similar to that of Warren (388).

For boric oxide there have been new determinations, which support the trigonal coördination scheme. Despujols (96) shows a completely resolved first maximum in the radial distribution function at 1.37 Å. which corresponds to 3 (observed 2.6) boron–oxygen pairs and Milberg and Meller (247) find much the same situation for $3B_2O_3{\cdot}H_2O$. The first two maxima are the same as for boric oxide, but the third moves out a bit for the hydrate, indicating a loosening of the network through addition of the extra oxygens. The radial distribution function of Herre and Richter (171) seems to indicate the trigonal coördination, but the function is so oscillatory as to have limited value, and not much confidence can be placed in their discussion of a layer structure.

Green (150) gives data for potassium borate glasses, which are similar to those for sodium borate glasses (24) in that they, too, show a shift from three to four-coördination with increasing oxygen content. Whether this occurs or not for lithium borate glasses is not clear since it was suggested (153) that there is actually a shift from four to three-coördination upon addition of lithium oxide to boric oxide. Later it was decided that the change, if it takes place, could not be proved from the data (214). Really the situation is probably much the same as for the other alkali metal oxides.

X-Ray study (34) of sodium metaphosphate glass, $NaPO_3$, shows the expected tetrahedron of oxygens around each phosphorus at a mean distance of 1.55 Å. Negatively charged linear phosphate polymers are proposed to be held together by sodium ions.

The structure of glassy arsenious oxide is like that of the mineral claudetite, in which arsenic forms a trigonal pyramid with 3 oxygen neighbors, and each oxygen has 2 arsenic neighbors (31, 267).

A similar structure is found (261) for arsenic sulfide glass and, upon addition of lead sulfide, the arsenic changes to tetrahedral coördination. Indeed, in the unusual natural glass revoredite, $5PbS{\cdot}3As_2S_3$, it seems that the structure is largely determined by a disordered close-packing of sulfurs in which lead occupies octahedral holes and arsenic occupies tetrahedral holes (261).

Another unusual glass which also does not seem to fit into Zachariasen's highly successful classification (398) is formed by tellurium oxide. Actually the glass does not form unless a modifier is added, and the glass studied (33) contains 10 mole per cent lithium oxide. Apparently the coördination is similar to the distorted octahedral one found in the crystal.

VIII. SUMMARY

> "Things are seldom what they seem.
> Skim milk masquerades as cream."
> "H.M.S. Pinafore"

The history of the application of diffraction techniques to liquids shows that its ability to furnish useful structural information depends first of all upon obtaining precise data for the coherent intensity to large values of *s* and upon attention to possible errors in data treatment. Indirectly it depends on the level of detail to which the structural questions are directed. For the main question, namely, how to describe the geometrical arrangement of nearly close-packed atoms where atom positions are constantly changing and exchanging, we must be content with a rather gross answer. In terms of the diffraction technique there is little operational justification for demanding too specific an answer, for to describe the average coördination geometry is a problem which does not have a unique solution if distribution functions alone are used. These restrictions are the most severe in the liquids which, chemically, are the simplest. The problem is that of the mathematician with more variables than relationships with which to determine them.

For other liquids, those containing molecules, it is possible to give a reasonable accounting of the intramolecular structure, but the interpretation of intermolecular structure remains ambiguous. Thus as we review Zernike and Prins' early classification (404) of ordering into two categories, (a) the arrangement of atoms in molecules, and (b) the arrangement of molecules relative to each other, we see that adequate descriptions can be given of the first category, but the last, which is the heart of the liquid structure problem, is too poorly defined to allow any but a statistical description incapable of suggesting unique structures.

Although these remarks may sound pessimistic, they are intended to emphasize the properties peculiar to the liquid state and the limitations they place not only upon the deductions that may be made from diffraction data but also upon the questions that may be asked legitimately of a diffraction experiment. They may also serve as a caution to the experimentalist, who, as Prins shrewdly observes (277), often finds that "it is difficult not to fall a victim to wishful analyzing." If the current development of inductive approaches to understanding of liquid structure is to proceed, however, further accurate determinations, and redeterminations, of distribution functions will be needed, and diffraction will continue to be important in gaining that understanding.

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