

## The Structure of Liquids. I

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The development of the X-ray diffraction methods for the investigation of the structure of matter exhibits certain peculiarities which are rather striking. The marked spots and sharp and well defined lines of the diagrams obtained from crystalline substances attracted, quite naturally, the interest of the scientists. The immediate result of this was the foundation of X-ray crystallography, which, in its turn, has furnished a vast amount of information concerning the constitution and properties of solid crystalline substances.

As early as 1915, Debye<sup>1</sup> and Ehrenfest<sup>2</sup> independently postulated that theoretically X-ray diagrams from non-crystalline substances should also possess a characteristic pattern from which certain conclusions concerning the distribution of the electrons in the substances in question could be drawn. However, little attention was paid to these results, and the possibility it offered of investigating the structure of liquids and other non-crystalline substances was not considered in the first decades.

The reason for this was certainly not lack of interest in the structure of liquids. It was probably due to the fact that the diffraction pattern from crystals was far more conspicuous to the naked eye than that produced by liquids. For this reason the interpretation of the latter requires a more advanced experimental technique.

The first attempt to determine the structure of a liquid by a Fourier-synthesis from experimental X-ray intensity data was made in 1930 by Debye and Menke<sup>3</sup>. Their investigation of liquid mercury represents, in fact, the first step towards a practical method for the determination of such structures. The small deviations between the results of Debye and Menke and later investigators in this field are quite negligible.

The application of Fourier-synthesis to X-ray data from liquids was originally proposed by Zernicke and Prins<sup>4</sup>. Their method, in a somewhat modified form, has been employed by Warren and Gingrich<sup>5</sup> and co-workers in their

determinations of atomic distribution functions for a great number of liquid elements and other liquids. Different authors have also reported the determination of atomic distribution functions for a series of more complicated substances by this method.

A structural interpretation of the atomic distribution functions has also been attempted in several cases, but with limited success, and Gingrich writes in a survey of the diffraction of X-rays by liquid elements<sup>6</sup>: 'These atomic distribution curves represent the time-averaged atomic environment about any given atom within the liquid, but this environment is neither permanent, as in a crystal, nor random, as in a gas, and hence no simpler description of liquid structures can now be given to supply the same information.'

A comparison of the atomic distribution functions for groups of similar substances seems to indicate that this statement is correct. On the other hand, such a conclusion seems rather strange from a physical point of view, especially as regards the structures of molten metals and liquid gases.

In recent years certain types of systematic errors which may enter into the Fourier-synthesis of the atomic distribution functions for liquids have been reported<sup>7</sup>, and such errors may well account for the difficulty of a structural interpretation of the distribution functions. Any discussion of these problems must be based on theoretical expressions for the intensity of the coherent and incoherent scattering of X-rays by a liquid. It will therefore be necessary to give some basic details of the scattering theory for monochromatic X-rays.



## II. THE SCATTERING OF X-RAYS BY A LIQUID

The intensity of the radiation scattered coherently by a system of electrons, when a parallel beam of X-rays of wavelength  $\lambda$  is falling on the system, may be expressed by the formula<sup>8</sup>:

$$I(s) = \frac{\epsilon^4 I_0}{\mu^2 c^4 R^2} \cdot \frac{1 + \cos^2 2\Theta}{2} \int_0^\infty \sigma(r) \frac{\sin sr}{sr} dr \quad (1)$$

$I(s)$  is the intensity of the radiation scattered coherently in a given direction,  $I_0$  the intensity of the primary beam,  $\epsilon$  and  $\mu$  the charge and mass of an electron,  $c$  the velocity of light,  $R$  the distance from the center of the electron system to the point where the intensity is observed (this distance must be great compared with the extent of the system),  $2\Theta$  the angle between the incident beam and the direction in which the intensity is observed,  $s$  is equal to  $\frac{4\pi \sin \Theta}{\lambda}$ ,  $r$  the distances occurring in the electron system, and  $\sigma(r) dr$  is the

probability of finding electrons in the system at a mutual distance between  $r$  and  $r + dr$ .

Applying the Fourier integral theorem we may write:

$$\sigma(r) = r \frac{4R^2 \mu^2 c^4}{\pi \epsilon^4 I_0} \cdot \int_0^{\infty} \frac{sI(s)}{1 + \cos^2 2\Theta} \sin sr \, ds \quad (2)$$

The function  $\sigma(r)$  should, according to its definition, give maxima for  $r$ -values corresponding to distances between greater densities of electrons in the system in question.

For an electron system consisting of two atoms with spherical electron distribution at a fixed mutual distance, the  $\sigma(r)$ -function possesses only one maximum, and this maximum is found at an  $r$ -value which is somewhat greater than the distance between the nuclei. This shift of the maximum with relation to the internuclear distance increases with decreasing distance. Its numerical value will, however, in practice never exceed 0.005 Å and may therefore, in the case of liquids, for all practical purposes be neglected. It has been proved that the positions of the maxima in the function  $\frac{\sigma(r)}{r}$  correspond exactly to the internuclear distances<sup>9</sup>. This function has, however, the disadvantage that the magnitude of maxima corresponding to the same two atoms is proportional to  $\frac{1}{r}$  and accordingly decreases rapidly with increasing  $r$ -values.

The distribution function  $\sigma(r)$  may be divided into terms in different ways. The electron system in question may, for instance, consist of atoms which are bound together to form molecules, and the molecules, in their turn, form still larger aggregates. The distribution function  $\sigma(r)$  for such a system must contain, first of all, the sum of the distribution functions for all its component atoms  $\sigma_{at}(r)$ . Secondly it must contain the sum of the distribution functions for all the molecules, the distance between electron densities in the same atom being left out in the calculation of the molecular distribution functions  $\sigma_m(r)$ .

The distribution function for the whole system may thus be written:

$$\sigma(r) = \sum_{at} \sigma_{at}(r) + \sum_m \sigma_m(r) + \sigma_i(r) \quad (3)$$

Where the term  $\sigma_i(r)$  results from all the inter molecular distances, *i. e.* distances between electron densities belonging to different molecules.

Introducing (3) in formula (1), leads to:

$$I(s) = \frac{\varepsilon^4 I_0}{\mu^2 c^4 R^2} \cdot \frac{1 + \cos^2 2\Theta}{2} \left[ \sum_{at} \int_0^\infty \sigma_{at}(r) \frac{\sin sr}{sr} dr + \sum_m \int_0^\infty \sigma_m(r) \frac{\sin sr}{sr} dr + \int_0^\infty \sigma_i(r) \frac{\sin sr}{sr} dr \right] \quad (4)$$

The term:

$$\frac{\varepsilon^4 I_0}{\mu^2 c^4 R^2} \cdot \frac{1 + \cos^2 2\Theta}{2} \int_0^\infty \sigma_{at}(r) \frac{\sin sr}{sr} dr \quad (5)$$

represents the intensity of the coherent scattering of one special atom or ion and may be replaced by the expression:

$$\frac{\varepsilon^4 I_0}{\mu^2 c^4 R^2} \cdot \frac{1 + \cos^2 2\Theta}{2} f_{at}^2 \quad (6)$$

where  $f_{at}$  is the atomic scattering factor for the special atom or ion in question<sup>10</sup>.

If the electron distribution of the system is altered during the exposure time or if more than one system contributes to the scattering, then the intensity of the total coherent scattering is represented by the weighted mean of the scattering corresponding to the individual electron distributions in the system. In that case the intensity may be expressed as:

$$I(s) = \frac{\varepsilon^4 I_0}{\mu^2 c^4 R^2} \cdot \frac{1 + \cos^2 2\Theta}{2} \int_0^\infty \sum_i a_i \sigma_i(r) \frac{\sin sr}{sr} dr \quad (7)$$

where the summation must be taken over all the systems or electron distributions.  $a_i$  is a factor equal to the probability of each individual distribution and  $\sigma_i(r)$  is the electron distribution function corresponding to this special electron distribution.

Formula (4) gives the intensity of the coherent scattering in a convenient form for our purpose. It should be noted, however, that certain structural problems may be simplified by splitting up the distribution function  $\sigma(r)$  in a different way.

The intensity which we are able to determine experimentally from X-ray diagrams is the total scattering; that is the sum of the coherent and the incoherent scattering.

The intensity of the incoherent scattering may be given by the expression <sup>11</sup>:

$$I_{\text{inc}} = \frac{\epsilon^4 I_0}{\mu^2 c^4 R^2} \cdot \frac{1 + \cos^2 2\Theta}{2} \cdot \frac{1}{\left(1 + \frac{h(1 - \cos 2\Theta)}{\mu c \lambda}\right)^3} \cdot \sum_{at} S_{at}(s) \quad (8)$$

The theoretical basis for the determination of the function  $S_{at}(s)$  has been given by Heisenberg <sup>12</sup>, and it is possible to determine the numerical values of this function for different atoms from a table given by Bewilouga <sup>13</sup>.

$\frac{1}{\left(1 + \frac{h(1 - \cos 2\Theta)}{\mu c \lambda}\right)^3}$  represents the Breit-Dirac correction factor where  $h$  is Planck's constant. The summation in the last term in formula (8) is to be taken over all the atoms in the system.

The total intensity of the scattering may now be written:

$$\begin{aligned} I_{\text{total}}(s) &= I(s) + I_{\text{inc}} = \\ &= \frac{\epsilon^4 I_0}{\mu^2 c^4 R^2} \cdot \frac{1 + \cos^2 2\Theta}{2} \left[ \sum_m \int_0^\infty \sigma_m(r) \frac{\sin sr}{sr} dr + \int_0^\infty \sigma_i(r) \frac{\sin sr}{sr} dr \right. \\ &\quad \left. + \sum_{at} (f_{at}^2 + \frac{1}{\left(1 + \frac{h(1 - \cos 2\Theta)}{\mu c \lambda}\right)^3} \cdot S_{at}(s)) \right] \quad (9) \end{aligned}$$

The last two terms in (9), representing the total scattering from all the isolated atoms in the system, can easily be calculated, as both  $f_{at}$  and  $S_{at}(s)$  are tabulated for most types of atoms.

### III. THE EXPERIMENTAL PROCEDURE

The X-ray diagrams for liquids may be obtained by an experimental technique which is similar to the powder method used in X-ray crystallography. The cameras and monochromators used by the different investigators for the study of liquids are of various types. In the following a brief description of the equipment used at the University of Oslo shall be given.

Between the X-ray tube, which was of the Müller Metallix type, and the camera, a monochromator was inserted a considerable distance into the camera. The distance between the focal spot of the tube and the sample in

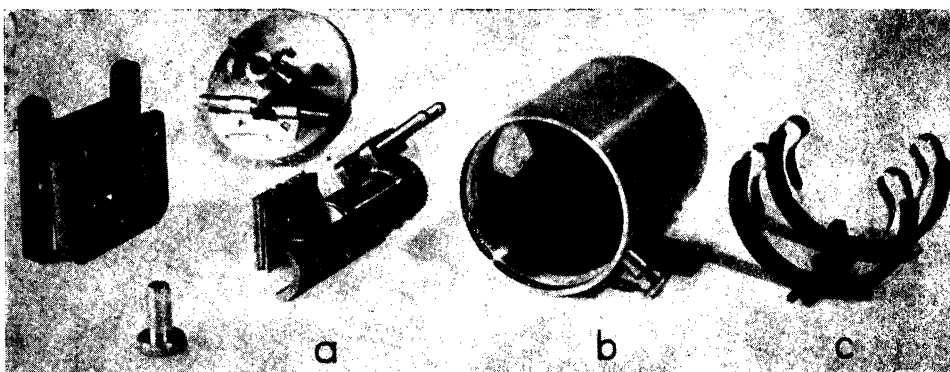


Fig. 1. Camera and monochromator.

the camera was only 8 cm. The different parts of the camera and the monochromator are illustrated in Fig. 1. The X-ray beam passes through three slits in the monochromator a, one between the tube and the reflecting crystal and two between the crystal and the sample. The monochromatic beam was the 200 reflection from a rocksalt crystal. The monochromator could be adjusted for any wavelength between 2 Å and 0.5 Å. The diameter of the cylindrical film was 57.3 mm and the film was held against the inner wall of the camera b by a spring system c.

The specimen was contained in a glass or rubber tube, the walls of which had a thickness of 0.02–0.01 mm. The diameter of the specimen ranged from 1 to 0.3 mm, depending on the absorption in the sample. The influence of the glass tube on the scattering could, in most cases, be neglected, but for substances which absorb X-rays strongly, effects due to scattering from the glass tube must be taken into consideration. This is also the case when rubber tubes are used.

The density  $D$  of the blackening of the film was determined by a Zeiss recording microphotometer, and the photometer reading,  $M$ , being transformed to density scale by the logarithmic formula:

$$D = -\log M + \log M_0 \quad (10)$$

where  $M_0$  is the photometer reading for an unexposed spot on the film.

For small values of  $D$ , the connection between the total intensity of the scattering,  $I_{\text{exp}}(s)$ , and  $D$  may be given by:

$$I_{\text{exp}}(s) = c_1 D + c_2 \quad (11)$$

where  $c_1$  and  $c_2$  are constants. This formula is, however, only an approximation and is valid only for a rather narrow range in  $I_{\text{exp}}(s)$ .

$$I_a < I_{\text{exp}}(s) < I_b \quad (12)$$

For  $I_{\text{exp}}(s) < I_a$  formula (11) gives too large values of  $I_{\text{exp}}(s)$ , and for  $I_{\text{exp}}(s) > I_b$  the values are too small. The general shape of the experimental intensity curve of the liquids allows, however, an adjustment of the exposure time of the film to the correct range in  $D$ . The experimental intensity curve shows a main fall with increasing  $s$ , and the magnitude of its maxima and minima decreases rapidly with increasing  $s$ . If, therefore, a diagram of short exposure-time gives too high values of the intensity for greater values of  $s$  compared with a diagram of longer exposure-time, then the diagram of short exposure-time is underexposed. If, on the other hand, a diagram of long exposure-time gives too small values of the intensity for smaller values of  $s$  compared with a diagram of shorter exposure-time, then the diagram of long exposure-time is overexposed. It is thus easy to pick out the diagrams of correct range in density  $D$  from a series of diagrams with different exposure-times. This procedure is, without doubt, laborious and requires the preparation of a considerable number of diagrams and photometer-records, of which a relatively large percentage must be rejected.

In order to increase the interval in  $s$  for which reliable observations of the intensity are available and also to check the observed intensity, sets of diagrams are always taken with both monochromatic  $\text{CuK}_\alpha$ - and  $\text{MoK}_\alpha$ -radiation. The best diagrams are then picked out from each set and used as the basis for the further treatment.

The reflection of the X-rays from the rock-salt crystal introduces a certain polarization to the monochromatic radiation, and the polarization factor,  $\frac{1 + \cos^2 2\theta}{2}$ , in formula (9) must be replaced by a factor

$$P(s) = \frac{1 + k \cos^2 2\theta}{2} \quad (13)$$

where  $k = 0.937$  for  $\text{MoK}_\alpha$ - and  $k = 0.723$  for  $\text{CuK}_\alpha$ -radiation<sup>14</sup>.

It should be remembered, however, that the radiation reflected in a given direction from a fixed crystal is not necessarily monochromatic. Bragg's formula for the reflection from a crystal-lattice may be written:

$$2d \sin \theta = n \lambda_0 \quad (14)$$

where  $n$  is a positive integer and  $d$  the distance between the reflecting planes in the crystal. In our case, the rock-salt crystal in the monochromator was set to reflect the desired wave-length  $\lambda_0$  by the plane (200) through the slit-system. This setting of the crystal not only permits the passage of the radiation with wave-length  $\lambda_0$  through the slits, but also all the wave-lengths  $\lambda_n$  which satisfy the condition:

$$\lambda_n = \frac{\lambda_0}{n} \quad (15)$$

where  $n$  again may be any positive integral number. This means that the wave-length  $\lambda_0$  and all its 'overtones' can pass through the slits. The intensity of the 'overtones' must therefore be suppressed as much as possible relative to the intensity of the desired wave-length. This may be accomplished by running the X-ray tube at the correct tension.

Powder diagrams of substances, the lattices of which are well known, may be used for the control of the radiation. Lines originating from the 'overtones' may easily be spotted on the diagrams, as their position would correspond to superstructures in the lattices in question. However, we have never been able to observe such lines.

The absorption of the radiation in the cylindrical sample is compensated for by introducing the factor  $A(s)$ , which may be determined from tables published by Blake<sup>15</sup>.

The intensity of the scattered radiation which is observed experimentally,  $I_{\text{exp}}(s)$  may be written according to formula (9) and (13):

$$I_{\text{exp}}(s) = \frac{\epsilon^4 I_0}{\mu^2 c^4 R^2} P(s) \cdot A(s) \left[ \sum_m \int_0^\infty \sigma_m(r) \frac{\sin sr}{sr} dr + \int_0^\infty \sigma_l(r) \frac{\sin sr}{sr} dr + \sum_{at} (f_{at}^2 + \frac{1}{(1 + \frac{h(1 - \cos 2\theta)}{\mu c \lambda})^3} S_{at}(s)) \right] \quad (16)$$

From formula (16) an expression for the terms:

$$\sum_m \int_0^\infty \sigma_m(r) \frac{\sin sr}{sr} dr + \int_0^\infty \sigma_l(r) \frac{\sin sr}{sr} dr = I_{m+l}(s) \quad (17)$$



may be deduced:

$$I_{m+l}(s) = I_{\text{exp}}(s) \frac{\mu^2 c^4 R^2}{I_0 \varepsilon^4 P(s) A(s)} - \sum_{at} (f_{at}^2 + \frac{1}{\left(1 + \frac{h(1 - \cos 2\Theta)}{\mu c \lambda}\right)^3} S_{at}(s)) \quad (18)$$

From formula (17) it is seen that the value of  $I_{m+l}(s)$  must decrease rapidly with increasing  $a$ . This again means that the two terms in formula (18) must approach each other rapidly with increasing  $s$ . The second term:

$$B(s) = \sum_{at} (f_{at}^2 + \frac{1}{\left(1 + \frac{h(1 - \cos 2\Theta)}{\mu c \lambda}\right)^3} S_{at}(s)) \quad (19)$$

may be calculated when the number of the different types of atoms or ions contained in the sample is known. Introducing (11), the first term in formula (18) may be written:

$$E(s) = \frac{c_1}{I_0} D(s) C(s) + \frac{c_2}{I_0} C(s) \quad (20)$$

where  $D(s)$  represents the blackening of the film and  $C(s)$  is given by:

$$C(s) = \frac{\mu^2 c^4 R^2}{\varepsilon^4 P(s) A(s)} \quad (21)$$

and may be determined when the experimental conditions are known. The two constants,  $\frac{c_1}{I_0}$  and  $\frac{c_2}{I_0}$ , are given such values by a trial and error method that the function  $E(s)$  coincides as close as possible to the function  $B(s)$  for greater values of  $s$ . This operation is easiest to effect in the case of the experimental blackening obtained by the MoK $_{\alpha}$ -radiation. The problem is somewhat more complicated in the case of CuK $_{\alpha}$  radiation. In practice therefore the MoK $_{\alpha}$ -curve is first adjusted to the function  $B(s)$  and then the CuK $_{\alpha}$ -curve is brought to coincidence with both the  $B(s)$  and the adjusted MoK $_{\alpha}$ -curve.

An investigation of the errors which may be introduced by this adjustment has led to the conclusion that if the adjustment is carried out with care, the errors are negligibly small. In the next part of this paper, this type of error and a method for its removal will be treated in greater detail.

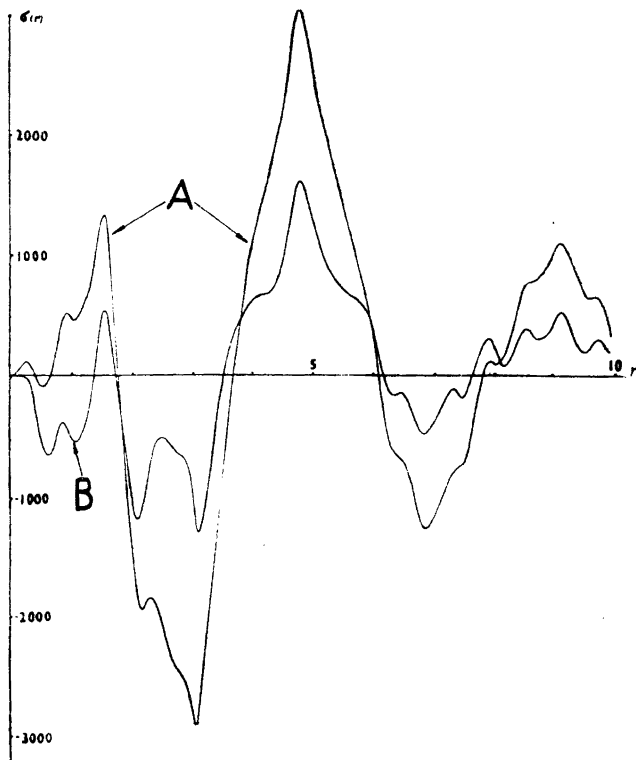


Fig. 2. Two electronic distribution curves for an aqueous solution of phosphoric acid. Curve A and B correspond to the intensity curves A and B in Fig. 3.

#### IV. A DISCUSSION OF CERTAIN SYSTEMATIC ERRORS

Both during the experimental procedure and as a result of the more theoretical treatment of the intensity curves, errors of different kinds may enter into the results of the Fourier synthesis. Some of these errors, like the influence of the exposure time on the form of the intensity curve, has already been mentioned. Others, as for instance the influence of the film type and the developing process on the intensity, are of a more general character, and have therefore been treated thoroughly in publications on X-ray crystallography.

There are, however, some systematic errors which may ruin a Fourier synthesis of the distribution function for a non-crystalline material.

The first type may originate from two different sources. It may be introduced by an incorrect adjustment of the term  $E(s)$ , (20) to the function  $B(s)$ , (19), and this in turn may be due to an incorrect exposure-time. The

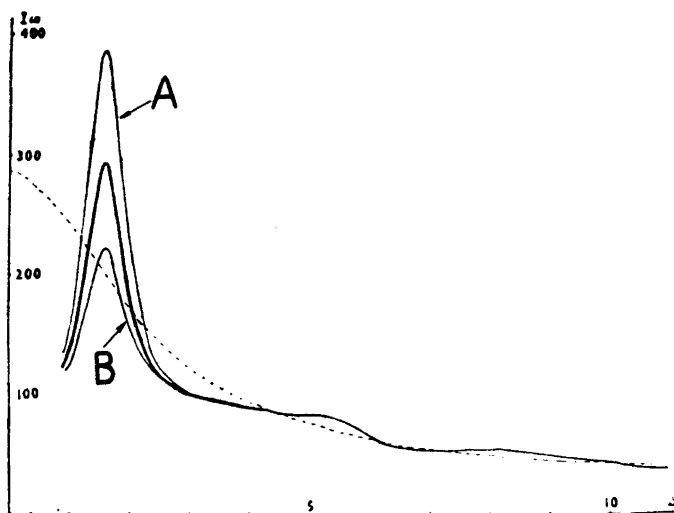


Fig. 3. Intensity curves visualizing the effect of various adjustments.

effect may also be caused by errors in the absorption factor,  $A(s)$ . The second of these two sources is certainly the more common.

The effect on the function  $I_{m+l}(s)$  is the addition or subtraction of a term which is equal to nought for  $s$  equal to zero, reaches its greatest value for  $s$  equal to  $1-2 \text{ \AA}^{-1}$ , where the intensity curve generally has its greatest peak, and decreases uniformly to zero with increasing  $s$ . The Fourier transformation of such a wedge-shaped term gives a function which has its greatest maxima and minima at smaller  $r$ -values, generally at  $0.3-1.0 \text{ \AA}$ . In this region neither  $\sigma_m(r)$  nor  $\sigma_l(r)$  can have any maximum or minimum.

The influence of an incorrect adjustment of the  $\text{MoK}_\alpha$ - and the  $\text{CuK}_\alpha$ -intensity curves has been demonstrated in a work published in 1944<sup>7</sup>, where overexposed  $\text{MoK}_\alpha$ - and underexposed  $\text{CuK}_\alpha$ -diagrams from aqueous phosphoric acid are used as an example. In Fig. 2 two distribution curves for an aqueous solution, containing 86 % phosphoric acid, are given, and the corresponding intensity curves are shown in Fig. 3. These two intensity curves are the results of two adjustments which, as will be seen, differ greatly from each other. It should be noted that the position of the maxima is not shifted in the direction of the  $r$ -axis by the various adjustments. Their magnitude, or their position in the direction perpendicular to the  $r$ -axis, shows, however, a great variation from one case to the other.

Debye and Menke, in their pioneer work on the structure of liquid mercury<sup>3</sup>, determined a probability function,  $W(r)$ , which is not identical with the

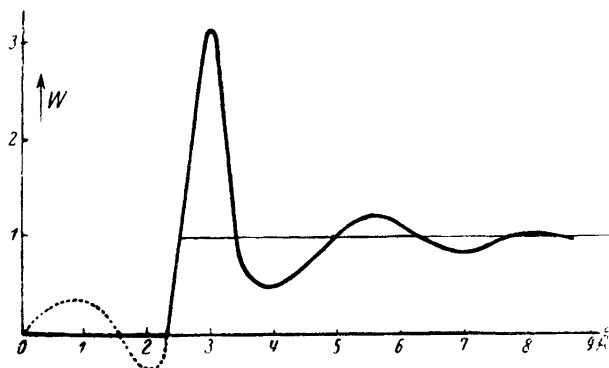


Fig. 4. Debye and Menkes probability function for liquid mercury.

distribution function,  $\sigma(r)$ . It is, however, derived from the intensity of the coherent scattering by a Fourier-transformation, which differs only slightly from the one by which the function  $\sigma(r)$  is determined. The functions  $W(r)$  and  $\sigma(r)$  for the same substance have therefore many common properties and are subject to the same types of errors. In Debye and Menke's probability function for liquid mercury, a spurious maximum is observed at about 0.6 Å, and ascribed by the authors to errors in the intensity function for greater values of  $s$ . This spurious maximum may, however, be explained as due to the addition of such a wedge-shaped term to the intensity function. That the maxima observed at 5.5 and 8.5 Å in the  $W(r)$  function may also arise from the same wedge-shaped term is not inconsistent with this explanation<sup>7</sup>.

The occurrence of spurious maxima and minima at small values of  $r$  in the distribution function indicates very strongly the presence of an erroneous wedge-shaped term in the function  $I_{m+i}(s)$ , and this again in general may be traced back to an incorrect adjustment of the experimental intensity curve or an error in the absorption factor  $A(s)$ . The inner part of the  $\sigma(r)$  curve should therefore be examined very carefully, and subsidiary maxima and minima in this part of the curve should always be taken into account.

The error in the absorption factor, which, as stated above, is the most common source of the wedge-shaped term, may be due to certain theoretical and experimental causes. Of these the most probable is perhaps the fact that the distribution of the intensity in the cross-section of the beam from the monochromator generally fails to meet the requirements of the theory. In the theoretical treatment it is assumed that the specimen is irradiated by a parallel beam of X-rays with constant intensity throughout its whole cross-section. A beam reflected from a plane crystal does not fulfill this require-

ment, as the intensity in a reflection from a crystal always decreases towards the edges.

The Fourier transformation in (2) requires that the intensity of the scattering be known from  $s = 0$  to  $s = \infty$ . The experimental intensity curve is, however, only known between the limits  $s = a$  to  $s = b$ . The value of  $a$  and  $b$  are, in general, of the magnitude  $a \approx 1 \text{ \AA}^{-1}$  and  $b \approx 12 \text{ \AA}^{-1}$ . When the upper limit of integration in (2) is changed from infinity to  $b$ , certain errors are introduced in the distribution functions. This error is of the same type as the diffraction effect met with in the Fourier synthesis of crystal lattices. It has been demonstrated by Bragg and West<sup>16</sup> that its influence may be reduced when the intensity is multiplied by a function  $e^{-ks^2}$ . Unfortunately this procedure also reduces the resolving power of the method. The reason for this is simply that the function  $e^{-ks^2}$  decreases rapidly with increasing  $s$ . Accordingly, it reduces the influence of the intensity on the distribution curve with increasing  $s$ , and this means a reduction of the resolving power. Warren, Gingrich and others<sup>5,17</sup>, on the other hand, multiply the intensity curve by a factor  $\frac{1}{f^2}$ , which increases rapidly with increasing  $s$ . The resolving power of the method is in this way increased considerably, but the increase in the diffraction error caused by the factor  $\frac{1}{f^2}$  has proved to be a great disadvantage, and may, as will be shown by a few examples, lead to serious difficulties in the interpretation of the experimental distribution curves.

The errors introduced in the distribution functions, when the lower limit of integration is changed from nought to  $a$  is not easily dealt with. Some estimate of its magnitude may be obtained by drawing two curves connecting the inner part of the observed intensity curve and the  $I(s)$  axis. The two curves should be drawn in such a manner that one of them represents a probable upper limit of the intensity curve in this region, and the other represents the corresponding lower limit. The integration in the Fourier transformation is then carried out, using both the upper and the lower of the two curves. In this way two distribution curves are obtained, and the difference between them should represent a fairly good estimate of the magnitude of this error. For greater interatomic distances this procedure may prove less expedient, but for distances up to about  $10 \text{ \AA}$  the method may be used safely.

In the following section some experimental results will be given, and, at the same time, some examples of the different kinds of errors discussed above will be shown. A more detailed discussion of the diffraction error, and its influence on the different types of distribution functions, is given by Viervoll<sup>9</sup>.

## SUMMARY

The theory of the scattering of monochromatic X-rays by a liquid is given and some details of the experimental method used at the University of Oslo for determination of electronic distribution functions are described. Some of the more common systematical errors are also discussed.

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