

## X-Ray Diffraction in Long Chain Liquids

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The diffraction of x-rays in long chain liquids is calculated by the method of Zernicke and Prins. In the liquid, the long cylindrical molecules are arranged quite at random in space and orientation, except in so far as the condition for relatively dense packing necessitates that about any one long molecule, the nearest neighbors be roughly parallel. The main peak is due to a concentration of scattering

matter at a distance about 8 percent larger than the lateral distance between chains. The inner peak, which is observed for the alcohols and the fatty acids, measures the distance from the heavy end group to the gap at the opposite end. For relatively long chains this distance becomes equal to the chain length.

### INTRODUCTION

THE x-ray diffraction halos produced by liquids have been studied by a number of workers. For a summary of the work up to 1928, reference should be made to the paper by Drucker.<sup>1</sup> For liquids in which the molecules are essentially spherical, it has been shown<sup>2, 3</sup> that the position of the principal diffraction peak is satisfactorily given by the Ehrenfest-Keesom<sup>4</sup> relation

$$\lambda = 0.814 \times 2a \sin \theta. \quad (1)$$

In this relation  $a$  is the mean distance between any one molecule and its nearest neighbors and under the assumption of a close packing of spheres is readily calculated from the molecular weight and the density.

$$a = 1.33(M/\rho)^{\frac{1}{3}}. \quad (2)$$

As would be expected, for molecules which depart appreciably from spherical shape, the two relations above lose their simple meaning, and the values of  $a$  calculated by the two methods no longer correspond.

In this paper we shall consider the diffraction of x-rays in three series of long chain liquids; the fatty acids, normal alcohols and normal paraffins. These series of long chain liquids seem particularly attractive because of the distinctive shape of the molecule, and also because excellent experimental scattering curves are available in a series of papers from the laboratory of G. W. Stewart.<sup>5, 6, 7</sup>

The method which we shall use in treating the problem of x-ray diffraction in liquids is a modification of the method which has been used successfully by Zernicke and Prins.<sup>8</sup> The intensity of coherent scattering from an array of atoms which takes all possible orientations in space is given by the expression

$$I = \sum_m \sum_n f_m f_n \frac{\sin(sr_{mn})}{sr_{mn}}; \quad s = \frac{4\pi \sin \theta}{\lambda}, \quad (3)$$

in which  $2\theta$  is the angle of scattering,  $f$  is the atomic scattering factor and the summation is taken with respect to any one atom over all the other atoms including the one singled out, and then the one singled out is in turn allowed to be each of the atoms in the array. For a liquid in which there is only one kind of atom present, and

<sup>1</sup> C. Drucker, *Phys. Zeits.* **29**, 273 (1928).

<sup>2</sup> W. Keesom and J. de Smedt, *Proc. Amsterdam* **25**, 118 (1922); **26**, 112 (1923); *Physica* **5**, 125 (1924).

<sup>3</sup> J. R. Katz, *Zeits. f. Physik* **45**, 97 (1927).

<sup>4</sup> Although the original derivation of this relation did not justify its application to liquid diffraction, its applicability to a liquid containing spherical molecules has since been fully established by the rigorous and elegant derivation of Zernicke and Prins.

<sup>5</sup> Stewart and Morrow, *Normal Alcohols*, *Phys. Rev.* **30**, 232 (1927).

<sup>6</sup> G. W. Stewart, *Normal Paraffins*, *Phys. Rev.* **31**, 174 (1928).

<sup>7</sup> G. W. Stewart, *Fatty Acids*, *Proc. Nat. Acad.* **13**, 787 (1927); *R. Morrow*, *Phys. Rev.* **31**, 10 (1928).

<sup>8</sup> Zernicke and Prins, *Zeits. f. Physik* **41**, 184 (1927).

if on the average each atom is surrounded in the same way as every other atom, then (3) reduces to

$$I = Nf^2 \sum_n \frac{\sin sr_n}{sr_n}, \quad (4)$$

where  $N$  is the total number of atoms. The distribution of surrounding atoms can be represented by a radial density function  $g'(r)$  in terms of which (4) becomes

$$I = Nf^2 \int_0^\infty g'(r) \frac{\sin sr}{sr} dr. \quad (5)$$

To facilitate convergence, we imagine a uniform density of negative scattering matter spread throughout the liquid and just equal and opposite to the average positive density. So long as this negative density has an indefinite outer boundary and we do not consider angles of scattering which are less than several seconds, it will, of course, give rise to no diffraction effects and hence does not alter the problem.<sup>9</sup> By introducing a resultant density  $q'(r)$ , Eq. (5) becomes

$$I = Nf^2 \int_0^\infty q'(r) \frac{\sin sr}{sr} dr, \quad (6)$$

where  $q'(r) = g'(r) - 4\pi r^2 \rho$ . At large distances the positive density just cancels the negative density, and  $q'(r)$  becomes zero. Hence it is only necessary to carry out the integration in (6) over small values of  $r$ .

In a liquid made up of spherical molecules in approximately close packing, there will be a positive peak in the radial density curve at a distance equal to the inter-molecular separation  $r = a$ . The intensity, as given by (6), will show a maximum at a value of  $(\sin \theta)/\lambda$  which gives the function  $\sin s\alpha/s\alpha$  a positive maximum and this occurs first at a value  $sa = 7.72$ .

$$4\pi a \frac{\sin \theta}{\lambda} = 7.72; \quad \lambda = 0.814 \times 2a \sin \theta. \quad (7)$$

This is the significance of the factor 0.814 in the Ehrenfest-Keesom relation.

<sup>9</sup> For any practical set-up the angle of scattering must be less than one second in order that the greatest path difference in the radiation scattered by different parts of the sample shall be less than one wave-length.

For small values of  $(\sin \theta)/\lambda$  it should be noted that the function  $\sin(sr)/sr$  approaches unity and (6) becomes

$$I = Nf^2 \int_0^\infty q'(r) dr.$$

But from the definition of  $q'(r)$  this integral is equal to zero and hence at small angles of scattering the intensity approaches zero.<sup>10</sup> The statements to be found in the literature that small scattering at small angles necessarily indicates a crystalline scatterer are grossly incorrect. It merely indicates that the atoms are close together as in a solid or liquid, rather than widely separated as in a gas.

#### LIQUID PARAFFINS

The scattering curves for the whole series of liquid paraffins<sup>6</sup> are essentially the same, regardless of the number of carbon atoms in the chain. There is a single strong peak occurring at roughly  $(\sin \theta)/\lambda = 0.108$ . This fact simplifies the problem enormously, because it shows that we can neglect end effects and hence treat a chain of indefinite length, along which all the carbon atoms are to be considered as equivalent. For a first approximation the effect of the hydrogens can be neglected. We will picture the chains as roughly cylindrical in shape and in a fairly dense packing in the liquid, such that about any one cylindrical chain, the six nearest neighbors are roughly parallel. (Fig. 1(a).)

The lateral inter-chain distance can be calculated from the effective cross-sectional area of the chain. From the molecular weight, density, and the known length of chain from measurements on crystalline paraffins, one obtains the area of  $21.4\text{A}^2$ , which checks well enough the value  $21.0\text{A}^2$  obtained by Adam<sup>11</sup> from measurements on surface films of fatty acids. Using an

<sup>10</sup> At angles of scattering less than several seconds this statement is, of course, not true since the introduction of the continuous negative density is justifiable only for angles greater than several seconds. In directions differing from that of the main beam by angles of a second or less, the atoms re-enforce to produce the strong "zero order" diffraction beam.

<sup>11</sup> N. K. Adam, Proc. Roy. Soc. **A99**, 336 (1921); **A101**, 452 (1922); **A103**, 676, 687 (1923).

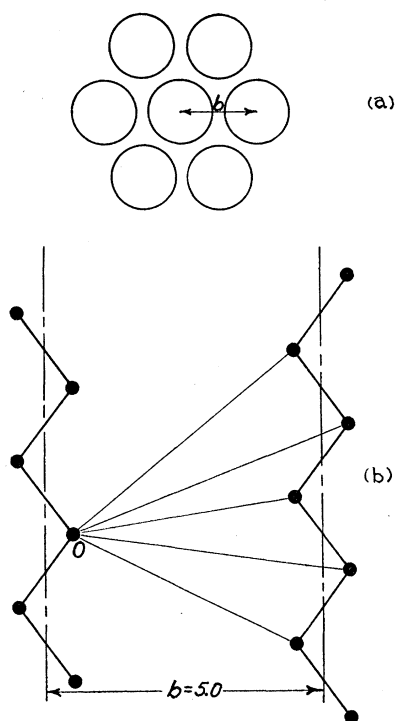


FIG. 1. Schematic representation of neighboring chains in a long chain liquid.

area of  $21.2\text{\AA}^2$  we obtain for the lateral separation

$$b = (2 \times 21.2 \times 3^{-\frac{1}{2}})^{\frac{1}{2}} = 5.0\text{\AA}.$$

We now fix our attention upon any one carbon atom, say at 0 (Fig. 1(b)) and proceed to tabulate the number of neighbors and their distances. In the same chain there will be 1 at distance zero, 2 at distance  $1.54\text{\AA}$ , 2 at distance  $2.50\text{\AA}$  and so on. On the six neighboring chains there will be 12 at distance  $5.0 \pm 0.9$ , 12 at distance  $5.3 \pm 0.9$  and so on. The radial density function  $g'(r)$  found in this way is represented graphically in Fig. 2(a), together with the radial negative density  $\rho'(r)$  which is to be subtracted from it. There is no assumption involved as to spherical symmetry in the function  $g'(r)$  since the fundamental diffraction equation (3) involves only the distances between atoms and not the relative orientations. It is seen at once that there is a marked positive peak in scattering matter at a distance of roughly  $5.4\text{\AA}$ , and it will turn out that it is just this concentration of scattering

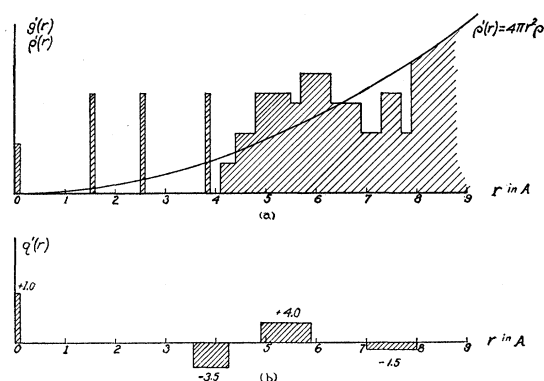


FIG. 2. Representation of radial density of scattering matter about any one carbon atom.

matter which gives rise to the main diffraction peak observed in the long chain liquids.

The resultant density function  $q'(r)$  would then be obtained by subtracting  $\rho'(r)$  from  $g'(r)$ . Actually, however, we have left out the random motion of the molecules, which of course tends to smooth out the irregularities in density. An attempt has been made to allow for this effect by retaining the essential features of Fig. 2(a) but making the concentrations considerably less pronounced. In choosing the final density function  $q'(r)$  there is of course the condition to be fulfilled,

$$\int_0^{\infty} q'(r) dr = 0.$$

The extent of smoothing out has but little effect on the position of the main peak and is carried out only far enough to satisfy the self consistency condition which is implied in assuming every atom surrounded in the same way as every other atom. The resultant density function  $q'(r)$  arrived at in this way is represented in Fig. 2(b). The integration of Eq. (6) is then carried out graphically<sup>12</sup> and, by taking the scattering factor for carbon from the table of James and Brindley,<sup>13</sup> the intensity is plotted out as a function of  $(\sin \theta)/\lambda$ . In Fig. 3 the resultant intensity curve is compared with the experimental curve of Stewart for pentadecane, which

<sup>12</sup> A most useful aid in this calculation is the new table of  $(\sin x)/x$  by J. Sherman, *Zeits. f. Krist.* **85**, 404 (1933).

<sup>13</sup> James and Brindley, *Zeits. f. Krist.* **78**, 470 (1931).

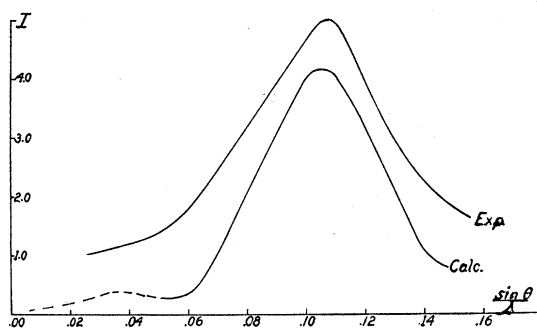


FIG. 3. Comparison of calculated and observed intensity curves for liquid paraffins.

is a typical curve for the whole series. The ordinates are, of course, in arbitrary units but the qualitative agreement is quite satisfactory. The exact shape of the curve at small angle is indefinite since it depends markedly upon the distribution at large distance.

The main peak, which occurs in the scattering curves for the normal alcohols and fatty acids at roughly the same position as in the paraffins, is, of course, to be explained in the same way. It should also be noted that the concentration of scattering matter at a distance 5.4Å, which is responsible for the main peak, would have been obtained roughly by direct application of the Ehrenfest-Keesom relation

$$a = [0.814 \times 2(\sin \theta)/\lambda]^{-1} = 5.65\text{Å}.$$

#### THE INNER PEAK

In the scattering curves from the normal alcohols<sup>5</sup> and fatty acids<sup>7</sup> there occurs a main peak at  $(\sin \theta)/\lambda = 0.108$  which we have already discussed and, in addition, a much weaker peak which occurs at smaller angle and which shifts continually to smaller and smaller angle as the number of carbons in the chain increases. This peak obviously has something to do with the length of the chain but direct application of the Ehrenfest-Keesom law gives a length which is roughly 5/3 the chain length as calculated by other methods.

To understand the origin of this peak two points should be noted. The peak occurs in the alcohols and fatty acids but not in the paraffins

and hence is dependent upon the heavy end group OH or COOH which is present in the first two cases but not in the third. It occurs at very small scattering angle and hence arises from some variation in the density of scattering matter which exists at a considerable distance from the heavy end group. In the region surrounding any heavy end group there is only one distinctive point at a definite long distance and this point is the other end of the chain. As is well known, the intermolecular distances in organic compounds are large and hence there occurs a relatively empty gap at the end of the chain. We have then a deficit of scattering matter rather than an accumulation, and occurring at a distance from the heavy end group which is roughly equal to the chain length. Such a distribution will of course give rise to a negative peak in the  $q'(r)$  density function. In carrying out the integration of (6), a positive peak in the intensity curve will be obtained at that value of  $(\sin \theta)/\lambda$  which gives the function  $(\sin sr)/sr$  a negative maximum, and this occurs at a value  $sr = 4.50$

$$4\pi r(\sin \theta)/\lambda = 4.50,$$

$$(2\pi/4.50)2r \sin \theta = \lambda. \quad (8)$$

Eq. (8) is, of course, the analogue of the Ehrenfest-Keesom relation applicable to density deficits. In Table I are tabulated the distances calculated by (8) from measurements on the normal alcohols.

The values of  $(\sin \theta)/\lambda$  for the alcohols are taken from the paper by Stewart and Morrow,<sup>5</sup> and to avoid the slight errors in the individual measurements the values have been read off their straight line plot. The length which is calculated from the inner peak is, of course, the distance from the heavy end group to the center of the gap, and it is only for long chain molecules that this distance becomes roughly equal to the chain length. As seen in Table I for chains of 5 carbon atoms or more, the agreement is quite satisfactory. In view of the difficulty in measuring relatively weak peaks at such small angles of scattering, the agreement in Table I is a tribute to the skill and care of Professor Stewart and his co-workers.

TABLE I. *Comparison of chain lengths of alcohols calculated from the inner peak and from the molecular volume.*

Number of carbons	From inner peak $l = \frac{1}{2.79 \sin \theta / \lambda}$	From Mol. Vol. $l = \frac{M}{\rho \times 0.606 \times 21.2}$
1	4.3A	3.2A
2	5.7	4.5
3	6.9	5.9
4	7.9	7.2
5	9.0	8.5
6	10.2	9.8
7	11.3	11.2
8	12.3	12.3
9	13.4	13.7
10	14.6	14.9

## GENERAL CONCLUSIONS

The agreement in Table I shows that, at least up to  $n=10$ , the chains remain essentially straight in the liquid. The picture of a long chain liquid, which we can draw from the above results, is one in which the positions and orien-

tations of the molecules are quite at random, except insofar as the condition for a fairly dense packing of such irregularly shaped molecules necessitates that the immediate neighbors about any one molecule shall be roughly parallel to it.

With such a picture of the liquid, the x-ray scattering curve is given quite satisfactorily by the theory of Zernicke and Prins. The main peak does not measure directly the lateral distance between chains but rather the distance to a concentration of scattering matter. The latter is about 8 percent larger than the lateral chain separation. The inner peak measures the distance from the heavy end group to the hole at the opposite end and, for sufficiently long chains, this distance becomes equal to the chain length. While our picture of the diffraction of x-rays in a long chain liquid differs from that which has been used by Stewart, the general significance of the two peaks has turned out to be the same.