

## The Structure of Liquids. II

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### V. THE EXPERIMENTAL RESULTS

The structural interpretation of the experimentally determined distribution curves seems, in the case of liquid elements, nearly always to lead to insuperable difficulties<sup>1</sup>. For more complicated structures, as for instance water and aqueous solutions of inorganic acids, bases and salts, such an interpretation has proved to be possible<sup>2</sup>. This situation must indeed be regarded as quite unusual, and should certainly not increase our confidence in the structures which have been reported for the more complicated substances. If, therefore, we are to accomplish anything in this field, it is obvious that the first problem which must be attacked is the structural interpretation of the distribution curves for the simplest possible liquids, namely the liquid noble gases and the molten metals.

The reason why a structural interpretation of these substances has not yet been possible may be due either to the complexity of the actual structures of even the simplest liquids, or to the fact that systematic errors of some sort have entered into the experimental distribution curves. The first reason is regarded as the only one of any importance by the great majority of the investigators, and the second has, as far as can be ascertained, only been considered by Campbell and Hildebrand<sup>3</sup>. In a discussion of some peculiar peaks which were observed in a great many of the experimental distribution curves for liquid elements, they state: 'One might be tempted to regard these subsidiary peaks as illusory, since they are so small as to suggest experimental errors, and they do not correspond to any expected geometrical structure. However, their occurrence again and again with different liquids and independent investigators make them appear real', and thus the second possibility is rejected by Campbell and Hildebrand also. The solution of the problem is, however, as will be seen later, to be found precisely in this direction.

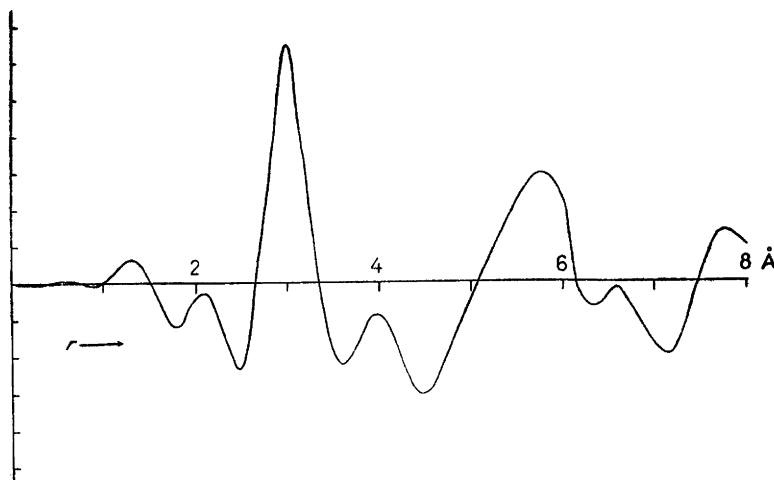


Fig. 1. Campbell and Hildebrand's atomic distribution curve for liquid mercury at  $-38^{\circ}\text{C}$ .

## VI. MOLTEN METALS AND LIQUID NOBLE GASES

Atomic distribution curves have been published for a considerable number of liquid noble gases and molten metals. Many of these distribution curves possess subsidiary peaks of the type mentioned above. For nine of these substances: lithium, argon, mercury, thallium, lead, indium, tin, bismuth and germanium, a complete recalculation of the distribution curves has been accomplished. The results for mercury at  $-38^{\circ}\text{C}$  and tin at  $280^{\circ}\text{C}$  will be discussed as examples.

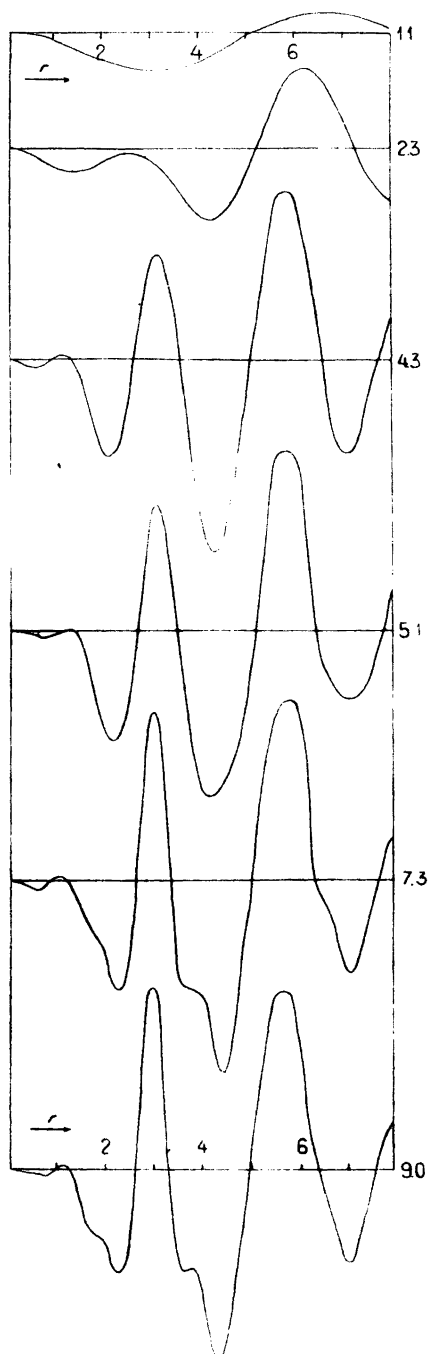
The reasons the distribution curve of mercury, determined by Campbell and Hildebrand<sup>3</sup>, was chosen are that the subsidiary peaks in this case are very marked, the diagrams are taken at a temperature which is only a few degrees above the meltingpoint of mercury, and that mercury melts at a comparatively low temperature and therefore should be expected to possess an extraordinarily high degree of order in the liquid state. Moreover the experimental distribution curve of mercury at  $-38^{\circ}\text{C}$ , as determined by Campbell and Hildebrand, offers a good example of the influence of an error in the absorption or in the adjustment.

The probability function  $W(r)$  of tin at  $280^{\circ}\text{C}$ , as determined by Hendus<sup>4</sup>, possesses three large maxima. Superimposed on the second and the third of these, is a ripple of constant period equal to about  $0.95\text{ \AA}$ . Such a ripple is very often met with in experimental distribution curves, and for this reason tin was used as the second example.

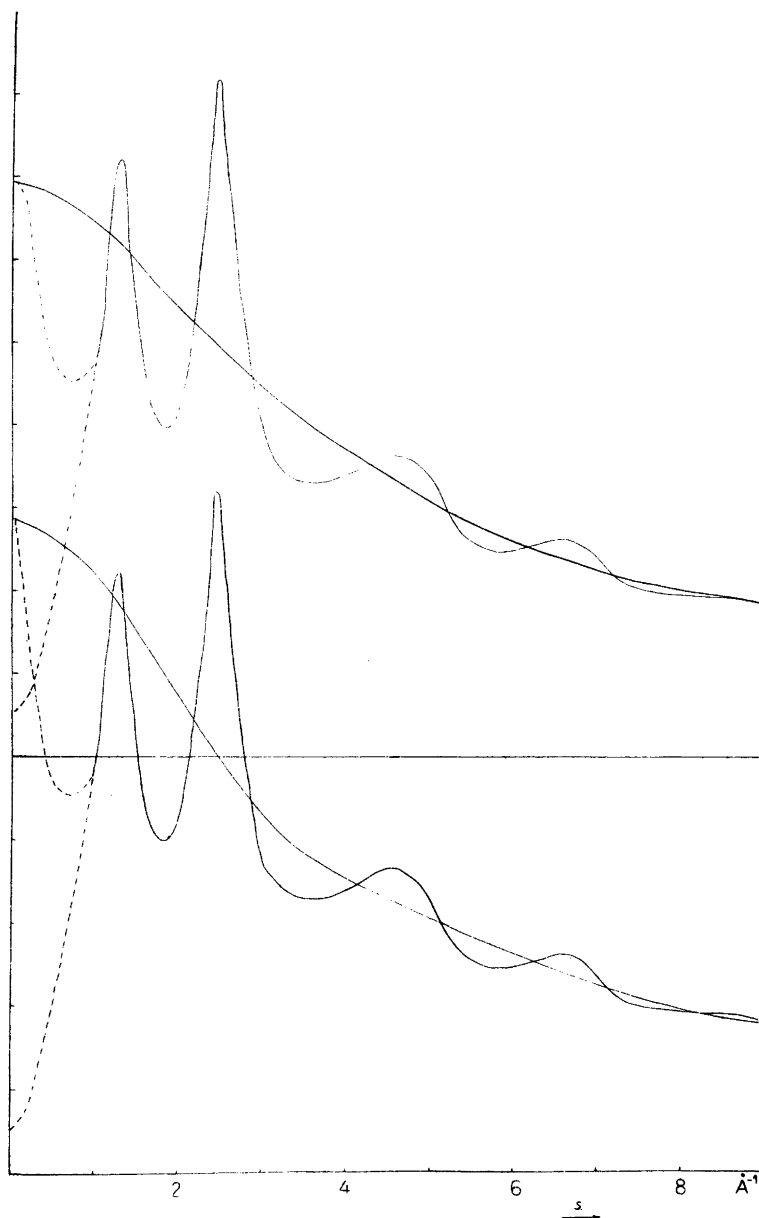
If the term  $4 \pi r^2 \rho_0$ , representing the distribution function of a constant average density of atoms equal to  $\rho_0$ <sup>5</sup>, is subtracted from the atomic distribution curve for liquid mercury at  $-38^\circ\text{C}$ , determined by Campbell and Hildebrand, then the curve given in Fig. 1 is obtained. The part of this curve  $r = 0$  to  $r = 2.5 \text{ \AA}$  is not given in the original paper, and has been determined from the intensity data published. The larger peaks of this distribution curve are observed at 3 and 5.7  $\text{\AA}$ . Smaller peaks are found at 0.6, 1.3, 2.1, 3.9, and 6.5  $\text{\AA}$ . The large peak at 3  $\text{\AA}$  corresponds very closely to the interatomic distances in the crystal lattice of solid mercury. The maximum at 2.1  $\text{\AA}$  and especially the comparatively large one at 1.3  $\text{\AA}$  are very difficult to explain as due to interatomic distances between mercury atoms. An interatomic distance of 1.3  $\text{\AA}$ , which would correspond to an atomic radius of the mercury atoms equal to 0.65  $\text{\AA}$ , is quite incompatible with the values derived from crystal lattices. The maxima at 0.6, 1.3, and 2.1  $\text{\AA}$  indicate, therefore, very strongly the presence of some error in the distribution curve. The fact that the small maxima at 2.1 and 3.9  $\text{\AA}$  are located symmetrically round the large peak at 3  $\text{\AA}$  makes the assumption that the atomic distribution curve is influenced by a diffraction error quite likely — the large maximum at 3  $\text{\AA}$  being real and the two subsidiary peaks at 2.1 and 3.9  $\text{\AA}$ , corresponding to the first maximum of the diffraction, ripples on both sides. From the observed distance 0.9  $\text{\AA}$  between the central peak and the first maximum in the ripple, an upper limit of integration equal to 8.6  $\text{\AA}^{-1}$  is computed — a result which is in the best accordance with the actual upper limit of integration equal to 9  $\text{\AA}^{-1}$ .

An electronic distribution curve was then determined from Campbell and Hildebrand's intensity data. The result is given in Fig. 2. The lower limit of integration for all curves was by an approximation to nought made equal, and the upper limits, which are different for the different curves, are indicated on the right of the respective curves. The maximum at 1.3  $\text{\AA}$  is already seen when the interval of integration is  $s = 0$  to  $s = 4.3 \text{ \AA}^{-1}$ , and this maximum is only slightly affected when the upper limit of integration is shifted even to  $s = 9 \text{ \AA}^{-1}$ . This proves that the maximum at 1.3  $\text{\AA}$  must be due namely to an error in the inner part of the intensity curve between  $s = 0$  and  $s = 4.3 \text{ \AA}^{-1}$ .

The subsidiary peaks at 2.1 and 3.9  $\text{\AA}^{-1}$  are considerably reduced in the electronic distribution curve, corresponding to an upper limit of integration equal to 9  $\text{\AA}^{-1}$ . The first one has nearly vanished, but the second is somewhat more persistent. This is exactly what would happen if the subsidiary peaks were actually caused by a diffraction effect. It should also be noted that when the upper limit of integration is  $s = 7.3 \text{ \AA}^{-1}$ , the two subsidiary maxima are moved to a distance of about 1.1  $\text{\AA}$  from the central peak.



*Fig. 2. The electronic distribution curves for liquid mercury at  $-38^\circ\text{C}$  determined from Campbell and Hildebrand's data.*



*Fig. 3. The upper curve represents Campbell and Hildebrand's intensity curve for liquid mercury at  $-38^{\circ}\text{C}$ , the lower one the corresponding curve with corrected atomic scattering,  $B(s)$ .*

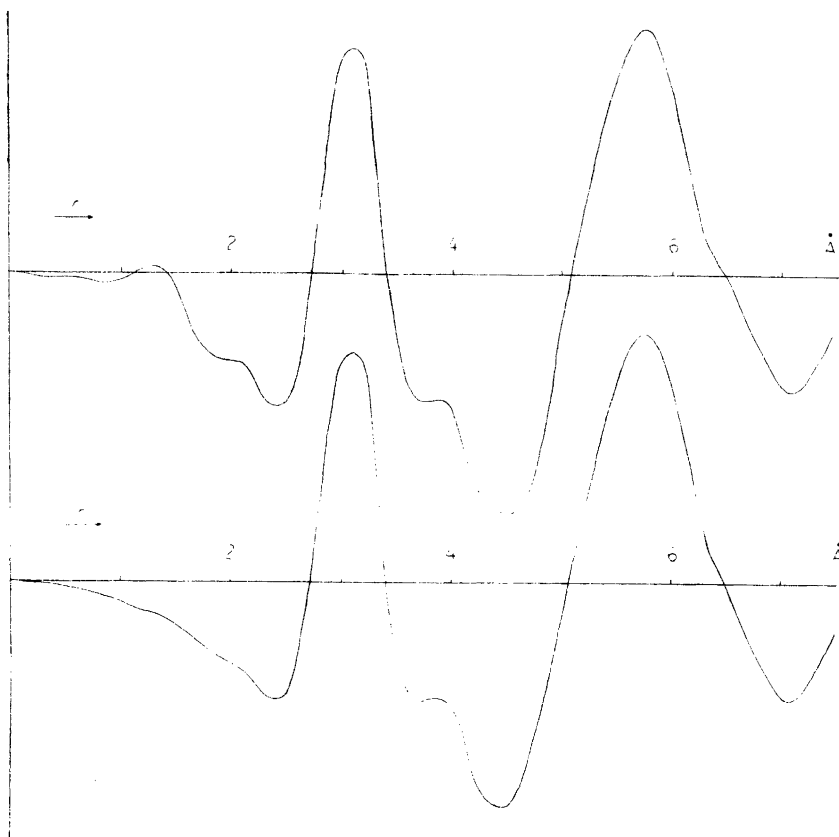


Fig. 4. Electronic distribution curves determined from the intensity curves in Fig. 3.

From this distance, an upper limit of integration, equal to  $7.0 \text{ \AA}^{-1}$ , is again computed. The maximum which was observed at  $6.5 \text{ \AA}$  in Campbell and Hildebrand's atomic distribution curve has vanished leaving only a flattening of the distribution curve in this region. The subsidiary peaks observed at  $2.1$ ,  $3.9$ , and  $6.5 \text{ \AA}$  are therefore undoubtedly due to a diffraction error of the ordinary type.

The peak at  $1.3 \text{ \AA}$ , which is also found in the electronic distribution curve, can hardly be caused by a diffraction effect. An error in the adjustment of the intensity curve or in the absorption factor  $A(s)$  would, as stated in part I, give rise to such maxima or minima.

Since the linear absorption coefficient,  $\mu$ , of mercury is large, an error of this type and of a magnitude sufficiently great to explain the occurrence of the peak at  $1.3 \text{ \AA}$  may easily enter into the intensity curve.

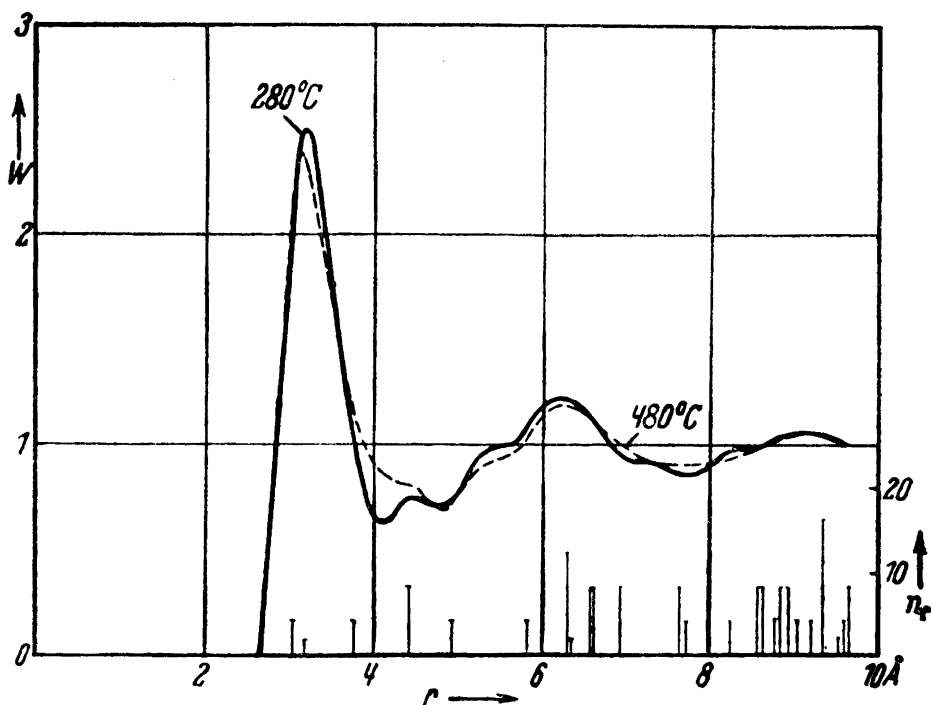


Fig. 5. Probability function,  $W(r)$  for liquid tin determined by Hendus.

The effect of an error in  $A(s)$  on the intensity curve should also increase rapidly with decreasing  $s$ , and as will be seen from Fig. 2, this is exactly what happens in our case. It is difficult to correct for such an error using the data given by Campbell and Hildebrand. The best we can do is to introduce a correction in the total atomic scattering curve  $B(s)$  and then make a new adjustment of the corrected atomic scattering curve to the observed intensity curve. In this way it is possible to find how a variation in the absorption factor alters the intensity curve. In order to determine the magnitude of the error in  $B(s)$ , a trial and error method must be applied. For each new value of  $B(s)$  a part of the distribution curve stretching to both sides from  $r = 1.3 \text{ \AA}$  must be computed, and the value of the function  $B(s)$ , which causes the subsidiary peak to vanish, is chosen for the final determination of the total distribution curve.

The upper curve in Fig. 3 is the intensity curve given by Campbell and Hildebrand. The lower one represents the same intensity curve with the corrected total atomic scattering curve  $B(s)$ . Fig. 4 gives the corresponding

Table 1.

Position of maxima observed	Difference in Å	Computed position
4.45	0.95	4.25
5.4	0.9	5.25
6.3	1.0	6.25
7.3	0.9	7.25
8.2	1.0	8.25
9.2		9.25
Mean difference	0.95 Å	

electronic distribution curves. The only difference between these two distribution curves is that the maximum at 1.3 Å has vanished completely and the small maximum at 2.1 Å has been reduced still further. This result does not prove with absolute certainty that an error in the absorption factor  $A(s)$  really is incorporated in the original intensity curve, but it makes such an assumption quite likely.

The structure of liquid tin has been studied by Gamertsfelder<sup>6</sup> and Hendus<sup>7</sup>. The probability function  $W(r)$  determined by Hendus (Fig. 5) for liquid tin at 280° C has its first and greatest maximum at 3.20 Å. The inner part of the function from  $r = 0$  to  $r = 2.8$  Å is not given by Hendus, and it is therefore difficult to judge whether the curve is influenced by some of the errors discussed above or not. From  $r \approx 4$  to  $r \approx 10$  Å the curve shows six smaller maxima which are superimposed on two broad maxima at about 6.2 and 9.2 Å. The position of the six small peaks are given in Table 1.

The six small maxima are, as will be seen from the table, approximately equidistant. An error in a narrow interval of the intensity curve always introduces a periodic term in the Fourier transformation, and thus gives rise to a sequence of small periodic maxima of equal amplitude. If the distance between these maxima is known, the position of the interval in the intensity curve from which the periodic maxima originate may easily be computed. In our case the period of the small peaks is approx. 0.95 Å, and the interval on the intensity curve from which they may originate would be found at approx.

$$s = \frac{2\pi}{0.95} \approx 2\pi \text{ Å}^{-1} \text{ or } \frac{\sin\theta}{\lambda} \approx 0.5 \text{ (Fig. 6). In this part of the intensity}$$



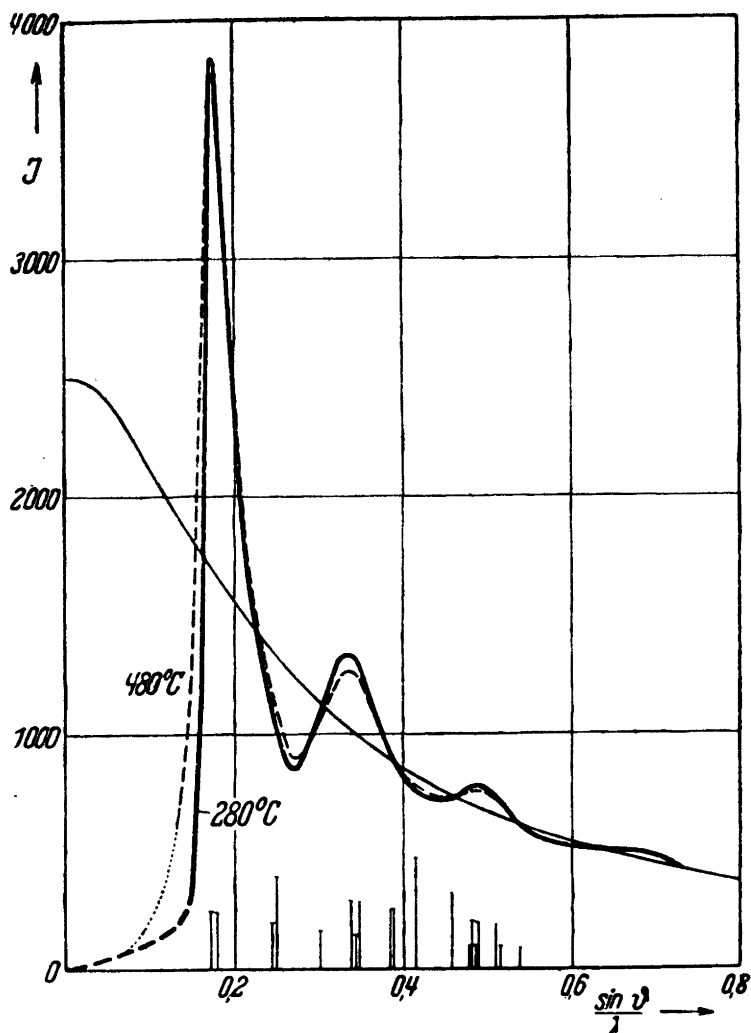


Fig. 6. The intensity curve from which  $W(r)$  in Fig. 5 was determined.

curve a maximum is found. If the magnitude of this maximum is too great, this would introduce a periodic term having maxima at the positions given in the third column in Table 1. The deviation between the observed and the computed position of the maxima at 4.45 and 5.4 Å may be due to the influence of a diffraction ripple from the great peak at 3.20 Å. The fact that the small maxima in the probability function  $W(r)$  may be caused by the maximum in the intensity curve at about  $s \approx 2\pi \text{Å}^{-1}$ , does not prove that the

small maxima are spurious. When, however, the method of computation used by Hendus is considered, such an assumption becomes quite likely. This method of computation has much in common with a method used by Warren, Gingrich and others <sup>5</sup>, and the distribution curves which are obtained by this procedure correspond to the distribution of the atoms, not to the electronic distribution in the system.

According to Warren and Gingrich, the atomic distribution function  $4\pi r^2 \sigma^1(r)$ , representing the difference between the actual distribution of the atoms in the sample and the distribution in a liquid with constant atomic density equal to the mean atomic density in the sample, is given by the expression:

$$4\pi r^2 \sigma^1(r) = \frac{2r}{N} \int_0^\infty \frac{s(I_{m+l}(s))}{f^2} \sin sr \, dr \quad (22)$$

The corresponding electronic density function may be deduced from formula (2) and (17).

$$\sum_m \sigma_m(r) + \sigma_l(r) = Cr \int_0^\infty s I_{m+l}(s) \sin sr \, ds \quad (23)$$

where  $C$  is a constant.

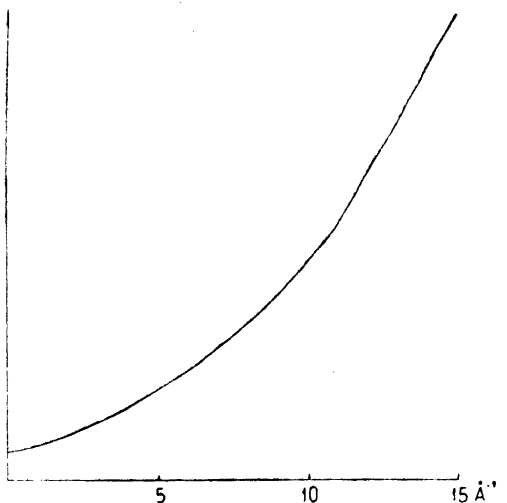
The difference between the integrals in (22) and (23) is that in (22) a factor  $\frac{1}{f^2}$  is introduced, where  $f$  is the atomic scattering factor. The factor  $\frac{1}{f^2}$  must therefore always increase rapidly with increasing  $s$ . In Fig. 7 the function  $\frac{1}{f^2}$  for tin is given.

The connection between the function  $I_{m+l}(s)$  and the experimentally observed intensity  $I_{\text{exp}}$  is given by (18). From this formula it will be seen that  $I_{\text{exp}}$  is multiplied by a factor

$$\frac{\mu^2 c^4 R^2}{I_0 \epsilon^4} \cdot \frac{1}{P(s)} \cdot \frac{1}{A(s)} \quad (24)$$

This factor is again, to a certain degree, dependent on the form and dimensions of the sample, the type of monochromator used, and other similar technical details of the experimental procedure. The factor is also greatly influenced by the absorption coefficient of the substances in question. In general, the best results are obtained when the value of this factor multiplied by  $s$  is as constant as possible for the whole interval in  $s$  for which intensities

Fig. 7. The function  $\frac{1}{f^2}$  for tin.



are observed. The reason for this is simply that equal weight must be attached to all parts of the experimentally observed intensity curve. If therefore, as in (22),  $I_{m+l}(s)$  is multiplied by a factor  $\frac{1}{f^2}$ , very great importance is assigned to the experimentally observed intensity for greater values of  $s$ , and the observations corresponding to smaller values of  $s$  are of little significance to the distribution curve. Under such circumstances an accidental error in the outer part of the experimental intensity curve may show up very clearly in the atomic distribution curve, whereas an error of equal magnitude in the inner part of the intensity curve does not count at all. This is, in fact, a great defect in this method, as the spurious maxima generated by an accidental error in the intensity corresponding to greater values of  $s$  are always sharp and well defined. The maxima caused by an error in the inner part of the intensity curve are necessarily of a considerable width, and for this reason are not so easily mistaken for marked interatomic distances. Both types of errors may, however, influence the magnitude of the maxima and minima in the distribution curve.

In the case of liquid tin at  $280^\circ\text{C}$ , an electronic distribution curve was then computed, making use of the intensity data published by Hendus. The result is given in Fig. 8. This curve shows maxima at 3.28, 6.21 and 9.15 Å. The six small periodic maxima observed in the probability function  $W(r)$  have totally vanished. A slight undulation of the electronic distribution curve in the interval  $r = 0$  to  $r = 2.5$  Å, having maxima at about 1.5 and 2.3 Å,

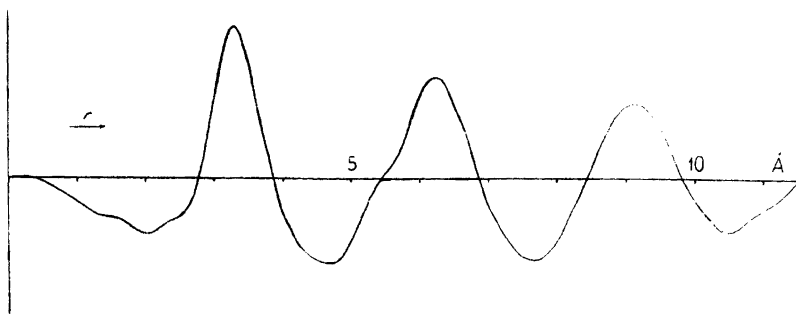


Fig. 8. Electronic distribution curves for tin.

seems to indicate a somewhat exaggerated value of the maximum in the region  $s \approx 2\pi\text{\AA}^{-1}$  of the intensity curve.

The small periodic maxima in the function  $W(r)$  of Hendus, may therefore, in all probability, be ascribed to a slight occasional error in the intensity curve at about  $s = 2\pi\text{\AA}^{-1}$ , and this rather negligible error is, owing to the special method of computation, made to interfere with the whole probability function.

Further typical examples of this error will be given in a subsequent part of this report, and for the sake of simplicity an error of this type will be termed general ripple.

A recomputation of the electronic distribution curves has, as mentioned above, been effected in nine cases. In all of these, the originally published atomic distribution curves have possessed marked subsidiary peaks or other individual peculiarities. In all nine cases it has been possible to show that the peculiarities of the distribution curves may be ascribed to diffraction ripples, general ripples, or to errors in the adjustment of the  $B(s)$  function or in the absorption factor  $A(s)$ .

For liquid lithium the recomputation was based on intensity data given by Gamertsfelder <sup>6</sup>, for argon at 91.8° K and 84.4° K the intensities were determined by Eisenstein and Gingrich <sup>7</sup>. A comparison of the atomic and electronic distribution curves, shows very strongly that the subsidiary peaks in these cases also are spurious, being due to diffraction ripples. The peak at 4.1 Å in the atomic distribution curve of lithium, at 4.5 Å in liquid argon at 91.8° K and at 5.1 Å in argon at 84.4° K are not found at all in the corresponding electronic distribution curves. Similar subsidiary peaks are also reported in the experimental distribution curves for some other liquid noble gases and molten metals; for instance in liquid sodium at 100° C <sup>8</sup> and in cadmium at 350° C <sup>6</sup>. In the case of sodium, the distribution curve has its greatest maximum

Table 2.

Substance	Position of second peak in diameters	Position of third peak in diameters	Position of first peak in Å
Li 200° C	1.80		3.24
Na 100° C	1.84		3.83
Na 400° C	1.87		3.90
Al 700° C	1.86		2.96
Ar 84.4° K	1.98		3.79
Ar 91.8° K	1.95		3.80
Ar 126.7° K	1.80		3.90
Ar 144.1° K	1.85	2.65	3.90
K 70° C	1.83	2.67	4.64
K 395° C	1.87	2.55	4.76
Zn 460° C	1.84	3.00	2.94
Ga 18° C	1.98	2.61	2.83
In 390° C	1.97		3.30
In 160° C	1.93		3.36
Sn 280° C	1.89	2.77	3.28
Sn 390° C	1.93		3.36
Hg -38° C	1.90		3.00
Hg 0° C	1.91		3.00
Hg 50° C	2.00		3.00
Hg 100° C	2.00		3.00
Hg 150° C	2.00		3.00
Hg 200° C	2.02		3.05
Mean	1.91	2.70	

at about 5 Å at a distance of 1.17 Å from the greater peak. This corresponds to an upper limit of integration  $s'_{\max} = 6.7 \text{ \AA}^{-1}$ , if the subsidiary peak is due to a diffraction effect, which agrees well with the actual limit of integration  $s = 6.28 \text{ \AA}^{-1}$ . For cadmium  $s'_{\max} = 8.6 \text{ \AA}^{-1}$  and  $s_{\max} = 7.54 \text{ \AA}^{-1}$ .

The agreement between the value  $s'_{\max}$  computed from the distance between the first large peak and its subsidiary maximum and the actual value  $s_{\max}$  is, as will be seen, on the whole remarkably good. Only in the case of cadmium is the deviation relatively large. An error of 0.13 Å in the distance between the two peaks would, however, account for this deviation, and it is indeed difficult to localize the small subsidiary maxima with greater accuracy from the curves in the publications.

From the above discussion it can be seen that there is good reason to believe that the subsidiary peaks observed in the atomic distribution curves of liquid noble gases and molten metals are spurious.

When the small extra maxima are removed, all these distribution curves become astonishingly similar and extremely simple. Only two or three maxima are left, and the ratio of their mutual distances is approximately the same, as will be seen from Table 2. In this table the position of the maxima along the  $r$ -axis are given, while the distance from the origin to the first and most marked peak in each curve is taken as unity. This coordinate may be termed diameters, by which is meant atomic diameters.

The interpretation of an atomic distribution curve possessing only two or three maxima ought to be simple. There is, however, a special type of error which may give rise to maxima in the same positions as the second and third peak in the experimental curves. It has been demonstrated<sup>9</sup> that if the first and greatest maximum of the experimental intensity curve is too great, smaller spurious maxima may occur at 0.26, 1.83 and 2.67 diameters, provided that the distribution curve possesses a maximum at 1 diameter. This special error must always give a maximum at about 0.26 diameters, and the magnitude of the maxima at about 1.8 and 2.6 diameters should always be small in comparison with the principal peak at 1 diameter. Unfortunately the inner part of the distribution curves is omitted in most of the publications. For sodium at 100° C and 400° C, potassium at 70° C and 395° C and for tin at 250° C and 390° C a sufficient number of points are given on the inner part of the distribution curves and in these six cases no maximum is observed at about 0.26 diameters. The final electronic distribution curve for mercury at — 38° C based on Campbell and Hildebrand's intensity data possesses no maximum in the critical interval. To this must be added the fact that the maximum which is observed at about 1.9 diameters for most of the substances is approximately of the same magnitude as the principal peak at 1 diameter and is not small in comparison with that maximum. It is obvious therefore that the error in question is not the cause of the maxima at about 1.9 and 2.7 diameters. These maxima can in any case be influenced by such an effect only to a slight degree.

The main source of the two maxima at approx. 1.9 and 2.7 diameters must, therefore, be found in some characteristic properties of the order of the atoms in the liquids. It follows therefore that it should be possible to construct a structure of similar atoms which would give a distribution function with maxima in the correct positions. As a first approximation, liquid noble gases and molten metals may be regarded as systems of hard spheres of the same size.

The formation of irregular packings of hard spheres of equal size has been given an extensive theoretical treatment by Kirkwood and Boggs<sup>10</sup>. The distribution curves for the centers of the spheres which Kirkwood and Boggs have determined on a wholly theoretical basis resemble the experimentally de-

Table 3.

Position of maxima in diameters.

First	Second	Third	
1	1.91	2.70	Mean of observations from Table 2.
1	1.71	2.44	Kirkwood and Boggs $\alpha = 0.72, \beta = 5.90$

terminated distribution curves for liquid noble gases and molten metals in a striking manner. The relative position of the maxima is, however, not in the best accordance with the experimental results.

In Table 3 the relative position of the maxima according to Kirkwood and Boggs are compared with the mean values from Table 2.

The positions of the maxima in the theoretical curve depend, to a certain degree, on some parameters which are introduced by Kirkwood and Boggs. The deviation between the experimental and theoretical relative position of the maxima may perhaps be eliminated by a variation in these parameters. The deviation may, however, also to some degree originate from uncertainty as to the location of the correct position of the maxima in the experimental distribution curves.

The results of Kirkwood and Boggs have subsequently been confirmed by Born and Green<sup>11</sup> in a more general theory of the liquids. A comparison between this theory and the experimental distribution curves for more complicated liquids will be given in the subsequent parts of the present paper.

## SUMMARY

Using liquid mercury at  $-38^{\circ}\text{C}$  and liquid tin at  $280^{\circ}\text{C}$  as examples, the effects of some types of systematical errors on the distribution curves of liquids are demonstrated. The subsidiary peaks observed in the distribution curves of a series of liquids are proved to be spurious. It is shown that when the influence of the systematical errors is removed the electronic distribution curves for molten metals and liquid noble gases are very simple and show great similarity.

The work on this publication was started in Cambridge in England in 1946, and I want to express my sincere thanks to Professor Sir W. Lawrence Bragg for his encourage-

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