Fundamental Study of the Structural Analysis of Monoatomic Liquids by X-ray Diffraction

Fundamental Study of the Structural Analysis of Monoatomic Liquids by X-ray Diffraction*

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Synopsis

This report presents an experimental procedure in X-ray diffraction study to determine the atomic distribution in monoatomic liquids. The methods for the corrections, normalization and the Fourier analysis on the X-ray scattering intensity from liquid sample (liquid mercury at 15°C) have been discussed in detail. The main results are as follows;

1) The atomic scattering factor should be modified by an anomalous dispersion effect.

2) Krogh-Moe-Morman's method is a useful one for the normalization of the X-ray scattering intensity.

3) When the different divergence-slits are used to measure the X-ray scattering intensity, the ratio of intensity obtained deviate from the value given from the ratio of the divergence; namely this ratio is a function of the scattering angle. Hence, this factor should be considered on the analysis within the experimental error.

I. Introduction

The liquid state of matters is the least understood of the three states of matter (solid, liquid, and gas). In the last few years, much theoretical effort has been devoted to the molecular theories of liquids and to the electronic properties of liquid metals. Especially the structural information is one of the most important knowledge to discuss these properties. X-ray diffraction is one of the useful methods that may be employed to study the liquid state of matters mainly from the point of view having an insight into their static structure (structure factor).

The review on the X-ray work including the experimental and analytical procedures in this field has been summarized by Gingrich[1] in 1943, and by Furukawa[2] in 1962. Recently, the accuracy in the measurement of X-ray scattering intensity has greatly progressed and some new methods for the X-ray Fourier analysis have been suggested.

From these reasons, it would be desirable to re-examine in detail, the analytical procedures of monoatomic liquids by X-ray diffraction which gives the radial distribution function about instantaneous three-dimentional structures averaged

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(1) N.S. Gingrich: Rev. Mod. Phys., **15** (1943), 90.

(2) K. Furukawa: Rep. Progr. Phys., **25** (1962), 395.

in time over many atomic configrations.

The main purpose of this work is to present a fundamental procedure in X-ray diffraction study to determine the atomic distribution in monoatomic liquids.

II. Analysis of X-ray intensity patterns

1. Fundamental scattering equation for monoatomic liquids

The method on the analysis for the observed X-ray intensity data was previously described by Furukawa[2]. The essential features are given below.

Expressed in electron units, a general form of X-ray intensity $I_{eu}^{coh}(K)$ scattered coherently from an array of atoms which takes all orientation is given by the following relation.

$$I_{eu}^{coh}(K)=\sum_n \sum_m f_n f_m \frac{\sin(K\cdot r_{mn})}{K\cdot r_{mn}}, \tag{1}$$

where $K=sin\theta/\lambda, \lambda$ is the wavelength, 2θ is the angle between the incident and diffracted X-rays, f_m and f_n are the respective coherent atomic scattering factors of the m-th and n-th atoms. Eq. (1) involves only the magnitudes of the distances r_m of each atom from every other atom. The summation in Eq. (1) should be performed at first for the origin atom itself and next extending to all atoms (N) in the system over all distances. In the case of one-component liquids, $f_m=f_n=f$ and $f_m f_n=f^2$. Summations for the origin atom lead to unity, since in the limits as $r_{mn}\to 0$, $sin\ (K.r_{mn})/K.r_{mn}\to 1$. So Eq. (1) may be written,

$$I_{eu}^{coh}(K)=Nf^2\left[1+\sum_m \frac{\sin(K\cdot r_{mn})}{K\cdot r_{mn}}\right], \tag{2}$$

On the other hand, the structure of non-crystalline materials is expressed by a density distribution function $\rho\ (r)$. Here $\rho\ (r)$ is the number of atoms per unit volume at a distance r from the reference atom, and $4\pi r^2\rho(r)$dr is the number of atoms contained in a spherical shell of radius r and thickness dr. The quantity $4\pi r^2\rho(r)$ is called the radial distribution function (RDF).

The distribution of atoms about any reference atom may be regarded as a continuous function and the summation in Eq. (2) replaced by an integral with the radial distribution function. Besides, by means of the Fourier integral theorem and RDF, Eq.(2) can be transformed to,

$$4\pi r^2\rho(r)=4\pi r^2\rho_0 g(r)=4\pi r^2\rho_0+\frac{2r}{\pi}\int_0^\infty K[a(K)-1]\sin(K\cdot r)\,dK \tag{3}$$

$$a(K)=\frac{I_{eu}^{coh}(K)}{Nf^2} \tag{4}$$

where $\rho\ (r)=\rho_0 g(r)$, $g\ (r)$ is the pair correlation function ρ_0 is the average density

of atoms and the quantity a (K) is called the structure factor. The structure factor a (K) can be obtained from X-ray diffraction experiments. Then, Eq.(3) is the fundamental equation for obtaining RDF of monoatomic liquids.

2. Corrections for polarization, absorption and fluorescence

The X-rays generated at the target are not polarized, but became polarizing after scattering by materials. Using the well-defined polarization factor (P), the measured X-ray intensities are corrected.

$$P=\frac{1}{2}(1+\cos^2 2\theta)\ , \tag{5}$$

where 2θ is the scattering angle.

The Bragg-Brentano focusing condition is maintained so that the absorption correction is constant throughout. The absorption for an infinitely absorbing material with a flat surface is given by[2],

$$A=\frac{1}{\mu}\frac{\sin(2\theta-\Delta)}{\sin\Delta+\sin(2\theta-\Delta)}\ , \tag{6}$$

where Δ is the angle between the specimen surface and the primary beam and μ is the linear absorption coefficient of the sample. When the Bragg-Brentano forcusing condition is employed, $\Delta=\theta$, and the absorption correction simplified to $A=1/(2\mu)$. Hence the absorption correction is angle-independent and not necessary for the Bragg-Brentano focusing system.

Fluorescent radiation from the sample is angle-dependent, but at present a numerical calculation of its intensity is impossible. Hence we should avoid it as far as possible by a suitable method. In this work, positioning of the filter in the diffracted beam eliminated the fluorescent scattering, most of the Compton scattering, as well as the contineous spectrum and the K_β radiation. Extraneous radiation was also eliminated by a pulse-height analyzer in the detecting circuit.

Accordingly, the corrected intensities I^{cor} are obtained by deviding the measured intensities I^{meas} by the polarization factor.

3. Normalization

The corrected intensities must be reduced to the electron units and expressed by the following relation,

$$\alpha I^{cor}=N(I_{eu}^{coh}+I_{eu}^{inc})\ , \tag{7}$$

where α is the convesion factor and often called the normalization constant. There are two methods for determining α.

(A) High-angle region method[3]

This method is based on the assumption that the total scattering (coherent

(3) C.N.J. Wagner, H. Ocken, and M.L. Joshi: Z. Naturf., **20a** (1965), 325.

and incoherent) intensities and the observed corrected intensities are matched together at large scattering angle ($K>10$ $\mathring{A}^{-1}$). The normalization constant can be calculated by dividing the area under the total scattering curve by the area under the observed corrected intensity curve in the region of large K where there are no longer modulations in the latter curve. The normalization constant α by the high-angle region method is given by,

$$\alpha = \frac{\int_{K\simeq 10}^{K_{max}} (f^2 + I_{eu}^{inc})\, dK}{\int_{K\simeq 10}^{K_{max}} I^{cor}\, dK} . \tag{8}$$

(B) Krogh-Moe-Norman's method[4],[5]

This method can be derived by considering the behaviour of the expression for the radial distribution function in the neighbourhood of $r=0$. At distance approaching zero, the atomic distribution function $\rho\ (r)$ is zero and sin $(K.r)=Kr$ and hence Eq.(12) will become

$$0 = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^{K_{max}} K[a(K)-1](K\cdot r)dK ,$$

hence,

$$-2\pi^2\rho_0 = \int_0^{K_{max}} K^2[a(K)-1]dK . \tag{9}$$

Using Eq. (4) and Eq. (7),

$$-2\pi^2\rho_0 = \int_0^{K_{max}} K^2\left[\frac{I^{cor}-N I_{eu}^{inc}}{Nf^2} - 1\right]dK ,$$

$$\alpha = \frac{-2\pi^2\rho_0 + \int_0^{K_{ma}} K^2\left[\frac{I_{eu}^{inc}}{f^2}+1\right]dK}{\int_0^{K_{max}} K^2\frac{I^{cor}}{f^2}\, dK} . \tag{10}$$

This relation is more exactly derived by Krogh-Moe[4] and Norman[5]. The normalization constant α is now determined by an analytical method.

4. Atomic scattering factor

The theoretical values of the coherent atomic scattering factor for X-rays are numerically calculated and listed. But, when the energy of the incident X-rays is similar to that of the electron in the specimen stoms, the coherent atomic scattering factor f will be modified by an abnormal dispersion effect. The atomic scattering factor corrected for the abnormal dispersion effect is in the following form,

(4) J. Krogh-Moe: Acta Cryst., **9** (1956), 951.
(5) N. Norman: Acta Cryst., **10** (1957), 370.

$$\left.\begin{aligned} f^{cor} &= f + f' + if'' \\ |f^{cor}|^2 &= (f+\Delta f')^2 + (\Delta f'')^2 \end{aligned}\right\}, \tag{11}$$

The new numerical values of $\Delta f'$ and $\Delta f''$ are given by Dauben and Templeton[6] and Cromer[7].

The wavelength of X-rays scattered by incoherent process is slightly longer than that of primary X-rays. The incoherent scattering intensity in electron units is given as,

$$\begin{aligned} I_{eu}^{inc} &= B[Z - \Sigma |f_k|^2] \\ B &= \left[1 + \frac{h}{8\pi^2 mc}\lambda K^2\right]^{-3}, \end{aligned} \tag{12}$$

where h is the Planck constant, c is the velocity of light, m is the electron mass, $K = 4\pi \sin\theta/\lambda$, and f_K is the scattering factor for the K-th electron in the atom and numerically given by Compton and Allison[8].

As shown in Eq. (12), a shorter wavelength radiation and larger scattering angle give rise to the increase of the incoherent scattering intensity. Hence the separation of this scattering intensity from the observed intensity is one of the important problems on the Fourier analysis of liquids.

III. Results and discussion

The methods as mentioned in the previous section were applied to the X-ray diffraction experiments for liquid mercury at 15°C observed by Waseda and Suzuki[9]. The experimental arrangment for the measurement of the scattered X-ray intensities from liquid metals was identical to the one described in the previous paper[10].

1. Correction for the abnormal dispersion effect

The coherent and incoherent scattering intensities of mercury were calculated by means of Eq. (11) and Eq. (12). These results are shown in Fig. 1. On the coherent scattering intensity in electron units, there is difference at the region of K less than 8.0 $Å^{-1}$ between the dispersion corrected atomic scattering factor and the uncorrected one. Hence, we attempted to convert the observed intensities into electron units by both of the atomic scattering factors and compare the results.

Fig. 2 shows the X-ray intensity curve of liquid mercury at 15°C in electron units. Normalization constant (α) was derived by the Krogh-Moe-Nornan's

(6) C.H. Dauben and D.H. Templeton: Acta Cryst., **8** (1955), 841.
(7) D.T. Cromer: Acta Cryst., **18** (1965), 17.
(8) A.H. Compton and S.K. Allison: X-ray in Theory and Experiments, D. Van Nostrand Co., New York (1935), 116.
(9) Y. Waseda and K. Suzuki: phys. stat. sol., **40** (1970), 183.
(10) Y. Waseda and K. Suzuki: Sci. Rep. RITU, **A23** (1971), 1.

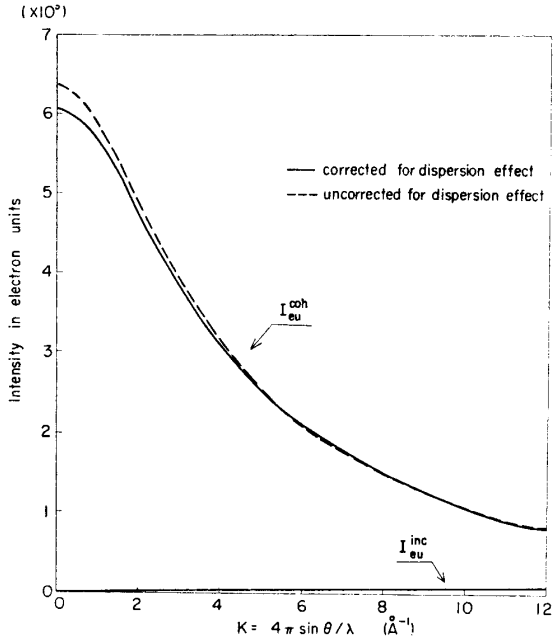

Fig. 1. Atomic scattering factor of mercury.
(——) corrected with the abnormal dispersion correction. (- - -) uncorrected with the abnormal dispersion correction.

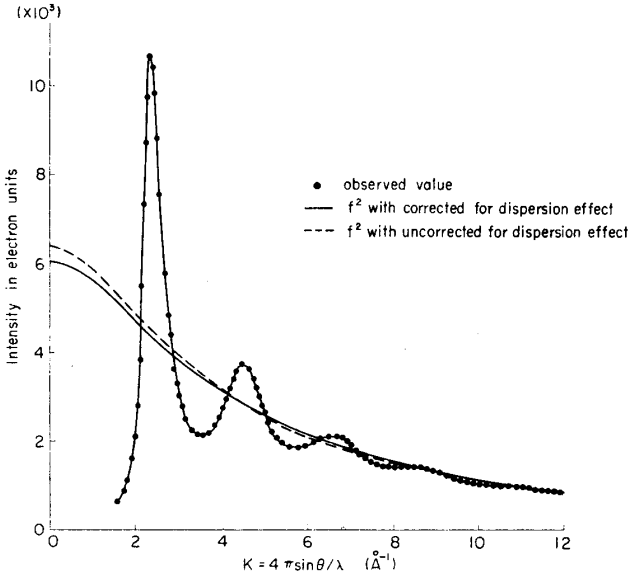

Fig. 2. Intensity pattern of liquid mercury at 15°C.

method. Fig. 3 shows the structure factor $a(K)$ obtained. Fig. 4 and Fig. 5 show the pair correlation function $g(r)$ and the atomic radial distribution function $4\pi r^2 \rho_0 g(r)$, respectively. As shown in these figures, the results with the dispersion corrected atomic scattering factor seems to be more reasonable because the spurious ripple in the pair correlation function at small r region is reduced. This is corresponding to the physical meaning that the atoms do not approach one another inside of the atomic diameter. Therefore this indicates that the correction for

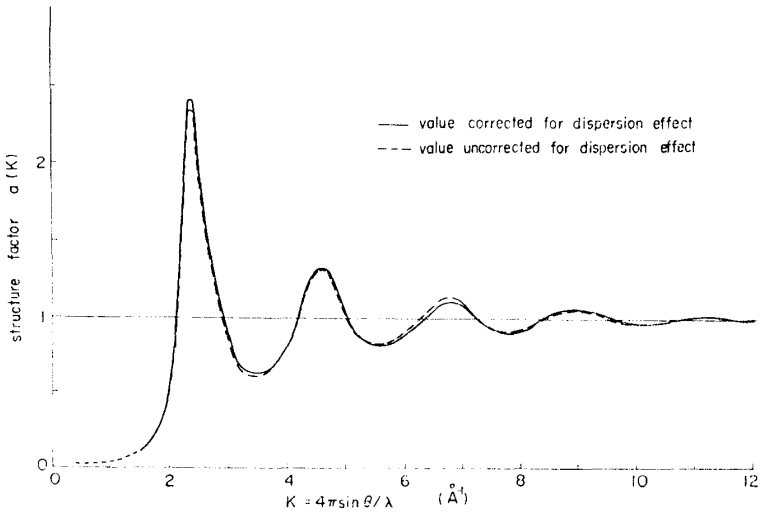

Fig. 3. Structure factor of liquid mercury at 15°C.

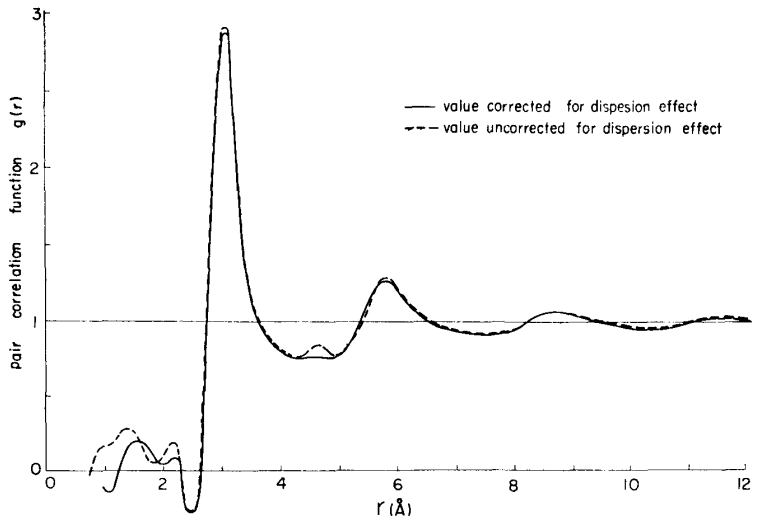

Fig. 4. Pair correlation function of liquid mercury at 15°C.

the abnormal dispersion effect on the coherent atomic scattering factor is important.

2. Problem of the divergence of the slits

Normalization is the sensitive factor for the derivation of the structure factor $a(K)$. In generally, normalization constant (α) required to convert each intensity curve to an absolute scale are obtained by two method as shown in section II–3. Here, the discussion on the Krogh-Moe-Norman's method being useful and analytical method are given.

The values of α for various values of K are given in Table 1-(A). As shown in Eq. (10) normalization constant should be constant for any values of K. However, the decrease of α is observed with increasing the values of K and this must be due to some systematic error which is connected with the scattering

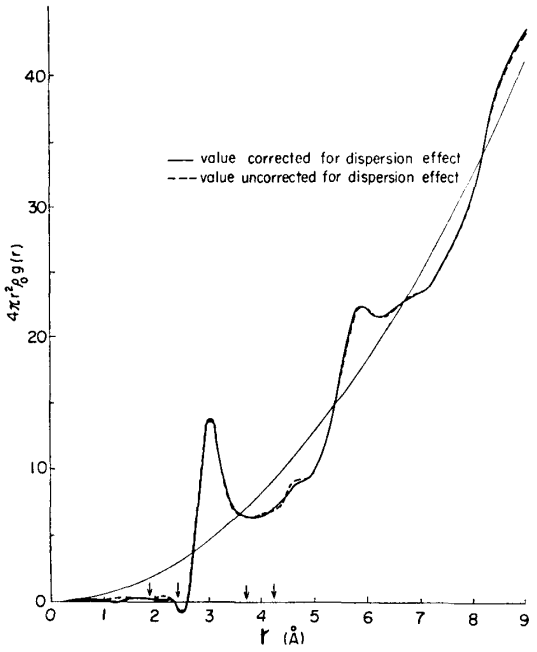

Fig. 5. Atomic radial distribution function of liquid mercury at 15°C.

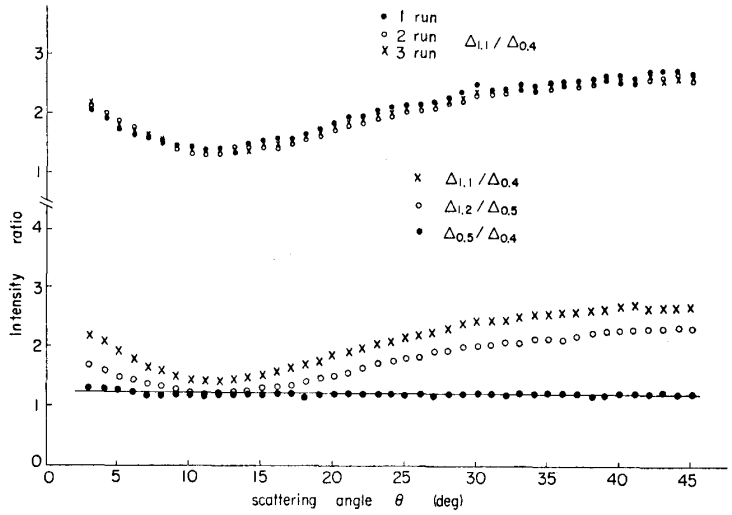

Fig. 6. Relation between the ratio of intenstities with various divergences and the scattering angle.

angle.

In order to clarify the existence of such an ambiguous error, the problem of the slits was considered. The relation between the ratio of intensities with various divergences and the scattering angle was obtained and the results are given in Fig. 6. As shown in this figure, when the receiving slits (Δ) were changed to give a different angular divergence, the ratio of intensities obtained did not have the value given from the ratio of the divergences and this ratio was a function of the scattering angle. This angular variation was significant in the larger

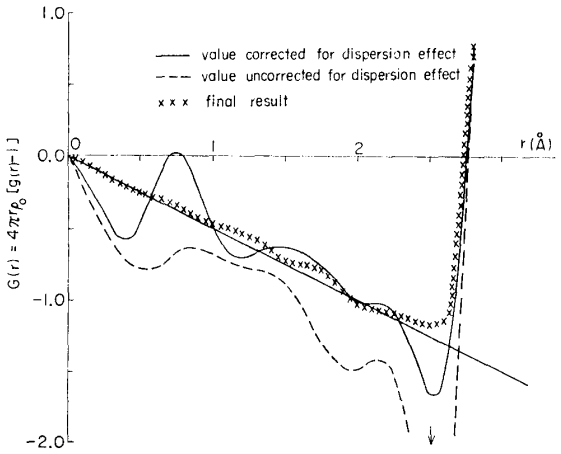

Fig. 7. Function G(r) in the region below the first peak of the pair correlation function of liquid mercury at 15°C.

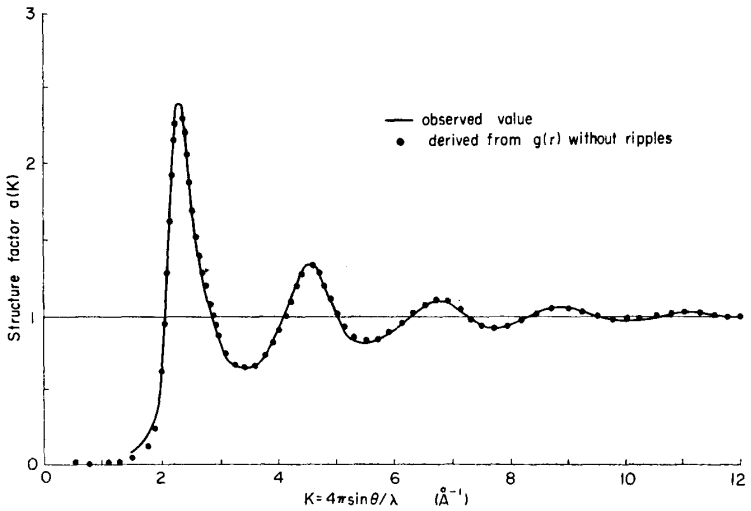

Fig. 8. Structure factor derived from g(r) with the spurious oscillations at small r removed of liquid mercury at 15°C.

Table 1. Normalization constant (α) obtained in the analysis of liquid Mercury at 15°C.

K (Å^{-1})	6.0	8.0	10.0	12.0
(A)	0.82	0.79	0.78	0.76
(B)	0.77	0.76	0.76	0.76

(A) values without the correction for the divergence-ratio factor.
(B) values with the correction for the divergence-ratio factor.

divergence. But this became almost negligibly small when the ratio of two small divergences (Δ=0.4 and 0.5) was taken. This change may be caused by the depth of penetration of X-ray beam in the specimen, curvature of the surface of the specimen, and so on. But these factors are not quantitatively separated. From

these reasons it was assumed that the values for the smallest divergence ($\Delta=0.4$) had no error and experimental values taken with larger divergences were corrected by the factor derived from the measurements (Fig. 6). Table 1-(B) shows the normalization constant obtained after correction for this divergence ratio factor. These results show moderately constant value.

In the most of the previous reports on X-ray diffraction study of liquids, this factor was not considered. But as above-mentioned, this factor should not be negligible within the experimental error on the accurate analysis of the structure of liquids by X-ray diffraction.

In case of the High-angle region method the normalization constant was 0.78. The use of this method with the Krogh-Moe-Norman's method at the same time seems to be very avaiable for the normalization-procedure.

3. Reliability of the radial distribution function

The radial distribution function calculated by Eq. (3) must be carefully examined before accepting as a final results, because usually it may include some doubtful phenomena originating from experimental errors, unsuitable treatments of several correction factors, or the termination effect which means the cutting-effect of integration in Eq. (3) at maximum of K (hereafter to be refered to as K_{max}) in place of infinity, and so on.

Such errors generally appear as spurious ripples or subsidiary maximum in the atomic radial distribution function. The spurious ripples can arise from the error in the measured intensity pattern at a discrete angular position as shown by Klug and Alexander[11] or from the use of an incorrect value for the normalization constant. The subsidiary maximum on either side of a main peak results from terminating the Fourier integral at a finite value of K.

Generally, the major soruce of error is the unsuitable correction for the absorption of the experimental data. But this is eliminated in the this work, as mentioned above, by operating the diffraction to maintain the Bragg-Brentano forcusing condition.

At first, the reliability of the radial distribution function is easily analyzed by the shape of the curve in the range near $r=0$, where $g(r)=0$ theoretically. A general shfit to positive or negative density in this region is possible, due to the mistakes in the normalization correction. In Fig. 4 the result with uncorrected dispersion effect shows the ripples in the range near $r=0$. that is larger than that of the result with corrected dispersion effect. This is due to the unsuitable normalization.

The reliability of $g(r)$ depends upon the accuracy of $a(K)$ directly and the range of the Fourier integral which has to be performed in the range from $K=0$ to ∞ as shown in Eq. (3), whereas in practice the available experimental data are

(11) K.P. Klung and L.E. Alexander: X-ray Diffraction Procedures, John Wiley and Sons Inc., New York (1954), 586,

limited to a lower value K_{min} and to a finite upper value K_{max} of K.

The significant errors arise from the inaccuracy of the extrapolation at the small angular range where the scattered intensity cannot be resolved from the primary beam and the abrupt termination of experimental data at the upper limit of the angular range at which the diffratometer can be operated.

In practice the observed intensity curve at value of K less than about 1.20Å^{-1} has been smoothly extrapolated to the K=0 value.

The value of $a(0)$ is connected with the coherent small-angle scattering due to the isothermal compressibility. This relation[2] is,

$$\lim_{K\to\infty} a(K) = a(0) = \rho_0 \chi_T kT \ , \tag{13}$$

where k is the Boltzmann constant, χ_T is the isothermal compressibility, ρ_0 is the average atomic density and T is the absolute temperature. Hence we performed the extrapolation with reference to the $a(0)$ value.

According to the work of Egelstaff et al.[12] the value of $a(0)$ is nearly equal to that of $a(K)$ at $K=(1/4)K_P$ for liquid metals, where K_P represents the position of the first peak in $a(K)$. Since $K_{min}>(1/4)K_p$ in this work, the extrapolation from $K=K_{min}$ to $K=0$ may contain the considerable uncertainty.

So in order to learn how sensitive the pair correlation function was to the extrapolation $g(r)$ was calculated for several values of x_T. It was verified that a reasonably possible change in the $a(0)$ level gives rise to changes in the resulting $g(r)$ which are not severe. As other researchers[13],[14] have also reproted, this is mainly due to the circumstance that the contribution to the integral in Eq. (3) from the region of small K is just a little hence the uncertainty for small angle coherent scattering is insignificant.

Subsidiary maximum arising from the termination error are relatively easy to trace as their positions are function of the upper limit of integration. They appear at $\Delta r=\pm 5\pi/2K_{max}\sim\pm 9\pi/2K_{max}$ according to the analysis of Sugawara[15] from the main peak position. These peaks are marked with an arrow in Fig. 5. But, this is the result for the discretely sharp peak, and the termination effect is not serious for the broad peak observed in liquid. This is theoretically discussed by Morimoto[16].

Often we find a general ripple of nearly constant amplitude superposed on the radial distribution function. As suggested by Finback[17], if the main diffraction peak is too high or too low due to experimental error, the ghost maxima or minima will appear at $(1/5)r_1$, $(1+4/5)r_1$, $(1+8/5)r_1,\ldots$, where r_1 is the position of the main peak in the radial distribution function. About the result of liquid

(12) P.A. Egelstaff, C. Duffill. V. Rainey, J.E. Enderby, and D.M. North: Phys. Lett., **21** (1966), 286.
(13) P. Ascarelli: Phys. Rev., **143** (1966). 36.
(14) G.T. Clayton and L. Heatom: Phys. Rev., **121** (1961), 649.
(15) T. Sugawara: Sci. Rep. RITU, **A3** (1951), 39.
(16) H. Morimoto: J. Phys. Soc. Japan, **13** (1958), 1015.
(17) C. Finback: Acta Chem Scandi., **3** (1949), 1279.

mercury at 15°C r_1 is equal to 3.07 Å. But as shown in Fig. 5 such the ghosts disappear. In this work, the obtained radial distribution function of liquid mercury at 15°C is almost free of ripples and hence the results seem to be reasonable.

We shows another method of the check of the validity for the obtained radial distribution function.

Kaplow et al.[18] used the function defined as follows,

$$F(K)=K[a(K)-1]=\int_0^\infty G(r)\,\sin(K\cdot r)\,dr\,, \tag{14}$$

and

$$G(r)=4\pi r\rho_0[g(r)-1]=\frac{2}{\pi}\int_0^\infty F(K)\,\sin\,(K\cdot r)dK\,, \tag{15}$$

in order to show clearly the reciprocity between $a(K)$ and $g(r)$ and to facilitate the Fourier transformation operation. For the pair correlation function in the region below the first peak $g(r)$ is zero. Hence in this region, we find,

$$G(r)=-4\pi\rho_0 r\,, \tag{16}$$

from which the average density ρ_0 of the liquid sample can be obtained, because the initial slope is $-4\pi\rho_0$. Therefore, the value of ρ_0 calculated by this mehod gives a criterion for the accuracy of $a(K)$ and $g(r)$. Fig. 7 shows the behaviour of $G(r)$ in the region of small r for liquid mercury at 15°C. From the slope illustrated in Fig. 7, the value of the average density ρ_0 is estimated at 0.041 atoms/Å^3, which is in good agreement with the observed value, 0.0407 atoms/Å^3. The usefulness of this method was also shown in the previous work concerning the X-ray Fourier analysis for several liquid metals[19],[20].

It is not possible to be certain, with experimental data, that all errors have been removed in fact, but the magnitude of remaining oscillations at small values of r and the value of ρ_0 in the final $G(r)$ may be used as the check of over-all efficiency of the procedures. Therefore, we ought to perform the Fourier transformation and the inverse Fourier transformation between $a(K)$ and $g(r)$ repeatedly within the experimental error. Fig. 8 shows the structure factor $a(K)$ derived from $g(r)$ with the spurious ripples at small r removed and this is in almost good agreement with the observed structure factor.

As shown in Fig. 5, the atomic radial distribution function of liquid mercury at 15°C remains some subsidiary maximum. But the structure of liquid mercury is somewhat different from those of simple liquid metals such as Al[19], Pb[19], alkali metals[21] and so on. This problem was discussed in detial in the previous papers

(18) R. Kaplow, S.L. Strong, and B.L. Averbach: Phys. Rev., **138** (1965), A1336.
(19) Y. Waseda and K. Suzuki: phys. stat. sol., **39** (1970), 669.
(20) Y. Waseda and K. Suzuki: phys. stat. sol., **49** (1972), 339.
(21) N.S. Gingrich and L. Heaton: J. Chem. Phys., **39** (1961), 873.

[9],[10]. Therefore, these subsidary maximum or ripples are due to not the experimental errors and the termination effect but the specific character of liquid mercury.

On the other hand, in order to obtain the information on the changes in the resulting $g(r)$ derived from the errors in the structure factor $a(K)$ the pair correlation function was calculated for several structure factors which were intentionally modified. It was found that the errors in $a(K)$ in the region of large K have severely influence on the resulting region of small r in $g(r)$. This suggests that the correction for normalization is very important and the atomic scattering factor should be corrected for the abnormal dispersion effect again. However the errors of $a(K)$ in the region of small K have frequently influence on the resulting region of small r in $g(r)$.

From these results, we should perform the Fourier transformation and the inverse Fourier transformation between $a(K)$ and $g(r)$ repeatedly within the experimental error and subsequently accept the radial distribution function obtained as a final result.

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