Profile Analysis of Amorphous Haloes by Means of a Fourier Transformation, with Special Reference to the Structures of Amorphous Pt–C and Ni–P

BY KENJI DOI
Division of Physics, Japan Atomic Energy Research Institute, Tokai-mura, 319-11, Japan

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A Fourier transform method is proposed for the analysis of halo profiles from amorphous materials, which is analogous to the Fourier method for the analysis of Debye–Scherrer line profiles as originally expounded by Warren & Averbach [J. Appl. Phys. (1950), 21, 595]. Applied to the first haloes of amorphous alloys, it gives radial distribution functions in which only those atom pairs are represented whose separations are atomic diameters or integral multiples thereof. The method is applied to the first haloes of amorphous Pt–C and Ni–P, which correspond to the nearest neighbour distances of metallic atoms. The result from amorphous Pt10C80 confirms the microcrystalline model with diameter 2×2.2 Å. The analysis of amorphous Ni33P17 gives a result less simple to understand. The correlation between neighbouring atoms extends as far as 5×2.2 Å, which explains the sharpness of the first halo observed. Directly neighbouring pair separations are found to be increased by 0.2–0.4 Å. The definition of amorphous scattering is discussed in relation to that in very broad Debye–Scherrer reflexions.

1. Introduction

It is established that the intensity profile of a given Debye–Scherrer (DS) line hkl contains structural information relevant to the reflecting plane (hkl), which we can derive from the observed profile via its Fourier transformation. For instance, coherent lengths (crystallite sizes) and lattice strains, both perpendicular to the reflecting plane, have been derived from the observed line profiles (Warren & Averbach, 1950; Wilson, 1963; Bertaut, 1950; Doi, 1961; Mori & Doi, 1964; Das, 1968; Yoda, Doi, Tamura & Kuriyama, 1973).

We can now expect that a similar Fourier method will apply to a halo profile from amorphous materials provided that the halo is unambiguously attributed to a single kind of atom rows, just as a DS line from crystalline materials is attributed to a single kind of lattice planes.

On the other hand there are problems left unsolved for the structure of amorphous materials. In particular, for some amorphous alloys structure models seem not to be well established regarding the first halo profiles. To cite, for the amorphous Ni–P system (a–Ni–P) the height and breadth of the first halo on the scattering pattern seem to be irreconcilable with the dense random packing (DRP) model (Sadoc, Dixmier & Guinier, 1973) as pointed out by Mráfkó & Duhaj (1975), although the DRP model should certainly be the most acceptable one in all other aspects (Dixmier, 1974). It is thus of interest to extract structural information from the first haloes of amorphous alloys which are attributed to the directly neighbouring atom pairs, in order to estimate the extent to which the profiles of the first haloes are consistent with proposed models.

In this paper a Fourier method for halo profile analysis, which is analogous to that for DS profile analysis, is presented. The method is applied to systems a–Pt–C and a–Ni–P as examples of amorphous alloy structures.

2. Method of analysis

We start from the general expression for scattering intensities from amorphous materials (Guinier, 1964):

\[ J(s) - 1 = \int_{-\infty}^{+\infty} \frac{2\pi x^2[\rho(x) - \rho_0]}{2\pi x} \sin 2\pi x \, dx, \]  

where \( J(s) \) is the interference function and other symbols have their usual meanings. Let us consider an atom row with neighbour separation \( a \) (Fig. 1a), its radial distribution function \( RDF = 2\pi x^2[\rho(x) - \rho_0] \) takes the form as represented schematically in Fig. 1(b) where the RDF (dotted curve) is shown approximated by a series of equally spaced peak functions of height \( P_n \). The RDF for an atom row as depicted in Fig. 1(b) shall hereafter be denoted by \( RDF(a) \) or \( 2\pi x^2[\rho(x) - \rho_0] \) and the Fourier inverse of RDF(a) by \( [J(s) - 1]_a \).

The interference function corresponding to the atom row is then written as:

\[ [J(s) - 1]_a = \sum_n P_n \sin \frac{2\pi s n \xi}{2\pi s \xi}, \]  

with \( P_n \) alternating in sign as shown in Fig. 1(b).

Let both sides of (2) be Fourier-transformed, then we have:

\[ P(x) = \sum_n P_n A_n(x), \]  

where

\[ P(x) = \int_{-\infty}^{+\infty} [J(s) - 1]_a \exp 2\pi i s x \, ds, \]
and
\[ \Delta_n(x) = \int_{-\infty}^{+\infty} \sin \frac{2\pi s n x}{2} \exp 2\pi i s x \, ds. \]  
\[ \tag{5} \]

The function \( \Delta_n(x) \) is a square function as represented by Fig. 1(c). The function \( P(x) \) given by (3) is shown schematically in Fig. 1(d) with coefficients \( G_n \) where the terms with even \( n \) and odd \( n \) are represented separately, the former being positive and the latter negative (see Fig. 1b). The resultant \( P(x) \) will have the shape shown in Fig. 1(e) specified by the coefficients \( g_n \).

From these figures follow the relations between the coefficients \( P_n, G_n \) and \( g_n \):
\[ g_n = G_n - |G_{n+1}|, \quad n \text{ even} \]
\[ g_n = G_{n+1} - |G_n|, \quad n \text{ odd} \]  
\[ \tag{6} \]
\[ \frac{1}{na} P_n = G_n - G_{n+2}, \quad n \text{ even} \]
\[ \frac{1}{na} P_n = |G_n| - |G_{n+2}|, \quad n \text{ odd}. \]  
\[ \tag{7} \]

As the function \( P(x) \) is directly related to the observed intensity distribution (equation 4), we have the possibility of deriving the coefficients \( g_n \) from observed intensities, and to derive the coefficients \( P_n \) via the relations (6) and (7), which will enable us to construct RDF(a) as in Fig. 1(b).

In place of \( P(x) \) [equation (4)] we define a function
\[ \mathcal{P}(x) = \int_{-\infty}^{+\infty} [J(s) - 1] \frac{\sin \pi a (s - s_a)}{\pi a (s - s_a)} \exp 2\pi i(s - s_a) x \, ds, \]  
\[ \tag{8} \]
with
\[ s_a = \frac{1}{a}, \]  
\[ \tag{9} \]
which is related to the maximum of the first halo \( s_1 \) by Ehrenfest’s relation (Guinier, 1964).
The expression in the central bracket \( \left[ \sin \frac{\pi a(s-s_a)}{\pi a(s-s_a)} \right] \)
in the integral of (8) is illustrated in Fig. 2 together with the observed \( J(s) - 1 \). It is seen that only the first halo of the scattering pattern effectively contributes to the integral of (8) because of the central bracket which decreases as \( 1/|s-s_a| \) with \( |s-s_a| \). It also justifies the neglect of the higher-order harmonics in \( [J(s) - 1]_a \) which should exist at

\[ s_m = ms_1 \quad (m \neq 1), \]

but which are hardly separated in observed intensity distributions. In particular, we can dispense with small-angle scatterings, if any, which correspond to \( m = 0 \). The relation (8) is rewritten by virtue of the convolution theorem (Doi, 1961):

\[
\Pi(x) = \int_{-\infty}^{+\infty} P(x') A_1(x-x') \exp \left( -2\pi i s_0 x' \right) dx'
\]

where \( \Delta_1(x) \) is given by:

\[
\Delta_1(x) = \int_{-\infty}^{+\infty} \sin \frac{\pi a s}{\pi a s} \exp 2\pi i s x dx.
\]

In Fig. 3 are shown a portion of \( P(x) \), \( ABCDEG \), and the function \( \Delta_1(x-n a/2) \) together with the real and imaginary parts of \( \exp -2\pi i s_0 x \). With the aid of these figures we have, making use of (12),

\[
\text{Re} \Pi \left( \frac{na}{2} \right) = 0
\]

\[
\text{Im} \Pi \left( \frac{na}{2} \right) = (-1)^{n-N} \frac{1}{\pi} (g_n - g_{n+1})
\]

where \( \text{Re} \) and \( \text{Im} \) mean real and imaginary parts, respectively. The above arguments show that, by constructing \( \Pi(x) \) from observed \( J(s) \) [equation (8)], and sampling its values at \( x = na/2 \) \( (n = 1, 2, 3, \ldots \text{ etc.}) \), we can make use of (6), (7) and (13) to derive \( P_n \) values which represent RDF(\( a \)) relevant to the atom rows with atomic separation \( a \).

The relation between the method of analysis here expounded and that for the DS line profile analysis is discussed in the Appendix.

### 3. The structure of \( \alpha\)-Pt\(_{20}\)C\(_{80}\)

The interference function of \( \alpha\)-Pt\(_{20}\)C\(_{80}\) evaluated from the observed intensities [Fig. 1(a), Dixmier (1974)] was processed as described in the previous section, the contributions from C atoms to the scattering intensities being neglected. The value adopted for \( a \) was 2.77 Å in accordance with both the diameter of the Pt atom (Pearson, 1958) and with the estimation from the Ehrenfest relation (10).

Fig. 4(a) and (b) shows the real and imaginary parts of the function \( \Pi(x) \) thus obtained. Although errors, mainly due to the truncations in the integrations of (8), are rather important, it is seen that the real part of \( \Pi(x) \) is effectively zero as required by the first of equations (13). It means that the function \( P(x) \) has really the rectangular form as shown by \( ABCDEG \) in Fig. 3(a), and that the distances between neighbouring atoms are well defined* in the structure of \( \alpha\)-Pt\(_{20}\)C\(_{80}\). The imaginary part vanishes for \( x \geq 3a \); which means:

\[
g_n - g_{n+1} = 0, \quad n \geq N
\]

with \( N = 6 \) in this case. If we assume that

\[
g_n = 0, \quad n \geq N
\]

* It is seen that when the distances between neighbouring atoms fluctuate around the mean value \( a \), the rectangles will be rounded symmetrically and (13) will still hold in its slightly modified form. See the discussion in § 6.

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Fig. 3. A portion of the function \( P(x) \) defined by (4) and shown in Fig. 1(e). The rectangular portion \( ABCDEG \) corresponds to the structure where the neighbour separation \( a \) is uniquely defined. When there are increases in neighbour separations the rectangle is deformed as \( ABFDG \), the curves \( BF \) and \( DG \) being approximated by Gaussian functions as shown. The figures are shown for even \( n \). The dotted \( B'F' \) refers to ‘thermal vibration’. (b) The function \( \Delta_1(x-na/2) \) defined by (5') and appearing in (12) in the text. (c), (d). The real and imaginary parts of \( \exp -2\pi i s_0 x \) appearing in (12).
we can deduce $g_n$ from $\text{Im} \, \Pi(x)$ by making use of the second of equations (13). The coefficients $g_n$ thus determined, we can obtain $G_n$ by (6) assuming further that
\[ G_n = 0, \quad n \geq N. \] 
(16)

Despite the truncation errors we can sample the values of $\text{Im} \, \Pi(x)$ at $x = na/2$ ($n = 1, 2, \ldots, N$), as shown by black spots in Fig. 4, and obtain the values of $G_n$. The coefficients $P_n$ are then calculated with (7), and the RDF(a) is constructed as shown in Fig. 5 where the correlation is seen to exist only within the range of about 2a.

The behaviour of RDF(a) described above is thoroughly consistent with the proposed model of $\alpha$-Pt$\text{C}_{80}$, where 13 Pt atoms are arranged in an f.c.c. or h.c.p. microcrystalline lattice with a well defined interatomic distance of 2.77 Å. It has been shown that the calculated intensities for these models are in agreement with those observed for values of $s$ up to 1.5 Å$^{-1}$ (Dixmier, 1974).

The present analysis of the first halo indicates that the structure of $\alpha$-Pt$\text{C}_{80}$ is constituted of atom rows of lengths up to $2a = 5.54$ Å. The atom rows may be interconnected with each other to produce a three-dimensional arrangement, which can explain the observed intensity distribution outside the first halo as well. The structure thus produced is in fact the close-packed 13 Pt atoms regularly arranged with interatomic distance 2.77 Å (microcrystals). The whole structure may be such that the microcrystals as described above are incoherently dispersed in the carbon matrix.

4. Effects of variations in interatomic distances

In the previous sections it was assumed that the function $P(x)$ defined in (4) has a rectangular form, as in Fig. 1(e), which proves to be the case for $\alpha$-Pt$\text{C}_{80}$. If the interatomic distances in atom rows are not well defined but are varied locally to a slight extent, the form of $P(x)$ will no longer be rectangular as $ABCDEG$ of Fig. 3(a); it will become rounded according to the variation of the interatomic distances. For instance, when the atom row is locally dilated, $ABCDEG$ is

\[ 2 \pi x f(P(x) - P_0) \, dx \]

Fig. 5. The RDF(a) derived from the first halo of $\alpha$-Pt$\text{C}_{80}$.
deformed to \textit{ABFDG} (Fig. 3a), with BF and DG expressed, without loss of generality, by Gaussian curves:

\[ (g_n - g_{n+1}) \exp \left( - \alpha_n^2 x^2 \right) \]  

(17a)

where the parameter \( \alpha_n \) is such that

\[ \frac{1}{\alpha_n} \leq \alpha. \]  

(17b)

Equation (13) is then modified as (Moriguchi, Udagawa & Hitotsumastu, 1956)

\[
\text{Re } \Pi \left( \frac{na}{2} \right) = (-1)^n \left\{ \left( g_n - g_{n+1} \right) \frac{\pi s_n}{2\alpha_n} \right. \\
\times \exp \left( - \frac{\pi^2 s_n^2}{\alpha_n^2} \right) \\
+ \left( g_n - g_{n-1} \right) \frac{\pi s_n}{2\alpha_{n-1}} \exp \left( - \frac{\pi^2 s_n^2}{\alpha_{n-1}^2} \right) \right\} 
\]

\[
\text{Im } \Pi \left( \frac{na}{2} \right) = (-1)^n \left\{ \frac{1}{\pi} \left( g_n - g_{n+1} \right) \\
- \left( g_n - g_{n-1} \right) \frac{s_n}{\alpha_{n-1}} \right. \\
\times \exp \left( - \frac{\pi^2 s_n^2}{\alpha_{n-1}^2} \right) \text{erf} \left( \frac{\pi s_n}{\alpha_{n-1}} \right) \\
- \left( g_n - g_{n-1} \right) \frac{s_n}{\alpha_n} \right. \\
\times \exp \left( - \frac{\pi^2 s_n^2}{\alpha_n^2} \right) \text{erf} \left( \frac{\pi s_n}{\alpha_n} \right) \left\} 
\]

(18)

For contractions in interatomic distances the signs are reversed in \( \text{Re } \Pi(x) \) and in the second and third terms of \( \text{Im } \Pi(x) \). It is noted that \( \text{Re } \Pi(x) \) no longer vanishes and that when all \( \alpha_n^{-1} \) are zero (18) is reduced to (13).

As we have \( 2N \) equations (18) for \( N \) sampling points, we have the possibility of deriving \( 2N \) parameters \( g_n \) and \( \alpha_n \) for \( N \) points, with which we can construct the RDF(\( a \)) when the variation in interatomic distances is present.

5. The structure of \( a\)-Ni\(_{83}\)P\(_{17}\)

The observed interference function of \( a\)-Ni\(_{83}\)P\(_{17}\) (Dixmier, Doi & Guinier, 1965) was analysed along the lines described in \( \S \S \) 2 and 4, neglecting the presence of metalloid atoms as in the analysis of \( a\)-Pt\(_{12}\)C\(_{80}\). There arose a problem that, with all possible choices of \( s_n \), the real part of \( \Pi(x) \) proved not to vanish, which apparently contradicted (13). As seen from the discussions in \( \S \) 4 this requires that the variations in interatomic distances should be taken into consideration, and the parameter \( \alpha_n \) should be attached to the function \( P(x) \), which is to be evaluated from the observed intensity distribution.

The parameter \( \alpha_n \) and therefore \( s_n \) should then be

\* For symmetric fluctuations in interatomic distances \( \text{Re } \Pi(x) \) vanishes for \( x = na/2 \).

Fig. 6. (a) The real and (b) the imaginary parts of the function \( \Pi(x) \) obtained from the first halo of \( a\)-Ni\(_{83}\)P\(_{17}\). Note that the real part does not vanish indicating the increase in neighbour separations, and that the imaginary part remains finite as far as \( x = 5a \). Black spots, crossed circles and open circles show the calculated values allowing for 0, 10 and 20\% increase respectively.
chosen in such a way that the values of \( \text{Re} \, II(x) \) (equation 8) are minimized for every point sampled:

\[
\sum_n \left| \text{Re} \, II \left( \frac{na}{2} \right) \right| = \text{minimum}, \tag{19}
\]

because \( a \) in this case is a mean value of interatomic distance from which the real distances may deviate. A systematic search of \( a \) satisfying the condition (19) was made, giving the result \( a = 2.20 \pm 0.05 \text{ Å} \), which is appreciably different from the distance of closest approach of Ni atoms, 2.50 Å (Pearson, 1958). The discrepancy between those two figures will be discussed later.

The value 2.20 Å of \( a \) gives \( x = 1.10 \) in the Ehrenfest relation (10) which is closer to \( x = 1.00 \) corresponding to an infinite range of correlation (Bragg relation) than the usually accepted value \( x = 1.23 \) corresponding to the correlation length \( a \) (diatomic molecules). This suggests that the correlation in \( a-\text{Ni}_{83}\text{P}_{17} \) along the atom row with separation \( a \) ranges much farther than that in \( a-\text{Pt}_{20}\text{C}_{80} \) where the \( x \)-value adopted is nearly equal to 1.23.

The function \( II(x) \) thus obtained is shown in Fig. 6. The real part is finite and positive for \( x < 2a \). For \( x > 2a \) where \( \text{Re} \, II(x) \) is practically zero and the form of \( P(x) \) is still considered rectangular, the analysis can be made in the same way as the analysis of \( a-\text{Pt}_{20}\text{C}_{80} \) (\( N = 10 \) in this case), and the values of \( G_n \) (\( n \geq 4 \)) are thereby obtained. For \( x < 2a \) (\( n \leq 3 \)) the positive values of \( \text{Re} \, II(x) \) suggest that the form is no longer rectangular but is rounded by variations in interatomic distances, which are in fact extensions. If they were contractions \( \text{Re} \, II(x) \) would be negative, and if interatomic distances fluctuated symmetrically around a mean value, \( \text{Re} \, II(x) \) would vanish as in the case of \( a-\text{Pt}_{20}\text{C}_{80} \).

A trial and error analysis of \( \text{Re} \, II(x) \) and \( \text{Im} \, II(x) \) was made for \( x = na/2 \) (\( n = 1, 2, 3 \)). First, the coefficients \( G_n \) were estimated by extrapolation from \( G_n \) for \( n \geq 4 \) (\( x \geq 2a \)), and

\[
\frac{1}{\alpha_n} = a \times 10^\% \quad (n = 1, 2, 3) \tag{20}
\]

was assumed. Then, with the same estimation of \( G_n \) (\( n = 1, 2, 3 \)) another assumption,

\[
\frac{1}{\alpha_n} = a \times 20^\% \quad (n = 1, 2, 3), \tag{21}
\]

was made. The calculated values of \( \text{Re} \, II(x) \) and \( \text{Im} \, II(x) \) on the basis of these assumptions are plotted in Fig. 6 by open and crossed circles respectively. Black spots correspond to

\[
\frac{1}{\alpha_n} = 0 \quad (n \geq 4). \tag{22}
\]

The agreement with the observed values of \( II(x) \) is satisfactory with both assumptions (20) and (21), in view of various sources of errors, viz the truncations, uncertainty in the value of \( a \), Gaussian assumption (17) and the neglect of P atoms (only the first of these being estimated by bars in Fig. 6).

The RDF(a) constructed is shown in Fig. 7, where the peaks corresponding to \( n = 1, 2, 3 \) are displaced outwards by an amount of \( 10 \sim 20\% \) of \( a \), i.e., \( 0.2 \sim 0.4 \text{ Å} \), and the heights of peaks remain finite as far as \( x = 5a = 11 \text{ Å} \). It is noted that in the RDF(a) of \( a-\text{Pt}_{20}\text{C}_{80} \) (Fig. 5) peaks are spaced regularly and vanish at about \( x = 7 \text{ Å} \). The longer range of correlation in \( a-\text{Ni}_{83}\text{P}_{17} \) (11 Å) may be responsible for the relatively high and relatively narrow profile of the first halo.

The RDF(a) of Fig. 7 represents an atom row as depicted schematically in Fig. 8. The increases in the direct neighbour distances are understood by a zigzag arrangement of atoms as shown, making the direct neighbour distance 2.5 Å ± 0.1 Å and leaving the distances of second, third, etc. neighbours approximately as 2 × 2.2, 3 × 2.2 Å, etc., respectively. The direct neighbour separation 2.5 Å agrees both with the position of the first peak in ordinary RDF (Dixmier et al., 1965) and with the diameter of Ni atom (Pearson, 1958).

Increases of this nature are suggested by Cargill & Cochrane (1974) and Polk & Boudreaux (1975) to be due to the presence of P atoms.

It is noted that the \( n \)-membered atom rows (\( n \sim 6 \)) as
shown in Fig. 8 have been found in DRP models as well. In fact, 4-, 5-, 6- and 7-membered atom rows are recognized in the laboratory-built DRP model of Bernal (1964).

In principle it is possible to derive from RDF(a) the number fraction of n-membered rows as a function of n, in a way analogous with that in which the distribution function of crystallite sizes is derived from the Fourier transform of a DS line profile. (Doi, 1961; Mori & Doi, 1964; Das, 1968; Yoda et al., 1973). In practice, however, we cannot proceed in this way because of the rather important errors in RDF(a) as mentioned above in relation to Fig. 6. Nevertheless it seems highly probable that the RDF(a) of Fig. 7 suggests many more fractions for the n-membered rows (n~6) than is estimated by an inspection of Bernal's model. As the RDF(a) for Pt20C80 (Fig. 5) is seen to be quite similar to that of Ni83P17 (Fig. 7), except for the outward displacements of central peaks, we can say that if the former can be related to microcrystals of 13 atoms of diameter 2a the latter may be well related to 'microcrystals' of diameter 5a with a zigzag arrangement of atoms. In fact the atom rows of Fig. 8 may be organized laterally to form a three-dimensional coherent domain (microcrystal) of diameter 5a in which atoms are arranged in a zigzag manner.

The above structural information for a-Ni83P17 is derived merely from the first halo of the scattering pattern, the rest of the scattering pattern being irrelevant. However, if we are permitted to proceed further with the analogy with the case of a-Pt20C80 (§ 3), we can expect that there exists a structure model which is effectively derived from the first halo and which is compatible with the intensity distribution outside the first halo, just as the analysis of the first halo of a-Pt20C80 indicated a microcrystalline model which gives calculated intensities agreeing well with the observed ones outside the first halo (Dixmier, 1974).

In fact the coherent domains described above may be identified with the 'crystallites' having heavily distorted lattices described by Dixmier et al. (1965) (see also Doi, 1966; Livage, Doi & Mazières, 1968) on which the model may be constructed. It is interesting to note that the parameters specifying the dimension of the 'crystallite' are found in the range 5.5~20 Å (Dixmier et al., 1965), which is consistent with the length of the atom row (5a = 11 Å) derived in the present analysis.

On the other hand, another model may be obtained starting from the DRP model by taking due account of the number fractions of n-membered atom rows or atomic collinearities (Bernal, 1964) so as to explain the sharpness of the first halo. The inhomogeneous packing of atoms suggested by Finnay (1975) might be an example. Those models should be regarded as two complementary descriptions of a single physical entity which will not conform to a structural model as straightforward as the one usually adopted to describe, for example, structures of crystals.

6. Summary and discussions

A Fourier analysis of the first halo corresponding to the direct neighbour distance a is shown to be feasible for a-Pt20C80 and a-Ni83P17. The principle of analysis is similar to that with which the Fourier analyses of DS line profiles are made. The radial distribution functions RDF(a) relevant to atom rows of neighbouring distance a are derived. For a-Pt20C80 the RDF(a) is composed of peaks regularly spaced by a = 2.77 Å which vanish beyond x = 2a. The RDF(a) is consistent with the proposed model for this structure, i.e. a microcrystal of diameter 2a constituted of 13 atoms arranged in regular f.c.c. or h.c.p. lattices. The structure of a-Ni83P17 proves to be less simple. The RDF(a) obtained reveals that there exists in the structure an appreciable amount of atom row as long as 5a (a = 2.2 Å), and that the direct neighbour separations in atom rows are increased by 0.2~0.4 Å. These findings do not allow an easy interpretation in terms of a simple structure model as for the structure of a-Pt20C80. Characteristic features of a-Ni83P17 structure disclosed by the present analysis are the unexpectedly long correlation range 5a (= 11 Å) as well as the extensions between directly neighbouring atom pairs, both of which should be taken into consideration in any realistic and reasonable descriptions of the structure.

It is to be noted here that the present method of analysis is not susceptible to `thermal vibrations' which make the interatomic distance fluctuate symmetrically around its mean value. In fact RDF(a) of Fig. 1(b) (dotted curve) is approximated by series of delta functions. The discussion of Fig. 3 will show readily that, when the rectangle is rounded symmetrically with respect to BC as shown by B'F', (13) still holds with slightly modified definition of g_n. Estimated from background in J(s)~1 [e.g. X'X' in Fig. 2(a)], these fluctuations are of the order of the 1/10 of a in the materials examined (Dixmier et al., 1965). This means that P_n in Figs. 5 and 7 and the displacements in Fig. 7 may suffer from errors of about 10% each. The conclusion arrived at should therefore be understood as merely semi-quantitative.

The present method of analysis will apply, in principle, to any halo profiles provided that the profile is ascribed to a single kind of atom rows. In practice, however, the application may be limited to first haloes of simple liquids and amorphous materials, otherwise haloes are produced by superposition of intensities from several kinds of atom rows whose interatomic distances are incommensurable with each other. Moreover the profile should really be of `amorphous' nature in the sense that it is describable by a Debye function [see equation (2)]. A discussion on this question is given in the Appendix.
Numerical calculations were performed by Fortran programs written by H. Tomimitsu to whom author’s thanks are due.

**APPENDIX**

A note on amorphous haloes and very broad Debye–Scherrer reflexions

One may argue here about the definitions of ‘amorphous’ and ‘crystalline’ reflexions, because in some cases scattering from ‘amorphous’ materials is treated as very broad crystalline reflexions and is analysed by a DS line profile technique (Doi, 1961).

It is said in quite a formal way that the scattering intensity from an amorphous material is expressed in terms of a Debye function \[ \text{Debye function} \]

\[ \sum P_n \sin \frac{2\pi sna}{2\pi s} \]

while for a crystalline material it is the Laue interference function (James, 1954)

\[ \sum P_n \sin^2 \frac{\pi sna}{\sin^2 \pi s} \]

which prescribes the diffracted intensity.

Let us consider an intensity distribution from a single scatterer spread out to some extent in reciprocal space (Fig. 9). The intensity is distributed around a point \( S \) with breadth \( \Delta s_1 \) in the direction \( \vec{OS} \) (\( O \) being the origin of the reciprocal space) and \( \Delta s_2, \Delta s_3 \) in lateral directions perpendicular to \( \vec{OS} \). For a crystalline material the point \( S \) is identified with a relpoint \( hkl \) around which the Laue–Bragg reflexion is more or less broadened. The DS line profile is constructed by integrating the intensities over spherical shells centred at \( O, SS' \) for instance (Fig. 9). If

\[ \Delta s_2 \ll 1 \]
\[ \Delta s_3 \ll 1 \]

(A3)

the integrations can be approximated by those taken over the planes perpendicular to \( \vec{OS} \) (such as \( SX \) in Fig. 9, for example). The line profile is then the Fourier transform of a one-dimensional lattice structure which is the projection of the whole of the structure onto a line parallel to \( \vec{OS} \) (Doi, 1961), and the intensity is expressed by the one-dimensional Laue interference function \( (A2) \). It is noted that the condition \( (A3) \) does not require that

\[ \Delta s_1 \ll 1 \]

(A4)

and therefore the DS reflexion can be very broad having the profile expressed by the Laue function \( (A2) \).

In fact it realizes a crystallite very thin in the direction \( [hkl] \), which was found to be the case with the ‘amorphous’ carbon (Doi, 1961).

When the conditions \( (A3) \) are not valid, \( i.e. \) the intensity is spread out in directions perpendicular to \( \vec{OS} \) in reciprocal space, the integration over the shell \( SS' \) can no longer be approximated by that over the tangential plane \( SX \) (Fig. 9), and the spherical integration in reciprocal space becomes essential. One must then have recourse to the Debye formula which expresses the result of this integration for each atom pair constituting the scatterer. It can be shown that when the lateral widths \( \Delta s_2, \Delta s_3 \) are reduced, the Debye function \( (A2) \) approaches the Laue function \( (A1) \) (James, 1954).

In practice, however, it is a subtle matter to decide whether an observed halo is really ‘amorphous’ or ‘crystalline’ in the sense defined here, because it requires one to decide whether the observed profile is expressible by the Debye function \( (A1) \) or the Laue function \( (A2) \) with suitable assignments of coefficients \( P_n \) attached to each term of \( (A1) \) or \( (A2) \).

References


