Calculation of Profiles of Two-Dimensional X-ray Reflections from Layered Structures

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An analytical expression has been derived for the number of interatomic (or inter-unit cell) distances of equal magnitude in finite (disc-shaped) layers. The expression facilitates greatly the calculation of the profiles of two-dimensional reflections from layered structures using the interatomic distance sum technique.

The powder patterns of layered structures yield somewhat abnormal profiles for the \( h00 \) reflections (\( c^* \) is taken normal to the layers). A theoretical expression for the profiles was first given by Warren (1941). His approach involved the lattice sum technique. With this technique, the intensity (in Thomson units) of X-rays scattered coherently is expressed as (Diamond, 1957)

\[
I(s) = (FF^*) \cdot (GG^*) \cdot (HH^*)
\]

in which \( F \) is the structure factor of the unit cell within the layer, \( G \) is the transform of the lattice and \( H \) is the transform of the shape of the layer. In general, \( I(s) \) is calculated as a function of the position vector \( s \) in reciprocal space and \( \langle I(s) \rangle \) is obtained by integration.

Generally, it becomes necessary for one to take the factor \( (FF^*) \) outside the integral and to make other simplifying assumptions (Warren, 1941; Wilson, 1949; Brindley & Mériné, 1951; Warren & Bodenstein, 1966; Ruland, 1967).

An alternate approach to the problem is the most primitive one, that is, to consider all of the interatomic distance vectors. The intensity is given by

\[
I(s) = \sum \sum f_m f_n \exp (i2\pi s \cdot r_{mn}),
\]

in which \( f \) is the atomic scattering factor and \( r_{mn} \) is the distance vector from \( m \) to \( n \). The advantage of this technique lies in the fact that the necessary integrations involved in obtaining \( \langle I(s) \rangle \) are often done without any simplifying assumptions and simple expressions.
are obtained. For example, if the distance vectors \( \mathbf{r} \) assume all possible orientations with equal probability, then

\[
\langle \exp (i2\pi \mathbf{s} \cdot \mathbf{r}) \rangle = \frac{1}{2\pi} \int_0^{2\pi} \exp(i2\pi sr \cos \alpha) \sin \alpha \, d\alpha
\]

and we obtain

\[
I(s) = \sum_m \sum_n f_m f_n \sin 2\pi sr \frac{2\pi sr}{2\pi sr}.
\]  

Equation (1) is the well-known Debye interference function and has been used in the analysis of liquids and some powder patterns. On the other hand if \( \mathbf{r} \) and \( \mathbf{s} \) make all possible angles with each other with equal probability, then

\[
\langle \exp (i2\pi \mathbf{s} \cdot \mathbf{r}) \rangle = \frac{1}{2\pi} \int_0^{2\pi} \exp(i2\pi sr \cos \alpha) \sin \alpha \, d\alpha
\]

and

\[
I(s) = \sum_m \sum_n f_m f_n J_0(2\pi sr),
\]

in which \( J_0 \) is the Bessel function of zero order. This case arises for samples of layered structures showing a very high degree of preferred orientation, for example when the layers are parallel to a plane as in some pyrolytic carbons or to an axis as in some special fibers (Ergun, 1970). When the sample is placed in such a manner that the diffraction vector \( \mathbf{s} \) lies in the plane of the layers, equation (2) becomes applicable. Fibers also show a cylindrical distribution of layers about the fiber axis. If the diffraction vector lies perpendicular to the fiber axis,

\[
\langle \exp (i2\pi \mathbf{s} \cdot \mathbf{r}) \rangle = \frac{1}{\pi} \int_0^\alpha \int_0^\beta \exp(i2\pi sr \sin \beta \cos \alpha) \, d\beta \, d\alpha
\]

and

\[
I(s) = \sum_m \sum_n f_m f_n J_0(\pi sr).
\]  

Similarly simple expressions are obtained when the diffraction vector makes any angle with the fiber axis (Ergun, 1970). It should also be noted that the interatomic distance sum technique yields the intensity at any given value of \( \mathbf{s} \), whereas the lattice sum technique yields the intensity as a function of \( \mathbf{s} \) and \( \mathbf{s}_z, s_0 \) being the value of \( \mathbf{s} \) that satisfies the Laue equation for the \( hkl \) reflections considered. In the latter case the spill-over from the other reflections must be added to obtain the intensity profiles.

For a structure containing \( N \) atoms (for example 280 in a graphite-like layer) there is a total of \( N^2 \) (\( \sim 80,000 \)) interatomic distances including \( m = n \) terms; many distances have the same magnitude and the number of different magnitudes is much less (\( \sim 132 \)) than \( N^2 \). Unless the distances having the same magnitude are grouped, the use of equations (1)–(3) becomes prohibitive for structures containing more than a few atoms. When grouped, for a structure containing one kind of atom equations (1)–(3) take the forms, respectively,

\[
i(s) = 1 + \sum_r n(r) \frac{\sin 2\pi sr}{2\pi sr}, \quad r \neq 0;
\]

\[
i(s) = 1 + \sum_r n(r) J_0(2\pi sr), \quad r \neq 0;
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\]

where \( i(s) = I(s)/Nf^2 \), the intensity in atomic units; \( n(r) = 1/N \sum_p \sum_q n_{pq} \) with \( |r_{pq}| = r \), i.e. the average number of neighboring atoms at a distance \( r \) to an atom. Diamond (1957) noted the advantages of the use of equation (4) and presented data for large aromatic molecules calculated by using \( n(r) \) obtained by counting \( n_{pq} \)'s. Thus, the main obstacle to the use of the interatomic distance sum technique has been the difficulty in counting the number of interatomic distances having equal magnitudes (Diamond, 1957; Warren & Bodenstein, 1966; Tiensuu, Ergun & Alexander, 1964). Diamond also gave a table showing the variation of \( n(r) \) with \( r \) based on counting the distances.

A solution to the problem is to develop an analytical expression for the number of identical distances as was done by Germer & White (1941) for the three-dimensional case. In a layer of infinite extent the different interatomic distances can be represented by a set; for example, for a graphite layer, if the bond distance is designated by \( r_0 \), the set of interatomic distances is given in set notation by

\[
\{r: r = (p^2 + q^2 + pq)^{1/2}r_0, \text{ where } p \text{ and } q \text{ are integers such that } p \geq 1 \text{ and } p \geq q \geq 0\}. \]

Fig. 1. Schematic illustration of the fractions of neighboring atoms at distances \( r \) from atoms A, B and C. The fractions are given by the arc that can be drawn inside the disc.
The average number \( n_0(\mathbf{r}) \) of atoms at a distance \( \mathbf{r} \) from any atom in a layer of infinite size can also be represented by a set. For example, for a graphite layer,

\[
\{n_0(\mathbf{r}) : \begin{array}{l}
n_0(\mathbf{r}) = 3 \text{ if } q = 0 \text{ and } p \equiv 3 \not\equiv 0 \\
6 \text{ if } q = p \text{ or } (q = 0 \text{ and } p \equiv 3 \not\equiv 0) \\
12 \text{ if } q \not= p \text{ and } (p-q) \equiv 0 \not\equiv 0,
\end{array}
\}
\tag{8}
\]

\( r \) being defined by equation (7).

In dealing with the layers having a finite size we must consider the conditions imposed upon the sets \( r \) and \( n_0(\mathbf{r}) \). We can readily impose an upper limit \( P \) to \( p \) and modify the conditions imposed on \( p \) and \( q \),

\[
1 \leq p \leq P \\
0 \leq q \leq \min \{p, (P^2 - \frac{1}{2}p^2)^{1/2} - \frac{1}{2}p\}.
\]

Modification of \( n_0(\mathbf{r}) \) can readily be accomplished for disc-shaped layers. We may define \( n(\mathbf{r}) = \varepsilon(\mathbf{r})n_0(\mathbf{r}) \), \( 0 \leq \varepsilon(\mathbf{r}) \leq 1 \). If we take an atom at a distance \( u \) from the center of the disc and consider the number of atoms at a distance \( r \) from it (see Fig. 1), \( \varepsilon(u, r) = 1 \) if \( u \geq R - r \), \( \varepsilon(u, r) = 0 \) if \( u \leq r - R \), and \( 0 < \varepsilon(u, r) < 1 \) otherwise. As seen in the Figure, \( \varepsilon(u, r) = \frac{\pi}{\pi} \) when \( 0 \leq \varepsilon(u, r) \leq 1 \). The average value of \( \varepsilon(\mathbf{r}) \) is obtained by carrying out the integral

\[
\varepsilon(\mathbf{r}) = \int_0^{2\pi} \int_0^R \varepsilon(u, r) 2\pi u \, du \, dr
\]

giving

\[
\varepsilon(\mathbf{r}) = \frac{2}{\pi} \left[ \cos^{-1} \left( \frac{r}{2R} \right) - \frac{r}{2R} \left( 1 - \frac{r^2}{4R^2} \right)^{1/2} \right], 0 \leq r \leq 2R.
\tag{9}
\]

Thus in equations (4)–(6) \( n(\mathbf{r}) \) may be replaced by

\[
n(\mathbf{r}) = n_0(\mathbf{r}) \varepsilon(\mathbf{r}).
\tag{10}
\]

For very small layers, equation (9) may yield values of \( \varepsilon(\mathbf{r}) \) such that \( n_0(\mathbf{r}) \varepsilon(\mathbf{r}) \) may differ from those obtained by actual counting. This is a trivial point, especially since the latter depends upon the choice of the center; however, if desired, it may be remedied by modifying \( \varepsilon(\mathbf{r}) \) so that \( Nn_0(\mathbf{r}) \varepsilon(\mathbf{r}) \) yields the nearest integer. Without resorting to such a correction, we have calculated \( \varepsilon(s) \) for the random case, i.e. equation (4), for \( R = 5 \) and \( 15 \) Å for a graphite-like layer, once using equations (9 and 10) and once using \( n(\mathbf{r}) \) values obtained by actual counts. The results for \( R = 5 \) Å are shown in Fig. 2. It is seen that the agreement is very good. As expected, the discrepancies are confined to small values of \( s \). In the case of \( R = 15 \) Å the two curves were identical.

In examining equation (9) we note that \( \varepsilon(\mathbf{r}) \) is equivalent to the overlap area of two discs of radius \( R \) separated by a distance \( r \) divided by the area of one of the discs (Warren & Bodenstein, 1965). Thus \( \pi R^2 \varepsilon(\mathbf{r}) \) is equal to the ghost area \( A(\mathbf{r}) \) defined by Wilson (1949) for a disc. Evidently the extension of Germer & White’s method to the two-dimensional case was overlooked even though an analytical expression for \( \varepsilon(\mathbf{r}) \) is readily derivable.

There is little or no difficulty involved in a set representation of \( r \) and \( n_0(\mathbf{r}) \) for a known lattice. In equation (10) \( \varepsilon(\mathbf{r}) \) may be designated to account for the effect on the intensity of the size and the shape of the layers as well as the size distribution. Equation (9) is for uniform disc-shaped layers. Other shapes may also be considered if the calculations are done by the procedure adapted in the derivation of equation (9) or by the method of Wilson (1949). However, even for the simplest non-circular shapes, e.g. triangles, parallelo-

![Fig. 2. Comparison of intensities computed using \( \varepsilon(\mathbf{r}) \) calculated by equation (4) (dots) and using \( \varepsilon(\mathbf{r}) \) obtained by actual counts (solid line).](image-url)
grams, etc., exceedingly cumbersome expressions are obtained that are difficult to use in profile analyses. For practical purposes it is necessary to choose a shape because the shapes of the layers are not known. In this regard Warren & Bodenstein (1966) consider a disc shape to be the most realistic shape. In case the observed and calculated intensity profiles differ significantly, it is more likely that the discrepancy is the result of a distribution of size rather than of a shape factor.

Evidently $\varepsilon(r)$ is also the transform of the size and shape in the lattice sum technique. We may demonstrate its use in the derivation of expressions for the profiles of the 000 reflections from disc shaped layers. The 000 reflections are important in the analysis of 00l reflections. Designating the atomic density of layers by $\phi(r)$, an atom would have $2\pi r \varepsilon(r) \phi(r) dr$ neighboring atoms at a distance between $r$ and $r+dr$. For the 000 reflections, $\phi(r)$ may be replaced by the average density and the summation in equation (4) may be replaced by an integral, viz.

$$i_{000}(s) = \int_0^{2R} \varepsilon(r) \frac{\sin 2\pi sr}{2\pi sr} 2\pi r dr. \quad (11)$$

Substituting (9) into (11) and integrating we obtain

$$i_{000}(s) = \frac{q}{2\pi s^2} \left[ 1 - \frac{J_1(4\pi s R)}{4\pi s R} \right]. \quad (12)$$

For large values of $s$, the term containing the Bessel function vanishes and the resulting expression assumes the form derived by Warren for the 000 reflections:

$$i_{000}(s) = \frac{q}{2\pi s^2}, \quad s \gg 0. \quad (13a)$$

The expression takes the form

$$i_{000}(s) = \pi R^2 q \left[ 1 - \frac{(2\pi s R)^2}{6} \right], \quad \text{for small } s. \quad (13b)$$

At $s=0$, the expression simply gives the number of atoms in the layer. The 002 reflections of carbons occur at values of $s$ for which equation (13a) yields results significantly different from those given by (11). Diamond (1956) had demonstrated the limitations of equation (13a) by comparing it with the results for the 000 reflections computed with the Debye equation. Equation (11) yields results identical to those obtained with the Debye equation.

For the case in which the reflection vector lies in the layers, $\sin 2\pi sr/2\pi sr$ is replaced by $J_0(2\pi s r)$ in equation (11). Upon integration, we obtain

$$i_{000}(s) = 4\pi R^2 q \frac{J_1^2(2\pi s R)}{(2\pi s R)^2}. \quad (14)$$

An equation identical to (14) was derived by Warren & Bodenstein (1966) in a different manner, not using $\varepsilon(r)$; however, its connection to the 000 reflections was not discussed. Equation (14) indicates that at large values of $s$, the 000 reflections become proportional to $1/s^3$; at $s=0$ it yields, as before, $\pi R^2 q$.

With an analytical expression available for $\varepsilon(r)$, the interatomic sum technique can be used advantageously for values of $R$ up to several hundred Ångstrom units. It is no longer necessary to resort to tabulated data.

References


