Analysis of Polymeric X-ray Diffraction Profiles. II. The Significance of the Fourth Moment–Range Function of the Diffraction Profile in the Analysis of First Order Reflexions*

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An expression has been developed for the fourth moment–range function of an X-ray diffraction profile in terms of the effects of finite crystal size and type II lattice distortions. A methodology has also been developed for its determination, which would be valuable in the analysis of the first order peaks from fibrous polymers. A computer program written in FORTRAN II for an IBM 1620 Computer, is described for this purpose.

Introduction

In the preceding paper (Kulshreshtha, Dweltz & Radhakrishnan, 1971, to be referred to as I), a general theory was developed for the analysis of X-ray diffraction profiles from fibrous polymers, which are ideal examples of anisotropic paracrystals. An analysis of variance–range functions of the profiles of multiple orders of 0k0 reflexions from a polynosic viscose, Tufcel, was also presented. It was concluded that it is not possible to separate the size and distortion effects from a study of the variance–range function of only one diffraction line, because both these effects contribute to the slope and the intercept, both of which basically contain equivalent information about fibre fine structure.

The theoretical significance of the fourth central moment as a measure of line broadening of X-ray diffraction profiles was first investigated by Mitra (1964), who obtained the expressions for the moment–range function* in terms of average crystallite size and type I distortions. The practical usefulness of this concept is clear from the work of Kagan & Snovidov (1965), who evaluated the fourth moment over the entire range of the profiles of the lines from low-temperature-tempered martensite. In the present paper, an expression has been developed for the moment–range function of the diffraction profile in terms of type II distortions. It is shown that the moment–range function, in conjunction with the variance–range function, can be used to obtain the average crystallite size $M_1$ and distortion parameter $g$ using only the profile of a first order reflexion. It is also shown that an analysis of the moment–range function yields additional information on the nature of lattice distortions to that given by the analysis of the variance–range function alone. Finally, a computer program is described for obtaining both these functions.

* This research was performed by A. K. Kulshreshtha as part of his research assignment leading to a Ph. D. degree of the Gujarat University.

* The fourth central moment of the diffraction profile evaluated as a function of range. Thus 'moment–range function' refers to the 4th central moment unless otherwise specified. This terminology will be used throughout this paper.
Theoretical

Let $\mu$ and $W$ represent the fourth central moment and variance respectively. If the line broadening is attributed to finite crystallite size and type II lattice distortions, the specimen line profile would then be a convolution of the line profiles which are obtained when each of these effects is separately considered. The additivity property of the cumulants gives the following relation for the fourth central moment of the pure diffraction profile (Cramer, 1962; Mitra, 1964).

$$\mu_{PD} = \mu_P + \mu_D + 6W_PW_D$$

where the suffixes $P$, $D$ indicate the components for crystallite size and type II distortions respectively.

The normalized line profile due to type II distortions is given in our previous paper [I, equation (12)], as:

$$I_D(s) = \frac{2\sigma}{\alpha^2 + 4\pi^2 s^2}, \quad \alpha = \frac{2\sigma^2 g^2 k^2}{b}$$

where $g$ denotes the coefficient of variation of the spacing between $(0k0)$ planes, and $b$ is the average spacing. We obtain

$$\int_{-\sigma_1}^{\sigma_2} I_D(s)ds = \frac{1}{\pi} \left[ \tan^{-1} \left( \frac{2\pi\sigma_1}{\alpha} \right) + \tan^{-1} \left( \frac{2\pi\sigma_2}{\alpha} \right) \right]$$

$$\approx 1, \text{ for large } \sigma_1 \text{ and } \sigma_2.$$

The line profile $I_D(s)$ is truncated over the range $-\sigma_1$ to $+\sigma_2$ in $s$ units. Now

$$\int_{-\sigma_1}^{\sigma_2} s^2 I_D(s)ds = \frac{\alpha(\sigma_1 + \sigma_2)}{2\pi^2} - \frac{\alpha^2}{4\pi^2} \int_{-\sigma_1}^{\sigma_2} I_D(s)ds$$

$$\approx \frac{\alpha(\sigma_1 + \sigma_2)}{2\pi^2} - \frac{\alpha^2}{4\pi^2}, \text{ for large } \sigma_1 \text{ and } \sigma_2.$$

Similarly,

$$\int_{-\sigma_1}^{\sigma_2} s^4 I_D(s)ds = \frac{\alpha(\sigma_1^3 + \sigma_2^3)}{6\pi^2} - \frac{\alpha^2}{4\pi^2} \int_{-\sigma_1}^{\sigma_2} s^2 I_D(s)ds$$

$$\approx \frac{\alpha(\sigma_1^3 + \sigma_2^3)}{6\pi^2} - \frac{\alpha^2(\sigma_1 + \sigma_2)}{8\pi^4} + 16\pi^4$$

for large $\sigma_1$ and $\sigma_2$.

Since $I_D(s)$ is symmetrical about the peak, for large $(\sigma_1 + \sigma_2)$ the second and fourth central moments of $I_D(s)$ are given by

$$W_D = \frac{\int_{-\sigma_1}^{\sigma_2} s^2 I_D(s)ds}{\int_{-\sigma_1}^{\sigma_1} I_D(s)ds} \approx \frac{\alpha(\sigma_1 + \sigma_2)}{2\pi^2} - \frac{\alpha^2}{4\pi^2}$$

(3)

and

$$\mu_D = \frac{\int_{-\sigma_1}^{\sigma_2} s^4 I_D(s)ds}{\int_{-\sigma_1}^{\sigma_1} I_D(s)ds} \approx \frac{\alpha(\sigma_1^3 + \sigma_2^3)}{6\pi^2} - \frac{\alpha^2}{4\pi^2} W_D$$

(4a)

Equation (4a) indicates that for a Cauchy profile, the moment–range function partly depends on the variance–range function. The corresponding quantities for crystallite size broadening are given by (Wilson, 1962; Mitra, 1964):

$$W_P = -\frac{1}{4\pi^2} \left[ \frac{2(\sigma_1 + \sigma_2)}{V'(0)} + \frac{\sigma_1 + \sigma_2}{V''(0)} \right]$$

and

$$\mu_P = -\frac{(\sigma_1^3 + \sigma_2^3)}{6\pi^2} \frac{V'(0)}{V(0)} + \frac{(\sigma_1 + \sigma_2)}{8\pi^4} \frac{V''(0)}{V(0)} + \frac{1}{16\pi^4} \frac{V''''(0)}{V(0)}.$$

It will be shown in a future paper that the autocorrelation function for particle size broadening, $V(t)/V(0)$, has an exponential form under the most general assumptions about the dispersion of crystallites in a polymer matrix. Therefore, from equation (6) of our previous paper (I)

$$V(t) = \exp\{-\beta |t|\}; \quad \beta = \frac{1}{M}$$

and we obtain

$$W_P = \frac{\beta(\sigma_1 + \sigma_2)}{2\pi^2} - \frac{\beta^2}{4\pi^2}$$

(6)

and

$$\mu_P = \frac{\beta(\sigma_1^3 + \sigma_2^3)}{6\pi^2} - \frac{\beta^3(\sigma_1 + \sigma_2)}{8\pi^4} + \frac{\beta^4}{16\pi^4}.$$

(7)

Combining equations (1), (3), (4b), (6) and (7), and substituting $\sigma_1 \simeq \sigma_2 = \sigma/2$, we obtain:

$$\mu_{PD} = \frac{(\alpha + \beta)\sigma^3}{24\pi^2} + \frac{3\alpha\beta}{2\pi^4} \sigma^2 - \frac{(\alpha^3 + 6\alpha^2\beta + 6\alpha\beta^2)}{8\pi^4} \sigma$$

$$+ \frac{(\alpha^4 + 6\alpha^3\beta + 6\alpha^2\beta^2)}{16\pi^6}.$$

(8)

It is easily seen from this expression that only the terms containing $\sigma^2$ and $\sigma^3$ will have appreciable magnitude, and the rest will be vanishingly small. Recently, Wilson (1969) has shown that the more accurate expression for variance contains a term proportional to $1/\sigma$ in addition to those contained in equations (3) and (6), and this is especially true for Cauchy profiles (Edwards & Toman, 1970). If we include this result in our calculations, it is easily seen that the moment–range function is represented by means of the polynomial:

$$\mu_{PD}(\sigma) = \sum_{n=-2}^{\eta-1} a_n \sigma^n$$

(9)

* Our notation in this regard is slightly different from that generally accepted, namely $\sigma_1 \simeq \sigma_2 \approx \sigma$; where the range is $\pm \sigma$ rather than $\pm \sigma/2$ in our notation.
Thus, two solutions are obtained for $g$ and $\bar{M}_i$. By physical reasoning it should be possible to reject one of these.

Therefore, by obtaining the variance– and moment–range functions for a single diffraction line, one can calculate the values of $\bar{M}_i$ and $g$. For type I distortions, the moment–range function does not have a term varying as $\sigma^2$ because the variance is independent of range. Therefore, by fitting the polynomial (9) in the observed moment–range function (corrected for instrumental aberrations), one can ascertain the nature of distortions present in the specimen.

**Methodology**

X-ray measurements for obtaining 0k0 diffraction line profiles from Tufcel and the corresponding instrument profiles have been described in our previous paper (1). The present method has been used to analyse the 020 diffraction profile, which is free from any contamination from neighbouring reflexions. It is an extension of the methods of Pike & Wilson (1959) for calculating the centroid and that of Langford & Wilson (1963) for determining the variance–range function.

After obtaining a record of intensity $I(x)$ versus $x$, where $x$ is in ($^\circ$2B) or in 2 sin $\theta$/2 units, one proceeds with the determination of the variance–range and moment–range functions as follows:

(i) The assumed background, $I_b(x)$, is subtracted from $I(x)$ and the line profile is obtained.

(ii) A starting point $x_a < x_p$, the peak, is chosen on the profile.

(iii) An upper limit $x'_g$ is chosen symmetrically about the peak, i.e., $x_p - x'_g = x_g - x_a$. The centroid of the profile truncated between the limits $x_a$ and $x'_g$ is calculated, say $x'_c$.

(iv) The mid-point of the range ($x'_a + x'_g$)/2 is compared with $x'_c$, and the difference $[(x'_a + x'_g)/2 - x'_c]$ is called the asymmetry of $x'_g$.

(v) The range $x_a$ to $x'_g$ is changed to a new range $x_a$ to $x'_g''$ by subtraction of twice the asymmetry of $x'_g$ from $x'_g$, i.e., $x'_g'' = x'_g - 2((x'_a + x'_g)/2 - x'_c)$. $x'_c$ is at the mid point of the new range.

(vi) The steps (iii)–(iv) are repeated with new upper limits $x'_g'$, $x'_g''$, $x'_g'''$, ..., until the asymmetry is $\leq \beta/20$, where $\beta$ is the integral breadth of the line profile. Let $x_g$ be the upper limit satisfying the condition

$$[(x_a + x_g)/2 - x_g] \leq \frac{\beta}{4}$$

where $x_g$ is the centroid corresponding to the final range ($x_g - x_a$).

(vii) The starting point $x_a$ is changed in discrete steps to values $x_{a1}$, $x_{a2}$, $x_{a3}$, ..., and for each starting point the corresponding final upper limits $x_{g1}$, $x_{g2}$, $x_{g3}$, ... are found by the procedure outlined.
in steps (iii)-(vi). For each range \((x_{gn} - x_{an})\), the values of integrated intensity, centroid, variance, and third and fourth central moments are calculated.

(viii) The procedure (i)-(vii) is repeated after subtracting different backgrounds until the variance-range curve obtained in step (vii) shows a significant linear portion. Thus, the 'true' background, \(I_B(x)\), is known and can be eliminated.

(ix) The line profile \([I(x) - I_B(x)]\) is corrected for Lorentz-polarization and absorption effects to give the corrected profile \(g(x)\) \([I\), equation (20)].

(x) Steps (ii)-(vii) are repeated to obtain the variance- and moment-range functions of the corrected line profile \(g(x)\).

Let \(W_b, W_t\) denote the variance-range functions and \(\mu_b, \mu_t\) represent the moment-range functions respectively for the observed fibre and instrument profiles.

For the 020 profile from Tufcel, these plots are shown in Fig. 1(A) and (B), which also illustrates the choice of range for the calculation of the moment-range function, \(\mu_{PD}\), of the specimen profile. The common range (confined between vertical dashed lines in Fig. 1) in which both \(W_b\) and \(W_t\) are linear, is used for calculating \(\mu_{PD}\) from the formula

\[
\mu_{PD}(\sigma') = (\mu_b - \mu_i) + 6W_t(W_b - W_t). \tag{12}
\]

Let

\[
\mu_{PD}(\sigma') = \sum_{n=3}^{N} \frac{\sigma^n}{\sigma^3} \tag{13}
\]

where \(\mu_{PD}\) and \(\sigma'\) have dimensions \((°20)^4\) and \((°20)^2\) respectively. Then, equation (13) can be converted into equation (9) by means of the transformation

\[
\mu_{PD} = K^4\mu_{PD}, \quad \sigma = K\sigma', \quad a_n = K^{a_n}a_n' \tag{14}
\]

where

\[
K = \left( \frac{\pi}{180} \times \cos \theta_0 \right), \lambda
\]

\(\theta_0\) being the centroid of the line profile and \(\lambda\) the wavelength of X-rays.

A program written in FORTRAN to perform the calculations outlined in steps (ii)-(vii) on an IBM 1620 computer is given in the Appendix. In addition to the intensity values \(I(x)\) or \(g(x)\) taken at intervals \(dx\), it requires the following data as input:

\[
N = \text{the total number of intensity values given in proper angular order} \quad (I_1, I_2, \ldots, I_N).
\]

\[
DX = dx, \quad \text{the steps at which the intensities are observed.}
\]

\[
X(1) = \text{the initial value of } x \text{ corresponding to } I_1.
\]

\[
KDX = \text{increment interval in half-range.}
\]

\[
M = \text{the total number of increments required in half-range.}
\]

\[
I_{\text{FMAX}} = P = \text{the suffix corresponding to the maximum value of intensity, } I_P, \text{ where } 1 < P < N.
\]

Typical input and output data tables are also given in the Appendix. In the output, the quantities mentioned in (vii) are printed as a function of the total range.

Results and discussion

The moment-range function of the intrinsic 020 profile \(\mu'_{PD}\) is shown in Fig. 1(C). The polynomial (13) was fitted to this curve by the method of least-squares and it was found that \(\mu_{PD}\) could be expressed as:

\[
\mu_{PD} = 0.00259\sigma'^2 + \frac{0.00185}{\sigma'} - \frac{0.00406}{\sigma'^2} - 0.00006.
\]

This gives \(a'_3 = 0\), and \(a'_2 = 0.00259\) \((°20)^2\) or \(a'_2 = 0.324 \times 10^{-6} \text{ Å}^{-2}\) using (14). From equation (10) we calculate

\[
a_{14} = \frac{2\pi^4}{3} a_2 = 0.211 \times 10^{-4} \text{ Å}^{-2}.
\]

For calculating the value of \((x + \beta)\), the slope of the variance-range function should be used. From (I), Table 3, we find for the 020 profile:

\[
k_{08} = \frac{(x + \beta)}{2\pi^2} = 0.603 \times 10^{-3} \text{ Å}^{-1}
\]

or

\[
(x + \beta) = 0.0119 \text{ Å}^{-1}.
\]

From these values of \(a_{14}\) and \((x + \beta)\), the following two solutions are obtained for \(g\) and \(\bar{M}_1\) [cf. equation (11)]:

\[
\bar{M}_1(\text{Å}) \quad g(\%)
\]

Solution I 461 3.56
Solution II 103 1.68

According to Bonart (1963), the number of orders of reflexions separable along the reciprocal axis is given by \(0.24/g(\%)).\)

Solution I can be rejected on this ground, since \(080\) is observable. Thus, solution II is the correct one, and within experimental error agrees with the values obtained by the multiple-order method of analysis (1, Tables 2 and 4).

For moderately large ranges used for calculating \(\mu_{PD}\), it is assumed that equation (I) is approximately valid. The fact that the coefficient of the \(\sigma^2\)-dependent term is appreciable lends support to the 'paracrystalline' theory of lattice distortions. The absence of the \(\sigma^3\)-dependent term may be attributed to slight errors in the choice of background and in the method of deconvolution.

APPENDIX

The term FX used in the program may correspond either to \(I(x)\) or \(g(x)\) described in the text. The program is reproduced below:
**DETERMINATION OF VARIANCE- AND MOMENT- RANGE FUNCTIONS**

1. Reading input data and initializing variables:

```plaintext
DIMENSION X(400), FX(400), XFX(400)

READ 1,N,M,K,IFMAX, X(1), DX
FORMAT(15,F10.0)

READ 2,FX(1), J#I,N
FORMAT(8F10.0)
```

2. Calculating range functions:

```plaintext
DO25 J#I,N
  XFX#J = X#J * FX#J
  X2FX#J = X#J * XFX#J
  X3FX#J = X#J * X2FX#J
  X4FX#J = X#J * X3FX#J
  X#J&Iu = X#J & DX
  ID#1FMAX
  IDP#IFMAX
  PUNCH6,N,M,K,ID,X#ID, FX#ID, DX
END
```

3. Calculating range and moment functions:

```plaintext
DO35 J#I,M
  ID#ID-K
  IDP#IDP&K
  RM2NE#X2FX#JEPlm & XCS*FXC*.5
  RM3NE#X3FX#JEPlm & XCC*FXC*.5
  RM4NE#X4FX#JEPlm & XFC*FXC*.5
  RM2NM#X2FX#JSMI & X2FX#JEPlm*.5
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  RM4NM#X4FX#JSMI & X4FX#JEPlm*.5
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  RM3NM#X3FX#JSM&X3FX#JEPlm*.5
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  PUNCH7,I,RANGE,CGD, CG, CM2, CM3, CM4
END
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4. Calculating output range data:

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5. Using type 8 format: 35

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PUNCH7,I,RANGE,CG, CG, CM2, CM3, CM4
```

6. Ending the program:

```plaintext
END
```
The authors wish to thank the Director of ATIRA for his permission to publish this paper. They also appreciate the kindly interest of Mr. T. Narasimham in this work and are grateful to Professor A. J. C. Wilson for sending in advance a prepublication typescript of Edwards & Toman's (1970) paper on the additivity of variances. They would also like to take this opportunity to thank Dr. T. Radhakrishnan for the many valuable suggestions he has made and for his abiding interest in this work. Finally, the financial assistance by the C.S.I.R. (India) to one of us (AKK) is gratefully acknowledged.

References


The Double-Crystal X-ray Spectrometer: Corrections, Errors, and Alignment Procedure*

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The theory of the X-ray double-crystal spectrometer is outlined. For a vertical rotation axis, crystal planes should be vertical and the X-ray beam horizontal. Geometrical errors are introduced by crystal tilts (departure from vertical) and misalignment (departure of central ray from horizontal). Even with perfect alignment a vertical divergence correction is required. A typographical error in Schwarzschild’s analysis of these geometrical effects led to erroneous results by Schnopper, later corrected in an erratum. The physical significance of this revision is considered here. The resulting expression for relative wavelength error indicates that, for zero tilt, misalignment produces no significant errors in relative wavelengths. Geometrical errors are shown to be negligible in recent measurements of Bearden and very small in earlier work of Bearden & Shaw. The Williams vertical divergence correction, used by Bearden, is proven valid; the Parratt form, preferred by Schnopper, is incorrect. An alignment procedure which can reduce geometrical errors below 1 part per million is described. It employs a precision engineer’s level (with autocollimating telescope) and a simple technique for grinding crystal faces parallel to atomic planes.

1. Introduction

The double-crystal X-ray spectrometer has been extensively used for high precision wavelength determinations and for other measurements requiring high resolving power \([\Delta \lambda/\lambda > 10^4]\). If equipped with almost perfect crystals, it can accept a broad X-ray beam, limited only by the width of these crystals. In problems with low intensities the signal-to-noise ratio is substantially improved (since the successive scattering from two crystals greatly reduces the incoherent radiation, which comprises most of the noise). Of course, the absolute diffracted intensity is also reduced in this process.

Allison (1931) has shown that the resolving power of the double-crystal spectrometer in the \((n, +n)\) position is superior to that of the single-crystal instrument used in the \(n\)th order. Depending on the exact form of the crystal window function, the improvement may run as high as 75%. Admittedly this comparison does not exhaust all cases of practical interest. For example, in the \((1, +n)\) double-crystal position the instrumental window is essentially determined by that of the first crystal; in the \(n\)th order single-crystal case the window is primarily fixed by the geometrical slit system. Hence in such a comparison the single-crystal instrument may often be superior, especially for longer wavelengths with a narrow-line focus X-ray tube; this point was discussed by Bearden, Henins, Marzolf, Sauder & Thomsen (1964) in describing precision wavelength determinations.