The Fourier Coefficients of Paracrystalline X-ray Diffraction*

By A. K. Kulshreshtha and N. E. Dweltz

up for Physics, Ahmedabad Textile Industry's Research Association (ATIRA), Ahmedabad-15, Gujarat, India

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Theoretical expressions are presented for the Fourier coefficients, derived in terms of a linear 'ideal paracrystal' lattice defined by Hosemann. These coefficients are related to the 'coordination statistic' or the probability density $h(t)$, $t = m\mathbf{b}$ denoting identically distributed according to the 'coordination statistic' or the probability density $h(t)$, $t = m\mathbf{b}$ denoting...
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a distance along the b axis. The higher partial statistic $h_a(t)$ is given by the multiple convolution of $h(t)$

$$h_a(t) = h(t)$$

and governs the distribution of the distance $S_m = X_1 + X_2 + \ldots + X_m$

between the origin and the mth lattice point. The expression on the right hand side of equation (1) means the self-convolution of $h(t)$, $|m| - $ times. Let $S_m$ denote the displacement of the mth lattice point from its ideal site, relative to the origin. Then

$$S_m = S_m - \langle S_m \rangle$$

where $b = \langle X_i \rangle$, is the average spacing between adjacent lattice points and the brackets denote the mathematical expectations of the term they enclose. Variance of $S_m$ is given by

$$D_m = \langle S_m^2 \rangle = |m|^2 \cdot$$

The coefficient of variation of the lattice spacing is

$$g = \frac{A}{b}$$

The Q-function, i.e. the distance-statistics function is given by

$$z(t) = \sum_{m = -\infty}^{\infty} h_a(t)$$

The Fourier transformation of $z(t)$ gives the expression for the interference function, i.e. the 'paracrystalline lattice factor' $Z(S)$, where $S = 2\sin \theta / \lambda$ is the distance of

$$Z(S) = \sum_{m = -\infty}^{\infty} F.T. \{h_a(t)\}$$

where

$$F.T. \{z(t)\} = \lim_{\infty} \int_{-\infty}^{\infty} z(t) \exp (-2\pi iSt) \, dt$$

denotes the Fourier transform of $z(t)$. The Fourier series representation of $Z(S)$ can be easily understood with the help of equation (6), which gives

$$Z(S) = \sum_{m = -\infty}^{\infty} [Y(k, m) \exp (-2\pi i m b S)]$$

where the distortion Fourier coefficients are

$$Y(k, m) = \sum_{m = -\infty}^{\infty} [H_m(S) - H_m^*(S)]$$

The asterisk (*) denotes the complex conjugate and the order of reflection. The meaning of $H_m(S)$ will be discussed in the Appendix. The line profile due to Type II distortions can thus be expressed as

$$Z(S) = \sum_{m = -\infty}^{\infty} [J(m) \cos 2\pi m b S - K(m) \sin 2\pi m b S]$$

where $s = (S-S_0)$ is the actual distance by which the node $S_0$ of the reciprocal lattice. The Gaussian approximation for $h_a(t+mb)$ will be valid if the displacements $S_m$ are small and for large $|m|$ by the virtue of the central limit theorem. In this case the imaginary coefficients $K(m)$ will be vanishingly small and the real coefficients (Kulshreshta, Dweltz & Radhakrishnan, 1971) will be

$$J(m) = \exp (-2\pi^2 \alpha^2 S_0^2 |m|)$$

or

$$J(t) = \exp (-\alpha^2 t^2) \left[ \frac{2\pi \alpha^2 S_0^2 \delta}{b} \right]$$

(The Appendix describes an alternative method of deriving the expressions for the distortion line profile and its Fourier coefficients).

The observed profile, obtained after correction for instrumental factors by the method of Stokes (1942), is a convolution of the size-broadened profile and distortion-broadened profile. The Stokes correction real (cos) and imaginary (sin) coefficients are therefore given by

$$F_r(t) = \frac{\langle V(t) \cos \theta \rangle}{\langle V(t) \rangle}$$

$$F_i(t) = \frac{\langle V(t) \sin \theta \rangle}{\langle V(t) \rangle}$$

Fig. 1. $-\ln F(m)$ vs $m$ plots for 110 and 220 reflexions of annealed 'Marlex 50' polyethylene filaments measured at -196 and 20°C.
THE FOURIER COEFFICIENTS OF PARACRYSTALLINE X-RAY DIFFRACTION

\[ F_r(t) = \frac{V(t)}{V(0)} \exp \left( -2\pi^2 S^2 \langle S_m^2 \rangle \right) \]

where \( V(t) \) is the volume common to the crystal and ghost obtained through a translation \( t = mb \) along a normal to the reflecting \((0k0)\) planes (Wilson, 1962).

For small degrees of distortion

\[ F_r(t) \approx \frac{V(t)}{V(0)} \exp \left( -2\pi^2 S^2 \langle S_m^2 \rangle \right) \]

\[ \ln F_r(t) = \ln \left[ \frac{V(t)}{V(0)} \right] - 2\pi^2 S^2 \langle S_m^2 \rangle \]  

(10)

Thus, if two orders of reflexion are available, equation (10) can be used to separate the size and distortion effects (Warren & Averbach, 1952). The resulting values \( \langle S_m^2 \rangle \) can be interpreted according to equation (13) for Type II distortions and \( F_r(t)/F(0) \) according to standard procedures (Bertaut, 1949; Smith & Simpson, 1955). However, if more than two orders are available, a separation of size and distortion effects is better achieved by Harrison’s (1967) method, which yields \( F(0)/F(0) \) and various even and odd moments of \( S_m \) which, in turn, can be utilized to synthesize the partial statistic \( h_m(t+mb) \).

The size coefficients can be approximated as

\[ \frac{V(t)}{V(0)} \approx \exp \left( -\beta t \right) \]

where

\[ \beta = \frac{1}{M_1} = \frac{1}{M} \langle g(M) \rangle \]  

(11)

and \( g(M) \) denotes the frequency function of crystallite lengths \( M \). Expression (11) is a good approximation of the case of fibrous polymers and can be derived in terms of various stochastic models for the placement of crystallites along the length of a fibre. Thus, from equations (8), (9a) and (11):

\[ F_r(t) \approx \exp \left( -\left(\alpha + \beta \right) t \right) \]

\[ \ln F_r(t) \approx \left[ \frac{2\pi^2 g^2 k^2}{\theta} + \frac{1}{M_1} \right] t \]  

(12)

The utility of this equation will be illustrated with the help of a suitable example. The methodology for computing the Fourier coefficients and thereby obtaining the co-ordination statistic and size distribution of paracrystallites will be discussed elsewhere.

Equilibrium paracrystallite size

Ehrlich (1966) defines the interaction radius \( t_M \) of a paracrystalline lattice as the region of order in \( z(t) \), outside which \( z(t) \) assumes a constant value, and obtains the following relation

\[ t_M = \frac{\sqrt{d_{HH}}}{(2\pi g)^2} \]

or

\[ \sqrt{t_M} \sqrt{d_{HH}} \approx 0.4 \]  

(13)

This relation shows that the average size of the coherently diffracting domains is inversely proportional to the degree of disorder \( g \), \( d_{HH} \) denoting the average spacing between the reflecting planes. In practice, however, one obtains the crystallite size values which are much smaller than predicted by equation (13). Hosemann, Loboda-Cackovic & Wilke (1968) define a dimensionless parameter \( \alpha' \) as

\[ \alpha' = \sqrt{L/d_{HH}} \]  

(14)

where \( L \) is the ‘weight-average’ size of the paracrystallites along the normal to the reflecting planes and is a measure of the micro-heterogeneity of the substance under examination. The use of this parameter is, however, open to criticism since it is obtained through interatomic breadth analyses which involve arbitrary assumptions regarding profile shapes. The moment and Fourier transform methods are theoretically sound and very suitable for studying the imperfections in paracrystalline substances and yield the number-average crystallite size \( M_1 \) (Guinier, 1963). We therefore define an analogous parameter \( \alpha'' \) as

\[ \alpha'' = \sqrt{M_1/d_{HH}} \]  

(15)

The relation between \( \alpha' \) and \( \alpha'' \) is obviously dependent upon the size distribution of paracrystallites. In general \( \alpha'' < \alpha' \), and for a Cauchy-like size profile, \( \alpha' = \sqrt{2\alpha''} \).

A reinterpretation of earlier results on the Fourier analysis of polyethylene and petroleum cokes

The first study on the Fourier analysis of polymeric X-ray diffraction profiles was carried out by Katayama (1961), who investigated the line broadening in annealed ‘Marlex 50’ polyethylene filaments at two different temperatures (−196°C and 20°C). He observed that the distortion line profiles had an approximately Cauchy form, but his interpretation of the Fourier coefficients was incorrect, being based on the stress-strain model of disorder. As a result of this erroneous interpretation, he obtained an infinite crystallite size in polyethylene and his estimate of strain was at least an order of magnitude higher than those found in cold-worked metals. Obviously, such a large crystallite size cannot be envisaged in fibres. Later Hosemann, Balta-Calleja & Wilke (1966) could prove by means of integral breadth analysis that lattice distortions in various linear and branched polyethylenes were ‘paracrystalline’ in character and obtained paracrystallite
Table 1. Condensed results of X-ray diffraction line-profile analysis on paracrystalline aggregates

<table>
<thead>
<tr>
<th>Reference</th>
<th>Substance</th>
<th>Sample specifications</th>
<th>Lattice planes</th>
<th>$d_{max}$</th>
<th>$L$</th>
<th>$M_1$</th>
<th>$g$</th>
<th>$\alpha$'</th>
<th>$\alpha$''</th>
</tr>
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<tr>
<td>Present work, data of Popovic (1969)</td>
<td>Petroleum coke powder</td>
<td>Heat-treated at</td>
<td>1190°C</td>
<td>002</td>
<td>3.47 Å</td>
<td>32 Å</td>
<td>4.12%</td>
<td>0.13</td>
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<td></td>
<td></td>
<td></td>
<td>1810</td>
<td>002</td>
<td>3.43</td>
<td>85</td>
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<td></td>
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<td>200</td>
<td>1.83</td>
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<td>2220</td>
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<td></td>
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<td></td>
<td>2550</td>
<td>002</td>
<td>3.37</td>
<td>435</td>
<td>1.14</td>
<td>0.13</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2850</td>
<td>002</td>
<td>3.36</td>
<td>565</td>
<td>1.02</td>
<td>0.13</td>
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<td>Present work, data of Katayama (1961)</td>
<td>Linear polyethylene</td>
<td>Marlex-50, studied at</td>
<td>-196°C</td>
<td>110</td>
<td>4.10</td>
<td>205</td>
<td>2.80</td>
<td>0.22</td>
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<tr>
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<td></td>
<td>20</td>
<td>110</td>
<td>4.10</td>
<td>295</td>
<td>2.60</td>
<td>0.20</td>
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<td>Hot-stretched 60:1</td>
<td>Component I</td>
<td>110</td>
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<td>91 Å</td>
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<td></td>
<td></td>
<td>Component II</td>
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<td>186</td>
<td>2.20</td>
<td>0.15</td>
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<td>Hostalen G</td>
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<td></td>
<td>Lupolen 6001 H</td>
<td>110</td>
<td>4.10</td>
<td>332</td>
<td>2.14</td>
<td>0.19</td>
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<td>Crystallized at 85°C, 24 hr</td>
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<td>Buchanan &amp; Miller (1966)</td>
<td>Isotactic polystyrene</td>
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<td>110</td>
<td>10.95</td>
<td>131</td>
<td>4.95</td>
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<td>110</td>
<td>10.95</td>
<td>162</td>
<td>2.80</td>
<td>0.11</td>
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<td>Kulshreshtha, Patil, Dweltz &amp; Radhakrishnan (1969)</td>
<td>Ramie</td>
<td>Bleached</td>
<td>020</td>
<td>5.15</td>
<td>460</td>
<td>0.80</td>
<td>0.08</td>
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<td>Kulshreshtha, Dweltz &amp; Radhakrishnan (1971a)</td>
<td>Polynosic viscose</td>
<td>Tufcel</td>
<td>020</td>
<td>5.15</td>
<td>125</td>
<td>1.66</td>
<td>0.08</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>020</td>
<td>5.15</td>
<td>90</td>
<td>1.37</td>
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<td></td>
<td>MnsFe2O4 spinels</td>
<td>$x = 1.88$</td>
<td>$h00$</td>
<td>3.01</td>
<td>1540</td>
<td>0.85</td>
<td>0.19</td>
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<td></td>
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<td></td>
<td>$\alpha\beta\gamma$</td>
<td>1.24</td>
<td>250</td>
<td>1.20</td>
<td>0.17</td>
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<tr>
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<td>$a\beta\gamma$</td>
<td>1.43</td>
<td>200</td>
<td>1.64</td>
<td>0.19</td>
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<tr>
<td>Hosemann, Loboda-Cackovic &amp; Wilke (1968)</td>
<td>$\alpha$-Fe + 3% Al2O3</td>
<td>Annealed at 400°C, 15 hr</td>
<td>$h00$</td>
<td>2.03</td>
<td>250</td>
<td>1.02</td>
<td>0.11</td>
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<td></td>
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<td>$\alpha\beta\gamma$</td>
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<td>$\alpha\beta\gamma$</td>
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<td>435</td>
<td>1.10</td>
<td>0.19</td>
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<td></td>
<td></td>
<td>$a\beta\gamma$</td>
<td>2.03</td>
<td>540</td>
<td>0.63</td>
<td>0.10</td>
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<td>Hosemann &amp; Lemm (1965)</td>
<td>Lead</td>
<td>223°C above melting point.</td>
<td>10</td>
<td>12.5</td>
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values in the range 200–500 Å with g-values of 2.8 and 2.6 \% respectively for the samples studied at −196 °C and 20 °C.

Popovic (1969) investigated powdered samples of petroleum coke, heat-treated at various temperatures, carrying out a Fourier analysis of the 00\ell\ell\ell\ell refractions. He plotted the values of \( \langle S^2 \rangle^{1/2} \) vs. t, \( \langle L \rangle^{1/2} \) vs. L in his notation for various samples obtained from the Fourier analysis [cf. equation (10)]. This way, he obtained curves which were far from linear. Fig. 2 illustrates \( \langle S^2 \rangle^{1/2} \) vs. t plots for various samples obtained after replotting the values taken from the original curves of Popovic (1969). These plots are all straight lines passing through the origin, as to be expected from the equation (3) for an 'ideal paracrystal'. g-values for various heat-treated samples can be obtained by making use of the slopes of these curves and the \( d_{002} \) values listed by Popovic (1969) for these samples. The values of \( L_e \), also listed by him, (L_e in his notation), would be complementary to the g-values in understanding the fine structure of these samples.

A summary of results of line-profile analyses on paracrystalline aggregates

Table 1 also lists the values of \( \alpha' \) and \( \alpha'' \) for various substances. It can be seen that for most of the substances, \( \alpha' \) or \( \alpha'' \) values are centred around 0.16, whereas for fibres of cellulosic origin they tend to lie around 0.08. A summary of these results is presented in Fig. 3, which shows a plot of the g-value against \( (d_{002}/M)_{1/2} \) or \( (d_{002}/L)_{1/2} \). A correlation coefficient of the order of 0.85 is obtained. The scatter of points, which becomes large as paracrystallite size decreases, may be due to (i) the substances belonging to different classes, (ii) the substances being investigated by different groups of workers and (iii) an inverse inter-relation between the errors in the two parameters.

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indebted to Dr T. Radhakrishnan for his valuable suggestions and guidance. The grant of a research fellowship to one of us (A.K.K.) by the C.S.I.R. (India) is also appreciated.

APPENDIX

The distance statistics function is

\[ z(t) = \delta(t-0) + \sum_{m=1}^{\infty} [h_m(t) + h_{-m}(t)]. \]

The lattice factor is

\[ Z(S) = F(T) \cdot [z(t)] \]

\[ = 1 + \sum_{m=1}^{\infty} F(T) \cdot [h_m(t)] + \sum_{m=1}^{\infty} F(T) \cdot [h_{-m}(-t)]. \]

The Fourier transforms of \( h_m(t) \) are called ‘statistic amplitudes’. Thus

\[ F_m(S) = F(T) \cdot [h_m(t)] = H_m(S) \exp \left( -2 \pi \text{m} S \right) \]

\[ = |F(S)|^m \]  \[ (16) \]

\[ F_{-m}(S) = F(T) \cdot [h_{-m}(t)] = H^*_m(S) \exp \left( 2 \pi \text{m} S \right) \]

\[ = |F(S)|^m \]

where

\[ H_m(S) = F(T) \cdot [h_m(t + mb)] \]

\[ H^*_m(S) = F(T) \cdot [h_m(t - t - mb)] \]

and * denotes the complex conjugate. We have

\[ Z(S) = \sum_{m=0}^{\infty} \left[ F^m(S) + F^*^m(S) \right] - 1 \]

\[ = \frac{1 - |F|^2}{1 + |F|^2 - 2 |F| \cos 2 \pi b S}, \quad S \neq 0. \]  \[ (17) \]

For a Gaussian coordination statistic, \( |F| \) is given by

\[ \exp \left( -2 \pi^2 g^2 k^2 \right) \]

\[ Z'(S) = \frac{\sinh(2 \pi^2 g^2 k^2)}{\cosh(2 \pi^2 g^2 k^2) - \cos 2 \pi b S}. \]  \[ (18) \]

The line-profile is obtained by replacing \( S \) by \( (S - S_0) \) and becomes, for small \( g \)-values

\[ Z'(S) \approx \frac{1}{b} \cdot \frac{2 \alpha}{(\alpha^2 + 4 \pi^2 b^2)} \; ; \; \alpha = \frac{2 \pi^2 g^2 k^2}{b}. \]  \[ (19) \]

The real distortion Fourier coefficients are

\[ J(t) = \left\{ Z'(S) \exp \left( 2 \pi \text{i} S t \right) \right\} ds \]

\[ = \exp \left( - \beta t \right) \]

since

\[ Z'(S) = \sum_{m=-\infty}^{\infty} \exp \left( - \beta S \right) \cdot \left| S \right| \cdot 2 \pi t \left| S \right| \]  \[ (\text{cf. equations (7c) and (16)).} \]
Analysis of Polymeric X-ray Diffraction Profiles.
I. Theory and Application of the Variance Method*

BY A.K. KULSHRESHTHA, N.E. DWELTZ AND T. RADHAKRISHNANT
Ahmedabad Textile Industry's Research Association (ATIRA), Ahmedabad-15, India

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In the field of polymer physics, X-ray diffraction line profile analysis methods have yet to acquire the significance which they possess in the analysis of the fine structure of metals and alloys. The present paper attempts to put these methods on a solid theoretical basis and to introduce new concepts in the analysis of polymeric X-ray diffraction profiles. The theory of paracrystals has been used to calculate the expressions for integral line breadth and variance-range-function of 000 diffraction profiles. The methodology is illustrated by an application of the integral breadth and variance methods to a polymeric viscos fibre, Tufcel, whose axial structure has been shown to be 'paracrystalline'. Special emphasis is laid on the elimination of diffuse background scatter, the correction of profiles for angular variation factors, the problem of overlapping reflexions etc. and the superiority of the variance method over the integral breadth method in the analysis of polymeric X-ray diffraction profiles is established.

Introduction

It is now well recognized that the crystallites in fibrous polymers are at best paracrystalline, that is, characterized by lattice distortions of the second kind which destroy long-range order (Hosemann & Bagchi, 1962; Boriart, 1963; Vainshtein, 1966). Paracrystalline structures are also found in polymer single crystals, liquid crystals, molten metals, graphitic carbons, Mn spinels, Fe–Al alloys, cold-worked metals and alloys generally possess such distortions as well as cold-worked metals are broadened as a result of small crystallite size and the presence of such distortions. There is thus a superficial similarity between the diffraction patterns given by polymers and polycrystalline structures (Viswanathan, 1967; Statton, 1968; II, 1969). However, a careful study of the line profiles shows that there are also profound differences between the kinds of broadening due to type I and type II distortions. These differences are also theoretically dictated. There is extensive theoretical work on the paracrystalline single-crystal X-ray diffraction lines from small crystals with type II distortions. This work has been used to estimate the dimensions of crystallites and their distortion parameters. The treatments are based on the paracrystalline analysis of line profiles (Warren & Averbach, 1963b) or on the more satisfactory variance analysis (Wilson, 1962a, b, c, 1963a, b, c, 1968; Langford, 1965, 8a, 6b). In the case of small crystallite domains with type II distortions, the theory is less developed. It has been shown, that for ideal paracrystals, integral line breadths increase as the square of the order of reflection (Bonart, Hosemann & McCullough, 1963). This result is not as yet very popular, especially in the case of polymeric X-ray diffraction profiles. However, most of the available experimental work for polymers has made no attempt to allow for distortion broadening in calculating the sizes of crystalline domains (Thielke & Billmeyer, 1964; Mori & Doi, 1964; Viswanathan & Venkataraman, 1966). In studies (Kulshreshtha, 1968; Kuriyama, 1961; Kuriyama, Tanaka & Nagai, 1963; Buchanan & Miller, 1966), where such a separation has been sought on Warren–Averbach lines, no attempts have been made to interpret the Fourier coefficients in terms of type II lattice distortions.

Apart from theoretical difficulties, there are also some practical hurdles in the analysis of polymeric X-ray diffraction lines. These are:

(i) absence of higher orders of reflexion
(ii) generally weak X-ray scattering power
(iii) occasional sample-to-sample variation in line positions and breadths
(iv) presence of a diffuse, structured background
(v) lack of reliable 'crystalline standards' to measured instrument broadening.

The present paper shows that the application of the variance-range analysis technique of Wilson and his colleagues may minimize some of these theoretical and experimental difficulties. A general calculation of the profiles of diffraction lines from small, ideal, paracrystalline samples is presented. Results are then derived connecting the variance of line profiles to crystalline dimensions and type II distortions. The formulae are applied to meridional reflexions from a polymeric viscous fibre. The results are shown to agree with those obtained from integral line breadths. Some improvements in ex-
perimental methods of determining line profiles are also described.

The theory for the analysis of X-ray diffraction from paracrystals

The X-ray diffraction patterns from fibrous polymers display certain peculiar features (Andreae & Iveronova, 1958; Roldan, Rahl & Paterson, 1965). Almost all the features can be explained by Hosemann's (1962) theory of an 'ideal paracrystal', which is especially suitable for fibrous polymers (Guinier, 1963). The basic postulate underlying this theory is that the edges of the unit cells of the perturbed crystal lattice vary statistically, in length and direction, about the ideal values independent of the values of their neighbouring cell edges. In the scattering pattern of a paracrystal, which is a function of lattice statistics, the characteristics of crystal interference and liquid interference are superimposed. The diffuse background under the reflexions is predicted to arise from the perturbation of the lattice.

Let us now consider a lattice which shows a 'paracrystalline' axial structure, i.e. irregularity in placement of lattice points along the b axis of the crystal lattice. (The electron density contents of a unit cell may be replaced by a representative point.) Let \( X_1, X_2, \ldots, X_m \ldots \) denote the distances between successive lattice points starting from the origin. In the model of an ideal paracrystal it is assumed that the positions of lattice points fluctuate independently, i.e. \( X_1, X_2, \ldots, X_m \ldots \) represent a sequence of independent random variables. It is further assumed that the random variables \( X_m \) are identically distributed and have the probability density \( h(t) \). They are constant in the limit and have finite variances, i.e.

\[
E(X_m) = \int \theta h(t) \, dt = b
\]

\[
E(X_m^2) = \int \theta^2 h(t) \, dt = b^2 + \Delta^2
\]

\[
\text{Var}(X_m) = E(X_m^2) - (E(X_m))^2 = \Delta^2
\]

where \( E(X_m) \) and \( \text{Var}(X_m) \) respectively denote the mathematical expectation and the variance of \( X_m \), and \( b \) is the average periodicity in the axial direction. The function \( h(t) \) is also called the 'coordination statistic' of the paracrystal in the b direction and governs the distribution of distance between nearest neighbours. Let \( S_m = X_1 + X_2 + \ldots + X_m \) represent the total distance between the origin and the \( m \)th lattice site. The probability–density function for \( S_m \) is given by

\[
h_m(t) = \frac{1}{m!} h(t)^m \cdot h(t) \cdot \ldots \cdot h(t) \cdot h(t)
\]

\[
= \text{self convolution of } h(t), \, m \text{ times}
\]

We find

\[
E(S_m) = \int \theta h(t) \, dt = \frac{mb}{2}
\]

\[
E(S_m^2) = \int \theta^2 h(t) \, dt = \frac{mb^2 + m\Delta^2}{2}
\]

and

\[
\text{Var}(S_m) = \frac{m\Delta^2}{2}.
\]

The diffraction line profile for an aggregate of imperfect crystals can be written as (Wilson, 1962; Guinier 1963)

\[
I_{PD}(s) = \frac{2C}{U} \int Y(t) \, I(t) \exp \{-2\pi st\} \, dt
\]

where

\[
V(t) = \text{volume common to the crystal and its glideplane obtained by a translation } t = mb \text{ in a direct normal to the reflecting (00l) planes.}
\]

\[
Y(t) = J(t) - iK(t) \text{ is the mean value of the product } F^*F \text{ of the structure factors of a pair of cells separated by the distance } t.
\]

\[
\lambda = \frac{2 \sin \theta}{\lambda}, \text{ where } \theta \text{ is the position of the intensity maximum and } \lambda \text{ the wavelength of X-rays.}
\]

\[
\tau = \text{upper limit of } t \text{ such that } V(t) = 0
\]

\[
U = \text{volume of the unit cell, and}
\]

\[
C = \text{angular variation factor containing the }
\]

\[
V(t) = \int \left\{ \left[ 1 - \frac{|t|}{M} \right] g(M) \right\} \, dM
\]

where \( V \) is the volume of the crystal, and \( g(M) \) d\( M \) the frequency function of crystallite sizes \( M \) along normal to the reflecting planes. For small \(|t|\), we obtain

\[
\frac{V(t)}{V} \approx \exp \{- \beta |t|\}, \quad \beta = \frac{1}{M_1} = \int_0^\infty \frac{1}{M} g(M) \, dM
\]

where the interpretation of \( M_1 \) has been discussed by Guinier (1963). Since the crystallite sizes in fibre polymers are very small (~ 100 Å), \( V(t) \) will be sharp and would have appreciable magnitude only small \(|t|\). The normalized line profile due to a distribution of crystallite sizes, which is the Fourier transform of \( V(t) \), can therefore be approximated by a Cauchy function:

\[
I_P(s) \approx \frac{2\beta}{\beta^2 + 4\pi^2 s^2}
\]

The variance of \( I_P(s) \) truncated between limits \( s = -\sigma \) and \( s = \sigma \) is

\[
W_p(s) = \int_{-\sigma}^{\sigma} I_p(s) \, ds = \int_{-\sigma}^{\sigma} I_p(s) \, ds
\]
ANALYSIS OF POLYMERIC X-RAY DIFFRACTION PROFILES.

\[
E(S_m') = \int h_m(t + mb) \, dt = 0
\]

\[
\text{Var}(S_m') = E(S_m'^2) = \int t^2 h_m(t + mb) \, dt - mA^2.
\]

where \( h_m(t + mb) \) gives the probability that the displacement distortion, \( S_m' \), of the \( m \)th lattice point lies between \( t \) and \( t + dt \), and \( S_0 = 2 \sin \theta / \lambda \) is the distance of point \( 0 \) from the origin of the reciprocal lattice. For small \( t \), i.e., for small displacement \( S_m' \), we obtain from equation (10a):

\[
Y(t) = |F|^2 \exp \left\{ -2\pi^2 k^2 A^2 \right\} = J(t), \quad \text{since it is entirely real.}
\]

For large \( t \), we will consider the limiting distribution of the sum \( S_m \). The limit theorems for the sums of dependent random variables (Gnedenko, 1962; Craig, 1962) state that irrespective of the nature of the distribution \( h(t) \), \( h_m(t) \) will converge to a Gaussian distribution having variance equal to \( mA^2 \), provided \( m \) is sufficiently large. Therefore, we can write:

\[
h_m(t + mb) \approx (2\pi mA^2)^{-1/2} \exp \left\{ -t^2 / 2mA^2 \right\}
\]

obtain from equation (10b):

\[
Y(t) = |F|^2 \frac{(2\pi mA^2)^{-1/2}} \exp \left\{ -t^2 / 2mA^2 \right\}
\]

\[
\times \exp \left\{ -2\pi i k \theta / \lambda \right\} \, dt
\]

\[
= |F|^2 \exp \left\{ -2\pi^2 g^2 k^2 \right\} = J(t).
\]

The same result is obtained whether we consider the variables \( X_m \) to the right or to the left of the origin.

Therefore,

\[
J(t) = |F|^2 \exp \left\{ -2\pi^2 g^2 k^2 m \right\},
\]

which after rearranging \( s_0 = k / \lambda, \quad g = 4 \lambda / \beta \) and \( m = \sigma / \beta \), becomes,

\[
J(t) = |F|^2 \exp \left\{ -a |t| \right\}, \quad a = 2\pi^2 g^2 k^2.
\]

where \( k \) denotes the order of reflexion. Thus we find that expression (11) for \( J(t) \) is approximately correct for all values of \( t \) even if the coordination statistic \( h(t) \) is not Gaussian. The function \( J(t) \) is a measure of the degree of correlation in the lattice.

The normalized line profile due to type II disorientations, which is the Fourier transform of \( J(t) \), is Cauchy in shape, and given by

\[
I_0(s) = \frac{2\pi^2}{\alpha^2 + 4\pi^2 s^2},
\]

(12)

The integral breadth of the distortion profile is

\[
\beta_0(s) = \frac{\int I_0(s) \, ds}{I_0(0)} = \frac{a}{2\pi^2 g^2 k^2}.
\]

This result is equivalent to that derived by Bonart, Hosemann & McCullough (1963), who have shown that if the line broadening is due to a small paracrystal, the integral breadth of a reflexion of the type \( 0 \)\( k \)\( 0 \) is given by

\[
\beta_{0k0} = \frac{1}{|L|^3} + \frac{\pi^2 g^2 k^2}{b},
\]

(14)

where \( g = \lambda / \beta \) is a measure of the degree of lattice disorder, \( \beta_{0k0} \) is the integral line breadth of the \( 0k0 \) reflexion, and \( L \) is the average of the dimensions of the paracrystallite along the normal to the \( 0k0 \) planes, given by (Guinier, 1963).

Fig. 1. Observed intensity distribution from Tufcel along the meridional direction. The broken curve shows the 'true' background.
The variance of the distortion profile is given by

\[ W_D(s) = \frac{\sigma^2}{2\pi^2} - \frac{\sigma^2}{4\pi^2} \text{, for large } \sigma \]

\[ = \frac{g^2k^2}{b} \left( 1 - \frac{\pi^2 g^2 k^4}{b^2} \right). \]

The variance of the intrinsic line profile, which is the convolution of \( I_D(s) \) and \( f(s) \), can be calculated from equation (4), which can be rearranged as

\[ I_D(s) = 2 \int_0^s A(t) \cos 2\pi t \, dt \]

with

\[ A(t) = C \int V(t) J(t) \]

\[ = C \int V(t) \exp \left[ -\pi |t| \right]. \]

The result is (Wilson, 1962c)

\[ W_{PD}(s) = -\frac{1}{4\pi^2} \left[ 2C^2 A''(0) + \frac{A''(0)}{A(0)} \right] \]

where the functions \( A'(0) \) and \( A''(0) \) represent the limits of the derivatives of \( A(t) \), as \( t \) goes to zero through positive values. From (176), we obtain

\[ A'(0) = \left[ V'(0) - \sigma \right] \]

and

\[ A''(0) = \left[ \sigma^2 - 2\pi V'(0) V(0) + \frac{V''(0)}{V(0)} \right]. \]

From (6), we find

\[ \frac{V'(0)}{V(0)} = \lim_{t \to 0^+} \left[ \frac{V'(t)}{V(t)} \right] = -\frac{1}{M_1} \]

and

\[ \frac{V''(0)}{V(0)} = \lim_{t \to 0^+} \left[ \frac{V''(t)}{V(t)} \right] = \frac{1}{M_1^2}. \]

The resulting expression for variance becomes, after substituting \( \sigma = 2\pi^2 g^2 k^2 \cdot b \),

\[ W_{PD}(s) = k_{so} \sigma(s) - W_{0s} \]

where

\[ k_{so} = \frac{g^2k^2}{b} + \frac{1}{2\pi M_1}. \]

and

\[ W_{0s} = \frac{\pi^2 g^2 k^4}{b^2} + \frac{g^2 k^2}{b M_1} + \frac{1}{4\pi^2 M_1^2}. \]

If one calculates \( W_{PD}(s) \) as a function of \( \sigma(s) \), the called variance-range function is obtained. In this case, \( k_{so} \) and \( W_{0s} \) represent the slope and the intercept, respectively, of the variance-range function. From (1).
(18c) it is found that

\[ n(x) = e^{-x} \]

\[ n(x) = e^{-x} \]

in fact, be obtained through (18) by putting \( g = 0 \), \( M_i = \infty \) respectively.

**Experimental**

Highly oriented fibres of Tufcel, a polynosic viscose, were chosen for line-profile studies for the following reasons: (i) they gave rise to four orders of reflection from longitudinal (0k0) planes, and (ii) they were found to be most ordered among the samples of polynosic viscose in a preliminary survey of X-ray fibre diagrams. The 0k0 profiles were recorded using a transmission goniometer, which has many obvious advantages over the conventional method of obtaining polymeric X-ray diffraction profiles (Wilchinsky, 1965). Intensity measurements were made at room temperature with a Philips diffractometer using a Geiger counter and Cu Kα x-ray tube at 35 kV and 25 mA. Monochromatization was achieved by means of balanced filters of nickel and art acetate. A single bundle of parallel fibres (~0.5 thick) was used and the axis of this bundle was oriented at an angle of 90° to the incident and diffracted beams. The following slit system employed: divergence slit 0.05°, receiving slit 0.3 cm, anticounter slit 1°. A fixed-count step scanning method (Parra, 1956; Wilson, 1967) was used to obtain intensities, which were determined at 0.05° intervals in the peak region and at 0.25° intervals between peaks. The total number of counts accumulated was fixed at 12800.

Quartz powder (average grain size > 10μ) was used as the instrumental standard. A thin uniform film of quartz powder dispersed in collodion was prepared. The film was mounted on the diffractometer in the manner described above and instrument profiles were obtained under identical conditions. The only difference in this case was that the film was rotated in its plane to eliminate the effects of preferred orientation and the intensities were determined at 0.05° intervals in the regions of the peaks. Variation of air temperature from different parts of the apparatus with 2θ also studied. Finally, the values of \( \mu \) (where \( \mu \) and \( \sigma \) denote the absorption coefficient and thickness of substance respectively) were obtained for the fibre and the quartz film.

**Method of analysis**

A programme was written for the IBM 1620 computer to convert the counting times into intensities (units. min⁻¹) and to correct the intensities for count dead time and white radiation contamination. Thus, \( I(2θ) \) versus 2θ plots were obtained to give the meridional scattering curve for the fibre and the radial scattering curve for quartz. Fig. 1 shows the meridional scattering curve for Tufcel from 13 to 42° 2θ:

**Elimination of background**

The special feature of the variance method is that the true background level can be determined very accurately. The procedure for the elimination of true background is incorporated in the Langford & Wilson method of analysis.
(1963) method of determining the variance-range functions, where the variation of background is assumed to be linear. The difficulty with polymeric X-ray diffraction is that the background, especially at low Bragg angles, has a curved shape. Therefore, the procedure of choosing the background has to be separated from the procedure of determining the variance-range functions. One can start with two or three visual estimates of background, which may be curved or linear depending on the angular range under investigation. After subtracting these backgrounds, different profiles are obtained and the variance-range functions are computed for each of these. The variance-range function corresponding to the subtraction of true background would exhibit a linear portion for moderately large ranges. Therefore, after having a look at these variance-range functions, one can suitably modify the initial estimate of background, until the variance-range function obtained is optimum, i.e., it shows a significant linear portion. Thus, after a few trials the true background can be estimated and then subtracted. This procedure is illustrated in Fig. 2, where three different backgrounds were subtracted and the variance-range functions of the corresponding 020 profiles were calculated and plotted. The true backgrounds under 040 and 080 reflexions were found to be linear. All the profiles were obtained after the subtraction of the 'true' background in each case.

Correction for Lorentz-polarization and absorption factors

All the profiles were corrected for these angular variation factors by means of a program written for the IBM 1620 computer. The corrected line profile is given by

\[ g(\theta) = \frac{[l(2\theta) - I_0(2\theta)]}{L(2\theta) P(2\theta) A_0(2\theta)} \]

where \(L(2\theta) = \frac{1}{\sin^2 \theta \cos \theta}\) is the Lorentz factor (Wolff, 1962; Ruland, 1967), \(P(2\theta) = (1 + \cos^2 2\theta)\) is the polarization factor, \(A_0(2\theta) = t \sec \theta \exp (-\mu s \cos \theta)\) is the absorption factor (Bragg & Packer, 1963), \(I_0(2\theta)\) is the experimental profile, and \(I_0(2\theta)\) the true background.

Tackling the problem of overlapping reflexions

020 and 080 profiles were free from any contamination from their neighbouring off-meridional reflexions but the higher angle tail of the 040 profile was corrupted slightly by a weak and very broad tail from the meridional 041 reflexion (Fig. 1). In order to obtain integral breadth of the 040 profile, it was necessary to resolve it from its neighbours. This resolution was attempted in the following way. From a knowledge of positions of the 020 and 080 peaks, the position of the peak was calculated. The difference in the position of the 040 and 041 peaks was assumed to be 1.4° in 2θ. 041 was assumed to be symmetric about its peak. Trial and error, one could arrive at the peak height 041 which would yield a satisfactory resolution of 040 profile (Fig. 3).

Such a resolution is necessary for obtaining the integral breadth where the entire range of a line profile used. A great advantage of the variance method is that a much shorter range is required to obtain the variance range function and, if there is only partial overlap, this fact can be used to eliminate the need of resolution. Thus, the variance–range function for the 040 profile (Fig. 5) has been determined for short ranges, with attempting its resolution. If the variation of background

![Fig. 5. Variance–range functions for observed 040 profiles (A) and for their corresponding instrument profiles (B); (i) 020, 040 and (iii) 080.](image-url)
ANALYSIS OF POLYMERIC X-RAY DIFFRACTION PROFILES. I

Table 1. Observed, instrumental and corrected integral breadths

<table>
<thead>
<tr>
<th>040</th>
<th>B°(2θ)</th>
<th>b°(2θ)</th>
<th>β_{ho} (Å⁻¹)</th>
<th>β_{ho} (Å⁻¹)</th>
<th>β_{ho} (Å⁻¹)</th>
<th>β_{ho} (Å⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>040</td>
<td>0.915</td>
<td>0.220</td>
<td>0.0091</td>
<td>0.0098</td>
<td>0.0092</td>
<td>0.0095</td>
</tr>
<tr>
<td>040</td>
<td>0.985</td>
<td>0.304</td>
<td>0.0938</td>
<td></td>
<td>0.0928</td>
<td>0.0075</td>
</tr>
<tr>
<td>050</td>
<td>2.158</td>
<td>0.328</td>
<td>0.0192</td>
<td>0.0189</td>
<td>0.0182</td>
<td>0.0162</td>
</tr>
</tbody>
</table>

a. Equation (21) b. Equation (22) c. Determined by Jones’s (1938) method
d. Equation (23)
Thus, $W_{00}$ and $k_w$ can be obtained by simple subtraction and interpreted in terms of crystallite size $M_1$ and distortion parameter $g$ by using equations (18). The corrected variance–range functions for 00k profiles are shown in Fig 6. The slopes and intercepts of the variance–range functions are listed in Table 3.

Table 3. Intercepts ($A^2 \times 10^6$) and slopes ($A^{-1} \times 10^3$) of linear variance–range functions

<table>
<thead>
<tr>
<th>Instrument profile</th>
<th>Specimen profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_{00}$</td>
<td>$k_{00}$</td>
</tr>
<tr>
<td>040</td>
<td>0.75</td>
</tr>
<tr>
<td>020</td>
<td>-0.47</td>
</tr>
<tr>
<td>080</td>
<td>-1.55</td>
</tr>
</tbody>
</table>

Results

The results of integral breadth measurements are listed in Tables 1 and 2 and plotted in Fig. 4. It can be noted that the square of the integral breadth $\beta_{00}$ varies as $k^4$ [see equation (14)] regardless of the procedure used for separating $\beta_{00}$. It may be thought that with only three points on the graph, the test of linearity is far from conclusive. However, when one looks at the enormous range of variation in $k^4$, the nature of the fit will be appreciated. It is a consequence of paracrystalline order that reflections of measurable intensity do not appear at still higher values of $k$. The intercepts of $\beta_{00} - k^4$ lines give the value of $L$, the average crystallite size defined by equation (15), and the slopes prove the value of $g$, the coefficient of variation of the $b$ rep. of the crystallite. The values of $g$ and $L$ are listed in Table 2 for each method of separation of $\beta_{00}$. It can be seen that, whereas all the methods give practically the same value of $g$, the values obtained for $L$ are widely different.

The values of $k_{00}$ and $\sqrt{W_{00}/\pi}$ are plotted against $k^2$ in Figs. 7 and 8 respectively. These plots are linear conformity with equations (18b) and (19). The slope of these lines yield $g^2/b$, hence the value of $g$, and the intercepts determine the value of $M_1$, the average crystallite size defined in equation (6). Table 4 summarises the values of $M_1$ and $g$ obtained through an analysis of slopes and intercepts of linear variance–range functions of 00k diffraction profiles.

Table 4. Values of crystallite size and lattice distortion parameter obtained from variance–range functions

<table>
<thead>
<tr>
<th>Values calculated</th>
<th>Crystallite size</th>
<th>Lattice distortion parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope of $k_{00}$ vs. $k^2$ plot</td>
<td>$M_1$ (A)</td>
<td>$\beta_{00}$ (arcsec)</td>
</tr>
<tr>
<td>1</td>
<td>1.35 [1-]</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Intercept of $k_{00}$ vs. $k^2$ plot</td>
<td>96 [94]</td>
</tr>
<tr>
<td>3</td>
<td>Slope of $\sqrt{W_{00}/\pi}$ vs. $k^2$ plot</td>
<td>-1.06 [1-]</td>
</tr>
<tr>
<td>4</td>
<td>Intercept of $\sqrt{W_{00}/\pi}$ vs. $k^2$ plot</td>
<td>111 [98]</td>
</tr>
</tbody>
</table>

The values in square brackets have been obtained after corrections to $W_{00}$ and $k_{00}$ for deconvolution errors (Edwards & Toman, 1970).

Discussion

We thus see that the slopes and the intercepts of the variance–range functions follow the behaviour predicted by equations (18) and (19). Equation (19) predicts that the same information is obtained from the analysis of the slopes and the intercepts of variance–range functions. Nevertheless, it should be pointed out that the information obtained through a comparison of the results obtained from the integral breadth analysis with the values obtained by the variance method, it is found to be more reliable than that obtained from the intercepts $W_{00}$ because if some residual strain is present in the crystals of the instrument standard, it would affect only the intercepts of observed variance–range functions. Moreover, the values of intercepts are subject to errors due to truncation (Wilson, 1965), non-additivity and the neglect of hyperbolic terms (Wilson, 1972) and (Edwards & Toman, 1970), which in the present case are not serious owing to predominant size broadening. This is obvious from a comparison of the results obtained from the integral breadth analysis with the values obtained by the variance method, where it is found...
that values obtained from the $k_m$, $k^2$ plot are in agreement with the integral breadth results. It would be kept in mind that for any general form of $F(t)$, $L = 2M_1$, but in the particular case when $F(t)$ is proportional to $\exp[-t/M_1]$, $L = 2M_1$. From equation (18), it can be seen that the slope of the variance-range function depends upon $M_1$ as well as upon $g$, like the case with type I distortions, for which it depends only on $M_1$. This fact, combined with equation (9), would mean that at least two orders of reflections are necessary to separate $M_1$ and $g$ from the slopes of variance-range functions. This result is disappointing, since in many cases (for example, the equatorial reflexions from fibrous polymers) only the first order peaks are observed. Equations (7) and (12) indicate that observed profiles would be approximately Cauchy in shape. It is reported in literature that the line profiles obtained from fibrous polymers in fact have a Cauchy shape (Gjønnes, Norman & Viervoll, 1958; Katayama, 61).

The suitability of Hosemann's paracrystalline model for fibrous polymers has been discussed by Kulshreshtha, weltz & Radhakrishnan (1969). Paracrystalline distortions have been found by other workers to exist in hydroxyethyl, propylene, polytetrafluoroethylene, nylon, terephthalamide, nylon, terephthalamide, and substituted vinyl polymers. The theoretical deductions in the present paper are based on an 'ideal paracrystalline' lattice, which involves the assumption that all the molecules in the polymer are identically deformed and consequently, all individual unit cells in the lattice are parallelepipeds. If there exists a partial correlation between the neighboring lattice points, a general paracrystalline lattice results, the unit cells of which are hitherto deformed parallelepipeds. According to Hosemann & Bagchi (1962), the deviations from the ideal model influence only the diffuse background scattering between the reflexions. So long as the fluctuations are not too strong ($i.e.$, $g < 3\%$) and crystallites contain more than five unit cells on the average, the effects of corrections on the crystalline reflexions can be considered negligible. Anyway, with a careful choice of the diffuse background and the analysis of the linear portion of variance-range curves for moderate ranges, one should still obtain quite meaningful results.

The advantages of the variance method over the integral breadth method in the analysis of polymeric x-ray diffraction profiles are obvious: (i) it helps in sussing the 'true' background; (ii) it is capable of tracing some useful information from unresolved profiles, and (iii) the corrections for instrument broadening are rigorous and simple.

Thus, from the X-ray line profile studies we can get a fine structure parameters $g$ and $M_1$ or $g$, which define 'order' in fibrous polymers in a more meaningful way than the 'degree of crystallinity'. These parameters define the lattice statistics of a paracrystal (Hosemann, 1962), which undergoes a change during quenching, annealing, or swelling-stretching treatments of fibres. The distortion parameter $g$ is related to the average conformation of the long-chain molecules and would therefore influence fibre properties. Evidence for the existence of a paracrystalline structure in fibres is offered by the present study, which serves to establish such a structure in the axial direction of Tufcel, and supports earlier line-profile studies on fibrous polymers (Kulshreshtha et al., 1968; Schnabel, 1969; Wilke, 1969).

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References

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*

By A. K. Kulshreshtha, N. R. Kothari and N. E. Dweltz

Ahmedabad Textile Industry’s Research Association (ATIRA), Ahmedabad-15, India

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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 & Radhishnan, 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 00l reflexions from a polynosic viscose fibre, was also presented. It was concluded that it was not possible to separate the size and distortion effects from a study of the variance-range function of any one diffraction line, because both these effects contribute to the slope and the intercept, both of which theoretically contain equivalent information about fibre 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 & Snowidov (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.

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*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 (Cramér, 1962; Mitra, 1964):

$$\mu_{PD} = \mu_P + \mu_D + 6W_P W_D$$

(1)

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:

$$I_D(s) = \frac{2\pi}{a^2 + 4\pi^2 s^2} \cdot \frac{a}{b}$$

(2)

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

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

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

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

Now

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

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

Similarly,

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

$$\simeq \frac{a(\sigma_1 + \sigma_2)}{6\pi^2} - \frac{\alpha^2(\sigma_1 + \sigma_2)}{8\pi^4} + \frac{\alpha^4}{16\pi^4}, \text{ for large } \sigma_1 \text{ and } \sigma_2.$$

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

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

and

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

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

$$V(0) = \exp\left\{ -\beta |h| \right\}, \quad \beta = \frac{1}{\kappa},$$

and we obtain

$$W_P = \frac{\mu_0}{2\pi^2} \frac{\sigma_1 + \sigma_2}{4\pi^2}$$

and

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

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

$$\mu_{PD} = \frac{(\alpha + \beta) \sigma^4}{24\pi^2} - \frac{3\sigma^2}{2\pi^2} \frac{\alpha^2}{8\pi^4} + \frac{\alpha^4}{16\pi^4} + \frac{(\alpha^2 + 6\sigma^2) \beta^2}{16\pi^4}$$

It is easily seen from this expression that only terms containing $\sigma^2$ and $\sigma^4$ will have appreciable magnitude, and the rest will be vanishingly small.

Recently, Wilson (1969) has shown that the most 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 exclude this result in our calculations, it is easily seen that the moment-range function is represented by the polynomial:

$$\mu_{PD}(\sigma) = \sum_{n=3}^{\infty} a_n \sigma^n.$$

* Our notation in this regard is slightly different from generally accepted, namely $\sigma_1 = \sigma_2 = \sigma$, where the range is rather than $\pm \sigma/2$ in our notation.
the coefficients of our interests are:

\[ a_2 = \frac{3\sigma \beta}{2\pi^2} \]

\[ a_3 = \frac{(\alpha + \beta)}{24\pi^2} \]

(10)

Thus, two solutions are obtained for \( g \) and \( M_I \). 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 \( M_I \) 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 060 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 \( ^\circ 20 \) or in \( 2\sin \theta/\lambda \) units, one proceeds with the determination of the variance-range and moment-range functions as follows:

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

(ii) A starting point \( x_s < x_p \) (the peak) is chosen on the profile.

(iii) An upper limit \( x'_U \) is chosen symmetrically about the peak, i.e., \( x'_U - x_p = x_p - x_s \). The centroid of the profile truncated between the limits \( x_s \) and \( x'_U \) is calculated, say \( x'_C \).

(iv) The mid-point of the range \( x'_U - x_s \) is compared with \( x'_C \), and the difference \( (x'_U - x'_C)/2 \) is called the asymmetry of \( x'_C \).

(v) The range \( x_s \) to \( x'_U \) is changed to a new range \( x_s' \) to \( x'_U' \) by subtraction of twice the asymmetry of \( x'_C \) from \( x_s' \), i.e., \( x'_U' = x'_U - 2[(x'_U + x'_C)/2 - x'_C] \), \( x'_C \) is at the mid-point of the new range.

(vi) The steps (iii)-(iv) are repeated with new upper limits \( x'_U, x'_U', x''_U, \ldots \) until the asymmetry is \( \leq dx/4 \), where \( dx \) is the step length used for numerical integration (\( dx = \beta/20 \), where \( \beta \) is the integral breadth of the line profile). Let \( x_c \) be the upper limit satisfying the condition

\[
[(x_c + x_b)/2 - x_c] \leq \frac{dx}{4}
\]

where \( x_c \) is the centroid corresponding to the final range \( (x_c - x_b) \).

(vii) The starting point \( x_s \) is changed in discrete steps to values \( x_{s1}, x_{s2}, x_{s3}, \ldots \), and for each starting point the corresponding final upper limits \( x'_{b1}, x'_{b2}, x'_{b3}, \ldots \) are found by the procedure outlined.
in steps (iii)-(vi). For each range \((x_{an} - x_{an})\), 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 Lorenz-polarization and absorption effects to give the corrected profile \(g(x)\) [1, equation (20)].

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

Let \(W_b\) and \(W_t\) denote the variance-range functions and \(\mu_b\) and \(\mu_t\) 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

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

Let

\[
\mu_{PD}(\sigma') = \sum_{s=-2}^{s=2} a_s\sigma'^s
\]

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

\[
\mu_{PD} = K^4\mu_{PD}, \quad \sigma = K\sigma', \quad a_n = K^{4n+4}a'_n
\]

where

\[
K = \frac{\pi}{180} \times \cos \theta_b
\]

\(\theta_b\) 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:

- \(N\) = the total number of intensity values given in proper angular order \((I_1, I_2, \ldots, I_N)\).
- \(DX\) = \(dx\), the steps at which the intensities are observed.
- \(X(1)\) = the initial value of \(x\) corresponding to \(I_1\).
- \(KDX\) = increment interval in half-range.
- \(M\) = the total number of increments required in half-range.
- \(IFMAX\) = \(P\) = the suffix corresponding to the maximum value of intensity, \(I_P\), 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) fitted to this curve by the method of least-squares it was found that \(\mu_{PD}\) could be expressed as

\[
\mu_{PD} = 0.00259\sigma^2 + \frac{0.00185}{\sigma^2} - 0.0006 - 0.0006
\]

This gives \(\alpha_3 = 0\), and \(\alpha_4 = 0.00259 (\text{°}2\theta)^2\) or \(\alpha_4 = 0.045 \times 10^{-4} \text{ Å}^{-2}\) using (14). From equation (10) we calculate

\[
a'b = \frac{2\pi^4}{3} - a_2 = 0.211 \times 10^{-4} \text{ Å}^{-2}
\]

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

\[
\kappa_{a'b} = \frac{\alpha + \beta}{2\pi^2} = 0.603 \times 10^{-3} \text{ Å}^{-1}
\]

or

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

From these values of \(a'b\) and \((\alpha + \beta)\), the following four solutions are obtained for \(g\) and \(\overline{M}_1\) [cf. equat (11)]:

<table>
<thead>
<tr>
<th>Solution</th>
<th>(\overline{M}_1(\text{Å}))</th>
<th>(g(%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>461</td>
<td>3.56</td>
</tr>
<tr>
<td>II</td>
<td>103</td>
<td>1.68</td>
</tr>
</tbody>
</table>

According to Bonart (1963), the number of orders reflections separable along the reciprocal axis is given by \(0.24\sqrt{g(\%)}\).

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

For moderately large ranges used for calculation of \(\mu_{PD}\), it is assumed that equation (1) is approximately valid. The fact that the coefficient of the \(\sigma^2\)-dependent term is appreciable lends support to the 'paracrystalline' line theory of lattice distortions. The absence of \(\sigma^2\)-dependent term may be attributed to slight error in the choice of background and in the method of convolution.

**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

```
* DIMENSION X%40Qa-,FX%40a,X2FX%40n,X3FX%40n,X4FX%40a
1,01 READ1,N,M,K>-IFMAX,X%ln.DX,~
1 FORMAT84I5.2F10.0Q
- D#DX*.25
2, READ2.%F*%Ua.J#l>Nn
2 -EORMATSSFlO.On
425 D025J#1.N
XFX*Jn*X*jo*FX#Jo
v  X2FX%Ja«X%Ja*XFX%Ja .
X3FX8Ja#xaJ°*X2FX8Ja
X4FX95Jn#X8jn4x3FX8jn
25 ' XS j&la#XSSUa&DX
ID0IFMAX
IDP#IFMAX
.  PUNCH6.N.MTK.lD.X*IDn.FXSl'Du.DX
6 FORMATSAI5.3E15.8a
PUNCH11
,11 FORMATS 1H a
435 D035J#1.M
XID1-K
IDP#IDP6K
RMID#X%1D6%X1DPA=*.5
FXC#FX6DPA
EMMOX
JS#ID1
JE1#IDP-2
CGNE#$FX%JE1=16FX%JE62=*.5
CGDE#$FX%JE1=6FX%JE62=*.5
41 CGM#FX%JE1=6FX%JE62=*.5
CGD#FX%JE1=6FX%JE62=*.5
D045J#JS+JE
CGM#FX%JE6CGM
CGDP#CGM#DX5CGDE=EM
CGF#CGM#DX5CGDE=EM/CGD
ASY#RMID-CG
IF%ABSFSASra-0a41.41.42
42 XC#XC*XCS
xec#xc*xcs ' XCF#XC*XCC
JEP10JE&1
JSM1#JS-1
RM2NE»SX2FXSJEPln&XCS*FXCa*.5
RM3N£*SX3FXSJEPln&X3FXSJEPln*.5
RM4NM#SX4FXSJEPln&X4FXSJEPln*.5
D055J#JS+JE
RM2X#FXSJE4RMXN
RM4X#FXSJE4RMXN
55 RM2X#FXSJE4RMXN
RM2E#RM4NMDXRX2MEfE/CGD
RM3#RM3NMDXRM3NEfE/CGD
RG#RM4NMDXDR4NEfE/CGD
CG2#CG2GCG
CG4#CG2GCG
CG6#CG6GCG
CM2#RM2-CG2
CM3#RM3-3.*RM2*CG2-#CG3
CM4#RM4-4.*RM5*CG6-#CG2-3.*CG4
RANGE#XC-9IDM
35 PUNCH7.I,RANGE,CGD,CGM2,CM3,CN,
7 FORMATS13+6E12.6a
PUNCH11
8 FORMATH4OVERn
GOTO101
END

INPUT DATA

34 10 1 14 34.0 0.05
2130 2520 2995 3595 4310 5150 6068 6900
7690 8400 9055 9615 10128 10400 10550 9959
9460 8770 8010 7155 6285 5435 4650 3990
1,0000 2950 2210 1905 1670 1465 1245 1140
1140 1,000

OUTPUT

34 10 1 14 3.46500000E601 1.04000000E04 5.00000000E-02
1 1.00000E-00 .3519595E0 3465010E02 .824536E-03 8.00000E-09 1.90000E-05
2 2.00000E00 .30341250E0 3465075E02 .824546E-03 278600E-05 .267000E-04
3 3.00000E00 .29772250E0 3465135E02 .762368E-02 .212480E-04 .141400E-03
4 4.00000E00 .3873955E0 3465185E02 .129799E-01 .317220E-04 .84200E-03
5 5.00000E00 .4701155E0 3465235E02 .195780E-01 .628440E-04 .70100E-03
6 6.00000E00 .5449755E0 3465285E02 .272137E-01 .105440E-03 .63420E-03
7 7.00000E00 .6105175E0 3465335E02 .358845E-01 .157040E-03 .25120E-02
8 8.00000E00 .6791255E0 3465385E02 .445927E-01 .210832E-03 .44600E-02
9 9.00000E00 .7165805E0 3465435E02 .537941E-01 .267344E-03 .59630E-02
10 1.00000E01 .7582375E0 3465525E02 .630890E-01 .318910E-03 .84096E-02
```
The authors wish to thank the Director of ATIRA for 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


Dear Sir:

February 25, 1969

The concept of a continuous spectrum of degree of order in cellulose [17] was utilized in only two basic models [4, 5]. Various kinds of paracrystalline models for cellulose have been proposed from time to time [4]. The theory of diffraction by paracrystalline structures has also been developed for linear synthetic high polymers [6]. However, no direct attempt has so far been made to apply these results to cellulose. The present work is a consequence of our earlier crystallinity studies [16] and concerns itself with the analysis of x-ray diffraction profiles of successive orders of 0k0 reflections from ramie which is the most highly ordered of the native cellulose fibers.

Our earlier technique for obtaining meridional x-ray scattering curves from fiber cross sections [15] showed that the half-maximum line breadths of the 040 and 080 reflections varied as a function of specimen length (AB...
in Fig. 1). This effect, which is attributed to the low x-ray absorption coefficient of cellulose \( (\mu \approx 8) \), could not be easily corrected by the Keating and Warren method \([9]\), and hence a refinement of our earlier technique was made in the following way:

Several uniformly thick flat bundles of parallel ramie fibers were prepared. Each bundle was sliced into two parts by pressing a microtome knife perpendicular to the length of the fibers. Only well-cut bundle cross sections (approx. \( 1 \times 0.05 \) cm), judged under low-power magnification, were selected.

Bundle cross sections and \( 0.008 \)-cm silver foils were packed in the specimen holder (2 \( \times \) 1-cm slct) such that there was a silver foil between every two adjacent fiber bundles (Fig. 1), and the edges of silver foils and the plane of bundle cross sections were kept flush with the surface of the specimen holder. The silver foil did not give any reflection in the angular range under investigation. Thus the broadening effect due to beam penetration was reduced to the case of a single bundle, while at the same time the intensity of diffraction was as from several bundles.

Intensity data for the 0k0 diffraction profiles were obtained at room temperature by a fixed-count step-scan method with a Philips diffractometer, using a Geiger counter and CuK\( \alpha \) radiation at 35 \( \times \) 25 mA. Monochromatization was carried out with balanced filters of nickel and cobalt-acetate. Half-degree divergence and anti-scatter slits and a receiving slit of 0.01-cm width were employed. Intensities were measured at 0.025\(^{\circ}\) to 0.05\(^{\circ}\) intervals in Bragg angles \( (2\theta) \) in the peak region and 0.30\(^{\circ}\) intervals between peaks. Total accumulated counts varied from 6,400 to 25,600 for different 0k0 profiles and also for different regions of the same profile. The weak 000 profile was obtained by using divergence and anti-scatter slits of 4\(^{\circ}\).

Quartz powder was used as an instrument standard. Those diffraction profiles of quartz, which were located at or near the 2\( \theta \)-values of the corresponding 0k0 profiles of ramie, were obtained under identical conditions. Intensities were determined at 0.01\(^{\circ}\) to 0.02\(^{\circ}\) intervals in \( 2\theta \) in the vicinity of the peaks and at 0.30\(^{\circ}\) elsewhere.

Intensities were plotted against \( 2\theta \) and a reasonable background was drawn. For meridional scattering from ramie between \( 2\theta \) from 14\(^{\circ}\) to 30\(^{\circ}\), the shape of the background was similar to the scattering curve for amorphous cellulose (Figure 2). After subtracting the background, the results were divided by \( (1 + \cos^2 2\theta) \sin 2\theta \) to correct for the Lorentz-polarization effect.

![Fig. 2. Observed intensity distribution from ramie along the meridional direction.](image)

The corrected intensities were plotted against \( 2 \sin \theta / \lambda \). The 0k0 profiles thus obtained are shown in Figure 3. The profiles of the standard were obtained similarly. Many of the profiles were found to be contaminated by the tails of the neighboring off-meridional reflections. The resolution of a meridional profile from its overlapping neighbors was done by trial and error. The 020 and 030 reflections were highly asymmetric because of a strong one-dimensional x-ray diffraction on the second and third layer lines \([10]\) and the corruption of these profiles by the tails of their respective strong peaks.

![Fig. 3. Corrected meridional profiles of 0k0 reflections from ramie.](image)
For these reflections, the first \( f \) of the profile (towards lower \( 2\theta \)) was drawn symmetrically about the peak on the other side (towards higher \( 2\theta \)) so as to assess correctly their true breadths. The 040 profile was free of contamination by neighboring reflections. The integral line breadths of all the 0k0 profiles from ramie as well as those of the standard were thus determined. These were then corrected for the effects of CuKa doublet broadening and instrument broadening according to standard procedures [8]. The results are given in Table I.

### TABLE I. Integral Line Breadths of 0k0 Profiles of Ramie Obtained by Using Reflection Geometry

<table>
<thead>
<tr>
<th>( k )</th>
<th>( \beta'(2\theta) )</th>
<th>( \beta''(2\theta) )</th>
<th>( \beta''''(2\theta) )</th>
<th>( \frac{2 \sin \theta}{\lambda} )</th>
<th>( \beta(\text{rad}) )</th>
<th>( \beta_{\text{max}}' )</th>
<th>( \beta_{\text{max}}'' )</th>
<th>( k^2 )</th>
<th>( 10^4 \beta_{\text{max}}''(\text{A}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.303</td>
<td>0.143</td>
<td>0.196</td>
<td>0.1917</td>
<td>0.00342</td>
<td>0.00220</td>
<td>16</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.439</td>
<td>0.136</td>
<td>0.347</td>
<td>0.3884</td>
<td>0.00605</td>
<td>0.00382</td>
<td>81</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.312</td>
<td>0.122</td>
<td>0.279</td>
<td>0.3842</td>
<td>0.00399</td>
<td>0.00248</td>
<td>256</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.591</td>
<td>0.106</td>
<td>0.543</td>
<td>0.5777</td>
<td>0.00947</td>
<td>0.00550</td>
<td>1296</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.558</td>
<td>0.099</td>
<td>0.516</td>
<td>0.7690</td>
<td>0.00900</td>
<td>0.00470</td>
<td>4096</td>
<td>2.21</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.066</td>
<td>0.182</td>
<td>0.992</td>
<td>0.8746</td>
<td>0.01731</td>
<td>0.00829</td>
<td>6561</td>
<td>6.87</td>
<td></td>
</tr>
</tbody>
</table>

To check the consistency of line breadth measurements, ramie and quartz profiles were also obtained for transmission geometry, by using a divergence slit width 1/30°. The result of integral line breadth measurement of 0k0 profiles using reflection and transmission techniques are compared in Table II. It can be seen that the agreement between the two is satisfactory, except in the case of the very weak 060 reflection which is difficult to resolve from its neighbors.

### TABLE II. A Comparison of Integral Line Breadths of 0k0 Profiles of Ramie Obtained by Using Reflection and Transmission Techniques

<table>
<thead>
<tr>
<th>Reflection geometry</th>
<th>Transmission geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta'(2\theta) )</td>
<td>( \beta''(2\theta) )</td>
</tr>
<tr>
<td>0.439</td>
<td>0.136</td>
</tr>
<tr>
<td>0.312</td>
<td>0.122</td>
</tr>
<tr>
<td>0.591</td>
<td>0.106</td>
</tr>
<tr>
<td>0.558</td>
<td>0.099</td>
</tr>
<tr>
<td>0.589</td>
<td>0.099</td>
</tr>
</tbody>
</table>

The "weight average" of paracrystallite sizes normal to the (0k0) planes has been calculated as 460 A and the lattice distortion factor \( g \) as 0.8%. This is in fair agreement with the average length of the crystallites (450 A–500 A) determined by electron microscopy [11] after the cellulose has been degraded by acid hydrolysis and ultrasonic waves. The value of \( g = 0.8\% \) implies that the fiber identity...
period can vary between 10.06 Å and 10.54 Å as 3r limits. Sterically, this would mean that there exists a whole range of configurations of the cellulose chain molecule, each configuration having a specific (equilibrium) value of the fiber identity period. This fact is confirmed by studies on x-ray absorption of deuterated samples of cellulose [7]. This also explains why attempts at a really unique determination of the crystal structure of cellulose have not met with any success so far.

The presence of distortions severely limits the accuracy of determination of the atomic coordinates as well as the space group. The screw symmetry in cellulose has been the subject of an unending controversy. The presence of odd-order reflections has been reported by some [14], but dismissed by others [12] as artifacts. In this connection, it is interesting to note that the 030 reflection and its higher order 090, which are "forbidden" by the space group P21, do not fit into the scheme of 020, 040, and 080, as they are weaker and far more diffuse (Figure 5). This suggests that 030 and 090 reflections may be caused by disorder in the axial direction, thus giving rise to a "pseudo screw symmetry." The presence of these distortions should be taken into account before making a comparison of calculated and observed structure factors, and the intensity of the 030 reflection must not be neglected.

Since many synthetic fibers have a paracrystalline structure [5], this work confirms Hosemann's idea that there is a similarity in the architecture of natural and synthetic fibers. There is evidence that enzymes which is by no means perfect, results in a paracrystalline and synthetic fibers. There is evidence that enzymes...
MODERN techniques of electron microscopy have demonstrated that the walls of many fibrous substances are built up of 'microfibrils', which are long and slender aggregates of polymer chains. The manner of packing of these polymer chains can best be described as partly crystalline or 'paracrystalline'. This inference can be made by studying the X-ray diffraction patterns exhibited by fibrous polymers. One of the most powerful tools of X-ray study of disorder is the analysis of line profiles, a technique which was first developed to study lattice distortion in cold-worked metals and alloys. However, the theory, and methodology of application of line profile analysis have to be considerably revised in the case of polymers for the main reason that the structure proposed should not only explain the characteristic features of the X-ray diffraction pattern, but also some of the unique physical and chemical properties of the material which suggest the coexistence of several states of order. Pioneering work in the theory of X-ray diffraction from fibrous polymers was carried out by Bonart et al. They considered a finite lattice with 'ideal paracrystalline' distortions and calculated the integral breadth of its diffraction lines. Their theory could be applied with success to filaments of polyethylene, polytetrafluoroethylene, Fe-Al alloys, and Mn spinels. Nevertheless, this theory has encountered criticism because arbitrary assumptions have been made about the shape of the line profile as well as its resolution from background scatter.

One way of avoiding arbitrary assumptions about the resolution of the background is to use the variance method of line profile analysis, which has found increasing favour in recent years. Another powerful technique is the Fourier transform method of deconvoluting a line profile. However, neither of these techniques has hitherto been applied to paracrystalline distortions. The present paper attempts to present a theoretical derivation of the shape of the profile of X-ray diffraction lines from 'ideal' paracrystallites and to calculate various measures of line broadening therefrom. It is shown that crystallite size and disorder parameters can be independently calculated if line profiles are available for at least 3 orders of a given reflection. The theory is presented only in outline; detailed derivations can be found in earlier papers. These calculations have been applied to some fresh experimental work in which some new techniques have been used in order to minimize instrumental line breadth in diffractometry. This work pertains to meridional reflections from a natural cellulosic fibre (ramie), a regenerated cellulosic fibre ('polynosic' viscose with the trade name of Tufcel) and a ligno-cellulosic fibre (jute). In the case of ramie, three different experimental arrangements have been used to minimize line broadening and their relative merits compared. The line profiles have been analysed by the methods of integral breadth, variance and Fourier transform and fine structural parameters calculated in each case. The numerical estimates of crystallite size and disorder obtained by the three different methods are shown to be reasonably consistent with one another.

Theoretical Analysis

Hosemann's model of an 'ideal paracrystal' has been assumed for the calculation of the distortion line profile generated by the imperfect specimen, because in recent years it has received widespread corroboration as the most acceptable model for the representation of the true state of order in fibrous polymers. Considering the one-dimensional case, it can be assumed that the electron density contents of various unit cells are concentrated at lattice points, which constitute an array (Fig. 1). According to Hosemann's theory, the distances $X_i$, in Fig. 1, between successive lattice points, constitute a sequence of independently and identically distributed random variables. (If we visualize the real physical structure of a fibrous polymer along the axial direction, this would imply a continuous change...
in the conformation of individual molecules because of the ability of the segments to rotate about carbon-carbon valence bonds.) The common frequency function of distance between successive lattice points is called the ‘coordination statistic’ \( h(t) \).

The higher partial statistic \( h_m(t) \) is given by the multiple convolution of \( h(t) \)

\[
\text{Var} S_m = <S_m^2> - (S_m)^2 = m \Delta^2 
\]

where \( \Delta^2 \) is the variance of spacing between the closest neighbours. The normalized distortion Fourier coefficients of the line profile are given by

\[
Y(t) = \frac{1}{\sqrt{2\pi\Delta^2}} \int e^{-t^2/2\Delta^2} e^{-2\pi i t s} ds
\]

For small \( t \), i.e. for small displacements \( S_m \), Eq. (4a) can be approximated by

\[
Y(t) \approx e^{-2\pi i t S_m} <S_m^2> 
\]

For large \( t \), according to the central limit theorem, \( h_m(t+mb) \) converges to a Gaussian distribution having a variance \( m\Delta^2 \). Therefore, we obtain using Eq. (4b)
The term \( g_b^2/b \) represents the contribution of lattice distortions to the slope of the variance-range function. The finite crystallite size adds to this a term \( 1/(2a nd) \) and the overall expression for the slope of the resultant variance-range function is:

\[
\kappa = \frac{1}{2\pi^2 M} + \frac{g_b^2}{b} \quad \text{...(13)}
\]

The specimen line profile, which is a convolution of \( I_F(s) \) and \( I_D(s) \), can be represented as a Fourier series with coefficients \( F(s)Y(s) \). The real Fourier coefficients of the specimen profile are:

\[
F_r(s) = F(s) e^{2\pi i s^a} <S^2_n> \quad \text{ ...(14a)}
\]

or by virtue of Eqs. (6) and (10)

\[
F_r(s) \approx e^{(a+\beta) s} \quad \text{with } a = \frac{2\pi^2}{b} \quad \text{and } \beta = \frac{1}{M} \quad \text{...(14b)}
\]

Taking the logarithms, we obtain from Eqs. (14a) and (14b)

\[
\ln F_r(s) = \ln F(0) - 2\pi^2 s^2 <S^2_n> \quad \text{...(15a)}
\]

\[
\approx - \left[ \frac{2\pi^2}{b} s^2 \right] + \frac{1}{M^2} \quad \text{...(15b)}
\]

Eq. (15a) forms the basis of the Warren-Averbach method of Fourier analysis, whereas the simplified form of Eq. (15b) can be used for only fibrous polymers. Thus, Eqs. (11), (13) and (15), which form the basis of three different methods of line profile analysis, require the use of multiple orders of reflection from the same set of reflecting planes.

**Experimental Procedure**

Intensity measurements were made at room temperature with a Philips diffractometer using CuK\( \alpha \) radiation at 35 kV and 25 mA. Three different instrumental geometries were used for obtaining the meridional profiles from fibrous polymers as explained in what follows.

(I) **Reflection Geometry**

*Symmetric Bragg case* — A Geiger counter was employed as a detector of X-rays and the monochromatization was achieved by the balanced filter method. The instrument line breadth was minimized by using the parafocusing reflecting geometry of the Philips diffractometer. In order to obtain the meridional profiles from fibrous polymers, the diffraction from a surface of fibre cross-sections was studied. Bleached ramie fibres were selected for this study. During this investigation it was noted that the observed line breadth varied as a function of specimen length. This effect was attributed to defocusing which would occur in reflection geometry on account of the low X-ray absorption coefficient of cellulose (\( \mu \approx 8 \)). To minimize this defocusing, a refinement of the reflection technique was made in the following way: a specimen holder having a rectangular adjustable slot of 1 cm fixed width was fabricated. Well cut fibre bundle cross-sections were packed in alternation with silver foils, 80 \( \mu \) thick, in the specimen holder such that the edges of the silver foils and the planes of the bundle cross-sections were kept flush with the surface of the holder (Fig. 2). The diffraction from this surface was recorded by the fixed-counts step scanning method using divergence and anti-scatter slits of 1/2° and a receiving slit of 0.1 mm. This procedure minimized the broadening effect due to beam penetration while at the same time maintaining the total intensity of diffraction at a satisfactory level.

(II) **Transmission Geometry**

*Symmetric Laue case* — Although the transmission method has certain advantages over the reflection method in obtaining polymeric X-ray diffraction profiles, a large amount of defocusing which is inherent in any transmission method cannot be avoided. Samples of ramie and Tufcel were selected for this study. A single bundle of parallel fibres was prepared and its axis was maintained at the angle (90° — 0°) with respect to the incident and diffracted beams. Again, as in the case of the reflection method, profiles were obtained employing a Geiger counter as a detector of X-rays. The following slit system was employed: divergence slit 1/6° for Tufcel and 1/30° for ramie, receiving slit 0.3 cm and anti-scatter slit 1°.

(III) **Transmission Geometry**

*Use of a curved crystal focalizer* — Philips (Eindhoven) have developed a focusing monochromator for transmission diffractometry which is called the...
curved crystal focalizer'. This accessory, when placed between sample and counter, considerably reduces instrumental broadening. In this paper an evaluation has been made of the effect of this monochromator on instrument broadening from cellulosic fibres. The diffraction geometry is illustrated in Fig. 3. Samples of bleached ramie and white jute were studied under this set-up. Intensity measurements were made using a scintillation counter and a pulse height discriminator, which eliminated the need for monochromatization. The slit system used was: divergence slit 2°, receiving slit 0.05 mm, with no anti-scatter slit. The profiles were obtained from chart scans which were recorded at the slowest possible scanning speed of 1/8° per min. Each profile was scanned thrice and the average profile was chosen as a true representation of the sample.

Processing of Data
The background under each profile was estimated and subtracted according to the modified Langford-Wilson technique. Corrections for specimen absorption and Lorentz polarization effects were made on all profiles, except those obtained from chart scans. The integral breadths of 006 profiles were obtained and corrected for instrumental effects by Jones' method, as described in an earlier paper. Variance-range functions for these profiles were obtained by means of a computer programme published earlier. Only the slopes of these functions were calculated and used for interpretation, because the intercepts are influenced by many errors — such as those due to non-additivity, deconvolution and finite range of profile truncation. Fourier coefficients were obtained by the Stokes method, as described in an earlier paper. Wilson technique was used; divergence slit 2°, receiving slit 0.05 mm, with no anti-scatter slit. The profiles were obtained from chart scans which were recorded at the slowest possible scanning speed of 1/2° per minute, chart speed 200 mm/hr.

Observations and Results
The meridional scattering curves (chart scans) for ramie and jute, as obtained using the curved crystal focalizer, are shown in Fig. 4. Focalizer chart scans of 020, 040 and 080 reflections from ramie and jute samples as obtained on the curved crystal focalizer [Operating conditions 35 kV, 25 mA, scanning speed 1/2° per minute, chart speed 200 mm/hr]. The slopes of the linear variance-range functions of ramie, jute and Tufcel are listed in Table 3 where \( k_0 \) and \( k_1 \) refer to the slopes of the variance-range functions of instrument and specimen profiles respectively. The plots of \( k_0 \) against \( k_1 \) are shown in Fig. 7 and within the limits of experimental

Table 2 — Integral Line Breadths of 006 Profiles of White Jute Obtained Using Curved Crystal Focalizer from Ramie, Jute and Tufcel are shown in Fig. 6. The plots are linear in accordance with the theory and confirm the existence of paracrystalline axial order in all these three cellulosic fibres.

The slopes of the linear variance-range functions of ramie, jute and Tufcel are listed in Table 3 where \( k_0 \) and \( k_1 \) refer to the slopes of the variance-range functions of instrument and specimen profiles respectively. The plots of \( k_0 \) against \( k_1 \) are shown in Fig. 7 and within the limits of experimental
Fig. 6 — Plots of $3$ versus $k^2$ for ramie, jute and Tufcel

Fig. 7 — Slope of variance-range function, $k_{os}$, plotted against $k^2$

Fig. 8 — (a) $\log_{10} F_0(t)$ plotted as a function of $S^4$ for various values of $t$; (b) function $\mathcal{V}(t)$ giving $M_1 = 90 \text{ Å}$ for Tufcel; and (c) a plot of $\log_{10} F_{080}(t)$ against $t$ for the $080$ reflection of Tufcel

Table 3 — Slopes ($[\text{Å}^{-1}] \times 10^6$) of Linear Variance-Range Functions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diffraction geometry</th>
<th>Slope of variance-range function of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$020$ Profile</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{oi}$</td>
</tr>
<tr>
<td>Ramie III</td>
<td>I</td>
<td>0.203</td>
</tr>
<tr>
<td>Jute III</td>
<td>I</td>
<td>0.203</td>
</tr>
<tr>
<td>Tufcel II</td>
<td>(Div. 1/6°)</td>
<td>0.350</td>
</tr>
</tbody>
</table>

Table 4 — Summary of Results of Line Profile Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method of analysis</th>
<th>Integral breadth</th>
<th>Variance</th>
<th>Fourier transform</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Weight average crystallite size $\bar{L}$, Å</td>
<td>Number average crystallite size $\bar{M}$, Å</td>
<td>Number average crystallite size $\bar{M}_1$, Å</td>
</tr>
<tr>
<td>Bleached ramie</td>
<td></td>
<td>560</td>
<td>390</td>
<td>90</td>
</tr>
<tr>
<td>White jute</td>
<td></td>
<td>310</td>
<td>180</td>
<td>—</td>
</tr>
<tr>
<td>Tufcel</td>
<td></td>
<td>178</td>
<td>94</td>
<td>90</td>
</tr>
</tbody>
</table>
error are linear as predicted by Eq. (13) derived for ideal paracrystallites.

In Fig. 8(a) the logarithms of the Fourier coefficients \( F_n(t) \) are plotted as a function of \( s^2 \) for various values of \( t \) at intervals of 20 Å. It can be seen that the plots are linear for \( t \leq 20 \) Å and also for \( t > 140 \) Å. This can be explained on the basis that for linear polymers like cellulose Eqs. (6) and (15a) are more accurate for very small as well as for very large values of \( t \) (as a consequence of the central limit theorem for the sums of independent random variables). The intercepts of these curves on the \( \log_{10} F_n(t) \)-axis yield the values of \( M_1 \) for Tufcel. Fig. 8(b) shows a plot of \( \log_{10} F_n(t) \) against \( t \) for the 000 reflection of Tufcel, which is linear in accordance with Eq. (15b). Taking \( M_1 \) as 90 Å, an analysis of the slope of this line yields a g-value of 1-5% for Tufcel.

Table 4 summarizes the results of line profile analysis on ramie, jute and Tufcel. It can be seen that the values of the fine structural parameters, \( g \) and \( L \) or \( M_1 \), obtained by different methods of profile analysis, are close to one another for the three samples. These results thus provide ample confirmation of the theoretical treatment presented in this paper.

**Conclusion**

1. The axial lattice structures of ramie, jute and Tufcel are "paracrystalline". The axial order is highest in ramie and lowest in Tufcel, with jute having intermediate order.

2. Different methodologies for obtaining the meridional profiles are basically equivalent. However, the use of chart scans in conjunction with a curved crystal focalizer and a pulse height discriminator appears to be most suitable for line profile studies.

3. The consistency and mutual agreement of results obtained using integral breadth, variance and Fourier methods of analysis provide a verification of the theoretical treatment.

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**References**