

Try (5 1 7).

1.  $(2 \times 5 + 4 \times 1 + 3 \times 7) \cdot 35 = -1$  modulo 6, and the origin may be fixed by this reflection.

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**Molecular orientation distribution derived from an arbitrary reflection.** By R. LOVELL and G. R. MITCHELL, *Department of Metallurgy and Materials Science, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, England*

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### Abstract

A straightforward method using Legendre series enables the orientation distribution in a specimen with uniaxial symmetry to be derived from the azimuthal profile of a single arbitrary reflection. Moreover, the moments of the distribution  $\langle P_{2n}(\cos \alpha) \rangle$  can be obtained directly from the azimuthal profile without needing to calculate the complete distribution.

Pole figures derived from X-ray diffraction measurements are the standard method of quantifying orientation in crystalline materials. Similarly, the azimuthal profiles of the diffuse arcs found for liquid crystals (Leadbetter & Wrighton, 1979) and non-crystalline polymers (Wilchinsky, 1968) have been used to give a measure of orientation.

In polymers and liquid crystals, it is usually the orientation distribution for the molecular axes which is required, but this is only obtained directly from a pole figure if there is a strong reflection from planes perpendicular to the molecular axes. However, Wilchinsky (1963) has shown that, provided the molecules are random about their axes, a single arbitrary reflection can give the value of  $\langle \cos^2 \alpha \rangle$ , where  $\alpha$  is the angle between the molecular axis and the specimen axis.

In this communication we show that, for a specimen with uniaxial symmetry, the higher moments of the orientation distribution can also be obtained from the azimuthal profile of an arbitrary reflection. Hence the full orientation distribution can be calculated without recourse to solving integral equations or inverting matrices.

The scattering from a distribution of independent molecules is given by a convolution of the orientation distribution of molecular axes with the scattering for a single molecule (Ruland & Tompa, 1968). If both the orientation distribution  $D(\alpha)$  and the molecular scattering  $I^m(\alpha)$  have cylindrical symmetry, then the resultant scattering  $I(\alpha)$  also has cylindrical symmetry (Deas, 1952) and all three functions can be expanded in series of even-order Legendre polynomials ( $P_{2n}$ ), e.g.

$$I(\alpha) = \sum_{n=0}^{\infty} I_{2n} P_{2n}(\cos \alpha),$$

where

$$I_{2n} = (4n + 1) \int_0^{\pi/2} I(\alpha) P_{2n}(\cos \alpha) \sin \alpha \, d\alpha.$$

Similar formulae apply to  $D(\alpha)$  and  $I^m(\alpha)$ .

It has been shown (Deas, 1952) that the coefficients of the three series are related by

$$I_{2n} = \frac{2\pi}{4n + 1} D_{2n} I_{2n}^m,$$

which implies that

$$\langle P_{2n} \rangle_I = \langle P_{2n} \rangle_D \langle P_{2n} \rangle_{I^m},$$

where

$$\langle P_{2n} \rangle_I = \frac{\int_0^{\pi/2} I(\alpha) P_{2n}(\cos \alpha) \sin \alpha \, d\alpha}{\int_0^{\pi/2} I(\alpha) \sin \alpha \, d\alpha}. \quad (1)$$

Hence, if  $I(\alpha)$  and  $I^m(\alpha)$  are known, we can derive the orientation parameters of the distribution:

$$\langle P_{2n} \rangle_D = \frac{\langle P_{2n} \rangle_I}{\langle P_{2n} \rangle_{I^m}}.$$

Now, a sharp reflection at angle  $\alpha_0$  to the molecular axis gives

$$\langle P_{2n} \rangle_{I^m} = P_{2n}(\cos \alpha_0)$$

and therefore the orientation parameters are given by

$$\langle P_{2n} \rangle_D = \frac{\langle P_{2n} \rangle_I}{P_{2n}(\cos \alpha_0)}. \quad (2)$$

For the special cases  $\alpha_0 = 0$  or  $\alpha_0 = \pi/2$  this becomes

*Meridional reflection* ( $\alpha_0 = 0$ ):  $\langle P_{2n} \rangle_D = \langle P_{2n} \rangle_I$ ;

*Equatorial reflection* ( $\alpha_0 = \pi/2$ ):

$$\langle P_{2n} \rangle_D = \frac{(-1)^n 2^{2n} (n!)^2}{(2n)!} \langle P_{2n} \rangle_I.$$

The expression for the equatorial case is easier to use than the methods previously proposed (Hermans, Hermans, Vermaas & Weidinger, 1946; Seitsonen, 1968). The first four orientation parameters are given by

$$\langle P_2 \rangle_D = -2 \langle P_2 \rangle_{\text{eq}}$$

$$\langle P_4 \rangle_D = \frac{8}{3} \langle P_4 \rangle_{\text{eq}}$$

$$\langle P_6 \rangle_D = \frac{16}{5} \langle P_6 \rangle_{\text{eq}}$$

$$\langle P_8 \rangle_D = \frac{128}{35} \langle P_8 \rangle_{\text{eq}}$$

where the  $\langle P_{2n} \rangle_{\text{eq}}$  are derived from (1) with  $\alpha$  measured from the meridian. The expression for  $\langle P_2 \rangle_D$  is implicit in Wilchinsky's (1963) formula for  $\langle \cos^2 \alpha \rangle$ .

For many non-crystalline polymers and perhaps also for some liquid crystals, it is unjustified to approximate the molecular scattering  $I^m(\alpha)$  by a sharp reflection. In these cases, particularly for liquid crystals and rigid-chain molecules, it may be possible to calculate the cylindrically averaged scattering from a molecule and thus derive a form for  $I^m(\alpha)$ . When this is not possible, however, an approximate correction factor for  $\langle P_2 \rangle$  can be estimated (Pick, Lovell & Windle, 1980) but no reliable values of  $\langle P_4 \rangle$ ,  $\langle P_6 \rangle$  etc. can be obtained.

When the molecular scattering can be taken to be a sharp reflection, the values of  $\langle P_{2n} \rangle_D$  derived from (2) may be used to give the coefficients in the Legendre series for  $D(\alpha)$ :

$$D_{2n} = \frac{4n+1}{2\pi} \langle P_{2n} \rangle_D$$

Thus the full orientation distribution function can be obtained:

$$\begin{aligned} D(\alpha) &= \frac{1}{2\pi} \sum_{n=0}^{\infty} (4n+1) \langle P_{2n} \rangle_D P_{2n}(\cos \alpha) \\ &= \frac{1}{2\pi} \sum_{n=0}^{\infty} (4n+1) \langle P_{2n} \rangle_I \frac{P_{2n}(\cos \alpha)}{P_{2n}(\cos \alpha_0)} \end{aligned} \quad (3)$$

For the special cases this becomes

*Meridional reflection:*

$$\begin{aligned} D(\alpha) &= \frac{1}{2\pi} \sum_{n=0}^{\infty} (4n+1) \langle P_{2n} \rangle_I P_{2n}(\cos \alpha) \\ &= \frac{I(\alpha)}{2\pi \int_0^{\pi/2} I(\alpha) \sin \alpha \, d\alpha} \end{aligned}$$

as expected.

*Equatorial reflection:*

$$\begin{aligned} D(\alpha) &= \frac{1}{2\pi} \sum_{n=0}^{\infty} (4n+1) \times \frac{(-1)^n 2^{2n} (n!)^2}{(2n)!} \langle P_{2n} \rangle_I P_{2n}(\cos \alpha) \\ &= \frac{1}{2\pi} \left[ 1 - 10 \langle P_2 \rangle_I P_2(\cos \alpha) + \frac{72}{3} \langle P_4 \rangle_I P_4(\cos \alpha) \right. \\ &\quad \left. - \frac{208}{3} \langle P_6 \rangle_I P_6(\cos \alpha) + \dots \right]. \end{aligned}$$

The number of terms needed in these series depends on the sharpness of  $D(\alpha)$ . It is unlikely that more than about seven terms will be needed to describe the  $D(\alpha)$  usually found.

No general method of deriving  $D(\alpha)$  from  $I(\alpha)$  seems to have been given previously. However, for an equatorial reflection, Hermans *et al.* (1946) have shown that Kratky's (1933) expression

$$I_{\text{eq}}(\alpha) = \int_{\pi/2-\alpha}^{\pi/2} \frac{D(\alpha') \sin \alpha' \, d\alpha'}{(\sin^2 \alpha' - \cos^2 \alpha)^{1/2}} \quad (4)$$

can be inverted to obtain

$$D(z) = \frac{1}{2\pi} \frac{d}{dz} \int_0^z \frac{y I_{\text{eq}}(y) \, dy}{(z^2 - y^2)^{1/2}} \quad (5)$$

where  $z = \cos \alpha'$  and  $y = \sin \alpha$ .

Seitsonen (1968, 1973) has given numerical methods for evaluating this, using points equally spaced in either  $y$  or  $\alpha$ . For  $N$  equal intervals in  $\alpha$ , the formulae are (after correction)

$$D(\alpha_{m+1/2}) = \frac{1}{\pi^2} \frac{N}{\sin \alpha_{m+1/2}} [S(m) - S(m+1)] \quad (6)$$

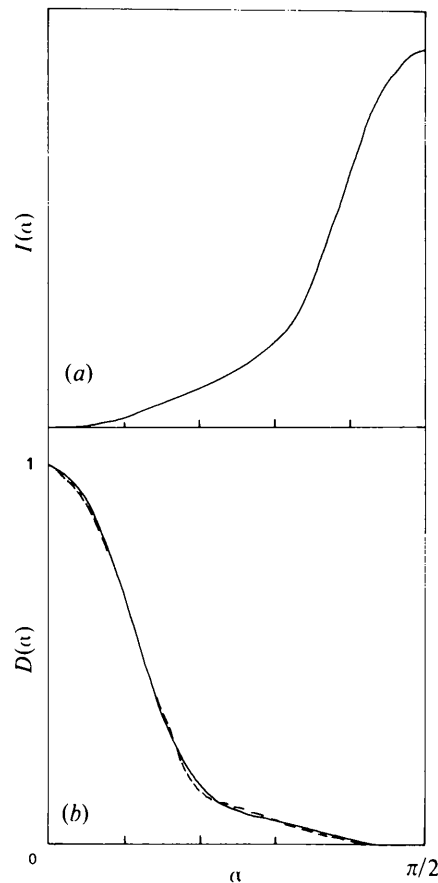


Fig. 1. Comparison of  $D(\alpha)$  derived from an equatorial arc  $I(\alpha)$  by two methods. (a) Azimuthal profile of equatorial arc of quenched *i*-PS (Lovell & Windle, 1976). (b) —  $D(\alpha)$  from equation (1) with  $N_1 = 20$  intervals and summing the first seven terms ( $n = 0-6$ ) of equation (3). ---  $D(\alpha)$  from Seitsonen's (1973) formulae [equations (6) and (7)] with  $N = 100$  intervals.

where  $0 \leq m \leq (N - 1)$ ,

$$S(m) = \sum_{n=m}^{N-1} I(\alpha_{N-n-1/2}) |(\cos^2 \alpha_m - \cos^2 \alpha_{n+1})^{1/2} - (\cos^2 \alpha_m - \cos^2 \alpha_n)^{1/2}| \quad (7)$$

and

$$\alpha_n = \left( \frac{n}{N} \right) \frac{\pi}{2}$$

This method uses a histogram approximation to  $I(\alpha)$  in evaluating the integral of (5) and a linear approximation in calculating the derivative. Moreover, the value of  $D(\alpha)$  at the end points ( $\alpha = 0$  or  $\pi/2$ ) cannot be calculated. For both these reasons, the value of  $N$  needs to be carefully chosen for accurate results.

A slightly different method of inverting (4) has recently been given by Biangardi (1980). This uses Fourier series and may be more accurate than Seitsonen's (1968) approximation.

For the Legendre-series method, the  $\langle P_{2n} \rangle_l$  were calculated from (1) with Simpson's rule with  $N_1$  intervals and the distribution  $D(\alpha)$  was obtained by summing the first few terms in (3).

The result of using (3) is compared with that of Seitsonen's formulae in Fig. 1. The methods were applied to the equatorial arc (at  $2\theta = 9^\circ$  for Cu  $K\alpha$  radiation) of quenched isotactic polystyrene (*i*-PS) oriented by extrusion (Lovell & Windle, 1976). It can be seen that the two methods are in

good agreement and in fact the shape of  $D(\alpha)$  is quite similar to  $I(\alpha)$ .

We conclude that the method based on Legendre series is easier to use if the  $\langle P_{2n} \rangle$  are all that are required, and even when the full orientation distribution is wanted this method is more straightforward than those used previously. No other method appears to have been proposed for a general reflection.

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#### Tensor properties and rotational symmetry of crystals. I and II. Erratum. By F. G. FUMI and C. RIPAMONTI, Istituto di Scienze Fisiche, Università di Genova, Italy and GNSM-CNR, Unità di Genova, Italy

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#### Abstract

In the two papers by Fumi & Ripamonti [*Acta Cryst.* (1980), **A36**, 535–551; 551–558] three errors have been printed. In paper I on page 543 in the last block of equations for Rank 6, the second term on the right-hand side of the fourth equation should read  $-\frac{1}{6}(x\dot{x}\dot{y}\dot{y}\dot{x})x$  rather than  $\frac{1}{6}(x\dot{x}\dot{y}\dot{y}\dot{x})x$

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#### Treatment of diffraction data from protein crystals twinned by merohedry: Erratum. By RICHARD G. FISHER\* and ROBERT M. SWEET, Department of Chemistry and Molecular Biology Institute, University of California, Los Angeles, California 90024, USA

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#### Abstract

A printer's error has occurred in Fisher & Sweet [*Acta Cryst.* (1980), **A36**, 755–780]. Seven lines from the bottom of the left-hand column of page 755 a bar has been omitted from *khil*. The sentence should read:

and the second term on the right-hand side of the fifth equation should read  $\frac{1}{6}(y\dot{y}\dot{x}\dot{y}\dot{x})x$  rather than  $\frac{1}{6}(y\dot{y}\dot{x}\dot{y}\dot{x})x$ . In paper II on page 553, Table I, part (b), the sixth line on the right-hand side should read  $c - (-1)^n p_1 c$  rather than  $c - (-1)^n p_1 c$ .

All information is given in the *Abstract*.

Although distinct twin domains can sometimes be distinguished in the polarizing microscope, the twinning is of the twin-lattice-symmetry type (Donnay & Donnay, 1974) in which reflection *hkil* of crystal I is superimposed onto reflection *khil* of crystal II.

All information is given in the *Abstract*.