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The Effect of Disorientation on the Intensity Distribution of Non-crystalline Fibres. I. Theory

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The intensity function in reciprocal space is derived for the case of non-crystalline fibres with a Gaussian distribution of orientations. An expression is found relating the observed intensity function with the weighted integral along a circle of the intensity derived from the molecular structure factor. From this result in the case where the layer-line width is very small a correction factor may be derived which, if applied to the observed intensity, yields the intensity which would be obtained from a perfectly orientated fibre. The general problem of correcting for disorientation can only be treated by a numerical deconvolution procedure.

Introduction

We are concerned with the problem of calculating the intensity to be observed in diffraction from slightly disorientated fibres and gels such as tobacco mosaic virus (see, for example, Franklin & Holmes, 1958) and non-crystalline DNA fibres (see Langridge, Wilson, Hooper, Wilkins & Hamilton, 1960). Typically, such molecules are periodic in their length, so that the diffraction is confined to layer lines. However, the degree of correlation between the positions of neighbouring particles is slight so that each particle scatters independently. Furthermore, there is no azimuthal correlation between particles so that one observes, essentially, the cylindrically averaged scattering from a single particle. The intensity along each layer line is continuous, being an expression of the molecular transform, and there are no Bragg reflexions. Inevitably, the particle axes are not exactly parallel, and each point on any layer line becomes smeared out in reciprocal space into an arc forming part of a Debye–Scherrer ring. The observed intensity is thus related to the molecular transform by a folding process which we investigate below.

The problem of calculating the intensity function from assemblages of molecules having partial alignment has been treated by Deas (1952). Deas expands the distribution function of particle axes in terms of spherical harmonics, and in order to apply his results one must also expand the calculated intensities in spherical harmonics. These methods are admirable for large disorientations, but are inconvenient for the case of small disorientations outlined above. Moreover, further analysis of the diffraction pattern frequently makes it desirable that one expresses one's results in cylindrical polar coordinates. Therefore the derivation given below does not follow Deas, but uses methods which allow the intensity to be expressed in cylindrical polar coordinates, and restricts discussion to the effects of small disorientations.

Below we assume that overlap of layer lines does not occur, and that the particle distribution function has a simple form (Gaussian).

The particle distribution function

We consider a sol wherein all the particles are orientated about a common axis but are subject to random Brownian motion. The distribution of particles is given by the Boltzmann law. Thus, if the restoring force is a linear function of displacement, the probability of finding particles at an angle α to the common axis in an element of solid angle $d\Omega$ is $N(\alpha)d\Omega/4\pi$, where

$$N(\alpha)=\frac{2}{\alpha_0^2}\exp\left(\frac{-\alpha^2}{2\alpha_0^2}\right) \qquad (1)$$

and where α_0 is a parameter depending upon concentration, *p*H, temperature, *etc.* that we shall call the disorientation parameter.

Calculation of the intensity in the disorientated pattern

Let the intensity function at the point B (Fig. 1) in reciprocal space be I. It is convenient to refer to B by two coordinate systems: the polar coordinates v and σ; and the Cartesian coordinates R and Z.

The total intensity at B is calculated by integrating over all possible particle orientations taking account of the density of particles in any particular direction and strength of the intensity (from the calculated transform) that such particles contribute at B. This integration may be effected by evaluating the calculated intensity for any one cone of particles lying at an angle γ to the line OB, by evaluating how many particles may lie between γ and $\gamma+d\gamma$, and by integrating over all such cones. The calculated intensity from a general particle may be conveniently written as a function of the two orthogonal coordinates l and s. l and s give the position of the point B referred to the axis of the particle. Clearly for all particles lying on a cone of constant γ, l and s are constant and the calculated intensity is constant. Furthermore γ, l, v and s are related by the right-angled triangle OAB so that

$$l=v\cos\gamma \qquad (2a)$$

$$s=v\sin\gamma\,. \qquad (2b)$$

The calculated intensity may be written as the product of two terms: $I_{\text{calc}}(s)$ describing the distribution along a layer line, and $f(l)$ describing the distribution across a layer line. Performing the operation described above we find the total intensity at the point B is

$$I=\int_{\Omega} I_{\text{calc}}(s)f(l)N(\alpha)\frac{\mathrm{d}\Omega}{4\pi} \tag{3}$$

$$=\frac{1}{4\pi}\int_{\varphi=0}^{2\pi}\int_{\gamma=0}^{\pi} I_{\text{calc}}(s)f(l)N(\alpha)\sin\gamma\,\mathrm{d}\gamma\mathrm{d}\varphi \tag{3a}$$

where α is the disorientation angle ($O''OC$ in Fig. 1) and where φ is the azimuthal coordinate around OB of the general particle with axis OC.

To proceed further in the evaluation of (3*a*) we transform variables so as to consider together all planes with height l in the calculated intensity distribution. If the thickness of such a plane is dl then the range (dγ) of particle orientations which can contribute to the point B by means of planes in the calculated intensity distributions at height l is found by differentiating (2*a*), *viz.*

$$-\frac{\mathrm{d}l}{v}=\sin\gamma\mathrm{d}\gamma\,.$$

Substituting l for γ in (3*a*) we get

$$I=\frac{1}{4\pi v}\int_{\phi=0}^{2\pi}\int_{l=0}^{v} I_{\text{calc}}(s)f(l)N(\alpha)\mathrm{d}l\mathrm{d}\varphi\;; \tag{4}$$

(4) is generally true. Now

$$N(\alpha)=\frac{2}{\alpha_0^2}\exp\left(-\frac{\alpha^2}{2\alpha_0^2}\right) \tag{1}$$

and referring to the stereogram (Fig. 2) we see that

$$\cos\alpha=\cos\gamma\cos\sigma+\sin\gamma\sin\sigma\cos\varphi\,. \tag{5}$$

Hence for small α, by substitution and expansion

$$\tfrac{1}{2}\alpha^2\simeq 1-\frac{zl}{v^2}-\frac{sR}{v^2}\cos\varphi\,. \tag{6}$$

Inserting (6) in (1) and (1) in (4) we obtain

$$I=\frac{1}{2\pi v\alpha_0^2}\int_{\phi=0}^{2\pi}\int_{l=0}^{v} I_{\text{calc}}(s)f(l)$$
$$\times\exp\left[-\frac{1}{\alpha_0^2}\left(1-\frac{zl}{v^2}-\frac{sR\cos\varphi}{v^2}\right)\right]\mathrm{d}l\mathrm{d}\varphi\,. \tag{7}$$

Using the integral representation of a Bessel function

$$I_0(x)=\frac{1}{2\pi}\int_{\phi=0}^{2\pi}\exp(x\cos\varphi)\mathrm{d}\varphi$$

[see Abramowitz & Stegun (1965), p. 374], (7) becomes

$$I=\frac{1}{v\alpha_0^2}\int_{l=0}^{v} I_{\text{calc}}(s)f(l)\exp\left[-\frac{1}{\alpha_0^2}\left(1-\frac{zl}{v^2}\right)\right]$$
$$\times I_0\left(\frac{sR}{v^2\alpha_0^2}\right)\mathrm{d}l\,. \tag{8}$$

Defining the function

$$i_0(x)=I_0(x)e^{-x}$$

we may regroup (8), giving

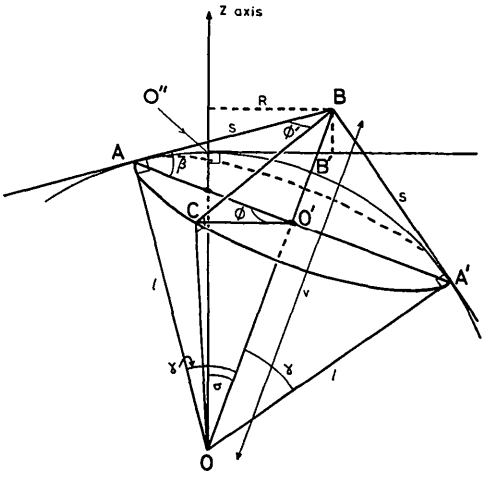

Fig. 1. The variables used in deriving the disorientation correction. The general point B may be described by the reciprocal-space Cartesian coordinates (R,Z) or the spherical polar coordinates $(v,\ \sigma)$. For any given particle the Cartesian coordinates of B in the *particle frame of reference* are (s,l). The particles contributing intensity to B may be grouped in cones of semi-angle γ corresponding to sheets of intensity at height l in the particle frame of reference. The angle of disorientation of a general particle (*e.g.*, a particle with axis OC) is $(O''CO=\alpha)$. φ is the azimuthal coordinate of the general particle OC measured around an axis defined by the vector v (OB).

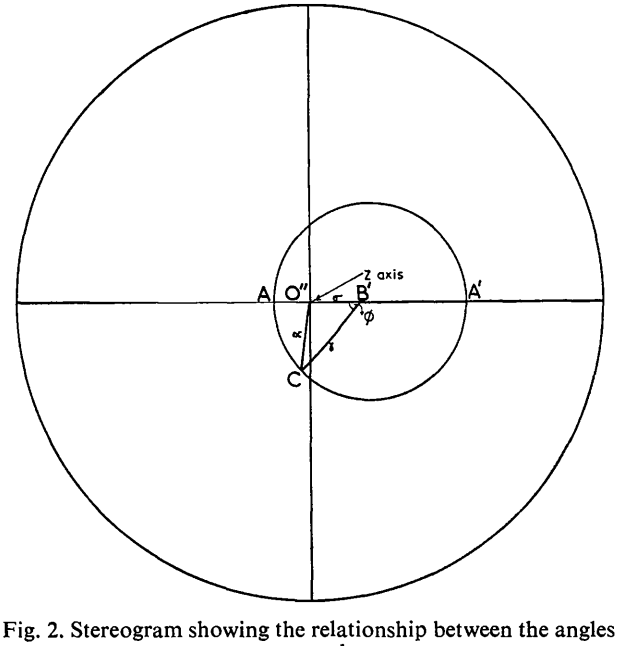

Fig. 2. Stereogram showing the relationship between the angles α, γ, φ and σ.

$$I=\frac{1}{v\alpha_0^2}\int_{l=0}^{v} I_{\text{calc}}(s)f(l)\exp\left[-\frac{(s-R)^2+(Z-l)^2}{2\alpha_0^2v^2}\right]\times i_0\left(\frac{sR}{v^2\alpha_0^2}\right)\mathrm{d}l. \quad (9)$$

Equation (9) is the required relationship between I_{calc} and I.

The structure of the integrand in equation (9) may be understood by reference to Fig. 3(*a*) which shows the geometrical relationships between the variables l,s,v, and γ embodied in equation (2). Furthermore Fig. 3(*a*) may be reinterpreted as representing a plane through the intensity field of a perfectly orientated fibre. As l varies between $l=0$ and $l=v$ the point of integration follows a circular arc. The point B in Fig. 3(*a*) represents the origin of the exponential factor in (9). Considering the general point X, if we replace the chord BX by the arc BX (which is valid if α_0 is small) the exponential term in (9) may be written

$$\exp-\frac{(\gamma-\sigma)^2}{2\alpha_0^2}. \quad (10)$$

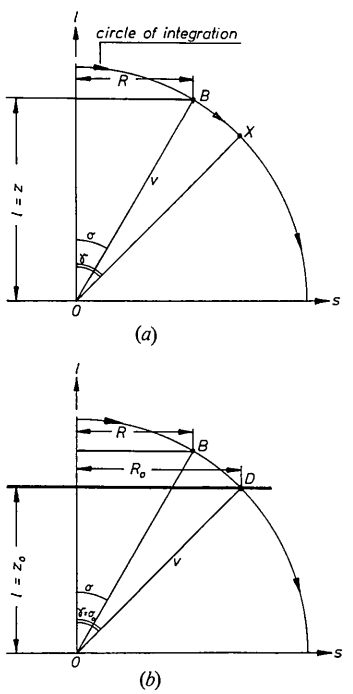

Fig. 3. (*a*) The circular arc shows the path of integration (equation 9) through the calculated intensity. The point B is the general point at which the observed intensity function is to be evaluated. The argument of the Gaussian weighting function in (9) is proportional to the square of the distance between B and a general point X on the circle of integration. This is approximately equal to the chord BX. (*b*) In many situations the calculated intensity can be represented by a very thin layer line (heavy line $l=Z_0$). The integration (equation 9) reduces to evaluating the factors of the integrand at the point (D) where the circle of integration intersects the layer line. This point corresponds to the place at which the Debye–Scherrer arc through the general point B intersects the layer line (height Z_0) from the perfectly orientated particle.

Returning to γ as a variable of integration,

$$I=\frac{1}{\alpha_0^2}\int_{\alpha=0}^{\pi} I_{\text{calc}}(s)f(l)\exp\left[-\frac{(\gamma-\sigma)^2}{2\alpha_0^2}\right]\times i_0\left[\frac{\sin\gamma\sin\sigma}{\alpha_0^2}\right]\sin\gamma\mathrm{d}\gamma \quad (11)$$

which demonstrates that I is related to the integral along a circular arc of the intensity of an ideal fibre with the weighting factor

$$\exp\left[-\frac{(\gamma-\sigma)^2}{2\alpha_0^2}\right]i_0\left[\frac{\sin\gamma\sin\sigma}{\alpha_0^2}\right]. \quad (12)$$

The case of the infinitely thin layer line

If $f(l)$ is very sharp (*e.g.* a delta function having unit weight where $l=Z_0$) then the integrand of equation (9) [or (11)] vanishes except where the circle of integration (of radius v) intersects the layer line (of height Z_0). This situation is shown in Fig. 3(*b*), point D. The coordinates of the point D are $s=R_0$, $l=Z_0$, $\gamma=\sigma_0$ where,

$$\cos\sigma_0=Z_0/v$$
$$R_0=v\sin\sigma_0.$$

If we substitute in (9) the form of the weighting factors (12) we obtain

$$I=\frac{1}{v\alpha_0^2}\int_{l=0}^{v} I_{\text{calc}}(s)f(l)\exp\left[-\frac{(\gamma-\sigma)^2}{2\alpha_0^2}\right]\times i_0\left[\frac{\sin\gamma\sin\sigma}{\alpha_0^2}\right]\mathrm{d}l. \quad (14)$$

If we introduce into (14) the condition that $f(l)$ vanishes except when $l=Z_0$ (*i.e.* at the point D), then

$$I=\frac{1}{v\alpha_0^2}I_{\text{int}}(R_0)\exp\left[-\frac{(\sigma-\sigma_0)^2}{2\alpha_0^2}\right]i_0\left[\frac{\sin\sigma\sin\sigma_0}{\alpha_0^2}\right] \quad (15)$$

where $I_{\text{int}}(R_0)$ is the value of the calculated intensity integrated across the layer line.

Except near the meridian

$$i_0\left[\frac{\sin\sigma_0\sin\sigma}{\alpha_0^2}\right]$$

is a slowly varying function of σ so that equation (15) demonstrates that the intensity variation along a Debye–Scherrer arc is a Gaussian centred on the perfectly orientated layer line. Away from the meridian (15) may be further simplified by making use of the asymptotic expansion of $i_0(x)$:

$$i_0(x)=\frac{1}{(2\pi x)^{\frac{1}{2}}} \quad (16)$$

putting

$$\sin\sigma_0\sin\sigma\simeq\frac{R_0^2}{v^2}$$

and using (16) we finally obtain

$$I=I_{\text{int}}(R_0)\frac{1}{(2\pi)^{\frac{1}{2}}}\exp-\frac{(\sigma-\sigma_0)^2}{2\alpha_0^2}\frac{1}{\alpha_0 R_0}. \quad (17)$$

Disorientation correction

For the limiting case discussed above I_{int} and I are related by a simple factor. Moreover $I_{\text{int}}(R_0)$ represents the intensity which would be observed from a perfectly orientated fibre. Therefore the intensity measured along the *middle of the layer line* [$I(R_0)$] may be used to calculate I_{int}. If we define the disorientation correction K as

$$K=I_{\text{int}}/I,$$

we see from equation (17) setting $\sigma=\sigma_0$ that

$$K=\frac{I_{\text{int}}}{I}=(2\pi)^{1/2}\alpha_0 R \quad (18)$$

[note that (18) is dimensionally correct because I_{int}/I has the dimension length^{-1}]. Within the validity of the approximations given above (*i.e.* not too near the meridian) (18) is the disorientation correction for fibres if the measurements are made at points along the middle of the layer line.

Geometrical meaning of the correction factor

The form of (18) may be illustrated by a simple geometrical construction (Fig. 4). The figure shows a section through the intensity in reciprocal space arising from three diffracting particles (*a*, *b*, and *c*). *b* is perfectly orientated, *a* and *c* are both disorientated through 5°. Each particle gives rise to a set of layer lines (0,1, 2, 3). By inspection of the zero layer line it is obvious that the fanning out of the layer lines will give rise to a relationship of the kind

$$I\propto\frac{I_{\text{int}}}{R}.$$

Rather more unexpectedly Fig. 4 demonstrates that this relationship is also valid on layer lines (1), (2) and (3) [on condition that $I_{\text{calc}}(s)$ is constant].

The simple correction factor (18) will break down near the meridian on upper layer lines because the layer lines form a caustic and not a point of intersection and because the delta function approximation to $f(l)$ is too crude. It is always possible by use of the full form of the relationship between I and I_{calc} (equation 9) to calculate I from I_{calc}. The inverse procedure near the meridian is only possible in favourable circumstances. In practice (18) also breaks down near the meridian because the X-ray spot on the film is relatively large. An investigation of this effect together with a numerical analysis of the validity of the various approximations used is given in the following paper (Stubbs, 1974).

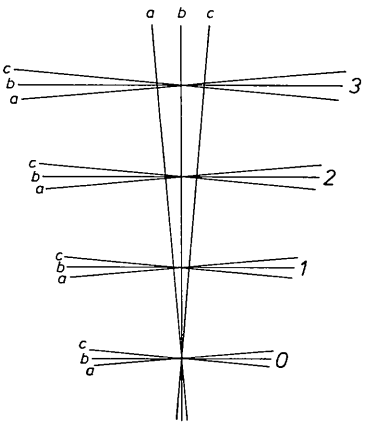

Fig. 4. A simple geometrical illustration that the disorientation correction is approximately proportional to R on all layer lines. The axes of three particles (a,b,c) are shown together with the disorientated layer lines (0,1,2,3) arising from these particles. If the density along these layer lines is uniform then it can be seen that the intensity will drop off as $1/R$ on all layer lines. Upper layer lines do not strictly intersect in a point but for small angles of disorientation the caustic formed is practically a point.

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