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Distorted Diffractors with Special Reference to Collagen Fibres

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The fan-shaped appearance of the low-angle X-ray diffraction patterns of dry collagen fibres, previously attributed to regions of disorder in the structure, is here considered to be due to regular shearing of the fibrils; it is shown that distortions of this kind lead to the observed diffraction spot shapes. First, the relation of low-angle to high-angle diffraction patterns is discussed and illustrated by optical analogues, and then the effects of longitudinal shear on two-dimensional diffractors is investigated and optical illustrations are also presented. Diffraction by a bundle of independent cylindrical fibrils, simply sheared, is discussed as a model of collagen which shows the fanning effect. Finally a particularly simple kind of random distortion is critically examined and the results compared with those of Bear & Bolduan (1951).

Introduction

It is well known that collagen fibres have a longitudinal periodic variation of structure observable by electron-microscopy, the repeat distance being about 640 Å. This large-scale variation is responsible for the low-angle X-ray diffraction pattern first resolved by Bear (1942). Later he and his colleagues used pin-hole collimation of the X-ray beam and observed that specimens of dried collagen sometimes yielded low-angle diffraction patterns in which the meridional spots were drawn out along the layer lines to an extent roughly proportional to the diffraction index, thus producing a so-called 'fanning' effect. These patterns may be found in a summary of this work by Bear (1952). It is to be emphasized that the intensities are spread along the layer lines and that this kind of distribution is distinct from the spreading of spots that may occur as a result of disorientation of fibrils in the specimen.

Bear & Bolduan (1950, 1951) have given a discussion of the fanning effect, attributing it to alternating regions of order and disorder in the fibre macro-period, and Bear (1952) has identified the assumed regions of disorder with the sites of uptake of phospho–tungstic acid which are readily observed by electron-microscopy. These authors postulated a particular kind of disordering of the structure and worked out in detail its effect upon the diffraction pattern showing that a fanning effect would result. However, their model is not the only one capable of accounting for the fanning effect for it may be inferred from simple geometrical consideration of the observed diffraction patterns that they could be produced by a regular longitudinal shearing of the fibres. This paper examines the consequences of such shearings of diffractors, usually taken to be two-dimensional, and also discusses critically a simple example of the kind of problem considered by Bear & Bolduan (1951).

Relation between low- and high-angle diffraction patterns

The high-angle diffraction pattern due to a fibrous material such as collagen results from an intra-molecular periodic structure on the atomic scale, and the low-angle pattern from a much coarser density distribution superimposed upon the fine structure. The diffractor may be regarded as an axially periodic structure of closely spaced scattering elements whose electron density, or number density, varies periodically with a much larger period; i.e. the fine-scale diffractor has its scattering power modulated by a large-scale periodic function. The electron density may then be represented by the product of two functions, and the resulting diffraction pattern, which is the Fourier transform of this product, is given by the convolution of the transforms of the two separate functions (see for example McLachlan, 1957). If the structure is assumed to be of infinite extent the transform of the fine-structure function is a set of discrete values, the infinitely sharp diffraction orders of a wide-angle pattern. These may be represented by a set of Dirac δ functions. If it is also assumed that the transform of the modulation function decreases so rapidly that it cannot significantly overlap two of the δ functions, then on convoluting it with these δ functions there results a pattern consisting of this transform, i.e. the low-angle pattern, spread about each order of the wide-angle pattern. These conclusions are graphically illustrated by the optical diffraction patterns of Fig. 1.

Fig. 1(a) shows the diffraction pattern due to an extended two-dimensional grating, the mask for which was produced by the 'fly's eye' technique. Fig. 1(b) is the diffraction pattern due to a triangular aperture in an opaque screen. On placing this screen over the extended grating, thus modulating the transparency of the latter by a function which is a constant within the triangle and zero elsewhere, the resulting diffraction pattern was as shown in Fig. 1(*c*), which clearly shows the transform of the modulating function centred on each point of the diffraction pattern of the small-period grating. Some allowance should be made for the limited intensity range that can be conveyed by a photographic print.

Thus any periodic structure in which the scattering power is modulated by any large-scale variation produces a diffraction pattern consisting of a low-angle pattern located about each order of the high-angle pattern. Furthermore if this low-angle pattern does not extend over two or more orders of the high-angle pattern, and if the latter is sufficiently sharp, it is then a faithful Fourier transform of the modulation. However, if the fine-scale periodic structure is imperfect its high-angle diffraction pattern will consist of broadened peaks and these convoluted with a small-angle pattern may produce a diffuse distribution of intensity in which the details of the low-angle pattern may be completely obscured. But whatever the degree of order in the fine-scale structure there is always a strong and very sharp zero-order diffraction maximum (James, 1950) and consequently a low-angle pattern centred on this should appear distinctly, again provided that it is not so extensive as to overlap higher orders of the high-angle pattern. This is precisely what is observed in diffraction by collagen fibres whether wet or dry. Furthermore the nature of this low-angle pattern depends entirely upon the large-scale modulation function and is quite independent of the detailed atomic arrangement.

Distortion and disorder in collagen fibres

The diffuseness of the high-angle pattern of collagen, and the detection of the low-angle pattern only in the centre of the field, clearly indicates that the fine structure is not well ordered. The effects of disorder on the high-angle pattern have been considered in detail by Andreeva & Iveronova (1957). But, as argued above, such disorder cannot affect the nature of the low-angle pattern. This can be modified only by distortions of the structure on a scale comparable with the macro-period, and fanning of the low-angle pattern must therefore be explained in terms of such relatively large distortions. These may be introduced either by regular displacements such as a shearing or twisting of the structure, or by making small random displacements of elements of the structure which are cumulative.

Electron-micrographs of teased-out collagen fibres often show fibrils having a longitudinal shear (Fig. 2) and although the treatment of the material in this case is different from that involved in preparing specimens for the X-ray diffraction camera it is clear that sheared configurations of fibrils readily occur. It may be emphasized that the production of fanned diffraction patterns of dried collagen depends upon somewhat ill-defined pre-treatment of the fibres (Bear, 1952) which could conceivably result in the production of a bundle of fibrils sheared like those of Fig. 2.

Sheared two-dimensional diffractors

In order to simplify the discussion of the effects of shearing attention will be directed mainly to two-dimensional gratings which when undistorted have a periodic density variation along one direction only. First a simple argument showing that shearing must result in a fanning effect will be presented.

Consider an infinitely extended grating consisting of parallel lines of scattering matter spaced at intervals d (Fig. 3). Such a grating produces in reciprocal space a set of points along the z^* axis with separation $d^* = 1/d$. If the grating is sheared along the z direction as shown the result is equivalent to a grating lying along OP with spacing $d \cos \alpha$. This grating yields a diffraction pattern represented in reciprocal space by the points along OP' with spacing $d^*/\cos \alpha$. The distortion of the grating has therefore translated the reciprocal lattice points along lines perpendicular to OZ^*. Thus a set of gratings with angles of shear uniformly distributed between $\pm \alpha$ and diffracting independently must produce a diffraction pattern in which the intensity maxima are drawn out along the layer lines by an amount proportional to the index of diffraction, i.e. a fanned pattern.

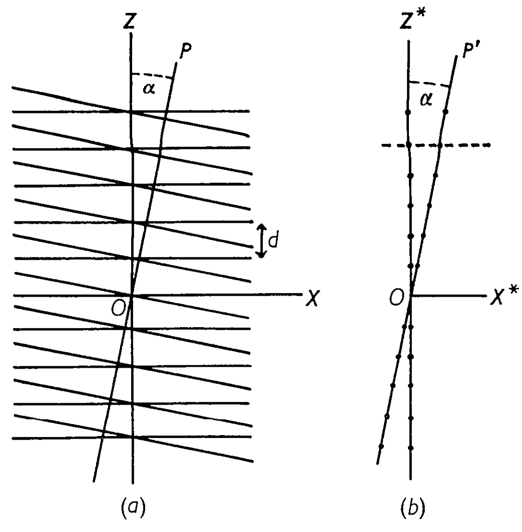

Fig. 3. (*a*) A plane grating of infinite extent lying along OZ sheared to become a grating lying along OP with spacing $d \cos \alpha$. (*b*) The intensity distribution in reciprocal space consisting of points along OZ^* for the undistorted grating, and along OP' after shearing. Corresponding points lie on lines parallel to OX^*.

In this simple example the distribution of intensity along the lines is uniform, but clearly non-uniform distributions of the shearing angles, or more elaborate distortions, would give other intensity distributions; in addition there is the possibility that the distorted

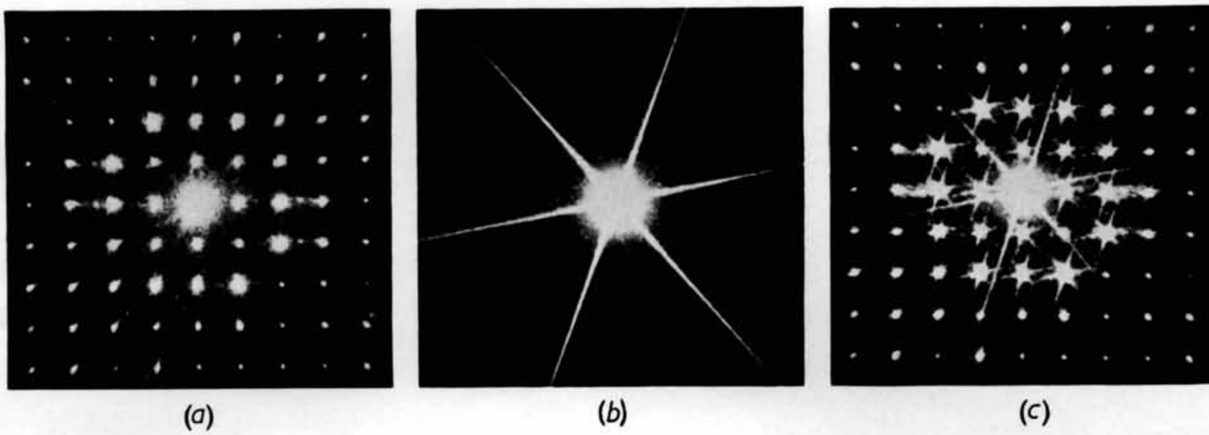

Fig. 1. (*a*) Optical diffraction pattern of an extended two-dimensional diffractor of small periodicity. (*b*) Optical diffraction pattern of a triangular aperture large compared with the period of the diffractor producing (*a*). (*c*) The diffraction pattern which results from superposing the triangular aperture on the two-dimensional diffractor.

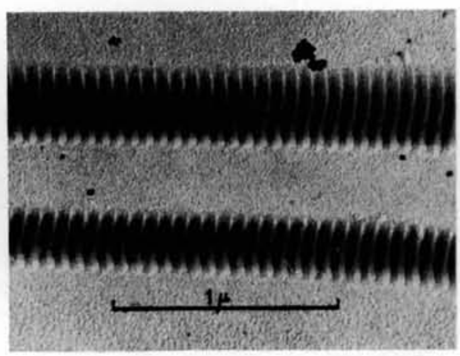

Fig. 2. Electron-micrographs of collagen fibres showing longitudinal shear.

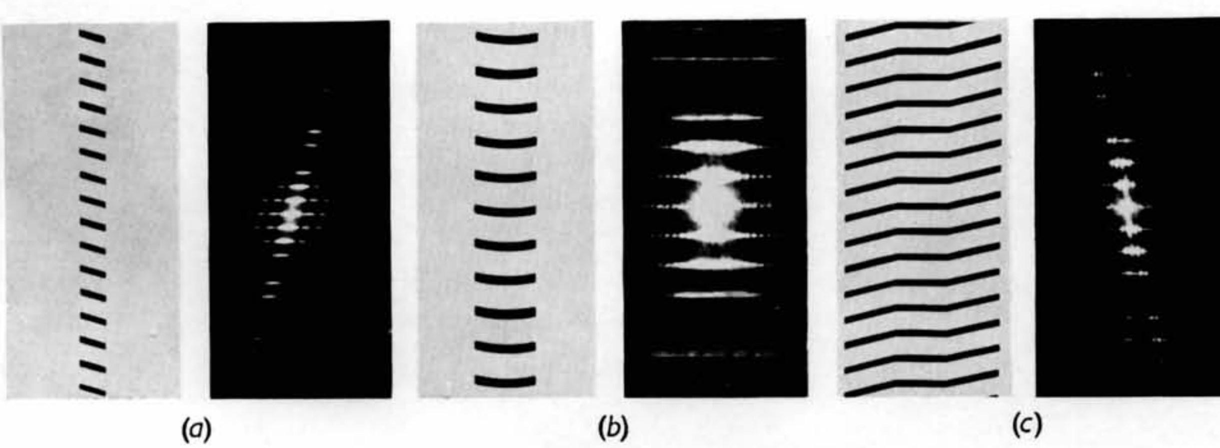

Fig. 7. Optical diffraction patterns and prints from the corresponding masks. (*a*) A linearly sheared grating to be compared with Fig. 3. (*b*) An approximately parabolically sheared grating to be compared with Fig. 5. (*c*) A grating consisting of an undistorted part and two-displaced linearly sheared sections illustrating interference effects in the off-axis part of the pattern.

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gratings of a set may not all diffract independently, in which case interference of diffracted beams reaching a given layer line would further modify the intensity distributions.

General expression for line shape due to shearing

Consider a two-dimensional object lying in an x, z plane which has electron density $\varrho(x, z)$. If $\mathbf{s}_0$ and $\mathbf{s}$ are unit vectors parallel to the incident X-ray beam and a diffracted beam respectively, and if $\mathbf{r}$ is the vector defining the point x, z then the intensity at the point $Q(R, \theta, \varphi)$, where R, θ and φ are defined by Fig. 4, is given by

$$|Y|^2 = I_0^2/(R^2) \left| \iint \varrho(x, z) \exp(-ik\mathbf{r}.\mathbf{s}-\mathbf{s}_0)\,dxdz \right|^2. \quad (1)$$

Here $k=2\pi/\lambda$ where λ is the wavelength of the incident radiation, and I_0 is the amplitude at unit distance of the wave scattered by one electron in the direction $\mathbf{s}$. I_0 is a function of direction but in considering low-angle diffraction θ and φ are so small that I_0 may be regarded as constant.

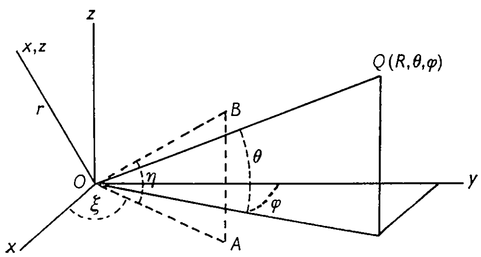

Fig. 4. Definition of coordinates and other variables.

The development of this formula for the case where ϱ is a function of z only, having a period of $2d$, is straightforward. For a grating extending from $x=-X$ to $x=X$, and from $z=-Nd$ to $z=Nd$ (i.e. having a large number N of complete periods) one finds for the intensity of the nth order of the diffraction pattern.

$$|Y_n|^2 = 4N^2X^2 \frac{I_0^2}{R^2} \left(\frac{\sin kX\varphi}{kX\varphi}\right)^2 |F_n|^2 , \quad (2)$$

where

$$F_n = \int_{-d}^{d} \varrho(z) \exp(-in\pi(z/d))\,dz .$$

The intensity variation in azimuth is that due to diffraction by a single slit of width $2X$ and is independent of the index of diffraction.

Suppose now that the diffractor is sheared parallel to OZ so that a line of constant ϱ which was previously parallel to OX becomes a curve. If $\Delta(x)$ (a function of x only) is the displacement at x parallel to OZ the intensity at Q due to the distorted grating is, by a modification of equation (1)

$$|Y|^2 = \frac{I_0^2}{R^2} \left| \int_{-X}^{X} \int_{-L}^{L} \varrho(z-\Delta) \exp(-ik\mathbf{r}.\mathbf{s}-\mathbf{s}_0)\,dxdz \right|^2 . \quad (3)$$

Write

$$\varrho(z) = \sum_{-\infty}^{\infty} A_p \exp(ip\pi(z/d))$$

and substitute into (3). Then since

$$\begin{aligned} \mathbf{r}.\mathbf{s}-\mathbf{s}_0 &= x\cos\theta\sin\varphi + z\sin\theta \\ &= x\varphi + z\theta \end{aligned}$$

for low-angle diffraction, and because the intensity maxima occur where

$$k\theta = n(\pi/d)$$

one finds for the intensity in the nth order

$$|Y_n|^2 = N^2 \frac{I_0^2}{R^2} |A_n|^2 \left| \int_{-x}^{x} \exp(-in\pi(\Delta/d) - ikx\varphi)\,dx \right|^2 .$$

Thus, in general, as the result of a longitudinal shear the intensity along the layer lines is given by the factor

$$\Phi_n^2 = \left| \int_{-x}^{x} \exp(-i(n\pi/d)\Delta(x) - ik\varphi x)\,dx \right|^2$$

which is independent of the linear density variation of the undistorted diffractor.

Some special cases of shearing

Φ_n^2 may be readily evaluated for the linear shearing function $\Delta=ax$ to give

$$\Phi_n^2 = 4X^2 \left[\frac{\sin(n\pi(a/d)+k\varphi)X}{(n\pi(a/d)+k\varphi)X}\right]^2$$

which yields a pattern of spots of the same shape as for the undistorted grating but shifted off-axis by an amount proportional to n. This is similar to the situation represented in Fig. 3 except that the grating is now of finite width.

Any kind of shearing which can be made up of linear displacements can be treated similarly. Among other shearing functions which are amenable a parabolic distortion $\Delta=ax^2$ has been considered. This gives Φ_n^2 in terms of Fresnel integrals:

$$\Phi_n^2 = \frac{2d}{na} \left\{ \left[\int_\beta^\gamma \cos\tfrac{1}{2}(\pi)y^2dy \right]^2 + \left[\int_\beta^\gamma \sin\tfrac{1}{2}(\pi)y^2dy \right]^2 \right\} ,$$

where

$$\beta = (-X+\xi)\left(\frac{2d}{n\pi}\right)^{\frac{1}{2}}, \quad \gamma = (X+\xi)\left(\frac{2d}{n\pi}\right)^{\frac{1}{2}}$$

$$\xi = \frac{1}{2a}\frac{kd}{n\pi}\varphi .$$

In Fig. 5 are shown the intensity profiles for the first eight orders of such a grating. The values of the parameters given were chosen for ease of calculation and correspond to the sketched grating. Evidently a slightly distorted object produces a well fanned diffraction pattern.

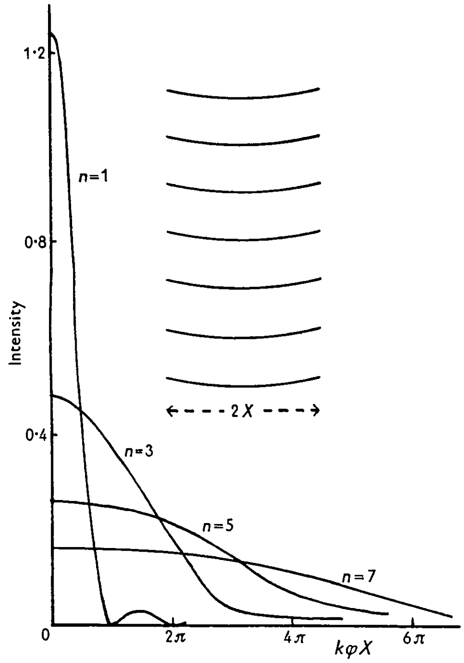

Fig. 5. The intensity distributions in the 1st, 3rd, 5th, and 7th orders of a diffractor sheared parabolically as shown. Fanning of the pattern is shown by the increasing widths of the distributions with order.

Further complication of the intensity profiles occurs when the shearing is such that two separated parts of the grating diffract into the same region of reciprocal space, so that interference occurs. An example of a distortion producing this kind of effect is afforded by a sinusoidal shearing function, conveniently taken as

$$\Delta = -a \sin \pi(x/X)$$

for which the grating is represented in Fig. 6 along with spot shapes calculated for two different orders of diffraction. The angular distribution function is

$$\Phi_n = 2X\mathbf{J}_\nu(z) ,$$

where $\nu = k\varphi X/\pi$, $z = n\pi(a/d)$ and $\mathbf{J}_\nu(z)$ is Anger's function (Watson, 1922). This function we have tabulated in sufficient detail to allow the plotting of Φ_n^2 for the first and tenth orders of a grating for which $a/d = 1/20$ (Fig. 6). These curves are sufficient to show the development of fanning with strong intensity variation along the layer lines.

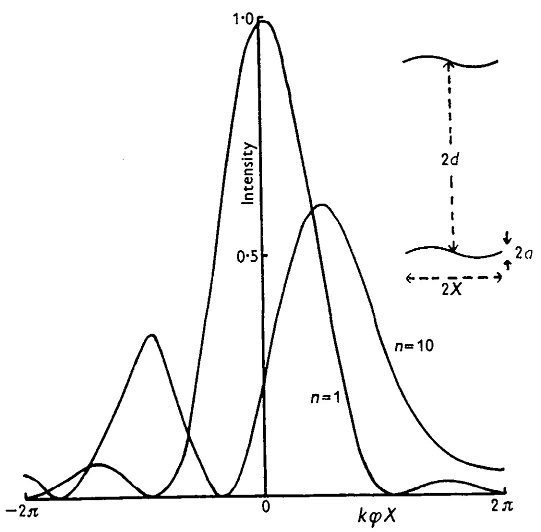

Fig. 6. The intensity distributions in the 1st and 10th orders of the pattern due to sinusoidal shearing. One period of the sheared grating is shown to scale. Fanning is evident, with the appearance of a double peak in the higher orders.

Replication of gratings

A set of gratings arranged with some degree of order must be expected to show further peculiarities of spot shapes as a result of interference between beams from different gratings. In this connection it is instructive to consider two similar gratings displaced relative to one another. Referring to Fig. 4, suppose the grating displaced so that its origin moves to the point in the x, z plane defined by the vector $\mathbf{t}$ while remaining parallel to OZ.

The diffracted wave amplitude at Q due to the displaced grating is, from (1),

$$Y_t = \frac{I_0}{R}\iint \varrho(\mathbf{r}+\mathbf{t}) \exp(-ik\mathbf{r}+\mathbf{t}.\mathbf{s}-\mathbf{s}_0)dxdz .$$

Since $\varrho(\mathbf{r}+\mathbf{t}) = \varrho(\mathbf{r})$

$$Y_t = \exp(-ik\mathbf{t}.\mathbf{s}-\mathbf{s}_0)Y.$$

The resultant intensity at Q due to the original and displaced gratings diffracting together is

$$|Y_r|^2 = |1+\exp(-ik\mathbf{t}.\mathbf{s}-\mathbf{s}_0)|^2|Y|^2$$
$$= 4\cos^2(\tfrac{1}{2}k\mathbf{t}.\mathbf{s}-\mathbf{s}_0)|Y|^2.$$

The pattern due to the single grating is modulated by the function $\cos^2(\frac{1}{2}k\mathbf{t}.\mathbf{s}-\mathbf{s}_0)$. If the two gratings are similarly sheared then the drawn out diffraction spots of the individual patterns might be broken up by the modulation function. For example two gratings like those of Fig. 5. placed side by side, so that $\mathbf{t}$ has only an x component of $2X$, would produce a pattern like that of Fig. 5, modulated by the function $4\cos^2 kX\varphi$. This would have the effect of breaking the higher orders into three or more spots along the layer lines.

The diffraction pattern due to a real collagen fibre is the result of diffraction by many fibrils. If these were arranged on a precise transverse lattice the diffraction effects could be calculated by an obvious extension of the above argument. Such regularity would cause a fine structure to appear in the diffraction spots, but this is not in fact observed. However, the individual fibrils cannot be completely disordered transversely, and the structure is in this respect not unlike that of a liquid, so that a coarse modulation of the pattern due to a single fibril might be expected in the higher orders of a fanned pattern.

Optical illustrations

The conclusions reached above have been verified by experiments with an optical diffractometer. The masks were made by photo-reduction of drawings of gratings, and were mounted in methyl benzoate between optical flats. Some of these results are shown in Fig. 7 and as illustrations of the previous discussions speak for themselves (see Plate 7).

The subsidiary maxima along the layer lines are more pronounced than would be the case if the gratings represented correctly the projected density of cylindrical fibres. For further relevant discussion of diffraction by curved edges see Sommerfeld's 'Optics' (1954).

Sheared cylindrical diffractors

We now have a sufficient basis for a qualitative discussion of the low-angle pattern due to a set of parallel cylindrical fibrils forming a fibre. Such a fibril lying along a z axis has, if undistorted, a Fourier transform consisting of a set of intensity discs centred on, and perpendicular to the z^* axis of reciprocal space (Bear & Bolduan, 1950). Suppose now that the cylindrical fibre is sheared so that a cross section is tilted about the y axis (Fig. 4). By analogy with the example of Fig. 7 the diffraction discs will be displaced off the z^* axis along lines parallel to x^* by amounts proportional to the indices of diffraction, the centres of the discs remaining in the x^*z^* plane. But this plane is effectively the sphere of reflection since we are concerned only with low-angle diffraction. Consequently the intersection of the sphere of reflection with the intensity discs is unaffected except for the displacement.

Next suppose the fibril to be sheared by tilting a cross section about the x axis. Now the diffraction discs will be displaced off the z^* axis along lines parallel to y^* and the centres of all the discs will then lie either behind, or in front of, the x^*z^* plane. The intersections with this plane, which is effectively the sphere of reflection, will be no longer through the diameters of the intensity discs, but through chords of decreasing length as the index of diffraction increases. Consequently the diffraction pattern will consist of spots which become narrower, and weaker in the higher orders, as compared with the pattern due to the undistorted fibril.

It follows that a fibre consisting of a set of independently diffracting fibrils equally sheared but with a variety of orientations of the planes of shearing would produce a diffraction pattern like that of Fig. 8. This figure shows results calculated for a shearing of $d/20$ and with all orientations of the plane of shear being equally likely. The derivation of the necessary formula is outlined in an appendix.

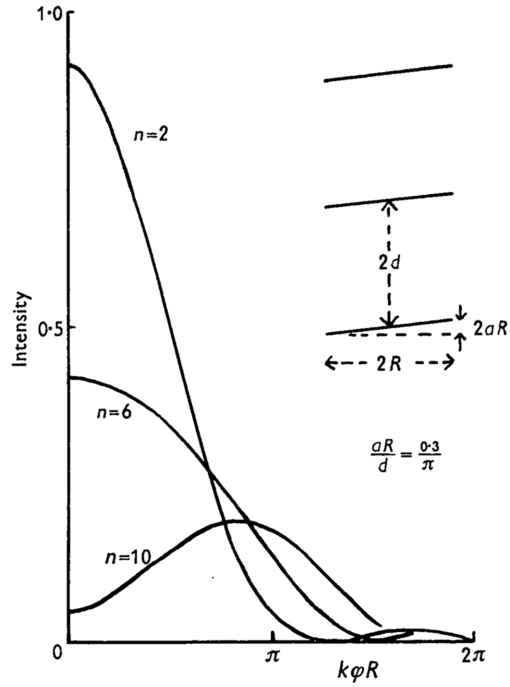

Fig. 8. Intensity distributions due to a set of linearly sheared cylinders distributed uniformly in orientation. The degree of shear is shown to scale in the insert. Fanning occurs with the development of two off-axis peaks in the higher orders.

This is a simple example of a sheared three-dimensional structure yielding a fanned low-angle diffraction pattern having a strong intensity variation across the spots. With a variety of shearing angles as well as orientations there would be a tendency to even out the intensity variations. On the other hand a particularly simple shearing function has been considered and earlier remarks on the possible interdependence of diffractors should not be forgotten.

Randomly disordered gratings

In this section a rigorous examination will be made of a particularly simple example of the kind of problem considered by Bear & Bolduan (1950, 1951), an example which avoids some of the mathematical complexity of their second paper, and which brings out an error in their procedure.

Suppose a two-dimensional grating lying in the x, z plane of Fig. 4 has a density variation $\varrho(z)$ which is a function of z only and has a period of $2d$. Imagine the grating divided into narrow strips parallel to OZ, of width $2w$. Each strip is then displaced parallel to

OZ by an amount $\pm\sigma$ relative to its neighbour, either sign of the displacement being equally likely. The problem is to determine the diffraction pattern due to an assembly of such gratings diffracting independently.

For one particular member of this assembly the diffraction pattern may be calculated by regarding the grating as sheared by a step-like shearing function. The angular distribution of intensity in the nth order is given by the following factor which is an obvious modification of equation (4):

$$\Phi_n^2 = \left| \sum_{r=0}^{N-1} \int_{(2r-1)w}^{(2r+1)w} \exp\left(-in(\pi/d)\Delta_r - ik\varphi x\right) dx \right|^2 ,$$

where Δ_r is the displacement of the rth strip. There are N strips and the integration across the full width of the grating is partly replaced by summations.

On carrying out the integration across a single strip, and putting

$$2k\varphi w = \alpha, \quad n(\pi/d) = \beta \quad \text{and} \quad W = 4w^2 (\sin \tfrac{1}{2}\alpha/\tfrac{1}{2}\alpha)^2$$

$$\Phi_n^2 = W \left| \sum_{r=0}^{N-1} \exp\left(-i\beta\Delta_r - i\alpha r\right) \right|^2 .$$

For the whole assembly of gratings the mean value of Φ_n^2 is

$$\overline{\Phi_n^2} = W \sum_s P \left| \sum_{r=0}^{N-1} \exp\left(-i\beta\Delta_r - i\alpha r\right) \right|^2 ,$$

where P is the probability of a given sequence of values of Δ_r, and $\sum_s$ means summation over all possible sequences.

If each strip is displaced $\pm\sigma$, with equal likelihood, relative to its neighbour, all possible sequences have the same probability of occurrence, viz. $(\frac{1}{2})^N$.

$$\therefore \overline{\Phi_n^2} = W(\tfrac{1}{2})^N \sum_s \sum_{p=0}^{N-1} \sum_{q=0}^{N-1} \exp\left[-i\beta(\Delta_p - \Delta_q) - i\alpha(p-q)\right].$$

To evaluate this, interchange the summations and consider

$$(\tfrac{1}{2})^N \sum_s \exp\left[-i\beta(\Delta_p - \Delta_q)\right].$$

Now $\Delta_p - \Delta_q = \nu\sigma$ where ν is an integer such that $-(p-q) \le \nu \le (p-q)$.

We need the number of sequences corresponding to a given ν. This is equivalent to asking how many ways are there of tossing N coins so that between the pth and qth throws there should be ν more heads than tails. The answer is (see for example Chandrasekhar, 1943)

$$2^{N-p-q} \binom{p-q}{\frac{1}{2}(p-q+\nu)}$$

$$\therefore (\tfrac{1}{2})^N \sum_s \exp\left[-i\beta(\Delta_p - \Delta_q)\right]$$

$$= \sum_{\nu=-(p-q)}^{p-q} (\tfrac{1}{2})^N 2^{N-p-q} \binom{p-q}{\frac{1}{2}(p-q+\nu)} \exp(-i\beta\sigma\nu)$$

$$= (\cos\beta\sigma)^{p-q} \quad \text{for} \quad p > q .$$

Since the number of sequences is the same for $p < q$ as for $p > q$, in general

$$(\tfrac{1}{2})^N \sum_s \exp\left[-i\beta(\Delta_p - \Delta_q)\right] = (\cos\beta\sigma)^{|p-q|}$$

$$\therefore \overline{\Phi_n^2} = W \sum_{p=0}^{N-1} \sum_{q=0}^{N-1} \exp\left[-i\alpha(p-q)\right] (\cos\beta\sigma)^{|p-q|} .$$

After some manipulation this leads to

$$\frac{1}{W}\overline{\Phi_n^2} = \frac{\begin{array}{l} N\sin^2\beta\sigma(1-2\cos\alpha\cos\beta\sigma+\cos^2\beta\sigma) \\ \quad -2\cos\alpha\cos\beta\sigma+4\cos^2\beta\sigma-2\cos\alpha\cos^3\beta\sigma \\ \quad +2\cos\overline{N+1}\alpha\cos^{N+1}\beta\sigma-4\cos N\alpha\cos^{N+2}\beta\sigma \\ \quad +2\cos\overline{N-1}\alpha\cos^{N+3}\beta\sigma \end{array}}{(1-2\cos\alpha\cos\beta\sigma+\cos^2\beta\sigma)^2} .$$

This result is given at length because it is rigorous and leads to conclusion distinctly different from those of Bear & Bolduan whose method of calculation involves approximations.

On taking N large and $\sin\beta\sigma$ not too small

$$\overline{\Phi_n^2} = W \frac{N\sin^2\beta\sigma}{1-2\cos\alpha\cos\beta\sigma+\cos^2\beta\sigma} .$$

Fig. 9 shows line profiles calculated from this last expression for $\sigma/d = 1/20$. Evidently fanning occurs and the higher orders show the development of off-meridian peaks. But the point of particular interest is that $\overline{\Phi_n^2}$ is a periodic function of $\beta\sigma$ so that when $\beta\sigma = 2\pi$ the intensity distribution is the same as for $\beta\sigma = 0$ which is the case of the undistorted grating. Thus initially the pattern fans outward to a maximum extension when $\beta\sigma = \pi$ and then contracts inwards again to the meridian, and so on. Physically, a periodicity is to be expected, for if $\sigma = 2d$ the displacements of adjacent strips are equal to the period of the grating, and the density distribution is unaltered by the disordering.

In applying the method of Bear & Bolduan (1951) to this particular problem the correct binomial distribution function used above is replaced by the approx-

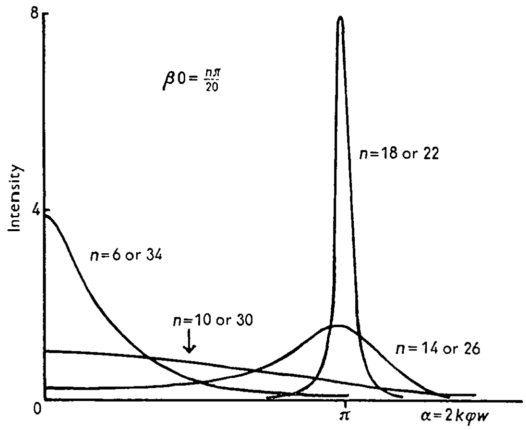

Fig. 9. Average intensity distributions from gratings divided lengthwise into narrow strips which are displaced parallel to their length in the manner of a random walk.

imate Gaussian distribution (Chandrasekhar, 1943), and the finite summations are replaced by integrations in which it is assumed that the limits may be extended to infinity. This procedure leads to

$$\overline{\Phi_u^2} = 16Nw^2 \frac{\beta^2\sigma^2}{\beta^4\sigma^4+(4k\varphi w)^2}$$

which is analogous to the formula quoted by Bear & Bolduan (1951) for the case of a diffractor comprised of cylindrical fibrils disordered in the same way as the strips of our two-dimensional grating. According to this last result fanning occurs but the line profiles are of similar shapes and there is never a double maximum of intensity as in Fig. 9 and no periodic dependence of the spot shape on diffraction index.

Conclusions

From a consideration of a number of simple cases of regular shearing of diffractors it is clear that distortions of this kind are entirely adequate to account for the phenomenon of fanning of low-angle X-ray diffraction patterns, and for the appearance of complex intensity distributions along the layer lines. Such distortions are commonly observed in electron-micrographs of teased fibrils and are of such magnitude as to make the choice of parameters used in the above computations distinctly conservative. Of course these fibrils have been subjected to severe treatment but evidently the shearing considered here is of a kind to which collagen fibres are demonstrably susceptible. Assuming a suitably dried fibre to consist of fibrils of various degrees of shear and orientation a fairly simple explanation of the observed fanning effects emerges.

The more elaborate explanation of Bear & Bolduan (1951) in terms of ordered and disordered regions of the fibrils is much more difficult to discuss quantitatively. They themselves point out some of the inadequacies of their model and there appears to be a significant error in their treatment of the problem which makes their results valid only if σ is small, although, again, another approximation requires that σ be not too small. But probably their formulae are fairly reliable for the relatively few orders (excluding the first three or four) of the diffraction patterns that have been observed. For higher orders there might be a considerable difference between the effects of regular shearing and the kind of disorder considered by Bear & Bolduan and exemplified by the above discussion of the two-dimensional grating.

It should be emphasized that the disorder of Bear & Bolduan is of a peculiar kind in that, although the individual displacements σ may be small, there are appreciable probabilities of building up relatively larger displacements of the kind which are responsible for observable effects in low-angle diffraction patterns. Small displacements of atoms or small groups of atoms about their mean ordered positions can have no effect upon the low-angle patterns, and this kind of disorder should be distinguished from the cumulative kind.

Since a simple shearing of fibrils appears to account for observed effects at least as well as a particular kind of disordering, and since shearing is an observable distortion of isolated fibrils, the notion of regions of order and disorder in collagen fibrils cannot be considered to be unambiguously supported by X-ray diffraction studies. It can be inferred from wide-angle diffraction patterns that there is some disorder in the form of fine scale displacements from regular positions, but this is unrelated to the characteristics of low-angle patterns which can be explained without postulating regions of order and disorder.

APPENDIX

Sheared cylindrical fibrils

A point in the cylinder is defined by cylindrical coordinates r, ψ, z and Fig. 4 defines other coordinates and shearing parameters. The cylinder of radius R is sheared so that a plane initially perpendicular to OZ is rotated about a line perpendicular to the direction ξ in the x, y plane so that OA is displaced to OB through an angle η.

The displacement of the point $r, \psi, 0$ is given by

$$\Delta = r\cos(\xi-\psi)\tan\eta = ar\cos(\xi-\psi)\,.$$

Following the treatment of the cylindrical diffractor given by Bear & Bolduan (1950) and introducing the shearing function as in the above discussion of two-dimensional diffractors the azimuthal distribution of intensity in the diffraction maxima is given by

$$\Phi_n^2 = \left| \int_0^R \int_0^{2\pi} \exp\left[-ikr\Psi\cos(\psi-\alpha) - in\pi(a/d)r\cos(\psi-\xi)\right] dr\, d\psi \right|^2,$$

where

$$\Psi\cos\alpha = \cos\theta\sin\varphi$$
$$\Psi\sin\alpha = \cos\theta\cos\varphi - 1\,.$$

On putting

$$k\Psi\cos(\psi-\alpha) + n\pi(a/d)\cos(\psi-\xi) = A\cos(\psi-\beta)$$

so that

$$A^2 = k^2\Psi^2 + (n\pi(a/d))^2 + 2k\Psi n\pi(a/d)\cos(\xi-\alpha)$$

the double integral can be evaluated to give

$$\Phi_n^2 = (2\pi R^2)^2\{J_1(AR)/AR\}^2.$$

This is the result for a single fibril sheared in the direction ξ. For a number of independent diffractors having a uniform distribution of ξ from 0 to 2π i.e. all possible directions of shear, the resultant intensity is given by

$$\int_0^{2\pi} \Phi_n^2 d\xi \propto \int_0^{2\pi} \{J_1(\omega)/\omega\}^2 d\gamma$$

where

$$\omega^2 = x^2 + y^2 - 2xy \cos\gamma$$

and

$$x = k\Psi R \simeq k\varphi R \text{ for low angle diffraction },$$
$$y = -n\pi(a/d)R ,$$
$$\gamma = \xi - \alpha .$$

The integral has been evaluated only in series form as follows:

From Watson (1922)

$$\frac{J_1(\omega)}{\omega} = \sum_{p=0}^{\infty} \frac{(xy\cos\gamma)^p}{p!} \frac{J_{p+1}(z)}{z^{p+1}} ,$$

where

$$z^2 = x^2 + y^2.$$

On squaring, the general even term in $\cos\gamma$ is

$$\frac{1}{z^{2p+2}}\left[\frac{J^2_{p+1}(z)}{(p!)^2} + 2\sum_{q=1}^{p} \frac{J_{p+1-q}(z)}{(p-q)!}\frac{J_{p+1+q}(z)}{(p+q)!}\right] (xy\cos\gamma)^{2p} .$$

Since

$$\int_0^\pi \cos^{2p}\gamma \, d\gamma = \frac{2p!}{(2^p p!)^2}\pi$$

$$\int_0^\pi \left[\frac{J_1(\omega)}{\omega}\right]^2 d\gamma = \pi \sum_{p=0}^{\infty} \frac{1}{(2^p p!)^2}$$
$$\times \left[\binom{2p}{p} J^2_{p+1}(z) + 2\sum_{q=1}^{p}\binom{2p}{p-q} J_{p+1-q}(z) J_{p+1+q}(z)\right] \frac{(xy)^{2p}}{z^{2p+2}} .$$

Introducing the function, tabulated by Jahnke & Emde (1945),

$$\Lambda_p(z) = 2^p p! \frac{J_p(z)}{z^p}$$

one finds for the first few terms of the series

$$\Phi_n^2 \propto \Lambda_1^2 + \tfrac{1}{48}(\tfrac{3}{2}\Lambda_2^2 + \Lambda_1\Lambda_3$$
$$+ 1/6{\cdot}144\,(10\Lambda_3^2 + 10\Lambda_2\Lambda_4 + \Lambda_1\Lambda_5)\,(xy/10)^4$$
$$+ 1/371{\cdot}6\,(87{\cdot}5\Lambda_4^2 + 105\Lambda_3\Lambda_5$$
$$+ 21\Lambda_2\Lambda_6 + \Lambda_1\Lambda_7)\,(xy/10)^6 + \ldots .$$

This is the expression from which the results of Fig. 8 were calculated. It is quite adequate to show the general trend of the diffraction pattern but with the parameters used proved to converge too slowly to be reliable for orders above the tenth.

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