The Application of Optical Transform Methods to the Interpretation of X-ray Fibre Photographs

By U. Mukhopadhyay* and C. A. Taylor,
Viriamu Jones Laboratory of Physics, University College, Cardiff, Wales

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A brief outline of the essential features of the geometry of X-ray fibre diffraction patterns is given and leads to a discussion of the beginnings of a systematic study, using optical diffraction patterns, of the correspondence between various features of the structure and effects in the X-ray scattering pattern.

Introduction

Optical diffraction methods have been used for studying fibre diffraction patterns from helical structures (e.g. Stokes, 1955; Wyckoff, Bear, Morgan & Carlstrom, 1957; Elliot & Malcolm, 1958; Hosemann, 1962) and also in interpreting small-angle X-ray patterns (e.g. Hosemann, 1962; Predecki & Statton, 1965). Hosemann has also described applications to the interpretation of some general features of fibre patterns, such as the production of background scattering, the effect of distortions, etc. Until recently, however, not much work had been done on scattering at wider angles. It has been pointed out (Taylor, 1966, 1967) that the basic problems are those of mask preparation and

* Present address: Indian Jute Industries’ Research Association, 17 Taratola Road, Calcutta-53, India

Fig. 1. (a) Mask representing a random arrangement of nearly parallel simple chains (one unit of which is shown at the side) and the corresponding diffraction pattern. (b) Mask representing a random arrangement of simple $7 \times 7$ square lattices (one cell of which is shown separated) and the corresponding diffraction pattern.
the relationship between the three-dimensional structure of the fibres themselves and the two-dimensional character of the masks which are used to represent them. Over the past year or two, a systematic study of these problems has been made and the purpose of the present paper is to discuss some of the solutions and results that have emerged. It will be convenient first to discuss the geometry of fibre diffraction before going on to discuss the question of mask making and the systematic study of the variables involved and their effects on the fibre photograph.

The geometry of fibre photographs

The essential common factor in fibre photographs is the cylindrical symmetry; there is no difference between a photograph taken with a stationary specimen and one for which the specimen is rotated about a fibre axis. We must assume, therefore, that there is a distribution of orientations either of the chain molecules or of the groups of molecules forming crystallites or fibrils, but with their long axes more-or-less parallel to each other. The reciprocal solid (the analogue of the reciprocal lattice for a non-periodic object) thus has cylindrical symmetry and any vertical section containing the fibre axis is equivalent to any other. A section of the reciprocal solid in diffraction space corresponds, of course, to a projection of the object in real space along a direction normal to the section. Thus, in order to simulate the X-ray diffraction pattern of the fibre by optical diffraction at a planar mask, the mask must be made to represent a projection of the structure along some direction perpendicular to the fibre axis. It turns out, however, that, if one assumes that the structure has some kind of homogeneity, it can be considered to be made up of layers roughly one 'molecule' thick and the diffraction pattern of any one layer is remarkably similar to that of the projection through a number of layers. (See Fig. 11 later). It follows, therefore, that one can make useful progress using single layers of units, though occasional checks with complete projections of three-dimensional arrangements must be made.

The remaining geometrical point which must be discussed is the relationship between the hole in the mask and the corresponding feature of the real structure (which is not necessarily a single atom but may be a group). It has been suggested (Taylor, 1966) that the most practicable optical approach is to ask the question 'what kind of diffracting object produced this X-ray pattern?' rather than the more usual ques-
tion 'is this X-ray photograph consistent with the particular model being proposed?'. If this approach is adopted, the problem of the relationship between the scattering factor of the hole and that of the atoms or groups of atoms may be deferred until after some semblance of agreement has been reached between the

Fig. 4.(a), (b), (c) Masks and diffraction patterns for 3 single chains.
optical diffraction pattern and the X-ray photograph. The nature of the atoms or groups of atoms of the monomer unit provides a function which has to be convoluted with the polymeric distribution and this leads, of course, to the multiplication of the whole resulting diffraction pattern by an overall form factor. It is therefore very convenient in the early trial stages to use very small holes in the mask and hence to eliminate the form factor altogether; this has the added advantage of minimizing the problem of overlapping of holes in the mask which will be discussed later. The fact that most masks used for this kind of work contain very large numbers of holes plus the advent of laser sources offsets the loss in light transmission arising from the use of very small holes which was one of the difficult problems in the early days of optical transform methods.

**Mask-making**

A consideration of these various geometrical factors leads to considerable simplification in the techniques of mask making. The conditions that need to be satisfied by any mask-making procedure are:

1. that it must be reasonably rapid,
2. that it should be possible to build-up overlapping layers or projections without the necessity of drawing the complete arrangement first and
3. the final product must consist of holes in opaque material or alternatively, of clear spots in an opaque photographic plate (in the latter case, in order to avoid phase problems, the mask must be immersed in cedar wood oil or a silicone oil of appropriate refractive index between optical flats).

Four principal methods have been used. The simplest method is direct punching using a pantograph (Hughes & Taylor, 1953). As was pointed out in the last section it turns out to be quite satisfactory to use very small holes and to make any necessary overall correction for the form factor afterwards. If one, therefore, uses a very small punch — say ½ mm — there is no problem with overlapping layers and surprisingly high concen-
trations of holes can be achieved; the only real limitation on the method is the time required to produce a mask. Fig. (1a) is an example of a mask produced by direct punching. It consists of about eighty identical simple straight chains randomly positioned in space with axes orientated within about 5° of the vertical. Although the mask as a whole appears to be a fairly random arrangement of holes in which identification of any one chain is difficult even when its shape is known, the diffraction pattern reveals the presence of the chains very clearly. Fig. (1b) shows a similar mask in which there are about 20 units, each of 49 holes arranged on a $7 \times 7$ square lattice; the units are random in both position and orientation. Although superficially the mask resembles that of Fig. (1a) and has roughly the same number of holes, the diffraction pattern

![Diffraction Patterns](image)

Fig. 6. (a) Mask and diffraction pattern for a crystalline arrangement based on the chain in Fig. 4(b). (b) As 6(a) but with random displacements in the vertical direction. (c) As 6(a) but with random displacements in the horizontal direction.
Fig. 7. (a) Mask and diffraction pattern for a crystalline arrangement based on the chain in Fig. 4(c). (b) As 7(a) but with chains not strictly parallel to each other. (c) As 7(a) but with randomly bent chains.

Pattern reveals the totally different structure. In both these examples, a single copy of the unit was drawn and moved to a new location on the pantograph table for each punching; part of each unit is shown at the side of the masks.

The second method involves the punching of a mask.
representing one layer or one repeat unit followed by a multiprinting on a photographic plate or film. A simple mechanical translation device on the baseboard of a photographic enlarger (used in fact to produce a reduced image of the mask) can be used and it is possible to use the same device several times so that quite large masks can be produced relatively rapidly. The final mask can be reproduced either by etching

Fig. 8. (a) As Fig. 7(a) but with 'conformal' bending. (b) As Fig. 7(a) but with random rotation of chains about their own long axes. (c) As Fig. 7(a) but with both bending and rotation about long axes of chains.
in copper foil (Harburn, Taylor & Yeadon, 1965) or on a photographic plate to be used in an immersion bath.

The third method involves direct photography of a model made of white polythene foam balls connected together with black spokes and viewed against a black background. Fig. 2 shows such a model of a cubic lattice mounted on a tripod and this clearly offers a useful technique which could be developed for structures with complex three-dimensional geometry.

The fourth method, which is really a variant of the first, is to use a computer to devise the arrangements and to use a graph-plotter output to prepare the relatively complex drawings resulting from multiply overlapped layers; the final drawing may then be used for handpunching on the photograph or for photographic reproduction if the dots can be made suitable clear. Fig. 3 shows a mask produced by handpunching from a graph-plotter output; it is based on a random three-dimensional arrangement of 300 identical pairs of atoms in parallel orientation which are placed within a sphere of a given radius and with a limit on their closest distance of approach. The computer program generates the three-dimensional coordinates of such pairs and extracts the two-dimensional projection onto a given plane to drive the graph plotter. As in Fig. 1(a) and (b), although there is little visual evidence of the pairs in the mask, the diffraction pattern gives striking evidence of their presence.

The relevant variables in fibre diagrams

In order to make progress in interpreting fibre diagrams it is necessary to make a systematic study of the contributions of all the various possible features of a fibre-like structure. The total number of variables is very large and the present sequence only indicates the principles and cannot be considered exhaustive.

We shall start with a single chain. Fig. 4 shows the diffraction patterns of three rather arbitrarily chosen chains. The periodicity along the chain, of course, defines the 'layer lines'; the chain unit governs the distribution of intensity along each line. This intensity distribution along the line is one of the dominant features which persists through a surprising range of modifications as will be seen later.
If the single chain is bent or twisted characteristic changes occur in this basic pattern. The main result is that the layer lines diverge as one moves away from the vertical centre-line of the pattern but for twisting the distribution along the layer lines becomes considerably disturbed as well. Fig. 5(a) and (b) show the effect using the chain unit as in Fig. 4(c).

We should now consider the effect of placing a series of chains side-by-side with a regular spacing to form a crystalline arrangement. Fig. 6(a) shows a completely regular arrangement and Fig. 6(b) shows the effect of random displacement of the chains vertically [the basic chain is that of Fig. 4(b)]; since the projection of each chain onto a horizontal centre line is unchanged by these displacements, the central horizontal row of spots is unaffected, though other rows develop a degree of fuzziness. In Fig. 6(c) we see the corresponding effect for random lateral displacements; here the projection of all the chains onto a vertical line will be unchanged and now it is the vertical row of spots on the fibre diagram that is unaffected while the rest of the layers develop streaks. Apart from the central vertical and horizontal rows the effect of the two types of random displacement is remarkably similar and the dominant feature remains the pattern of the single chain.

The effect of lack of parallelism of the chains and of bending of the chains is somewhat similar though the bent chains produce a rather more blurred effect than the inclination of straight chains. Fig. 7 illustrates these points using the basic chain unit of Fig. 4(c). If the bending is not done in a random way but with the chains remaining parallel - 'conformal bending' - the result is streaks along the vertical rows as shown in Fig. 8(a). The effect of rotation of the chains about their axes while remaining fixed in lateral position is shown in Fig. 8(b). This is rather interesting from the diffraction standpoint because it leads to sharp spots along the odd layer lines and diffuse streaks along the even layers including the zero layer. This effect how-

Fig. 10.(a) Mask and diffraction pattern for a single chain as in Fig. 4(c) with random changes in the periodicity along the chain length. (b) Mask and diffraction pattern for a single chain as in Fig. 4(c) with variations in the chain unit though the 'repeat' remains constant.
ever, is characteristic of the particular chain unit that has been chosen; the odd layer lines are only receiving contributions from the holes which lie along the axis of each chain unit whereas the even layers receive contributions from all the holes. When the chains are rotated, the axial holes are unaffected and hence, the spots on the odd layer lines remain sharp.

The combined effect of bending and rotation of the chains is shown in Fig. 8(c). Fig. 9 shows the effect of twists in the chain, first with chains at equal distances from each other and later combined with bending, Fig. 9(b). Finally, Fig. 10(a) and (b) illustrate the effect of two kinds of irregularity in the chains themselves - a change in the periodicity without change in the basic chain element and a change in the element without a change in the periodicity.

It was pointed out earlier that there is very little difference between the pattern produced by a single layer of a structure and by a large number of similar, though not identical, layers superimposed on each other. Fig. 11 demonstrates this point for a particular arrangement. It certainly demonstrates that, at least in the early stages of an investigation, it is unnecessary to use vast numbers of chains superimposed; relatively few chains can be used to make quick tests of ideas with reasonable safety.

Some general conclusions

The first point to be made – no doubt a very obvious one but nevertheless important – is that the presence of diffraction maxima distributed along layer lines is not related to crystallinity in the ordinary sense of the word. Layer lines may simply be an indication of periodicities along individual chains and an indication that the chains have some degree of parallelism with each other. The second point is that diffuse scattering may arise from a number of different causes such as bending, twisting, irregularities in the chains, and similarly general background scatter can arise from distortion in the chain units or from randomness in the arrangement. It therefore seems inappropriate to continue to refer to the diffuse maxima that occur in fibre photographs as 'reflexions'; it also becomes clear that
one cannot easily separate the so called 'crystalline' and 'amorphous' regions or determine their relative proportions by very simple measurements of the presence of sharp and diffuse spots. This point may be demonstrated very forcibly by Fig. 12. The diffraction patterns Fig. 12(a) and (b) are not at all dissimilar and both consist of sharp spots on a diffuse background. For (a) however there is a single perfect crystallite surrounded by completely amorphous material whereas in (b) all the 'atoms' present lie at the possible sites from the crystallite as in (a) but a proportion of the sites, selected at random remain unfilled. In (b) there is no amorphous material at all nor is there any perfectly crystalline material!

The third point that emerges from this work is that it is possible to produce patterns with strong superficial similarities from a number of quite different structural arrangements. This point should not be over-emphasized but it does support the general thesis referred to earlier in the paper that one should really be asking questions about the origin of particular diffraction effects in order to suggest lines of development of structural models rather than using the existence of particular diffraction effects as absolute confirmation of a particular model.

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References