

## ORDER-DISORDER TRANSITIONS IN STRUCTURES CONTAINING HELICAL MOLECULES

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The most commonly considered types of disorder in a crystal containing long-chain molecules are those in which the individual chain molecules are either rotated about their long axes or else translated along the fibre axis. However, since many fibrous polymers are helical in structure, we should also expect the possibility of screw disorder; that is, a combination of the above two types. A disorder of this kind can be shown to exist in orientated gels of tobacco mosaic virus and in fibres of polytetrafluoroethylene (PTFE) at 20°C. The method by which screw disorder may be deduced from X-ray diagrams is described, and the order-disorder transitions in the two substances discussed. The mechanism of the transition in PTFE is of particular interest in connection with its remarkably low coefficient of friction.

Attention is also drawn to a related type of disorder found in stretched fibres of deoxyribonucleic acid.

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Two types of disorder are commonly recognized in crystal structures consisting of long-chain molecules. The first arises when the individual molecules are randomly rotated about their long axes. Thus the transition that occurs in paraffin hydrocarbons<sup>1</sup> and related molecules<sup>2</sup> a few degrees below the melting point is believed to be due to the onset of rotation of the molecules about their long axes. The second kind of disorder is that in which the molecules are variably displaced along their long axes. When the number of monomer units in the "fibre" axis repeat period is large, it is not possible, by X-ray diffraction methods, to distinguish between rotational and translational order.

Besides straightforward rotational or translational disorder it is clearly possible to have a combination of the two types, that is, screw disorder. Indeed we should expect this to happen when the molecules have a helical structure and are packed rather closely together. Examples of a screw disorder of this kind can be deduced from the X-ray diagrams of tobacco mosaic virus (TMV) and of the polymer polytetrafluoroethylene (PTFE). The effect with TMV has already been described elsewhere,<sup>3</sup> and is recapitulated here in more general terms to serve as an introduction to the order-disorder transition<sup>4</sup> in PTFE at room temperature. The latter is of interest in connection with the remarkable frictional properties of the substance.

### THE INTERLOCKING OF PARTICLES OF TMV

It is well known that particles of TMV are rods of diameter<sup>5</sup> about 150 Å and length<sup>6</sup> about 3000 Å. More recent work<sup>7</sup> has shown that the virus protein is composed of sub-units set in helical array around the long axis of the particles. It has also been shown<sup>3</sup> that the previously accepted value<sup>5</sup> of 152 Å for the diameter refers to the packing diameter between particles in the dry state, and that in fact the maximum radius<sup>8,9</sup> of the particle exceeds this packing radius. The TMV particle bears on its surface a helical array of protuberances, one for each sub-unit, projecting well beyond the mean radius, and so presents a system of helical ridges and grooves. Two neighbouring particles can thus interlock and approach each other to within a distance smaller than the maximum diameter.

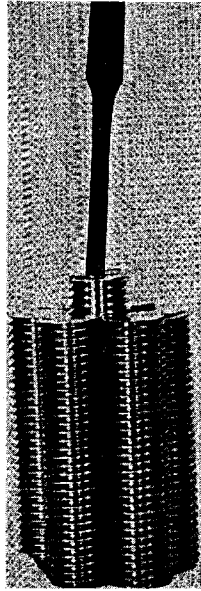


FIG. 1.—A model to illustrate the interlocking in a close-packed array formed by rods bearing helical grooves of small pitch angle. The central rod in the model can be screwed in and out by means of a screw-driver.

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the nature of this interlocking and its effects on the X-ray diffraction diagram that we shall be concerned with here.

X-ray diffraction diagrams of oriented, wet TMV gel indicate that the particles are in random orientation about their long axes, since the pattern obtained is characteristic of the scattering by independent particles (continuous Fourier transform). Evidence that the particles are in fact probably oscillating or rotating about their long axes may be deduced from an observation of Bernal and Hankuchen.<sup>5</sup> They showed that the distance between the particles in the so-called "equilibrium gels" could be varied by changing the pH or the salt concentration and that the distance of closest approach in strong salt solution was found to be 173 Å, a value which is greater than the packing diameter (152 Å) of the particle. Even more striking is the fact that variation of interparticle distance with pH shows a distinct minimum of 185 Å at the isoelectric point. Since it is now known<sup>9</sup> that the maximum radius of the TMV particles is about 90 Å, it seems clear that the observed minimum distance represents the closest approach of two TMV particles rotating or oscillating about their long axes.

When a gel of TMV is dried, the X-ray diagram shows that the particles move closer together to form a close-packed two-dimensional hexagonal array. In so far as the TMV particles may be regarded as uniform density rods, the structure will behave as a single crystal in two dimensions but the actual intramolecular X-ray pattern observed indicates that the particles are still in a state of rotational and/or translational disorder with respect to their long axes.

As mentioned above, the interparticle distance in dry gel is a good deal less than the maximum diameter of the particles and this implies that a considerable degree of interlocking takes place. It has been shown by Franklin and Klug,<sup>3</sup> from a study of the X-ray diagram of dry TMV, that the particles interlock because each bears a helical groove on its surface. It is perhaps not immediately obvious why the existence of grooves and ridges should produce any interlocking, for, when two parallel particles are brought into contact, the direction of the ridges on one particle crosses that of the grooves on the other. The interlocking in TMV is possible only because the helical groove involved makes an angle of only 22° with the horizontal and is thus very nearly flat. The flatness of the helix means that a particle may interlock with all the six neighbours surrounding it in a hexagonal array. This is illustrated by the model in fig. 1 which shows seven helically grooved rods fully interlocked. The central rod can (with the aid of a screw-driver) be screwed in and out among its six neighbours without altering the packing of the rods.

The original paper should be consulted for details of the effect of the interlocking on the X-ray diagram, and we shall here outline the type of reasoning used in terms applicable to general screw disorder in helical structures.

#### THE DETECTION OF SCREW DISORDER IN X-RAY DIAGRAMS

The model in fig. 1 forms a truly crystalline structure, and screwing one of the rods (considered infinitely long) in or out with respect to its neighbours would not destroy the crystallinity of the arrangement. Any real structure consists, of course, of discrete atoms, so that a screw movement of this kind would destroy the coherence between different particles. The X-ray diffraction pattern would thus for the greater part correspond to the continuous transform of the individual particles. There would be, however, a region of the X-ray diagram in which the crystalline character is still evident.

It has been shown<sup>10</sup> that the diffraction pattern of a helical structure can be usefully thought of as a sum of contributions each of which corresponds to a particular "helical projection" of the structure. To define a helical projection we consider a space-filling set of helices all of the same pitch, and let each atom be projected along the helix passing through it on to either an axial or equatorial

plane. Formally, the Bessel function contribution of order  $n$  on the  $l$ th layer-line corresponds to the projection down a set of helices of direction denoted by  $(n, l)$  and of pitch  $nc/l$ .

Consider now what happens when we have an assembly of molecules arranged at the lattice points of a crystal and a variable screw disorder is introduced. In general, the three-dimensional crystalline order is destroyed. But the projection of the molecules along the helix corresponding to the screw motion will remain unchanged. Hence that part of the X-ray diagram corresponding to this helical projection will still resemble diffraction by a crystal and show sharp reflections (i.e. the continuous transform of the molecule is sampled at the points of the reciprocal lattice of the crystal), while the rest of the X-ray diagram will show areas of diffuse scattering (continuous transform of the molecule).

For simplicity, we have dealt first with the change from full crystalline order to a disordered state. It is, however, the converse process that takes place when orientated TMV gel is dried. The change here is from a state in which no orientational order is present to a partially ordered state brought about by the interlocking between particles.

#### A SCREW TRANSITION IN POLYTETRAFLUOROETHYLENE AT 20°C

The molecular and crystal structure of PTFE has recently been worked out by Bunn and Howells.<sup>4</sup> PTFE is crystalline below 20°C but at that temperature shows a first-order transition. By a comparison of the X-ray diagrams above and below this temperature, Bunn and Howells showed that the transition is one from fully crystalline three-dimensional order to a lower degree of order. They further concluded that the disorder consists either of a variable displacement of the molecules along their chain axes or a variable rotation about these axes. We wish, however, to point out that the experimental results clearly indicate that what happens at the transition temperature is the onset of a *screw* disorder. This may be inferred from the X-ray diagrams by reasoning along the lines given above.

The molecular configuration determined by Bunn and Howells<sup>4</sup> is shown as a radial projection<sup>10</sup> in fig. 2. To obtain this diagram the atoms have been projected radially on to a cylindrical surface centred on the chain axis, and the surface then cut open parallel to the axis and opened out flat. The axial repeat period is 16.8 Å, and in this distance are contained 13  $>CF_2$  groups lying along six turns of the basic helix of pitch 2.8 Å. The carbon atoms lie at a radius of 0.42 Å and the fluorine atoms at a radius of 1.64 Å. This is, of course, a purely geometrical description of the structure, but it is the most appropriate for our purposes.

Bunn and Howells observed that when the temperature is raised to 25°C the equatorial reflections and those on the 6th and 7th layer-lines remain sharp, but that all those on intermediate layer-lines become diffuse. The areas of diffuse scattering are in the same place as the sharp reflections of the crystal structure, showing that the molecular configuration is unchanged, but that the overall crystallinity has been destroyed.

The sharpness of the reflections on the 6th and 7th layer-lines indicates that, as far as these parts of the diagram are concerned, the structure has remained crystalline. That is, the corresponding helical projections are unchanged by the transition at 20°C. The direction of the helical projection corresponding to the 6th layer-line is shown by the full lines in fig. 2, and that corresponding to the 7th by the dotted lines. These are then the directions in which the screw motion responsible for the disorder takes place. In the notation of Klug, Crick and Wyckoff<sup>10</sup> the helical directions are (1, 6) and (-1, 7), the Bessel functions on the 6th and 7th layer-lines both being of the first order.

Although the results indicate that *two* screw displacements with respect to the original position in the low-temperature crystal lattice are possible, it should be noted that any one molecule can only undergo one of these screw motions at a time. It is not, however, possible to decide from the X-ray results whether there

distinct domains in a crystal, each of which contains only one direction of screw disorder, or whether the two classes of disordered molecules are interdispersed throughout one crystal.

The question naturally arises as to why the screw disorder takes place. The answer is not entirely obvious, but must clearly be bound up with the helical nature of the molecular configuration. Several points seem worth noting.

The fact that the transition occurs at a temperature ( $20^{\circ}\text{C}$ ) so far below the melting point ( $330^{\circ}\text{C}$ ) evidently means that the relatively rigid PTFE molecules are able to slip past, or roll round, one another very easily. Bunn and Howells attributed the ease with which this happens to the smooth profile of the approximately cylindrical surface of the fluorocarbon chain. While there may indeed be

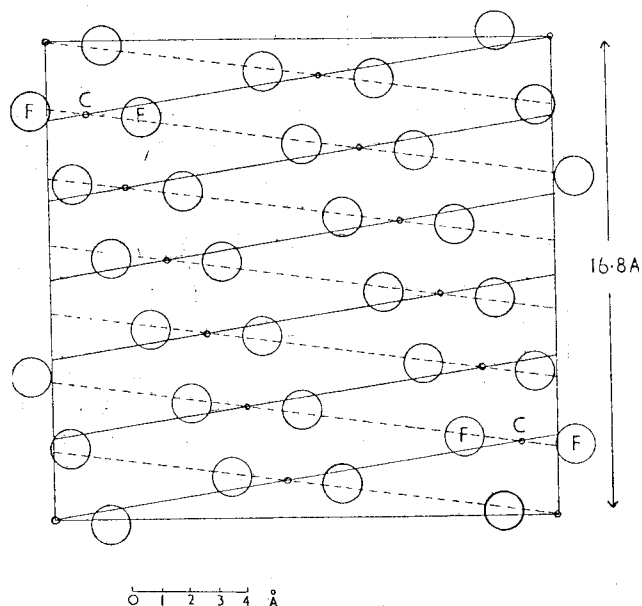


FIG. 2.—The radial projection (see text) of one axial repeat period of a molecule of polytetrafluoroethylene, drawn on a cylindrical surface of diameter equal to the intermolecular distance. The sections of the van der Waals spheres of the fluorine atoms are shown as large circles. The full and dotted lines represent the helices (1,6) and (-1,7) respectively.

free rotation at higher temperatures, this is surely not the case at  $20^{\circ}\text{C}$  for, as we have seen, the molecules appear to be screwed in and out with respect to their neighbours. Since the molecules are held together only by van der Waals forces, this would happen only if there were in fact some degree of interlocking between neighbours.

The packing of PTFE molecules may be conveniently illustrated by means of the radial projection in fig. 2. This was drawn on a cylindrical surface of diameter 16.8 Å equal to the intermolecular distance, so that the line of contact between two neighbours lies in the surface chosen. In the figure, we have also drawn the sections of the van der Waals spheres of the fluorine atoms by this surface so that the diagram is a fairly realistic representation of the bumps or knobs on the outside of a PTFE molecule. It will be seen from the figure (or from Bunn and Howells' drawing<sup>4</sup>) that the molecule bears grooves in the two helical directions (1,6) and (-1,7) in which the screw disorder takes place. There are, of course, others as well, but the two helices mentioned are those of the smallest pitch angle. Neither of these two helical grooves is as flat as that present on the surface of the TMV

particle and the ridge on a molecule of PTFE cannot interlock efficiently with the corresponding grooves on its neighbours. Interlocking is in this case facilitated by the presence of the two grooves since they are of opposite tilt and similar pitch. (The helix  $(-1,7)$  has a pitch equal to  $6/7$ ths of that of the helix  $(1,6)$  and is of opposite sense; see fig. 2.) This means that when two parallel molecules are in contact, the set of ridges belonging to the one helix can fit approximately into the grooves of the other. If the fit were exact, there would be no difficulty at all in surrounding a molecule by six interlocking neighbours.

The approximate way in which two molecules can pack together may be illustrated by making a copy of fig. 2 on transparent paper, and turning it over before

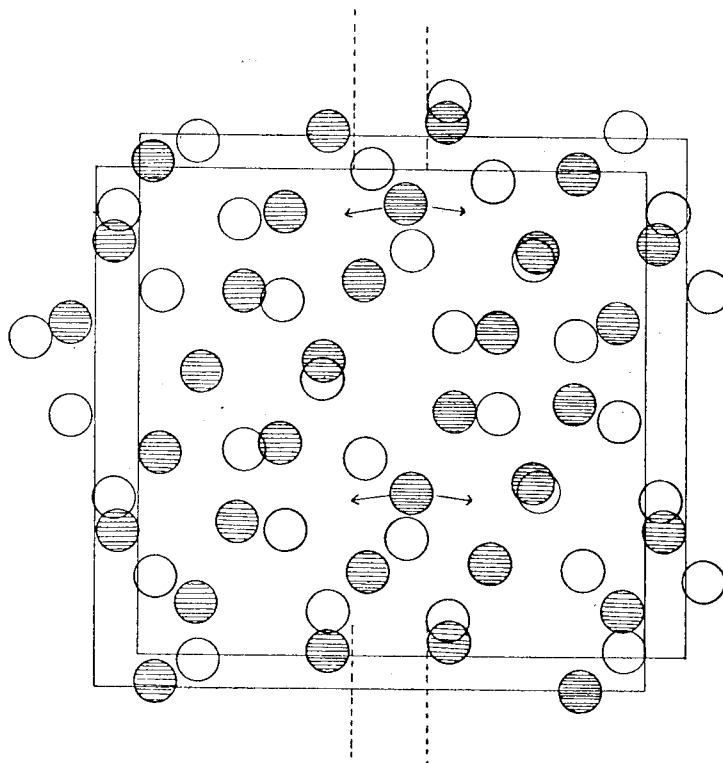


FIG. 3.—The pattern formed by the fluorine atoms of two PTFE molecules in one of the many possible positions of contact. The line of contact may be anywhere between the dotted lines. The arrows denote the helical directions  $(1,6)$  and  $(-1,7)$  along which the screw disordering displacements take place.

superimposing the two diagrams (since it is the outsides of both cylindrical surfaces that must come into contact). It is found that there are a large number of positions containing a narrow band in which the knobs of one molecule fall nicely between the knobs of the second. One of these positions is shown in fig. 3 which shows the two radial projections superimposed. The vertical line of contact can be taken to be anywhere between the pair of dotted lines, which subtend an angle of approximately  $50^\circ$  at the axis.

However, by considering the contact between only two molecules at a time, it is not possible to understand precisely how the molecules pack in a hexagonal lattice, except on the general grounds given above. A molecule has 13-fold screw symmetry about its axis, so that the 6 contacts between a molecule and its neighbours cannot all be the same. Since 13 is not far from a multiple of 6, there may

be an approximately hexagonal system of contacts. It would not be profitable to pursue this matter further without a detailed study of the packing in the pseudo-hexagonal crystalline form of PTFE occurring at temperatures below the transition point.

It ought to be mentioned, for completeness, that if the PTFE is racemic, helices of opposite sense will be present. However, it seems likely that in this case the racemate would be at least partially resolved on crystallization.

Finally, on the question as to why it is along the helices of smallest pitch that the screw disordering motion takes place, it might be valid to introduce some kinetic considerations, besides the steric ones mentioned. It is easy to show that, for a given total displacement of a point on the surface of the molecule, the kinetic energy is the smaller, the smaller the pitch angle of the motion. Thus, if the disorder were not merely static, but some form of hindered oscillation (similar to that found in paraffin crystals<sup>2</sup>), the particular screw motions adopted would be partly accounted for. This assumption might not at first sight seem very plausible at a temperature as low as 20°C, but the extremely streamlined nature of the fluorocarbon surface ought to be borne in mind. Bunn and Howells<sup>4</sup> also discovered a similar transition to that observed in PTFE in crystals of perfluoroacetane, C<sub>16</sub>F<sub>34</sub>. Here the transition temperature is -170°C, indicating that, because of their lower molecular weight (800), the molecules are able to undergo the disordering motions at a lower temperature than in PTFE. The low absolute value of the transition temperature does suggest that it is extremely easy to set fluorocarbon molecules in a crystal into rotational or translational motion—or a combination of both—and that kinetic considerations might thus be relevant in discussing the screw disorder in PTFE.

#### PARTIAL DISORDER IN DEOXYRIBONUCLEIC ACID

Other types of disorder are possible which lead to X-ray diagrams showing sharp reflections in some regions and continuous scattering in others. An example of this occurs when long chain molecules in a crystal are displaced along their long axes, by translations which are not random but related to the repeat distance along the molecular chain. An effect of this kind has been observed by Wyckoff<sup>11</sup> with stretched fibres of DNA in the B form. On the X-ray diffraction pattern even layer-lines are observed to have sharp spots on them, while odd layer-lines are diffuse.

The simplest explanation of this again involves the interlocking of helical grooves, but in a slightly different way. The double-strand helix of DNA bears two approximately equally spaced grooves,<sup>12</sup> one deeper than the other. In spite of the fact that these grooves are rather steep, helical interlocking as described above can take place because both grooves are relatively very deep. The existence of the bulges and depressions on the surface of the molecule means that neighbouring molecules can pack together in such a way that the large ridge fits *either* into the deep groove or into the shallow one (and similarly for the small ridge). If it is assumed that these possibilities are equally likely in the stretched fibres examined by Wyckoff, then this is equivalent to giving each molecule a random displacement of either 0 or  $\pm \frac{1}{2}c$ . This would lead to crystal reflections on even layer-lines and to continuous scattering on odd ones, as observed.

The effect is analogous to that observed with some *layer* structures such as cobalt<sup>13</sup> or certain clays.<sup>14</sup> Here the layers, which have hexagonal symmetry, have random *lateral* displacement of  $\pm \frac{1}{2}$  in the 110 direction, and only every third layer-line shows sharp reflections. With DNA, however, the experimental data are rather sparse, and more complicated models could doubtless be devised to explain the results.

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- <sup>1</sup> Müller, *Proc. Roy. Soc. A*, 1932, **138**, 514.
- <sup>2</sup> for a review see Daniel, *Adv. in Physics*, 1953, **2**, 450.
- <sup>3</sup> Franklin and Klug, *Biochim. Biophys. Acta*, 1956, **19**, 403.
- <sup>4</sup> Bunn and Howells, *Nature*, 1954, **174**, 549.
- <sup>5</sup> Bernal and Fankuchen, *J. Gen. Physiol.*, 1941, **25**, 111.
- <sup>6</sup> Williams and Steere, *J. Amer. Chem. Soc.*, 1951, **73**, 2057.
- <sup>7</sup> Watson, *Biochim. Biophys. Acta*, 1954, **13**, 10. Franklin and Holmes, *Biochim. Biophys. Acta*, 1956, **21**, 405.
- <sup>8</sup> Caspar, *Nature*, 1956, **177**, 475.
- <sup>9</sup> Franklin, Klug and Holmes, in *The Nature of Viruses* (Ciba Foundation Symposium, J. and A. Churchill, London, 1956), p. 39. Franklin, to be published.
- <sup>10</sup> Klug, Crick and Wyckoff, *Acta Cryst.*, 1958, **11**, 199.
- <sup>11</sup> Wyckoff, *Thesis* (Massachusetts Institute of Technology, 1955).
- <sup>12</sup> for a review see Wilkins, *Cold Spring Harbor Symposia*, 1956, **21**, 75.
- <sup>13</sup> Wilson, *X-ray Optics* (Methuen, London, 1949).
- <sup>14</sup> Brindley and Robinson, *Trans. Brit. Ceram. Soc.*, 1947, **46**, 49; *Miner. Mag.*, 1948, **28**, 393.

*Note added in proof*

More recent work on PTFE (for references, see Bunn and Holmes, this Discussion) has shown that the molecule is slightly untwisted just above the transition point at 20°C, so that the axial repeat period contains 15 CF<sub>2</sub> groups distributed over 7 turns of the basic helix. The actual physical change in the internal configuration is, however, very small, and the argument for the intermolecular screw disorder is not affected.