CHAPTER 8

INFERENCES ON COTTON FINE STRUCTURE

SCOPE

This chapter is a review of some of the findings on cotton fibre structure derived from the present studies of wide angle X-ray diffraction from decrystallised fibres. It is shown that these findings are broadly in accord with the picture of a "fringed fibril fine structure" \(1\) of cotton. It is also shown that this picture can be extended in a natural and unforced manner to give a plausible model of the observed decrease in crystallinity and dimensions of crystallites which follow the swelling-deswelling sequence.

1 SWELLING OF COTTON FIBRES AND
THE TWO - PHASE THEORY

An outstanding feature of the present investigation is the observation that the wide angle X-ray diffraction pattern from cotton fibres which have been subjected to a variety of decrystallization treatments can in all
FIGURE 1.
SCHEMATIC DIAGRAM OF THE TWO-PHASE STRUCTURE.

BEFORE SWELLING.

AFTER SWELLING.
cases be well synthesized from the diffraction curves of highly crystalline and pure amorphous cellulose, provided that the line breadths of the crystalline reflections are suitably adjusted. There has been no need to invoke the concept that cotton fibres may contain material with intermediate degrees of order. The existence of material with intermediate order is, however, by no means disproved. It may well be that the observed intensities of diffraction exhibit good or better agreement with the intensities calculated for a model characterized by a continuous rather than a bimodal spectrum of order. However, the simplest model which fits the data in hand is the modified bimodal one in which micro-crystallites of varying dimensions are embedded in varying proportions of an amorphous matrix of cellulose chains. Fig. 1 is a schematic of this simple model of the structure of cotton fibres before and after swelling.

It will be noted that the crystallites in Fig. 1 are shown with reduced dimensions after swelling. There is a corresponding increase in the volume of the disordered regions. However, the number of crystalline sites has

130
been shown as unmodified by swelling. This representation is based on the findings that (a) line breadths of crystalline reflections increase with decreasing crystallinity (Chapter 6) in such a manner that there is good correlation between crystallinity and crystallite volume; (b) the accord between calculated and observed intensities for highly decrystallised samples improves when the crystallite size in the standard is appropriately reduced (Chapter 6). Thus decrystallisation is pictured as resulting from the reduction in size of the crystalline regions by swelling. This picture is what one would expect if the action of the swelling agent was confined to intercrystalline regions and the fringes of crystallites. But it cannot be so easily anticipated when one remembers that the powerful intracrystalline swelling agents used in the present study penetrate the cellulose lattice and destroy all trace of it (Chapter 6). Notwithstanding this disruption of order, the tendency to recrystallise seems to persist and asserts itself when the swelling agent is removed. Probably the sites of recrystallisation are the same as earlier sites of crystallisation in the untreated fibre as pictured in Fig. 1. However, the tendency towards crystallisation around these sites is
less prevalent than in the parent fibre. It now remains
to see how far this plausible, but by no means proven,
picture of de-crystallisation and re-crystallisation during
the swelling-deswelling sequence, fits in with modern
notions of a fringed fibril structure for cotton.

8 THE FRINGED FIBRIL STRUCTURE
OF COTTON FIBRES

Though the circumstances which led to the proposal of
the fringed fibril structure have been mentioned
previously (Chapter 1) they are recalled here for the sake
of continuity. Over a period of many years the working
model of fibre fine structure was the fringed micelle
structure. Though it was not possible to make direct
observation on the fringed micelles or crystallites it
was intuitively assumed that they were present in the
fibre body, alternating between low ordered or amorphous
regions according to the famous "bundle of ropes"
analogy of Astbury. This structure was helpful in
explaining many phenomena, e.g., the sharp crystalline
peaks superimposed on a diffuse scatter due to amorphous
substance observed in the X-ray diffraction pattern of
fibres. The crystalline regions, which would correspond
to the well ordered core of micelles, were shown to be about 50 Å wide by over 600 Å long in native cotton fibres. In the last two decades or so, direct observations on fibre structure became possible after the advent of electron microscopy. The electron microscope revealed the fact that many fibrous substances are made up of fine strands known as fibrils or microfibrils. Cotton fibres have been examined by the electron microscope in two ways:

(i) after mechanically degrading the fibre by wet beating or ultrasonic treatment

(ii) after chemical degradation (i.e., acid hydrolysis) followed by ultrasonic treatment.

When cotton fibres are subjected only to mechanical disintegration, it has been confirmed that: (a) fibrils or microfibrils are about 50-80 Å wide, but with a length so large that it is indeterminate in the electron microscope (b) these fibrils, which are packed in circular lamellar sheets, run spirally along the fibre axis with an occasional and rather abrupt change in the direction of spiral. When cotton is subjected to acid hydrolysis followed by ultrasonic disintegration, it is
observed that, depending upon the severity of the acid treatment, the very long fibrils (observed in case-i) break down into shorter fragments with a certain length distribution. These fragments are variously referred to as microfibrils, elementary fibrils or fibrillar fragments. Under more drastic hydrolysis the fibrils break down into sharply defined tablet-shaped particles with the same width as that of the parent fibril (i.e., 50-80 Å), but with length only of the order of a few hundred Ångström units. The dimensions of these crystalline particles agree well with those observed in recent X-ray investigations [5, 6].

These direct observations on the internal architecture of native fibres led Hearle to propose the fringed fibril structure (loc. cit.) (See Fig. 11, Chapter 1). On the basis of this structure, the lamellae of the secondary wall in native fibres are made up of continuous fringed crystalline regions or fibrils embedded in a continuous network consisting of chain molecules of lower order. The chains may enter or leave at any point along the length of a fibril. There are no abrupt discontinuities caused by these entries or departures; i.e., the transition from a high order to a low order is gradual.
The success of the two-phase model in the present investigation, however, indicates that the transition from a high order to a low order in cotton fibres may be more abrupt than originally envisaged. The finding of different line breadths for different orders of meridional reflections in cotton, as in contrast to ramie (Chapter 6) seems to indicate that the above mentioned transitions are likely to be sharper in the case of ramie than in cotton fibres. The increase in line breadth of ogo reflections in cotton fibres with higher k may possibly be due to the gradual fringing of the crystallite.

After the swelling-deswelling sequence is completed, it seems plausible to assume that the cotton fibre reverts to a fringed fibril structure. However, the "crystalline" cores of these fibrils are smaller in extent or less well organized (or both) than in the parent fibre. Careful observations of decrystallised cotton fibres under the electron microscope would be decisive in this connection.

Finally, a word of caution would not be out of place in looking at these results. It is rarely possible to say
that a certain model of fibre fine structure would be acceptable to the exclusion of all others. Otherwise the proliferation of para-crystalline models which we now have \(^7\), including the total denial of crystallinity \(^8\), would never have occurred. The fact that so many models are there reflects on (a) the difficulties of adequately describing the "coordination statistics" of fibres in terms of minimum detail and maximum generality (b) the difficulties of obtaining enough experimental data on which to base these descriptions. In the present investigation with X-rays, for example, the "crystalline standard" as calculated has not been experimentally realized. There have been indications that more than one "amorphous standard" may exist. The calculation of crystallite sizes is complicated by the poor resolution of the pattern, the need to use half-maximum rather than integral line breadths, possible heterogeneity in size as well as line broadening due to other causes than size. The inferences on fine structure which have been made in this thesis are, therefore, only qualitative and somewhat speculative on account of these limitations.