Small-Angle Neutron Scattering of Selectively Deuterated Cellulose‡, [1]

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ABSTRACT: The extent of hydrogen–deuterium exchange depends on the accessibilities of the ordered and less ordered regions of the cellulose fibers. Because of the difference between the coherent scattering lengths of H and D the deuterium exchange raises the scattering contrast in a neutron small-angle scattering experiment. Selectively deuterated samples exhibit meridional long spacing reflections in the range of 150 to 200 Å: These reflections are not given by untreated samples. The intensity analysis of the first layer line yields a lateral fibril dimension of 34 Å in the case of Fortisan. The central diffuse scattering of natural cellulose can be explained by lozenge-shaped voids which could be related to 120° kinks in the microfibrils.

1. Introduction

The problem of the supermolecular structure of native and regenerated cellulose has been extensively studied during the past 50 years. The beginning of macromolecular science is marked by arguments on the relationship between the crystallite size of cellulose in the chain direction and the length of the cellulose molecules.[3a] Already in 1928 Hengstenberg and Mark[3b] found a crystallite length of 600 Å for Ramie from the line width of the x-ray diffraction pattern and concluded that this dimension is given by the length of the chain molecules, whereas Staudinger[3c] postulated that this length must be 4000 Å at least. The question was resolved by adapting the fringed micelle model to the structure of cellulose.[4] For the case of synthetic polymers in the drawn, highly oriented state the idea of chain folded structures was introduced by Bonart et al.[5] The concept of folded molecules has also been proposed for cellulose,[6,7] but according to other views the molecules are fully extended in the axial direction of the protofibrils.[8,9]

In contrast to most synthetic fibers the crystalline fibrils of native or regenerated cellulose do not show a meridional small-angle x-ray reflection in general, although in some special cases a very weak long spacing reflection could be detected for regenerated cellulose.[10,11,27] Normally the meridional maximum appears only after hydrolytic degradation of the regenerated cellulose, whereby the degree of polymerization approaches the value corresponding to the long spacing.[12] This observation is explained by the assumption[11,13] that the difference of electron density between the "amorphous" and "crystalline" regions is too weak to give rise to a small-angle reflection, but the distinction in chain order causes a selectivity with respect to the chemical degradation.

On the other hand the differences of accessibility have been used by Mark et al.[14] for the estimation of the degree of crystallinity of cellulose by means of the hydrogen–deuterium exchange of the hydroxyl groups. In contrast to the hydrolytic degradation this exchange has been proved to be reversible so long as only the amorphous regions are involved.[15]

We suppose that such selective deuteration will reveal new information on the structure of cellulose if scattering experiments are done by neutrons instead by x rays. The difference between the coherent scattering length of the proton and the deuteron should create a scattering contrast that is not available in the x-ray experiment. Suitable equipment for small-angle neutron scattering (SANS) has been constructed and is available for experiments.[16,17]

The main aims of our investigations are the following: (i) detecting the long spacing of native and regenerated cellulose and measuring the density difference between the crystalline and disordered regions; (ii) searching for the longitudinal periodicity of 30–40 Å revealed in the high-resolution electron microscopy of cellulose protofibrils;[6] and (iii) evaluation of the lateral width of the protofibrils and their arrangement in the cellulose fibers.

The present paper describes preliminary results obtained by the new method and is mainly intended to demonstrate its power and usefullness.

2. Experimental Methods

Experiments were carried out with native (Ramie) and regenerated (Fortisan and Rayon) celluloses.

Vapor-phase deuteration of the samples was carried out in glass tubes which were then sealed in order to avoid rehydrogenation on exposure to atmospheric moisture. As shown by Mann and Marrinan[15] it is the advantage of this technique compared with deuteration in heavy water that one can deuterate the amorphous regions without appreciable deuteration of the crystalline regions. Quartz glass was chosen for the sample tubes for two reasons; first, because it does not exhibit angularly dependent scattering in the small-angle range, and second, because most other forms of glass contain boron which is very efficient in capturing neutrons. The procedure for deuterating the samples was essentially as follows. The cellulose samples were retained in quartz tubes (3 mm in diameter and 100 mm in length) fitted with standard taper joints at both ends. The sample tube was connected to an apparatus similar to that used by Mann and Marrinan[15] as shown in Figure 1. The sample was first thoroughly dried by continuous pumping with an oil backing-pump for about 2 h, a trap cooled in liquid nitrogen being placed between the cellulose and the pump. The hydrogen–deuterium exchange was then carried out by bubbling dry nitrogen at a constant rate through 99.7% heavy water and passing the moist gas over the sample for a certain time between 0.5 and 5 h. The deuteration was stopped by isolating the heavy water from the system (taps T_2 and T_3) and the cellulose was partially dried with the stream of dry nitrogen. When most of the surplus heavy water had been removed the sample was thoroughly dried with the oil backing-pump as described above. Finally the sample tube was sealed near both ends with a torch.

About ten of the sample tubes were fitted in a close-packed parallel arrangement in a frame, in order to get a sufficiently large scattering volume with respect to the effective beam cross section of about 1.5 cm^2. The neutron scattering experiments were carried out on the D11 apparatus of the ILL in Grenoble.

This small-angle scattering camera includes a two-dimensional multidetector for the registration of the scattered neutrons. Five positions at different distances up to 40 m behind the sample are possible. The neutrons come from a cold source and are collimated between two diaphragms of variable distance. Monochromatization is achieved by a velocity selector. The wavelength can be changed between about 0.4 nm and 2 nm with a resolution of about 9% fwhm. For other details of the arrangement we refer to the publication of Ibel.[16]

The presented measurements are carried out with sample–detector distances between 170.0 and 2052.5 cm connected with wavelengths between 0.43 and 1.83 nm. The total relevant range of momentum transfer was 0.023 to 2.8 nm^{-1}. A typical measuring time for one spectrum was about 20 min.

‡ Dedicated to Dr. Maurice L. Huggins on his 80th birthday.

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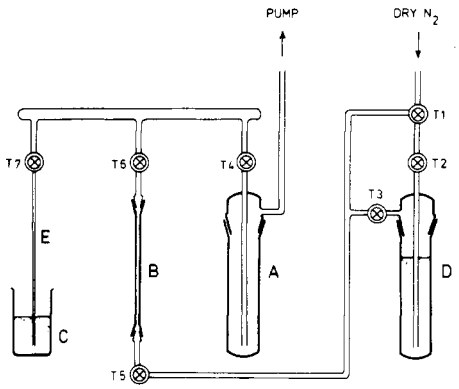

Figure 1. Drawing of the apparatus used for vapor-phase deuteration of the cellulose samples: A, trap cooled in liquid nitrogen; B, quartz sample tube; C, mercury seal to prevent moist air entering and causing rehydrogenation of the sample; D, bubbling tube containing heavy water; E, narrow bore tubing; T_1 to T_7, stopcocks.

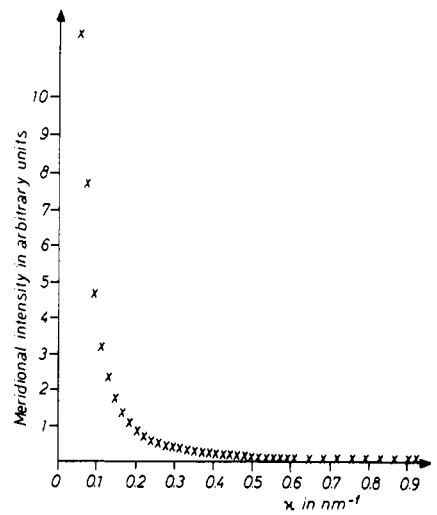

Figure 2. Meridional small-angle x-ray curve of regenerated cellulose fibers (Fortisan).

3. Results and Discussion

The meridional small-angle x-ray scattering curve of Fortisan is shown in Figure 2 as obtained my means of a Kratky camera. As often described in the literature, only a continuous scattering is observed without indication of a long-range periodicity. The small-angle neutron scattering pattern shows the same behavior (see Figure 3 curve a) in the case of the untreated Fortisan fibers. After the hydrogen–deuterium exchange, however, a strong meridional long spacing reflection is observed by SANS, as shown in Figure 3 curve b. Bragg's equation yields a long period of 165 Å. A similar effect of the deuterium exchange was observed in the case of Rayon fibers, as shown in Figure 4, where the long spacing corresponds to an axial periodicity of 193 Å. The appearance of these reflections is evidently caused by the increase in the scattering contrast between the amorphous and crystalline regions.

The results clearly indicate the existence of periodically arranged regions of different accessibility for the heavy water vapor. Surprisingly, the density difference between these regions is vanishingly small, since a completely smooth curve in this κ region is observed in the cases of SANS or SAXS of the original fiber. There is no indication of structural periodicity before "staining" by means of the H–D exchange. Further studies will be concerned with the investigation of the nature of the disordered regions. From measurements of the absolute intensity of the scattered peak as a function of the extent of D exchange, the density of the "amorphous" regions

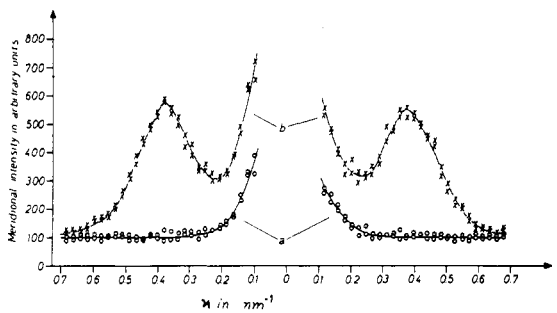

Figure 3. Meridional SANS curves of Fortisan: (a) untreated; (b) after 5 h of treatment with heavy water vapor and selective hydrogen–deuterium exchange. $\kappa = (4\pi/\lambda) \sin(\theta/2)$.

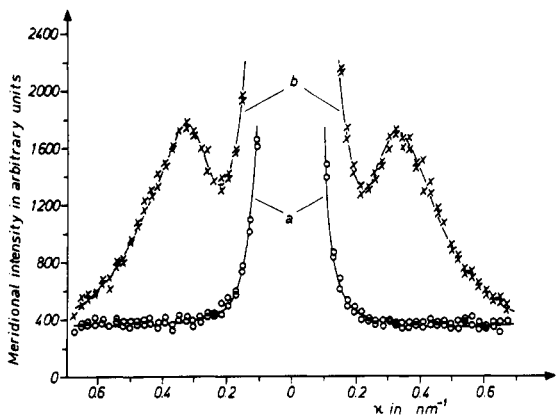

Figure 4. Meridional SANS curves of Rayon: (a) untreated; (b) deuterated for 5 h.

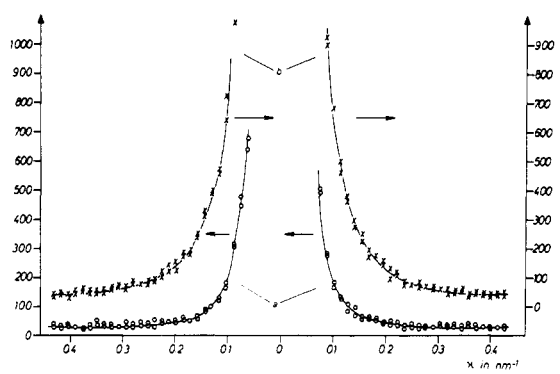

Figure 5. Meridional SANS curves of native cellulose (Ramie): (a) untreated; (b) deuterated for 5 h.

can be evaluated in a similar way as done for the case of SAXS by iodine stained polyethylene fibers.[18] These data will be very valuable for further discussion of the structure of the regenerated cellulose. Up to now our experiments did not show a change of scattered neutron intensity as a function of time of heavy water treatment. Obviously already after 0.5 h all accessible hydroxyl groups were deuterated and further treatment had no effect. The origin of the long spacing reflection is not yet known. In the case of synthetic polymers the existence of partially folded chains is generally assumed to be responsible for the density difference between the "amorphous" and the "crystalline" regions. But on the base of our present knowledge the "fringed micelle model" [4] cannot be refused.

In the case of native cellulose fibers (Ramie) no long spacing reflection was revealed by the D exchange as shown in Figure 5 in the κ range 0.1 to 0.45 nm^{-1}; only a strong increase of intensity due to deuteration is observed. There are also no re-

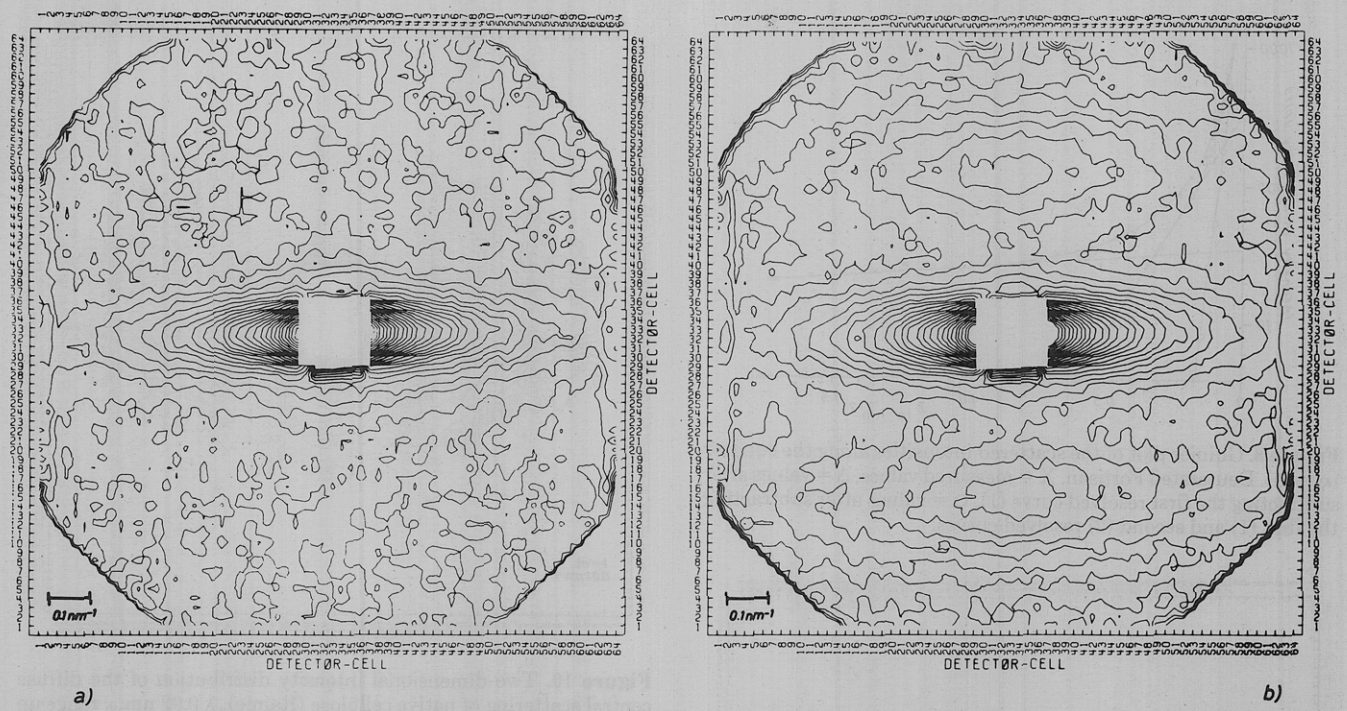

Figure 6. Two-dimensional intensity distribution of the the neutron scattering pattern of regenerated cellulose (Fortisan); λ 1.15 nm, κ range up to $\kappa \simeq 0.69$ nm^{-1} in both directions. Logarithmic scale of equiintensity curves: (a) untreated, (b) deuterated for 5 h. Fiber direction, vertical.

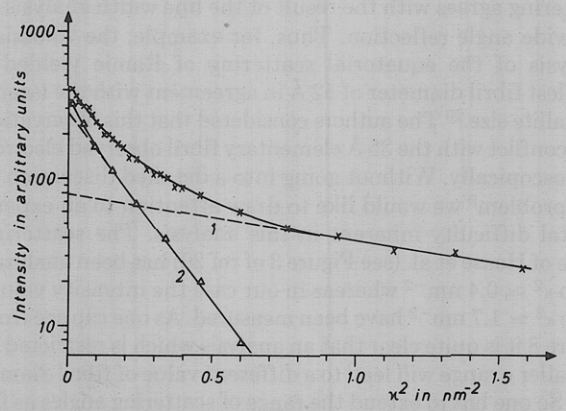

Figure 7. Guinier plot of the scattered intensities along the layer line ($\kappa_3 = 0.38$ nm^{-1}) in the horizontal direction. Deuterated Fortisan. X = measured values, Δ = values after subtracting the first resolved curve (1).

markable changes in the shape of the scattering curves if κ ranges are studied which correspond to Bragg spacing between 20 and 100 Å. So far no periodicities of this order of magnitude have been found in any of the fibers investigated. The absence of a long spacing peak may be either due to the fact that native cellulose does not have periodically arranged regions of different accessibility or due to the concealing effect of the void scattering. This diffuse scattering is very strong for small values of κ where periodicities in the range of 500–700 Å should show up. Within this range crystallite sizes of native cellulose have been found.[3b,19,20] There is some indication that the scattering curve of deuterated native cellulose includes a small component caused by different scattering power of the crystalline and amorphous regions in addition to the void scattering, in so far as the shape of the meridional scattering curve is changed to a small extent by the deuteration. There is, however, no clear answer to this problem at the moment.

Besides the possibility of contrast variation without irreversible chemical degradation, the multidetector of the D11 apparatus in Grenoble[16] allows the measurement of the whole intensity distribution in a plane of the reciprocal space. Figures 6a and 6b show lines of equal intensities for the untreated and deuterated Fortisan. The diffuse equatorial scattering and the meridional layer lines of the deuterated sample can be recognized quite clearly.

From the scattering data the intensity distribution in a horizontal direction can be easily evaluated. Under the assumption that no longitudional space correlation of neighboring fibrils exists, the Guinier plot of the intensity distribution along the layer line yields an estimate of the crystal dimensions in the lateral direction.[22] In the Gaussian approximation one obtains

$$I(\kappa) \sim \exp(-\kappa^2 R_D^2), \quad \kappa = (4\pi/\lambda) \sin(\theta/2)$$

where R_D is the radius of gyration with respect to the direction of the scattered beam. For fibrils with circular cross section of radius R, the radius of gyration is equal to

$$R_D^2 = R^2/4$$

Figure 7 shows the analysis of the layer line profile in the horizontal direction for $\kappa_3 = 0.38$ nm^{-1} [28] corresponding to a Bragg long distance of $L = 165$ Å.

There does not exist a single exponential decay, which is typical for a monodisperse system, but an analysis for the polydisperse system can be made by resolving the curve into successive tangents.[10,21,22] From the slope of the outer part of the curve in Figure 7 a diameter of the crystalline arrays of 34 Å can be derived in excellent agreement with electron microscopical studies which have revealed the existence of 35-Å diameter elementary fibrils as subunits of the microfibrils.[6,9,24] The mean lateral dimension of the crystals determined by Haase et al.[23] from the broadening of the x-ray wide-angle reflections is 50 Å for the case of Fortisan. The small difference is not regarded as a relevant discrepancy in consideration of the experimental errors inherent in both methods. From the experimental curve in Figure 7 a second monodisperse component can be derived by subtracting the contribution of the 34-Å component. The slope yields a diameter of 98 Å ($\sim 8^{1/2}35$ Å) which can be interpreted as caused by fibrils consisting of about eight elementary fibrils. The relative distribution of elementary fibrils and the aggregates can be estimated from

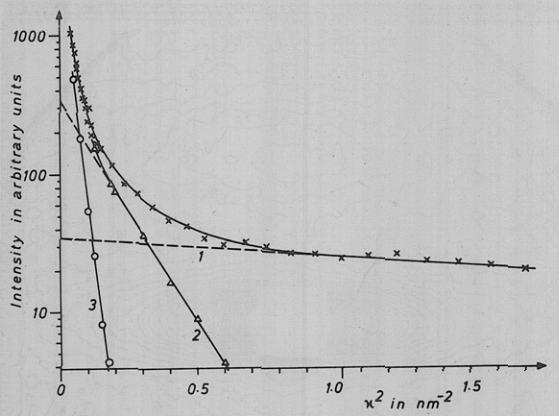

Figure 8. Guinier plot of the scattered intensities along the equator (κ_3 = O). Deuterated Fortisan. X = measured values, Δ = values after subtracting the first resolved curve (1), O = values after subtracting the first (1) and second (2) resolved curves.

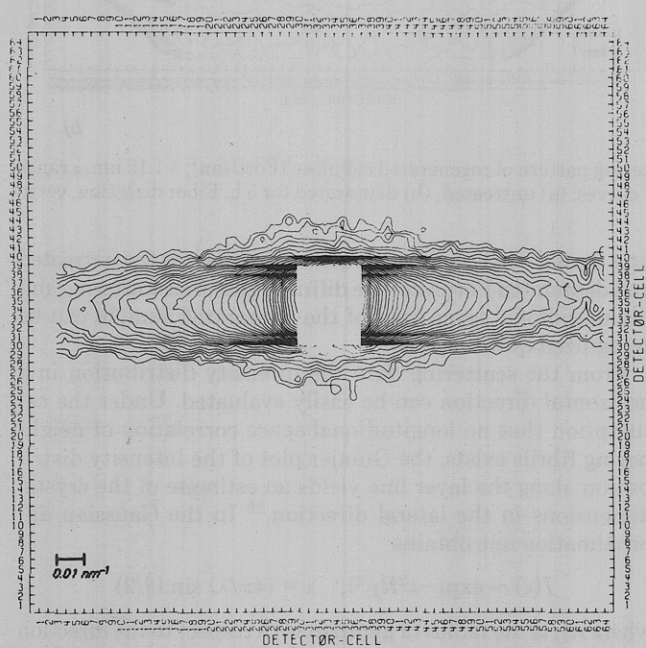

Figure 9. Two-dimensional intensity distribution of the diffuse central scattering of Fortisan. λ 0.92 nm, κ range up to $\kappa \simeq 0.11$ nm^{-1} in both directions. Logarithmic scale of equiintensity curves. Fiber direction, vertical.

the intensity ratio at $\kappa_r = 0$ taking into account the fact that the intensities at the meridian should be proportional to the square of the cross section for each fibril,[22] that means proportional to the fourth power of the diameter. The extrapolated intensity values show that about 71% of the regenerated cellulose is built up of elementary fibrils.

A similar analysis can also be carried out for the diffuse equatorial scattering. Figure 8 shows the experimental values and the successively constructed tangents yielding particle diameters of 22 Å [45%], 110 Å [19%], and 246 Å [36%]. The values in brackets indicate the relative frequency estimated from the intensity ratios.

Whereas the profile of the layer line is due to the shape of the microfibrils, the diffuse low-angle scattering on the equator can be either interpreted as due to the microfibrils neglecting the interparticular interferences[13,23,25] or due to a "dilute" system of microvoids or holes in a dense system.[10,26] Both assumptions have been used for the evaluation of the equatorial small-angle x-ray scattering of cellulose. The first view is apparently supported by the observation of Haase et al.[20,23] that the smallest dimension revealed from the diffuse

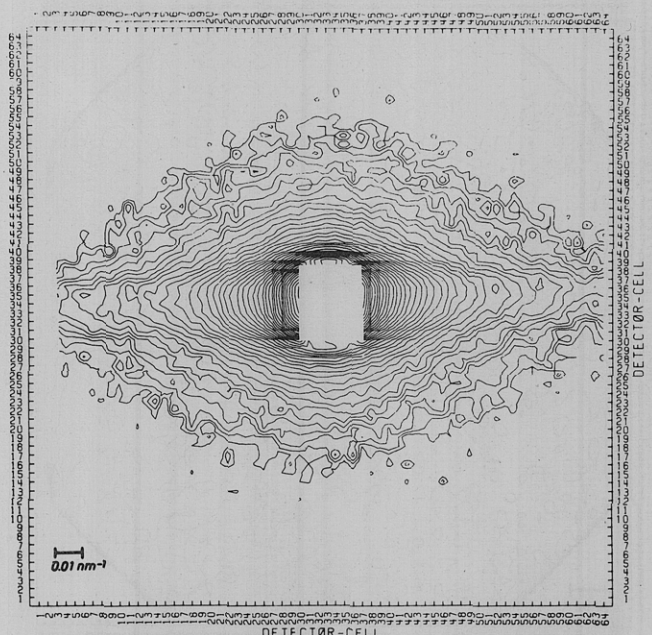

Figure 10. Two-dimensional intensity distribution of the diffuse central scattering of native cellulose (Ramie). λ 0.92 nm, κ range up to $\kappa \simeq 0.11$ nm^{-1} in both directions. Logarithmic scale of equiintensity curves. Fiber direction, vertical.

scattering agrees with the result of the line width analysis of the wide angle reflection. Thus, for example, the Gaussian analysis of the equatorial scattering of Ramie yielded a smallest fibril diameter of 52 Å in agreement with the lateral crystallite size.[20] The authors considered that this observation is in conflict with the 35 Å elementary fibril observed electron microscopically. Without going into a detailed discussion of this problem[9] we would like to draw attention to an experimental difficulty inherent in this analysis. The scattering curve of Haase et al. (see Figure 3 of ref 20) has been analyzed up to $\kappa^2 \simeq 0.4$ nm^{-2} whereas in our case the intensity values up to $\kappa^2 \simeq 1.7$ nm^{-2} have been measured. As one can see from Figure 8 it is quite clear that an analysis which is restricted to a smaller κ range will lead to a different value of fibril diameters. So one has to extend the range of scattering angles as far as possible.

In the case of the Fortisan sample studied in our experiments a definite discrepancy exists between the smallest lateral dimensions calculated from the first layer line on the one hand and from the equatorial scattering on the other hand, namely 35 and 22 Å, respectively. This observation seems to indicate that the continuous equatorial scattering, is caused by microvoids as assumed already by other authors.[10,26] This interpretation is supported by the shape of the two-dimensional intensity distribution for small κ, at least for the case of natural cellulose. Whereas the scattering pattern of Fortisan, see Figure 9, can probably be interpreted as caused by long fibrils with a small cross section, this is no more the case for the scattering pattern of natural cellulose, see Figure 10. The curves of constant intensity are lozenge shaped and indicate that the longitudinal and lateral dimensions of the scattering "particles" are roughly in a ratio of 2:1.

Such a type of scattering cannot be caused by ellipsoidal voids since in that case ellipsoid-shaped equiintensity curves are expected. The pattern of Figure 10 can be explained, however, if lozenge-shaped voids are assumed. This is demonstrated by a light-scattering experiment. The mask of Figure 11a has been constructed from two uncorrelated sets of random variables for the heights and widths of the lozenges. The mean values were in the ratio 2:1; the standard deviation was 50% in both cases. Figure 11b shows the optical diffraction

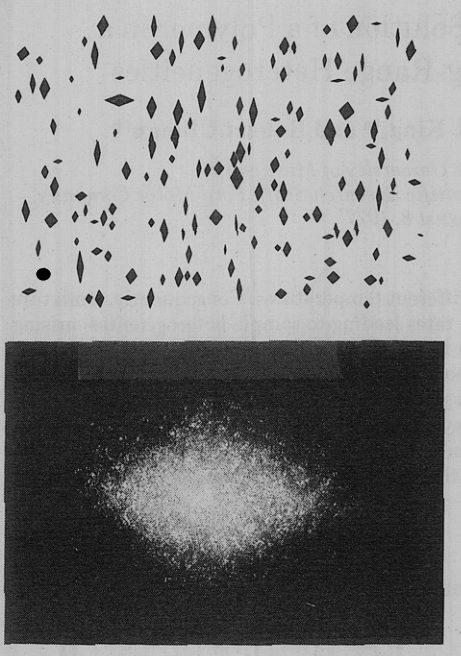

Figure 11. Model experiment by laser light scattering: (a) top, scattering mask, (b) bottom, scattering pattern.

diagram of the mask in Figure 11a; it agrees qualitatively with the observed neutron scattering pattern of Figure 10.

The origin of the lozenge-shaped voids in natural cellulose is not quite clear, but it could be related to the electron microscopical observation[6,7] of rather regular kinks in the microfibrils of Valonia and other kinds of cellulose. The kink angles generally lie in the range of 100–150 °C. If one assumes that the voids are caused by the packing of kinked microfibrils, the kink angle being 120° on the average, a similar scattering pattern could result.

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References and Notes

(1) (a) The measurements were carried out at the D11 instrument of the Institute Laue-Langevin in Grenoble; (b) The scattering experiments are a part of the thesis of P. Herchenröder, Universität Mainz, West Germany.
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(28) κ_3 stands for the component of the scattering vector κ in the direction parallel to the chain direction. Accordingly κ_r means the component of κ in the equatorial plane.