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### Cylindrically symmetrical distribution functions and their application in the structure investigation of cellulose. By N. NORMAN\*, *Department of Physics, University of Oslo, Norway*

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Wrinch (1946) and Vineyard (1951) have shown that if the Patterson distribution function

$$D(\mathbf{r}) = \int \rho(\mathbf{u})\rho^*(\mathbf{u}+\mathbf{r})d\mathbf{u} = \int I(\mathbf{r}^*) \exp[-2\pi i\mathbf{r}\mathbf{r}^*]d\mathbf{r}^* \quad (1)$$

of the density distribution  $\rho(\mathbf{r})$  has cylindrical symmetry, it can be written

$$D(x, z) = 4\pi \int_0^\infty \int_0^\infty x^* I(x^*, z^*) J_0(2\pi x x^*) \cos(2\pi z z^*) dx^* dz^* \quad (2)$$

$I(x^*, z^*)$  is the coherently scattered radiation at the point  $\mathbf{r}^*$  of reciprocal space which has cylindrical coordinates  $(x^*, z^*, \varphi^*)$  and polar coordinates  $(r^*, \theta^*, \varphi^*)$ . The point  $\mathbf{r}$ , of physical space, has similar coordinates, but without an asterisk. Both  $I(\mathbf{r}^*)$  and  $D(\mathbf{r})$  have therefore cylindrical symmetry and a centre of inversion at the origin, so that each may be expanded as a series of even Legendre polynomials; thus,

$$I(\mathbf{r}^*) = I(r^*, \theta^*) = \sum_{n=0}^{\infty} I_{2n}(r^*) P_{2n}(\cos \theta^*) \quad (3)$$

and

$$D(\mathbf{r}) = D(r, \theta) = \sum_{n=0}^{\infty} D_{2n}(r) P_{2n}(\cos \theta), \quad (4)$$

where, for example,

$$I_{2n}(r^*) = \frac{4n+1}{2} \int_0^\pi I(r^*, \theta^*) P_{2n}(\cos \theta^*) \sin \theta^* d\theta^* \quad (5)$$

Further (cf. Deas, 1952, equation (7)), it can be shown that

$$D_{2n}(r) = 2\pi r^{-1/2} (-1)^n \int_0^\infty (r^*)^{3/2} I_{2n}(r^*) J_{2n+1/2}(2\pi r r^*) dr^* \quad (6)$$

The expansion (4) is particularly suitable if the symmetry is not too far from spherical, as the series then converges rapidly.  $D_0(r)$  is equal to the radial distribution function for liquids (Debye & Pirene, 1938).

If  $\rho(\mathbf{r})$  is periodic in  $z$ , the intensity can be written

$$I'(x^*, z^*) = \frac{\sin^2(N_1 \pi c z^*)}{\sin^2(\pi c z^*)}$$

$I'(x^*, z^*)$  is the scattering from the atoms within the repeating unit,  $N_1$  the number of periods and  $c$  the length of the unit of repeat. For large  $N_1$ , the substitution of the above expression in equation (2) results in

$$D(x, z) = 2\pi \frac{N_1}{c} \sum_{l=-\infty}^{\infty} \cos 2\pi l \frac{z}{c} \int_0^\infty x^* I' \left( x^*, \frac{l}{c} \right) J_0(2\pi x x^*) dx^* \quad (7)$$

Formula (7) was first given by MacGillavry & Bruins (1948).

This communication is to report that cylindrically

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symmetrical distribution functions have been used in the structure determination of native and regenerated cellulose. The X-ray scattering from oriented ramie fibers (native cellulose) showed great diffuseness, whereas the diffracted intensity from Fortisan (regenerated cellulose) to a fair degree of approximation was on layer lines in a rotation photograph. Calculations in accordance with (2) for ramie and (7) for Fortisan were therefore performed, and in addition the first three terms in (4) for ramie were determined in order to compare the two methods (2) and (4). The intensities for ramie were obtained through a combination of normal-beam rotation photographs and Weissenberg photographs where the fibers were oscillated  $\pm 60^\circ$  from their initial position normal to the incident beam. Copper  $K\alpha$  radiation was used. In the rotation photographs the radiation was monochromatized by reflexion from a plane rocksalt crystal, and the camera could be either evacuated or filled with hydrogen. The Weissenberg camera was equipped with an additional

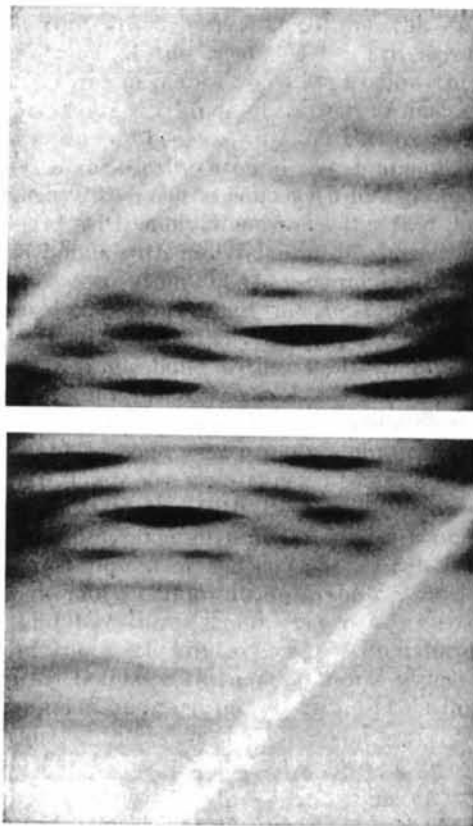


Fig. 1. Weissenberg photograph of ramie fibers oscillated about an axis normal to the fiber axis. Divergence of monochromatic incident beam  $2.5^\circ$ , height of irradiated sample 2 mm. and thickness 0.15 mm. Distance between layer-line screens 1.3 mm. Cu  $K\alpha$  radiation, 40 kVp. and 20 mA. Exposure 120 hr.

vacuum-tight cylinder inside the layer-line screens, and a bent rocksalt crystal focused the incident beam on the sample, which consisted of parallel fibers mounted in a frame. Each spot on the film therefore corresponds to the average intensity in a small volume in reciprocal space, the size of the volume element depending on the divergence of the incident beam, the height of the irradiated sample and the distance between the layer-line screens. Fig. 1 is a Weissenberg photograph for which  $|\Delta r^*|$  is of the order of  $0.03 \text{ \AA}^{-1}$ . For Fortisan the diffracted intensities were recorded on normal- and inclined-beam rotation photographs. The observed intensities were normalized, and the incoherent and the structure independent scattering  $I_{inc}$  and  $\Sigma f_j^2$  were subtracted. Tabulated values for  $I_{inc}$  and  $f_j$  were used.

Figs. 2 and 3 show the results of these calculations for ramie, using equations (2) and (4) respectively; only the first three terms in (4) were used. The contour plots have been compared with vector maps of different models, but so far it has been impossible to make any final decision. The chain structure proposed by Meyer & Misch (1937)



Fig. 2. Ramie. Cylindrical distribution. Negative regions are shaded. (Equation (2).)

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### Crystallographic data for two compounds related to deoxyribonucleic acids.\* By J. S. ROLLETT, Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena 4, California, U.S.A.

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Nucleotides and alkyl diesters of phosphoric acid are being investigated in these laboratories to provide data on the dimensions of groupings in the structures of nucleic acids, nucleoproteins and viruses. Preliminary investigations of two such compounds are here reported.

#### Deoxycytidine 5'-phosphate, $C_9H_{15}O_7N_3P$

A specimen was kindly supplied by Prof. A. R. Todd and his co-workers. Flat needle crystals were obtained by slow evaporation of aqueous solution. The symmetry is monoclinic with

$$a = 21.5, b = 11.2, c = 7.0 \text{ \AA}, \beta = 93^\circ 15'$$

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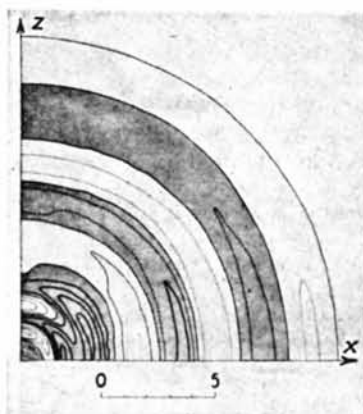


Fig. 3. Ramie. Cylindrical distribution. Negative regions are shaded. (First three terms of equation (4).)

did not fit the experimental data too well. A better agreement between model and contour plots was obtained when every other pyranose ring in the above structure was rotated, but when the twofold screw axis of the molecular chain is abandoned a large number of possibilities has to be tried. Further work on the interpretation of the distribution function is now in progress.

#### References

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Systematic absences determine the space group as  $P2_1$  or  $P2_1/m$ , but the latter is impossible because the molecule is asymmetric.

#### Potassium diethyl thiono-phosphate, $(C_2H_5O)_2POSK$

A specimen was made available by Dr Francis Gunther of the Citrus Experimental Station, Riverside, California. Lath-shaped needles were obtained by evaporation of solutions in acetone at room temperature. The symmetry is monoclinic with

$$a = 21.8, b = 6.6, c = 13.4 \text{ \AA}, \beta = 90^\circ 40'$$

and the crystals are twinned on (100). Systematic absences determine the space group as  $P2_1/n$ .

No further work on these two compounds is contemplated.