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Abstract

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X-RAY DIFFRACTION BY REGIONS CONSISTING OF LONG MOLECULES

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Consideration of the modern data on the structure of linear polymers leads to the conclusion that the structural unit of a number of polymers is an aggregate —a bundle of chains simultaneously passing through regions with different order ([1]). In connection with such a model, it is of interest to calculate the diffraction by regions consisting of long molecules whose axes are parallel to one another. One may imagine packings of parallel chain molecules with various degrees of order. One of the cases—diffraction by a "textured liquid" —was considered by N. S. Andreeva and V. I. Iveronova ([2]).

In the present work a calculation is made of X-ray diffraction by an aggregate of regions forming an axial texture. The regions are identical and are built of long molecules whose axes are parallel to the texture axis. The following cases are considered:

I. Within each region there is complete three-dimensional order. The axes of the chains form a regular lattice. The azimuthal rotations of the chains about their axes and the shifts of the chains along the axis are strictly regular.

II. Free rotation and regular shift of the chains—the chains rotate freely about their axes, but the shift along the axis remains regular.

III. Free rotation and arbitrary shift—this is the case of one-dimensional diffraction, when both the azimuthal rotation and the shift along the axis are arbitrary. The case of arbitrary shift and strict azimuthal order is not considered, as being clearly unrealistic.

I. Let us suppose that there are Z regions, each consisting of n chains. A chain, in turn, consists of N identical groups of atoms, with N large. This repeating group of P atoms will be called the unit cell of the chain. As shown in ([3]), only two types of packing of the projections of chains in the equatorial plane are possible. In one case all chains are translationally identical; in the other case there are two groups of translationally identical chains. Chains are translationally related if they are transformed into one another by means of a vector perpendicular to the chain axis, i.e., lying in the equatorial plane. Chains not translationally related differ by a shift along the texture axis and by a rotation about this same axis.

Let us consider the general case, assuming that all chains in a region can be divided into two groups of translationally identical chains. The scattering intensity of one region, in electronic scattering units, is

$$I = \sum_{kk'} f_k f_{k'} \exp\left(isR_{kk'}\right),$$

where f_k is the atomic factor; $s = 4\pi \sin\theta/\lambda$, and $R_{kk'}$ is the interatomic vector. Let us divide I into two parts: $I = I' + I''$. Into I' will enter all terms relating to summation over atoms of translationally related chains, and into I'' all terms relating to pairs of atoms of chains not translationally related.

Consider I''. Any interatomic vector $\mathbf{R}_{kk'}$ can be represented in the form:

$$\mathbf{R}_{kk'} = \vec{\rho}_{mm'} + l_{kk'}\mathbf{b} + \eta_{mm'}\mathbf{b} + \mathbf{r}_{kk'}.$$

By the indices m and m' we number the chains, and by k and k' the atoms; $\vec{\rho}$ is the interchain vector in the equatorial plane; $\mathbf{b}$ is the vector along the axis, equal to the period of the chain; l is an integer; $|\eta_{mm'}| < 1$. Denote the component of $\mathbf{s}$ along the molecular axis by s_b, and in the equatorial plane by s_r: $\mathbf{s} = s_b + s_r$; similarly for $\mathbf{r}_{kk'}$: the component along the axis is $\eta_{kk'}\mathbf{b}$, in the plane $\vec{\rho}_{kk'}$: $\mathbf{r}_{kk'} = \vec{\rho}_{kk'} + \eta_{kk'}\mathbf{b}$, $\vec{\rho}_{mm'kk'} = \vec{\rho}_{mm'} + \vec{\rho}_{kk'}$, and $\eta_{mm'kk'} = \eta_{mm'} + \eta_{kk'}$. Any pair of cells gives the same set of $\mathbf{r}_{kk'}$, therefore the summation over mm' and kk' can be separated, and after transformations we obtain (ξ is the layer-line number)

$$I'' = N^2 \sum_{mm'} \sum_{kk'} f_k f_{k'} \exp\left[i\left(s_r \vec{\rho}_{mm'kk'} + 2\pi\xi\eta_{mm'kk'}\right)\right].$$

For translationally identical chains $\eta_{mm'} = 0$ and

$$I' = N^2 \sum_{mm'} \sum_{kk'} f_k f_{k'} \exp\left[i\left(s_r \vec{\rho}_{mm'kk'} + 2\pi\xi\eta_{kk'}\right)\right].$$

The rotation of the regions about the texture axis is disordered. The mean intensity scattered by all the regions is: $\overline{I} = \overline{I'} + \overline{I''}$; φ is the azimuthal angle in the equatorial plane. Since

$$\frac{1}{2\pi} \int_0^{2\pi} \exp\left[is_r \vec{\rho}_{mm'kk'}\right] d\varphi = J_0(s_r \rho_{mm'kk'}) \quad (J_0 \text{ is a Bessel function}),$$

then, as a result of averaging, we obtain

$$\overline{I''} = N^2 Z \sum_{mm'} \sum_{kk'} f_k f_{k'} J_0(s_r \rho_{mm'kk'}) \exp\left[i2\pi\xi\eta_{mm'kk'}\right]; \tag{1}$$

$$\overline{I'} = N^2 Z \sum_{mm'} \sum_{kk'} f_k f_{k'} J_0(s_r \rho_{mm'kk'}) \exp\left[i2\pi\xi\eta_{kk'}\right]. \tag{2}$$

Of interest are further transformations of (1) and (2) with the aid of the known expansion of J_0.

$$\rho_{mm'kk'} = \sqrt{\rho^2_{mm'} + \rho^2_{kk'} - 2\rho_{mm'}\rho_{kk'} \cos\varphi_{mm'kk'}},$$

where, if $\alpha_{mm'kk'}$ is the angle between $\vec{\rho}_{mm'}$ and $\vec{\rho}_{kk'}$, then $\varphi_{mm'kk'} = 180^\circ - \alpha_{mm'kk'}$; then

$$J_0(s_r\rho_{mm'kk'}) = J_0(s_r\rho_{mm'})J_0(s_r\rho_{kk'}) + 2\sum_{n=1}^{\infty} J_n(s_r\rho_{mm'})J_n(s_r\rho_{kk'}) \cos n\varphi_{mm'kk'}. \tag{3}$$

First, using (3), let us transform $\overline{I'}$. Since for translationally identical chains $\rho_{kk'} = \rho_{k'k}$ and $\eta_{kk'} = -\eta_{k'k}$, then

$$\sum_{mm'} \sum_{kk'} f_k f_{k'} J_0(s_r\rho_{mm'}) J_0(s_r\rho_{kk'}) \exp\left[i2\pi\xi\eta_{kk'}\right] =$$

$$= \left[n + 2 \sum_{\substack{mm' \\ m'>m}} J_0(s_r\rho_{mm'})\right] \left[\sum_{k=1}^{p} f_k^2 + 2 \sum_{\substack{kk' \\ k'>k}} f_k f_{k'} J_0(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{kk'}\right].$$

$\varphi_{mm'kk'} = 180^\circ - \varphi_{mm'k'k}$, hence the sum $\cos n\varphi_{mm'kk'} + \cos n\varphi_{mm'k'k}$ is equal to zero for odd n, and to $2\cos n\varphi_{mm'kk'}$ for even n. Thus, summation

for translationally related chains gives:

$$\overline{I'} = N^2 Z \left\{ \left[n + 2 \sum_{mm'}^{m'>m} J_0(s_r\rho_{mm'})\right] \left[\sum_{k=1}^{p} f_k^2 + 2 \sum_{kk'}^{k'>k} f_{kf_{k'}} J_0(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{kk'}\right] + \right.$$

$$\left. +8 \sum_{mm'}^{m'>m} \sum_{kk'}^{k'>k} \sum_{\substack{n \\ \text{even}}} f_{kf_{k'}} J_n(s_r\rho_{mm'}) J_n(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{kk'} \cos n\varphi_{mm'kk'} \right\}. \tag{4}$$

Let us now consider $\overline{I''}$. Since (1) contains summation over chains that are not translationally related, then, generally speaking, $\rho_{kk'} \neq 0$, $\eta_{kk'} = 0$, and $m \neq m'$, but $\rho_{mm'kk'} = \rho_{m'mk'k}$ and $\eta_{mm'kk'} = -\eta_{m'mk'k}$.

Grouping all terms by the pairs $mm'kk'$ and $m'mk'k$ and expanding $J_0(s_r\rho_{mm'kk'})$ in a series according to (3), we obtain:

$$\overline{I''} = 2N^2 Z \left[\sum_{mm'}^{m'>m} \sum_{kk'} f_{kf_{k'}} J_0(s_r\rho_{mm'}) J_0(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{mm'kk'} + \right.$$

$$\left. +2 \sum_{mm'}^{m'>m} \sum_{kk'} \sum_{n} f_{kf_{k'}} J_n(s_r\rho_{mm'}) J_n(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{mm'kk'} \cos n\varphi_{mm'kk'} \right]. \tag{5}$$

It is not possible in the general case to carry out simplifications for $\overline{I''}$ of the same kind as for $\overline{I'}$, since, if $\eta_{kk'} = -\eta_{k'k}$, then $\rho_{kk'} \neq \rho_{k'k}$, and similarly for $\eta_{mm'}$ and $\rho_{mm'}$.

II. In this case, among the quantities characterizing the interchain and interatomic distances, $\rho_{mm'}$, $\eta_{mm'}$, and $\eta_{kk'}$ will remain unchanged, while $\varphi_{mm'kk'}$ and $\rho_{kk'}$ will vary.

In considering the cases of free rotation and one-dimensional diffraction, we do not consider the effect on the intensity of changes in the positions of the chain centers in the equatorial plane. Let us note that the formulas obtained below remain valid also in the case when the regular arrangement of the chain axes is disturbed; $\varphi_{mm'kk'}$ assumes any values from 0 to 2π. The mean value $\overline{\cos n\varphi_{mm'kk'}} = 0$. We single out the terms with $m = m'$. Then

$$\overline{I'} = n \left[\sum_{k=1}^{p} f_k^2 + 2 \sum_{kk'}^{k'>k} f_{kf_{k'}} J_0(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{kk'} \right] +$$

$$+2 \sum_{mm'}^{m'>m} \sum_{kk'} f_{kf_{k'}} J_0(s_r\rho_{mm'}) J_0(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{kk'},$$

$$\rho_{kk'} = \sqrt{\rho_k^2 + \rho_{k'}^2 - 2\rho_k\rho_{k'} \cos\psi_{kk'}},$$

where $\vec{\rho}_k$ and $\vec{\rho}_{k'}$ are the projections of $\vec{r}_k$ and $\vec{r}_{k'}$ onto the equatorial plane, and $\psi_{kk'} = 180^\circ - \gamma_{kk'}$, where $\gamma_{kk'}$ is the angle between $\vec{\rho}_k$ and $\vec{\rho}_{k'}$. $\rho_{kk'}$ is not constant, since under independent rotation of the chains $\psi_{kk'}$ varies from 0 to 2π if atoms k and k' belong to different chains. Therefore each $J_0(s_r\rho_{kk'})$ entering the sum must be averaged

$$\sum_{mm'}^{m'>m} \sum_{kk'} f_{kf_{k'}} J_0(s_r\rho_{mm'}) J_0(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{kk'} \; \overline{J_0(s_r\rho_{kk'})} = J_0(s_r\rho_k) J_0(s_r\rho_{k'}).$$

As a result, in the case of free rotation we obtain:

$$\overline{I'} = N^2 Z \left\{ n \left[\sum_{k=1}^{p} f_k^2 + 2 \sum_{kk'}^{k'>k} f_{kf_{k'}} J_0(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{kk'} \right] + \right.$$

$$\left. +2 \sum_{mm'}^{m'>m} J_0(s_r\rho_{mm'}) \sum_{kk'} f_{kf_{k'}} J_0(s_r\rho_k) J_0(s_r\rho_{k'}) \cos 2\pi\xi\eta_{kk'} \right\}. \quad (6)$$

Arguing analogously, for $\overline{I''}$ we obtain:

$$\overline{I''} = 2N^2 Z \sum_{mm'}^{m'>m} \sum_{kk'} f_k f_{k'} J_0(s_r\rho_{mm'}) J_0(s_r\rho_k) J_0(s_r\rho_{k'}) \cos 2\pi\xi\eta_{mm'kk'}. \quad (7)$$

III. Since the averaging for the case of free rotation has been carried out, it remains to consider how formulas (6) and (7) change if the displacement of the molecule along the axis is arbitrary. The result of the averaging is different for $\xi = 0$ and $\xi \neq 0$. If $\xi \neq 0$, then, as is seen from (7), $\overline{I''} = 0$, since

$$\overline{\cos 2\pi\xi\eta_{mm'kk'}} = 0.$$

$$\overline{\cos 2\pi\xi\eta_{kk'}} = 0,$$

if atoms k and k' are from different chains, and

$$\overline{I} = \overline{I'} = N^2 Z n \left[\sum_{k=1}^{p} f_k^2 + 2 \sum_{kk'}^{k'>k} f_k f_{k'} J_0(s_r\rho_{kk'}) \cos 2\pi\xi\eta_{kk'} \right].$$

For $\xi = 0$

$$\overline{I} = \overline{I'} + \overline{I''} = N^2 Z \left\{ n \left[\sum_{k=1}^{p} f_k^2 + 2 \sum_{kk'}^{k'>k} f_k f_{k'} J_0(s_r\rho_{kk'}) \right] + \right.$$

$$+2\sum_{mm'}^{m'>m} J_0(s_r\rho_{mm'})\sum_{kk'} f_k f_{k'} J_0(s_r\rho_k)J_0(s_r\rho_{k'})\Bigg\}.$$

Here the summation is over all chains, since in this case all chains are equivalent.

In conclusion, let us note a characteristic feature of the expressions for $\overline{I'}$ and $\overline{I''}$ in the case of three-dimensional order. In formulas (4) and (5), the terms of the sum over n contain higher orders of Bessel functions. It is known that, as the order increases, the first maximum of the function becomes smaller and shifts to larger values of the argument. Therefore the first term, consisting of functions of zeroth order and independent of the azimuthal order, essentially characterizes the entire intensity curve for small s_r, i.e., small θ. The contribution of the other terms of the sum belongs to the larger θ, the larger the order of this term. The principal result of free rotation consists in the absence of terms with J_n for $n \geq 1$, i.e., in a limitation of the diffraction field. Averaging as a result of changes in $\rho_{kk'}$ will have little effect on the intensity curve. The result of oscillations of the chains within some interval of angles around the texture axis will also be a limitation of the diffraction field, since small changes in $\varphi_{mm'kk'}$ "average out" $\cos n\varphi_{mm'kk'}$ the more strongly, the larger n is.

For calculations by the obtained formulas it is necessary to know the interchain and interatomic distances. If these quantities are known, then, by comparing the results of calculations with experiment, one can study the degree of order in different regions of the polymer. This question will be considered elsewhere.

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Note: Figure translations are in progress. See original paper for figures.