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X-ray Diffraction by Assemblages of Line Scatterers with Application to Linear Polymers*

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The principal halo in the X-ray scattering pattern of a densely packed amorphous linear polymer arises mainly from interferences between adjacent molecular chains. Therefore the relationship between the intensity distribution in the halo and the orientation of the molecules may be analyzed in terms of bundles of parallel line scatterers. This approach takes no account of diffraction effects arising from the structural features of an individual molecular chain.

An expression is derived giving the idealized intermolecular interference pattern as a function of the degree of preferred orientation assumed by the line scatterers. It is shown that the azimuthal intensity distributions predicted by the theory for the limiting cases of (1) randomly and (2) highly oriented molecular bundles are confirmed by experiment.

The theory of X-ray diffraction by assemblages of line scattering elements is of direct interest in connection with the phenomenon of preferred orientation of linear polymer molecules. It is now recognized that in some linear polymers various degrees of preferred orientation can be induced without the occurrence of crystallization (Hill, 1953; Alexander, Ohlberg & Taylor, 1955; Goldstein & Davies, 1955; Ohlberg, Alexander & Warrick, 1958). Thus, in certain elastomers a considerable amount of such 'amorphous' orientation occurs upon elongation of the specimens at temperatures above their melting points. Upon subsequent cooling, the rate of conversion of such oriented regions to the crystalline state is likely to differ from that in the sample as a whole.

Because of the intimate connection that necessarily exists between molecular orientation and actual crystallization, it was deemed worth while to investigate the nature of the X-ray scattering that might be expected from uncrystallized linear polymers. It was recognized that any success which might be achieved in this effort would provide some basis for the experimental evaluation of preferred molecular orientation from the distribution of intensity in the X-ray diffraction pattern.

The form of the X-ray scattering by well-oriented crystalline fibers has been investigated theoretically by a number of investigators (MacGillavry & Bruins, 1948; Vineyard, 1951; James, 1954, pp. 571–89; Norman, 1954). Oster & Riley (1952) have computed the scattering functions for assemblages of parallel solid cylinders and other cylindrically symmetric elements, with emphasis on aggregations of cylindrical particles oriented normally to the X-ray beam and arranged with various degrees of two-dimensional order. For complex aggregations of parallel cylinders displaying random orientations they demonstrated qualitatively that the X-ray interference function must be conically symmetrical about the direct X-ray beam vector, leading to circularly symmetric diffraction patterns when recorded on a flat film.

By analogy to the demonstrable relationship between the azimuthal intensity distribution, $I(\beta)$, in paratropic diffraction arcs and the distribution of orientations, $dN(\varphi)$, in a partially oriented crystalline fiber (Hermans, 1946), it has been proposed in a prior paper (Ohlberg, Alexander & Warrick, 1958) that $I(\beta)$ in the principal amorphous halo and $dN(\varphi)$ for a noncrystalline linear polymer should be related as follows:

$$dN(\varphi) = k \sin \beta I(\beta) d\beta \,. \tag{1}$$

In this expression $dN(\varphi)$ is the number of molecules

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oriented between the angles φ and $\varphi+d\varphi$ to the fiber axis, β is the azimuthal angle measured from the equator of the diffraction pattern, k is a constant, and φ is set equal to β. According to (1), the number of molecules oriented between the angles φ and $\varphi+d\varphi$ is proportional to the intensity in the principal amorphous halo at the azimuth $\beta = \varphi$ weighted by the factor $\sin \beta$.

We may visualize an amorphous linear polymer as comprising a tangled mass of molecular chains in which there is a tendency for chain segments to align themselves into small bundles of roughly parallel segments with a fairly definite nearest neighbor distance. The constituent chain segments are not sufficiently extended or so straight as to permit the development of longitudinal periodicity for appreciable distances; if this were true, as James has shown (James, 1954, p. 583), definite layer lines would appear in the scattering pattern of a preferentially oriented specimen, and experiment does not bear this out. Furthermore, since periodicity along individual chains is effectively absent, there can exist no regular relationship between the longitudinal positions of adjacent chains. Finally, the chains comprising a bundle are not so well packed as to constitute an actual close-packing in a two-dimensional sense, for, were this the case, there would appear in the equatorial plane discrete reflections capable of being indexed on the basis of a two-dimensional lattice.

Since we are primarily interested in the external interference effects, that is to say, interference between X-rays scattered from adjacent chains, let us eliminate from the model any details of structure within a chain. This move is justified as well on the grounds that there is no regular relationship between the longitudinal positions of adjacent chains. Hence, we shall typify any actual linear configuration (zigzag, helix, chain with side groups, etc.) as degenerating in effect to a line-like assemblage of scattering matter. A small bundle of chain segments can then be represented by two parallel lines separated by a distance a and free to revolve about each other. Second, third, etc., nearest neighbors will be excluded from the model to prevent the mathematical development from becoming too unwieldy. This step is also warranted because of the progressively greater variability in the vectors $\mathbf{a}_2$, $\mathbf{a}_3$, etc., between chains separated by greater distances, which will result in only secondary and broadened interference effects. We shall consider first a single bundle of molecules oriented normally to the incident X-ray beam.

1. Molecular axis parallel to the fiber axis and normal to the X-ray beam

The geometrical properties of the model for this case are illustrated in Fig. 1. Let $\mathbf{s}_0$ and $\mathbf{s}$ be unit vectors defining the directions of the direct and scattered X-ray beams respectively. Then $\mathbf{h} = \mathbf{s}-\mathbf{s}_0$ defines a point in reciprocal space with cylindrical coordinates ζ, ξ, γ_0 at which the scattered X-ray intensity is to be evaluated. Let the scattering matter be represented by two like atoms p and q which can appear with uniform probability at any points on the two parallel lines shown, which are of length $2z_0$ and separated by a distance a. In addition, let the line containing atom q rotate freely about the line containing p, which for sake of simplicity we shall make coincident with the Z axis of a cylindrical coordinate system in atomic space.

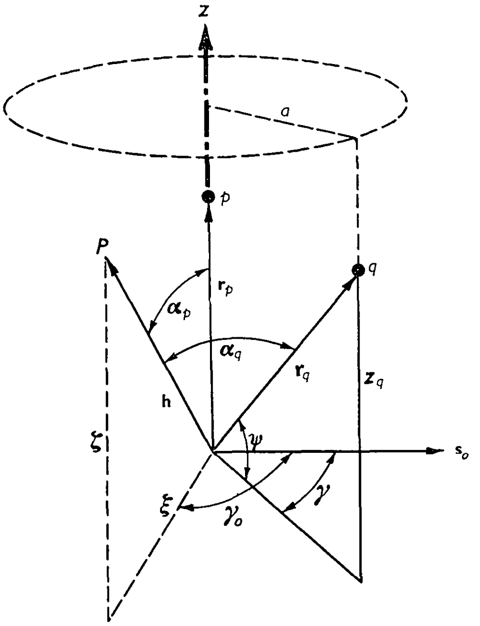


Fig. 1. Geometrical properties of simple model: Molecular axis parallel to the fiber axis and normal to the X-ray beam.

In general, the scattering function for two atoms confined in volumes V_r and $V_{r'}$, where f and f' are their respective scattering factors and $\mathbf{r}$ and $\mathbf{r}'$ their momentary positions relative to some arbitrary origin, may be written (James, 1954, p. 466)

$$I(\mathbf{h}) = \iint ff' \exp\left[i\varkappa\mathbf{h}.(\mathbf{r}-\mathbf{r}')\right] \frac{dv_r}{V_r}\frac{dv_{r'}}{V_{r'}} \,. \tag{2}$$

Here $\varkappa = 2\pi/\lambda$, λ being the wavelength of the X-rays. Making the appropriate substitutions in (2) to describe the present model, we have

$$\begin{aligned} \bar{I} = 2f^2+2f^2 \Bigg[& \int_{-z_0}^{+z_0} \exp\,(i\varkappa\zeta r_p)\,\frac{dr_p}{z_0} \\ & \times \int_{-\pi}^{+\pi}\int_{-\Psi_0}^{+\Psi_0} \exp\left\{-i\varkappa a[\xi\cos(\gamma_0-\gamma)+\zeta\tan\Psi]\right\} \\ & \times \frac{a\sec^2\Psi\,d\gamma\,d\Psi}{2\pi z_0}\Bigg] \,. \end{aligned} \tag{3}$$

Integration of (3) gives

$$\bar{I} = 2f^2\left[1+\frac{\sin^2\varkappa\zeta z_0}{(\varkappa\zeta z_0)^2}J_0(\varkappa a\xi)\right] , \tag{4}$$

wherein J_0 is a Bessel function of zeroth order. The first maximum in J_0 at $\varkappa a\xi = 7{\cdot}0$ corresponds to the principal amorphous halo of the diffraction pattern. For the equatorial section through the diffraction pattern $\zeta = 0$ and $\xi = 2\sin\theta$, so that (4) reduces to

$$\bar{I} = 2f^2[1+J_0(2\varkappa a\sin\theta)]\,, \tag{5}$$

which resembles closely Oster & Riley's (1952) equation (15) for a pair of parallel cylinders.

At non-equatorial azimuths the coefficient $(\sin^2\varkappa\zeta z_0)/(\varkappa\zeta z_0)^2$ in (4) decreases in magnitude rapidly as ζ increases, with the result that the second term becomes negligible except very near the equator. At any appreciable distance from the equator only the continuous independent scattering function, $2f^2$, is observable. This demonstrates that when the molecular axes are oriented normal to the X-ray beam, an interference pattern due to neighboring molecular chains will be observed only on or very near the equator. Oster & Riley (1952) postulate this to be the case for assemblages of cylindrical scatterers but without formal proof. Such an ideal state of molecular orientation in the amorphous state is, of course, not realized experimentally, but lesser degrees of orientation in some polymers are commonly observed, as indicated by a pronounced intensification of the principal amorphous halo on the equator accompanied by diminution of intensity at other azimuths, especially on the meridian (see Fig. 2).

2. Generalized model with a distribution of molecular orientations, $g(\varphi)$

The geometrical properties of this model are so much more complex than in case 1 that it is inadvisable to reproduce here the necessary drawings and the detailed mathematical development. Again substituting the proper quantities in equation (2), we obtain for the scattering as a function of ζ and ξ and the inclination angle φ:

$$\bar{I}(\varphi,\zeta,\xi) = 2f^2\left[1+\int\frac{\sin^2\varkappa z_0 D}{(\varkappa z_0 D)^2}J_0(\varkappa aE)\,d(\gamma_0-\gamma)\right], \tag{6}$$

where

$$D = \zeta\cos\varphi+\xi\cos(\gamma_0-\gamma)$$

and

$$E = \frac{\xi+\zeta\cos(\gamma_0-\gamma)\tan\varphi}{\cos(\gamma_0-\gamma)\{\sec^2\varphi+\tan^2(\gamma_0-\gamma)\}^{\frac{1}{2}}}\,.$$

If it is assumed that the probability of any orientation is a function of φ only, for a particular distribution of orientations, $g(\varphi)$, expression (6) can be written

$$\bar{I}(\zeta,\xi) = 2f^2\left[1+\iint\frac{\sin^2\varkappa z_0 D}{(\varkappa z_0 D)^2}J_0(\varkappa aE)g(\varphi)\,d(\gamma_0-\gamma)\,d\varphi\right]. \tag{7}$$

A test of the validity of this generalized expression is to evaluate it for the case of random orientations, in which event it is required that the diffraction pattern shall have circular symmetry, as is well known from empirical diffraction experiments. This condition may be expressed as

$$I(\zeta,\xi) = G(\zeta^2+\xi^2)\,.$$

For random orientations $g(\varphi) = \sin\varphi$ (Ohlberg, Alexander & Warrick, 1958). Integration of equation (7) after making this substitution is rather involved; hence, details of the process must be omitted here for lack of space. Suffice it to say that if w is defined by the expression

$$w = -\frac{\xi}{\zeta}\cos(\gamma_0-\gamma)\tan\varphi\,,$$

and if $q = \varkappa z_0\zeta(1-w)$ and $x = \cos\varphi$, the scattered intensity can be expressed as

$$\bar{I}(w,\zeta,\xi) = 2f^2\left[1+J_0\left(a\varkappa\frac{\xi^2+\zeta^2 w}{\{\zeta^2w^2+\xi^2\}^{\frac{1}{2}}}\right)\times\int_0^{\frac{\xi}{(\zeta^2w^2+\xi^2)^{\frac{1}{2}}}}\frac{\sin^2(qx)\,\zeta x\,dx}{(qx)^2\{\xi^2-x^2(\xi^2+\zeta^2w^2)\}^{\frac{1}{2}}}\right]. \tag{8}$$

Letting $z = qx$, and expanding $\sin^2(qx)$ in terms of the series expansion for $\cos 2qx$, we can integrate (8) termwise with the result:

$$\bar{I}(w,\zeta,\xi)=2f^2\left[1+J_0\left(a\varkappa\frac{\xi^2+\zeta^2w}{\{\zeta^2w^2+\xi^2\}^{\frac{1}{2}}}\right)\frac{\zeta}{\xi}\sum_{n=1}^{\infty}a_n p^{2n-2}b^{2n}\right], \tag{9}$$

in which

$$p = \varkappa z_0\zeta\cos\varphi\,,$$
$$b = \xi/\{\zeta^2w^2+\xi^2\}^{\frac{1}{2}},$$
$$a_n = (-1)^n 2^{2n-1}\frac{(2n-2)(2n-4)\ldots 2}{(2n)!\,1.3.5\ldots 2n-3}\,.$$

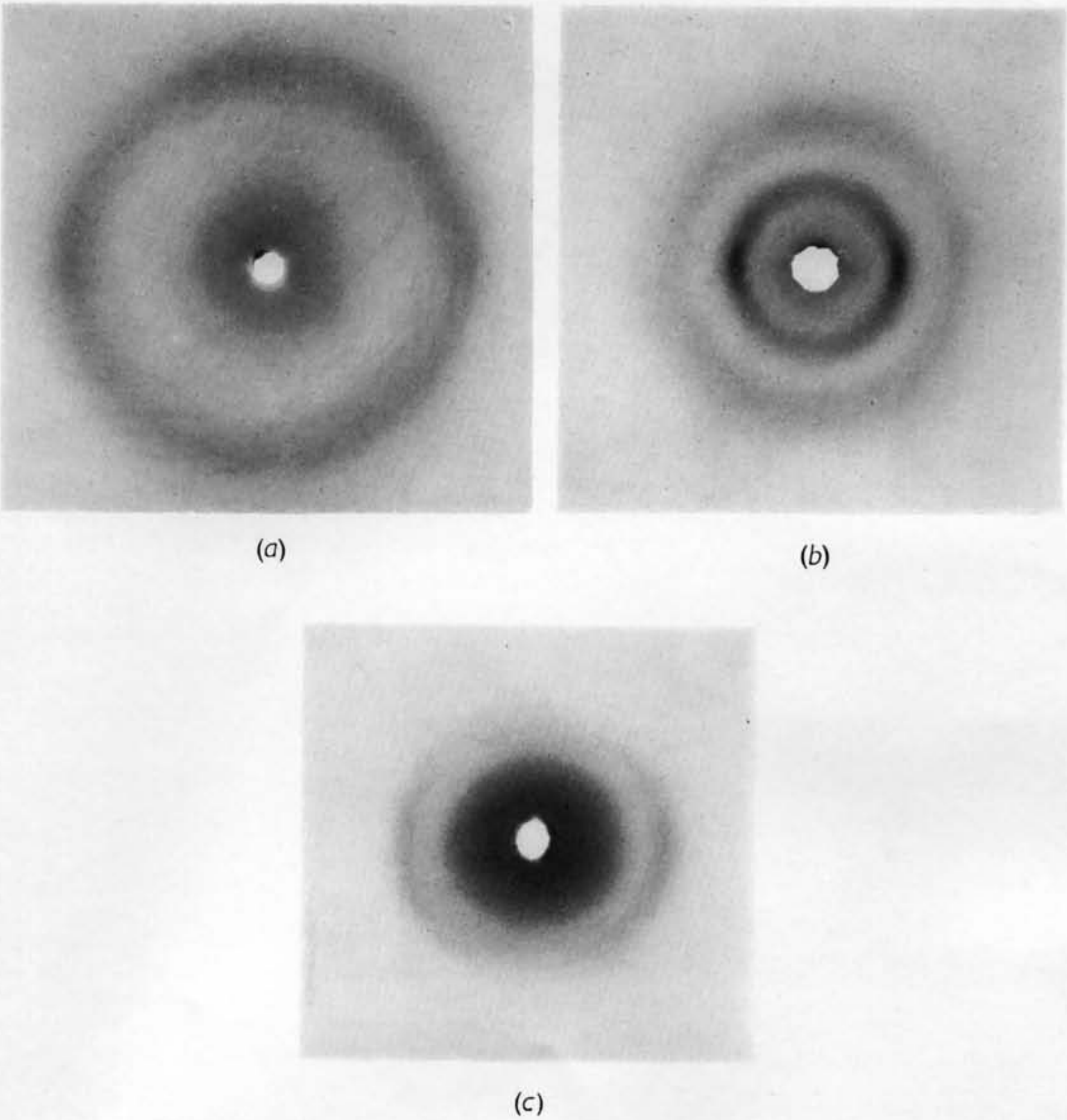
As $w\to\infty$ it can be seen that the Bessel function in (9) approaches the value $J_0(a\varkappa\zeta)$, while for $w\to-\infty$ it approaches the value $J_0(-a\varkappa\zeta)$. Therefore, since $J_0(-x) = J_0(x)$, it follows that a good approximation for the intensity from (9) is

$$\bar{I}(\zeta,\xi) = 2f^2\left[1+\overline{J_0\left(a\varkappa\frac{\xi^2+\zeta^2w}{\{\zeta^2w^2+\xi^2\}^{\frac{1}{2}}}\right)}\frac{\zeta}{\xi}\times\int_{-\infty}^{+\infty}\sum_{n=1}^{\infty}(\varkappa z_0)^{2n-2}a_n\zeta^{2n-1}\xi^{2n-1}\frac{(1-w)^{2n-2}}{(\xi^2+\zeta^2w^2)^n}\,dw\right]. \tag{10}$$

An obvious substitution of the form $w = (\xi/\zeta)\tan\varepsilon$ and some further simplification yield the final result:

$$\bar{I}(\zeta,\xi) = 2f^2\left[1+\overline{J_0\left(a\varkappa\frac{\xi^2+\zeta^2w}{\{\zeta^2w^2+\xi^2\}^{\frac{1}{2}}}\right)}\times\sum_{n=1}^{\infty}(-1)^n\frac{(2\varkappa\xi_0)^{2n-2}}{(2n)!}(\zeta^2+\xi^2)^{n-1}\right]. \tag{11}$$

This expression is a function of the quantity $(\zeta^2+\xi^2)$, as anticipated at the beginning of this section, and so the diffraction pattern of a system of randomly



(a)

(b)

(c)

Fig. 2. Diffraction patterns showing preferred molecular orientation in the amorphous state. Fiber axis vertical. (*a*) Polybutadiene elongated 535 %, (*b*) silicone elastomer elongated 540 %, (*c*) sodium metaphosphate glass fiber.

oriented bundles of line scatterers is shown to be circularly symmetrical.

Equation (7) for the generalized model with a distribution of orientations cannot be integrated directly except when $g(\varphi)$ assumes certain favorable forms (such as $\sin \varphi$); neither does it generally lend itself to inversion by the Fourier–Bessel theorem. Therefore the present mathematical analysis does not lead to a definite conclusion concerning the validity of equation (1).

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The Direct Determination, by Optical-Transform Methods, of the Structure of the Red Form of 5-Methoxy-2-Nitrosophenol. I. Determination of the Trial Structure

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The direct determination of the crystal structure of a compound $C_7O_3NH_7$ has been carried out using optical-diffraction principles without recourse to knowledge of the chemical configuration. The $h0l$ weighted reciprocal-lattice section showed that the molecule probably contained a plane hexagonal ring of atoms and that it was elongated parallel to the c axis. With this assumption, the position of the ring was found by a molecular-location method, signs of the structure factors were deduced from optical transforms, and a Fourier synthesis was performed. Possible positions of the remaining atoms were selected from this and the most likely ones tested by optical-transform methods. This procedure led to a trial structure which, after re-application of the molecular-location method, was refined by normal Fourier methods.

1. Introduction

This investigation was deliberately conceived as an attempt to see whether optical methods could be used to determine a structure directly—in other words, to see whether a structure can be recognized from its X-ray diffraction pattern. The compound was chosen because preliminary work showed that there was some possibility of success, and it was felt to be better to attempt a problem of this sort rather than one of greater difficulty which might not provide as much experience. Two of the authors (K. A. M. & C. A. T.) were kept in ignorance of the probable chemical configuration, being given only the empirical formula, $C_7O_3NH_7$. An outline of the earlier stages of the work has already been published (Crowder, Morley & Taylor, 1957).

2. Preliminary crystallographic results

Oscillation and Weissenberg photographs showed that the space group is $P2_12_12_1$, the unit-cell dimensions being $a = 17{\cdot}11$, $b = 3{\cdot}80$, $c = 10{\cdot}67$ Å. The density, $1{\cdot}46$ g.cm.$^{-3}$, showed that there are four molecules of $C_7O_3NH_7$ in the unit cell.

The short b axis indicated that the (010) projection was likely to be the most informative, and thus a $h0l$ weighted reciprocal-lattice section was derived. The first photographs taken were rather underexposed and gave only about 70 measurable reflexions out of a possible total of 230; this number was however considered reasonable to start with. The intensities were estimated visually and the weighted reciprocal-lattice section using approximate unitary structure factors derived from them is shown in Fig. 1.