

ing on the original choice of w , with or without Jaswon's restriction on the size of t . The simplest way of plotting centred lattices is temporarily to ignore the centring, choose u, v, w as lattice vectors, with integral components, which define a unit cell of volume equal to that of the centred unit cell, and plot the lattice planes so described. Then, centre each of the seven vectors $u, v, w, u+v, v+w, w+u, u+v+w$ that satisfies the conditions in Table 1. Finally, plot extra nets of points based on each of the centring points.

Table 1. Conditions under which a lattice vector with integral components s_1, s_2, s_3 will be centred

Lattice	Condition	Number of tested vectors that will be centred
Body-centred	s_1, s_2, s_3 of same parity	1
Face-centred	$s_1 + s_2 + s_3$ even	3
Base (C)-centred	$s_1 + s_2$ and s_3 , both even	1

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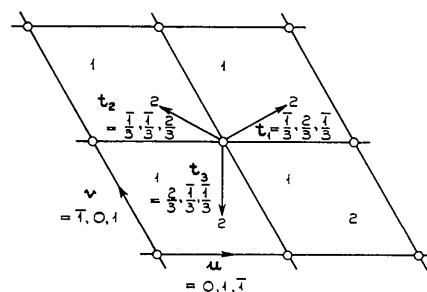


Fig. 2. Plot of (111) planes in a body-centred cubic lattice; the numbers show lattice points in successive planes with ones representing body-centre sites. Three possible shift vectors [as defined by equations (2) and (6)] t_1, t_2, t_3 are shown, all being of equal length. The lattice vector joining successive layers is clearly not $\frac{1}{2}u$ but could be $\frac{1}{2}(t_1+v)$ or $\frac{1}{2}(t_2+u+v)$ or $\frac{1}{2}(t_3+u)$.

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One-Dimensional Models for Small-Angle X-ray Diffraction from Crystalline Polymers.

I. General Model

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The relationship between a one-dimensional model for predicting small-angle X-ray scattering from crystalline polymers and a three-dimensional structure containing a one-dimensional periodicity is discussed. The basic features of previous models are reviewed. Based on the approach of Hosemann for a simple two-phase system, a model is formulated in which the density variation within the crystalline regions is described by an arbitrary function $\zeta(y)$.

Introduction

This article is concerned with the formulation of a general one-dimensional model suitable for describing discrete small-angle X-ray scattering from crystalline polymers. The diffraction occurs at angles around one degree and is generally attributed to a regular alternation in texture every 100–300 Å between crystalline and amorphous-like intercrystalline regions. In most types

of sample, the periodicity within each local scattering sequence is essentially one-dimensional. This is well illustrated by the case of samples made by sedimenting a suspension of solution grown polymer crystals. In their simplest form, the crystals are about 100 Å thick, bordered on their planar surface by thin layers of amorphous-like material (Keller, 1968). Thus on sedimenting, the crystals stack on top of one another to form a periodic crystalline–amorphous structure perpendicular

to the lamellar planes. However both the crystalline and amorphous thickness can fluctuate in size throughout the sample, so that the periodicity is imperfect and the resulting diffraction peaks are broad.

It is an obvious simplification to represent the periodicity within such polymer structures with a one-dimensional model and to overlook the structural details in the other two dimensions. The approach allows the nature of the periodicity to be described and visualized with the minimum number of parameters. Most previous treatments of this kind have considered two distinct phases where the mean electron density changes abruptly at each crystal-amorphous phase boundary. This leads to models where the one-dimensional variation in electron density traces a rectangular step function. The main aim of the present article is to generalize this approach so that the variation in density of the crystalline regions can be described by an arbitrary function ξ . This provides a framework for considering more subtle structural features, such as a gradual rather than an abrupt change in density between the crystalline and amorphous regions [part II, Blundell (1970)].

The article is in three main parts. The first part reviews the basis for representing three-dimensional structures with one-dimensional models, and shows that the models must represent the projection of the electron density onto a line perpendicular to the incident beam. The second part reviews the characteristics and merits of previous models where the density variation is a rectangular step function. Finally a two phase model by Hosemann (1949) is used as basis for formulating the more general model.

Relation between three-dimensional structure and one-dimensional model

For polymer samples consisting of crystalline and amorphous phases, it is possible to simplify the scattering problem by considering only the excess in electron density over the background amorphous value, since the additional scatter associated with the amorphous background only occurs at angles which are too small for observation (Guinier, 1963, p. 323). The complete sample will consist of many separate structures possessing a one-dimensional periodicity. Consider one such sequence where the mean excess electron density is given by $\varrho(\mathbf{r})$, and where the periodicity occurs along the component r_3 of the space vector \mathbf{r} . The angle of scatter can be defined by the customary reciprocal space vector $\mathbf{s} = (\mathbf{S} - \mathbf{S}_0)/\lambda$, whose length $s = |\mathbf{s}| = 2 \sin \theta/\lambda$; where \mathbf{S}_0 and \mathbf{S} are the unit direction vectors of the incident and scattered rays respectively, and 2θ is the total angle of scatter. Omitting the absolute constant of proportionality, the amplitude of the scattered radiation in the direction \mathbf{S} will be given by

$$a(\mathbf{s}) = \iiint \varrho(\mathbf{r}) \exp[-2\pi i \mathbf{s} \cdot \mathbf{r}] d\mathbf{r}.$$

For small angle scattering where $\theta \rightarrow 0$, \mathbf{s} becomes ap-

proximately perpendicular to \mathbf{S}_0 . The discrete diffraction of interest occurs when \mathbf{s} is parallel to the direction of component r_3 . If r_3 is therefore arranged to be perpendicular to \mathbf{S}_0 and provided the approximation of \mathbf{s} being perpendicular to \mathbf{S}_0 is good, then the discrete meridional scatter for \mathbf{s} parallel to r_3 will be given by:

$$a(s) = \iiint \varrho(r_1 r_2 r_3) dr_1 dr_2 \exp[-2\pi i s r_3] dr_3.$$

By integrating with respect to r_1 and r_2 , this can now be reduced to a one-dimensional problem:

$$a(s) = \int \varrho(r_3) A(r_3) \exp[-2\pi i s r_3] dr_3 \quad (1)$$

where $A(r_3)$ is the cross-sectional area of the structure at the point r_3 , and $\varrho(r_3)$ is now the mean excess electron density over the whole area $A(r_3)$.

Equation (1) can now be thought of in terms of a one-dimensional model. It represents exactly the amplitude of the meridional scatter from a line of non-overlapping scattering rods arranged perpendicular to \mathbf{S}_0 . The rods can be considered as representing the projection of the excess density of the crystalline regions of the three-dimensional structure, while the gaps between the rods represent the intervening amorphous regions (Bonart, 1966). If for simplicity it is assumed that the cross-sectional area A is constant over the whole length of the three-dimensional structure, then the variations in the rod density will reflect only changes in the projected crystallinity. Thus if the boundary between crystalline and amorphous phases is sharp and perfectly planar, $\varrho(r_3)$ will be a rectangular step function. If on the other hand the boundaries meander or genuine intermediate phases occur, the density profile of the rods will be smoothed out accordingly.

It should be noted that equation (1) only maps out the amplitude for scattering directions where \mathbf{s} is strictly parallel to the r_3 component. However since the cross-sectional area in real space is finite, the value of the intensity in the plane $s_3 = \text{constant}$ of Fourier space will fall off on either side of the central position where $s_1 = s_2 = 0$. For a typical sample the orientations of the individual scattering sequences will be such that all these neighbouring positions in Fourier space will be cut by the Ewald sphere. It is well known that if the area of the scatterer in real space is A , the total spot intensity for a given s_3 is equivalent to that obtained by making the intensity remain constant at its maximum value over a restricted region of Fourier space of area $1/A$ (Guinier, 1963). The total meridional diffracted intensity for one scattering sequence can therefore be obtained from (1) by calculating the quantity $(a^*a)/A$. To obtain the observed intensity for a sample containing many scattering sequences one must also take account of the relevant Lorentz factor for the distribution of orientations (Hosemann & Bagchi, 1962, p. 440).

Previous models

Most previous treatments have effectively considered scattering rods of constant density inferring that there is an abrupt change in projected density at amorphous-crystalline boundaries. Historically the first treatment of the one-dimensional problem was by Zernike & Prins (1927), who effectively considered an infinite number of rods of constant density. They assumed the length of the gaps between the rods fluctuated from place to place according to an exponential distribution, while the length of the rods remained constant. Later Hermans (1944) considered the case where both the rod and gap lengths varied. The most complete and general treatment of this kind has been given by Hosemann (1949) (see also Hosemann & Bagchi, 1962, p. 410). He considered constant density rods of finite number N , where the statistics of the rod and gap lengths were given by independent general distribution functions H and h respectively. The distinguishing feature of this theory of Hosemann is that there is no correlation between any two lengths, whether rods or gaps, except that they should randomly obey their respective distributions H and h . Each periodic length, from the beginning of one rod to the beginning of the next, depends on the individual lengths taken by both the intervening rod and gap. A similar situation exists in the study by Vonk & Kortleve (1967) and Kortleve & Vonk (1968) in which a comparison is made between theoretical and experimental correlation functions.

However there is also a slightly different approach to the problem, whereby the rods are considered as forming a one-dimensional paracrystal (see Hosemann & Bagchi, 1962, p. 302). This approach begins by defining an array of lattice points where the periodic distance fluctuates from place to place according to a specified distribution. The rod scatterers are then placed at the lattice points; the rod lengths can fluctuate amongst themselves, but their distribution is independent of, and cannot be correlated with, the previously defined statistics of the lattice. The resulting intensity expression is simpler than for the previously mentioned model of Hosemann in that the effects of the lattice statistics and the rods lengths can be separated into independent factors. For reasons of simplicity the paracrystal approach may therefore be preferred. However a paracrystal is basically unsound for representing polymer structures since it places more importance on the rods than on the gaps between them. In real samples the amorphous regions as represented by the gaps, are equally as important as the crystalline regions in spacing out the periodic structure. The model formulated in this article is therefore based on the former approach of Hosemann (1949).

General model

The model discussed here is an extension of the treatment in Hosemann & Bagchi (1962, p. 408). Consider

N scattering rods denoted individually by subscript j , which are arranged along an axis u perpendicular to S_0 (Fig. 1). Each rod is of length Y_j and has its left side located at the point u_j ; it is separated from the rod on the left by a gap of length Z_{j-1} and from the rod on the right by Z_j . However whereas Hosemann considered rods of constant density, the situation is generalized by describing the density by the arbitrary function $\xi(y_j, Y_j)$, where y_j is a variable defined from zero to Y_j . The lengths Y_j and Z_j are assumed to vary randomly from rod to rod from zero to infinity according to the normalized general distribution functions $H(Y_j)$ and $h(Z_j)$ respectively. There is no correlation between any particular Y_j or Z_j . Thus the distance between any two scatterers will depend on the values taken independently by all the intervening Y_j and Z_j . It will be noted that the dependence of ξ on Y_j will involve ξ suffering an appropriate affine type of transformation from rod to rod.

Let us assume for simplicity that the cross-sectional area A in equation (1) is unity, so that the rods can be considered purely as a one-dimensional problem. The amplitude of the scattered radiation is then given exactly by

$$a(s) = \int_{u_1}^{u_{N+1}} \rho(u) \exp[-2\pi i s u] du \\ = \sum_{j=1}^N \int_{u_j}^{u_{j+1}} \rho(u) \exp[-2\pi i s u] du.$$

Since $\rho(u)$ is only non-zero in the rods themselves, *i.e.* in the region $0 < y_j < Y_j$, then

$$a(s) = \sum_{j=1}^N \int_0^{Y_j} \xi(y_j) \exp[-2\pi i s (u_j + y_j)] dy_j \\ = \sum_{j=1}^N \exp[-2\pi i s u_j] f_j(Y_j, s),$$

where

$$f_j = \int_0^{Y_j} \xi(y_j) \exp[-2\pi i s y_j] dy_j$$

which is the scattering amplitude of rod j .

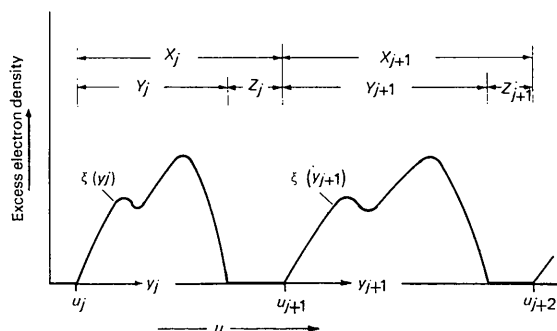


Fig. 1. Model of rod scatterers with general density profile $\xi(y)$.

The resulting intensity will therefore be

$$i(s) = a(s) \cdot a^*(s) \\ = \sum_{j=1}^N \sum_{k=1}^N \exp[-2\pi i s(u_j - u_k)] f_j f_k^* .$$

The expectation value of this double summation can be evaluated by considering the terms in groups.

First consider the terms with $k=j$, which will be equal to $\sum_{j=1}^N f_j f_j^*$. Since f_j is a function of Y_j , and the values taken by Y_j are given statistically by the distribution $H(Y_j)$, the expectation value of these terms will be equal to NJ , where $J = \int_0^\infty |f_j|^2 H(Y_j) dY_j$.

Now consider the $(N-1)$ terms with $k=(j-1)$ which will have the general form

$$\exp[-2\pi i s(Y_{j-1} + Z_{j-1})] f_j f_{j-1}^* .$$

Each length Y_{j-1} and Z_{j-1} will be given statistically by $H(Y_j)$ and $h(Z_j)$ respectively. The expectation value of all terms will therefore be

$$(N-1) \left\{ \int_0^\infty f_{j-1}^* H(Y_{j-1}) \exp[-2\pi i s Y_{j-1}] dY_{j-1} \right\} \\ \times \left\{ \int_0^\infty h(Z_{j-1}) \exp[-2\pi i s Z_{j-1}] dZ_{j-1} \right\} \\ \times \left\{ \int_0^\infty f_j(Y_j) H(Y_j) dY_j \right\} = (N-1) G_y F_z \gamma_y$$

where quite generally, for any j ,

$$G_y = \int_0^\infty f_j^* H \exp[-2\pi i s Y_j] dY_j \\ F_z = \int_0^\infty h \exp[-2\pi i s Z_j] dZ_j \\ \gamma_y = \int_0^\infty f_j H dY_j .$$

Similarly for terms with $k=(j+1)$, the expectation value amounts to the conjugate quantity:

$$(N-1) G_y^* F_z^* \gamma_y^* .$$

Hence the sum of all terms with $k=j \pm 1$ will have an expectation value:

$$= 2(N-1) \operatorname{Re}\{G_y F_z \gamma_y\} .$$

Next consider terms where $k=(j-2)$, there will be $(N-2)$ terms of the form

$$\exp[-2\pi i s(Y_{j-2} + Z_{j-2} + Y_{j-1} + Z_{j-1})] \\ f_j(Y_j) f_{j-2}^*(Y_{j-2}) .$$

There is no correlation between Y_{j-2} , Y_{j-1} , Z_{j-2} , Z_{j-1} , so the expectation value for these terms will be

$$(N-2) G_y F_z F_y F_z \gamma_y$$

where the factor $F_y = \int_0^\infty H \exp[-2\pi i s Y_j] dY_j$.

The terms with $k=(j+2)$ give the conjugate of this quantity, so that the expectation value of all terms with $k=(j \pm 2)$ will therefore be

$$2(N-2) \operatorname{Re}\{G_y \gamma_y F_z^2 F_y\} .$$

Similarly the sum of all terms with $k=(j \pm r)$ will be

$$2(N-r) \operatorname{Re}\{G_y \gamma_y F_z^r F_y^{r-1}\} .$$

Hence the sum of all terms with $k \neq j$ will amount to

$$\operatorname{Re}\{2G_y \gamma_y F_z \sum_{r=0}^{N-1} (N-r-1) (F_y F_z)^r\} .$$

This summation reduces to

$$\operatorname{Re}\left\{2G_y \gamma_y F_z \left[\frac{N}{(1-F_y F_z)} - \frac{1-(F_y F_z)^N}{(1-F_y F_z)^2} \right]\right\} .$$

Thus by adding now the term for $j=k$, the expectation value of the total intensity is found to be the sum of two intensity terms i_B and i_C , where

$$i_B = \operatorname{Re}\left\{N \left[J + \frac{2G_y \gamma_y F_z}{(1-F_y F_z)} \right]\right\} \\ \text{and} \\ i_C = \operatorname{Re}\left\{ \frac{2G_y \gamma_y F_z [1-(F_y F_z)^N]}{(1-F_y F_z)^2} \right\} . \quad (2)$$

If $\xi(y)$ is made constant, these two terms degenerate into those with similar notation in the analysis of Hosemann & Bagchi (1962). i_B is directly proportional to N and in simple cases can be shown to obey Babinet's Principle in that it is unchanged if the density variation along the rods is inverted. i_B is mainly responsible for the first and higher order diffraction peaks (if resolvable). The shape and width of these peaks depends on the degree of imperfection in the periodicity. The intensity term i_C gives the zero order scatter; it also contains contributions which broaden the peaks of i_B in a similar way to crystal size effects in atomic lattices. If N is sufficiently large and/or if the distribution functions H and h are sufficiently broad, then i_C can be neglected. The conditions for neglecting i_C are fully discussed by Hosemann & Bagchi (1962).

In order to use these results for three-dimensional structures, equations (2) must be interpreted as representing the total meridional scatter for a structure of unit area of cross section. If \bar{X} is the mean periodic length, the length of the structure will be $N\bar{X}$. Thus the total meridional scatter per unit volume of scattering sequence will be given by

$$I_B(s) = \operatorname{Re}\left\{ \frac{1}{\bar{X}} \left[J + \frac{2G_y \gamma_y F_z}{(1-F_y F_z)} \right] \right\} \quad (3)$$

and

$$I_C(s) = \operatorname{Re}\left\{ \frac{2G_y \gamma_y F_z [1-(F_y F_z)^N]}{N\bar{X}(1-F_y F_z)^2} \right\} .$$

For crystalline polymers the main term of interest outside the zero order scatter will be I_B . Equation (3) has, therefore, been evaluated in part II (Blundell, 1970) for the particular case when $\xi(y)$ has a trapezium-like profile. This case represents a structure whose projected density shows a gradual linear change in density on going from the amorphous to the crystalline values.

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One-Dimensional Models for Small-Angle X-ray Diffraction from Crystalline Polymers. II. Model with Continuous Density Changes between Phases

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The small angle X-ray scatter from crystalline polymers is evaluated by using a one-dimensional model where the density between crystal and amorphous phases changes linearly over a finite transition range t , and where the sizes of the crystal and amorphous regions fluctuate according to independent Gaussian distributions. The calculation is based on the general model formulated in part I. Approximate expressions are derived for the width and area of the diffraction peaks. The dependence on t occurs in the factor $\sin^2 \pi st / (\pi st)^2$ which affects only the peak intensities. An analysis is made to find how the factor will modify theoretical interpretations based on experimental intensity measurements.

1. Introduction

When X-rays are scattered from crystalline polymers, diffraction maxima are observed at small angles corresponding to Bragg spacings of a few hundred Ångströms. This scatter is generally attributed to an alternation in texture between crystalline and amorphous-like intercrystalline regions, in which both regions fluctuate in thickness about their respective mean values. Most theoretical treatments consider the phenomenon in terms of one-dimensional models where the mean density changes abruptly between the crystalline and amorphous values, giving a rectangular step density profile. The model discussed in this article introduces, between each phase, a transition zone where there is linear change in density from the crystalline to amorphous value, thus giving a repeated trapezium shape to the density profile.

The review of the basic scattering situation in part I (Blundell, 1970) showed that the periodicity within a typical polymer sample can be represented by a one-dimensional model consisting of a line of non-overlapping scattering rods arranged parallel to the period-

icity. The line of rods can then be interpreted as representing the projection onto the line of the excess in electron density over the background amorphous value. Part I concluded by formulating a general expression for the scattered intensity of a model where the density along a rod was given by an arbitrary function ξ . In the present work ξ is taken to have a trapezium profile in which there are transition zones of length t at the ends of each rod. Such a transition length has also been considered by Tsvankin (1964 *a, b*) in a model which is based on slightly different assumptions from those used in part I, and which employed different distribution statistics from those used here. However in Tsvankin's conclusions, the effects of t are not clearly resolved from the other parameters in his model. In the present article particular attention is paid to the ways in which the intensity curves for a simple rectangle profile must be modified when a transition zone is introduced.

In this article particular reference is made to the conditions prevailing in samples made by sedimenting solution grown crystals (particularly polyethylene), since of all polymer systems these have the most well char-