

## 4. DIFFUSE SCATTERING AND RELATED TOPICS

particular level depending on the layers present at adjacent levels. This is a one-dimensional disordered structure that can be used to describe a random copolymer. Blackwell and co-workers have developed a similar theory in terms of a one-dimensional paracrystalline model (Hosemann & Bagchi, 1962) for diffraction by random copolymers (Blackwell *et al.*, 1984; Biswas & Blackwell, 1988a), and this is the theory described here.

Consider a random copolymer made up of monomer units (residues) of  $N$  different types. Since the disorder is along the length of the polymer, some of the main characteristics of diffraction from such a molecule can be elucidated by studying the diffraction along the meridian of the diffraction pattern. The meridional diffraction is the intensity of the Fourier transform of the polymer chain projected onto the  $z$  axis and averaged over all possible monomer sequences. The diffraction pattern depends on the monomer (molar) compositions, denoted by  $p_i$ , the statistics of the monomer sequence (described by the probability of the different possible monomer pairs in this model) and the Fourier transform of the monomer units. Development of this model shows that the meridional diffracted intensity  $I(Z)$  can be written in the form (Blackwell *et al.*, 1984; Biswas & Blackwell, 1988a; Schneider *et al.*, 1991)

$$I(Z) = \sum_i p_i |F_i(Z)|^2 + 2 \sum_i \sum_{j \neq i} \Re\{F_i(Z)F_j^*(Z)T_{ij}(Z)\}, \quad (4.5.2.30)$$

where the summations are over the different monomer types and  $F_i(Z)$  is the axial Fourier transform of the  $i$ th monomer unit (each referenced to a common origin). The  $T_{ij}(Z)$  are most conveniently described by defining them as the  $ij$ th element of an  $N \times N$  matrix  $\mathbf{T}$ , which is given by

$$\mathbf{T} = \frac{\mathbf{PMX}(Z)}{\mathbf{I} - \mathbf{MX}(Z)}, \quad (4.5.2.31)$$

where  $\mathbf{P}$ ,  $\mathbf{M}$ ,  $\mathbf{X}(Z)$  and  $\mathbf{I}$  are  $N \times N$  matrices.  $\mathbf{I}$  is the unit matrix and  $\mathbf{P}$  is a diagonal matrix with elements  $p_i$ . The elements  $M_{ij}$  of  $\mathbf{M}$  are the probabilities of forming  $ij$  monomer pairs and can be generated for different kinds of random sequence (*e.g.* chemical restrictions on the occurrence of particular monomer pairs, random chains, varying degrees of blockiness, tendency towards alternating sequences *etc.*) (Schneider *et al.*, 1991). The matrix  $\mathbf{X}(Z)$  is diagonal with elements equal to  $\langle \exp(i2\pi Z\zeta_i) \rangle$  where the  $\zeta_i$  are the projected monomer lengths and the average is over all chain conformations.

Equation (4.5.2.30) can be used to calculate the meridional diffraction for a particular random copolymer. The most important result of such a calculation is that intensity maxima are spaced irregularly along the meridian. The positions of the maxima depend on the monomer proportions, the sequence statistics and the projected monomer lengths.

The full cylindrically averaged diffraction pattern, denoted by  $I(R, Z)$ , from a noncrystalline specimen containing oriented random copolymer chains can be calculated by replacing  $F_i(Z)$  in equation (4.5.2.30) by  $F_i(R, Z)$ , *i.e.*

$$I(R, Z) = \sum_i p_i |F_i(R, Z)|^2 + 2 \sum_i \sum_{j \neq i} \Re\{F_i(R, Z)F_j^*(R, Z)T_{ij}(Z)\} \quad (4.5.2.32)$$

(Biswas & Blackwell, 1988a). Note that we write  $I(R, Z)$  rather than  $I_l(Z)$  since the pattern cannot be indexed on the basis of regularly spaced layer lines. The  $F_i(R, Z)$  in equation (4.5.2.32) depend on the chain conformation, since this affects the range of monomer orientations and hence their average diffraction. Chivers & Blackwell (1985) have considered two extreme cases,

one corresponding to fixed conformations between monomers and the other corresponding to completely random conformations between monomers, and have derived expressions for the diffracted intensity in both cases. Equation (4.5.2.32) allows one to calculate the fibre diffraction pattern from an array of parallel random copolymers that exhibit no lateral ordering. The diffraction pattern consists of irregularly spaced layer lines whose spacings (in  $Z$ ) are the same as those described above for the meridional maxima. Measurement of layer-line spacings and intensities and comparison with calculations based on the constituent monomers allows chain conformations to be estimated (Biswas & Blackwell, 1988a).

Diffraction patterns from liquid-crystalline random copolymers often contain sharp Bragg maxima on the layer lines. This indicates that, despite the random sequence and the possible dissimilarity of the component monomers, the chains are able to pack together in a regular way (Biswas & Blackwell, 1988b,c). Expressions that allow calculation of diffraction patterns for arrays of polymers with minimal registration, in which short, non-identical sequences form layers, have been derived (Biswas & Blackwell, 1988b,c). Calculation of diffracted intensities, coupled with molecular-mechanics modelling, allows chain conformations and packing to be investigated (Hofmann *et al.*, 1994).

## 4.5.2.4.4. Partially crystalline fibres

In this section we address disorder in the packing of the molecules in a polycrystalline fibre. The presence of disorder within the crystallites modifies the intensities of the Bragg reflections, as well as introducing continuous diffraction. The dominant effect, sometimes seen on fibre diffraction patterns (Stroud & Millane, 1995a), is for Bragg reflections to remain at low resolution but to be replaced by continuous diffraction at high resolution. There are two distinct cases to consider. The first is where the distortions at different lattice points in the crystallite are uncorrelated, and the second is where they are correlated.

Disorder within a crystallite in a polycrystalline fibre may consist of (1) deviations in the positions of the molecules (which are treated as rigid bodies) from their positions in a regular lattice, (2) rotations of the molecules about their molecular axes from their rotational positions in an ordered crystal, and (3) random orientations (up or down) of the molecules. The first of these is called *lattice disorder*, and the second and third are components of *substitution disorder*.

Uncorrelated disorder has been treated by a number of authors (Clark & Muus, 1962; Tanaka & Naya, 1969; Fraser & MacRae, 1973; Arnott, 1980). A rather complete model has been described by Millane & Stroud (1991) and Stroud & Millane (1995b), which is presented here. If the lattice and substitution disorders are independent, and the lattice and substitution distortions at different lattice sites are uncorrelated, then the cylindrically averaged layer-line intensities  $I_l(R)$  diffracted from a fibre can be written as a sum of Bragg and diffuse (continuous) intensities (Tanaka & Naya, 1969):

$$I_l(R) = I_l^B(R) + I_l^D(R). \quad (4.5.2.33)$$

The profiles of the Bragg reflections are independent of the position of the reflection in reciprocal space. If the Cartesian components of the lattice distortions are independent, normally distributed, and the  $x$  and  $y$  components have equal variances, cylindrical averaging of the diffracted intensity can be performed analytically.

The lattice disorder consists of distortions of the two-dimensional lattice (in the lateral plane) into three-dimensional space, and in the *absence* of substitution disorder the Bragg component is given by (Stroud & Millane, 1995b)

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$$I_l^B(R) = I_l(R_{hk})w_{\text{lattice}}(R_{hk}, l/c) \quad (4.5.2.34)$$

where  $I_l(R_{hk})$  is given by equation (4.5.2.24), the *lattice disorder weight*,  $w_{\text{lattice}}(R, Z)$ , is given by

$$w_{\text{lattice}}(R, Z) = \exp[-4\pi^2(R^2\sigma_{\text{lat}}^2 + Z^2\sigma_{\text{axial}}^2)], \quad (4.5.2.35)$$

where  $\sigma_{\text{lat}}^2$  and  $\sigma_{\text{axial}}^2$  are the variances of the lattice distortions normal ('lateral') and parallel ('axial') to the  $z$  axis, respectively. The diffuse component is given by

$$I_l^D(R) = (1/A_{\text{cryst}})I_l(R)[1 - w_{\text{lattice}}(R, l/c)], \quad (4.5.2.36)$$

where  $I_l(R)$  is given by equation (4.5.2.17) and  $A_{\text{cryst}}$  is the average cross-sectional area of the crystallites. Inspection of equations (4.5.2.34) and (4.5.2.36) shows that the effect of the lattice disorder is to weight the amplitudes of the Bragg reflections down with increasing  $R$  and  $l$ , and to introduce a continuous intensity component whose amplitude increases with  $R$  and  $Z$ . Furthermore, the amplitude of the diffuse component relative to the Bragg component is inversely proportional to  $A_{\text{cryst}}$ , and therefore is not significant unless the crystallites are small.

If substitution disorder is also present, then equation (4.5.2.33) still applies but equations (4.5.2.34) and (4.5.2.36) are replaced by

$$I_l^B(R) = \left| \sum_n w_{nl} G_{nl}^2(R_{hk}) \exp[in(\psi_{hk} + \pi/2)] \right|^2 w_{\text{lattice}}(R_{hk}, l/c) \quad (4.5.2.37)$$

and

$$I_l^D(R) = (1/A_{\text{cryst}}) \sum_n |G_{nl}(R)|^2 [1 - |w_{nl}|^2 w_{\text{lattice}}(R, l/c)], \quad (4.5.2.38)$$

respectively, where the *substitution disorder weight*,  $w_{nl}$ , is given by

$$w_{nl} = \int_0^{c/2\pi} \int_0^z p(\varphi, z) \exp[i(2\pi z l/c - n\varphi)] d\varphi dz. \quad (4.5.2.39)$$

In equation (4.5.2.39),  $p(\varphi, z)$  is the probability density function (p.d.f.) that describes the substitution disorder, *i.e.* the p.d.f. for a molecule being rotated by  $\varphi$  about and translated by  $z$  along the molecular axis relative to its position in the undistorted lattice. Inspection of equations (4.5.2.37) and (4.5.2.38) shows that the substitution disorder weights the different contributing Bessel terms differently. This can lead to quite complicated effects on the diffraction pattern for various kinds of substitution disorder, resulting in different distributions and amplitudes of Bragg and diffuse diffraction over the diffraction pattern (Stroud & Millane, 1995b). If one assumes either uniform or normal distributions for  $\varphi$  and  $z$ , then expressions can be obtained for the  $w_{nl}$  in terms of the variances of the distributions of  $\varphi$  and  $z$  (Stroud & Millane, 1995b). The cases where distortions in  $\varphi$  are correlated with distortions in  $z$  (*e.g.* 'screw disorder'), and directional (up and down) disorder, can also be accommodated. This model has been shown to be capable of predicting diffraction patterns which are in good agreement with those measured from some disordered polycrystalline fibres (Stroud & Millane, 1995a).

We consider now the case of correlated packing disorder. As a result of intermolecular contacts within a polycrystalline

specimen, it is possible that distortions at one lattice site will affect the degree of distortion at neighbouring sites. Coupling between distortions at different lattice sites can be included in the model of disorder by allowing the distortions at different lattice sites to be correlated. The effect of correlated distortions on diffraction patterns is that the diffracted intensity does not separate into Bragg and diffuse components as it does in the case of uncorrelated distortions [equation (4.5.2.33)]. The intensity can be described as being diffuse on the whole diffraction pattern, with (often broad) maxima occurring at some of the reciprocal-lattice points, but with no significant maxima at other reciprocal-lattice points. The widths of the profiles of the maxima generally increase with increasing resolution, whereas the widths of the Bragg maxima resulting from uncorrelated disorder as described above are independent of resolution. A broadening of diffraction maxima with increasing resolution and blending into continuous diffraction is sometimes seen on diffraction patterns from polycrystalline fibres, indicating the presence of correlated disorder (Stroud & Millane, 1996b).

Correlated lattice disorder consists of correlated distortions of the two-dimensional lattice into three-dimensional space. A flexible model of crystalline disorder is that based on the perturbed lattice approach (Welberry *et al.*, 1980). While formulating perturbed lattices with only nearest-neighbour interactions is complicated, a more tractable approach is to base the statistics on an imposed correlation field (de Graaf, 1989; Stroud & Millane, 1996a). This approach has been used to describe cylindrically averaged diffraction from polycrystalline fibres that contain correlated lattice disorder and uncorrelated substitution disorder (Stroud & Millane, 1996a,b), and is presented here.

To develop a flexible and tractable theory for diffraction from crystallites with correlated disorder, it is necessary to formulate the problem in real space. The size and shape of a crystallite in the  $xy$  (lateral) plane is described by a *shape function*  $s_{\text{lat}}(\mathbf{r})$ , where  $\mathbf{r}$  denotes the position vector in real space, which is equal to unity inside the crystallite and zero outside. The autocorrelation of the shape function,  $t(\mathbf{r})$ , is given by

$$t(\mathbf{r}) = \int s(\mathbf{r}') s(\mathbf{r} + \mathbf{r}') d\mathbf{r}'. \quad (4.5.2.40)$$

The correlations between the  $x$  components, and between the  $y$  components, of the distortions at any two lattice sites are taken to be identical. The correlations between distortion vectors are defined in terms of lateral,  $\rho_{\text{lat}}(\mathbf{r})$ , and axial,  $\rho_{\text{axial}}(\mathbf{r})$ , correlation fields such that the correlation coefficients between components of the distortions in the  $x$  (or  $y$ ) and  $z$  directions, respectively, are equal to the correlation field evaluated for  $\mathbf{r}$  equal to the inter-site vector. Various functional forms for the correlation fields are possible, but exponential correlation functions are usually used (Stroud & Millane, 1996a). If  $t(\mathbf{r})$  and the correlation fields are circularly symmetric, then cylindrical averaging of the diffracted intensity can be performed analytically.

For a polycrystalline fibre with correlated lattice disorder and uncorrelated substitution disorder, the diffracted intensity is given by (Stroud & Millane, 1996b)

$$\begin{aligned} I_l(R) &= \sum_{j,k} t(r_{jk}) w_{\text{lat}}(R, r_{jk}) w_{\text{axial}}(l/c, r_{jk}) \\ &\times \sum_{m,n} J_{n-m}(2\pi R r_{jk}) \Re\{w_{ml} w_{nl}^* G_{ml}(R) G_{nl}^*(R)\} \\ &\times \exp[i(m-n)\varphi_{jk}] \end{aligned} \quad (4.5.2.41)$$

where  $r = |\mathbf{r}|$ , the sum over  $(j, k)$  is over all the sites of the undistorted lattice within the region occupied by the autocorrelation function,  $(r_{jk}, \varphi_{jk})$  are the polar coordinates of the

