

## 4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

$$F_l(\mathbf{H}) = \sum_j \sum_n f_j J_n(2\pi H_r r_j) \exp\{-in\psi_j\} \\ \times \exp(2\pi i l z_j) \exp\{in[\Psi + (\pi/2)]\} \quad (4.2.4.35)$$

or

$$F_l(\mathbf{H}) = \sum_n (\alpha_n + i\beta_n) \exp\{in\Psi\}$$

$$\alpha_n = \sum_j f_j J_n(2\pi H_r r_j) \cos\{n[(\pi/2) - \psi_j] + 2\pi l z_j\}$$

$$\beta_n = \sum_j f_j J_n(2\pi H_r r_j) \sin\{n[(\pi/2) - \psi_j] + 2\pi l z_j\}.$$

Intensity in the  $l$ th diffuse layer is given by

$$I_l = \sum_n \sum_{n'} [(\alpha_n \alpha_{n'} + \beta_n \beta_{n'}) + i(\alpha_{n'} \beta_n - \alpha_n \beta_{n'})] \\ \times \exp\{i(n - n')\Psi\}. \quad (4.2.4.36)$$

(a) *Cylinder symmetry* (free rotating molecules around the chain axis or statistical averaging with respect to  $\psi$  over an assembly of chains). Only component  $F_{0l}$  occurs:

$$F_{0l}(H_r, L) = 2\pi \int \int \langle a_M \rangle J_0(2\pi H_r r) \exp\{2\pi i l z\} r \, dr \, dz$$

or

$$F_{0l}(H_r, L) = \sum_j f_j J_0(2\pi H_r r_j) \exp\{2\pi i l z_j\}.$$

In particular,  $F_{00}(H_r)$  determines the radial component of the molecule projected along  $z$ :

$$F_{00}(H_r) = \sum_j f_j J_0(2\pi H_r r_j).$$

(b) *p-fold symmetry* of a plane molecule (or projected molecule) as outlined previously: only components  $np$  instead of  $n$  occur. Bessel functions  $J_0$  and  $J_p$  are sufficient in most cases.

(c) *Vertical mirror plane*: see above.

(d) *Horizontal mirror plane* (perpendicular to the chain): Exponentials  $\exp\{2\pi i l z\}$  in equation (4.2.4.32) may be replaced by  $\cos 2\pi l z$ .

(e) *Twofold symmetry axis* perpendicular to the chain axis (at positions  $\psi = 0, 2\pi/p, \dots$ ). Exponentials in equation (4.2.4.32),  $\exp\{-i(np\psi - 2\pi l z)\}$ , are replaced by the corresponding cosine term  $\cos(np\psi + 2\pi l z)$ .

Formulae concerning the reverse method (Fourier synthesis) are not given here (see, e.g., Vainshtein, 1966). Usually there is no practical use in diffuse-scattering work because it is very difficult to separate out a single component  $F_{nl}$ . Every diffuse layer is affected by all components  $F_{nl}$ . There is a chance if one diffuse layer corresponds predominantly to one Bessel function.

#### 4.2.4.3.2. Disorder within randomly distributed collinear chains

Deviations from strict periodicities in the  $z$  direction within one chain may be due to loss of translational symmetry of the centres of the molecules along  $z$  and/or due to varying orientations of the molecules with respect to different axes, such as azimuthal misorientation, tilting with respect to the  $z$  axis or combinations of both types. As in 3D crystals, there may or may not exist 1D structures in an averaged sense.

##### 4.2.4.3.2.1. General treatment

All formulae given in this section are only special cases of a 3D treatment (see, e.g., Guinier, 1963). The 1D lattice (4.2.4.12) is

replaced by a distribution:

$$d(z) = \sum_\nu \delta(z - z_\nu)$$

$$D(L) = \sum_\nu \exp\{2\pi i L z_\nu\} \quad (4.2.4.37)$$

$$F(\mathbf{H}) = F_M(\mathbf{H})D(L).$$

The Patterson function is given by

$$P(\mathbf{r}) = [a_M(\mathbf{r}) * a_M - (\mathbf{r})] * [d(z) * d - (z)]. \quad (4.2.4.38)$$

Because the autocorrelation function  $w = d * d$  is centrosymmetric

$$w(z) = N\delta(z) + \sum_\nu \sum_\mu \delta[z - (z_\nu - z_\mu)] + \sum_\nu \sum_\mu \delta[z + (z_\nu - z_\mu)], \quad (4.2.4.39)$$

the interference function  $W(L) (= |D(L)|^2)$  is given by

$$W(L) = N + 2 \sum_\nu \sum_\mu \cos 2\pi [L(z_\nu - z_\mu)] \quad (4.2.4.40)$$

$$I(\mathbf{H}) = |F_M(\mathbf{H})|^2 W(L). \quad (4.2.4.41)$$

Sometimes, e.g. in the following example of orientational disorder, there is an order only within domains. As shown in Section 4.2.3, this may be treated by a box or shape function  $b(z) = 1$  for  $z \leq z_N$  and 0 elsewhere.

$$d(z) = d_\infty b(z)$$

$$a(\mathbf{r}) = a_M(\mathbf{r}) * [d_\infty b(z)] \quad (4.2.4.42)$$

$$F(\mathbf{H}) = F_M(\mathbf{H})[D_\infty * B(L)]$$

with

$$b(z) * b - (z) \leftrightarrow |B(L)|^2 \quad (4.2.4.43)$$

$$I = |F_M(\mathbf{H})|^2 |D_\infty * B(L)|^2.$$

If the order is perfect within one domain one has  $D_\infty(L) \simeq \sum \delta(L - l)$ ;  $(D_\infty * B) = \sum D(L - l)$ ; i.e. each reflection is affected by the shape function.

##### 4.2.4.3.2.2. Orientational disorder

A misorientation of the chain molecules with respect to one another is taken into account by different structure factors  $F_M$ .

$$I(\mathbf{H}) = \sum_\nu \sum_\mu F_\nu(\mathbf{H}) F_\mu(\mathbf{H})^+ \exp\{2\pi i L(z_\nu - z_\mu)\}. \quad (4.2.4.44)$$

A further discussion follows the same arguments outlined in Section 4.2.3. For example, a very simple result is found in the case of uncorrelated orientations. Averaging over all pairs  $F_\nu F_\mu^+$  yields

$$I(\mathbf{H}) = N(\langle |F|^2 \rangle - \langle |F|^2 \rangle) + \langle |F|^2 \rangle L(L), \quad (4.2.4.44a)$$

where

$$\langle |F|^2 \rangle = 1/N^2 \langle F_\nu F_\mu^+ \rangle \\ = \sum_\nu \alpha_\nu F_\nu(\mathbf{H}) \sum_\mu \alpha_\mu F_\mu^+(\mathbf{H}) \quad (\nu \neq \mu)$$

$$\langle |F|^2 \rangle = 1/N \langle F_\nu F_\nu^+ \rangle = \sum_\nu \alpha_\nu |F_\nu(\mathbf{H})|^2.$$

Besides the diffuse layer system there is a diffuse background modulated by the  $\mathbf{H}$  dependence of  $[\langle |F(\mathbf{H})|^2 \rangle - \langle |F(\mathbf{H})|^2 \rangle]$ .

#### 4. DIFFUSE SCATTERING AND RELATED TOPICS

##### 4.2.4.3.2.3. Longitudinal disorder

In this context the structure factor of a chain molecule is neglected. Irregular distances between the molecules within a chain occur owing to the shape of the molecules, intrachain interactions and/or interaction forces *via* a surrounding matrix. A general discussion is given by Guinier (1963). It is convenient to reformulate the discrete Patterson function, *i.e.* the correlation function (4.2.4.39).

$$w(z) = N\delta(z) + \sum_{\nu} \delta[z \pm (z_{\nu} - z_{\nu+1})] + \sum_{\nu} \delta[z \pm (z_{\nu} - z_{\nu+2})] + \dots \quad (4.2.4.39a)$$

in terms of continuous functions  $a_{\mu}(z)$  which describe the probability of finding the  $\mu$ th neighbour within an arbitrary distance

$$w'(z) = w(z)/N = \delta(z) + a_1(z) + a_{-1}(z) + \dots + a_{\mu}(z)a_{-\mu}(z) + \dots \quad (4.2.4.45)$$

$$[\int a_{\mu}(z) dz = 1, a_{\mu}(z) = a_{-\mu}(-z)].$$

There are two principal ways to define  $a_{\mu}(z)$ . The first is the case of a well defined one-dimensional lattice with positional fluctuations of the molecules around the lattice points, *i.e.* long-range order is retained:  $a_{\mu}(z) = \mu c_0 + z_{\mu}$ , where  $z_{\mu}$  denotes the displacement of the  $\mu$ th molecule in the chain. Frequently used are Gaussian distributions:

$$c' \exp\{-(z - \mu c_0)^2/2\Delta^2\}$$

( $c'$  = normalizing constant;  $\Delta$  = standard deviation). Fourier transformation [equation (4.2.4.45)] gives the well known result

$$I_d \sim (1 - \exp\{-L^2\Delta^2\}),$$

*i.e.* a monotonically increasing intensity with  $L$  (modulation due to a molecular structure factor neglected). This result is quite analogous to the treatment of the scattering of independently vibrating atoms. If (short-range) correlations exist between the molecules the Gaussian distribution is replaced by a multivariate normal distribution where correlation coefficients  $\kappa^{\mu}$  ( $0 < \kappa < 1$ ) between a molecule and its  $\mu$ th neighbour are incorporated.  $\kappa^{\mu}$  is defined by the second moment:  $\langle z_0 z_{\mu} \rangle / \Delta^2$ .

$$a_{\mu}(z) = c'' \exp\{-(z - \mu c_0)^2/2\Delta^2(1 - \kappa^{\mu})\}.$$

Obviously the variance increases if the correlation diminishes and reaches an upper bound of twice the single site variance. Fourier transformation gives an expression for diffuse intensity (Welberry, 1985):

$$I_d(L) \sim \exp\{-L^2\Delta^2\} \sum_j (-L^2\Delta^2)^j / j! \times (1 - \kappa^{2j}) / (1 + \kappa^{2j} - 2\kappa^j \cos 2\pi L c_0). \quad (4.2.4.46)$$

For small  $\Delta$ , terms with  $j > 1$  are mostly neglected. The terms become increasingly important with higher values of  $L$ . On the other hand,  $\kappa^j$  becomes smaller with increasing  $j$ , each additional term in equation (4.2.4.46) becomes broader and, as a consequence, the diffuse planes in reciprocal space become broader with higher  $L$ .

In a different way – in the paracrystal method – the position of the second and subsequent molecules with respect to some reference zero point depends on the *actual* position of the predecessor. The variance of the position of the  $\mu$ th molecule relative to the first becomes unlimited. There is a continuous transition to a fluid-like behaviour of the chain molecules. This 1D paracrystal (sometimes called distortions of second kind) is only a special case of the 3D paracrystal concept (see Hosemann & Bagchi, 1962; Wilke, 1983). Despite some difficulties with this

concept (Brämer, 1975; Brämer & Ruland, 1976) it is widely used as a theoretical model for describing diffraction of highly distorted lattices. One essential development is to limit the size of a paracrystalline grain so that fluctuations never become too large (Hosemann, 1975).

If this concept is used for the 1D case,  $a_{\mu}(z)$  is defined by convolution products of  $a_1(z)$ . For example, the probability of finding the next-nearest molecule is given by

$$a_2(z) = \int a_1(z') a_1(z - z') dz' = a_1(z) * a_1(z)$$

and, generally:

$$a_{\mu}(z) = a_1(z) * a_1(z) * a_1(z) * \dots * a_1(z)$$

( $\mu$ -fold convolution).

The mean distance between next-nearest neighbours is

$$\langle c \rangle = \int z' a_1(z') dz'$$

and between neighbours of the  $\mu$ th order:  $\mu \langle c \rangle$ . The average value of  $a_{\mu} = 1/\langle c \rangle$ , which is also the value of  $w(z)$  for  $z > z_k$ , where the distribution function is completely smeared out. The general expression for the interference function  $G(L)$  is

$$G(L) = 1 + \sum_{\mu} \{F^{\mu} + F^{+\mu}\} = \text{Re}\{(1 + F)/(1 - F)\} \quad (4.2.4.47)$$

with  $F(L) \leftrightarrow a_1(z)$ ,  $F^{\mu}(L) \leftrightarrow a_{\mu}(z)$ .

With  $F = |F|e^{i\chi}$  ( $\chi = L\langle c \rangle$ ), equation (4.2.4.47) is written:

$$G(L) = [1 - |F(L)|^2] / [1 - 2|F(L)| \cos \chi + |F(L)|^2]. \quad (4.2.4.47a)$$

[Note the close similarity to the diffuse part of equation (4.2.4.5), which is valid for 1D disorder problems.]

This function has maxima of height  $(1 + |F|)/(1 - |F|)$  and minima of height  $(1 - |F|)/(1 + |F|)$  at positions  $lc^*$  and  $(l + \frac{1}{2})c^*$ , respectively. With decreasing  $|F|$  the oscillations vanish; a critical  $L$  value (corresponding to  $z_k$ ) may be defined by  $G_{\max}/G_{\min} \lesssim 1.2$ . Actual values depend strongly on  $F(\mathbf{H})$ .

The paracrystal method is substantiated by the choice  $a_1(z)$ , *i.e.* the disorder model. Again, frequently used is a Gaussian distribution:

$$a_1(z) = 1/\sqrt{2\pi}\Delta \cdot \exp\{-(z - \langle c \rangle)^2/2\Delta^2\}$$

$$a_{\mu}(z) = 1/\sqrt{\mu} \cdot 1/\sqrt{2\pi}\Delta \cdot \exp\{-(z - \mu\langle c \rangle)^2/2\mu\Delta^2\}$$

$$(4.2.4.48)$$

with the two parameters  $\langle c \rangle$ ,  $\Delta$ .

There are peaks of height  $1/[\pi^2 L^2 (\Delta/\langle c \rangle)^2]$  which obviously decrease with  $L^2$  and  $(\Delta/\langle c \rangle)^2$ . The oscillations vanish for  $|F| \simeq 0.1$ , *i.e.*  $1/\langle c \rangle \simeq 0.25/\Delta$ . The width of the  $m$ th peak is  $\Delta_m = \sqrt{m}\Delta$ . The integral reflectivity is approximately  $1/\langle c \rangle [1 - \pi^2 L^2 (\Delta/\langle c \rangle)^2]$  and the integral width (defined by integral reflectivity divided by peak reflectivity) (background subtracted!)  $1/\langle c \rangle \pi^2 L^2 (\Delta/\langle c \rangle)^2$  which, therefore, increases with  $L^2$ . In principle the same results are given by Zernike & Prins (1927). In practice a single Gaussian distribution is not fully adequate and modified functions must be used (Rosshirt *et al.*, 1985).

A final remark concerns the normalization [equation (4.2.4.39)]. Going from (4.2.4.39) to (4.2.4.45) it is assumed that  $N$  is a large number so that the correct normalization factors  $(N - |\mu|)$  for each  $a_{\mu}(z)$  may be approximated by a uniform  $N$ . If this is not true then

$$G(L) = N + \sum_{\mu} (N - |\mu|) (F^{\mu} + F^{+\mu}) = N \text{Re} \{(1 + |F|)/(1 - |F|)\} - 2 \text{Re} \{|F|(1 - |F|^N)/(1 - |F|^2)\}. \quad (4.2.4.49)$$

## 4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

The correction term may be important in the case of relatively small (1D) domains. As mentioned above, the structure factor of a chain molecule was neglected. The  $\mathbf{H}$  dependence of  $F_m$ , of course, obscures the intensity variation of the diffuse layers as described by (4.2.4.47a).

The matrix method developed for the case of planar disorder was adapted to 2D disorder by Scaringe & Ibers (1979). Other models and corresponding expressions for diffuse scattering are developed from specific microscopic models (potentials), *e.g.* in the case of  $\text{Hg}_{3-6}\text{AsF}_6$  (Emery & Axe, 1978; Radons *et al.*, 1983), hollandites (Beyeler *et al.*, 1980; Ishii, 1983), iodine chain compounds (Endres *et al.*, 1982) or urea inclusion compounds (Forst *et al.*, 1987).

### 4.2.4.3.3. Correlations between different almost collinear chains

In real cases there are more or less strong correlations between different chains at least within small domains. Deviations from a strict (3D) order of chain-like structural elements are due to several reasons: shape and structure of the chains, varying binding forces, thermodynamical or kinetic considerations.

Many types of disorder occur. (1) Relative shifts parallel to the common axis while projections along this axis give a perfect 2D ordered net ('axial disorder'). (2) Relative fluctuations of the distances between the chains (perpendicular to the unique axis) with short-range order along the transverse  $\mathbf{a}$  and/or  $\mathbf{b}$  directions. The net of projected chains down to the  $ab$  plane is distorted ('net distortions'). Disorder of types (1) and (2) is sometimes correlated owing to non-uniform cross sections of the chains. (3) Turns, twists and torsions of chains or parts of chains. This azimuthal type of disorder may be treated similarly to the case of azimuthal disorder of single-chain molecules. Correlations between axial shifts and torsions produce 'screw shifts' (helical structures). Torsion of chain parts may be of dynamic origin (rotational vibrations). (4) Tilting or bending of the chains in a uniform or non-uniform way ('conforming/non-conforming'). Many of these types and a variety of combinations between them are found in polymer and liquid crystals and are treated therefore separately. Only some simple basic ideas are discussed here in brief.

For the sake of simplicity the paracrystal concept in combination with Gaussians is used again. Distribution functions are given by convolution products of next-nearest-neighbour distribution functions. As long as averaged lattice directions and lattice constants in a plane perpendicular to the chain axis exist, only two functions  $a_{100} = a_1(xyz)$  and  $a_{010} = a_2(xyz)$  are needed to describe the arrangement of next-nearest chains. Longitudinal disorder is treated as before by a third distribution function  $a_{001} = a_3(xyz)$ . The phenomena of chain bending or tilting may be incorporated by an  $x$  and  $y$  dependence of  $a_3$ . Any general fluctuation in the spatial arrangement of chains is given by

$$a_{mpq} = a_1 * \dots * a_1 * a_2 * \dots * a_2 * a_3 * \dots * a_3. \quad (4.2.4.50)$$

( $m$ -fold,  $p$ -fold,  $q$ -fold self-convolution of  $a_1, a_2, a_3$ , respectively.)

$$w(\mathbf{r}) = \delta(\mathbf{r}) \sum_m \sum_p \sum_q [a_{mpq}(\mathbf{r}) + a_{-mpq}(\mathbf{r})]. \quad (4.2.4.51)$$

$a_\nu$  ( $\nu = 1, 2, 3$ ) are called fundamental functions. If an averaged lattice cannot be defined, more fundamental functions  $a_\nu$  are needed to account for correlations between them.

By Fourier transformations the interference function is given by

$$G(\mathbf{H}) = \sum_m \sum_p \sum_q F_1^m F_2^p F_3^q = G_1 G_2 G_3; \quad (4.2.4.52)$$

$$G_\nu = \text{Re}\{(1 + |F_\nu|)/(1 - |F_\nu|)\}.$$

If Gaussian functions are assumed, simple pictures are derived. For example:

$$a_1(\mathbf{r} + \langle \mathbf{a} \rangle) = 1/(2\pi)^{3/2} \cdot 1/(\Delta_{11}\Delta_{12}\Delta_{13}) \\ \times \exp\{-\frac{1}{2}[(x^2/\Delta_{11}^2) + (y^2/\Delta_{12}^2) + (z^2/\Delta_{13}^2)]\} \quad (4.2.4.53)$$

describes the distribution of neighbours in the  $x$  direction (mean distance  $\langle a \rangle$ ). Parameter  $\Delta_{13}$  concerns axial,  $\Delta_{11}$  and  $\Delta_{12}$  radial and tangential fluctuations, respectively. Pure axial distribution along  $\mathbf{c}$  is given by projection of  $a_1$  on the  $z$  axis, pure net distortions by projection on the  $x - y$  plane. If the chain-like structure is neglected the interference function

$$G_1(\mathbf{H}) = \exp\{-2\pi^2(\Delta_{11}^2 H^2 + \Delta_{12}^2 K^2 + \Delta_{13}^2 L^2)\} \quad (4.2.4.54)$$

describes a set of diffuse planes perpendicular to  $\mathbf{a}^*$  with mean distance  $1/\langle a \rangle$ . These diffuse layers broaden along  $H$  with  $m\Delta_{11}$  and decrease in intensity along  $K$  and  $L$  monotonically. There is an ellipsoidal-shaped region in reciprocal space defined by main axes of length  $1/\Delta_{11}, 1/\Delta_{12}, 1/\Delta_{13}$  with a limiting surface given by  $|F| \simeq 0.1$ , beyond which the diffuse intensity is completely smeared out. The influence of  $a_2$  may be discussed in an analogous way.

If the chain-like arrangement parallel to  $\mathbf{c}$  [equation (4.2.4.12)] is taken into consideration,

$$l(z) = \sum_{n_3} \delta(z - n_3 c);$$

the set of planes perpendicular to  $\mathbf{a}^*$  (and/or  $\mathbf{b}^*$ ) is subdivided in the  $L$  direction by a set of planes located at  $l \cdot 1/c$  [equation (4.2.4.15)].

Longitudinal disorder is given by  $a_3(z)$  [equation (4.2.4.48),  $\Delta_{33} = \Delta$ ] and leads to two intersecting sets of broadened diffuse layer systems.

Particular cases like pure axial distributions ( $\Delta_{11}, \Delta_{12} \sim 0$ ), pure tangential distributions (net distortions:  $\Delta_{11}, \Delta_{13} \sim 0$ ), uniform bending of chains or combinations of these effects are discussed in the monograph of Vainshtein (1966).

### 4.2.4.4. Disorder with three-dimensional correlations (defects, local ordering and clustering)

#### 4.2.4.4.1. General formulation (elastic diffuse scattering)

In this section general formulae for diffuse scattering will be derived which may best be applied to crystals with a well ordered average structure, characterized by (almost) sharp Bragg peaks. Textbooks and review articles concerning defects and local ordering are by Krivoglaz (1969), Dederichs (1973), Peisl (1975), Schwartz & Cohen (1977), Schmatz (1973, 1983), Bauer (1979), and Kitaigorodsky (1984). A series of interesting papers on local order is given by Young (1975) and also by Cowley *et al.* (1979). Expressions for polycrystalline sample material are given by Warren (1969) and Fender (1973).

Two general methods may be applied:

(a) the average difference cluster method, where a representative cluster of scattering differences between the average structure and the cluster is used; and

(b) the method of short-range-order correlation functions where formal parameters are introduced.

Both methods are equivalent in principle. The cluster method is generally more convenient in cases where a single average cluster is a good approximation. This holds for small concentrations of clusters with sufficient space in between. The method of short-range-order parameters is optimal in cases where isolated clusters are not realized and the correlations do not extend to long distances. Otherwise periodic solutions are more convenient in most cases.

In any case, the first step towards the solution of the diffraction problem is the accurate determination of the average structure. As