

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 μ 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_{μ} denotes the displacement of the μ th molecule in the chain. Frequently used are Gaussian distributions:

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

(c' = normalizing constant; Δ = 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 κ^{μ} ($0 < \kappa < 1$) between a molecule and its μ th neighbour are incorporated. κ^{μ} 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 Δ , terms with $j > 1$ are mostly neglected. The terms become increasingly important with higher values of L . On the other hand, κ^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 μ 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:

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

(μ -fold convolution).

The mean distance between next-nearest neighbours is

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

and between neighbours of the μ 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 $\langle c \rangle$, Δ .

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_ν ($\nu = 1, 2, 3$) are called fundamental functions. If an averaged lattice cannot be defined, more fundamental functions a_ν 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 Δ_{13} concerns axial, Δ_{11} and Δ_{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