4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

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

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 lth diffuse layer is given by

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

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

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

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 $\psi = 0$, $2\pi/p$, ...). 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:

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

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

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

The Patterson function is given by

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

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

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

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

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

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

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 $z \le z_N$ and 0 elsewhere.

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

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

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

with

$$b(z) * b - (z) \leftrightarrow |B(L)|^2$$
$$(4.2.4.43)$$
$$I = |F_M(\mathbf{H})|^2 |D_\infty * B(L)|^2.$$

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.

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

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

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

where

$$\langle |F| \rangle^2 = 1/N^2 \langle F_\nu F_\mu^+ \rangle$$

$$= \sum_\nu \alpha_\nu F_\nu(\mathbf{H}) \sum_\mu \alpha_\mu F_\mu^+(\mathbf{H}) \quad (\nu \ne \mu)$$

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

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

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