– If the complete structure is recognized, but of poor quality, a conventional Fourier synthesis may be used to obtain refined parameters.

– If only a fragment is recognized (say less than 60% of the total scattering power), this fragment may be used as input to *DIRDIF*.

– If the structure is not recognized, one should pay attention to the printed statistical quantities, and examine the input model. Large B_p and small p_{exp}^2 indicate a bad model. Too large or too small B_r values or an $|E_r|^2$ average which deviates too much from unity are often related to scaling problems: in this case the user may supply reasonable values for B_p and B_r and rerun *DIRDIF* with a severe sin θ/λ cut-off. The following rerun options may be considered:

* If the model consists of one or more heavy atoms, which appear to be shifted by more than 0·1 Å, the new positions may be used as input.

* For a light-atom fragment the same option can be applied and one may also reject the atoms that return low in the peak list, and include some higher peaks.

* If the input fragment completely returns in the *DIRDIF* Fourier, with atomic shifts less than 0·1 Å, we suggest adding a number of high peaks to the known fragment: this number may be 10, 20% of the total number of non-hydrogen atoms, or 50% of the number of atoms of the input model, depending on the problem at hand.

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General Lattice Factor of the Ideal Paracrystal

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Abstract

The lattice factor of a paracrystalline lattice with oblique axes and with general orientation of the fluctuation tensor ellipsoid is calculated. Directly applicable formulas for the special case of a monoclinic (macro) lattice, which is of interest in connexion with the small-angle scattering of oriented semicrystalline polymers, are given.

1. Introduction

The ideal paracrystal is a model of a statistical distorted crystal lattice or macro lattice (Hosemann & Bagchi, 1962). The distortions are described by the cell-edge statistics $H_k(\mathbf{x})$ ($k = 1, 2, 3$) and the mean cell-edge vectors are

$$\mathbf{a}_k = \int \mathbf{x} H_k(\mathbf{x}) \, d^3 \mathbf{x}. \tag{1}$$

For statistics $H_k(\mathbf{x})$ having a center of symmetry, the statistical amplitude $F_K(\mathbf{b})$, the Fourier transform, $\mathscr{F}\{H_k(\mathbf{x})\}$, can be expressed in the form

$$F_k(\mathbf{b}) = |F_k(\mathbf{b})| \exp |-2\pi i \mathbf{b} \cdot \mathbf{a}_k|, \tag{2}$$

where, for statistics $H_k(\mathbf{x})$ Gaussian (otherwise as an approximation),

$$|F_k(\mathbf{b})| = \exp |-2\pi^2 \mathbf{b} \cdot \mathbf{T}(k) \cdot \mathbf{b}|. \tag{3}$$

The analytical part of the lattice factor is given by

$$Z(\mathbf{b}) = \prod_{k=1}^{3} \frac{1 - |F_k(\mathbf{b})|^2}{[1 - |F_k(\mathbf{b})|]^2 + 4|F_k(\mathbf{b})| \sin^2[\pi(\mathbf{b} \cdot \mathbf{a}_k)]}. \tag{4}$$

The principal values of the three symmetric fluctuation tensors $T(k)$, with regard to orthogonal coordinate systems $\mathring{\mathbf{e}}_j(k)$ parallel to the directions of the principal axes (Fig. 1), are

$$\mathring{\Delta}_{jj}^2(k) = \int [\mathring{\mathbf{e}}_j(k) \cdot (\mathbf{x} - \mathbf{a}_k)]^2 H_k(\mathbf{x}) \, d^3 \mathbf{x}. \tag{5}$$

The principal axes of these tensors in general do not coincide with the crystallographic axes $\mathbf{a}_k$.

The distortion of the paracrystal is defined by the nine values $\mathring{\Delta}_{jj}(k)$ and the directions $\mathring{\mathbf{e}}_j(k)$, but for the calculation of the scattering intensity the lattice factor and therefore the expression $\mathbf{b} \cdot T(k) \cdot \mathbf{b}$ in the general case of oblique cell-edge vectors $\mathbf{a}_k$ is needed. Up to now only orthorhombic cells were taken into consideration. In the following the general formula for $\mathbf{b} \cdot T(k) \cdot \mathbf{b}$ is derived. As an example the explicit expression for a monoclinic lattice will be given. This special case is of interest in connexion with the small-angle scattering from fibrillar and lamellar superstructures in semicrystalline polymers (Jung-nickel, Teichgräber & Ruscher, 1973).

2. Theory

In real space three coordinate systems are used:

1. A basic Cartesian system, unit vectors $\mathbf{e}_i$.
2. Principal-axes systems of the fluctuation tensors $T(k)$ with unit vectors $\mathring{\mathbf{e}}_i(k)$ ($k = 1, 2, 3$) (Fig. 1).

The calculations can be done with a common origin of these coordinate systems, because the shift of the tensor ellipsoids to $\mathbf{a}_k$ is taken into account by (2).
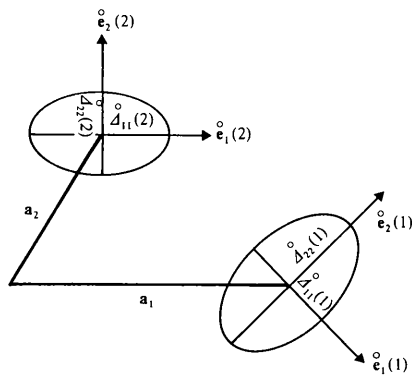

Fig. 1. Two-dimensional representation of the fluctuation tensor ellipsoids.

The systems $\mathring{\mathbf{e}}_i(k)$ are rotated relative to the system $\mathbf{e}_i$. The rotations are specified by

$$\mathring{\mathbf{e}}_i(k) \cdot \mathbf{e}_j = \cos \varphi_{ij}(k) = \alpha_{ij}(k). \tag{6}$$

The $\mathring{\mathbf{e}}_i(k)$ and $\mathbf{e}_i$ are expressed as

$$\mathring{\mathbf{e}}_i(k) = \sum_{j=1}^{3} \alpha_{ij}(k) \, \mathbf{e}_j := \alpha_{ij}(k) \, \mathbf{e}_j \tag{7}$$

$$\mathbf{e}_i = \alpha_{ji}(k) \, \mathring{\mathbf{e}}_j(k). \tag{8}$$

3. The lattice system with base vectors $\mathbf{a}_i$.

In terms of the Cartesian unit vectors $\mathbf{e}_i$, the cell-edge vectors $\mathbf{a}_i$ are given by

$$\mathbf{a}_i = \sum_{j=1}^{3} a_i^j \, \mathbf{e}_j = a_i^j \, \mathbf{e}_j. \tag{9}$$

The elements of the metric tensor G_{ij} (Price, 1982) are defined as

$$G_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j = G_{ji}. \tag{10}$$

The base vectors of the reciprocal space are $\mathbf{a}^i$. The following relations are valid:

$$\mathbf{a}_i \cdot \mathbf{a}^j = \delta_i^j = \begin{cases} 1 \text{ if } i = j \\ 0 \text{ if } i \neq j \end{cases} \tag{11}$$

$$\mathbf{a}^i = G^{ij} \, \mathbf{a}_j$$
$$= G^{ij} a_j^l \, \mathbf{e}_l$$
$$= c^{il} \, \mathbf{e}_l, \tag{12}$$

where

$$c^{il} = G^{ij} a_j^l. \tag{13}$$

The reciprocal-space metric tensor G^{ij} is the inverse of G_{ij}:

$$G^{ij} = (G_{ij})^{-1}. \tag{14}$$

A vector in reciprocal space can be written

$$\mathbf{b} = h_i \, \mathbf{a}^i \tag{15}$$

with h_i as continuous variables. At the nodes of the reciprocal lattice they become integers (Miller indices). Insertion of (11) in (14) results in

$$\mathbf{b} = h_i \, c^{il} \, \mathbf{e}_l$$
$$= b^l \, \mathbf{e}_l \tag{16}$$

$$b^l = h_i \, c^{il}$$
$$= h_i \, G^{ij} a_j^l. \tag{17}$$

To calculate $\mathbf{b} \cdot T(k) \cdot \mathbf{b}$, the transformation of $T(k)$ from the principal-axes coordinate system $\mathring{\mathbf{e}}_i(k)$ to the basic Cartesian system $\mathbf{e}_i$ must be done as a first step. The principal values and the direction of the principal axes are given in the form

$$\hat{T}(k) = \begin{pmatrix} \mathring{A}_{11}(k) & 0 & 0 \\ 0 & \mathring{A}_{22}(k) & 0 \\ 0 & 0 & \mathring{A}_{33}(k) \end{pmatrix} \qquad (18)$$

and

$$\hat{\mathbf{e}}_i(k) = \alpha_{ij}(k)\,\mathbf{e}_j. \qquad (19)$$

Using the transformation rules for tensor components and bearing in mind the diagonal form of $\hat{T}(k)$, one obtains the components $T_{ij}(k)$ expressed in the $\mathbf{e}_i$ coordinate system:

$$T_{ij}(k) = [T(k)]_{ij} = \mathring{A}_{ij}^2(k)$$
$$= \alpha_{li}(k)\,\alpha_{mj}(k)\,\mathring{A}_{lm}^2(k)$$
$$= \alpha_{li}(k)\,\alpha_{lj}(k)\,\mathring{A}_{ll}^2(k). \qquad (20)$$

This result with (16) and (17) allows the calculations of $\mathbf{b}.\,T(k).\,\mathbf{b}$ in a straightforward manner:

$$\mathbf{b}.\,T(k).\,\mathbf{b} = b^i\,\mathbf{e}_i.\,T_{lm}(k)\,\mathbf{e}_l\,\mathbf{e}_m.\,b^j\,\mathbf{e}_j$$
$$= b^i\,b^j\,T_{lm}(k)\,\mathbf{e}_i.\mathbf{e}_l\,\mathbf{e}_m\cdot\mathbf{e}_j$$
$$= b^i\,b^j\,T_{ij}(k)$$
$$= b^i\,b^j\,\alpha_{li}(k)\,\alpha_{lj}(k)\,\mathring{A}_{ll}^2(k)$$
$$= h_m\,c^{mi}\,h_n\,c^{nj}\,\alpha_{li}(k)\,\alpha_{lj}(k)\,\mathring{A}_{ll}^2(k)$$
$$= h_m\,G^{mp}\,a_p^i\,h_n\,G^{nq}\,a_q^j\,\alpha_{li}(k)\,\alpha_{lj}(k)\,\mathring{A}_{ll}^2(k)$$
$$= h_m\,h_n\,G^{mp}\,G^{nq}\,a_p^i\,a_q^j\,\alpha_{li}(k)\,\alpha_{lj}(k)\,\mathring{A}_{ll}^2(k) \qquad (21)$$

(summation over all repeated indices, regardless of position).

For a specific paracrystalline lattice the values $\mathring{A}_{ll}^2(k)$ and $\alpha_{ij}(k)$, which describe the distortion tensor ellipsoids, are fixed. The values of G^{ij} and a_i^j are determined by the lattice type. The lattice factor is then obtained by inserting (20) into (3) and the resulting $|F_k(\mathbf{b})|$ into (4). For the special case of an orthorhombic lattice and fluctuation tensors with principal axes parallel to the cell-edge vectors $[\alpha_{ij}(k) = \delta_{ik}]$ we obtain the well known result

$$\mathbf{b}.\,T(k).\,\mathbf{b} = \frac{\mathring{A}_{ll}^2(k)}{|\mathbf{a}_l|^2}\,h_l^2. \qquad (22)$$

3. Application to a monoclinic lattice

In some cases the analysis of the small-angle X-ray scattering from oriented semicrystalline polymers can be carried out by using a monoclinic paracrystalline macro lattice as structure model (Jungnickel, Teichgräber & Ruscher, 1973). The often observed fibrillar and lamellar structures are special cases of such a superlattice (Fig. 2). In the case of uniaxial oriented samples rotational symmetry about the fiber axis ($\mathbf{a}_3$ direction) exists and the minimum set of fluctuation tensor componence consists of

$$\mathring{A}_{11}(1) = \mathring{A}_{11}(2) = \mathring{A}_{22}(1) = \mathring{A}_{22}(2) := \mathring{A}_r$$
$$\mathring{A}_{33}(1) = \mathring{A}_{33}(2) := \mathring{A}_{a3}$$
$$\mathring{A}_{33}(3) = \mathring{A}_{33}$$
$$\mathring{A}_{11}(3) = \mathring{A}_{22}(3) = 0. \qquad (23)$$

Furthermore, we set $|\mathbf{a}_1|\sin\beta = |\mathbf{a}_2|$ because of the rotational symmetry.

To characterize the statistical fluctuations of a paracrystalline lattice usually the relative fluctuations

$$\frac{\mathring{A}_r}{|\mathbf{a}_1|\sin\beta} = \frac{\mathring{A}_r}{|\mathbf{a}_2|} = g_r, \qquad (24)$$

$$\frac{\mathring{A}_{33}}{|\mathbf{a}_3|} = g_{33}, \qquad (25)$$

$$\frac{\mathring{A}_3}{|\mathbf{a}_3|} = g_3 \qquad (26)$$

are introduced.

A fibrillar structure is defined by $g_3 \gg g_{33}$ [for isolated fibrils $(g_3$ and $g_r) \gg g_{33}$] and a lamellar structure by $g_3 \ll 1$.

The edge vectors of the monoclinic lattice cell relative to the basic Cartesian coordinate system are chosen in the following way:

$$\mathbf{a}_1 = a_1^1\,\mathbf{e}_1 + a_1^3\,\mathbf{e}_3 \qquad (27)$$

$$\mathbf{a}_2 = a_2^2\,\mathbf{e}_2 = |\mathbf{a}_2|\,\mathbf{e}_2 \qquad (28)$$

$$\mathbf{a}_3 = a_3^3\,\mathbf{e}_3 = |\mathbf{a}_3|\,\mathbf{e}_3,$$

where

$$a_1^1 = |\mathbf{a}_1|\sin\beta = |\mathbf{a}_2| \qquad (29)$$

$$a_1^3 = |\mathbf{a}_1|\cos\beta \qquad (30)$$

and $\beta = \angle(\mathbf{a}_1, \mathbf{a}_3)$.

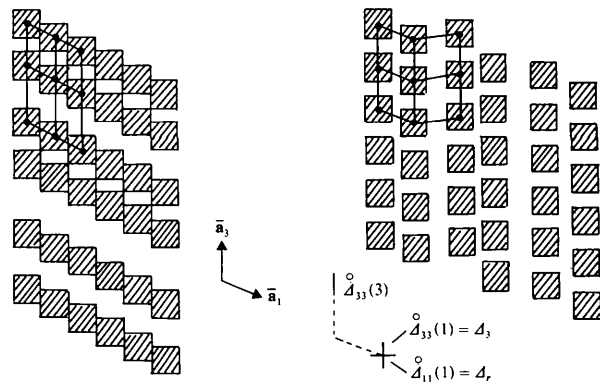The reciprocal-space metric tensor follows from (10) and (14):

Fig. 2. Schematic representation of paracrystalline monoclinic macro lattices: lamellar (left) and fibrillar (right) structure.

$$G^{ij} = \begin{pmatrix} \dfrac{1}{|a_1|^2 \sin^2 \beta} & 0 & -\dfrac{\cos \beta}{|a_1| \, |a_3| \sin^2 \beta} \\ 0 & \dfrac{1}{|a_2|^2} & 0 \\ -\dfrac{\cos \beta}{|a_1| \, |a_3| \sin^2 \beta} & 0 & \dfrac{1}{|a_3|^2 \sin^2 \beta} \end{pmatrix}. \tag{31}$$

The reciprocal-lattice vectors are calculated with (12) and (27)–(31):

$$a^1 = G^{11} a_1 + G^{12} a_2 + G^{13} a_3$$

$$= \frac{1}{|a_1| \sin \beta} e_1. \tag{32}$$

In a similar way results for a^2 and a^3

$$a^2 = \frac{1}{|a_2|} \cdot e_2 \tag{33}$$

$$a^3 = -\frac{\cot \beta}{|a_3|} e_1 + \frac{1}{a_3} \cdot e_3. \tag{34}$$

The vector b is obtained by inserting (32)–(34) into (15):

$$b = h_1 a^1 + h_2 a^2 + h_3 a^3$$

$$= \left[\frac{h_1}{|a_1| \sin \beta} - \frac{h_3 \cot \beta}{|a_3|} \right] \cdot e_1$$

$$+ \frac{h_2}{|a_2|} \cdot e_2 + \frac{h_3}{|a_3|} \cdot e_3. \tag{35}$$

The directions $\dot{e}_1(k)$ of the principal axes of the fluctuation tensors for the case in question must be fixed parallel to the unit vectors e_i of the basic Cartesian system, hence [compare with (8)],

$$\alpha_{ij}(k) = \delta_{ij}. \tag{36}$$

Equation (21) reduces to

$$b.T(k).b = h_m h_n G^{mp} G^{nq} a_p^i a_q^j \delta_{li} \delta_{lj} \Delta_{li}^2(k)$$

$$= h_m h_n G^{mp} G^{nq} a_p^l a_q^l \Delta_{ll}^2(k). \tag{37}$$

As an example, the calculation of $b.T(3).b$ is worked out in the following.

$$b.T(3).b = h_m h_n G^{mp} G^{nq} a_p^3 a_q^3 \Delta_{33}^2$$

$$= \Delta_{33}^2 h_m h_n G^{mp} a_p^3 (G^{n1} a_1^3 + G^{n3} a_3^3)$$

$$= \Delta_{33}^2 h_m h_n (G^{n1} a_1^3 + G^{n3} a_3^3)$$

$$\times (G^{m1} a_1^3 + G^{m3} a_1^3)$$

$$= \Delta_{33}^2 [h_1 G^{11} a_1^3 + h_1 G^{13} a_3^3 + h_3$$

$$\times G^{31} a_1^3 + h_3 G^{33} a_3^3]^2$$

$$= \Delta_{33}^2 \left[\frac{h_3(1 - \cos^2 \beta)}{|a_3| \sin^2 \beta} \right]^2$$

$$= \frac{\Delta_{33}^2}{|a_3|^2} h_3^2 = g_{33}^2 h_3^2. \tag{38}$$

In the same way, but by a more lengthy calculation, the formula for $b.T(1).b = b.T(2).b$ is obtained:

$$b.T(1).b = b.T(2).b$$

$$= g_r^2 \left\{ \left[h_1 - \frac{|a_1| \cos \beta}{|a_3|} h_3 \right]^2 + h_2^2 \right\} + g_3^2 h_3^2. \tag{39}$$

Finally, in the denominator of the lattice factor $Z(b)$ the term proportional to $\sin^2 [\pi(b.a_k)]$ occurs and must be written as a function of the variables h_l. The result follows immediately from (11) and (15):

$$b.a_k = h_k. \tag{40}$$

The explicit formula for the lattice factor $Z(b)$ follows from (38)–(40) together with (3) and (4). The small-angle scattering intensity is obtained by specifying the bricks of the lattice (e.g. cylindrical crystallites) and working out some averaging processes (Wilke & Göttlicher, 1981). The details of this procedure are outside the scope of this paper.

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