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Distribution and interference functions for two-dimensional hexagonal paracrystals

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The notion of a paracrystal is particularly well adapted to the calculation of the scattering interference function of distorted crystallographic lattices in which the long-range order does not exist. However, classical paracrystal modelling cannot be used directly for hexagonal lattices because it does not respect the hexagonal symmetry. Here an analytical determination of the distribution and interference functions for two-dimensional hexagonal paracrystals is presented.

1. Introduction

The notion of the paracrystal was developed about 50 years ago by Hoseman (1950) for modelling X-ray scattering patterns produced by distorted crystallographic lattices in which the long-range order is non-existent. Contrary to classical crystals, for which the lattice geometry is fixed, paracrystals allow fluctuations of the lengths and orientations of lattice vectors, and thus make it possible to account for slight amplitude distortions as well as larger ones in the lattice by a change in parameters. This description is elegant since the distribution function of the lattice nodes is analytical, as is its Fourier transform (interference function) in the widely acceptable approximation of Gaussian first-node distribution functions. Remembering that the scattered intensity is equal to the product of the interference function and the square modulus of the unit-cell form factor, the paracrystal model appears very well adapted to the analysis of X-ray scattering by disordered media.

The mathematical bases of the modelling can be reviewed in Hoseman (1950), Hoseman & Bagchi (1962) and Vainshtein (1966), whose notations are used here. In short, in the approximation for ideal two-dimensional paracrystals, the position of the (m, n) node in lattice $(\mathbf{a}, \mathbf{b})$ is not equal to $\mathbf{r} = m\mathbf{a} + n\mathbf{b}$ as in a classical crystal but depends on the actual position of the neighbouring nodes, the parallelogram shape of each unit cell being retained. This condition can be translated mathematically in a simple way. By calling $h^a(\mathbf{r})$ and $h^b(\mathbf{r})$ the distribution functions of the first lattice nodes along axes $\mathbf{a}$ and $\mathbf{b}$, which are characterized by their parameter sets $(\langle a\rangle, \sigma_a^a, \sigma_b^a)$ and $(\langle b\rangle, \sigma_a^b, \sigma_b^b)$, respectively average values and standard deviations along $\mathbf{a}$ and $\mathbf{b}$, the distribution function around node (m, n) is given by the convolution product of h^a self-convoluted m times and h^b self-convoluted n times. The complete distribution function is therefore written as:

$$Z(\mathbf{r}) = \delta_0 + \sum_m \sum_n [h^a(\mathbf{r})]^{*m} * [h^b(\mathbf{r})]^{*n},$$

where $*$ means convolution product.

The Fourier transform of $z(\mathbf{r})$ gives the interference function $Z(\mathbf{S})$:

$$Z(\mathbf{S}) = \{1 + 2\Re[H^a/(1 - H^a)]\}\{1 + 2\Re[H^b/(1 - H^b)]\},$$

where H^a and H^b are the Fourier transforms of h^a and h^b, $\Re$ represents the real part of complex quantities.

Assuming Gaussian distribution functions, *i.e.*

$$h^a(\mathbf{r} - \langle a\rangle\mathbf{a}) = G(u, \sigma_a^a)G(v, \sigma_b^a)$$

with

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b}$$

and

$$G(x, \sigma) = [1/\sigma(2\pi)^{1/2}]\exp(-x^2/2\sigma^2),$$

we have

$$H^a(\mathbf{S}) = \exp(-2\pi^2h^2\sigma_a^{a2})\exp(-2\pi^2k^2\sigma_b^{a2}),$$

where h and k are the reduced components of the scattering vector $\mathbf{S}$. A symmetric expression is found for H^b.

The interference function $Z(\mathbf{S})$ displays a series of maxima centred around the reciprocal nodes; their widths increase when the indices (m, n) increase and they diminish rapidly as the standard deviations become larger. In Fig. 1(*a*) is shown an example of a two-dimensional interference function, represented using a grey scale, which has been calculated for a hexagonal lattice, assuming identical isotropic Gaussian distribution functions along $\mathbf{a}$ and $\mathbf{b}$. As expected, the widths of the reflections increase starting from the centre, but the sixfold symmetry is not respected. This anomaly is due to the fact that, in the general paracrystal formulation given above, the distribution function for node $(1, 1)$ is calculated as the convolution of $h^a(\mathbf{r})$ and $h^b(\mathbf{r})$, whilst it should be exactly the same as $h^a(\mathbf{r})$ or $h^b(\mathbf{r})$ for hexagonal symmetry reasons. The general calculation of the distribution and interference functions for paracrystals, as formulated initially, does not respect the equivalence of $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{a} + \mathbf{b}$ axes in the hexagonal lattice.

Hoseman & Bagchi (1962) have extended their model to non-ideal paracrystals. They have briefly described the case of hexagonal lattices as an application of this 'real' paracrystal in which the symmetry is restored by taking into account an additional diagonal term and then by calculating an average value of the interference function after successive rotations of 60°. This calculation has several shortcomings: first, it does not provide an expression for the distribution function in real space. Second, it does not respect the hexagonal symmetry throughout the whole calculation but reintroduces it in the end by averaging over the hexagonal lattice. Third, the authors provide a formula for the interference function that involves first-node functions $H(\mathbf{S})$ which do not possess the hexagonal symmetry, making it very problematic to use.

These difficulties represent a problem in the case of most biological tissues which are characterized by a hexagonal-type lateral packing of elementary units, as for instance in muscles, keratin fibres and collagen tissues. Extending and complementing the general theory of paracrystals, we present here an analytical determination of the distribution and interference functions for two-dimensional hexagonal paracrystals that fully respects the hexagonal symmetry, first in the general case, then in the Gaussian approximation.

2. Theory for the ideal two-dimensional hexagonal paracrystal

We define the hexagonal lattice by the usual two vectors **a** and **b**, but we will also use a third vector **c** in order to preserve the symmetry between the three equivalent nodes (1, 0), (0, 1) and (1, 1) of the lattice (Fig. 2). To make the calculations straightforward, we rename the vectors as:

$$\mathbf{w}_1 = \mathbf{a}, \quad \mathbf{w}_2 = \mathbf{c}, \quad \mathbf{w}_3 = \mathbf{b}, \quad \mathbf{w}_4 = -\mathbf{a}, \quad \mathbf{w}_5 = -\mathbf{c},$$
$$\mathbf{w}_6 = -\mathbf{b} = \mathbf{w}_0$$

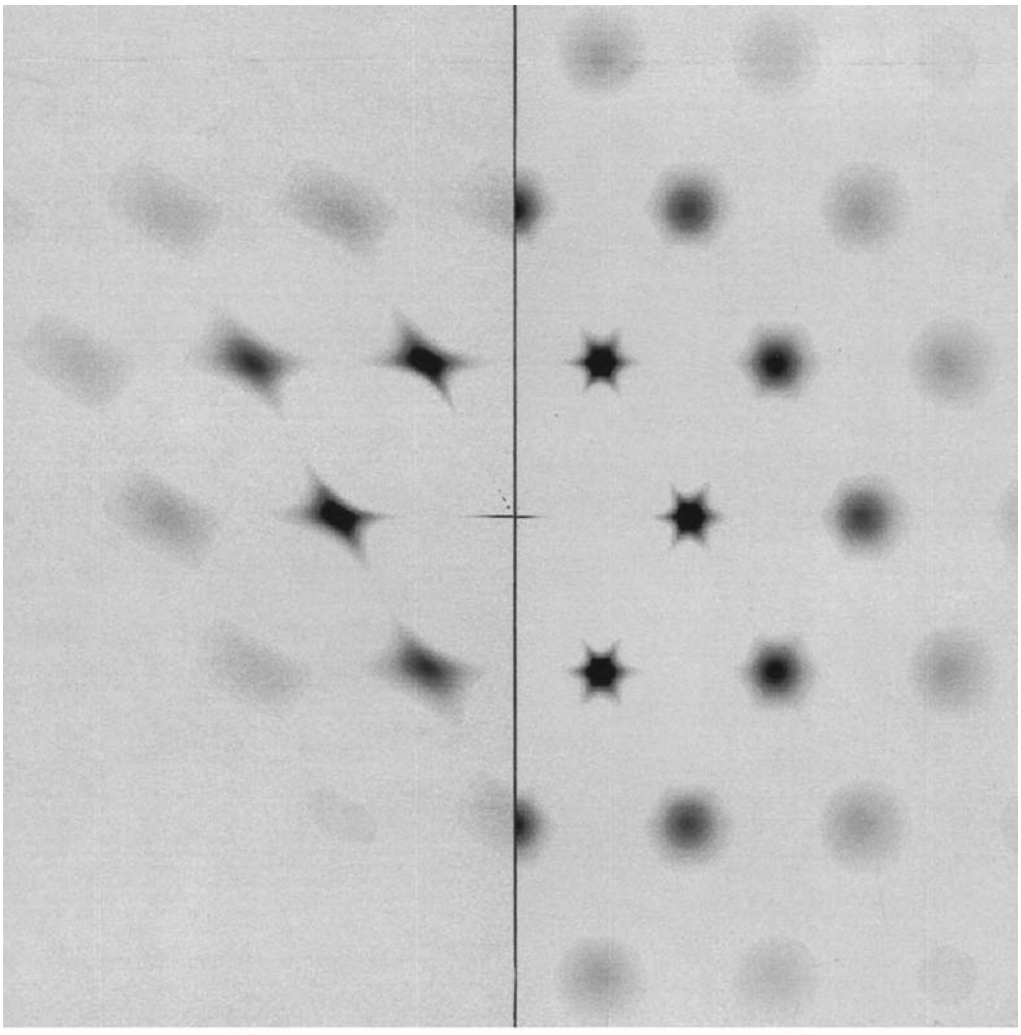

Figure 1
Split two-dimensional modelling in linear grey-scale representation of the interference function for two-dimensional hexagonal paracrystal lattices. All the standard deviations are chosen equal to 14% of the parameter length. (*a*) Modelling using the classical formulation. The sixfold symmetry is lost in the interference function. (*b*) Modelling using the special formulation for the hexagonal paracrystals developed in this paper. The sixfold symmetry is now fulfilled.

and we separate the plane in six equivalent sections (Fig. 2), sector i being the area limited by $\mathbf{w}_{i-1}$ and $\mathbf{w}_i$. The distribution function then follows:

$$z(\mathbf{r}) = \sum_{i=1}^{6} z_i(\mathbf{r}) + \sum_{i=1}^{6} z_{\mathbf{w}_i}(\mathbf{r}) + \delta_0, \tag{1}$$

where z_i, $z_{\mathbf{w}_i}$ and δ_0 represent respectively the distribution functions of sector i (axes excluded), axis $\mathbf{w}_i$ (centre excluded) and centre alone.

The z_i functions are defined by

$$z_i(\mathbf{r}) = \sum_{m=1}^{+\infty} [h_{\mathbf{w}_{i-1}}(\mathbf{r})]^{*m} * \sum_{n=1}^{+\infty} [h_{\mathbf{w}_i}(\mathbf{r})]^{*n}, \quad 1 \le i \le 6, \tag{2}$$

where $*$ means convolution product.

The $h_{\mathbf{w}_i}(\mathbf{r})$ first-node functions characterize the distributions of the positions around the six first-order nodes defined by the $\mathbf{w}_i$ vectors. Note that $h_{\mathbf{w}_i}(\mathbf{r}) = h^0_{\mathbf{w}_i}(\mathbf{r} - \mathbf{w}_i)$, where $h^0_{\mathbf{w}_i}$ is calculated at the origin of the lattice. It follows that

$$z_{\mathbf{w}_i}(\mathbf{r}) = \sum_{m=1}^{+\infty} [h_{\mathbf{w}_i}(\mathbf{r})]^{*m}. \tag{3}$$

For the interference function $Z(\mathbf{S})$, it follows by application of the Fourier-transform properties that

$$Z(\mathbf{S}) = \sum_{i=1}^{6} Z_i(\mathbf{S}) + \sum_{i=1}^{6} Z_{\mathbf{w}_i}(\mathbf{S}) + 1 \tag{4}$$

with

$$\begin{aligned} Z_i(\mathbf{S}) &= \sum_{m=1}^{+\infty} (H_{\mathbf{w}_{i-1}})^m(\mathbf{S}) \sum_{n=1}^{+\infty} (H_{\mathbf{w}_i})^n(\mathbf{S}) \\ &= \{H_{\mathbf{w}_{i-1}}(\mathbf{S})/[1 - H_{\mathbf{w}_{i-1}}(\mathbf{S})]\}\{H_{\mathbf{w}_i}(\mathbf{S})/[1 - H_{\mathbf{w}_i}(\mathbf{S})]\} \end{aligned} \tag{5}$$

and

$$Z_{\mathbf{w}_i}(\mathbf{S}) = \sum_{m=1}^{+\infty} [H_{\mathbf{w}_i}(\mathbf{S})]^m = \{H_{\mathbf{w}_i}(\mathbf{S})/[1 - H_{\mathbf{w}_i}(\mathbf{S})]\}. \tag{6}$$

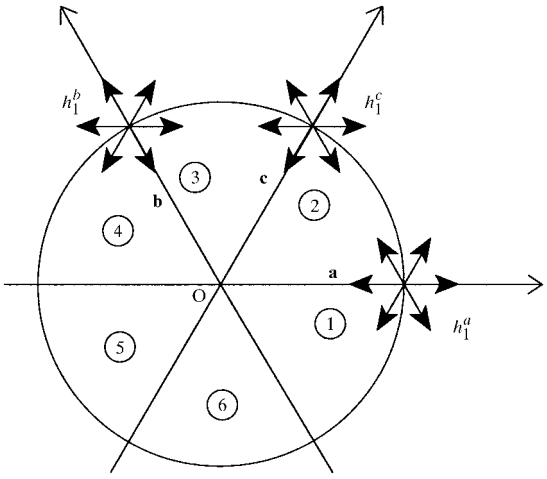

Figure 2
Notation used for axes and sectors in the modelling of the distribution for a two-dimensional hexagonal paracrystalline lattice.

Since it is possible to write

$$H_{\mathbf{w}_i}(\mathbf{S}) = H^0_{\mathbf{w}_i}(\mathbf{S}) \exp(-2i\pi \mathbf{S} \cdot \mathbf{w}_i),$$

the calculation of the total interference function is then conditioned by the modelling of six first-node functions $H^0_{\mathbf{w}_i}$ in the reciprocal space.

Taking into account the centre of inversion of all lattices, the above formulas are greatly simplified; thus, for $1 \le i \le 3$,

$$h_{\mathbf{w}_{i+3}}(\mathbf{r}) = h_{\mathbf{w}_i}(-\mathbf{r}) \quad \text{and} \quad H_{\mathbf{w}_{i+3}}(\mathbf{S}) = \overline{H_{\mathbf{w}_i}}(\mathbf{S}),$$

where the bar means complex conjugation.

Finally, the interference function is calculated by

$$\begin{aligned} Z(\mathbf{S}) = 2\Re\left[\sum_{i=1}^{3} \frac{H_{\mathbf{w}_{i-1}}(\mathbf{S})}{1 - H_{\mathbf{w}_{i-1}}(\mathbf{S})} \frac{H_{\mathbf{w}_i}(\mathbf{S})}{1 - H_{\mathbf{w}_i}(\mathbf{S})}\right] \\ + 2\Re\left[\sum_{i=1}^{3} \frac{H_{\mathbf{w}_i}(\mathbf{S})}{1 - H_{\mathbf{w}_i}(\mathbf{S})}\right] + 1. \end{aligned} \tag{7}$$

Therefore, the full definition of $Z(\mathbf{S})$ only requires three functions $H_{\mathbf{a}}$, $H_{\mathbf{b}}$ and $H_{\mathbf{c}}$. Equation (7) is equivalent to (79) in Hoseman & Bagchi (1962), but obtained in a straightforward manner, compatible with the hexagonal symmetry as long as the $h_{\mathbf{w}_i}$ (or $H_{\mathbf{w}_i}$) functions are also compatible with this symmetry.

In the simplest but most useful case for the modelling of biological samples, all the first-order nodes are generally considered equivalent, which means that all the $h^0_{\mathbf{w}_i}$ (or $H^0_{\mathbf{w}_i}$) functions are equal to a unique h^0 (or H^0); in addition, h^0 (or H^0) is isotropic in order to fulfil the average circular symmetry of the cylinder-shaped objects. It is important to avoid any confusion between the geometry of the average unit cell, which is used to build the paracrystal and the final average geometry of the unit cells in the paracrystal. In our case, the geometry of the initial unit cell is hexagonal, but if the distribution functions were not identical, or were characterized by anisotropic standard deviations, then we would not expect a paracrystal with an average hexagonal unit cell. The most common case corresponds to the hexagonal isotropic case, but anisotropic distortions can be considered, for example to account for a one-direction induced stress.

3. Distribution and interference functions in the Gaussian approximation

In the Gaussian approximation, each first-node function is taken as the normalized product of three Gaussian distributions corresponding to the three directions **a**, **b** and **c**. Calling $G^{\sigma}(x)$ the Gaussian function with standard deviation σ and fixing by convention **a** and **c** as the coordinate vectors, all the first-node functions can be written as

$$h_{\mathbf{w}_i}(\mathbf{r}) = D G^{\sigma_1}_{\mathbf{w}_i}(u) G^{\sigma_2}_{\mathbf{w}_i}(v) G^{\sigma_3}_{\mathbf{w}_i}(u + v) \tag{8}$$

with $\mathbf{r} = u\mathbf{a} + v\mathbf{c}$ and where D is a normalization factor.

In order to easily calculate and handle the Fourier transform of the first-node functions, we have chosen to impose $||\mathbf{a}^*|| = ||\mathbf{c}^*|| = 1$. Writing $\mathbf{S} = k\mathbf{a}^* + h\mathbf{c}^*$, we have:

$$H^0_{\mathbf{w}_i}(\mathbf{S}) = H^0_{\mathbf{w}_i}(h,k) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} h^0_{\mathbf{w}_i}(u,v)\exp[-2i\pi(hu+kv)](2/3^{1/2})\,\mathrm{d}u\,\mathrm{d}v \tag{9}$$

$$H^0_{\mathbf{w}_i}(h,k) = [2D/(2\pi)^{3/2}\sigma_1\sigma_2\sigma_3 3^{1/2}] \times \int_{-\infty}^{+\infty}\exp(-u^2/2\sigma_1^2)[J]\exp(-2i\pi hu)\,\mathrm{d}u, \tag{10}$$

where the J integral is given by

$$J = \int_{-\infty}^{+\infty}\exp[-v^2/2\sigma_2^2 - (u+v)^2/2\sigma_3^2]\exp(-2i\pi kv)\,\mathrm{d}v. \tag{11}$$

To perform the calculation of this integral, we rewrite it as the Fourier transform (FT) of a Gaussian function

$$J = (2\pi)^{1/2}\sigma_{2,3}\exp[-u^2/2(\sigma_2^2+\sigma_3^2)] \times \mathrm{FT}\{G^{\sigma_{2,3}}[v + u(\sigma_{2,3}/\sigma_3^2)]\}(k), \tag{12}$$

where $1/\sigma_{2,3}^2 = 1/\sigma_2^2 + 1/\sigma_3^2$. According to the rules for the Fourier transform of a Gaussian function:

$$J = (2\pi)^{1/2}\sigma_{2,3}\exp[-u^2/2(\sigma_2^2+\sigma_3^2)]\exp[2i\pi ku(\sigma_{2,3}^2/\sigma_3^2)] \times \exp(-2\pi^2\sigma_{2,3}^2k^2). \tag{13}$$

Then the first-node function as a whole can also be rewritten in the same way:

$$H^0_{\mathbf{w}_i}(h,k) = \frac{2D\sigma_{2,3}\sigma_{1,2,3}}{3^{1/2}\sigma_1\sigma_2\sigma_3(2\pi)^{1/2}}\exp(-2\pi^2\sigma_{2,3}^2k^2) \times \mathrm{FT}[G^{\sigma_{1,2,3}}(u)][h - k(\sigma_{2,3}^2/\sigma_3^2)], \tag{14}$$

where $1/\sigma_{1,2,3}^2 = 1/\sigma_1^2 + 1/(\sigma_2^2+\sigma_3^2)$, and which gives, after simplification,

$$H^0_{\mathbf{w}_i}(h,k) = \frac{2D}{3^{1/2}(\sum_{i=1}^3\sigma_1^2)^{1/2}(2\pi)^{1/2}} \times \exp\left(-2\pi^2\frac{\sigma_1^2\sigma_3^2h^2 + \sigma_2^2\sigma_3^2k^2 + \sigma_1^2\sigma_2^2(h-k)^2}{\sigma_1^2+\sigma_2^2+\sigma_3^2}\right). \tag{15}$$

The D factor is necessary for the first-node function in direct space to have a unit integral over the whole plane, which means that its Fourier transform is unity at the origin of the reciprocal space. Then, the value of D follows:

$$D = (2\pi)^{1/2}(3^{1/2}/2)(\sigma_1^2+\sigma_2^2+\sigma_3^2)^{1/2}. \tag{16}$$

3.1. A particular case: sixfold symmetry, isotropic first-node functions

We consider here the simplification of the previous calculations in the case of an isotropic lattice, where all the direct-space (or reciprocal-space) first-node functions and all the σ_i values are equal to h^0 (or H^0) and σ.

The direct-space first-node function is then

$$h^0(\mathbf{r}) = DG^\sigma(u)G^\sigma(v)G^\sigma(u+v) = [D/(2\pi)^{3/2}\sigma^3]\exp\{-[u^2+v^2+(u+v)^2]/2\sigma^2\} \tag{17}$$

and, with the value of D [from (16)] and the relation

$$\mathbf{r}^2 = (u\mathbf{a}+v\mathbf{c})^2 = u^2+v^2+uv = \tfrac{1}{2}[u^2+v^2+(u+v)^2], \tag{18}$$

the isotropic lattice function becomes

$$h^0(\mathbf{r}) = (3/4\pi\sigma^2)\exp(-r^2/\sigma^2). \tag{19}$$

The reciprocal-space first-node function can be derived as

$$H^0(h,k) = \exp\{-2\pi^2\sigma^2[h^2+k^2+(h-k)^2]/3\} = \exp(-4\pi^2\sigma^2S^2/3). \tag{20}$$

We remark that both functions are cylindrically symmetric around the origin of their lattices. The whole interference function is calculated using formula (7). The lattice functions in that case are then only described by one parameter σ. In Fig. 1(*b*) is represented the interference function calculated with our modelling in the isotropic hexagonal case with the same standard deviations as those chosen for Fig. 1(*a*). The effect of our modelling is quite clear since, contrary to Fig. 1(*a*), the hexagonal symmetry is respected.

4. Discussion

The direct determination of the distribution and interference functions described above for hexagonal paracrystals, in both the isotropic and general cases, allows the use of this model for a wide range of applications related to distorted two-dimensional hexagonal crystals including biological samples and liquid crystals.

Some authors have pointed out that Hoseman's theory imposes restraints on the allowed deformations of the crystal unit cell, which remains a parallelogram in the ideal case exposed above (Brämer, 1975). It must be stressed that the paracrystal is a model, which means that it is conceived as an efficient tool to account for an actual distorted crystal through its distribution and interference functions (which are indeed average functions over a large number of lattice cells). In that respect, the limitation of the unit-cell shape must be seen as a selection of a certain class of allowed deformations which present the advantage of making an analytical calculation possible. Other deformations may have consequences on the actual positions of lattice nodes in a particular crystal, but the average behaviour in terms of distribution and interference functions remains essentially the same. Other models exist to account for systematic distortions in crystals, such as the hexatic lattice model, but they are more difficult to handle, especially because they need more input parameters than the paracrystal.

The behaviour of the paracrystal interference function for small values of $\|\mathbf{S}\|$ may also appear as a potential problem of the model (Welberry, 1985). Even though it does go to infinity when $\|\mathbf{S}\|$ goes to zero, as is expected for a perfect crystal, some authors have claimed that, for a homogeneous disorder, the small-angle signal should have a finite value related to the density fluctuations, as for liquids and gases (Perret & Ruland, 1971; Brämer & Ruland, 1976). This criticism was recently ruled out in a more sophisticated one-dimensional paracrystal model that also takes into account the limited size of the diffraction units (Mu, 1998). However, great care must still be taken to interpret the paracrystal structure. It should not be interpreted as anything more than a distorted crystal, in which the long-range order has faded but long-range correlations still remain between any two nodes through a statistical law. In that respect, we think that the paracrystal model is a powerful tool as long as it is used only for samples to which it can be applied and in that case it provides quantitative results. Strictly speaking, such samples can be defined as distorted crystals in which the crystalline order has not disappeared and for which the behaviour of the interference function at small angles is then coherent. In particular, we think that the paracrystal model can indeed only partially account for gases, liquids and related structures.

Keeping in mind that the paracrystal is a modelling method that must only be applied to appropriate samples, it has proved very useful so far to quantitatively account for experimental X-ray scattering data. For example, it has been shown that cylindrically averaged interference functions from a two-dimension hexagonal paracrystal with isotropic first-node functions (Briki *et al.*, 1998) are very close to those calculated from the actual positions of keratin microfibrils on an electron micrograph (Fraser *et al.*, 1964), which strongly supports the general study of the hexagonal paracrystal presented here.

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