If disordering is time dependent exclusively, $\langle\rho\rangle$ represents the time average, whereas $\langle F\rangle$ gives the pure elastic scattering part [*cf.* equation (4.2.2.8)] and ΔF refers to inelastic scattering only.

4.2.3. General treatment

4.2.3.1. *Qualitative interpretation of diffuse scattering*

Any structure analysis of disordered structures should start with a qualitative interpretation of diffuse scattering. This problem may be facilitated with the aid of Fourier transforms and their algebraic operations (see, *e.g.*, Patterson, 1959). For simplicity the following modified notation is used in this section: functions in real space are represented by small letters, *e.g.* $a(\mathbf{r})$, $b(\mathbf{r})$, . . . except for $F(\mathbf{r})$ and $P(\mathbf{r})$ which are used as general symbols for a structure and the Patterson function, respectively; functions in reciprocal space are given by capital letters $A(\mathbf{H})$, $B(\mathbf{H})$; $\mathbf{r}$ and $\mathbf{H}$ are general vectors in real and reciprocal space, respectively, $Hz + Ky + Lz$ is the scalar product $\mathbf{H}\cdot\mathbf{r}$; d$\mathbf{r}$ and d$\mathbf{H}$ indicate integrations in three dimensions in real and reciprocal space, respectively. Even for X-rays the electron density $\rho(\mathbf{r})$ will generally be replaced by the scattering potential $a(\mathbf{r})$. Consequently, anomalous contributions to scattering may be included if complex functions $a(\mathbf{r})$ are admitted. In the neutron case $a(\mathbf{r})$ refers to a quasi-potential. Using this notation we obtain the scattered amplitude and phase $A(\mathbf{H})\exp i\varphi$

$$A(\mathbf{H}) = \int_{\mathbf{r}} a(\mathbf{r})\exp\{2\pi i\mathbf{H}\cdot\mathbf{r}\}\,\mathrm{d}\mathbf{r} \qquad (4.2.3.1a)$$

$$a(\mathbf{r}) = \int_{\mathbf{H}} A(\mathbf{H})\exp\{-2\pi i\mathbf{H}\cdot\mathbf{r}\}\,\mathrm{d}\mathbf{H} \qquad (4.2.3.1b)$$

(constant factors are omitted).

$a(\mathbf{r})$ and $A(\mathbf{H})$ are reversibly and uniquely determined by Fourier transformation. Consequently equations (4.2.3.1) may simply be replaced by $a(\mathbf{r}) \leftrightarrow A(\mathbf{H})$, where the double-headed arrow represents the two integrations given by (4.2.3.1) and means: $A(\mathbf{H})$ is the Fourier transform of $a(\mathbf{r})$, and *vice versa.* The following relations may easily be derived from (4.2.3.1):

$$a(\mathbf{r}) + b(\mathbf{r}) \leftrightarrow A(\mathbf{H}) + B(\mathbf{H}) \quad \text{(law of addition)} \qquad (4.2.3.2)$$

$$\beta a(\mathbf{r}) \leftrightarrow \beta A(\mathbf{H}) \quad \text{(law of scalar multiplication)} \qquad (4.2.3.3)$$

(β = scalar quantity).

On the other hand, the multiplication of two functions does not yield a relation of similar symmetrical simplicity:

$$a(\mathbf{r})b(\mathbf{r}) \leftrightarrow \int A(\mathbf{H}')B(\mathbf{H}-\mathbf{H}')\,\mathrm{d}\mathbf{H}' = A(\mathbf{H}) * B(\mathbf{H}) \qquad (4.2.3.4a)$$

$$a(\mathbf{r}) * b(\mathbf{r}) = \int a(\mathbf{r}')b(\mathbf{r}-\mathbf{r}')\,\mathrm{d}\mathbf{r}' \leftrightarrow A(\mathbf{H})B(\mathbf{H}) \qquad (4.2.3.4b)$$

(laws of convolution and multiplication).

Since $a(\mathbf{r})b(\mathbf{r}) = b(\mathbf{r})a(\mathbf{r})$:

$$\int A(\mathbf{H}')B(\mathbf{H}-\mathbf{H}')\,\mathrm{d}\mathbf{H}' = \int B(\mathbf{H}')A(\mathbf{H}-\mathbf{H}')\,\mathrm{d}\mathbf{H}'$$

and *vice versa.* The convolution operation is commutative in either space.

For simplicity the symbol $a(\mathbf{r}) * b(\mathbf{r})$ instead of the complete convolution integral is used. The distribution law $a(b+c) = ab + ac$ is valid for the convolution as well:

$$a(\mathbf{r}) * [b(\mathbf{r}) + c(\mathbf{r})] = a(\mathbf{r}) * b(\mathbf{r}) + a(\mathbf{r}) * c(\mathbf{r}). \qquad (4.2.3.5)$$

The associative law of multiplication does not hold if mixed products (convolution and multiplication) are used:

$$a(\mathbf{r}) * [b(\mathbf{r})c(\mathbf{r})] \neq [a(\mathbf{r}) * b(\mathbf{r})]c(\mathbf{r}). \qquad (4.2.3.6)$$

From equations (4.2.3.1) one has:

$$a(\mathbf{r}-\mathbf{r}_0) \leftrightarrow A(\mathbf{H})\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_0)$$
$$A(\mathbf{H}-\mathbf{H}_0) \leftrightarrow a(\mathbf{r})\exp(-2\pi i\mathbf{H}_0\cdot\mathbf{r}) \qquad (4.2.3.7)$$

(law of displacements).

Since symmetry operations are well known to crystallographers in reciprocal space also, the law of inversion is mentioned here only:

$$a(-\mathbf{r}) \leftrightarrow A(-\mathbf{H}). \qquad (4.2.3.8)$$

Consequently, if $a(\mathbf{r}) = a(-\mathbf{r})$, then $A(\mathbf{H}) = A(-\mathbf{H})$. In order to calculate the intensity the complex conjugate $A^+(\mathbf{H})$ is needed:

$$a^+(\mathbf{r}) \leftrightarrow A^+(-\mathbf{H}) \qquad (4.2.3.9a)$$

$$a^+(-\mathbf{r}) \leftrightarrow A^+(\mathbf{H}). \qquad (4.2.3.9b)$$

Equations (4.2.3.9) yield the relationship $A^+(-\mathbf{H}) = A(\mathbf{H})$ ('Friedel's law') if $a(\mathbf{r})$ is a *real* function. The multiplication of a function with its conjugate is given by:

$$a(\mathbf{r}) * a^+(-\mathbf{r}) \leftrightarrow |A(\mathbf{H})|^2,$$

with

$$a(\mathbf{r}) * a^+(-\mathbf{r}) = \int a(\mathbf{r}')a(\mathbf{r}'-\mathbf{r})\,\mathrm{d}\mathbf{r}' = P(\mathbf{r}). \qquad (4.2.3.10)$$

Note that $P(\mathbf{r}) = P(-\mathbf{r})$ is not valid if $a(\mathbf{r})$ is complex. Consequently $|A(-\mathbf{H})|^2 \neq |A(\mathbf{H})|^2$. This is shown by evaluating $A(-\mathbf{H})A^+(-\mathbf{H})$

$$A(-\mathbf{H})A^+(-\mathbf{H}) \leftrightarrow a(-\mathbf{r}) * a^+(\mathbf{r}) = P(-\mathbf{r}). \qquad (4.2.3.11)$$

Equation (4.2.3.11) is very useful for the determination of the contribution of anomalous scattering to diffuse reflections.

Most of the diffuse diffraction phenomena observed may be interpreted qualitatively or even semi-quantitatively in a very simple manner using a limited number of important Fourier transforms, given below.

4.2.3.1.1. *Fourier transforms*

(1) *Normalized Gaussian function*

$$(\pi^{3/2}\alpha\beta\gamma)^{-1}\exp\{-(x/\alpha)^2 - (y/\beta)^2 - (z/\gamma)^2\}. \qquad (4.2.3.12)$$

This plays an important role in statistics. Its Fourier transform is again a Gaussian:

$$\exp\{-\pi^2(\alpha^2H^2 + \beta^2K^2 + \gamma^2L^2)\}. \qquad (4.2.3.12a)$$

The three parameters α, β, γ determine the width of the curve. Small values of α, β, γ represent a broad maximum in reciprocal space but a narrow one in real space, and *vice versa.* The constant has been chosen such that the integral of the Gaussian is unity in real space. The product of two Gaussians in reciprocal space

$$\exp\{-\pi^2(\alpha_1^2H^2 + \beta_1^2K^2 + \gamma_1^2L^2)\} \times \exp\{-\pi^2(\alpha_2^2H^2 + \beta_2^2K^2 + \gamma_2^2L^2)\} = \exp\{-\pi^2[(\alpha_1^2+\alpha_2^2)H^2 + (\beta_1^2+\beta_2^2)K^2 + (\gamma_1^2+\gamma_2^2)L^2]\} \qquad (4.2.3.12b)$$

again represents a Gaussian of the same type, but with a sharper profile. Consequently its Fourier transform given by the convolution of the transforms of the two Gaussians is itself a Gaussian with a broader maximum. It may be concluded from this discussion that the Gaussian with $\alpha, \beta, \gamma \to 0$ is a δ function in real space, and its Fourier transform is unity in reciprocal space. The convolution of two δ functions is again a δ function.

(2) *Lattices*

Lattices in real and reciprocal space may be described by δ functions

$$l(\mathbf{r}) = \sum_{\mathbf{n}} \delta(\mathbf{r} - \mathbf{n})$$

and

$$L(\mathbf{H}) = \sum_{\mathbf{h}} \delta(\mathbf{H} - \mathbf{h}),$$

where $\mathbf{n}$, $\mathbf{h}$ represent the components of the displacement vectors in real and reciprocal space, respectively. The Fourier transforms of lattices with orthogonal basis vectors of unit length and an infinite number of points in all three dimensions correspond to each other. In the following the relation $l(\mathbf{r}) \leftrightarrow L(\mathbf{H})$ is used in this generalized sense.

The Fourier transforms of *finite* lattices are given by

$$\frac{\sin \pi N_1 H}{\sin \pi H} \frac{\sin \pi N_2 K}{\sin \pi K} \frac{\sin \pi N_3 L}{\sin \pi L}, \tag{4.2.3.13}$$

which is a periodic function in reciprocal space, but, strictly speaking, non-periodic in real space. It should be pointed out that the correspondence of lattices in either space is valid only if the origin coincides with a δ function. This fact may easily be understood by applying the law of displacement given in equation (4.2.3.7).

(3) *Box functions*

The Fourier transform of a box function $b(\mathbf{r})$ with unit height is:

$$b(\mathbf{r}) \leftrightarrow \frac{\sin \pi \alpha H}{\pi H} \frac{\sin \pi \beta K}{\pi K} \frac{\sin \pi \gamma L}{\pi L}. \tag{4.2.3.14}$$

α, β, γ describe its extension in the three dimensions. This function is real as long as the centre of symmetry is placed at the origin, otherwise the law of displacement has to be used. The convolution of the box function is needed for the calculation of intensities:

$$\begin{aligned} t(\mathbf{r}) &= b(\mathbf{r}) * b(-\mathbf{r}) \\ &\leftrightarrow \left(\frac{\sin \pi \alpha H}{\pi H}\right)^2 \left(\frac{\sin \pi \beta K}{\pi K}\right)^2 \left(\frac{\sin \pi \gamma L}{\pi L}\right)^2. \end{aligned} \tag{4.2.3.15}$$

$t(\mathbf{r})$ is a generalized three-dimensional 'pyramid' of doubled basal length when compared with the corresponding length of the box function. The top of the pyramid has a height given by the number of unit cells covered by the box function. Obviously, the box function generates a particle size in real space by multiplying the infinite lattice $l(\mathbf{r})$ by $b(\mathbf{r})$. Fourier transformation yields a particle-size effect well known in diffraction. Correspondingly, the termination effect of a Fourier synthesis is caused by multiplication by a box function in reciprocal space, which causes a broadening of maxima in real space.

(4) *Convolutions*

It is often very useful to elucidate the convolution given in equations (4.2.3.4) by introducing the corresponding pictures in real or reciprocal space. Since $1 \cdot f(\mathbf{r}) = f(\mathbf{r}), \delta(\mathbf{H}) * F(\mathbf{H}) = F(\mathbf{H})$ the convolution with a δ function must result in an identical picture of the second function, although the function is used as $f(-\mathbf{r})$ in the integrals of equations (4.2.3.4), $f(\mathbf{r} - \mathbf{r}')$ with $\mathbf{r}'$ as variable in the integral of convolution. The convolution with $f(-\mathbf{r})$ brings the integral into the form

$$\int f(\mathbf{r}') f(\mathbf{r}' - \mathbf{r}) \, \mathrm{d}\mathbf{r}', \tag{4.2.3.16}$$

which is known as the Patterson function (or self- or auto-convolution) and represents the generalized Patterson function including anomalous scattering [*cf.* equation (4.2.3.10)].

The change of the variable in the convolution integral may sometimes lead to confusion if certain operations are applied to the arguments of the functions entering the integral. Hence, it seems to be useful to mention the invariance of the convolution integral with respect to a change of sign, or a displacement, respectively, if applied to $\mathbf{r}'$ in both functions. Consequently, the convolution with the inverted function $a(\mathbf{r}) * b(-\mathbf{r})$ may be determined as follows:

$$\begin{aligned} b'(\mathbf{r}) &= b(-\mathbf{r}) \\ a(\mathbf{r}) * b(-\mathbf{r}) &= a(\mathbf{r}) * b'(\mathbf{r}) = \int a(\mathbf{r}') b'(\mathbf{r} - \mathbf{r}') \, \mathrm{d}\mathbf{r}' \\ &= \int a(\mathbf{r}') b(\mathbf{r}' - \mathbf{r}) \, \mathrm{d}\mathbf{r}' = P'(\mathbf{r}). \end{aligned} \tag{4.2.3.17}$$

This equation means that the second function is displaced into the positive direction by $\mathbf{r}$, then multiplied by the first function and integrated. In the original meaning of the convolution the operation represents a displacement of the second function into the positive direction and an inversion at the displaced origin before multiplication and subsequent integration. On comparing both operations it may be concluded that $P'(\mathbf{r}) \neq P'(-\mathbf{r})$ if the second function is acentric. For real functions both have to be acentric. In a similar way it may be shown that the convolution of

$$\begin{aligned} a(\mathbf{r} - \mathbf{m}) * b(\mathbf{r} - \mathbf{m}') &= \int_{\mathbf{r}'} a(\mathbf{r}' - \mathbf{m}) b(\mathbf{r} - \mathbf{m}' - \mathbf{r}') \, \mathrm{d}\mathbf{r}' \\ &= \int_{\mathbf{r}''} a(\mathbf{r}'') b(\mathbf{r} - \mathbf{m}' - \mathbf{m} - \mathbf{r}'') \, \mathrm{d}\mathbf{r}''. \end{aligned} \tag{4.2.3.18}$$

Equation (4.2.3.18) indicates a displacement by $\mathbf{m}' + \mathbf{m}$ with respect to the convolution of the undisplaced functions. Consequently

$$\delta(\mathbf{r} - \mathbf{m}) * \delta(\mathbf{r} - \mathbf{m}') = \delta(\mathbf{r} - \mathbf{m} - \mathbf{m}'). \tag{4.2.3.19}$$

Obviously, the commutative law of convolution is obeyed; on the other hand, the convolution with the inverted function yields

$$\delta(\mathbf{r} - \mathbf{m}' + \mathbf{m}),$$

indicating that the commutative law (interchange of $\mathbf{m}$ and $\mathbf{m}'$) is violated because of the different signs of $\mathbf{m}$ and $\mathbf{m}'$.

The effectiveness of the method outlined above may be greatly improved by introducing further Fourier transforms of useful functions in real and reciprocal space (Patterson, 1959).

4.2.3.1.2. *Applications*

(1) *Clusters in a periodic lattice (low concentrations)*

The exsolution of clusters of equal sizes is considered. The lattice of the host is undistorted and the clusters have the same lattice but a different structure. A schematic drawing is shown in Fig. 4.2.3.1. Two different structures are introduced by

$$\begin{aligned} F_1(\mathbf{r}) &= \sum_{\nu} \delta(\mathbf{r} - \mathbf{r}_\nu) * F_\nu(\mathbf{r}) \\ F_2(\mathbf{r}) &= \sum_{\mu} \delta(\mathbf{r} - \mathbf{r}_\mu) * F_\mu(\mathbf{r}). \end{aligned}$$

Their Fourier transforms are the structure factors $F_1(\mathbf{H})$, $F_2(\mathbf{H})$. The bold lines in Fig. 4.2.3.1 indicate the clusters, which may be represented by box functions $b(\mathbf{r})$ in the simplest case. It should be pointed out, however, that a more complicated shape means nothing other than a replacement of $b(\mathbf{r})$ by another shape function $b'(\mathbf{r})$ and its Fourier transform $B'(\mathbf{H})$. The distribution of clusters is represented by

references