4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

diffuse scattering. Alternatively, computer simulations may be helpful, as discussed in Section 4.2.7. The most important step is the separation of the distribution function from the molecular scattering. Since this information may be derived from a careful comparison of low-angle diffraction with the remaining sharp reflections, this task is not too difficult. If the influence of the distribution function is unknown, the reader is strongly advised to disregard the immediate neighbourhood of Bragg peaks in the first step of the interpretation. Obviously information may be lost in this way but, as has been shown in the past, much confusion caused by an attempt to interpret the scattering near the Bragg peaks with specific structural properties of a cluster or molecular model is avoided. The inclusion of this part of diffuse scattering can be made after a complete interpretation of the change of the influence of the distribution function on diffraction in the wide-angle region.

4.2.5. Quantitative interpretation

4.2.5.1. Introduction

In these sections, quantitative interpretations of the elastic part of X-ray and neutron diffuse scattering are outlined. Although similar relations are valid for the magnetic scattering of neutrons, this particular topic is excluded. Obviously, all disorder phenomena are strongly temperature-dependent if thermal equilibrium is reached. Consequently, the interpretation of diffuse scattering should include a statistical thermodynamical treatment. Unfortunately, no quantitative theory for the interpretation of structural phenomena is so far available: all quantitative solutions introduce formal order parameters such as correlation functions or distributions of defects. At low temperatures (*i.e.* with a low concentration of defects) the distribution function plays the dominant role in diffuse scattering. With increasing temperature the number of defects increases with corresponding strong interactions between them. Therefore, correlations become increasingly important, and phase transformations of first or higher order may occur which need a separate theoretical treatment. In many cases, large fluctuations of structural properties occur that are closely related to the dynamical properties of the crystal. Theoretical approximations are possible, but their presentation is far beyond the scope of this article. Hence we restrict ourselves to formal parameters in the following.

Point defects or limited structural units, such as molecules, clusters of finite size *etc.*, may only be observed in diffraction if there is a sufficiently large number of defects. This statement is no longer true in high-resolution electron diffraction, where single defects may be observed either by diffraction or by optical imaging if their contrast is high enough. Hence electron microscopy and diffraction are valuable methods in the interpretation of disorder phenomena.

The arrangement of a finite assembly of structural defects is described by its structure and its three-dimensional (3D) distribution function. Structures with a strict 1D periodicity (chain-like structures) need a 2D distribution function, while for structures with a 2D periodicity (layers) a 1D distribution function is sufficient. Since the distribution function is the dominant factor in statistics with correlations between defects, we define the dimensionality of disorder as that of the corresponding distribution function. This definition is more effective in diffraction problems because the dimension of the disorder problem determines the dimension of the diffuse scattering: 1D diffuse streaks, 2D diffuse layers or a general 3D diffuse scattering.

Strictly speaking, completely random distributions cannot be realized, as shown in Section 4.2.3. They occur approximately if the following conditions are satisfied:

(1) The average volume of all defects including their surrounding strain fields NcV_d (where N is the number of unit cells, c is the concentration of defects and V_d is the volume of the defect with $V_d > V_c$, V_c being the volume of the unit cell) is small in comparison with the total volume NV_c of the crystal, or $V_c \gg cV_d$.

(2) Interactions between the defects are negligible. These conditions, however, are valid in very rare cases only, *i.e.* where small concentrations and vanishing strain fields are present. Remarkable exceptions from this rule are real point defects without interactions, such as isotope distribution (which can be studied by neutron diffraction) or the system AuAg at high temperature.

As already mentioned, disorder phenomena may be observed in thermal equilibrium. Two completely different cases have to be considered:

(1) The concentration of defects is given by the chemical composition, *i.e.* impurities in a closed system.

(2) The number of defects increases with temperature and also depends on pressure or other parameters, *i.e.* interstitials, voids, static displacements of atoms, stacking faults, dislocations *etc.*

In many cases, the defects do not occur in thermal equilibrium. Nevertheless, their diffuse scattering is temperature-dependent because of the anomalous thermal movements at the boundary of the defect. Hence the observation of a temperature-dependent behaviour of diffuse scattering cannot be taken as a definite criterion of thermal equilibrium without further careful interpretation.

Ordering of defects may take place in a very anisotropic manner. This is demonstrated by the huge number of examples of 1D disorder. As shown by Jagodzinski (1963), this type of disorder cannot occur in thermal equilibrium for the infinite crystal. This type of disorder is generally formed during crystal growth or mechanical deformation. Similar arguments may be applied to 2D disorder. This is a further reason why the Ising model can hardly ever be used to obtain interaction energies of structural defects. From these remarks it becomes clear that order parameters are formal parameters without strict thermodynamical meaning.

The following section is organized as follows: first we discuss the simple case of 1D disorder where reliable solutions of the diffraction problem are available. Intensity calculations for diffuse scattering from 2D disorder by chain-like structures follow. Finally, the 3D case is treated, where formal solutions of the diffraction problem have been tried and applied successfully to metallic systems to some extent. A short concluding section concerns the special phenomenon of orientational disorder.

4.2.5.2. Layered structures: one-dimensional disorder

As has been pointed out above, it is often useful to start the interpretation of diffuse scattering by checking the diffraction pattern with respect to the dimensionality of the disorder concerned. Since each disordered direction in the crystal demands a violation of the corresponding Laue condition, this question may easily be answered by looking at the diffuse scattering. Diffuse streaks in reciprocal space are due to a one-dimensional violation of the Laue conditions, and will be called one-dimensional disorder. This kind of order is typical for layer structures, but it is frequently observed in cases where several sequences of layers do not differ in the interactions of next-nearest neighbours. Typical examples are structures which may be described in terms of close packing, *e.g.* hexagonal and cubic close packing.

For a quantitative interpretation of diffuse streaks we need one-dimensional correlation functions, which may be determined uniquely if a single independent correlation function is active. According to equation (4.2.3.50), Fourier transformation yields the information required. In all other cases, a specific model has to be suggested for a full interpretation of diffuse streaks. It is worth noting that disorder parameters can be defined uniquely

only if the diffraction pattern allows for a differentiation between long-range and short-range order. This question can be answered at least partly by studying the line width of sharp reflections at very good resolution. Since integrated intensities of sharp reflections have to be separated from the diffuse scattering, this question is of outstanding importance in most cases. Inclusion of diffuse parts in the diffraction pattern during intensity integration of sharp reflections may lead to serious errors in the interpretation of the average structure.

The existence of diffuse streaks in more than one direction of reciprocal space means that the diffraction problem is no longer one-dimensional. Sometimes the problem may be treated independently if the streaks are sharp and no interference effects are observed in the diffraction pattern in areas where the diffuse streaks do overlap. In all other cases, there are correlations between the various directions of one-dimensional disorder which can be determined with the aid of a model covering more than one of the pertinent directions of disorder.

Before starting the discussion of the quantitative solution of the one-dimensional problem, some remarks should be made about the usefulness of quantitative disorder parameters. It is well known from statistical thermodynamics that a one-dimensional system cannot show long-range order above $T = 0$ K. Obviously, this statement is in contradiction with many experimental observations of long-range order even in layer structures. The reason for this behaviour is given by the following arguments, which are valid for any structure. Let us assume a structure with strong interactions at least in two directions. From the theoretical treatment of the two-dimensional Ising model it is known that such a system shows long-range order below a critical temperature T_c. This statement is true even if the layer is finite, although the strict thermodynamic behaviour is not really critical in the thermodynamical sense. A three-dimensional crystal can be constructed by adding layer after layer. Since each layer has a typical two-dimensional free energy, the full statistics of the three-dimensional crystal may be calculated by introducing a specific free energy for the various stackings of layers. Obviously, this additional energy also has to include terms describing potential and entropic energies. They may be formally developed into contributions of next, next-but-one *etc.* nearest neighbours. The contribution to entropy must include configurational and vibrational parts, which are strongly coupled. As long as the layers are finite, there is a finite probability of a fault in the stacking sequence of layers which approaches zero with increasing extension of the layers. Consequently, the free energy of a change in the favourite stacking sequence becomes infinite quadratically with the size of the layer. Therefore, the crystal should be either completely ordered or disordered; the latter case can only be realized if the free energies of one or more stacking sequences are exactly equal (this is very rare but is possible over a small temperature range during phase transformations). An additional positive entropy associated with a deviation from the periodic stacking sequence may lead to a kind of competition between entropy and potential energy, in such a way that periodic sequences of faults result. This situation occurs in the transition range of two structures differing only in their stacking sequence. On the other hand, one must assume that defects in the stacking sequence may occur if the size of the layers is small. This situation occurs during crystal growth, but one should remember that the number of stacking defects should decrease with increasing size of the growing crystal. Apparently, this rearrangement of layers may be suppressed as a consequence of relaxation effects. The growth process itself may influence the propagation of stacking defects and, consequently, the determination of stacking-fault probabilities, with the aim of interpreting the chemical bonding, seems to be irrelevant in most cases.

The quantitative solution of the diffraction problem of one-dimensional disorder follows a method similar to the Ising model. As long as next-nearest neighbours alone are considered, the

solution is very simple if only two possibilities for the structure factors are to be taken into account. Introducing the probability of equal pairs 1 and 2, α, one arrives at the known solution for the *a priori* probability p_μ and *a posteriori* probabilities $p_{\mu\mu'}(\mathbf{m})$, respectively. In the one-dimensional Ising model with two spins and the interaction energies $(U \mp \Delta U)/k_B T$, defining the pair probability $[\alpha = p_{11}(\mathbf{1})]$ as

$$\alpha = \frac{\exp\{\pm\Delta U/k_B T\}}{[\exp\{+\Delta U/k_B T\} + \exp\{-\Delta U/k_B T\}]},$$

the full symmetry is $p_1 = p_2 = \frac{1}{2}$ and $p_{11}(\mathbf{m}) = p_{22}(\mathbf{m})$.
Consequently

$$p_{12}(\mathbf{m}) = p_{22}(\mathbf{m}) = 1 - p_{11}(\mathbf{m}).$$

The scattered intensity is given by

$$I(\mathbf{H}) = L(h, k) \sum_{\mathbf{m}} \langle FF_m^+ \rangle (N - |m|) \exp\{-2\pi iml\}, \qquad (4.2.5.1)$$

where $\mathbf{m} = m\mathbf{c}$, N is the number of unit cells in the $\mathbf{c}$ direction and $\langle FF^+ \rangle$ depends on λ_1, λ_2, which are the eigenvalues of the matrix

$$\begin{pmatrix} \alpha & 1 - \alpha \\ 1 - \alpha & \alpha \end{pmatrix}.$$

From the characteristic equation

$$\lambda^2 - 2\alpha\lambda - 1 + 2\alpha = 0 \qquad (4.2.5.2)$$

one has

$$\lambda_1 = 1; \quad \lambda_2 = 2\alpha - 1. \qquad (4.2.5.2a)$$

λ_1 describes a sharp Bragg reflection (from the average structure) which need not be calculated. Its intensity is simply proportional to $\langle F(\mathbf{H}) \rangle$. The second characteristic value yields a diffuse reflection in the same position if the sign is positive ($\alpha > 0.5$) and in a position displaced by $\frac{1}{2}$ in reciprocal space if the sign is negative ($\alpha < 0.5$). Because of the symmetry conditions only $p_{11}(\mathbf{m})$ is needed; it may be determined with the aid of the boundary conditions

$$p_{11}(\mathbf{0}) = 1, \quad p_{11}(\mathbf{1}) = \alpha,$$

and the general relation

$$p_{\mu\mu'}(\mathbf{m}) = c'_{\mu\mu'}\lambda_1^m + c''_{\mu\mu'}\lambda_2^m.$$

The final solution of our problem yields simply

$$p_{11}(\mathbf{m}) = \frac{1}{2} + \frac{1}{2}\lambda_2^m = p_{22}(\mathbf{m}),$$
$$p_{12}(\mathbf{m}) = \frac{1}{2} - \frac{1}{2}\lambda_2^m = p_{21}(\mathbf{m}).$$

The calculation of the scattered intensity is now performed with the general formula

$$I(\mathbf{H}) = L(h, k) \sum_m \sum_{\mu, \mu'} p_\mu p_{\mu\mu'}(\mathbf{m}) F_\mu F_{\mu'}^+ (N - |m|) \exp\{-2\pi iml\}.$$

$$(4.2.5.3)$$

Evaluation of this expression yields

$$I(\mathbf{H}) = L(h, k) \sum_m (N - |m|) \exp\{-2\pi iml\}$$
$$\times [|\tfrac{1}{2}(F_1 + F_2)|^2 \lambda_1^m + |\tfrac{1}{2}(F_1 - F_2)|^2 \lambda_2^m]. \qquad (4.2.5.4)$$

Since the characteristic solutions of the problem are real,

$$I(\mathbf{H}) = L(\mathbf{G})|(F_1 + F_2)/2|^2$$
$$+ L(h, k)|(F_1 - F_2)/2|^2$$
$$\times \frac{1 - |\lambda_2|^2}{1 - 2\lambda_2 \cos 2\pi l + |\lambda_2|^2}. \quad (4.2.5.5)$$

The particle-size effect has been neglected in (4.2.5.5). This result confirms the fact mentioned above that the sharp Bragg peaks are determined by the averaged structure factor and the diffuse ones by its mean-square deviation.

For the following reason there are no examples of quantitative applications: two different structures generally have different lattice constants, so the original assumption of an undisturbed lattice geometry is not valid. The only case known to the authors is the typical lamellar structure of plagioclases reported by Jagodzinski & Korekawa (1965). The authors interpret the well known 'Schiller effect' as a consequence of optical diffraction. Hence, the size of the lamellae is of the order of 2000 Å. This long-period superstructure cannot be explained in terms of next-nearest-neighbour interactions. In principle, however, the diffraction effects are similar: instead of the diffuse peak as described by the second term in equation (4.2.5.5), satellites of first and second order *etc.* accompanying the Bragg peaks are observed. The study of this phenomenon (Korekawa & Jagodzinski, 1967) has in the meantime found a quantitative interpretation (Burandt *et al.*, 1992; Kalning *et al.*, 1997).

Obviously, the symmetry relation used in the formulae discussed above is only valid if the structures described by the F_μ are related by symmetries such as translations, rotations or combinations of the two. The type of symmetry has an important influence on the diffraction pattern.

(1) *Translation parallel to the ordered layers*

If the translation vector between the two layers in question is such that $2\Delta\mathbf{r}$ is a translation vector parallel to the layer, there are two relevant structure factors:

$$F_1, F_2 = F_1 \exp\{2\pi i\mathbf{H} \cdot \Delta\mathbf{r}\}.$$

$\mathbf{H} \cdot \Delta\mathbf{r}$ may be either an integer or an integer $+ \frac{1}{2}$. Since any integer may be neglected because of the translation symmetry parallel to the layer, we have $F_1 = F_2$ in the former case and $F_1 = -F_2$ in the latter. As a consequence, either the sharp reflections given in equation (4.2.5.4) vanish, or the same is true for the diffuse ones. Hence the reciprocal lattice may be described in terms of two kinds of lattice rows, sharp and diffuse, parallel to the reciprocal coordinate l.

Disorder of this type is observed very frequently. One of the first examples was wollastonite, $CaSiO_3$, studied by Jefferey (1953). Here the reflections with $k = 2n$ are sharp Bragg peaks without any diffuse scattering. Diffuse streaks parallel to $(h00)$, however, are detected for $k = 2n + 1$. In the light of the preceding discussion, the translation vector is $\frac{1}{2}\mathbf{b}$ and the plane of ordered direction (the plane of intergrowth of the two domains) is (100). Hence the displacement is parallel to this plane. Since the intensity of the diffuse lines does not vary according to the structure factor involved, the disorder cannot be random. The maxima observed are approximately in the position of a super-structure generated by large domains without faults in the stacking sequence mutually displaced by $\frac{1}{2}\mathbf{b}$ (antiphase domains). This complicated ordering behaviour is typical for 1D order and may easily be explained by the above-mentioned fact that an infinitely extended interface between two domains causes an infinite unfavourable energy (Jagodzinski, 1964*b*, p. 188). Hence a growing crystal should become increasingly ordered. This consideration explains why the agreement between a 1D disorder theory and experiment is often so poor.

Examples where more than one single displacement vector occur are common. If these are symmetrically equivalent all symmetries have to be considered. The most important cases of displacements differing only by translation are the well known close-packed structures (see below). A very instructive example is the mineral maucherite (approximately Ni_4As_3). According to Jagodzinski & Laves (1947), the structure has the following disorder parameters: interface (001), displacement vectors [000], [$\frac{1}{2}$00], [0$\frac{1}{2}$0], [$\frac{1}{2}\frac{1}{2}$0]. From equation (4.2.5.5) we obtain

$$\langle F(\mathbf{H})\rangle = [1 + \exp\{\pi ih\} + \exp\{\pi ik\} + \exp\{\pi i(h + k)\}]/4.$$

Hence there are sharp reflections for h, k = even and diffuse ones otherwise. Further conclusions may be drawn from the average structure.

(2) *Translation perpendicular to the ordered layers*

If the translation is $\mathbf{c}/2$ the structure factors are

$$F_2 = F_1 \exp\{2\pi il\},$$
$$F_1 = F_2 \text{ for } l = \text{even},$$
$$F_1 = -F_2 \text{ for } l = \text{odd}.$$

There are sharp ($l = 2n$) *and* diffuse ($l = 2n + 1$) reflections on all reciprocal-lattice rows discussed above.

Since the sharp and diffuse reflections occur on the same reciprocal line, the behaviour is completely different compared with the preceding case. In general, a component of any displacement vector perpendicular to the interface gives rise to a change in chemical composition, as shown in the next example: in a binary system consisting of A and B atoms with a tendency towards an alternating arrangement of A and B layers, any fault in the sequence $BABAB|BABAB|B$ increases the number of B atoms (or A atoms). In general, such kinds of defects will lead to an interface with a different lattice constant, at least in the direction perpendicular to the interface. Consequently, the exact displacement vectors of $\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$ are rare. Since ordered structures should be realized in the 1D case, incommensurate super-structures will occur; these are very abundant during ordering processes. An interesting example has been reported and interpreted by Cowley (1976*a,b*), where the displacement vector has a translational period of $\frac{1}{4}$ perpendicular to the plane of inter-growth. Reflections 00*l* and 22*l* with $l = 4n$ are sharp, all remaining reflections more or less diffuse. Since the maxima ($\bar{1}11$), ($\bar{1}33$) show a systematically different behaviour, there is also a displacement component parallel to the plane of inter-growth in question. A semiquantitative interpretation was given in his papers.

(3) *Rotations*

Layers related by a twofold rotation parallel to **c** may easily be discussed by simply considering their structure factors. Since the layers do not obey the twofold symmetry, their structure factors are generally different; unless they become equal accidentally there are sharp and diffuse reflections according to the values of $\langle F\rangle$ and ΔF, respectively. Obviously, $F_1 = F_2$ is valid only if $h = k = 0$; consequently there is just one reciprocal-lattice row free from diffuse scattering.

(4) *Asymmetric case*

In the asymmetric case, the symmetry conditions used above are no longer valid:

$$p_1 \neq p_2, \quad p_{12} \neq p_{21}, \quad p_{11} \neq p_{22}.$$

However, there is one condition which may be derived from the invariance of the numbers of pairs in the relevant and its opposite direction:

$$p_\mu p_{\mu\mu'}(\mathbf{m}) = p_{\mu'}p_{\mu'\mu}(-\mathbf{m}).$$

This equation does not require that $p_{\mu\mu'}(\mathbf{m})$ should be symmetric in **m**. The calculation of characteristic values yields

$$\lambda_1 = 1, \qquad \lambda_2 = (\alpha_1 + \alpha_2) - 1. \quad (4.2.5.6)$$

The *a priori* probabilities are now different from $\frac{1}{2}$ and may be calculated by considering $p_{\mu\mu'}(\mathbf{m}) \rightarrow p_{\mu'}(\mathbf{m} \rightarrow \infty)$:

$$p_1 = \alpha_1/(\alpha_1 + \alpha_2); \quad p_2 = \alpha_2/(\alpha_1 + \alpha_2).$$

The intensity is given by an expression very similar to (4.2.5.5):

$$I(\mathbf{H}) = L(\mathbf{G})|[\alpha_1/(\alpha_1 + \alpha_2)]F_1 + [\alpha_2/(\alpha_1 + \alpha_2)]F_2|^2$$
$$+ L(h,k)|[\alpha_1/(\alpha_1 + \alpha_2)]F_1 - [\alpha_2/(\alpha_1 + \alpha_2)]F_2|^2$$
$$\times (1 - |\lambda_2|^2)/(1 - 2\lambda_2 \cos 2\pi l + |\lambda_2|^2). \qquad (4.2.5.7)$$

Again, there are sharp Bragg reflections and diffuse ones in the same positions or in a displaced position depending on the sign of λ_2.

From a discussion of the next-nearest-neighbour Ising model, one may conclude that a detailed study of the qualitative behaviour of sharp and diffuse reflections may give additional information on the symmetry of the layers involved.

In the case of translations between neighbouring layers not fulfilling the condition $\mathbf{h} \cdot \mathbf{r}$ = integer, where $\mathbf{r}$ is parallel to the layer, more than two structure factors have to be taken into account. If $n\mathbf{h} \cdot \mathbf{r}$ = integer, where n is the smallest integer fulfilling the said condition, n different structure factors have to be considered. The characteristic equation has formally to be derived with the aid of an $n \times n$ matrix containing internal symmetries, which may be avoided by adding the phase factors $\varepsilon = \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}/n\}$, $\varepsilon^+ = \exp\{-2\pi i \mathbf{H} \cdot \mathbf{r}/n\}$ to the probability of pairs. The procedure is allowed if the displacements $\mathbf{r}$ and $-\mathbf{r}$ are admitted only for neighbouring layers. The matrix yielding the characteristic values may then be reduced to

$$\begin{pmatrix} \alpha_1\varepsilon & (1 - \alpha_1)\varepsilon^+ \\ (1 - \alpha_2)\varepsilon & \alpha_2\varepsilon^+ \end{pmatrix}$$

and yields the characteristic equation

$$\lambda^2 - \lambda(\alpha_1\varepsilon + \alpha_2\varepsilon^+) - 1 + \alpha_1 + \alpha_2 = 0. \qquad (4.2.5.8)$$

Equation (4.2.5.8) gives sharp Bragg reflections for $\mathbf{H} \cdot \mathbf{r}/n$ = integer; the remaining diffuse reflections are displaced according to the phase of the complex characteristic value. Equation (4.2.5.8) has been used in many cases. Qualitative examples are the mixed-layer structures published by Hendricks & Teller (1942). An example of a four-layer-type structure is treated by Dubernat & Pezerat (1974). A first quantitative treatment with good agreement between theory and experimental powder diffraction data has been given by Dorner & Jagodzinski (1972) for the binary system TiO_2–SnO_2. In the range of the so-called spinodal decomposition, the chemical compositions of the two domains and the average lengths of the two types of domains could be determined. Another quantitative application was reported by Jagodzinski & Hellner (1956) for the transformation of $RhSn_2$ into a very complicated mixed-layer type. A good agreement of measured and calculated diffuse scattering (with asymmetric line profiles and displacement of maxima) could be found over a wide angular range of single-crystal diffraction.

4.2.5.2.1. Stacking disorder in close-packed structures

From an historical point of view, stacking disorder in close-packed systems is most important. The three relevant positions of ordered layers are represented by the atomic coordinates $|0,0|$, $|\frac{1}{3}, \frac{2}{3}|$, $|\frac{2}{3}, \frac{1}{3}|$ in the hexagonal setting of the unit cell, or simply by the figures 1, 2, 3 in the same sequence. Structure factors F_1, F_2, F_3 refer to the corresponding positions of the same layer:

$$F_2 = F_1 \exp\{2\pi i(h - k)/3\},$$
$$F_3 = F_1 \exp\{-2\pi i(h - k)/3\},$$

hence

$$F_1 = F_2 = F_3 \quad \text{if } h - k \equiv 0 \pmod 3.$$

According to the above discussion, the indices 1, 2, 3 define the reciprocal-lattice rows exhibiting sharp reflections only, as long as the distances between the layers are exactly equal. The symmetry conditions caused by the translation are normally

$$p_1 = p_2 = p_3, \qquad p_{11} = p_{22} = p_{33},$$
$$p_{12} = p_{23} = p_{31}, \quad p_{13} = p_{21} = p_{32}.$$

For the case of close packing of spheres and some other problems any configuration of $\mathbf{m}$ layers determining the *a posteriori* probability $p_{\mu\mu'}(\mathbf{m})$, $\mu = \mu'$, has a symmetrical counterpart where μ is replaced by $\mu' + 1$ (if $\mu' = 3$, $\mu' + 1 = 1$).

In this particular case, $p_{12}(\mathbf{m}) = p_{13}(\mathbf{m})$ and equivalent relations generated by translation.

Nearest-neighbour interactions do not lead to an ordered structure if the principle of close packing is obeyed (no pairs are in equal positions) (Hendricks & Teller, 1942; Wilson, 1942). Extension of the interactions to next-but-one or more neighbours may be carried out by introducing the method of matrix multiplication developed by Kakinoki & Komura (1954, 1965) or the method of overlapping clusters (Jagodzinski, 1954). The latter procedure is outlined in the case of interactions between four layers. A given set of three layers may occur in the following 12 combinations:

$$123, 231, 312; \quad 132, 213, 321;$$
$$121, 232, 313; \quad 131, 212, 323.$$

Since three of them are equivalent by translation, only four representatives have to be introduced:

$$123; \quad 132; \quad 121; \quad 131.$$

In the following, the new indices 1, 2, 3, 4 are used for these four representatives for the sake of simplicity.

In order to construct the statistics layer by layer, the next layer must belong to a triplet starting with the same two symbols with which the preceding one ended, *e.g.* 123 can only be followed by 231 or 232. In a similar way, 132 can only be followed by 321 or 323. Since both cases are symmetrically equivalent, the probabilities α_1 and $1 - \alpha_1$ are introduced. In a similar way, 121 may be followed by 212 or 213 *etc.* For these two groups the probabilities α_2 and $1 - \alpha_2$ are defined. The different translations of groups are considered by introducing the phase factors as described above. Hence the matrix for the characteristic equation may be set up as follows. As a representative cluster of each group the one having the number 1 at the centre is chosen, *e.g.* 312 is the representative for the group 123, 231, 312; in a similar way 213, 212 and 313 are the remaining representatives. Since this arrangement of three layers is equivalent by translation, it may be assumed that the structure of the central layer is not influenced by the statistics to a first approximation. The same arguments hold for the remaining three groups. On the other hand, the groups 312 and 213 are equivalent by rotation only. Consequently, their structure factors may differ if the influence of the two neighbours has to be taken into account. A different situation exists for the groups 212 and 313, which are correlated by a centre of symmetry, which causes different corresponding structure factors. It should be pointed out, however, that the structure factor is invariant as long as there is no influence of neighbouring layers on the structure of the central layer. The latter is often observed in close-packed metal structures or in compounds like

512

ZnS, SiC and others. For the calculation of intensities $p_\mu p_{\mu\mu'}$ and $F_\mu F_{\mu'}^+$ are needed.

According to the following scheme of sequences, any sequence of pairs is correlated with the same phase factor for FF^+ due to translation if both members of the pair belong to the same group. Consequently, the phase factor may be attached to the sequence probability such that FF^+ remains unchanged and the group may be treated as a single element in the statistics. In this way, the reduced matrix for the solution of the characteristic equation is given by

It should be pointed out that clusters 1 and 3 describe a cubic arrangement of three layers in the case of simple close packing, while clusters 2 and 4 represent the hexagonal close packing. There may be a small change in the lattice constant c perpendicular to the layers. Additional phase factors then have to be introduced in the matrix for the characteristic equation and a recalculation of the constants is necessary. As a consequence, the reciprocal-lattice rows $(h - k) \equiv 0 \,(\mathrm{mod}\ 3)$ become diffuse if $l \neq 0$ and the diffuseness increases with l. Similar behaviour results for the remaining reciprocal-lattice rows.

F_μ	$F_{\mu'}^+$ (1) 312, $123(\varepsilon^+)$, $231(\varepsilon)$	(2) 212, $323(\varepsilon^+)$, $131(\varepsilon)$	(3) 213, $321(\varepsilon^+)$, $132(\varepsilon)$	(4) 313, $121(\varepsilon^+)$, $232(\varepsilon)$
(1) 312, $123(\varepsilon)$, $231(\varepsilon^+)$	$\alpha_1\varepsilon^+$	0	0	$(1-\alpha_1)\varepsilon^+$
(2) 212, $323(\varepsilon)$, $131(\varepsilon^+)$	$(1-\alpha_2)\varepsilon^+$	0	0	$\alpha_2\varepsilon^+$
(3) 213, $321(\varepsilon)$, $132(\varepsilon^+)$	0	$(1-\alpha_2)\varepsilon$	$\alpha_1\varepsilon$	0
(4) 313, $121(\varepsilon)$, $232(\varepsilon^+)$	0	$\alpha_2\varepsilon$	$(1-\alpha_2)\varepsilon$	0

There are three solutions of the diffraction problem:

(1) If $h - k = 0 \,(\mathrm{mod}\ 3)$, $\varepsilon = +1$, there are two quadratic equations:

$$\lambda^2 - (\alpha_1 + \alpha_2)\lambda - 1 + \alpha_1 + \alpha_2 = 0,$$
$$\lambda^2 - (\alpha_1 - \alpha_2)\lambda + 1 - \alpha_1 - \alpha_2 = 0,$$
(4.2.5.9)

with solutions

$$\lambda_1 = 1, \qquad \lambda_2 = \alpha_1 + \alpha_2 - 1,$$
$$\lambda_{3/4} = \frac{\alpha_1 - \alpha_2}{2} \pm \left[\frac{(\alpha_1 - \alpha_2)^2}{4} - 1 + \alpha_1 - \alpha_2\right]^{1/2}. \qquad (4.2.5.10)$$

λ_1 and λ_2 are identical with the solution of the asymmetric case of two kinds of layers [*cf.* equation (4.2.5.6)]. They yield sharp reflections for l = integer and diffuse ones in a position determined by the sequence probabilities α_1 and α_2 (with a position of either l = integer or $l = \frac{1}{2}$ + integer, respectively). The remaining two characteristic values may be given in the form $\lambda = |\lambda| \exp\{2\pi i\varphi\}$, where φ determines the position of the reflection. If the structure factors of the layers are independent of the cluster, λ_2, λ_3 and λ_4 become irrelevant because of the new identity of the F's and there is no diffuse scattering. Weak diffuse intensities on the lattice rows $h - k = 0 \,(\mathrm{mod}\ 3)$ may be explained in terms of this influence.

(2) The remaining two solutions for $\varepsilon = \exp\{\pm 2\pi i(h - k)/3\}$ are equivalent and result in the same characteristic values. They have been discussed explicitly in the literature; the reader is referred to the papers of Jagodzinski (1949*a,b,c*, 1954).

In order to calculate the intensities, one has to reconsider the symmetry of the clusters, which is different to the symmetry of the layers. Fortunately, a threefold rotation axis is invariant against the translations, but this is not true for the remaining symmetry operations in the layer if there are any more. Since we have two pairs of inequivalent clusters, namely 312, 213 and 212, 313, there are only two different *a priori* probabilities $p_1 = p_3$ and $p_2 = p_4 = \frac{1}{2}(1 - 2p_1)$.

The symmetry conditions of the new clusters may be determined using 'probability trees' as described by Wilson (1942) and Jagodzinski (1949*b*). For example: $p_{11} = p_{33}, p_{22} = p_{44}, p_{13} = p_{31}, p_{24} = p_{42}$ *etc.*

The final solution of the diffraction problem results in the following general intensity formula:

$$I(\mathbf{H}) = L(h, k)N \sum_\nu \{A_\nu(\mathbf{H})(1 - |\lambda_\nu|^2)$$
$$\times [1 - 2|\lambda_\nu|\cos 2\pi(l - \varphi_\nu) + |\lambda_\nu|^2]^{-1}$$
$$- 2B_\nu(\mathbf{H})|\lambda_\nu|\sin 2\pi(l - \varphi_\nu)$$
$$\times [1 - 2|\lambda_\nu|\cos 2\pi(l - \varphi_\nu) + |\lambda_\nu|^2]^{-1}\}. \qquad (4.2.5.11)$$

Here A_ν and B_ν represent the real and imaginary part of the constants to be calculated with the aid of the boundary conditions of the problem. The first term in equation (4.2.5.11) determines the symmetrical part of a diffuse reflection with respect to the maximum and is completely responsible for the integrated intensity. The second term causes an antisymmetrical contribution to intensity profiles but does not influence the integrated intensities. These general relations enable a semiquantitative interpretation of the sharp and diffuse scattering in any case, without performing the time-consuming calculations of the constants, which may only be done in more complicated disorder problems with the aid of a computer program evaluating the boundary conditions of the problem.

This can be carried out with the aid of the characteristic values and a linear system of equations (Jagodzinski, 1949*a,b,c*), or with the aid of matrix formalism (Kakinoki & Komura, 1954; Takaki & Sakurai, 1976). As long as only the line profiles and positions of the reflections are required, these quantities may be determined experimentally and fitted to characteristic values of a matrix. The size of this matrix is given by the number of sharp and diffuse maxima observed, while $|\lambda_\nu|$ and $\exp\{2\pi i\varphi_\nu\}$ may be found by evaluating the line width and the position of diffuse reflections. Once this matrix has been found, a semiquantitative model of the disorder problem can be given. If a system of sharp reflections is available, the averaged structure can be solved as described in Section 4.2.3.2. The determination of the constants of the diffraction problem is greatly facilitated by considering the intensity modulation of diffuse scattering, which enables a phase determination of structure factors to be made under certain conditions.

The theory of close-packed structures with three equivalent translation vectors has been applied very frequently, even to

systems that do not obey the principle of close-packing. The first quantitative explanation was published by Halla *et al.* (1953). It was shown there that single crystals of $C_{18}H_{24}$ from the same synthesis may have a completely different degree of order. This was true even within the same crystal. Similar results were found for C, Si, CdI_2, CdS_2, mica and many other compounds. Quantitative treatments are less abundant [*e.g.* CdI_2 (Martorana *et al.*, 1986); MX_3 structures (Conradi & Müller, 1986)]. Special attention has been paid to the quantitative study of polytypic phase transformations in order to gain information about the thermodynamical stability or the mechanism of layer displacements, *e.g.* Co (Edwards & Lipson, 1942; Frey & Boysen, 1981), SiC (Jagodzinski, 1972; Pandey *et al.*, 1980*a*,*b*,*c*), ZnS (Müller, 1952; Mardix & Steinberger, 1970; Frey *et al.*, 1986) and others.

Certain laws may be derived for the reduced integrated intensities of diffuse reflections. 'Reduction' in this context means a division of the diffuse scattering along l by the structure factor, or the difference structure factor if $\langle F \rangle \neq 0$. This procedure is valuable if the number of stacking faults rather than a complete solution of the diffraction problem is required.

The discussion given above has been made under the assumption that the full symmetry of the layers is maintained in the statistics. Obviously, this is not necessarily true if external lower symmetries influence the disorder. An important example is the generation of stacking faults during plastic deformation. Problems of this kind need a complete reconsideration of symmetries. Furthermore, it should be pointed out that a treatment with the aid of an extended Ising model as described above is irrelevant in most cases. Simplified procedures describing the diffuse scattering of intrinsic, extrinsic, twin stacking faults and others have been described in the literature. Since their influence on *structure determination* can generally be neglected, the reader is referred to the literature for additional information.

A different approach to the analysis of planar disorder in close-packed structures is given by Varn *et al.* (2002). With simplifying assumptions, *e.g.* that spacings between identical defect-free layers are independent of local stacking arrangements, average correlations between them are extracted from experimental diffractograms *via* Fourier analysis. Spatial patterns of the layers are then constructed by a so-called epsilon machine, which reproduces the correlations with minimal states of the stacking process. The basic statistical description of the ensemble of spatial patterns produces the stacking distribution. With this technique, stacking sequences are generated which are compared with the correlation factors and the diffractograms. The authors report an improved matching of calculated and experimental data for ZnS.

4.2.5.3. Chain-like structures: two-dimensional disorder

In this section, disorder phenomena that are related to chain-like structural elements in crystals are considered. This topic includes the so-called '1D crystals', where translational symmetry (in direct space) exists in one direction only – crystals in which highly anisotropic binding forces are responsible for chain-like atomic groups, *e.g.* compounds that exhibit a well ordered 3D framework structure with tunnels in a unique direction in which atoms, ions or molecules are embedded. Examples are compounds with platinum, iodine or mercury chains, urea inclusion compounds with columnar structures (organic or inorganic), 1D ionic conductors, polymers *etc.* Diffuse-scattering studies of 1D conductors have been carried out in connection with investigations of stability/instability problems, incommensurate structures, phase transitions, dynamic precursor effects *etc.* These areas are not treated here. For general reading about diffuse scattering in connection with these topics see, *e.g.*, Comes & Shirane (1979) and references therein. Also excluded are specific problems related to polymers or liquid crystals (meso-

phases) (see Chapter 4.4) and magnetic structures with chain-like spin arrangements.

Trivial diffuse scattering occurs as 1D Bragg scattering (diffuse layers) by internally ordered chains. Diffuse phenomena in reciprocal space are due to 'longitudinal' disordering within the chains (along the unique direction) as well as to 'transverse' correlations between different chains over a restricted volume. Only static aspects are considered; diffuse scattering resulting from collective excitations or diffusion-like phenomena which are of inelastic or quasielastic origin are not treated here.

4.2.5.3.1. Randomly distributed collinear chains

As found in any elementary textbook of diffraction, the simplest result of scattering by a chain with period c,

$$l(\mathbf{r}) = l(z) = \sum_{n_3} \delta(z - n_3 c), \qquad (4.2.5.12)$$

is described by one of the Laue equations:

$$G(L) = |L(L)|^2 = \sin^2 \pi NL / \sin^2 \pi L, \qquad (4.2.5.13)$$

which gives broadened profiles for small N. In the context of phase transitions the Ornstein–Zernike correlation function is frequently used, *i.e.* (4.2.5.13) is replaced by a Lorentzian:

$$1/[\xi^2 + 4\pi^2(L - l)^2], \qquad (4.2.5.14)$$

where ξ denotes the correlation length.

In the limiting case $N \to \infty$, (4.2.5.13) becomes

$$\sum_l \delta(L - l). \qquad (4.2.5.15)$$

The scattering by a real chain $a(\mathbf{r})$ consisting of molecules with structure factor F_M is therefore determined by

$$F_M(\mathbf{H}) = \sum_j f_j \exp\{2\pi i(Hx_j + Ky_j + Lz_j)\}. \qquad (4.2.5.16)$$

The Patterson function is

$$
\begin{aligned}
P(\mathbf{r}) = {}&(1/c) \int\int |F_0(H, K)|^2 \cos 2\pi(Hx + Ky)\, dH\, dK \\
&+ (2/c) \sum_l \int\int |F_l|^2 \exp\{2\pi i(Hx + Ky)\} \\
&\times \exp\{-2\pi i l z\}\, dH\, dK, \qquad (4.2.5.17)
\end{aligned}
$$

where the index l denotes the only relevant position $L = l$ (the subscript M is omitted).

The intensity is concentrated in diffuse layers perpendicular to $\mathbf{c}^*$ from which the structural information may be extracted. Projections are:

$$\int a(\mathbf{r})\, dz = \int\int F_0(H, K) \exp\{2\pi i(Hx + Ky)\}\, dH\, dK, \quad (4.2.5.18)$$

$$\int\int a(\mathbf{r})\, dx\, dy = (2/c) \sum_l F_l(00l) \exp\{-2\pi i l z\}. \qquad (4.2.5.19)$$

Obviously the z parameters can be determined by scanning along a meridian $(00L)$ through the diffuse sheets (*e.g.* by a diffractometer recording). Owing to intersection of the Ewald sphere with the set of planes, the meridian cannot be recorded on *one* photograph; successive equi-inclination photographs are necessary. Only in the case of large c spacings is the meridian well approximated in one photograph.

There are many examples where a tendency to cylindrical symmetry exists: chains with p-fold rotational or screw symmetry around the preferred direction or assemblies of chains (or domains) with a statistical orientational distribution around the texture axis. In this context, it should be mentioned that symmetry operations with rotational parts belonging to the 1D rod groups actually occur, *i.e.* not only $p = 2, 3, 4, 6$.

In all these cases a treatment in the frame of cylindrical coordinates is advantageous (see, *e.g.*, Vainshtein, 1966):

Direct space	Reciprocal space
$x = r \cos \psi$	$H = H_r \cos \Psi$
$y = r \sin \psi$	$K = H_r \sin \Psi$
$z = z$	$L = L$

$$a(r, \psi, z) = \int \int \int F(\mathbf{H}) \exp\{-2\pi i [H_r r \cos(\psi - \Psi) + Lz]\}$$
$$\times H_r \, dH_r \, d\Psi \, dL, \qquad (4.2.5.20)$$

$$F(\mathbf{H}) = \int \int \int a(r, \psi, z) \exp\{2\pi i [H_r r \cos(\psi - \Psi) + Lz]\}$$
$$\times r \, dr \, d\psi \, dz. \qquad (4.2.5.21)$$

The integrals may be evaluated by the use of Bessel functions:

$$J_n(u) = \tfrac{1}{2} \pi i^n \int \exp\{i(u \cos \varphi + n\varphi)\} \, d\varphi$$

$(u = 2\pi r H_r; \varphi = \psi - \Psi)$.

The 2D problem $a = a(r, \psi)$ is treated first; an extension to the general case $a(r, \psi, z)$ is easily made afterwards.

Along the theory of Fourier series one has

$$a(r, \psi) = \sum_n a_n(r) \exp\{in\psi\},$$
$$a_n(r) = \frac{1}{2\pi} \int a(r, \psi) \exp\{-in\psi\} \, d\psi, \qquad (4.2.5.22)$$

or with

$$\alpha_n = \frac{1}{2\pi} \int a(r, \psi) \cos(n\psi) \, d\psi,$$
$$\beta_n = \frac{1}{2\pi} \int a(r, \psi) \sin(n\psi) \, d\psi,$$
$$a_n(r) = |a_n(r)| \exp\{-i\psi_n(r)\},$$
$$|a_n(r)| = \sqrt{a_n^2 + \beta_n^2},$$
$$\psi_n(r) = \arctan \beta_n/\alpha_n.$$

If contributions to anomalous scattering are neglected $a(r, \psi)$ is a real function:

$$a(r, \psi) = \sum_n |a_n(r)| \cos[n\psi - \psi_n(r)]. \qquad (4.2.5.23)$$

Analogously, one has

$$F(H_r, \Psi) = \sum_n |F_n(H_r)| \exp\{in\Psi\}. \qquad (4.2.5.24)$$

$F(H_r, \Psi)$ is a complex function; $F_n(H_r)$ are the Fourier coefficients that are to be evaluated from the $a_n(r)$:

$$F_n(H_r) = \frac{1}{2\pi} \int F(H_r, \Psi) \exp\{-in\Psi\} \, d\Psi$$

$$= \exp\{in\pi/2\} \int a_n(r) J_n(2\pi r H_r) 2\pi r \, dr,$$

$$F(H_r, \Psi) = \sum_n \exp\{in[\Psi + (\pi/2)]\}$$
$$\times \int a_n(r) J_n(2\pi r H_r) 2\pi r \, dr, \qquad (4.2.5.25)$$

$$a(r, \psi) = \sum_n \exp\{in[\Psi - (\pi/2)]\}$$
$$\times \int F_n(H_r) J_n(2\pi r H_r) 2\pi H_r \, dH_r. \qquad (4.2.5.26)$$

The formulae may be used for calculation of the diffuse intensity distribution within a diffuse sheet, in particular when the chain

molecule is projected along the unique axis [*cf.* equation (4.2.5.18)].

Special cases are:
(1) *Complete cylinder symmetry*

$$F(H_r) = 2\pi \int a(r) J_0(2\pi r H_r) r \, dr \qquad (4.2.5.27),$$
$$a(r) = 2\pi \int F(H_r) J_n(2\pi r H_r) H_r \, dH_r. \qquad (4.2.5.28)$$

(2) *p-fold symmetry of the projected molecule*, where $a(r, \psi) = a[r, \psi + (2\pi/p)]$

$$F_p(H_r, \Psi) = \sum_n \exp\{inp[\Psi + (\pi/2)]\}$$
$$\times \int a_{np}(r) J_{np}(2\pi r H_r) 2\pi r \, dr, \qquad (4.2.5.29)$$

$$a_p(r, \psi) = \sum_n |a_{np}(r)| \cos[np\psi - \psi_{np}(r)]. \qquad (4.2.5.30)$$

Only Bessel functions $J_0, J_p, J_{2p}, \ldots$ occur. In most cases J_{2p} and higher orders may be neglected.

(3) *Vertical mirror planes*

Only cosine terms occur, *i.e.* all $\beta_n = 0$ or $\psi_n(r) = 0$.

The *general 3D expressions* valid for extended chains with period c [equation (4.2.5.12)] are found in an analogous way,

$$a(r, \psi, z) = a_M(r, \psi, z) * l(z),$$

$$F(\mathbf{H}) = F_l(H_r, \Psi, L) = F_M(\mathbf{H}) L(L)$$
$$= \int \int \int a_M(r, \psi, z) \exp\{2\pi i [H_r r \cos(\psi - \Psi) + Lz]\}$$
$$\times 2\pi r \, dr \, d\psi \, dz. \qquad (4.2.5.31)$$

Using a series expansion analogous to (4.2.5.23) and (4.2.5.24),

$$a_{nl}(r) = \frac{1}{2\pi} \int \int a_M \exp\{-i(n\psi - 2\pi lz)\} \, d\psi \, dz, \qquad (4.2.5.32)$$

$$F_{nl}(H_r) = \exp\{in\pi/2\} \int a_{nl}(r) J_n(2\pi H_r r) 2\pi r \, dr, \qquad (4.2.5.33)$$

one has

$$F_l(\mathbf{H}) = \sum_n \exp\{in[\Psi + (\pi/2)]\} \int a_{nl}(r) J_n(2\pi H_r r) 2\pi r \, dr.$$
$$(4.2.5.34)$$

In practice the integrals are often replaced by discrete summation of j atoms at positions $r = r_j$, $\psi = \psi_j$, $z = z_j$ $(0 \le z_j < c)$:

$$F_l(\mathbf{H}) = \sum_j \sum_n f_j J_n(2\pi H_r r_j) \exp\{-in\psi_j\}$$
$$\times \exp\{2\pi ilz_j\} \exp\{in[\Psi + (\pi/2)]\} \qquad (4.2.5.35)$$

or

$$F_l(\mathbf{H}) = \sum_n (\alpha_n + i\beta_n) \exp\{in\Psi\},$$

$$\alpha_n = \sum_j f_j J_n(2\pi H_r r_j) \cos\{n[(\pi/2) - \psi_j] + 2\pi lz_j\},$$

$$\beta_n = \sum_j f_j J_n(2\pi H_r r_j) \sin\{n[(\pi/2) - \psi_j] + 2\pi lz_j\}.$$

Intensity in the lth diffuse layer is given by

$$I_l = \sum_n \sum_{n'} [(\alpha_n \alpha_{n'} + \beta_n \beta_{n'}) + i(\alpha_{n'} \beta_n - \alpha_n \beta_{n'})]$$
$$\times \exp\{i(n - n')\Psi\}. \qquad (4.2.5.36)$$

(*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:

$$F_{0l}(H_r, L) = 2\pi \int \int \langle a_M \rangle J_0(2\pi H_r r) \exp\{2\pi ilz\} r \, dr \, dz$$

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 (4.2.5.32) may be replaced by $\cos 2\pi l z$.

(e) *Twofold symmetry axis* perpendicular to the chain axis (at positions $\psi = 0, 2\pi/p, \ldots$). Exponentials $\exp\{-i(np\psi - 2\pi l z)\}$ in equation (4.2.5.32) 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). There is usually no practical use for this 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 of doing so only if *one* diffuse layer corresponds predominantly to *one* Bessel function.

4.2.5.3.2. 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.

(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 (4.2.5.12) is replaced by a distribution:

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

$$D(L) = \sum_\nu \exp\{2\pi i L z_\nu\}, \qquad (4.2.5.37)$$

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

The Patterson function is given by

$$P(\mathbf{r}) = [a_M(\mathbf{r}) * a_M(-\mathbf{r})] * [d(z) * d(-z)]. \qquad (4.2.5.38)$$

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

$$w(z) = N\delta(z) + \sum_\nu \sum_\mu \delta[z - (z_\nu - z_\mu)] + \sum_\nu \sum_\mu \delta[z + (z_\nu - z_\mu)],$$
$$(4.2.5.39)$$

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

$$W(L) = N + 2 \sum_\nu \sum_\mu \cos 2\pi[L(z_\nu - z_\mu)], \qquad (4.2.5.40)$$

$$I(\mathbf{H}) = |F_M(\mathbf{H})|^2 W(L). \qquad (4.2.5.41)$$

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.

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

$$a(\mathbf{r}) = a_M(\mathbf{r}) * [d_\infty b(z)], \qquad (4.2.5.42)$$

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

with

$$b(z) * b(-z) \leftrightarrow |B(L)|^2,$$
$$I = |F_M(\mathbf{H})|^2 |D_\infty * B(L)|^2. \qquad (4.2.5.43)$$

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.

(2) *Orientational disorder*

A misorientation of the chain molecules with respect to one another is taken into account by different structure factors F_M.

$$I(\mathbf{H}) = \sum_\nu \sum_\mu F_\nu(\mathbf{H})F_\mu(\mathbf{H})^+ \exp\{2\pi i L(z_\nu - z_\mu)\}. \qquad (4.2.5.44)$$

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

$$I(\mathbf{H}) = N(\langle|F|^2\rangle - \langle|F|\rangle^2) + \langle|F|\rangle^2 L(L), \qquad (4.2.5.44a)$$

where

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

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

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

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

(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 (4.2.5.39),

$$w(z) = N\delta(z) + \sum_\nu \delta[z \pm (z_\nu - z_{\nu+1})]$$
$$+ \sum_\nu \delta[z \pm (z_\nu - z_{\nu+2})] + \ldots \qquad (4.2.5.39a)$$

in terms of continuous functions $a_\mu(z)$ that describe the probability of finding the μth neighbour within an arbitrary distance,

$$w'(z) = w(z)/N = \delta(z) + a_1(z) + a_{-1}(z) + \ldots$$
$$+ a_\mu(z) + a_{-\mu}(z) + \ldots \qquad (4.2.5.45)$$

$[\int a_\mu(z)\,dz = 1, a_\mu(z) = a_{-\mu}(-z)]$.

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 μth molecule in the chain. Gaussian distributions are frequently used:

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

where c' is a normalizing constant and Δ is the standard deviation. Fourier transformation of equation (4.2.5.45) gives the well known result

$$I_D \simeq (1 - \exp\{-L^2\Delta^2\}),$$

i.e. a monotonically increasing intensity with L (any modulation due to a molecular structure factor is 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 μth 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 the diffuse intensity (Welberry, 1985):

$$I_D(L) \simeq \exp\{-L^2\Delta^2\} \sum_j (-L^2\Delta^2)^j / j!$$
$$\times (1 - \kappa^{2j}) / (1 + \kappa^{2j} - 2\kappa^j \cos 2\pi L c_0). \quad (4.2.5.46)$$

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 (4.2.5.46) 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 μth molecule relative to the first becomes unlimited. There is a continuous transition to a fluid-like behaviour of the chain molecules. This 1D paracrystal (these are sometimes called distortions of the 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 by 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,

$$a_\mu(z) = a_1(z) * a_1(z) * a_1(z) * \ldots * a_1(z)$$

(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 μth order it is $\mu \langle c \rangle$. 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

$$G(L) = 1 + \sum_\mu \{F^\mu + F^{+\mu}\} = \text{Re}\{(1 + F)/(1 - F)\} \quad (4.2.5.47)$$

with $F(L) \leftrightarrow a_1(z)$, $F^\mu(L) \leftrightarrow a_\mu(z)$.

With $F = |F| \exp\{i\chi\}$ ($\chi = L\langle c \rangle$), equation (4.2.5.47) is written

$$G(L) = [1 - |F(L)|^2] / [1 - 2|F(L)| \cos \chi + |F(L)|^2]. \quad (4.2.5.47a)$$

[Note the close similarity to the diffuse part of equation (4.2.5.5), 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, a Gaussian distribution is frequently used:

$$a_1(z) = (1/\sqrt{2\pi}\Delta) \exp\{-(z - \langle c \rangle)^2 / 2\Delta^2\}$$
$$a_\mu(z) = (1/\sqrt{\mu})(1/\sqrt{2\pi}\Delta) \exp\{-(z - \mu\langle c \rangle)^2 / 2\mu\Delta^2\}$$
$$(4.2.5.48)$$

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 mth 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!) is $1/\langle c \rangle \pi^2 L^2 (\Delta/\langle c \rangle)^2$ 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).

Our final remark concerns the normalization [equation (4.2.5.39)]. Going from (4.2.5.39) to (4.2.5.45) 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

$$G(L) = N + \sum_\mu (N - |\mu|)(F^\mu + F^{+\mu})$$
$$= N \, \text{Re}\{(1 + |F|)/(1 - |F|)\} \quad (4.2.5.49)$$
$$- 2 \, \text{Re}\{|F|(1 - |F|^N)/(1 - |F|^2)\}.$$

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 (4.2.5.47a).

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 $Hg_{3-\delta}AsF_6$ (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; Weber *et al.*, 2000).

4.2.5.3.3. Correlations between almost collinear chains

In real cases there are quite 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: the shape and structure of the chains, varying binding forces, and 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 nonuniform cross sections of the chains. (3) Turns, twists and torsions of chains or parts of chains. This azimuthal type of disorder may be treated in a similar way 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 (such as rotational vibrations). (4) Tilting or bending of the chains in a uniform or nonuniform way ('conforming/nonconforming' disorder). Many of these types and a variety of combinations between them are found in polymer and liquid crystals, and are therefore treated 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

$$a_{mpq} = a_1 * \ldots * a_1 * a_2 * \ldots * a_2 * a_3 * \ldots * a_3. \quad (4.2.5.50)$$

(m-fold, p-fold, q-fold self-convolution of a_1, a_2, a_3, respectively.)

$$w(\mathbf{r}) = \delta(\mathbf{r}) \sum_m \sum_p \sum_q [a_{mpq}(\mathbf{r}) + a_{-mpq}(\mathbf{r})]. \quad (4.2.5.51)$$

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

$$G(\mathbf{H})\, G_\nu = \mathrm{Re}\{(1 + |F_\nu|)/(1 - |F_\nu|)\}. \quad (4.2.5.52)$$

If Gaussian functions are assumed, simple pictures are derived. For example

$$a_1(\mathbf{r} + \langle \mathbf{a} \rangle) = [1/(2\pi)^{3/2}][1/(\Delta_{11}\Delta_{12}\Delta_{13})]$$
$$\times \exp\left\{-\tfrac{1}{2}[(x^2/\Delta_{11}^2) + (y^2/\Delta_{12}^2) + (z^2/\Delta_{13}^2)]\right\}$$
$$(4.2.5.53)$$

describes the distribution of neighbours in the x direction (with a mean distance $\langle a \rangle$). Parameters Δ_{13}, Δ_{11} and Δ_{12} concern axial, 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 are given by projection on the xy plane. If the chainlike structure is neglected, the interference function

$$G_1(\mathbf{H}) = \exp\{-2\pi^2(\Delta_{11}^2 H^2 + \Delta_{12}^2 K^2 + \Delta_{13}^2 L^2)\} \quad (4.2.5.54)$$

describes a set of diffuse planes perpendicular to $\mathbf{a}^*$ with a mean distance of $1/\langle a \rangle$. These diffuse layers broaden along H with $m\Delta_{11}$ and decrease in intensity along K and L monotonically. There is an ellipsoid-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 (4.2.5.12)] 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 $l(1/c)$ [equation (4.2.5.15)].

Longitudinal disorder is given by $a_3(z)$ [equation (4.2.5.48), $\Delta_{33} = \Delta$] and leads to two intersecting sets of broadened diffuse layer systems.

Particular cases like pure axial distributions ($\Delta_{11}, \Delta_{12} \simeq 0$), pure tangential distributions (net distortions: $\Delta_{11}, \Delta_{13} \simeq 0$), uniform bending of chains or combinations of these effects are discussed in the monograph by Vainshtein (1966).

4.2.5.4. Defects, short-range ordering, clustering: three-dimensional disorder

4.2.5.4.1. General formulation (elastic diffuse scattering)

In this section general formulae for diffuse scattering will be derived that 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, 1996a,b), Dederichs (1973), Peisl (1975), Schwartz & Cohen (1977), Schmatz (1973, 1983), Bauer (1979), Kitaigorodsky (1984) and Schweika (1998). A series of interesting papers on local order is given by Young (1975) and also by Cowley et al. (1979). Expressions for polycrystalline samples 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.

The two 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. In the literature this problem is treated in terms of fluctuations of the distribution functions as will be discussed below (Section 4.2.5.4.6). The most convenient way to derive the distribution function correctly from experimental data is the use of low-angle scattering, which generally shows one or more clear maxima caused by partly periodic properties of the distribution function. For the deconvolution of the distribution function, achieved by Fourier transformation of the corrected diffuse low-angle scattering, the reader is referred to the relevant literature. However, deconvolutions are not unique and some reasonable assumptions are necessary for a final solution.

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 described in Section 4.2.4, important information on fractional occupations, interstitials and displacements of atoms (shown by unusual thermal parameters) may be derived. Unfortunately, all defects contribute to diffuse scattering; hence one has to start with the assumption that the disorder to be interpreted is predominant. Fractional occupancy of certain lattice sites by two or more kinds of atoms plays an important role in the literature, especially in metallic or ionic structures. Since vacancies may be treated as atoms with zero scattering amplitude, structures containing vacancies may be formally treated as multicomponent systems.

Since the solution of the diffraction problem should not be restricted to metallic systems with a simple (primitive) structure, we have to consider the structure of the unit cell – as given by the average structure – and the propagation of order according to the translation group separately. In simple metallic systems this difference is immaterial. It is well known that the thermodynamic problem of propagation of order in a three-dimensional crystal can hardly ever be solved analytically in a general way. Some solutions have been published with the aid of the Ising model using next-nearest-neighbour interactions. They are excellent for

an understanding of the principles of order–disorder phenomena, but they can rarely be applied quantitatively in practical problems. Hence, methods have been developed to derive the propagation of order from the diffraction pattern by means of Fourier transformation. This method has been described qualitatively in Section 4.2.3.1 and will be used here for a quantitative application. In a first approximation, the assumption of a small number of different configurations of the unit cell is made, represented by the corresponding number of structure factors. Displacements of atoms caused by the configurations of the neighbouring cells are excluded. This problem will be treated subsequently.

The finite number of structures of the unit cell in the disordered crystal is given by

$$F_\nu(\mathbf{r}) = \sum_j \sum_\mu \pi^\nu_{j\mu} f_\mu(\mathbf{r} - \mathbf{r}_j). \qquad (4.2.5.55)$$

Note that $F_\nu(\mathbf{r})$ is defined in real space and $\mathbf{r}_j$ gives the position vector of site j; $\pi^\nu_{j\mu} = 1$ if in the νth structure factor the site j is occupied by an atom of kind μ, and 0 elsewhere.

In order to apply the laws of Fourier transformation adequately, it is useful to introduce the distribution function of F_ν,

$$\pi_\nu(\mathbf{r}) = \sum_{\mathbf{n}} \pi_{\mathbf{n}\nu} \delta(\mathbf{r} - \mathbf{n}), \qquad (4.2.5.56)$$

with $\pi_{\mathbf{n}\nu} = 1$ if the cell $\mathbf{n} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ has the F_ν structure and $\pi_{\mathbf{n}\nu} = 0$ elsewhere.

In the definitions given above $\pi_{\mathbf{n}\nu}$ are numbers (scalars) assigned to the cell. Since all these are occupied we have

$$\sum_\nu \pi_\nu(\mathbf{r}) = l(\mathbf{r})$$

where $l(\mathbf{r})$ is the lattice in real space.

The structure of the disordered crystal is given by

$$\sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}). \qquad (4.2.5.57)$$

$\pi_\nu(\mathbf{r})$ consists of $\alpha_\nu N$ points, where $N = N_1 N_2 N_3$ is the total (large) number of unit cells and α_ν denotes the *a priori* probability (concentration) of the νth cell occupation.

It is now useful to introduce

$$\Delta \pi_\nu(\mathbf{r}) = \pi_\nu(\mathbf{r}) - \alpha_\nu l(\mathbf{r}) \qquad (4.2.5.58)$$

with

$$\sum_\nu \Delta \pi_\nu(\mathbf{r}) = \sum_\nu \pi_\nu(\mathbf{r}) - l(\mathbf{r}) \sum_\nu \alpha_\nu = l(\mathbf{r}) - l(\mathbf{r}) = 0.$$

Introducing (4.2.5.58) into (4.2.5.57) gives

$$\sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) = \sum_\nu \Delta \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) + l(\mathbf{r}) \sum_\nu \alpha_\nu F_\nu(\mathbf{r})$$

$$= \sum_\nu \Delta \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) + l(\mathbf{r})\langle F(\mathbf{r})\rangle. \qquad (4.2.5.59)$$

Similarly

$$\Delta F_\nu(\mathbf{r}) = F_\nu(\mathbf{r}) - \langle F(\mathbf{r})\rangle,$$

$$\qquad (4.2.5.60)$$

$$\sum_\nu \alpha_\nu \Delta F_\nu(\mathbf{r}) = \sum_\nu \alpha_\nu F_\nu(\mathbf{r}) - \sum_\nu \alpha_\nu \langle F(\mathbf{r})\rangle = 0.$$

Using (4.2.5.60) it follows from (4.2.5.58) that

$$\sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) = \sum_\nu \Delta \pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r})$$

$$+ \sum_\nu \Delta \pi_\nu(\mathbf{r}) * \langle F(\mathbf{r})\rangle + l(\mathbf{r}) * \langle F(\mathbf{r})\rangle$$

$$= \sum_\nu \Delta \pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) + l(\mathbf{r}) * \langle F(\mathbf{r})\rangle.$$

$$\qquad (4.2.5.61)$$

Comparison with (4.2.5.59) yields

$$\sum_\nu \Delta \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) = \sum_\nu \Delta \pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}).$$

Fourier transformation of (4.2.5.61) gives

$$\sum_\nu \Pi_\nu(\mathbf{H}) F_\nu(\mathbf{H}) = \sum_\nu \Delta \Pi_\nu(\mathbf{H}) \Delta F_\nu(\mathbf{H}) + L(\mathbf{H})\langle F(\mathbf{H})\rangle$$

with

$$\sum_\nu \Delta \Pi_\nu(\mathbf{H}) = 0, \quad \sum_\nu \Delta F_\nu(\mathbf{H}) = 0.$$

The expression for the scattered intensity is therefore

$$I(\mathbf{H}) = \left| \sum_\nu \Delta \Pi_\nu(\mathbf{H}) \Delta F_\nu(\mathbf{H}) \right|^2 + |L(\mathbf{H})\langle F(\mathbf{H})\rangle|^2$$

$$+ L(\mathbf{H}) \left\{ \langle F^+(\mathbf{H})\rangle \sum_\nu \Delta \Pi_\nu(\mathbf{H}) F_\nu(\mathbf{H}) \right.$$

$$\left. + \langle F^+(\mathbf{H})\rangle \sum_\nu \Delta \Pi^+_\nu(\mathbf{H}) F^+_\nu(\mathbf{H}) \right\}. \qquad (4.2.5.62)$$

Because of the multiplication by $L(\mathbf{H})$, the third term in (4.2.5.62) contributes to sharp reflections only. Since they are correctly given by the second term in (4.2.5.62), the third term vanishes. Hence the diffuse part is given by

$$I_D(\mathbf{H}) = \left| \sum_\nu \Delta \Pi_\nu(\mathbf{H}) \Delta F_\nu(\mathbf{H}) \right|^2. \qquad (4.2.5.63)$$

For a better understanding of the behaviour of diffuse scattering it is useful to return to real space:

$$i_D(\mathbf{r}) = \sum_\nu \Delta \pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) * \sum_{\nu'} \Delta \pi_{\nu'}(-\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})$$

$$= \sum_\nu \sum_{\nu'} \Delta \pi_\nu(\mathbf{r}) * \Delta \pi_{\nu'}(-\mathbf{r}) * \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})$$

$$\qquad (4.2.5.64)$$

and with (4.2.5.58):

$$i_D(\mathbf{r}) = \sum_\nu \sum_{\nu'} [\pi_\nu(\mathbf{r}) - \alpha_\nu l(\mathbf{r})] * [\pi_{\nu'}(-\mathbf{r}) - \alpha_{\nu'} l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}). \qquad (4.2.5.65)$$

Evaluation of this equation for a single term yields

$$[\pi_\nu(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - \alpha_\nu l(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r})$$

$$- \alpha_{\nu'} l(\mathbf{r}) * \pi_\nu(\mathbf{r}) + \alpha_\nu \alpha_{\nu'} l(\mathbf{r}) * l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(\mathbf{r}). \qquad (4.2.5.66)$$

Since $l(\mathbf{r})$ is a periodic function of points, all convolution products with $l(\mathbf{r})$ are also periodic. For the final evaluation the decrease of the number of overlapping points (maximum N) in the convolution products with increasing displacements of the functions is neglected (it is assumed that there is no particle-size effect). Then (4.2.5.66) becomes

$$[\pi_\nu(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - N\alpha_\nu\alpha_{\nu'}l(\mathbf{r}) - N\alpha_\nu\alpha_{\nu'}l(\mathbf{r}) + N\alpha_\nu\alpha_{\nu'}l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})$$

$$= [\pi_\nu(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - N\alpha_\nu\alpha_{\nu'}l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}). \tag{4.2.5.67}$$

If the first term in (4.2.5.67) is considered, the convolution of the two functions for a given distance $\mathbf{n}$ counts the number of coincidences of the function $\pi_\nu(\mathbf{r})$ with $\pi_{\nu'}(-\mathbf{r})$. This quantity is given by $Nl(\mathbf{r})\alpha_\nu p_{\nu\nu'}(-\mathbf{r})$, where $\alpha_\nu p_{\nu\nu'}(\mathbf{r})$ is the probability of a pair occupation in the $\mathbf{r}$ direction.

Equation (4.2.5.67) then reads

$$[Nl(\mathbf{r})\alpha_\nu p_{\nu\nu'}(-\mathbf{r}) - N\alpha_\nu\alpha_{\nu'}l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})$$

$$= N\alpha_\nu[p'_{\nu\nu'}(-\mathbf{r})l(\mathbf{r})]$$

$$* [\Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})] \tag{4.2.5.68}$$

with $p'_{\nu\nu'}(\mathbf{r}) = p_{\nu\nu'}(\mathbf{r}) - \alpha_{\nu'}$. The function $\alpha_\nu p'_{\nu\nu'}(\mathbf{r})$ is usually called the pair-correlation function $g \leftrightarrow \alpha_{\nu\nu'|\mathbf{nn}'}$ in physics.

The following relations hold:

$$\sum_\nu \alpha_\nu = 1; \tag{4.2.5.69a}$$

$$\sum_{\nu'} \alpha_\nu p_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu'}; \quad \sum_{\nu'} \alpha_\nu p'_{\nu\nu'}(\mathbf{r}) = 0 \tag{4.2.5.69b}$$

$$\sum_\nu \alpha_\nu p_{\nu\nu'}(\mathbf{r}) = \alpha_\nu; \quad \sum_\nu \alpha_\nu p'_{\nu\nu'}(\mathbf{r}) = 0 \tag{4.2.5.69c}$$

$$\alpha_\nu p_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu'} p_{\nu'\nu}(-\mathbf{r}). \tag{4.2.5.69d}$$

Functions normalized to unity are also in use. Obviously the following relation is valid: $p'_{\nu\nu'}(0) = \delta_{\nu\nu'} - \alpha_{\nu'}$.

Hence

$$\alpha_{\nu\nu'|\mathbf{nn}'} = \alpha_{\nu'}p'_{\nu\nu'}(\mathbf{r})/(\delta_{\nu\nu'} - \alpha_{\nu'})$$

is unity for $\mathbf{r} = 0$ $(\mathbf{n} = \mathbf{n}')$. This property is especially convenient in binary systems.

With (4.2.5.68), equation (4.2.5.64) becomes

$$i_D(\mathbf{r}) = N \sum_\nu \sum_{\nu'} [\alpha_\nu p'_{\nu\nu'}(-\mathbf{r})l(\mathbf{r})] * [\Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})] \tag{4.2.5.70}$$

and Fourier transformation yields

$$I_D(\mathbf{H}) = N \sum_\nu \sum_{\nu'} [\alpha_\nu P'_{\nu\nu'}(-\mathbf{H}) * L(\mathbf{H})] \Delta F_\nu(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}).$$

$$\tag{4.2.5.71}$$

It may be concluded from equations (4.2.5.69) that all functions $p'_{\nu\nu'}(\mathbf{r})$ may be expressed by $p'_{11}(\mathbf{r})$ in the case of two structure factors F_1, F_2. Then all $p'_{\nu\nu'}(\mathbf{r})$ are symmetric in $\mathbf{r}$; the same is true for the $P'_{\nu\nu'}(\mathbf{H})$. Consequently, the diffuse reflections described by (4.2.5.71) are all symmetric. The position of the diffuse peak depends strongly on the behaviour of $p'_{\nu\nu'}(\mathbf{r})$; in the case of cluster formation Bragg peaks and diffuse peaks coincide. Diffuse superstructure reflections are observed if the $p'_{\nu\nu'}(\mathbf{r})$ show some damped periodicities.

It should be emphasized that the condition $p'_{\nu\nu'}(\mathbf{r}) = p'_{\nu\nu'}(-\mathbf{r})$ may be violated for $\nu \neq \nu'$ if more than two cell occupations are involved. As shown below, the possibly asymmetric functions may be split into symmetric and antisymmetric parts. From equation (4.2.3.8) it follows that the Fourier transform of the antisymmetric part of $p'_{\nu\nu'}(\mathbf{r})$ is also antisymmetric. Hence, the convolution in the two terms in square brackets in (4.2.5.71) yields an antisymmetric contribution to each diffuse peak, generated by the convolution with the reciprocal lattice $L(\mathbf{h})$.

Obviously, equation (4.2.5.71) may also be applied to primitive lattices occupied by two or more kinds of atoms. Then the structure factors F_ν are merely replaced by the atomic scattering factors f_ν and the α_ν are equivalent to the concentrations of atoms c_ν. In terms of the $\alpha_{\nu\nu'|\mathbf{nn}'}$ (Warren short-range-order parameters) equation (4.2.5.71) reads

$$I_D(\mathbf{H}) = N(\overline{f^2} - \bar{f}^2) \sum_\mathbf{n} \sum_{\mathbf{n}'} \alpha_{\nu\nu'|\mathbf{nn}'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}.$$

$$\tag{4.2.5.71a}$$

In the simplest case of a binary system A, B,

$$\alpha_{\mathbf{nn}'} = (1 - p_{AB|\mathbf{nn}'})/c_B = (1 - p_{BA|\mathbf{nn}'})/c_A;$$

$$c_A p_{AB} = c_B p_{BA}; \quad p_{AA} = 1 - p_{AB};$$

$$I_D(\mathbf{H}) = Nc_A c_B (f_A - f_B)^2 \sum_\mathbf{n} \sum_{\mathbf{n}'} \alpha_{\mathbf{nn}'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}.$$

$$\tag{4.2.5.71b}$$

[The exponential in (4.2.5.71b) may even be replaced by a cosine term owing to the centrosymmetry of this particular case.]

It should be mentioned that the formulations of the problem in terms of pair probabilities, pair-correlation functions, short-range-order parameters or concentration waves (Krivoglaz, 1969, 1996a,b) are equivalent. The Patterson function may also be used when using continuous electron (or nuclear) density functions where site occupancies are implied (Cowley, 1981).

4.2.5.4.2. Random distribution of defects

As shown above in the case of random distributions, all $p'_{\nu\nu'}(\mathbf{r})$ are zero except for $\mathbf{r} = 0$. Consequently, $p'_{\nu\nu'}(\mathbf{r})l(\mathbf{r})$ may be replaced by

$$\alpha_\nu p'_{\nu\nu'}(\mathbf{r}) = \alpha_\nu \delta_{\nu\nu'} - \alpha_\nu\alpha_{\nu'}. \tag{4.2.5.72}$$

According to (4.2.5.59) and (4.2.5.61), the diffuse scattering can be given by the Fourier transformation of

$$\sum_\nu \sum_{\nu'} \Delta\pi_\nu(\mathbf{r}) * \Delta\pi_{\nu'}(-\mathbf{r}) * F_\nu(\mathbf{r}) * F_\nu(-\mathbf{r})$$

$$= \sum_\nu \sum_{\nu'} p'_{\nu\nu'}(\mathbf{r}) * F_\nu(\mathbf{r}) * F_{\nu'}(-\mathbf{r})$$

or with (4.2.5.72)

$$i_D(\mathbf{r}) = N \sum_\nu \sum_{\nu'} [\alpha_\nu \delta_{\nu\nu'} - \alpha_\nu\alpha_{\nu'}] * F_\nu(\mathbf{r}) * F_{\nu'}(-\mathbf{r}).$$

Fourier transformation gives

$$I_D(\mathbf{H}) = N \left\{ \sum_\nu \alpha_\nu |F_\nu(\mathbf{H})|^2 - \sum_\nu \alpha_\nu F_\nu(\mathbf{H}) \sum_{\nu'} \alpha_{\nu'} F_{\nu'}^+(\mathbf{H}) \right\}$$

$$= N\{\langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2\}. \tag{4.2.5.73}$$

This is the most general form of any diffuse scattering by systems ordered randomly ('Laue scattering'). Occasionally it is called 'incoherent scattering' (see Section 4.2.2).

4.2.5.4.3. Short-range order in multicomponent systems

The diffuse scattering of a disordered binary system without displacements of the atoms has already been discussed in Section 4.2.5.4.1. It could be shown that all distribution functions $p'_{\nu\nu'}(\mathbf{r})$ are mutually dependent and may be replaced by a single function [cf. (4.2.5.69)]. In that case $p'_{\nu\nu'}(\mathbf{r}) = p'_{\nu\nu'}(-\mathbf{r})$ was valid for all. This condition, however, may be violated in multicomponent systems. If a tendency towards an $F_1 F_2 F_3$ order in a ternary system is assumed, for example, $p_{12}(\mathbf{r})$ is apparently different from $p_{12}(-\mathbf{r})$. In this particular case it is useful to introduce

$$\langle p'_{vv'}(\mathbf{r}) \rangle = \tfrac{1}{2}[p'_{vv'}(\mathbf{r}) + p'_{vv'}(-\mathbf{r})],$$

$$\Delta p'_{vv'}(\mathbf{r}) = \tfrac{1}{2}[p'_{vv'}(\mathbf{r}) - p'_{vv'}(-\mathbf{r})]$$

and their Fourier transforms $\langle P'_{vv'}(\mathbf{H}) \rangle$, $\Delta P'_{vv'}(\mathbf{H})$, respectively.

The asymmetric correlation functions are therefore expressed by

$$p'_{vv'}(\mathbf{r}) = \langle p'_{vv'}(\mathbf{r}) \rangle + \Delta p'_{vv'}(\mathbf{r});$$

$$p'_{vv'}(-\mathbf{r}) = \langle p'_{vv'}(\mathbf{r}) \rangle - \Delta p'_{vv'}(\mathbf{r});$$

$$\Delta p'_{vv}(\mathbf{r}) = 0.$$

Consequently, $i_D(\mathbf{r})$ (4.2.5.70) and $I_D(\mathbf{H})$ (4.2.5.71) may be separated according to the symmetric and antisymmetric contributions. The final result is

$$I_D(\mathbf{H}) = N\Big\{ \sum_v \alpha_v [P'_{vv}(\mathbf{H}) * L(\mathbf{H})]|F_v(\mathbf{H})|^2$$

$$+ \sum_{v>v'} \alpha_v[\langle P'_{vv'}(\mathbf{H}) \rangle * L(\mathbf{H})]$$

$$\times [\Delta F_v(\mathbf{H})\Delta F_{v'}^+(\mathbf{H}) + \Delta F_v^+(\mathbf{H})\Delta F_{v'}(\mathbf{H})]$$

$$+ \sum_{v>v'} \alpha_v[\Delta P'_{vv'}(-\mathbf{H}) * L(\mathbf{H})]$$

$$\times [\Delta F_v(\mathbf{H})\Delta F_{v'}^+(\mathbf{H}) - \Delta F_v^+(\mathbf{H})\Delta F_{v'}(\mathbf{H})]\Big\}. \qquad (4.2.5.74)$$

Obviously, antisymmetric contributions to line profiles will only occur if structure factors of acentric cell occupations are involved. This important property may be used to draw conclusions with respect to the structure factors involved in the statistics. It should be mentioned here that the Fourier transform of the antisymmetric function $\Delta p'_{vv'}(\mathbf{r})$ is imaginary and antisymmetric. Since the last term in (4.2.5.74) is also imaginary, the product of the two factors in brackets is real, as it should be.

4.2.5.4.4. Displacements: general remarks

Even small displacements may have an important influence on the problem of propagation of order. Therefore, no structural treatments other than the introduction of formal parameters (*e.g.* Landau's theory) have been published in the literature. Most of the examples with really reliable results refer to binary systems and even these represent very crude approximations, as will be shown below. For this reason we shall restrict ourselves here to binary systems, although general formulae where displacements are included may be developed in a formal way.

Two kinds of atoms, $f_1(\mathbf{r})$ and $f_2(\mathbf{r})$, are considered. Obviously, the position of any given atom is determined by its surroundings. Their extension depends on the forces acting on the atom under consideration. These may be very weak in the case of metals (repulsive forces, the 'size effect'), but long-range effects have to be expected in ionic crystals. For the development of formulae authors have assumed that small displacements $\Delta\mathbf{r}_{vv'}$ may be assigned to the pair-correlation functions $p'_{vv'}(\mathbf{r})$ by adding a phase factor $\exp\{2\pi i\mathbf{H} \cdot \Delta\mathbf{r}_{vv'}\}$, which is then expanded in the usual way:

$$\exp\{2\pi i\mathbf{H} \cdot \Delta\mathbf{r}_{vv'}\} \simeq 1 + 2\pi i\mathbf{H} \cdot \Delta\mathbf{r}_{vv'} - 2[\pi\mathbf{H} \cdot \Delta\mathbf{r}_{vv'}]^2. \qquad (4.2.5.75)$$

The displacements and correlation probabilities are separable if the change of atomic scattering factors in the angular range considered may be neglected. The formulae in use are given in the next section. As shown below, this method represents nothing other than a kind of average over certain sets of displacements. For this purpose, the correct solution of the problem has to be discussed. In the simplest model the displacements are due to
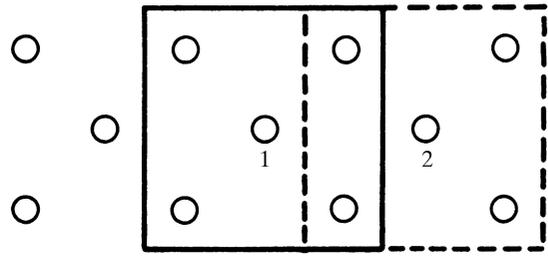

Fig. 4.2.5.1. Construction of the correlation function in the method of overlapping clusters.

next-nearest neighbours only. It is further assumed that the configurations rather than the displacements determine the position of the central atom and a general displacement of the centre of the first shell does not occur (there is no influence of a strain field). Obviously, the formal correlation function of pairs is not independent of displacements. This difficulty may be avoided either by assuming that the pair-correlation function has already been separated from the diffraction data, or by theoretical calculations of the correlation function (the mean-field method) (Moss, 1966; de Fontaine, 1972, 1973). The validity of this procedure is subject to the condition that the displacements have no influence on the correlation functions themselves.

The observation of a periodic average structure justifies the definition of a periodic array of origins, which normally depends on the degree of order. Local deviations of origins may be due to fluctuations in the degree of order and due to the surrounding atoms of a given site. For example, a b.c.c. lattice with eight nearest neighbours is considered. It is assumed that only these have an influence on the position of the central atom owing to different forces of the various configurations. With two kinds of atoms, there are $2^9 = 512$ possible configurations of the cluster (the central atom plus 8 neighbours). Symmetry considerations reduce this number to 28. Each is characterized by a displacement vector. Hence their *a priori* probabilities and the propagation of 28 different configurations have to be determined. Since each atom has to be considered as the centre once, this problem may be treated by introducing 28 different atomic scattering factors as determined from the displacements: $f_v(\mathbf{r}) \exp\{2\pi i\mathbf{H} \cdot \Delta\mathbf{r}_{vv'}\}$. The diffraction problem has to be solved with the aid of the propagation of order of overlapping clusters. This is demonstrated by a two-dimensional model with four nearest neighbours (Fig. 4.2.5.1). Here the central and the neighbouring cluster (full and broken lines) overlap with two sites in, for example, the x direction. Hence only neighbouring clusters with the same overlapping pairs are admitted. These restrictions introduce severe difficulties into the problem of propagation of cluster ordering which determines the displacement field. Since it was assumed that the problem of pair correlation had been solved, the cluster probabilities may be derived by calculating

$$\alpha_v l(\mathbf{r}) \prod_{\mathbf{n}\neq 0} p'_{vv'}(\mathbf{r} - \mathbf{n}). \qquad (4.2.5.76)$$

Only next-nearest neighbours have to be included in the product. This must be performed for the central cluster ($\mathbf{r} = 0$) *and* for the reference cluster at $\mathbf{r} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$, because all are characterized by different displacements. So far, possible displacement of the centre has not been considered; this may also be influenced by the problem of propagation of cluster ordering. These displacement factors should best be attached to the function describing the propagation of order which determines, in principle, the local fluctuations of the lattice constants (the strain field *etc.*). This may be understood by considering a binary system with a high degree of order but with atoms of different size. Large fluctuations of lattice constants are involved in the case of

exsolution of the two components because of their different lattice parameters, but they become small in the case of super-structure formation where a description in terms of antiphase domains is reasonable (with equal lattice constants). This example demonstrates the mutual dependence of ordering and displacements, which is mostly neglected in the literature.

The method of assigning phase factors to the pair-correlation function is now discussed. Pair-correlation functions average over all pairs of clusters having the same central atom. An analogous argument holds for displacements: using pair correlations for the determination of displacements means nothing other than aver-aging over all displacements caused by various clusters around the same central atom. There remains the general strain field due to the propagation of order, whereas actual displacements of atoms are realized by fluctuations of configurations. Since large fluctuations of this type occur in highly disordered crystals, the displacements become increasingly irrelevant. Hence the formal addition of displacement factors to the pair-correlation function does not yield much information about the structural basis of the displacements. This situation corresponds exactly to the rela-tionship between a Patterson function and a real structure: the structure has to be found which explains the quite complicated function completely, and its unique solution is rather difficult. We state these points here because in most publications related to this subject these considerations are not taken into account adequately. Displacements usually give rise to antisymmetric contributions to diffuse reflections. As pointed out above, the influence of displacements has to be considered as phase factors which may be attached either to the structure factors or to the Fourier transforms $P'_{vv'}(\mathbf{H})$ of the correlation functions in equa-tion (4.2.5.71). As has been mentioned in the context of equation (4.2.5.74), antisymmetric contributions will occur if acentric structure factors are involved. Apparently, this condition is met by the phase factors of displacements. In consequence, antisym-metric contributions to diffuse reflections may also originate from the displacements. This fact can also be demonstrated if the assignment of phase factors to the Fourier transforms of the correlation functions is advantageous. In this case, equations (4.2.5.69a,b) are no longer valid because the functions $p'_{vv'}(\mathbf{r})$ become complex. The most important change is the relation corresponding to (4.2.5.69):

$$\alpha_v p'_{vv'}(\mathbf{r}) = \alpha_{v'} p'^{+}_{vv'}(-\mathbf{r}) \leftrightarrow \alpha_v P'_{vv'}(\mathbf{H}) = \alpha_{v'} P'^{+}_{v'}(\mathbf{H}). \quad (4.2.5.77)$$

Strictly speaking, we have to replace the *a priori* probabilities α_v by complex numbers $\alpha_v \exp\{2\pi i \Delta \mathbf{r}_v \cdot \mathbf{H}\}$, which are determined by the position of the central atom. In this way, all correlations between displacements may be included with the aid of the clusters mentioned above. To a rough approximation it may be assumed that no correlations of this kind exist. In this case, the complex factors may be assigned to the structure factors involved. Averaging over all displacements results in diffraction effects that are very similar to a static Debye–Waller factor for all structure factors. On the other hand, the thermal motion of atoms is treated similarly. Obviously, both factors affect the sharp Bragg peaks. Hence this factor can easily be determined by the average structure, which contains a Debye–Waller factor including static and thermal displacements. It should be pointed out, however, that these static displacements cause elastic diffuse scattering, which cannot be separated by inelastic neutron-scattering tech-niques.

A careful study of the real and imaginary parts of

$$\langle p'_{vv'}(\mathbf{r}) \rangle = \langle p'_{vv'}(\mathbf{r}) \rangle_{R} + \langle p'_{vv'}(\mathbf{r}) \rangle_{I}$$

and

$$\Delta p'_{vv'}(\mathbf{r}) = \Delta p'_{vv'}(\mathbf{r})_{R} + \Delta p'_{vv'}(\mathbf{r})_{I}$$

and their Fourier transforms results, after some calculations, in the following relation for diffuse scattering:

$$I_{D} \simeq N \sum_v \alpha_v |\Delta F_v(\mathbf{H})|^2 \{[\langle P'_{vv}(\mathbf{H})\rangle - \Delta P'_{vv}(\mathbf{H})] * L(\mathbf{H})\}$$
$$+ 2N \sum_{v>v'} \alpha_v (\Delta F_v \Delta F_{v'}^{+})_{R}$$
$$\times \{[\langle P'_{vv'}(\mathbf{H})\rangle_{R} - \Delta P'_{vv'}(\mathbf{H})_{I}] * L(\mathbf{H})\}$$
$$+ 2N \sum_{v>v'} \alpha_v (\Delta F_v \Delta F_{v'}^{+})_{I}$$
$$\times \{[\langle P'_{vv'}(\mathbf{H})\rangle_{I} - \Delta P'_{vv'}(\mathbf{H})_{R}] * L(\mathbf{H})\}. \quad (4.2.5.78)$$

It should be noted that all contributions are real. This follows from the properties of Fourier transforms of symmetric and antisymmetric functions. All $\Delta P_{vv'}(\mathbf{H})$ are antisymmetric; hence they generate antisymmetric contributions to the line profiles. In contrast to equation (4.2.5.75), the real *and* the imaginary parts of the structure factors contribute to the asymmetry of the line profiles.

4.2.5.4.5. Distortions in binary systems

In substitutional binary systems (with a primitive cell with only one sublattice) the Borie–Sparks method is widely used (Sparks & Borie, 1966; Borie & Sparks, 1971). The method is formulated in the short-range-order-parameter formalism. The diffuse scat-tering may be separated into two parts (*a*) owing to short-range order and (*b*) owing to static displacements.

Corresponding to the expansion (4.2.5.75), $I_{D} = I_{sro} + I_2 + I_3$, where I_{sro} is given by equation (4.2.5.71*b*) and the correction terms I_2 and I_3 relate to the linear and the quadratic term in (4.2.5.75). The intensity expression will be split into terms of A–A, A–B, ... pairs. More explicitly $\Delta \mathbf{r}_{vv'} = \mathbf{u}_{nv} - \mathbf{u}_{n'v'}$ and with the following abbreviations

$$\delta_{nn'|AA} = \mathbf{u}_{n|A} - \mathbf{u}_{n'|A} = x_{nn'|AA}\mathbf{a} + y_{nn'|AA}\mathbf{b} + z_{nn'|AA}\mathbf{c}$$
$$\delta_{nn'|AB} = \mathbf{u}_{n|A} - \mathbf{u}_{n'|B} = \ldots$$
$$F_{nn'|AA} = [f_A^2/(f_A - f_B)^2][(c_A/c_B) + \alpha_{nn'}]$$
$$F_{nn'|BB} = [f_B^2/(f_A - f_B)^2][(c_B/c_A) + \alpha_{nn'}]$$
$$F_{nn'|AB} = [2f_A f_B/(f_A - f_B)^2](1 - \alpha_{nn'}) = F_{nn'|BA}$$

one finds (where the short-hand notation is self-explanatory):

$$I_2 = 2\pi i c_A c_B (f_A - f_B)^2 \sum_{n}\sum_{n'} \{H[F_{nn'|AA}\langle x_{nn'|AA}\rangle$$
$$+ F_{nn'|BB}\langle x_{nn'|BB}\rangle + F_{nn'|AB}\langle x_{nn'|AB}\rangle] + K[\text{'}y\text{'}]$$
$$+ L[\text{'}z\text{'}]\} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}, \quad (4.2.5.79)$$

$$I_3 = c_A c_B (f_A - f_B)^2 (-2\pi)^2 \sum_{n}\sum_{n'} \{H^2[F_{nn'}\langle x^2_{nn'|AA}\rangle$$
$$+ F_{nn'|BB}\langle x^2_{nn'|BB}\rangle + F_{nn'|AB}\langle x^2_{nn'|AB}\rangle]$$
$$+ K^2[\text{'}y^2\text{'}] + L^2[\text{'}z^2\text{'}]$$
$$+ HK[F_{nn'|AA}\langle (xy)_{nn'|AA}\rangle + F_{nn'|BB}\langle (xy)_{nn'|BB}\rangle$$
$$+ F_{nn'|AB}\langle (xy)_{nn'|AB}\rangle]$$
$$+ KL[\text{'}yz\text{'}] + LH[\text{'}zx\text{'}]\}$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}. \quad (4.2.5.80)$$

With further abbreviations

$$\gamma_{\mathbf{nn'}|x} = 2\pi(F_{\mathbf{nn'}|AA}\langle x_{\mathbf{nn'}|AA}\rangle + F_{\mathbf{nn'}|BB}\langle x_{\mathbf{nn'}|BB}\rangle$$
$$+ F_{\mathbf{nn'}|AB}\langle x_{\mathbf{nn'}|AB}\rangle)$$

$$\gamma_{\mathbf{nn'}|y} = \ldots$$

$$\gamma_{\mathbf{nn'}|z} = \ldots$$

$$\delta_{\mathbf{nn'}|x} = (-2\pi^2)(F_{\mathbf{nn'}|AA}\langle x^2_{\mathbf{nn'}|AA}\rangle + F_{\mathbf{nn'}|BB}\langle x^2_{\mathbf{nn'}|BB}\rangle$$
$$+ F_{\mathbf{nn'}|AB}\langle x^2_{\mathbf{nn'}|AB}\rangle)$$

$$\delta_{\mathbf{nn'}|y} = \ldots$$

$$\delta_{\mathbf{nn'}|z} = \ldots$$

$$\varepsilon_{\mathbf{nn'}|xy} = (-4\pi^2)(F_{\mathbf{nn'}|AA}\langle(xy)_{\mathbf{nn'}|AA}\rangle + F_{\mathbf{nn'}|BB}\langle(xy)_{\mathbf{nn'}|BB}\rangle$$
$$+ F_{\mathbf{nn'}|AB}\langle(xy)_{\mathbf{nn'}|AB}\rangle)$$

$$\varepsilon_{\mathbf{nn'}|yz} = \ldots$$

$$\varepsilon_{\mathbf{nn'}|zx} = \ldots$$

$$I_2 = c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n'}} i(\gamma_{\mathbf{nn'}|x} + \gamma_{\mathbf{nn'}|y} + \gamma_{\mathbf{nn'}|z})$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n'})\}$$

$$I_3 = c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n'}} (\delta_{\mathbf{nn'}|x} H^2 + \delta_{\mathbf{nn'}|y} K^2$$
$$+ \delta_{\mathbf{nn'}|z} L^2 + \varepsilon_{\mathbf{nn'}|xy} HK + \varepsilon_{\mathbf{nn'}|yz} KL$$
$$+ \varepsilon_{\mathbf{nn'}|zx} LH) \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n'})\}.$$

If the $F_{\mathbf{nn'}|AA}, \ldots$ are independent of $|\mathbf{H}|$ in a range of measurement which is better fulfilled with neutrons than with X-rays (see below), γ, δ, ε are the coefficients of the Fourier series:

$$Q_x = \sum_{\mathbf{n}} \sum_{\mathbf{n'}} i\gamma_{\mathbf{nn'}|x} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n'})\};$$

$$Q_y = \ldots; \qquad Q_z = \ldots;$$

$$R_x = \sum_{\mathbf{n}} \sum_{\mathbf{n'}} \delta_{\mathbf{nn'}|x} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n'})\};$$

$$R_y = \ldots; \qquad R_z = \ldots;$$

$$S_{xy} = \sum_{\mathbf{n}} \sum_{\mathbf{n'}} \varepsilon_{\mathbf{nn'}|xy} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n'})\};$$

$$S_{yz} = \ldots; \qquad S_{zx} = \ldots.$$

The functions Q, R, S are then periodic in reciprocal space.

The double sums over $\mathbf{n}$, $\mathbf{n'}$ may be replaced by $N\sum_{m,n,p}$ where m, n, p are the coordinates of the interatomic vectors $(\mathbf{n} - \mathbf{n'})$ and I_2 becomes

$$I_2 = -N c_A c_B (f_A - f_B)^2 \sum_m \sum_n \sum_p (H\gamma_{lmn|x} + \ldots + \ldots)$$
$$\times \sin 2\pi(Hm + Kn + Lp). \qquad (4.2.5.81)$$

The intensity is therefore modulated sinusoidally and increases with scattering angle. The modulation gives rise to an asymmetry in the intensity around a Bragg peak. Similar considerations for I_3 reveal an intensity contribution h_i^2 times a sum over cosine terms which is symmetric around the Bragg peaks ($i = 1, 2, 3$ with $h_1 = h$, $h_2 = k$, $h_3 = l$). This term shows a quite analogous influence of local static displacements and thermal movements: an increase of diffuse intensity around the Bragg peaks and a reduction of Bragg intensities, which is not discussed here. The second contribution I_2 has no analogue owing to the nonvanishing average displacement. The various diffuse intensity contributions may be separated by symmetry considerations. Once they are separated, the single coefficients may be determined by Fourier inversion. Owing to the symmetry constraints, there are relations between the displacements $\langle x \ldots \rangle$ and, in turn, between the γ and Q components. The same is true for the δ, ε and R, S components. Consequently, there are symmetry conditions for the individual contributions of the diffuse intensity which may be used to distinguish them. In general, the total diffuse intensity may be

split into only a few independent terms. The single components of Q, R, S may be expressed separately by combinations of diffuse intensities that are measured in definite selected volumes in reciprocal space. Only a minimum volume must be explored in order to reveal the behaviour over the whole reciprocal space. This minimum repeat volume is different for the single components: I_{sro}, Q, R, S or combinations of them.

The Borie–Sparks method has been applied very frequently to binary and even ternary systems; some improvements have been communicated by Bardhan & Cohen (1976). The diffuse scattering of the historically important metallic compound Cu_3Au was been studied by Cowley (1950a,b) and the pair-correlation parameters could be determined. The typical fourfold splitting was found by Moss (1966) and explained in terms of atomic displacements. The same splitting has been found for many similar compounds such as Cu_3Pd (Ohshima et al., 1976), Au_3Cu (Bessière et al., 1983) and $Ag_{1-x}Mg_x$ ($x = 0.15$–0.20) (Ohshima & Harada, 1986). Similar pair-correlation functions have been determined. In order to demonstrate the disorder parameters in terms of structural models, computer programs were used (e.g. Gehlen & Cohen, 1965). A similar microdomain model was proposed by Hashimoto (1974, 1981, 1983, 1987). According to approximations made in the theoretical derivation, the evaluation of diffuse scattering is generally restricted to an area in reciprocal space where the influence of displacements is of the same order of magnitude as that of the pair-correlation function. The agreement between calculation and measurement is fairly good, but it should be remembered that the amount and quality of the experimental information used is low. No residual factors are so far available; these would give an idea of the reliability of the results.

The more general case of a multicomponent system with several atoms per lattice point was treated similarly by Hayakawa & Cohen (1975). Sources of error in the determination of the short-range-order coefficients are discussed by Gragg et al. (1973). In general, the assumption of constant $F_{\mathbf{nn'}|AA}, \ldots$ produces an incomplete separation of the order- and displacement-dependent components of diffuse scattering. By an alternative method, by separation of the form factors from the Q, R, S functions and solving a large array of linear relationships by least-squares methods, the accuracy of the separation of the various contributions is improved (Tibbals, 1975; Georgopoulos & Cohen, 1977; Wu et al., 1983). The method does not work for neutron diffraction. The case of planar short-range order with corresponding diffuse intensity along rods in reciprocal space may also be treated along the Borie & Sparks method (Ohshima & Moss, 1983).

Multiwavelength methods taking advantage of the variation of the structure factor near an absorption edge (anomalous dispersion) are discussed by Cenedese et al. (1984). The same authors show that in some cases the neutron method allows contrast variation by using samples with different isotope substitution.

In general, X-ray and neutron methods are complementary. The neutron method is helpful in the cases of hydrides, oxides, carbides, Al–Mg distributions etc. In favourable cases it is possible to suppress (nuclear) Bragg scattering of neutrons when isotopes are used so that $\sum_v c_v f_v = 0$ for all equivalent positions. Another way to separate Bragg peaks is to record the diffuse intensity, if possible, at low $|\mathbf{H}|$ values. This can be achieved either by measurement at low angles or by using long wavelengths. For reasons of absorption the latter are the domain of neutron scattering. Bragg scattering is ruled out by exceeding the Bragg cut-off. In this way, 'diffuse' background owing to multiple Bragg scattering is avoided. Other diffuse-scattering contributions that increase with the $|\mathbf{H}|$ value [thermal diffuse scattering (TDS) and scattering due to long-range static displacements] are thus also minimized. Neutrons are preferable in cases where X-rays show only a small scattering contrast: (heavy) metal lattice distortions,

Huang scattering and so on should be measured at large values of $|\mathbf{H}|$. TDS can be separated by purely elastic neutron methods within the limits given by the energy resolution of an instrument. This technique is of particular importance at higher temperatures where TDS becomes remarkably strong. Neutron scattering is a good tool only in cases where (isotope/spin-) incoherent scattering is not too strong. In the case of magnetic materials, confusion with paramagnetic diffuse scattering could occur. This is also important when electrons are trapped by defects which themselves act as paramagnetic centres.

4.2.5.4.6. Comparison with the cluster method

In the general formula for diffuse scattering from random distributions equation (4.2.3.23a,b) may be used. Here $|\langle F(\mathbf{H})\rangle|^2$ describes the sharp Bragg maxima, while $|\Delta F(\mathbf{H})|^2 = \langle|F(\mathbf{H})|^2\rangle - |\langle F(\mathbf{H})\rangle|^2$ represents the contribution to diffuse scattering. Correlation effects can also be taken into account by using clusters of sufficient size if their distribution may be considered as random to a good approximation. The diffuse intensity is then given by

$$I_D(\mathbf{H}) = \sum_\nu p_\nu |F_\nu(\mathbf{H})|^2 - \left|\sum_\nu p_\nu F_\nu(\mathbf{H})\right|^2, \qquad (4.2.5.82)$$

where $F_\nu(\mathbf{H})$ represents the difference structure factor of the νth cluster and p_ν is its a priori probability. Obviously equation (4.2.5.82) is of some use in only two cases. (1) The number of clusters is sufficiently small and meets the condition of a nearly random distribution. In principle, the structure may then be determined with the aid of refinement methods according to equation (4.2.5.82). Since the second term is assumed to be known from the average structure, the first term may be evaluated by introducing as many parameters as there are clusters involved. A special computer program for incoherent refinement has to be used if more than one representative cluster has to be introduced. In the case of more clusters constraints are necessary. (2) The number of clusters with similar structures is not limited. It may be assumed that their size distribution may be expressed by fluctuations using well known analytical expressions, e.g. Gaussians or Lorentzians. The distribution is still assumed to be random.

An early application of the cluster method was the calculation of the diffuse intensity of Guinier–Preston zones, where a single cluster is sufficient (see, e.g., Gerold, 1954; Bubeck & Gerold, 1984). Unfortunately, no refinements of cluster structures have so far been published. The full theory of the cluster method was outlined by Jagodzinski & Haefner (1967).

A different approach to analysing extended defects in crystals is simply to construct analytically disorder models that include chemical substitution and atomic displacements around an atomic defect as consequence of the surrounding local distortions. This method works if the number of 'shells' of the first, second, ... neighbours is limited and if short- or long-range correlations between different clusters are neglected. After subtracting the underlying average structure and the calculation of the Fourier transform of the difference structure ΔF, the intensities can be fitted to the observed diffuse diffraction pattern and the parameters of the disorder model (occupancies and displacements) can be determined. For examples of this method see Neder et al. (1990) or Kaiser-Bischoff et al. (2005). Short-range correlations may simply be included by approximating the distribution function by summing over a finite number of defects (clusters) (Goff et al., 1999).

4.2.5.5. Molecular crystals: orientational disorder

Molecular crystals show in principle disorder phenomena similar to those discussed in previous sections (i.e. substitutional or displacement disorder). Here we have to replace the structure factors $F_\nu(\mathbf{H})$ used in the previous sections by the molecular structure factors in their various orientations. These are usually rapidly varying functions in reciprocal space which may obscure the disorder diffuse scattering. Disorder in molecular crystals is treated by Guinier (1963), Amorós & Amorós (1968), Flack (1970), Epstein et al. (1982), Welberry & Siripitayananon (1986, 1987) and others.

A particular type of disorder is very common in molecular and also in ionic crystals: the centres of masses of molecules or ionic complexes form a perfect 3D lattice but their orientations are disordered. Sometimes these solids are called plastic crystals. In comparison, the liquid-crystalline state is characterized by an orientational order in the absence of long-range positional order of the centres of the molecules. A clear-cut separation is not possible in cases where translational symmetry occurs in a low dimension, e.g. in sheets or parallel to a few directions in crystal space. For discussion of these mesophases see Chapter 4.4.

An orientationally disordered crystal may be pictured by freezing molecules in different sites in one of several orientations. Local correlations between neighbouring molecules and correlations between position and orientation may be responsible for orientational short-range order. Thermal reorientations of the molecules are often related to an orientationally disordered crystal. Thermal vibrations of the centres of masses of the molecules, librational or rotational excitations around one or more axes of the molecules, jumps between different equilibrium positions or diffusion-like phenomena are responsible for diffuse scattering of dynamic origin. As mentioned above, the complexity of molecular structures and the associated large number of thermal modes complicate a separation from static disorder effects.

In general, high Debye–Waller factors are typical for scattering by orientationally disordered crystals. Consequently only a few Bragg reflections are observable. A large amount of structural information is stored in the diffuse background. It has to be analysed with respect to an incoherent and coherent part, elastic, quasielastic or inelastic nature, short-range correlations within one and the same molecule and between orientations of different molecules, and cross correlations between positional and orientational disorder scattering. Combined X-ray and neutron methods are therefore highly recommended.

(1) General expressions

On the assumption of a well ordered 3D lattice, a general expression for the scattering by an orientationally disordered crystal with one molecule per unit cell may be given. This is a very common situation. Moreover, orientational disorder is frequently related to molecules with an overall 'globular' shape and consequently to crystals of high (in particular, averaged) spherical symmetry. In the following, the relevant equations are given for this situation; these are discussed in some detail in a review article by Fouret (1979). The orientation of a molecule is characterized by a parameter ω_l, e.g. the set of Eulerian angles of three molecular axes with respect to the crystal axes: $l = 1, \ldots, D$ (for D possible different orientations). The equilibrium position of the centre of mass of a molecule in orientation ω_l is given by $\mathbf{r}_l$, the equilibrium position of atom k within a molecule l in orientation ω_l by $\mathbf{r}_{lk}$ and a displacement from this equilibrium position by $\mathbf{u}_{lk}$. Averaging over a long time, i.e. supposing that the lifetime of a discrete configuration is long compared with the period of atomic vibrations, the observed intensity may be deduced from the intensity expression corresponding to a given configuration at time t:

$$I(\mathbf{H}, t) = \sum_l \sum_{l'} F_l(\mathbf{H}, t) F_{l'}^+(\mathbf{H}, t)$$
$$\times \exp\{2\pi i\mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}, \qquad (4.2.5.83)$$

$$F_l(\mathbf{H}, t) = \sum_k f_k \exp\{2\pi i\mathbf{H} \cdot (\mathbf{r}_{lk} + \mathbf{u}_{lk})\}. \qquad (4.2.5.84)$$

Averaging procedures must be carried out with respect to the thermal vibrations (denoted by an overbar) and over all configurations (symbol $\langle \rangle$). The centre-of-mass translational vibrations and librations of the molecules are most important in this context. (Internal vibrations of the molecules are assumed to be decoupled and remain unconsidered.)

$$I(\mathbf{H}, t) = \sum_l \sum_{l'} \langle \overline{F_l(\mathbf{H}, t)F_{l'}^+(\mathbf{H}, t)} \rangle$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}. \qquad (4.2.5.83a)$$

Thermal averaging gives (*cf.* Chapter 4.1)

$$I = \sum_l \sum_{l'} \overline{F_l F_{l'}^+} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\},$$
$$\overline{F_l F_{l'}^+} = \sum_k \sum_{k'} f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}$$
$$\times \overline{\exp\{2\pi i \mathbf{H} \cdot (\mathbf{u}_{lk} - \mathbf{u}_{l'k'})\}}. \qquad (4.2.5.85)$$

In the harmonic approximation $\exp\{\overline{2\pi i \mathbf{H} \cdot \Delta\mathbf{u}}\}$ is replaced by $\exp\{\frac{1}{2}|2\pi \mathbf{H} \cdot \Delta\mathbf{u}|^2\}$. This is, however, a rather crude approximation because strongly anharmonic vibrations are quite common in an orientationally disordered crystal. In this approximation $\overline{F_l F_{l'}^+}$ becomes

$$\overline{F_l F_{l'}^+} = \sum_k \sum_{k'} f_k f_{k'} \exp\{-B_k(\omega_l)\}$$
$$\times \exp\{-B_{k'}(\omega_{l'})\} \exp\{D_{lk;\, l'k'}\}. \qquad (4.2.5.86)$$

B_k is equal to $\frac{1}{2}\overline{(2\pi \mathbf{H} \cdot \mathbf{u}_{lk})^2}$ (the Debye–Waller factor) and depends on the specific configuration ω_l. $D_{lk;\, l'k'} = \overline{(2\pi \mathbf{H} \cdot \mathbf{u}_{lk})(2\pi \mathbf{H} \cdot \mathbf{u}_{l'k'})}$ includes all the correlations between positions, orientations and vibrations of the molecules.

Averaging over different configurations demands a knowledge of the orientational probabilities. The probability of finding molecule l in orientation ω_l is given by $p(\omega_l)$. The double probability $p(\omega_l, \omega_{l'})$ gives the probability of finding two molecules l, l' in different orientations ω_l and $\omega_{l'}$, respectively. In the absence of correlations between the orientations we have $p(\omega_l, \omega_{l'}) = p(\omega_l)p(\omega_{l'})$. If correlations exist, $p(\omega_l, \omega_{l'}) = p(\omega_l)p'(\omega_l|\omega_{l'})$, where $p'(\omega_l|\omega_{l'})$ defines the conditional probability that molecule l' has the orientation ω_l if molecule l has the orientation $\omega_{l'}$. For long distances between l and l' $p'(\omega_l|\omega_{l'})$ tends to $p(\omega_{l'})$.

The difference $\Delta(\omega_l|\omega_{l'}) = p'(\omega_l|\omega_{l'}) - p(\omega_{l'})$ characterizes, therefore, the degree of short-range orientational correlation. Note that this formalism corresponds fully to the $p_\mu, p_{\mu\mu'}$ used in the context of translational disorder.

The average structure factor, sometimes called averaged form factor, of the molecule is given by

$$\langle F_l \rangle = \sum_{\omega_l} p(\omega_l)F_l(\omega_l). \qquad (4.2.5.87)$$

(*a*) Negligible correlations between vibrations of different molecules (Einstein model):

$$D_{lk;\, l'k'} = 0 \text{ for } l \neq l'.$$

From (4.2.5.86) it follows that (the prime symbol takes the Debye–Waller factor into account)

$$\overline{\langle I \rangle} = N^2 |\langle F' \rangle|^2 L(\mathbf{G})$$
$$+ N\Big\{ \sum_k \sum_{k'} \sum_{\omega_l} p(\omega_l)f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{lk'})\}$$
$$\times \exp\{D_{lk;\, lk'}\} - |\langle F' \rangle|^2 \Big\}$$
$$+ N \sum_{\Delta l \neq 0} \sum_{\omega_l} \sum_{\omega_{l'}} p(\omega_l)\Delta(\omega_l|\omega_{l'})$$
$$\times F_l'(\omega_l)F_{l'}^+(\omega_{l'})$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}. \qquad (4.2.5.88)$$

$L(\mathbf{G})$ is the reciprocal lattice of the well defined ordered lattice. The first term describes Bragg scattering from an averaged structure. The second term governs the diffuse scattering in the absence of short-range orientational correlations. The last term takes the correlation between the orientations into account.

If rigid molecules with centre-of-mass translational displacements and negligible librations are assumed, which is a first approximation only, $|\langle F \rangle|^2$ is no longer affected by a Debye–Waller factor.

In this approximation the diffuse scattering may therefore be separated into two parts:

$$N(\langle F^2 \rangle - |\langle F' \rangle|^2) = N(F^2 - |\langle F \rangle|^2) + N(|\langle F \rangle|^2 - |\langle F' \rangle|^2)$$
$$(4.2.5.89)$$

with

$$\langle F^2 \rangle = \sum_{\omega_l} \sum_{\omega_{l'}} \sum_k \sum_{k'} f_k(\omega_l)f_{k'}(\omega_{l'})p(\omega_l)$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}. \qquad (4.2.5.90)$$

The first term in (4.2.5.89) gives the scattering from equilibrium fluctuations in the scattering from individual molecules (diffuse scattering without correlations), the second gives the contribution from the centre-of-mass thermal vibrations of the molecules.

(*b*) If intermolecular correlations between the molecules cannot be neglected, the final intensity expression for diffuse scattering is very complicated. In many cases these correlations are caused by dynamical processes (see Chapter 4.1). A simplified treatment assumes the molecule to be a rigid body with a centre-of-mass displacement $\mathbf{u}_l$ and neglects vibrational–librational and librational–librational correlations: $D_{l;\, l'} = \overline{(2\pi \mathbf{H} \cdot \mathbf{u}_l)(2\pi \mathbf{H} \cdot \mathbf{u}_{l'})}$ $(l \neq l')$. The following expression approximately holds:

$$\overline{\langle I \rangle} = N^2 |\langle F' \rangle|^2 L(\mathbf{G})$$
$$+ \Big\langle \sum_l \sum_{l'} F_l'(\omega_l)F_{l'}^{'+}(\omega_{l'}) \exp\{D_{l;\, l'}\} \Big\rangle \{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}$$
$$+ N\Big[\sum_{\omega_l} \sum_{k, k'} p(\omega_l)f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}$$
$$\times \exp\{D_{lk;\, l'k'}\} - \sum_{\omega_l} \sum_{\omega_{l'}} \sum_k \sum_{k'} p(\omega_l)p(\omega_{l'})f_k f_{k'}$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}$$
$$\times \exp\{D_{lk;\, l'k'}\}\Big] + \sum_{l \neq l'} \sum_{\omega_l} \sum_{\omega_l} p(\omega_l)\Delta(\omega_l|\omega_{l'})$$
$$\times F_l'(\omega_l)F_{l'}^{'+}(\omega_{l'})$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\} \exp\{D_{l;\, l'}\}. \qquad (4.2.5.91)$$

Again, the first term describes Bragg scattering and the second corresponds to the average thermal diffuse scattering in the disordered crystal. Because just one molecule belongs to one unit cell only acoustic waves contribute to this part. To an approximation, the result for an ordered crystal may be used by replacing F by $\langle F' \rangle$ [Chapter 4.1, equation (4.1.3.4)]. The third term corresponds to random-disorder diffuse scattering. If librations are neglected this term may be replaced by $N(\langle F^2 \rangle - \langle F \rangle^2)$. The

last term in (4.2.5.91) describes space correlations. Omission of $\exp\{D_{l;\,l'}\}$ or expansion to $\sim(1 + D_{l;\,l'})$ are further simplifying approximations.

In either (4.2.5.88) or (4.2.5.91) the diffuse-scattering part depends on a knowledge of the conditional probability $\Delta(\omega_l | \omega_{l'})$ and the orientational probability $p(\omega_l)$. The latter may be found, at least in principle, from the average structure factor.

(2) *Rotational structure (form) factor*

In certain cases and with simplifying assumptions, $\langle F \rangle$ [equation (4.2.5.87)] and $\langle \Delta F^2 \rangle$ [equation (4.2.5.90)] may be calculated. Assuming only one molecule per unit cell and treating the molecule as a rigid body, one derives from the structure factor of an ordered crystal F_l

$$\langle F \rangle = \sum_k f_k \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\}\rangle \qquad (4.2.5.92)$$

and

$$\langle \Delta F^2 \rangle = \sum_k \sum_{k'} f_k f_{k'} [\langle \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}\rangle$$
$$- \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\}\rangle \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{l'k'}\}\rangle]. \qquad (4.2.5.93)$$

If the molecules have random orientation in space the following expressions hold [see, *e.g.*, Dolling *et al.* (1979)]:

$$\langle F \rangle = \sum_k f_k j_0(\mathbf{H} \cdot \mathbf{r}_k) \qquad (4.2.5.94)$$

$$\langle |\Delta F|^2 \rangle = \sum_k \sum_{k'} f_k f_{k'} \{ j_0[\mathbf{H} \cdot (\mathbf{r}_k - \mathbf{r}_{k'})]$$
$$- j_0(\mathbf{H} \cdot \mathbf{r}_k) j_0(\mathbf{H} \cdot \mathbf{r}_{k'}) \}. \qquad (4.2.5.95)$$

$j_0(z)$ is the zeroth order of the spherical Bessel functions and describes an atom k uniformly distributed over a shell of radius r_k.

In practice the molecules perform finite librations about the main orientation. The structure factor may then be found by the method of symmetry-adapted functions [see, *e.g.*, Press (1973), Press & Hüller (1973), Dolling *et al.* (1979), Prandl (1981, and references therein)].

$$\langle F \rangle = \sum_k f_k 4\pi \sum_\nu \sum_{\mu=-\nu}^{+\nu} i^\nu j_\nu(\mathbf{H} \cdot \mathbf{r}_k) C_{\nu\mu}^{(k)} Y_{\nu\mu}(\theta, \varphi). \qquad (4.2.5.96)$$

$j_\nu(z)$ is the νth order of spherical Bessel functions, the coefficients $C_{\nu\mu}^{(k)}$ characterize the angular distribution of $\mathbf{r}_k$ and $Y(\theta, \varphi)$ are the spherical harmonics where $|\mathbf{H}|$, θ, φ denote polar coordinates of $\mathbf{H}$.

The general case of an arbitrary crystal, site and molecular symmetry and the case of several symmetrically equivalent orientationally disordered molecules per unit cell are treated by Prandl (1981); an example is given by Hohlwein *et al.* (1986). As mentioned above, cubic plastic crystals are common and therefore mostly studied up to now. The expression for $\langle F \rangle$ may then be formulated as an expansion in cubic harmonics $K_{\nu\mu}(\theta, \varphi)$:

$$\langle F \rangle = \sum_k f_k 4\pi \sum_\nu \sum_\mu i^\nu j_\nu(\mathbf{H} \cdot \mathbf{r}_k) C_{\nu\mu}^{'(k)} K_{\nu\mu}(\theta, \varphi), \qquad (4.2.5.97)$$

where $C'_{\nu\mu}$ are modified expansion coefficients.

Taking into account isotropic centre-of-mass translational displacements, which are not correlated with the librations, we obtain

$$\langle F' \rangle = \langle F \rangle \exp\{-\tfrac{1}{6} H^2 \langle U^2 \rangle\}. \qquad (4.2.5.98)$$

U is the mean-square translational displacement of the molecule. Correlations between translational and vibrational displacements are treated by Press *et al.* (1979).

Equivalent expressions for crystals with symmetry other than cubic may be found from the same concept of symmetry-adapted functions [tables are given by Bradley & Cracknell (1972)].

(3) *Short-range correlations*

The final terms in equations (4.2.5.88) and (4.2.5.91) concern correlations between the orientations of different molecules. Detailed evaluations need knowledge of a particular model. Examples are compounds with nitrate groups (Wong *et al.*, 1984; Lefebvre *et al.*, 1984), CBr$_4$ (More *et al.*, 1980, 1984) and many others (see Sherwood, 1979). The situation is even more complicated when a modulation wave with respect to the occupation of different molecular orientations is superimposed. A limiting case would be a box-like function describing a pattern of domains. Within one domain all molecules have the same orientation. This situation is common in ferroelectrics where molecules exhibit a permanent dipole moment. The modulation may occur in one or more directions in space. The observed intensity in this type of orientationally disordered crystal is characterized by a system of more or less diffuse satellite reflections. The general scattering theory of a crystal with occupational modulation waves follows the same lines as outlined in Section 4.2.3.5.1.

4.2.6. Disorder diffuse scattering from aperiodic crystals

The preceding sections of this chapter have either been related to disorder phenomena in conventional crystals defined by the presence of 3D translational symmetry, *i.e.* by a 3D lattice function, at least in the averaged sense, or to solids with crystalline order in only lower (2 or 1) dimensions where the ordering principle along 'nonperiodic' directions shows a gradual transition from long- to short-range order, in particular to a liquid-like behaviour and, finally, to an (almost) random ordering behaviour of structural units. So-called aperiodic crystals do not fit this treatment because aperiodicity denotes a different type of order, which is nonperiodic in 3D space but where translational order may be restored in higher-dimensional ($n > 3$) direct space. Three types of solids are commonly included in the class of aperiodic structures: (i) incommensurately modulated structures (IMSs), where structural parameters of any kind (coordinates, occupancies, orientations of extended molecules or subunits in a structure, atomic displacement parameters) deviate periodically from the average ('basic') structure and where the modulation period is incommensurate compared to that of the basic structure; (ii) composite structures (CSs), which consist of two (or more) intergrown incommensurate substructures with mutual interactions giving rise to mutual (incommensurate) modulations; and (iii) quasicrystals (QCs), which might simply be viewed as made up by n (≥ 2) different tiles – analogous to the elementary cell in crystals – which are arranged according to specific matching rules and which are decorated by atoms or atomic clusters. Most common are icosahedral (i-type) quasicrystals with 3D aperiodic order (3D 'tiles') and decagonal quasicrystals (d-phases) with 2D aperiodicity and one unique axis along which the QC is periodically ordered. The basic 'crystallography' of aperiodic crystals is given in Chapter 4.6 of this volume; see also the review articles by Janssen & Janner (1987) and van Smaalen (2004) (and further references therein). We only point out some of the aspects here to provide the background for a short discussion about disorder diffuse scattering in aperiodic crystals.

As outlined in Section 4.6.1, a d-dimensional (dD) ideal aperiodic crystal can be defined as a dD irrational section of an nD ('hyper'-)crystal with nD crystal symmetry. Corresponding to the section of the nD hypercrystal with the dD ($d = 1, 2, 3$) direct physical (= 'external' or 'parallel') space we have a projection of the (weighted) nD reciprocal hyperlattice onto the dD reciprocal physical space. The occurrence of Bragg reflections as a signature