4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS
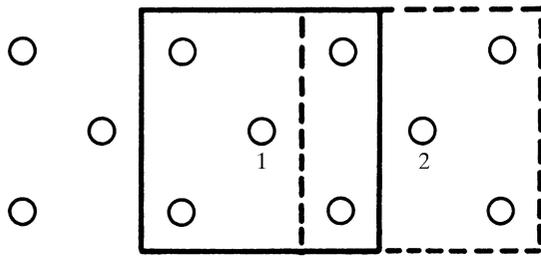

Fig. 4.2.4.1. Construction of the correlation function in the method of overlapping clusters.

In the product only next-nearest neighbours have to be included. 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 (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 superstructure formation where a description in terms of antiphase domains is reasonable (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 averaging 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 too much information about the structural basis of the displacements. This situation corresponds exactly to the relationship between a Patterson function and a real structure: the structure has to be found which explains the more or less complicated function completely, and its unique solution is rather difficult. These statements seem to be necessary 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 $P'_{\nu\nu'}(\mathbf{H})$ of the correlation functions in equation (4.2.4.71). As has been mentioned in the context of equation (4.2.4.74) antisymmetric contributions will occur if acentric structure factors are involved. Apparently, this condition is met by the phase factors of displacements. In consequence, antisymmetric 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 (4.2.4.69a,b) are no longer valid because the functions $p'_{\nu\nu'}(\mathbf{r})$ become complex. The most important change is the relation corresponding to (4.2.4.69):

$$\alpha_\nu p'_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu'}p'^{+}_{\nu\nu'}(-\mathbf{r}) \leftrightarrow \alpha_{\nu'}P'_{\nu\nu'}(\mathbf{H}) = \alpha_{\nu'}P'^{+}_{\nu'}(\mathbf{H}). \quad (4.2.4.77)$$

Strictly speaking we have to replace the *a priori* probabilities α_ν by complex numbers $\alpha_\nu \exp(2\pi i \Delta \mathbf{r}_\nu \cdot \mathbf{H})$ 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 which 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 techniques.

A careful study of the real and imaginary parts of

$$\langle p'_{\nu\nu'}(\mathbf{r}) \rangle = \langle p'_{\nu\nu'}(\mathbf{r}) \rangle_R + \langle p'_{\nu\nu'}(\mathbf{r}) \rangle_I$$

and

$$\Delta p'_{\nu\nu'}(\mathbf{r}) = \Delta p'_{\nu\nu'}(\mathbf{r})_R + \Delta p'_{\nu\nu'}(\mathbf{r})_I$$

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

$$I_d \simeq N \sum_\nu \alpha_\nu |\Delta F_\nu(\mathbf{H})|^2 \{[\langle P'_{\nu\nu}(\mathbf{H}) \rangle - \Delta P'_{\nu\nu}(\mathbf{H})] * L(\mathbf{H})\}$$
$$+ 2N \sum_{\nu > \nu'} \alpha_\nu (\Delta F_\nu \Delta F^+_{\nu'})_R$$
$$\times \{[\langle P'_{\nu\nu'}(\mathbf{H}) \rangle_R - \Delta P'_{\nu\nu'}(\mathbf{H})_I] * L(\mathbf{H})\}$$
$$+ 2N \sum_{\nu > \nu'} \alpha_\nu (\Delta F_\nu \Delta F^+_{\nu'})_I$$
$$\times \{[\langle P'_{\nu\nu'}(\mathbf{H}) \rangle_I - \Delta P'_{\nu\nu'}(\mathbf{H})_R] * L(\mathbf{H})\}. \quad (4.2.4.78)$$

It should be noted that all contributions are real. This follows from the properties of Fourier transforms of symmetric and antisymmetric functions. All $\Delta P_{\nu\nu'}(\mathbf{H})$ are antisymmetric; hence they generate antisymmetric contributions to the line profiles. In contrast to equation (4.2.4.75), the real *and* the imaginary parts of the structure factors contribute to the asymmetry of the line profiles.

4.2.4.4.5. *Distortions in binary systems*

In substitutional binary systems (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 scattering may be separated into two parts (*a*) owing to short-range order and (*b*) owing to static displacements.

Corresponding to the expansion (4.2.4.75), $I_d = I_{\text{sro}} + I_2 + I_3$, where I_{sro} is given by equation (4.2.4.71*b*) and the correction terms I_2 and I_3 relate to the linear and the quadratic term in (4.2.4.75). The intensity expression will be split into terms of A–A, A–B, ... pairs. More explicitly $\Delta_{\nu\nu'}\mathbf{r} = \mathbf{u}_{\mathbf{n}\nu} - \mathbf{u}_{\mathbf{n}'\nu'}$ and with the following abbreviations:

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

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

$$I_2 = 2\pi i c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \{H \cdot [F_{\mathbf{nn}'|AA} \langle x_{\mathbf{nn}'|AA} \rangle$$

$$+ F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB} \rangle + F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB} \rangle] + K \cdot [`y`]$$
$$+ L \cdot [`z`]\} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\} \qquad (4.2.4.79)$$

$$I_3 = c_A c_B (f_A - f_B)^2 (-2\pi)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \{H^2 [F_{\mathbf{nn}'} \langle x_{\mathbf{nn}'|AA}^2 \rangle$$

$$+ F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB}^2 \rangle + F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB}^2 \rangle]$$
$$+ K^2 \cdot [`y^2`] + L^2 \cdot [`z^2`]$$
$$+ HK [F_{\mathbf{nn}'|AA} \langle (xy)_{\mathbf{nn}'|AA} \rangle + F_{\mathbf{nn}'|BB} \langle (xy)_{\mathbf{nn}'|BB} \rangle$$
$$+ F_{\mathbf{nn}'|AB} \langle (xy)_{\mathbf{nn}'|AB} \rangle]$$
$$+ KL [`(yz)`] + LH [`(zx)`]\}$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}. \qquad (4.2.4.80)$$

With further abbreviations

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

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

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

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

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

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

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

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

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

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

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

If the $F_{\mathbf{nn}'|AA}, \ldots$ are independent of $|\mathbf{H}|$ in the range of measurement which is better fulfilled with neutrons than with X-rays (see below), $\gamma, \delta, \varepsilon$ 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

$$I_2 = -N c_A c_B (f_A - f_B)^2 \sum_m \sum_n \sum_p (H\gamma_{lmn|x} + \ldots + \ldots)$$

$$\times \sin 2\pi (Hm + Kn + Lp). \qquad (4.2.4.81)$$

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. This term shows quite an 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 non-vanishing 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. Generally 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 which 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 has 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 multi-component 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. Also, the case of planar short-range order with corresponding diffuse intensity along rods in reciprocal space may be treated along the Borie & Sparks method (Ohshima & Moss, 1983).

Multi-wavelength 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 for a contrast variation by using samples with different isotope substitution.

4.2.4.4.6. *Powder diffraction*

Evaluation of diffuse-scattering data from powder diffraction follows the same theoretical formulae developed for the determination of the radial distribution function for glasses and liquids (Debye & Menke, 1931; Warren & Gingrich, 1934). The final formula for random distributions may be given as (Fender, 1973)

$$I_d^p = \{\langle|F(\mathbf{H})|^2\rangle - |\langle F(\mathbf{H})\rangle|^2\} \sum_i s_i \sin(2\pi H r_i)/(2\pi H r_i).$$

$$(4.2.4.82)$$

s_i represents the number of atoms at distance r_i from the origin. An equivalent expression for a substitutional binary alloy is

$$I_d^p = \alpha(1-\alpha)\{|f_2(\mathbf{H}) - f_2(\mathbf{H})|^2\} \sum_i s_i \sin(2\pi H r_i)/(2\pi H r_i).$$

$$(4.2.4.83)$$

4.2.4.4.7. *Small concentrations of defects*

In the literature small concentrations are treated in terms of fluctuations of the functions $\pi_{\mathbf{n}\nu}$ as defined in equation (4.2.4.56). Generally we prefer the introduction of the distribution function of the defects or clusters. Since this problem has already been treated in Section 4.2.4.4.3 only some very brief remarks are given here. 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, received by Fourier transformation of the corrected diffused low-angle scattering, the reader is referred to the relevant literature. Since deconvolutions are not unique some reasonable assumptions are necessary for the final solution. Anomalous scattering may be very helpful if applicable.

4.2.4.4.8. *Cluster method*

As mentioned above, the cluster method may be useful for the interpretation of disorder problems. In the general formula of diffuse scattering of random distributions equation (4.2.2.13) 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 in good approximation. The diffuse intensity is then given by

$$I_d(\mathbf{H}) = \sum_\nu p_\nu |F_\nu(\mathbf{H})|^2 - |\sum_\nu p_\nu F_\nu(\mathbf{H})|^2, \qquad (4.2.4.84)$$

where $F_\nu(\mathbf{H})$ represents the difference structure factor of the νth cluster and p_ν is its *a priori* probability. Obviously equation (4.2.4.84) is of some use in two cases only. (1) The number of clusters is sufficiently small and meets the condition of nearly random distribution. In principle, its structure may then be determined with the aid of refinement methods according to equation (4.2.4.84). 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 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).

Some remarks on the use of residual factors should be added here. Obviously the diffuse scattering may be used for refinements in a similar way as in conventional structure determination. For this purpose a sufficiently small reciprocal lattice has to be defined. The size of the reciprocal cell has to be chosen with respect to the maximum gradient of diffuse scattering. Then the diffuse intensity may be described by a product of the real intensity distribution and the small reciprocal lattice. Fourier transformation yields the convolution of the real disordered structure and a large unit cell. In other words, the disordered structure is subdivided into large units and subsequently superimposed ('projected') in a single cell. In cases where a clear model of the disorder could be determined, a refinement procedure for atomic and other relevant parameters can be started. In this way a residual factor may be determined. A first approach has been elaborated by Epstein & Welberry (1983) in the case of substitutional disorder of two molecules.

The outstanding limiting factor is the collection of weak intensity data. The amount increases rapidly with the complexity of the structure and could even exceed by far the amount which is needed in the case of protein structure refinement. Hence, it seems to be reasonable to restrict the measurement to distinct areas in reciprocal space. Most of these publications, however, use too little information when compared with the minimum of data which would be necessary for the confirmation of the proposed model. Hence, physical and chemical considerations should be used as an additional source of information.

4.2.4.4.9. *Comparison between X-ray and neutron methods*

Apart from experimental arguments in favour of either method, there are some specific points which should be mentioned in this context. The diffuse scattering in question must be separated from Bragg scattering and from other diffuse-scattering contributions. Generally both methods are complementary: neutrons are preferable in cases where X-rays show only a small scattering contrast: (heavy) metal hydrides, oxides, carbides, Al–Mg distribution *etc*. In favourable cases it is possible to suppress (nuclear) Bragg scattering of neutrons when isotopes are used so that $\sum_\nu c_\nu f_\nu = 0$ 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 θ angles or by using long wavelengths. For reasons of absorption the latter point is the domain of neutron scattering. Exceeding the Bragg cut-off, Bragg scattering is ruled out. In this way 'diffuse' background owing to multiple Bragg scattering is avoided. Other diffuse-scattering contributions which increase with the $|\mathbf{H}|$ value are thus also minimized: thermal diffuse scattering (TDS) and scattering due to long-range static displacements. On the other hand, lattice distortions, Huang scattering, . . . should be measured at large values of $|\mathbf{H}|$. TDS