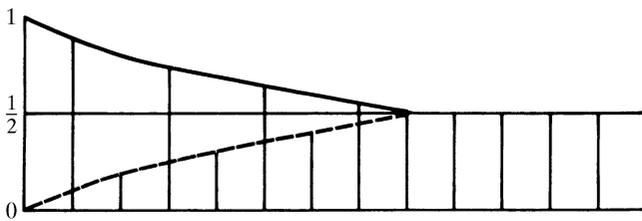4. DIFFUSE SCATTERING AND RELATED TOPICS

Fig. 4.2.3.7. The same distribution (*cf.* Fig. 4.2.3.5) in the case of superstructure formation.

where I_1, I_2 represent the two solutions discussed for the assembly of crystals and have to be added with the probability $\frac{1}{2}$; the intensities of sharp reflections become

$$I = (I_1 + I_2)/2. \qquad (4.2.3.52)$$

Introducing equation (4.2.3.51) into (4.2.3.52), we obtain

$$I \simeq |\tfrac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]|^2 + s^2|F_1(\mathbf{H}) - F_2(\mathbf{H})^2|^2. \qquad (4.2.3.53a)$$

$s = 0$ corresponds to the well known behaviour of sharp reflections, $s = \frac{1}{2}$ (maximum long-range order) gives

$$I \simeq \tfrac{1}{2}[|F_1(\mathbf{H})|^2 + |F_2(\mathbf{H})|^2]. \qquad (4.2.3.53b)$$

This result reveals some difficulties for the determination of the averaged structure as long as s is different from zero or $\frac{1}{2}$, since in the former case the use of integrated sharp Bragg intensities yields a correct average structure. If $s = \frac{1}{2}$, a correct structure determination can only be performed with a refinement allowing for an incoherent superposition of two different structures. Having subtracted all periodic contributions to $p_{\mu\mu'}(\mathbf{r})$, new functions that describe the remaining nonperiodic parts have to be introduced (Fig. 4.2.3.6b). In order to obtain a clear overview of intensities, $p'_{\mu\mu'}(\mathbf{r})$ is again defined:

$$p'_{\mu\mu'}(\mathbf{r}) = cp_{\mu\mu'}(\mathbf{r}) - p_{\mu\mu'}(\infty),$$

where c should be chosen such that $p_{\mu\mu'}(\mathbf{0}) = 1$. By this definition a very simple behaviour of the diffuse scattering is obtained:

$$p'_{11}(\mathbf{r}): \tfrac{1}{2} - s; \quad p'_{12}(\mathbf{r}): -(\tfrac{1}{2} - s);$$
$$p'_{22}(\mathbf{r}): \tfrac{1}{2} + s; \quad p'_{21}(\mathbf{r}): -(\tfrac{1}{2} + s).$$

With the definitions introduced above it is found that

$$p'_{11}(\mathbf{r}) = p'_{22}(\mathbf{r}).$$

The diffuse scattering is given by

$$I_{1D}(\mathbf{H}) = (\tfrac{1}{4} - s^2)|F_1(\mathbf{H}) - F_2(\mathbf{H})|^2[P'_{11}(\mathbf{H}) * L(\mathbf{H})]. \qquad (4.2.3.54)$$

Since equation (4.2.3.54) is symmetrical with respect to an interchange of F_1 and F_2, the same result is obtained for I_{2D}. Diffuse reflections occur in the positions of the sharp ones; the integrated intensities of sharp and diffuse reflections are independent of the special shape of $P'_{11}(\mathbf{H})$, hence

$$1 = \int P'_{11}(\mathbf{H}) \exp\{2\pi i \mathbf{0} \cdot \mathbf{H}\} \, d\mathbf{H} = \int P'_{11}(\mathbf{H}) \, d\mathbf{H}$$

since $p_{11}(\mathbf{0}) = 1$.

(6) *Lamellar domains with long-range order: tendency to superorder*

So far it has been tacitly assumed that the crystal shows a preference for equal neighbours. If there is a reversed tendency (*i.e.* pairs of unequal neighbours are more probable), the whole procedure outlined above may be repeated as shown in Fig. 4.2.3.7 for the one-dimensional example. With the same probability of an unlike pair as used for the equal pair in the preceding example, the order process approaches an alternating structure

such that the even-order neighbours have the same pair probabilities, while the odd ones are complementary for equal pairs (Fig. 4.2.3.7). In order to calculate intensities, it is necessary to introduce a new lattice with the doubled lattice constant and the corresponding reciprocal lattice with $b^{*'} = b^*/2$. In order to describe the probability $p_{\mu\mu'}(\mathbf{r})$, one has to introduce two lattices in real space – the normal lattice with the undisplaced origin and the displaced one. Fourier transformation of the new functions yields the following very similar results:

Sharp Bragg reflections
(*a*) $k' =$ even

$$I_S = |\tfrac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]|^2. \qquad (4.2.3.55a)$$

(*b*) $k' =$ odd

$$I_S = s^2|\tfrac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]|^2. \qquad (4.2.3.55b)$$

Diffuse reflections
(*c*) $k' =$ odd

$$I_D = (\tfrac{1}{4} - s^2)|\tfrac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]|^2. \qquad (4.2.3.55c)$$

In contrast to (5), this is the better situation for the determination of the averaged structure, which may be performed without any difficulty regardless of whether s is different from zero or not. For this purpose, even reflections (or reflections in the old setting) may be used. The inclusion of odd reflections in the structure determination of the superstructure is also possible if convenient **H**-independent scaling factors are introduced in order to compensate for the loss in intensity which is unavoidable for the integration of the diffuse scattering.

A few comments should be made on the physical meaning of the formulae derived above. All formulae may be applied to the general three-dimensional case, where long-range and short-range order is a function of the relevant thermodynamical parameters. In practice, long-range order will never be realized in a real crystal consisting of mosaic blocks which may behave as small subunits in order–disorder transitions. Another reason to assume partly incoherent areas in single crystals is the possible presence of strains or other distortions at the interfaces between domains, which should cause a decrease of the averaged areas of coherent scattering. All these effects may lead to diffuse scattering in the neighbourhood of Bragg peaks, similar to the diffuse scattering caused by domain structures. For this reason, an incoherent treatment of domains is probably more efficient, although considerable errors in intensity measurements may occur. A very careful study of line profiles is generally useful in order to decide between the various possibilities.

4.2.3.5.5. Two-dimensional disorder

The subject of two-dimensional disorder refers to predominantly one-dimensional structural elements, *e.g.* extended macromolecules and chain- or column-like structural units. A short introduction to this subject and some examples taken from inorganic structures are given in Section 4.2.5.3. Most important in this context, however, would be a treatment of disorder diffuse scattering of polymer/fibre structures. These are subjects in their own right and are treated in Chapter 4.5 of this volume and in Chapter 19.5 of Volume F.

4.2.3.5.6. Three-dimensional disorder

The solution of three-dimensional disorder problems is generally more demanding, although it may start with the formulation given above. Various algorithms have been developed to tackle these problems at least approximately, most of them restricted to particular models. Both real-space (cluster) and reciprocal-space (fluctuation wave) methods are employed and will be briefly addressed in Section 4.2.5.4. The more recently

references