

## 4. DIFFUSE SCATTERING AND RELATED TOPICS

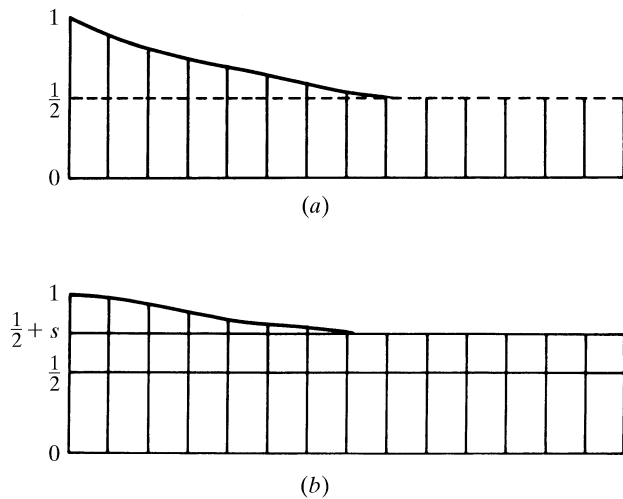


Fig. 4.2.3.5. Typical distributions of mixed crystals (unmixing): (a) upper curve: short-range order only; (b) lower curve: long-range order.

interpretation of the diffraction pictures this correlation may be derived from the diffraction pattern itself. The  $p_{\mu\mu'}(\mathbf{m})$  are separable into a strictly periodic and a monotonically decreasing term approaching zero in both cases. This behaviour is shown in Figs. 4.2.3.6(a), (b). The periodic term contributes to sharp Bragg scattering. In the case of short-range order the symmetry relations given in equation (4.2.3.25) are valid. The convolution in real space yields with factors  $t(\mathbf{r})$  (equations 4.2.3.21):

$$\begin{aligned} & \frac{1}{2}t(\mathbf{r})\left[\sum_{\mathbf{m}}\delta(\mathbf{r}+\mathbf{m})p'_{11}(\mathbf{m})\right]*F_1(\mathbf{r})*F_1(-\mathbf{r}) \\ & + \frac{1}{2}t(\mathbf{r})\left[\sum_{\mathbf{m}}\delta(\mathbf{r}+\mathbf{m})p'_{12}(\mathbf{m})\right]*F_1(\mathbf{r})*F_2(-\mathbf{r}) \\ & + \frac{1}{2}t(\mathbf{r})\left[\sum_{\mathbf{m}}\delta(\mathbf{r}+\mathbf{m})p'_{21}(\mathbf{m})\right]*F_2(\mathbf{r})*F_1(-\mathbf{r}) \\ & + \frac{1}{2}t(\mathbf{r})\left[\sum_{\mathbf{m}}\delta(\mathbf{r}+\mathbf{m})p'_{22}(\mathbf{m})\right]*F_2(\mathbf{r})*F_2(-\mathbf{r}), \end{aligned}$$

where  $p'_{\mu\mu'}(\mathbf{m})$  are factors attached to the  $\delta$  functions:

$$\begin{aligned} p'_{11}(\mathbf{m}) &= p_{11}(\mathbf{m}) - \frac{1}{2} = p'_{22}(\mathbf{m}) \\ p'_{12}(\mathbf{m}) &= p'_{21}(\mathbf{m}) = -p'_{11}(\mathbf{m}). \end{aligned}$$

The positive sign of  $n$  in the  $\delta$  functions results from the convolution with the inverted lattice [cf. Patterson (1959, equation 32)]. Fourier

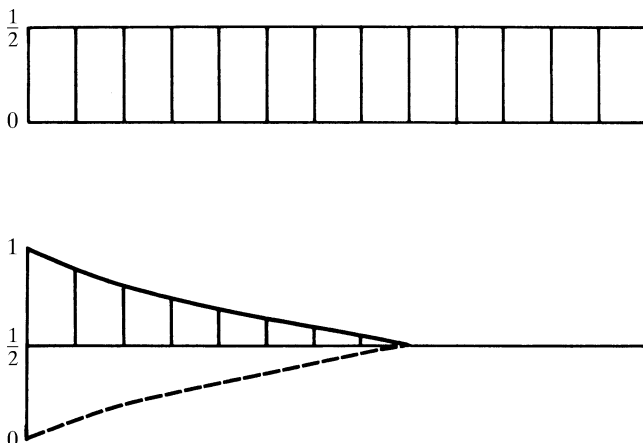


Fig. 4.2.3.6. Decomposition of Fig. 4.2.3.5(a) into a periodic and a rapidly convergent part.

transformation of the four terms given above yields the four corresponding expressions ( $\mu, \mu'$ ):

$$\frac{1}{2}[T(\mathbf{H}) * \sum_{\mathbf{m}} p'_{\mu\mu'}(\mathbf{m}) \exp\{-2\pi i\mathbf{H} \cdot \mathbf{m}\}] F_{\mu}(\mathbf{H}) F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.27a)$$

Now the summation over  $\mathbf{m}$  may be replaced by an integral if the factor  $l(\mathbf{m})$  is added to  $p'_{\mu\mu'}(\mathbf{m})$ , which may then be considered as the smoothest continuous curve passing through the relevant integer values of  $\mathbf{m}$ :

$$\sum \rightarrow \int l(\mathbf{m}) p'_{\mu\mu'}(\mathbf{m}) \exp\{-2\pi i\mathbf{H} \cdot \mathbf{m}\} d\mathbf{m}$$

since both  $l(\mathbf{m})$  and  $p'_{\mu\mu'}(\mathbf{m})$  are symmetric in our special case we obtain

$$\sum = L(\mathbf{H}) * P'_{\mu\mu'}(\mathbf{H}).$$

Insertion of the sum in equation (4.2.3.27a) results in

$$\frac{1}{2}[L(\mathbf{H}) * T(\mathbf{H}) * P'_{\mu\mu'}(\mathbf{H})] F_{\mu}(\mathbf{H}) F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.27b)$$

Using all symmetry relations for  $p'_{\mu\mu'}(\mathbf{m})$  and  $P'_{\mu\mu'}(\mathbf{H})$ , respectively, we obtain for the diffuse scattering after summing over  $\mu, \mu'$

$$I_d \approx [L(\mathbf{H}) * T(\mathbf{H}) * P'_{11}(\mathbf{H})] |\Delta F(\mathbf{H})|^2 \quad (4.2.3.28)$$

with  $\Delta F(\mathbf{H}) = \frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]$ .

It should be borne in mind that  $P'_{11}(\mathbf{H})$  decreases rapidly if  $p'_{11}(\mathbf{r})$  decreases slowly and *vice versa*. It is interesting to compare the different results from equations (4.2.3.21b) and (4.2.3.28). Equation (4.2.3.28) indicates diffuse maxima at the positions of the sharp Bragg peaks, while the multiplication by  $D(\mathbf{H})$  causes satellite reflections in the neighbourhood of Bragg maxima. Both equations contain the factor  $|\Delta F(\mathbf{H})|^2$  indicating the same influence of the two structures. More complicated formulae may be derived for several cell occupations. In principle, a result similar to equation (4.2.3.28) will be obtained, but more interdependent correlation functions  $p_{\mu\mu'}(\mathbf{r})$  have to be introduced. Consequently, the behaviour of diffuse intensities becomes more differentiated in so far as all  $p'_{\mu\mu'}(\mathbf{r})$  are now correlated with the corresponding  $\Delta F_{\mu}(\mathbf{r}), \Delta F_{\mu'}(-\mathbf{r})$ . Hence the method of correlation functions becomes increasingly ineffective with increasing number of correlation functions. Here the cluster method seems to be more convenient and is discussed below.

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

The Patterson function of a disordered crystal exhibiting long-range order is shown in Fig. 4.2.3.5(b). Now  $p_{11}(\infty)$  converges against  $\frac{1}{2} + s$ , the *a priori* probability changes correspondingly. Since  $p_{12}(\infty)$  becomes  $\frac{1}{2} - s$ , the symmetry relation given in equation (4.2.3.25) is violated:  $p_{11}(\mathbf{r}) \neq p_{22}(\mathbf{r})$  for a finite crystal; it is evident that another crystal shows long-range order with the inverted correlation function,  $p_{22}(\infty) = \frac{1}{2} + s$ ,  $p_{21}(\infty) = \frac{1}{2} - s$ , respectively, such that the symmetry  $p_{11}(\mathbf{r}) = p_{22}(\mathbf{r})$  is now valid for an assembly of finite crystals only. According to Fig. 4.2.3.5(b) there is a change in the intensities of the Bragg peaks.

$$\begin{aligned} I_1 &\sim |(\frac{1}{2} + s)F_1(\mathbf{H}) + (\frac{1}{2} - s)F_2(\mathbf{H})|^2 \\ I_2 &\sim |(\frac{1}{2} + s)F_2(\mathbf{H}) + (\frac{1}{2} - s)F_1(\mathbf{H})|^2, \end{aligned} \quad (4.2.3.29)$$

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

$$I = (I_1 + I_2)/2. \quad (4.2.3.30)$$

Introducing equation (4.2.3.29) into (4.2.3.30) we obtain