$$W(\Delta) = \frac{1}{\eta\sqrt{2\pi}} \exp\left(-\frac{\Delta^2}{2\eta^2}\right), \qquad (6.4.8.2)$$

where Δ is the angular deviation of the block from the mean orientation of all blocks in the crystal, and η is the standard deviation of the distribution. (The assumption of a Gaussian distribution is not critical to the argument that follows.)

Let the crystal be a cube of side L, and let α be the probability that a ray reflected by the first block is reflected again by a subsequent block. The effective size of the crystal for Bragg scattering of a single incident ray is then

$$\langle L \rangle = \ell + (L - \ell)\alpha, \qquad (6.4.8.3)$$

while the size of the crystal for all other attenuation processes is L, since, for them, the Bragg condition does not apply. The probability of re-scattering, α, can readily be expressed in terms of crystallographic quantities. The full width at half-maximum intensity of the Darwin reflection curve is given, after conversion to the glancing-angle (θ) scale, by Zachariasen (1945) as

$$\Delta\theta = \frac{3\lambda^2 N_c F}{\pi\sqrt{2}\sin 2\theta} \text{ (radians)}. \qquad (6.4.8.4)$$

The full width at half-maximum (FWHM) of the mosaic-block distribution (6.4.8.2) is derived in the usual way, and the parameter g ($= 1/2\eta\sqrt{\pi}$) is introduced to clear (to 1%) numerical constants. Then α, which is equal to the ratio of the widths, is given by

$$\alpha = \frac{g N_c \lambda^2 F}{\sin 2\theta}. \qquad (6.4.8.5)$$

Insertion of $\langle L \rangle$ [equation (6.4.8.3)] in place of ℓ in equation (6.4.8.1) for x leads to

$$x = [N_c \lambda F \ell + g Q_\theta (L - \ell)]^2, \qquad (6.4.8.6)$$

where $Q_\theta = N_0^2 \lambda^3 F^2 / \sin 2\theta$.

6.4.9. Secondary extinction

A separate treatment of secondary extinction is required only in the uncorrelated block model, and the method given by Hamilton (1957) is used in this work. The coupling constant in the H–D equations is given by $\sigma(\Delta\theta) = Q_\theta E_p W(\Delta\theta)$, where $Q_\theta = N_c^2 \lambda^3 F^2 / \sin 2\theta$ for equatorial reflections in the neutron case, E_p is the correction for primary extinction evaluated at the angle θ, and $W(\Delta\theta)$ is the distribution function for the tilts between mosaic blocks. The choice of this function has a significant influence on the final result (Sabine, 1985), and a rectangular or triangular form is suggested.

In the following equations for the secondary-extinction factor,

$$x = E_p Q_\theta G D, \qquad (6.4.9.1)$$

and A and B are given by equations (6.4.5.6) and (6.4.5.7). The average path length through the crystal for the reflection under consideration is D and G is the integral breadth of the angular distribution of mosaic blocks. It is important to note that A should be set equal to one if the data have been corrected for absorption, and B should be set equal to one if absorption-weighted values of D are used. If D for each reflection is not known, the average dimension of the crystal may be used for all reflections.

For a rectangular function, $W(\Delta\theta) = G$, for $|\Delta\theta| \le 1/2G$, $W(\Delta\theta) = 0$ otherwise, and the secondary-extinction factor becomes

$$E_L = \frac{\exp(-\mu D)}{2x}[1 - \exp(-2x)], \qquad (6.4.9.2)$$

$$E_B = \frac{A}{1 + Bx}. \qquad (6.4.9.3)$$

For a triangular function, $W(\Delta\theta) = G(1 - |\Delta\theta| G)$, for $|\Delta\theta| \le 1/G$, $W(\Delta\theta) = 0$ otherwise, and the secondary-extinction factor becomes

$$E_L = \frac{\exp(-\mu D)}{x}\left\{1 - \frac{1}{2x}[1 - \exp(-2x)]\right\}, \qquad (6.4.9.4)$$

$$E_B = \frac{2A}{(Bx)^2}[Bx - \ln|1 + Bx|]. \qquad (6.4.9.5)$$

6.4.10. The extinction factor

6.4.10.1. *The correlated block model*

For this model of the real crystal, the variable x is given by equation (6.4.8.6), with ℓ and g the refinable variables. Extinction factors are then calculated from equations (6.4.5.3), (6.4.5.4), and (6.4.5.5). For a reflection at a scattering angle of 2θ from a reasonably equiaxial crystal, the appropriate extinction factor is given by (6.4.7.1) as $E(2\theta) = E_L \cos^2 2\theta + E_B \sin^2 2\theta$.

It is a meaningful procedure to refine both primary and secondary extinction in this model. The reason for the high correlation between ℓ and g that is found when other theories are applied, for example that of Becker & Coppens (1974), lies in the structure of the quantity x. In the theory presented here, x is proportional to F^2 for pure primary extinction and to Q_θ^2 for pure secondary extinction.

6.4.10.2. *The uncorrelated block model*

When this model is used, two values of x are required. These are designated x_p for primary extinction and x_s for secondary extinction. Equation (6.4.8.1) is used to obtain a value for x_p. The primary-extinction factors are then calculated from (6.4.5.3), (6.4.5.4) and (6.4.5.5), and $E_p(2\theta)$ is given by equation (6.4.7.1). In the second step, x_s is obtained from equation (6.4.9.1), and the secondary-extinction factors are calculated from either (6.4.9.2) and (6.4.9.3) or (6.4.9.4) and (6.4.9.5). The result of these calculations is then used in equation (6.4.7.1) to give $E_s(2\theta)$. It is emphasised that x_s includes the primary-extinction factor. Finally, $E(2\theta) = E_p(2\theta) E_s[E_p(2\theta), 2\theta]$.

Application of both models to the analysis of neutron diffraction data has been carried out by Kampermann, Sabine, Craven & McMullen (1995).

6.4.11. Polarization

The expressions for the extinction factor have been given, by default, for the σ-polarization state, in which the electric field vector of the incident radiation is perpendicular to the plane defined by the incident and diffracted beams. For this state, the polarization factor is unity. For the π-polarization state, in which the electric vector lies in the diffraction plane, the factor is $\cos 2\theta$. The appropriate values for the extinction factors for this state are given by multiplying F by $\cos 2\theta$ wherever F occurs.

For neutrons, which are matter waves, the polarization factor is always unity.

For an unpolarized beam from an X-ray tube, the observed integrated intensity is given by $I^{\rm obs} = \frac{1}{2} I_\theta^{\rm kin}\left(E_\sigma + E_\pi \cos^2 2\theta\right)$. In the kinematic limit, $E_\sigma = E_\pi = 1$, and the power to which $\cos 2\theta$