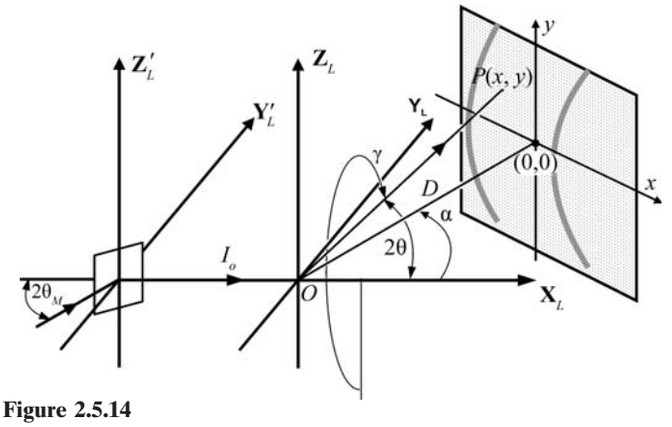

Figure 2.5.14
Geometric relationship between the monochromator and detector in the laboratory coordinates.

and effectively cancel each other. Therefore, it is not necessary to perform the Lorentz correction to the frame before integration if relative intensities equivalent to a conventional Bragg–Brentano diffractometer are expected. The Lorentz correction can be done on the integrated diffraction profiles in the same way as on the diffraction profiles collected with conventional diffractometers.

When a non-polarized X-ray beam is scattered by matter, the scattered X-rays are polarized. The intensity of the diffracted beam is affected by the polarization; this effect is expressed by the polarization factor. In two-dimensional X-ray diffraction the diffraction vectors of the monochromator diffraction and sample crystal diffraction are not necessarily in the same plane or perpendicular planes. Therefore, the overall polarization factor is a function of both 2θ and γ. Fig. 2.5.14 illustrates the geometric relationship between the monochromator and detector in the laboratory coordinates, X_L, Y_L, Z_L. The monochromator is located at the coordinates X_L, Y'_L, Z'_L, which is a translation of the laboratory coordinates along the X_L axis in the negative direction. The monochromator crystal is rotated about the Z'_L axis and $2\theta_M$ is the Bragg angle of the monochromator crystal. The diffracted beam from the monochromator propagates along the X_L direction. This is the incident beam to the sample located at the instrument centre O. The 2D detector location is given by the sample-to-detector distance D and swing angle α. The pixel $P(x, y)$ represents an arbitrary pixel on the detector. 2θ and γ are the corresponding diffraction-space parameters for the pixel. Since a monochromator or other beam-conditioning optics can only be used on the incident beam, the polarization factor for 2D-XRD can then be given as a function of both θ and γ:

$$P(\theta, \gamma) = \frac{(1 + \cos^2 2\theta_M \cos^2 2\theta)\sin^2\gamma + (\cos^2 2\theta_M + \cos^2 2\theta)\cos^2\gamma}{1 + \cos^2 2\theta_M}. \quad (2.5.27)$$

If the crystal monochromator rotates about the Y'_L axis, *i.e.* the incident plane is perpendicular to the diffractometer plane, the polarization factor for two-dimensional X-ray diffraction can be given as

$$P(\theta, \gamma) = \frac{(1 + \cos^2 2\theta_M \cos^2 2\theta)\cos^2\gamma + (\cos^2 2\theta_M + \cos^2 2\theta)\sin^2\gamma}{1 + \cos^2 2\theta_M}. \quad (2.5.28)$$

In the above equations, the term $\cos^2 2\theta_M$ can be replaced by $\left|\cos^n 2\theta_M\right|$ for different monochromator crystals. For a mosaic crystal, such as a graphite crystal, $n = 2$. For most real monochromator crystals, the exponent n takes a value between 1 and 2. For near perfect monochromator crystals, n approaches 1 (Kerr & Ashmore, 1974). All the above equations for polarization factors may apply to multilayer optics. However, since multilayer optics have very low Bragg angles, $\left|\cos^n 2\theta_M\right|$ approximates to unity. The γ dependence of the polarization factor diminishes in this case. The polarization factor approaches

$$P(\theta, \gamma) \simeq \frac{1 + \cos^2 2\theta}{2}. \quad (2.5.29)$$

2.5.3.3.5. *Air scatter*

X-rays are scattered by air molecules in the beam path between the X-ray source and detector. Air scatter results in two effects: one is the attenuation of the X-ray intensity, the other is added background in the diffraction pattern. Air scatter within the enclosed primary beam path – for instance, in the mirror, monochromator housing or collimator – results in attenuation of only the incident beam. The enclosed beam path can be purged by helium gas or kept in vacuum to reduce the attenuation so that no correction is necessary for this part of the air scatter. The open beam between the tip of the collimator and the sample generates an air-scatter background pattern, which is the major part of the air scatter. In the secondary beam path, the air scatter from the diffracted beam may generate background too, but the main effect of the air scatter is inhomogeneous attenuation of the diffraction pattern due to the different beam path lengths between the centre and the edge of the detector.

The background generated by air scattering from the open incident-beam path has a strong 2θ dependence. The specific scattering curve depends on the length of the open primary beam path, the beam size and the wavelength of the incident beam. There are two approaches to correct air scatter. One is to collect an air-scatter background frame under the same conditions as the diffraction frame except without a sample. The background frame is then subtracted from the diffraction frame. Another approach is to remove the background from the integrated profile, since the background is 2θ dependent.

The attenuation of the diffracted beam by air absorption depends on the distance between the sample and pixel. For a flat detector, air absorption can be corrected by

$$p_c(x, y) = p_o(x, y)\exp\left[\mu_{\rm air}(D^2 + x^2 + y^2)^{1/2}\right], \quad (2.5.30)$$

where $p_o(x, y)$ is the original pixel intensity of the pixel $P(x, y)$ and $p_c(x, y)$ is the corrected intensity. The detector centre is given by $(0, 0)$. $\mu_{\rm air}$ is the linear absorption coefficient of air. The value of $\mu_{\rm air}$ is determined by the radiation wavelength. By approximation, for air with 80% N_2 and 20% O_2 at sea level and at 293 K, $\mu_{\rm air}$ = 0.01 cm^{-1} for Cu $K\alpha$ radiation. Air scatter and absorption increases with increasing wavelength. For example, $\mu_{\rm air}$ = 0.015 cm^{-1} for Co $K\alpha$ radiation and 0.032 cm^{-1} for Cr $K\alpha$ radiation. The absorption coefficient for Mo $K\alpha$ radiation, $\mu_{\rm air}$ = 0.001 cm^{-1}, is only one-tenth of that for Cu $K\alpha$ radiation, so an air-absorption correction is not necessary. Alternatively, the absorption correction may be normalized to the absorption level in the beam centre as

$$p_c(x, y) = p_o(x, y)\exp\left\{\mu_{\rm air}\left[(D^2 + x^2 + y^2)^{1/2} - D\right]\right\}. \quad (2.5.31)$$

In this normalized correction the attenuation by air scatter is not fully corrected for each pixel, but rather corrected to the same attenuation level as the pixel in the detector centre. This means that the effect of path-length differences between the detector centre pixel and other pixels are eliminated.

2.5.3.3.6. *Sample absorption*

The absorption of X-rays by the sample reduces the diffracted intensity. Many approaches are used to calculate and correct the absorption effect for various sample shapes and geometries [*International Tables for Crystallography* Volume C, Chapter 6.3 (Maslen, 1992); Ross, 1992; Pitschke *et al.*, 1996; Zuev, 2006]. The sample absorption can be measured by the transmission coefficient (also referred to as the absorption factor):

$$A = (1/V) \int_V \exp(-\mu\tau)\, \mathrm{d}V, \tag{2.5.32}$$

where A is the transmission coefficient, μ is the linear absorption coefficient and τ is the total beam path in the sample, which includes the incident-beam path and diffracted-beam path. Fig. 2.5.15(a) shows reflection-mode diffraction with a flat-plate sample. The thickness of the plate is t. z is the distance of the element dV from the sample surface. The normal to the reflection surface is **n**. The incident beam is represented by the unit vector $\mathbf{s}_o$ and the diffracted beam by the unit vector **s**. The transmission coefficient is given as (Maslen, 1992)

$$A = \frac{1 - \exp\{-\mu t[(1/\cos\eta) + (1/\cos\zeta)]\}}{\mu[(\cos\zeta/\cos\eta) + 1]}, \tag{2.5.33}$$

where η is the angle between the incident beam and the normal to the sample surface, and ζ is the angle between the diffracted beam and the sample normal. For two-dimensional X-ray diffraction, there is a single incident-beam direction at a time, but various diffracted-beam directions simultaneously, so

$$\cos\eta = \sin\omega\cos\psi \tag{2.5.34}$$

and

$$\cos\zeta = -\cos 2\theta \sin\omega\cos\psi - \sin 2\theta \sin\gamma\cos\omega\cos\psi - \sin 2\theta\cos\gamma\sin\psi. \tag{2.5.35}$$

The transmission coefficient from equation (2.5.33) contains a length unit, which creates ambiguity if such transmission coefficients are used to correct the intensity pixel-by-pixel. In order to make the relative intensity comparable to the results from Bragg–Brentano geometry, we introduce a new transmission coefficient, which is normalized by the transmission coefficient of the Bragg–Brentano geometry, $A_{\rm BB} = 1/(2\mu)$. This normalized transmission coefficient is also a numerical factor without units. The transmission coefficient with normalization will be denoted by T hereafter in this chapter. The transmission coefficient for reflection-mode diffraction with a flat sample of thickness t is then given as

$$T = A/A_{\rm BB} = \frac{2\cos\eta\big(1 - \exp\{-\mu t[(1/\cos\eta) + (1/\cos\zeta)]\}\big)}{\cos\eta + \cos\zeta}. \tag{2.5.36}$$

For a thick plate or material with a very high linear absorption coefficient, the transmission through the sample thickness is negligible and the above equation becomes

$$T = \frac{2\cos\eta}{\cos\eta + \cos\zeta}. \tag{2.5.37}$$

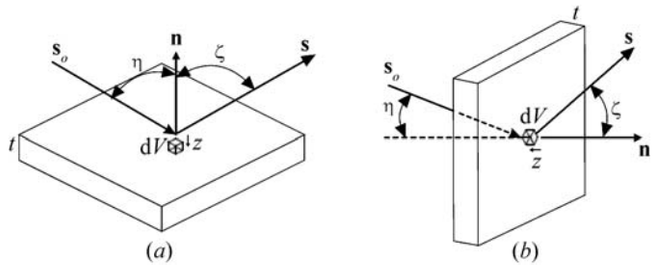

Figure 2.5.15
Absorption correction for a flat slab: (a) reflection; (b) transmission.

Fig. 2.5.15(b) shows transmission-mode diffraction with a flat-plate sample. The thickness of the plate is t. The normal to the reflection surface is represented by the unit vector **n**. The incident beam is represented by the unit vector $\mathbf{s}_o$ and the diffracted beam by the unit vector **s**. η is the angle between the incident beam and the normal of the sample surface, and ζ is the angle between the diffracted beam and the sample normal.

The transmission coefficient normalized by $A_{\rm BB} = 1/(2\mu)$ is given by (Maslen, 1992; Ross, 1992)

$$T = \frac{2\sec\eta[\exp(-\mu t\sec\eta) - \exp(-\mu t\sec\zeta)]}{\sec\zeta - \sec\eta} \quad \text{for } \sec\zeta \neq \sec\eta. \tag{2.5.38}$$

For two-dimensional X-ray diffraction in transmission mode

$$\cos\eta = \sin\omega\sin\psi\sin\varphi + \cos\omega\cos\varphi \tag{2.5.39}$$

and

$$\cos\zeta = (\sin\omega\sin\psi\sin\varphi + \cos\omega\cos\varphi)\cos 2\theta + (\cos\omega\sin\psi\sin\varphi - \sin\omega\cos\varphi)\sin 2\theta\sin\gamma - \cos\psi\sin\varphi\sin 2\theta\cos\gamma. \tag{2.5.40}$$

It is very common practice to set the incident angle perpendicular to the sample surface, *i.e.* $\eta = 0$. For most transmission-mode data collection, equation (2.5.40) becomes

$$T = \frac{2[\exp(-\mu t) - \exp(-\mu t\sec\zeta)]}{\sec\zeta - 1}. \tag{2.5.41}$$

When $\eta = \zeta$, both the numerator and denominator approach zero, and the transmission coefficient should be given by

$$T = 2\mu t\sec\zeta\exp(-\mu t\sec\zeta). \tag{2.5.42}$$

It is common practice to load the sample perpendicular to the incident X-ray beam at the goniometer angles $\omega = \psi = \varphi = 0$. Therefore, $\cos\eta = 1$ and $\cos\zeta = \cos 2\theta$, and the transmission coefficient becomes

$$T = \frac{2\cos 2\theta[\exp(-\mu t) - \exp(-\mu t/\cos 2\theta)]}{1 - \cos 2\theta}. \tag{2.5.43}$$

The maximum scattered intensity occurs when

$$t = \frac{\cos 2\theta\ln\cos 2\theta}{\mu(\cos 2\theta - 1)}. \tag{2.5.44}$$

This equation can be used to select the optimum sample thickness for transmission-mode diffraction. For example, if the measurement 2θ range is between 3 and 50°, the preferred sample thickness should be given by μt = 0.8–1.0.

references