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):

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

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 $\mathrm{d}V$ 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)

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

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

$$\cos\eta = \sin\omega\cos\psi \qquad (2.5.34)$$

and

$$\cos\zeta = -\cos 2\theta\sin\omega\cos\psi - \sin 2\theta\sin\gamma\cos\omega\cos\psi - \sin 2\theta\cos\gamma\sin\psi. \qquad (2.5.35)$$

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

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

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

$$T = \frac{2\cos\eta}{\cos\eta+\cos\zeta}. \qquad (2.5.37)$$

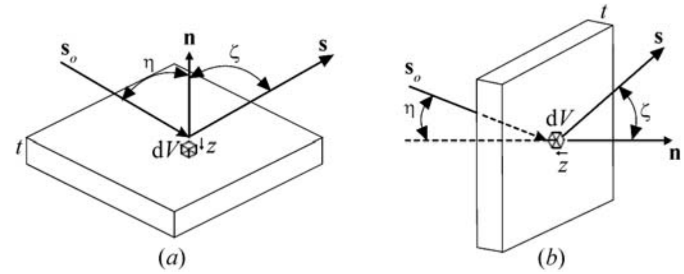

Figure 2.5.15
Absorption correction for a flat slab: (*a*) reflection; (*b*) transmission.

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)

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

For two-dimensional X-ray diffraction in transmission mode

$$\cos\eta = \sin\omega\sin\psi\sin\varphi + \cos\omega\cos\varphi \qquad (2.5.39)$$

and

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

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

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

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

$$T = 2\mu t\sec\zeta\exp(-\mu t\sec\zeta). \qquad (2.5.42)$$

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

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

The maximum scattered intensity occurs when

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

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.

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