3.1   Detector corrections

The measured scattering data needs to be corrected for any distortions introduced by the experimental setup, detector effects as well as a geometric correction accounting for the solid angle covered by each pixel.
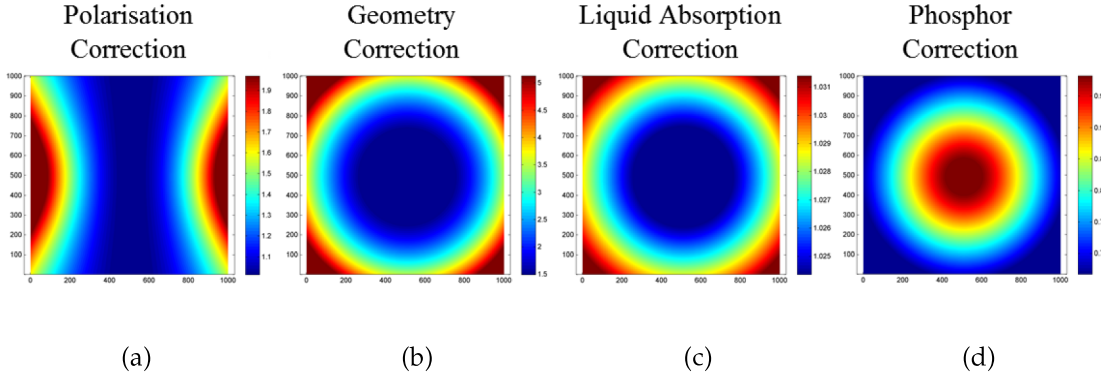

Polarisation Correction	Geometry Correction	Liquid Absorption Correction	Phosphor Correction
(a)	(b)	(c)	(d)

Figure 3.1: 2D Detector corrections needed at a synchrotron source (ID09b at ESRF)

The necessary corrections are applied after the dark and gain corrections have been accounted for. The full detector correction is given by:

$$I^{Corrected}_{pixel} = \frac{I^{measured}_{pixel} - Dark_{pixel}}{Gain_{pixel}} \cdot Corrections_{pixel} \tag{3.1}$$

where $Dark_{pixel}$ is the measured intensity with no incident photons and $Gain_{pixel}$ is the sensitivity of the pixels. All pixels can be treated simultaneously when all individual components are defined in a vector or array:

$$I^{Corrected} = \frac{I^{measured} - Dark}{Gain} \cdot Corrections \tag{3.2}$$

For an established beamline with a commercial detector, Dark and Gain are usually taken care of with a Dark and Flatfield measurement, yielding a partially corrected Image:

$$I^{measured}_{Dark,Gain} = \frac{I^{measured}_{pixel} - Dark_{pixel}}{Gain_{pixel}} \tag{3.3}$$

where $I^{measured}_{Dark,Gain}$ is the partially corrected images obtained from a calibrated detector e.g. the FRELON at ID09b and other commercial CCD detectors. These images still need the remaining detector corrections prior to analysis:

$$I^{Corrected} = I^{measured}_{Dark,Gain} \cdot Corrections \tag{3.4}$$

$$Corrections = C^{Polarisation} \cdot C^{Geometry} \cdot C^{Absorption} \cdot C^{Phosphor} \tag{3.5}$$

In the following the individual corrections are introduced.

X-ray polarisation - $C^{Polarisation}$

Scattering is dependent on the polarisation and is highest when the X-ray polarisation is perpendicular to the azimuthal angle to a given pixel and smallest at 90 degrees to the incoming beam along the direction of polarisation. This is why X-ray emission spectroscopy is ideally measured at this angle to avoid background scattering in the measured signal. The polarisation is given by the following equation from Hura et al. [22]:

$$C^{Polarisation} = P \left[1 - (sin(2\theta)sin(\phi))^2 \right] + (1 - P) \left[1 - (cos(2\theta)sin(\phi))^2 \right] \quad (3.6)$$

where P is the X-ray polarisation and θ and ϕ are the X-ray scattering angle and azimuthal angle respectively.

Pixel geometry - $C^{Geometry}$

The geometry correction accounts for the relative solid angle covered by the individual pixel projected onto a sphere. The projection can be divided into the relative area of a pixel $\frac{1}{cos(t\theta)^2}$ and the relative area facing the scattering source due to the angle of the pixel given by $\frac{1}{cos(t\theta)}$.

The geometry correction is given by the ratio of a normalised spherical angle covered by a pixel in the following equation from Bosecke et al. [23]:

$$C^{Geometry} = \frac{1}{cos(2\theta)^3} \quad (3.7)$$

The geometric correction increases at large angles and results in relatively poor signal to noise at high angles, even though the higher angles cover a larger number of pixels per spherical angle.

Sample absorption - $C^{Absorption}$

The scattered X-rays on a liquid sheet will have different path-lengths through the liquid. Given the X-ray transmission of the liquid the differences in path-length result in different transmissions. This has been solved analytically for a perpendicular "plate-like sample geometry" by Pauw et al. [24].

$$C^{Absorption} = \frac{\mu D - \mu D / cos(2\theta)}{exp(\mu D)[-exp(\mu D) + exp(\mu D / cos(2\theta))]} \quad (3.8)$$

where $C^{Absorption}$ is calculated for a perpendicular liquid sheet of thickness D and only accounts for different path-lengths through the sample and not for multiple scattering. This correction has a large effect with angles larger than 2θ and when the transmission through the sample is low.

In case of a non-perpendicular liquid sheet the correction gets complicated and divides the absorption into three cases: when the scattered radiation passes through the liquid sheet, parallel to the liquid sheet and returning out the back

of the liquid sheet. This problem can be solved numerically by finding positive and negative scattering angles with regards to the liquid sheet and bounding all scattering lengths with the liquid sheet parameters (width and thickness).

Phosphor correction - $C^{Phosphor}$

The phosphor correction corrects for the probability of absorption in a detection layer. The phosphor correction is exemplified by the phosphor layer in front of X-ray CCD's, converting hard X-ray to detectable visible photons, but can also be used to account for the detection probability in the detection layer of a detector when the probability is less than unity. This correction calculates the ratio between the detection probability in the direct beam and scattered intensities of a perpendicular detector, due to differing path-lengths in the detection layer of each pixel:

$$C^{Phosphor} = \frac{1 - exp^{(} - \mu \cdot D_p)}{1 - exp^{(} - \mu \cdot D_p / cos(2\theta))}$$

(3.9)

where D_p is the thickness of the detection layer.

3.2   Constructing scattering curves

The Debye equation assumes that the sample is rotationally isotropic, meaning that the scattering signal is isotropic along the azimuthal angle around the normal of the X-ray beam. Thus, after applying the corrections described in the previous chapter, the 2D images can be reduced to 1D scattering curves by azimuthal integration. This azimuthal integration collapses each 2D image into a 1D curve according to the scattering angle to each pixel $S(2\theta)$. With the relation between momentum transfer and scattering angle given by:

$$Q = \frac{4pi \cdot sin(\frac{2\theta}{2})}{\lambda}$$

(3.10)

where 2θ is the scattering angle and λ is the X-ray wavelength.

The scattering curves measured at ID09b at the ESRF for neat water where compared to the data published in [22] while developing reduction and analysis code, to verify the applied corrections.

The total X-ray scattering can be analysed to extract the sample structure as radial distribution functions, as done by Skinner et al. in a recent article studying neat water [25]. Since XDS is a global structural probe, a global description of the system is necessary to analyse the total scattering. For TR-XDS there are many other complication factors, so instead the data is converted into difference scattering curves, essentially cancelling out all static contributions.

Hence, when measuring TR-XDS difference scattering, static background effects can be neglected since they cancel out when taking the difference. It can however be beneficial to study the full or radially integrated images to identify and remove any sources to background, since they may fluctuate over time or increase the noise in specific regions.