Integrated Intensity:

In real diffraction experiments, it is often difficult to measure the true peak intensity because of instrumental resolution, among other things. Therefore often we use the integrated intensity, which is essentially the area under a diffraction curve.

In \((hkl)\) units, the integrated intensity is simply the peak of the interference function multiplied by its width:

\[
J_{hkl} = \left\lfloor \left\lfloor I(hkl) \right\rfloor dhdkdl = \left| F_H \right|^2 N^2 \cdot 1/N = \left| F_H \right|^2 \frac{V}{V_c}.
\]

The integrated intensities can take slightly different forms with different geometric factors, depending on how the integration is performed in a real experiment.

The basic integrated intensity is the one with respect to reciprocal space volume:

\[
J_0 = \left\lfloor \left\lfloor \left\lfloor I(hkl) \right\rfloor dV^* = \left\lfloor \left\lfloor \left\lfloor I(hkl) \right\rfloor \frac{1}{V_c} dhdkdl = \left| F_H \right|^2 \frac{V}{V_c^2}.
\]

Two commonly used integration methods are (1) rocking curve measurements and (2) powder diffraction method.

Rocking curve measurements: As shown below, the detector accepts a solid angle \(d\Omega\) plus rocking the specimen by \(d\theta\).

\[
J_0 = \left\lfloor \left\lfloor I(hkl) \right\rfloor d\theta d\Omega.
\]

\[
d\theta = \frac{dq_1}{H} = \frac{dq_1}{2k \sin\theta},
\]

\[
d\Omega = \frac{dq_2 dq_3}{k^2},
\]

Volume element, as shown at right, in reciprocal space is

\[
dV^* = dq_1 dq_2 dq_3 \cos\theta,
\]

thus:

\[
d\theta d\Omega = \frac{dq_1 dq_2 dq_3}{2k^3 \sin\theta} = dV^* \frac{\lambda^3}{\sin 2\theta}.
\]
Taking into account the polarization factor for an unpolarized incident beam: 
\[(1+\cos^2\theta)/2,\] we obtain the expression for integrated intensity in a rocking curve:

\[J_\theta = \int \int \int I(hkl) d\theta d\Omega = \int \int \int I(hkl) dV^* \cdot \lambda^3 \frac{1+\cos^2\theta}{2\sin2\theta} = \frac{\lambda^3 |F_H|^2}{\nu^2_c} V \left( \frac{1+\cos^2\theta}{2\sin2\theta} \right).\]

The factor in parenthesis is often called the **Lorentz-Polarization factor**.

**Powder diffraction**: A powder or polycrystalline specimen can be viewed as an extreme case of mosaic crystal with a mosaic spread of \(4\pi\) solid angle.

Integrated intensity of a complete powder diffraction ring is given by:

\[J_p = \frac{\lambda^3 |F_H|^2}{\nu^2_c} V \left( \frac{1+\cos^2\theta}{2\sin2\theta} \right).\]

However, if only a portion of the ring is measured with a detector with an out-of-plane acceptance width \(\Delta w\), then one needs to introduce an additional factor that depends on the size of the powder diffraction ring:

\[J_w = J_p \cdot \frac{\Delta w}{2\pi R \sin2\theta}.\]
In addition, we need to take into account the “degeneracy” of $\mathbf{H}$ reflection: e.g. for cubic structures, all $(100)$, $(010)$, $(0-10)$, $(001)$, $(00-1)$ reflections contribute to the $(100)$ powder ring intensity. For this purpose, we introduce a multiplicity factor $m_{hkl}$ and the integrated intensity for powder diffraction becomes:

$$J_w = \frac{\lambda^3 |F_H|^2 V}{\nu^2 V_c} \left(1 + \frac{\cos^2 2\theta}{2 \sin \theta}\right) \frac{1}{\sin 2\theta} \cdot m_{hkl} \propto \frac{\lambda^3 |F_H|^2 V}{\nu^2 V_c} \left(1 + \frac{\cos^2 2\theta}{\sin^2 \theta \cos \theta}\right) m_{hkl}.$$ 

**Temperature effects:**

So far we have ignored the effects due to atomic vibrations, and treating all atoms as stationary. We know this is not true.

When an atom thermally vibrates, it effectively displays a somewhat larger atomic size to x-rays, thus giving rise to an atomic scattering form factor that decreases more rapidly at higher momentum transfers $Q$. This can be understood with the basic Fourier transform properties.

The decrease in atomic form factor due to thermal vibrations is characterized by a Debye-Waller factor:

$$f \rightarrow f e^{-M}$$

$$I \propto f^2 e^{-2M}$$

where $M = 8\pi^2 \left(\frac{u^2}{\lambda}\right) \frac{\sin \theta}{\lambda^2}, \left\langle u^2 \right\rangle$ is the mean square vibrational amplitude of the atom. Typically $\left\langle u^2 \right\rangle$ is on the order of 0.1 Angstroms, so the Debye-Waller factor affects higher-order reflections more than the low-angle ones.

**Basic concepts in crystallography:**

- Measure integrated $I(hkl)$ for as many $(hkl)$’s as possible;
- Deduce magnitudes of structure factors $|F(hkl)|$, taking account of scaling factors.
Solve the phase problem \( \Rightarrow \) phase of \( F(hkl) \): this is a considerably difficult step for large structures since there is no general solution to the phase problem so far. Still an active area of current research;

Commonly used methods for phasing crystal structures are: auto-correlation function (Patterson map) and direct methods (based on math-statistical prediction of phases) for small molecules, and heavy-atom methods (based on anomalous dispersion of heavy-atoms in the structure) for macromolecules.

Produce an electron density map: \[ \rho(r) = \frac{1}{V_c} \sum_{\mathbf{H}} F_{\mathbf{H}} e^{-i\mathbf{H} \cdot \mathbf{r}}, \]

once the phases of \( F(hkl) \) are figured out.