The Debye-Waller Factor (after Kittel)

The structure factor $F$ has the term

$$f_j \exp(-i\vec{q} \cdot \vec{r}_j)$$

where $f_j$ is the form factor of the atom $j$ at a site described by $\vec{r}_j$, and $\vec{q}$ is the scattering wave vector ($|\vec{q}| = 2\pi/d$). Now in a real crystal, the atom $j$ is not precisely at the site described by $\vec{r}_j$, but rather, oscillating about some mean position so that we can write

$$\vec{r}_j(t) = \vec{r}_j + \vec{u}(t)$$

where $\vec{r}_j(t)$ describes the instantaneous position of the atom at time $t$, and $\vec{u}(t)$ is the displacement at that time. $\vec{r}_j$ is then the mean position of the atom, or the “frozen” position.

The thermal average of the structure factor is written using $\langle$quantity$\rangle$, so that the term in the structure factor expression becomes:

$$f_j \exp(-i\vec{q} \cdot \vec{r}_j) \langle \exp(-i\vec{q} \cdot \vec{u}) \rangle$$

we expand the term $\langle \exp(-i\vec{q} \cdot \vec{u}) \rangle$ as a series:

$$\langle \exp(-i\vec{q} \cdot \vec{u}) \rangle = 1 - i\langle \vec{q} \cdot \vec{u} \rangle - \frac{1}{2}\langle (\vec{q} \cdot \vec{u})^2 \rangle + \ldots$$

Now $\langle \vec{q} \cdot \vec{u} \rangle = 0$ since the displacements are uncorrelated and random. If we drop higher terms in the expansion, we have the term in the structure factor $\frac{1}{2}\langle (\vec{q} \cdot \vec{u})^2 \rangle$, which can be simplified:

$$\langle (\vec{q} \cdot \vec{u})^2 \rangle = q^2 \langle u^2 \rangle \langle \cos^2 \theta \rangle = \frac{1}{3} \langle u^2 \rangle q^2$$

The term $\frac{1}{3}$ arises by taking the geometrical average of $\cos^2 \theta$ over a sphere.

We now write:

$$\exp(-\frac{1}{6} \langle u^2 \rangle q^2) = 1 - \frac{1}{6} \langle u^2 \rangle q^2 + \ldots$$
It can be shown from comparing (4) and (6) that for a harmonic oscillator, all the individual terms in the two are identical. This means that the structure factor term is now:

$$f_j \exp(-i\vec{q} \cdot \vec{r}_j) \exp(-\frac{1}{6} \langle u^2 \rangle q^2)$$  \hspace{1cm} (7)

The intensity of the scattered radiation comes by squaring terms such as the one in equation (7):

$$I \sim f_j \exp(-i\vec{q} \cdot \vec{r}_j)f_j \exp(i\vec{q} \cdot \vec{r}_j) \exp(-\frac{1}{3} \langle u^2 \rangle q^2) = I_0 \exp(-\frac{1}{3} \langle u^2 \rangle q^2)$$  \hspace{1cm} (8)

Where $I_0$ is the intensity from a rigid lattice.

The intensity drop-off in x-ray diffraction with increasing $|\vec{q}| = 2\pi/d$ or $s = |\vec{q}|/4 = \frac{\sin \theta}{\lambda}$ therefore arises both from the drop in the form factor as well as the Debye-Waller factor.

In the case of neutron diffraction, the drop off is purely due to the Debye-Waller factor.

What causes the motion of the atom? There is both a phonon contribution that increases as temperature increases, as well as the quantum-mechanical zero-point motion.

There are other ways in which the Debye-Waller factor is presented. In crystallography, it is common to write:

$$f = f_0 \exp[-B(\frac{\sin \theta}{\lambda})^2]$$  \hspace{1cm} (9)

Where $B = 8\pi^2 U$ and has the units of Å$^2$. Here $U = \langle u^2 \rangle$, the mean-squared displacement of the atom with respect to its equilibrium position. $B$ is called the atomic temperature factor, and typical values are between 0.20 and 3.0 Å$^2$.

When written as above, the assumption is that the thermal parameter is isotropic, or spherical. In crystals, it is a tensor quantity, represented by the matrix:

$$U = \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ 0 & U_{22} & U_{23} \\ 0 & 0 & U_{33} \end{pmatrix}$$

Depending on site symmetry of the atom, some of the terms in the matrix can be redundant.

Experimentally determined thermal parameters can be used to plot so-called thermal ellipsoids. Here are some 50% probability ellipsoids from a protein crystal:
The Debye-Waller factor starts making its presence felt at high angles:

![Graph showing Debye-Waller factor vs. s]

The Lorentz correction (after Giacovazzo)

Diffraction arises when points in the reciprocal lattice are intersected by the Ewald sphere. In experiments, for different points in the reciprocal space, the time that the points spend satisfying the Bragg condition (crossing the Ewald sphere) is not constant across all the points. This requires a small correction to the intensity, usually a function of $2\theta$. In certain simple cases (meaning simple diffraction geometries):

$$L = \frac{1}{\sin 2\theta}$$
**The Polarization Correction after Giacovazzo**

X-rays incident on a crystal or powder in an x-ray experiment may or may not be polarized. The reflected X-rays, coming out from the crystal/powder are polarized however. This affects the intensity. If the radiation is not monochromatized (no crystal on the incident side), the polarization correction takes on the form:

\[
P = \frac{1}{2} (1 + \cos^2 2\theta)
\]

This is the simplest case, and is plotted below:

![Graph of polarization correction](image)

Usually, the Lorentz and Polarization corrections are grouped together as \(LP\), and the correction for intensity is:

\[
|F_{\text{relative}}| = \sqrt{\frac{I_{hkl}}{LP}}
\]

This follows Stout and Jensen.

**The Rietveld formula (after Giacovazzo)**

Powder x-ray diffraction data is step scanned to obtain a large number of observed intensities \(y_{io}\). The calculated intensities are:

\[
y_{ic} = s \sum_k LP_k |F_k|^2 G(\Delta\theta_{ik}) + y_{ib}
\]
where \( s \) is the scale factor, \( LP_k \) is the Lorentz-Polarization factor, \( F_k \) is the structure factor, and \( y_{ib} \) is the background intensity. \( \Delta \theta_{ik} = 2\theta_i - 2\theta_k \) where \( 2\theta_k \) is the scattering angle where the Bragg condition is fulfilled (corrected for instrumental errors), and \( 2\theta_i \) represents neighboring regions. \( G(\Delta \theta_{ik}) \) is then the profile function.

The profile function given by Caglioti requires three parameters, \( u, v \) and \( w \):

\[
\Gamma(\theta) = \sqrt{u \tan^2(\theta/2) + v \tan(\theta/2) + w}
\]

Where \( \Gamma(\theta) \) is the FWHM.

For a pseudo-Voigt peakshape (Gaussian + Lorentzian), the intensity looks like:

\[
I_{PV}(\theta_1; \theta_2 - \theta_1) = \frac{2\sigma\Gamma(\theta_1)}{\pi[\Gamma(\theta_1)^2 + 4(\theta_1 - \theta_2)^2]} + (1 - \sigma)\sqrt{\frac{4\ln(2)}{\pi\Gamma(\theta_1)^2}} \exp \left( -\frac{4\ln(2)(\theta_1 - \theta_2)^2}{\Gamma(\theta_1)^2} \right)
\]

The structural model (reflected in \( F_{hkl} \) is improved until the fit is good. The factor that is minimized is the residual:

\[
S = \sum w_i |y_{io} - y_{ic}|^2
\]

where \( w_i \) is some suitable weighting.

**Anomalous scattering (after Giacovazzvo)**

Electrons are quantum creatures that can be considered as natural oscillators. The idea that x-rays scatter off electron density like the atoms were points is accurate only if there is no resonance consition between the x-ray and the quantum states of electron. This is not always true. The correct expression for the atomic form factor is:

\[
f = f_a + \Delta f' + f''
\]

where \( \Delta f' \) and \( f'' \) are called the real and imaginary dispersion corrections. Please see the handout.