1 Derivation of scattering intensities for different types of disorder

1.1 The ideal lattice

The intensity of scattered X-rays as a function of the wave vector, $\vec{q}$, from an ideal lattice can be described by:

$$I(\vec{q}) = |\sum_{n=1}^{N} f(\vec{q}) e^{i\vec{q}\cdot\vec{r_n}}|^2 \tag{1}$$

where $\vec{r_n}$ is a unit lattice vector: $\vec{r_n} = \vec{r_o} + h\vec{r_x} + k\vec{r_y} + l\vec{r_z}$, with h, k, and l corresponding to the unit cell dimensions. The vector $\vec{r_o}$ can be taken to be the origin without any loss of generality. In one dimension, the above can be simplified to:

$$I(\vec{q}) = |f(\vec{q})|^2 |\sum_{h} e^{ih\theta}|^2 \tag{2}$$

by rewriting the dot product as an angle, $\theta = \vec{q}\cdot\vec{r_x}$, where θ is real and h is an integer. Consider the following two cases: when $\theta = 2\pi$, the exponential term is unity and there is constructive interference that scales with the number of unit cells, N. When $\theta \neq 2\pi$, the exponent averages to 0, resulting in zero intensity due to destructive interference.

1.2 Lattice with translational disorder

Assume that each unit cell is displaced from its mean lattice position, and that these displacements sample an independent and identically distributed (i.i.d.) Gaussian. In this case, a displacement term is added to the unit lattice vector: $\vec{r_h} = h\vec{r_x} + \vec{\Delta_h}$. The intensity of scattered X-rays is:

$$\begin{aligned} I(\vec{q}) = |\sum_{n=1}^{N} f(\vec{q}) e^{i\vec{q}\cdot(h\vec{r_x}+\vec{\Delta_h})}|^2 &= |f(\vec{q})|^2 \sum_{h} e^{i\vec{q}\cdot(h\vec{r_x}+\vec{\Delta_h})} \sum_{h'} e^{-i\vec{q}\cdot(h'\vec{r_x}+\vec{\Delta_{h'}})} \\ &= |f(\vec{q})|^2 \sum_{h}\sum_{h'} e^{i\vec{q}\cdot\vec{r_x}(h-h')+i\vec{q}\cdot(\vec{\Delta_h}-\vec{\Delta_{h'}})} \\ &= |f(\vec{q})|^2 [\sum_{h} e^0 + \sum_{h}\sum_{h',h'\neq h} e^{i\vec{q}\cdot\vec{r_x}(h-h')+i\vec{q}\cdot(\vec{\Delta_h}-\vec{\Delta_{h'}})}] \end{aligned}$$

Because $\vec{\Delta_h}$ and $\vec{\Delta_{h'}}$ are i.i.d. Gaussians with means of zero, their difference is also an i.i.d. Gaussian with a mean of zero and standard deviation of $2\sigma^2$: $\vec{\Delta_{h,h'}} \sim N(0,\sigma^2)$, and $G_{h-h'} = (\vec{\Delta_h} - \vec{\Delta_{h'}}) \sim N(0, 2\sigma^2)$. Note that the characteristic function, $\phi(t)$, of a random variable is the Fourier transform of its probability density function. In the case of a normal distribution, the characteristic function evaluates to:

$$\phi(t) = \int p(t) e^{it\cdot x} = e^{i\mu t} \cdot e^{\frac{-1}{2}\sigma^2 h^2} \tag{3}$$

The above, along with substitution of $\vec{q}\cdot\vec{r_x} = \theta$, can then be used to simplify the equation for the scattered intensity as follows:

$$\begin{aligned} I(\vec{q}) = |f(\vec{q})|^2 [N + \sum_{h}\sum_{h',h'\neq h} e^{i\vec{q}\cdot\vec{r_x}(h-h')+i\vec{q}G_{hh'}}] &= |f(\vec{q})|^2 [N + \sum_{h}\sum_{h',h'\neq h} e^{ih\theta} \int p(G_{hh'}) e^{i\vec{q}G_{hh'}} dG_{hh'}] \\ &= |f(\vec{q})|^2 [N + \sum_{h}\sum_{h',h'\neq h} e^{ih\theta} e^{-\sigma^2\vec{q}^2}] = |f(\vec{q})|^2 [N + e^{-\sigma^2\vec{q}^2} \sum_{h}\sum_{h',h'\neq h} e^{ih\theta}] \\ &= |f(\vec{q})|^2 [N(1 - e^{-\sigma^2\vec{q}^2}) + e^{-\sigma^2\vec{q}^2} \sum_{h}\sum_{h'} e^{ih\theta}] \end{aligned}$$

The first term corresponds to the Fourier transform of a single unit cell and does not contain phase information. The second term is the Bragg component and scales with N^2 due to the double sum, in contrast to the first term which scales with N, so dominates at $\theta = 2\pi$ conditions. It is modulated by the $e^{-\sigma^2\vec{q}^2}$ term, which diminishes the Bragg intensities with increasing resolution and displacement.

1.3 Lattice with configurational disorder

Assume that each atom is displaced from its mean position. The intensity of a single unit cell can be expressed as:

$$I_{cell}(\vec{q}) = \langle |\sum_k f_k(\vec{q}) e^{i\vec{q}\cdot\vec{r_k}}|^2 \rangle \tag{4}$$

where f_k is the atomic form factor and $\vec{r_k} = \vec{\mu_k} + \vec{\delta_k}$. Expanding the above,

$$I_{cell}(\vec{q}) = \sum_k f_k(\vec{q}) e^{i\vec{q}\cdot(\vec{r_k}+\vec{\delta_k})} \sum_{k'} f_{k'}(\vec{q}) e^{-i\vec{q}\cdot(\vec{r_{k'}}+\vec{\delta_{k'}})} = \sum_k \sum_{k'} f_k f_{k'} e^{i\vec{q}[(\vec{r_k}-\vec{r_{k'}})+(\vec{\delta_k}-\vec{\delta_{k'}})]} \tag{5}$$

Let $x_0 = \vec{r_k} - \vec{r_k'}$, $x = \vec{\delta_k} - \vec{\delta_{k'}}$, and P(x) be a multivariate Gaussian model for the atomic positional probabilities. Then the exponential term becomes:

$$\int dx P(x) e^{i\vec{q^T}(\vec{x_0}+\vec{x})} = e^{i\vec{q^T}x_0} \int dx \frac{e^{\frac{-1}{2}\vec{x^T}V^{-1}\vec{x}} \cdot e^{i\vec{q^T}\vec{x}}}{\int dx e^{\frac{1}{2}\vec{x^T}V^{-1}\vec{x}}} = e^{i\vec{q^T}\vec{x_0}} \cdot Z^{-1} \int \frac{dx \cdot e^{\frac{-1}{2}\vec{x^T}V^{-1}\vec{x}+i\vec{q^T}\vec{x}}}{Z^{-1} \cdot e^{-\frac{1}{2}\vec{q^T}V\vec{q}}} \tag{6}$$

where $Z = \int dx e^{\frac{1}{2}x^T v x}$ is a normalization constant integrated over all of q-space. Because $x^T v$ is symmetric and positive matrix, the expression in the integrand can be simplified to $e^{-\frac{1}{2}\vec{q^T}V_{kk'}\vec{q}}$, where $V_{kk'} = \langle \vec{x}\vec{x^T} \rangle$, by the definition of an n-dimensional Gaussian integral. Thus,

$$I_{ensemble}(\vec{q}) = \sum_k \sum_{k'} f_k f_{k'} e^{i\vec{q}(\vec{r_k}-\vec{r_{k'}})} e^{-\frac{1}{2}\vec{q^T}V_{kk'}\vec{q}} \tag{7}$$

$V_{kk'}$ is the interatomic displacement covariance matrix between atoms k and k':

$$V_{kk'} = \langle (\delta_k - \delta_k'^T)(\delta_k - \delta_k'^T) \rangle = \langle \delta_k \delta_k^T \rangle + \langle \delta_k' \delta_k'^T \rangle - 2\langle \delta_k \delta_k'^T \rangle \tag{8}$$

where each term in the expansion is a 3 x 3 symmetric covariance matrix of interatomic displacements. Thus, $I(q)$ can be rewritten as follows:

$$I_{ensemble}(\vec{q}) = \sum_k \sum_{k'} f_k e^{-W_k} f_{k'} e^{-W_k'} e^{i\vec{q}(\vec{r_k}-\vec{r_{k'}})} e^{\vec{q^T}\langle \delta_k \delta_k'^T \rangle \vec{q}} \tag{9}$$

where $W_k = \frac{1}{2}\vec{q^T}\langle \delta_k \delta_k^T \rangle \vec{q}$ is the Debye-Waller factor.

In the case of a model that only has sufficient resolution to account for isotropic disorder, eq. 7 can be rewritten by relating $C_{kk'}$, the N x N correlation matrix (where N is the number of atoms) to anisotropic displacement covariance matrix, V as follows:

$$C_{kk'} = \frac{Tr(\langle \delta_k \delta_k'^T \rangle)}{(Tr(\langle \delta_k \delta_k^T \rangle) Tr(\langle \delta_k' \delta_k'^T \rangle))^{\frac{1}{2}}} = \frac{\langle \delta_k \delta_{k'}^T \rangle}{B_k^{\frac{1}{2}} B_{k'}^{\frac{1}{2}}} \tag{10}$$

where $B_k = \langle \delta_k \delta_k^T \rangle$, and thus related to the B-factor. Then,

$$I_{ensemble}(\vec{q}) = \sum_k \sum_{k'} f_k f_{k'} e^{i\vec{q}(\vec{r_k}-\vec{r_{k'}})} e^{-\frac{1}{2}\vec{q}^2(B_k+B_{k'}-2C_{kk'}(B_k B_{k'})^{\frac{1}{2}})} \tag{11}$$