Consider the scattering of x-rays from a crystal in the far-field. A general form of the scattered intensity, I, at some wavevector $\mathbf{q}$ in reciprocal space is:

$$I(\mathbf{q}) = \left| \sum_c e^{-i\mathbf{q}\cdot\mathbf{u_c}} \sum_i f_i e^{-i\mathbf{q}\cdot\mathbf{r}_i} e^{-i\mathbf{q}\cdot\boldsymbol{\delta}_{c_i}} \right|^2 \tag{1}$$

where $\mathbf{u_c}$ is the vector from the origin of the coordinate system to the origin of unit cell c, f_i is the atomic form factor of atom i, r_i is the vector that describes the mean position of atom i relative to origin of the unit cell, and $\boldsymbol{\delta}_{c_i}(t)$ is the instantaneous displacement vector of atom i in unit cell c.

Adopting the compact notation $x_{ij} = x_i - x_j$ for $\mathbf{u}$, $\mathbf{r}$, and $\boldsymbol{\delta}$, we may write the time (or, equivalently, ensemble) averaged scattering

$$\langle I(\mathbf{q}) \rangle = \left\langle \sum_{c,d} e^{-i\mathbf{q}\cdot\mathbf{u}_{cd}} \sum_{i,j} f_i f_j e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} e^{-i\mathbf{q}\cdot\boldsymbol{\delta}_{c_i d_j}} \right\rangle \tag{2}$$

We make three critical assumptions about the structure of the statistical ensemble of atomic displacements $\boldsymbol{\delta}$:

1. The correlation range of atomic displacements is small with respect to the size of the crystal. Equivalently, the correlation between atomic displacements in different unit cells are independent,

   $$\langle \boldsymbol{\delta}_{c_i}^T \boldsymbol{\delta}_{d_j} \rangle = \mathbf{0} \text{ if } c \neq d$$

   and therefore we may write the displacements simply using their atomic index, for instance δ_i. Note that if correlations exist between what might traditionally be considered a minimal unit cell, and one wishes to consider these correlations, it is possible to simply define a larger unit cell that encompasses the entire correlated region.

2. Atoms in different unit cells behave identically in a statistical fashion, so $p(\boldsymbol{\delta}_{ci}) = p(\boldsymbol{\delta}_{di})$ for all i.

3. The atom displacements may be described by a pairwise multivariate normal distribution, with zero mean and covariance matrix $V_{ij} = \langle \boldsymbol{\delta}_i^T \boldsymbol{\delta}_j \rangle \in \mathcal{R}^{3\times 3}$

   $$p(\boldsymbol{\delta}_i, \boldsymbol{\delta}_j) \sim \text{MVN}(\mathbf{0}, V_{ij})$$

   this is the simplest model that takes into account anisotropic correlations between atoms.

We may re-write eq. 2 as

$$\langle I(\mathbf{q}) \rangle = \sum_{c,d} e^{-i\mathbf{q}\cdot\mathbf{u}_{cd}} \sum_{i,j} f_i f_j e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} \iint p(\boldsymbol{\delta}_{c_i}, \boldsymbol{\delta}_{d_j}) e^{-i\mathbf{q}\cdot(\boldsymbol{\delta}_{c_i} - \boldsymbol{\delta}_{d_j})} d\boldsymbol{\delta}_{c_i}\, d\boldsymbol{\delta}_{d_j} \tag{3}$$

in appendix A1 we show

$$\iint p(\boldsymbol{\delta}_{c_i}, \boldsymbol{\delta}_{d_j}) e^{-i\mathbf{q}\cdot(\boldsymbol{\delta}_{c_i} - \boldsymbol{\delta}_{d_j})} d\boldsymbol{\delta}_{c_i}\, d\boldsymbol{\delta}_{d_j} = \exp\left\{ -\frac{1}{2}\mathbf{q}^T V_{c_i c_i}\mathbf{q} - \frac{1}{2}\mathbf{q}^T V_{d_j d_j}\mathbf{q} + \mathbf{q}^T V_{c_i d_j}\mathbf{q} \right\} \tag{4}$$

under our assumptions, $V_{c_i d_j} = \mathbf{0}$ if $c \neq d$, and $V_{c_i c_i}$ is identical for all c, such that we may write $V_{c_i c_i} = V_{ii}$ (and similarly $V_{d_j d_j} = V_{jj}$). Thus, it is natural to split eq. 2 into two parts – one expressing interference *between* unit cells (where $V_{c_i d_j} = \mathbf{0}$), and one expressing interference *within* repeats of a single cell,

$$\langle I(\mathbf{q}) \rangle = \sum_{c,d\neq c} e^{-i\mathbf{q}\cdot\mathbf{u}_{cd}} \sum_{i,j} f_i f_j e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} e^{-\frac{1}{2}\mathbf{q}^T V_{ii}\mathbf{q} - \frac{1}{2}\mathbf{q}^T V_{jj}\mathbf{q}} \tag{5}$$

$$+ N \sum_{i,j} f_i f_j e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} e^{-\frac{1}{2}\mathbf{q}^T V_{ii}\mathbf{q} - \frac{1}{2}\mathbf{q}^T V_{jj}\mathbf{q} + \mathbf{q}^T V_{ij}\mathbf{q}} \tag{6}$$

$$= \sum_{c,d} e^{-i\mathbf{q}\cdot\mathbf{u}_{cd}} \sum_{i,j} f_i f_j e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} e^{-\frac{1}{2}\mathbf{q}^T V_{ii}\mathbf{q} - \frac{1}{2}\mathbf{q}^T V_{jj}\mathbf{q}} \tag{7}$$

$$+ N \sum_{i,j} f_i f_j e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} e^{-\frac{1}{2}\mathbf{q}^T V_{ii}\mathbf{q} - \frac{1}{2}\mathbf{q}^T V_{jj}\mathbf{q}} \left[e^{\mathbf{q}^T V_{ij}\mathbf{q}} - 1 \right] \tag{8}$$

with N being the number of unit cells. [Note: I may be missing a normalizing factor].

The astute reader will notice the first term as the traditional crystallographic scattering

$$I(\mathbf{q})_{\text{Bragg}} = \sum_{c,d} e^{-i\mathbf{q}\cdot\mathbf{u}_{cd}} \sum_{i,j} f_i f_j e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} e^{-\frac{1}{2}\mathbf{q}^T V_{ii}\mathbf{q} - \frac{1}{2}\mathbf{q}^T V_{jj}\mathbf{q}} \tag{9}$$

$$= \left| \left(\sum_c e^{-i\mathbf{q}\cdot\mathbf{u}_c} \right) \left(\sum_i f_i e^{-i\mathbf{q}\cdot\mathbf{r}_i} e^{-\frac{1}{2}\mathbf{q}^T V_{ii}\mathbf{q}} \right) \right|^2 \tag{10}$$

$$= |S(\mathbf{q})|^2 |F(\mathbf{q})|^2 \tag{11}$$

where V_{ii} is an anisotropic B-factor (also called the Debye Waller factor). $|S(\mathbf{q})|^2$ becomes a Dirac comb as the number of unit cells grows, showing this scattering is localized to discrete regions of $\mathbf{q}$.

The remaining scattering $\langle I(\mathbf{q})\rangle - I(\mathbf{q})_{\text{Bragg}}$ is typically termed the diffuse scattering

$$I_{\text{diffuse}}(\mathbf{q}) = N \sum_{i,j} f_i f_j e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} e^{-\frac{1}{2}\mathbf{q}^T V_{ii}\mathbf{q} - \frac{1}{2}\mathbf{q}^T V_{jj}\mathbf{q}} \left[e^{\mathbf{q}^T V_{ij}\mathbf{q}} - 1 \right]$$

There are two notable features of the diffuse scattering. First, lacking the lattice transform $|S(\mathbf{q})|^2$ it is *not* localized in reciprocal space. Second, it is non-trivial only if there is correlated displacements between the atoms $V_{ij} \neq \mathbf{0}$.

1 Diffuse Scatter in Special Cases

1.1 No Cross-Correlation

In the case V_{ij} is $\mathbf{0}$ for all $\{i, j\}$, then all $i \neq j$ terms vanish, and

$$I_{\text{diffuse}}(\mathbf{q}) = N \sum_i f_i^2 \left[1 - e^{-\mathbf{q}^T V_{ii}\mathbf{q}} \right]$$

just a relatively unstructured background remains, proportional to the anisotropic B-factors. Note anisotropy is still possible if the individual atomic displacements are highly anisotropic. The diffuse scatter will, however, lack the "speckle" features that normally distinguish it from background scattering.

1.2 Rigid Bodies

1.3 Isotropic Real Space Correlation Length

2 Appendix A1

We prove

$$\iint p(\boldsymbol{\delta}_{c_i}, \boldsymbol{\delta}_{d_j}) e^{-i\mathbf{q}\cdot(\boldsymbol{\delta}_{c_i} - \boldsymbol{\delta}_{d_j})} d\boldsymbol{\delta}_{c_i}\, d\boldsymbol{\delta}_{d_j} = \exp\left\{ -\frac{1}{2}\mathbf{q}^T V_{c_i c_i}\mathbf{q} - \frac{1}{2}\mathbf{q}^T V_{d_j d_j}\mathbf{q} + \mathbf{q}^T V_{c_i d_j}\mathbf{q} \right\} \tag{12}$$