

Supplementary Information for: Periodic Lattices of Arbitrary Nano-objects: Modeling and Applications for Self-Assembled Systems

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Appendix A Derivation of Lattice Factor

In order to see how the lattice factor (a sum over hkl Miller indices) arises from the sum over unit cells, consider a crystal shaped like a parallelepiped with edge-lengths N_1a , N_2b , and N_3c , where \mathbf{a} , \mathbf{b} , and \mathbf{c} are the vectors that define the unit cell. Note that selecting a parallelepiped simplifies the exposition, but the sequence of arguments would be the same for any crystal shape or unit cell shape. Starting from Equation 6 in the main text, the intensity is converted into a sum over the three dimensions of the crystal:

$$I(\mathbf{q}) = \left| \mathcal{U}(\mathbf{q}) \sum_{n_1=1}^{N_1} e^{i\mathbf{q}\cdot n_1\mathbf{a}} \sum_{n_2=1}^{N_2} e^{i\mathbf{q}\cdot n_2\mathbf{b}} \sum_{n_3=1}^{N_3} e^{i\mathbf{q}\cdot n_3\mathbf{c}} \right|^2 \quad (1)$$

Each summation takes the form of a geometric progression. Re-indexing to start from zero, we obtain:

$$\sum_{n_1=0}^{N_1-1} e^{i\mathbf{q}\cdot n_1\mathbf{a}} = 1 + (e^{i\mathbf{q}\cdot\mathbf{a}})^1 + (e^{i\mathbf{q}\cdot\mathbf{a}})^2 + \dots + (e^{i\mathbf{q}\cdot\mathbf{a}})^{N_1} \quad (2)$$

$$= \frac{1 - (e^{i\mathbf{q}\cdot\mathbf{a}})^{N_1}}{1 - (e^{i\mathbf{q}\cdot\mathbf{a}})}$$

Each sum is multiplied by its complex conjugate, resulting in terms like:

$$\begin{aligned} \left| \sum_{n_1=0}^{N_1-1} e^{i\mathbf{q}\cdot n_1\mathbf{a}} \right|^2 &= \left(\frac{1 - (e^{i\mathbf{q}\cdot\mathbf{a}})^{N_1}}{1 - (e^{i\mathbf{q}\cdot\mathbf{a}})} \right) \left(\frac{1 - (e^{-i\mathbf{q}\cdot\mathbf{a}})^{N_1}}{1 - (e^{-i\mathbf{q}\cdot\mathbf{a}})} \right) \\ &= \frac{1 - e^{-i\mathbf{q}\cdot\mathbf{a}N_1} - e^{+i\mathbf{q}\cdot\mathbf{a}N_1} + e^0}{1 - e^{-i\mathbf{q}\cdot\mathbf{a}} - e^{+i\mathbf{q}\cdot\mathbf{a}} + e^0} \\ &= \frac{2 - 2\cos(\mathbf{q}\cdot\mathbf{a}N_1)}{2 - 2\cos(\mathbf{q}\cdot\mathbf{a})} \\ &= \frac{\sin^2(\mathbf{q}\cdot\mathbf{a}N_1/2)}{\sin^2(\mathbf{q}\cdot\mathbf{a}/2)} \end{aligned} \quad (3)$$

Combining the results:

$$\begin{aligned} I(\mathbf{q}) &= |\mathcal{U}(\mathbf{q})|^2 \frac{\sin^2(\mathbf{q}\cdot\mathbf{a}N_1/2)}{\sin^2(\mathbf{q}\cdot\mathbf{a}/2)} \frac{\sin^2(\mathbf{q}\cdot\mathbf{b}N_2/2)}{\sin^2(\mathbf{q}\cdot\mathbf{b}/2)} \frac{\sin^2(\mathbf{q}\cdot\mathbf{c}N_3/2)}{\sin^2(\mathbf{q}\cdot\mathbf{c}/2)} \\ &= |\mathcal{U}(\mathbf{q})|^2 L_s(\mathbf{q}\cdot\mathbf{a}, N_1)L_s(\mathbf{q}\cdot\mathbf{b}, N_2)L_s(\mathbf{q}\cdot\mathbf{c}, N_3) \end{aligned} \quad (4)$$

The function:

$$L_s(x, N) = \frac{\sin^2(Nx/2)}{\sin^2(x/2)} \quad (5)$$

defines a peak when $x = 2\pi$ (or multiple thereof). The width of the peak is controlled by N : for small values of N , the peak is broad. As N increases, the peak becomes narrower, in the limit approaching a delta function. Physically, this corresponds to the constructive interference between the unit cells of the crystal: as more cells interfere constructively, the reciprocal-space peak becomes sharper. Although the function has oscillations beyond the central lobe, these are usually ignored and the peak-shape, L , described using a Gaussian or Lorentzian. The width of the peak function is then converted into a correlation length (which can frequently be interpreted as an average crystal grain size) using a Debye-Scherrer analysis (Langford & Wilson, 1978; Smilgies, 2009). Note that N in L_s controls the peak height, and we thus extract it as a prefactor while converting to the normalized peak shape L . In order to re-introduce

the periodicity, in reciprocal space, of the peak function L_s , we note that L_s has maxima when the following relations are satisfied:

$$\begin{aligned}\mathbf{q} \cdot \mathbf{a} &= 2\pi h \\ \mathbf{q} \cdot \mathbf{b} &= 2\pi k \\ \mathbf{q} \cdot \mathbf{c} &= 2\pi l\end{aligned}\tag{6}$$

Where h , k , and l are integers. We define reciprocal-space vectors:

$$\mathbf{u} = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}\tag{7}$$

$$\mathbf{v} = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}\tag{8}$$

$$\mathbf{w} = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}\tag{9}$$

and consider \mathbf{q} expressed in terms of these reciprocal vectors:

$$\mathbf{q} = (\mathbf{q} \cdot \mathbf{a})\mathbf{u} + (\mathbf{q} \cdot \mathbf{b})\mathbf{v} + (\mathbf{q} \cdot \mathbf{c})\mathbf{w}\tag{10}$$

Combining with the three Laue equations (6) yields:

$$\begin{aligned}\mathbf{q}_{hkl} &= (2\pi h)\mathbf{u} + (2\pi k)\mathbf{v} + (2\pi l)\mathbf{w} \\ &= 2\pi(h\mathbf{u} + k\mathbf{v} + l\mathbf{w}) \\ &= 2\pi\mathbf{H}_{hkl}\end{aligned}\tag{11}$$

Where \mathbf{H}_{hkl} is a vector that defines the position of Bragg reflection hkl for the reciprocal-lattice. Now that we are considering only the positions where scattering appears in reciprocal-space, we can convert the intensity to a sum over the reciprocal-space positions of the peaks.

$$I(\mathbf{q}) = N_1 N_2 N_3 \sum_{\{hkl\}} |\mathcal{U}(\mathbf{q}_{hkl})|^2 L(\mathbf{q} - \mathbf{q}_{hkl})\tag{12}$$

Where the $\{hkl\}$ denotes the indices of the reciprocal-space lattice. This allows us to generalize to an arbitrary lattice type. The effect of lattice symmetry is to define the

positions of the reciprocal-space peaks via the $\{hkl\}$ indices and the corresponding rules for \mathbf{q}_{hkl} . For powder-like samples, the beam probes grains at all possible orientations. The observed scattering then depends only on the magnitude of q . We thus introduce an orientation average, denoted by angled brackets (with subscript o):

$$\begin{aligned}
 I(q) &= \langle I(\mathbf{q}) \rangle_o \\
 &= \left\langle N_n \sum_{\{hkl\}}^{m_{hkl}} |\mathcal{U}(\mathbf{q}_{hkl})|^2 L(\mathbf{q} - \mathbf{q}_{hkl}) \right\rangle_o \\
 &= \frac{N_n}{\Omega q^{d-1}} \sum_{\{hkl\}}^{m_{hkl}} |\mathcal{U}(\mathbf{q}_{hkl})|^2 L(q - q_{hkl})
 \end{aligned} \tag{13}$$

Where Ωq^{d-1} is a Lorentz factor accounting for the orientational averaging (Ω is a solid angle, and d is dimensionality). Generally we consider three-dimensional lattices, and an isotropic (spherically symmetric) orientational average, wherein $d = 3$ and $\Omega = 4\pi$. This can be intuitively understood by considering the surface area of spherical averaging, in reciprocal space. The scattering intensity from lattice peaks at a particular q will be spread out over an area $\int_0^{2\pi} \int_0^\pi q^2 \sin \theta d\theta d\phi = 4\pi q^2$, and we thus divide the sum of peak intensities by that area. Different orientational symmetries can give rise to different correction factors. Finally, we express position within the unit cell in terms of our new reciprocal-space definitions, by defining fractional coordinates x_j , y_j , and z_j , for the three axes of the unit cell:

$$\mathbf{r}_j = x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c} \tag{14}$$

Such that:

$$\begin{aligned}
 \mathbf{q}_{hkl} \cdot \mathbf{r}_j &= 2\pi(h\mathbf{u} + k\mathbf{v} + l\mathbf{w}) \cdot (x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c}) \\
 &= 2\pi(hx_j + ky_j + lz_j)
 \end{aligned} \tag{15}$$

Which leads to the following expression for the intensity (and the definition of the

lattice factor shown in equation 7 of the main text):

$$I(q) = \frac{N_n}{\Omega q^{d-1}} \sum_{\{hkl\}}^{m_{hkl}} \left| \sum_{j=1}^{N_j} F_j(\mathbf{q}_{hkl}) e^{2\pi i(x_j h + y_j k + z_j l)} \right|^2 L(q - q_{hkl}) \quad (16)$$

Appendix B Generalized Peak Shape Function

We describe here the peak-shape function introduced in the literature to allow for a generalized shape that can mix Gaussian and Lorentzian character (Micha, 1998; Forster et al., 2005). The defining equation is:

$$L_{hkl}(q) = \frac{2}{\pi\delta} \prod_{n=0}^{\infty} \left(1 + \frac{\gamma_\nu^2}{(n + \nu/2)^2} \frac{4q_s^2}{\pi^2\delta^2} \right)^{-1} \quad (17)$$

$$= \frac{2}{\pi\delta} \left| \frac{\Gamma[\nu/2 + i\gamma_\nu(4q_s^2/\pi^2\delta^2)]}{\Gamma[\nu/2]} \right|^2 \quad (18)$$

Where $q_s = (q - q_{hkl})$, δ describes the peak width, and ν describes the peak shape. The function is normalized ($\int_{-\infty}^{+\infty} L_{hkl}(q) dq = 1$). The parameter γ_ν is a ratio of gamma functions:

$$\gamma_\nu = \sqrt{\pi} \frac{\Gamma[(\nu + 1)/2]}{\Gamma[\nu/2]} \quad (19)$$

The limiting cases for peak shape are:

$$L_{hkl}(q_s) = \begin{cases} \frac{\delta/2\pi}{q_s^2 + (\delta/2)^2} & \text{for } \nu \rightarrow 0 \quad (\text{Lorentzian}) \\ \frac{2}{\pi\delta} \exp\left[-\frac{4q_s^2}{\pi\delta^2}\right] & \text{for } \nu \rightarrow \infty \quad (\text{Gaussian}) \end{cases} \quad (20)$$

Thus the parameter ν allows one to vary continuously between a Lorentzian peak shape and a Gaussian peak shape. For $\nu > 200$, a pure Gaussian becomes an acceptable approximation, and for $\nu < 0.005$, a simple Lorentzian can be used. The peak width parameter, δ , in the Lorentzian limit is simply the full-width at half-maximum (FWHM): $\delta_{\text{lorentz}} = \text{FWHM}_{\text{lorentz}}$. In the Gaussian limit, δ is related to the standard deviation (σ) as:

$$\delta_{\text{gauss}} = \sqrt{\frac{8}{\pi}} \sigma_{\text{gauss}} = \frac{\text{FWHM}_{\text{gauss}}}{\sqrt{\pi \ln 2}} \quad (21)$$

This versatile peak shape allows one to account for the various contributions to peak broadening (instrumental resolution, grain size, grain shape, microstrain). Of course, when comparing to experimental data, it is preferable (where possible) to convolve the simulated curve with the known instrumental resolution function, and to then use a physically-grounded peak shape function.

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