Scattering from amorphous materials:

Two types of length scales show up in scattering intensities from a piece of amorphous material: (1) inter-atomic distances (1-10 Angstroms) that give rise to Wide Angle X-ray Scattering (WAXS or WAS), and (2) particle size and interpartical distances (10²-10⁴ Angstroms) that dominate the Small Angle X-ray Scattering regime (SAXS or SAS).

Wide-Angle Scattering:

Let us consider a diatomic molecule with identical scattering form factor $f$ from each atom. The two atoms are separated by a distance $a$.

The scattering amplitude from this molecule

$$S(Q) = f + fe^{iQa} = f\left(1 + e^{iQa \cos \theta}\right),$$

and the intensity is:

$$I_s(Q) = f^2 \left(1 + e^{iQa \cos \theta}\right)\left(1 + e^{-iQa \cos \theta}\right) = 2f^2 \left[1 + \cos(Qa \cos \theta)\right].$$

In a liquid or gas, all molecules are randomly oriented, so the total scattered intensity is a spherical average of that from a single molecule:

$$I(Q) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \sin \theta d\theta d\phi \cdot 2f^2 \left[1 + \cos(Qa \cos \theta)\right] = 2f^2 \left(1 + \frac{\sin(Qa)}{Qa}\right).$$

The scattering per atom is

$$\frac{I(Q)}{2} = f^2 \left(1 + \frac{\sin(Qa)}{Qa}\right).$$

This is the so-called liquid scattering factor, and its first peak is located at $Qa = 2\pi \times 1.23$. A schematic plot of this scattering factor is shown below.

For $N$ atoms, we define $a_i =$ distance to $i$th neighbors, and $Y_i =$ population of the $i$th neighbors, then

$$\frac{I(Q)}{N} = f^2 \left(1 + \sum \frac{Y_i \sin(Qa_i)}{Qa_i}\right).$$
Small-Angle Scattering:

We use an example to illustrate basic concepts in small angle scattering. We consider scattering from a sphere of radius $R$ and uniform density $\rho_0$. The scattering amplitude from such a sphere is simply

$$S(Q) = \int \rho_0 e^{iQr} \, dr = \int \rho_0 e^{iQr\cos\theta} \, dr.$$ 

Again we perform spherical average and obtain:

$$S(Q) = \rho_0 \frac{2\pi}{V} \frac{R}{\pi} \int_0^\pi d\theta \int_0^R r^2 \, dr \cdot e^{iQr\cos\theta}$$

$$= 2\pi \rho \frac{R}{\pi} \int_0^\pi \sin\theta \, d\theta \int_0^R r^2 \, dr \cdot e^{iQr\cos\theta}$$

$$= 4\pi \rho_0 \frac{R}{\pi} \int_0^\pi \sin Qr \, d\theta$$

$$= 4\pi \rho_0 \frac{\sin QR - QR \cos QR}{QR^3}$$

$$= V \rho_0 \frac{3}{(QR)^2} \left( \frac{\sin QR}{QR} - \cos QR \right),$$

where $V = \frac{4\pi R^3}{3}$ is the volume of the scattering object, which is a sphere in our case. The scattered intensity is thus

$$I(Q) = V^2 \rho_0^2 \frac{9}{(QR)^4} \left( \frac{\sin QR}{QR} - \cos QR \right)^2.$$ 

The following are two commonly used analysis regimes in small angle scattering:

(1) **Guinier analysis**: for very small angles, or $QR << 1$

In the case of $QR << 1$, we have:

$$\frac{\sin QR}{QR} \approx 1 - \frac{Q^2 R^2}{3!} + \frac{Q^4 R^4}{5!} - \cdots,$$

$$\frac{\cos QR}{QR} \approx 1 - \frac{Q^2 R^2}{2!} + \frac{Q^4 R^4}{4!} - \cdots.$$
and the scattered intensity becomes:

\[ I(Q) \approx V^2 \rho_0^2 \left( 1 - \frac{Q^2 R^2}{10} \right)^2 \approx V^2 \rho_0^2 \left( 1 - \frac{Q^2 R^2}{5} \right) \approx V^2 \rho_0^2 e^{-\frac{Q^2 R^2}{5}}. \]

Using a definition of \textit{radius of gyration}: \( \langle R_G^2 \rangle = \frac{1}{V} \int r^2 dV \), which gives the equivalent moment of inertia of an object to a point located at \( R_G \) from center of mass. For a sphere of radius \( R \), it can be shown that \( R_G = \sqrt{\frac{3}{5}} R \). Substituting into the equation above gives us an express that is valid for any scattering object with an arbitrary shape:

\[ I(Q) \approx V^2 \rho_0^2 e^{-\frac{Q^2 R_G^2}{3}}. \]

In practice, one plots \( \ln I(Q) \) vs. \( Q^2 \), and the slope in the very small angle region is given by \( -\frac{R_G^2}{3} \). From this Guinier analysis method, a characteristic length scale \( R_G \) of the scattering object can be obtained.

(2) \textbf{Porod analysis:} for larger angles, or \( QR \gg 1 \) (but still in small-angle regime)

In the case of \( QR \gg 1 \), we have:

\[ I(Q) \approx V^2 \rho_0^2 \frac{9\langle \cos^2 QR \rangle}{Q^4 R^4} \approx V^2 \rho_0^2 \frac{9}{2Q^4 R^4}, \]

where we have taken the average value of \( \cos^2 QR \) to be \( \frac{1}{2} \). This is the so-called Porod’s \( Q^{-4} \) law for small angle scattering. Using the expressions for volume \( V = 4\pi R^3 / 3 \) and surface area \( S = 4\pi R^2 \), again we write the above equation in a form that is valid for any scattering object with arbitrary shape:

\[ I(Q) \approx \frac{2\pi \rho_0^2 S}{Q^4}. \]

We see in Porod’s region, the scattering is determined by the total surface area of the object, or the porosity of the material.

In practice, one plots out \( \ln I \) vs. \( \ln Q \), and obtains the power-law behavior in the Porod’s region.
Overall picture of scattering from amorphous materials:

Note: for scattering from polymers, the two regions for SAXS and WAXS are less well defined because of some well-defined correlations of intermolecule distances.