Surface Sensitive X-ray Diffraction:

We now go back to x-ray diffraction and scattering techniques that are surface sensitive. We’ll cover two such techniques: crystal truncation rod and x-ray reflectivity.

Crystal truncation rod (CTR):

Let us consider scattering from many atomic layers or monolayers. We assume the scattering factor from each layer is unity. These layers are separated by spacing $a$.

For a crystal with an infinite size, the scattering amplitude is

$$S(Q_z) = \sum_{n=-\infty}^{\infty} e^{iQ_zan} = \delta \left( Q_z - \frac{2\pi l}{a} \right), \text{ where } l \text{ is an integer.}$$

So the diffraction pattern is a set of delta functions located at reciprocal lattice points in reciprocal space.

However, no crystal has an infinite size. For a crystal that is truncated by a surface $z=0$, the scattering amplitude becomes:

$$S(Q_z) = \sum_{n=0}^{\infty} e^{iQ_zan} = \frac{1}{1 - e^{iQ_za}},$$

and the intensity becomes $I(Q_z) = \left| \frac{1}{1 - e^{iQ_za}} \right|^2 = \frac{1}{4\sin^2(Qza/2)}$, as shown in the figure below.
Thus a truncated crystal would give rise to diffuse scattering streaks, or rods, around Bragg peaks. The direction of the rods are running perpendicular to the surface. These rods are called crystal truncation rods.

The fact that the crystal truncation rods are surface sensitive can be seen by calculating the scattering amplitude at so-called anti-Bragg points, $Q_z a = \pi, 3\pi, \ldots$. For example, at $Q_z a = \pi$,

$$S(Q_z = \pi / a) = \frac{1}{1 - e^{i\pi}} = \frac{1}{2}.$$  

This means that a semi-infinite crystal would give a scattering amplitude at anti-Bragg points that is equivalent to that from a $\frac{1}{2}$ monolayer. Therefore the intensity at anti-Bragg points are very surface sensitive.

Layer-by-layer crystal growth: Now let us add a $\frac{1}{2}$ monolayer on top of the surface, then the scattering amplitude at anti-Bragg point becomes:

$$S(Q_z = \pi / a) = \frac{1}{2} + \frac{1}{2} e^{-i\pi} = \frac{1}{2} - \frac{1}{2} = 0.$$  

This is why the intensity at anti-Bragg points would oscillate during a layer-by-layer crystal growth, commonly known as RHEED oscillations, with each oscillation period indicating the completion of a complete monolayer. These oscillations can also be seen with x-ray diffraction.

**Specular X-ray Reflectivity (XR):**

A specular surface with a sharp interface can be represented by a step function in the density profile normal to the surface:

$$\rho_0(z) = \begin{cases} \rho_0 & z \geq 0 \\ 0 & z < 0 \end{cases}$$
A rough surface can be described by the convolution of the sharp interface with a width function \( w(z) \):

\[
\rho(z) = \rho_0(z) \ast w(z) = \int_{-\infty}^{\infty} dz' \rho_0(z - z')w(z') = \rho_0 \int_{-\infty}^{z} dz'w(z')
\]

So we see that the width function can be written as the gradient of \( \rho(z) \):

\[
w(z) = \frac{1}{\rho_0} \frac{\partial \rho}{\partial z}.
\]

Scattering amplitude from a rough surface is given by

\[
S(Q_z) = FT\{\rho_0(z)\} \cdot FT\{w(z)\} = S_0(Q_z) \cdot FT\left\{ \frac{1}{\rho_0} \frac{\partial \rho(z)}{\partial z} \right\}
\]

where \( S_0(Q_z) \) is the Fresnel reflection amplitude from a perfectly flat surface. This result indicates that x-ray reflectivity from a real surface is related to the density gradient (or changes) in the surface normal direction. Thus by measuring the x-ray reflectivity, density profile normal to the surface can be obtained.