Topic 3-2: Scattering Density
Kittel Pages: 26-30

Summary: Now that we developed an expression for the amplitude at the detector, in video 3-1, we need to look more closely at the term $n(\vec{r})$, our scattering density. We begin with an infinitely periodic solid and define our scattering density as a Fourier series in terms of the reciprocal space vectors, $\vec{G}$, which are defined to preserve the periodicity of our sample. We then look at our reciprocal space vectors in terms of our real space lattice vectors. Finally, we look at graphine in an example concerning scattering density.

- Looking more closely at the scattering density, $n(\vec{r})$
    - Scattering density depends on the type of incident wave. X-rays scatter off the electrons (both valence and core states). Neutron 'waves' scatter off of the nucleus and don't 'see' the electrons. For each flavor of wave, there is a function $n(\vec{r})$ that spatially maps a samples tendency to scatter that source wave.
    - $n(\vec{r})$ is important because it contains structural information about the material that we ultimately want to know
- Have already developed an expression for the intensity at the detector in terms of $n(\vec{r})$ and $\Delta\vec{k}$
- So far we have made no assumptions about $n(\vec{r})$
    - Could put a crystal, solid, liquid, etc into our diffractometer and the expression for intensity would still be true
- Start with a crystal that is infinitely periodic in all directions
    - This means that $n(\vec{r}) = n(\vec{r}+\vec{T})$ where $\vec{T}=n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ and n_i is an integer
    - Our goal is to get an analytic expression for intensity
- We don't know $n(\vec{r})$ but we know it is periodic so we can build it from other periodic functions
    - This indicates the use of a Fourier series
    - This will take the form of

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \qquad\qquad [1]$$

- o $n_{\vec{G}}$ will be the Fourier coefficients that determine each terms contribution to the total scattering density

- $\vec{G}$ creates the Fourier space that we build our wave in for $n(\vec{r})$

  - o So far, we don't know much about $\vec{G}$

  - o However, $\vec{G}$ must be constrained to preserve the periodicity $\vec{T}$ in the sample

- To test how to preserve this periodicity, we plug in $(\vec{r}+\vec{T})$ for $\vec{r}$

$$n(\vec{r} + \vec{T}) = \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G}\cdot(\vec{r}+\vec{T})} \qquad [2]$$

  - o From Euler's formula we know that $e^{i2\pi m} = 1$ for any integer m

  - o Thus if $\vec{G} \cdot \vec{T} = 2\pi m$, translational symmetry is maintained when the exponential is separated

$$n(\vec{r} + \vec{T}) = \sum_{\vec{G}} n_{\vec{G}} (e^{i\vec{G}\cdot(\vec{r})})(e^{i\vec{G}\cdot\vec{T}}) = \sum_{\vec{G}} n_{\vec{G}} \left(e^{i\vec{G}\cdot(\vec{r})} \right)(1) = n(\vec{r}) \qquad [3]$$

- Since $\vec{G} \cdot \vec{T} = 2\pi m$ where m is an **integer**, the Fourier space must be discrete.

- Let us arbitrarily define $\vec{G}$ as so:

$$\vec{G} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3 \qquad [4]$$

  - o where *h, k*, and *l* are integers (due to the discrete nature of the $\vec{G}$-space)

- Now that we have expressions for both terms in the dot product, we can put them together
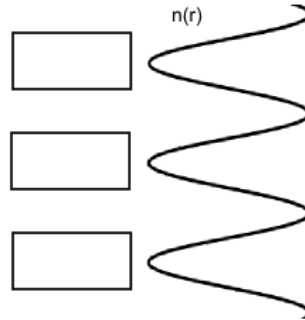
$$\vec{G} \cdot \vec{T} = (h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3) \cdot (n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3) = 2\pi m \qquad [5]$$

  - o This suggests that we should choose a $\vec{G}$ such that $\vec{g}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$ where $\delta_{i=j} = 1$ and $\delta_{i \neq j} = 0$ (Kronecker delta function)

- This gives $2\pi h n_1 + 2\pi k n_2 + 2\pi l n_3 = 2\pi m$.

  - o Nice, defining *h, k*, and *l* as integers did make sense (recall n_i are integers)

- Since $\vec{g}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$, then $\vec{g}_i$ can be described using our real space vectors $\vec{a}_j$

- For i$\neq$j $g_i \perp a_j$ so the dot product equals zero

- For example, $\vec{g}_1 \perp \vec{a}_2$ and $\vec{a}_3$ so $\vec{g}_1 \parallel \vec{a}_2 \times \vec{a}_3$

  - o In a cubic system this means $\vec{g}_1 \parallel \vec{a}_1$

- This leads to the expression:

$$\vec{g}_1 = \frac{2\pi\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \qquad [6]$$

- o which is the above factor over the volume of the cell

- If you dot $\vec{g}_1 \cdot \overrightarrow{a_1} = \frac{2\pi \vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \cdot \overrightarrow{a_1} = 2\pi$ Nice!

- This means a bigger cell in real space results in a smaller cell in reciprocal space. Additionally, when you consider the units on $\vec{g}_i$, you finds reciprocal length units. For these reasons, the Fourier space $\vec{G}$ is referred to as reciprocal space

- Example concerning n($\vec{r}$): layers of graphine stacked in $\vec{a}_3$

n(r)

- Let's coarsely approximate n($\vec{r}$) along $\vec{a}_3$ as a sine wave. There is high electron density in the graphine slab, but between the slabs there is little electron density. Within this simple treatment, we can generally state:

  - o The n_{001} term is non-zero, and all higher terms (e.g. n_{002}, n_{003}) are close to zero, since we don't need higher order terms to approximate a sine wave.

  - o We don't know anything about the electron density in $\vec{a}_1$ or $\vec{a}_2$, so we can't say anything about $n_{\vec{G}_{hkl}}$ for non-zero h and k. If we assume (crazily) that the individual slabs are featureless, then we're left with just n_{001} and the series in n(r) drops to a single term where G = 001.

Questions to Ponder

1. Where does the space spanned by $\vec{G}$ exist? Is it infinite? Why or why not? It may help to consider units.

2. What can we say about the magnitude of $\vec{G}$ compared to the wavelength we use in diffraction?