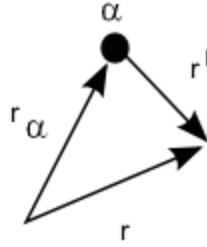


Topic 3-4: Structure Factor  
Kittel Pages: 39,40

- Now that we have an expression for  $n(\vec{r})$  we need to determine how to solve for  $n_{\vec{G}}$
- Invoking constructive interference only when  $\Delta\vec{k} = \vec{G}$ 
  - Inserting Fourier series expression for  $n(\vec{r})$  and converting amplitude to intensity:
  - $I(\Delta\vec{k}) \propto \left| \sum_{\vec{G}} n_{\vec{G}} \int_V e^{i(\vec{G}-\Delta\vec{k})\cdot\vec{r}} d\vec{r} \right|^2$
  - If  $\Delta\vec{k} = \vec{G}$   $I \propto |n_{\vec{G}}|^2 V^2$  (note the complex exponential becomes  $e^0=1$ )
  - If  $\Delta\vec{k} \neq \vec{G}$   $I = 0$  (In short, the integral across  $\vec{r}$  when the complex exponential remains leads to destructive interference and no net intensity)
- Can solve for  $n_{\vec{G}}$  by using an inverse Fourier transform of  $n(\vec{r})$ 
  - $n_{\vec{G}_{h,k,l}} = \frac{1}{V_{cell}} \int_{cell} n(\vec{r}) e^{-i\vec{G}_{h,k,l}\cdot\vec{r}} d\vec{r}$  where  $\vec{G}_{h,k,l}$  denotes a specific G vector
  - Since we are invoking an infinitely periodic solid we can put a 1 over the volume term out front and integrate over just one unit cell
- To check this, we can again insert the Fourier series for  $n(\vec{r})$

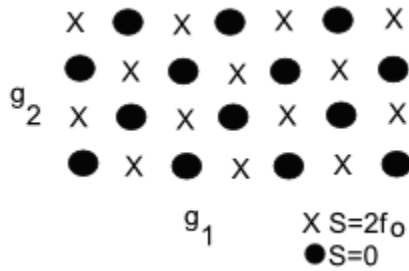
$$n_{\vec{G}_{h,k,l}} = \frac{1}{V_{cell}} \sum_{\vec{G}} \int_{cell} n_{\vec{G}} e^{-i(\vec{G}-\vec{G}_{h,k,l})\cdot\vec{r}} d\vec{r}$$


- For this integral there is only one non-zero solution, when  $\vec{G} = \vec{G}_{h,k,l}$ 
  - Same logic as above – when the exponent remains, the integration across  $r$  leads destructive interference and a net zero value.
- This gives  $n_{\vec{G}_{h,k,l}} = \frac{1}{V_{cell}} \int_{cell} n_{\vec{G}_{h,k,l}} d\vec{r} = \frac{1}{V_{cell}} n_{\vec{G}_{h,k,l}} V_{cell} = n_{\vec{G}_{h,k,l}}$  so we are on the right track. Now you can see why we have  $1/V_{cell}$  out front as well.
- With  $n_{\vec{G}_{h,k,l}} = \frac{1}{V_{cell}} \int_{cell} n(\vec{r}) e^{-i\vec{G}_{h,k,l}\cdot\vec{r}} d\vec{r}$  the integral represents the scattering density within one unit cell, which we will call the **structure factor**  $S_{h,k,l}$
- Challenge: We need to estimate  $n(\vec{r})$  within the cell! With  $n(\vec{r})$  established, we can predict intensities at the detector.
- Approach: Develop an approximation to  $n(\vec{r})$  that doesn't invoke any bonding, just the core electrons. Start with a coordinate system for atom positions, develop a local approximation for electron density, sum the densities.
- We will assume that the atoms don't interact with each other and have their own local charge density of  $n_{\alpha}(\vec{r}')$  where this local vector  $\vec{r}'$  points from the atom to some position vector  $\vec{r}$  and  $\vec{r}_{\alpha}$  points from the origin to atom  $\alpha$ .



- Then  $\vec{r}' = \vec{r} - \vec{r}_\alpha$
- Total  $n(\vec{r})$  is then  $\sum_\alpha n_\alpha(\vec{r} - \vec{r}_\alpha)$
- This makes our structure factor equal to  $S_{h,k,l} = \sum_\alpha \int_{cell} n_\alpha(\vec{r}') e^{-i\vec{G}_{h,k,l} \cdot \vec{r}} d\vec{r}$
- We want to separate this into terms concerning  $r_\alpha$  (where the atoms are centered) and  $r'$  (the local charge density associated with atom  $\alpha$ ); to do so we multiply by  $1 = e^{-i\vec{G}_{h,k,l} \cdot \vec{r}_\alpha} e^{i\vec{G}_{h,k,l} \cdot \vec{r}_\alpha}$ :
- This gives  $S_{h,k,l} = \sum_\alpha e^{i\vec{G}_{h,k,l} \cdot \vec{r}_\alpha} \int_{cell} n_\alpha(\vec{r}') e^{-i\vec{G}_{h,k,l} \cdot \vec{r}'} d\vec{r}'$ 
  - The sum term includes  $\vec{r}_\alpha$ , which is where the atom is within the cell
  - The integral term includes  $\vec{r}'$  which gives a term called the **atomic form factor**,  $f$
- Example 1: One atom in cell at position  $\vec{r}_\alpha = (0,0,0)$ 
  - $\vec{G}_{h,k,l} \cdot \vec{r}_\alpha = 0$
  - $S_{h,k,l} = f_{o,\alpha} e^0 = f_{o,\alpha}$  for all h,k,l
  - So for every case where  $\Delta\vec{k} = \vec{G}_{h,k,l}$   $I \propto |n_{\vec{G}_{h,k,l}}|^2 \propto |S_{h,k,l}|^2 \propto |f_o|^2$
- Example 2: Cesium Chloride: Cs at (0,0,0), Cl at (1/2,1/2,1/2) within the cell
  - Cesium atom gives  $f_o$  as in previous example
  - $S_{h,k,l} = f_{o,Cs} + e^{-i\vec{G}_{h,k,l} \cdot \vec{r}_{Cl}} f_{o,Cl}$
  - Chlorine atom gives  $e^{-i\pi(h+k+l)}$  since  $\vec{g}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$  ( $2 \times \frac{1}{2}$  yields unity...)
  - This gives  $S_{h,k,l} = f_{o,Cs} + e^{-i\pi(h+k+l)} f_{o,Cl}$
  - From Euler's we know:  $e^{-i\pi \text{ odd integer}} = -1$  and  $e^{-i\pi \text{ even integer}} = 1$
  - So  $S_{h,k,l} = f_{o,Cs} + f_{o,Cl}$  if  $h+k+l = \text{even}$  and  $S_{h,k,l} = f_{o,Cs} - f_{o,Cl}$  if  $h+k+l = \text{odd}$
  - Moving  $\Delta k$  out in reciprocal space (via shifting source/detector positions), we could pass through a set of  $G = (h, 0, 0)$  points in reciprocal space. The first point,  $\Delta k = G_{100}$  will be weak, the second point at  $G_{200}$  will be strong,  $G_{300}$  will be strong, etc.

- If instead of CsCl, we considered a BCC cell (where the two  $f$  are identical, we will see systematic absences of atoms as shown below in the  $\vec{g}_3$  slice



 Sketch the  $\Delta k = h00$  path in reciprocal space, picking an appropriate origin and highlighting the strong reflections

- **Practical application:** When we measure intensity, we lose the phase information in the amplitude at the detector. As such, we can't simply take the inverse Fourier transform to obtain the scattering density
- In practice, one guesses the structure, uses the structure factor to calculate the intensity pattern, compares that to experimental data and then changes the guess until experimental and calculated intensities match.
- Since it's a fitting procedure rather than an exact transformation, there are the usual issues of initial guess choice, number of free parameters, local vs global minima, etc.