Physics 489 S 04 Lecture 6
Determination of Crystal Structures (Ashcroft and Mermin, chapter 6)

1. Experiments probe matter by scattering of waves
   Waves useful for scattering from crystals: X-rays, neutrons, high-energy electrons

   - Must penetrate into the solids to be sensitive to the structure
   - Neutrons penetrate very well (except for a few elements) - low energy thermal neutrons have wavelength $\lambda \approx$ atomic spacing
   - X-rays penetrate fairly well - the absorption causes some problems in analysis, but we will ignore absorption - kilovolt X-rays have wavelength $\lambda \approx$ atomic spacing - now tunable sources at synchrotrons
   - High-energy electrons (kilovolts) penetrate but experiments and analysis are difficult due to losses- will not be dealt with explicitly here

2. Bragg scattering: elastic scattering - no loss of energy - scattered wave has same energy (wavelength) as incident wave:
   Analysis as scattering from planes spaced by distance d:
   Well known formula: $n\lambda = 2d\sin(\theta)$

3. More useful expression in general cases:
   Conservation of "crystal momentum": $\mathbf{k}_i - \mathbf{k}_s = \mathbf{G}$, where $\mathbf{G}$ is a reciprocal lattice vector

4. Elastic scattering: $E_i = E_s$; $|\mathbf{k}_i| = |\mathbf{k}_s|$

   - Ewald construction - orientation of crystal to satisfy $\mathbf{k}_i - \mathbf{k}_s = \mathbf{G}$
   - Bragg law where 2θ is scattering angle:
     $2d\sin(\theta) = n\lambda$ or $\sin(\theta) = \frac{\lambda}{4\pi}|\mathbf{G}|$
   - Leads to characteristic ratios of $\sin(\theta_n)$ for each Bravais lattice, where n denotes different scattering angles

5. Experimental methods

   - Rotating crystal
   - Powder pattern (Debye-Scherrer)
   - Energy range for probe waves (Laue)
   - Tunable energy for probe waves - Now widely used at synchrotrons

6. Bragg planes and Brillouin Zones

   - Another way to formulate Bragg law: $2\mathbf{k} \cdot \mathbf{G} = |\mathbf{G}|^2$, where $\mathbf{k}$ is either $\mathbf{k}_i$ or $\mathbf{k}_s$
   - Leads to scattering only for $\mathbf{k}$ on Bragg planes defined as bisectors of $\mathbf{G}$ vectors
   - Volumes enclosed by Bragg planes are Brillouin Zones

- First Brillouin Zone is smallest volume enclosed by Bragg planes

7. First Brillouin Zone (BZ) = Wigner-Seitz cell of Reciprocal lattice
   - No Bragg scattering occurs for any $\mathbf{k}$ inside first Brillouin Zone (BZ)
   - Bragg scattering occurs for $\mathbf{k}$ on surface of BZ
   - Examples of BZ: simple cubic, fcc, bcc

8. Form factors and structure factors
   - Scattering amplitude of a single atom is given by the form factor $f(|\mathbf{k}_i - \mathbf{k}_s|)$ where f depends upon the type of scattering probe
   - Scattering amplitude for a solid is the coherent scattering from all the atoms, $j = 1, ...$
     $\sum_j f_j(\mathbf{k}_i - \mathbf{k}_s) e^{i(\mathbf{k}_i - \mathbf{k}_s)\cdot\mathbf{R}_j}$
   - For a crystal scattering is non-zero only for $\mathbf{k}_i - \mathbf{k}_s = \mathbf{G}$ and the scattering amplitude is given by N_{cells} times the scattering per cell
     $\sum_j f_j(\mathbf{G}) e^{i(\mathbf{k}_i - \mathbf{k}_s)\cdot\mathbf{R}_j}$,
     where the sum is over all the atoms in a primitive cell
   - Approximate correct to treat scattering from each atom in the solid as spherically symmetric, i.e., $f_j(\mathbf{G}) = f_j(|\mathbf{G}|)$ and the same for all atoms of the same chemical species
   - Then the scattering for all atoms of the same type can be written as the form factor $f_j(|\mathbf{G}|)$ multiplied by a geometrical structure factor $S(\mathbf{G})$:
     $S(\mathbf{G}) = \sum_j e^{i\mathbf{G}\cdot\mathbf{R}_j}$,
     where the sum is over atoms of the same type
   - Example: diamond structure

9. Phase problem:
   - In general scattering experiments only measure intensities $\propto |amplitude|^2$
   - Nobel prize in chemistry in 1988 for method to determine three-dimensional structure of complex crystals such as proteins
   - If the phase can be measured, amplitudes can be determined, and the structure in real space can be determined by inverse Fourier transform of the scattering amplitude in Fourier space
   - Current research to find ways to measure the phases