Chapter 3
Structure of Crystalline Solids

• Crystal Structures
• Points, Directions, and Planes
• Linear and Planar Densities
• X-ray Diffraction
  • How do atoms assemble into solid structures? (for now, focus on metals)
  • How does the density of a material depend on its structure?
  • When do material properties vary with the sample (i.e., part) orientation?
Energy and Packing

- **Non dense, random packing**

- **Dense, regular packing**

Dense, regular-packed structures tend to have lower energy.
Materials and Packing

**Crystalline** materials...
- atoms pack in periodic, 3D arrays
- typical of:  
  - metals
  - many ceramics
  - some polymers

**Noncrystalline** materials...
- atoms have no periodic packing
- occurs for:  
  - complex structures
  - rapid cooling

"Amorphous" = Noncrystalline
Metallic Crystals

• tend to be densely packed.

• have several reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.

• have the simplest crystal structures.

  We will look at four such structures...
Simple Cubic Structure (SC)

- Unit Cell (small repeat entity)
- Rare due to poor packing (only Po has this structure)
- Close-packed directions are cube edges.
  
  Coordination # = 6
  (# nearest neighbors)
Atomic Packing Factor (APF)

\[
APF = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}
\]

*assume hard spheres

- APF for a simple cubic structure = 0.52

\[
APF = \frac{\frac{4}{3} \pi (0.5a)^3}{a^3} = \frac{1}{8} \times 8 = 1 \text{ atom/unit cell}
\]
Body Centered Cubic Structure (BCC)

- Close packed directions are cube diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

- Coordination # = 8
APF of BCC

• APF for a body-centered cubic structure = 0.68

Close-packed directions:
length = 4R
= \sqrt{3} \ a

Unit cell contains:
1 + 8 \times \frac{1}{8}
= 2 \ atoms/unit \ cell

APF = \frac{2 \times \left(\frac{4}{3} \ \pi \ (\frac{3a}{4})^3\right)}{a^3} \ \frac{volume}{atom}
Face Centered Cubic Structure (FCC)

- Close packed directions are face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

- Coordination # = 12
APF of FCC

• APF for a body-centered cubic structure = 0.74

Close-packed directions:
length = 4R
  = \sqrt{2} \ a

Unit cell contains:
6 x 1/2 + 8 x 1/8
  = 4 atoms/unit cell

\[
\text{APF} = \frac{4 \frac{4}{3} \pi (\sqrt{2}a/4)^3}{a^3}\]

\text{unit cell volume} 
\text{atom volume}
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

A sites
B sites
C sites

- FCC Unit Cell
Hexagonal Closed-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection
- 2D Projection

- Coordination # = 12
  - APF = 0.74
Theoretical Density

\[ \rho = \frac{nA}{V_c N_A} \]

# atoms/unit cell

Atomic weight (g/mol)

Volume/unit cell (cm\(^3\)/unit cell)

Avogadro's number (6.023 x 10\(^{23}\) atoms/mol)

Example: Copper

Data from Table inside front cover of Callister (see next slide):

- crystal structure = FCC: 4 atoms/unit cell
- atomic weight = 63.55 g/mol (1 amu = 1 g/mol)
- atomic radius \( R = 0.128 \) nm (1 nm = 10\(^{-7}\) cm)

\[ V_c = a^3 ; \text{For FCC, } a = 4R\sqrt{2} ; \quad V_c = 4.75 \times 10^{-23} \text{cm}^3 \]

Result: theoretical \( \rho_{\text{Cu}} = 8.89 \text{ g/cm}^3 \)

Compare to actual: \( \rho_{\text{Cu}} = 8.94 \text{ g/cm}^3 \)
Seven Crystal Systems

Cubic  \( a = b = c \)  \( \alpha = \beta = \gamma = 90^\circ \)

Hexagonal  \( a = b \neq c \)  \( \alpha = \beta = 90^\circ, \gamma = 120^\circ \)

Tetragonal  \( a = b \neq c \)  \( \alpha = \beta = \gamma = 90^\circ \)

Rhombohedral  \( a = b = c \)  \( \alpha = \beta = \gamma \neq 90^\circ \)

Orthorhombic  \( a \neq b \neq c \)  \( \alpha = \beta = \gamma = 90^\circ \)

Monoclinic  \( a \neq b \neq c \)  \( \alpha = \gamma = 90^\circ \neq \beta \)

Tri clinic

\( a \neq b \neq c \)  \( \alpha \neq \beta \neq \gamma \neq 90^\circ \)
Crystallographic Points

- Be specified in terms of its coordinates
- Fractional multiples of the unit cell edge length
Crystallographic Directions

Steps to determine the direction
- Let the vector pass origin
- Project to the axes
- Reduce the number to the smallest integer values
- Enclose in Square Brackets
- Use upper bar for negative value

Direction family: use Angle Brackets
\(<100>: [100], [\overline{1}00], [010], [\overline{0}10], [001], [\overline{0}01]\)

Four-axis system for hexagonal crystal
Crystallographic Planes

Steps to determine the plane

• Choose right origin
• Intercept to the axes
• Take reciprocals
• Reduce the number to the smallest integer values
• Enclose in Parentheses
• Use upper bar for negative value

Plane family: use Braces

\{111\}: (\overline{1}11), (\overline{1}1\overline{1}), (1\overline{1}1), (111)……

Four-axis system for hexagonal crystal
Linear and Planar Densities

• Linear Density

\[ \text{LD} = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}} \]

• Planar Density

\[ \text{PD} = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}} \]
X-ray Diffraction

Diffraction Phenomenon

• A series regularly spaced obstacles
  • Spacing ~ wavelength

• Constructive interference
  Path length difference ~ \( n \lambda \)

• Destructive interference
  Path length difference ~ \( n/2 \lambda \)
Bragg’s Law

Constructive interference:

\[ n\lambda = \overline{SQ} + \overline{QT} \]

\[ n\lambda = d_{hkl} \sin \theta + d_{hkl} \sin \theta \]

\[ = 2d_{hkl} \sin \theta \]

For cubic system:

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]
Diffractometer

- Measurement of: Critical angles, $\theta_c$, for X-rays provide atomic spacing, $d$.

$$d = n \frac{\lambda}{2 \sin \theta_c}$$

x-ray intensity (from detector)