Chapter 3: The Structure of Crystalline Solids

ISSUES TO ADDRESS...

• How do atoms assemble into solid structures?
• Examples of dependence of material property on its crystal structure
Crystalline vs. Noncrystalline (Amorphous) Materials

**Crystalline** materials...
- atoms pack in periodic, 3D arrays with long-range translational symmetry
- typical of:
  - Most metals
  - Many ceramics
  - Some polymers

**Noncrystalline** materials...
- atoms have no long-range periodic packing
- occurs for:
  - All glasses
  - Some polymer

"Amorphous" = Noncrystalline
Energy & Packing for Crystalline vs. Noncrystalline (Amorphous) Materials

- **Crystalline material**: Ordered packing, higher density
  - Typical neighbor bond length
  - Typical neighbor bond energy
  - Higher density and lower energies (more stable)

- **Amorphous material**: Random packing, lower density
  - Typical neighbor bond length
  - Typical neighbor bond energy

Orderly packed crystalline structures tend to have higher density and **lower** energies (more stable)
Single Crystal Materials

- Periodic arrangement of atoms throughout the entire material
  -- diamond single crystals for industrial abrasives
  (Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)
  -- turbine blades
  Fig. 8.33(c), Callister & Rethwisch 8e. (Fig. 8.33(c) courtesy of Pratt and Whitney).

- Single crystal silicon wafer for semiconductor

Polycrystalline Materials

• **Most** engineering materials are **polycrystalline**, i.e., they contain many individual grains or small crystals

  ![Polycrystalline Nb-Hf-W plate with an electron beam weld.](image)

  1 mm

• Each "grain" is a single crystal

• Grain size ranges from ~1 nm to ~1 cm

Adapted from Fig. K, color inset pages of *Callister 5e*. (Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

Casted polycrystalline Si

Polycrystalline Si wafer

http://pveducation.org
Hard Sphere Model for Crystal Structures

• Hard-sphere model
  – Atoms are hard spheres
  – Atoms “touch” nearest neighbors
  – **Periodic with translational symmetry**

• Exercise:
  – Draw 1D arrangement
  – Draw 2D arrangement
Crystal Lattice, Unit Cell, & Coordination Number (CN)

- **Crystal lattice**: an array of points coincide with atoms (or a certain set of atoms or molecules) representing geometric configuration in crystals.

- **Unit cell**: Smallest (simplest) repeating unit in a lattice that satisfy the followings:
  - Represent/reflect symmetry in crystal
    - Translational
    - Rotational
    - Mirror
  - Opposite faces (for 3D)/edges are parallel
  - Each point is identical in its environment

- **Coordination Number (CN)**
  - Number of nearest (or touching) neighboring atoms for an atom within a crystal.
Crystal Systems

Unit cell in 3D typically parallelepipeds

4 3-fold axis of rotation
1 4-fold axis of rotation
3 2-fold axis of rotation

Cubic

Tetragonal Orthorhombic

Monoclinic
Triclinic
Rhombohedral (Trigonal)
Hexagonal

1 mirror plane
None
1 3-fold axis of rotation
1 6-fold axis of rotation

a, b, and c are the lattice constants
α, β, γ are angles

Adapted with changes from
http://crystalinehealing.blogspot.com/2014/06/blog-post_11.html
Simple Cubic Structure (SC)

- Cubic crystal system
- Simple
- Rare for metals (only Po has this structure)
- Close-packed directions are cube edges
  - Coordination number (CN, or the # nearest/touching neighbors) = 6

If same types of atoms (e.g., pure metal)
  - Edge length \(a\)
  - Atom radius \(R\)

\[ a = 2R \]

On average: 1 atoms per unit cell: 8 corners x 1/8 = 1
Crystal Structure Application Problem 2
Atomic Packing Factor (APF) for Simple Cubic Structure

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

*assume hard spheres

- APF for a simple cubic structure = 0.52

Adapted from Fig. 3.24, Callister & Rethwisch 8e.

[Diagram showing close-packed directions.]

The unit cell contains \( 8 \times \frac{1}{8} = 1 \) atom.

Volume of an unit cell

Volume of each atom

\[ \text{APF} = \frac{1}{6} \pi (0.5a)^3 \approx 0.52 \]
Visualizing Simple Cubic (SC) Lattice

Filling balls for SC lattice

Ball-Stick model for SC lattice

Unit cell for SC lattice

srinivaseducation.blogspot.com

http://www2.ucdsb.on.ca/tiss/stretton/CHEM2/arch19.htm
Body Centered Cubic (BCC) Structure

- Atoms touch each other along cube diagonals.

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

ex: Cr, W, Fe ($\alpha$), Tantalum, Molybdenum

- Coordination number $\text{CN} = 8$

On average, 2 atoms per unit cell: 1 center + 8 corners x $1/8$

https://www.nde-ed.org/EducationResources/CommunityCollege/Materials/Structure/metallic_structures.htm

Adapted from Fig. 3.2, Callister & Rethwisch 8e.
Crystal Structure Application Problem 2
Atomic Packing Factor (APF) for BCC

- APF for a body-centered cubic structure = 0.68

Along close-packed direction:

\[ 4R = \sqrt{3} \cdot a \]

# of atoms per unit cell

\[
\text{APF} = \frac{2 \cdot \frac{4}{3} \pi \left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3} \pi}{8} \approx 0.68
\]

Adapted from Fig. 3.2(a), Callister & Rethwisch 8e.
Face Centered Cubic (FCC) Structure

- Atoms touch each other along face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination number $CN = 12$

On average: 4 atoms per unit cell: 6 face $x$ $1/2 + 8$ corners $x$ $1/8$

https://www.nde-ed.org/EducationResources/CommunityCollege/Materials/Structure/metallic_structures.htm
Crystal Structure Application Problem 2
Atomic Packing Factor (APF) for FCC

• APF for a face-centered cubic structure = 0.74
  maximum achievable APF

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

Adapted from Fig. 3.1(a), Callister & Rethwisch 8e.

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

\[ = \frac{\sqrt{2}\pi}{6} \approx 0.74 \]

# of atoms per unit cell

Volume of each atom

Volume of an unit cell

Volume of an atom
Densities of Material Classes

In general
\[ \rho_{\text{metals}} > \rho_{\text{ceramics}} > \rho_{\text{polymers}} \]

Why?

Metals have...
- close-packing (metallic bonding)
- often large atomic masses

Ceramics have...
- less dense packing
- often lighter elements

Polymers have...
- low packing density (often amorphous)
- lighter elements (C,H,O)

Composites have...
- intermediate values

Data from Table B.1, Callister & Rethwisch, 8e.

Based on data in Table B1, Callister *GFRE, CFRE, & AFRE are Glass, Carbon, & Aramid Fiber-Reinforced Epoxy composites (values based on 60% volume fraction of aligned fibers in an epoxy matrix).