Outline (Chapter 3)

- **Crystalline & Amorphous Structures**
- **Crystal Structures**
  - ✓Basic Concepts
    - o Unit Cell
    - o Single Cubic **(SC)**
    - o Coordination number
    - o Atomic packing factor
    - o Crystal density
  - ✓Body Centered Cubic **(BCC)**
  - ✓Face Centered Cubic **(FCC)**
  - ✓Hexagonal Close-Packed **(HCP)**

Crystalline vs. Amorphous

➢ **Crystalline Structure:**

If atoms bonded together in a regular 3-D pattern they form a **CRYSTAL**

➢ **Amorphous Structure:**

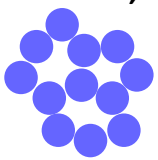
If atoms bonded to each other but there is no repeating pattern (**short range order)** . e.g. water, glasses **(AMORPHOUS - non-crystalline)**

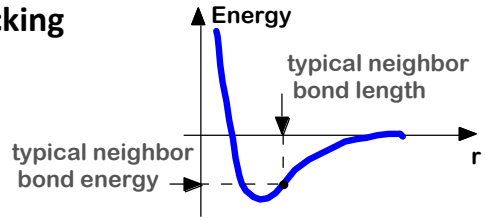
- o Metals: (>99%) → **Crystalline**
- o Ceramics: **Crystalline** (except glasses → Amorphous)
- o Polymers: **Semi-crystalline** (mixed of crystalline and amorphous) or **Amorphous**

o In gases, atoms have no order (Amorphous).

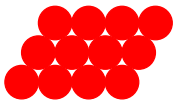
Crystalline vs. Amorphous

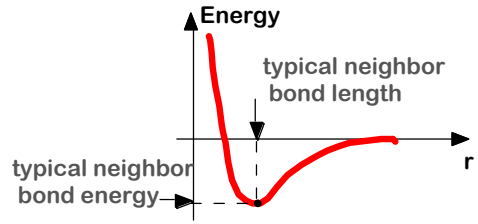
- **Non dense, random packing**





- **Dense, regular packing**

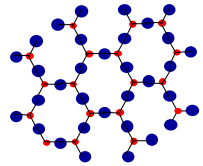




Dense, regular-packed structures tend to have lower energy.

Crystalline vs. Amorphous

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

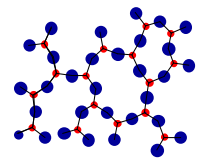


crystalline SiO_2

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

"Amorphous" = Noncrystalline

• Si • Oxygen



noncrystalline SiO_2

Crystal Structures

• **Motivation:** Many of the properties of materials (*especially mechanical) are determined by the arrangement of the* constituent atoms.

✓***This arrangement is called the material's crystal structure.***

• **An important distinction…**

– **Atomic structure** relates to the number of protons and neutrons in the nucleus of an atom, as well as the number and probability distributions of the electrons.

– **Crystal structure** pertains to the arrangement of atoms in the crystalline solid material.

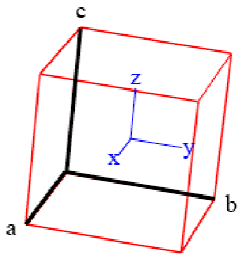
What is Unit Cell?

• **Unit cell: The smallest group of atoms** which can generate the entire crystal by translation.

• **Lattice parameter: The length of each unit cell axis**

✓ In other words, **unit cell** is the smallest repetitive volume which contains the complete **lattice pattern** of a crystal.

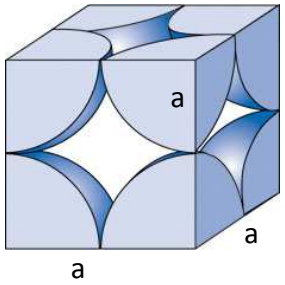
✓ *To illustrate the concept of crystal structure and lattice systems, we first identify a* ***coordinate system (x, y, z)***

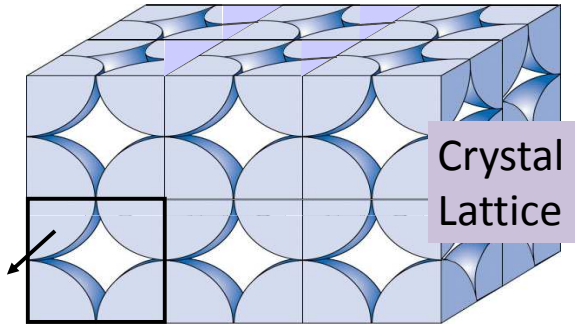


– ***a, b,*** and ***c*** are the ***lattice parameters***.
– *In cubic systems, all three orthogonal lattice parameters are equal.*
– Lattice parameters are typically on the order of a few tenths of a nanometer (10^{-9} m) (or a few Angstroms - 10^{-10} m)

What is Unit Cell?

Unit cell of:
Simple cubic (SC)





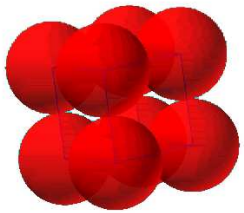
In Simple Cubic Structure:
• Atoms "touch" along the crystal axes
• These directions are referred to as "close-packed" in the simple cubic system

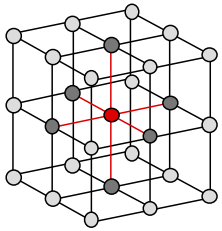
Simple Cubic Structure (SC)

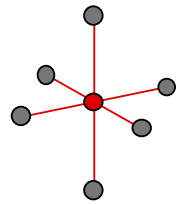
• Rare due to poor packing (only Po has this structure)
• Close-packed directions are cube edges.

Coordination number (CN): Number of touching atoms surrounding one atom

✓ Large atoms tend to have larger CN, small atoms usually have small CN. Because, it's easier to surround a big atom with lots of atoms than a smaller one.





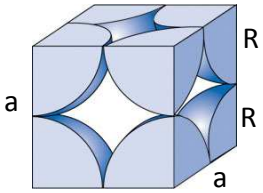


• **Coordination number = 6**
(# nearest neighbors)

Simple Cubic Structure (SC)

- **Number of Atoms in Unit Cell (n):** In SC, unit cell contains 1 full atom (8 x 1/8 atoms)
- **Atomic Packing Factor (APF):** Volume of unit cell occupied by atoms over total unit cell volume **(the higher APF ⇨ the higher the density)**

APF = volume of unit cell occupied by atoms / total unit cell volume



a = 2R

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

- **APF for a SC structure = 0.52**

Crystal Structures

- **Crystal Density:** The true density, ρ, of material (free from defects) can be calculated knowing its crystal structure.

$$\rho = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{\frac{\#\text{ of atoms}}{\text{unit cell}} \cdot \text{Atomic weight (g/mol)}}{N_A \cdot \frac{\text{volume}}{\text{unit cell}}}$$

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

volume / unit cell (cm^3/unit cell)

n = number of atoms in unit cell
A = Atomic Weight of element (g/mol)
V_c = volume of unit cell ($=a^3$ for cubic system)
N_{av} = Avogadro's number (6.022×10^{23} atoms/mol)

$\rho_{metals} > \rho_{ceramics} > \rho_{polymers}$

Summary: Crystal Structures
(Basic Concepts)

- **Unit cell:** The smallest repetitive volume which contains the complete lattice pattern of a crystal.
- **Coordination number (CN):** Number of touching atoms surrounding one atom
- **Atom/Unit Cell (n):** Number of Atoms in Unit Cell
- **Atomic Packing Factor (APF):** Volume of unit cell occupied by atoms over total unit cell volume
- **Crystal Density:** The true density, ρ, of material (free from defects) can be calculated knowing its crystal structure.

Crystal Structures

- **Simple Cubic (SC):**

a = 2R, APF = 0.52, coordination # = 6, n=1

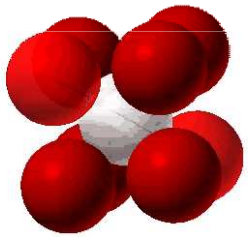
Metallic Crystal Structures:
- **Body Centered Cubic (BCC)**
- **Face Centered Cubic (FCC)**
- **Hexagonal Close-Packed (HCP)**

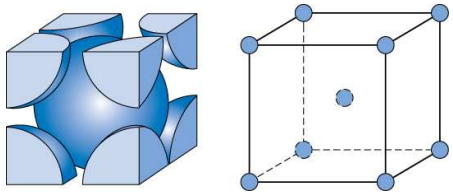
✓ Most metals crystallize into one of these three densely packed structures

Body Centered Cubic (BCC)

- 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 (α), Tantalum, Molybdenum

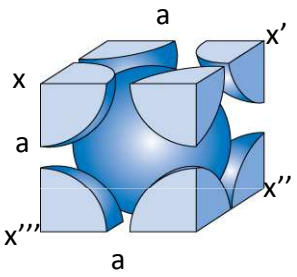




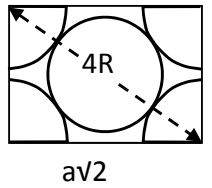
- **Coordination number = 8**
  (# nearest neighbors)

- **# of atoms/unit cell (n) = 2**
  (1 atom + 8 x 1/8 atoms)

Body Centered Cubic (BCC)



plane x, x', x'', x'''



$4R = a\sqrt{3}$

so $R = \frac{a\sqrt{3}}{4}$

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} = \frac{2 \cdot \frac{4}{3}\pi(\sqrt{3}a/4)^3}{a^3}$$

4R = a√3

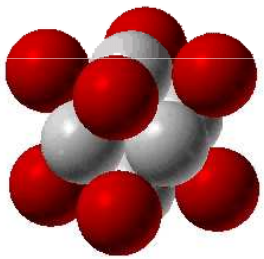
- **APF for a BCC structure = 0.68**

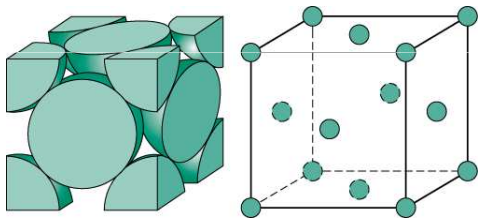
Face Centered Cubic (FCC)

- Atoms touch each other along face diagonals.

Note: All atoms are identical; face-centered atoms are shaded differently only for ease of viewing.

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

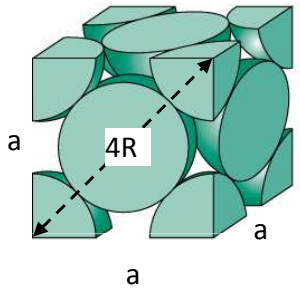




- **Coordination number = 12**
  (# nearest neighbors)

- **# of atoms/unit cell (n) = 4**
  (6 face x 1/2 + 8 corners x 1/8)

Face Centered Cubic (FCC)



$4R = a\sqrt{2}$

so $R = \frac{a\sqrt{2}}{4}$

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} = \frac{4 \cdot \frac{4}{3}\pi(\sqrt{2}a/4)^3}{a^3}$$

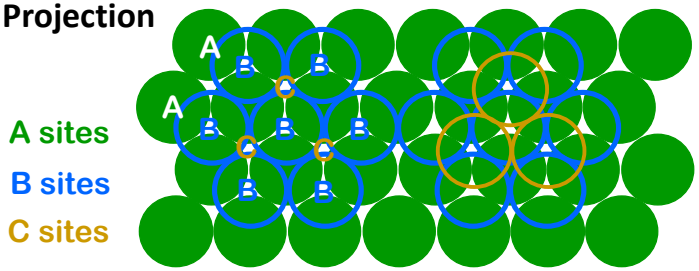
4R = a√2

- **APF for a FCC structure = 0.74**

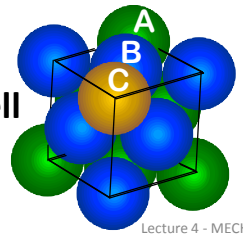
maximum achievable APF

Face Centered Cubic (FCC)

- ABC-ABC... Stacking Sequence
- 2D Projection



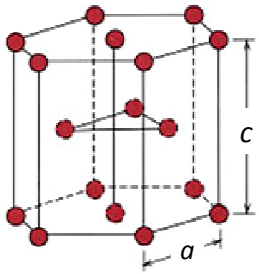
- FCC Unit Cell

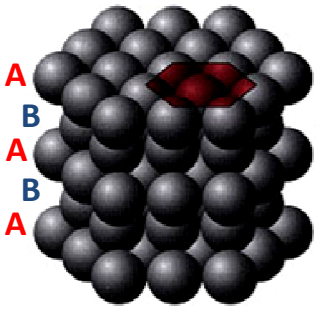


Close-packed plane of atoms

Hexagonal Close-Packed Structure (HCP)

➢ Hexagonal arrangement (not cubic), have 2 lattice parameters "a" , & "c"





- AB-AB... Stacking Sequence

examples: Cd, Mg, Ti, Zn

- Coordination number = 12 (# nearest neighbors)
- c/a = 1.633
- # of atoms/unit cell (n) = 6 (2x1/2 + 12cornerx 1/6 + 3)
- APF for an HCP structure = 0.74 (Same as FCC)

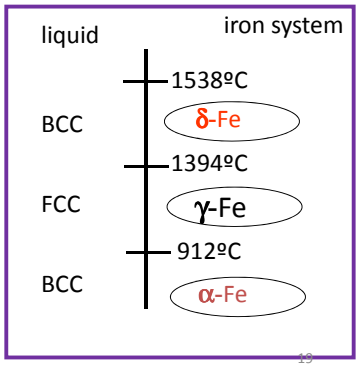
Crystal Structures

- **Polymorphism:** When some metals (or non-metals) have more than one crystal structure. *(depending on **Pressure** and **Temperature** condition)*
- **Allotropy:** When more than one crystal structure found in elemental solids

Examples:

Carbon: Forms as Graphite (at ambient pressure) & Diamond (at high pressure)

Iron: Various structures at different temperatures



Can be IMPORTANT as some crystal structures more dense (better packing, higher APF) than others.
So a change in crystal structure can often result in volume change of material.
APF (FCC) =0.74
APF (BCC) = 0.68
i.e. expands on transforming from FCC to BCC.

Crystal Structures (review problem)

- **Calculate the Theoretical Density, ρ, of Copper (Cu). Cu has an atomic radius 0.128 nm an FCC crystal structure & an atomic weight of 63.5 g/mol.**

Note: Use the data in Table 3.1 (Callister 9th edition)

$$\rho = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{n\,A}{N_A\,V_c}$$

n: # of atoms / unit cell
A: Atomic weight (g/mol)
N_A: Avogadro's number (6.023×10^{23} atoms/mol)
V_c: volume / unit cell (cm^3/unit cell)