Outline:

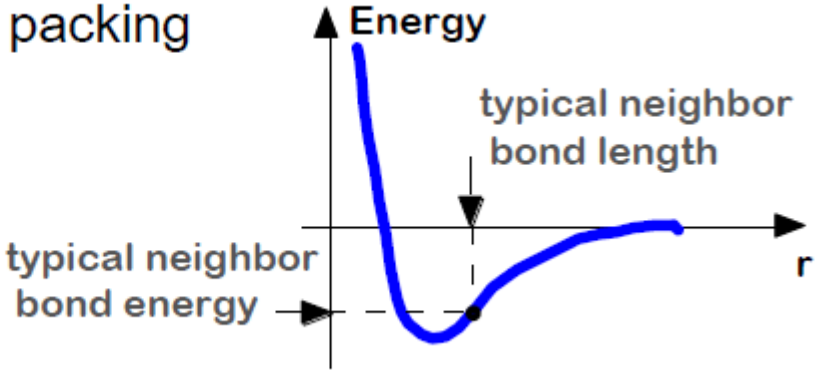
- Crystalline versus amorphous structures

- Crystal structure
  - Unit cell
  - Coordination number
  - Atomic packing factor

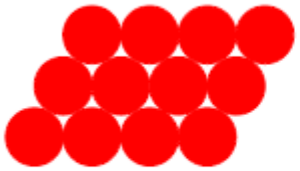
- Crystal systems

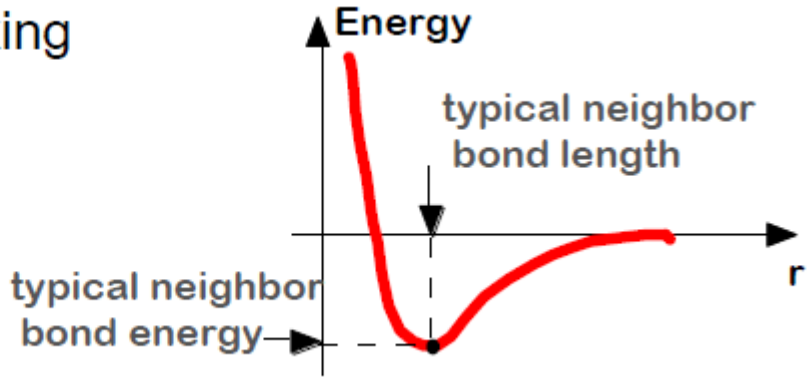
ENERGY AND PACKING

- Non dense, random packing



- Dense, regular packing





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

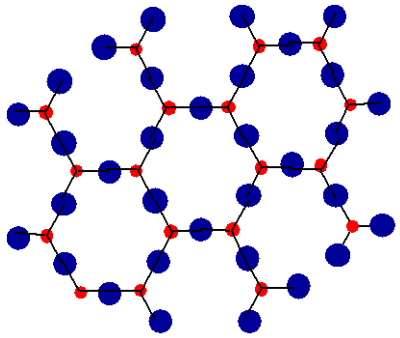
CRYSTAL STRUCTURES & PROPERTIES

How do materials assemble?

Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of:

  -metals
  -many ceramics
  -some polymers



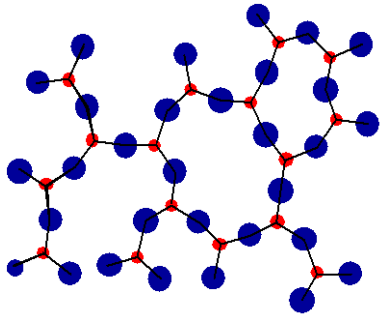
crystalline SiO_2

• **Si** • **Oxygen**

Noncrystalline (amorphous) materials...

- atoms have no periodic packing occurs for:

  -complex structures
  -rapid cooling



noncrystalline SiO_2

Crystal Structure

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.

– **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 constituent electrons.

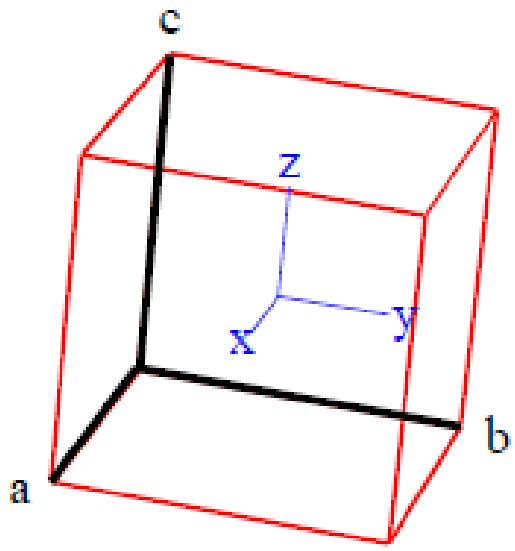
– On the other hand, **crystal structure** pertains to the arrangement of atoms in the crystalline solid material.

Crystal Structure

- We need a way to specify crystallographic directions and planes.

- Let's start with the hard sphere model (in which nearest neighbour atoms "touch" each other)…

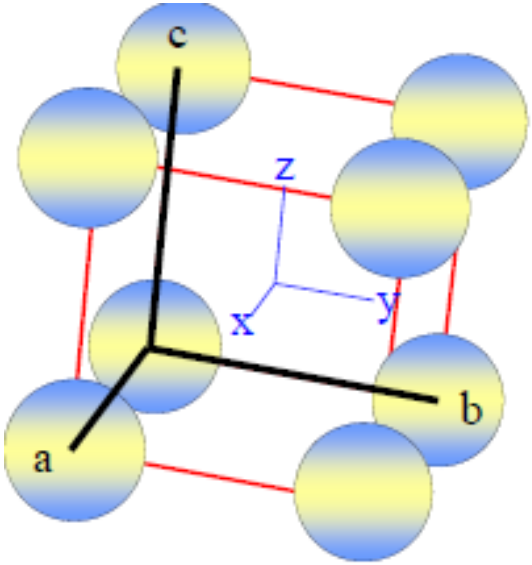
To illustrate the concept of z crystal structure and lattice systems, we first identify a coordinate system (x, y, z):



We can't specify directions or planes without knowing what the reference system is.

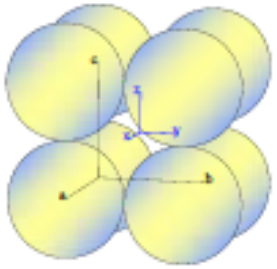
Crystal Structure

Now place an atom at each corner…



This represents the "hard sphere" model of a simple crystal system

- Atoms "touch" along the crystal axes
- These directions are referred to as "close-packed" in the simple cubic system



not many examples of simple cubic systems in nature, except for Po

The above diagram represents a simple cubic crystal structure

What is Unit Cell?

• A unit cell is the smallest entity that exhibits the chemical and physical properties of the material.

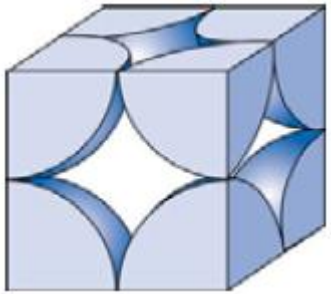
– *Unit cells are the most elementary arrangement of atoms which can generate the entire crystal upon application of suitable translation, rotation, mirror, or inversion operations.*

Definition:
the length of each unit cell axis is called a lattice

– *In cubic systems, all three orthogonal lattice parameters are equal*

– Lattice parameters are typically on the order of a few Angstroms (or a few tenths of a nanometer)

Simple Cubic Unit Cell



How many atoms does the simple cubic unit cell contain?

You should be able to convince yourself that a simple cubic structure contains … atom/unit cell.

(Remember, a part of each atom is shared by another unit cell!)

- The number of atoms/unit cell is an important quantity and determines many physical properties.
- In general, the number of atoms/unit cell, N, is given by

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

Where: N_i = # interior atoms,
N_f = # face atoms,
N_c = # corner atoms

Simple Cubic Unit Cell

- volume of the unit cell = a^3
  - where a is the lattice parameter

- coordination # = 6
  - for simple cubic structures

✓CN is the number of nearest-neighbor atoms

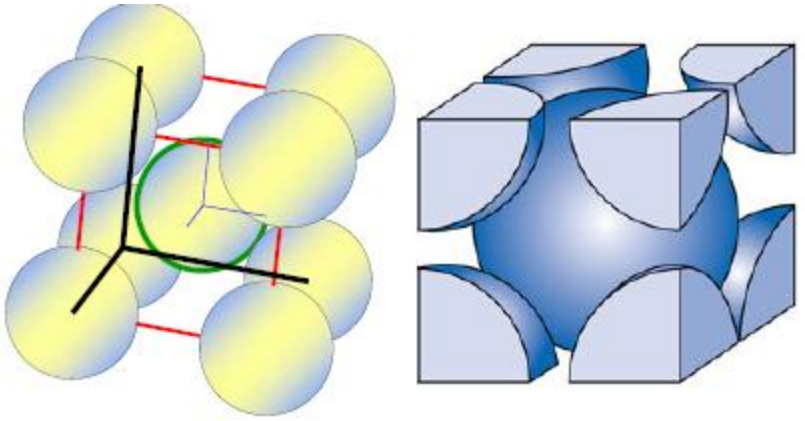
✓ Coordination number is important in determining the structure of crystalline materials.

✓ Large atoms tend to have large CN, small atoms usually have small CN

it's easier to surround a big atom with lots of atoms than a smaller one.

BODY CENTERED CUBIC STRUCTURE (BCC)

Now, suppose we add another atom at the **center** of the cube



We no longer have a simple cubic structure but instead, a .... (BCC) structure

Examples of BCC systems: Cr, W, Mo, Ta, Fe (αFe T_m below 912°C)

Notice that in the BCC structure, atoms touch along the body diagonals. These are the close-packed directions in the body-centered cubic structure.

BCC unit cells have a CN = ..**8**...

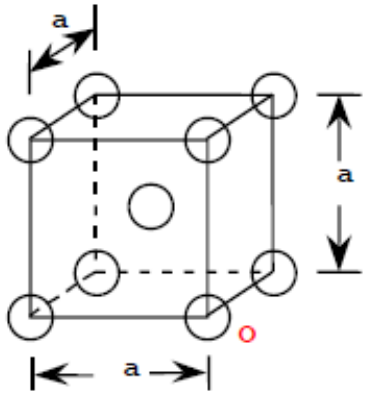
2 atoms in unit cell

Atomic Packing Factor

$$\text{Atomic Packing Factor (APF or APE)} = \frac{\text{total "sphere" volume}}{\text{total cell volume}}$$

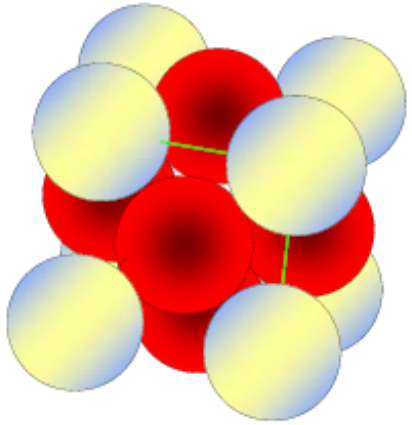
"total sphere volume" is just the volume per atomic "sphere" multiplied by the number of atoms in the unit cell

Example: Calculate the APF for a BCC unit cell:



Face Centered Cubic Unit Cell

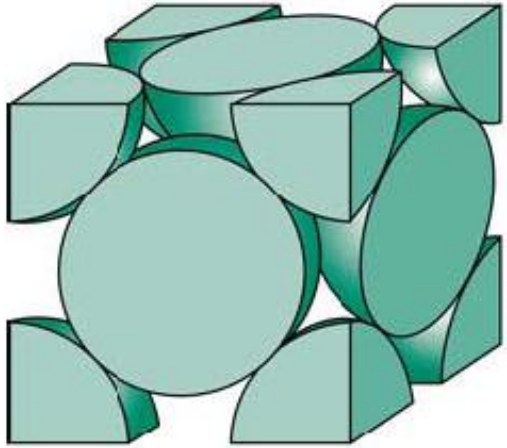
Now suppose we place equivalent atoms at the corners of the unit cell, AND in the center of each face:



This is a ..... (FCC) crystal structure

- Examples of FCC metals: Cu, Ni, Au, Ag, Fe (T_m above 912°C)
- Close-packed directions in FCC metals are along face diagonals

Face Centered Cubic Unit Cell



- Q: How many atoms per unit cell in the FCC structure?

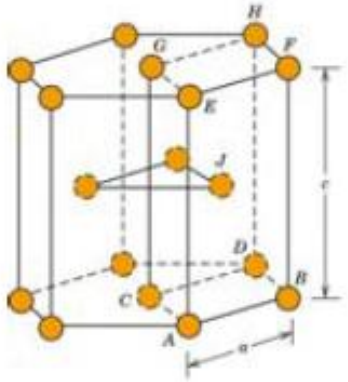
$$\text{recall, } N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

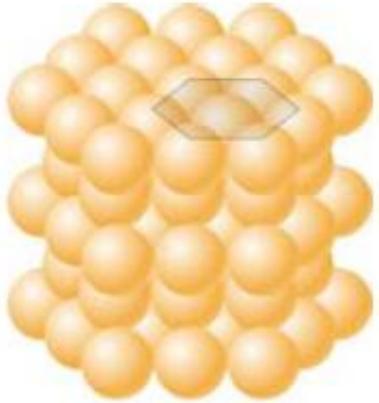
- FCC unit cells have a CN = 12 and an APF = 0.75
  - *maximum packing efficiency for monosized spheres*

Hexagonal Unit Cell

- There are other ways in which atoms can be arranged to form unit cells:
  - For example…

This represents an HCP (…….. ..packed..) structure





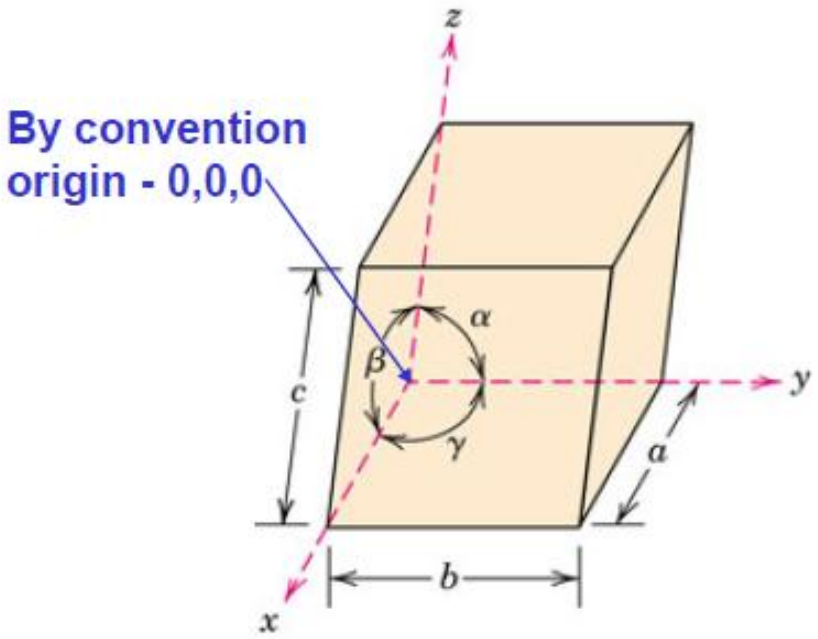
- Examples of HCP systems ***(Mg, Co, Ti, Zn, Zr, RE)***

- The HCP unit cell consists of 6 atoms forming the corners of a hexagon in the basal planes + 1 atom in the center. In addition, there are 3 interior atoms midway between basal planes along the c-axis.

  # atoms/unit cell = (1/6)*12 (corner atoms) + (1/2)*2 (center face atoms) + 3 (interior atoms) = …….

- Coordination # = ……12

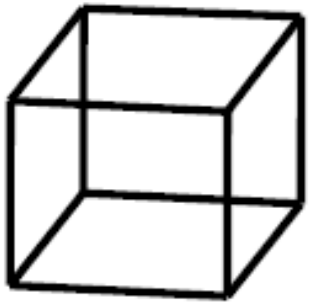
General convention for unit cell axis and angle notation:



In total, there are 7 distinct and unique crystal systems:

cubic represents only one of the 7

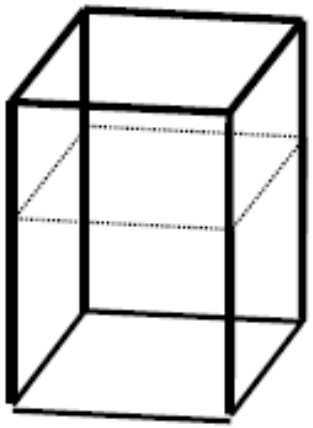
Crystal Systems



Cubic

a=b=c

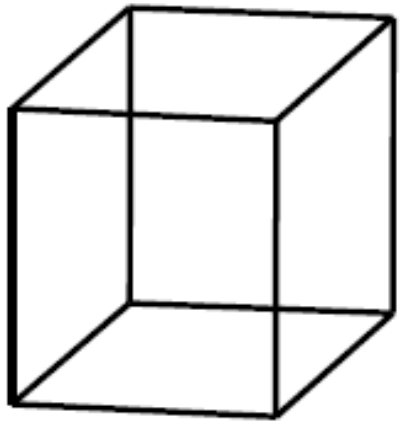
$\alpha=\beta=\gamma=90$



Tetragonal

a=b≠c

$\alpha=\beta=\gamma=90$

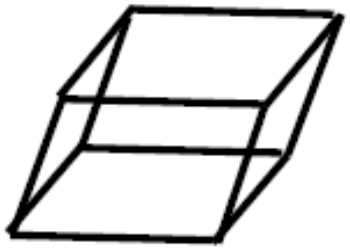


Orthorhombic

a≠b≠c

$\alpha=\beta=\gamma=90$

Crystal Systems

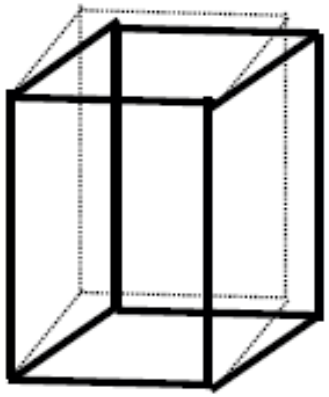


Rhombohedral

a=b=c

$\alpha=\beta=\gamma \neq 90$

"Pushed over" cube



Hexagonal

a=b≠c

$\alpha=\beta=90 \quad \gamma=120$

"Squished" tetragonal

Monoclinic

a≠b≠c

$\alpha=\gamma = 90, \beta \neq 90$

"Pushed over" orthorhombic (in one direction)

Triclinic

a≠b≠c

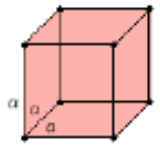
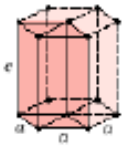
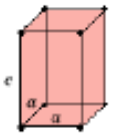
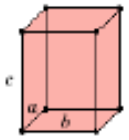
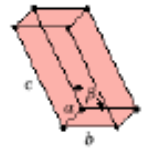
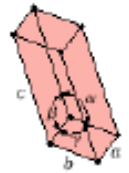
$\alpha \neq \beta \neq \gamma \neq 90$

"Pushed over" orthorhombic (in two directions)

Crystal Systems

Note that these 7 crystal systems do not account for all the possible lattice types

for example, the cubic system contains SC, FCC, and BCC as subsets

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Crystal Systems

There are 14 unique lattice types from this framework of 7 crystal systems (called Bravais lattices):

Crystal system	Types of possible lattice arrangements
Cubic	SC, BCC, FCC
Hexagonal	HCP
Tetragonal	Simple, body-centered
Orthorhombic	Simple, base-centered, BC, FC
Rhombohedral	Simple
Monoclin	Simple, base-centered
Triclinic	Simple

We will mainly be concerned with cubic and hexagonal systems in this class. But you need to realize that many other types of symmetries exist!