The Structure of Crystalline Solids

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Outline

- **Fundamental concepts and language**
- **Unit cells**
- **Crystal structures**
  - ➤ **Face-centered cubic**
  - ➤ **Body-centered cubic**
  - ➤ **Hexagonal close-packed**
- **Close packed crystal structures**
- **Density computations**
- **Types of solids**

  Single crystal

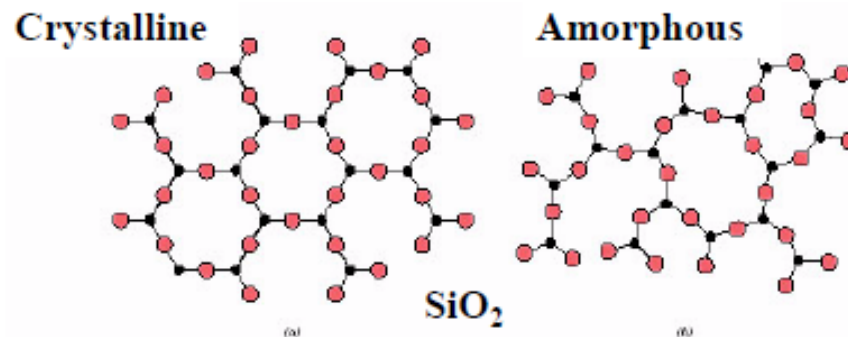 **Polycrystalline**

  Amorphous

Types of solids

Crystalline material: atoms self-organize in a periodic array

Single crystal: atoms are in a repeating or periodic array over the entire extent of the material

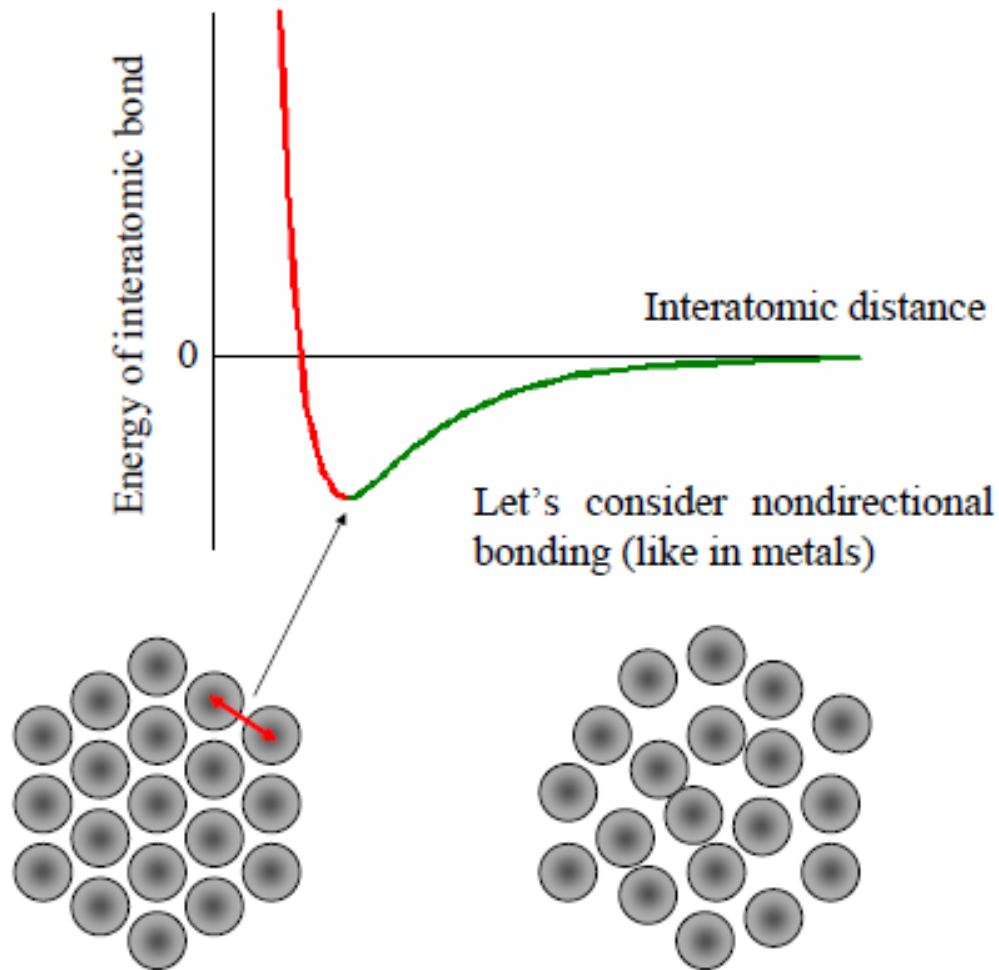**Polycrystalline material**: comprised of many small crystals or **grains**


Amorphous: disordered – lack of a systematic atomic arrangement

Crystalline   Amorphous

SiO_2

Crystal structures

Why do atoms assemble into ordered structures (crystals)?

Interatomic distance

Let's consider nondirectional bonding (like in metals)

Energy of the crystal < Energy of the amorphous solid

To discuss crystalline structures it is useful to consider atoms as being hard spheres with well-defined radii. In this hard-sphere model, the shortest distance between two like atoms is one diameter of the hard sphere.

2R — hard-sphere model
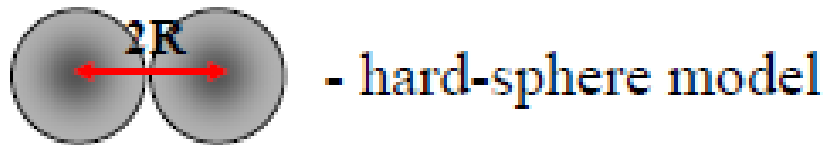
We can also consider crystalline structure as a lattice of points at atom/sphere centers.
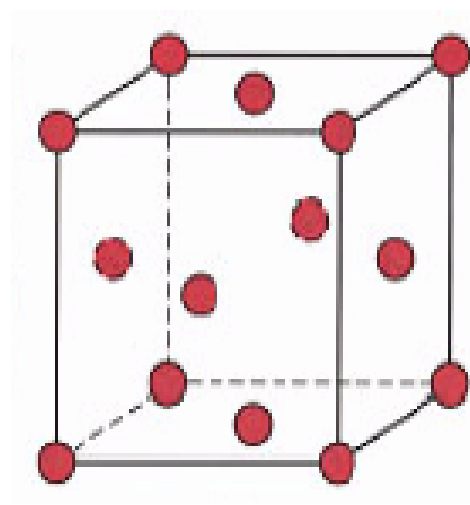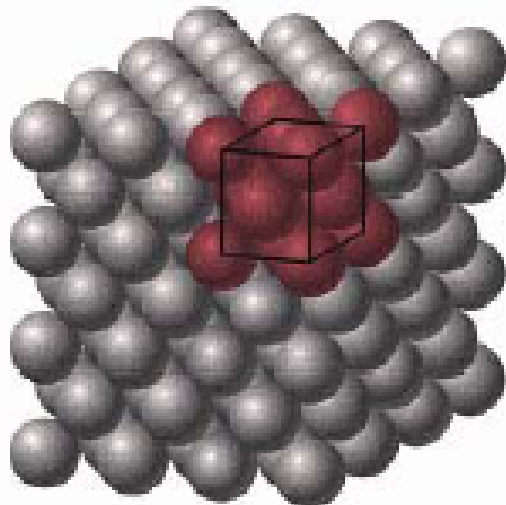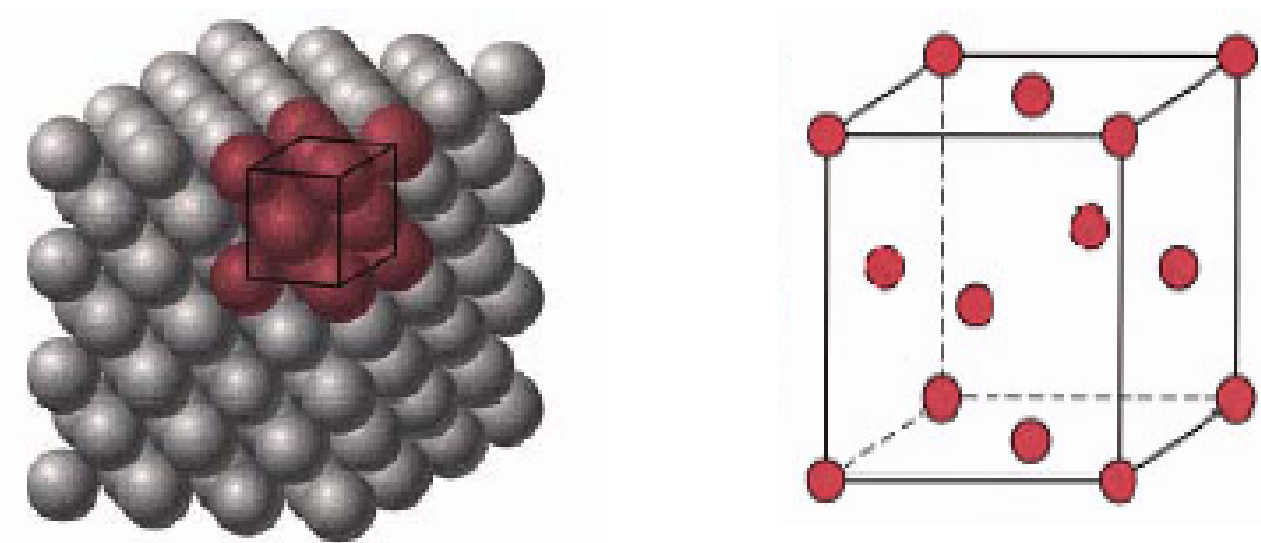
Unit cell

The unit cell is a structural unit or building block that can describe the crystal structure. Repetition of the unit cell generates the entire crystal.

Example: 2D honeycomb net can be represented by translation of two adjacent atoms that form a unit cell for this 2D crystalline structure
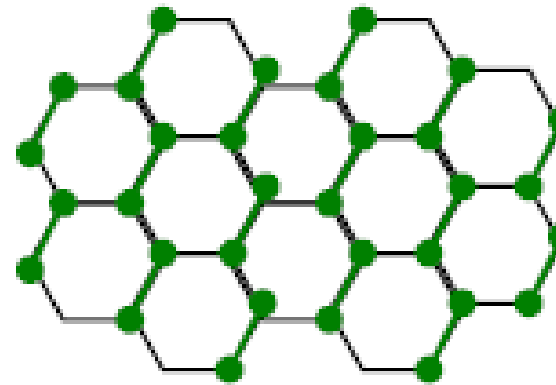
Example of 3D crystalline structure:

Different choices of unit cells possible, we will consider parallelepiped unit cell with highest level of symmetry

Metallic crystalline structure

➢ Metals are usually (poly)crystalline; although formation of amorphous metals is possible by rapid cooling

➢ As we learned in Chapter 2, the atomic bonding in metals is non-directional ⇒ no restriction on numbers or positions of nearest-neighbor atoms ⇒ large number of nearest neighbors and dense atomic packing

➢ **Atomic (hard sphere) radius, R**, defined by ion core radius - typically 0.1 - 0.2 nm

➢ The most common types of unit cells are
- faced-centered cubic (FCC)
- body-centered cubic (BCC)
- hexagonal close-packed (HCP).

Face-centered Cubic (FCC) Crystal Structure (I)

➢ Atoms are located at each of the corners and on the centers of all the faces of cubic unit cell

➢ Cu, Al, Ag, Au have this crystal structure

Two representations of the FCC unit cell
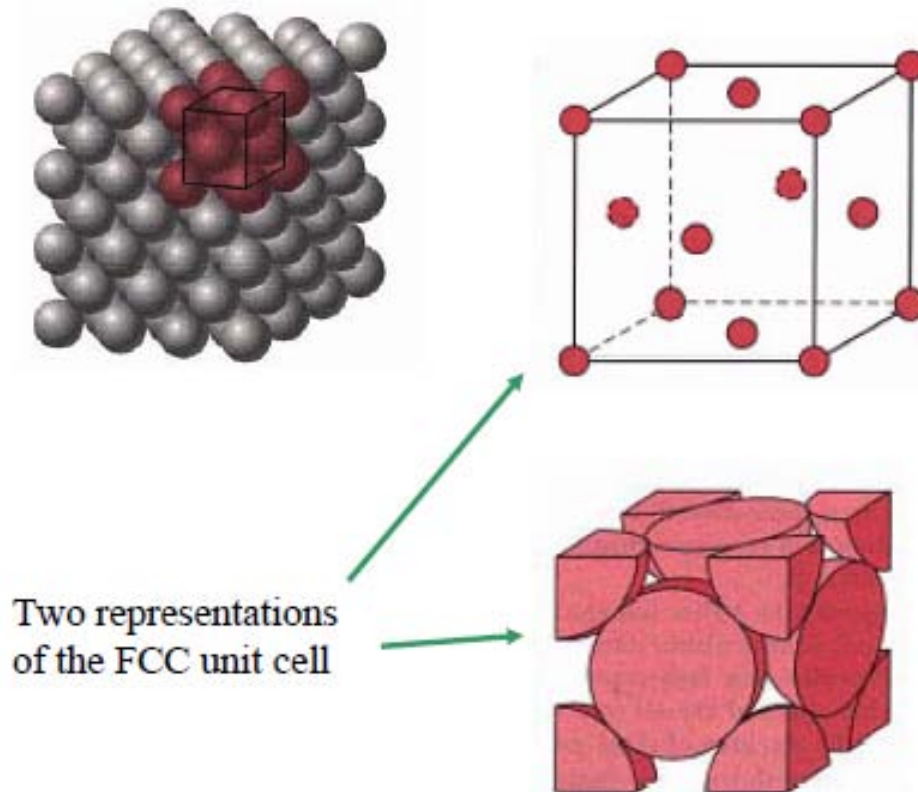
Face-centered Cubic (FCC) Crystal Structure (II)
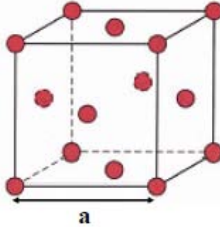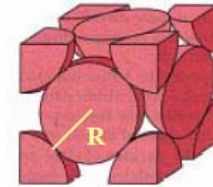
➤ **The coordination number, CN** = the number of closest neighbors to which an atom is bonded = number of touching atoms, **CN = 12**

➤ **Number of atoms per unit cell, n = 4**. (For an atom that is shared with m adjacent unit cells, we only count a fraction of the atom, $1/m$). In FCC unit cell we have:

6 face atoms shared by two cells: $6 \times 1/2 = 3$

8 corner atoms shared by eight cells: $8 \times 1/8 = 1$

➤ **Atomic packing factor, APF** = fraction of volume occupied by hard spheres = (Sum of atomic volumes)/(Volume of cell) = **0.74** (maximum possible)

Face-centered Cubic (FCC) Crystal Structure (III)
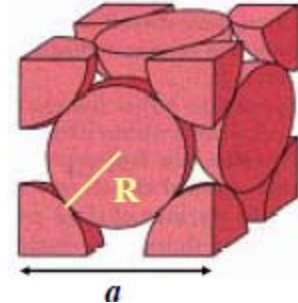
$$a = 2R\sqrt{2}$$

- Let us calculate the Atomic packing factor (APF) for FCC crystal.

APF = (Sum of atomic volumes)/(Volume of unit cell)

Volume of 4 hard spheres in the unit cell: $4 \times \dfrac{4}{3}\pi R^3$

Volume of the unit cell: $a^3 = 16R^3\sqrt{2}$

$$APF = \frac{16}{3}\pi R^3 \Big/ 16R^3\sqrt{2} = \pi/3\sqrt{2} = 0.74$$

maximum possible packing of hard spheres

Face-centered Cubic (FCC) Crystal Structure (IV)

➤ Corner and face atoms in the unit cell are equivalent

➤ FCC crystal has APF of 0.74, the maximum packing for a system equal-sized spheres ⇒ FCC is a **close-packed structure**

➤ FCC can be represented by a stack of **close-packed planes** (planes with highest density of atoms)
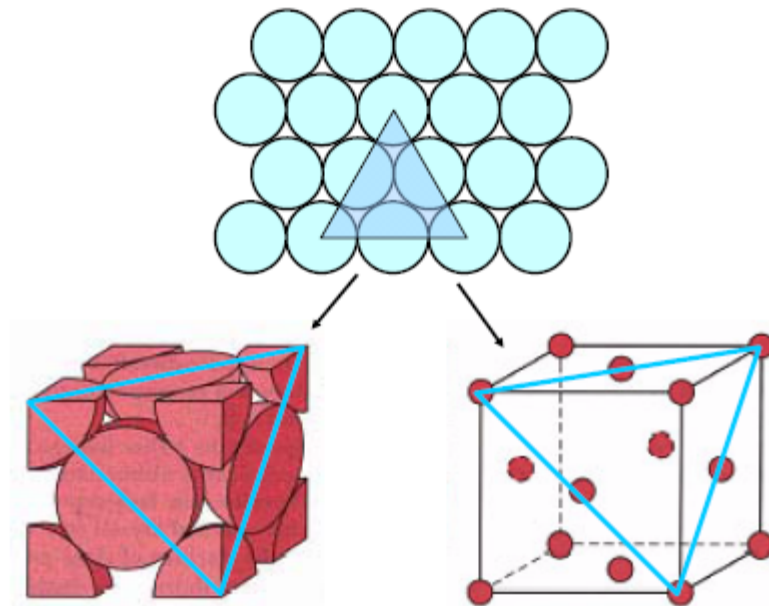
Body-centered Cubic (BCC) Crystal Structure (I)

Atom at each corner and at center of cubic unit cell

Cr, α-Fe, Mo have this crystal structure
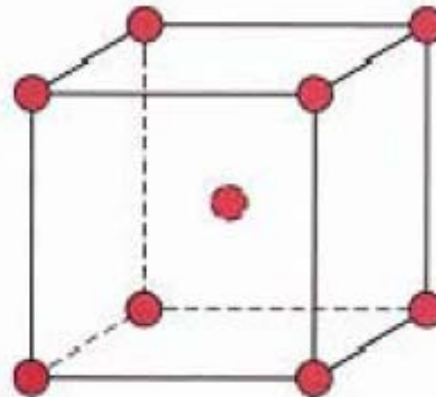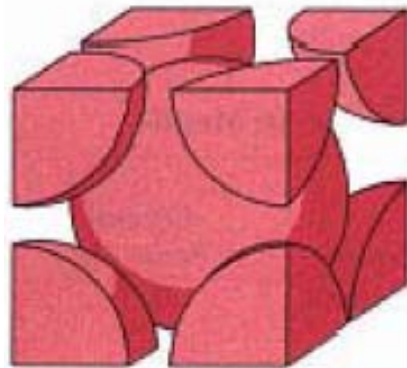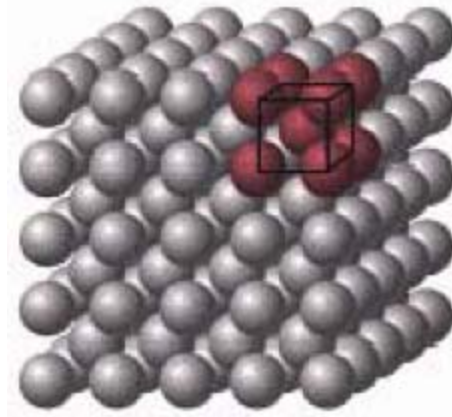
Body-centered Cubic (BCC) Crystal Structure (II)

➢ The hard spheres touch one another along cube diagonal $\Rightarrow$ the cube edge length, $a = 4R/\sqrt{3}$

➢ **The coordination number, CN = 8**

➢ **Number of atoms per unit cell, n = 2**

   Center atom (1) shared by no other cells: $1 \times 1 = 1$
   8 corner atoms shared by eight cells: $8 \times 1/8 = 1$

➢ **Atomic packing factor, APF = 0.68**

➢ Corner and center atoms are equivalent
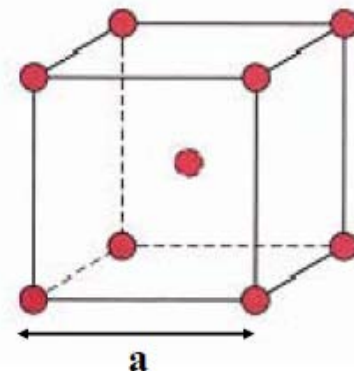
Hexagonal Close Packed Crystal Structure (I)

➢ HCP is one more common structure of metallic crystals

➢ Six atoms form regular hexagon, surrounding one atom in center. Another plane is situated halfway up unit cell (c-axis), with 3 additional atoms situated at interstices of hexagonal (close-packed) planes

➢ Cd, Mg, Zn, Ti have this crystal structure
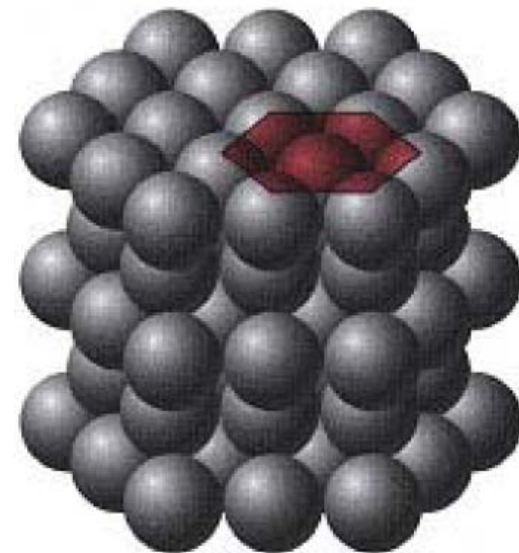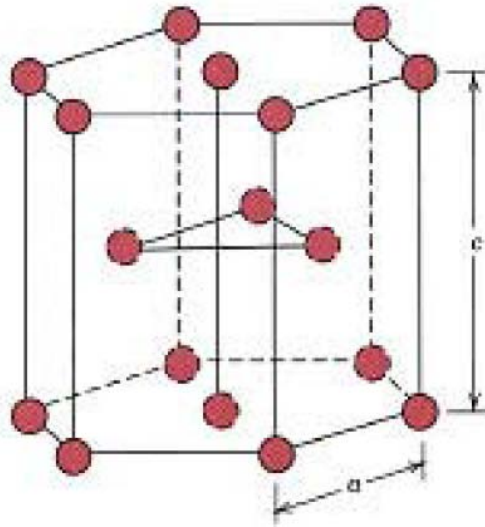
Hexagonal Close Packed Crystal Structure (II)

➢ Unit cell has two lattice parameters a and c. Ideal ratio c/a = 1.633

➢ **The coordination number, CN = 12 (same as in FCC)**

➢ **Number of atoms per unit cell, n = 6.**
   3 mid-plane atoms shared by no other cells: $3 \times 1 = 3$
   12 hexagonal corner atoms shared by 6 cells: $12 \times 1/6 = 2$
   2 top/bottom plane center atoms shared by 2 cells: $2 \times 1/2 = 1$

➢ **Atomic packing factor, APF = 0.74 (same as in FCC)**

➢ All atoms are equivalent

Close-packed Structures (FCC and HCP)

➢ Both FCC and HCP crystal structures have atomic packing factors of 0.74 (maximum possible value)

➢ Both FCC and HCP crystal structures may be generated by the stacking of close-packed planes

➢ **The difference between the two structures is in the stacking sequence**

FCC: Stacking Sequence ABCABCABC…
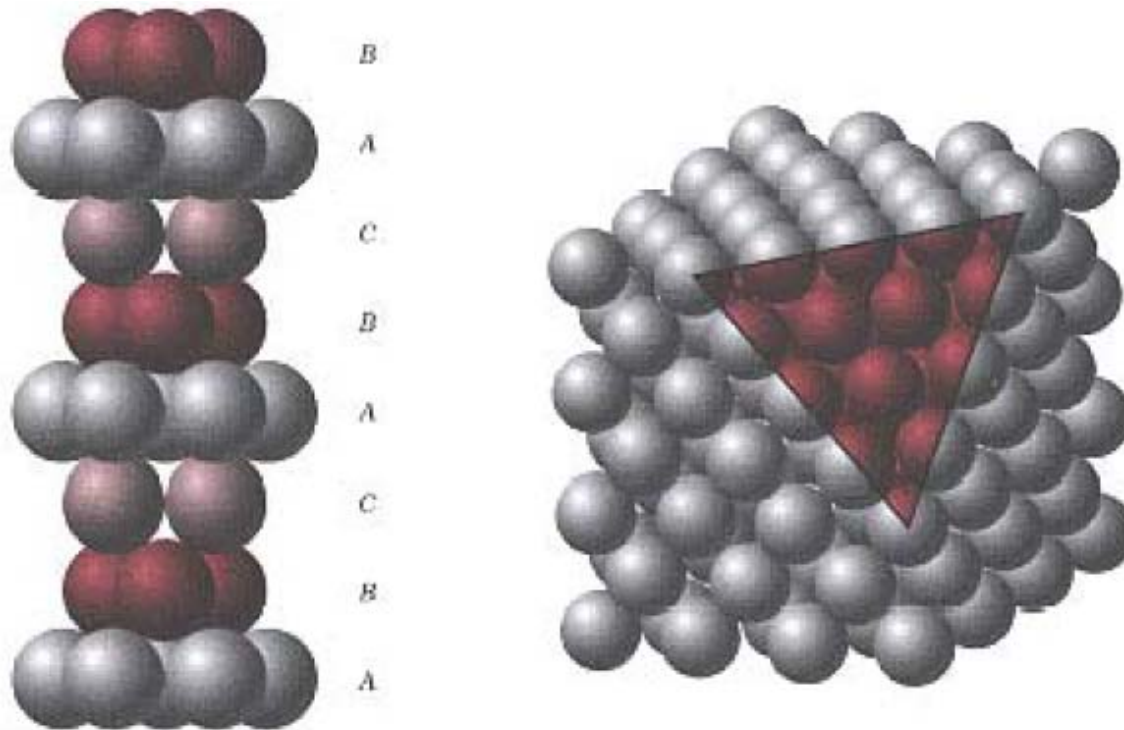
Third plane is placed above the "holes" of the first plane not covered by the second plane.

HCP: Stacking Sequence ABABAB...
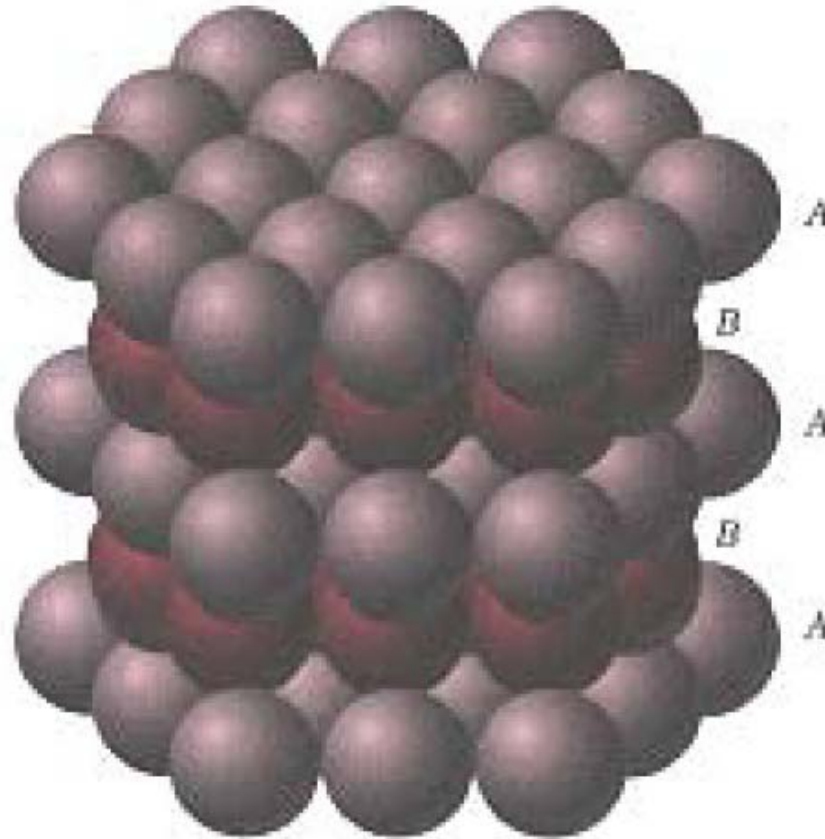
Third plane is placed directly above the first plane of atoms.

Density Computations

Since the entire crystal can be generated by the repetition of the unit cell, the density of a crystalline material, ρ = the density of the unit cell = (atoms in the unit cell, n) × (mass of an atom, M) / (the volume of the cell, V_c)

Atoms in the unit cell, n = 2 (BCC); 4 (FCC); 6 (HCP)

Mass of an atom, M = Atomic weight, A, in amu (or g/mol) is given in the periodic table. To translate mass from amu to grams we have to divide the atomic weight in amu by the Avogadro number N_A = 6.023×10^{23} atoms/mol

Density Computations

The volume of the cell, $V_c = a^3$ (FCC and BCC)

   $a = 2R\sqrt{2}$ (FCC); $a = 4R/\sqrt{3}$ (BCC)

   where R is the atomic radius

Thus, the formula for the density is:

$$\rho = \frac{nA}{V_c N_A}$$

Atomic weight and atomic radius of many elements you can find in the table at the back of the textbook front cover.

Polymorphism and Allotropy

- Some materials may exist in more than one crystal structure, this is called **polymorphism.** If the material is an elemental solid, it is called **allotropy**.

- An example of allotropy is carbon, which can exist as diamond, graphite, and amorphous carbon.

Diamond

Graphite

Buckminsterfullerene
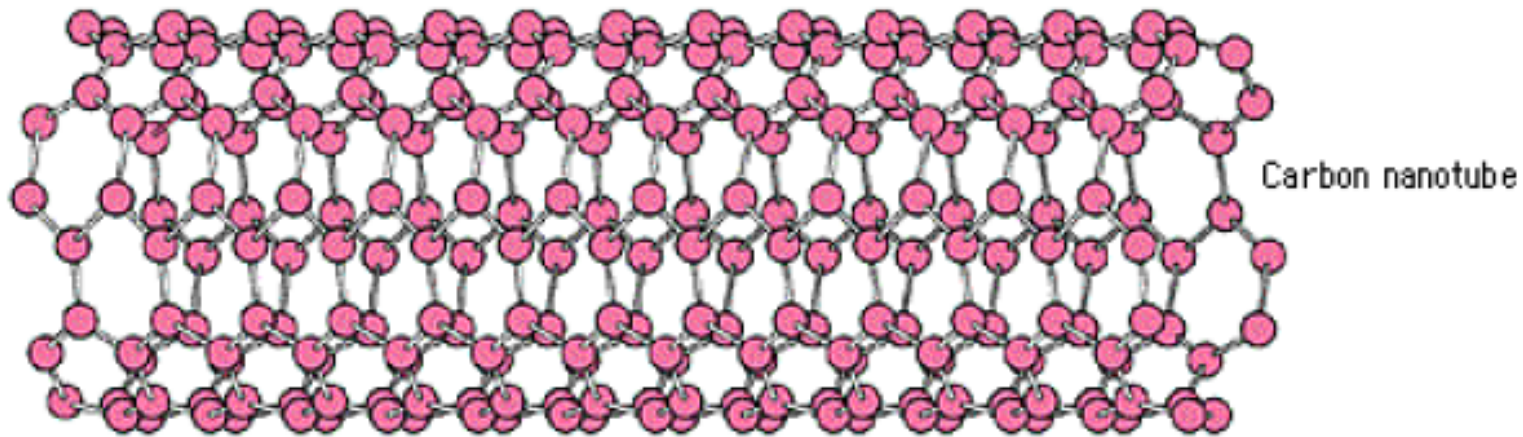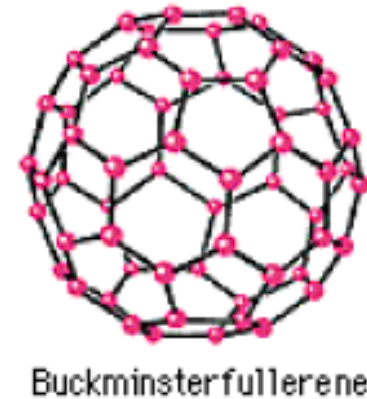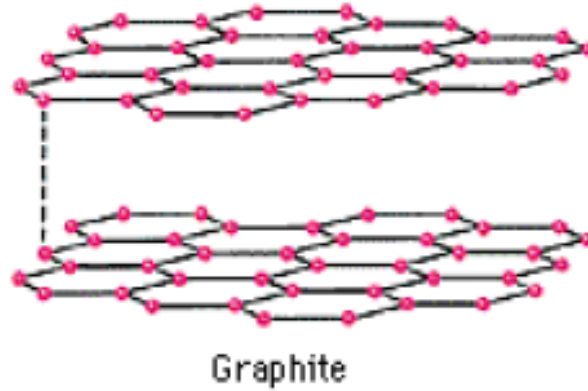
Carbon nanotube

Pure, solid carbon occurs in three crystalline forms – diamond, graphite; and large, hollow fullerenes. Two kinds of fullerenes are shown here: buckminsterfullerene (buckyball) and carbon nanotube.

Single Crystals and Polycrystalline Materials

- Single crystal: atoms are in a repeating or periodic array over the entire extent of the material.

- Polycrystalline material: comprised of many small crystals or grains. The grains have different crystallographic orientation. There exist atomic mismatch within the regions where grains meet. These regions are called grain boundaries.

Grain Boundaries

Grain Boundary

"Grains"
(Differently Oriented Crystals)
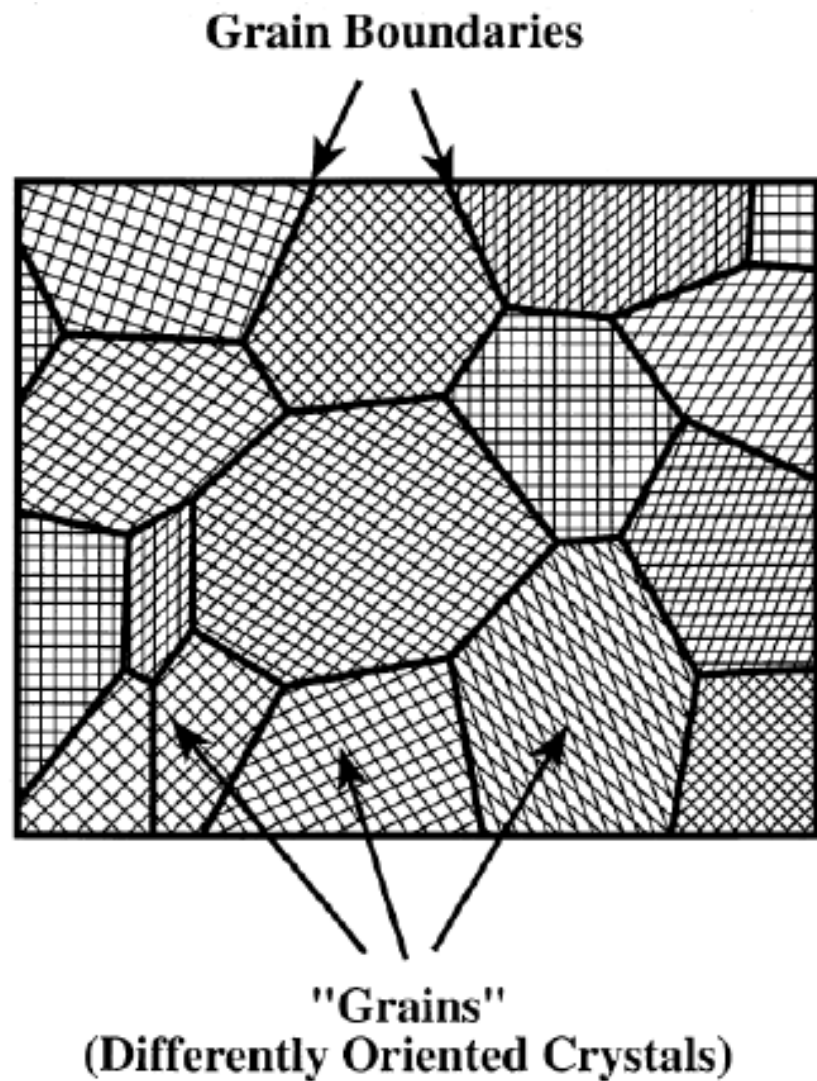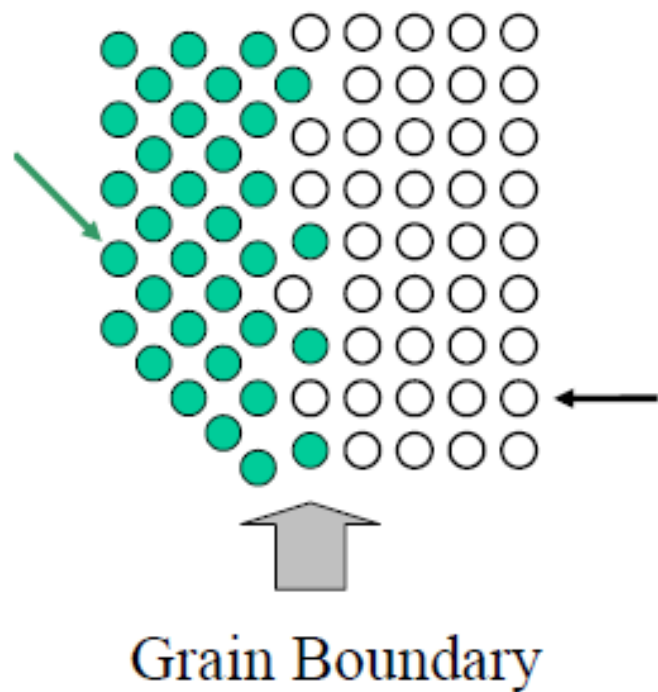
Polycrystalline Materials
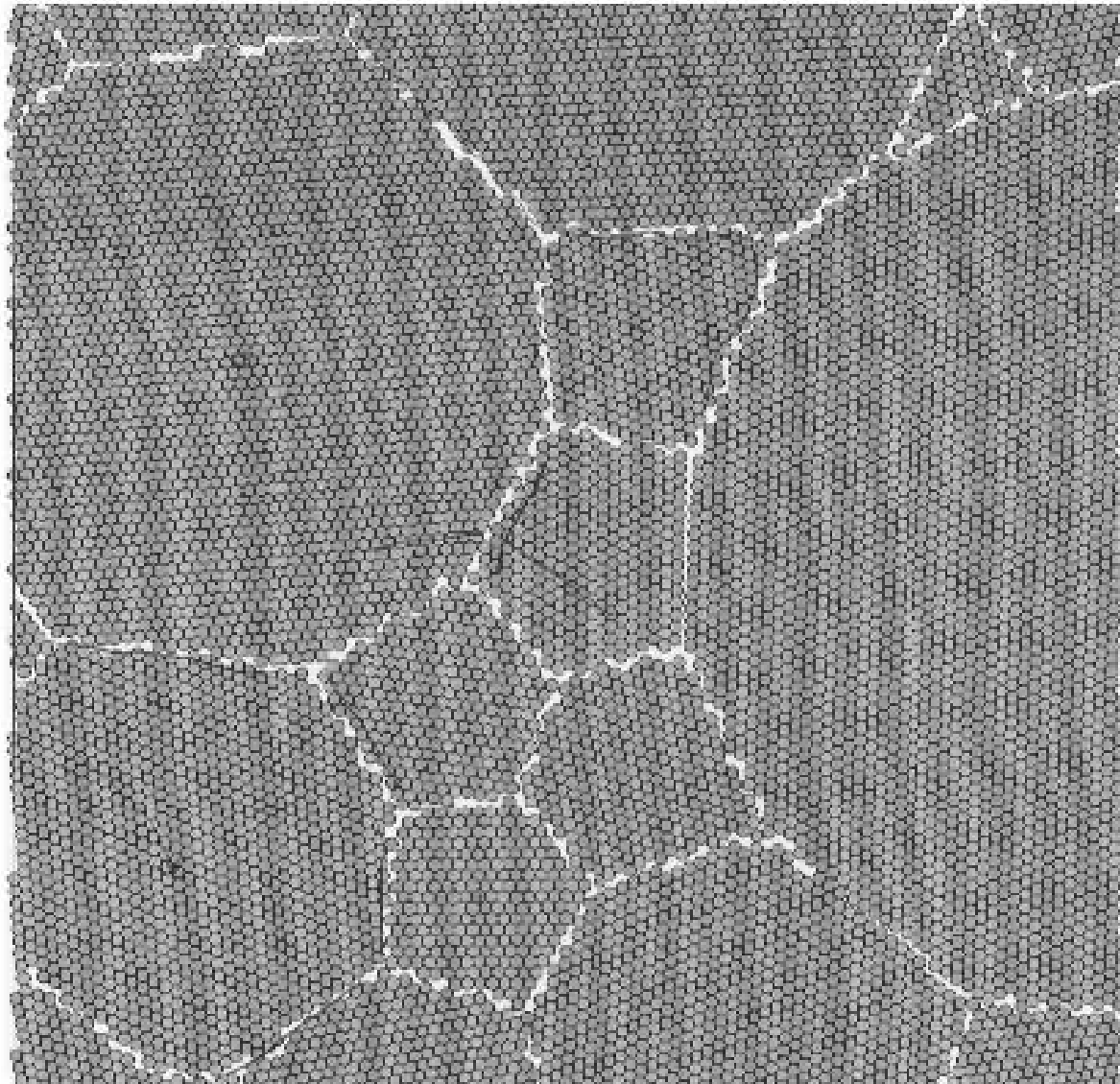
Atomistic model of a nanocrystalline solid by Mo Li, JHU

Polycrystalline Materials

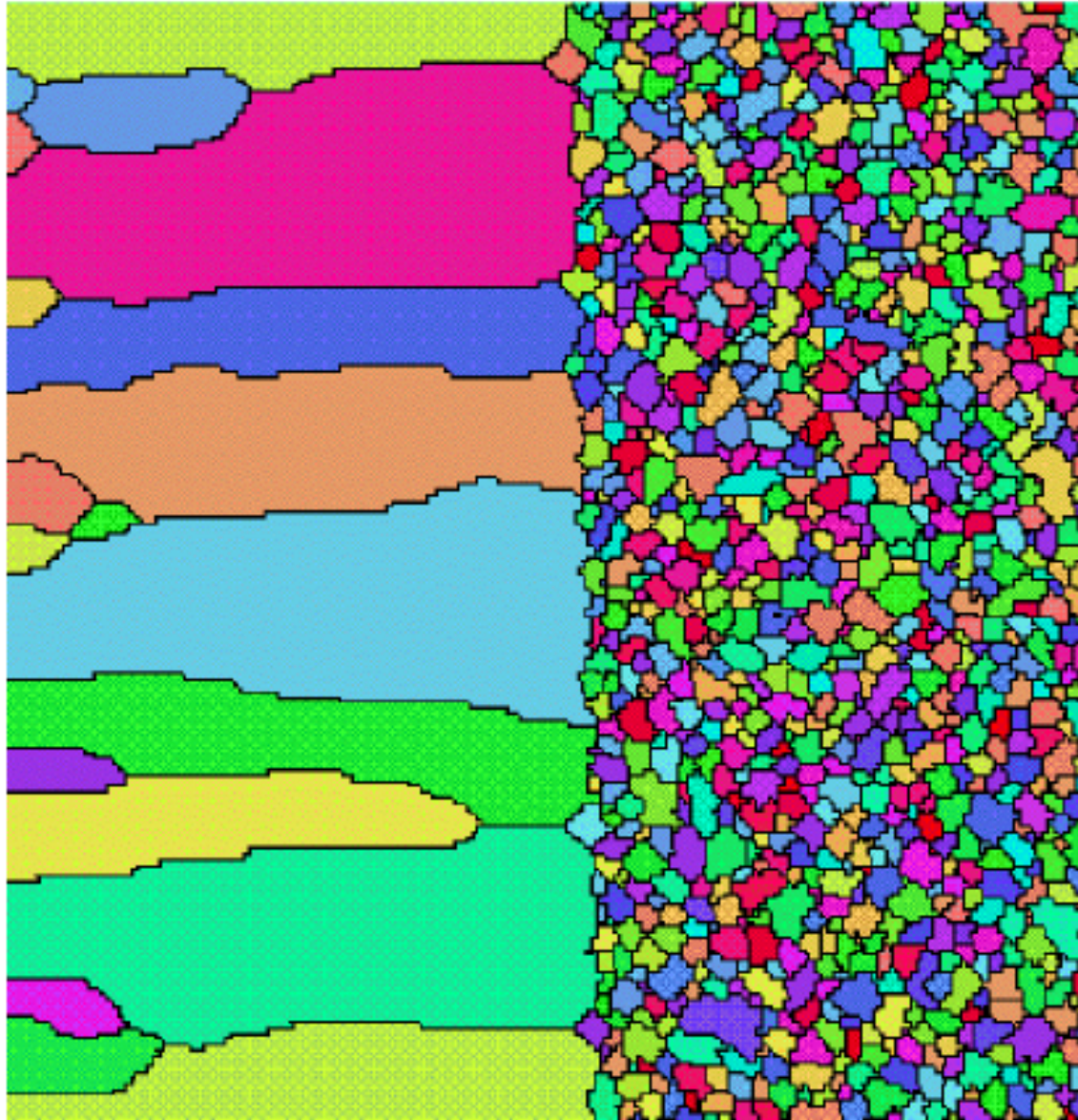Simulation of annealing of a polycrystalline grain structure
from http://cmpweb.ameslab.gov/cmsn/microevolproj.html (link is dead)

Anisotropy

- Different directions in a crystal have different packing. For instance, atoms along the edge of FCC unit cell are more separated than along the face diagonal. This causes anisotropy in the properties of crystals, for instance, the deformation depends on the direction in which a stress is applied.

- In some polycrystalline materials, grain orientations are random, so bulk material properties are isotropic.

- Some polycrystalline materials have grains with preferred orientations (texture), so properties are dominated by those relevant to the texture orientation and the material exhibits anisotropic properties.

Non-Crystalline (Amorphous) Solids

- In amorphous solids, there is no long-range order. But amorphous does not mean random, in many cases there is some form of short-range order.
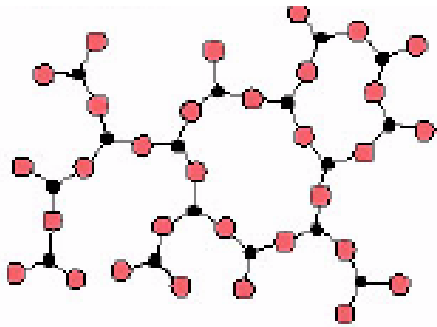
Schematic picture of amorphous SiO_2 structure
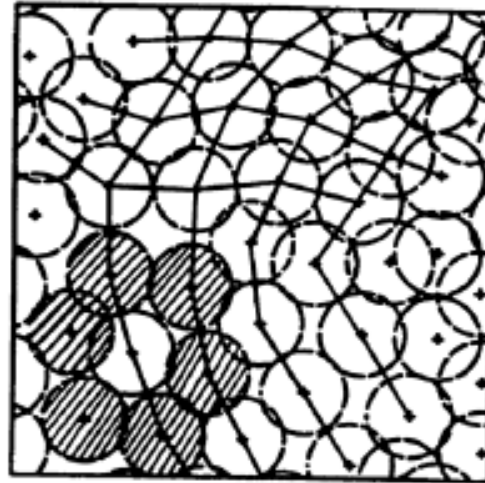
Amorphous structure from simulations by E. H. Brandt

Summary

Make sure you understand language and concepts:

- Allotropy
- Amorphous
- Anisotropy
- Atomic packing factor (APF)
- Body-centered cubic (BCC)
- Coordination number
- Crystal structure
- Crystalline
- Face-centered cubic (FCC)
- Grain
- Grain boundary
- Hexagonal close-packed (HCP)
- Isotropic
- Lattice parameter
- Non-crystalline
- Polycrystalline
- Polymorphism
- Single crystal
- Unit cell

Reading for next class:

Chapter 4: Imperfections in Solids

      Point defects (vacancies, interstitials)

      Dislocations (edge, screw)

      Grain boundaries (tilt, twist)

      Weight and atomic composition

Homework (1)

2.15 For an $Na^+ - Cl^-$ ion pair, attractive and repulsive energies E_A and E_R, respectively, depend on the distance between the ions r, according to

$$E_A = -\frac{1.436}{r}$$

$$E_R = \frac{7.32 \times 10^{-6}}{r^8}$$

For these expressions, energies are expressed in electron volts per $Na^+ - Cl^-$ pair, and r is the distance in nanometers. The net energy E_N is just the sum of the two expressions above.

(a) Superimpose on a single plot E_N, E_R, and E_A versus r up to 1.0 nm.

(b) On the basis of this plot, determine (i) the equilibrium spacing r_0 between the Na^+ and Cl^- ions, and (ii) the magnitude of the bonding energy E_0 between the two ions.

(c) Mathematically determine the r_0 and E_0 values using the solutions to Problem 2.14 and compare these with the graphical results from part (b).

2.20 Make a plot of bonding energy versus melting temperature for the metals listed in Table 2.3. Using this plot, approximate the bonding energy for molybdenum, which has a melting temperature of 2617°C.

3.7 Molybdenum has a BCC crystal structure, an atomic radius of 0.1363 nm, and an atomic weight of 95.94 g/mol. Compute and compare its theoretical density with the experimental value found inside the front cover.

3.17 Beryllium has an HCP unit cell for which the ratio of the lattice parameters c/a is 1.568. If the radius of the Be atom is 0.1143 nm, **(a)** determine the unit cell volume, and **(b)** calculate the theoretical density of Be and compare it with the literature value.