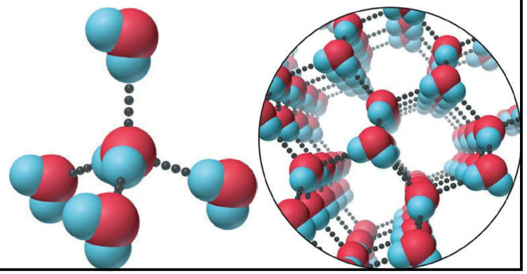
12.5 The Unique Properties of Water

- **Solvent** properties of water
  - Dissolves ionic compounds through ion-dipole forces (salts, minerals, acids, bases, …)
  - Dissolves molecular compounds
    - Through H-bonding and dipole-dipole forces (sugars, alcohols, proteins, …)
    - Through Dipole-induced dipole forces (O_2, CO_2, …)
- **Thermal** properties of water
  - Very high **heat capacity** – it takes a lot of heat to warm or cool water (due to strong H-bonding)
    - Oceans help maintain a narrow ***T*** range on Earth
  - Very high ΔH_{vap} – it takes a lot of heat to vaporize water (due to strong H-bonding)
    - Sweating helps maintain body temperature

- **Surface** properties of water
  - Very high **surface tension** (strong H-bonding)
    - Provides excellent capillary action (moisture in soil)
- **Density** of water
  - Ice has lower density than liquid water due to the open ice structure (hexagonal network of H-bonds); the liquid is packed more efficiently

- Negative slope of solid liquid-phase boundary (rare)
- Ice floats on the surface of lakes and prevents total freezing



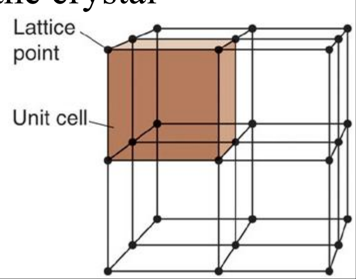
12.6 The Solid State

- **Amorphous solids** – random arrangement of structural units (rubber, plastics, …)
- **Crystalline solids** – structural units arranged in regular arrays (crystals with well defined shapes and surfaces)

- **Crystal lattice** – a system of points defining the geometric pattern of the crystal

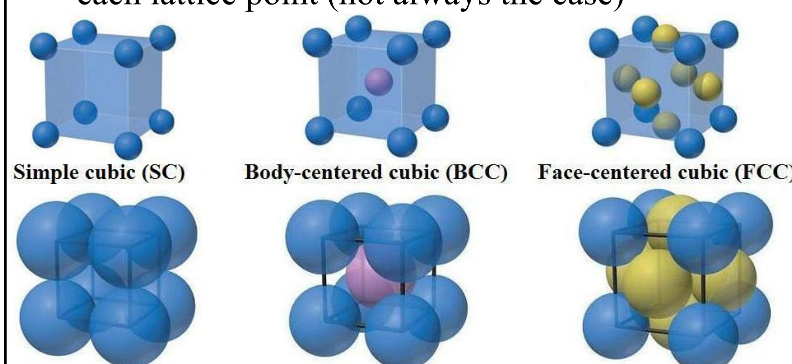
➢ **Lattice points** – points with identical surroundings (can be occupied by atoms, ions or molecules)

➢ **Unit cell** – a small set of lattice points sufficient to reproduce the entire lattice

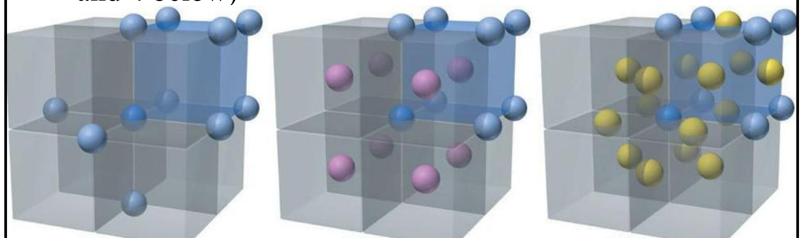


➢ There are 7 **crystallographic systems** with different lattices occurring in nature

- **Cubic system** – the unit cell is a cube
  - There are three types of cubic unit cells
  - Let's assume that a spherical particle occupies each lattice point (not always the case)

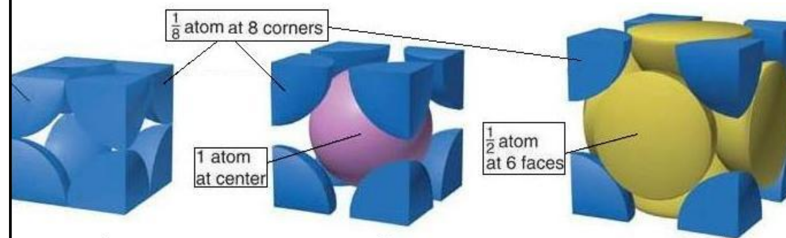


- **Coordination number** – the number of nearest neighbors of a particle in the lattice
  - **SC → coord. # = 6** → each particle touches 6 other particles (4 in the same layer, 1 above and 1 below)
  - **BCC → coord. # = 8** → each corner particle touches 8 particles in the body centers of the 8 cells it belongs to
  - **FCC → coord. # = 12** → each corner particle touches 12 particles in the face centers (4 in the same layer, 4 above and 4 below)



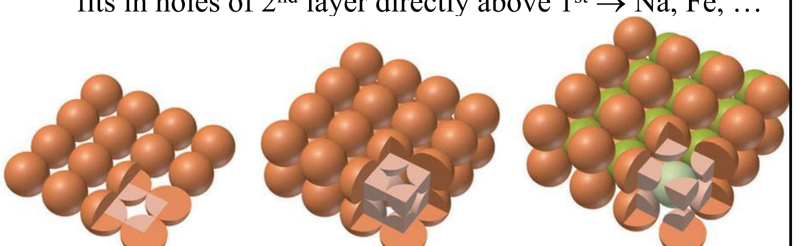
SC **BCC** **FCC**

- **Lattice points per unit cell (*n*)**
  - Corner points belong to 8 cells → 1/8 of the corner points
  - Face points belong to 2 cells → 1/2 of the corner points
  - Body points belong to 1 cell → all body points
- **SC → *n* = (1/8)*8** corners **= 1**
- **BCC → *n* = (1/8)*8** corners **+ 1** body point **= 1+1 = 2**
- **FCC → *n* = (1/8)*8** corners **+ (1/2)*6** face points **= 1+3 = 4**



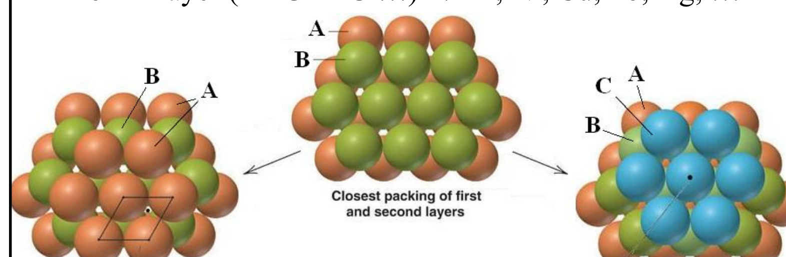
n = 1 **n = 2** **n = 4**

- **Packing efficiency** – part of the total volume of the crystal that is occupied by the particles
  - For spherical particles of the same size, the efficiency **increases with the coordination #**
- **SC & BCC** – in each layer, the particles form squares with diamond-shaped holes between them
  - **SC** → 2^{nd}, 3^{rd}, … layers directly on top of 1^{st} layer
  - **BCC** → 2^{nd} layer fits in holes of 1^{st} layer, and 3^{rd} layer fits in holes of 2^{nd} layer directly above 1^{st} → Na, Fe, …



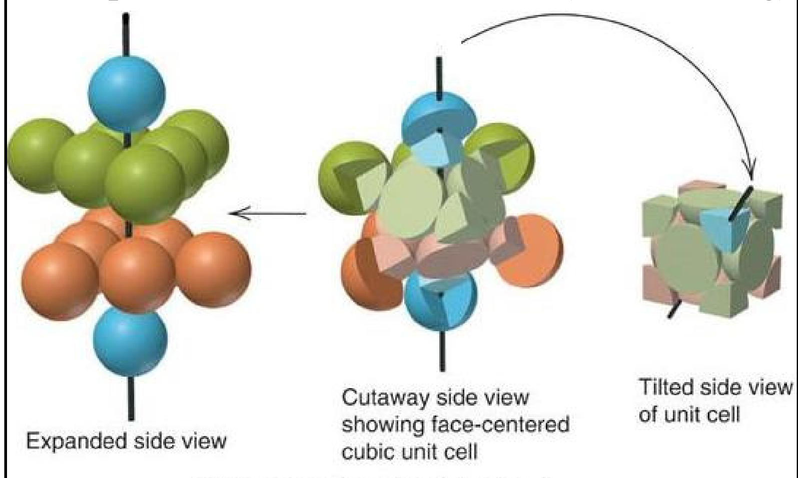
SC (52%) **BCC (68%)**

- **Closest packing** structures – in each layer, the particles form rhombi with triangular holes between them (more efficient)
  - **Hexagonal closest packing** (**hcp**) – 2^{nd} layer fits in holes of 1^{st} layer, and 3^{rd} layer fits in holes of 2^{nd} layer directly above 1^{st} layer (**ABAB** …) → Zn, Mg, Ti, …
  - **Cubic closest packing** (**ccp**) – 2^{nd} layer fits in holes of 1^{st} layer; 3^{rd} layer fits in holes of 2^{nd} layer above holes of 1^{st} layer (**ABCABC** …) → Al, Ni, Cu, Pb, Ag, …



hcp (74%) **ccp (74%)**

- **hcp** is based on the **hexagonal** unit cell
- **ccp** is based on the **FCC** unit cell (the same thing)



Cubic closest packing (*abcabc*...)

- **Density** of unit cells (***d***) – same as that of the crystal
  - $m \rightarrow$ mass of unit cell; $m_p \rightarrow$ mass of 1 particle
  - $V \rightarrow$ volume of unit cell; $V_p \rightarrow$ volume of 1 particle
  - $V_o \rightarrow$ volume of unit cell occupied by particles
  - $n \rightarrow$ # of particles per unit cell
  - $M \rightarrow$ molar mass; $N_a \rightarrow$ Avogadro's number
  - $Eff \rightarrow$ packing efficiency; $r \rightarrow$ radius of a particle

$$V_o = V \times Eff = n \times V_p \quad \Rightarrow \quad V = \frac{n \times V_p}{Eff}$$

$$d = \frac{m}{V} = \frac{n \times m_p}{V} = \frac{n \times (M / N_a)}{V} = \frac{\cancel{n} \times M \times Eff}{\cancel{n} \times V_p \times N_a}$$

$$V_p = \frac{4}{3} \pi \times r^3 \quad \Rightarrow \quad \boxed{d = \frac{3}{4} \times \frac{M \times Eff}{\pi \times r^3 \times N_a}}$$

Example: **Fe** has a density of **7.90 g/cm³** and crystallizes in a **BCC** lattice. Calculate the atomic radius of **Fe**.

$M \rightarrow 55.85$ g/mol; $Eff \rightarrow 0.68$; $r \rightarrow$???

$$d = \frac{3}{4} \times \frac{M \times Eff}{\pi \times r^3 \times N_a} \quad \Rightarrow \quad r = \sqrt[3]{\frac{3}{4} \times \frac{M \times Eff}{\pi \times d \times N_a}}$$

$$r = \sqrt[3]{\frac{3}{4} \times \frac{55.85\ \text{g/mol} \times 0.68}{3.14 \times 7.90\ \text{g/cm}^3 \times 6.022 \times 10^{23}\ /\text{mol}}}$$

$$r = 1.24 \times 10^{-8}\ \text{cm} = 124\ \text{pm}$$

- The structure of the unit cell can be studied by **x-ray diffraction**
  - The crystal is irradiated with a narrow beam of x-rays and the resulting diffraction pattern consists of dark and bright spots
  - The condition for constructive interference (bright spot in the pattern) is given by the **Bragg Equation:**

$$2d \sin\theta = n\lambda$$ $\rightarrow$ **d** – distance between layers
$\rightarrow$ **n** – whole number