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 (O2, CO2, …)

• **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 $\Delta H_{\text{vap}}$ – 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 \(\rightarrow\) coord. \# = 6 \(\rightarrow\) each particle touches 6 other particles (4 in the same layer, 1 above and 1 below)
- BCC \(\rightarrow\) coord. \# = 8 \(\rightarrow\) each corner particle touches 8 particles in the body centers of the 8 cells it belongs to
- FCC \(\rightarrow\) coord. \# = 12 \(\rightarrow\) each corner particle touches 12 particles in the face centers (4 in the same layer, 4 above and 4 below)

Lattice points per unit cell \((n)\)
- Corner points belong to 8 cells \(\rightarrow\) 1/8 of the corner points
- Face points belong to 2 cells \(\rightarrow\) 1/2 of the corner points
- Body points belong to 1 cell \(\rightarrow\) all body points
- SC \(\rightarrow n = (1/8)*8\) corners = 1
- BCC \(\rightarrow n = (1/8)*8\) corners + 1 body point = 1+1 = 2
- FCC \(\rightarrow n = (1/8)*8\) corners + (1/2)*6 face points = 1+3 = 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 \(\rightarrow\) 2nd, 3rd, … layers directly on top of 1st layer
  - BCC \(\rightarrow\) 2nd layer fits in holes of 1st layer, and 3rd layer fits in holes of 2nd layer directly above 1st \(\rightarrow\) Na, Fe, …

Closest packing structures – in each layer, the particles form rhombi with triangular holes between them (more efficient)
- Hexagonal closest packing (hcp) – 2nd layer fits in holes of 1st layer, and 3rd layer fits in holes of 2nd layer directly above 1st layer \((ABAB \ldots)\) \(\rightarrow\) Zn, Mg, Ti, …
- Cubic closest packing (ccp) – 2nd layer fits in holes of 1st layer; 3rd layer fits in holes of 2nd layer above holes of 1st layer \((ABCABC \ldots)\) \(\rightarrow\) Al, Ni, Cu, Pb, Ag, …
- **hcp** is based on the **hexagonal** unit cell
- **ccp** is based on the **FCC** unit cell (the same thing)

![Diagram of hexagonal and FCC unit cells]

**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

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

\[ d = \frac{m}{V} = \frac{n \times m_p}{V} = \frac{n \times (M / N_a)}{V} \quad \Rightarrow \quad \frac{n \times M \times Eff}{n \times V_p \times N_a} \]

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

**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; $Eff \rightarrow 0.68$ ; $r \rightarrow ???$

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

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

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

**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**:

\[ 2d \sin \theta = n \lambda \quad \rightarrow \quad d \rightarrow \text{distance between layers} \]

\[ n \rightarrow \text{whole number} \]

![Diagram of x-ray diffraction](image)