

Chapter 11
Intermolecular Forces, Liquids, and Solids

11.1 A Molecular Comparison of Liquids and Solids

- Gases characterized by rapidly moving, widely-spaced particles
- Solids characterized by a regular array of closely-spaced, fixed particles
- Liquids are somewhere in-between, but with some special properties of their own
- Why do liquids and solids exist? Why is all matter not in the gaseous state?

Changes of State

- Converting a gas into a liquid or solid requires the molecules to get closer to each other:
 - cool or compress.
- Converting a solid into a liquid or gas requires the molecules to move further apart:
 - heat or reduce pressure.
- The forces holding solids and liquids together are called intermolecular forces.

11.2 Intermolecular Forces

- Intermolecular forces are weaker than bonds, but have profound effects on the properties of liquids
- Polar liquids have a higher boiling point and higher heat of vaporization than non-polar liquids.
- Polar liquids dissolve ionic solids and polar liquids.

Ion-Dipole Forces

- Ions have full charges that are attracted to the partial charge on polar molecules (dipoles)
- Explains solubility of ionic salts in polar solvents
- Metal ions are hydrated in solution; this hydrate often is found in solid metal salts as well. Some hydrates actually form coordinate-covalent bonds and are very stable.
- $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is an example
- $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is so stable that it takes many hours to exchange a bonded water molecule for one in the solvent water

Hydrated Iron(III) Ion

- The water molecules are attracted so strongly in this case that they donate electron pairs to the iron ion and form a coordinate covalent bond.

Dipole-Dipole Forces

- Molecules that are permanent dipoles can also induce dipoles in other molecules
- Permanent dipoles attract one another
- Pure substance or mixture
- Strength of these forces depend on the dipole moment of the molecules
- Explains why polar liquids are more soluble in polar liquids than in non-polar liquids
 - It takes 2000 mL of H_2O to dissolve 1 mL of CCl_4

- It takes 50 mL of H₂O to dissolve 1 mL of CH₂Cl₂
- Which member of each pair has the stronger intermolecular forces?
SiCl₄, SiHCl₃
CO₂, SO₂

London Dispersion Forces

- London dispersion forces are present in all molecules; temporary partial charges give temporary polarity
- Strength increases with polarizability (squishiness of the electron cloud)
- Only force in non-polar molecules and in unbonded atoms
- London forces become stronger, the larger the atom or molecule (larger electron clouds are easier to deform)
- Found in mixtures or pure substances.
- The magnitude of London forces explains why Cl₂ is a gas, Br₂ is a liquid, and I₂ is a solid.
- Explain the order of the boiling points of the halogens and noble gases.

Boiling Points

- Boiling point increases with the size of molecules because of increases in London forces with larger electron clouds.

London Dispersion Forces

- Which member of each pair has the stronger London forces?
Ne, Kr
F₂, Cl₂
CH₄, SiCl₄
N₂, O₂ N₂ b.p. = 77.4 K O₂ b.p. = 90.2 K

Hydrogen Bonding

- Hydrogen bond is an especially strong dipole-dipole force, as shown by the trend in boiling points of polar molecules
- H-bonding is observed for HF, H₂O, NH₃, but not CH₄
- Conditions for occurrence:
 - H attached to a small, highly electronegative element in one molecule
 - Small, highly electronegative element with one or more unshared electron pairs in the other molecule
- Observed for the elements: F, O, N (rarely S and Cl)
- Which of the following molecules will hydrogen-bond in the pure substance?
H₂O
H₂Se
HF
HBr
NH₃
PF₃

Hydrogen Bonding in Liquid Water

- H points at the electron pair on the atom in the other molecule
- In liquid water, each water molecule is surrounded by an average of 4 other water molecules; structure is not rigid.
- Longer than covalent bond.
- Average of 4 hydrogen bonds in liquid water

Hydrogen Bonding

- Fluoride ion is hydrogen-bonded to water in solution
- Molecules hydrogen-bond to themselves or to other molecules.

Structure of Ice

- The water molecules in ice are fixed into a tetrahedral arrangement as a result of hydrogen bonding. Open structure makes ice less dense than water.
- The open structure of ice leaves channels of empty space through the crystals.

Identify Type of Intermolecular Forces

- What types of intermolecular forces are observed for each of the following molecules?

(A molecule may have more than one.)

H ₂ O	HF
HBr	NH ₃
PF ₃	CH ₃ OH
F ₂	CO
CO ₂	N ₂

Strengths of Intermolecular Forces

- Intermolecular forces generally increase in strength as
London < Dipole-Dipole < H-bonding < Ion-Dipole < Ionic Bonding
- The forces are cumulative. All molecules have London forces. Polar molecules have both London and dipole-dipole forces. ...

Trends in Intermolecular Forces

- Which member of each pair has the larger intermolecular forces (boiling point, heat of vaporization)?

CH₃OH, CH₃SH
 F₂, Kr
 F₂, CO
 CO, HF
 CO₂, NH₃
 N₂, NH₃

11.3 Some Properties of Liquids

- Properties intermediate between those of gases and solids
- Intermolecular forces and distance between particles are also intermediate
- Viscosity - resistance to flow
- Values depend on size and intermolecular forces

- Water is about average (high intermolecular forces, but small size)

Surface Tension

- Caused by intermolecular forces, which are larger in the bulk of the liquid than at the surface.
- Molecules must break IM forces in order to move to the surface and increase the surface area.
- Why are water droplets spherical?
- How does a water strider stay on the top of the water?
- Why does the needle float?
- Why does soap make the paper clip sink?

Capillary Action

- Why do liquids rise in a capillary?
- Competing forces:
 - Between liquid molecules
 - Between liquid molecules and glass
 - $\text{H}_2\text{O-Glass} > \text{H}_2\text{O-H}_2\text{O}$
 - $\text{Hg-Glass} < \text{Hg-Hg}$
- Height determined by net liquid-glass forces opposing gravity
- Which forces in each system are greater?

11.4 Phase Changes

- Physical states of a substance can co-exist under a variety of conditions of pressure and temperature.
- Phases: different forms (gas, liquid, solid, etc.) of a substance that co-exist in a heterogeneous system.
- Transitions between phases are called phase changes
 - evaporation: liquid \rightarrow gas (reverse = condensation)
 - melting: solid \rightarrow liquid (reverse = freezing)
 - sublimation: solid \rightarrow gas (reverse = deposition)

Heat of Vaporization

- Is evaporation exothermic or endothermic?
- ΔH_{vap} = heat needed to evaporate 1 mol of liquid at constant temperature
- Energy used to overcome intermolecular forces during evaporation
- Larger molecules have higher ΔH_{vap} because of higher London forces
- Polar $\Delta H_{\text{vap}} >$ nonpolar ΔH_{vap} if molecular size is similar
- H-bonded $\Delta H_{\text{vap}} >$ polar ΔH_{vap}

Heat of Fusion

- Generally heat of fusion (enthalpy of fusion) is less than heat of vaporization: it takes more energy to completely separate molecules, than partially separate them.

Freezing

- Cooling liquids decreases their kinetic energy
- When intermolecular forces become greater than kinetic energy, the liquid freezes and becomes solid.
- Freezing point = temperature at which solid and liquid are in a state of equilibrium
- Normal freezing point = f.p. at pressure of 1 atm.
- Pressure has a small effect on the freezing point.
- Effect depends of the relative densities of the liquid and solids.
- Most substances have higher density for solid; increased pressure increases the freezing point and at constant temperature, pressure makes the solid harder (more frozen).
- Water has a lower density for the solid; pressure causes the freezing point to decrease and may melt the solid.

Critical Temperature and Pressure

- Gases liquefied by increasing pressure at some temperature.
- Critical temperature: the minimum temperature for liquefaction of a gas using pressure
- Critical pressure: pressure required for liquefaction

11.5 Vapor Pressure

- Evaporation: loss of higher kinetic energy molecules, so the liquid cools (unless energy is supplied) (The process is endothermic.)
- Evaporative cooling, perspiration, alcohol bath, canvas water bags, wind chill factor

Evaporation

- Open container: evaporates completely
- Closed container: reach a state of equilibrium

Vapor Pressure

- Equilibrium: rate of evaporation = rate of condensation
- P at equilibrium = vapor pressure
- When $P_{\text{vap}} = P_{\text{atm}}$, T = boiling point
- When $P_{\text{vap}} = 1 \text{ atm}$, T = normal boiling point
- In Phoenix, boiling point of $\text{H}_2\text{O} = 99^\circ\text{C}$
- At sea level, b.p. of $\text{H}_2\text{O} = 100^\circ\text{C}$
- At 9000 ft elevation, b.p. of $\text{H}_2\text{O} = 91^\circ\text{C}$
(needs a pressure cooker to speed up cooking)
- Vapor pressure varies with temperature and intermolecular forces

11.6 Phase Diagrams

- Phase diagram: plot of pressure vs. Temperature summarizing all equilibria between phases.
- Given a temperature and pressure, phase diagrams tell us which phase will exist.
- lines: equilibrium between two phases

- areas: only one phase is stable
- triple point (confluence of 3 lines): equilibrium between three phases

Phase Diagram Features

- Features of a phase diagram:
 - Triple point: temperature and pressure at which all three phases are in equilibrium.
 - Vapor-pressure curve: generally as pressure increases, temperature increases.
 - Critical point: critical temperature and pressure for the gas.
 - Melting point curve: as pressure increases, the solid phase is favored if the solid is more dense than the liquid.
 - Normal melting point: melting point at 1 atm.

Phase Diagram of Water

- Shows conditions of stability of phases and conditions of equilibrium
- What phase changes are represented by the arrows?
- Label features.

Phase Diagram of Carbon Dioxide

- Describe the various points, lines, and areas on the diagram. How can we melt Dry Ice?

11.7 Structures of Solids

- Definite and rigid shapes and sizes
- Not very compressible
- Do not flow
- Two types of solids
 - amorphous (without form)
 - crystalline (orderly arrays)
- Demo: NiTiNOL

Crystals

- Crystal - an orderly, repeating, 3-dimensional array of particles
- Lattice - pattern formed by the array
- Unit cell - smallest repeating unit that reproduces the lattice

Cubic Crystal Systems

- Seven crystal systems
- Cubic is the most common
- Three forms of cubic crystals - simple or primitive, body-centered, face-centered
- How many atoms in a unit cell? Coordination number?

Simple Cubic Unit Cell Movie

- One atom per unit cell

Lattice Planes

- Lattice planes - different planes are found for different structures
- Cleavage of crystals when hit occurs along these planes
- Lattice planes determine the external shape of the crystal

X-Ray Diffraction

- Crystals diffract x-rays as they are rotated through a beam
- Diffraction caused by constructive and destructive interference of waves
- Diffraction pattern correlates with the repeating pattern of the diffracting object

Metal Structures

- Most metals have a structure that involves closest-packing, the most efficient use of space
- Same as used by a flock of penguins to keep warm (see photo)
- One layer as close as possible; the next layer fills in the depressions in the first layer

Structure of Gold

- What is the coordination number of gold in one layer?

First Closest-Packed Layer

Second Closest-Packed Layer in B

- Can only occupy one type of position.
- In this case, the 2nd layer occupies B positions.

Second Closest-Packed Layer in C

- Can only occupy one type of position.
- In this case, the 2nd layer occupies C positions.

Third Closest-Packed Layer in C

- If 2nd layer is in B, third can be in C or A.
- This layer is in C
- Cubic Closest Packed: ABCABC...

Cubic Closest Packed

- CCP is the same as the face-centered cubic structure

Third Closest-Packed Layer in A

- If 2nd layer is in B, third can be in C or A.
- This layer is in A
- Hexagonal Closest Packed: ABABAB...

Structures of Ionic Crystals

- Many can be described as a simple cubic or face-centered cubic array of one ion with the second fitting into holes in the structure.

- Closest packed structures use 74% of the volume. The other 26% is available for occupation by another particle.
- The structure of an ionic crystal is often dictated by the size of the holes in the structure, which must match the size of the ion to fit into the holes.

Holes in Closest Packed Arrays

- Tetrahedral holes are surrounded by four spheres.
- Octahedral holes are surrounded by six spheres.
- Two tetrahedral holes and 1 octahedral hole per sphere in the array

Holes That Can Be Used for Ionic Crystal Structures

- Two tetrahedral holes and 1 octahedral hole per sphere in the array
- These holes occur at the B and C positions in the closest-packed array.
- Cubic closest-packed has 4 spheres, 8 tetrahedral holes, and 4 octahedral holes per unit cell
- Octahedral holes are larger than tetrahedral holes
- Good fit in holes maximizes coulombic attractions with efficient use of space

Ionic Crystal Structures

- Two different representations of crystal structure. Which is more accurate?

Sodium Chloride Structure (NaCl)

- Face-centered cubic arrangement of chloride ions with sodium ions in all octahedral holes
- How many formula units per unit cell?
- Coordination number of Cl ?
- ... of Na ?

Zinc Blende Structure (ZnS)

- CCP sulfide ions
- Zinc ions in 1/2 the tetrahedral holes
- How many formula units per unit cell?
- Coordination number of S ?
- ... of Zn ?

Fluorite Structure (CaF₂)

- CCP calcium ions
- Fluoride ions in all the tetrahedral holes
- How many formula units per unit cell?
- Coordination number of F ?
- ... of Ca ?

Cesium Chloride Structure (CsCl)

- Simple cubic arrangement of chloride ions
- Cesium ions in the body center (too large for CCP holes)

- Also a simple cubic array of Cs with Cl in the body center
- How many formula units per unit cell?
- Coordination number of Cl ? ... of Cs ?

11.8 Bonding in Solids

- Properties of solids correlate with the types of forces holding the fundamental particles together.
- Classes: Particles:
 molecular single atoms or molecules
 network covalent covalently bonded atoms in large arrays
 ionic ions
 metallic metal atoms

Crystalline Solids

- Classes: Forces:
 molecular intermolecular forces
 network covalent covalent bonds
 ionic ionic bonds
 metallic metallic bonds

Brittleness, Ductility

- Ionic crystals are brittle, metallic crystals are ductile
- Diamond is hard, graphite is soft