Chapter 11. Intermolecular Forces, Liquids, and Solids

A Molecular Comparison of Gases, Liquids, and Solids

- Physical properties of substances are understood in terms of kinetic-molecular theory:
  - Gases are highly compressible and assume the shape and volume of their container.
  - Gas molecules are far apart and do not interact much with one another.
  - Liquids are almost incompressible, assume the shape but not the volume of the container.
  - Liquids molecules are held together more closely than gas molecules but not so rigidly that the molecules cannot slide past each other.
  - Solids are incompressible and have a definite shape and volume.
  - Solid molecules are packed closely together.
  - The molecules are so rigidly packed that they cannot easily slide past each other.
- Solids and liquids are condensed phases.
- Solids with highly ordered structures are said to be crystalline.
- Converting a gas into a liquid or solid requires the molecules to get closer to each other.
  - We can accomplish this by cooling or compressing the gas.
- Converting a solid into a liquid or gas requires the molecules to move further apart.
  - We can accomplish this by heating or reducing the pressure on the gas.
- The forces holding solids and liquids together are called intermolecular forces.
- Physical properties of liquids and solids are due to intermolecular forces.
  - These are forces between molecules.

11.2 Intermolecular Forces

- The attraction between molecules is an intermolecular force.
  - Intermolecular forces are much weaker than ionic or covalent bonds.

Slide 1

- When a substance melts or boils, intermolecular forces are broken.
- When a substances condenses, intermolecular forces are formed.
  - Boiling points reflect intermolecular force strength.
    - A high boiling point indicates strong attractive forces.
- Melting points also reflect the strength of attractive forces.
  - A high melting point indicates strong attractive forces.

Slide 2
van der Waals forces are the intermolecular forces that exist between neutral molecules.

These include London dispersion forces, dipole–dipole forces, and hydrogen-bonding forces.

Ion–dipole interactions are important in solutions.

These are all weak (<15% as strong as a covalent or ionic bond) electrostatic interactions.

**Lets go from weak to strong forces**

**London-Dispersion Forces  Slide 3**

These are the weakest of all intermolecular forces.

It is possible for two adjacent neutral molecules to affect each other.

- The nucleus of one molecule (or atom) attracts the electrons of the adjacent molecule (or atom).
- For an instant, the electron clouds become distorted.
- In that instant a dipole is formed (called an *instantaneous* dipole).
- One instantaneous dipole can induce another instantaneous dipole in an adjacent molecule (or atom).
- These two temporary dipoles attract each other.

The attraction is called the London dispersion force, or simply a dispersion force.

London dispersion forces exist between all molecules.

What affects the strength of a dispersion force?

Molecules must be very close together for these attractive forces to occur.

Deviation in the ideal Gas law: Notice H2, N2, vs CO2

- **Polarizability** is the ease with which an electron distribution can be deformed.
  - The larger the molecule (the greater the number of electrons) the more polarizable it is.
    - London dispersion forces increase as molecular weight increases.
    - London dispersion forces depend on the shape of the molecule.
  - The greater the surface area available for contact, the greater the dispersion forces.
    - London dispersion forces between spherical molecules are smaller than those between more cylindrically shaped molecules.

**Dipole–Dipole Forces**

- **Dipole–dipole forces** exist between neutral polar molecules.
• Polar molecules attract each other.
  • The partially positive end of one molecule attracts the partially negative end of another.

• Polar molecules need to be close together to form strong dipole–dipole interactions.

• If two molecules have about the same mass and size, then dipole–dipole forces increase with increasing polarity.

• For molecules of similar polarity, those with smaller volumes often have greater dipole–dipole attractions.

**Hydrogen Bonding**

• Experiments show that the boiling points of compounds with H–F, H–O, and H–N bonds are abnormally high.
  • Their intermolecular forces are abnormally strong.

• **Hydrogen bonding** is a special type of intermolecular attraction
  • This is a special case of dipole–dipole interactions.

• H-bonding requires:
  • H bonded to a small electronegative element (most important for compounds of F, O, and N).
  • an unshared electron pair on a nearby small electronegative ion or atom (usually F, O, or N on another molecule).

• Electrons in the H–X bond (X is the more electronegative element) lie much closer to X than H.
  • H has only one electron, so in the H–X bond, the H⁺ presents an almost bare proton to the X⁻.
  • Bond energies of hydrogen bonds vary from about 4 kJ/mol to 25 kJ/mol.
  • They are much weaker than ordinary chemical bonds.

• Intermolecular and intramolecular hydrogen bonds have exceedingly important biological significance.
  • They are important in stabilizing protein structure, in DNA structure and function, etc.

• An interesting consequence of H-bonding is that the density minimum of water is at 4 °C and ice floats.

**Explain the properties of water related to the ecology of lakes.**
**Ion-Dipole Forces - the strongest forces**

- An **ion–dipole** force is an interaction between an ion (e.g., Na\(^+\)) and the partial charge on the end of a polar molecule/dipole (e.g., water).
- It is especially important for solutions of ionic substances in polar liquids.
  - Example: NaCl\((aq)\)

**Comparing Intermolecular Forces**

- Dispersion forces are found in all substances.
  - Their strength depends on molecular shapes and molecular weights.
- Dipole–dipole forces add to the effect of dispersion forces.
  - They are found only in polar molecules.
- H-bonding is a special case of dipole–dipole interactions.
  - It is the strongest of the intermolecular forces involving neutral species.
  - H-bonding is most important for H compounds of N, O, and F.
- If ions are involved, ion–dipole (if a dipole is present) and ionic bonding are possible.
  - Ion–dipole interactions are stronger than H-bonds.
  - **Keep in mind that ordinary ionic or covalent bonds are much stronger than these interactions!**

**Some Properties of Liquids**

**Viscosity** slide 12 and 13

- **Viscosity** is the resistance of a liquid to flow.
- A liquid flows by sliding molecules over one another.
- Viscosity depends on:
  - the attractive forces between molecules.
  - The stronger the intermolecular forces, the higher the viscosity.
  - the tendency of molecules to become entangled.
  - Viscosity increases as molecules become entangled with one another.
  - the temperature.
  - Viscosity usually decreases with an increase in temperature.

**Surface Tension**

- Bulk molecules (those in the liquid) are equally attracted to their neighbors.
- Surface molecules are only attracted inward towards the bulk molecules.
Therefore, surface molecules are packed more closely than bulk molecules. This causes the liquid to behave as if it had a “skin.”

- **Surface tension** is the amount of energy required to increase the surface area of a liquid by a unit amount.
- Stronger intermolecular forces cause higher surface tension.
  - Water has a high surface tension (H-bonding)
  - Hg(l) has an even higher surface tension (there are very strong metallic bonds between Hg atoms).
- Cohesive and adhesive forces are at play.
  - **Cohesive forces** are intermolecular forces that bind molecules to one another.
  - **Adhesive forces** are intermolecular forces that bind molecules to a surface.
  - Illustrate this by looking at the meniscus in a tube filled with liquid.
    - The *meniscus* is the shape of the liquid surface.
    - If adhesive forces are greater than cohesive forces, the liquid surface is attracted to its container more than the bulk molecules. Therefore, the meniscus is U-shaped (e.g., water in glass).
    - If cohesive forces are greater than adhesive forces, the meniscus is curved downwards (e.g., Hg(l) in glass)

- **Capillary action** is the rise of liquids up very narrow tubes.
  - The liquid climbs until adhesive and cohesive forces are balanced by gravity.

Think about how this works! Make the tube very small. How does this work in plants?

**Phase Changes**

- **Phase changes** are changes of state.
  - Matter in one state is converted into another state.
    - **Sublimation**: solid $\rightarrow$ gas.
    - **Melting or fusion**: solid $\rightarrow$ liquid.
    - **Vaporization**: liquid $\rightarrow$ gas.
    - **Deposition**: gas $\rightarrow$ solid.
    - **Condensation**: gas $\rightarrow$ liquid.
    - **Freezing**: liquid $\rightarrow$ solid.

**Energy Changes Accompanying Phase Changes**

- Energy changes of the system for the above processes are:
  - **melting or fusion**: $\Delta H_{\text{fus}} > 0$ (endothermic).
    - The enthalpy of fusion is known as the **heat of fusion**.
  - **vaporization**: $\Delta H_{\text{vap}} > 0$ (endothermic). **Ethanol Demo**
    - The enthalpy of vaporization is known as the **heat of vaporization**.
  - **sublimation**: $\Delta H_{\text{sub}} > 0$ (endothermic).
• The enthalpy of sublimation is called the **heat of sublimation**.

  • *deposition*: $\Delta H_{\text{dep}} < 0$ (exothermic).
  • *condensation*: $\Delta H_{\text{con}} < 0$ (exothermic).
  • *freezing*: $\Delta H_{\text{fre}} < 0$ (exothermic).

• Generally the heat of fusion (enthalpy of fusion) is less than heat of vaporization.
  • It takes more energy to completely separate molecules than to partially separate them.

**And these relationships are due to intermolecular forces.**

**Heating Curves**

• Plot of temperature change versus heat added is a *heating curve*.

heat capacity of ice 2.05 J/g K
The **molar heat of fusion of ice** is 6.01 kJ/mol
heat capacity of water 4.19 J/g K
The **molar heat of vap of water** is 40.65 kJ/mol
heat capacity of ice 2.05 J/g K
heat capacity of steam 1.966 J/g K

• During a phase change adding heat causes no temperature change.
  • The added energy is used to break intermolecular bonds rather than cause a temperature change.
  • These points are used to calculate $\Delta H_{\text{fus}}$ and $\Delta H_{\text{vap}}$.
  • *Supercooling*: When a liquid is cooled below its freezing point and it still remains a liquid. DUCKS

### 11.6 Phase Diagrams

• A **phase diagram** is a plot of pressure vs. temperature summarizing all equilibria between phases.

• Phase diagrams tell us which phase will exist at a given temperature and pressure.

• Features of a phase diagram include:
  • vapor-pressure curve: generally as temperature increases, vapor pressure increases.
  • **critical point**: critical temperature and pressure for the gas.
  • **normal melting point**: melting point at 1 atm.
  • **triple point**: temperature and pressure at which all three phases are in equilibrium.
  • Any temperature and pressure combination not on a curve represents a single phase.

**Phase Diagrams of H$_2$O and CO$_2$**

• **Water**:
  • In general, an increase in pressure favors the more compact phase of the material.
    • This is usually the solid.
  • Water is one of the few substances whose solid form is less dense than the liquid form.
    • The melting point curve for water slopes to the left.
  • The triple point occurs at 0.0098 °C and 4.58 mm Hg.
  • The normal melting (freezing) point is 0 °C.
• The normal boiling point is 100 °C.
• The critical point is 374 °C and 218 atm.
• Carbon Dioxide:
  • The triple point occurs at –56.4 °C and 5.11 atm.
  • The normal sublimation point is –78.5 °C. (At 1 atm CO₂ sublimes, it does not melt.)
  • The critical point occurs at 31.1 °C and 73 atm.
  • Freeze drying: Frozen food is placed in a low pressure (< 4.58 torr) chamber.
    • The ice sublimes.

Critical Temperature and Pressure
• Gases may be liquefied by increasing the pressure at a suitable temperature.
• Critical temperature is the highest temperature at which a substance can exist as a liquid.
• Critical pressure is the pressure required for liquefaction at this critical temperature.
  • The greater the intermolecular forces, the easier it is to liquefy a substance.
  • Thus the higher the critical temperature.