

# 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 substance 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 H<sub>2</sub>, N<sub>2</sub>, vs CO<sub>2</sub>

- **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<sup>+</sup> presents an almost bare proton to the X<sup>-</sup>.
    - 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.,  $\text{Na}^+$ ) 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:  $\text{NaCl}(aq)$

## 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<sub>2</sub>O and CO<sub>2</sub>

- *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 CO<sub>2</sub> sublimates, 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 sublimates.

### **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.