

## Chapter 11: Intermolecular Forces

### Lecture Outline

#### 11.1 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 containers.
    - Gas molecules are far apart and do not interact much with one another.
  - Liquids are almost incompressible; they assume the shape, but not the volume of the container.
    - Liquid 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 solid.
- 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.
- 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.
- 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.

#### Ion-Dipole 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:  $\text{NaCl (aq)}$

#### 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.

- Dipole-dipole forces are weaker than ion-dipole forces.
- 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.

### London-Dispersion Forces

- 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.
  - **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 are.
    - London-dispersion forces between spherical molecules are smaller than those between more cylindrically shaped molecules.
      - Example: *n*-pentane vs. neopentane

### 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  $H^{\oplus+}$  presents an almost bare proton to the  $X^{\ominus-}$ .
    - H-bonds are strong interactions.
      - 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 ice floats.
  - The molecules in solids are usually more closely packed than those in liquids.
    - Therefore, solids are usually more dense than liquids.
  - Ice is ordered with an open structure to optimize H-bonding.
    - In ice the H-O bond length is 1.0 Å.

- The O | | | | H hydrogen bond length is 1.8 Å.
- Water molecules in ice are arranged in an open, regular hexagon.
  - Each  $\delta^+$  H points towards a lone pair on O.
- Therefore, ice is less dense than water.
- Ice floats, so it forms an insulating layer on top of lakes, rivers, etc. Therefore, aquatic life can survive in winter.
- Water expands when it freezes.
  - Frozen water in pipes may cause them to break in cold weather.

### 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!

## 11.3 Some Properties of Liquids

### Viscosity

- **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 are, 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.

## 11.4 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).
    - 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.
- All phase changes are possible under the right conditions (e.g., water sublimates when snow disappears without forming puddles).
  - The following sequence is endothermic:  
heat solid  $\rightarrow$  melt  $\rightarrow$  heat liquid  $\rightarrow$  boil  $\rightarrow$  heat gas
  - The following sequence is exothermic:  
cool gas  $\rightarrow$  condense  $\rightarrow$  cool liquid  $\rightarrow$  freeze  $\rightarrow$  cool solid

### Heating Curves

- Plot of temperature change versus heat added is a *heating curve*.
- 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* is when a liquid is cooled below its freezing point and it still remains a liquid.

### 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.

## 11.5 Vapor Pressure

### Explaining Vapor Pressure on the Molecular Level

- Some of the molecules on the surface of a liquid have enough energy to escape the attraction of the bulk liquid.
  - These molecules move into the gas phase.
- As the number of molecules in the gas phase increases, some of the gas phase molecules strike the surface and return to the liquid.
- After some time the pressure of the gas will be constant.
  - A **dynamic equilibrium** has been established.
    - Dynamic equilibrium is a condition in which two opposing processes occur simultaneously at equal rates.
    - In this case, it is the point when as many molecules escape the surface as strike the surface.
  - **Vapor pressure** of a liquid is the pressure exerted by its vapor when the liquid and vapor are in dynamic equilibrium.
    - The pressure of the vapor at this point is called the equilibrium vapor pressure.

### Volatility, Vapor Pressure, and Temperature

- If equilibrium is never established, then the vapor continues to form.
  - Eventually, the liquid evaporates to dryness.
- Liquids that evaporate easily are said to be **volatile**.
  - The higher the temperature, the higher the average kinetic energy, the faster the liquid evaporates.

### Vapor Pressure and Boiling Point

- Liquids boil when the external pressure at the liquid surface equals the vapor pressure.
  - The **normal boiling point** is the boiling point at 760 mm Hg (1 atm).
- The temperature of the boiling point increases as the external pressure increases.
- Two ways to get a liquid to boil are to:
  - increase temperature or decrease pressure.
    - Pressure cookers operate at high pressure.
    - At high pressure the boiling point of water is higher than at 1 atm.
    - Therefore, food is cooked at a higher temperature.

## 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  $100^{\circ}\text{C}$ .
- The critical point is  $374^{\circ}\text{C}$  and 218 atm.
- *Carbon Dioxide*:
  - The triple point occurs at  $-56.4^{\circ}\text{C}$  and 5.11 atm.
  - The normal sublimation point is  $-78.5^{\circ}\text{C}$ . (At 1 atm  $\text{CO}_2$  sublimates, it does not melt.)
  - The critical point occurs at  $31.1^{\circ}\text{C}$  and 73 atm.
  - Freeze drying: Frozen food is placed in a low pressure ( $< 4.58$  torr) chamber.
    - The ice sublimates.

### 11.7 Structures of Solids

- A **crystalline solid** has a well-ordered, definite arrangements of molecules, atoms or ions.
  - Examples are quartz, diamond, salt, and sugar.
  - The intermolecular forces are similar in strength.
    - Thus, they tend to melt at specific temperatures.
- In an **amorphous solid** molecules, atoms or ions do not have an orderly arrangement.
  - Examples are rubber and glass.
  - Amorphous solids have intermolecular forces that vary in strength.
    - Thus, they tend to melt over a range of temperatures.

### Unit Cells

- Crystalline solids have an ordered, repeating structure.
- The smallest repeating unit in a crystal is a **unit cell**.
  - The unit cell is the smallest unit with all the symmetry of the entire crystal.
  - The three-dimensional stacking of unit cells is the **crystal lattice**.
    - Each point in the lattice is a *lattice point* which represents an identical environment within the solid.
- There are three types of cubic unit cells.
  - **Primitive cubic**
    - The lattice points are at the corners of a simple cube with each atom shared by eight unit cells.
  - **Body-centered cubic (bcc)**
    - Lattice points occur at the corners of a cube and in addition there is a lattice point at the center of the body of the cube. The corner lattice points are shared by eight unit cells and the center atom is completely enclosed in one unit cell.
  - **Face-centered cubic (fcc)**
    - There are lattice points at the corners of a cube plus one lattice point in the center of each face of the cube. Eight unit cells share the corner lattice points and two unit cells share the face lattice points.

### The Crystal Structure of Sodium Chloride

- It has a face-centered cubic lattice.
- There are two equivalent ways of defining this unit cell:
  - $\text{Cl}^-$  (larger) ions at the corners of the cell, or
  - $\text{Na}^+$  (smaller) ions at the corners of the cell.
- The cation to anion ratio in a unit cell is the same for the crystal.
  - In NaCl each unit cell contains the same number of  $\text{Na}^+$  and  $\text{Cl}^-$  ions.
- Note that the unit cell for  $\text{CaCl}_2$  needs twice as many  $\text{Cl}^-$  ions as  $\text{Ca}^{2+}$  ions.

### Close Packing of Spheres

- Crystalline solids have structures that maximize the attractive forces between particles.
- Their particles can be modeled by spheres.

- Each atom or ion is represented by a sphere.
- Molecular crystals are formed by close packing of the molecules.
- Maximum intermolecular forces in crystals are achieved by the close packing of spheres.
  - A crystal is built up by placing close-packed layers of spheres on top of each other.
  - There is only one place for the second layer of spheres.
  - There are two choices for the third layer of spheres:
    - The third layer eclipses the first (ABAB arrangement).
      - This is called **hexagonal close packing** (hcp).
    - The third layer is in a different position relative to the first (ABCABC arrangement).
      - This is called **cubic close packing** (ccp).
      - Note: The unit cell of a ccp crystal is face-centered cubic.
  - In both close-packed structures, each sphere is surrounded by 12 other spheres (6 in one plane, 3 above and 3 below).
- **Coordination number** is the number of spheres directly surrounding a central sphere.
  - When spheres are packed as closely as possible, there are small spaces between adjacent spheres (interstitial holes).
  - If unequally sized spheres are used, the smaller spheres are placed in the interstitial holes.
    - For example:  $\text{Li}_2\text{O}$ 
      - The larger  $\text{O}^{2-}$  ions assume the cubic close-packed structure with the smaller  $\text{Li}^+$  ions in the holes.

### 11.8 Bonding in Solids

- The physical properties of crystalline solids depend on the:
  - attractive forces between particles and on
  - the arrangement of the particles.

#### Molecular Solids

- **Molecular solids** consist of atoms or molecules held together by intermolecular forces.
- Weak intermolecular forces give rise to low melting points.
  - Intermolecular forces include dipole-dipole, London-dispersion, and H-bonds.
  - Molecular solids are usually soft.
  - They are often gases or liquids at room temperature.
- Efficient packing of molecules is important (since they are not regular spheres).
- Molecular solids show poor thermal and electrical conductivity.
- Examples are  $\text{Ar}(s)$ ,  $\text{CH}_4(s)$ ,  $\text{CO}_2(s)$ , and sucrose.

#### Covalent-Network Solids

- **Covalent-network solids** consist of atoms held together, in large networks or chains, with covalent bonds.
- They have much higher melting points and are much harder than molecular solids.
  - This is a consequence of the strong covalent bonds that connect the atoms.
- Examples are diamond, graphite, quartz ( $\text{SiO}_2$ ), and silicon carbide ( $\text{SiC}$ ).
- In diamond:
  - each C atom has a coordination number of 4.
  - each C atom is tetrahedral.
  - there is a three-dimensional array of atoms.
  - Diamond is hard, and has a high melting point ( $3550^\circ\text{C}$ ).
- In graphite:
  - each C atom is arranged in a planar hexagonal ring.
  - layers of interconnected rings are placed on top of each other.

- the distance between adjacent C atoms in the same layer is close to that seen in benzene ( $1.42 \text{ \AA}$  vs.  $1.395 \text{ \AA}$  in benzene).
- electrons move in delocalized orbitals (good conductor).
- the distance between layers is large ( $3.41 \text{ \AA}$ ).
- the layers are held together by weak dispersion forces.
  - They slide easily past each other.
  - Graphite is a good lubricant.

### Ionic Solids

- **Ionic solids** consist of ions held together by ionic bonds.
  - They are hard, brittle and have high melting points.
- Ions (spherical) are held together by electrostatic forces of attraction.
- Recall:

$$E = k \frac{Q_1 Q_2}{d}$$

- The larger the charges ( $Q_1$ ,  $Q_2$ ) and smaller the distance ( $d$ ) between ions, the stronger the ionic bond.
- The structure of the ionic solid depends on the charges on the ions and on the relative sizes of the atoms.
- Examples of some ionic lattice types are:
  - NaCl structure.
    - Each ion has a coordination number of six.
    - It has a face-centered cubic lattice.
    - The cation to anion ratio is 1:1.
    - Other similar examples are LiF, KCl, AgCl and CaO.
  - CsCl structure.
    - $\text{Cs}^+$  has a coordination number of eight.
    - It is different from the NaCl structure ( $\text{Cs}^+$  is larger than  $\text{Na}^+$ ).
    - The cation to anion ratio is 1:1.
  - Zinc blende ( $\text{ZnS}$ ) structure.
    - $\text{S}^{2-}$  ions adopt a face-centered cubic arrangement.
    - $\text{Zn}^{2+}$  ions have a coordination number of four.
    - The  $\text{S}^{2-}$  ions are placed in a tetrahedron around the  $\text{Zn}^{2+}$  ions.
    - Another example is CuCl.
  - Fluorite ( $\text{CaF}_2$ ) structure.
    - $\text{Ca}^{2+}$  ions are in a face-centered cubic arrangement.
    - There are twice as many  $\text{F}^-$  ions as  $\text{Ca}^{2+}$  ions in each unit cell.
    - Other examples are  $\text{BaCl}_2$  and  $\text{PbF}_2$ .

### Metallic Solids

- **Metallic solids** consist entirely of metal atoms.
  - Metallic solids are soft or hard.
  - They have high melting points.
  - They show good electrical and thermal conductivity.
  - They are ductile and malleable.
    - Examples are all metallic elements (i.e., Al, Cu, Fe, Au).
- Metallic solids have metal atoms in hexagonal close-packed, face-centered cubic or body-centered cubic arrangements.
  - Thus, the coordination number for each atom is either eight or twelve.
- Problem that needs to be explained:



- The bonding is too strong to be explained by London-dispersion forces and there are not enough electrons for covalent bonds.
- Resolution:
  - The metal nuclei float in a sea of delocalized valence electrons.
  - Metals conduct heat and electricity because the valence electrons are delocalized and are mobile.

### **X-Ray Diffraction**

- When waves are passed through a narrow slit they are diffracted.
- When waves are passed through a diffraction grating (many narrow slits in parallel) they interact to form a diffraction pattern (areas of light and dark bands).
- Efficient diffraction occurs when the wavelength of light is close to the size of the slits.
- The spacing between layers in a crystal is  $2 - 20 \text{ \AA}$ , which is the wavelength range for X-rays.
- X-ray diffraction (X-ray crystallography):
  - X-rays are passed through the crystal and are detected on a photographic plate.
  - The photographic plate has one bright spot at the center (incident beam), as well as a diffraction pattern.
  - Each close-packing arrangement produces a different diffraction pattern.
  - Knowing the diffraction pattern, we can calculate the positions of the atoms required to produce that pattern.
  - We calculate the crystal structure based on a knowledge of the diffraction pattern.