Chapter 11

Intermolecular Forces
States of Matter

Dependent on 2 things:
- Closeness
- Motion

Strength of intermolecular attractions increasing

Gas
- Chlorine, Cl₂
  - Particles far apart; possess complete freedom of motion

Liquid
- Bromine, Br₂
  - Particles are closely packed but randomly oriented; retain freedom of motion; rapidly change neighbors

Crystalline solid
- Iodine, I₂
  - Particles are closely packed in an ordered array; positions are essentially fixed
States of Matter

Liquid & solid: atoms/molecules/ions perpetually touching. condensed phases.

Droplet of water on a solid surface Shows how liquid molecules stick together
The States of Matter

- The *state* of matter depends on:
  - temperature
  - pressure
  - The kinetic energy of the particles.
  - The strength of the attractions between the particles.

<table>
<thead>
<tr>
<th>State</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Assumes both volume and shape of its container</td>
</tr>
<tr>
<td></td>
<td>Expands to fill its container</td>
</tr>
<tr>
<td></td>
<td>Is compressible</td>
</tr>
<tr>
<td></td>
<td>Flows readily</td>
</tr>
<tr>
<td></td>
<td>Diffusion within a gas occurs rapidly</td>
</tr>
<tr>
<td>Liquid</td>
<td>Assumes shape of portion of container it occupies</td>
</tr>
<tr>
<td></td>
<td>Does not expand to fill its container</td>
</tr>
<tr>
<td></td>
<td>Is virtually incompressible</td>
</tr>
<tr>
<td></td>
<td>Flows readily</td>
</tr>
<tr>
<td></td>
<td>Diffusion within a liquid occurs slowly</td>
</tr>
<tr>
<td>Solid</td>
<td>Retains own shape and volume</td>
</tr>
<tr>
<td></td>
<td>Does not expand to fill its container</td>
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<td></td>
<td>Is virtually incompressible</td>
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<td>Does not flow</td>
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<td></td>
<td>Diffusion within a solid occurs extremely slowly</td>
</tr>
</tbody>
</table>
Intermolecular Forces

Molecules/atoms can stick to each other. But much more weakly than a bond.

Covalent bond strength: 50-200 kJ/mole
Intermolecular force: 1-12 kJ/mole
Intermolecular Forces

But these weak interactions control many critical properties:

- boiling and melting points,
- vapor pressures,
- viscosities, etc.
Intermolecular Forces

All weak intermolecular forces are called: van der Waals forces.
van der Waals Forces
Two major forms:

• Dipole–dipole interactions
  – Hydrogen bonding
• London dispersion forces
Dipole–Dipole Interactions

- Molecules that have permanent dipoles are attracted to each other.
  - The positive end of one is attracted to the negative end of the other, and vice versa.
  - These forces are only important when the molecules are close to each other.
Dipole–Dipole Interactions

The more polar the molecule, the higher its boiling point.
Hydrogen Bonding

- The dipole–dipole interactions experienced when H is bonded to N, O, or F are unusually strong.
- We call these interactions hydrogen bonds.
Hydrogen bonding result of high electronegativity of nitrogen, oxygen, and fluorine.
Ion–Dipole Interactions

- Ion–dipole interactions (stronger type of electrostatic interaction) are important in solutions of ions.
- The strength of these forces is what makes it possible for ionic substances to dissolve in polar solvents.

Positive ends of polar molecules are oriented toward negatively charged anion

Negative ends of polar molecules are oriented toward positively charged cation
London Dispersion Forces

While the electrons in the 1s orbital of helium would repel each other (and, therefore, tend to stay far away from each other), it does happen that they occasionally wind up on the same side of the atom.
London Dispersion Forces

At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side.
Another helium atom nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.
London Dispersion Forces

London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole.
London Dispersion Forces

- These forces are present in all molecules, whether they are polar or nonpolar.
- Tendency of an electron cloud to distort in this way is called polarizability.
Factors Affecting London Forces

• Shape matters. Long, skinny molecules (like $n$-pentane) pack together more efficiently.
  – Stronger interaction

• Short fat ones pack less well
  – Weaker interaction
Factors Affecting London Forces

- Increases with increased molecular weight.
- Larger atoms more electrons to slosh around easier to polarize.

<table>
<thead>
<tr>
<th>Period</th>
<th>Element</th>
<th>Boiling Point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Ne (27 K)</td>
<td>F₂ (85 K)</td>
</tr>
<tr>
<td>3</td>
<td>Ar (87 K)</td>
<td>Cl₂ (239 K)</td>
</tr>
<tr>
<td>4</td>
<td>Kr (121 K)</td>
<td>Br₂ (332 K)</td>
</tr>
<tr>
<td>5</td>
<td>Xe (166 K)</td>
<td>I₂ (458 K)</td>
</tr>
</tbody>
</table>
Which Have a Greater Effect?  
Dipole–Dipole Interactions or Dispersion Forces

• If two molecules are of comparable size and shape, dipole–dipole interactions will likely be the dominating force.
• If one molecule is much larger than another, dispersion forces will likely determine its physical properties.
How Do We Explain This?

- The nonpolar series (SnH$_4$ to CH$_4$) follow the expected trend.
- The polar series follow the trend until you get to the smallest molecules in each group.
Summarizing Intermolecular Forces

Are ions present?
- Yes
- No
  - Are polar molecules present?
    - Yes
      - Are H atoms bonded to N, O, and F atoms?
        - Yes
          - Hydrogen bonding
            - Examples: NaCl dissolved in H₂O
        - No
          - Dispersion forces only
            - Examples: CH₄, Br₂
    - No
      - Dipole–dipole forces
        - Examples: CH₃F, HBr
  - No
    - van der Waals forces

Increasing interaction strength
Intermolecular Forces Affect Many Physical Properties

The strength of the attractions between particles can greatly affect the properties of a substance or solution.
Viscosity

- Resistance of a liquid to flow is called **viscosity**.
- It is related to the ease with which molecules can move past each other.
- Viscosity increases with stronger intermolecular forces and decreases with higher temperature.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>Viscosity (kg/m-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₃</td>
<td>3.26 × 10⁻⁴</td>
</tr>
<tr>
<td>Heptane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>4.09 × 10⁻⁴</td>
</tr>
<tr>
<td>Octane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>5.42 × 10⁻⁴</td>
</tr>
<tr>
<td>Nonane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>7.11 × 10⁻⁴</td>
</tr>
<tr>
<td>Decane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>1.42 × 10⁻³</td>
</tr>
</tbody>
</table>
Surface Tension

Surface tension results from the net inward force experienced by the molecules on the surface of a liquid.

On any surface molecule, there is no upward force to cancel the downward force, which means each surface molecule “feels” a net downward pull.

On any interior molecule, each force is balanced by a force pulling in the opposite direction, which means that interior molecules “feel” no net pull in any direction.