Scientists are interested in how matter behaves under unusual circumstances. For example, before the space station could be built, fundamental research into materials properties had to be undertaken.
Solids and Liquids

Intermolecular Forces
- Ion-ion, Ion-dipole, dipole-dipole and H-bonding, dipole-induced dipole, induced dipole-induced dipole

Liquids
- Vapor pressure and temperature, Critical T & P, Surface tension and viscosity

Phase Diagrams
- Show relation of solid, liquid, and gas phases with change in T and P

Solids
- Unit cells, metal structures, formulas and structures of ionic compounds, Molecular, network, and amorphous solids

Properties of Solids
- Lattice energy, heat of fusion, melting point

Summary of Intermolecular Forces

<table>
<thead>
<tr>
<th>Type of Interaction</th>
<th>Principal Factors Responsible for Interaction Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion</td>
<td>Ion charge; dipole moment</td>
</tr>
<tr>
<td>Dipole</td>
<td></td>
</tr>
<tr>
<td>Dipole (including H-bonding)</td>
<td>Dipole moment</td>
</tr>
<tr>
<td>Dipole</td>
<td></td>
</tr>
<tr>
<td>Induced dipole</td>
<td>Dipole moment; polarizability</td>
</tr>
<tr>
<td>Induced dipole</td>
<td></td>
</tr>
</tbody>
</table>

Van der Waal's forces

Dispersion forces

Increasing strength of interaction
Chapter Outline

- **6.1 London Dispersion Forces: They’re Everywhere**
  - Nonpolar molecules – polarizability and temporary dipoles
- **6.2 Interactions Involving Polar Molecules**
  - Polar molecules – ion-dipole, dipole-dipole, hydrogen bonds
- **6.3 Trends in Solubility**
- **6.4 Phase Diagrams: Intermolecular Forces at Work**
- **6.5 Some Remarkable Properties of Water**

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**London Dispersion Forces: They’re Everywhere**

Even nonpolar molecules and uncombined atoms have attractive forces between them, otherwise they would never condense or solidify.

<table>
<thead>
<tr>
<th>Noble Gas</th>
<th>Atomic View</th>
<th>Z</th>
<th>Boiling Point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>🌔</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Ne</td>
<td>🌑</td>
<td>10</td>
<td>27</td>
</tr>
<tr>
<td>Ar</td>
<td>🌒</td>
<td>18</td>
<td>87</td>
</tr>
<tr>
<td>Kr</td>
<td>🌓</td>
<td>36</td>
<td>120</td>
</tr>
<tr>
<td>Xe</td>
<td>🌔</td>
<td>54</td>
<td>165</td>
</tr>
<tr>
<td>Rn</td>
<td>🌕</td>
<td>86</td>
<td>211</td>
</tr>
</tbody>
</table>
**Polarizability** - a measure of the extent to which the electron cloud of an atom or molecule can be distorted by an external electric charge.

In general, *larger atoms or molecules are more easily polarizable* than smaller ones (more shells, etc), and so experience larger dipole-induced dipole interactions.

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**Temporary Dipoles**

Momentary shift in e\(^-\) density = "**temporary dipole**"
The Importance of Shape

Which alkane has greater attractive intermolecular forces?

Pentane
Boiling point 309 K

2-Methylbutane
Boiling point 301 K

2,2-Dimethylpropane
Boiling point 282 K
Viscosity: the measure of a fluid’s resistance to flow


Viscosities of some liquid alkanes

<table>
<thead>
<tr>
<th>Molar Mass (g/mol)</th>
<th>Viscosity @ 20°C (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>86</td>
<td>0.29</td>
</tr>
<tr>
<td>114</td>
<td>0.54</td>
</tr>
<tr>
<td>142</td>
<td>0.92</td>
</tr>
</tbody>
</table>
Chapter Outline

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Interactions Involving Polar Molecules

- **Ion-Dipole:**
  - Interaction between an ion and the partial charge of a molecule with a permanent dipole.

- **Sphere of Hydration:**
  - Cluster of water molecules surrounding an ion as it dissolves in aqueous solution.
  - *Sphere of solvation* if solvent other than \( \text{H}_2\text{O} \).
Ion-Dipole Interactions

Sphere of Hydration

- Inner hydration sphere
- Outer hydration sphere
- Bulk water
- Ion–dipole interaction
- Dipole–dipole interaction
Dipole-Dipole Interactions

- **Dipole-Dipole:**
  - Attractive forces between polar molecules.

- **Hydrogen Bond:**
  - Special class of dipole-dipole interactions due to strength.
  - Requires H atom covalently bonded to strongly electronegative atom.
    - Example: F, O, N.

The strongest type of dipole-dipole interaction involving a hydrogen and either F, O, or N

<table>
<thead>
<tr>
<th>Types of Hydrogen Bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>N—H···N—</td>
</tr>
<tr>
<td>N—H···O—</td>
</tr>
<tr>
<td>N—H···F—</td>
</tr>
</tbody>
</table>

About 10 % as strong as an ordinary covalent bond so approximately 15-40 kJ/mol.
More Examples of H-Bonding

A dimer of acetic acid

Network of hydrogen bonds in ammonia

Boiling Points of Binary Hydrides

Graph showing boiling points of binary hydrides for different groups.
The Double Helix of DNA is held together by hydrogen bonding

The polymer Nylon is also held together by hydrogen bonding
Sample Exercise 6.1

Dimethyl ether (C$_2$H$_6$O) has a molar mass of 46.07 g/mol and a boiling point of 248 K. Ethanol (C$_2$H$_6$O) has the same formula and molar mass but a boiling point of 351 K. Explain this difference in boiling points.

Dimethyl ether
CH$_3$OCH$_3$
Boiling point 248 K

Ethanol
CH$_3$CH$_2$OH
Boiling point 351 K

Ethanol
Polar and capable of hydrogen bonding

Dimethyl ether
Polar
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Solutions

A *solution* is a homogenous mixture of 2 or more substances.

The *solute* is(are) the substance(s) present in the smaller amount(s).

The *solvent* is the substance present in the larger amount.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Solvent</th>
<th>Solute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft drink (l)</td>
<td>H₂O</td>
<td>Sugar, CO₂</td>
</tr>
<tr>
<td>Air (g)</td>
<td>N₂</td>
<td>O₂, Ar, CH₄</td>
</tr>
<tr>
<td>Soft Solder (s)</td>
<td>Pb</td>
<td>Sn</td>
</tr>
</tbody>
</table>
Sample Exercise 6.2: Distinguishing Solute from Solvent

The liquid inside of an automobile engine is a homogeneous mixture that is 30% by mass water and 70% by mass ethylene glycol. The freezing point of the mixture is \(-50 \, ^\circ\text{C} (-60 \, ^\circ\text{F})\). Which ingredient is the solvent?

Solubility Behavior

- **Hydrophobic** ("water-fearing")
  - Interaction that repels water, diminishes water solubility.
- **Hydrophilic** ("water-loving")
  - Interaction that attracts water, promotes water solubility.
Polarity and Solubility

Two liquids that mix completely together are said to be **MISCIBLE** - otherwise they are **IMMISCIBLE**.

Mixing of Polar Liquids

Polar molecules can break up groups of other polar molecules through dipole-dipole interactions, resulting in a thorough mixing.
Mixing of Polar and Nonpolar Liquids

The weak London forces present in the CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{3} molecules are not strong enough to break the hydrogen bonds, so the two liquids are immiscible.

Dipole-Induced Dipole Intermolecular Forces

What little solubility a nonpolar organic molecule has in a polar solvent (such as water), is increased by what are known as dipole-induced dipole interactions
London forces are the only interactions, but the strength of these forces between $\text{CCl}_4$ molecules is comparable to those between $\text{C}_6\text{H}_{14}$ molecules, so the two liquids are miscible with each other.

General Observation:
Predicting Solubility

Which of these compounds should be very soluble in water and which should have limited solubility in water: carbon tetrachloride (CCl₄), ammonia (NH₃), hydrogen fluoride (HF), oxygen (O₂)?

More than one intermolecular force may need to be considered when examining solubility.

Solubility decreases as relative energy of H-bonding decreases and dispersion increases.
Extensive dispersion forces limit solubility of octanol in water.

Concept Test

Rank these alcohols from most to least soluble in water.
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**Pressure = force/unit area**

Molecules collide with the inside surface of the container. The force of the collision is measured as pressure.

\[ P = \text{force/unit area} \]
Units of Pressure: \( P = \text{force/unit area} \)

<table>
<thead>
<tr>
<th>Units</th>
<th>Pressure at Sea Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pounds/in(^2) (psi)</td>
<td>14.7 psi</td>
</tr>
<tr>
<td>Atmospheres (atm)</td>
<td>1 atm</td>
</tr>
<tr>
<td>Pascals (N/m(^2))</td>
<td>(101.325 \times 10^3) Pa</td>
</tr>
<tr>
<td>Torr (mmHg)</td>
<td>760 mmHg</td>
</tr>
</tbody>
</table>

Phase Diagrams

States of matter as a function of temperature and pressure
Phase Diagram of Water

- Triple Point
- Critical Point
- Critical Temperature
- Critical Pressure
- Supercritical Fluid
- Equilibrium Lines

Slope of the solid-liquid boundary:

Concept Test, p. 255

Explain how the wire connected by heavy weights can pass completely through the block of ice without cutting it in two!
Sample Exercise 6.3: Interpreting Phase Diagrams

Phase Diagram for CO₂

Critical point
(31°C, 73 atm)

Supercritical region

Solid

Liquid

Gas

Triple point
(−57°C, 5.1 atm)
1. Positive slope for the solid-liquid interface (normal)

2. Sublimation occurs at room temperature under 1 atm of pressure.

3. There is a “critical point” at 73 atm and 31 °C (varies from substance to substance).

4. Above the critical point the substance is known as a “supercritical fluid” (not a liquid; not a gas). Increasing the pressure normally would convert a gas to a liquid but doesn’t happen.

5. Supercritical fluids have enhanced solvation abilities, i.e. the fluid will dissolve greater amounts of solute than normal.

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On the left is water; water is unusual because the solid is less dense than the liquid. For most substances, the solid is more dense than the liquid like for benzene (on the right).
Surface Tension

The ability of a surface of a liquid to resist an external force pressing down on it. Quantitatively it's the energy required to stretch a surface by a unit area (e.g. cm$^2$, in$^2$, etc).

Capillary Action

The rise of a liquid in a thin tube as a result of cohesive forces within the liquid and adhesive forces between the liquid and the surface of the tube. Both depend on intermolecular forces.

Meniscus:

Cohesive forces:

Adhesive forces:
**Unique Property of Water**  
- density decreases when it freezes -

H-bonding results in cage-like structure in solid state; less dense than liquid state.

**Water and Aquatic Life**

- Importance of Density:
  - Lakes/rivers freeze from top down, allowing fish and aquatic life to survive below.
  - As surface waters warm or cool, nutrient-rich bottom waters cycle to the surface; oxygen-rich surface waters cycle to the bottom.