Intermolecular vs. intramolecular forces

To understand condensed phases, we need to understand their interactions

- **Intramolecular forces**: interactions between atoms in a molecule
- **Intermolecular forces**: interactions between individual molecules

**Intermolecular vs Intramolecular**

- 41 kJ to vaporize 1 mole of water (inter)
- 930 kJ to break all O-H bonds in 1 mole of water (intra)

Generally, **inter**molecular forces are much weaker than **intra**molecular forces.

However, **intermolecular forces** are primarily responsible for the bulk properties of matter (i.e. melting point and boiling point).
Intermolecular forces

- Ionic bonds
- Ion-dipole interactions
- Hydrogen bonds
- Dipole-dipole interactions
- Dipole-induced dipole interactions
- Dispersion forces (aka van der Waals forces)
Intermolecular forces: Ionic bonds

- Ionic bonds are **very strong** intermolecular forces—similar to **covalent bonds**.
- Requires both species to have a full charge.
Ionic solids have extremely high melting points. All solids are held together by forces between atoms or molecules. Being made of lattices of ions, ionic solids have some of the strongest possible attractive forces holding them together.
Intermolecular forces: Ion-dipole interactions

- Ionic bonds
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Decreasing Strength

- Ion-dipole interactions are strong (~25% of a covalent bond).
- These forces are responsible for the ability of water to dissolve many ionic solids.

Polar molecules orient toward ions so that the positive end of the dipole is near an anion and ...

... the negative end of the dipole is near a cation.
Water as a solvent

Figure 2-6
Lehninger Principles of Biochemistry, Seventh Edition
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Intermolecular forces: Hydrogen bonds

- Ionic bonds
- Ion-dipole interactions
- **Hydrogen bonds**
- Dipole-dipole interactions
- Dipole-induced dipole interactions
- Dispersion forces (aka van der Waals forces)

Hydrogen bonds do not involve full charges, but they are the strongest possible type of **polar interaction** (~10% of a covalent bond).

- Requires an H bonded to N, O, or F.
- Also requires an N, O, or F on a second molecule.
Intermolecular forces: Hydrogen bonds

Which of the following can form hydrogen bonds with water?

\[ \text{Li}^+ \quad \text{F}_2 \quad \text{CH}_3\text{OH} \]

\[ \text{CH}_3\text{Cl} \quad \text{HCOOH} \]
Intermolecular forces: Weak dipole interactions

- Ionic bonds
- Ion-dipole interactions
- Hydrogen bonds
- Dipole-dipole interactions
- Dipole-induced dipole interactions
- Dispersion forces (aka van der Waals forces)

**Decreasing Strength**

- Dipole-dipole interactions are also known as **polar** interactions.
- These interactions just require two **polar molecules**.
- These are weaker, but still significant (~1% of a covalent bond).

Polar molecules can also **induce** dipoles in nonpolar molecules if they come into close proximity.

Polar molecules **attract** one another when they orient with unlike charges close together, but ...  
... they **repel** one another when they orient with like charges together.
Intermolecular forces: Dispersion forces

- Ionic bonds
- Ion-dipole interactions
- Hydrogen bonds
- Dipole-dipole interactions
- Dipole-induced dipole interactions
- **Dispersion forces**
  (aka van der Waals forces)

Averaged over time, the electron distribution in a Br$_2$ molecule is **symmetrical**.

At any given instant, the electron distribution in a molecule may be **unsymmetrical**, resulting in a temporary dipole and inducing a complementary attractive dipole in neighboring molecules.
Intermolecular forces are very important in large molecules!
What is the **strongest** intermolecular force found in each of the following substances?

- Water
- Acetone \((\text{CH}_3)_2\text{CO}\)
- Water and acetone mixture
- Solid sodium chloride
- Aqueous sodium chloride
- Cyclohexane \((\text{C}_6\text{H}_{12})\)
Phases of matter

In **gases**, the particles feel little attraction for one another and are free to move about randomly.

In **liquids**, the particles are held close together by attractive forces but are free to move around one another.

In **solids**, the particles are held in an ordered arrangement.
Phase Changes

Solid
- Freezing
- Melting
- Deposition

Liquid
- Evaporation

Gas
- Sublimation
- Condensing
Phase changes and thermodynamics

Enthalpy (Heat) of Fusion ($\Delta H_{\text{fus}}$):

The amount of energy required to overcome enough intermolecular forces to convert a solid into a liquid.

Enthalpy (Heat) of Vaporization ($\Delta H_{\text{vap}}$):

The amount of energy necessary to convert a liquid into a gas.
It is customary to show phases of a substance on a PT plot, called a phase diagram.

A phase diagram summarizes the conditions at which a substance exists as a solid, liquid, or gas.
Last topic: Phase Diagrams

- **Lines in a phase diagram**
  - Set of $T, P$ at which two phases can coexist indefinitely
  - Triple point: all three phases coexist indefinitely

- **Supercritical fluid**
  - Fourth phase of matter
  - A fluid; neither liquid nor gas
  - No meniscus
The triple point: where 3 phases exist at once!

https://www.youtube.com/watch?v=BLRqpJN9zeA
Supercritical Fluids: Neither Liquid nor Gas

https://www.youtube.com/watch?v=GEr3NxsPTOA
Phase Diagram of Carbon Dioxide

At 1 atm:
\[ \text{CO}_2 (s) \rightarrow \text{CO}_2 (g) \]

Unique feature of \( \text{CO}_2 \):
**Review of Concepts**

Which phase diagram corresponds to a substance that will sublime rather than melt as it is heated at 1 atm?

(a)  
(b)  
(c)