

Chemistry 1000 Lecture 17: Intermolecular forces

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Intermolecular forces

- The properties of chemical systems are strongly affected by the forces that act **between** molecules in these systems.
- Forces can act between molecules of the same or different kinds.
- There are different kinds of intermolecular forces, and they have different characteristic strengths.
- In the next several slides, we will look at the major intermolecular forces in **descending order of strength**.

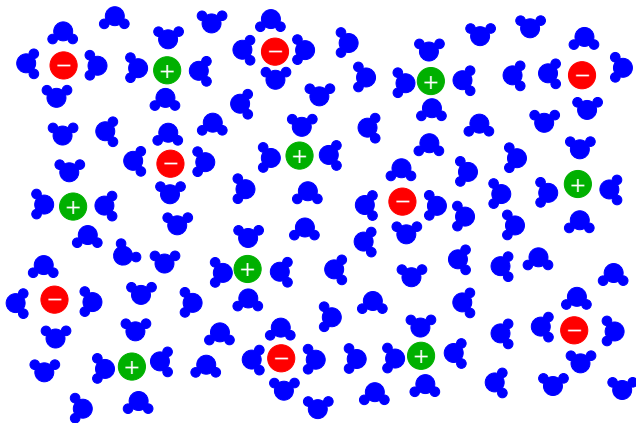
Ion-ion forces

- The Coulomb force is the strongest one that operates on the length scales of interest to chemists.

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}$$

- Because of the strength of this force, ionic compounds typically have high boiling points.
- When we dissolve an ionic compound in a solvent, forces between the ions result in a relatively organized state where, on average, anions are closer to cations than to other anions.

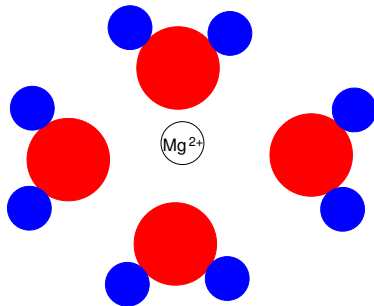
Ion-ion forces (continued)



- This organized state leads to screening of a charge by its “ionic atmosphere”, leading to an exponentially rapid falloff of the force between two ions in solution.

Ion-dipole forces

- There are also fairly strong forces between ions and dipoles, with a force that is proportional to the charge of the ion and to the strength of the dipole (size of the dipole vector).
- This force falls off faster than the ion-ion force.
- When we dissolve an ionic compound in a polar solvent, this results in substantial organization of the solvent around the ions.

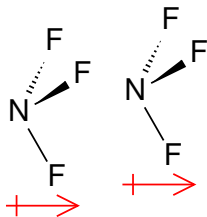


Ion-dipole forces (continued)

- For the case of an ion in a polar solvent, this can be the dominant intermolecular force in the solution due to the short distance between the ion and solvent dipole.

Dipole-dipole forces

- Dipoles exert forces on each other.
- Dipoles tend to align themselves so that the positive end of one is close to the negative end of another.

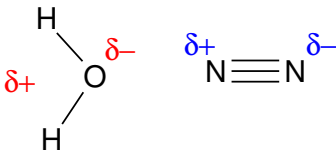


Dipole-induced dipole forces

- If we place a molecule next to a polar molecule, the electric field of the dipole exerts a force on the electrons of the other molecule, resulting in an **induced dipole**.
- The **polarizability** is a measure of how large an induced dipole is produced for a given electric field.
- The more loosely held the electrons are, the larger the polarizability. \implies atomic polarizability increases as we move down a group.
- All other things being equal, the polarizability will be larger for long molecules because a small charge separation over a large distance can result in a large dipole moment ($\mu = |q|d$).

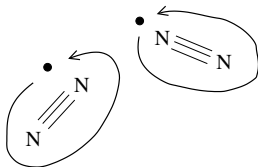
Dipole-induced dipole forces (continued)

- The induced dipole's orientation will always generate an attractive force to the polar molecule.



London dispersion forces

- If two molecules are close together, the motion of their electrons becomes correlated, i.e. the electrons will **tend** to move in the same direction at the same time.



- The following is a rough mental picture: When, by accident, one molecule develops a small dipole moment because more of its electrons move in one direction than the other, the same happens to the other molecule. They therefore have dipole moment vectors pointing in roughly the same direction, resulting in an attractive induced-dipole-induced dipole force.

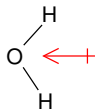
London dispersion forces (continued)

- The strength of dispersion forces depends on the polarizability.
- In large molecules, London dispersion forces can be large!
Example: Large hydrocarbons are solids at room temperature (waxes).

London dispersion forces (continued)

- Dispersion forces can occur even in ions or in molecules that have a permanent dipole moment.
- Induced dipoles in directions perpendicular to a permanent dipole moment are particularly important since there might not be any other forces acting in those directions.

Example: In H_2O , there is a permanent dipole moment parallel to the symmetry axis of the molecule.

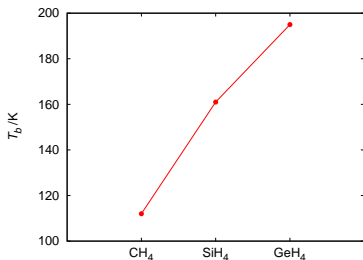


Dipole moment components can be induced perpendicular to this axis (perpendicular to molecular plane, or parallel to the H-H axis).

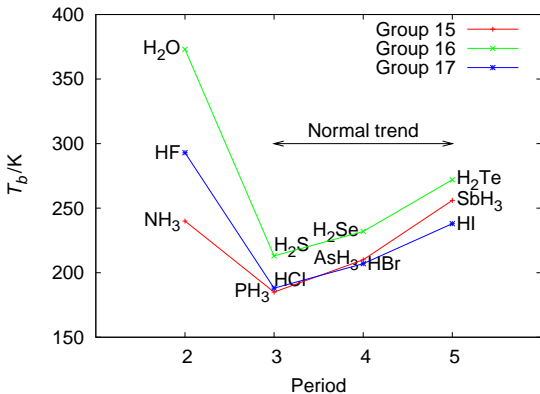
Boiling points

- All other things being equal, boiling points will be higher if the intermolecular forces are larger because it takes more energy to remove a molecule from the liquid.

Example: Group 14 boiling points



(Why?)



Why do NH_3 , H_2O and HF break the trend?

Hydrogen bonding

- In molecules containing O-H and N-H bonds and in HF, we observe dramatically increased intermolecular forces.
- We call this additional type of intermolecular force **hydrogen bonding**.
- Molecules involved in hydrogen bonding are much closer together than molecules experiencing (e.g.) dipole-dipole interactions, but not as close as covalent bonding distances.
(Known from X-ray and neutron scattering experiments)

Hydrogen bonding (continued)

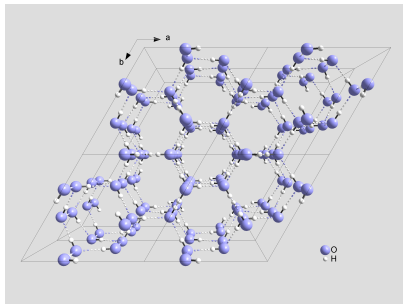
- Hydrogen bonding is due to a combination of factors:
 - Large electronegativity of N, O and F
 - No core orbitals in H
 - Availability of lone pairs on N, O and F
- The first two factors result in a very small electron density on the side of H away from a covalent bond to N, O or F.
- This allows H to interact with a lone pair. This interaction is partly a dipole-dipole interaction, but also has some covalent character.
- Hydrogen bonding is directional, i.e. there are preferred angles for this interaction.

Hierarchy of intermolecular forces

- 1 Ion-ion
 - 2 Ion-dipole
 - 3 Hydrogen bonding
 - 4 Dipole-dipole
 - 5 Dipole-induced dipole
 - 6 Induced dipole-induced dipole (London dispersion)
- Higher members of the hierarchy are stronger (except for dispersion, which can lead to very large forces in larger molecules).
 - Higher members are usually accompanied by some or all of the lower members.
- Example:** Water is subject to all the forces from hydrogen bonding to London dispersion.

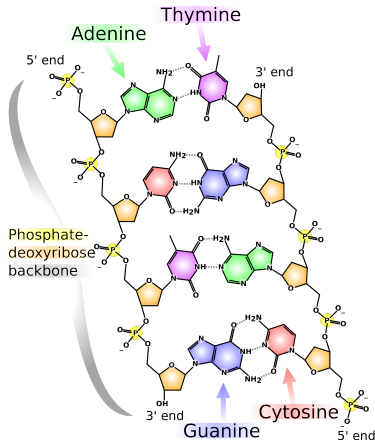
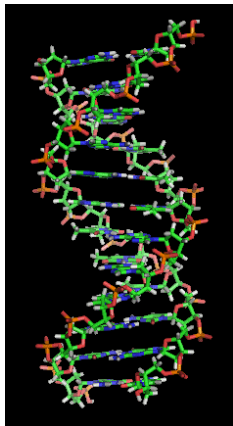
Why is ice less dense than water?

- This is unusual!
- Crystal structure of ice:



Source: Wikimedia commons,
http://en.wikipedia.org/wiki/File:Cryst_struct_ice.png

DNA and hydrogen bonding



Source: Wikimedia commons, http://en.wikipedia.org/wiki/File:DNA_orbit_animated_static_thumb.png and http://en.wikipedia.org/w/index.php?title=File:DNA_chemical_structure.svg&page=1

Why does DNA form a double helix?

- It's **not just** the hydrogen bonding!
- Hydrogen bonding to water would be just as good, and the higher entropy of single strands would tend to favor separated strands over a double helix.
- The bases are hydrophobic.
 - Nonpolar molecules tend to be hydrophobic because their presence in solution disrupts water's hydrogen bonding network.
 - "Burying" the hydrophobic bases is therefore a strong driving force in forming the double helix.
 - A full explanation of this effect requires entropy, to be discussed in CHEM 2000.
- There are fairly strong London dispersion forces between the stacked bases we get in the double helix, which also favors this structure.