
Intermolecular Forces

Intermolecular forces are generally ***much weaker*** than covalent bonds

- Only 16 kJ/mol of energy is required to overcome the intermolecular attraction between HCl molecules in the liquid state (i.e. the energy required to vaporize the sample)
- However, 431 kJ/mol of energy is required to break the covalent bond between the H and Cl atoms in the HCl molecule

Thus, when a molecular substance changes states the atoms within the molecule are unchanged

The temperature at which a liquid boils reflects the kinetic energy needed to overcome the attractive intermolecular forces (likewise, the temperature at which a solid melts).

Thus, the strength of the intermolecular forces determines the physical properties of the substance

Attractive forces between ***neutral*** molecules

- ***London dispersion*** forces
- ***Dipole-dipole*** forces
- ***Hydrogen bonding*** forces

Typically, dipole-dipole and dispersion forces are grouped together and termed ***van der Waals forces*** (sometimes the hydrogen bonding forces are also included with this group)

Attractive forces between ***neutral*** and ***charged*** (ionic) molecules

- ***ion-dipole*** forces

Note that all of these forces will be <u>electrostatic</u> in nature

<u>London Dispersion Forces</u>

Nonpolar molecules would not seem to have any basis for attractive interactions.

- However, gases of nonpolar molecules can be liquefied indicating that if the kinetic energy is reduced, some type of attractive force can predominate.
- Fritz London (1930) suggested that the motion of electrons within an atom or non-polar molecule can result in a transient dipole moment

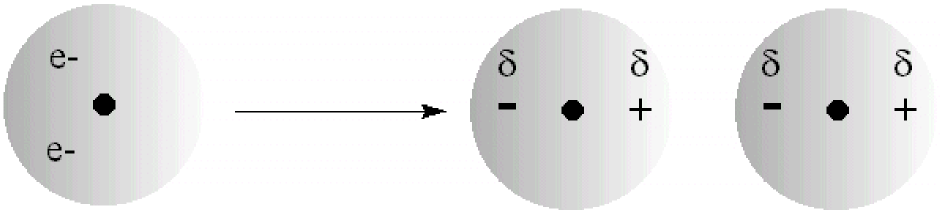
A Model To Explain London Dispersion Forces:

Helium atoms (2 electrons)

- Consider the ***particle*** nature of electrons
- The ***average*** distribution of electrons around each nucleus is spherically symmetrical
- The atoms are non-polar and posses no dipole moment
- The distribution of electrons around an individual atom***, at a given instant in time***, may ***not*** be perfectly symmetrical
    - Both electrons may be on one side of the nucleus
    - The atom would have an apparent dipole moment at that instant in time (i.e. a ***transient*** dipole)
    - A close neighboring atom would be influenced by this apparent dipole - the electrons of the neighboring atom would move away from the negative region of the dipole

Due to electron repulsion, a temporary dipole on one atom can induce a similar dipole on a neighboring atom

- This will cause the neighboring atoms to be ***attracted to one another***
- This is called the London dispersion force (or just dispersion force)
- It is significant only when the atoms are ***close together***



Instantaneous uneven distribution of electrons in He atom

Instantaneous dipole

Induced dipole on neighboring He atom. Resultant attractive force

The ease with which an external electric field can induce a dipole (alter the electron distribution) with a molecule is referred to as the "polarizability" of that molecule

- The ***greater*** the polarizability of a molecule the ***easier*** it is to induce a momentary dipole and the ***stronger*** the dispersion forces
- Larger molecules tend to have greater polarizability
    - Their electrons are further away from the nucleus (any asymmetric distribution produces a larger dipole due to larger charge separation)
    - The number of electrons is greater (higher probability of asymmetric distribution)

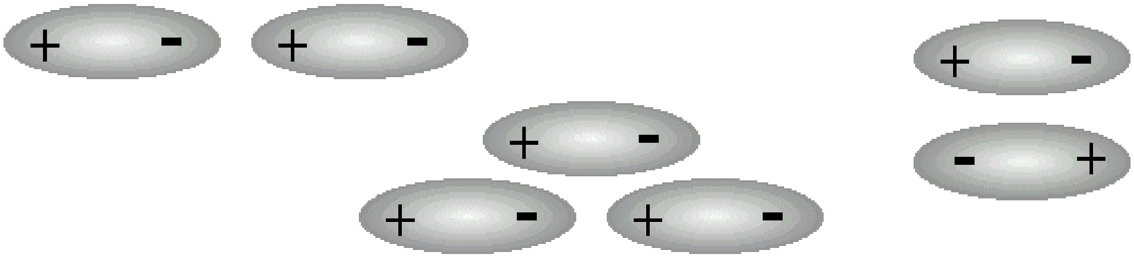
thus, dispersion forces tend to increase with increasing molecular mass

- Dispersion forces are also present between polar/non-polar and polar/polar molecules (i.e. between all molecules)

Dipole-Dipole Forces

A dipole-dipole force exists between neutral polar molecules

- Polar molecules attract one another when the partial positive charge on one molecule is near the partial negative charge on the other molecule
- The polar molecules must be in close proximity for the dipole-dipole forces to be significant
- Dipole-dipole forces are characteristically weaker than ion-dipole forces
- Dipole-dipole forces increase with an increase in the polarity of the molecule



Attractive Dipole-Dipole Interactions

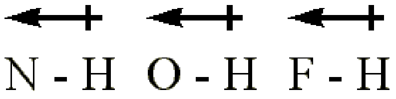
Boiling points increase for polar molecules of similar mass, but increasing dipole:

Substance	Molecular Mass (amu)	Dipole moment, *u* (D)	Boiling Point (°K)
Propane	44	0.1	231
Dimethyl ether	46	1.3	248
Methyl chloride	50	2.0	249
Acetaldehyde	44	2.7	294
Acetonitrile	41	3.9	355

Hydrogen Bonding

A hydrogen atom in a polar bond (e.g. H-F, H-O or H-N) can experience an attractive force with a neighboring electronegative molecule or ion which has an unshared pair of electrons (usually an F, O or N atom on another molecule)

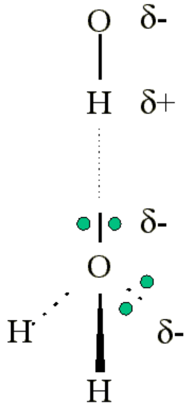
Hydrogen bonds are considered to be dipole-dipole type interactions

- A bond between hydrogen and an electronegative atom such as F, O or N is quite polar:
- 

- The hydrogen atom has no inner core of electrons, so the side of the atom facing away from the bond represents a virtually naked nucleus
- This positive charge is attracted to the negative charge of an electronegative atom in a nearby molecule
- Because the hydrogen atom in a polar bond is electron-deficient on one side (i.e. the side opposite from the covalent polar bond) this side of the hydrogen atom can get quite close to a neighboring electronegative atom (with a partial negative charge) and interact strongly with it (remember, the closer it can get, the stronger the electrostatic attraction)
    - Hydrogen bonds vary from about 4 kJ/mol to 25 kJ/mol (so they are still weaker than typical covalent bonds.
    - But they are stronger than dipole-dipole and or dispersion forces.
    - They are very important in the organization of biological molecules, especially in influencing the structure of proteins

Water is unusual in its ability to form an extensive hydrogen bonding network

- As a liquid the kinetic energy of the molecules prevents an extensive ordered network of hydrogen bonds
- When cooled to a solid the water molecules organize into an arrangement which maximizes the attractive interactions of the hydrogen bonds
    - This arrangement of molecules has greater volume (is less dense) than liquid water, thus water expands when frozen
    - The arrangement has a hexagonal geometry (involving six molecules in a ring structure) which is the structural basis of the six-sidedness seen in snow flakes
    - Each water molecule can participate in four hydrogen bonds
        - One with each non-bonding pair of electrons
        - One with each H atom

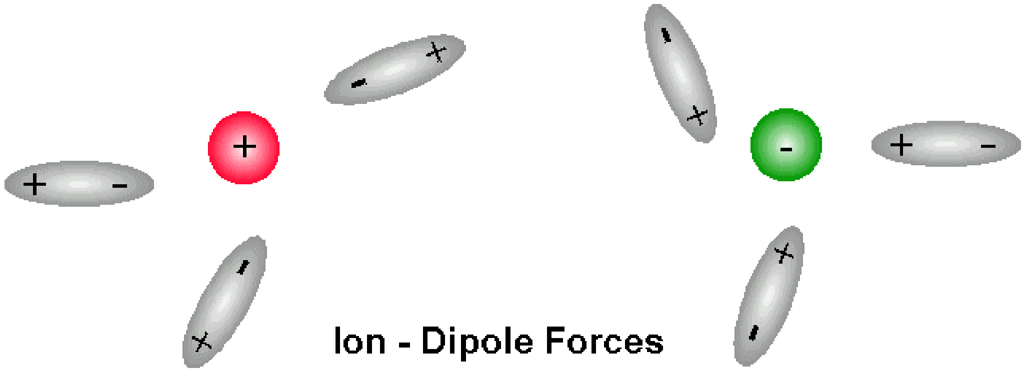


Ion-dipole

- Involves an interaction between a ***charged ion*** and a ***polar molecule*** (i.e. a molecule with a ***dipole***)
- Cations are attracted to the negative end of a dipole
- Anions are attracted to the positive end of a dipole
- The magnitude of the interaction energy depends upon the charge of the ion (***Q***), the dipole moment of the molecule (***u***) and the distance (***d***) from the center of the ion to the midpoint of the dipole

$$E \propto \frac{Qu}{d^2}$$

- Ion-dipole forces are important in solutions of ionic substances in polar solvents (e.g. a salt in aqueous solvent)



Ion - Dipole Forces

Ion-ion

1996 Michael Blaber