

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.

Intermolecular forces are electrical forces that exist between molecules that would cause one molecule to influence another. Such forces will cause a gas to deviate from Ideal Gas behavior. These forces are stronger in the liquid and solid state.

Intermolecular forces are called Van Der Waals forces . They are attractive forces between *neutral* molecules. There are three such types of Van Der Waals forces:

1. London Dispersion Forces which are forces that exist between non-polar molecules or non-bonding atoms as result of positive nuclei of one molecule attracting the electrons of another molecule. All molecular substances exhibit London Forces which are the weakest of the Van Der Waals forces.
2. Dipole-Dipole interactions which are forces that exist between polar molecules where the positive end of one molecule attracts the negative end of another molecule. Only polar molecules can exhibit this type of Van Der Waals forces and is considered the second strongest.
3. Hydrogen bonding interactions are forces that exist between molecules that have a hydrogen atom bonded to a highly electronegative atom such as Oxygen, Nitrogen, or Fluorine. This represents a strong dipole that will have the Hydrogen end (positive) attracting the negative end (O,N, or F) of other molecules. This type of Van Der Waals force represents one of the strongest type.

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

- *ion-dipole* forces

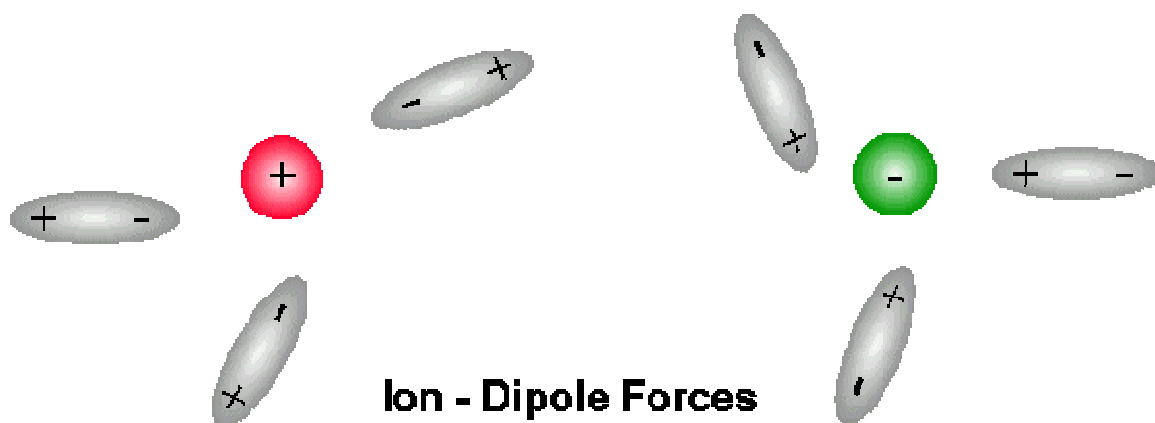
Note that all of these forces will be electrostatic in nature

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

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

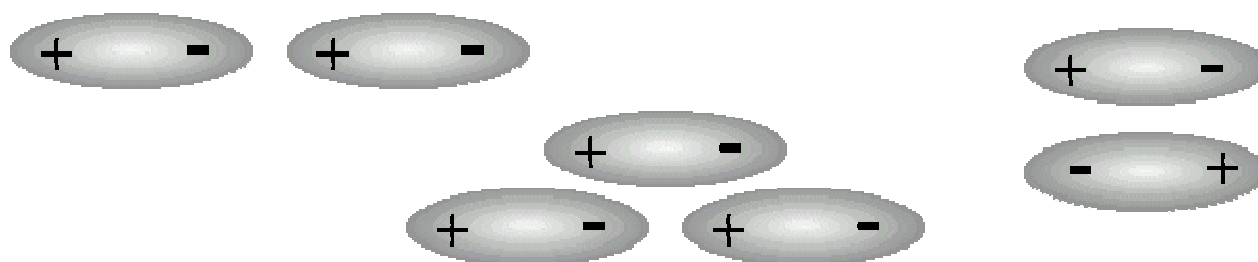
- Ion-dipole forces are important in solutions of ionic substances in polar solvents (e.g. a salt in aqueous solvent)



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, μ (D)	Boiling Point ($^{\circ}$ 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

London Dispersion Forces

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

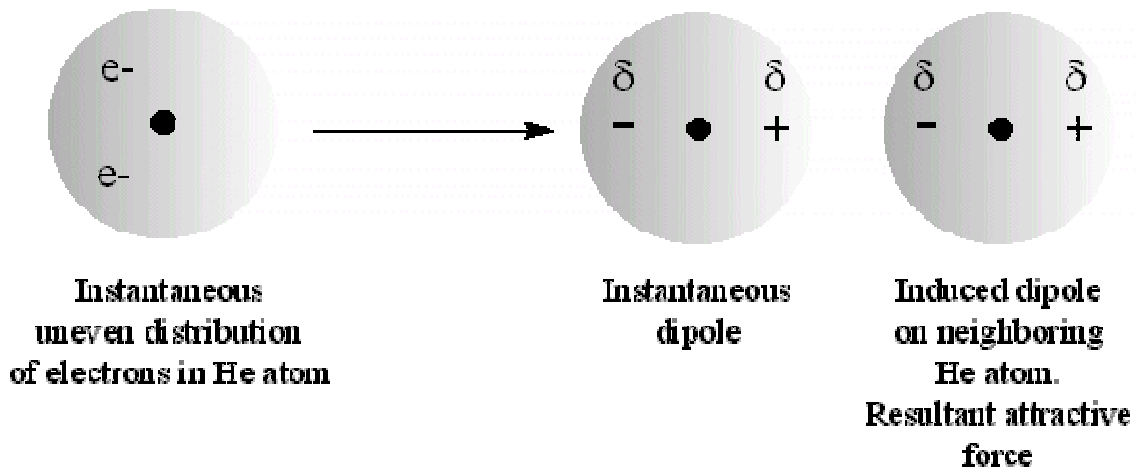
A Model To Explain London Dispersion Forces:

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 possess 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*



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)

Hydrophobic Interactions

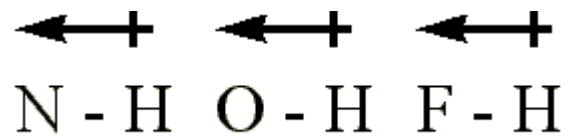
Nonpolar molecules cannot form H-bonds with H₂O, and are therefore insoluble in H₂O. These molecules are known as hydrophobic (water hating), as opposed to water loving hydrophilic molecules which can form H-bonds with H₂O. Hydrophobic molecules tend to aggregate together in avoidance of H₂O molecules; hydrophobic interactions are clearly demonstrated when you put an oil drop on water. This attraction/repulsion is known as the hydrophobic (fear of water) force. To understand the energetics driving this interaction, visualize the H₂O molecules surrounding a "dissolved" molecule attempting to form the greatest number of hydrogen bonds with each other. The best energetic solution involves forcing all of the nonpolar molecules together, thus reducing the total surface area that breaks up the H₂O H-bond matrix.

Hydrogen Bonding

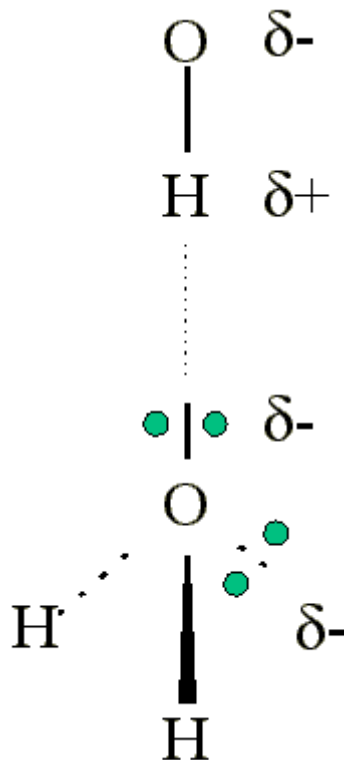
A hydrogen atom in a polar bond (e.g. H-F, H-O or H-N) can experience an attractive force with a neighboring electronegative molecule or ion which has an unshared pair of electrons (usually an F, O or N atom on another molecule)

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

Example 1. Which substances experience dipole-dipole intermolecular forces?

SiF₄, CHCl₃, CO₂, SO₂

Solution:

SiF₄ tetrahedral Si-F bonds are polar, but no molecular dipole; bond dipoles cancel
 CO₂ linear C-O bonds are polar, but no molecular dipole; bond dipoles cancel
 SO₂ bent S-O bonds are polar and do not cancel. Sulfur lone pair dipole only partially offsets net bond dipole.
 CHCl₃ tetrahedral C-H and C-Cl bonds are polar and do not cancel

SO₂ and CHCl₃ experience dipole-dipole intermolecular forces.

Example 2. Arrange the following non-polar molecules in order of increasing melting point.

SiF₄, CS₂, Cl₄, GeCl₄

Solution. None of these molecules is expected to have a dipole moment. Only dispersion forces will operate, and these increase with increasing molecular mass. The molar masses of these substances follow:

Substance	MM
SiF ₄	104.077
CS ₂	76.131
Cl ₄	519.631
GeCl ₄	214.402

The intermolecular forces, and the melting points, should increase in the following order:

CS₂ < SiF₄ < GeCl₄ < Cl₄

The experimentally determined melting points are -110.8, -90, -49.5, and 171 °C, respectively.
