Behavior of Liquids and Solids

Describe the difference between intra- and intermolecular forces, explain how these foresees influence molecular properties

Intermolecular forces are those that exist between molecules, whereas intramoleuclar forces that exist between atoms in a molecule, holding a molecule together. Strong intermolecular forces make a substance difficult to break apart and form either a liquid or a solid. In other words, the molecules are more attracted to each other; they stick together; they are harder to separate from each other. A substance with a strong intermolecular force has a high melting point, boiling point, heat of vaporization and fusion, low vapor pressures, and high surface tension.

Types of forces:

Ion-dipole: *a force between an ion and the partial charge on the end of a polar molecule. Ion-dipole forces are important when considering solutions of ionic substances.*

Dipole-dipole forces*: polar molecules align themselves so that the ∂- end of one molecule is near the ∂+ end of other molecules. The molecules are thus attracted to each other. Dipole-dipole forces exist between polar molecules. The greater the polarity of the molecule, the stronger the dipole-dipole forces between the molecules.*

London forces: a temporary dipole on one molecule (formed by the random motion of electrons in the molecule) induces a temporary dipole on neighboring molecules. These temporary dipoles experience attraction for each other. London forces exist between all types of molecules the strength of the London force depends on the molar mass of the molecule and to a lesser extent, on the surface area of the molecule. The higher the molar mass the more electrons in the molecule; the more electrons in the molecule, the more polarizable the molecule; the more polarizable the molecule, the stronger the London force. Temporary dipoles are more easily created in large molecules, especially those with high atomic numbers. The outer electrons are far from the nucleus and not held firmly. We picture these loosely held electrons as delocalized through out the entire molecule. The molecule is polarizable because not all the electrons are held in the same strength. Size and molecular mass go hand in hand, so as the size increase, the mass should increase, and the molecule should be more polarizable because there are more electrons.

Shape affects London forces by surface area. The larger the surface area for the same molar mass, the stronger the London force. Electrons in linear molecules are delocalized over a larger area. These molecules have more contact than a spherical molecule, which is more compact.

Hydrogen bonding*: this is a special (stronger case) of dipole-dipole forces. It can exist between a molecule with a hydrogen atom directly attached to an N, O or F atom and another molecule with a lone pair of electrons on an N, O, or F. The atoms N, O, and F are all very electronegative and very small. When a hydrogen atom is bonded to an N, O, or F, the resulting bond is especially polar. The ∂+ hydrogen atom is "shared between two atoms of n, o, f; the hydrogen atom has a covalent bond to one and a hydrogen bond to the other. Hydrogen bonds are very directional; three atoms must lie in a straight line.*

Hydrogen bonds are the strongest (15-40kJ), followed by dipole-dipole (0.01-0.2 kJ) and the third are London forces (0.4 kJ-10kJ).

In general: when MM and shapes are close, London forces are less important in determining van-der-Waals interactions. Dispersion forces are approximately equal. Differences in the dipole-dipole interactions are more important.
When molecular masses and shapes are different, dispersion forces tend to be more important.

State conditions that lead to hydrogen bonds, explain how hydrogen bonds differ form other types of intermolecular forces, and describe the effect of hydrogen bonds on physical properties.

Hydrogen bonds are formed when a hydrogen atom bound to an F, O, or N atom is attracted to another F, O, or N atoms. A Cl or S atom may substitute for F, O, or N atom but the resulting hydrogen bond is very very weak, almost non-existent. The hydrogen bond can be seen as being divided into two parts: one molecule contributes an electron pair attraction, while the other contributes a hydrogen attraction.

One explanation for H bonds is that the high electronegativity of F, O, or N pulls so much of the bond pair of electrons toward it that the hydrogen nucleus is almost a bare proton. Thus, a very intense dipole is created. However, this is not the full explanation.

The hydrogen bond is very strong, ranging from 15kJ to 40kJ. Strengths of other intermolecular forces rarely exceed 10kJ. It is common to see a fixed limit on the number of hydrogen bonds formed. Hydrogen bonds have reasonably will defined length 2.74Å between oxygen atoms in ice. Dipole attractions normally show a range of lengths. The required distance and number of hydrogen bonds make the structure of ice more open than that of liquid water. Thus, ice floats on water. The strength of the hydrogen bond results in unusually high melting and boiling points and heats of vaporization for substance comprised of small molecules.

What to do when you are asked to compare boiling points or vapor pressures for a set of molecules:

1) *Find the approximate molar mass of each molecule.*

2) *Determine the molecular geometry.*
3) *Determine the types of intermolecular forces present for each molecule*
4) *All molecules have London forces. Polar molecules have dipole-dipole forces. Molecules with hydrogen atoms attached to N, O, F and free lone pairs can Hydrogen bond.*
5) *If the molecules have similar molar masses, their London forces have similar strengths. Look at the types of intermolecular forces each molecule has. The one with the most types of forces has the strongest INTERMOLECULAR Force's overall*
6) *If the molecules have similar molar masses and they are all non polar, consider the shaper. The more stretched out the (least compact) molecule has the higher surface area and thus will have stronger London forces and stronger intermolecular forces overall, since London forces are the only type of forces they have. If the molecules have similar molar masses and similar types of intermolecular forces, look for the one that his the most polar or that has the most electronegative atoms or the most hydrogen bonding groups. That one will have the strongest intermolecular forces overall.*
7) *If the molecules have very different molar mass, by a factor of 2 or more, they will have very different London forces strengths. In this case, the one with the much higher molar mass will have the strongest intermolecular forces*

Examples:

$CH_3CH_2CH_3$	CH_3CH_2F	CH_3CH_2OH
44amu, bp –42°C	*48 amu, bp –38°C*	*46 amu, bp 78°C*
These molecules have very similar molar masses so their London Forces are similar. However, the first one is nonpolar, and has only London Forces. The second one is polar because it contains F, but it cannot Hydrogen bond because it does not have H attached directly to the F. The last one is polar and can have hydrogen bonding because of the OH group. The one that can hydrogen bond has the highest boiling point, the polar molecule has the medium bp and the non polar one has the lowest bp.		

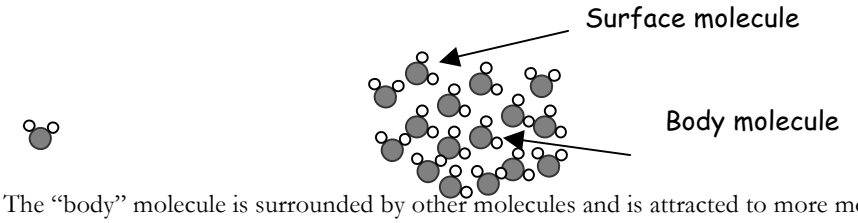
CH_3CH_2OH		CH_3OCH_3
MM 46, BP 78°C		*MM46, BP –25°C*
These molecules have the same molar mass. The first one can hydrogen bond, but the second one cannot (even though it is polar). Since the first one can hydrogen bond, it has stronger IMF/s overall and a higher boiling point. (Note what a huge difference there is in the boiling points!)		

$CH_3(CH_2)_5CH_3$		CH_3CH_2OH
MM 100, BP 98°C		*MM 46, BP 78°C*
These molecules have very different molar masses. The molar mass of the first one is more than two times the molar mass of the second one. Even though the second one can hydrogen bond and the first one is non polar, the fist one has stronger imf's overall. The one with the higher molar mass has much stronger London forces than the other one.		

$CH_3CH_2CH_2CH_3$ *58 amu, bp –0.5°C*		CH_3—$CH(CH_3)$—CH_3 *58 amu, bp –12°C*
These molecules are both non polar and have the same molar mass. However, the first one is more stretched out and the second one is more compact. The first one has a higher surface area and therefore stronger London forces and a higher boiling point. Since they are non polar, the only imf they have is London forces.		

Explain surface tension and describe several phenomena based on it:

Energy is given off when atoms are attracted to each other. Liquid molecules are moving slow enough so the cloud densities of one molecule can affect the cloud densities of the molecules around it. Forces of attraction exist between molecules and even between individual UN–bonded atoms; they are stronger for polar molecules than for non-polar molecules. A molecule could be considered to have an overall low energy if it is attracted to many other molecules; the "bound" molecule is more stable than a "free" molecule. We can consider two types of molecules in a liquid: a molecule in the body of a liquid and a surface molecule.



The "body" molecule is surrounded by other molecules and is attracted to more molecules than the "surface" molecule. The surface molecule can be considered to be less stable. The over all energy of the liquid is reduced (stabilized) if the liquid can decrease its surface area, and therefore, the number of surface molecules by changing more surface molecules

to body molecules. Liquids tend to form drops because it decreases the surface area. The resistance of a liquid to increase its surface area is called **surface tension.** Liquids with high intermolecular forces will have high surface tensions. The larger the surface area, the lower the surface tension. We are interested in the effect of other material on the surface tension of the liquid. When forces to another substance (adhesive forces) are stronger than forces within the liquid (cohesive forces) the liquid will wet that surface; the surface tension is reduced. In this case, a liquid will rise in a capillary tube in a vain attempt to decrease the extra surface created by the liquid rising to meet the wall of the tube. Drops of water will bead on a waxed surface because the opposite is happening. The cohesive force is stronger than the adhesive force and the surface tension is increased. If you use Cascade or some other soap with strong "wetting" ingredients, again the surface tension is decreased. [surfactants! We want the water to sheet, not bead in this case.]

Explain what occurs when a liquid vaporizes in a closed container: the dynamic equilibrium between a liquid and its vapor

A liquid in an open container, in contact with the atmosphere, will eventually vaporize. All of the liquid will go to the gas phase and the liquid will "disappear". In a closed container, the vapor molecules cannot escape. Eventually the concentration of the molecules the vapor state increases. At some point in time, the vapor molecules lose KE and condense back to liquid. Eventually, molecules condense from the vapor to the liquid state just as rapidly as they vaporized to the gas state. The vapor above the liquid is saturated; it can hold no more gas than what this equilibrium allows. The vapor concentration is proportion to the vapor pressure by the ideal gas law. The pressure of the saturated vapor is known as the liquid's vapor pressure. At this point the rate of vaporization = the rate of condensation. The rate of vaporization depends on three factors: temperature, forces between molecules and the surface are of the liquid. Increasing the temperature causes liquid to vaporize more rapidly. Vaporization also occurs more rapidly for a large surface area than for a small one. The rate of condensation depends on the pressure of the vapor and on the surface area. High pressure and large surface area both increase the rate of condensation. In the first case, there are more molecules present in the vapor that can condense; in the second case, the area that the molecules must hit in order to condense is larger.

Explain how vapor pressure and temperature are related and the meaning of boiling

As the temperature increases, the vaporization rate increases and so does the vapor pressure. Vapor pressure is often tabulated against temperature. When the vapor pressure of the liquid reaches atmospheric pressure bubbles of vapor form within the liquid and the liquid boils. This occurs at the normal boiling point, at 1 atm. The **Clausius-Clapeyron** equation is important because it permits us to predict the vapor pressure of a liquid at several different temperatures and it has the same form as the Arrhenius equation, which predicts the rated constant of a reaction at different temperatures and the van't Hoff equation which predicts the equilibrium constant of a chemical reaction at different temperatures (you will see these next semester)

Describe the significance of the critical point

A gas will not condense to a liquid no matter how much pressure is exerted above the critical point. The matter will get denser and may become as dense as a liquid by it will never show a meniscus. Similarly, above the critical pressure, the familiar process of vaporization and condensation do not occur no matter how the temperature changes. This is the pressure required to produce liquefaction at the critical temperature. The critical temperature represents a very high kinetic energy of the molecules. Their speeds are so large that the short-range intermolecular forces are not strong enough to hold molecules together.

Predict relative lattice energies of ionic compounds and relate their magnitudes to the physical properties of those compounds (melting point, molar enthalpy of vaporization, and solubility in water).

The lattice energy of an ionic compound is the energy of the reaction in which gaseous cations and gaseous anions unite to form one mole of the solid compound. Since this reaction releases energy, lattice energies are invariably exothermic. Lattice energies can be determined form experimental data with the Born-Haber cycle. Lattices energies can also be obtained from the crystal structure of the compound. Compounds that contain small highly charged ions would have large lattice energy.

This means that the ions are firmly bonded into the crystal. Hence, the crystal will be difficult to disrupt and will have a high melting point and a large heat of fusion. Because the ions also must be separated when the compound dissolve in water, we should expect a large lattice energy would predict a low solubility in water. Here there are some exceptions because solubility also depends on the attractions between the ions and the water molecules. These ion molecule attractions also are strong for small, highly charged molecules. Thus, although it may require a great deal of energy to separate the ions, most of that energy may be released when the ions are hydrated.

Interpret simple phase diagrams and use phase diagrams to predict changes when a substance is heated, cooled or undergoes a change in pressure.

A phase diagram summarizes the changes in phase of a given substance. The liquid-vapor curve is determined by the Clausius-Clapeyron equation, if ΔH sub is used for ΔHvap. The slop of the fusion line is given by

$$\frac{\Delta P}{\Delta T} = \frac{\Delta Hfus}{T\Delta V}$$

In the equation, ΔV is the volume increase of one mole on melting. The line between solid and liquid is straight enough to draw with a ruler. This line usually slopes upward and to the right, a positive slope, with water being one of the few examples that has a negative slope. In the case of water, the volume for fusion is negative, and the fusion curve slops upward and to the left. This means the volume decreases as the ice melts to form water; ice floats. The point where the vapor pressure, sublimation and fusion curves met is the triple point where solid, liquid and vapor exist together.

A heating curve is a plot of temperature verse energy when heat is added to a sample at a constant rate. The specific heat of ice or of steam is about half the specific heat of liquid water, meaning that the temperature of ice or steam will rise about twice as rapidly as will the temperature of the liquid. The molar heat of vaporization is 40.67 kJ/mol at 100°C while it s molar heat of fusion is 6.01 kJ/mol at 0°C, meaning that the vaporization temperature will be maintained about 7 times longer than the melting temperature.

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Work sheet for intermolecular forces:

1) List the properties of water that stem from hydrogen bonding.[i]

2) Predict the order of increasing boiling points of noble gases.[ii]

3) Which of the following has the highest boiling point: H_2, He, Ne, Xe, CH_4?[iii]

4) Which one in each of the following pairs is expected to exhibit hydrogen bonding, explain: CH_3CH_2OH or CH_3OCH_3, CH_3NH_2 or CH_3SH, CH_3OH or $(CH_3)_3N$?[iv]

5) In which molecule is London forces most likely to be the most important in determining the melting point and boiling point: ICl, Br_2, HCl, H_2S, or CO?[v]

6) The heat of vaporization of liquid chlorine ($Cl_{2(l)}$), liquid hydrogen ($H_{2(l)}$), and liquid nitrogen ($N_{2(l)}$), are 20.4 kJ/mol, 0.9 kJ/mole, and 5.6 kJ/mol respectively. Using the information about intermolecular forces, explain which force is probably holding the molecules in the liquid phase, and if these numbers see reasonable, and why.[vi]

7) For each of the following substances, list the kinds of intermolecular forces expected: Boron trifluoride, Isopropyl alcohol $CH_3CHOHCH_3$, hydrogen iodide gas, Krypton[vii]

8) Arrange the following substances in order of increasing power of London forces, $SiCl_4$, CCl_4, $GeCl_4$.[viii]

9) Describe the formation of hydrogen bonds in propanol $CH_3CH_2CH_2OH$. Represent possible hydrogen bonding structures in propanol by using structural formulas and the conventional notation for a hydrogen bond.[ix]

10) Ethylene glycol (CH_2OHCH_2OH, is a slightly viscous liquid that bois at 198°C. Pentane (C_5H_{12}), which has about the same molecular weight as ethylene glycol, is a non-viscous liquid that boils at 36°. Explain the differences in physical characteristics of these two compounds[x]

Answers to questions: the small roman numerals match the Aramaic numbers.

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[i] High melting point, high boiling point, high heat of vaporization, low density of ice compared to water, high specific heat, pH.

[ii] The greater the atomic number, the greater the number of electrons in each atom, and the greater is the London force. The greater the forces between molecules, the higher the boiling point, so this should be a trend expected with the noble gases, even though they are monatomic particles.

[iii] Xe, all are nonmetal polar particles but Xe has the greatest London forces because it has the most electrons.

[iv] Ethanol, [H is connected to O], methyl amine [N is connected to H, S is not electronegative enough to form H bonds, lone pairs are to diffuse,], methanol, [no H on the nitrogen atom in the trimethyl amine]

[v] Bromine, each of the other molecules has a dipole in addition to London forces. Only in bromine are the London forces the only intermolecular force.

[vi] The heat of vaporization is the energy needed to change a liquid into a gas. matter that has high vaporization energy has a large intermolecular force. All of these molecules exhibit only London forces. The larger the molecule, the more electrons, and the stronger the London force. The order makes sense because chlorine is the largest molecule and hydrogen is the smallest. Chlorine should have the largest heat of vaporization, hydrogen should have the smallest heat of vaporization, and nitrogen should be somewhere in-between.

[vii] All of these molecules will exhibit London forces. Boron trifluoride has a molecular geometry of trigonal planar. It is a symmetrical molecule; each of the bonds to fluorine is the same, and there are no lone pairs. Boron trifluoride should exhibit London forces only. Isopropyl alcohol has an OH group. OH groups are good hydrogen bonders. Isopropyl alcohol will exhibit hydrogen bonding. Hydrogen iodide is a polar molecule and will exhibit dipole-dipole interaction. Krypton is a large atom. it will exhibit only London forces.

[viii] The order will be based on mass. The molecule with the largest mass will have the most electrons, and therefore, the highest London forces: germanium tetrachloride, silicon tetrachloride, and the lowest LF, with carbon tetrachloride.

[ix] See drawing-okay, I will probably just put the drawing on the board.

[x] The shape these two compounds are around the same. The molar mass of ethylene glycol is about 62 g/mol, while the molar mass of pentane is about 72 g/mol we would expect the heavier molecule to have the larger London force and the larger boiling point. But that is not what is observed. The difference in the boiling points comes from the different types of molecular interactions. Pentane is non-viscous liquid, held together by very weak London forces. This is evident by the low boiling point. ethylene glycol is a viscous liquid, held together by London forces and very strong hydrogen bonding. There are two OH groups in this molecule, each capable of hydrogen bonding. Hydrogen bonding is strong. It takes a lot of energy to vaporize ethylene glycol, which is why it is great antifreeze. it does not freeze until the temperature is really, really cold, and takes a lot of energy to boil.