CHEM 116 How Intermolecular Forces Explain Behaviors of Particles in Condensed Phases (Liquids & Solids)

Note for printing lecture slides before coming to class:

At lecture 6 last week, we did not get all the way through the lecture slides. I have placed the slides we didn't get to at the beginning of today's slides. If you wish to avoid printing those because you already printed lecture 6, then just print pages 1, 2, 5 and 6 of this set of notes, and bring your lecture 6 notes from last week with you to class.

p.s. Don't forget your i>clicker.

Lecture 7 Prof. Sevian



Today's agenda

Finish chapter 11

- Reminder of polar vs. nonpolar molecules which you learned in first semester chemistry
- Reminder of types of units: atoms, molecules, ions
- Arrangements of units in materials
 - Single substance solids: ionic vs. molecular
 - Single substance liquids
 - Gray areas:
 - When solids change into liquids
 - When the bonding is somewhere in between polar and ionic
- Intermolecular attractions occurring in solutions
 - Polar solute in a polar solvent
 - Nonpolar solute in a polar solvent
 - Ionic solute in a polar solvent
- FSG is offered:
 - Mondays 11:00-11:50am
 - Tuesdays 3:30-4:20pm
 - Both in S-1-89

A clicker question to bring your mind back to material from first semester chemistry that we will build on in this lecture

Which molecule has the strongest dipole moment?

- (A) CCl₄
- $(\mathsf{B}) \quad CH_3OH$
- (C) CH₃OCH₃
- (D) CO_2

Explaining macroscopic (lab level) behavior by particle level interactions

Solids (crystals) : long range order Liquids : short range order Gases (vapors) : no order

- Solids vs. liquids vs. gases
 - Comparison of macroscopic properties with particle level explanation for why those properties arise <u>http://www.chem.purdue.edu/gchelp/liguids/character.html</u>
 - Comparison of radial distribution functions (average density of atoms at r given that another atom is located at the origin) determined by molecular dynamics simulations http://matdl.org/matdlwiki/index.php/softmatter:Radial_Distribution_Function
- Models of particle-particle interactions that have been used to explain and predict behavior of solids, liquids and gases
 - Dipole-dipole attractions predominate
 - small molecules with large dipoles
 - London dispersion attractions predominate
 - small molecules with nearly zero dipoles
 - large molecules, whether they have dipoles or not
 - van der Waals repulsions
 - not covered until graduate school, but there is a fairly readable explanation by Chandler, Weeks & Andersen in Science, 220, p. 787 (May 20, 1983)

Particle level: materials composed of Molecules

- Solid state
 - Molecules arranged in lattice
 - Individual molecules are neutral
 - Molecules restricted to vibration in lattice space
 - To change to liquid, must overcome molecule-molecule attraction that bind molecules to each other in solid state
- Liquid state
 - · Molecules occupy similar amount of space as in solid
 - Molecules have enough kinetic energy to surmount energetic barrier and move past each other
- Gas state
 - Molecules are in rapid random motion and travel in straight lines until they collide with something (each other, walls)
 - The space that an individual molecule occupies is negligible compared with the space available for the molecule to move in

Reminder: What is a dipole?

Molecules can be dipoles or non-polar (actually, it's more about the degree of polarity)



Particle level: materials composed of lons

- Solid state
 - Ions arranged in lattice, with individual ions occupying lattice points
 - lons have alternating arrangement (+ then then +, etc.) in such a way that every + ion is surrounded by – ions, and vice versa
 - Individual ions are charged
 - Ions restricted to vibration in lattice space
 - To change to liquid, must overcome positive ion negative ion attractions that bind ions to each other in solid state
- Liquid state
 - Ions occupy similar amount of space as in solid
 - Molecules have enough kinetic energy to surmount very large energetic barrier and move past each other
- Gas state
 - Mostly a theoretical construct

Some examples of ionic solids (particle level illustrations)

Sodium chloride (NaCl)



Ammonium chloride (NH₄Cl)



From Chemistry & Chemical Reactivity 5th edition by Kotz / Treichel. C 2003, Reprinted with permission of Brooks/Cole, a division of Thomson Learning: <u>www.thomsonrights.com</u>. Fax 800-730-2215.

Particle level: materials composed of metal atoms

- Solid state
 - Metal ions (missing valence electrons) arranged in lattice, with individual metal ions occupying lattice points
 - Every lattice point is occupied by a + charged metal ion
 - Valence electrons from all the metal atoms surround the metal ions (a "sea" of electrons)
 - Metal ions restricted to vibration in lattice space
 - Electrons free to roam and can be influenced by static charge or by voltage potential across the metal
 - To change to liquid, must overcome metal ion negative electron sea attractions that bind metal ions to bulk solid

Forces that hold units together in condensed states of matter: The basic idea

- Strength of attractive force governs difficulty of breaking the force (amount of energy required)
- Several factors matter in determining the strength of the attractive force:
 - <u>Separation</u> (distance) between the units (or subunits) that are held together by attractions
 - <u>Strengths</u> (magnitudes of the point charges or dipoles) of the units (or subunits) that are held together by attractions
 - <u>Timeframe</u>: how fast the particles are moving vs. timeframe of the measurement, this is beyond the scope of this course
- There are significant mathematical differences in strength between how these factors manifest in dipoles (neutral molecules with a permanent dipole moment, or neutral atoms with a temporary dipole moment) and monopoles (charged ions, point charges)
- In this course, we will either compare units within a single class, or particles of approximately the same size in different classes

What classes of "units" and "subunits" are we talking about?

- lons
 - Unit in an ionic compound is the neutral combination of simplest ratio of cations (+) and anions (-)
 - In the solid, crystal lattice sites are occupied either by a cation or by an anion
 - Subunits are the individual ions, which are held together by mutual attraction
- Molecules
 - Unit is an individual molecule
 - In the solid, every crystal lattice site has a molecule at it
 - Polar (small molecule with a dipole moment)
 - Nonpolar (lone atom or a molecule that does not have a dipole moment)
 - Gray area (large molecules which may have dipoles in them, but nonpolar parts of the molecules are more important because they are large)

Ion-ion attractions



Explaining macroscopic behavior by reasoning based on ion-ion attractions

Lattice energies* of some ionic compounds

(You can think of lattice energy as the amount of energy required to break apart an ionic crystal into its separated constituent ions far apart, *i.e.*, in the gas phase)

Compound	Lattice energy (kJ/mol)*
LiF	1037
LiCl	852
LiBr	815
LiI	761



*Actually, lattice energy is defined as the energy to do exactly the opposite, so the values are all negative. But the main point here is to look at the magnitudes of the numbers.

Polar molecule – polar molecule attractions

- For small molecules that have permanent dipole moments, these attractive forces are the strongest ones at work (but not the only ones)
- Often called dipole-dipole interactions
- Remember that dipoles are permanent
- Bar magnets are magnetic dipoles, polar molecules are electric dipoles, the behavior is analogous mathematically



Explaining macroscopic behavior by reasoning based on dipole-dipole attractions

The stronger the permanent dipole, the stronger the attractions

	dipole mome	ent
Molecule	(debyes)	<u>b.p. (°C)</u>
HCI	1.08	-84.9
HF	1.92	19.5

Which are stronger?

- Attractions between HCI and other HCI molecules, or
- Attractions between HF and other HF molecules

Compare HCI and HF



Question to consider: In which liquid does it require more energy to break intermolecular forces and move molecules into the gas state?

Explaining macroscopic behavior by reasoning based on dipole-dipole attractions

The stronger the permanent dipole, the stronger the attractions

Molecule	dipole moment (debyes)	b.p. (⁰C)		
HCI	1.08	-84.9		
HF	1.92	19.5		
NO NO ₂	0.16 0.29	-151.8 21.2	•	A
H₂S H₂O	1.10 1.87	-60.7 100		
H_2O_2	2.13	150.2 🧹	◚ੑੑੑੑੑੑੑ	

Some dipole-dipole interactions are very strong

They get their own special name: hydrogen bonding

- Hydrogen bonding is a category of dipole-dipole IM forces
- It is just the strongest of the dipole-dipole interactions
- When H is bonded to either N, O, F or Cl in a molecule
- Examples of substances in which there is hydrogen bonding
 - HCI
 - H₂O
 - CH₃COOH
 - NH₃
 - NH₂Cl
- Dipole-dipole attractions that are not hydrogen bonding (why not?)
 - CH₃-O-CH₃

Non-polar molecule – Non-polar molecule attractions (also called London dispersion forces)

- These can be considered to be the only significant force of attraction between nonpolar molecules
- · First, let's consider small molecules that are nonpolar
- A non-polar molecule can have a momentary, fleeting dipole
- When it does, it can induce a dipole in a neighboring molecule
- Two momentary dipoles attract each other during the brief time that



Source: http://www.chem.purdue.edu/gchelp/liquids/disperse.html

More about non-polar – non-polar attractions

- Often called London dispersion forces
- Sometimes called induced dipole induced dipole attractions
 To *induce* means to cause
- The larger the molecule, the greater the possible separation of partial electric charge, therefore the larger the momentary dipole moment can be
 - Caution: molecular mass is often, but not always, a good indicator of molecular size
- The stronger the temporary dipoles, the stronger the attractions

Comparing dispersion forces



four 5-carbon molecules



four 9-carbon molecules

n-pentane, C ₅ H ₁₂		
m.p.	-130ºC	
b.p.	36°C	

n-nonane, C₉H₂₀ m.p. -54°C b.p. 151°C

Explaining macroscopic behavior by reasoning about intermolecular forces

name	formula	melting point
lauric acid	C ₁₁ H ₂₃ COOH	44° C
myristic acid	C ₁₃ H ₂₇ COOH	58° C
palmitic acid	C ₁₅ H ₃₁ COOH	63° C
stearic acid	C ₁₇ H ₃₅ COOH	70° C

- What is "melting point"?
- If one substance has a higher melting point than another, what can you say about the substance with the higher melting point?
- What trend exists in the melting points of the fatty acids listed? (As ____, the melting points _____.)
- · What is the cause of the trend seen in the melting points of the fatty acids listed?

Reasoning based on IM forces

- As the number of carbons increases in a series of fatty acids...
- the melting point increases.
- This is because... •

materials are significant?

How the particles are arranged

and how the differences you

pointed out cause the particles

to interact differently

Why this causes the

differences in the

observed macroscopic behavior

- as the number of carbons increases, the chains get longer. When the chains are longer, the molecules are bigger.
- The larger the molecule, the greater the dispersion forces.
- When the attractive forces holding particles together is greater, you have to get to a higher temperature to break those forces, so the melting point is higher.

- State the trend
- State the physical property that is changing
- Point out the important point about the particles that is different
- Explain which IM forces are different and how they are
- Explain why that causes the physical property to be different



The structure of scientific explanations (in chemistry)

What things are the same about the materials? What things are different?

What kinds of interactions are there? Which of these are affected by the differences in the materials?

> Questions to help you think about what to say



Summarizing

From weakest to strongest

Comparing substances

What do you predict to be the order of normal boiling points for these substances? Put them in order by placing a 1 for the lowest boiling point and a 4 for the highest. Then explain why.



Explaining macroscopic behavior: viscosity

- Viscosity is the resistance to flow in liquids
- Viscosity is dependent on more than just molecule size it also depends on the kinds of attractive forces between molecules
- Viscosities of various liquids at 20°C (in centipoise)

Liquid	Viscosity (cp)	Type of IM attraction
water	1.002	H-bonding & London
tetrachloromethane (CCI_4) 0.969		London
mercury	1.526	metallic
olive oil	84	London
oleic acid	25	London
glycerine	1490	H-bonding & London

Comparing the London forces



Practice telling which IM forces

i₊clicker



7. 2-butanol, CH_3 -CHOH-CH₂-CH₃ T_{boil}=372K



Key points about IM forces of attraction

- Intermolecular forces (IM forces) are <u>attractive forces that act</u> <u>between one particle (e.g. molecule) and another</u> in the liquid and solid phases
- What kinds of IM forces exist depends on what kinds of particles they are
 - Molecular particles
 - Non-polar molecules
 - Polar molecules
 - Polar molecules that have an H bonded to either N, O, F or Cl
 - Ionic particles

chemical formula: C4H10O

- Some IM forces are stronger than others
- If a molecular compound has dipole-dipole (or H-bonding category of d-d) forces, it also has London dispersion forces
- In larger molecules, the London dispersion forces predominate, even if dipole-dipole forces are present