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.

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
(B) CH₃OH
(C) CH₃OCH₃
(D) CO₂

Explaining macroscopic (lab level) behavior by particle level interactions

- Solids vs. liquids vs. gases
  - Comparison of macroscopic properties with particle level explanation for why those properties arise
  - Comparison of radial distribution functions (average density of atoms at a given that another atom is located at the origin) determined by molecular dynamics simulations

- 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)

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

- C-H bonds are not very polar
- Even if they were, molecule is symmetric so dipole moments would cancel
Particle level: materials composed of ions

- Solid state
  - Ions arranged in lattice, with individual ions occupying lattice points
  - Ions 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)
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:
  - Separation (distance) between the units (or subunits) that are held together by attractions
  - Strengths (magnitudes of the point charges or dipoles) of the units (or subunits) that are held together by attractions
  - Timeframe: 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?

- Ions
  - 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

Coulomb’s Law:

\[ F = \frac{k Q_+ Q_-}{r^2} \]

- Force of attraction
- Charge on positive ion
- Charge on negative ion
- distance between ions

Is the force of attraction stronger or weaker? Should this ionic compound require greater or smaller “lattice energy” than the \((+1)(-1)\) original?
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)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice energy (kJ/mol)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>1037</td>
</tr>
<tr>
<td>LiCl</td>
<td>852</td>
</tr>
<tr>
<td>LiBr</td>
<td>815</td>
</tr>
<tr>
<td>LiI</td>
<td>761</td>
</tr>
</tbody>
</table>

*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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>dipole moment (debyes)</th>
<th>b.p. (°C)</th>
</tr>
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<tbody>
<tr>
<td>HCl</td>
<td>1.08</td>
<td>-84.9</td>
</tr>
<tr>
<td>HF</td>
<td>1.92</td>
<td>19.5</td>
</tr>
</tbody>
</table>

Which are stronger?
• Attractions between HCl and other HCl molecules, or
• Attractions between HF and other HF molecules

Compare HCl 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

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<td>19.5</td>
</tr>
<tr>
<td>NO</td>
<td>0.16</td>
<td>-151.8</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.29</td>
<td>21.2</td>
</tr>
<tr>
<td>H₂S</td>
<td>1.10</td>
<td>-60.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.87</td>
<td>100</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>2.13</td>
<td>150.2</td>
</tr>
</tbody>
</table>

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
  - HCl
  - 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 they have momentary dipoles

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

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

n-pentane, $C_5H_{12}$
m.p. -130ºC
b.p. 36ºC

n-nonane, $C_9H_{20}$
m.p. -54ºC
b.p. 151ºC

Explaining macroscopic behavior by reasoning about intermolecular forces

<table>
<thead>
<tr>
<th>name</th>
<th>formula</th>
<th>melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>lauric acid</td>
<td>$C_{11}H_{23}COOH$</td>
<td>44º C</td>
</tr>
<tr>
<td>myristic acid</td>
<td>$C_{13}H_{27}COOH$</td>
<td>58º C</td>
</tr>
<tr>
<td>palmitic acid</td>
<td>$C_{15}H_{31}COOH$</td>
<td>63º C</td>
</tr>
<tr>
<td>stearic acid</td>
<td>$C_{17}H_{35}COOH$</td>
<td>70º C</td>
</tr>
</tbody>
</table>

- 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...
  - 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)

- Observed macroscopic behavior
- Comparison of properties exhibited by two materials or Trend in properties exhibited by a series of related materials
- Which differences between the materials are significant?
- What things are the same about the materials? What things are different?
- How the particles are arranged and how the differences you pointed out cause the particles to interact differently
- What kinds of interactions are there? Which of these are affected by the differences in the materials?
- Why this causes the differences in the observed macroscopic behavior
- 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.

____ CCl₄
____ CH₃OH
____ CH₃OCH₃
____ CH₄

-162°C = 111 K
-24°C = 249 K
65°C = 338 K
77°C = 350 K
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)

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Viscosity (cp)</th>
<th>Type of IM attraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>1.002</td>
<td>H-bonding &amp; London</td>
</tr>
<tr>
<td>tetrachloromethane (CCl₄)</td>
<td>0.969</td>
<td>London</td>
</tr>
<tr>
<td>mercury</td>
<td>1.526</td>
<td>metallic</td>
</tr>
<tr>
<td>olive oil</td>
<td>84</td>
<td>London</td>
</tr>
<tr>
<td>oleic acid</td>
<td>25</td>
<td>London</td>
</tr>
<tr>
<td>glycerine</td>
<td>1490</td>
<td>H-bonding &amp; London</td>
</tr>
</tbody>
</table>

Comparing the London forces

Carbon tetrachloride, CCl₄

Oleic acid, C₁₇H₃₃COOH

Olive oil (oleic acid triglyceride)

Glycerine, HOCH₂CH(OH)CH₂OH
Practice telling which IM forces

What kinds of intermolecular forces hold the following condensed phases together?

1. \( \text{H}_2\text{O} \ (l) \)
2. \( \text{CO}_2 \ (s) \)
   a) \( \text{CO}_2 \ (g) \) dissolved in water [known as \( \text{CO}_2 \ (aq) \)]
3. \( \text{NH}_3 \ (l) \)
   a) \( \text{NH}_3 \ (g) \) dissolved in water [known as \( \text{NH}_3 \ (aq) \)]
4. \( \text{CaCl}_2 \ (s) \)
5. Octane, \( \text{C}_8\text{H}_{18} \ (l) \)
6. Diethyl ether, \( \text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3 \) \( T_{\text{boil}} = 308 \text{K} \)
7. 2-butanol, \( \text{CH}_3\text{-CHOH-CH}_2\text{-CH}_3 \) \( T_{\text{boil}} = 372 \text{K} \)

Note that both of these have the same chemical formula: \( \text{C}_4\text{H}_{10}\text{O} \)

Key points about IM forces of attraction

- Intermolecular forces (IM forces) are attractive forces that act between one particle (e.g., molecule) and another 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
- 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.