FROM SIMPLE MOLECULES TO LIQUIDS AND SOLIDS—
INTERMOLECULAR FORCES and PHASE TRANSITIONS

AN ESSAY TO ENCOURAGE EVERYDAY MYSTICISM

Part I—Pure Substances

We have seen in the last section that ionic and metallic bonding at room temperature immediately leads to the formation of networks of solid crystals and metals. But what of covalent bonding with its sharing of electrons? It leads to molecules, literally those "little lumps of matter", but these are not extensively connected to one another. *On their own,* the molecules would be expected to be gaseous at room temperature, and indeed many of them are when moving at sufficient speeds, demonstrating their essential independence from one another. And yet, so many, even small molecules like H_2O, are surprisingly liquid. Others like common table sugar, sucrose, $C_{12}H_{22}O_{11}$, are solid. The presence of these liquid and solid states is an indicator of additional intermolecular forces, i.e. forces *between* the molecules. Even these well-separated pure molecular substances cannot resist coming together at the next level!

Everyone is familiar with the three states of matter: solid, liquid, and gas. What you may not realize is the next level of attraction, intermolecular forces, creates these possibilities for molecules.

- As already mentioned, when essentially little attraction occurs between the molecules compared to their motion, a *gaseous* state occurs where the particles move freely and essentially completely independent of one another.
- If the temperature is lowered and the molecules begin to move more slowly and they come closer together, they begin to experience the forces among themselves, but the particles can still move past one another. This is the *liquid* state: somewhat coherent and taking the shape of its container and yet fluid enough for the particles to maintain some motion relative to one another. This is visible in the flow of any liquid.
- These first two states, gas and liquid, are called *fluids*, because of their ability to flow from place to place.
- As molecules move ever more slowly as the temperature decreases, the attractions between them now dominate and the particles stop moving from place *to* place (that is, they lose their flow) and now they simply vibrate *in* place, producing a solid.

Molecule Dance—children modelling solids, liquids and gases https://www.youtube.com/watch?v=9fGCbspu58E

Some transitions from one state of matter to another are associated with great delight. Consider:

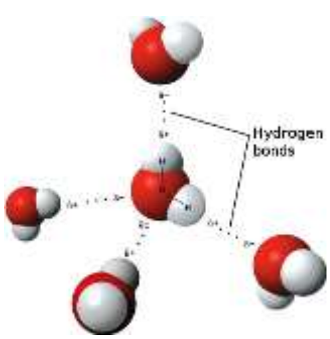
- the melting of ice cream…Next time you have a cone or sundae concentrate on how the higher temperature of your body melts this delight into a fluid as it is licked bit-by-bit by your tongue!

- the melting of chocolate…Ever wondered why those specialty chocolates with the "liquid" center are so good? Differential melting points! Translation: The outer layer of chocolate has a higher melting point than the center. By the time the mouth has warmed up the outside, the inside has liquified already, leading to the sensation of a chocolatey liquid center, once the outside has been consumed.
- the boiling of water for tea or coffee…At normal pressure, once water reaches 212^0F (100^0C), it begins to boil.
- the condensation of water vapor back to water…Next time watch the rain (from the inside or while outside…it doesn't matter). Consider that when the vapor in the atmosphere cools enough, it condenses back to water and falls as precipitation. Maybe you'll dance in the rain like Gene Kelly!
- the sublimation of dry ice…the what? the conversion of a solid directly into a gas without the intermediate state of a liquid! What a great trick, right? Dry ice is used to pack meats, candy, or ice cream for shipment. When dry ice is placed into water, you can also enjoy the effect of "white smoke" hugging a concert floor. (The white smoke is the result of very fine particles of water vapor which have condensed due to the cold dry ice.)
- the evaporation of sweat from your body to regulate body temperature…Yes, we can release heat by evaporating sweat. This cools down the body, preventing heat stroke. In fact, one sign of moving from heat exhaustion to heat stroke is the eventual lack of sweat while exerting the body greatly.
- the conversion of ice to water while it is under extreme pressure, as when under an ice-skate, gives us the ability to glide across the surface with great ease!

However, there are also times when phase transitions are dangerous.

- Anyone who has forgotten the kettle on the stove knows that the water eventually boils away, filling the room with steam, and possibly ruining the pot if not caught quickly!
- At body temperature, saturated fats tend to be solids; unsaturated fats, liquids. This difference in melting points can be dangerous for the person who has ingested too many saturated fats. The fatty deposits can clog up arteries, leading to arteriosclerosis.
- The freezing of a sidewalk in the winter…When the temperature drops below 32^0F (0^0C), water freezes on sidewalks and roadways, causing them to become dangerously slippery.

Hydrogen Bonding in Water



http://www.sciencekids.co.nz/images/pictures/chemistry/hydrogenbonds.jpg

The Molecular Dance of Water

https://www.youtube.com/watch?v=D3mbOzOYzQ0

Hydrogen bonding is so important let's talk more about its effect on the properties of water.

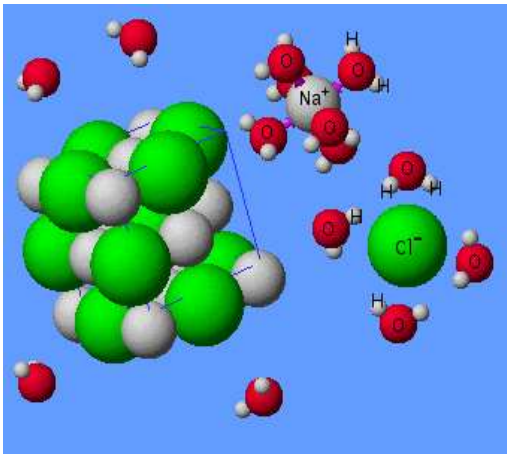
- For its mass and shape, water has an unusually high melting and boiling point. Lakes, rivers, and oceans exist at moderate temperatures because of this very strong intermolecular force.
- Unlike almost all other substances, solid H_2O (ice) floats on liquid H_2O (water) because the hydrogen bonding expands the solid when it cools. Consequently, lakes do not freeze from the bottom up but rather from the top down, providing a place for fish and other creatures to live when the conditions above the surface of the pond are below freezing!
- Because of its attraction for itself, it takes much heat to make liquid water move faster (achieve a higher temperature). This very high specific heat capacity moderates the temperature as water is heated. Consequently, the temperature in the ocean is regulated within a narrower range. And, expect the water for your pasta will take a while to boil.
- Water has the highest surface tension for all liquids, except mercury, so subsequently water molecules are very cohesive. Every child, usually to the consternation of his or her siblings, discovers you can overfill a glass slightly with water before it spills over!
- Hydrogen bonding makes water an excellent solvent, not only for salts, but also for other polar molecules. This dissolution of salts can lead under the right circumstances to the formation of magnificent underground caves.

Not only does hydrogen bonding drive the properties of water, the most common molecule in living creatures, it is also essential to the architecture of biomolecules (next stop on the tour).

Part II—Mixtures

In addition to the attraction among pure substances, two unlike substances *may* interact. For example, table salt (NaCl) readily dissolves in water. But *how* can that happen? How does water take apart ion-by-ion the structure so carefully constructed by ionic bonding? The answer is quite Lilliputian in nature…the result of many small forces is an effective larger force!

- In a crystal of table salt (NaCl), each sodium ion is connected to 6 chloride ions and each chloride ion is connected to 6 sodium ions. (See the picture below.)
- Water is, of course, attracted to itself by *hydrogen bonding*.
- Roughly speaking, when NaCl is dissolved in water each sodium ion (Na^+) is surrounded by a good half-dozen water molecules *and* each chloride ion (Cl^-) is separated surrounded by a good half-dozen water molecules.
- Because the total of these latter "ion-dipole" attractions of salt ions with water are stronger than the total original attractions holding salt and water together separately, the salt dissolves in the water!



http://chemistry.elmhurst.edu/vchembook/images2/171saltdissolve2.gif

- We say simply salt is "soluble" in water, rather than saying "the intermolecular forces between salt and water are stronger than those between salt and water as pure substances."   It's a lot simpler, right?

For other ionic substances (also called salts) like lead sulfate, $PbSO_4$, the ion-dipole forces between that salt's ions and water are *weaker* than the ionic force between the salt ions (Pb^{+2} and SO_4^{2-}) and the hydrogen bonding in the water, each as pure substances. Said more simply, $PbSO_4$ is "insoluble" (not soluble) in water! It sinks to the bottom of the container, unable to interact effectively with the water.

Metals, like the insoluble $PbSO_4$, are also insoluble in water because the bonds within the metals and the hydrogen bonding within water are stronger than the possible interactions of metals with water. Yes, sometimes metals like sodium can react with water but that's a different (and exciting) story involving a chemical reaction where the properties of the substances change!

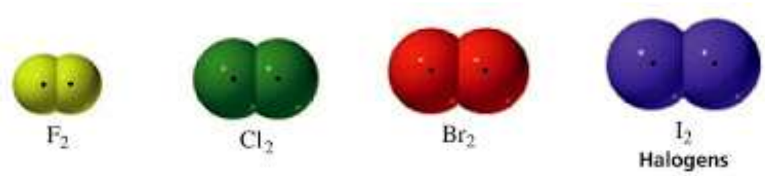
What difference does the relative strength of these interactions between *different* substances make in your daily life? Consider these interesting examples:

- Enjoying a good cup of tea or coffee…Tea and coffee are basically extractions of the flavors from tea leaves and coffee beans; that is, they are the result of certain flavorings being *soluble* in water. The flavors are even more soluble in hot water than cold water. So, the flavor is extracted from the tea leaves or coffee with hotter water.
- In addition, making ones tea or coffee sweet depends on the dissolvability of sucrose (a.k.a. solubility of sucrose) in water.   The multiple hydrogen bonds formed between sucrose and water are able to overcome the original hydrogen bonds among sucrose and water themselves.
- Doing your laundry…You know the ability to get clean clothes depends on the ability of detergents and other cleaners to remove stains from clothing. In other words, the material in the stain must be more soluble in the detergent-filled water than in the clothes. Since the make-up of stains varies widely, so does the stain-buster that can dissolve it or react with it, to remove it from clothing.
- Our conception…that's right, your dad's sperm (collectively) dissolved the protective coating on your mother's egg, so that the "lucky" first sperm through could fertilize it.
- Changing of the freezing point and the boiling point by addition of a substance has to do with the additional intermolecular forces between the particles that require
    - a higher boiling point to separate the solvent molecules *and*
    - a lower melting point to break the solid phase of the solvent apart. That's why we throw salt on the sidewalk to melt the ice at a lower temperature!

Bless the Lord, all you, liquids and solids,
Those with London dispersion forces, bless the Lord,
Those with dipole-dipole forces, bless the Lord,
Those with hydrogen bonds, bless the Lord,
Praise and exult God above all forever!

MORE SCIENCE BEHIND THE ESSAY

We have seen thus far that the attraction from one level of complexity to the next is often driven by electrical attraction, also known as Coulombic attraction. Recall that protons with their positive charge are attracted to electrons with their negative charge to form atoms, and atoms form molecules by exchanging or sharing electrons, thus disrupting or redistributing in some way the electrical balance of the original atoms. So too, this current level of association between simple molecules is dependent on the separation of charge.



http://4.bp.blogspot.com/-0PKJyyxihzM/UUV_9Ilc-EI/AAAAAAAAAO0/dmcOBKKgFoI/s400/Reactivity.jpg

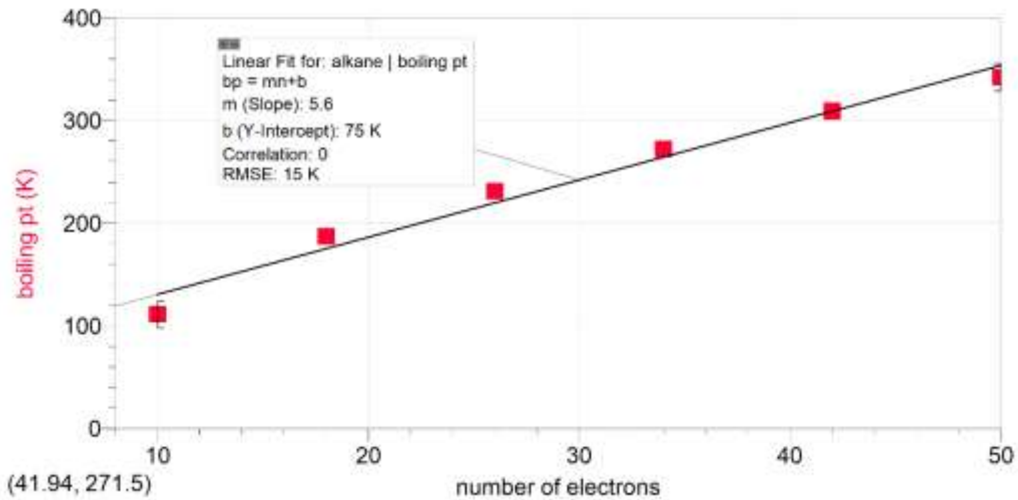
Molecules which do *not* have a permanent separation of charge, or *dipole*, within their structures are called *nonpolar*. However, even in simple nonpolar molecules, such as F_2, Cl_2, Br_2 and I_2, this separation of charge can be *temporarily* produced, or induced, by the shifting of electron density from one side of the molecule to the other. This drives a temporary shift away from electrical neutrality in neighboring molecules. Since a fleeting separation of charge, or *polarizability*, is momentarily induced, the molecules can associate with one another through a very weak electrical attraction. This is a way that one molecule can respond to the presence of other molecules around it. This polarizability leads to the weakest of intermolecular forces (forces between molecules) called the *induced dipole-induced dipole force*, also named as *London dispersion forces*, for Fritz London, who first explained the mutual attraction of noble gases, known for their isolated behavior.

This is also the reason that at sufficiently low temperatures, gases always turn into liquids and eventually into solids! The greater the number of electrons, the greater the attractive force associated with their polarizability. So, F_2 (18 electrons total), Cl_2 (34 electrons total), Br_2 (70 electrons total) and I_2 (106 electrons total) form liquids at increasingly warmer temperatures: F_2 at a very chilly -188^{0}C, Cl_2 at an Antarctic frigid temperature of -35^{0}C, Br_2 at a scalding 59^{0}C and I_2 at the oven-setting temperature +184^{0}C.

If the temperature becomes even lower, they also form solids:

- F_2 at -220^{0}C,
- Cl_2 at -101^{0}C,
- Br_2 at -7^{0}C and
- I_2 at 114^{0}C.

alkane	number of electrons	boiling point (K)
CH_4, methane	10	111
C_2H_6, ethane	18	184
C_3H_8, propane	26	231
C_4H_{10}, butane	34	273
C_5H_{12}, pentane	42	309
C_6H_{14}, hexane	50	342
C_7H_{16}, heptane	58 (not shown)	371
C_8H_{18}, octane	66 (not shown)	399
C_9H_{20}, nonane	74 (not shown)	424
$C_{10}H_{22}$, decane	82 (not shown)	447



These London dispersion forces are the same reason the boiling points for the hydrocarbon *alkanes*, molecules with the general formula C_nH_{2n+2}, increase in temperature in a predictable fashion. The first four alkanes are gases at room temperature, 298 K. These include common methane gas burned for energy, propane gas used in gas grills and butane found in charcoal lighters. The other six alkanes are all liquid at room temperature, although pentene boils around human body temperature (310 K = 98.6 ^{0}F). Octane as a fuel for automobiles is probably the most familiar of this liquid part of the alkane family.

By contrast, in polar molecules, where the separation of charge, or *polarity*, within a molecule is *permanent*, the attraction between molecules is stronger than the polarizability in nonpolar molecules, where the attraction is caused by only a *momentary* separation of charge. The resulting *dipole-dipole force for a similar number of electrons* leads to the formation of liquids and solids at higher temperatures than when only polarizability is operative. When we, therefore, compare polar ICl with nonpolar Br_2, both with 70 electrons, we find

- ICl has a warmer melting point at 27^0C than Br_2 at -7^0C. and
- ICl has a warmer boiling point at 97^0C than Br_2 at 59^0C

Now we can explain the hydrogen bonding in water. We find a surprise in the trend of boiling points for the group(VI) hydrides:

H_2O (100^0C), H_2S (-61^0C), H_2Se (-41^0C) and H_2Te (-2^0C)

The boiling point of H_2O isn't lower than -61^0C; it is incredibly higher at 100^0C (212^0F)! Here, there is a special case of dipole-dipole interaction between hydrogen atoms attached to highly electronegative atoms and the available electron pairs in other molecules. These include fluorine, oxygen, nitrogen— "FON" elements which have, of all the elements on the periodic table, the greatest ability to attract electrons in a bond. This exceptionally strong dipole-dipole force leads to a boiling point at a higher energy and therefore, at a higher temperature.

This hydrogen bonding is not unique to water, but water, as we know, is a unique substance because of it.