Chapter 10 - Liquids and Solids

10.1   Intermolecular Forces

We take for granted the three states of matter. But why are there solids, liquids, and gases rather than just one or two of the three? Furthermore, why are some materials solids at ambient temperature, while others are liquids, and still others gases? The answer follows a pattern of physical behavior we began exploring in CHM 211.

There exist attractive, intermolecular forces between all molecules. Intermolecular forces (IMF) are attractions between species that are not chemically bonded to one another. At a given temperature, molecules with strong intermolecular forces are more likely to be liquids or solids. The environmental factor that determines the physical state of a material is energy. i.e. Is there enough thermal energy around the molecules to overcome the intermolecular forces between the molecules? When too little energy exists (i.e. it is too cold), the material exists as a solid. If there is plenty of energy, it exists as a gas. If there is enough energy to disrupt the forces between molecules, but not enough to completely overcome them, a liquid exists. We next discuss the different types and strengths of intermolecular forces.

There are several types of intermolecular forces, although each operates using the same basic principle, which is very similar to how a chemical bond works and how an atom holds together. In a chemical bond, the nucleus of a one atom or ion attracts the electrons on a second atom or ion. Intermolecular forces arise from the attraction of electrons on a molecule or ion for the nuclei on a second ion or molecule. Intermolecular forces between atoms and molecules are sometimes collectively called van der Waals forces. They operate with a wide range of strengths, although almost never approaching the strength of a chemical bond. In Chapter 9, you saw that intermolecular forces influence the ideality of gases. They are the primary contributor to boiling and melting points and explain a range of other physical properties. As you might expect, as intermolecular forces become stronger, melting and boiling points increase. In many cases,

multiple intermolecular forces operate simultaneously. We will see how to determine which ones are more important for different molecules.

While there is basically one conceptual basis for IMF (electrostatic attraction), there are usually a number of types presented which are named after the interacting species. Your book lists three, but most books provide four, which I do below. The added one is typically the strongest and is important.

Ion-Dipole Forces

These forces operate between an ion and a polar molecule and usually occur when an ionic compound dissolves in a polar solvent (e.g. sodium chloride in water). The negative end of the dipole will point towards a cation and the positive end towards an anion. The strength increases as the ion charge and the dipole moment increase. The energy released from this interaction is what permits ionic compounds to dissolve. Ion-dipole forces operate over the longest distance of any of the intermolecular forces. Your book covers this in Section 11.2.
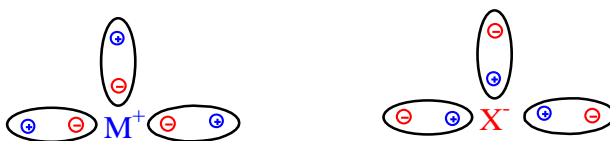
Dipole-Dipole Forces

These forces exist between two polar molecules and may occur either within a pure substance (e.g. CH_2Cl_2) or in a mixture (NH_3 dissolved in CH_2Cl_2). These are much weaker than ion-dipole forces and occur when dipoles line up positive end to negative end. Because they are weak, these alignments are only temporary and break-up and reform frequently. They operate over fairly short distances and increase in strength with increasing dipole moment.
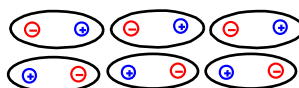
London Dispersion Forces

What force holds nonpolar molecules together? For example, gasoline is composed solely of nonpolar molecules, yet is a liquid at room temperature. Why?

Helium atoms provide the simplest way to illustrate how this works. On average, the electrons on a helium atom spend equal amounts of time at every position at some fixed distance from the nucleus. In other words, the electrons are distributed spherically about the nucleus. But two electrons can't be everywhere at the same time; so if, for an instant, both happen to be on the same side of the atom (see left atom below) the atom will have a dipole that will last only until the electrons redistribute. This happens incredibly quickly and so the dipole is called an instantaneous dipole. If another molecule of helium is very close by, the positive end of the instantaneous dipole pulls the other atom's electrons towards itself causing a brief and weak attraction. Such attractions are called London dispersion forces.
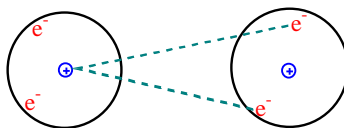
London dispersion forces tend to become stronger as molecules get larger. This may sound counterintuitive at first, but it is reasonable. Helium is very small and if both electrons are on the same side of the atom they can't be far from each other. They will repel and move away from each other. Both neon and argon have 8 valence electrons, but the outer shell of argon is larger. Therefore, it is more likely that an uneven distribution of electrons will occur at random or that such an arrangement can be induced by a nearby dipole. Also, consider xenon, which has 54 elections, all moving rapidly. Imagine putting a plane through the nucleus. What are the odds that exactly 27 electrons would be on each side of that plane? Many times, there would be 26/28 or 25/29 splits for brief periods. London dispersion forces can become so large that for very large molecules, such as molecular iodine, the material may even be a solid at ambient

temperature.

The book lists increasing mass and size as the causes for stronger dispersion forces. By far and away, molecular size is the primary driver of London dispersion forces, however. For example, H_2 and D_2 are both the same size, but have molecular weights of 2 and 4 g/mol, respectively. Their boiling points are 20 K and 22 K, respectively. Thus, doubling weight only increases boiling point by 10%. This topic is complicated. For example, the book provides a graph in Example 10.1 (p. 526) which is almost linear. The trend is real, the linearity almost certainly occurs by random chance.

Molecular shape also affects London dispersion forces. Molecules with large surface areas have greater forces than those with smaller surface areas, because there are more sites to affect the distribution of electron density. Thus, other things being equal, chains have stronger forces than rings which have stronger forces than "balls" or cages (Figure 10.7, p. 527).

London dispersion forces act on all molecules by all molecules. For small polar molecules they can be ignored, but in large, polar molecules (e.g. CHI_3) they are actually more important than the dipole. Thus, care must be used when comparing intermolecular forces between molecules.

Hydrogen Bonding

The final intermolecular force we will discuss is hydrogen bonding. Small molecules with N-H, O-H, and F-H groups have unexpectedly high boiling points. Hydrogen bonding occurs when a molecule containing one of these bonds has a hydrogen atom on one molecule associate with the lone pair on a second molecule. The effect decreases with increasing molecular size. i.e. The effect is larger in water (HOH) than methanol (CH_3OH).
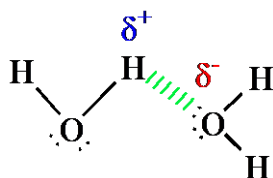
These interactions can be so strong that the hydrogen atoms transfer between molecules. For example, within seconds of mixing equal amounts of H_2O and D_2O, the solution consists of H_2O, D_2O, and HOD in a 1:1:2 ratio. Still, it is important to remember that hydrogen bonding is an intermolecular force and so is always weaker than normal chemical bonding.

Why does this occur? Hydrogen is unique in that it has no electron core. Thus, when it bonds there is little electron density on the far side of the nucleus (opposite to the bond). When N, O, or F bonds to hydrogen, electron density is farther drawn away from the hydrogen, further exposing the nucleus on the far side of the atom. The exposed positive electrical charge is then attracted/attracts a lone pair on a nearby molecule.

Water is a very special substance and its unusual properties arise from hydrogen bonding. For example, from Figure 10.11 (p. 531) you would expect the boiling point of water to be about -80º. Hydrogen bonding also accounts for ice having a lower density than water. Read the rest of this section on your own.

Like Dissolves Like

When mixing two liquids or attempting to dissolve a solid in a liquid, the old adage "like dissolves like" provides a good basis for making an initial guess as to whether mixing (or dissolution) will occur. (It is important to remember this is an observation NOT a physical cause for the tendency to dissolve.) What this means is that polar solvents typically do a good job of dissolving polar solutes, while nonpolar solvents dissolve nonpolar solutes. Why is this so?

Recall that polar molecules have a dipole, while non-polar molecules typically don't. (Some nonpolar molecules have offsetting bond dipoles (e.g. CO_2), but this is rare.)   Nonpolar

molecules are usually held together by London dispersion forces (instantaneous dipole – induced dipole forces). In small molecules, the attraction between two dipoles is stronger than the attraction between two nonpolar molecules. Polar molecules are attracted to nonpolar molecules by a force similar to London dispersion forces (dipole-induced dipole forces). However, these forces are typically much weaker than dipole-dipole attractions. When one attempts to mix a nonpolar substance into a polar one, weaker dipole-induced dipole forces would have to replace strong dipole-dipole forces. This is energetically unfavorable. When hydrogen bonding is involved, the attraction between the polar molecules is so strong that the energy cost associated with mixing is too great to overcome and the nonpolar liquid will not dissolve. For more weakly polar molecules, e.g. CH_3COCH_3 (acetone), the cost is small and there is enough thermal energy in the air to cause mixing.

One must be careful here. Implicit in "like dissolves like" is that polar and non-polar compounds won't mix. In fact polar, liquids and nonpolar liquids will frequently mix to some extent and polar/nonpolar liquids will many times dissolve nonpolar/polar solids. Only for the most polar liquids (e.g. water) is this true. Again, "like dissolves like" is an alright rule of thumb, but don't push it too far because it has a lot of exceptions.

10.2   Properties of Liquids

Viscosity is the resistance to flow by a liquid. Stronger intermolecular forces cause molecules to stick together more forcefully, making it more difficult for them to move past each other. Thus, viscosity increases as intermolecular forces become stronger. As temperature increases, there is more energy available to disrupt the intermolecular forces, so viscosity decreases with increasing temperature.

<u>Surface tension</u>

As you've seen, when a drop of water is placed on a newly waxed car it beads up. On the other hand, it usually spreads out on a kitchen countertop. Why the difference? First consider any generic liquid and imagine what it looks like at the molecular level.

surface of the liquid
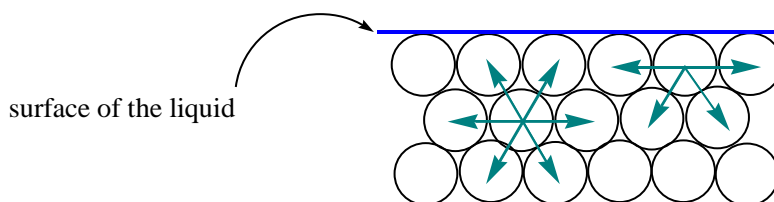
A molecule in the "middle" is pulled equally in all directions, but those at the surface are pulled preferentially inward (towards the bulk). As a result, the molecules at the surface pack a little more tightly (are more dense) and the liquid behaves as if it has a skin. The <u>surface tension</u> of a liquid is the energy required to increase the surface area by a unit amount. The stronger are intermolecular forces, the higher is surface tension.

Here is another experiment you can do at home. Fill a glass with water until it is just about full (it should be very close to the top). Take a thin, flat sewing needle (not pin) and wash and dry it. Make sure there is no soap on the needle. Using a clean pair of tweezers, grasp the needle by the eyehole and holding it as close to parallel to the water surface as possible, very gently place the needle on the water and let go. The needle should float, although it takes awhile to get the hang of doing this. Solid steel needles will float even though the steel is denser than water. Finally, take a pin and insert it in a bar of soap and withdraw it. Knock off any visible pieces of soap if you'd like. Insert the needle, tip first, into the water away from the needle. The needle should sink almost instantly because the soap disrupts the intermolecular forces and lowers the surface tension below a level that can support the needle.

There is one more place where you will commonly encounter the affects of intermolecular forces. If a thin glass tube is partly filled with water, the water will form a shallow well called a

meniscus at the surface. The well forms because the water adheres to the glass (adhesion) more strongly than the water molecules are attracted to each other (cohesion), so the water climbs the walls of the tube. When mercury is placed in an identical tube, an upward bulge forms. This occurs because the cohesion of the mercury atoms is greater than their adhesion to the glass. Thus, to answer the question posed at the beginning of this section; this property explains why water beads on wax (to which it adheres poorly) and spreads out on a kitchen counter (to which it adheres well).

Ignore the equation on p. 539. I think it was put there to scare students.

10.3   Phase Transitions

Phase transitions (sometimes phase changes) occur when a substance changes state (e.g. gas → liquid). As you already know, putting thermal energy into a substance typically raises its temperature. What you may not realize is that at the melting and boiling points, energy continues to go into the substance, but its temperature doesn't change. This extra energy is used to disrupt the intermolecular forces sufficiently to cause the phase change.

There is some terminology you'll need for this section, most of which you'll be familiar with, but others may have a slightly different technical meaning than you are accustomed to. Vaporization is the conversion of a liquid into a gas, while condensation is the conversion of a gas into a liquid. Melting is the conversion of a solid into a liquid and freezing is the reverse process. Finally, sublimation is the direct conversion of a solid into a gas (it is never liquid), while the conversion of a gas directly into a solid is called deposition.

In sealed containers, these pairings reach equilibrium if there is sufficient material present. For example, take a jar and put a few drops of water in it and wait a while. Some of the water will evaporate and enter the gas phase, but that process eventually stops and the mass of water in

the drops doesn't change over time. The pressure of a gas over the same substance as a liquid is called its <u>vapor pressure</u>. In reality, what is occurring is that for every liquid water molecule that breaks free of the drop, another gaseous water molecule strikes the drop and sticks. The vapor pressure remains constant because as many molecules gain enough energy through collisions to leave the liquid phase as stick to the liquid when gas molecules collide with the liquid surface. Vapor pressures decrease as intermolecular forces become stronger.

The energy change associated with melting a solid is called its <u>heat of fusion</u>. For the boiling of a liquid it is called the <u>heat of vaporization</u>. The direct conversion of a solid to a gas requires the addition of its <u>heat of sublimation</u>. For the reverse processes the name remains the same, but the sign on the value reverses.

Boiling and evaporation both result in the conversion of a liquid to a gas. When the external pressure equals the vapor pressure of a substance, the substance <u>boils</u>. When the external pressure is greater than the vapor pressure the substance evaporates. The <u>normal boiling point</u> is the temperature at which a substance boils when the external pressure is 1 atmosphere. Under normal conditions, a gas cannot be cooler than its boiling point and a liquid cannot be warmer than its boiling point. These basic ideas apply to melting and sublimation points. Ignore the discussion about the Clausius-Clapeyron equation on pp. 543-545.

Every liquid at its melting point possesses more energy than the solid of the same substance at the same temperature. Likewise, at its boiling point any gas possesses more energy than the liquid at the same temperature. This explains why steam burns are worse than boiling water burns. When steam strikes the body it also releases the heat of vaporization into the skin.

The process of adding thermal energy to a substance can be shown graphically as:
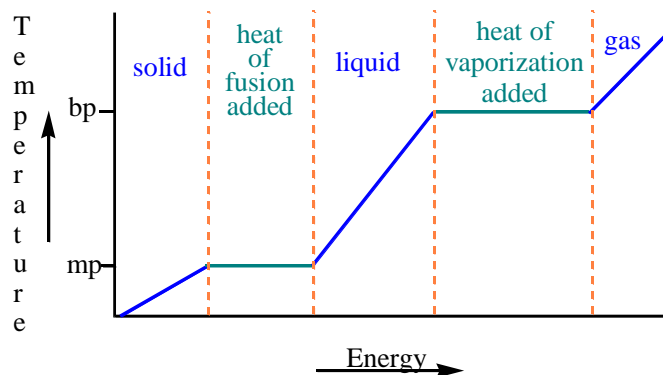
10.4   Phase Diagrams

Phase diagrams are a plot of melting, boiling, and sublimation temperatures as a function of pressure. A number of such points are measured and plotted on a graph like that below. The points are then connected by a straight or curved line (as appropriate) allowing the melting point, boiling point, or sublimation point of a substance to be determined at a pressure that had not before been examined.
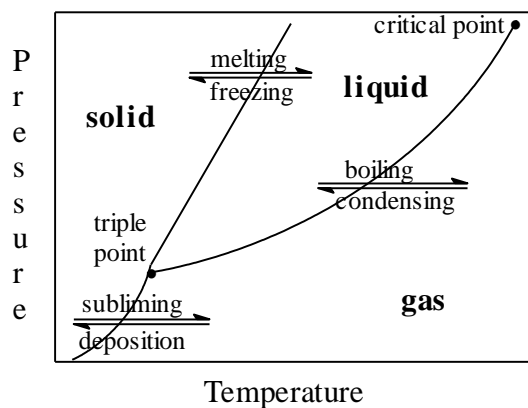
The <u>triple point</u> is the temperature and pressure at which all three phases are in equilibrium. The <u>critical point</u> occurs at the critical temperature and critical pressure. Under almost all conditions phase changes occur according to one of the arrows shown in the figure above. The critical point offers a unique phase change however. Imagine a gas with a temperature and pressure where the word "gas" appears in the figure above. If that gas is (1) heated above the critical temperature, (2) the pressure increased above the critical pressure, (3) the temperature

lowered below the critical temperature, and finally (4) the pressure lowered below the critical pressure, the gas becomes a liquid without condensing. If the reverse pathway is followed the liquid becomes a gas without boiling. In the region beyond the critical point, the substance is said to be a supercritical fluid, rather than a liquid or gas.

Critical Temperature and Pressure

Earlier, when we talked about gases, you learned that if enough pressure were applied to a gas it would liquefy. While usually true, there is a condition under which a gas won't liquefy. The critical temperature of a substance is the highest temperature at which it can exist as a liquid. Above this temperature, no pressure will cause the substance to condense to a liquid because the molecules possess so much energy that even if touching, intermolecular forces are overcome. The critical pressure is the pressure required to liquefy a substance at its critical temperature.

At this point, we learn about a fourth state of matter, which doesn't occur naturally. If a substance is heated in a sealed container the pressure rises as the substance vaporizes. If you look inside the container you see a distinct boundary between the liquid and gaseous phases as the substance warms. For many substances, at some temperature the line disappears as the phases combine into a new one, called a supercritical fluid.

10.5   The Solid State of Matter

Solids come in two basic types: crystalline and amorphous. The materials that comprise those solids come in four basic types: ionic, metallic, molecular, and covalent network. A crystal is an ordered array of atoms or molecules in the solids phase. The key to this definition is the phrase "ordered array." If the atoms or molecules are randomly arranged the solid is amorphous. Wax is an amorphous solid. Almost all substances can form crystals, but some do so much more readily than others. If external forces (e.g. ionic bonding) constrain a particular arrangement, crystals form relatively easily. Likewise, if the shape of a molecule encourages ordering (e.g. a

Platonic solid), crystals form more readily.

Ionic Solids - Ionic solids are generally hard and brittle and held together by ionic bonds. There are numerous arrangements of ions, several of which are shown in Section 10.6. One of the easier ones to visualize is the sodium chloride lattice shown below. It consists of sheets of alternating sodium (grey) and chloride (yellow-green) ions (Figure 1). To displace any ion at

Figure 1   Figure 2
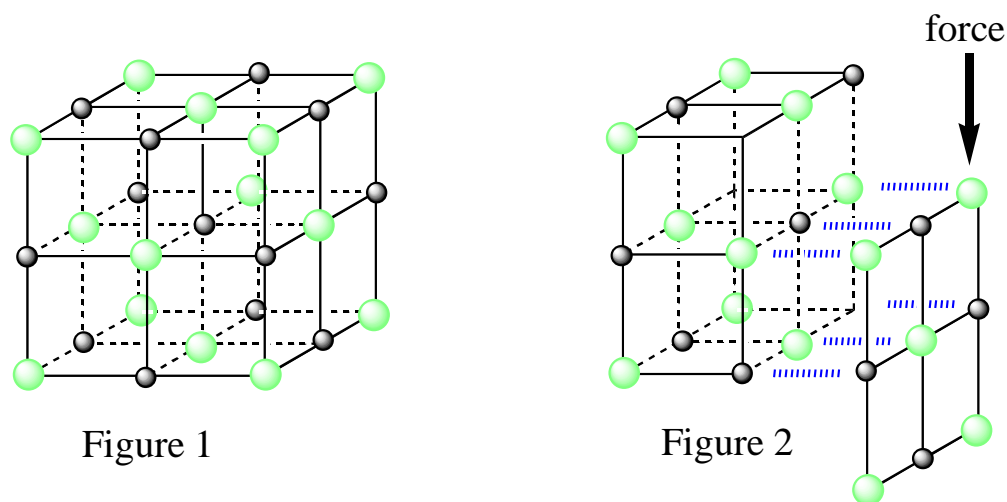
the surface of the lattice would require disrupting 5 strong interactions (4 in-plane, 1 directly below). Perhaps, it is easiest to see the nature of a salt crystal by what would happen if a downward force were applied to a face on a crystal. Imagine positioning the crystal in Figure 1 such that only the right-hand face was hanging over the edge of a table. If a downward force were applied to the top of that face, what would happen (Figure 2)? It would be resisted because each ion is close to an ion of opposite charge on the neighboring face. Moving the face would lengthen the distance between ions, making the interaction weaker (less stable). A second effect would be to bring ions of the same charge closer to one another. That would further destabilize the crystal because of the increased electrostatic repulsions. When the face had slipped exactly one bond length the attraction between the faces would reach a minimum while the repulsion would reach a maximum and the face would shear off (brittleness). This is why, when a salt crystal is hit, it shatters; yielding pieces with flat faces. The large amount of energy that must be

put into a crystal in order to cause shearing accounts for the hardness of the crystal.

Metallic solids

Since this is an array of metal atoms, no electrostatic interactions are involved. Likewise, the attachments are not covalent bonds. Perhaps the best way to think about these solids follows. The atoms will pack together much like balls will arrange in a box. Each atom will have 6 atoms form a hexagon around it and 3 atoms will cap it from above and below. Each atom has orbitals that will interact with orbitals on all of these 12 neighbors. The result is a material that has the properties we associate with metals. The nature of the bonding between metals atoms is not important for this course.

Molecular solids are held together only by van der Waals forces. As a result, they tend to have low melting points and be soft. Nearly all substances that are gases and liquids at room temperature form molecular solids when cooled.

Why do molecular solids have these two properties? Molecular solids may or may not be crystalline. Long, chain molecules, such as those in candle wax $(CH_3(CH_2)_{16}CH_3)$, tend to coil and undulate, rather than stretch out so that stacks can form. The result is an amorphous solid.

In a crystalline, molecular solid the molecules arrange themselves into an ordered array. Consider benzene (C_6H_6), a hexagonally shaped, flat molecule. As you can see from the figure,
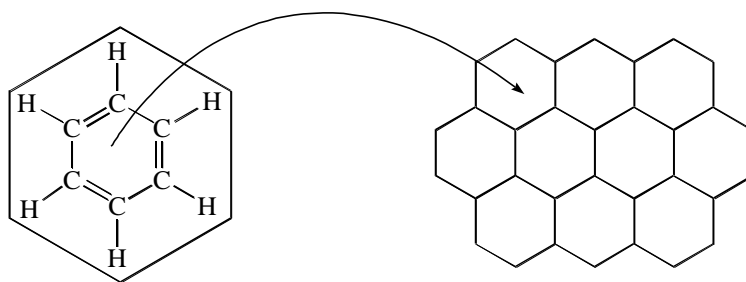
the molecule is flat; allowing easy stacking and the hexagon around the molecule on the left shows how the two dimensional array could be generated on the right (each hexagon contains one benzene molecule). Less symmetrical molecules are more difficult to crystallize because

arrays are harder to generate. For example, replacing one of the hydrogen atoms in benzene with a CH_3 group would have such an effect. Do you see why?

Because the van der Waals forces between the molecules are weak, moving the molecules past one another is relatively easy. This allows molecules in molecular solids to readily displace one another. Thus, pressure on the surface of the crystal causes the molecules directly beneath the pressure point to move deeper into the crystal. Likewise, molecules beneath the surface layer move readily both downward and to the sides. This makes it simple to generate depressions in molecular solids. You can test this by pressing a spoon into the side of a candle.

Covalent network solids

Not all hard, high melting solids are ionic. Can you think of an example? Diamonds and quartz are two classic examples. Why do they have the properties they do? In a sense, diamond and quartz crystals are one giant molecule. If you looked at either at the atomic level, you would see a near infinite array of atoms all bound by covalent bonds. Figure 10.43 (p. 563) shows such an array for diamond and graphite very nicely. (There are also movable images on the CHM 212 website.) In order to displace an atom, a covalent bond would have to be broken. Unlike molecular crystals where each molecule is a complete unit that can be moved by shifting a stack, the atoms in a covalent-network solid can't be moved nearly as easily because each site has an atom held in place by a covalent atom. The result is a rigid, hard lattice.

10.6 Lattice Structures in Crystalline Solids - Skip

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