NOTES 7: **Thermodynamics.**

- These are supplementary notes only, they do not take the place of reading the text book.
- Like learning to ride a bicycle, you can only learn physics by practicing. There are worked examples in the book, homework problems, problems worked in class, and problems worked in the student study guide to help you practice.

Key concepts:

1. Pressure in Pascals (Pa = N/m^2) is defined to be force per area: P = F/A.
2. Other units of pressure:
   1 atmosphere = 1.013x10^5 Pa
   1 mmHg (millimeter of mercury) = 133.3 Pa
   1 Torr = 133.3 Pa
3. Pressure at a depth h in a liquid of density ρ is P = P$_{atm}$ + h ρ g where P$_{atm}$ is the pressure of the atmosphere acting on the top of the liquid.
4. Because pressure increases with depth, the pressure and therefore the force on the bottom of a submerged object is greater than the force on the top. This results in an extra upward force called the **buoyant force**. If the buoyant force is larger than the object's weight it floats. If the buoyant force is less than the weight the object still sinks but it has a smaller apparent weight (e.g. rocks seem lighter under water).
5. **Archimedes principle** says that one way to calculate the buoyant force on an object submerged in a liquid is to first find the volume of the object (or the part that is submerged if it is only partly submerged). The buoyant force is equal to the weight of <u>liquid</u> (not the object!) of the same volume as the object (or the volume of the part submerged).
6. Pressure of a gas is determined by the force the molecules exert on the sides of the container. This leads to a definition of temperature (see supplemental material below).
7. Temperature is the average kinetic energy of the molecules in a sample: 3/2 k$_B$ T = <1/2 m v^2> where k$_B$ = 1.38x10^{-23} J/K is Boltzmann's constant, the temperature is in Kelvin and the brackets <> mean average. Note that some molecules will have kinetic energy higher than the average and others lower. In other words there is a **distribution** of velocities (see supplemental material below).
8. The ideal gas law is a relationship between the force with which the molecules strike the wall (pressure) and the average kinetic energy of the molecules (temperature): PV = nRT where V is the volume, n is the number of moles of molecules (Avogadro's number, N$_A$ = 1 mole = 6.02x10^{23} molecules) and R = 8.3 J/K mol is the idea gas constant.
9. Internal energy, U, includes all the energy in a system of molecules. For example kinetic (which is linked to temperature), rotational energy, chemical potential energy, vibrational energy, electrical potential energy, etc.
10. Heat is defined to be the energy transfered from one object to another due to a temperature difference. There are four means of transferring heat:
    - Conduction: dQ/dt = kAΔT/L where dQ/dt is the rate of energy flow or power (J/s or Watts) through a material of area A and thickness L, k is a constant which depends on the material, and ΔT is the temperature difference from one side of the material to the other.
    - Convection: dQ/dt = kAΔT where k is a different constant which depends on the nature and surface of the object in W/m^{2}K and A is surface area.
    - Radiation: dQ/dt = P = σAeT^4 where A is the area of the radiating object, T is the temperature in Kelvin and σ is the Stefan-Boltzmann constant, σ = 5.669x10^{-8} W/m^{2}K^4. e is a unit less number called the emissivity and tells the fraction of absorbed radiation. Emissivity varies

between zero (perfectly reflecting) and one (perfectly absorbing) and depends on the surface properties.

- Evaporation (see below). The average kinetic energy is lowered because the faster molecules escape. Temperature is defined as the average kinetic energy so the temperature is lower. In this case the substance also loses mass.

11. The energy gain by an object due to heat transfer can cause different things to happen:
     - The temperature could go up: $Q = mC\Delta T$ where Q is the heat flow (in Joules), m is the mass being heated, C is the specific heat (for gases there are two values, one for constant pressure, the other if the volume is constant) and ΔT is the change in temperature.
     - The substance could change from a solid to a liquid at the melting temperature: $Q = mL_f$ where L_f is the heat of fusion.
     - The substance could change from a liquid to a vapor at the vaporization temperature: $Q = mL_v$ where L_v is the heat of vaporization.

Applications and examples done in class, on quizzes, etc:

1. Sharp knives versus dull knives. Pressure is force per area. If the area is smaller then the pressure is higher. A sharp knife has a smaller surface area on the cutting edge than a dull knife.
2. Brownian motion. The biologist Brown noticed that small objects (pollen, dust, etc.) viewed under a microscope appear to constantly jiggle, never stopping. The motion was called Brownian motion and was explained by Einstein in 1905 using statistical arguments. Small objects tend to jiggle because they are being bombarded with even smaller objects, namely molecules. This was considered to be the first direct proof of the existence of molecules and lead to the creation of the field of statistical dynamics.
3. Thermal expansion. Temperature is average kinetic energy of the molecules so as an object is heated the molecules constituting the object have more kinetic energy. In a solid below the melting temperature this means the molecules vibrate more. Because of this extra motion the average location of the molecule shifts to a point further away from its neighbors, causing the solid to expand (see supplemental material below).
4. Change of phase. As the temperature of a solid is raised some the molecules will have energies high enough to start breaking their bonds with other atoms. Once enough atoms can move about the solid starts to melt.
5. Surface tension. At the interface between a liquid and air the molecules in the liquid are more strongly bonded to the surrounding molecules than with the air. This gives rise to surface effects such as surface tension.
6. The heat lost by radiation mentioned above and given by the equation $P = \sigma A e T^4$ is called **black body radiation**. All objects above zero Kelvin give off a wide spectrum of electromagnetic waves (or electromagnetic radiation). For very hot objects some of these waves fall in the visible part of the spectrum which is why very hot objects glow. A tungsten light bulb filament is hot enough to emit waves in the visible spectrum. Cooler objects also give off electromagnetic waves but not in a part of the spectrum we can see with our eyes. These waves can be detected however and this is the basis of some kinds of night vision technology. Living creatures are warmer than their surroundings and so emit different electromagnetic frequencies, allowing them to be detected against a cooler background. As we will see later, black body radiation is also the mechanism by which greenhouse gases in the atmosphere cause the earth's surface to be warmer than it would be otherwise.

Supplementary material

The Maxwell-Boltzmann speed distribution.
    Maxwell figured out how to measure the speeds of molecules in a gas. He came up with the following graph of the number of molecules with a particular speed (speed is x10^3 m/s on the x-axis and number with that speed as a fraction of a mole is shown on the y-axis). As you can see, few molecules have a speed of zero and few have very large speeds. The maximum speed occurs at 1x10^3 m/s for the graph on the left (low temperature) and 0.75 of the mole have this speed. You will notice that the curve is not symmetric. Maxwell also found that the curve looks slightly different for different temperatures (the second graph is higher and shifts to the right as temperature increases).
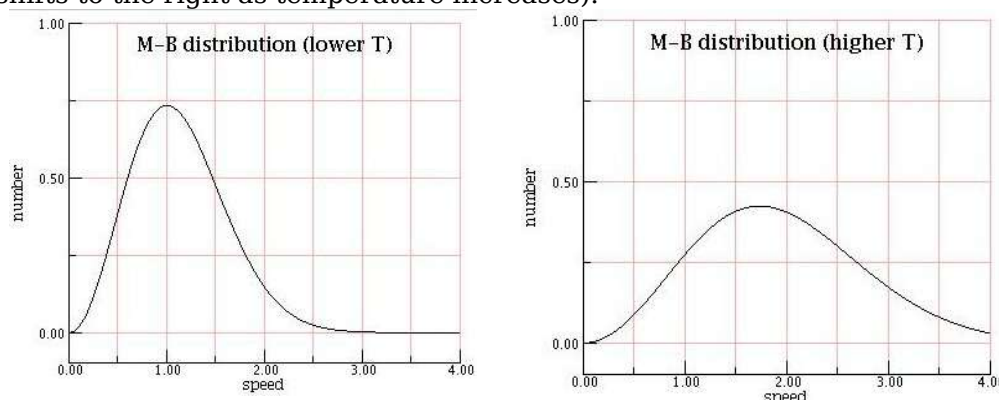
The formula Maxwell and Boltzmann came up with for this curve is called the

Maxwell-Boltzmann distribution of speeds: $F(v) = A\, v^2 \exp\left(\dfrac{-1/2\, mv^2}{kT}\right)$ where

$A = 4\pi N \left(\dfrac{m}{2\pi k_B T}\right)^{3/2}$ and m is the mass of the molecules, k_B is Boltzmann's

constant (duh!) and N is the total number of molecules. From this distribution we can calculate several useful quantities:
- Finding the maximum of the distribution (by setting the derivative equal to zero and solving for v) gives the speed of the maximum (the most probable speed): $v_{max} = \sqrt{\dfrac{2k_B T}{m}}$
- Integrating the distribution (equivalent to adding all the molecules that have each speed- the area under the curve) gives the total number of molecules, N.
    Solving for v gives the average speed: $v_{ave} = \sqrt{\dfrac{8k_B T}{\pi m}}$
- Integrating v^2 times the distribution and solving for $\sqrt{v^2}$ gives the square root of the mean squared value (root mean square or rms) of the speed:
    $v_{rms} = \sqrt{\dfrac{3kT}{m}}$ (notice this can be rearranged to give our previous definition of temperature, $3/2\ k_B T = <1/2\ m\ v^2>$ as above).
- Notice that the square root of the average squared values of a collection of numbers is not the same as the average of those numbers. Try it!
- Now we can explain evaporation quantitatively. The faster molecules escape which shifts the distribution to the left. This means the averages also shift to the left. But average kinetic energy is temperature so the temperature has to go down.

The link between pressure and temperature at the microscopic level.
    Suppose we have one atom moving at velocity **v** in a box of length L Since

$x = v_xt$, it crosses the box in a time $t = L/v_x$ where v_x is the x component of velocity. It goes from one side to the other and back in a time $\Delta t = 2L/v_x$. When it hits the wall there is an impulse on the wall of $F_x\Delta t = \Delta p = p_f - p_i$. If the collision is elastic then the atom rebounds with the same velocity and the change in momentum is $\Delta p = mv_x - (-mv_x) = 2mv_x$. So the impulse on the wall is $F_x\Delta t = F_x2L/v_x = 2mv_x$. So the force on the wall of the box is $F_x = mv_x^2/L$ due to this one molecule.

Now if we imagine filling the box with molecules which do not interact with each other (an ideal gas) then the force on the wall will be $F_x = \Sigma\, m_iv_{xi}^2/L$ where i is an index that tells us which molecule we are talking about. If there are N molecules then we can write $F_x = N<mv_x^2>/L$ where the brackets $<>$ mean average. For a large number of atoms probability theory tells us that $<v_x^2> = <v_y^2> = <v_z^2> = <v^2>/3$. From this we can write $F_x = N<mv^2>/3L$. Dividing by the area of the wall of the box gives the pressure on the wall: $P = F_x/A = N<mv^2>/3LA$. LA is the volume of the box so we can write $P = N<mv^2>/3V$. Or throwing in a couple of factors of 2 we see that pressure is a measure of the average kinetic energy of a gas: $P = 2N<1/2mv^2>/3V$

The ideal gas law tells us that $PV = nRT$ so we also have that $PV = nRT = 2N<1/2mv^2>/3$. The number of molecules is equal to the number of moles times Avogadro's number (above): $N = nN_A$. So we have $nRT = 2nN_A. <1/2mv^2>/3$. With a little rearranging and defining a new constant, Boltzmann's constant, $k_B = R/N_A = = 1.38 \times 10^{-23}$ J/K we end up with the relationship given above between average kinetic energy and temperature: $3/2k_BT = <1/2mv^2>$. Note that this is more useful than the equation for pressure because we don't have to know the number of molecules, N.

A little solid state physics.

As a simple model of a solid, imagine a bunch of small masses (the atoms) held together by springs (the inter atomic forces holding the solid together). For a Hooke's law force the force is $F_x = -kx$ where k is the spring constant (there are similar forces to the left and right and in the y and z directions but lets just look at one force for now). The potential for this force is $U = 1/2\,kx^2$. Here is a plot of the potential:
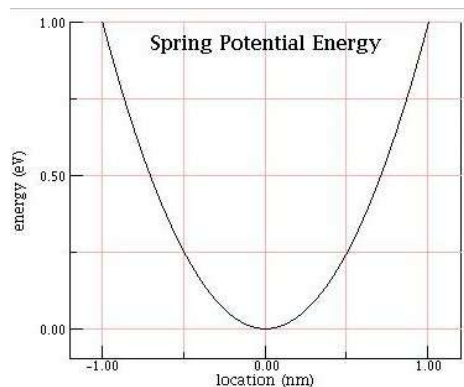
What does this tell us? Well if the temperature is absolute zero (the atom has no kinetic energy) it stays in its equilibrium position at $x = 0$. If we raise the temperature (add kinetic energy) it will oscillate back and forth around its equilibrium point. For and energy of 0.5 eV the atom will oscillate between -0.7 nm and +0.7 nm which are called the turning points. Raising the temperature makes the turning points further away from $x = 0$.

The above model is not very good in several respects:

1. Even though the turning points get further away as the temperature increases the average location of the atom is in the middle, at $x = 0$. A solid with this kind of inter atomic forces would not expand when heated.

2. No matter how high the temperature the atom can never escape. Adding more energy takes the atom higher in the potential and the turning points are further apart but the atom never can get out of the potential. A solid with this kind of

inter atomic force would never melt.

3. The equilibrium point is at x = 0. Since x is the distance from the atom to the next atom for this model each atom sits right on top of the next atom, there is no distance between atoms.

A more realistic potential is a Van der Waal like potential, $U = A/x^6 - B \exp(-x/C)$ where A, B and C are constants (the energy units are normally eV = electron volts, 1 eV = 1.6×10^{-19} J):
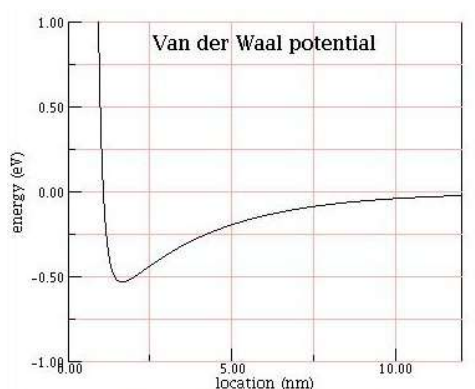
This potential is much more realistic:

1. The equilibrium position is at 1.6 rather than x = 0; the atoms are 1.6 nm apart at zero Kelvin.

2. The potential goes to infinity at about x = 1nm meaning that the atoms can get no closer than 1nm apart (the bump into each other).

3. The equilibrium point at 1.6 nm has a negative energy of about -0.5 eV. If we add +0.5 eV the atom will be able to escape to the right and be a free particle (with zero energy). This solid can melt. Another way to say this is that 0.5 eV is the binding energy for this potential.

4. Compare the turning points for an energy of -0.25 eV with the turning points for a higher energy of -0.1 eV. For -0.25 eV the turning points are about 1 nm and 4 nm for an average location of 2.5 nm. For energy of -0.1 eV the turning points are about 1nm and 7 nm for an average location of about 4 nm. As this solid is heated (the atoms oscillate higher in the potential) the average distance between molecules increases meaning that this inter atomic potential predicts the solid will expand.