Ideal Gases
Overview
Physics 223

The plan:
This week we'll talk about ideal gases. They are used to illustrate most of the examples in thermodynamics, because their behavior is simple. This has the unfortunate side effect of obscuring the question of which behaviors are true in general *(i.e.*, for all materials) and which ones apply only to ideal gases.

Two ideal gas laws:
Consider two equations that describe ideal gases:

$p = (N/V)kT$	The "equation of state"
$U = \alpha nkT$	The internal energy.

I've rewritten the $pV = NkT$ equation to demonstrate three points:
- N/V is the number of molecules per unit volume, *i.e.*, the particle density. Call it ρ: $p = k\rho T$.
- The pressure depends on the density and the pressure. In other situations, the pressure might depend on other quantities as well (for example an applied magnetic field).
- The internal energy depends only on the temperature, not on the density.

One might then ask:
- What conditions must be satisfied for $p = k\rho T$?
- Why does U not depend on ρ?
- Why is U proportional to T?
- Does U really $\rightarrow 0$ as $T \rightarrow 0$?

Underlying these questions is this one:
- Why don't other quantities, such as the size and mass of the molecules or the charge of the electron, appear in these equations?

Derivation of the ideal gas law:

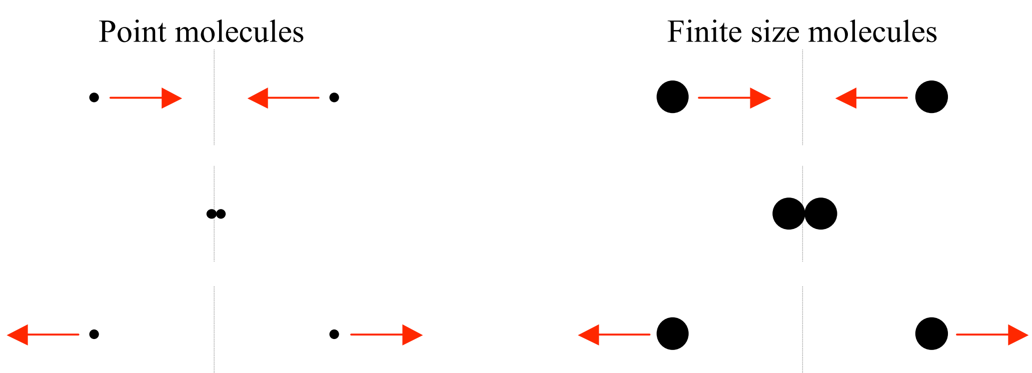
In P213 lecture, we make this argument:

- Suppose the gas in a cubical box of side L ($V = L^3$).
- The $\langle KE \rangle$ of a molecule (which means $\frac{1}{2}m\langle v^2 \rangle$) is proportional to T.
- The direction of motion is random, so $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \langle v^2 \rangle/3$, proportional to T.
- Consider collisions of a single molecule with a wall that is perpendicular to the x-axis.
- The average time, t, (actually, what we call the root-mean-square time) between collisions with this wall is $2L/\sqrt{\langle v_x^2 \rangle}$. This is roportional to L and inversely proportional to $\sqrt{T}$.
- The momentum transferred to the wall in each collision is $2p$ (momentum), which is proportional to $\sqrt{T}$.
- The time average force exerted on the wall by this molecule is $\langle F \rangle = 2p/t$. It is proportional to T and inversely proportional to L.
- The pressure exerted by this molecule is thus: $p = \langle F \rangle/L^2 = kT/L^3 = kT/V$. Boltzmann's constant, k, is just a proportionality constant.
- If the gas has N molecules, the pressure is thus, $p = NkT/V$.

Let's examine some of the assumptions.

Is it necessary that the direction of motion be random?
What would happen, for example, if the molecules were electrically charged and we applied a magnetic field? They would move in spirals around the magnetic field, and the whole argument falls apart. A question to ponder: What about gravity? There is a preferred direction for the air in the room; how does this affect the problem?

Do collisions between the gas molecules affect the argument?
Can we neglect them? Suppose two molecules collide at some point in the box, and the direction of motion afterwards is random. I claim that this has no effect, because the direction of motion is already random, so $\langle v_x^2 \rangle$ is unchanged. (This is a statistical argument; we're talking about averages.) The time between wall collisions remains $t = 2L/\sqrt{\langle v_x^2 \rangle}$. Another affect does modify t, however. The **molecules have a finite size**. Look at the figure below, which depicts head on collisions between point molecule (on the left) and finite size molecules (on the right):



For point molecules, the collision does not affect the time it takes to hit the wall. The path length remains unchanged. For finite size molecules, however, the time is reduced, because the center of the molecule never reaches the collision point (at the dotted line in the figure). This effect was first analyzed by Johannes van der Waals in 1873. In a nutshell, the effect results from the reduction of the volume available to molecules, so the ideal gas law is modified like this:

$$p(V\text{-}bN) = NkT = pV(1\text{-}b\rho)$$

In 1873, molecular sizes were not well known, so b was an empirical constant. Here are two values:

Ar: $b = 0.0322\ \ell/\text{mol} = 5.34\times10^{-29}\ \text{m}^3/\text{atom}$

CO_2: $b = 0.0427\ \ell/\text{mol} = 7.08\times10^{-29}\ \text{m}^3/\text{molecule}$

How big is the effect? Consider gas at room temperature (300 K) and atmospheric pressure (10^5 Pa). Using $pV = NkT$, $\rho = N/V = 2.41\times10^{25}$ atoms/m^3. This gives $(1\text{-}b\rho) = 0.9987$ for argon, a small effect. One must go to high density (high pressure and/or low temperature) to observe it.

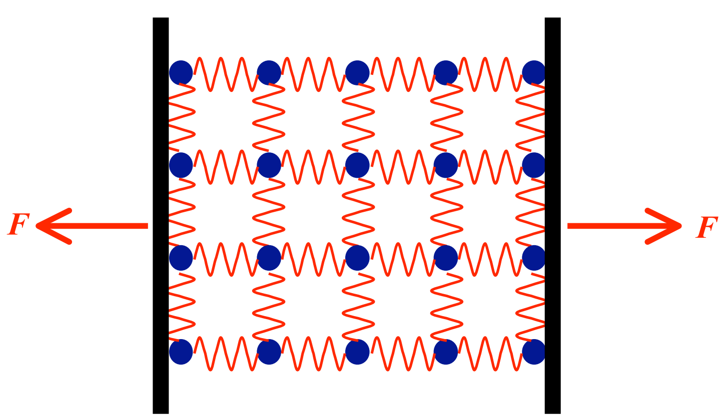
Comments:

- We need Avogadro's number to calculate ρ. That was first measured in 1827 by analyzing Brownian motion.

- How big is the argon atom? Using $b = 4\pi r^3/3$, I calculate $r_{\text{Ar}} = 2.4\times10^{-10}$ m. This is a bit too big; the radius is closer to 1.0×10^{-10} m (one Ångström).

Another assumption is that the molecules are free except during collisions.
In the ideal gas derivation, the pressure results only from the molecular motion. That's why p is inversely proportional to V. However, there are other possible sources of pressure. Here's an example in which the thermal molecular motion plays no role at all:

Consider, a material consisting of a bunch of atoms connected by springs. The springs are somewhat compressed, so to hold the material in place, it is confined between two walls. For simplicity, let's only consider one dimension.



Because the springs are compressed, there is pressure on the walls. This does not result from thermal effects, but from the interaction between the atoms. This interaction does not have to be springs; it can be any force (*e.g.*, chemical binding forces). The force can be either attractive or repulsive, which means that it can either increase or decrease the pressure. This modifies the equation of state to be:

$$(p+a\rho^2) = k\rho T$$

The correction to the pressure is proportional to ρ^2, because the density of interacting pairs of atoms is proportional to ρ^2. Positive a gives a p that is smaller than in the ideal case.

The van der Waals modified equation of state is thus:

$$(p+a\rho^2)\,(1-b\rho) = k\rho T$$

How big is the interaction effect? Here are two empirical values for a:

Ar: $a = 1.345\ \ell^2\cdot\text{Atm/mol}^2 = 3.75\times10^{-49}\ \text{m}^6\cdot\text{Pa/molecule}^2$
CO_2: $a = 3.59\ \ell^2\cdot\text{Atm/mol}^2 = 10.0\times10^{-49}\ \text{m}^6\cdot\text{Pa/molecule}^2$

Using $\rho = 2.41\times10^{25}$ molecules/m^3 (room temperature and pressure, as above) $a\rho^2 = 2.2\times10^2$ Pa for argon and 5.8×10^2 Pa for CO_2. This is an 0.6%, effect for CO_2.

Note that argon is not very inert. For comparison, helium's a is a factor of 40 smaller.

Internal energy:

The internal energy will also be modified by the molecular interactions. The derivation of the expression $U = \alpha nkT$ only includes kinetic energy (center of mass and rotational motion). Now there will be a density dependent correction that depends on how the potential energy varies with separation between molecules, $PE = f(r)$. As the density increases, the average separation, <r> is proportional to $\rho^{-1/3}$. An attractive interaction reduces U, because PE < 0.

Another effect gives nonlinear dependence of U on temperature. Remember that the proportionality constant, α, is determined by counting the number of modes that can absorb thermal energy. The number of available modes depends on the spacing of the quantum energy levels compared with the available thermal energy, ½kT, per mode. Consider a diatomic molecule, which we model as two masses connected by a spring (the chemical bond).

So far, we've only considered the KE due to rotation and CM motion. We ignored vibrations, because the harmonic oscillator energy levels are quantized. Molecular transitions betwen these vibrational states typically emit infrared or visible light. That is, the energy spacing is on the order of $\Delta E = hc/\lambda \sim 1$ eV. At room temperature, kT = 0.026 eV. Thus, there is not enough thermal energy to excite the vibrational states of typical diatomic molecules. At high temperatures, the vibrational mode becomes available and α increases from 5/2 to 7/2. It increases by 1 unit, because there is both KE and PE in vibrational motion.

In a similar vein, at very low temperatures (assuming the gas hasn't condensed), the rotational modes "freeze out," because *kT* becomes smaller than their level spacing.

We'll return to this problem in a couple of weeks, after you've learned how to calculate the excitation probability.

You'll learn how to calculate the energy spacing in P214, the quantum mechanics part of the course. We'll find that quantum mechanics can have a large influence on the themal properties of materials.