Week 3

Kinetic Theory of Gases

3.1 Maxwell-Boltzmann Distribution

1/24:

- Applying the molecular partition function to the heat capacity of a water molecule.
  - A water molecule has three vibrational modes, which we will denote by ν_1, ν_2, ν_3 (corresponding to symmetric stretch, antisymmetric stretch, and bend).
  - Main takeaway: Heat capacity can change with temperature.
  - After a while (at several thousand kelvin), it will level off (see Figure 18.7).
- Considers CO_2's vibrational modes, too.
  - The infrared absorption of the bending mode is what's associated with the Greenhouse Effect.
  - The symmetric stretch is IR inactive due to its lack of change of dipole moment.
  - Raman active: Change in the polarizability of the molecule.
- The Maxwell-Boltzmann distribution.
  - Maxwell derived it long before Boltzmann, but Boltzmann's thermodynamic derivation is much easier.
  - We know from the boltzmann factor that $p(E) \propto \mathrm{e}^{-E/k_BT}$.
  - Thus, to get the probability $p(v)$ of some speed v, we should have $p(v) \propto \mathrm{e}^{-mv^2/2k_BT}$ times a constant giving the number of molecules of each speed? This yields

    $$p(v) = A4\pi v^2 \mathrm{e}^{-mv^2/2k_BT}$$

    where A is a normalization constant.
  - The Maxwell-Boltzmann distribution is such that

    $$\begin{aligned}
    1 &= \int_0^\infty p(v)\,\mathrm{d}v \\
    &= A\int_0^\infty 4\pi v^2 \mathrm{e}^{-mv^2/2k_BT}\,\mathrm{d}v \\
    &= A\int_0^\infty 4\pi \left(\frac{2k_BT}{m}\right)^{3/2} u^2 \mathrm{e}^{-u^2}\,\mathrm{d}u \\
    &= A4\pi \left(\frac{2k_BT}{m}\right)^{3/2} \int_0^\infty u^2 \mathrm{e}^{-u^2}\,\mathrm{d}u \\
    &= A4\pi \left(\frac{2k_BT}{m}\right)^{3/2} \frac{\sqrt{\pi}}{4}
    \end{aligned}$$

$$A = \left(\frac{m}{2\pi k_B T}\right)^{3/2}$$

- Therefore,

$$p(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \mathrm{e}^{-mv^2/2k_B T}$$

- Any distribution that doesn't look like this isn't in thermal equilibrium.

- A system with all particles having $v = 0$ is at thermal equilibrium with $T = 0\,\mathrm{K}$.
- A system with all particles having constant velocity in the same direction is at thermal equilibrium with $T = 0\,\mathrm{K}$.
  - Think relativity; if you're moving with them, it looks like they're not moving and thus this case is the same as the last one because you're movement doesn't affect the thermodynamics of that system.
- A system with all particles having constant velocity in different directions is not at thermal equilibrium since it does not fit the bell curve but is rather a spike.