Week 2

Partition Functions and Ideal Gases

2.1 System Partition Functions

1/19:

- Decomposing the partition function of a molecule into the product of separate sums as partitioned by degrees of freedom (e.g., translation, rotation, vibration, and electronic).
- The partition functions of **independent**, distinguishable/indistinguishable molecules.
  - We should not double count the same states.
  - The $N!$ in $Q = q^N/N!$ is not important when calculating energy (because of the properties of the ln function), but it is very important when calculating quantities such as entropy.
- **Independent** (particles): A set of particles that do not interact with one another.
- Discusses bosons and fermions.
  - We can have a two fermions in the state $|1,1\rangle$ because it is a symmetric state.
- Recall the Fermi level, the boundary between the filled and unfilled electronic states in a solid.
  - If T is small, this level is a hard boundary.
  - If T is large, electrons can easily be excited and the Fermi level is a soft boundary.
- Does the 3D particle in a box derivation for the translation molecular partition function.
  - Note that since the de Broglie wavelength $\lambda_{\text{DB}} = \sqrt{h^2/2mk_BT}$, we may write
$$q_x = \sum_{n_x} \mathrm{e}^{-h^2/8mk_BTL_x^2} = \sum_{n_x} \mathrm{e}^{-\lambda_{\text{DB}}^2 n_x^2/4L_x^2}$$
- The number of states are occupied/have energy within k_BT of the ground state.
  - $-\lambda_{\text{DB}}^2 n_x^2/4L_x^2$ is on the order of 1, implying that n_x is on the order of $2L/\lambda_{\text{DB}}$.
  - It follows if L is on a macroscopic scale (e.g., $L \approx 1\,\text{m}$) and λ_{DB} is on a sub-angstrom scale that n_x is on the order of 10^{10}. When n_x is at such a scale, $\mathrm{e}^{-\lambda_{\text{DB}}^2 n_x^2/4L_x^2} \approx 1/\mathrm{e}$.
  - It follows that in a $1\,\text{m}^3$ box, we will have about 10^{30} states, so we really are in a regime where the number of states is larger than the number of molecules.
- More precisely, we want
$$N \ll n_x n_y n_z = \left(\frac{8mk_BT}{h^2} \right)^{3/2} L_x L_y L_z$$
where the middle term approximates the number of states so that
$$\frac{N}{V} \ll \left(\frac{8mk_BT}{h^2} \right)^{3/2}$$

- Approximating the translational energy with an integral.
  - Concludes with the translational partition function.
  - Since we can approach this problem from a classical perspective (as we did last Friday) or quantum mechanically (as we did today) to achieve the same result, this system again demonstrates the relation between quantum and classical mechanics.