Today

I. No class Wednesday or Friday; Last Time
II. The Ideal Gas from a Canonical Perspective
III. Spencer's Guest Lecture: The Gibbs Factor and the Grand Canonical Partition Function

I. Zak gave a guest lecture on the relationship between the partition function and the Helmholtz free energy. Gave a nice motivation that compared the Boltzmann counting of microstates and the design of the of partition function. The proof was via showing that both $\tilde{F} = -kT \ln Z$ and F satisfied the same PDE.

We also explored noninteracting, identical particles and their partition functions: $Z_{tot} = \frac{1}{N!}(Z_1)^N$.

II. At a technical level noninteracting decomposed the total energy into a sum of energies for each particle. We'll use this same idea again, this time separating the translational and internal motions. Here internal refers to all forms of energy for a single particle that aren't translational, e.g., rotational or vibrational modes within the molecule. This splits up the Boltzmann factor

$$e^{-\beta E(s)} = e^{-\beta E_{tr}(s)} e^{-\beta E_{int}(s)}.$$

Then we get a simpler partition function

$$Z_1 = Z_{tr} Z_{int}.$$

Let's repeat the calculation of the contribution of the translational modes, this time via partition function. To do that we need the quantum mechanics of translational motions in a box. First let's do the 1D case, then we'll do 3D.

II. The general wavelength of a wavefunction in a 1D box is

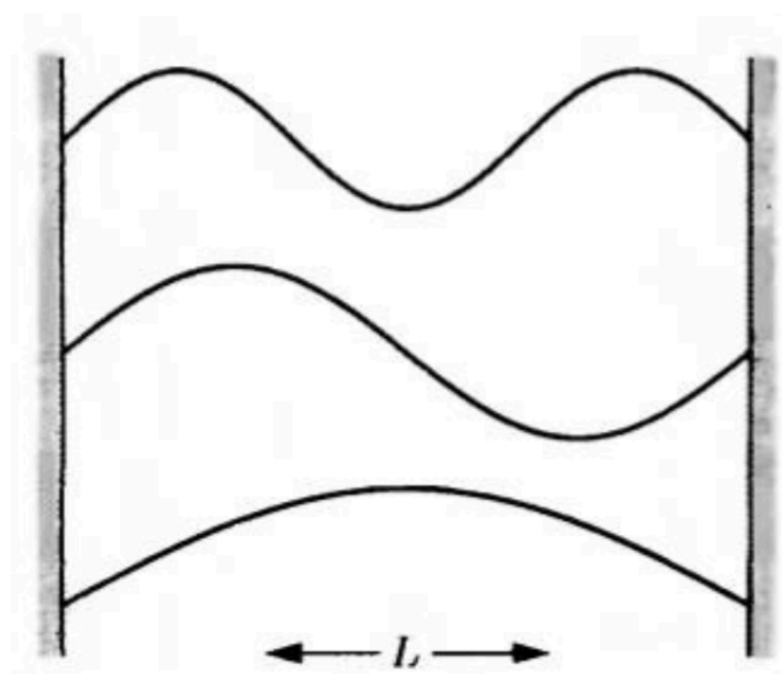
$$\lambda_n = \frac{2L}{n}, \text{ where } n = 1,2,3,....$$

According to de Broglie

$$p_n = \frac{h}{\lambda_n} = \frac{nh}{2L}, n = 1,2,3,....$$

Our free particle only has kinetic energy:

$$E_n = \frac{p_n^2}{2m} = \frac{n^2h^2}{8mL^2}, n = 1,2,3,....$$



$\lambda_3 = \frac{2L}{3}$

$\lambda_2 = \frac{2L}{2}$

$\lambda_1 = 2L$

II. With the energy spectrum in hand,

$$E_n = \frac{p_n^2}{2m} = \frac{n^2h^2}{8mL^2},\ n = 1,2,3,...,$$

we can compute the partition function. We find

$$Z_{1d} = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta \frac{h^2n^2}{8mL^2}}.$$

Converting this to an integral approximation we have

$$Z_{1d} \approx \int_0^\infty e^{-\beta \frac{h^2n^2}{8mL^2}} dn = \frac{\sqrt{\pi}}{2}\sqrt{\frac{8mL^2kT}{h^2}} = \sqrt{\frac{2\pi mkT}{h^2}}L \equiv \frac{L}{\ell_Q}.$$

Let's guess how it goes for the 3D box:

$$Z_{tr} = \frac{L_x}{\ell_Q}\frac{L_y}{\ell_Q}\frac{L_z}{\ell_Q} = \frac{V}{v_Q}.$$

Focusing, on ℓ_Q for a moment, we have $\ell_Q = \frac{h}{\sqrt{2\pi mkT}}$, this is the de Broglie wavelength of a thermal atom or molecule.

II. Using this partition function we can find the chemical potential (amongst many other things):

$$\mu = -kT \ln\left(\frac{V}{N}\frac{Z_{int}}{v_Q}\right).$$

See additional slides from Spencer's guest lecture too!