1 Intro to statistical methods

- Goal: Study systems consist of many particles (magnitude of moles) that interact with each other.
- Stat Mech bridges the gap between the Macroscopic and Microscopic Description of a system.

Macroscopic Description > µm:

- Temperature, Pressure, Volume Entropy, etc.

Microscopic Description Å:

Worksheet

(1) Avogadro's number: $N_A = 6.022 \times 10^{23}$ e.g. in 12g of carbon-12, there are N_A atoms!
1 mole of air : 22.4 L at 273 K, 1 atm.
e.g. Say a room is 5m x 5m x 8m = 200 m^3 = 200×10^3 L, how many moles of air are in the room? $\sim 10000 N_A$

(2) $k_B = 1.38 \times 10^{-23}$ J/K
Physical Meaning: $k_B T$ will roughly gives us the energy in one atom

(3) On a number line with 1 and $+\infty$, where is N_A?
In mathematics, we would place N_A closer to 1, but in physics we would place it closer to $+\infty$ because this number is huge in the context of physics.

(4) In the physics convention, we use θ as the polar angle and ϕ as the azimuthal angle. So a volume element in a sphere is

$$r^2 \sin\theta \mathrm{d}r \mathrm{d}\theta \mathrm{d}\phi$$

Thus the volume of a sphere is

$$V = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_0^R r^2 \sin\theta \mathrm{d}r \mathrm{d}\theta \mathrm{d}\phi = \frac{4}{3}\pi R^3$$

(5) The ideal gas law comes in two forms:

$$PV = N k_B T$$

$$PV = nRT$$

where $n = \frac{N}{N_A}$, and N is the number of particles in the system.

(6) The container with gas confined to half a container at $t = 0$ releases the gas to fill the whole container at $t > 0$. What is the change in entropy?
The equation for the change in entropy is

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T}$$

but this doesn't tell us much...

Basic Statistical Concepts : "statistical ensemble"

Example: Fair coin toss (50/50) N times. The expected value of heads is $N/2$. Repeating this many times gives a Gaussian distribution centered at $N/2$.

Random walk in 1D Starting at $x = 0$, we have a probability p to move one unit to the right and probability $(1-p) = q$ to move left.

For a 'trajectory'

- n_L: # of steps left
- n_R: # of steps right
- $N = n_L + n_R$
- Displacement: $x = n_R - n_L$

Each step is independent: "no memory", "Markovian/Markov process"

The probability of a specific trajectory is

$$p \cdot p \cdots p \cdot q \cdots q = p^{n_R} q^{n_L}$$

How many ways this (n_R, n_L) can be arranged?

$$\binom{N}{n_R} = \frac{N!}{n_R! n_L!}$$

So the probabilty of taking n_R steps to the right is

$$W_N(n_R) = \frac{N!}{n_R! n_L!} p^{n_R} q^{n_L}$$

Finishing the Random Walk

$$W_N(n_R) = \frac{N!}{n_R! n_L!} p^{n_R} q^{n_L}$$

is indeed the "Binomial distribution".

The mean displacement (or expected value) is

$$\bar{m} = \bar{n}_R - \bar{n}_L = pN - qN = N(p-q)$$

How do we define variance/dispersion?

$$\begin{aligned}\overline{(\Delta n_R)^2} = \overline{(n_R - \bar{n}_R)^2} &= \overline{n_R^2 - 2n_R\bar{n}_R + \bar{n}_R^2} \\ &= \overline{n_R^2} - 2\bar{n}_R^2 + \bar{n}_R^2 \\ &= \overline{n_R^2} - \bar{n}_R^2 = Npq\end{aligned}$$

So the deviation or width is roughly $\sim \sqrt{Npq}$

For large N, the distribution can be approximated a continuous:

$$\left.\frac{\mathrm{d}W(n_R)}{\mathrm{d}n_R}\right|_{\bar{n}_R} = 0$$

or equivalently

$$\left.\frac{\mathrm{d}\ln W(n_R)}{\mathrm{d}n_R}\right|_{\bar{n}_R} = 0$$

And using

$$n_R \equiv \bar{n}_R + \xi$$

where ξ is the deviation from the mean.

So now we can Taylor expand $\ln W$:

$$\ln W(n_R) = \ln W(\bar{n}_R) + \cancel{\left.\frac{\mathrm{d}\ln W(n_R)}{\mathrm{d}n_R}\right|_{\bar{n}_R}(n_R - \bar{n}_R)} + \frac{1}{2}B_2\xi^2 + \dots$$

where

$$W(n_R) \equiv W_{max} e^{-\frac{1}{2}B_2\xi^2}, \quad B_2 = \frac{1}{Npq}$$

This yields the Gaussian distribution approximation.

$$P(m) = W(n_R) = (2\pi Npq)^{-1/2} e^{-\frac{[m-N(p-q)]^2}{8Npq}}$$

Worksheet

1. If a coin is flipped 400 times, what's the probability of getting 215 heads?

   $N = 215 + 185 = 400$, $p = 0.5$, $q = 0.5$, $m = 215 - 185 = 30$

   Plugging in the numbers gives $P(30) = 1.295\%$