Lecture 2 - Microcanonical Ensemble

Last time:

$\vec{X} = \{x_1, \ldots, x_{3N}, p_1, \ldots, p_{3N}\}$ is microstate of the system

A is an observable, $A(X)$

$\langle A \rangle = \int d\vec{X}\, A(x) P(x)$ is value measured

$P(x)$ depends only on Macro State

for constant N, V, T - $P(x) = \frac{1}{Z} e^{-\beta \mathcal{H}(x)}$

$$Z = \int dx\, e^{-\beta \mathcal{H}(x)}$$

$$\langle \varepsilon \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{-1}{Z}\frac{\partial Z}{\partial \beta} = \frac{1}{Z}\int dx\, \mathcal{H}(x) e^{-\beta \mathcal{H}(x)}$$

Eg $\mathcal{H} = p^2/2m + \frac{1}{2}kx^2$

$$Z = 2\pi \cdot \frac{1}{\beta \omega}$$

$$-\log Z = -\log(2\pi/\omega) + \log(\beta)$$

$$\langle \varepsilon \rangle = -\frac{\partial \log Z}{\partial \beta} = \frac{1}{\beta} = k_B T$$

Average energy does not depend on k! (or m) Very important physical fact

$\vec{X}$ is not always continuous

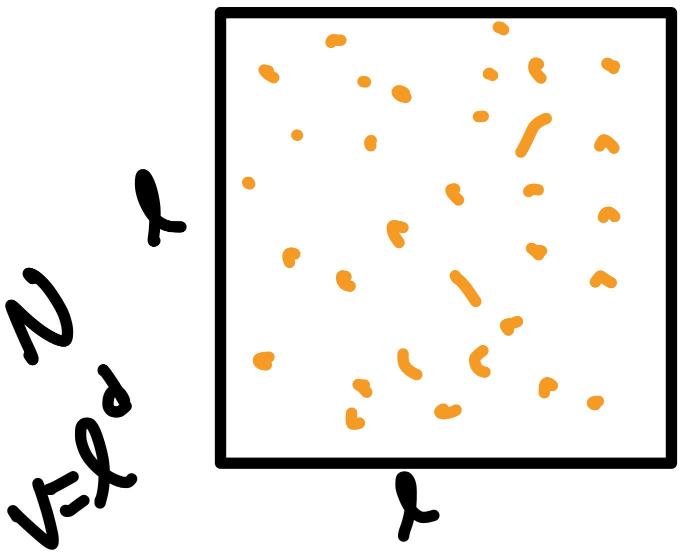
Eg quantum harmonic oscillator

$$\varepsilon_n = \hbar\omega\left(n + \frac{1}{2}\right), \quad n = 0, \ldots, \infty$$

$$Z = \sum_{i \in \text{states}} A_i P(i)$$ ← HW

$$= \sum_n \varepsilon_n e^{-\beta \varepsilon_n} / Z$$

Now lets return to a system of atoms or molecules we want to study



N particles in closed isolated box

closed ↑ no particle exchange

isolated ↑ no energy exchange

These N particles follow Newton's laws, so if we know $\vec{X}(t)$ we know $\vec{X}$ at all times in theory

If we know particle positions & momenta we know everything

Classical Mechanics:

$$F_i = m_i a_i = m_i \dot{v}_i = m_i \ddot{x}_i$$

$$v = \dot{x} = \frac{dx}{dt}$$

integrate!

const v

$$x(t) - x(0) = vt \Rightarrow d = vt$$

$$x_2 = x_1 + vt$$

$$v(t) - v(0) = at \quad \leftarrow \text{const } a$$

$$v_2 = v_1 + at$$

$$\dot{x}(t) = v_1 + at \Rightarrow d = v_1 t + \frac{1}{2} a t^2$$

Newton's laws conserve energy. So even if we cannot solve, $\mathcal{E}$ stays constant [no external forces]

Macrostate: $N, V, \mathcal{E}$

microstate: any configuration $\vec{X} = \{\vec{x}, \vec{p}\}$ where

$x_i \in$ box (eq $0 \le q \le L$) $\forall i$

$\mathcal{H}(\vec{X}) = \mathcal{E}$

Express this constraint as

$$\delta(\mathcal{H}(X) - \mathcal{E})$$

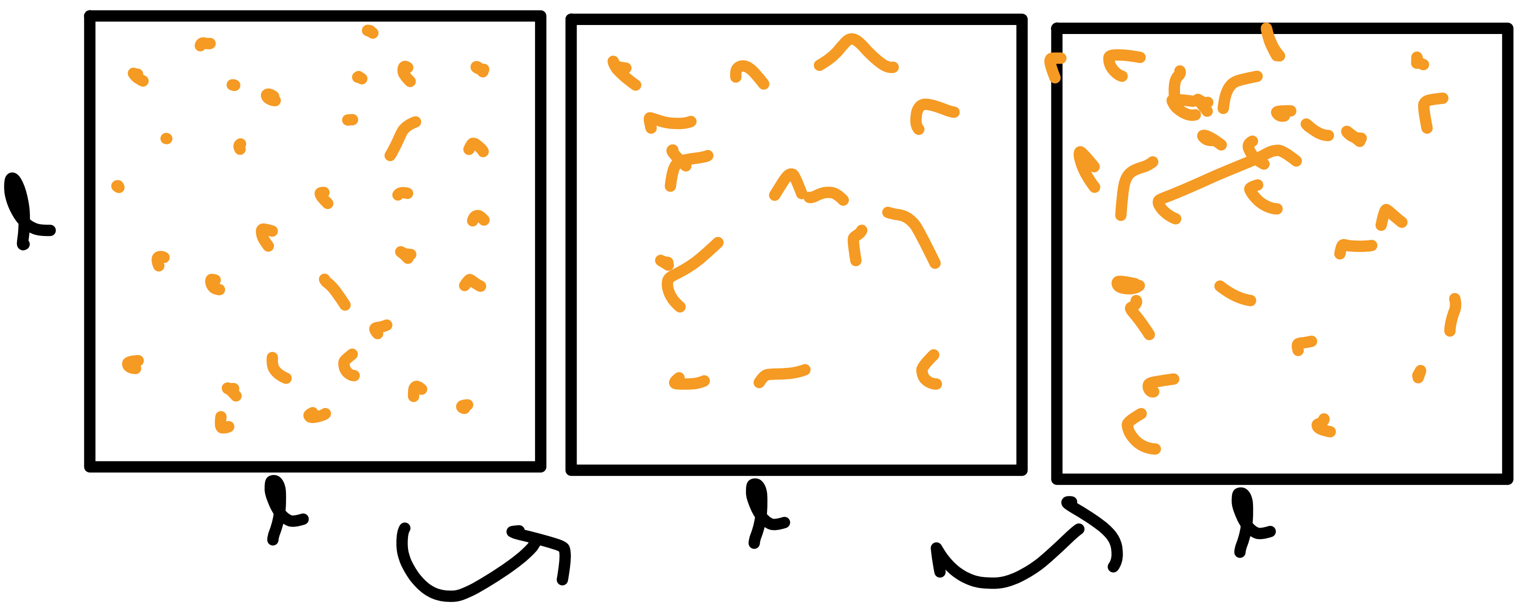
How many states are there?
"Count" every state where this is true. for continuous, this is an integral

$$\int d\vec{x} \int d\vec{p}\, \delta(\mathcal{H}(x,p) - \mathcal{E}) = Z$$

What is the probability of a state. Assumption: "equal a priori possibilities" - why should any one state be special?

So for N, V, E

$$P(\vec{X}) = \begin{cases} 1/Z & \text{if } \mathcal{H}(X) = E \\ 0 & \text{otherwise} \end{cases}$$



Z counts all allowed configurations

If we can also take snapshots of dynamics, we would get representative configurations

Ergodic - in principle, all possible configurations eventually visited

If we have a long "movie" or "trajectory"

Take snapshots x_i, p_i

and to average, do

eg $$\frac{1}{N_t} \sum_{i=1}^{N_t} A(x_i) = \langle A \rangle_{time}$$

If ergodic

$$\langle A \rangle = \langle A \rangle_{time}$$