# Lecture 2 – Microcanical Ensemble

Last time

Microstate:

$$\vec{X} = \{x_1, \ldots, x_{3N}, p_1, \ldots, p_{3N}\}$$

$A(\vec{X})$ measurable quantity

Observable quantity

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

$P(x)$ depends only on the <u>Macro</u> state

Eg const $N, V, T$ [canonical ensemble]

$$P(x) = \frac{1}{Z} e^{-\beta \mathcal{H}(x)}$$

$\mathcal{H} \leftarrow$ total energy

$\beta \leftarrow \frac{1}{k_B T}$ high $T$ - small $\beta$

harmonic oscillator - 1d

$$\mathcal{H}(x,p) = \frac{1}{2}kx^2 + p^2/2m$$

$$Z = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \; e^{-\beta \mathcal{H}(x,p)}$$

$$\omega = \sqrt{k/m}$$

$$Z = 2\pi \frac{k_B T}{\omega}$$

$$\langle E \rangle = \frac{1}{Z} \int d\vec{x} \, \mathcal{H}(\vec{x}) \, e^{-\beta \mathcal{H}(\vec{x})}$$

$$\langle E \rangle = -\frac{\partial \log Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$= +\frac{1}{Z}\int dx\, \mathcal{H}(x)\, e^{-\beta \mathcal{H}(x)}$$

no m, k

$$\langle E \rangle$$

$$\| $$

$$Z_{SHO} = 2\pi \frac{k_B T}{\omega} = 2\pi \cdot \frac{1}{\beta \omega}$$

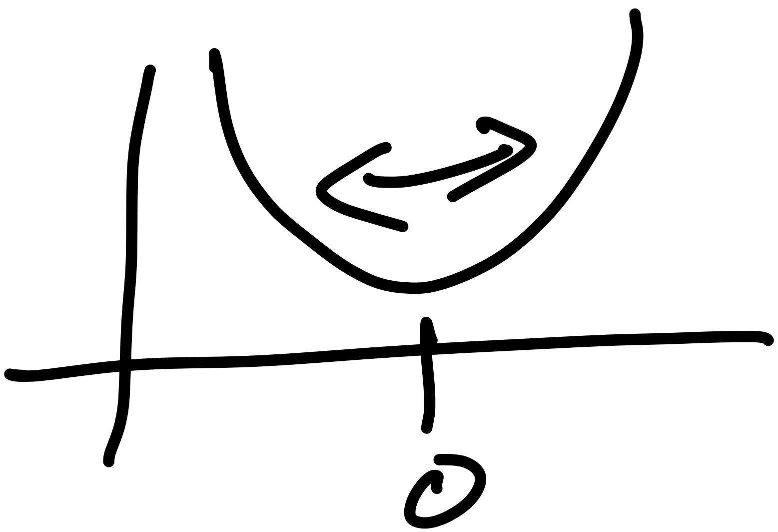
$$-\frac{\partial \log Z}{\partial \beta} = \frac{-\partial(-\log \beta)}{\partial \beta} = \frac{1}{\beta} = k_B T$$

$$\log Z = \log\left(\frac{2\pi}{\beta \omega}\right) = \log\left(\frac{2\pi}{\omega}\right) - \log \beta$$

$$\langle A \rangle = \frac{1}{Z}\int d\vec{x}\, A(\vec{x})\, e^{-\beta \mathcal{H}(\vec{x})} = \int dx\, A(x)\, P(x)$$

$$\langle x \rangle = \frac{1}{Z}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp\; x\; e^{-\beta\left[\frac{1}{2}kx^2 + p^2/2m\right]}$$

$$u = x^2 \quad du = 2x\,dx$$




$$\langle u \rangle = \int dx \int dp\, \frac{1}{2}kx^2 e^{---}$$

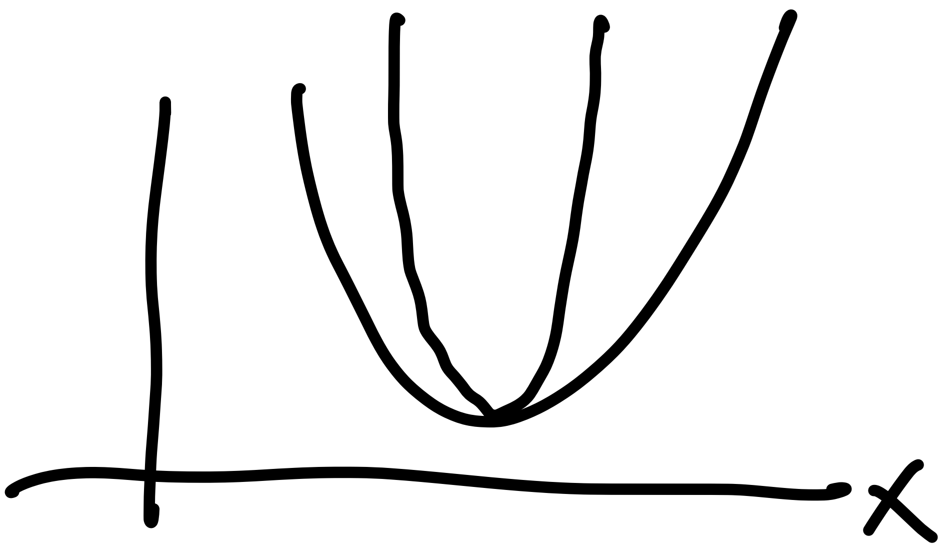
$$\int dx\, x^2 e^{-ax^2}$$

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

$$\mathcal{H} = -\frac{e^2}{4\pi\varepsilon r}$$

can't solve directly

$$\langle \varepsilon \rangle = k_B T$$




$$Z = 2\pi \frac{k_B T}{\omega}$$

$Z \sim$ number of states

$\vec{x}$ particular state of system

classical mechanics – continuous

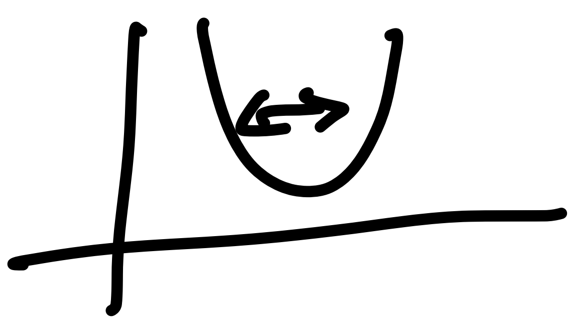
quantum mechanics – discretized

$$\mathcal{H} = P^2/2m + \tfrac{1}{2}kx^2$$ ← s.h.o. quantum

$$\varepsilon_n = \hbar\omega(n+\tfrac{1}{2})$$

$\hbar\omega/2$ ← zero point energy

$h\nu$

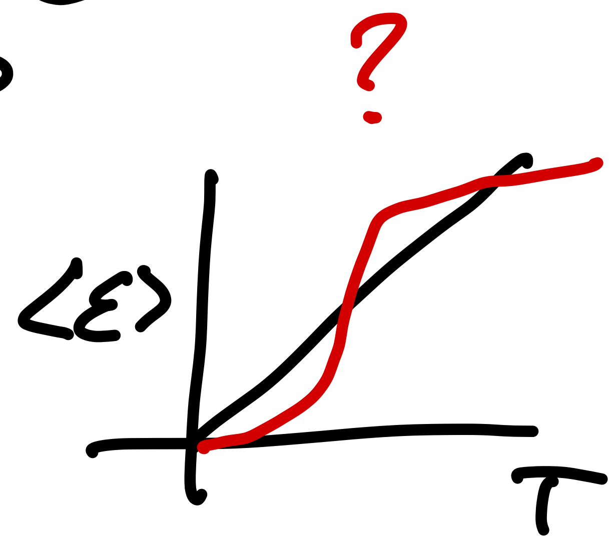


$$P(\text{state}) = \frac{1}{Z} e^{-\beta \mathcal{H}(\text{state})}$$

$n = 0, \dots, \infty$

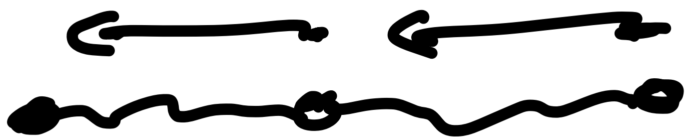
$$Z = \sum_{n=0}^{\infty} e^{-\beta \epsilon_n} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega \left(n + \frac{1}{2}\right)}$$

$$\langle \varepsilon \rangle = \frac{1}{Z} \underbrace{\sum_{n=0}^{\infty} \epsilon_n e^{-\beta \epsilon_n}}$$




HW: solve $Z$ exactly

$\langle \varepsilon \rangle$ by $-\partial \log Z / \partial \beta$



sum over springs

$$\mathcal{H} = \sum_{i=1}^{3} \vec{p}_i^{\,2}/2m_i + \sum_{i=1}^{2} \frac{1}{2} k_i (l_i - l_0)^2$$

$$\parallel$$

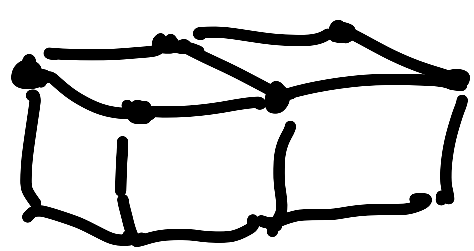
dist rest

N H.O. in ~ any dimensions $\longrightarrow$

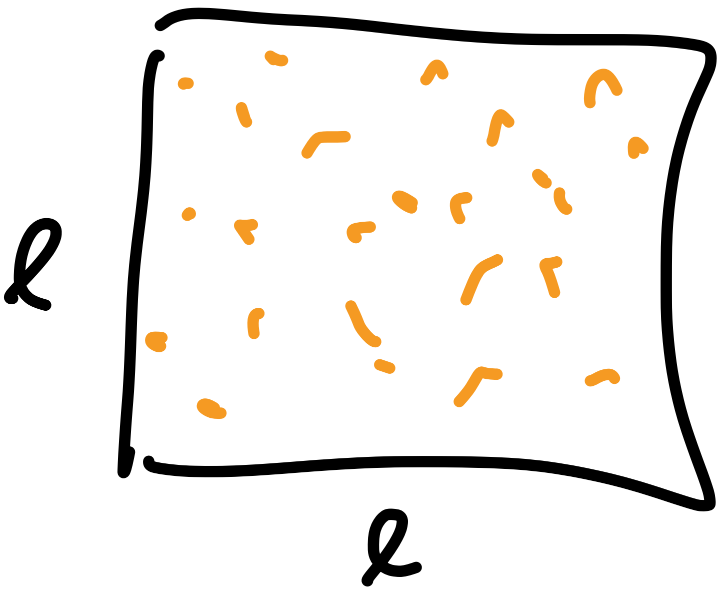
$$\sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{2} k_{ij} (r_{ij} - r_{ij}^{0})^2$$

$$\mathcal{E} = \frac{1}{2} \sum_{i=1}^{N} k_i' \, \tilde{u}_i^{2}$$

$\tilde{u}_i \sim$ normal mode



Return to system of N particles in a box




assert:

box is closed no exchange of #'s

is isolated no exchange of E (heat)

N in box volume $V = \ell^d$

N particles follow Newton's equations of motion

Classical mechanics:

$$F_i = \underline{m_i a_i} \qquad \vec{F} = m\vec{a}$$

$$X_0 = \{ \overset{x,y,z\ldots}{x_1, \ldots, x_{3N}}, \overset{p_x, p_y, p_z}{p_1 \ldots p_{3N}} \} \text{ @ time } 0$$

know $X$ from $t \in (-\infty, \infty)$

$$= \{ \vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots \vec{p}_N \}$$

$(x, y, z)_1$ $(p_x, p_y, p_z)_N$

$$a_i = \frac{dv_i}{dt} = \frac{1}{m}\frac{dp_i}{dt}$$

$$F = -\nabla U(\vec{x}_1, \dots, \vec{x}_N)$$

$$\nabla = \left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \dots \frac{\partial}{\partial x_N}\right)$$

$$F_i = m_i a_i = m_i \frac{dv_i}{dt} = m_i \frac{d^2 x_i}{dt^2}$$

$$v = \frac{dx}{dt} \qquad \int_0^\tau dt\, v = \int_0^\tau dt \frac{dx}{dt}$$

integrate: $x(\tau) - x(0) = v\tau$

"$d = vt$"

$$\left[ d = v_i t + \frac{1}{2} a t^2 \right.$$

$$a = \frac{dv}{dt} \Rightarrow v(\tau) - v(0) = a\tau$$

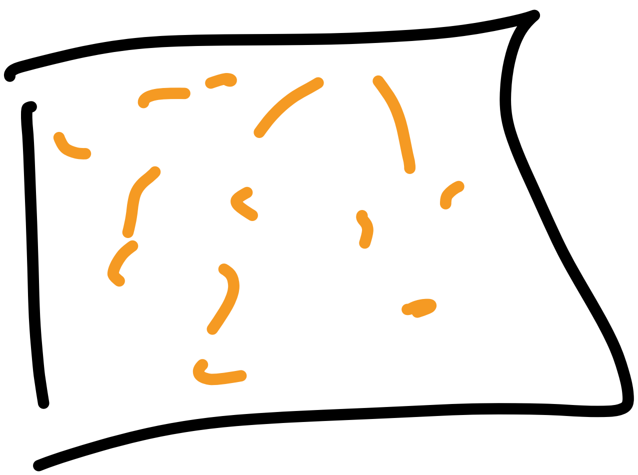
$r_1$ $\quad$ $r_2$ $\quad$ $r_3$

!! three body problem!

$$U = -\frac{Gmm}{r}$$

$$F = \frac{Gmm}{r^2}$$

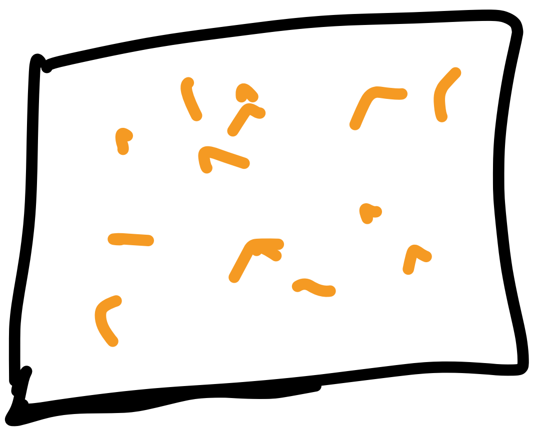
$$F = -\frac{\partial U}{\partial r} = \frac{G m_1 m_2}{|r_1 - r_2|^2}$$



$$N \sim N_A$$

No external forces!

Newton's equations conserve $E_{total}$



State :

$N, V, E$

Microcanonical ensemble

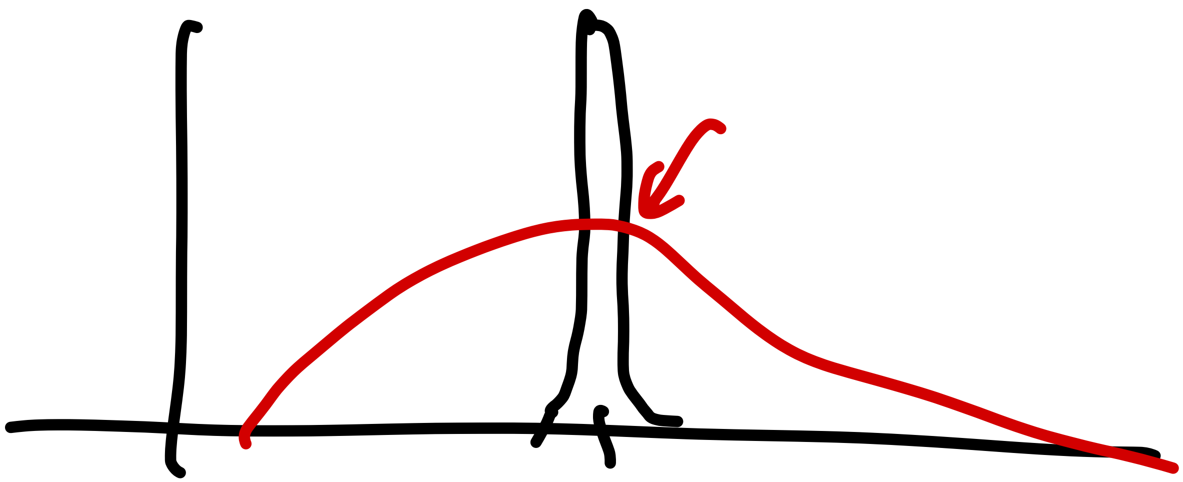
How many microstates are there

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

can solve particle in box

number of states

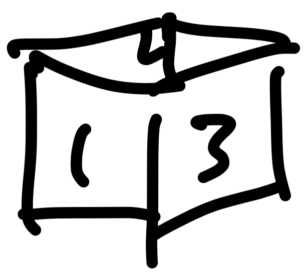
$$\delta(x) \sim \begin{cases} 1 & \text{when } x = 0 \\ 0 & \text{when } x \neq 0 \end{cases}$$




$$\int_{-\infty}^{\infty} dx\, \delta(x) = 1 \qquad \int_{-\infty}^{\infty} dx\, f(x)\, \delta(x-a) = f(a)$$

$$P(\vec{x}) = \begin{cases} \frac{1}{Z} & \text{if } \mathcal{H}(x) = E \\ 0 & \text{if not} \end{cases}$$

$$\int P(x)\, d\vec{x} = 1$$

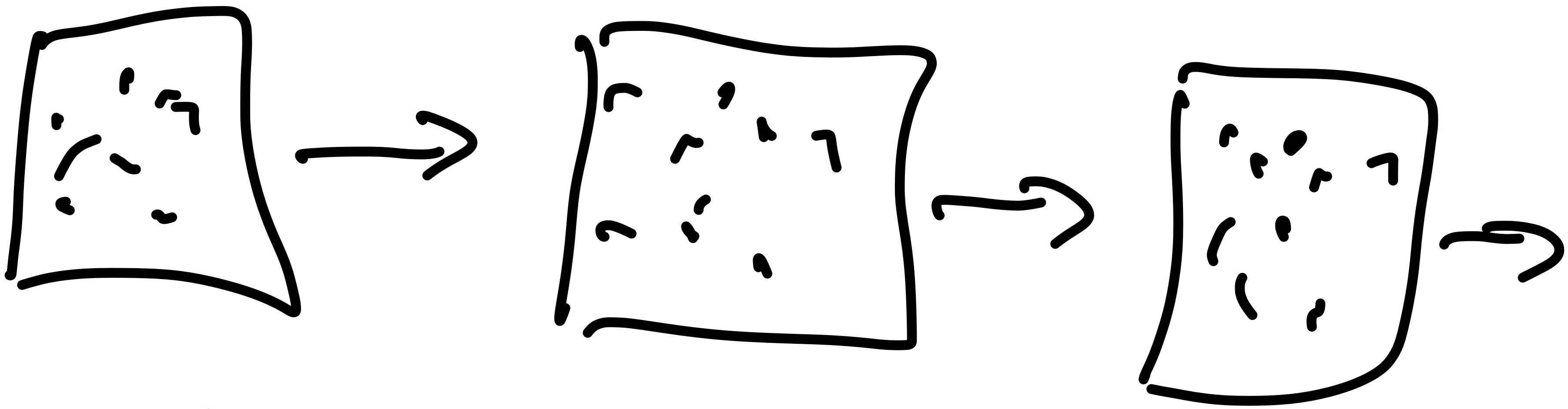



$$P(1, \dots, 6) = \frac{1}{6}$$

X weighted dice

$$P(1) = 5/6$$

$$P(2 \dots 6) = \frac{1}{30}$$



w/ Newton's equations

trajectory

$$X(t) \sim \underset{\epsilon}{\underset{\downarrow}{X(t=0)}},\ \underset{\epsilon}{\underset{\downarrow}{X(t=1)}},\ \underset{\epsilon}{\underset{\downarrow}{X(t=2)}}$$

$\langle KE \rangle$ by thermometer

$\propto T$

$$\langle KE \rangle_{time} = \frac{1}{N_t} \sum_{i=1}^{N_t} KE(t)$$

if system can access all allowed states

assume $t \to \infty$

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