Introduction

What is statistical mechanics?

A "system" obeys E.O.M.
like <u>Newton's Eqns</u>, S.E.

Classical: initial conditions
+ EOM → everything

Idea: properties of a system

property is independent of

the "state" system

(micro)

$$\underline{X} = \{x_1, x_2, \ldots, x_{3N}, p_1, p_2, \ldots, p_{3N}\}$$

Only depends on "Macroscopic"

variable, (N, V, T)

Properties only depend on averages over states

Statistical properties of the system

Average:

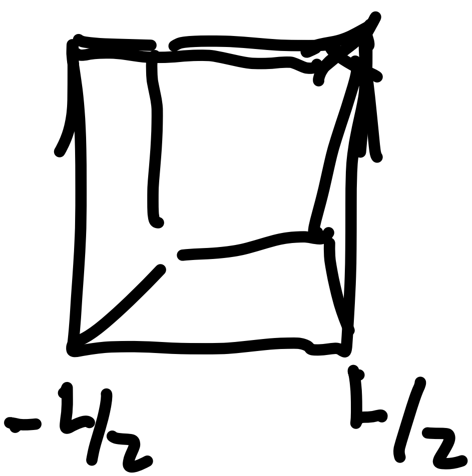
$A(\underline{X})$ an "observable"

can measure

What we measure is average of A over all microstates

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

$$\int d\vec{X} = \int_{-L/2}^{L/2} dx_1 \int dx_2 \int \cdots \int dx_{3N} \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} p_{3N} \;(\quad)$$



$$V = L \cdot L \cdot L$$

If Quantum mechanicanical:
States are discrete

	ε
— $+1/2$	$\hbar/2$
— $-1/2$	$-\hbar/2$

$$\langle A \rangle = \sum_{i=1}^{n\,states} A_i \, P(i)$$

$$\sum_{i=1}^{2} \varepsilon_i \, P(i)^{\varepsilon?}$$

Clearly we need to know $P(\underline{X}_n)$ if $P(\underline{X}_n)$ is simple we can compute any average property of our system

Probality Distribution:

$$P(\underline{X}) \leq 1 \qquad P(x) \geq 0$$

$$\int d\underline{X}\, P(\underline{X}) = 1$$

Example @ N, V, T constant

$$P(X) \propto e^{-\mathcal{H}(X)/k_B T}$$

$\mathcal{H}$ total energy $= U + K.E.$
potential

T temperature

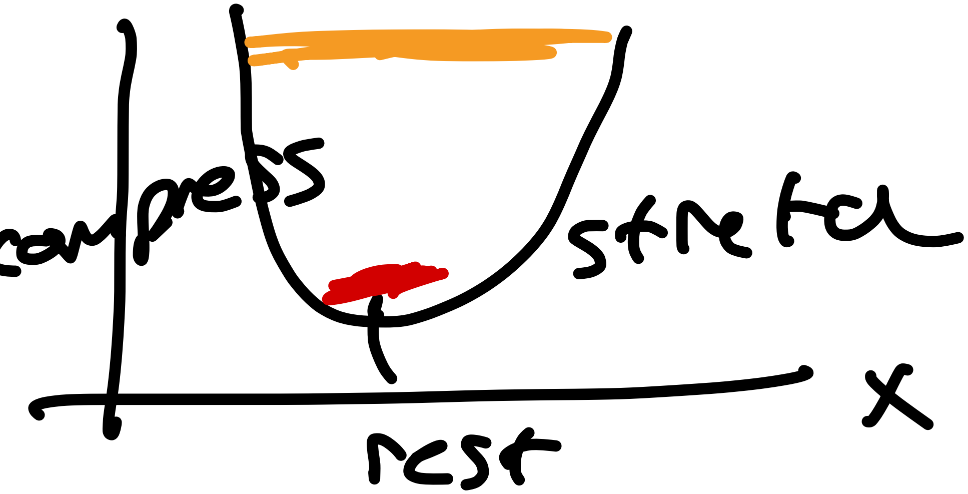
k_B Boltzmann's constant

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

$$\int P(x)\,dx = 1 \Rightarrow \frac{1}{Z} \int dx\, e^{-\mathcal{H}(x)/k_BT} = 1$$

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

Partition function

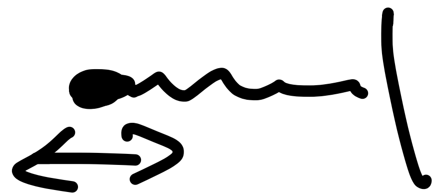


$$U(x) = \frac{1}{2}kx^2$$

$p = mv$

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

Harmonic oscillator



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

$$Z = \int_{-\infty}^{\infty} \underline{dp} \int_{-\infty}^{\infty} \underline{dx}\; e^{-\frac{1}{k_B T}\left[\frac{p^2}{2m} + \frac{1}{2} k x^2\right]}$$

$$= 2\pi k_B T \cdot \sqrt{m/k}$$

$$e^{A+B} = e^A e^B$$

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

$$\varepsilon \cdot t$$

$$= \int_{-\infty}^{\infty} dp\, e^{-p^2/2mk_BT} \int_{-\infty}^{\infty} dx\, e^{-\frac{kx^2}{2k_BT}}$$

gaussian

$$e^{-x^2/2\sigma^2} \qquad \frac{1}{\sqrt{2\pi\sigma^2}}$$

$$\sqrt{2\pi m k_B T} \qquad \sqrt{2\pi \frac{k_B T}{k}}$$

Z is a # $\rightarrow$ how does this tell us anything

Example $\langle \varepsilon_{total} \rangle = \langle \mathcal{H} \rangle$

$$\langle \varepsilon \rangle = \int dx\, P(x)\, \mathcal{H}(x) =$$

$$\frac{1}{Z} \int dx\, \mathcal{H}(x) e^{-\mathcal{H}(x)/k_B T}$$

$$\beta = (k_B T)^{-1}$$

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

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

$$\frac{d e^{ax}}{dx} = a e^{ax}$$

$$\frac{\partial Z}{\partial \beta} = \int dx \left(-\mathcal{H}(x)\right) e^{-\beta \mathcal{H}(x)}$$

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

for HO

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

for next time

What is $\langle \varepsilon \rangle$?