Lecture 1 - Introduction to Statistical Mechanics

What is statistical mechanics:

Chemists care about the behavior of collections of atoms & molecules

In principle, a system has an equation of motion, Newton/S.E.

If classical & initial conditions are known, all behavior is known

But: cannot solve Eqns of motion analytically for large N in most cases

Idea: Properties of a system only depend on a few macro variables eg N, V, T

Measure property like heat capacity or stiffness of an object and it is always same

So: properties must depend on <u>Average</u> over particle positions

Hence, we care about statistical properties of the system only

Average:

Suppose $\vec{X}$ represents the state of a system and $A(\vec{X})$ is something we can measure ("Observable")

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

If states are discrete as in QM: $\langle A \rangle = \sum_{i=1}^{n} A_i P(i)$

Clearly, need to know $P(\vec{x})$ and then if $P(\vec{x})$ is simple we can compute any average property of our system

Properties of Probability distribution

- $P(x) \leq 1$
- $P(x) \geq 0$
- $\int_{\text{all values}} d\vec{x}\, P(x) = 1$

Example: we will show that for constant N, V, T

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

$$\mathcal{H} = U + KE$$

Has to be normalized, let $1/Z$ be the const of prop. so

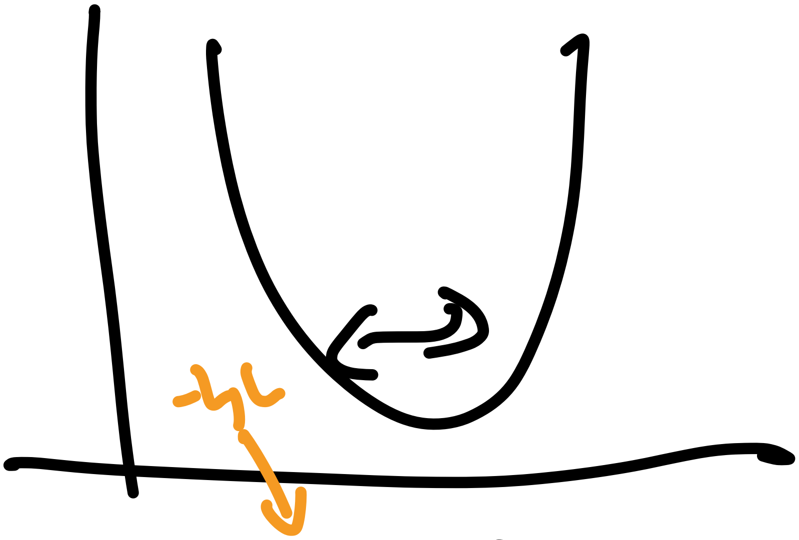
$$P(x) = e^{-\mathcal{H}(x)/k_BT}/Z$$

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

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

This is called the "partition function" and if we know it we can compute any property of the system

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



Harmonic Oscillator

$$Z = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp\, e^{-\frac{1}{k_BT}\left[\frac{1}{2m}p^2 + \frac{1}{2}kx^2\right]}$$

$$= \underbrace{\int_{-\infty}^{\infty} dv\, e^{-\frac{1}{2k_BTm}p^2}}_{\sqrt{2\pi k_BTm}} \int_{-\infty}^{\infty} dx\, e^{-\frac{k}{2k_BT}x^2}$$

$$\sqrt{2\pi k_BTm}\,\sqrt{2\pi\frac{k_BT}{k}}$$

$\left[\omega = \sqrt{k/m}\right.$

$$= 2\pi k_BT \cdot \sqrt{\frac{m}{k}} = 2\pi\frac{k_BT}{\omega}$$

units $E \cdot t$

How does this help us calculate properties? Just a number...

Want Eg $\langle E \rangle$

$$\langle E_{tot} \rangle = \langle H \rangle = \frac{\int d\vec{x}\, \mathcal{H}(\vec{x})\, e^{-\mathcal{H}(x)/k_B T}}{\int dx\, e^{-\mathcal{H}(x)/k_B T}}$$

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

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

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

This means $-\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \langle H \rangle$

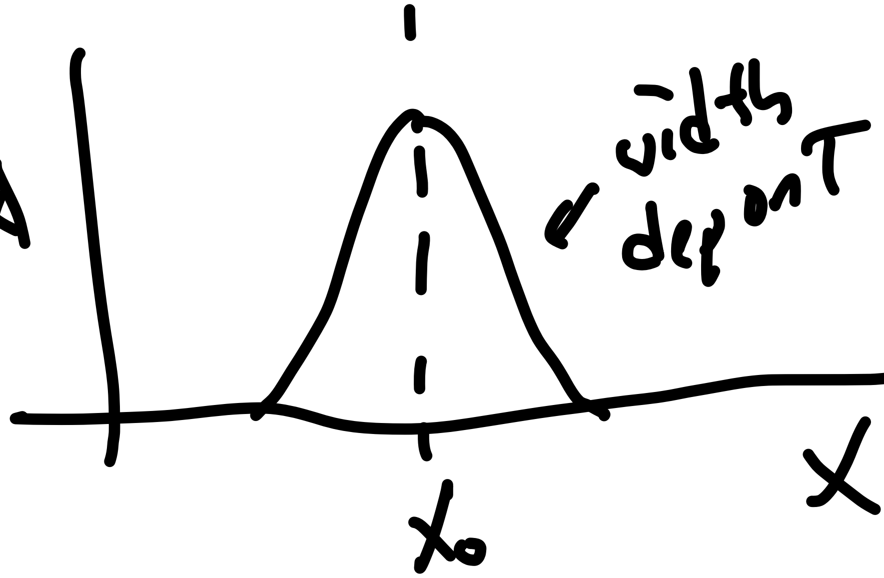
and $= -\frac{\partial \ln Z}{\partial \beta} = \langle \varepsilon \rangle$

For H.O., $Z = \frac{k_B T}{\omega} \cdot 2\pi = \frac{2\pi}{\omega \beta}$

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

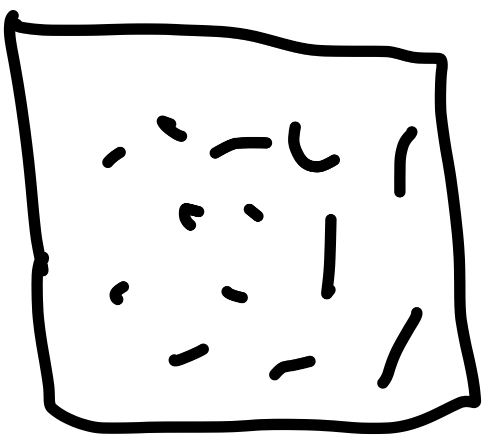
$\langle \varepsilon \rangle = \frac{1}{\beta} = \underline{\underline{k_B T}}$ doesn't depend on ω

Very important physical fact



HW: Show for N H.O. that $\langle E_{tot} \rangle = N k_B T$ from derivative of Z

Where does $P(x) \propto e^{-\beta \mathcal{H}}$ come from? Have to first consider a system of particles in box



N, V

closed system

1st law of thermodynamics

$d\mathcal{E} = \delta q + \delta w$

energy in

work done

for this system $d\mathcal{E} = 0$!

$\mathcal{E}$ is constant (or SE)

Particles obey Newton's Law

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

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

$$x_2 = x_1 + vt$$

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

$$v_2 = v_1 + at$$

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

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 $\vec{X} = \{\vec{q}, \vec{p}\}$ where

$q_i \in$ box (eg $0 \le q \le L$) $\forall i$

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

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

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

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

So for N, V, E

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

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

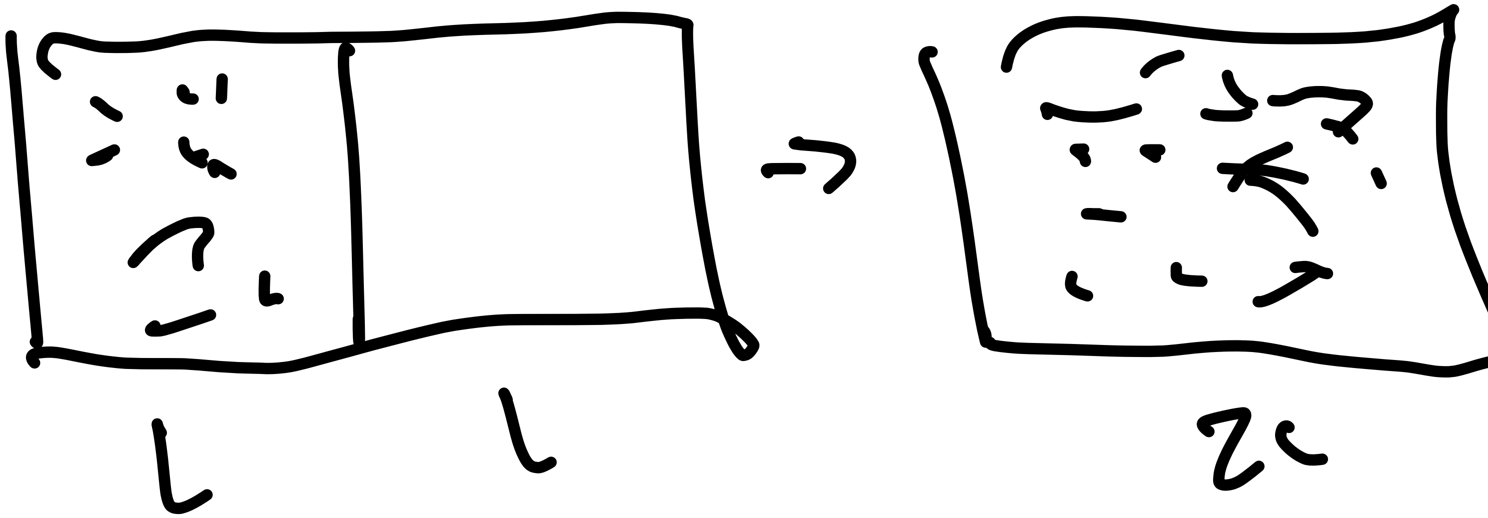
Take snapshots X_i, p_i

and to average, do

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

Does this work for any initial conditions?

What about



Mystery, why does gas only spread out and not go back

2nd law $dS \geq 0$ (more later)

Does this try count? ...