Lecture #1:

Introduction to Statistical Mechanics

First:

1. Introduction, my background and current position
2. Survey
3. Quick, stand & introduce selves to eachother
4. Go through syllabus

What is statistical mechanics?
(statistical physics, statistical thermo ...)

In chemistry we are interested in atoms & molecules:
how molecules interact with one another

We know properties of atoms & small molecules in isolation can be computed using QM

Most chemistry experiments involve large collections of molecules, $\sim \mathcal{O}(10^{23})$, so we cannot compute anything about this

directly using QM or even
Classical Mechanics (Newton)

However! we know many
properties of systems can be
measured that have nothing to
do with the precise coordinates
of all the 10^{23} molecules in a box
(e.g. phase transition temperature,
heat capacity)

Hence we might surmise these
properties arise when averaging
some quantity over all the possible
positions of every molecule in the system
(lets assume no reactions for now)

In this class:

look @ how measurable quantities arise for systems of molecules

connect classical mechanics with

① thermodynamic quantities (e.g. entropy, free-energies, heat capacities etc) → emerge from avg interactions

② look at non-thermodynamic properties such as spectra, rates of going between states

③ learn about how computer simulations can help generate solutions for problems that cannot be solved exactly

<u>Real examples</u>

① What is the structure of a liquid, and how does this connect to how it is measured

(2) general principles of how polymers behave in solution, including how proteins fold

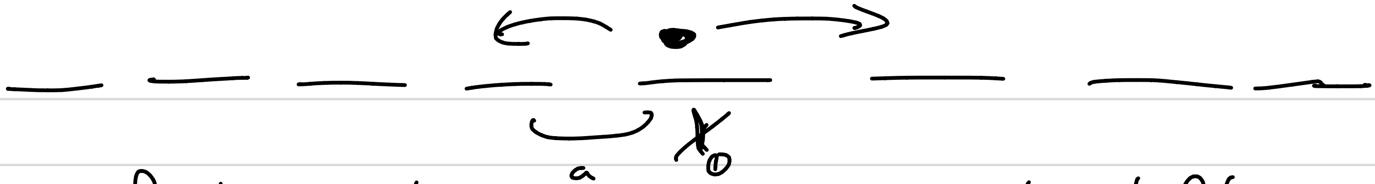
(3) how do things; melt, freeze self assemble, how does this depend on dimension? (eg confinement)

Crucial to understand statistical quantities used in this class,

Real example, diffusion:

later we may cover diffusion in 3D, particle w/ brownian motion, Einstein 1905

Consider the simpler case of something trapped in one dimension



moves distance "a" with prob p to left or right, lets call $p = 1/2$

How far does it get in T steps on avg?

This is the same as flipping a coin N times

particular time seq might be:

$$\text{moves} = \{\overset{m_1}{L}, \overset{m_2}{R}, R, R, L, \ldots\} = \{m_i\}$$

$$\text{trajectory, seq of positions: } \{\overset{x_0}{0}, \overset{x_1}{-a}, \overset{x_2}{0}, a, 2a, 1a, \ldots\} = \{x_i\}$$

time avg:

$$\langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \sum_{i=1}^{T} A(x_i)$$

$$\text{displacement } d_i = \sum_{j=1}^{i} m_j = aN_+^i - aN_-^i$$

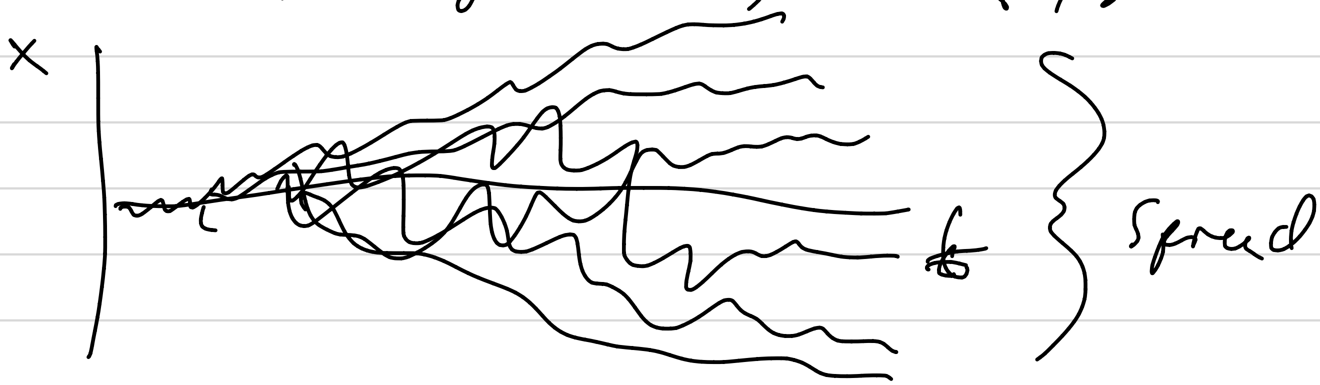
$$\langle d_T \rangle = \lim_{T \to \infty} \frac{1}{T} \sum_{i=1}^{T} aN_+^i - aN_-^i \sim [ap - a(1-p)]T^{\to \infty}$$

$$\approx a[2p-1]T$$

$$= 0 \text{ if } p = 0$$

order didn't matter

however, if you actually do expt, you will find



Measure this by RMS d, $\langle d^2 \rangle$

this is an avg over many trials

for most problems in stat mech, we will imagine many copies of the system w/ diff init conditions / random seeds

Then we perform an "ensemble" avg

$$\langle A \rangle_{ensemble} = \sum_{\substack{n \\ \text{states}}} P_n A_n \quad \star$$

for this problem & others, we expect

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

if this is true for any A, it is

called ~~an~~ "ergodic" system

Usually, cannot show a system is ergodic but we believe it to be true for most systems

$$d_T = \sum_{i=1}^{T} a m_i \sim a N_+ - a N_-$$

$$P_{N+} = \binom{T}{N_+} \underbrace{p^{N^+}(1-p)^{T-N^+}}_{(1/2)^T} \propto \text{num sequences with } N_+$$

$\langle N_+ \rangle \to Tp = T/2, \quad \langle d_T \rangle = a(T/2) - a(T/2) = 0$

$$\langle (d_T)^2 \rangle = a^2 \langle (N_+ - N_-)^2 \rangle$$

$N_- = T - N_+$

$$= a^2 \langle (2N_+ - T)^2 \rangle = a^2 \langle (4N_+^2 - 4N_+ T + T^2) \rangle$$

$$= a^2 (\langle 4N_+^2 - \underset{4T^2}{4N_+ T} + \underline{T^2} \rangle)$$

$$\text{Var } N_+ = Tp(1-p) = \langle N_+^2 \rangle - \langle N_+ \rangle^2$$

$$- T^2 p^2 (1-p)$$

$$\Rightarrow \langle N_+^2 \rangle = Tp(1-p) + T^2 p^2 \quad \propto T^2$$

$$= a^2 (4(Tp(1-p) + 4T^2 p^2 - 4T^2 p + T^2$$

$$+ 4T^2 p(1-p) + T^2$$

$$\langle d^2 \rangle \propto T^2 \Rightarrow \sqrt{\langle d^2 \rangle} \propto T$$

This is an example of a standard deviation, def^n

$$\sigma^2 = Var(\underset{\sim}{X}) \equiv \frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2$$

where $\underset{\sim}{X} = \{x_1, x_2, \dots, x_N\} = \{x_i\}$

and $\mu = \frac{1}{N}\sum_{i=1}^{N} x_i$

Important:

$$\frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2 = \frac{1}{N}\sum(x_i^2 - 2x_i\mu + \mu^2)$$

$$= \underbrace{\frac{1}{N}\sum x_i^2}_{\langle x^2\rangle} - 2\mu \underbrace{\sum x_i}_{\mu} + \frac{1}{N}\underbrace{\sum \mu^2}_{N\mu^2}$$

$$= \langle x^2\rangle - \mu^2 = \langle x^2\rangle - \langle x\rangle^2$$

① $\boxed{Var(x) = \langle x^2\rangle - \langle x\rangle^2}$

② $Var(x) \geq 0 \Rightarrow \langle x^2\rangle \geq \langle x\rangle^2$ *

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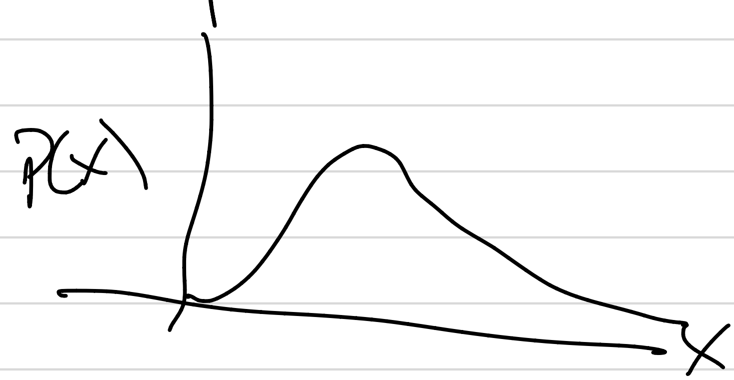
Measurements X_i are assumed to come from an underlying probability distribution $P(X)$, eg



Properties:

① likelyhood $X \in (a,b) = \int_a^b P(x)\,dx$

② normalized, $\int_{-\infty}^{\infty} P(x)\,dx = 1$

← or range of def^n

Avg: $\langle A \rangle = \int A(x)\,P(x)\,dx$

Mean: $\mu = \langle x \rangle = \int x\,P(x)\,dx$

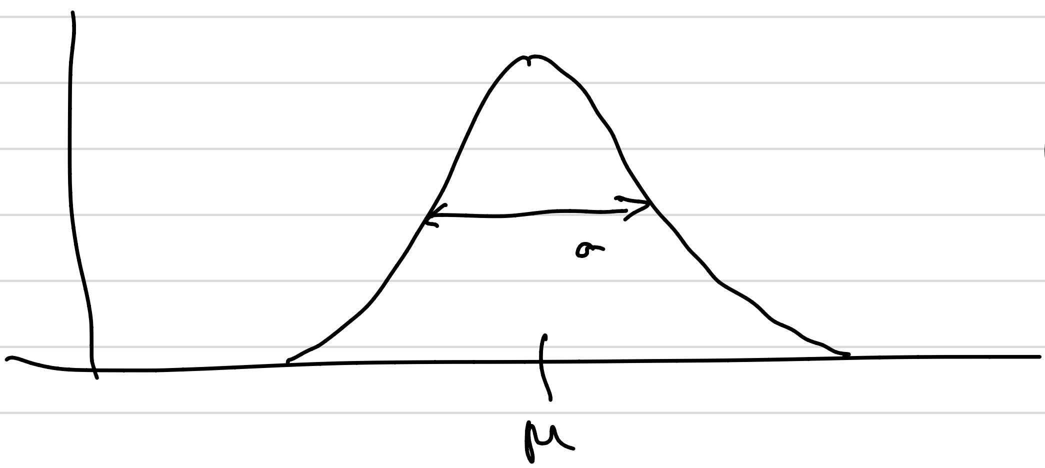
Var: $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = \int x^2 P(x)\,dx - \mu^2$

$= \int (x-\mu)^2 P(x)\,dx$

Very important distribution,

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2} \sim \mathcal{N}(\mu, \sigma^2)$$

normal distribution



(HW, prove normalization const)

Central limit theorem!

Suppose x_i from any $P(x)$

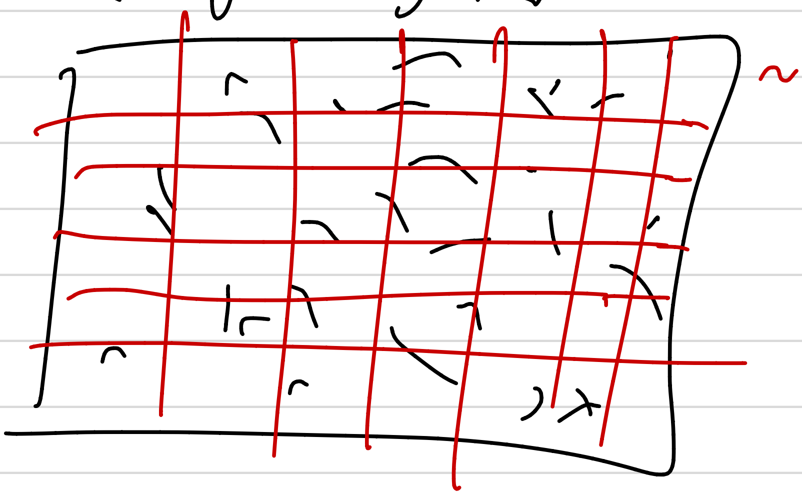
Sample mean $\mu_N = \frac{1}{N}\sum_{i=1}^{N} x_i$

$$P(\mu_N - \mu) \xrightarrow[N\to\infty]{} \mathcal{N}(0, \sigma^2/N)$$

which means avg error on mean

$\langle(\mu_N - \mu)^2\rangle = \sigma^2/N \rightarrow$ std dev of mean $\propto 1/\sqrt{N}$

In stat mech, we imagine taking our large system



$N_{boxes} = V/\xi^d$

$\propto N_{molecules}$

Compute A_i on avg subsystem

Then $\sqrt{\langle A - \langle A \rangle \rangle^2} \sim 1/\sqrt{N}$

Hence for a large system we always measure the avg quantity

(if ξ can be sufficiently small)