

Phase Space volume is conserved:

$$\frac{dP(\underline{p}, \underline{q}, t)}{dt} \rightarrow \text{Total time derivative of phase space density is zero}$$

What is equilibrium:

$$\langle O(\underline{p}, \underline{q}) \rangle = \text{Time independent}$$

$$\downarrow \text{Ensemble average} = \int P(\underline{p}, \underline{q}, t) O(\underline{p}, \underline{q}) d\Gamma$$

\downarrow
 $P_{eq}(\underline{p}, \underline{q})$

$$P_{eq} \equiv P_{eq}(H) \rightarrow \text{Hamiltonian of the system}$$

$$H \rightarrow \text{Constant of motion} \quad \frac{dH}{dt} = 0$$

$$E = H \Rightarrow P_{eq} \sim \delta(H - E)$$

Canonical ensemble, $P_{eq} \sim e^{-\beta H}$ $\beta = \frac{1}{k_B T}$ \rightarrow Boltzmann distribution

Microcanonical ensemble

Isolated System

(N, V, E)

First Postulate of Statistical Mechanics:

Time average = Ensemble average

↘ Distribution fn $P(\underline{p}, \underline{q}) \rightarrow$ System following classical mechanics
But if the system is quantum mechanical
↘ eigenfunctions and energy eigen values

$$\langle X \rangle = \frac{1}{N} \sum_{i=1}^N p_i x_i$$

$$\langle x \rangle = \frac{\sum p_i x_i}{\sum p_i} \quad \sum p_i = N$$

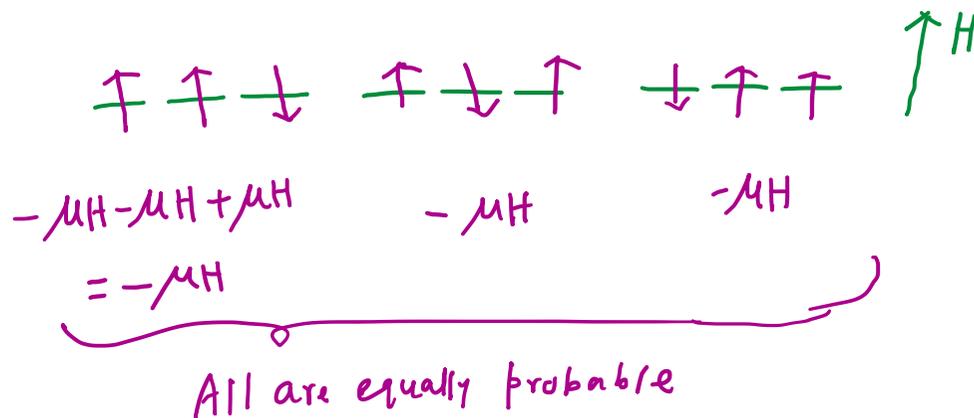
Microcanonical ensemble:

Postulate of equal a priori

Systems of the ensemble are distributed uniformly, that is with equal probability over all possible microscopic states of the system. In the language of time trajectory, each state is visited an equal number of times if waited enough.

$$E = -\mu H$$

$H \rightarrow$ Magnetic field
 $\mu \rightarrow$ Magnetic moment



Ergodic Hypothesis:

During its trajectory, in phase space, a system is free to explore all the microscopic states and given a sufficiently long period of time, spends time in a state that is proportional to the volume of the phase space.

state in

$$dpdq \sim h \rightarrow \text{Planck's Const}$$

$$d^{3N}p d^{3N}q \sim h^{3N}$$

→ smallest vol^m element



Energy landscape of glass
(Rugged energy landscape)

"Non-ergodic"

^ Supercooled liquid ^

n possible outcomes, each with probability p_j , where $j=1, 2, \dots, n$

If the experiment is repeated indefinitely,

→ Discrete prob. distribution

$$p_j = \lim_{N \rightarrow \infty} \frac{N_j}{N} \quad j=1, 2, \dots, n$$

$N_j \rightarrow$ is the # of times of outcome j

$N \rightarrow$ total # of repetitions of the expt.

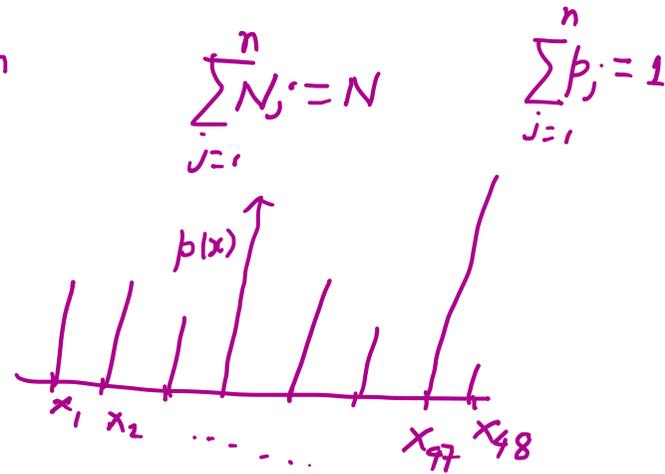
Average x

$$\langle x \rangle = \sum_{j=1}^n x_j p_j$$

↓
First moment of this distribution

$$\langle x^2 \rangle = \sum_{j=1}^n x_j^2 p_j$$

↳ second moment



Second central moment or Variance:

$$\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle = \sum_{j=1}^n (x_j - \langle x \rangle)^2 p_j \rightarrow \text{positive definition}$$

↳ measure of the spread of the distribution

$$\sigma_x^2 = \sum_{j=1}^n (x_j^2 - 2x_j \langle x \rangle + \langle x \rangle^2) p_j = \underbrace{\sum_{j=1}^n x_j^2 p_j}_{\langle x^2 \rangle} - 2 \underbrace{\left(\sum_{j=1}^n x_j p_j \right)}_{\langle x \rangle} \langle x \rangle + \langle x \rangle^2 \underbrace{\sum_{j=1}^n p_j}_1$$

$$= \langle x^2 \rangle - 2\langle x \rangle^2 + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2 \geq 0$$

$$\langle x^2 \rangle \geq \langle x \rangle^2$$

Continuous distribution

$$\text{Prob}(x, x+dx) = p(x) dx$$
$$-\infty \leq x \leq \infty$$

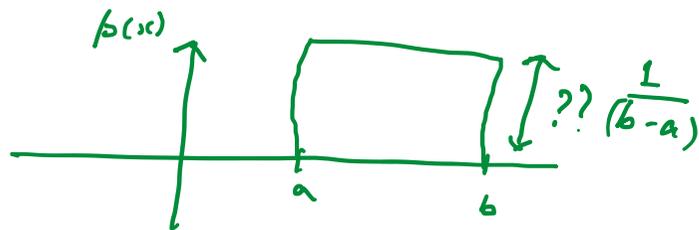
$$\int_{-\infty}^{+\infty} p(x) dx = 1 \quad (\text{normalized / total prob} = 1)$$
$$\int_{-\infty}^{+\infty} x p(x) dx = \langle x \rangle$$
$$\int_{-\infty}^{+\infty} x^2 p(x) dx = \langle x^2 \rangle$$
$$\int_{-\infty}^{+\infty} x^n p(x) dx = \langle x^n \rangle \rightarrow n^{\text{th}} \text{ moment}$$

Example:

$$p(x) = A \quad a \leq x \leq b$$
$$= 0 \quad \text{otherwise}$$

$$\int_a^b p(x) dx = A \int_a^b dx = 1 \Rightarrow A(b-a) = 1$$
$$\text{or } A = \frac{1}{(b-a)}$$

$$\langle x \rangle = \frac{1}{(b-a)} \int_a^b x dx = \frac{1}{(b-a)} \left[\frac{x^2}{2} \right]_a^b = \frac{b^2 - a^2}{2(b-a)} = \frac{1}{2}(b+a)$$



$$\langle x^2 \rangle = \frac{1}{b-a} \int_a^b x^2 dx = \frac{1}{(b-a)} \frac{1}{3} (b^3 - a^3) = \frac{(b-a)(b^2 + ab + a^2)}{3(b-a)} = \frac{1}{3} (b^2 + ab + a^2)$$

Variance

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{3} (b^2 + ab + a^2) - \frac{1}{4} (b + 2ab + a^2)$$

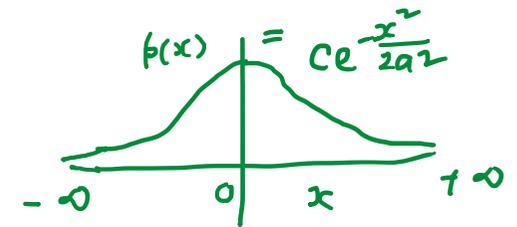
$$= \frac{(b-a)^2}{12}$$

$$\sqrt{\sigma_x^2} = \text{Standard deviation}$$

$$= \frac{1}{\sqrt{12}} (b-a)$$

* Most common continuous prob. distribution \rightarrow Gaussian or a normal distribution

$$p(x) = C e^{-x^2/2a^2} \quad -\infty < x < \infty$$



$$\int_{-\infty}^{+\infty} p(x) dx = 1 = C \int_{-\infty}^{+\infty} e^{-\frac{x^2}{2a^2}} dx$$

$$1 = C \sqrt{\pi} \frac{1}{\sqrt{\frac{1}{2a^2}}}$$

$$1 = C \sqrt{\pi} \sqrt{2} a$$

$$\Rightarrow C = \frac{1}{\sqrt{2\pi a^2}}$$

$\langle x \rangle = ?$ $\langle x^3 \rangle = 0$ $\langle x^n \rangle = 0$ if n is odd (Integration of an odd integrand within symmetric limits)

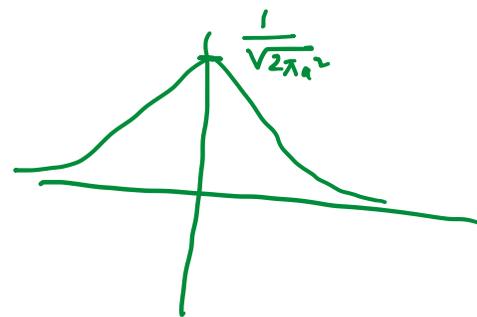
$$\alpha \equiv \frac{1}{2a^2}$$

Standard Integral

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}}$$

$$p(x) = \frac{1}{\sqrt{2\pi a^2}} e^{-\frac{x^2}{2a^2}}$$

at $x=0$ $p(0) = \frac{1}{\sqrt{2\pi a^2}}$



$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 \frac{1}{\sqrt{2\pi a^2}} e^{-\frac{x^2}{2a^2}} dx = \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{+\infty} x^2 e^{-\frac{x^2}{2a^2}} dx$$

$$I = \int_{-\infty}^{+\infty} e^{-\alpha x^2} = \left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}}$$

$$\frac{dI}{d\alpha} = \int_{-\infty}^{+\infty} -x^2 e^{-\alpha x^2} \Rightarrow \int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} = -\frac{dI}{d\alpha} = +\frac{1}{2} \sqrt{\pi} \alpha^{-3/2} = \frac{1}{2\alpha} \left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}}$$

$$\alpha \equiv \frac{1}{2a^2}$$

$$\langle x^2 \rangle = \frac{1}{\sqrt{2\pi a^2}} \frac{1}{2 \cdot \frac{1}{2a^2}} \left(\frac{\pi}{\frac{1}{2a^2}}\right)^{\frac{1}{2}} = \frac{1}{\sqrt{2\pi a^2}} a^2 \sqrt{2\pi a^2} = a^2$$

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = a^2 - 0 = a^2 \Rightarrow f(x) = \frac{1}{\sqrt{2\pi \sigma^2}} e^{-\frac{x^2}{2\sigma^2}} \quad \sigma^2 \equiv \text{variance}$$