NO QUIZ TODAY

→ READ CHAP. 3

CLOSED SYSTEM (FIXED N, V, E)

→ MICROCANONICAL ENSEMBLE

PHASE SPACE (CLASSICAL) of N PARTICLES

$6N$ DIMENSIONAL $\vec{Q}$, $\vec{P}$

$$\vec{Q} = \{q_1, q_2, \dots q_{3N}\}$$

positions

$$\vec{P} = \{p_1, p_2, \dots p_{3N}\}$$

$\Omega(E)$ =: PHASE SPACE VOLUME OF ALL (MICRO) STATES WITH ENERGY E

CLASSICAL HAMILTONIAN

$$\Omega(E) = \int d\mathbb{P}\, d\mathbb{Q}\; \delta(E - \mathcal{H}(\mathbb{P}, \mathbb{Q}))$$

ENSEMBLE AVERAGE OF PROPERTY $\mathcal{O}$ "OBSERVABLE"

HAMILTONIAN

HAMILTONIAN

$$\langle O \rangle = \frac{1}{\Omega(E)} \int d\mathbb{P}\, d\mathbb{Q}\, \delta(E - \mathcal{H})\, O(\mathbb{P}, \mathbb{Q})$$

FREQUENTLY IT IS MORE CONVENIENT TO DEFINE $\Omega(E)$ AS THE LIMIT $\delta E \to 0$ OF A FINITE ENERGY SHELL WITH RANGE $(E, E + \delta E)$

$$\Omega(E) \cdot \delta E = \int_{E < \mathcal{H} < E + \delta E} d\mathbb{P}\, d\mathbb{Q}$$

$$\langle O \rangle = \frac{1}{\Omega(E)\, \delta E} \int_{E < \mathcal{H} < E + \delta E} O(\mathbb{P}, \mathbb{Q})\, d\mathbb{P}\, d\mathbb{Q}$$

$\Omega(E)$ typically $\propto \exp(E)$

$\delta E \propto E^0$ but even $\propto E^1$

IN THE LIMIT $N \to \infty$

$E \propto N$, WE CAN USE $\Omega(E)$ OR $\Omega(E)\delta E$ INTERCHANGARLY.

CLASSICAL HAMILTONIAN

$$H(\mathbb{P},\mathbb{Q}) = \frac{\mathbb{P}^2}{2m} + U(\mathbb{Q})$$

$$= \sum_{j=1}^{3N} \frac{p_j^2}{2m} + U(q_1, q_2, \dots q_{3N})$$

MATH ON PARTICLES

Example for U ALL PARTICLES ARE DISTINGUISHABLE → INDEX

$$U = \frac{1}{2} \sum_{\nu \neq \mu} U_{pair}(\vec{q}_\nu, \vec{q}_\mu)$$

atomic indices

$$+ \sum_{\nu=1}^{N} U_{ext}(\vec{q}_\nu)$$

IDEAL GAS

$$U(\mathbb{Q}) = \text{CONST} = 0$$

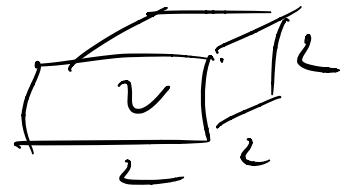
"PROCESS TOWARDS EQUILIBRIUM REQUIRES LONG TIME LIMIT BEFORE TURNING OFF WEAK INTERACTIONS"

$$\Omega(E)\,\delta E = \int_{E<\mathcal{H}<E+\delta E} dP\,dQ$$

$$= \int dQ \int_{E<\mathcal{H}<E+\delta E} dP$$

→ treat Q and P PART SEPERATELY

$$\int dQ = L^{3N} = V^N$$



$\rho(Q)$ FOR A PARTICULAR CONFIGURATION

$$\rho(Q) = \frac{1}{\int dQ} = \frac{1}{V^N}$$

N	0
$V/2$	$V/2$

V, N

1 particle : $\frac{V/2}{V} = \frac{1}{2}$

N particles : $\left(\frac{V/2}{V}\right)^N = \frac{1}{2^N} = \left(\frac{1}{2}\right)^N$

$N/2$	$N/2$
$V/2$	$V/2$

$$\binom{N}{\frac{N}{2}}\left(\frac{1}{2}\right)^{N/2}\left(\frac{1}{2}\right)^{N/2} = \dots$$

GENERALIZATION

$2N, 2V$

$N-m$	$N+m$
V	V

$$P_m = \frac{1}{2^N}\binom{2N}{N+m} = \frac{1}{2^N}\frac{(2N)!}{(N+m)!\,(N-m)!}$$

STIRLING FORMULA

$$n! = \left(\frac{n}{e}\right)^n \sqrt{2\pi n} \approx \left(\frac{n}{e}\right)^n$$

LEADING ORDER → BUT MESSES UP NORMALIZATION

WILL BE CORRECTED

2016

$\rightarrow$ FIX NORMALIZATION $\sum_m p_m = 1$

$$p_m = p_0 \frac{1}{\cancel{2^{2N}}} \frac{\left(\frac{\cancel{2}N}{\cancel{e}}\right)^{2N}}{\left(\frac{N+m}{\cancel{e}}\right)^{N+m}\left(\frac{N-m}{\cancel{e}}\right)^{N-m}}$$

$$= p_0 N^{2N} \underbrace{(N+m)^{-(N+m)}}_{N \gg m} \underbrace{(N-m)^{-(N-m)}}$$

$$= p_0 \cancel{N^{2N}} \cancel{N^{-(N+m)}} \left(1+\frac{m}{N}\right)^{-(N+m)} \cancel{N^{-(N-m)}} \times \left(1-\frac{m}{N}\right)^{-(N-m)}$$

$$= p_0 \underbrace{\left(1+\frac{m}{N}\right)^{-N}\left(1-\frac{m}{N}\right)^{-N}}_{\left(1-\frac{m^2}{N^2}\right)^{-N}} \left(1+\frac{m}{N}\right)^{-m}\left(1-\frac{m}{N}\right)^{+m}$$

$$= p_0 \left(1-\frac{m^2}{N^2}\right)^{-N}\left(1+\frac{m}{N}\right)^{-m}\left(1-\frac{m}{N}\right)^{+m}$$

$e^x \approx 1 + x + O(x^2) \quad x \ll 1$

SINCE $\frac{m}{N} \ll 1$!

$$= p_0 \cancel{\left(e^{+\frac{m^2}{N^2}}\right)^{+\frac{N}{2}}} \cancel{\left(e^{+\frac{m}{N}}\right)^{-m}} \left(e^{-\frac{m}{N}}\right)^{+m}$$

$$= p_0 e^{-\frac{m^2}{N}}$$

$$1 \overset{!}{=} \sum_{m=-N}^{N} p_m \approx \int_{-\infty}^{\infty} p_0 e^{-\frac{m^2}{N}} dm$$

$$= p_0 \sqrt{\pi N}$$

$$p_m = \frac{1}{\sqrt{2\pi}\,\frac{N}{2}} e^{-\frac{m^2}{2\left(\frac{N}{2}\right)}}$$

p_m is normal distribution

WITH MEAN $m = 0$

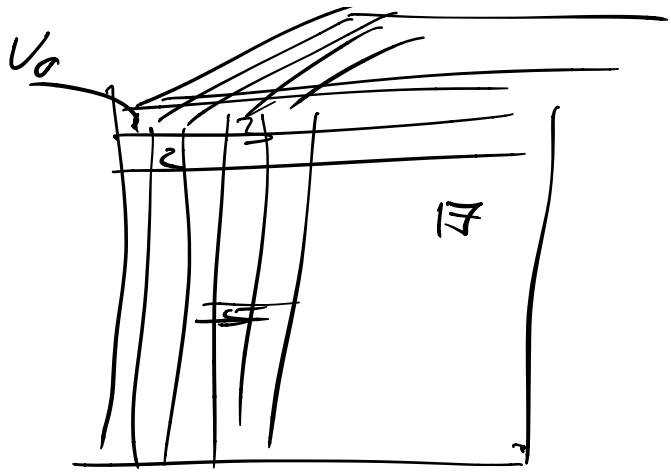
AND VARIANCE $\sigma^2 = \frac{N}{2}$

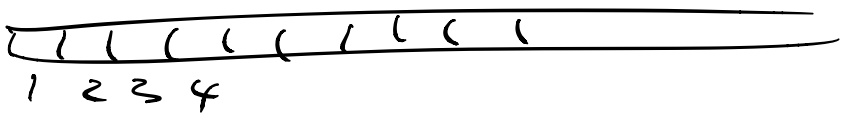
STANDARD DEVIATION is

$\propto \sqrt{N}$

RELATIVE DEVIATION $\propto \frac{1}{\sqrt{N}}$

$N \sim 10^{24}$ $\quad m \approx \sqrt{N} = 10^{12}$





ARRANGEMENT OF SMALL VOLUMES IS ARBITRARY

→ LAW 4. last

~~MICRO → $\left(\frac{W}{m}\right)$~~

CANONIC $Z = \sum_{\alpha} e^{-\beta E_\alpha}$