Statistical Ensemble

Property of collection of molecules

Statistical thermo - important properties average over molecular configurations

phase, optical properties, electronic physical properties

→ In a particular <u>State</u>

State set of thermo variables
(macro)

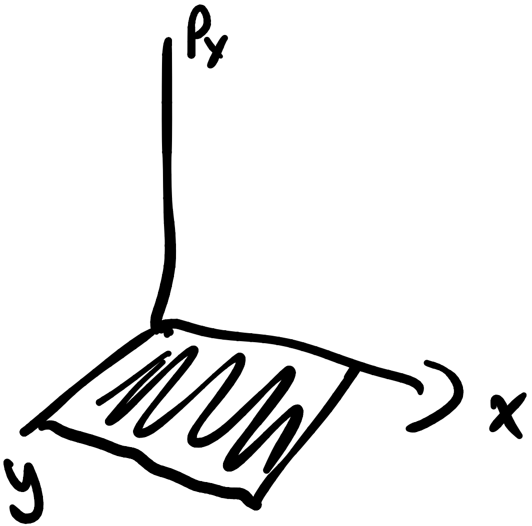
N, V, E N, V, T

N_1, N_2, N_3, P, T

$d+2$ variables to define a state

microstate particular arrangement
particular velocity/momentum

$6N_{tot}$ ← atoms
degrees of freedom



State
N, V, E

x, y, z inside a "box"
of size $L_x \cdot L_y \cdot L_z = V$

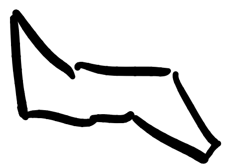
$E_{total} = KE + PE$

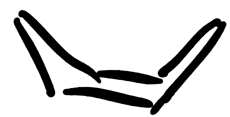
$\frac{1}{2} m (v_x^2 + v_y^2) \leq E_{total}$ (bonds constraints

1 atom in 2d

Averages

Enumerate every state of system





C_6H_{12} - 3.18 $\rightarrow$ 2 important states

possible states is $2 \cdot 2 \cdot 2 \cdots 2$

$= 2^N$

distinguishable states $2^N/N!$

N molecules

m boat

N-m chair

$$\varepsilon = m \cdot \varepsilon_{boat} + (N-m)\varepsilon_{chair}$$

Enumerate states

Average of $O(\text{state})$

$$\langle O \rangle = \sum_{i=1}^{M_{\text{states}}} O_i P_i$$

$$\vec{X} = \{x_1\ y_1\ z_1 \ldots \ldots x_N\ y_N\ z_N\}$$

or

$$= \int dx_1 dy_1 dz_1 \ldots\ldots dx_N dy_N dz_N \ldots dp_x^1 dp_y^1 dp_z^1 \ldots\ldots dp_x^N dp_y^N dp_z^N \left[O(\vec{X}) P(\vec{X}) \right]$$

$$\int d\vec{x}^{3N} d\vec{p}^{3N}\, O(\vec{X},\vec{P})\, P(\vec{X},\vec{P})$$

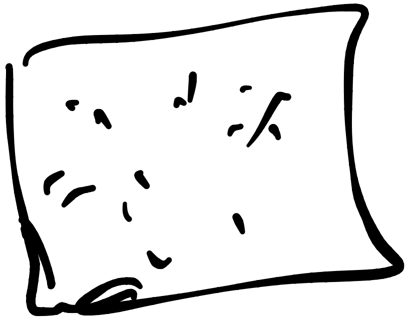
How likely is each microstate

→ depends on type of state

$$\underbrace{N, V, E}_{\text{Microcanonical Ensemble}} \qquad \underbrace{N, V, T}_{\text{Canonical Ensemble}}$$

Isolated

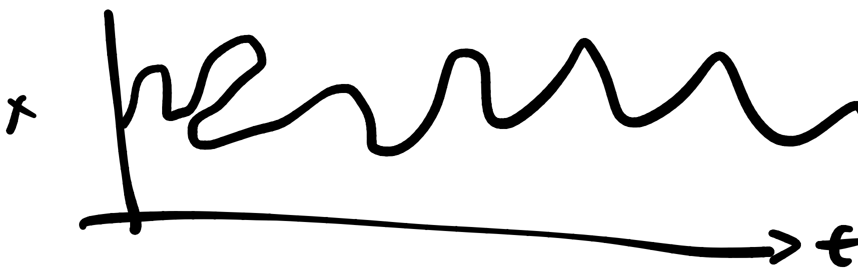
N, V, E - isolated



Newton's equations

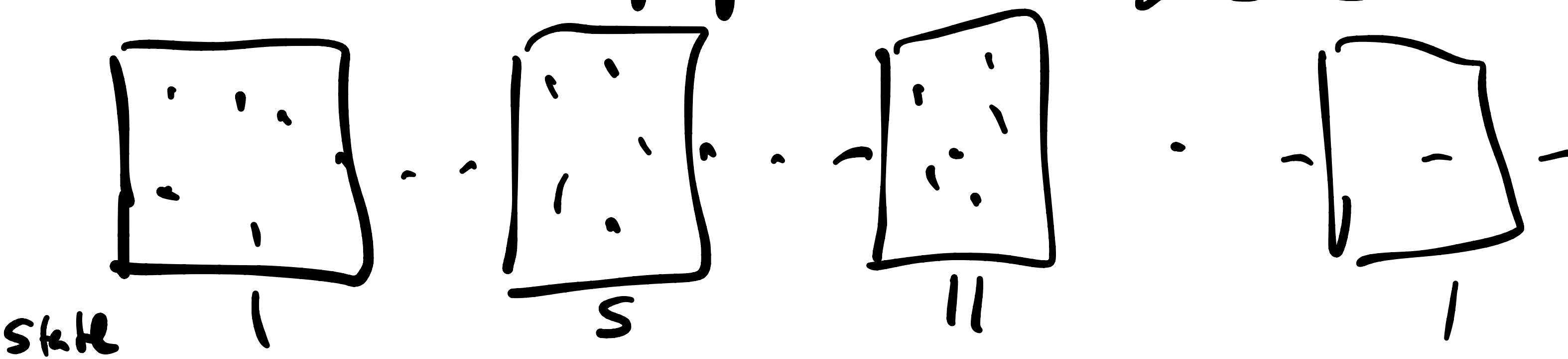
$$\vec{F} = m\vec{a}$$

know $\vec{X}_0^{3N}, \vec{P}_0^{3N}$



Ensemble "many" copies of system
all in possible configurations
correct proportion

A copies



how likely is state k?

$$P_k = \frac{M_k}{A}$$

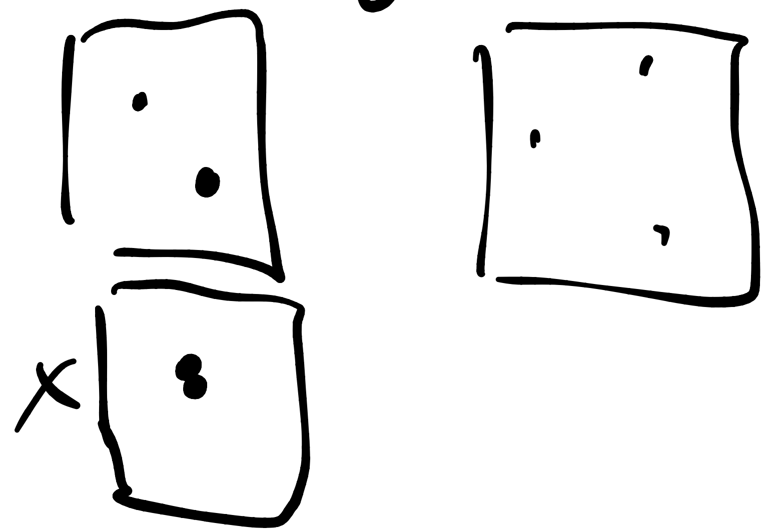
M_k: how many k

$$\sum_{k=1}^{\#\,\text{possible}} M_k = A$$

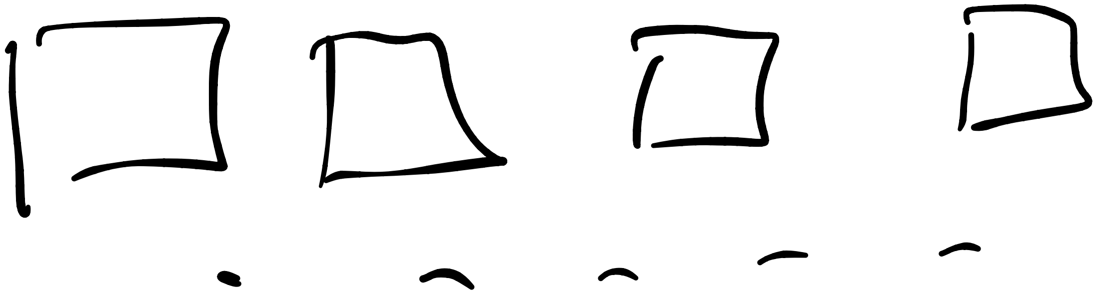
Microcanonical Ensemble

Every microstate equally likely

$\underline{N}, \underline{V}, \underline{E}$



Ensemble



entropy: $S = k_B \ln W$

Statistically state ensemble will maximize entropy

$$W = \frac{A!}{M_1!\, M_2!\, M_3! \cdots M_{\#}!}$$ (multinomial distribution)

A copies

order them in $A!$

possible states, can't distiguish $M_1, M_2 \ldots$

maximize S : $\frac{\partial S}{\partial M_k} = 0$ for each k

$\Rightarrow$ makes M_k as large as possible for every k

Maximize $f(x)$ constraint

$h(x) = h$

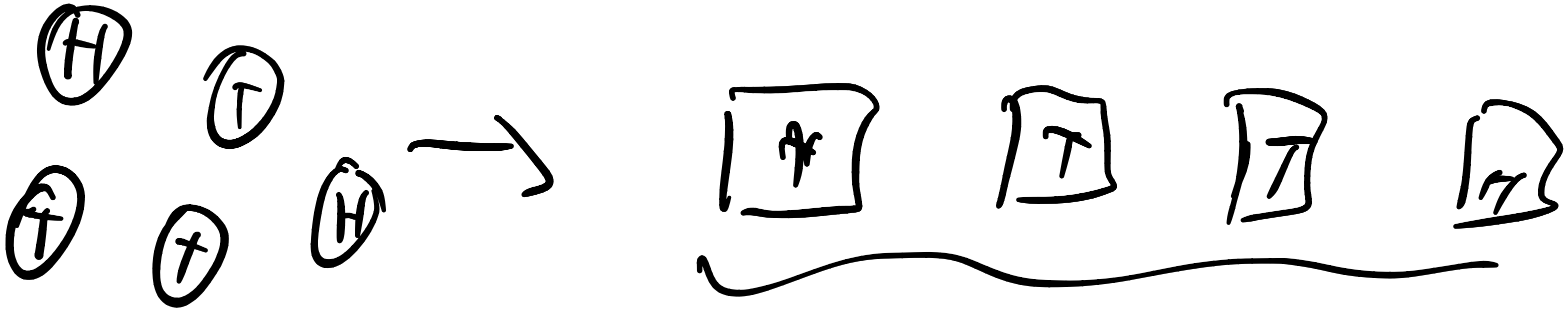
$$g(x, \alpha) = f(x) - \alpha(h(x) - A)$$

maximize g instead of f

Lagrange multipliers

$$\partial g / \partial x = \frac{\partial f(x)}{\partial x} - \frac{\partial}{\partial x}\left(\alpha(h(x) - h)\right) = 0$$

$$\partial g / \partial \alpha = 0 = h(x) - h \Rightarrow h(x) = h$$



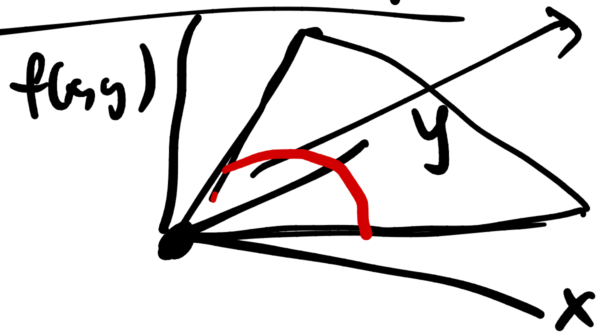
100,000

$$W = \frac{100{,}000!}{M_H!\,M_T!}$$

$$g = S = k \ln W - \alpha\left(M_H + M_T - 100000\right)$$

$$\frac{\partial \ln W}{\partial M_H} = 0 \qquad \frac{\partial \ln W}{\partial M_T} = 0 \qquad \frac{\partial g}{\partial \alpha} = 0 \Rightarrow M_H + M_T = 100000$$

Classic Example



If $x^2+y^2=1$

$f(x,y) = x+y$

where is this max or min

$\frac{\partial f}{\partial x} = 1 \qquad \frac{\partial f}{\partial y} = 1$

$$g(x,y) = \underbrace{f(x,y)}_{x+y} - \alpha(x^2+y^2-1)$$

$$\frac{\partial g}{\partial x} = 1 - 2\alpha x^* = 0 \quad \Rightarrow x^* = 1/2\alpha$$

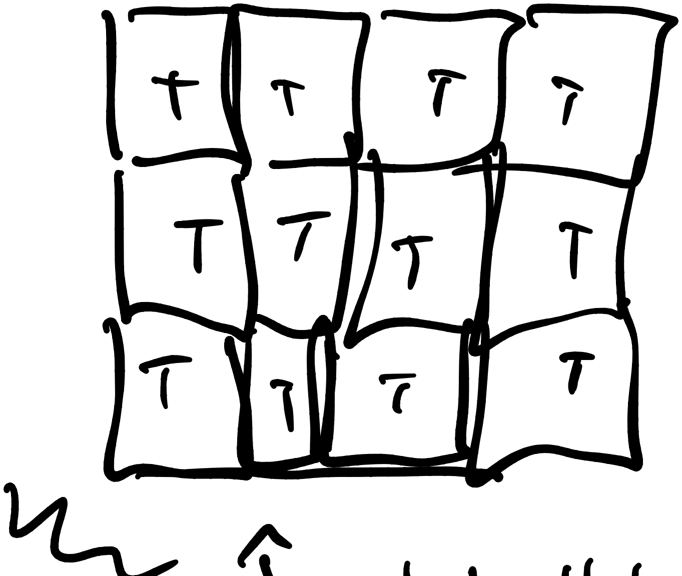
$$\frac{\partial g}{\partial y} = 1 - 2\alpha y^* = 0 \quad y^* = 1/2\alpha$$

$$\frac{\partial g}{\partial \alpha} = x^{*2} + y^{*2} - 1 = 0$$

$$\frac{1}{4\alpha^2} + \frac{1}{4\alpha^2} - 1 = 0 \Rightarrow \alpha = \pm 1/\sqrt{2}$$

f is max at $\sqrt{2}/2, \sqrt{2}/2$ if $x^2+y^2=1$

Canonical Ensemble (ch 10)



$\mathcal{A}$ copies

→ can exchange energy

N, V, E

whole thing isolated

How likely is a microstate

$$S(M_1, M_2, \ldots, M_\#)$$
$$- \alpha \left(\sum M_i - A \right)$$
$$- \beta \left(\sum M_i \varepsilon_i - \varepsilon_{tot} \right)$$

Boltzmann distribution

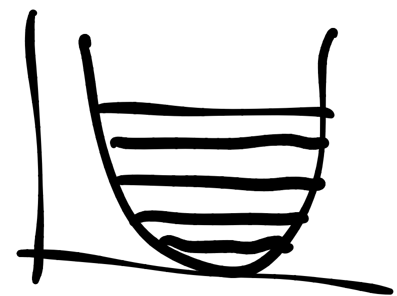
Maximize: $P_i = \frac{M_i}{A} \propto e^{-\beta \varepsilon_i}$

$\sum P_i = 1$

$$P_i = e^{-\beta \varepsilon_i} \Big/ \sum_{i=1}^{\#} e^{-\beta \varepsilon_i}$$

$$Q = \sum_i e^{-\beta \varepsilon_i} = \sum_i e^{-\varepsilon_i / k_B T}$$

partition function



$$\varepsilon_n = h\nu\left(\tfrac{1}{2} + n\right)$$

turns out $\beta = 1/k_B T$

$$w_i = e^{-\beta \epsilon_i}$$

relative weight

$$P_i = w_i / Q = e^{-\beta \epsilon_i} \Big/ \sum_i e^{-\beta \epsilon_i}$$