Statistical connection between microscopic & macroscopic properties

Microscopic (atomistic) - molecular properties

x, y, z of each atom or $v_x, v_y, v_z \ldots$

spin of each of each atom

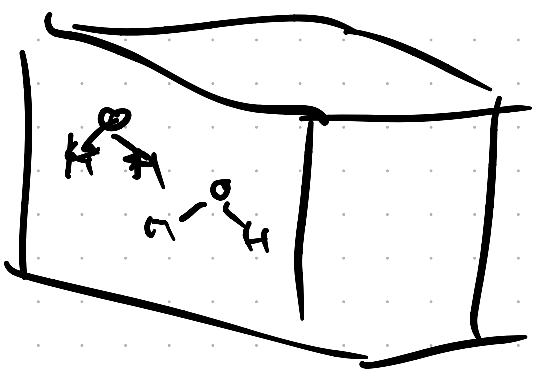
Macroscopic (Thermodynamic)

T, P, heat capicity, coefficient of thermal expansion

Macrostates - characterizes the thermodynamic system

$N, V, T \qquad N, p, T$

Microstate - particular configuration of your system



N_{H_2O}, $V = 1\,l$

$T = 25°C$

x_1, y_1, z_1

x_2, y_2, z_2

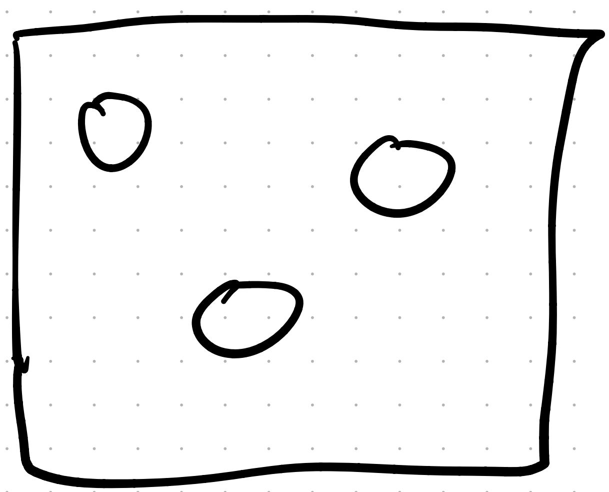
$\vdots$

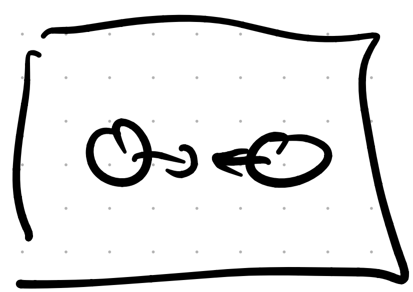
x_N, y_N, z_N

<u>Ergodicity</u> explores all accessible states in ∞ time

<u>Ergodic hypothesis</u> systems are big enough that they're effectively ergodic

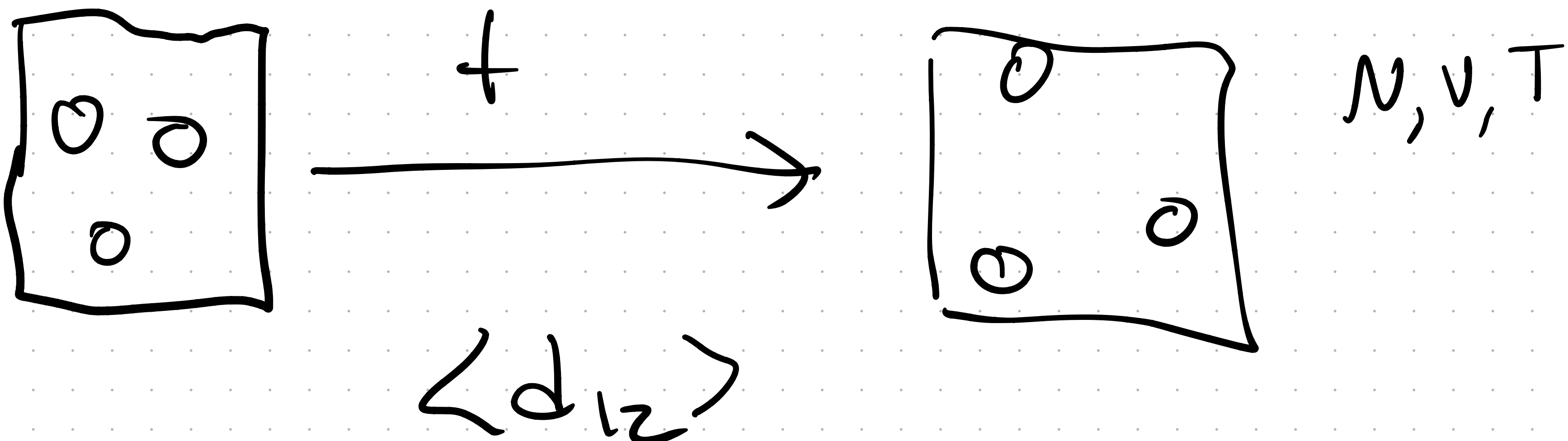
Billiard Ball Problem

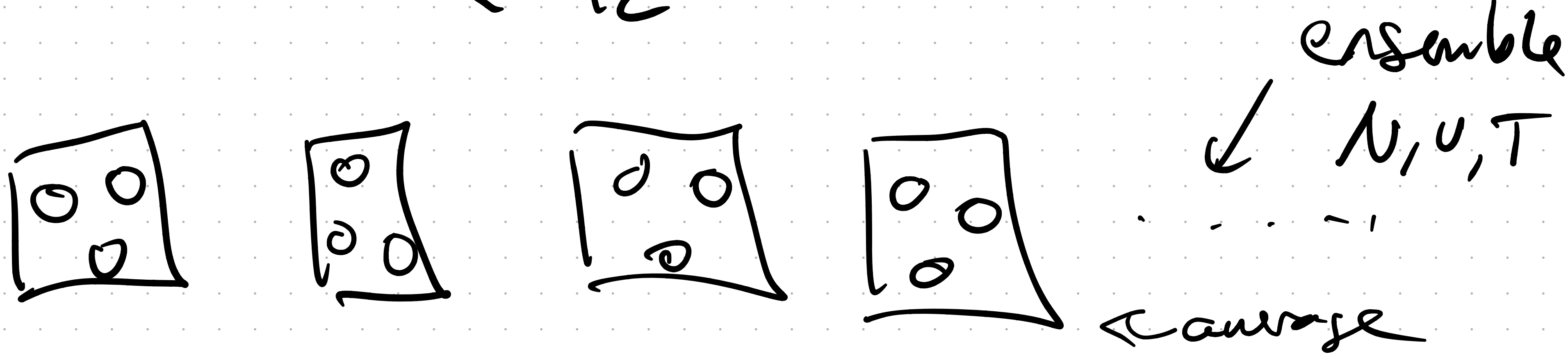




Ensemble Method

If you have many copies of a system
average a property over that ensemble
Same answer as 1 system for $t \to \infty$





have been talking about continuous systems

meaning, $\vec{x}, \vec{y}, \vec{z}$

start with discrete systems

discrete number of possible states

Consider a system that can be

in <u>M</u> microstates

<u>A</u> total copies

State →	5	7	11	...	$m/3$
	1	2	3		A

N_i is the # in state i

$$\sum_{i=1}^{m} N_i = A$$

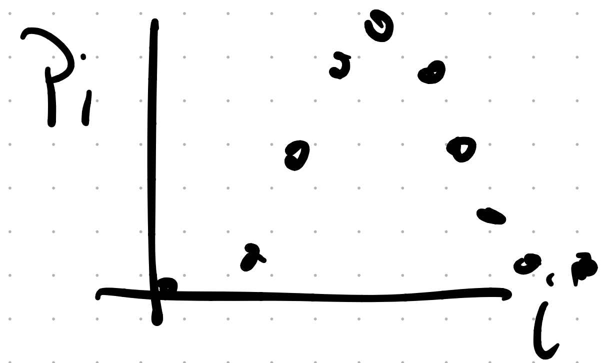
$$\{N_i\} = \{N_1, N_2, \ldots, N_m\}$$

$$\{P_i\} = \{P_1, \ldots P_m\} = \left\{\frac{N_1}{A}, \frac{N_2}{A}, \ldots \frac{N_m}{A}\right\}$$

$m = 6$

Ensemble Average

Property y_i for each i



$$\langle y \rangle_{ensemble} = \frac{1}{m} \sum_{i=1}^{m} y_i P_i$$

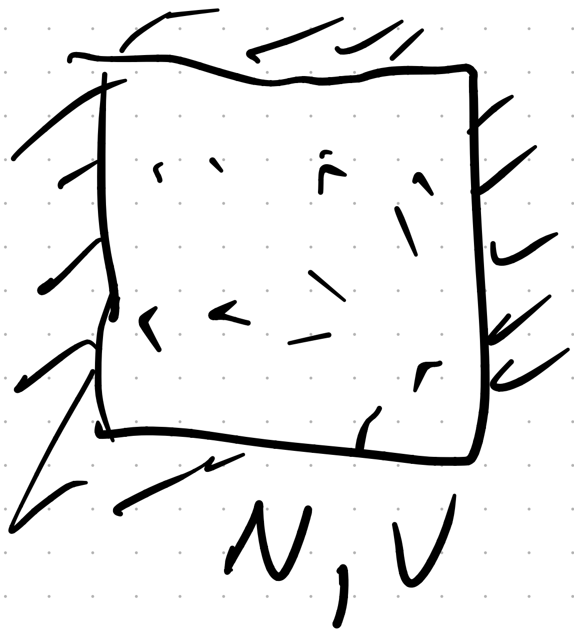
Contrast to a time average

$$y(t_1),\ y(t_2),\ \ldots\ldots,\ y(t_{N_t})$$

$$\langle y \rangle_{time} = \frac{1}{N_t} \sum_{i=1}^{N_t} y(t_i)$$

Microcanonical Ensemble

Ensemble where every copy has the same N, V, E – isolated system



all molecules follow newton's equations

$F = ma$

or schrodinger equation

Both case E is constant

Learned previously that entropy

$S = k \ln \Omega$ is a thermodynamic potential for N, V, E systems

S is maximized at equilibrium

copies of this system maximize entropy

$\Rightarrow$ $P_1, P_2, \ldots, P_m$ for our system

$$S = k_B \ln W$$

N copies and N_1 in state 1
N_2 in state 2 ...

$$W = \frac{A!}{N_1! N_2! N_3! N_4! \cdots N_m!}$$ (multinomial distribution)

$$\sum_{i=1}^{m} N_i = A$$

A & $\{N_i\}$ large

Sterling's approximation is okay

$$W = \frac{A!}{N_1!\,N_2!\,N_3!\,N_4!\cdots N_m!}$$

$\ln X! \approx X\ln X - X$

$$S = k_B \ln W = \left(A\ln A \cancel{-A} - \sum_{i=1}^{m}(N_i\ln N_i \cancel{-N_i})\right) k_B$$

$$S/k_B = A\ln A - \sum_{i=1}^{m} N_i \ln N_i$$

$$\frac{\partial S/k_B}{\partial N_j} = 0$$

$$S/k_B \approx A\ln A - \sum_{i=1}^{m} N_i \ln N_i$$

$$A = \sum_{i=1}^{m} N_i$$

$$\frac{\partial S/k_B}{\partial N_j} = A\frac{\partial \ln A}{\partial N_j} + \frac{\partial A}{\partial N_j}\ln A \qquad \frac{\partial A}{\partial N_j} = 1$$

$$- \frac{N_j}{N_j} - 1 \cdot \ln N_j$$

maximize N_j to get $S \to 0$

$$= 1 + \ln A - 1 - \ln N_j$$

$$= \ln A - \ln N_j = \ln\left(A/N_j\right)$$

Want to maximize all N_j

but $\sum_{j=1}^{m} N_j = A$ ← constraint

Method of Lagrange Multipliers

$f(x)$ ← want to find max or min with a constraint

max or min $\quad I = f(x) - \alpha(\text{constraint})$

$S = k \ln W$ w/ constraint

$$\sum_{i=1}^{M} N_i = A \rightarrow \left(\sum_{i=1}^{m} N_i - A \right) = 0$$

$$I = k \ln W - \alpha \left(\sum_{i=1}^{M} N_i - A \right)$$

$$\frac{\partial I}{\partial N_j} = \ln A - \ln N_j - \alpha = 0 \text{ for every } N_j$$

$$\alpha = \ln\left(A / N_j \right) \Leftrightarrow N_j = A e^{-\alpha}$$

$$N_j = Ae^{-\alpha}$$

$$\sum_{i=1}^{m} N_j - A = 0 \Leftarrow \text{constraint}$$

$$\sum_{i=1}^{m} Ae^{-\alpha} = A \Rightarrow mAe^{-\alpha} = A$$

$$e^{\alpha} = m \qquad \alpha = \ln(m)$$

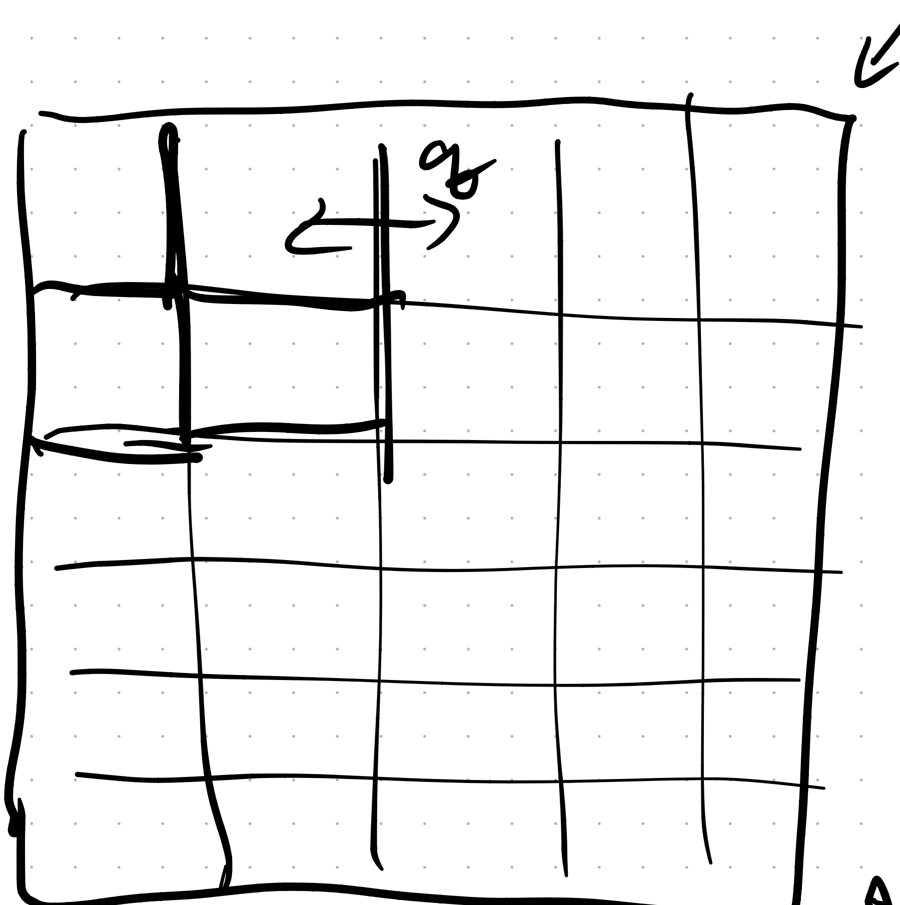
$$P_i = \frac{N_i}{A} = \frac{Ae^{-\alpha}}{A} = \frac{1}{e^{\alpha}} = \frac{1}{m}$$

Chapter 16 Canonical Ensemble

a system of interest has constant

N, V, T

isolated



$N, V, \mathcal{E}$ overall

heat transfers until each system has same T

one system @ eq

$\tilde{N}, \tilde{V}, T$

$N = A\tilde{N}$ $V = A\tilde{V}$ $\mathcal{E} = \sum_{i=1}^{A} \mathcal{E}_i$

Whole system is N, V, E

Maximize $S = k \ln \Omega$

constraints ① $\sum_{i=1}^{m} N_i = A$

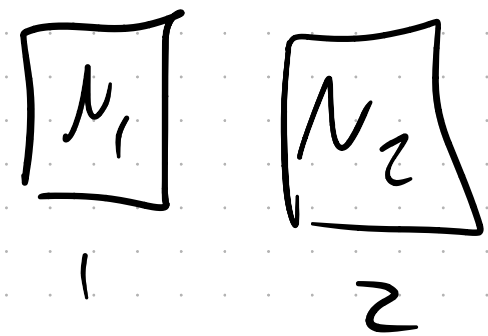
② ~~$\sum_{i=1}^{m} \varepsilon_i = \varepsilon_{total}$~~ constant

Lagrange multipliers (2 constraints)

~~$S = k \ln \Omega - \alpha\left(\sum N_i - A\right) - \beta\left(\sum \varepsilon_i - \varepsilon_t\right)$~~

Energy constraint

$$\mathcal{E}_{total} = \sum_{i=1}^{A} \tilde{\mathcal{E}}_i$$



$$\mathcal{E}_{total} = \sum_{i=1}^{M} N_i \mathcal{E}_i$$

$$S = k \ln W - \alpha\left(\sum N_i - A\right) - \beta\left(\sum N_i \mathcal{E}_i - \mathcal{E}_{total}\right)$$

$$\frac{\partial S}{\partial N_j} = \ln(A/N_j) - \alpha - \beta \mathcal{E}_j = 0$$

$$\ln(A/N_j) - \alpha - \beta\varepsilon_j = 0$$

$$N_j = e^{-\alpha} e^{-\beta\varepsilon_j} \cdot A$$

$$\sum_{j=1}^{m} N_j = A = A e^{-\alpha} \sum_{j=1}^{m} e^{-\beta\varepsilon_j}$$

$$1 = e^{-\alpha} \sum_{j=1}^{m} e^{-\beta\varepsilon_j}$$

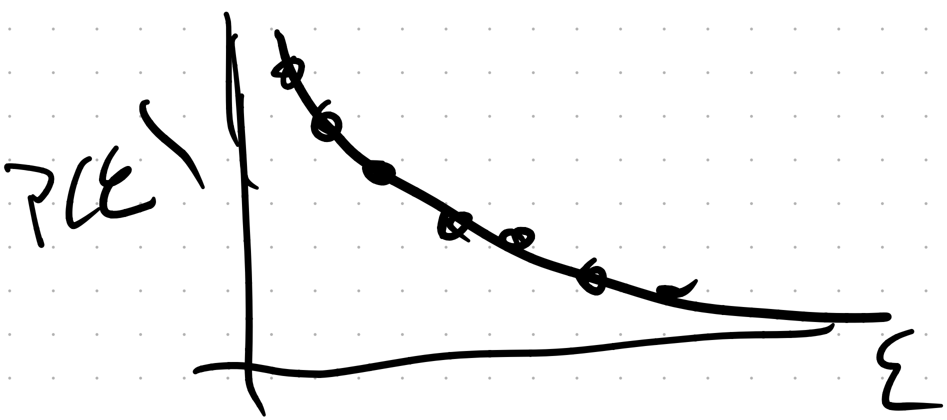
$$e^{\alpha} = \sum_{j=1}^{m} e^{-\beta\varepsilon_j}$$

$$P_j = \frac{N_j}{A} = e^{-\alpha} e^{-\beta\varepsilon_j}$$

$$= e^{-\beta\varepsilon_j} \Big/ \sum_{j=1}^{m} e^{-\beta\varepsilon_j}$$

$$P_j = \frac{e^{-\beta \varepsilon_j}}{\sum_{j=1}^{m} e^{-\beta \varepsilon_j}}$$ ☆

$$Q = \sum_{j=1}^{m} e^{-\beta \varepsilon_j}$$ "partition function"



$e^{-\beta \varepsilon_j}$ is called

Boltzmann factor

(relative weight)

for Micro canonical

Bolzmann factor $=1$ like $\beta=0$

$$Q=\sum_{i=1}^{m} BF_i = m$$

$$\langle y\rangle=\sum_{i=1}^{m} y_i P_i=\sum_{i=1}^{m} y_i e^{-\beta \epsilon_i}/Q$$

$$\langle \varepsilon\rangle=\sum_{i=1}^{m} \epsilon_i e^{-\beta \epsilon_i}/Q$$

$$\beta=1/k_B T$$

$$Q = \sum_{i=1}^{M} e^{-\beta \varepsilon_i}$$

can derive thermodynamic quantities from the partition function

$$\langle \varepsilon \rangle = \sum_{i=1}^{M} \varepsilon_i e^{-\beta \varepsilon_i} / Q$$

$$-\frac{\partial Q}{\partial \beta} = \sum_{i=1}^{M} \varepsilon_i e^{-\beta \varepsilon_i}$$

$$\frac{\partial \log Q}{\partial x} = \frac{1}{Q} \frac{\partial Q}{\partial x}$$

$$-\frac{\partial \ln Q}{\partial \beta} = \frac{\sum_{i=1}^{m} \epsilon_i e^{-\beta \epsilon_i}}{Q} = \langle \varepsilon \rangle$$

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

Gibbs Entropy

$S = k \ln W$ micro

$$S = -k_B \sum_{i=1}^{M} p_i \ln p_i \qquad \sum p_i y_i = \langle y \rangle$$

$$p_i = e^{-\beta \varepsilon_i} / Q$$

$$= -k_B \sum p_i \left[-\beta \varepsilon_i - \ln Q \right]$$

$$= k_B \beta \sum p_i \varepsilon_i + k_B \ln Q$$

$$= k_B \beta \langle \varepsilon \rangle + k_B \ln Q$$

entropy

$$S = k_B \beta \langle \varepsilon \rangle + k_B \ln Q$$

$$T = \left(\frac{\partial U}{\partial S} \right)_V = \frac{\partial U}{\quad}$$