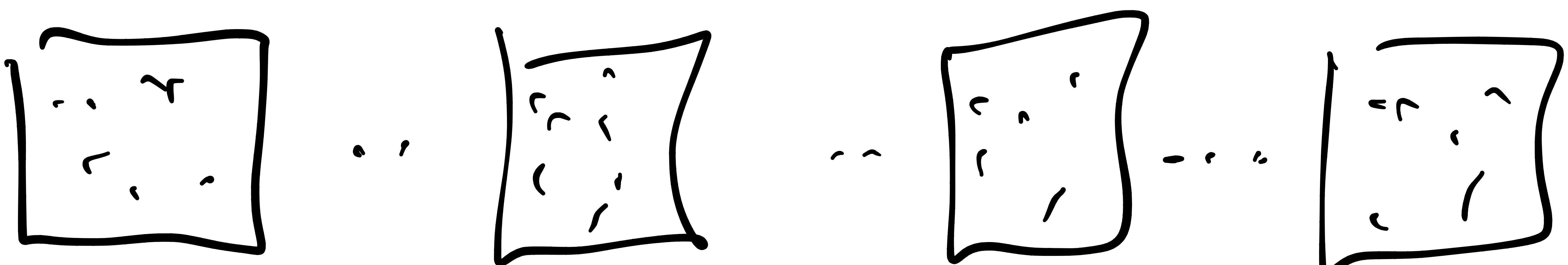
Lecture 21 - Thermodynamic Ensembles

Imagine - many copies of system



$$\underbrace{\qquad\qquad\qquad\qquad\qquad}_{A}$$

Same "macro state"

isolated - N, V, E

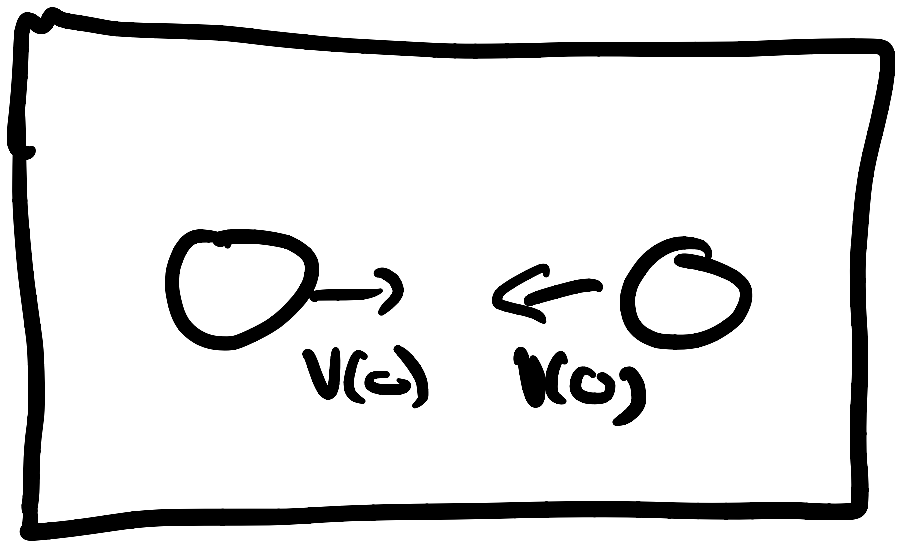
Ensemble average

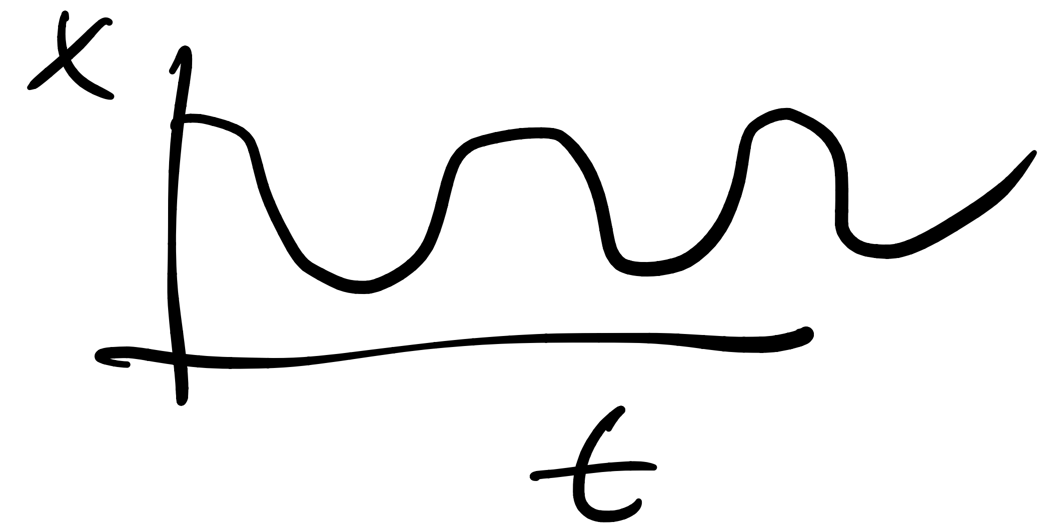
$$\langle O \rangle_{ensemble} = \frac{1}{A} \sum_{i=1}^{A} O(\vec{X}_i)$$

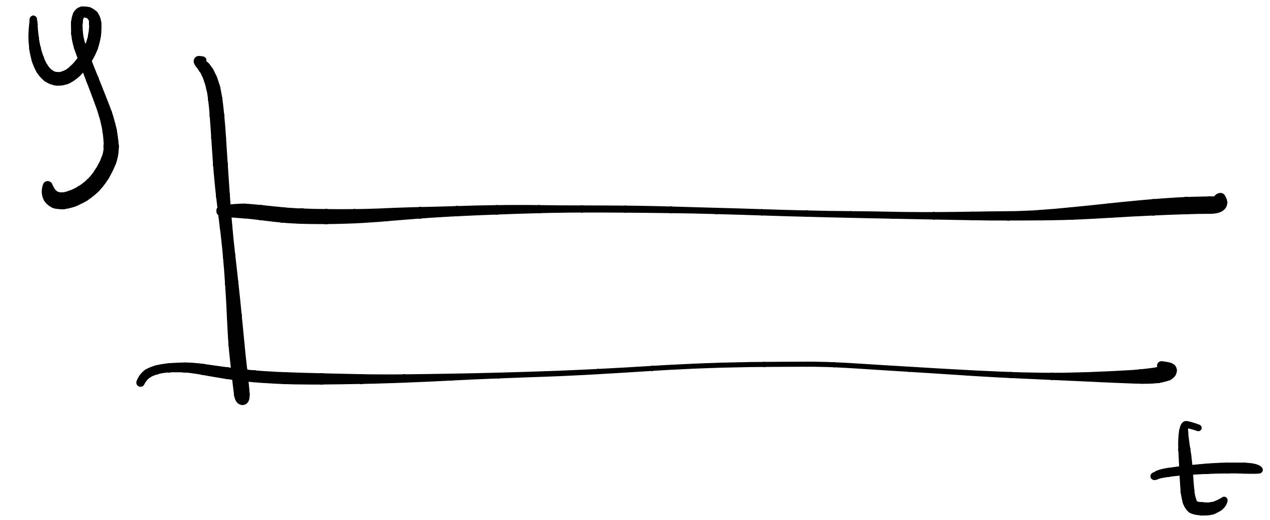
Time average $$\langle O \rangle_{time} = \frac{1}{T} \sum_{t=1}^{T} O(\vec{X}(t))$$

"Ergotic" hypothesis - over long times

T, $\langle O \rangle_{ensemble} = \langle O \rangle_{time}$

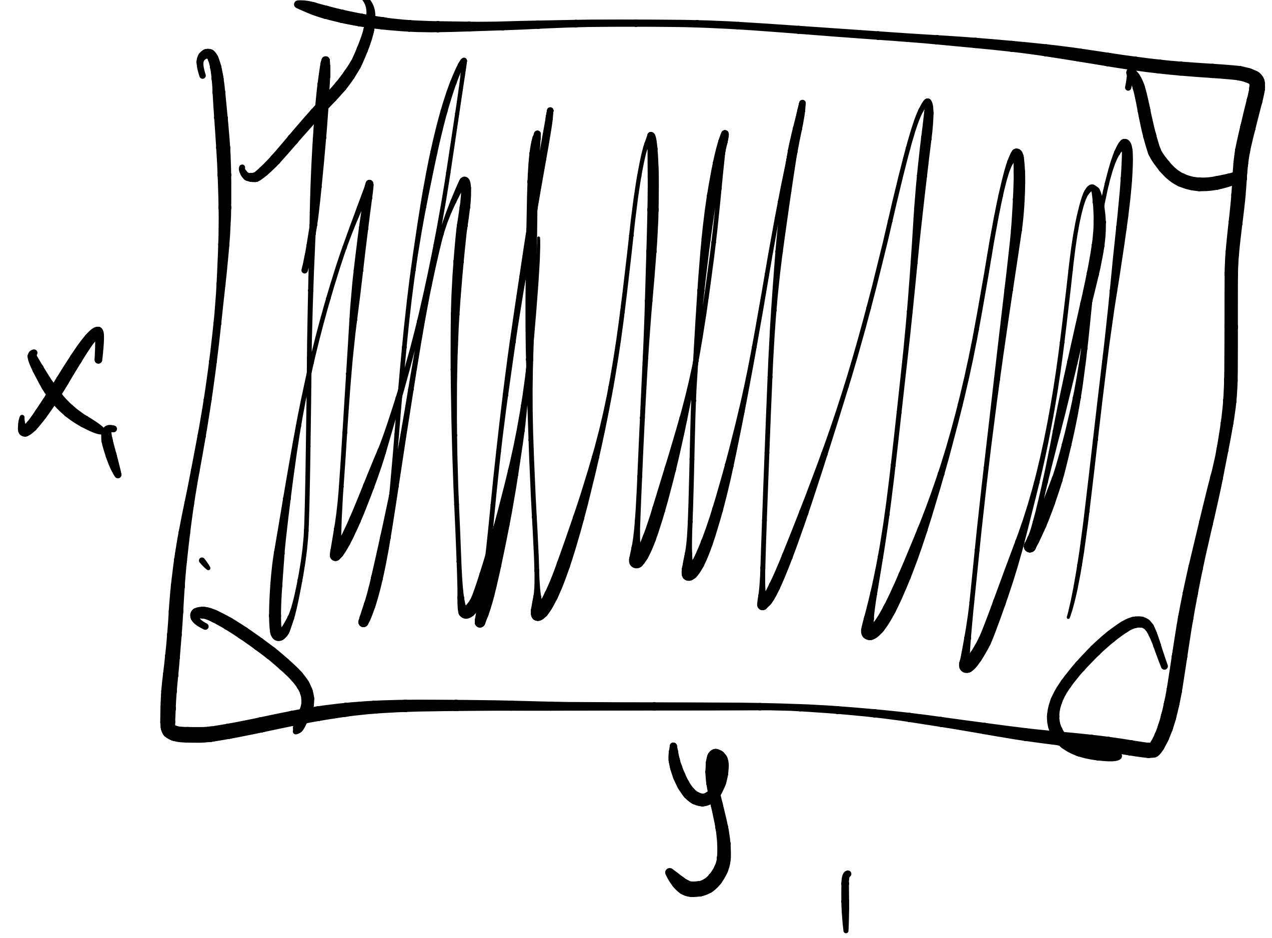


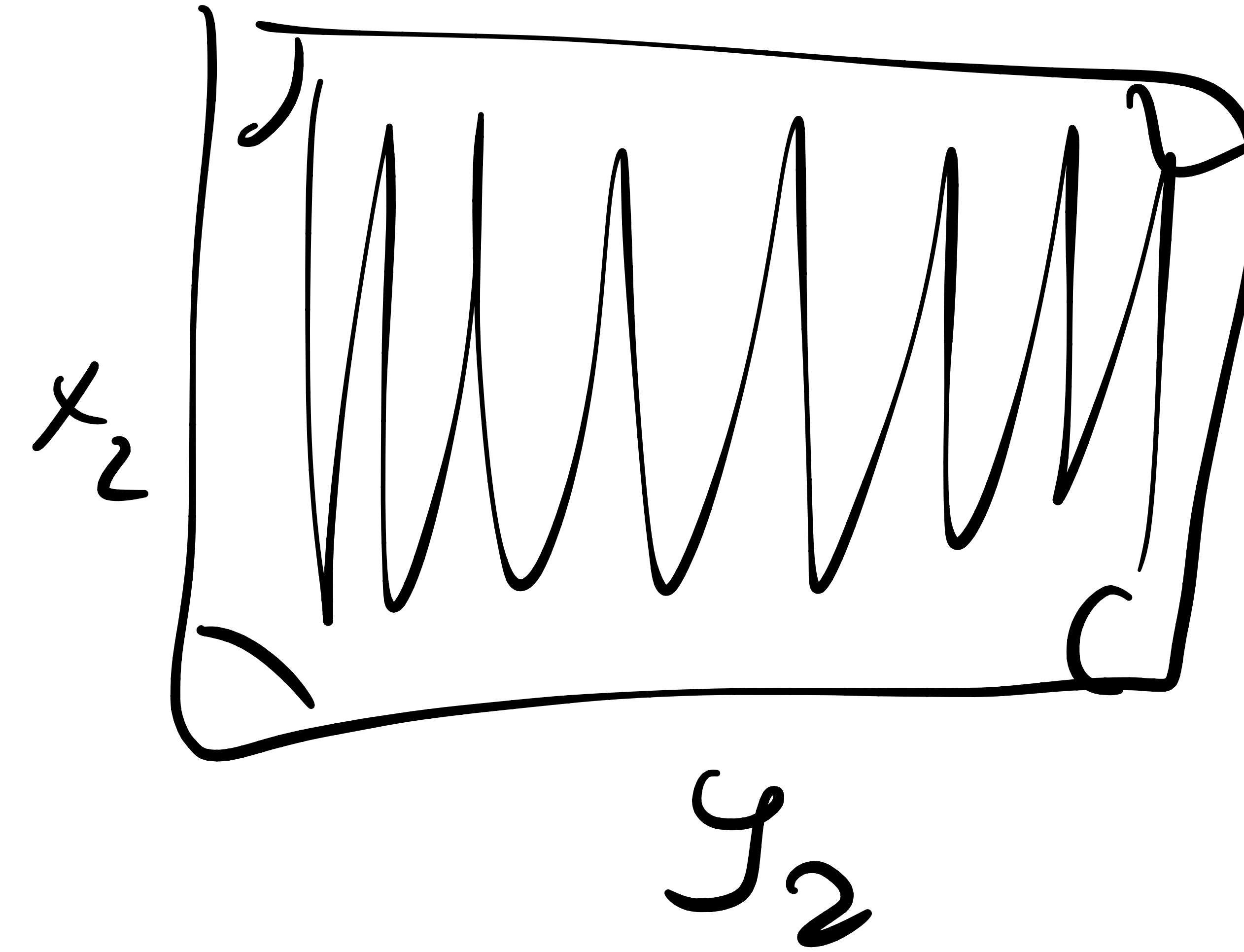




In this case, every (x_1, y_1, x_2, y_2) should be equally likely

Histogram

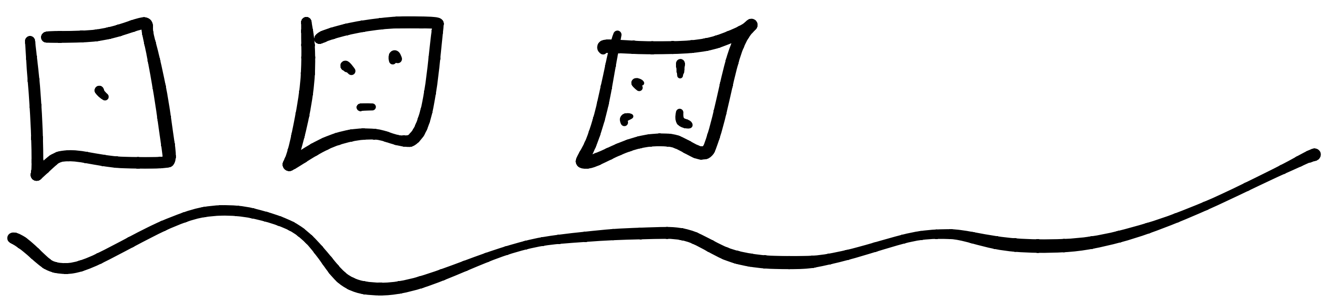




Ergodic <u>hypothesis</u>

Organize system into "states"

P_i likelihood of state i



macro state is N dice

micro state $\{\underset{1-6}{m_1}, m_2, \dots, \underset{1-6}{m_N}\}$

2 dice

state total sum is 12 $P_{z=12} = \frac{1}{36}$

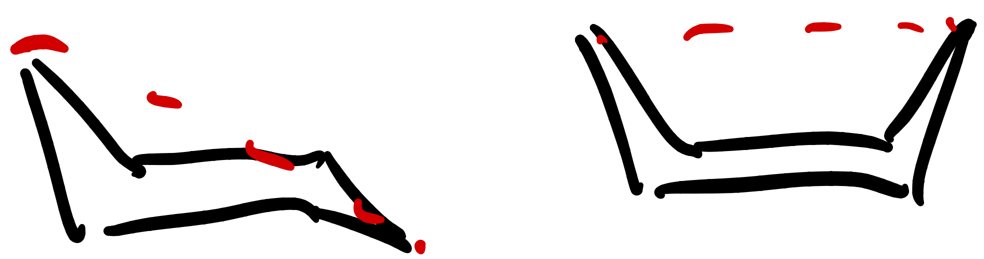
$$\langle O \rangle_{ensemble} = \frac{1}{A} \sum_{i=1}^{A} O(x_i)$$

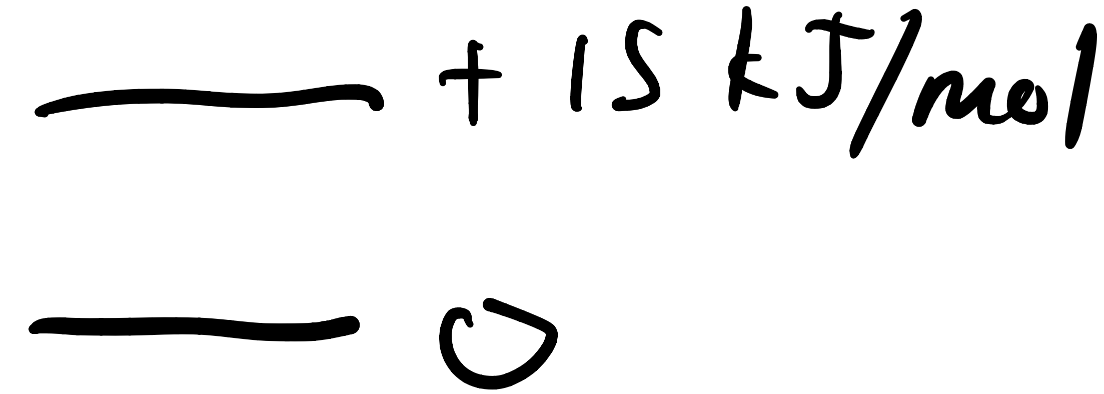
$$= \sum_{j=1}^{M_{states}} O(s_j) \, P(s_j)$$

e) binomial dist

Example: at const Temperature

$$P(\varepsilon_i) \propto e^{-\varepsilon_i / k_B T}$$

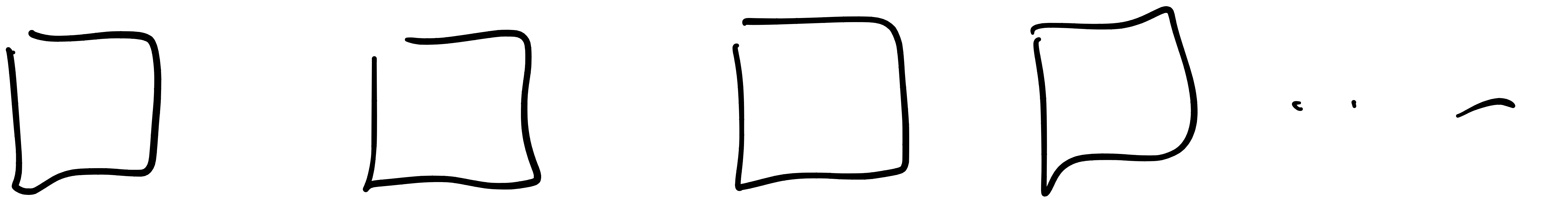




example "0" distance between C_1 and C_4

$$\langle d \rangle_{temperature} = d_{boat} P_{boat} + d_{chair} P_{chair}$$

How likely is a particular state?



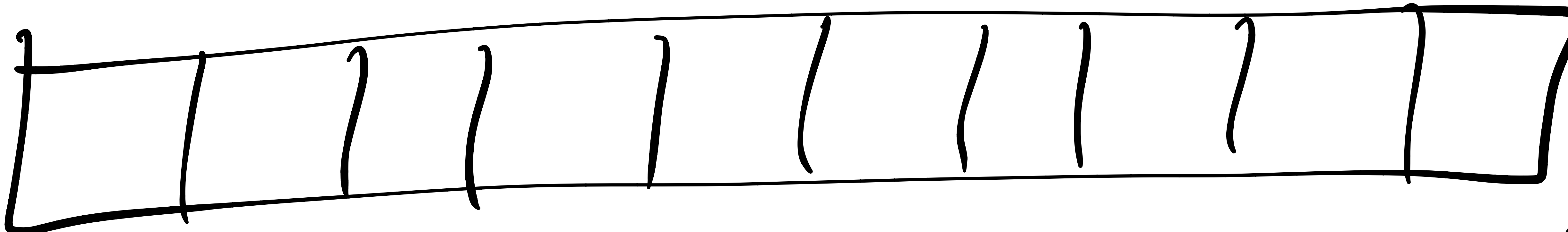
A copies

isolated ⇐ "microcanonical ensemble"

every system has constant N, V, E

Each can be in a different state

Scenario 2



A copies

in contact, $\mathcal{E}$ can flow

@ eq everything is at the same temp

Each has const N, V, T individually

The full system of A copies has const $\mathcal{E}$

Maximize entropy of whole A copies of system to see how many are in each possible state

M possible states