

L19: review

Average \leftarrow $A = \sum_{j=1}^w p_j A_j$ \leftarrow Probability of state j \leftarrow Value of observable A in state j

Postulate #1: laws of motion ($F=ma$; $\hat{H}\psi = E\psi$)

apply to an isolated system as $N \rightarrow \infty$

\Rightarrow energy conservation (1st law of thermo)

Postulate #2: In an isolated system all the

microstates are equally possible: $p_j = \frac{1}{w}$,

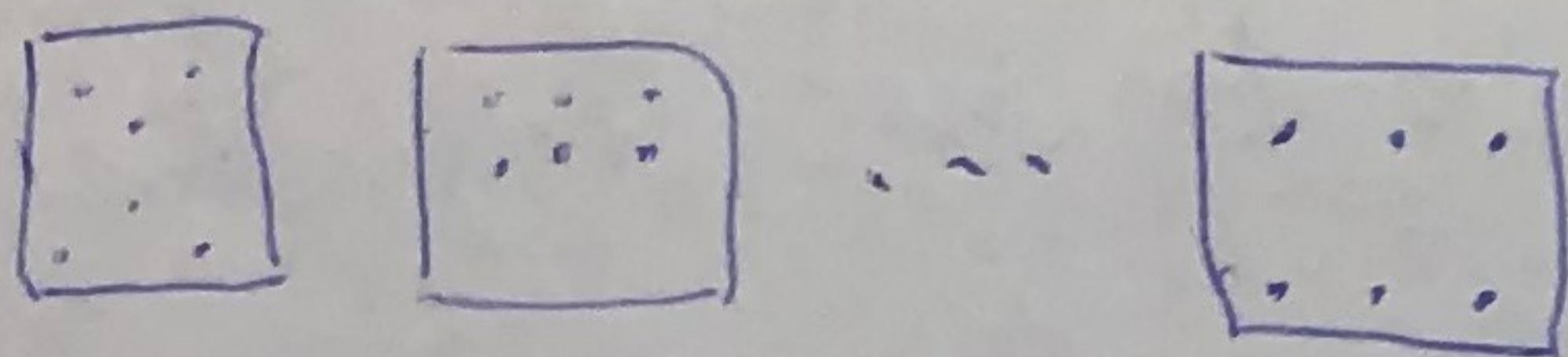
where w is the total number of accessible states. w is also called the

"partition function".

\hookrightarrow Strong form: averaging over time

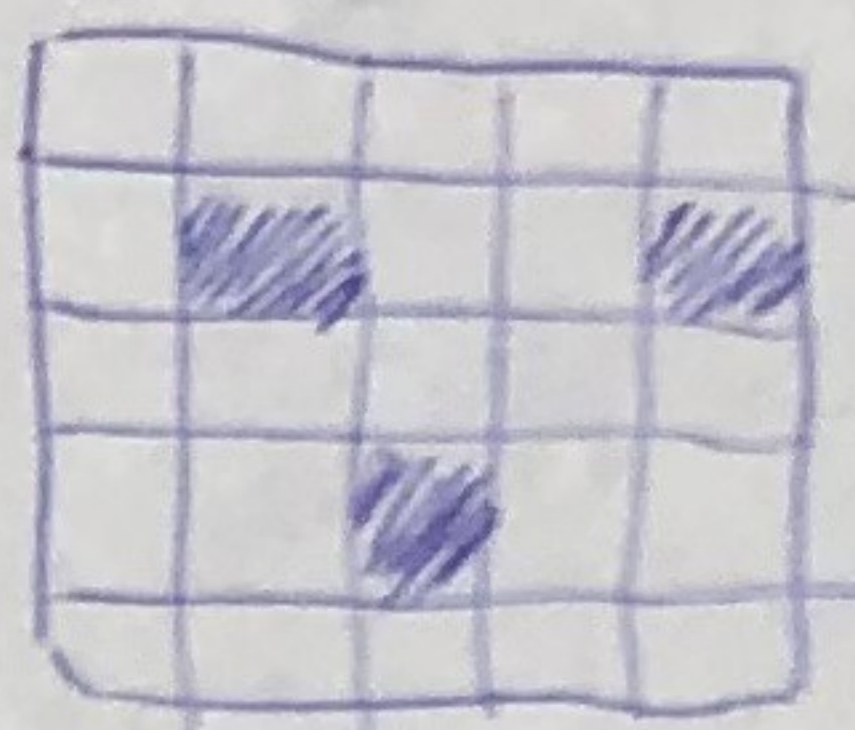
is the same as averaging over

all microstates



Today: Properties of w and the entropy S

ex:



$$\left. \begin{aligned} M &= 5 \times 5 = 25 \\ N &= 3 \end{aligned} \right\} N \ll M$$

volume: V ; volume of one cell, V_0 :

$$V_0 = \frac{V}{M} \quad \text{or} \quad M = \frac{V}{V_0}$$

Number of arrangements of N identical

particles in the box is: $\frac{25 \times 24 \times 23}{3!}$

In general, $\frac{M!}{(M-N)! N!} = w$

For large factorials, $n! \approx n^n e^{-n}$ \Rightarrow

$$\Rightarrow w = \frac{M!}{(M-N)! N!} \approx \frac{M^M e^{-M}}{(M-N)^{M-N} e^{-(M-N)} N^N e^{-N}}$$

$$\frac{e^{-N+M}}{N^{-N} e^N} \approx \frac{M^M}{(M-N)^{M-N} N^N}$$

* In a lot of applications, e.g. gas phase or dilute liquid solutions, $N \ll M$

$$\Rightarrow M-N \approx M$$

$$\Rightarrow W \approx \frac{M^N}{N^N} \approx \left(\frac{M}{N}\right)^N$$

Plugging in realistic numbers:

$$\left. \begin{aligned} V_0 &= 10 \text{ \AA}^3 = 10^{-29} \text{ m}^3 \\ V &= 1 \text{ cm}^3 = 10^{-6} \text{ m}^3 \end{aligned} \right\} \Rightarrow M = \frac{V}{V_0} = 10^{23}$$

In a gas at 1 atm, or a solution of 0.05M: ^{molar}

$$N \approx 10^{19} \text{ molecules per cm}^3 \Rightarrow \frac{M}{N} = \frac{10^{23}}{10^{19}} = 10^4 \gg 1$$

v molecule (velocity at room temperature) $\approx 300 \text{ m/s}$

$$\Rightarrow \Delta t = \frac{L_0}{v} = \frac{V_0^{1/3}}{v} \approx 10^{-12} \text{ s} = 1 \text{ fs}$$

↓
time it takes
for molecules to hop
from one cell to
the next

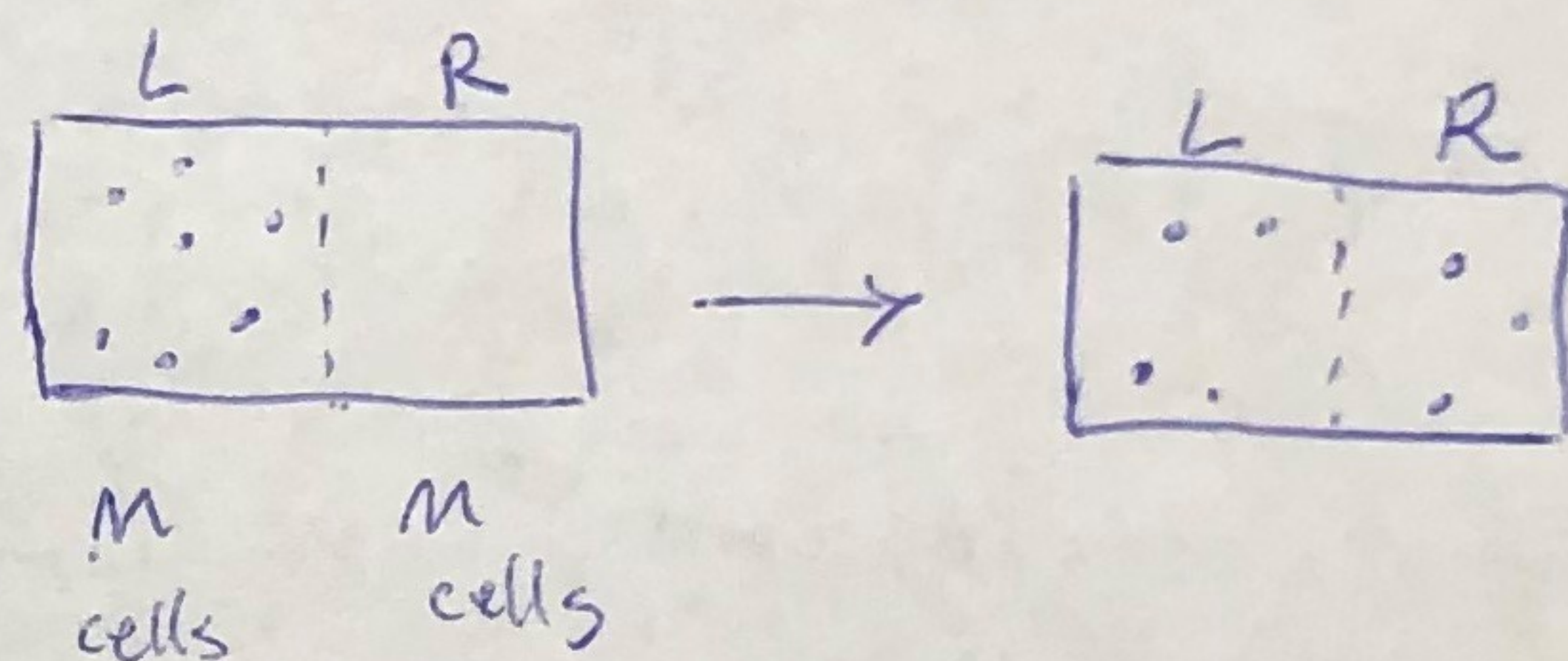
* Max. observation time is lifetime of universe, 10^{18} seconds. The number of configurations we can measure is $10^{18} / 10^{-12} = 10^{30}$

How many configurations are there in the ensemble?

$$\hookrightarrow W \approx \left(\frac{M}{N}\right)^N = (10^4)^{10^{19}} \gg 10^{30}$$

therefor in any given experiment we are sampling a very small fraction of the possible states of the system but the observable microstates are mostly ones closer to the ensemble average; the example below illustrates this point.

* In-class exercise



$$W_{\text{left}} = W_{\text{right}}$$

$$W_{\text{total}} = W_{\text{after}}$$

Initially, each molecule has only one possibility of where to be: L

Later, each molecule has two possibilities of where to be: L and R

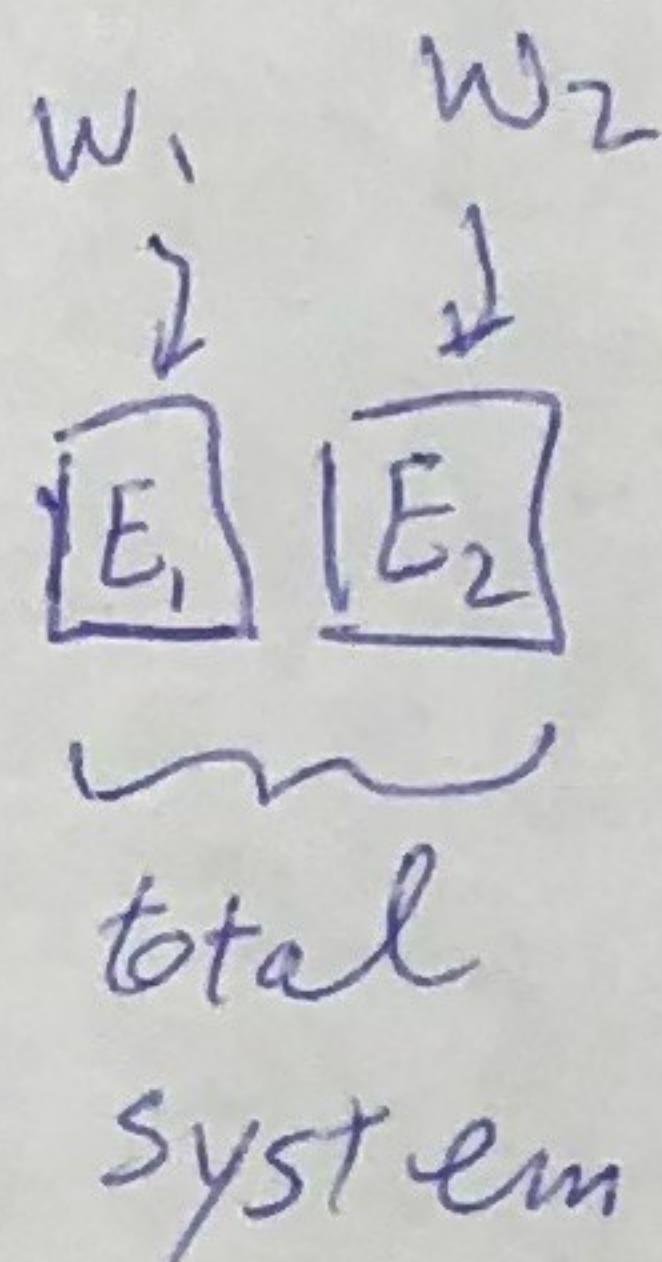
For N particles, There are 2^N more possibilities of being anywhere in the box, not just in the left side.

$$p_{\text{left}} = \frac{W_{\text{before}}}{W_{\text{after}}} = \frac{W_{\text{left}}}{W_{\text{total}}} = \frac{1}{2^N}$$

\Rightarrow by removing the barrier, $W(t > 0) > W(t = 0)$

W and S

Energy is additive: $E_{\text{tot}} = E_1 + E_2$
(or extensive)



W is multiplicative: $W_{\text{tot}} = W_1 \cdot W_2$

Since chemists refrain from multiplicative variables they prefer $\ln W$ over W :

$$\boxed{S \equiv k_B \ln W} \Rightarrow S_{\text{tot}} = S_2 + S_1$$

definition

* Boltzmann constant, k_B , converts the unit of S from ~~entropy~~ into Joule/Kelvin

* note that logarithm is monotonic; therefore, $S(t > 0) > S(t = 0)$