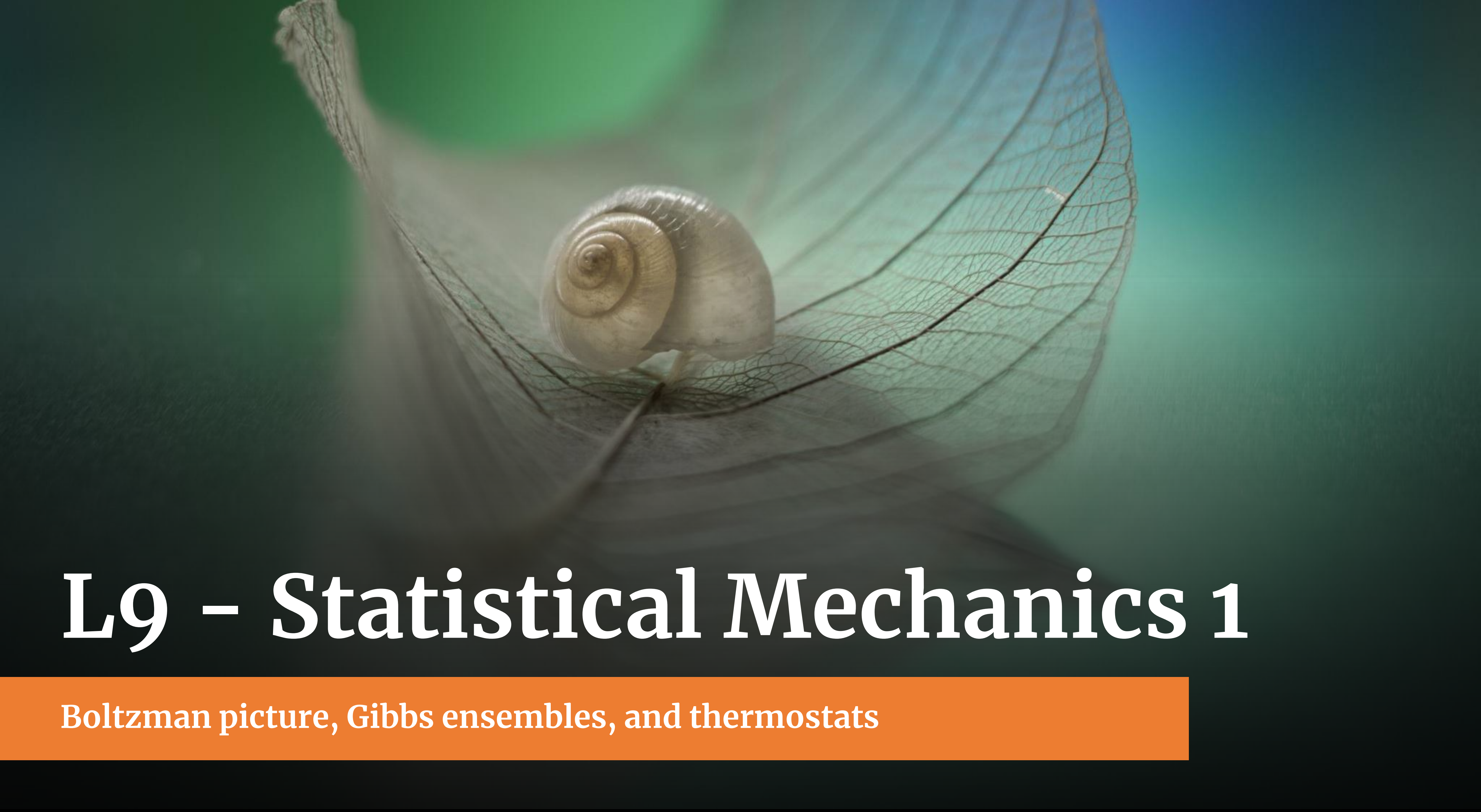


L9 - Statistical Mechanics 1

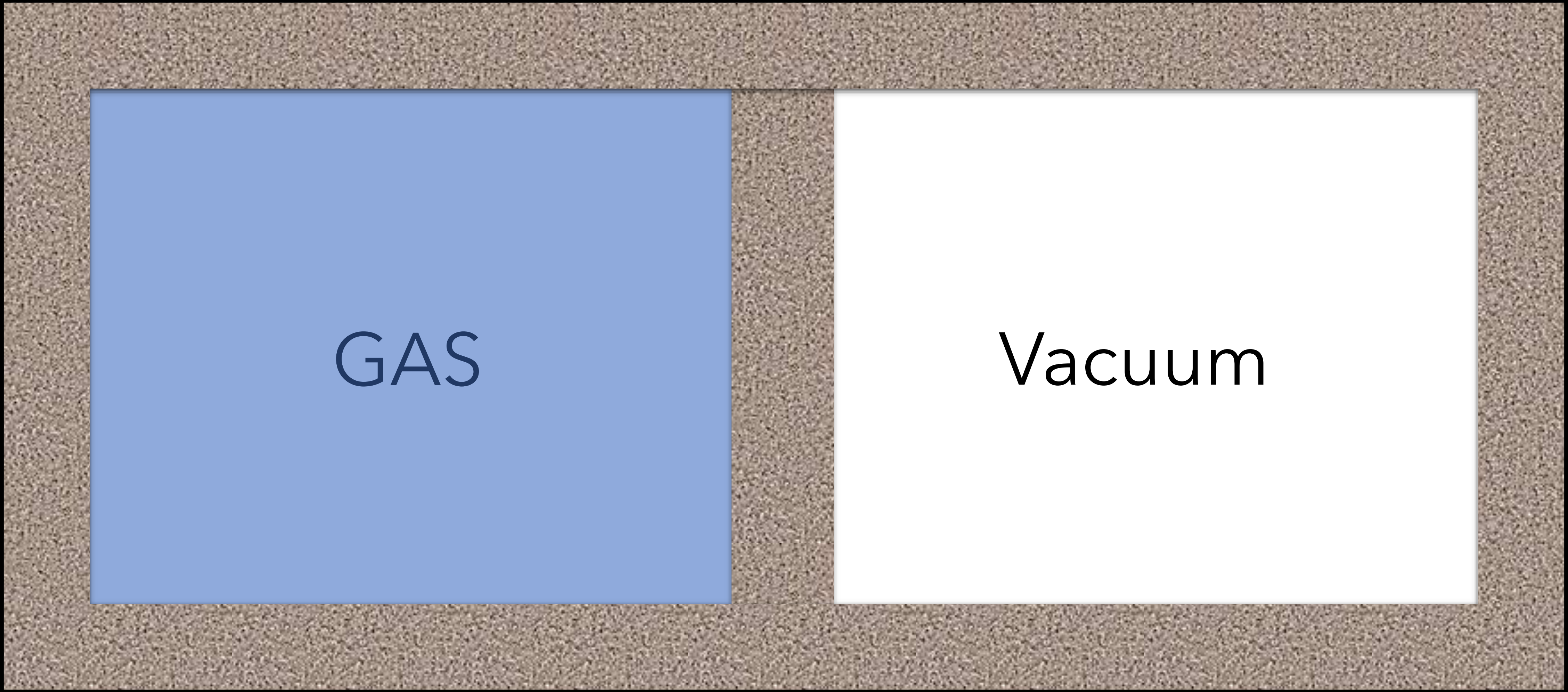
Boltzman picture, Gibbs ensembles, and thermostats

"Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

Perhaps it will be wise to approach the subject cautiously"

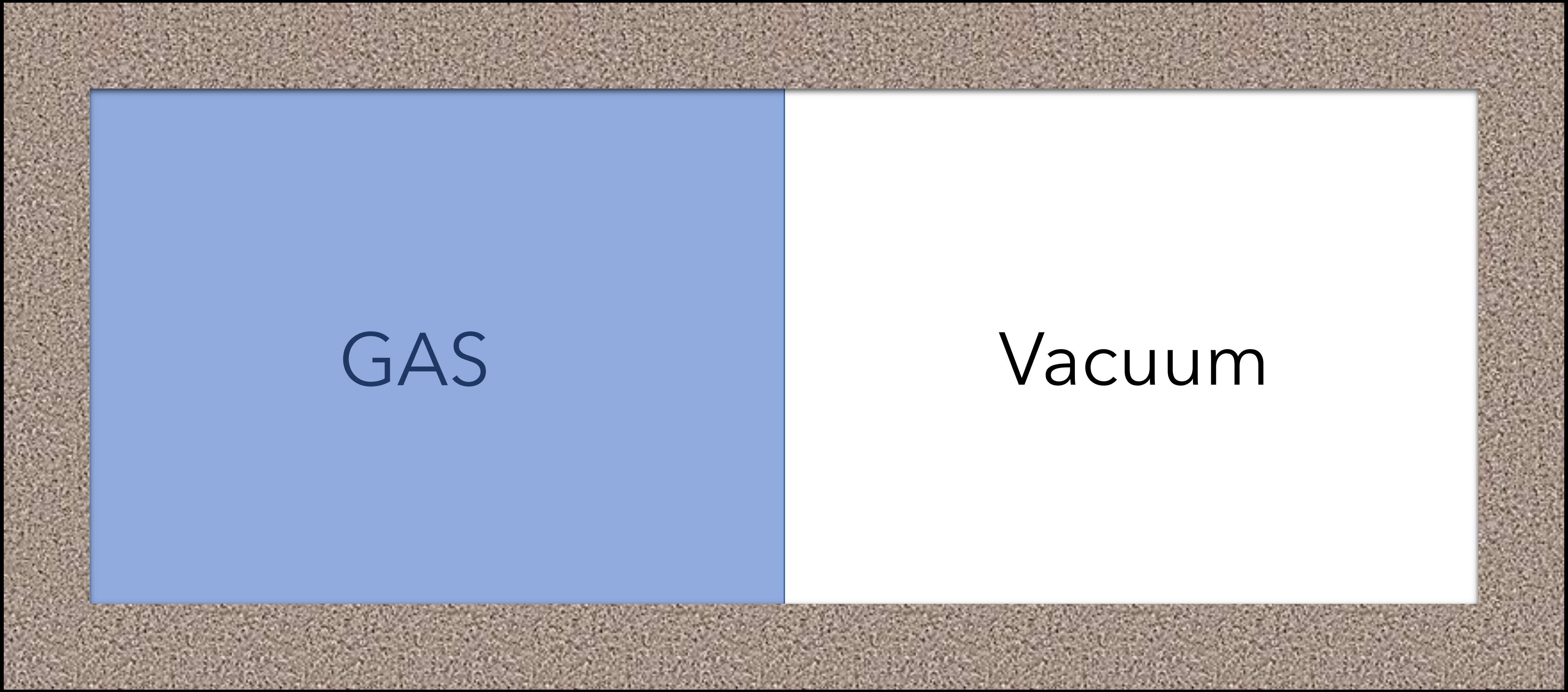
David L. Goodstein – States of Matter, 2014

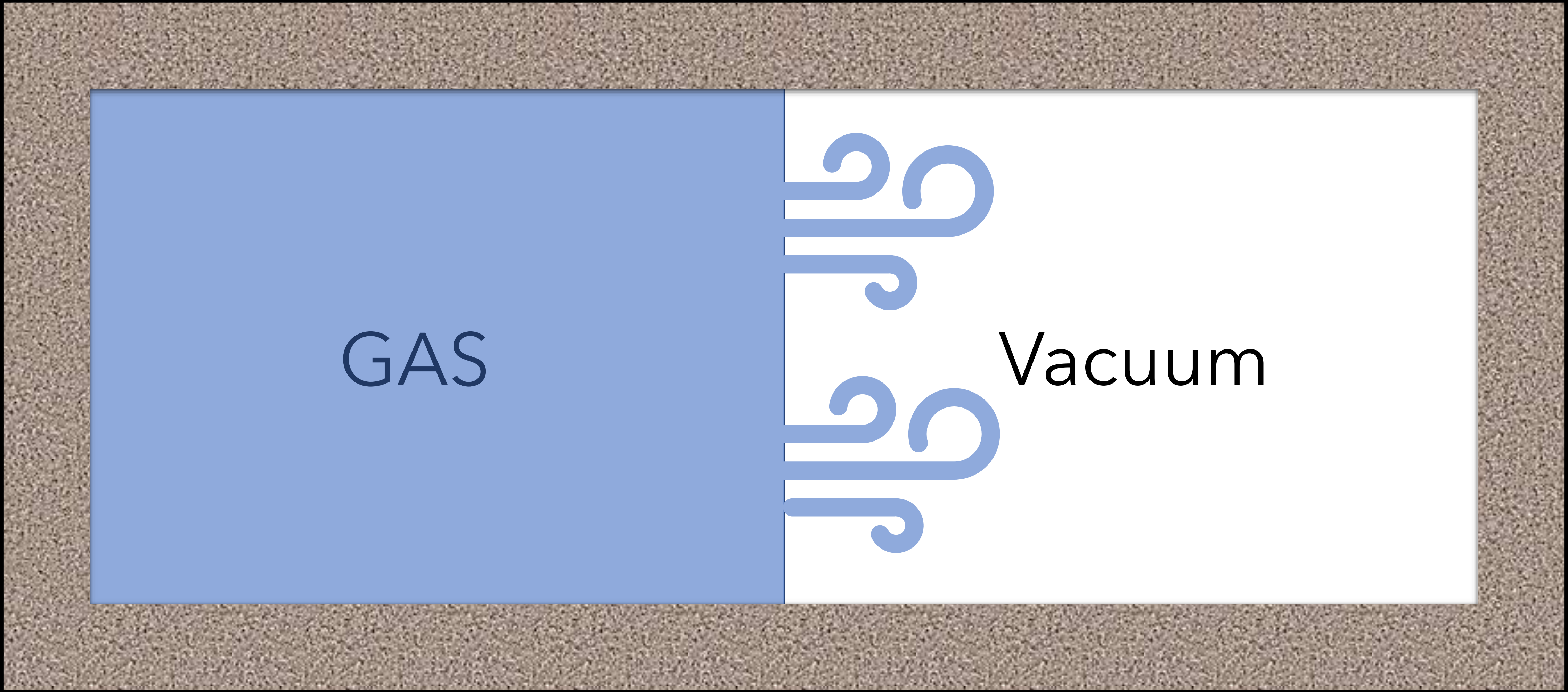
The Boltzmann picture

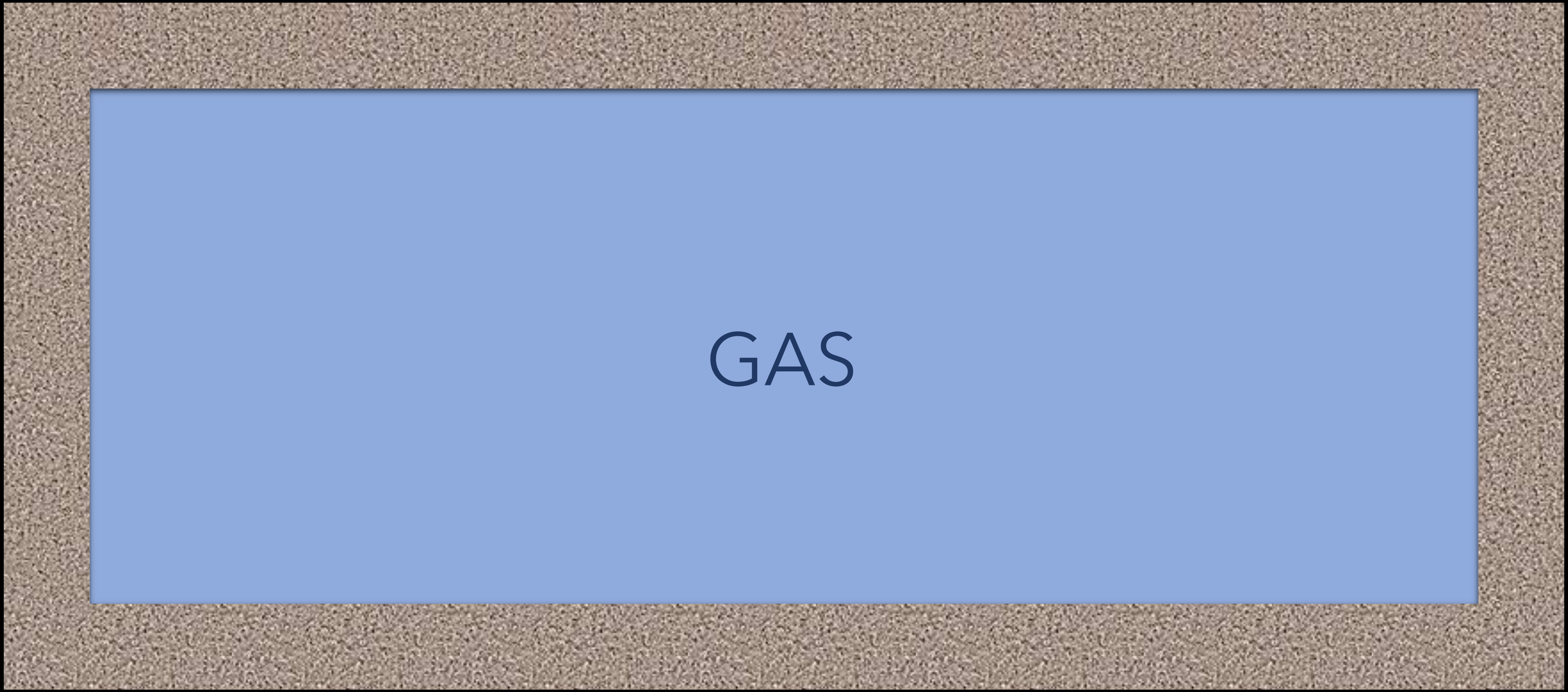


GAS

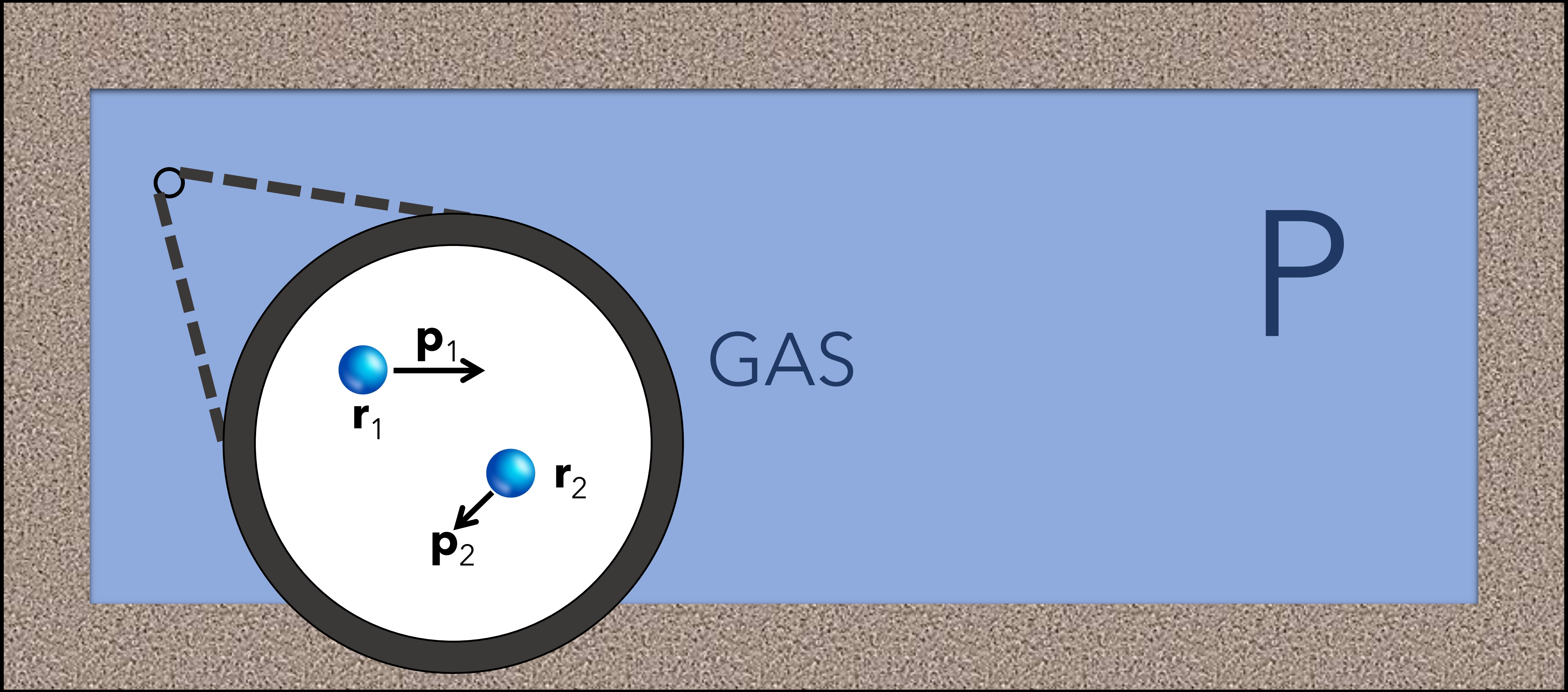
Vacuum


GAS
Vacuum


GAS
Vacuum



GAS


$\mathbf{p}_1$
$\mathbf{r}_1$
$\mathbf{r}_2$
$\mathbf{p}_2$
GAS
P

Macroscopic state: P

Microscopic state: $\mathbf{x} = (\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots, \mathbf{r}_N, \mathbf{p}_N)$

A microstate corresponds to a single macrostate

$\mathbf{x}_1 = (\mathbf{r}_{11}, \mathbf{p}_{11}, \mathbf{r}_{12}, \mathbf{p}_{12}, \ldots , \mathbf{r}_{1N}, \mathbf{p}_{1N}) \rightarrow P_a$

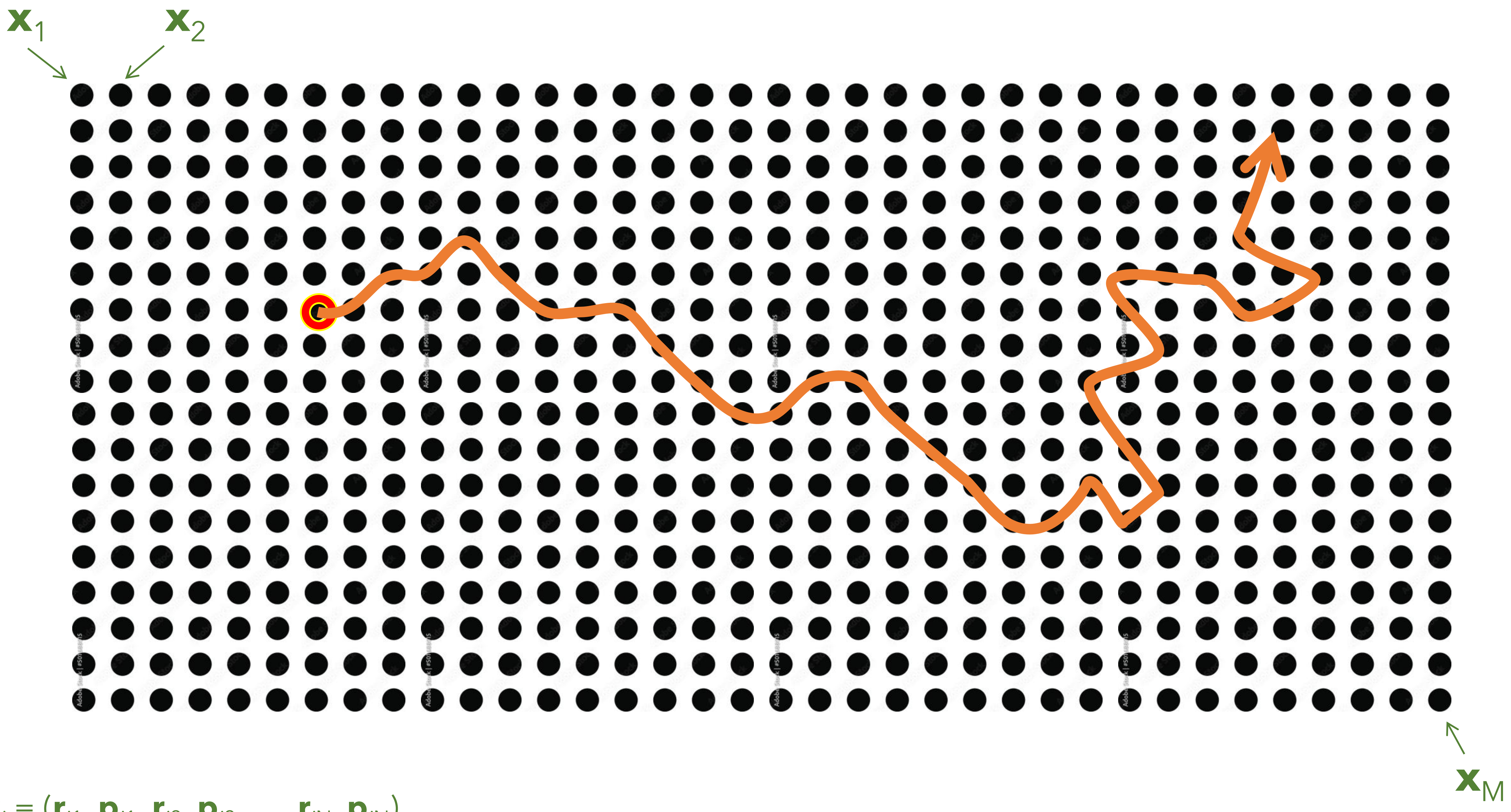
Many microstates may yield the same macrostate

$\mathbf{x}_1 \rightarrow P_a$

$\mathbf{x}_2 \rightarrow P_a$

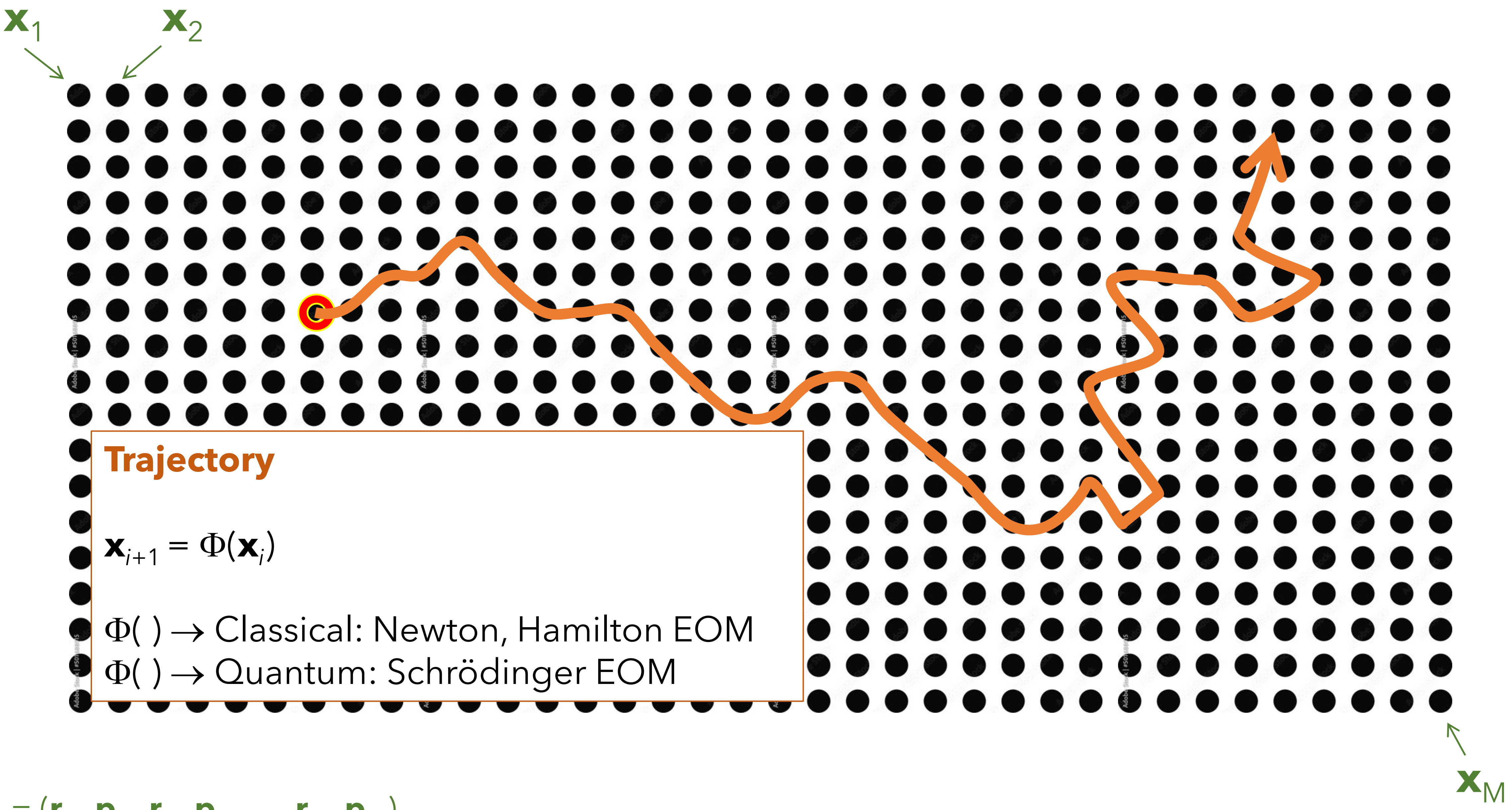
$\mathbf{x}_3 \rightarrow P_a$

Microstate space



$\mathbf{x}_i = (\mathbf{r}_{i1}, \mathbf{p}_{i1}, \mathbf{r}_{i2}, \mathbf{p}_{i2}, \ldots, \mathbf{r}_{iN}, \mathbf{p}_{iN})$

Microstate space



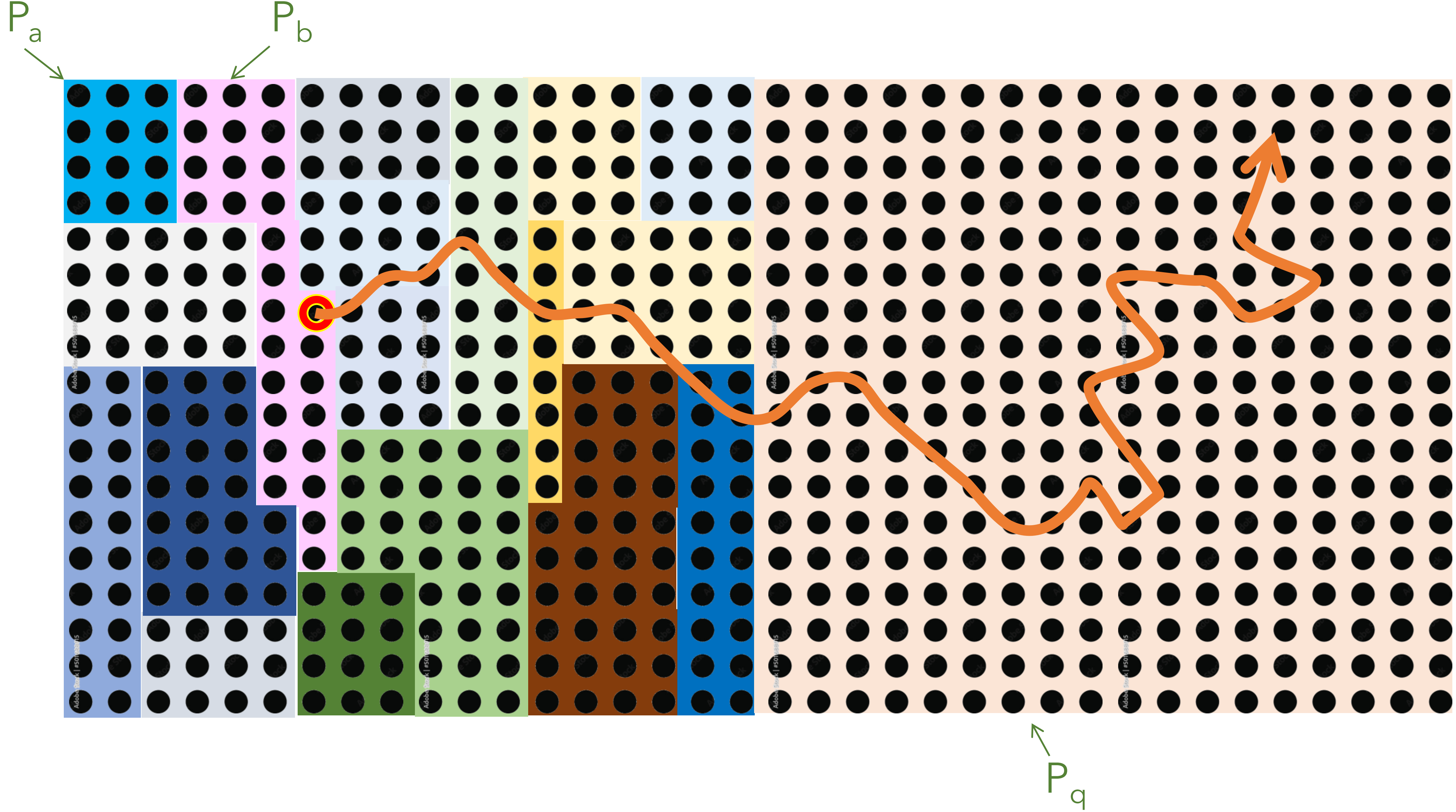
Trajectory

$\mathbf{x}_{i+1} = \Phi(\mathbf{x}_i)$

$\Phi(\ )$ → Classical: Newton, Hamilton EOM
$\Phi(\ )$ → Quantum: Schrödinger EOM

$\mathbf{x}_i = (\mathbf{r}_{i1}, \mathbf{p}_{i1}, \mathbf{r}_{i2}, \mathbf{p}_{i2}, \dots, \mathbf{r}_{iN}, \mathbf{p}_{iN})$

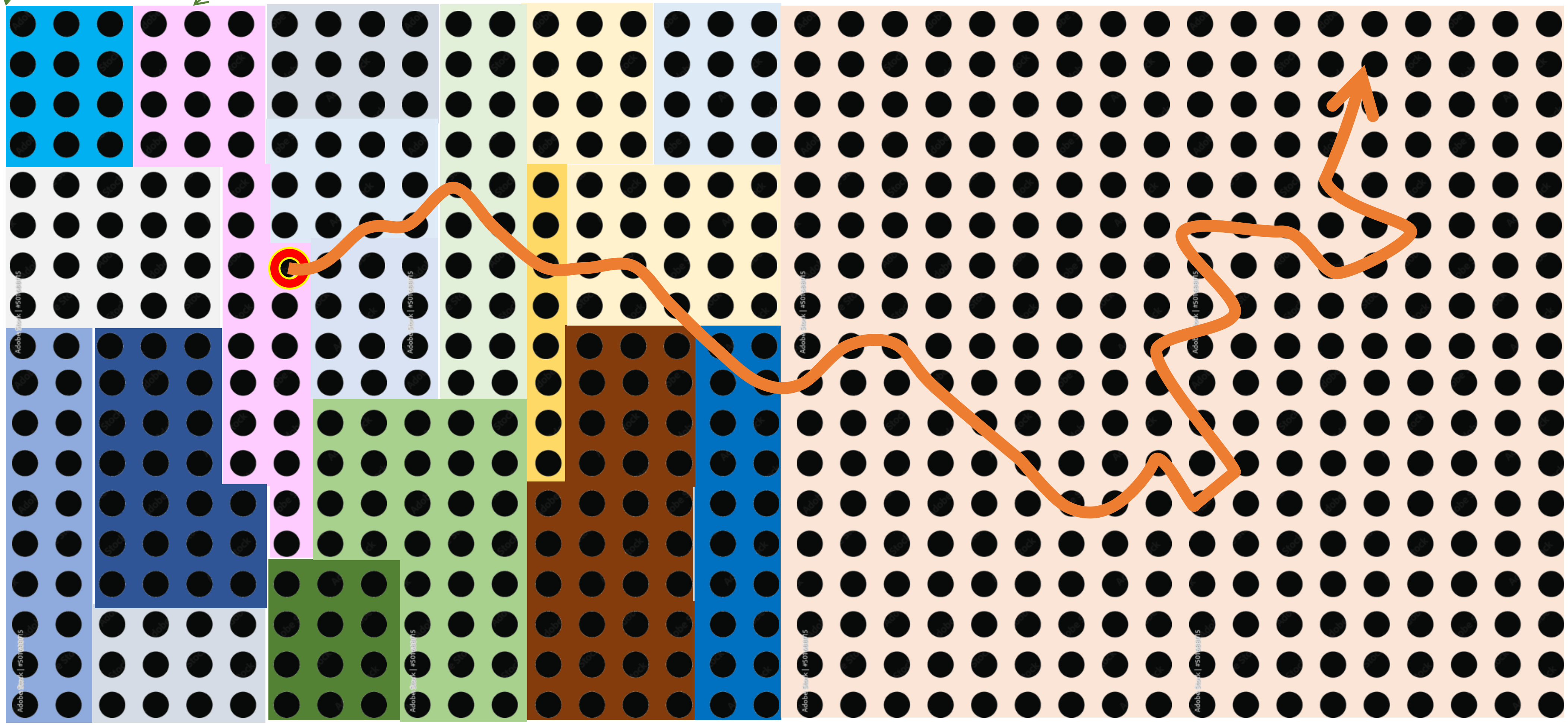
Microstate space



Microstate space

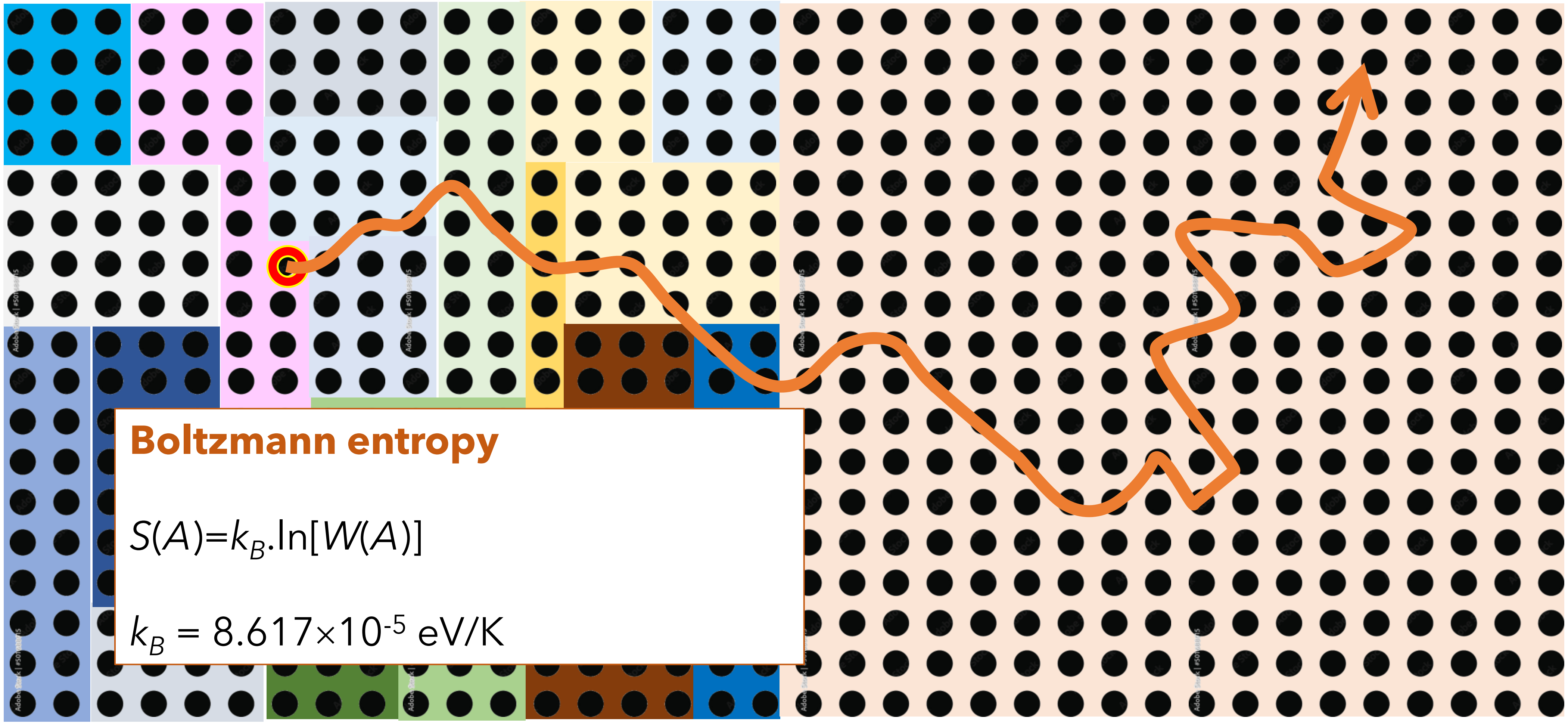
$W(P_a)=12$

$W(P_b)=28$



$W(P_q)=324$

Microstate space



$S(P_a)=k_B.\ln(12)$
$=2.49\ k_B$

$S(P_b)=3.33\ k_B$

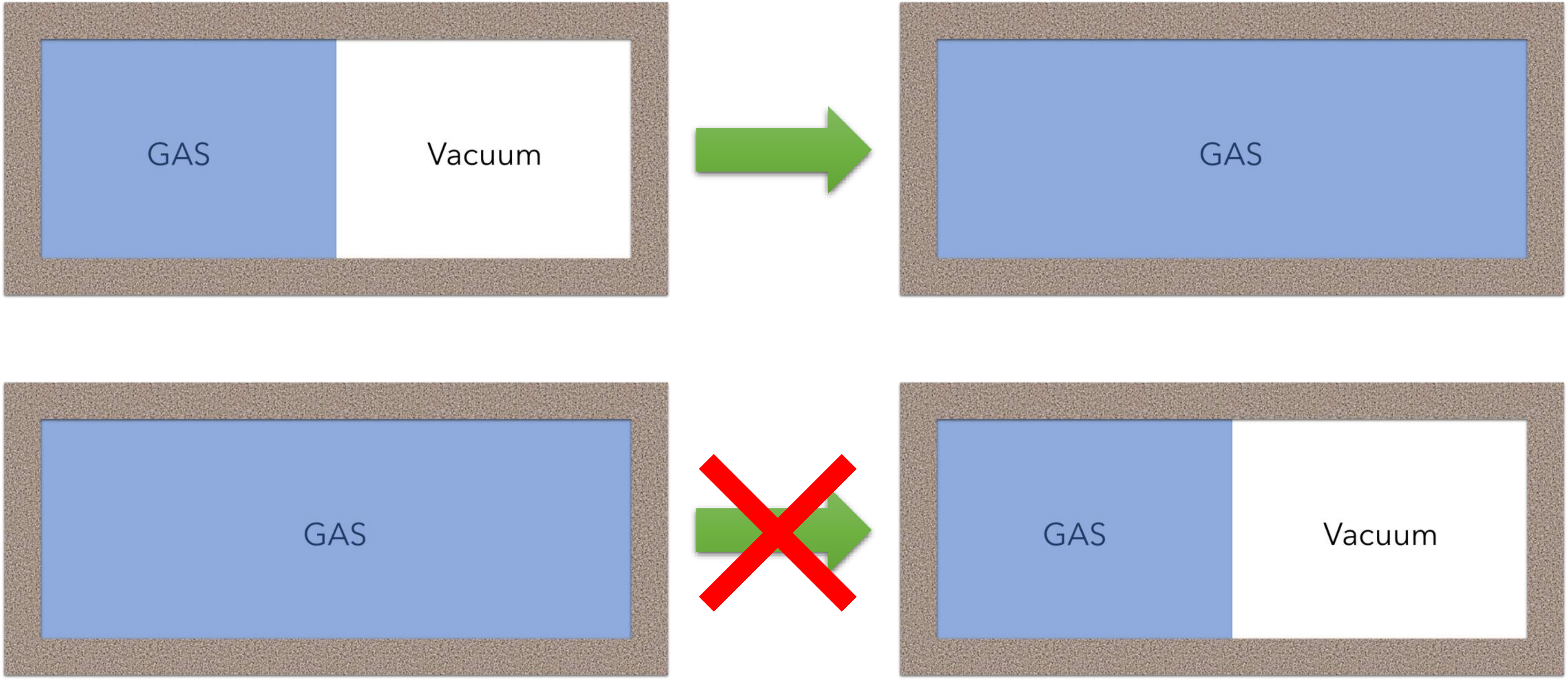
$S(P_q)=5.78\ k_B$

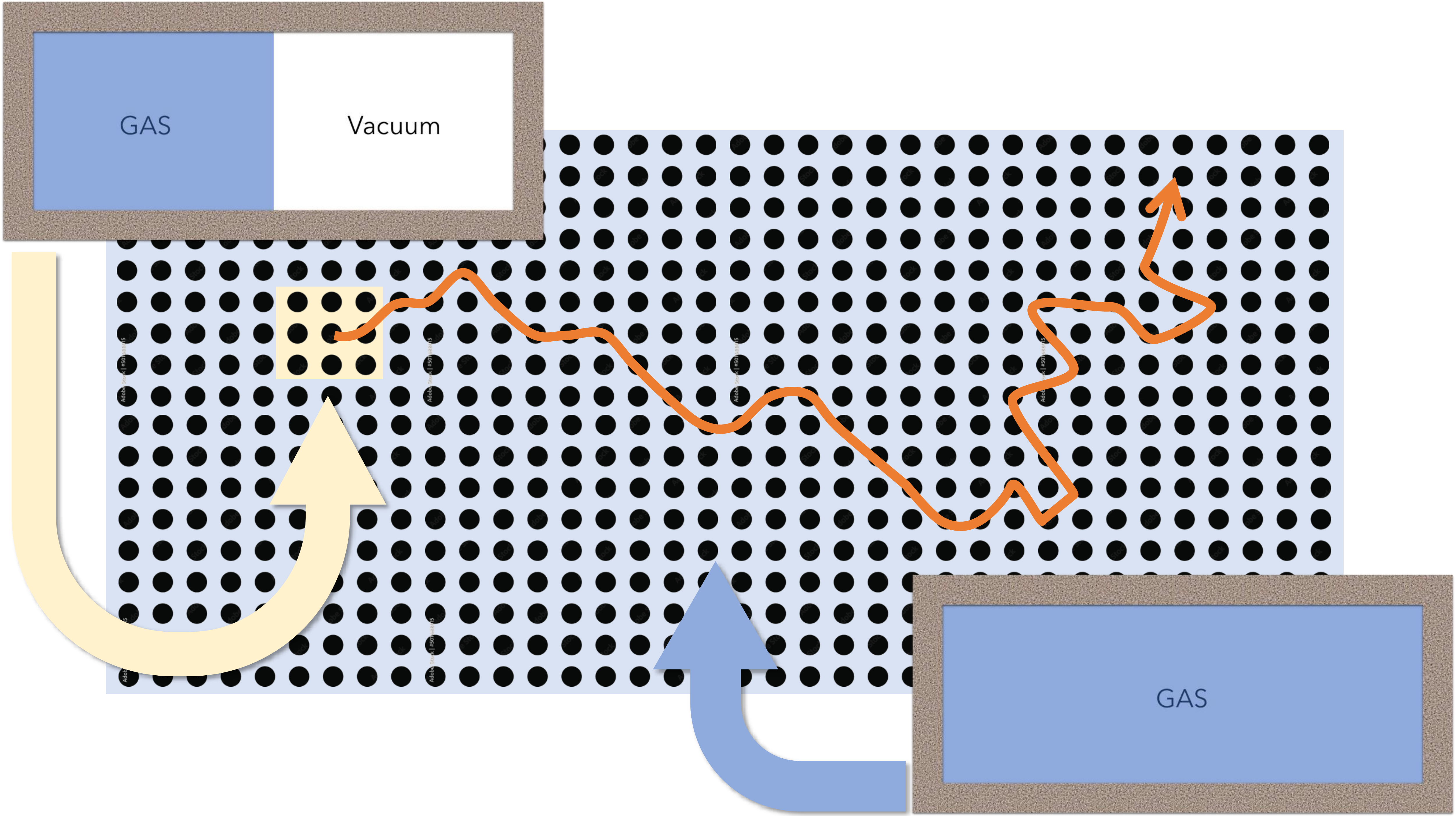
Boltzmann entropy

$S(A)=k_B.\ln[W(A)]$

$k_B = 8.617\times10^{-5}$ eV/K

Why does time flow in a single direction?




GAS
Vacuum
GAS

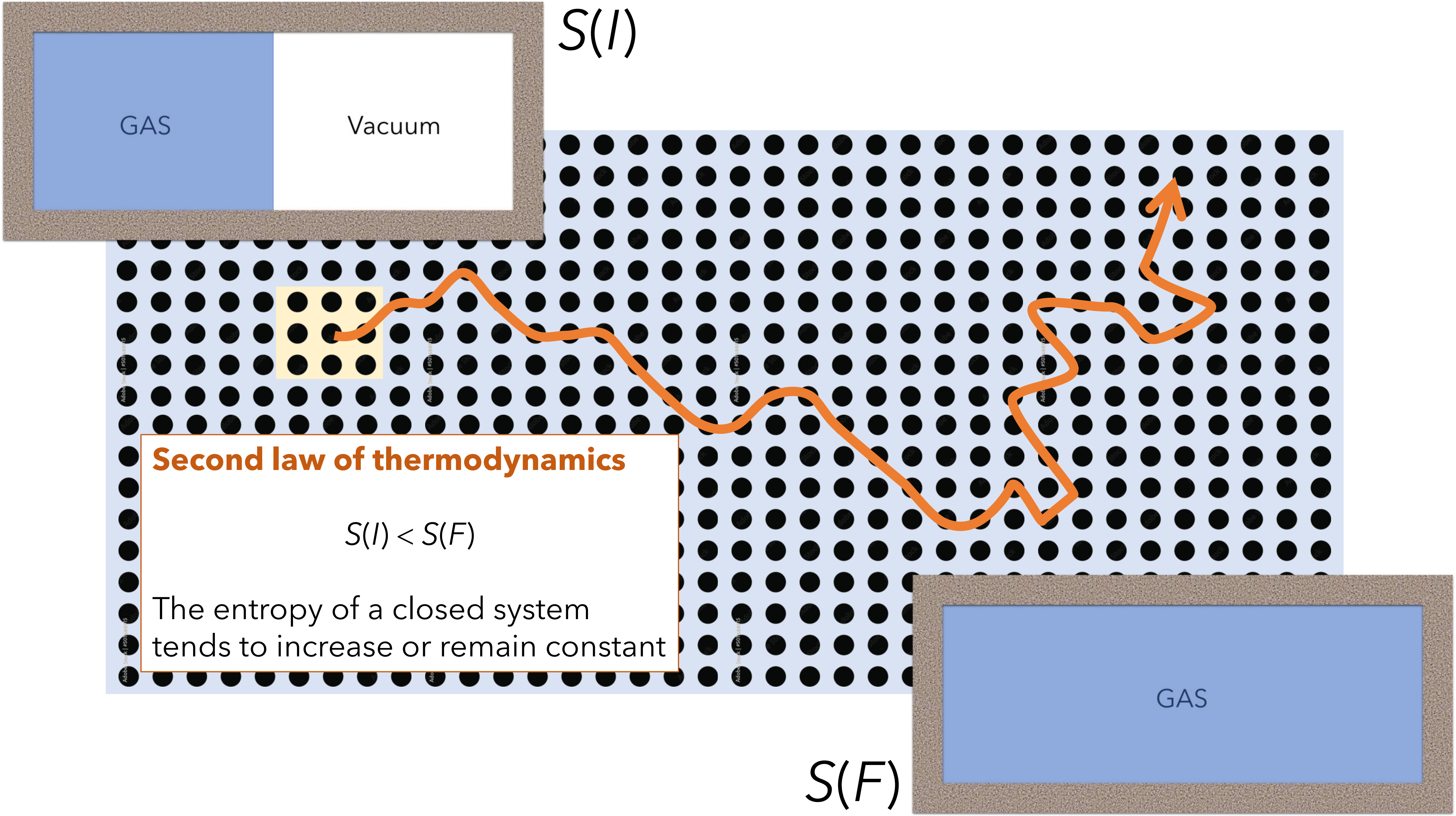
Why does time flow in a single direction?

The equilibrium region of the microstate space is so large that it consists almost entirely of equilibrium microstates.

For this reason, a system that starts its time-evolution in a non-equilibrium state always evolves into the equilibrium region and stays there for a very long time.

A trajectory may take longer than the universe's lifetime to return to the initial non-equilibrium region.

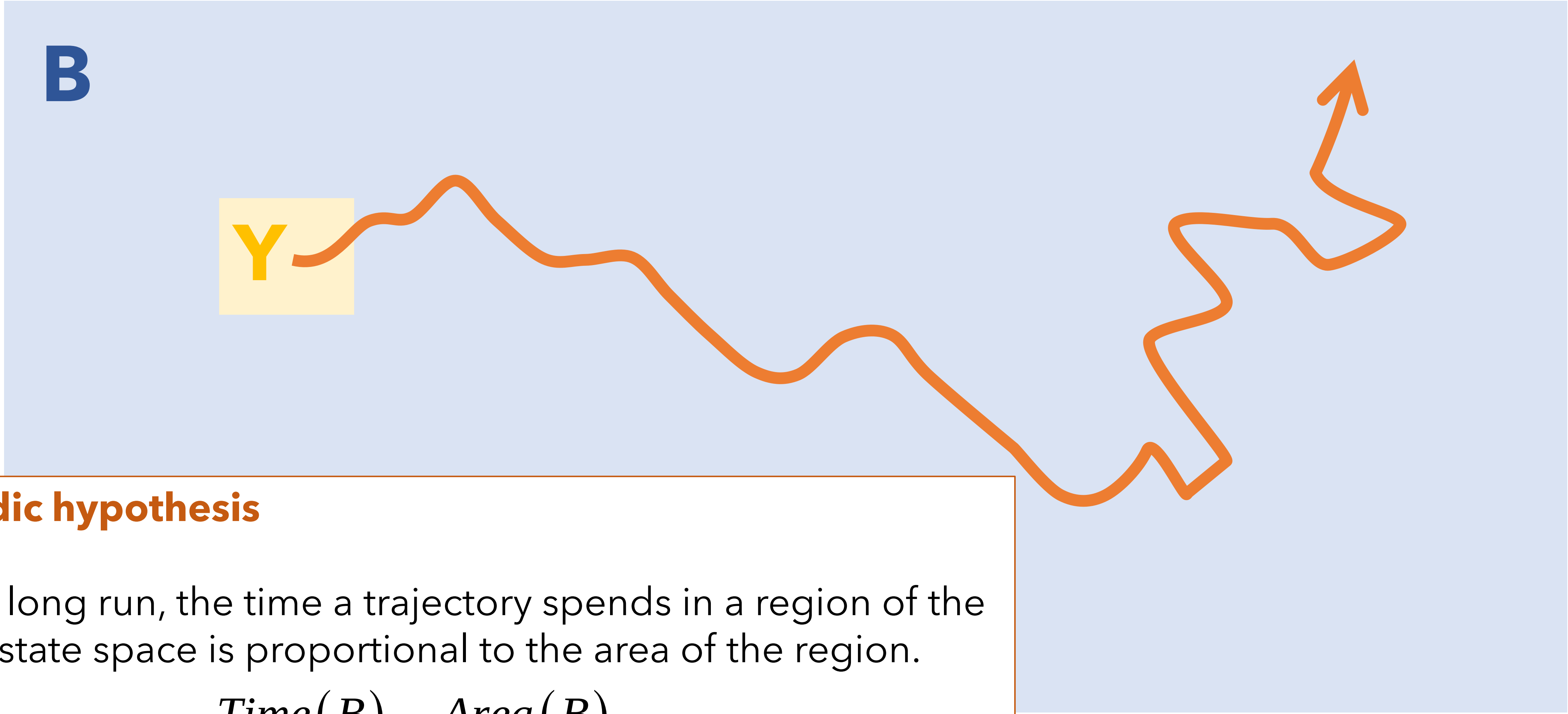
plato.stanford.edu/entries/statphys-statmech



Second law of thermodynamics

$$S(I) < S(F)$$

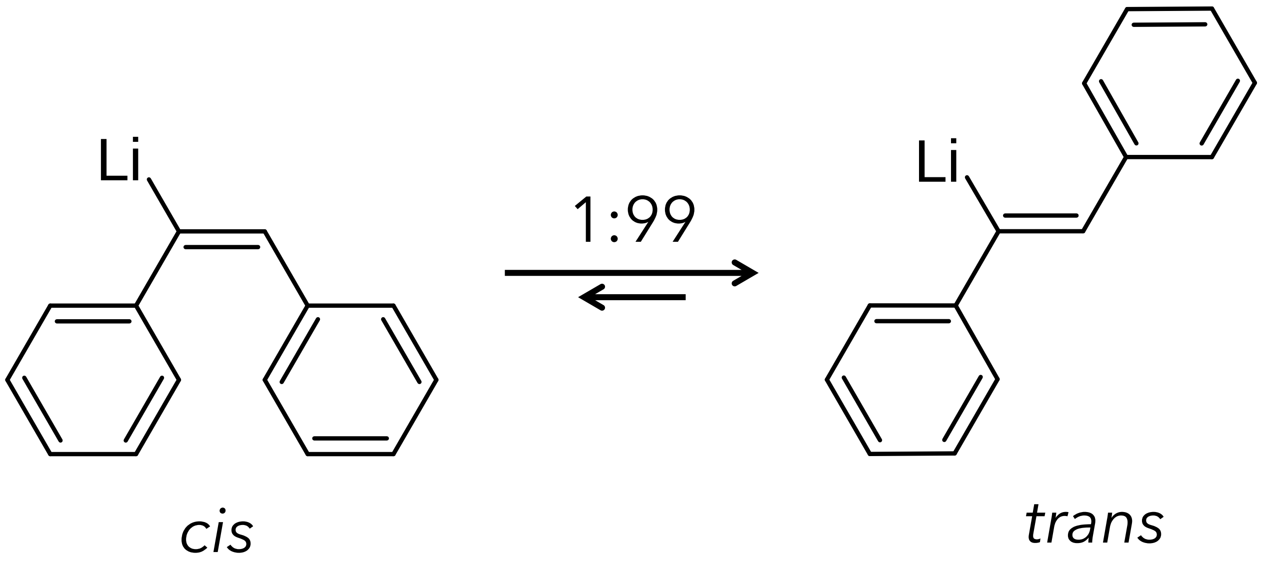
The entropy of a closed system tends to increase or remain constant



Ergodic hypothesis

In the long run, the time a trajectory spends in a region of the microstate space is proportional to the area of the region.

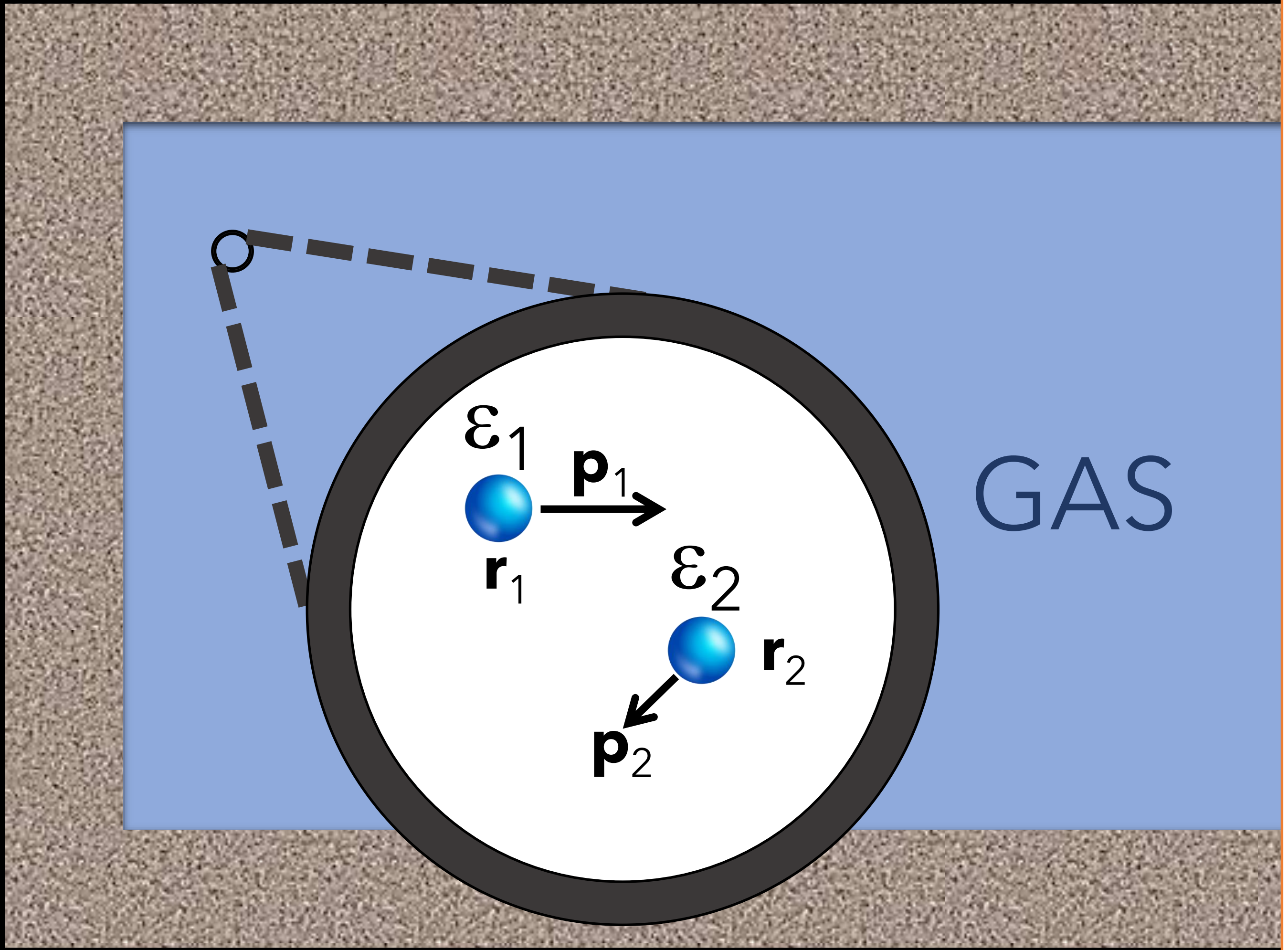
$$\frac{Time(B)}{Time(Y)} = \frac{Area(B)}{Area(Y)}$$

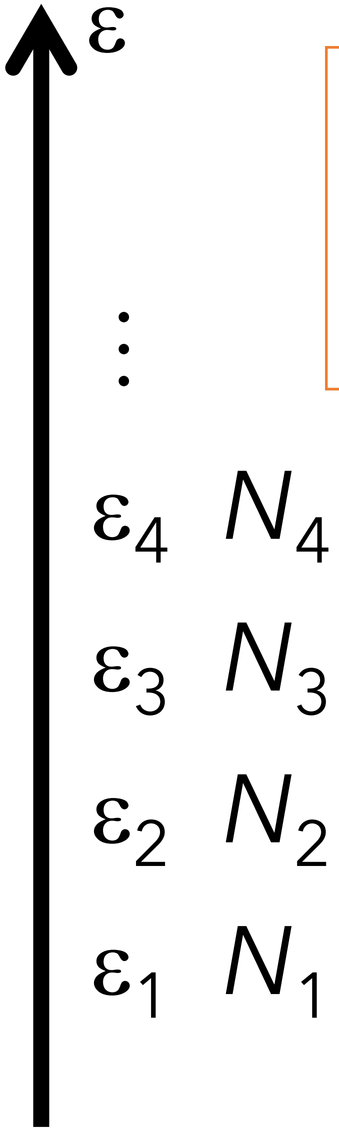


1) If we random sample Li-stilbene according to the 1:99 probability ratio, we get 1% of *cis* and 99% of *trans*.

2) If we run a long molecular dynamics trajectory, Li-stilbene remains 1% of the time in *cis* and 99% of the time in *trans*.

Maxwell-Boltzmann statistics

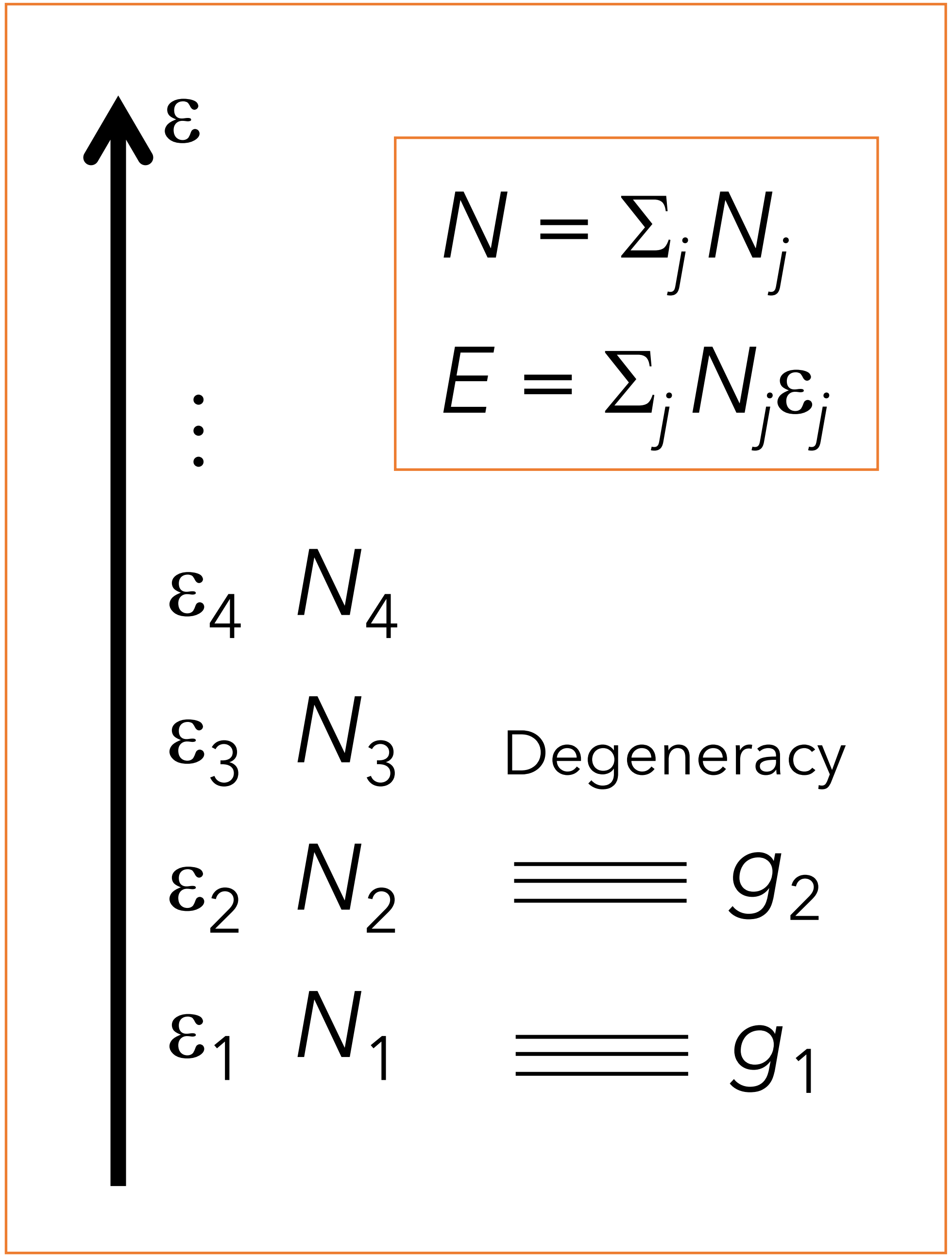




$$N = \Sigma_j N_j$$

$$E = \Sigma_j N_j \varepsilon_j$$

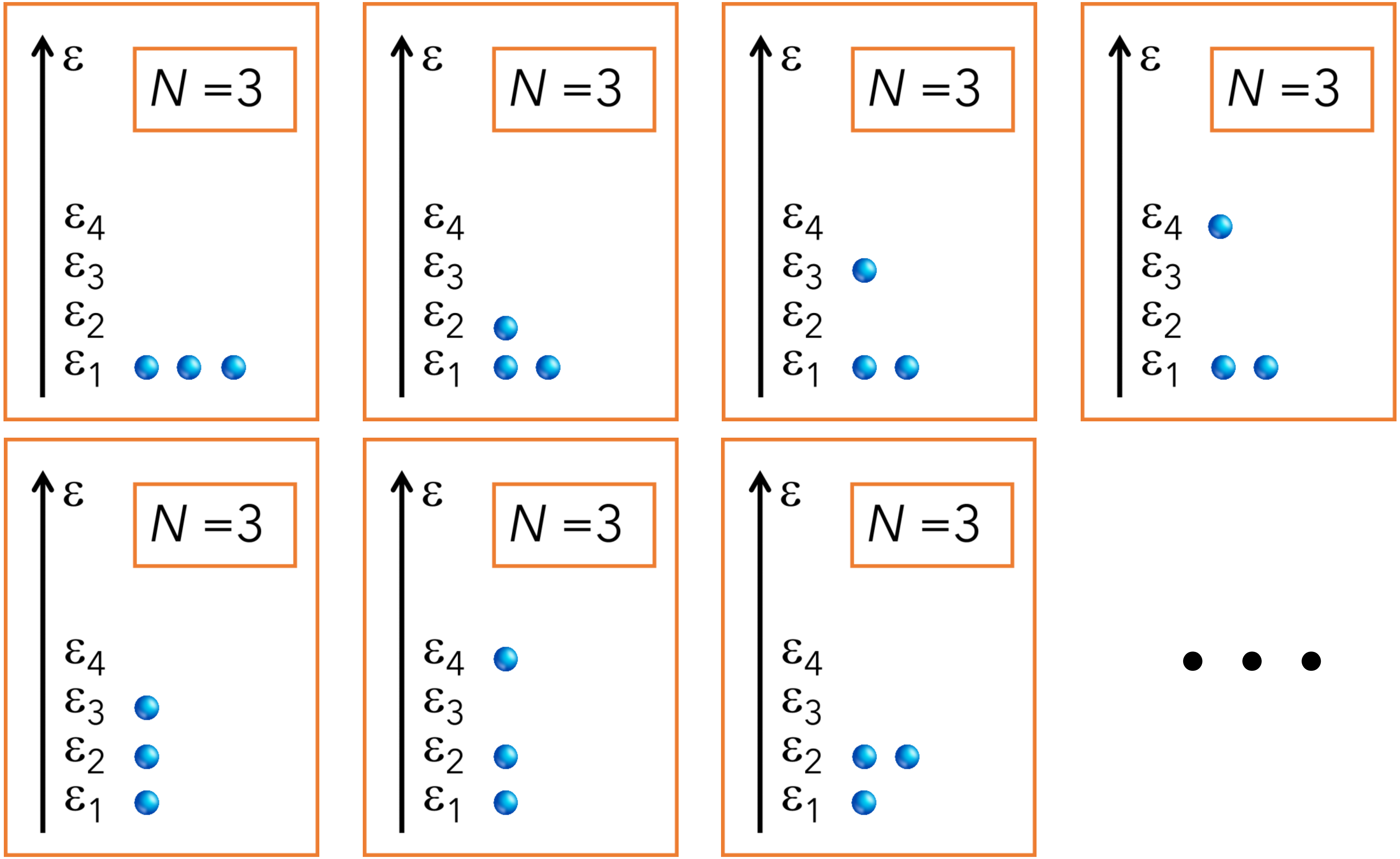
If the system is in equilibrium,
how many particles N_i
have energy ε_i?



$$N = \Sigma_j N_j$$

$$E = \Sigma_j N_j \varepsilon_j$$

en.wikipedia.org/wiki/Maxwell-Boltzmann_statistics


ε
N =3
ε4
ε3
ε2
ε1
ε
N =3
ε4
ε3
ε2
ε1
ε
N =3
ε4
ε3
ε2
ε1
ε
N =3
ε4
ε3
ε2
ε1
ε
N =3
ε4
ε3
ε2
ε1
ε
N =3
ε4
ε3
ε2
ε1
ε
N =3
ε4
ε3
ε2
ε1
• • •

The distribution of microstates is

$$W = \prod_i \frac{g_i^{N_i}}{N_i!} \quad \left(\text{for } g_i \gg N_i\right)$$

en.wikipedia.org/wiki/Maxwell-Boltzmann_statistics

We have many W distributions

$$W = \prod_i \frac{g_i^{N_i}}{N_i\,!}$$

For example, for N = 3 and 4 energy levels, each with g_i = 10:

$$W_1 = \frac{10^3}{3!} \times \frac{10^0}{0!} \times \frac{10^0}{0!} \times \frac{10^0}{0!} \approx 167$$

$$W_2 = \frac{10^2}{2!} \times \frac{10^1}{1!} \times \frac{10^0}{0!} \times \frac{10^0}{0!} = 500$$

$$W_3 = \frac{10^2}{2!} \times \frac{10^0}{0!} \times \frac{10^1}{1!} \times \frac{10^0}{0!} = 500$$

$$\vdots$$

$$W_M = \frac{10^0}{0!} \times \frac{10^0}{0!} \times \frac{10^0}{0!} \times \frac{10^3}{3!} \approx 167$$

In equilibrium,
S = k_B ln W is the largest.

We should search for the N_is that give the biggest ln W.

To find the maximum, we must solve

$$\frac{\partial}{\partial N_j}\left[\ln\left(\prod_i \frac{g_i^{N_i}}{N_i!}\right)\right]=0$$

However, to ensure that the total number of particles and energy are constant, we must solve

$$\frac{\partial}{\partial N_j}\left[\ln\left(\prod_i \frac{g_i^{N_i}}{N_i!}\right)+\alpha\left(N-\sum_i N_i\right)+\beta\left(E-\sum_i N_i\varepsilon_i\right)\right]=0$$

Lagrange multipliers
youtu.be/yuqB-d5MjZA

We get the Maxwell-Boltzmann distribution

$$\boxed{N_j = g_j \exp\left(\frac{-\left(\varepsilon_j - \mu\right)}{k_B T}\right)}$$

See the derivation in the Appendix to this presentation.

Two extremely important results are

$$\frac{N_j}{N_k} = \frac{g_j}{g_k} \exp\left(\frac{-\left(\varepsilon_k - \varepsilon_j\right)}{k_B T} \right)$$

$$\frac{N_j}{N} = \frac{g_j \exp\left(\frac{-\varepsilon_j}{k_B T} \right)}{\sum_i g_i \exp\left(\frac{-\varepsilon_i}{k_B T} \right)}$$

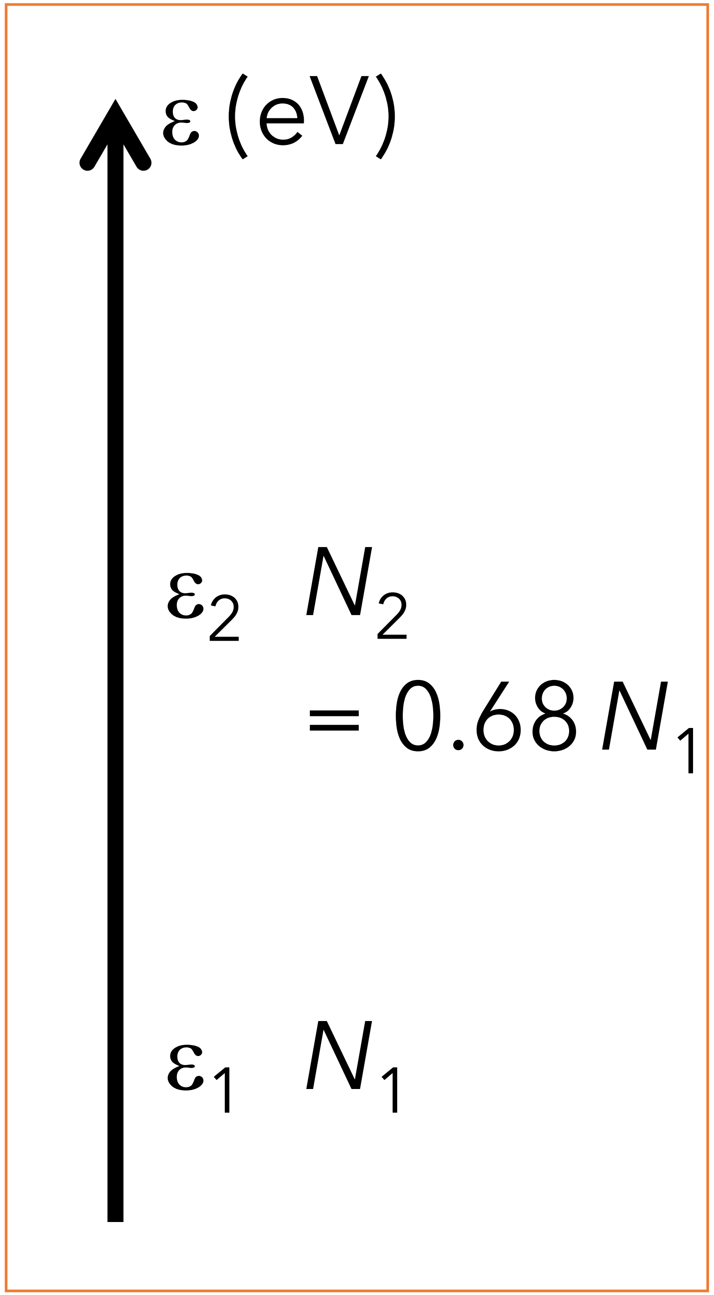
Example: If a gas is equilibrated at 300 K, which fraction of molecules (relative to the ground state) is at the first vibrational excited state 0.01 eV above the ground state? The states are equally degenerated.

$$\frac{N_j}{N_k} = \frac{g_j}{g_k} \exp\left(\frac{-\left(\varepsilon_k - \varepsilon_j\right)}{k_B T} \right)$$

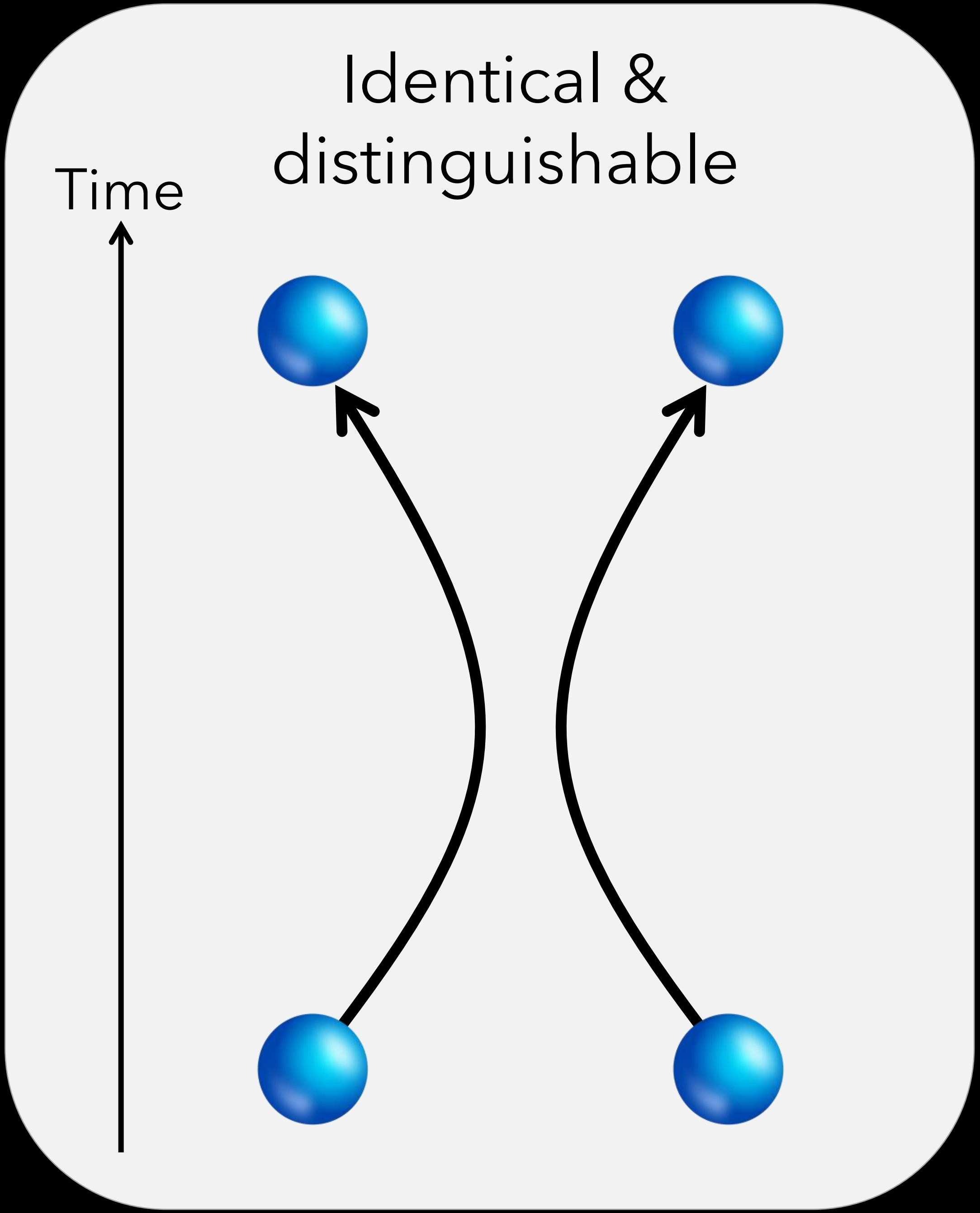
$$\frac{N_2}{N_1} = \exp\left(\frac{-\left(\varepsilon_2 - \varepsilon_1\right)}{k_B T} \right)$$

$$= \exp\left(\frac{-0.01\ \mathrm{eV}}{8.617 \times 10^{-5}\ \mathrm{eV/K} \times 300\ \mathrm{K}} \right)$$

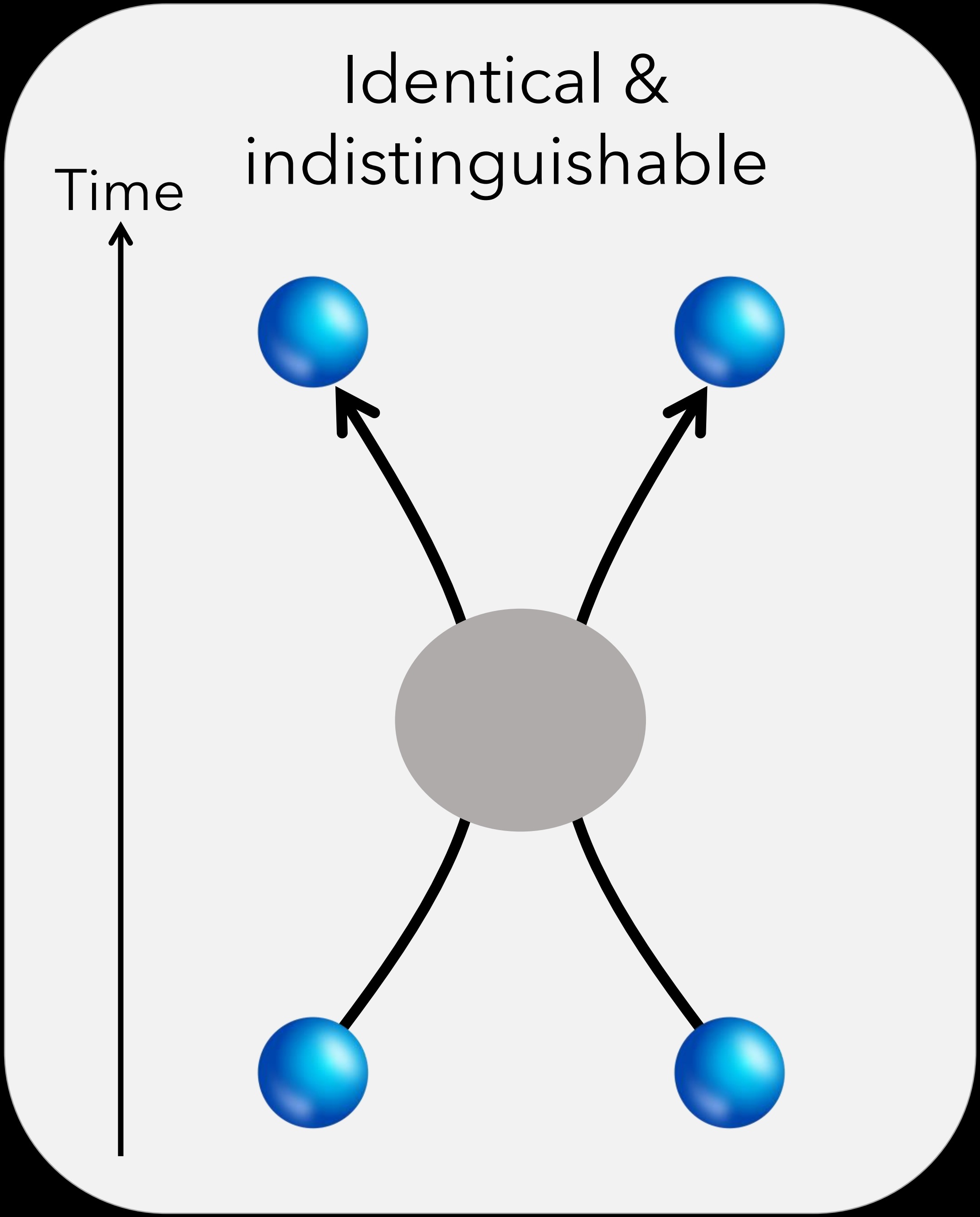
$$= 0.68$$



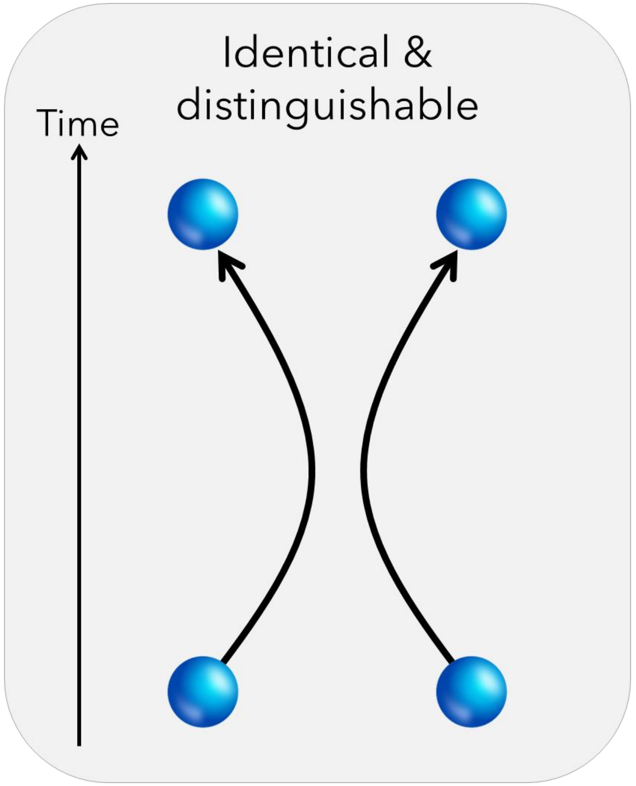
Particle distributions



Identical & distinguishable



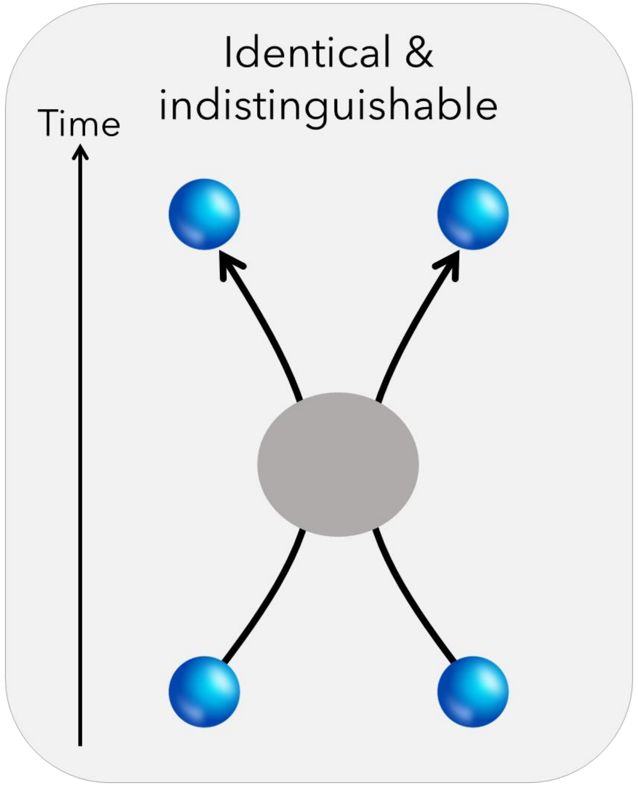
Identical & indistinguishable



Number of microstates

$$W = N! \prod_i \frac{g_i^{N_i}}{N_i!}$$

Wrong entropy! (Gibbs paradox)



Number of microstates

$$W = \prod_i \frac{g_i^{N_i}}{N_i!}$$

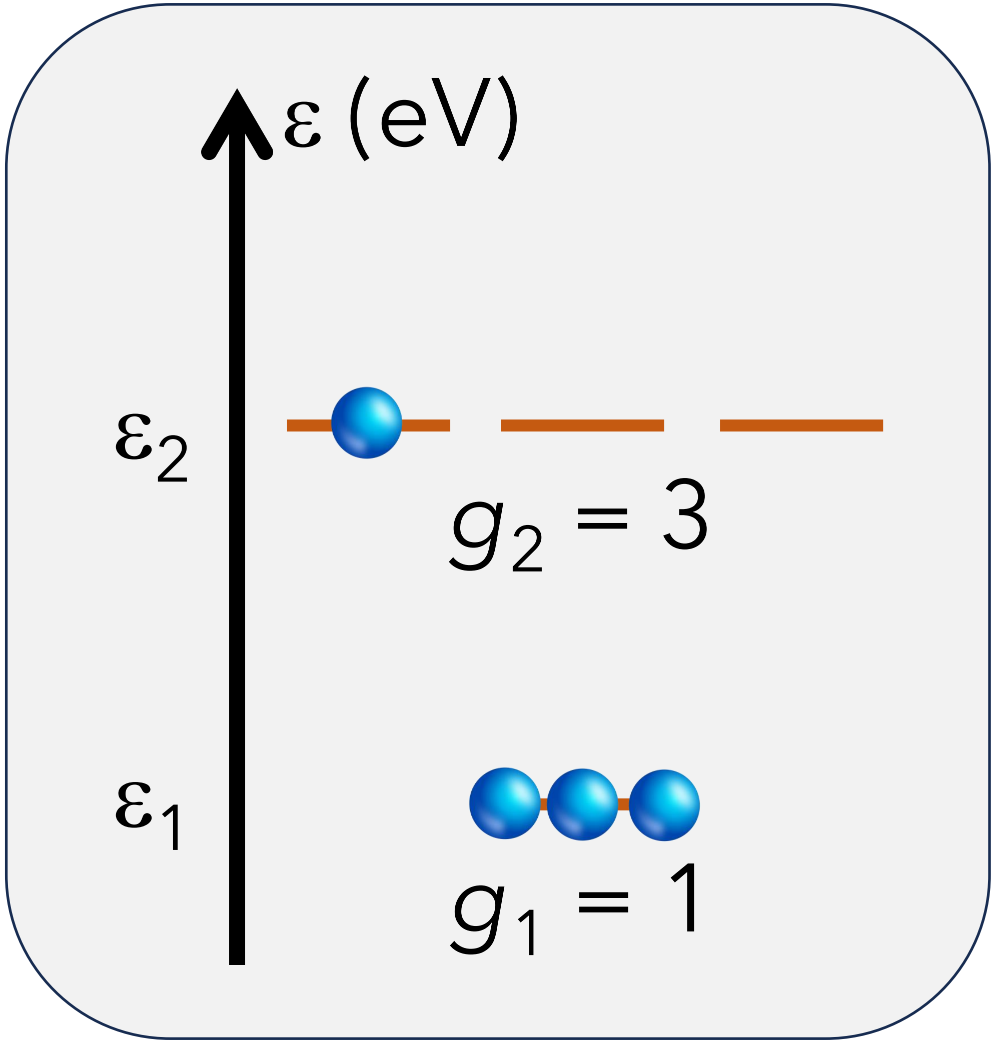
Correct entropy!

Indistiguibility is needed to describe classical systems statistically.

Gibbs discovered that in 1874!

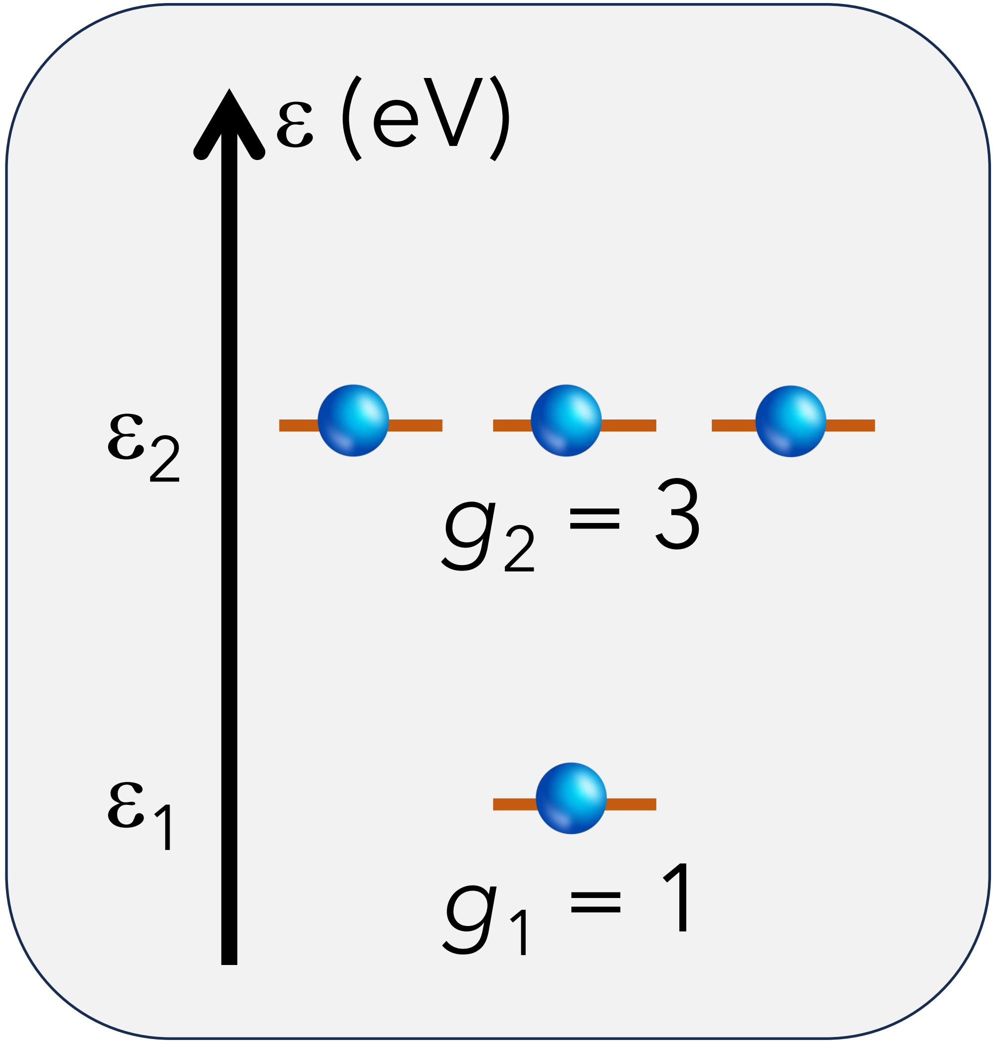
Jaynes, In *Maximum entropy and Bayesian methods, Springer, 1992*

Bosons



As many as we want in each sublevel.

Fermions



One per sublevel.

Bosons

As many as we want in each sublevel.

Fermions

One per sublevel.

$$W_{BE} = \prod_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

$$W_{FD} = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!}$$

$$\frac{\partial}{\partial N_j}\left[\ln(W) + \alpha\left(N - \sum_i N_i\right) + \beta\left(E - \sum_i N_i \varepsilon_i\right)\right] = 0$$

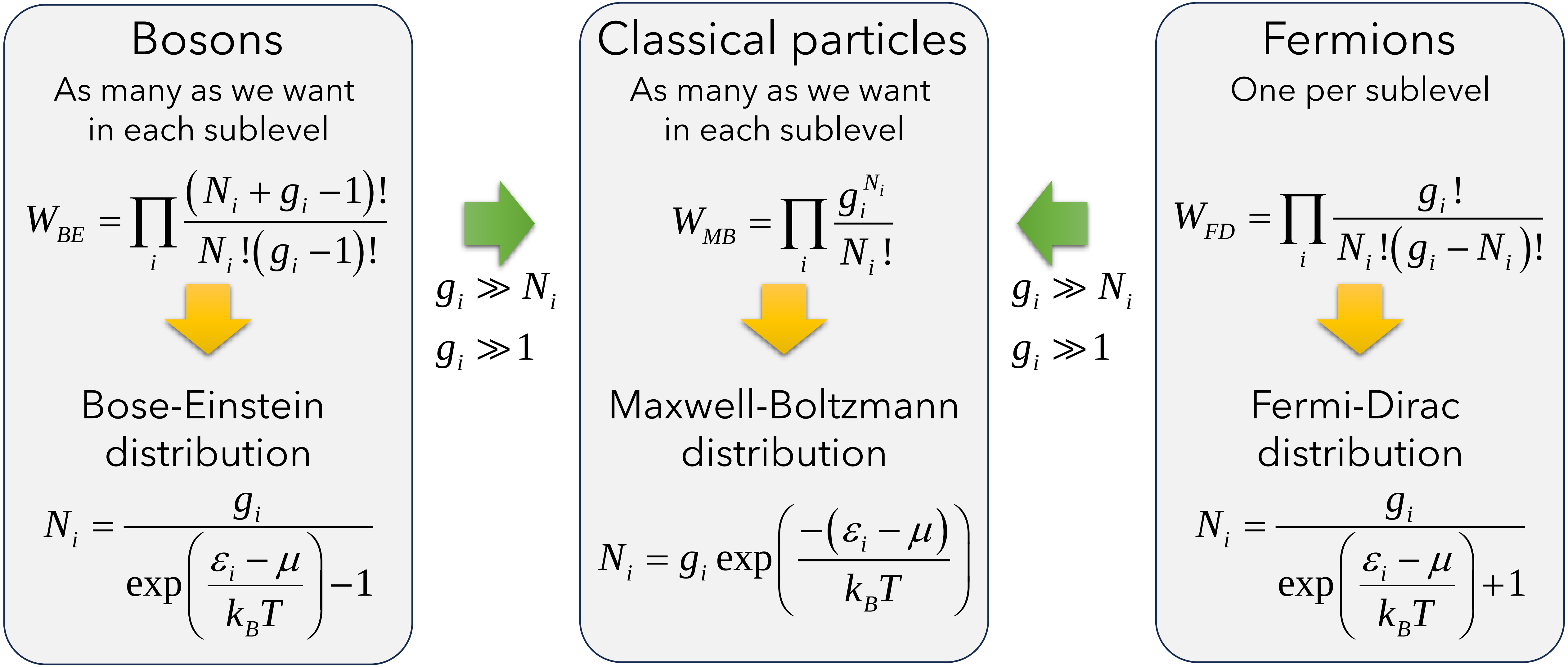
Bose-Einstein distribution

$$N_i = \frac{g_i}{\exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right) - 1}$$

Fermi-Dirac distribution

$$N_i = \frac{g_i}{\exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right) + 1}$$

en.wikipedia.org/wiki/Bose-Einstein_statistics
en.wikipedia.org/wiki/Fermi-Dirac_statistics



Bosons

As many as we want
in each sublevel

$$W_{BE} = \prod_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

Bose-Einstein
distribution

$$N_i = \frac{g_i}{\exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right) - 1}$$

$g_i \gg N_i$

$g_i \gg 1$

Classical particles

As many as we want
in each sublevel

$$W_{MB} = \prod_i \frac{g_i^{N_i}}{N_i!}$$

Maxwell-Boltzmann
distribution

$$N_i = g_i \exp\left(\frac{-(\varepsilon_i - \mu)}{k_B T}\right)$$

$g_i \gg N_i$

$g_i \gg 1$

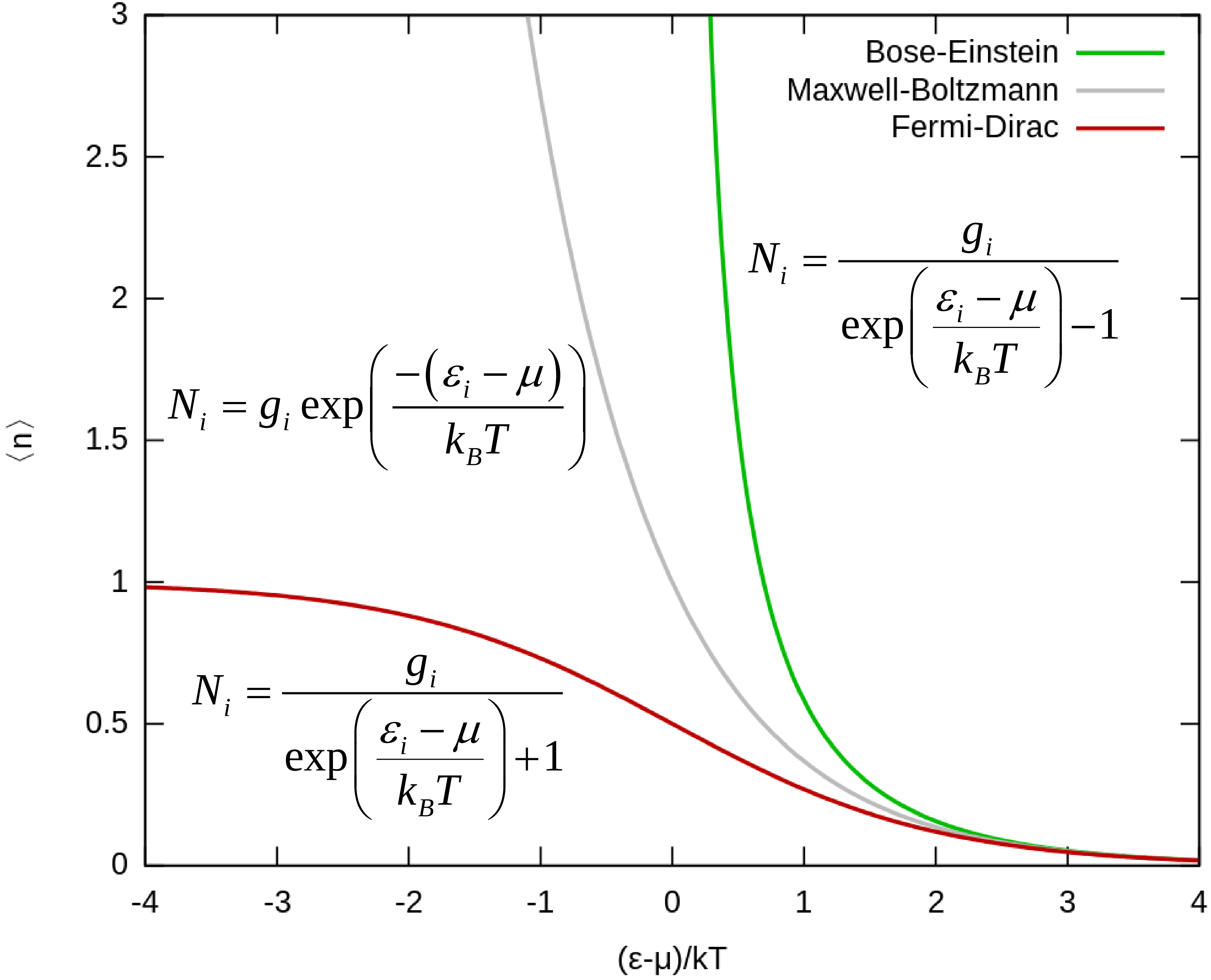
Fermions

One per sublevel

$$W_{FD} = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!}$$

Fermi-Dirac
distribution

$$N_i = \frac{g_i}{\exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right) + 1}$$



$$N_i = \frac{g_i}{\exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right) - 1}$$

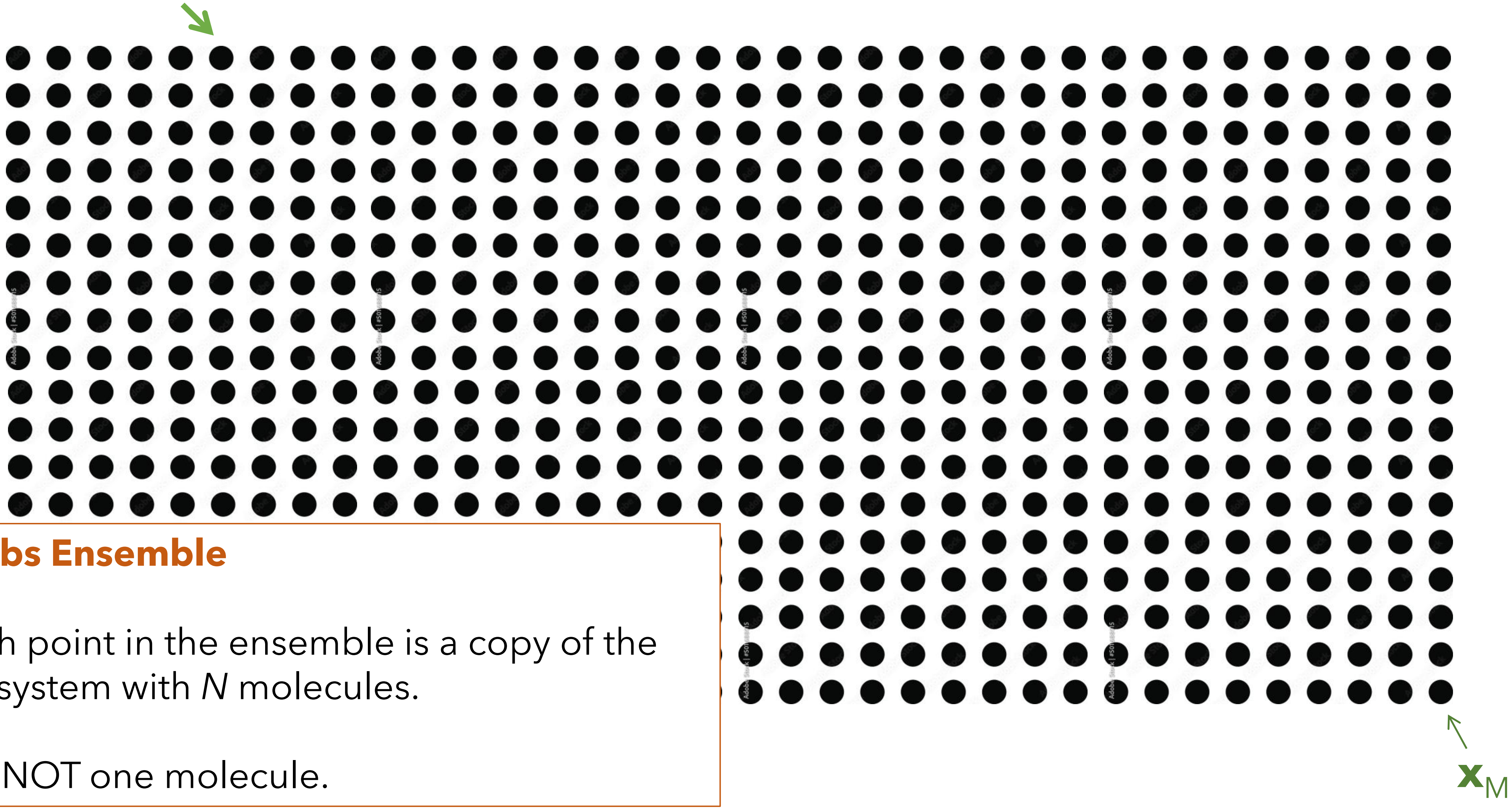
$$N_i = g_i \exp\left(\frac{-(\varepsilon_i - \mu)}{k_B T}\right)$$

$$N_i = \frac{g_i}{\exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right) + 1}$$

The Gibbs picture

Ensemble

$\mathbf{x}_i = (\mathbf{r}_{i1}, \mathbf{p}_{i1}, \mathbf{r}_{i2}, \mathbf{p}_{i2}, \ldots, \mathbf{r}_{iN}, \mathbf{p}_{iN})$



Gibbs Ensemble

Each point in the ensemble is a copy of the full system with *N* molecules.

It is NOT one molecule.

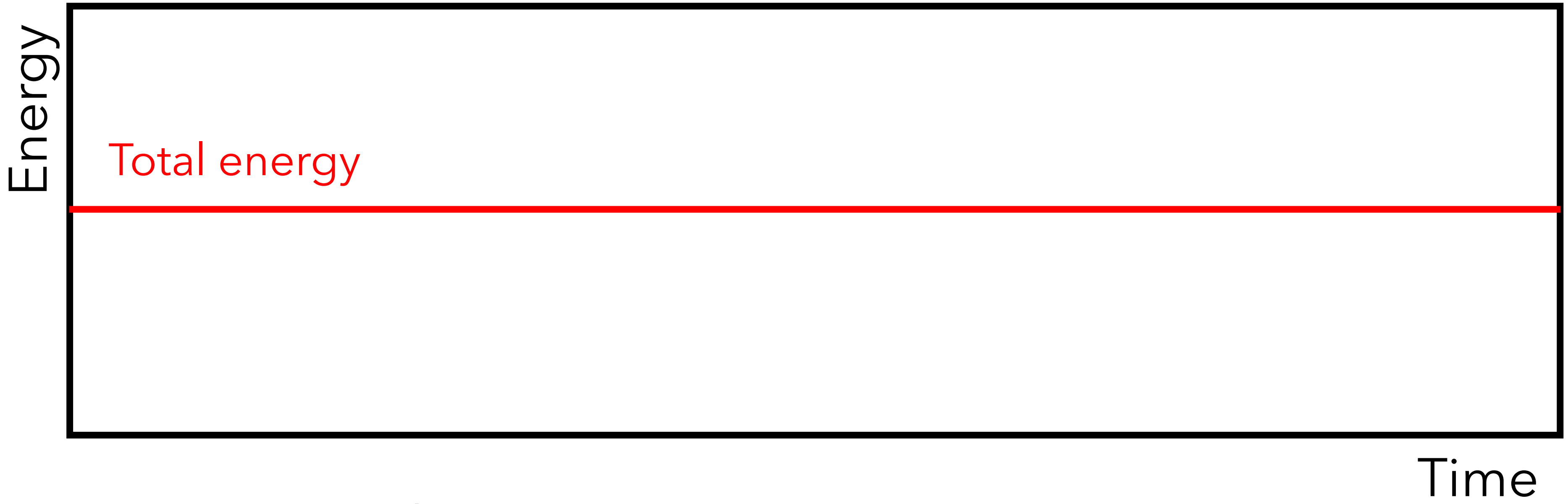
Microcanonical (or *NVE*) ensemble: all points have the same number of molecules and total energy.

Canonical (or *NVT*) ensemble: all points have the same number of molecules and temperature. They may have different total energies.

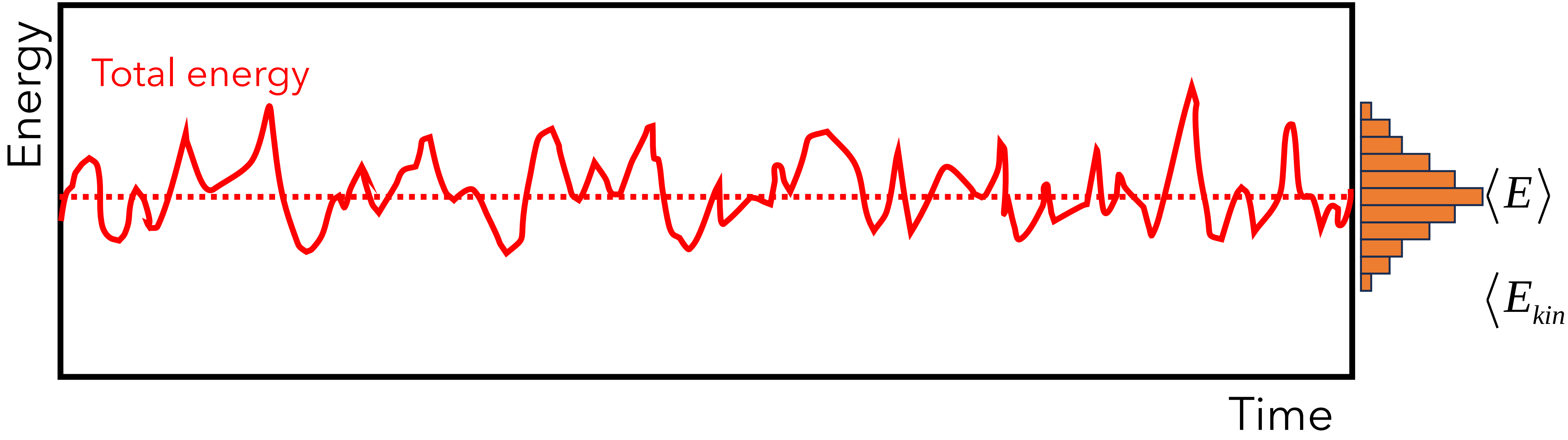
Grand-canonical (or μ*VT*) ensemble: all points have the same temperature and chemical potential. They may have a different number of molecules and total energies.

Thermostats

Microcanonical ensemble (NVE)



Canonical ensemble (NVT)



$$\langle E_{kin} \rangle = \frac{3}{2} k_B T$$

How can we run molecular dynamics with constant temperature?

Thermostats are algorithms that couple the system to an external bath, allowing energy exchange and thermalization.

Many thermostats are available in MD programs.

Some of the most popular are:

- Andersen [Andersen. *J Chem Phys* **1980**, *72*, 2384]
- Lowe-Andersen [Lowe. *Europhys Lett* ***1999***, *47*, 145]
- Nosé-Hoover [Hoover. *Phys Rev A* **1985**, *31*, 1695]

	Nosé-Hoover	**Andersen**	**Lowe-Andersen**
Conserves momentum	Yes	No	Yes
Galilean invariant	No	No	Yes
Global/Local	Global	Local	Local
Enhances viscosity	No	No	Yes
Deterministic/Stochastic	Deterministic	Stochastic	Stochastic

Lowe. *Europhys Lett* ***1999***, *47*, 145

Andersen thermostat

1. Define a collision frequency Γ
2. Integrate dynamics in one step Δt (eg, Velocity Verlet)
3. For each atom, sample a uniform random number r_0 between 0 and 1.
   If $r_0 > \Gamma\Delta t$, do not change the velocity
   If $r_0 \leq \Gamma\Delta t$, change the velocity as

$$\mathbf{v}_{\alpha}^{(new)} = \left(v_{\alpha,x}^{(new)}, v_{\alpha,y}^{(new)}, v_{\alpha,z}^{(new)}\right) = \sqrt{\frac{k_B T}{M_{\alpha}}} \times \left(r_x, r_y, r_z\right)$$

   where r_x, r_y, and r_z are Gaussian random numbers of unit variance;
   M_{α} is the mass of atom α

Andersen. *J Chem Phys* **1980**, *72*, 2384

$$\mathbf{v}_\alpha^{(new)} = \sqrt{\frac{k_B T}{M_\alpha}} \times \left(r_x, r_y, r_z\right)$$

The rationale for this formula is that for a system following Maxwell-Boltzmann statistics, the velocity is distributed as

$$f\left(\mathbf{v}\right) d^3\mathbf{v} = \left[\frac{M}{2\pi k_B T}\right]^{3/2} \exp\left(-\frac{Mv^2}{2K_B T}\right)$$

This is a Gaussian distribution with standard deviation

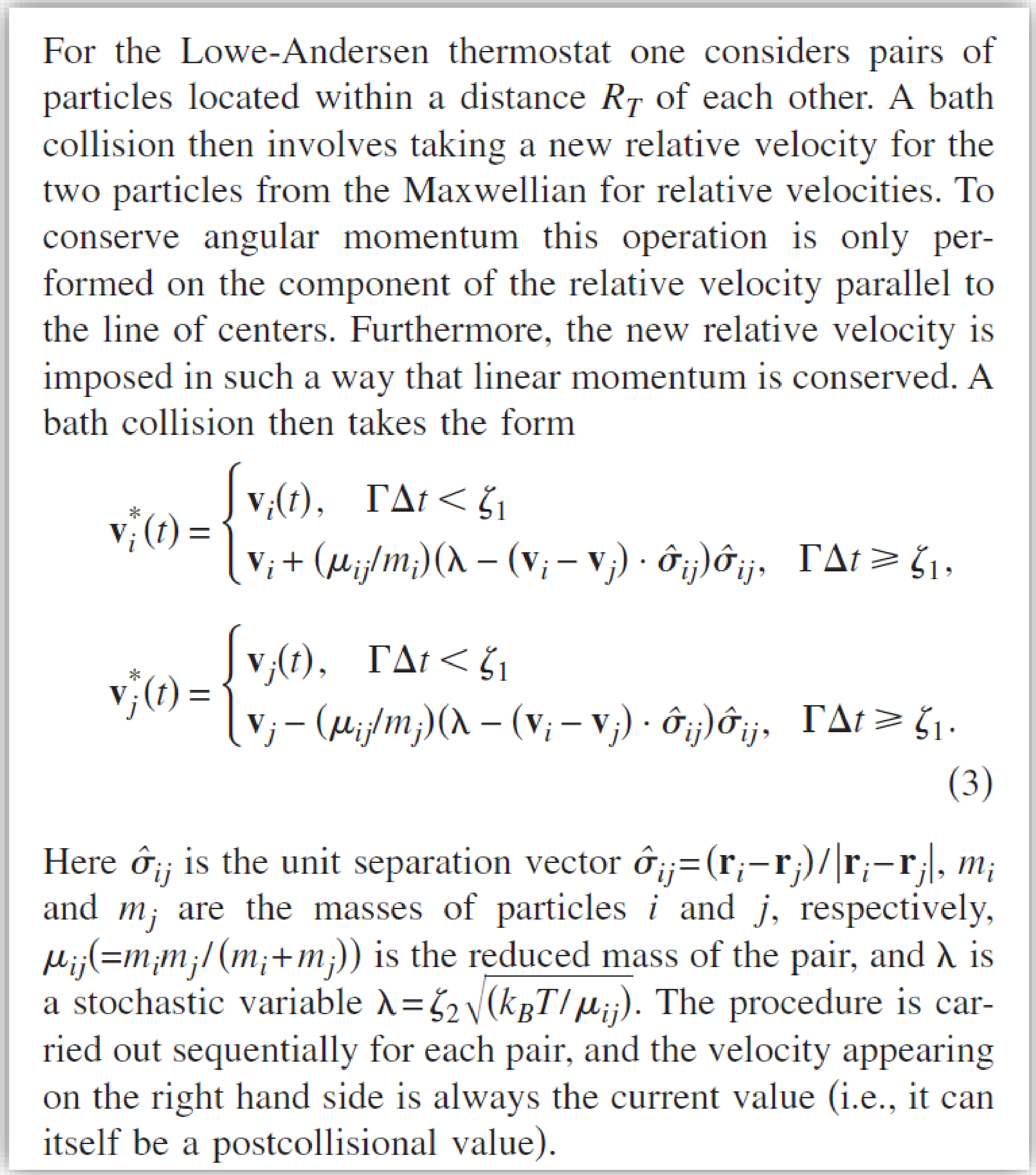
$$\sigma = \sqrt{\frac{k_B T}{M}}$$

Thus, the Andersen thermostat is spreading the velocity as a Gaussian around the mean value **v** = 0

The Lowe-Anderson thermostat works similarly but with a more complicated velocity change.

It is done in the direction between atoms to conserve momentum.

Koopman; Lowe. *J Chem Phys* **2006**, *124*, 204103



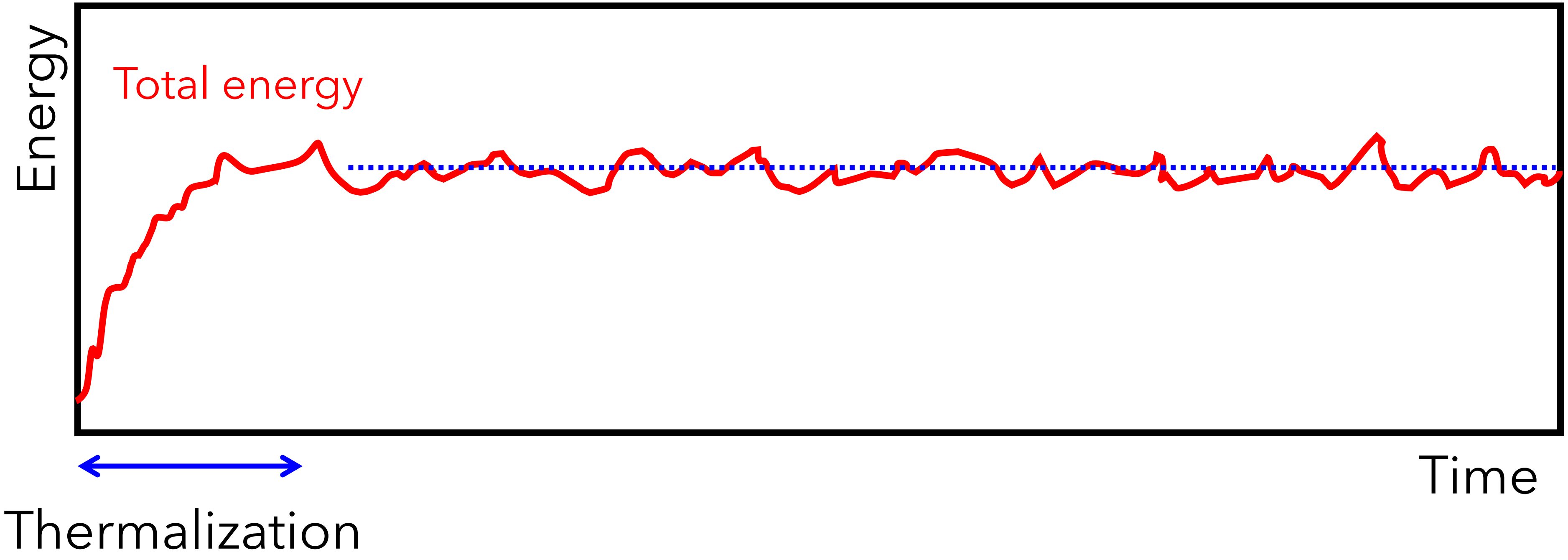
For the Lowe-Andersen thermostat one considers pairs of particles located within a distance R_T of each other. A bath collision then involves taking a new relative velocity for the two particles from the Maxwellian for relative velocities. To conserve angular momentum this operation is only performed on the component of the relative velocity parallel to the line of centers. Furthermore, the new relative velocity is imposed in such a way that linear momentum is conserved. A bath collision then takes the form

$$\mathbf{v}_i^*(t) = \begin{cases} \mathbf{v}_i(t), & \Gamma\Delta t < \zeta_1 \\ \mathbf{v}_i + (\mu_{ij}/m_i)(\lambda - (\mathbf{v}_i - \mathbf{v}_j)\cdot\hat{\sigma}_{ij})\hat{\sigma}_{ij}, & \Gamma\Delta t \geqslant \zeta_1, \end{cases}$$

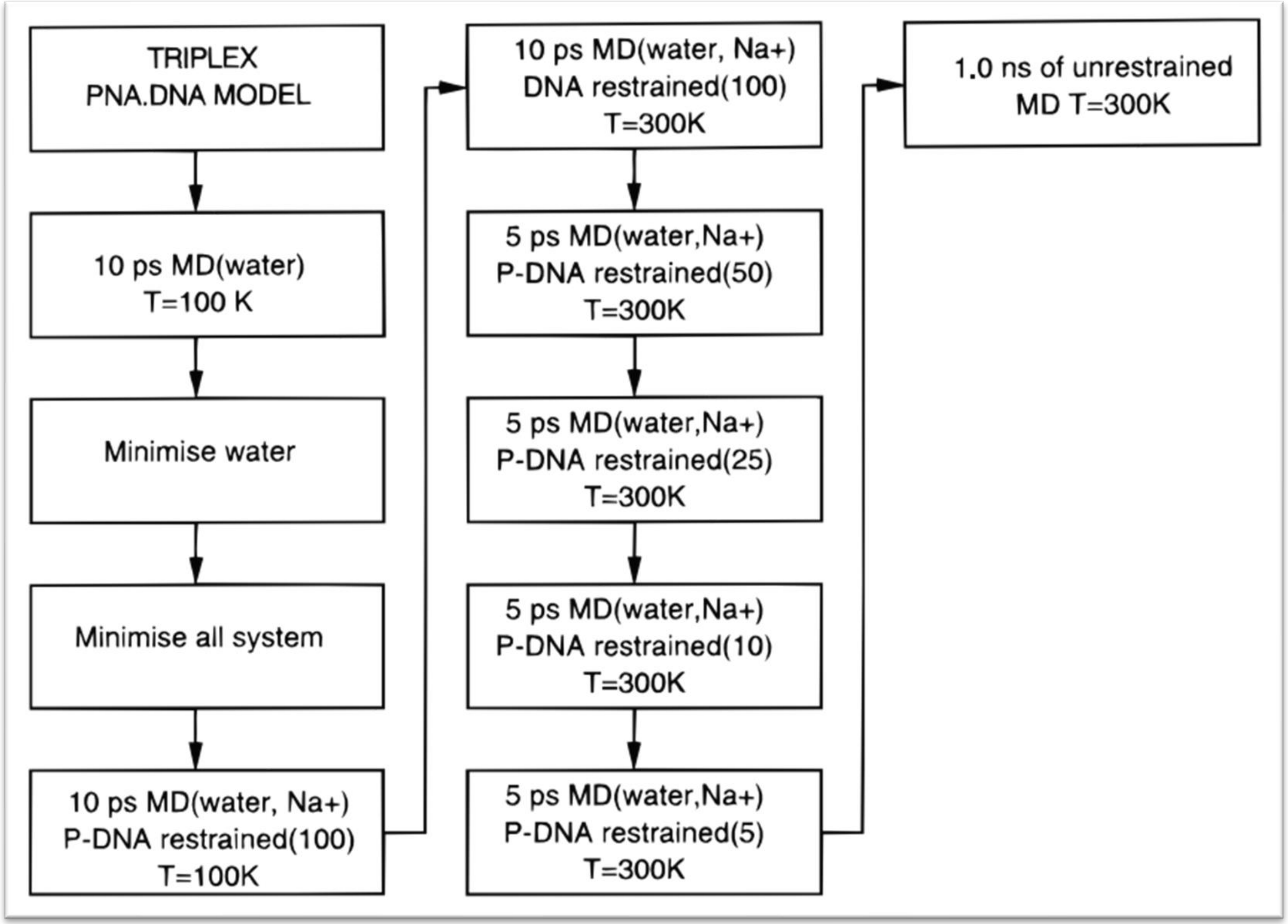
$$\mathbf{v}_j^*(t) = \begin{cases} \mathbf{v}_j(t), & \Gamma\Delta t < \zeta_1 \\ \mathbf{v}_j - (\mu_{ij}/m_j)(\lambda - (\mathbf{v}_i - \mathbf{v}_j)\cdot\hat{\sigma}_{ij})\hat{\sigma}_{ij}, & \Gamma\Delta t \geqslant \zeta_1. \end{cases} \tag{3}$$

Here $\hat{\sigma}_{ij}$ is the unit separation vector $\hat{\sigma}_{ij}=(\mathbf{r}_i-\mathbf{r}_j)/|\mathbf{r}_i-\mathbf{r}_j|$, m_i and m_j are the masses of particles i and j, respectively, $\mu_{ij}(=m_i m_j/(m_i+m_j))$ is the reduced mass of the pair, and λ is a stochastic variable $\lambda=\zeta_2\sqrt{(k_B T/\mu_{ij})}$. The procedure is carried out sequentially for each pair, and the velocity appearing on the right hand side is always the current value (i.e., it can itself be a postcollisional value).

Canonical ensemble (NVT)



Thermalization may require several steps.



Shields *et al. J Am Chem Soc* **1998**, *120*, 5895
Asha *et al. J Phys Chem B* **2022**, *126*, 10608

To know more:

Philosophical perspective on statistical mechanic

- plato.stanford.edu/entries/statphys-statmech

The different statistics

- en.wikipedia.org/wiki/Maxwell-Boltzmann_statistics
- en.wikipedia.org/wiki/Bose-Einstein_statistics
- en.wikipedia.org/wiki/Fermi-Dirac_statistics

Lagrange multipliers:

- youtu.be/yuqB-d5MjZA

Papers available for download at:
amubox.univ-amu.fr/s/xXAiMZrDPb9RMRX (Ask me for the password)

Appendix
Deriving Maxwell-Boltzmann distribution

In equilibrium,
$S = k_B \ln(W)$ is the largest.

We should search for the largest $\ln(W)$

Which value of N_j does maximize W
under the constraint that N and E are constant?

$$\frac{\partial}{\partial N_j}\left[\ln(W)+\alpha\left(N-\sum_i N_i\right)+\beta\left(E-\sum_i N_i\varepsilon_i\right)\right]=0$$

Lagrange multipliers: youtu.be/yuqB-d5MjZA

To find the maximum of ln *W*, we need ln *W*:

$$\ln(W) = \ln\left(\prod_i \frac{g_i^{N_i}}{N_i!}\right)$$

$$= \sum_i \left(\ln\left(g_i^{N_i}\right) - \ln(N_i!)\right)$$

$$\approx \sum_i \left(N_i \ln(g_i) - N_i \ln(N_i) + N_i\right)$$

Remember

$$\ln(ab) = \ln(a) + \ln(b)$$

Stirling's approximation

$$\ln(N!) \approx N \ln(N) - N_i \text{ for } N \gg 1$$

We must solve

$$\frac{\partial}{\partial N_j}\left[\sum_i\left(N_i\ln\left(g_i\right)-N_i\ln\left(N_i\right)+N_i\right)+\alpha\left(N-\sum_i N_i\right)+\beta\left(E-\sum_i N_i\varepsilon_i\right)\right]=0$$

First, we compute the derivative

$$\frac{\partial}{\partial N_j}\left[\sum_i\left(N_i\ln\left(g_i\right)-N_i\ln\left(N_i\right)+N_i\right)+\alpha\left(N-\sum_i N_i\right)+\beta\left(E-\sum_i N_i\varepsilon_i\right)\right]$$

$$=\frac{\partial}{\partial N_j}\sum_i N_i\left(\ln\left(g_i\right)-\ln\left(N_i\right)+1\right)+\alpha\frac{\partial}{\partial N_j}\left(N-\sum_i N_i\right)+\beta\frac{\partial}{\partial N_j}\left(E-\sum_i N_i\varepsilon_i\right)$$

$$=\frac{\partial}{\partial N_j}N_j\left(\ln\left(g_j\right)-\ln\left(N_j\right)+1\right)-\alpha\frac{\partial}{\partial N_j}N_j-\beta\varepsilon_j\frac{\partial}{\partial N_j}N_j$$

$$=\left(\ln\left(g_j\right)-\ln\left(N_j\right)+1\right)+N_j\frac{\partial}{\partial N_j}\left(\ln\left(g_j\right)-\ln\left(N_j\right)+1\right)-\alpha-\beta\varepsilon_j$$

$$=\ln\left(g_j\right)-\ln\left(N_j\right)+1-\frac{N_j}{N_j}-\alpha-\beta\varepsilon_j$$

$$=\ln\left(g_j\right)-\ln\left(N_j\right)-\alpha-\beta\varepsilon_j$$

Solving

$$\frac{\partial}{\partial N_j}\left[\ln(W)-\alpha\left(N-\sum_i N_i\right)-\beta\left(E-\sum_i N_i\varepsilon_i\right)\right]=\ln\left(g_j\right)-\ln\left(N_j\right)-\alpha-\beta\varepsilon_j=0$$

gives N_j that maximizes W under constant N and E:

$$N_j=g_j\exp\left(-\left(\alpha+\beta\varepsilon_j\right)\right)$$

To find α and β:

$$\ln\left(W\right) \approx \sum_i N_i \left(\ln\left(g_i\right) - \ln\left(N_i\right) + 1\right)$$

$$= \sum_i g_i e^{-\left(\alpha+\beta\varepsilon_\iota\right)} \left(\ln\left(g_i\right) - \ln\left(g_i e^{-\left(\alpha+\beta\varepsilon_\iota\right)}\right) + 1\right)$$

$$= \sum_i g_i e^{-\left(\alpha+\beta\varepsilon_\iota\right)} \left(\ln\left(g_i\right) - \ln\left(g_i\right) - \ln\left(e^{-\left(\alpha+\beta\varepsilon_i\right)}\right) + 1\right)$$

$$= \sum_i g_i e^{-\left(\alpha+\beta\varepsilon_i\right)} \left(\alpha + \beta\varepsilon_i + 1\right)$$

$$= \left(\alpha+1\right) \sum_i g_i e^{-\left(\alpha+\beta\varepsilon_\iota\right)} + \beta \sum_i g_i e^{-\left(\alpha+\beta\varepsilon_\iota\right)} \varepsilon_i$$

$$= \left(\alpha+1\right) \sum_i N_i + \beta \sum_i N_i \varepsilon_i$$

$$= \left(\alpha+1\right) N + \beta E$$

Solve it to *E*:

$$E = \frac{\ln(W)}{\beta} - \frac{N}{\beta} - \frac{\alpha N}{\beta}$$

$$= \frac{S}{k_B \beta} - \frac{N}{\beta} - \frac{\alpha N}{\beta}$$

Remember

$$S = k_B \ln W$$

Compare to the ideal gas:

$$E = TS - PV + \mu N$$

$$= TS - N k_B T + \mu N$$

T = temperature
μ = chemical potential

$$\beta = \frac{1}{k_B T}$$

$$\alpha = -\frac{\mu}{k_B T}$$