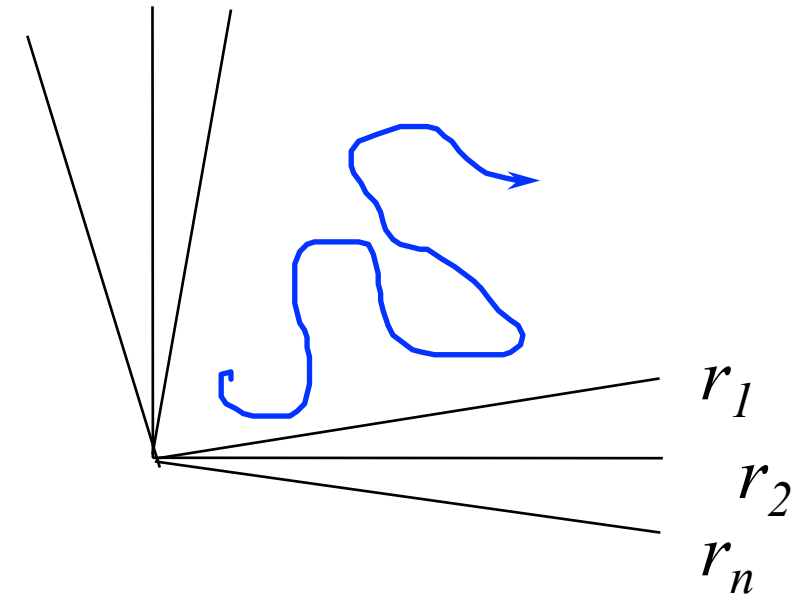


2. Thermodynamics

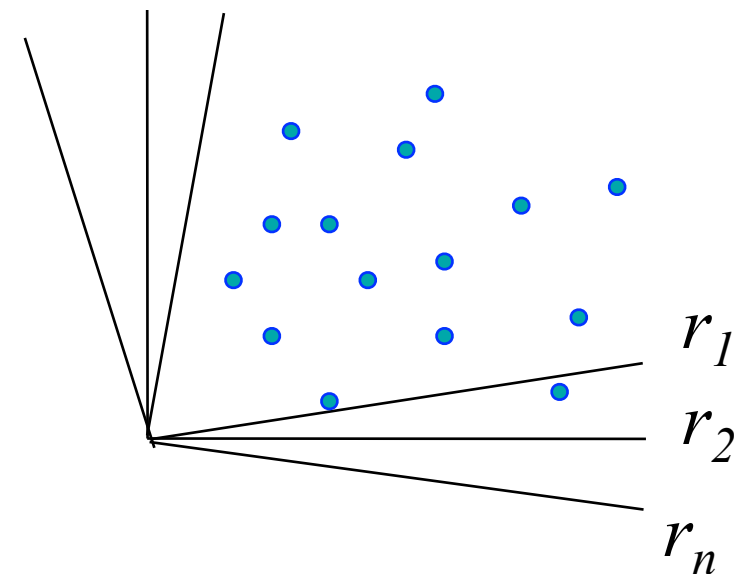
Introduction

Molecular Simulations

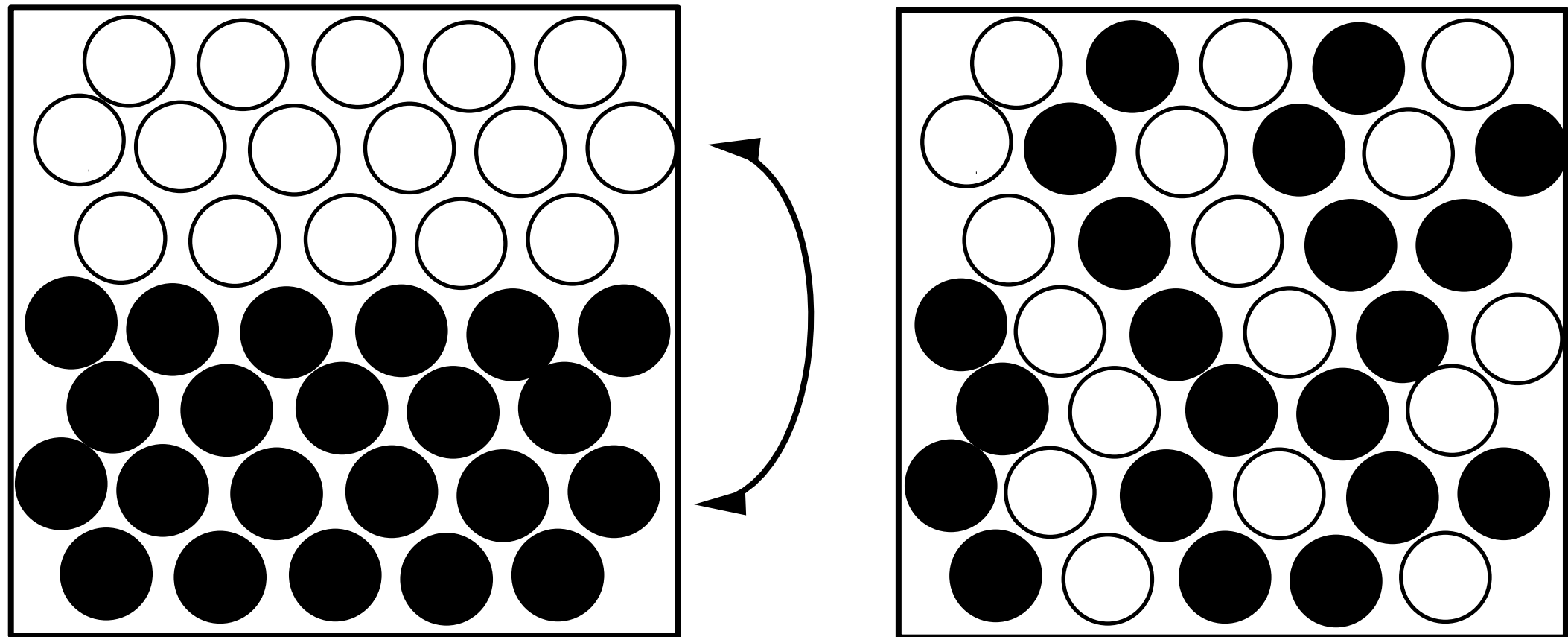
➔ **Molecular dynamics:**
solve equations of motion



➔ **Monte Carlo:** importance sampling

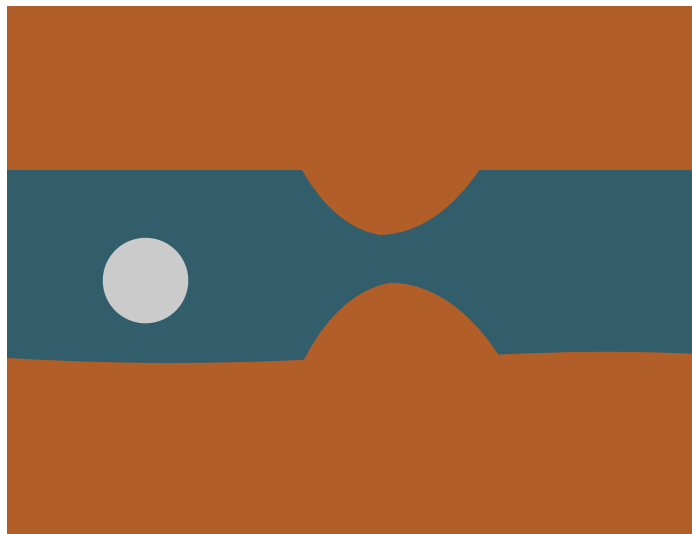


Monte Carlo versus Molecular Dynamics

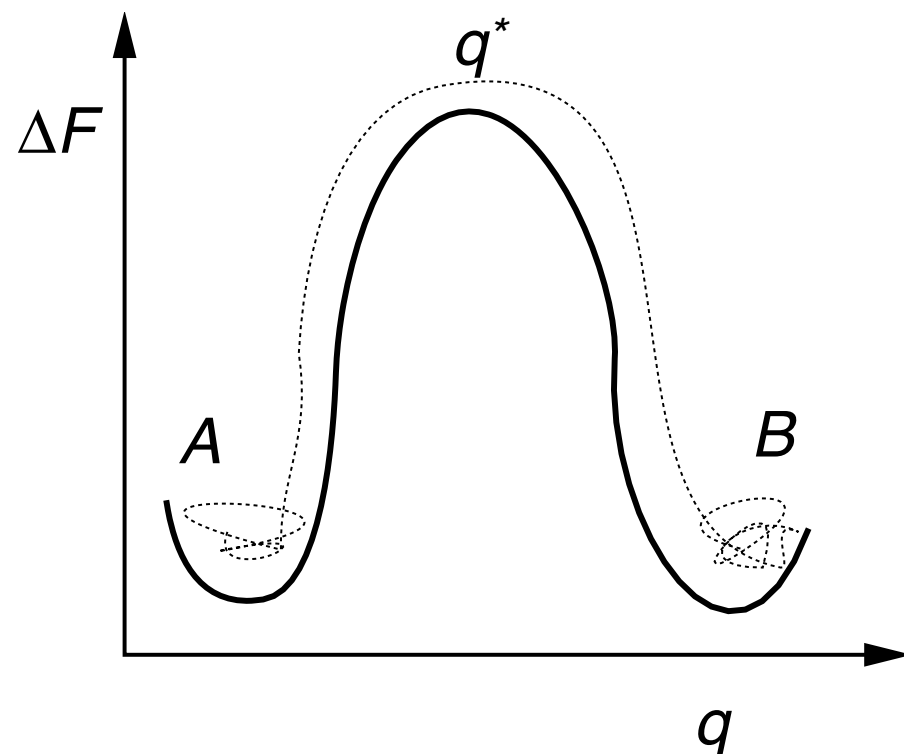
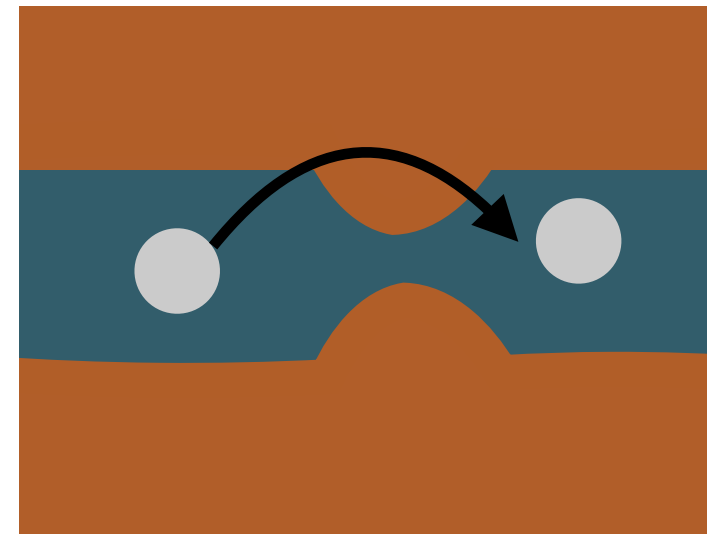


Particle in a pore

molecular dynamics



Monte Carlo



How do we know our simulation is correct?

- **Molecular Dynamics:**

- if the force field is correct we follow the “real” dynamics of our system,
- if we simulate sufficiently long, we can compute the properties of interest

Statistical
Thermodynamics

- **Monte Carlo:**

- what is the distribution we need to sample?
- how do we sample this distribution?

Importance Sampling

Outline

2. Thermodynamics

2.1. Introduction

2.2. Forces and Thermodynamics

2.3. Statistical Thermodynamics

2.3.1. Basic Assumption

2.3.2. Equilibrium

2.4. Ensembles

2.4.1. Constant temperature

2.4.2. Constant pressure

2.4.3. Constant chemical potential

2. Thermodynamics

2.2 Forces and Thermodynamics

Outline

2. Thermodynamics

2.1. Introduction

2.2. Forces and Thermodynamics

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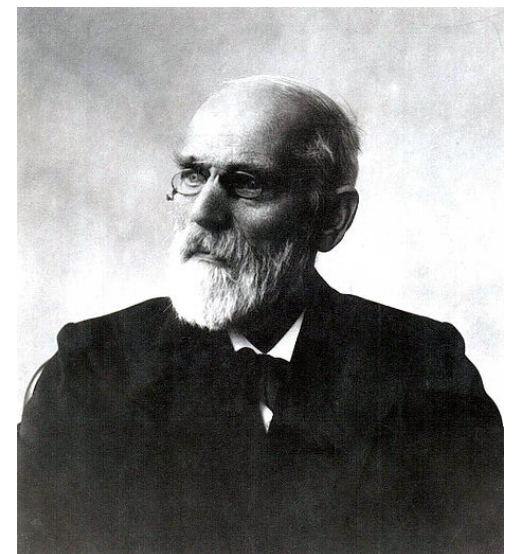
Atoms and Thermodynamics

History: thermodynamics was first atoms came later

Question: how would things have looked if atoms where first?



Nicolas Léonard Sadi Carnot
1796-1832 (wikipedia)



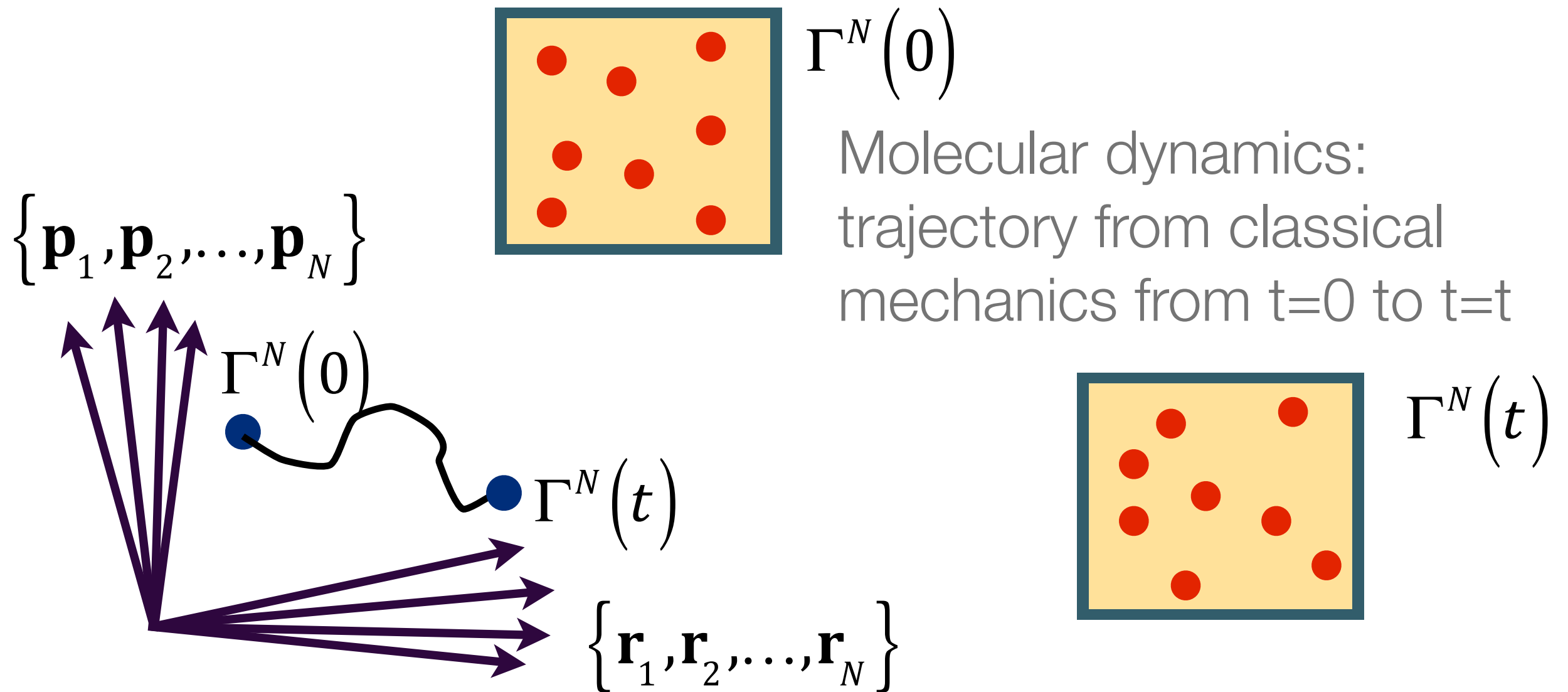
Johannes van der Waals
1837-1923 (wikipedia)

2. Thermodynamics

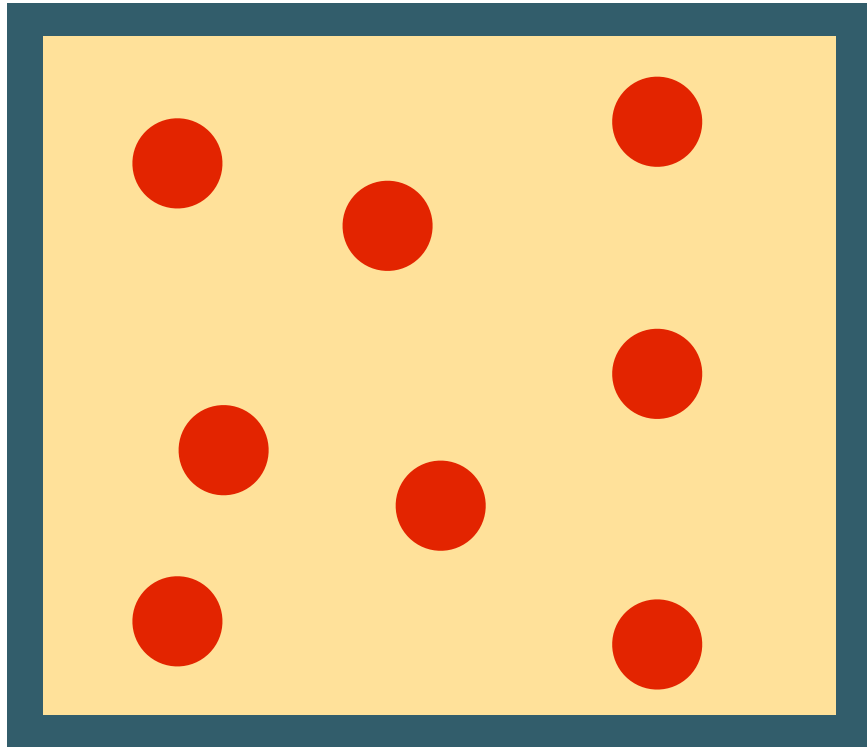
2.2.1 Thermodynamics: first law of thermodynamics

Phase space

Point in phase space: $\Gamma = \{r_1, r_2, \dots, r_N, p_1, p_2, \dots, p_N\}$



The first law: a box of particles



Our system:

- Isolated box with a volume V
- In which we put N particles
 - the particles interact through a given intermolecular potential
- no external forces

Newton: equations of motion

$$\mathbf{F}(\mathbf{r}) = -\nabla U(\mathbf{r})$$

$$m \frac{d^2 \mathbf{r}}{dt^2} = \mathbf{F}(\mathbf{r})$$

Consequence: Conservation of total energy E

NVE: micro-canonical ensemble

2. Thermodynamics

2.2.2 Thermodynamics: Gibbs phase rule

Intermezzo 1: The Gibbs Phase Rule

The Gibbs Phase Rule gives us for a thermodynamic system the number of degrees of freedom



Phase rule: $F=2-P+C$

Example: boiling water

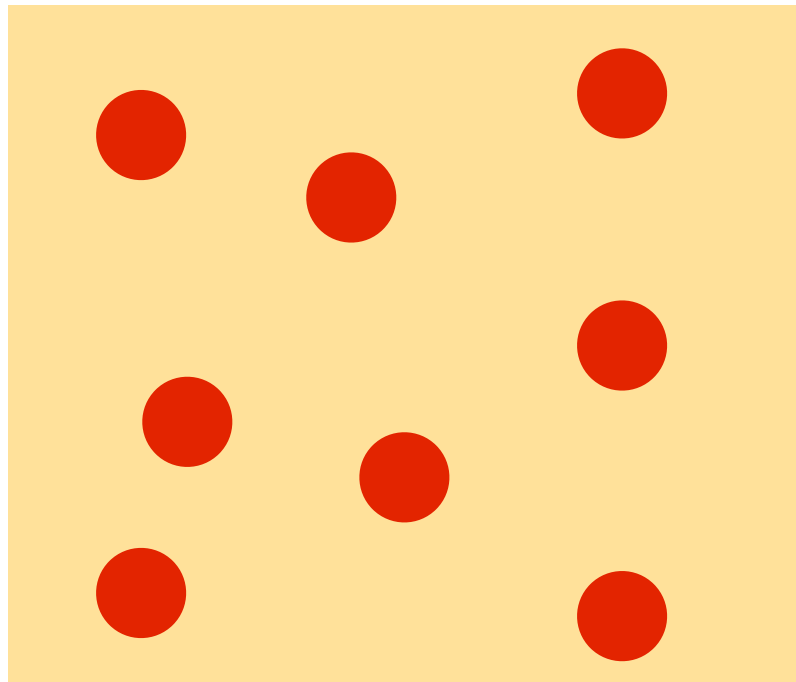
- F: degrees of freedom
- P: number of phases
- C: number of components

- $P = 2$ (water and steam)
- $C = 1$ (pure water)
- $F=2-2+1=1$

Hence, if we fix the pressure all other thermodynamic variables are fixed (e.g., temperature and density)

→ **Question:** why is there the 2?

Making a gas



What do we need to specify to fully define a thermodynamic system?

1. Specify the volume V
2. Specify the number of particles N
3. Give the particles:
 - ♦ initial positions
 - ♦ initial velocities

More we cannot do: Newton takes over!

System will be at constant:

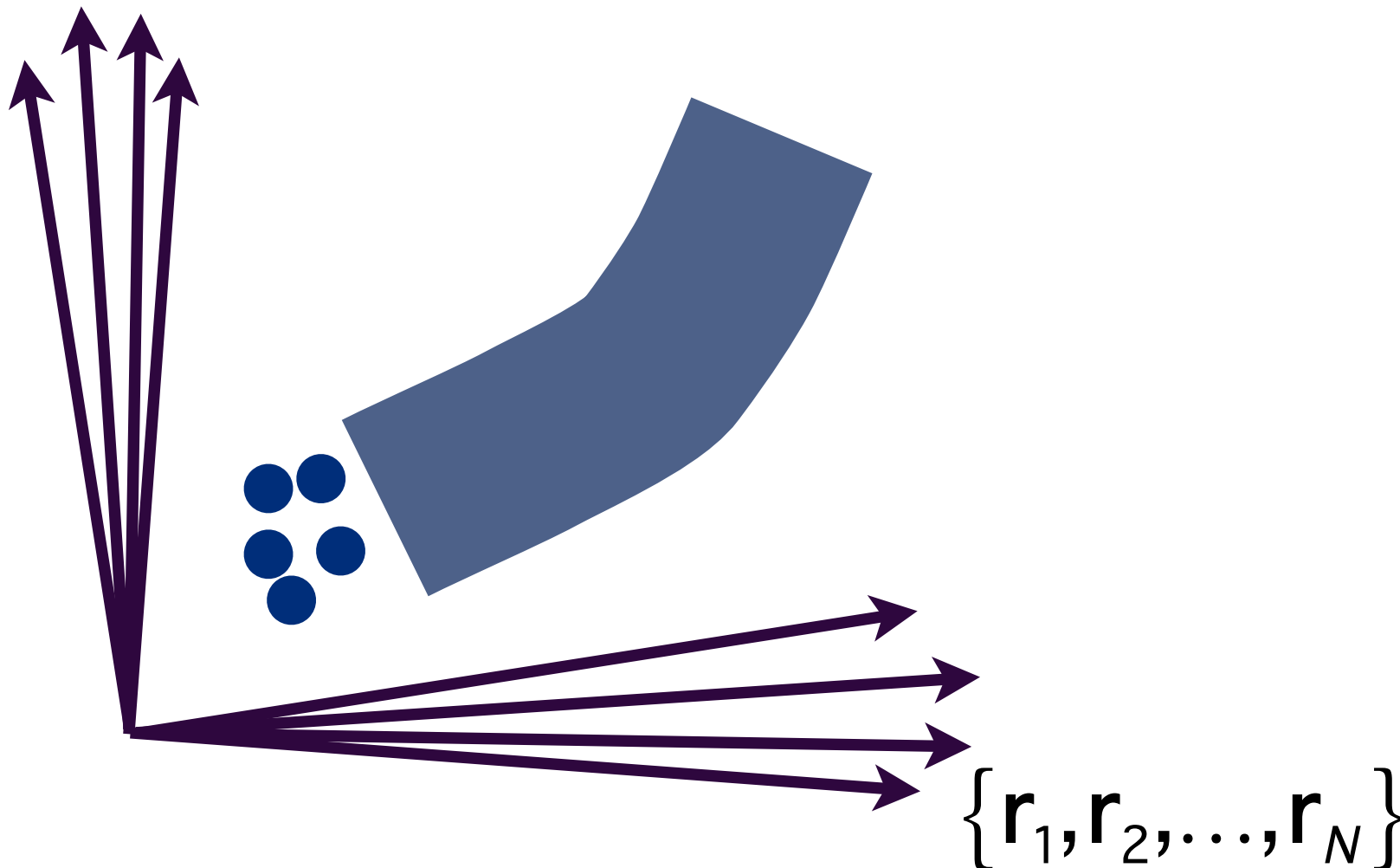
N, V, E

(micro-canonical ensemble)

All trajectories with the same initial total energy should describe the same thermodynamic state

These trajectories define a probability density in phase space

$\{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N\}$

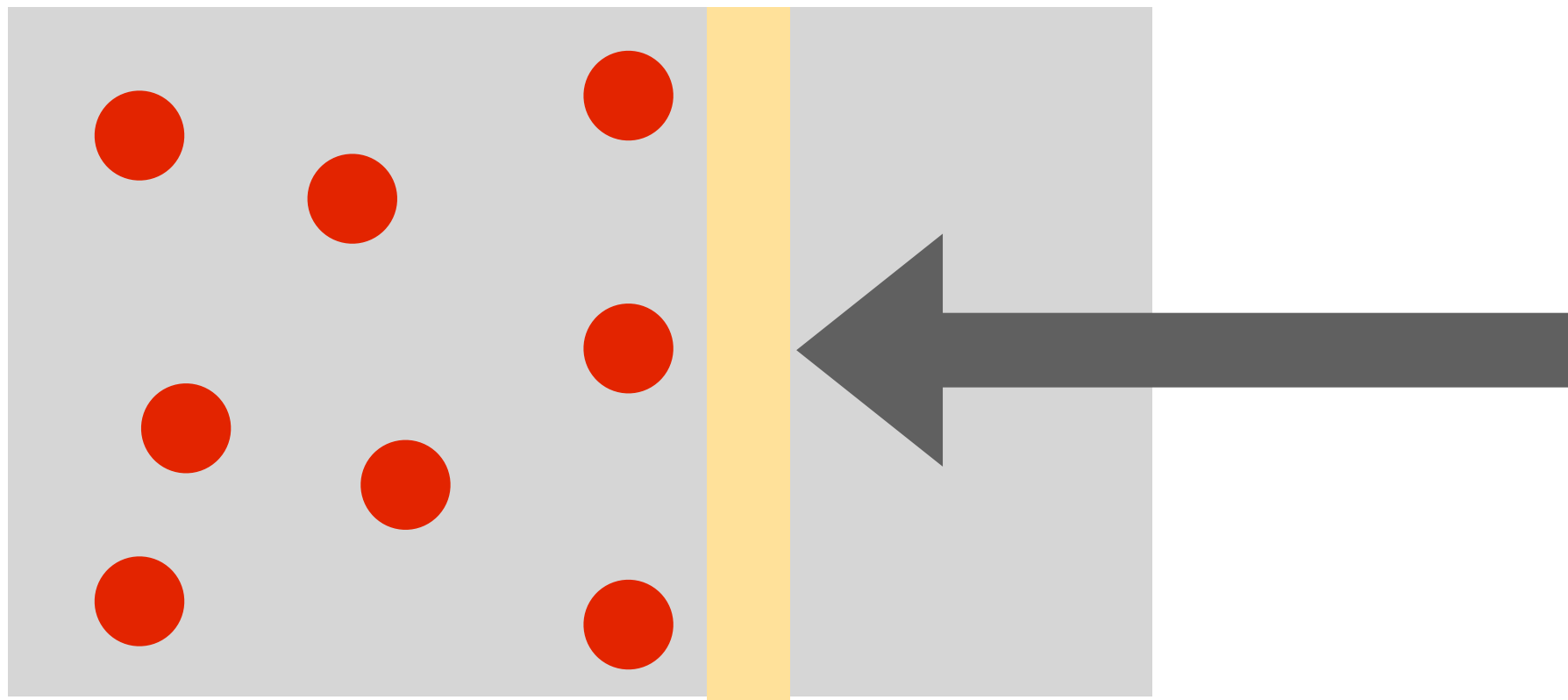


2. Thermodynamics

2.2.3 Thermodynamics: pressure

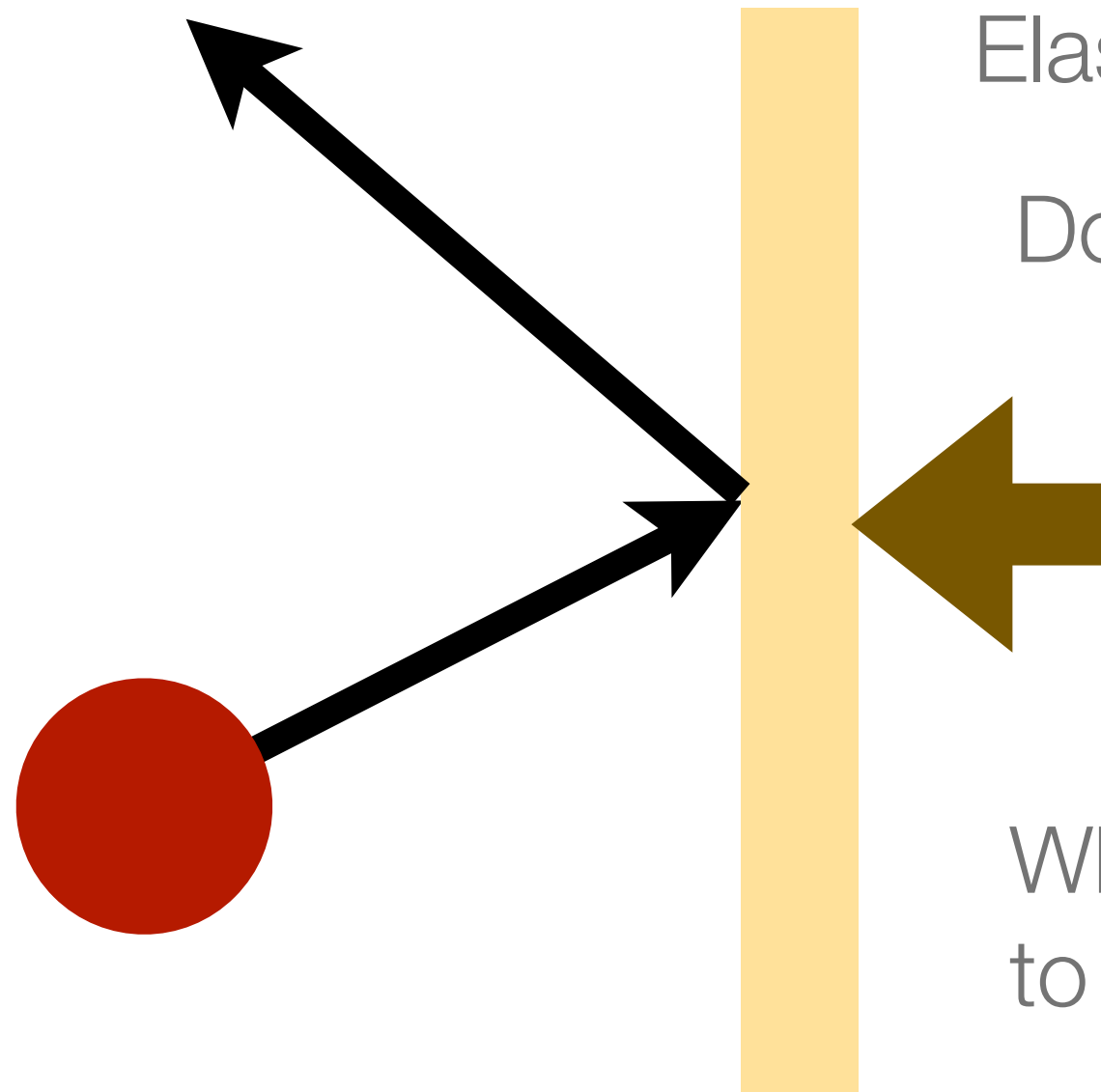
Pressure

What is the force I need to apply to prevent the wall from moving?



How much work I do?

Collision with a wall

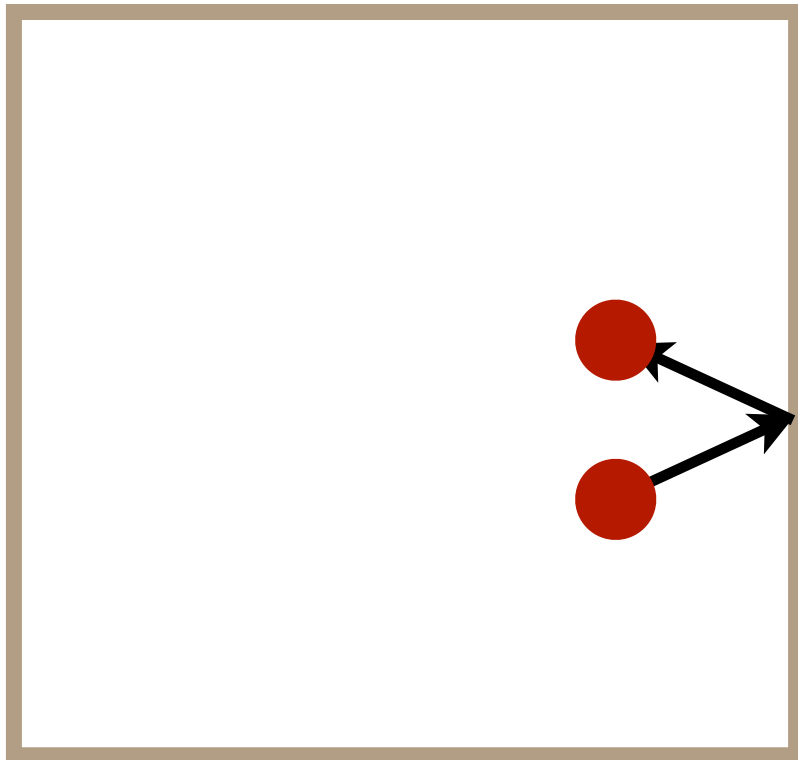


Elastic collisions:

Does the energy change?

What is the force that we need to apply on the wall?

Pressure



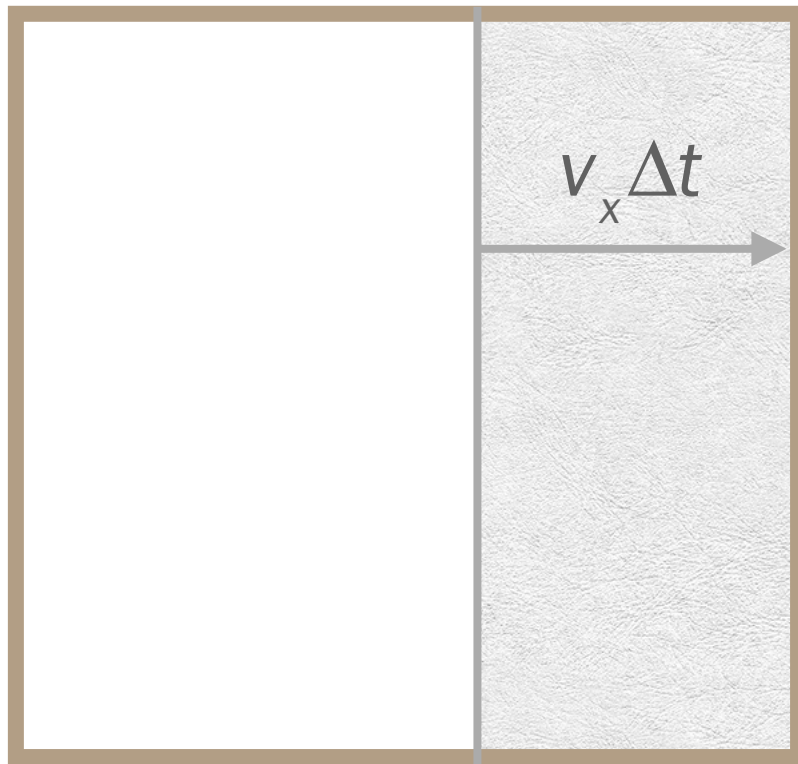
We need to compute the impulse over a time Δt

If we have one particle:

$$2mv_x = F\Delta t$$

But now an (ideal) gas with density ρ

We need to estimate the total number of particles that collide in a time Δt



If we assume that all particles have a velocity v_x :

Number of particles in this volume:

$$V = v_x \Delta t A$$

$$N_c = 0.5 v_x \Delta t A \rho$$

Impulse:

$$F \Delta t = (2 m v_x) (0.5 v_x \Delta t A \rho)$$

This give for the pressure:

If we use for temperature:

$$\frac{1}{2} m v_x^2 = \frac{1}{2} k_B T$$

$$p = \frac{F}{A} = m v_x^2 \rho$$

ideal gas law

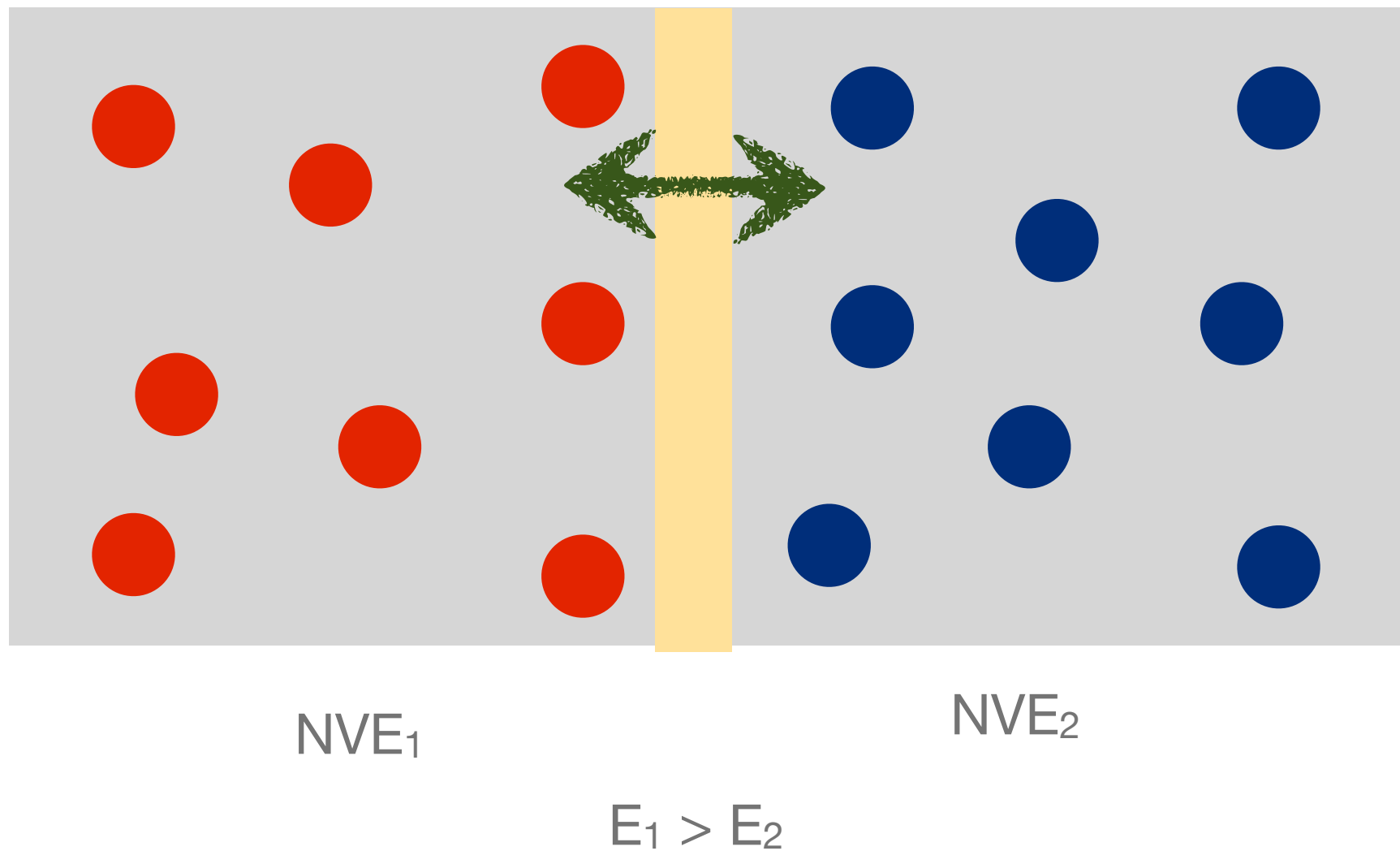
We get:

$$p = k_B T \rho$$

2. Thermodynamics

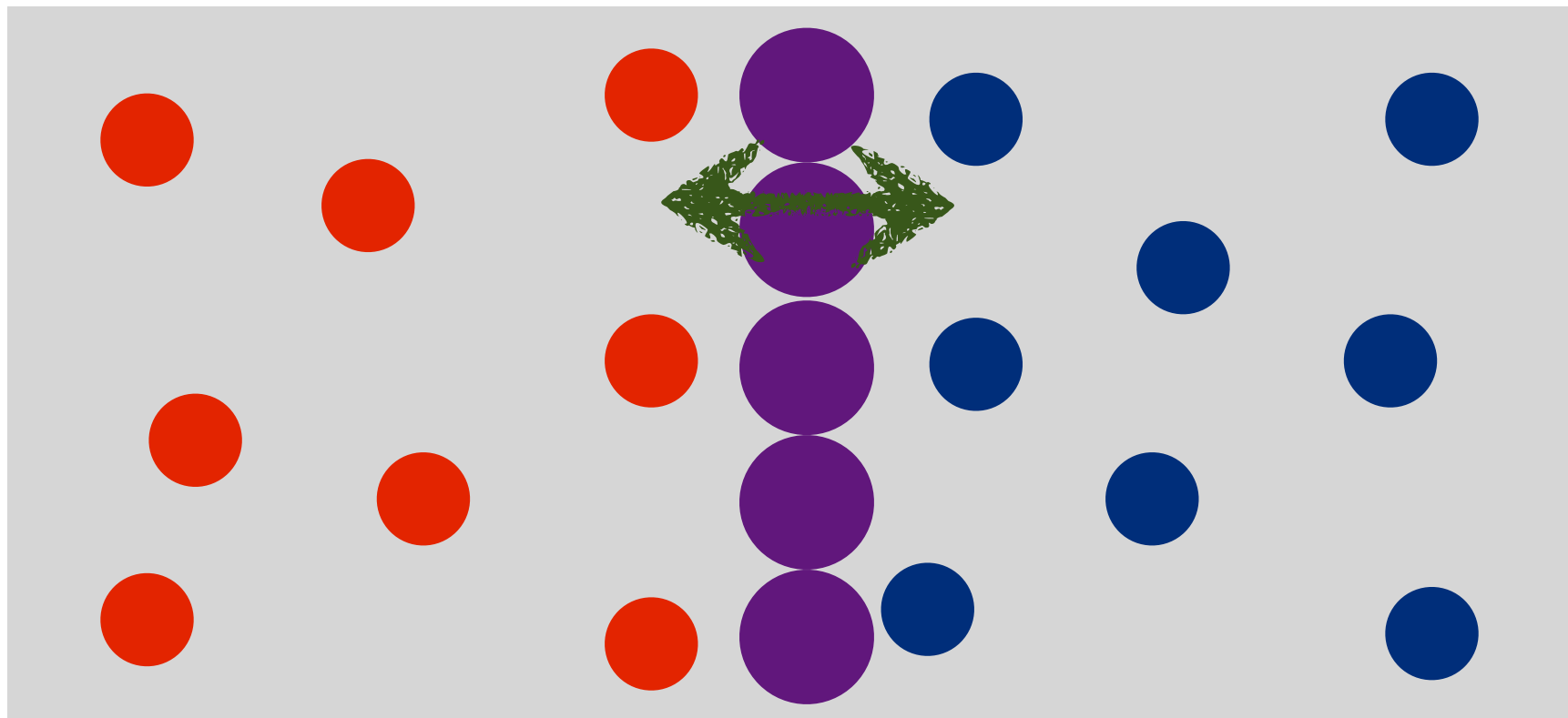
2.2.3 Thermodynamics: equilibrium

Experiment



What will the moveable (isolating) wall do?

Experiment (2)



NVE_1

$E_1 > E_2$

NVE_2

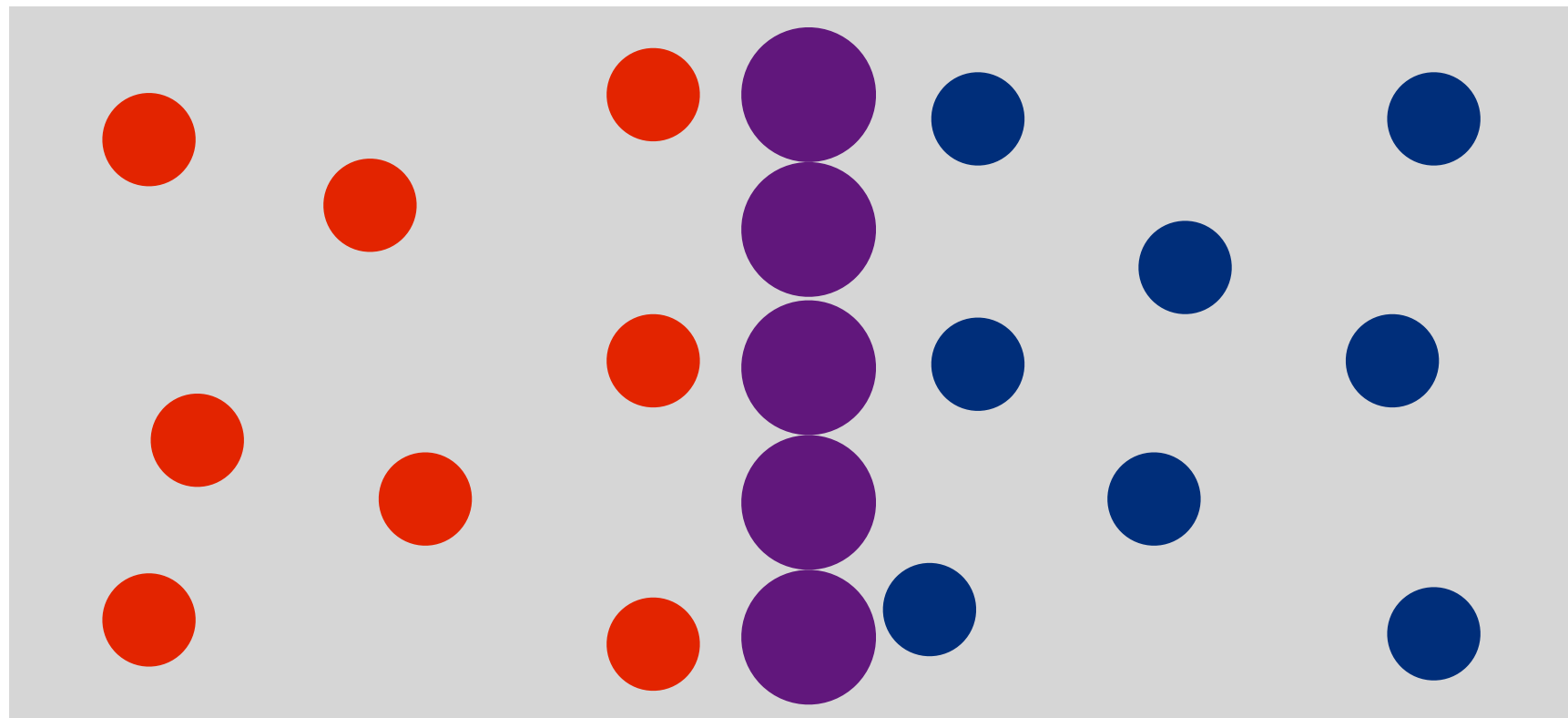
Now the wall are heavy molecules

What will the moveable wall do?

Newton + atoms

- We have a natural formulation of the first law
- We have discovered pressure
- We have discovered another equilibrium properties related to the total energy of the system

Experiment



NVE_1

$E_1 > E_2$

NVE_2

The wall can move and exchange energy:
what determines equilibrium ?

Classical Thermodynamics

- 1st law of Thermodynamics
 - Energy is conserved
- 2nd law of Thermodynamics
 - Heat spontaneously flows from hot to cold

Classical Thermodynamics

The first law:

$$\Delta U = Q + W$$

If we carry out a **reversible** process:

Carnot: Entropy difference
between two states:

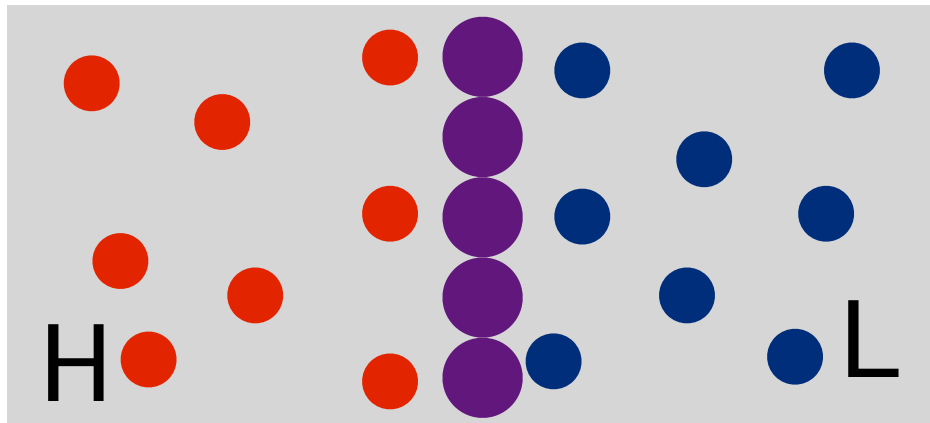
$$\Delta S = S_A - S_B = \int_A^B \frac{dQ_{rev}}{T}$$

$$dU = TdS + dW$$

If we have work by a expansion of a fluid

$$dU = TdS - pdV$$

Equilibrium



Let us look at the very initial stage
 dq is so small that the temperatures of
the two systems do not change

For system H $dS_H = -\frac{dq}{T_H}$

For system L $dS_L = \frac{dq}{T_L}$

Hence, for the total system:

Heat goes from warm to
cold: or if $dq > 0$ then $T_H > T_L$

$$dS = dS_L + dS_H = dq \left(\frac{1}{T_L} - \frac{1}{T_H} \right)$$

This gives for the entropy change:

$$dS \geq 0$$

Hence, the entropy increases until
the two temperatures are equal

2. Thermodynamics

2.3 Statistical Thermodynamics

Statistical Thermodynamics

Basic Assumption:

For an isolated system any microscopic configuration is equally likely

... but classical thermodynamics is based on laws

Consequence:

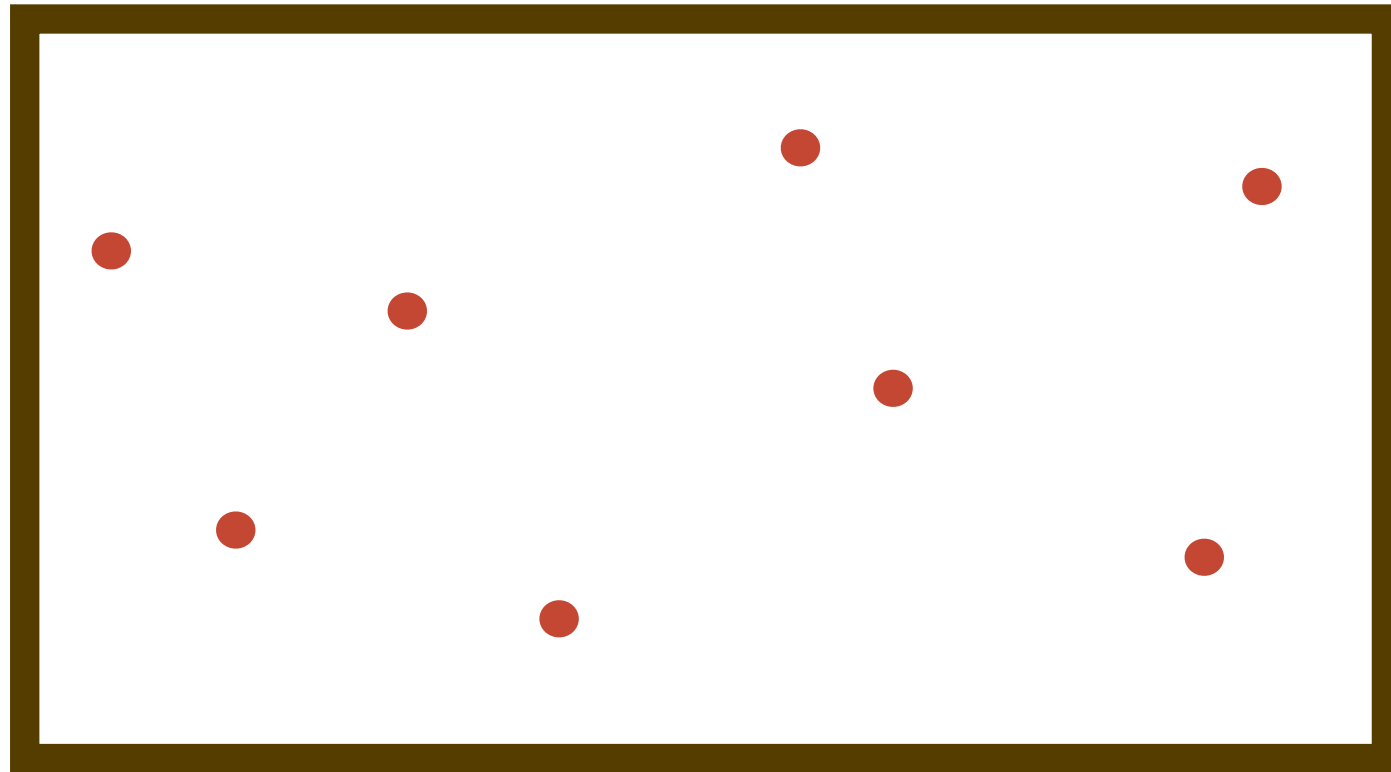
All of statistical thermodynamics and equilibrium thermodynamics

2. Thermodynamics

2.3.1 Statistical Thermodynamics: Basic Assumption

Ideal gas

Let us again make an ideal gas



We select:

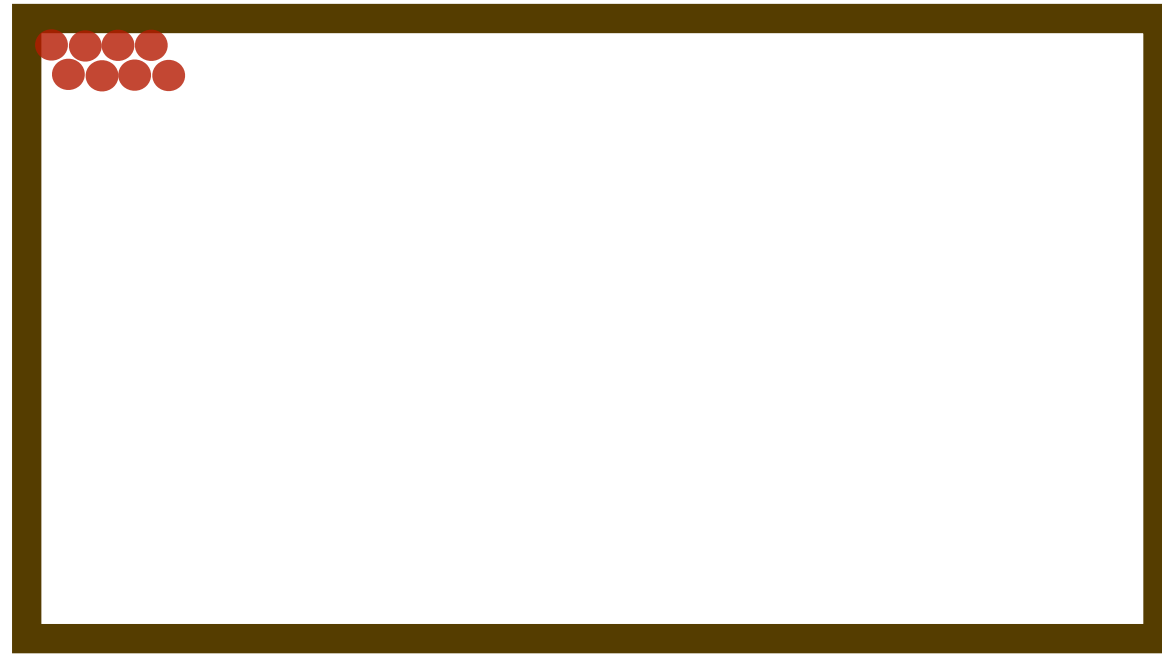
- (1) N particles,
- (2) Volume V ,
- (3) initial velocities
+ positions

This fixes: V/N , U/N

Basic Assumption:

For an isolated system each microscopic configuration is equally likely

What is the probability to find this configuration?



The system has the same energy as the previous one!!

Our basis assumption states that this configuration is equally likely as any other configuration

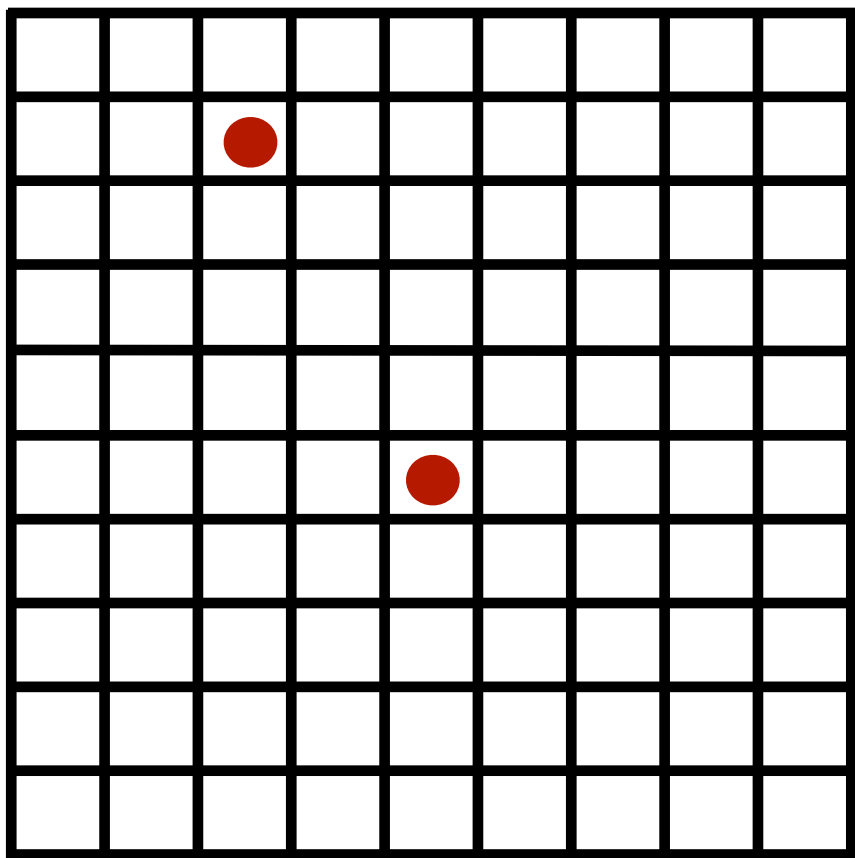
But having all atoms in the corner of our system seems to be very unlikely

.... and very dangerous

Our basic assumption must be seriously wrong!

Question: How to compute the probabilities of a particular configuration?

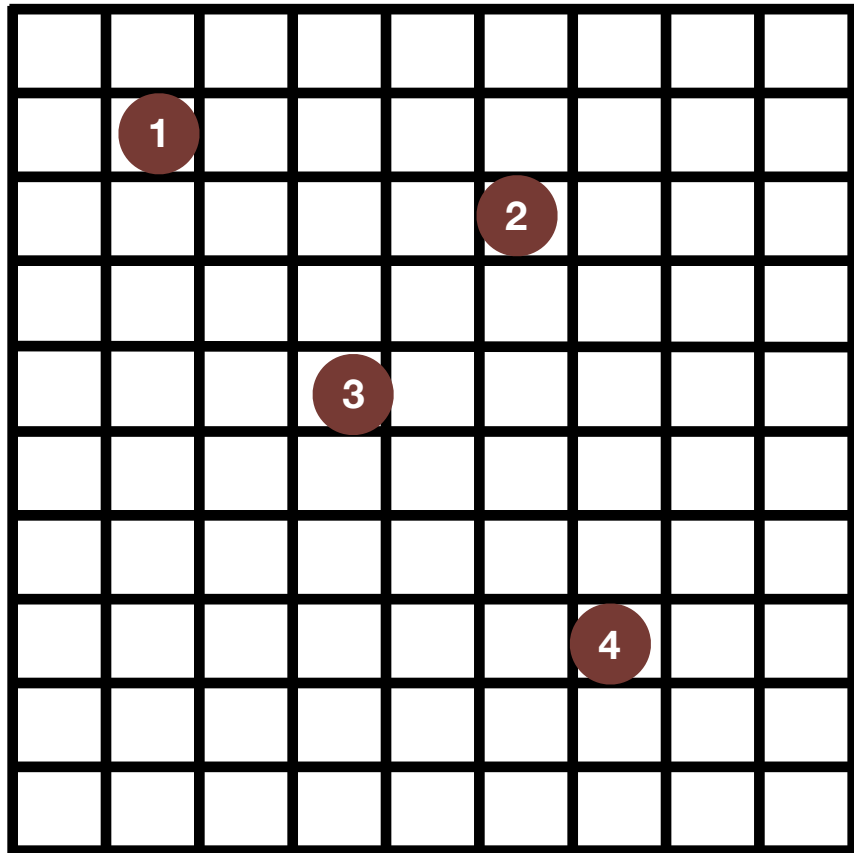
Use a lattice model to make the counting the number of possible confirmations easier



Assumptions:

- the position of a molecule is given by the lattice site
- there is no limit in the number of molecules per lattice site

Question: what is the probability of a given configuration?



Basic assumption:

$$P = \frac{1}{\text{Total \# of configurations}}$$

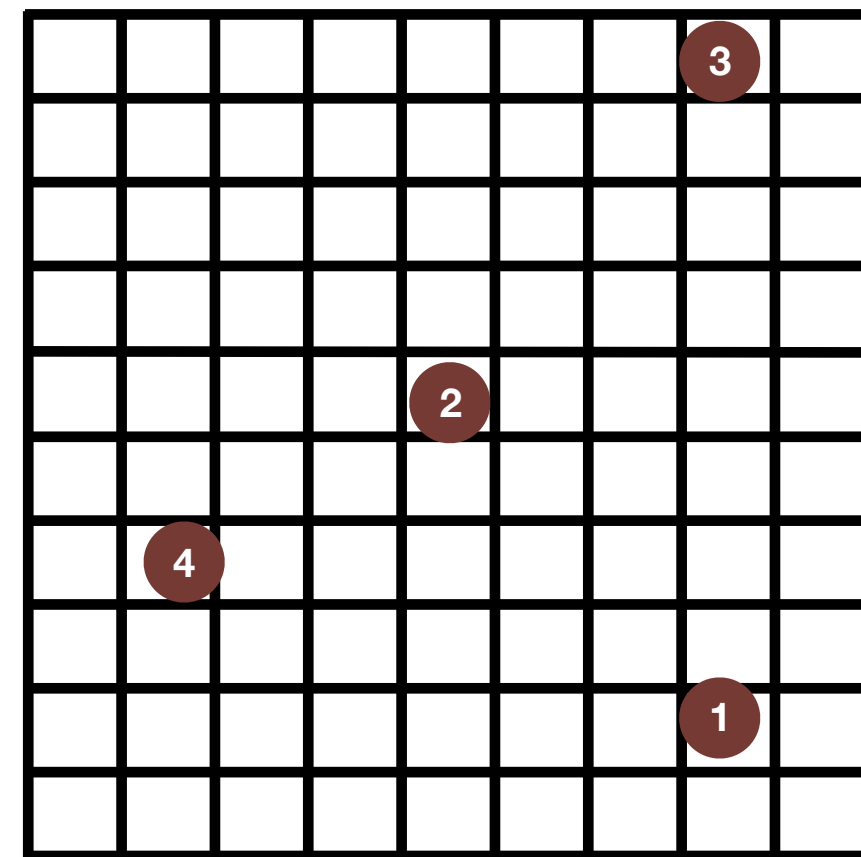
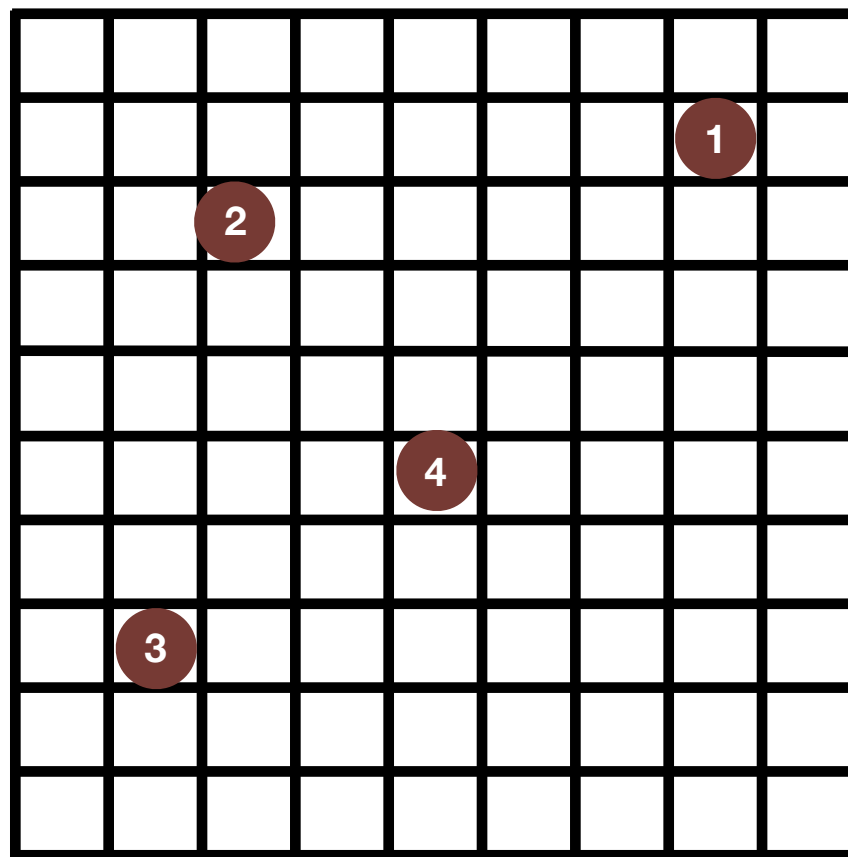
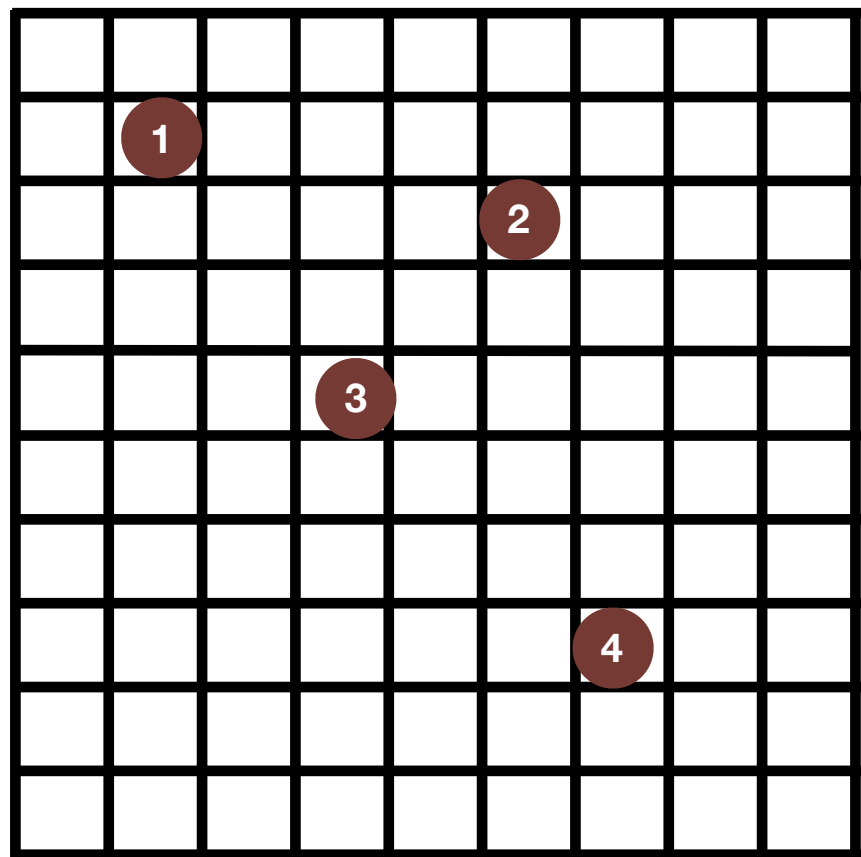
particle number 1 can be put in M positions, number 2 at M positions, etc.

For N particle the total number of configurations is: M^N

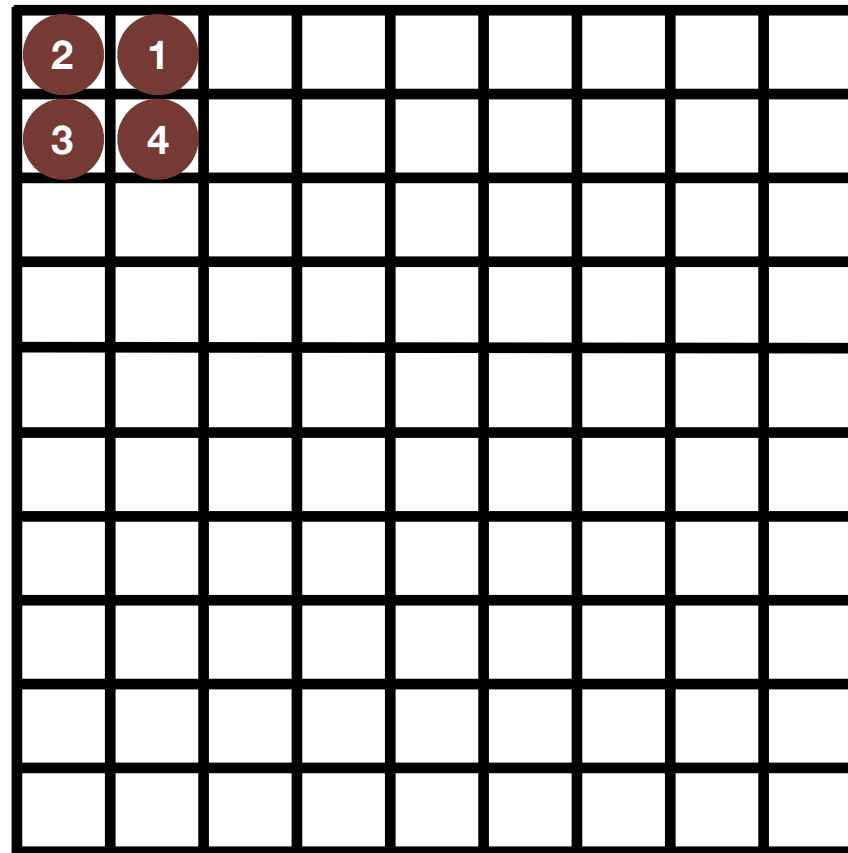
Hence the probability is: $P = \frac{1}{M^N}$

→ **Question:** how does the statistics change if the particles are indistinguishable ?

→ Question: What are the probabilities of these configurations ?



➡ ... and this one ?



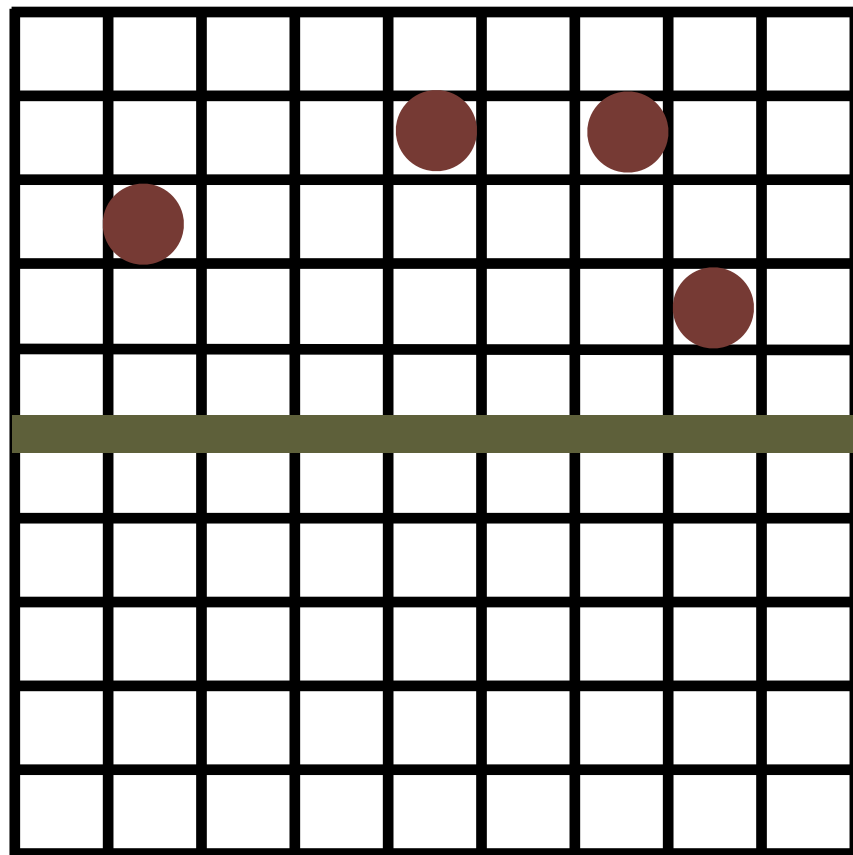
Is there a real danger that all the oxygen atoms are all in one part of the room?

Are we asking the right question?

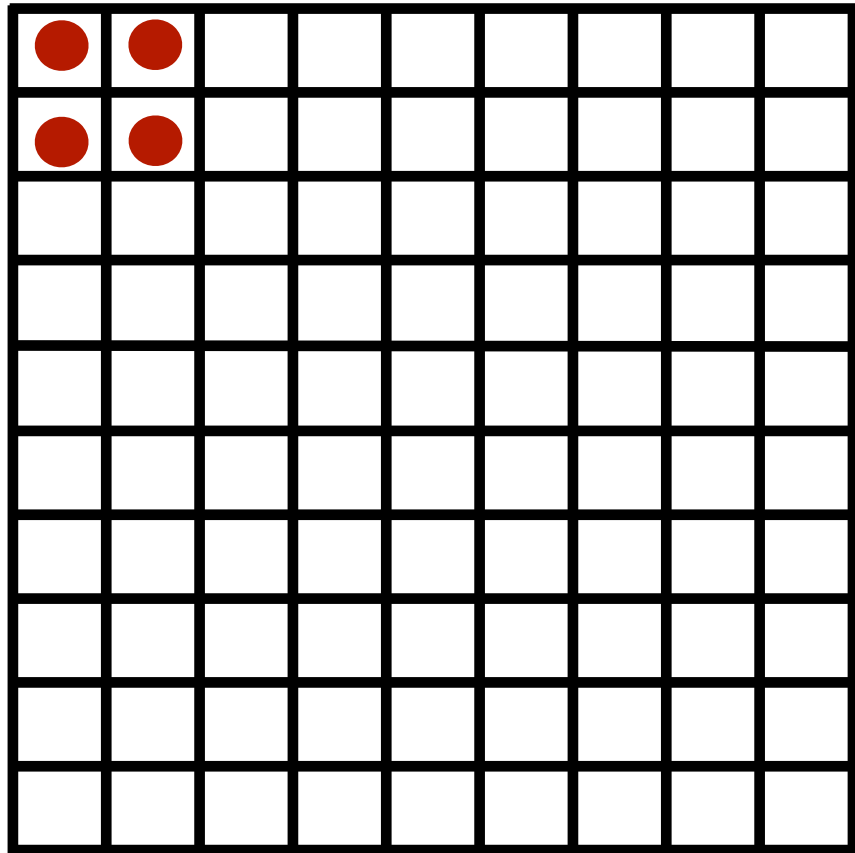
Thermodynamic is about **macroscopic properties**:

These are averages over many configurations

Measure densities: what is the probability that we have all our N gas particle in the upper half?



N	P(empty)
1	0.5
2	0.5×0.5
3	$0.5 \times 0.5 \times 0.5$
1000	10^{-301}



What is the probability to find this configuration?

exactly equal as to any other configuration!!!!!!

This is reflecting the microscopic reversibility of Newton's equations of motion. A microscopic system has no "sense" of the direction of time

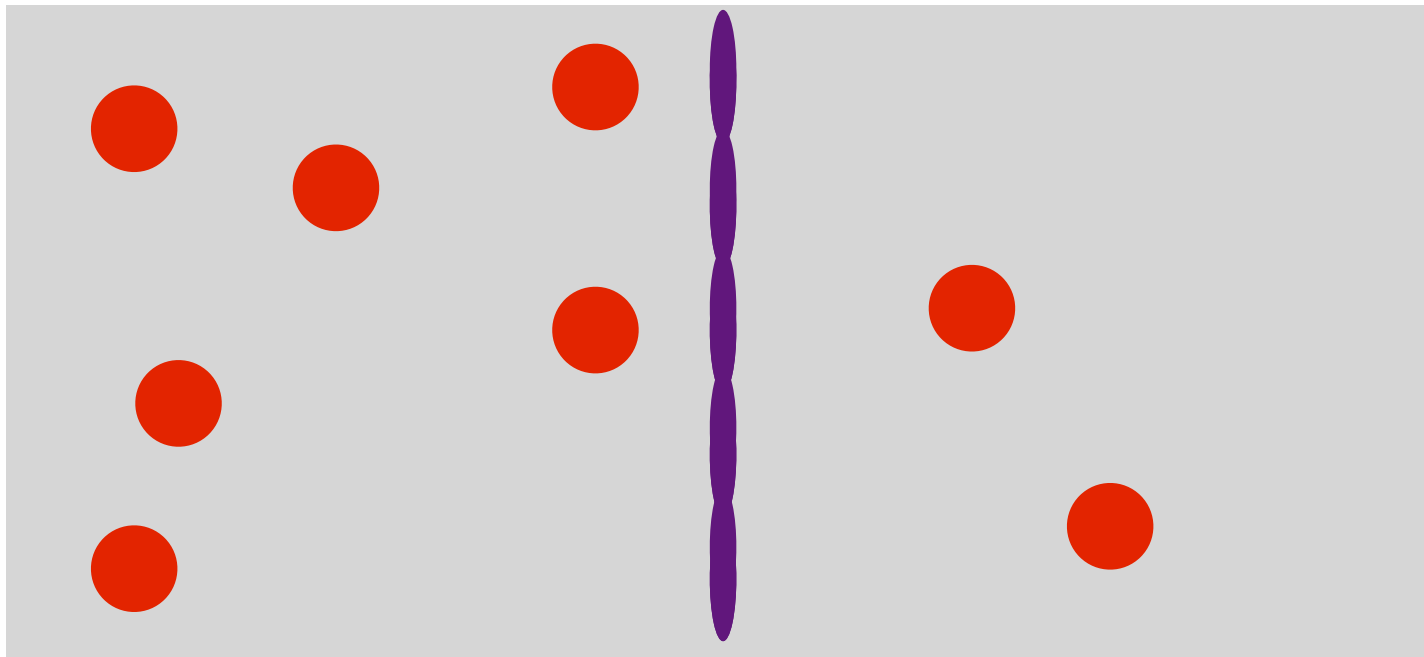
Summary

- On a **microscopic level** all configurations are equally likely
- On a **macroscopic level**; as the number of particles is extremely large, the probability that we have a fluctuation from the average value is **extremely** low
- Let us now quantify this

2. Thermodynamics

2.2 Statistical Thermodynamics: Equilibrium

Question



If all configurations are equally likely what will be then the energy we will observe in the two boxes?

Discussion: equilibrium (1)



We have a closed and isolated system

Basic Assumption: every configuration is equally likely

Discussion: equilibrium (2)



We have a closed and isolated system, but heat can flow between system 1 and 2

Basic Assumption: every configuration is equally likely:

→ **Questions:**

- How do we know the system is in equilibrium?
- how does this tell us what will be the macroscopic properties (e.g., temperature) of the two systems?

Solution:



All micro states **are** equally likely!

... but the number of micro states that give an particular density or energy distribution over the 2 systems **are not** ...

Macroscopically we will observe the **most likely** one



$P(E_1, E_2)$ The probability to find E_1 in volume 1 and E_2 in volume 2

$N_1(E_1)$ The number of configurations that result in an energy E_1 in volume 1.

$E_2 = E - E_1$ The total energy E is constant

$$P(E_1, E_2) = \frac{N_1(E_1)N_2(E - E_1)}{\sum_{E_1=0}^{E_1=E} N_1(E_1)N_2(E - E_1)} = CN_1(E_1)N_2(E - E_1)$$

Experimentally we will observe the most likely configuration; which is given by the maximum

We need to find:

$$\frac{dP(E_1, E_2)}{dE_1} = 0$$

Finding:

$$\frac{dP(E_1, E_2)}{dE_1} = 0$$

with:

$$P(E_1, E_2) = CN_1(E_1)N_2(E - E_1)$$

Is equivalent in finding:

$$\frac{d\ln(P(E_1, E_2))}{dE_1} = 0$$

or:

$$\frac{d\ln(N_1(E_1))}{dE_1} + \frac{d\ln(N_2(E - E_1))}{dE_1} = 0$$

with $E_2 = E - E_1$

$$\frac{d\ln(N_1(E_1))}{dE_1} - \frac{d\ln(N_2(E - E_1))}{dE_2} = 0$$

The solution of this equation gives the energies in volume 1 and 2 that are most likely, i.e., the largest number of configurations have these energies

Let us define a property
(almost S, but not quite) :

$$S^* = \ln(N(E))$$

Equilibrium if:

$$\frac{d \ln(N_1(E_1))}{dE_1} = \frac{d \ln(N_2(E - E_1))}{dE_2}$$

or

$$\left(\frac{\partial S_1^*}{\partial E_1} \right)_{N_1, V_1} = \left(\frac{\partial S_2^*}{\partial E_2} \right)_{N_2, V_2}$$

And for the total system:

$$S^* = S_1^* + S_2^*$$

For a system at constant energy, volume and number of particles S^* increases until it has reached its maximum value at equilibrium

What is this magic property S^* ?

Defined a property S^* (that is almost S):

$$S^*(E_1, E - E_1) = \ln(N(E_1, E - E_1))$$

Question 1: Why is maximising S^* the same as maximising N ?

Answer: The logarithm is a monotonically increasing function.

Question 2: Why is the logarithm a convenient function?

Answer: makes S^* additive! Leads to extensivity.

Question 3: Why is S^* not quite entropy?

Answer: Units! The logarithm is just a unit-less quantity.

$$S = k_B S^* = k_B \ln(N(E))$$

For a partitioning of E between 1 and 2, the number of configuration is maximized when:

$$\left(\frac{\partial S_1^*}{\partial E_1} \right)_{N_1, V_1} = \left(\frac{\partial S_2^*}{\partial E_2} \right)_{N_2, V_2}$$

What do these partial derivatives relate to?

$$dE = TdS - pdV + \sum_{i=1}^{i=M} \mu_i dN_i$$

Temperature

$$T = \left(\frac{\partial E}{\partial S} \right)_{N_i, V} \quad \text{or} \quad \frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N_i, V}$$

Thermal equilibrium \rightarrow equal temperature of system 1 and 2!

$$S = k_B S^* = k_B \ln(N(E))$$

Question: How large is $N(E)$ for a glass of water?

How to estimate $N(E)$

- Number of molecules of the order 10^{23}
- Make a grid of 10^6 cells ($100 \times 100 \times 100$)

$$N(E) \gg (10^6)^{10^{23}}$$

Summary:

- For macroscopic systems $N(E)$ is super-astronomically large
- Macroscopic deviations from the second law of thermodynamics are not forbidden, but they are extremely unlikely.

2. Thermodynamics

2.4 Ensembles

The 2nd law

Entropy of an isolated system can only **increase**; until equilibrium where it takes its maximum value

Most systems are at constant temperature and volume or pressure?

When do we have equilibrium for such a system?

Other ensembles?

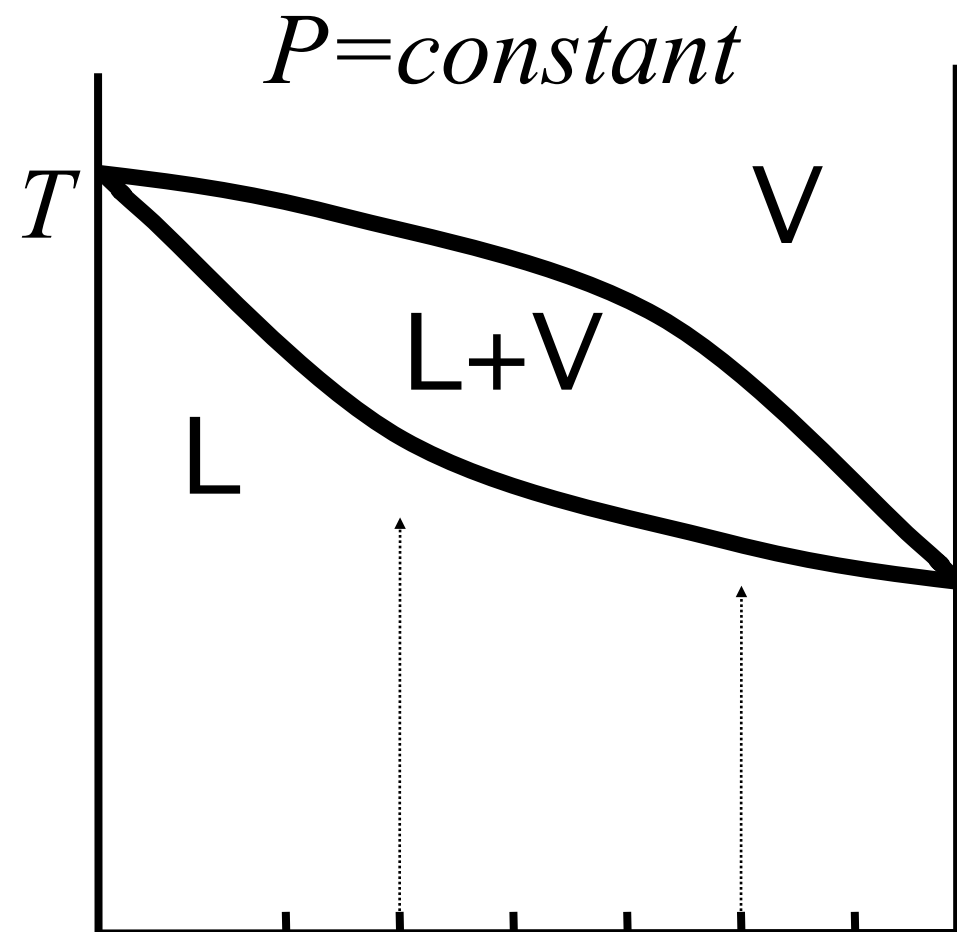
In the thermodynamic limit the thermodynamic properties are independent of the ensemble: so buy a bigger computer ...

However, it is most of the times much better to think and to carefully select an appropriate ensemble.

For this it is important to know how to simulate in the various ensembles.

But for doing this we need to know the Statistical Thermodynamics of the various ensembles.

Example (1): vapour-liquid equilibrium mixture



vapour(V)-liquid (L) Phase
diagram of a binary mixture
at (fixed) temperature T

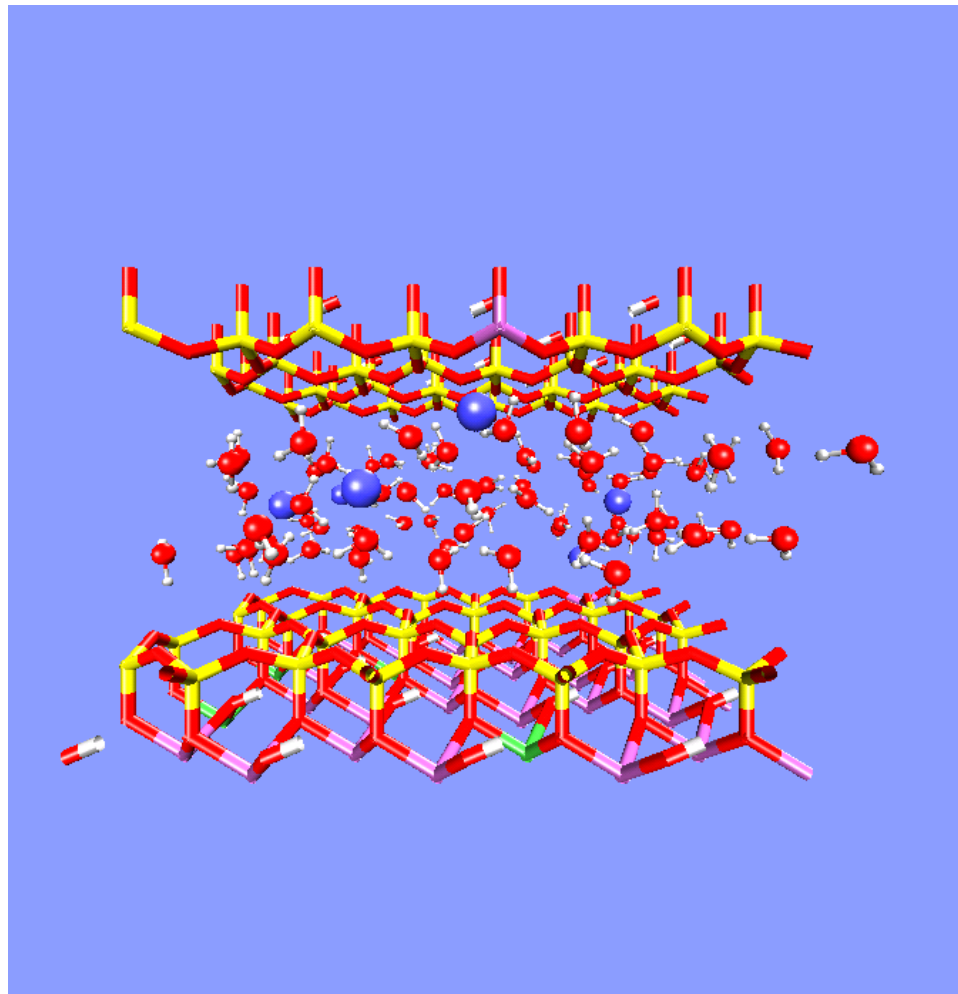
Question:

- if we have a 50%-50% mixture how many degrees of freedom if we have V-L coexistence?

Experiment: determine the composition of the coexisting vapour and liquid phases if we start with a homogeneous liquid of two different compositions but the same temperature:

- How to mimic this with the N, V, T ensemble?
- What is a better ensemble?

Example (2): adsorption in porous media



water adsorbed in clay
layers

Question:

- What are the equilibrium conditions

Experiments: Deep in the earth clay layers can swell upon adsorption of water:

- How to mimic this in the N, V, T ensemble?
- What is a better ensemble to use?

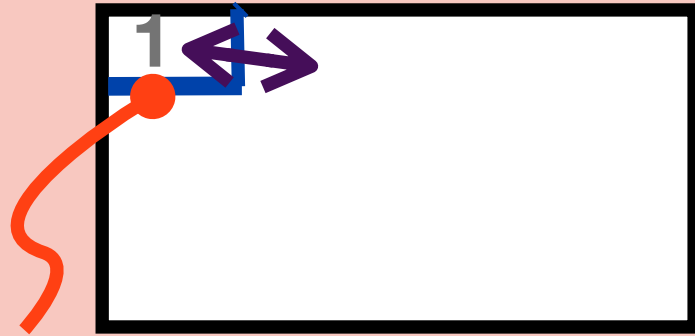
Ensembles

- Micro-canonical ensemble: E, V, N
- Canonical ensemble: T, V, N
- Constant pressure ensemble: T, P, N
- Grand-canonical ensemble: T, V, μ

2. Thermodynamics

2.4.1 Ensembles: constant temperature

Canonical ensemble: classical thermodynamics



fixed volume but can exchange energy

Our entire system is isolated (NVE), but our subsystems (box 1 and bath) can exchange energy

First law $dU = TdS - pdV$

Second law $dS \geq 0$

Box 1: *constant volume and temperature*

1st law: $dU = dU_1 + dU_b = 0$ or $dU_1 = -dU_b$

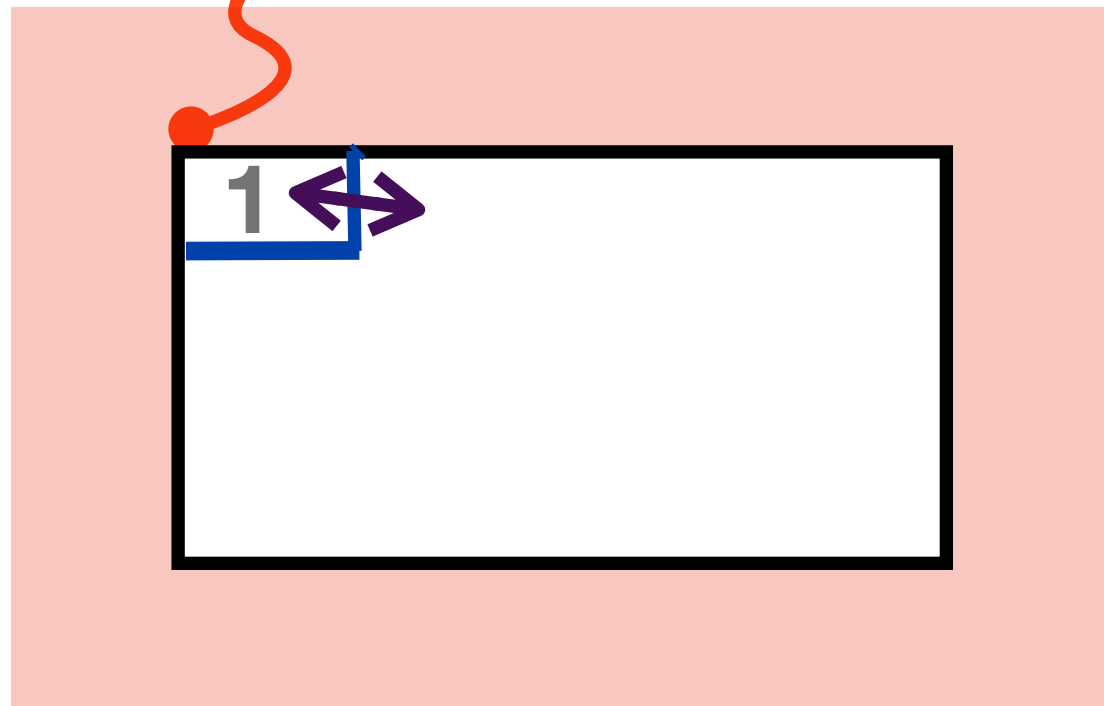
The bath is so large that the heat flow does not influence the temperature of the bath + the process is reversible

2nd law: $dS = dS_1 + dS_b \geq 0$ or $dS_1 + dS_b = dS_1 + \frac{dU_b}{T} = dS_1 - \frac{dU_1}{T} \geq 0$

Giving: $TdS_1 - dU_1 \geq 0$

we have a criteria that only depends on box 1

fixed volume but can
exchange energy



Total system is isolated and the
volume is constant

Box 1: *constant volume and
temperature*

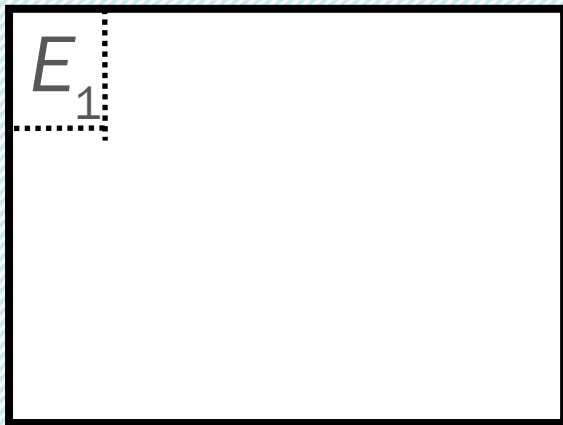
2nd law: $TdS_1 - dU_1 \geq 0$
 $d(U_1 - TS_1) \leq 0$

Let us define the Helmholtz free energy (F): $F \equiv U - TS$

For box 1 we can write: $dF_1 \leq 0$

Hence, for a system at *constant temperature and volume*
the Helmholtz free energy decreases and takes its
minimum value at equilibrium

Canonical ensemble: statistical mechanics



Consider a small system that can exchange energy with a big reservoir

$$\ln \Omega(E_1, E - E_1) = \ln \Omega(E) - \left(\frac{\partial \ln \Omega}{\partial E} \right) E_1 + \dots$$

$$= 1/k_B T$$

If the reservoir is very big we can ignore the higher order terms:

$$\frac{\ln \Omega(E_1, E - E_1)}{\ln \Omega(E)} = -\frac{E_1}{k_B T}$$

Hence, the probability to find E_1 :

$$P(E_1) = \frac{\Omega(E_1, E - E_1)}{\sum_i \Omega(E_i, E - E_i)} = \frac{\Omega(E_1, E - E_1) / \Omega(E)}{\sum_i \Omega(E_i, E - E_i) / \Omega(E)} = C \frac{\Omega(E_1, E - E_1)}{\Omega(E)}$$

$$P(E_1) \propto \exp\left[-\frac{E_1}{k_B T}\right] \propto \exp[-\beta E_1]$$

$$\beta = 1/k_B T$$

Thermodynamics

What is the average energy of the system?

$$\begin{aligned}\langle E \rangle &\equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} \\ &= - \frac{\partial \ln \left[\sum_i \exp(-\beta E_i) \right]}{\partial \beta} = - \frac{\partial \ln Q_{NVT}}{\partial \beta}\end{aligned}$$

Classical thermodynamics:

$$dF = -SdT - pdV$$

$$\left(\frac{\partial F}{\partial T} \right)_{N,V} = -S$$

$$\left(\frac{\partial F/T}{\partial 1/T} \right) = -T^2 \left(\frac{\partial F/T}{\partial T} \right) = -T^2 \left(-\frac{F}{T^2} + \frac{1}{T} \left(\frac{\partial F}{\partial T} \right) \right)$$

$$\left(\frac{\partial F/T}{\partial 1/T} \right) = F + TS = U$$

$$\beta F = -\ln Q_{NVT}$$

The link between statistical
and classical thermo

From states to atoms

We have assumed that we can count states

Quantum Mechanics: energy discrete

What to do for classical model such as an ideal gas, hard spheres, Lennard-Jones?

Energy is continuous:

- potential energy
- kinetic energy

Particle in a box:

$$\epsilon_n = \frac{(nh)^2}{8mL^2}$$

What are the energy levels for Argon in a 1-dimensional box of 1 cm?

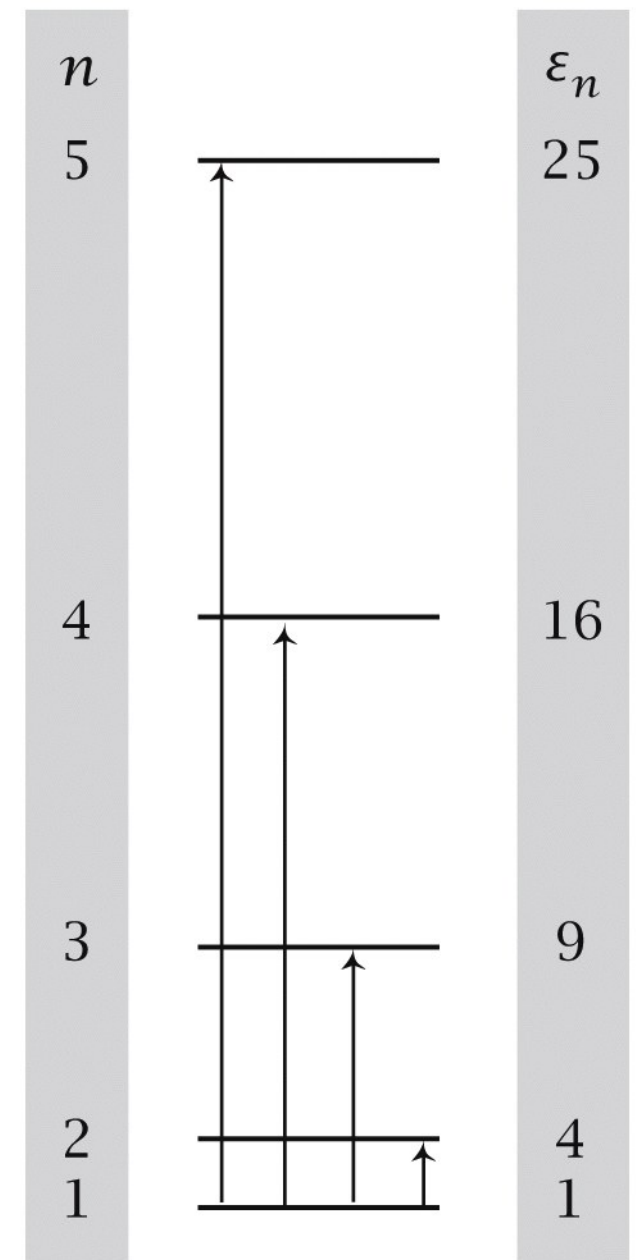


Figure 11.4 Molecular Driving Forces 2/e (© Garland Science 2011)

What are the energy levels for Argon in a 1-dimensional box of 1 cm?

$$\epsilon_n = \frac{(nh)^2}{8mL^2}$$

(Argon: $m=40 \text{ g/mol}=6.63 \times 10^{-26} \text{ kg}$ $h=6.63 \times 10^{-34} \text{ J s}$)

$$\epsilon_n = 5 \times 10^{-39} n^2 (\text{J})$$

Kinetic energy of Ar at room temperature $\approx 4.14 \times 10^{-21} \text{ J}$

$$q_{\text{translational}} = \sum_{n=1}^{\infty} e^{-\frac{(nh)^2}{8mL^2 k_B T}}$$

Many levels are occupied: only at very low temperatures or very small volumes one can see quantum effect!

$$q_{\text{translational}} = \int_0^{\infty} e^{-\frac{(nh)^2}{8mL^2 k_B T}} dn$$

$$q_{\text{translational}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} L$$

3D:

$$q_{\text{translational}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} L^3 = \frac{V}{\Lambda^3}$$

de Broglie wavelength

Partition function: $q = \sum_{n=1}^{\infty} e^{-\frac{E_n}{k_B T}} = \int_0^{\infty} e^{-\frac{E_n}{k_B T}} dn$

we assume that the potential energy does **not** depend on the velocity

Hamiltonian: $H = U_{\text{kin}} + U_{\text{pot}} = \sum_{i=1}^N \frac{p_i^2}{2m} + U_{\text{pot}}(r^N)$

one atom: $Z_{1,V,T} = C \iint e^{-\frac{H}{k_B T}} dp^3 dr^3 = C \int e^{-\frac{p^2}{2mk_B T}} dp^3 \int e^{-\frac{U_{\text{pot}}(r)}{k_B T}} dr^3$

one ideal gas atom: $U_p(r)=0$

$$Z_{1,V,T}^{\text{ideal gas}} = C \int e^{-\frac{p^2}{2mk_B T}} dp^3 \int 1 dr^3 = CV \int e^{-\frac{p^2}{2mk_B T}} dp^3 = CV (2\pi mk_B T)^{\frac{3}{2}}$$

Compare:

$$q_{\text{translational}} = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} V = \frac{V}{\Lambda^3}$$

if we define $C=1/h^3$

$$Z_{1,V,T}^{\text{ideal gas}} = CV (2\pi mk_B T)^{\frac{3}{2}} = \frac{V}{\Lambda^3}$$

N gas molecules:

$$Z_{N,V,T} = \frac{1}{h^{3N}} \iint e^{-\frac{H}{k_B T}} dp^{3N} dr^{3N}$$

wrong: particles are indistinguishable

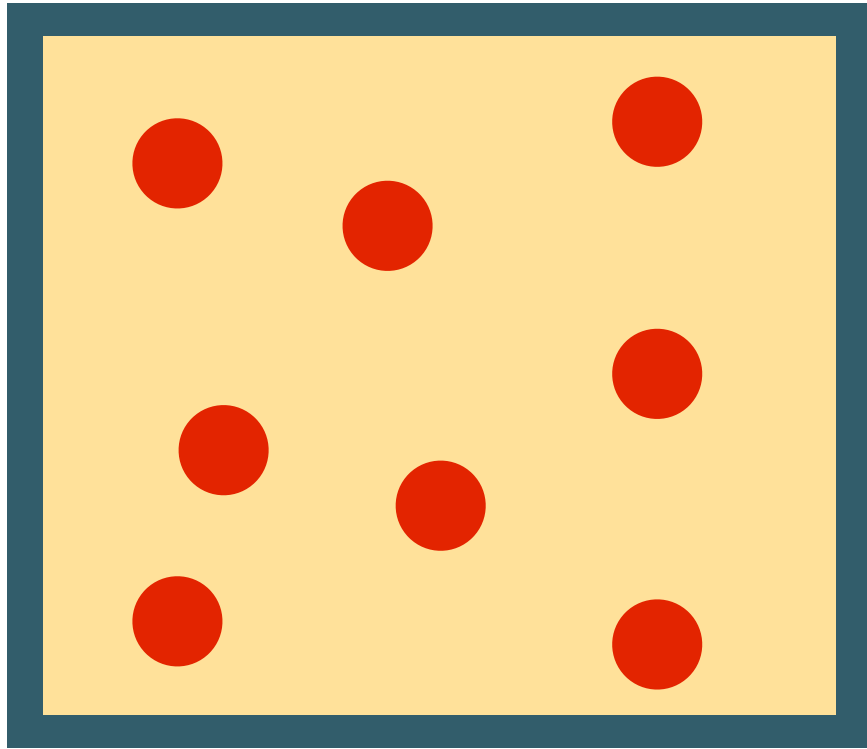
if we swap the position of two particles we do not have a new configuration!

$$Z_{N,V,T} = \frac{1}{h^{3N} N!} \iint e^{-\frac{H}{k_B T}} dp^{3N} dr^{3N}$$

Configurational part of the partition function:

$$Q_{N,V,T} = \frac{1}{\Lambda^{3N} N!} \int e^{-\frac{U(r)}{k_B T}} dr^{3N}$$

Probability to find a particular configuration



Partition function:

$$Q_{N,V,T} = \frac{1}{\Lambda^{3N} N!} \int e^{-\frac{U(r)}{k_B T}} dr^{3N}$$

Probability to find configuration R^N

$$P(R^N) = \frac{1}{Q_{N,V,T}} \frac{1}{\Lambda^{3N} N!} \int \delta(R^N - r^N) e^{-\frac{U(r^N)}{k_B T}} dr^{3N} \propto e^{-\frac{U(R^N)}{k_B T}}$$

As expected we get the Boltzmann factor

Intermezzo: Stirling's approximation

In general N is a large number:

$$\ln(N!) = \ln N + \ln(N-1) + \ln(N-2) + \cdots + \ln 1$$

$$\ln(N!) = \sum_{n=1}^N \ln(i) \approx \int_1^N \ln x dx = x \ln x - x \Big|_1^N = N \ln N - N + 1 \approx N \ln N$$

Hence, for large N we will use:

$$\ln(N!) \approx N \ln N$$

Question

- For an ideal gas, calculate:
 - the partition function
 - the pressure
 - the energy
 - the chemical potential

Ideal gas molecules:

$$Q_{N,V,T}^{\text{ideal gas}} = \frac{1}{\Lambda^{3N} N!} \int e^0 dr^{3N} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy:

$$F^{\text{ideal gas}} = k_B T \ln \Lambda^3 - k_B T \ln \left(\frac{V^N}{N!} \right)$$

This is the (absolute) reference state of the free energy: F^0 , which only depends on temperature

For $N!$ we can use Stirling's approximation

$$= F^0 + k_B T N \ln \left(\frac{N}{V} \right) = F^0 + k_B T N \ln \rho$$

Pressure:

Thermo: $p = - \left(\frac{\partial F}{\partial V} \right)_{T,N}$

$$p = \frac{k_B T N}{V}$$

Ideal gas law

Energy:

Thermo: $U = \left(\frac{\partial F/T}{\partial 1/T} \right)$

$$U = 3k_B N \left(\frac{\partial \ln \Lambda}{\partial 1/T} \right)$$

with

$$\ln \Lambda = \ln \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{1}{2}} = C + \frac{1}{2} \ln \left(\frac{1}{T} \right)$$

Giving:

$$U = \frac{3}{2} N k_B T$$

Chemical potential:

Thermo $\mu = -\left(\frac{\partial F}{\partial N}\right)_{T,V}$

For an ideal gas we have:

$$\beta F^{\text{ideal gas}} = N \ln \Lambda^3 + N \ln \left(\frac{N}{V} \right)$$

$$\beta \mu^{\text{ideal gas}} = \beta \mu^0 + \ln \rho$$

Summary: Canonical ensemble (N,V,T)

Partition function:

$$Q_{N,V,T} = \frac{1}{\Lambda^{3N} N!} \int e^{-\frac{U(r)}{k_B T}} dr^{3N}$$

Probability to find a particular configuration:

$$P(R^N) \propto e^{-\frac{U(R^N)}{k_B T}}$$

Ensemble average:

$$\langle A \rangle_{N,V,T} = \frac{\frac{1}{\Lambda^{3N} N!} \int A(r) e^{-\frac{U(r)}{k_B T}} dr^{3N}}{Q_{N,V,T}} = \frac{\int A(r) e^{-\beta U(r)} dr^{3N}}{\int e^{-\beta U(r)} dr^{3N}}$$

Free energy:

$$\beta F = -\ln Q_{NVT}$$

Summary: micro-canonical ensemble (N,V,E)

Partition function:

$$Q_{N,V,E} = \frac{1}{h^{3N} N!} \iint \delta(E - H(p^{3N}, r^{3N})) dp^{3N} dr^{3N}$$

Probability to find a particular configuration

$$P(P^N, R^N) \propto 1$$

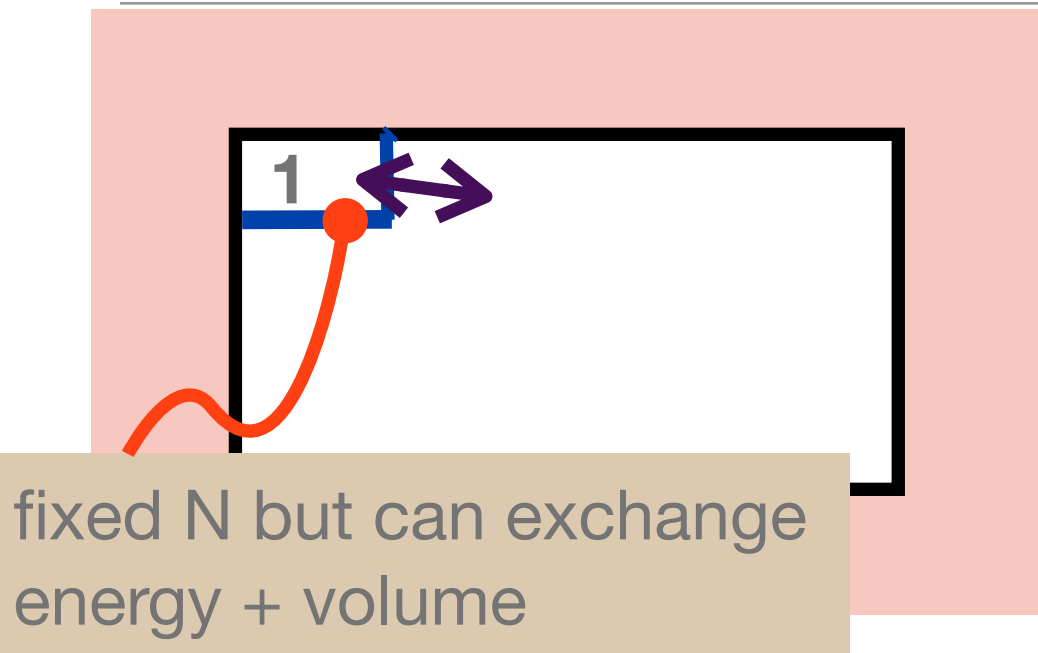
Free energy

$$S = k_B \ln Q_{NVE}$$

2. Thermodynamics

2.4.2 Ensembles: constant pressure

Constant: T and p



We have our system (1) and a bath (b)

Total system is isolated and the volume is constant

First law $dU = dq - pdV = 0$

Second law $dS \geq 0$

Box 1: *constant pressure and temperature*

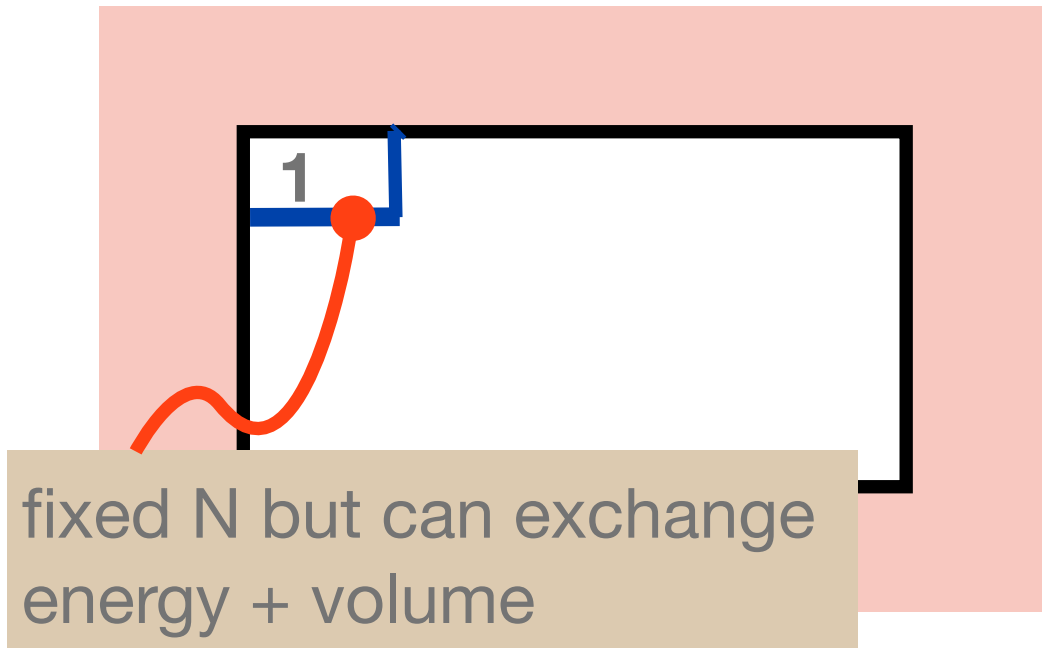
1st law: $dU_1 + dU_b = 0$ or $dU_1 = -dU_b$

$dV_1 + dV_b = 0$ or $dV_1 = -dV_b$

The bath is very large and the small changes do not change P or T; in addition the process is reversible

2nd law: $dS_1 + dS_b = dS_1 + \frac{dU_b}{T} + \frac{p}{T}dV_b \geq 0$

$$TdS_1 - dU_1 - pdV_1 \geq 0$$



Total system is isolated and the volume is constant

Box 1: *constant pressure and temperature*

2nd law: $TdS_1 - dU_1 - pdV_1 \geq 0$

$$d(U_1 - TS_1 + pV_1) \leq 0$$

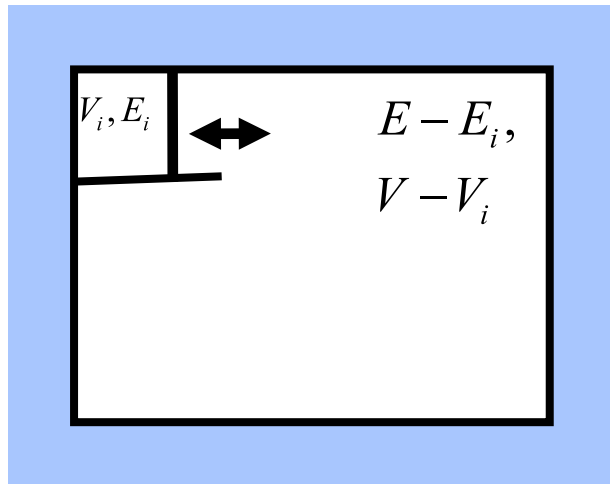
Let us define the **Gibbs free energy**: G

$$G \equiv U - TS + pV$$

For box 1 we can write $dG_1 \leq 0$

Hence, for a system at *constant temperature and pressure* the Gibbs free energy decreases and takes its minimum value at equilibrium

N, P, T ensemble



Consider a small system that can exchange volume and energy with a big reservoir

$$\ln \Omega(V - V_1, E - E_1) = \ln \Omega(V, E) - \left(\frac{\partial \ln \Omega}{\partial E} \right) E_1 - \left(\frac{\partial \ln \Omega}{\partial V} \right) V_1 + \dots$$

The terms in the expansion follow from the connection with thermodynamics:

$$S = k_B \ln \Omega$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum \frac{\mu_i}{T} dN_i$$

We have:

$$\left(\frac{\partial S}{\partial U} \right)_{V, N_i} = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V} \right)_{N, E} = \frac{p}{T}$$

$$\ln \Omega(V - V_1, E - E_1) = \ln \Omega(V, E) - \left(\frac{\partial \ln \Omega}{\partial E} \right)_{V, N} E_1 - \left(\frac{\partial \ln \Omega}{\partial V} \right)_{E, N} V_1 + \dots$$

$$\ln \Omega(V - V_1, E - E_1) = \ln \Omega(V, E) - \frac{1}{k_B T} E_1 - \frac{p}{k_B T} V_1 + \dots$$

$$\ln \left(\frac{\Omega(V - V_1, E - E_1)}{\Omega(V, E)} \right) = -\frac{E_1}{k_B T} - \frac{p V_1}{k_B T}$$

Hence, the probability to find E_i, V_i :

$$P(V_1, E_1) = \frac{\Omega(V - V_1, E - E_1)}{\sum_{i,j} \Omega(V - V_i, E - E_j)} = \frac{\Omega(V - V_1, E - E_1) / \Omega(V, E)}{\sum_{i,j} \Omega(V - V_i, E - E_j) / \Omega(V, E)} = C e^{-\frac{1}{k_B T} (E_1 + p V_1)}$$

$$P(V_1, E_1) \propto e^{-\beta(E_1 + p V_1)}$$

Partition function:

$$\Delta(N, p, T) = \sum_{i,j} e^{-\frac{1}{k_B T} (E_i + pV_j)}$$

Ensemble average:

$$\langle V \rangle = \frac{\sum_{i,j} V_j e^{-\frac{1}{k_B T} (E_i + pV_j)}}{\sum_{i,j} e^{-\frac{1}{k_B T} (E_i + pV_j)}} = -k_B T \left(\frac{\partial \ln \Delta(N, p, T)}{\partial p} \right)_{N, T}$$

$$dG = -SdT + Vdp - \sum \mu_i dN_i$$

Thermodynamics

$$V = \left(\frac{\partial G}{\partial p} \right)_{N, T}$$

Hence:

$$G = -k_B T \ln \Delta(N, p, T)$$

Summary

In the classical limit, the partition function becomes

$$Q(N, p, T) = \frac{1}{\Lambda^{3N} N!} \int dV e^{-\beta p V} \int dr^N e^{-\beta U(r^N)}$$

The probability to find a particular configuration:

$$P(r^N, V) \propto e^{-\beta [pV + U(r^N)]}$$

The link to thermodynamics:

$$G = -k_B T \ln \Delta(N, p, T)$$

2. Thermodynamics

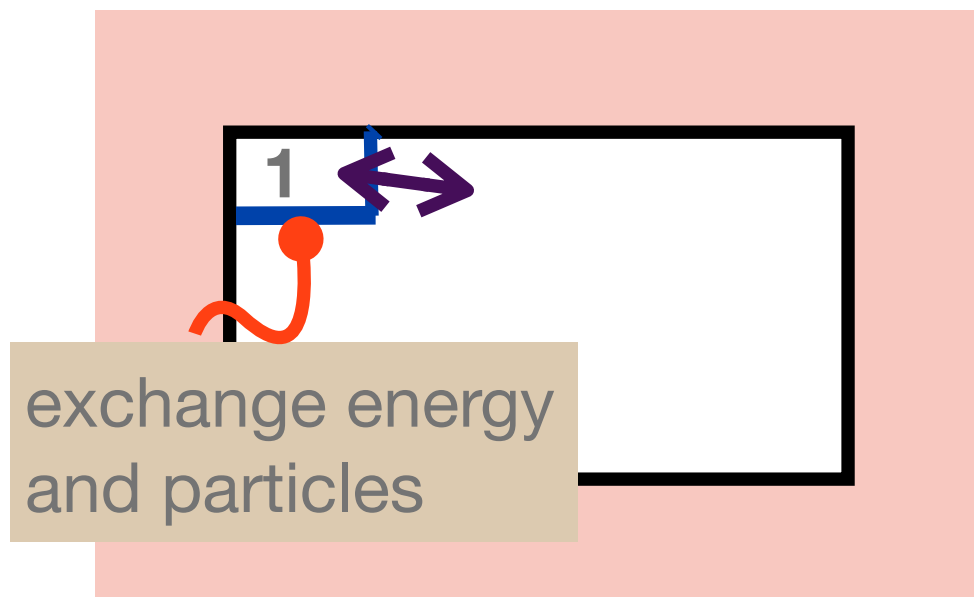
2.4.3 Ensembles: constant chemical potential

Grand-canonical ensemble

Classical: A small system that can exchange **heat and particles** with a large bath

Statistical: Taylor expansion of a small reservoir

Constant: T and μ



Total system is isolated and the volume is constant

First law $dU = TdS - pdV + \mu dN = 0$

Second law $dS \geq 0$

Box 1: *constant chemical potential and temperature*

1st law: $dU_1 + dU_b = 0$ or $dU_1 = -dU_b$

$dN_1 + dN_b = 0$ or $dN_1 = -dN_b$

The bath is very large and the small changes do not change μ or T ; in addition the process is reversible

2nd law:
$$dS = dS_1 + dS_b = dS_1 + \left[\frac{dU_b}{T} - \mu \frac{dN_b}{T} \right] \geq 0$$

$$dS = dS_1 + dS_b = dS_1 + \left[\frac{dU_b}{T} - \mu \frac{dN_b}{T} \right] \geq 0$$

We can express the changes of the bath in terms of properties of the system

$$dS_1 + \left[-\frac{dU_1}{T} + \mu \frac{dN_1}{T} \right] \geq 0 \quad \begin{aligned} d(TS_1 - U_1 + \mu N_1) &\geq 0 \\ d(U_1 - TS_1 - \mu N_1) &\leq 0 \end{aligned}$$

For the Gibbs free energy we can write:

$$G \equiv U - TS + pV$$

$$G = \mu N$$

$$\text{or} \quad -pV = U - TS - \mu N$$

Giving:

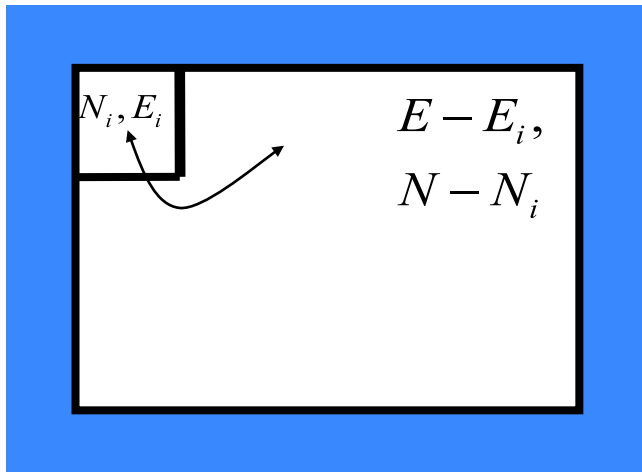
$$d(-pV) \leq 0$$

or

$$d(pV) \geq 0$$

Hence, for a system at *constant temperature and chemical potential* pV increases and takes its maximum value at equilibrium

μ, V, T ensemble



Consider a small system that can exchange *particles* and energy with a big reservoir

$$\ln \Omega(N - N_1, E - E_1) = \ln \Omega(N, E) - \left(\frac{\partial \ln \Omega}{\partial E} \right) E_1 - \left(\frac{\partial \ln \Omega}{\partial N} \right) N_1 + \dots$$

The terms in the expansion follow from the connection with Thermodynamics:

$$S = k_B \ln \Omega$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN$$

Giving:

$$\left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial N} \right)_{V,T} = -\frac{\mu}{T}$$

$$\ln \Omega(N - N_1, E - E_1) = \ln \Omega(N, E) - \left(\frac{\partial \ln \Omega}{\partial E} \right) E_1 - \left(\frac{\partial \ln \Omega}{\partial N} \right) N_1 + \dots$$

$$\ln \Omega(N - N_1, E - E_1) = \ln \Omega(N, E) - \frac{E_1}{k_B T} + \frac{\mu N_1}{k_B T} + \dots$$

$$\ln \left[\frac{\Omega(N - N_1, E - E_1)}{\Omega(N, E)} \right] = -\frac{1}{k_B T} (E_1 - \mu N_1)$$

Hence, the probability to find E_1, N_1 :

$$P(N_1, E_1) = \frac{\Omega(N - N_1, E - E_1)}{\sum_{i,j} \Omega(N - N_i, E - E_j)} = \frac{\Omega(N - N_1, E - E_1) / \Omega(N, E)}{\sum_{i,j} \Omega(N - N_i, E - E_j) / \Omega(N, E)} = C e^{-\frac{1}{k_B T} (E_1 - \mu N_1)}$$

$$P(N, E) \propto C e^{-\beta(E - \mu N)}$$

In the classical limit, the partition function becomes

$$Q(\mu, V, T) = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N} N!} \int dr^N e^{-\beta U(r^N)}$$

The probability to find a particular configuration:

$$P(N, r^N) \propto e^{-\beta[U(r^N) - \mu N]}$$