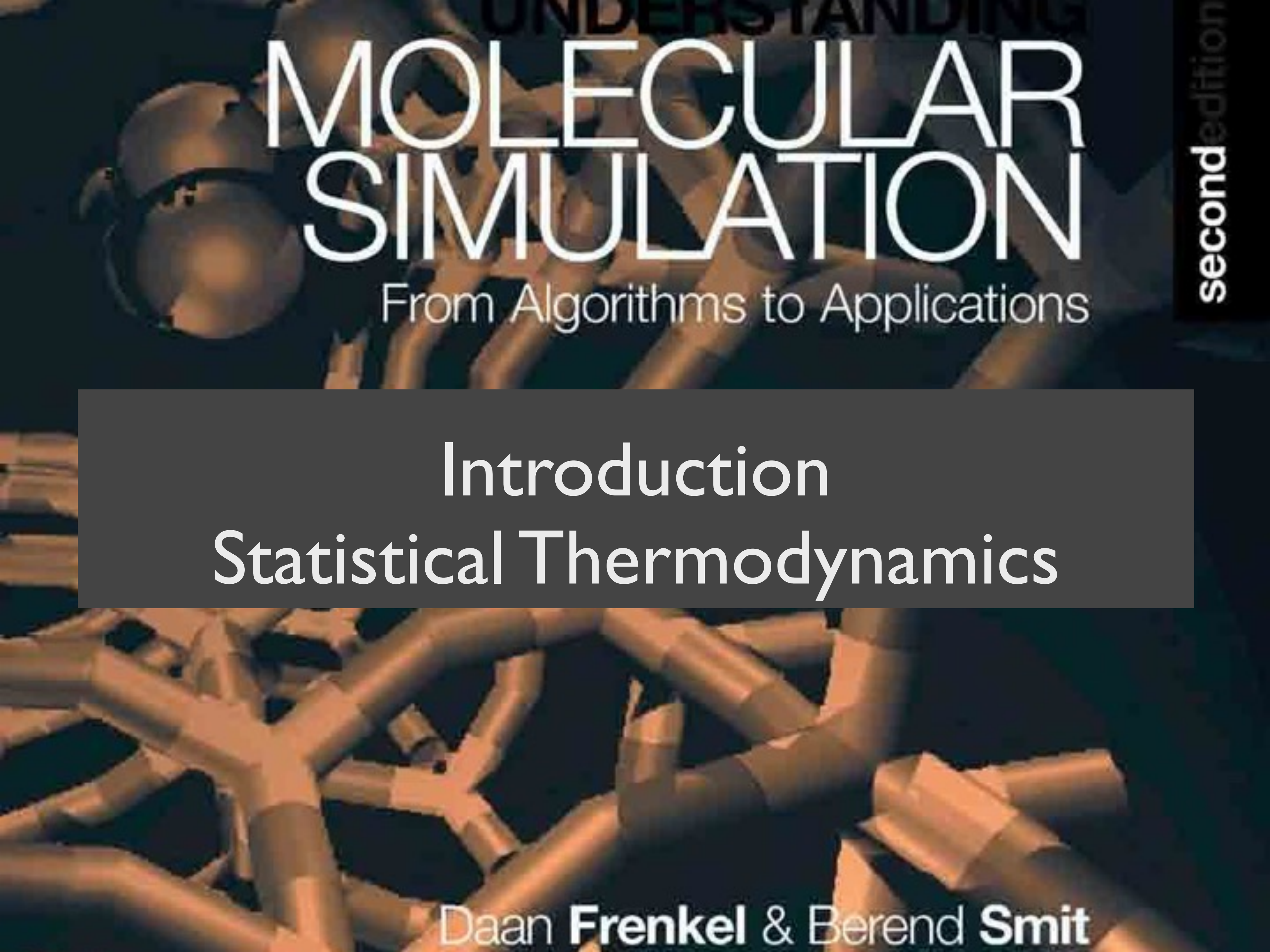
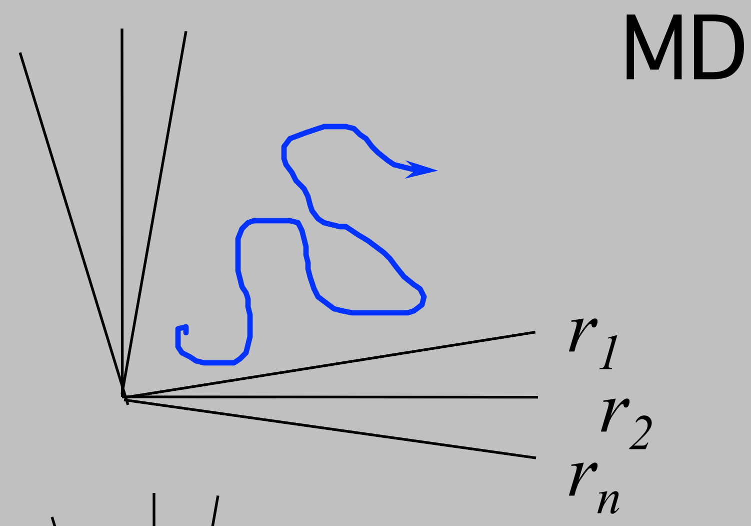


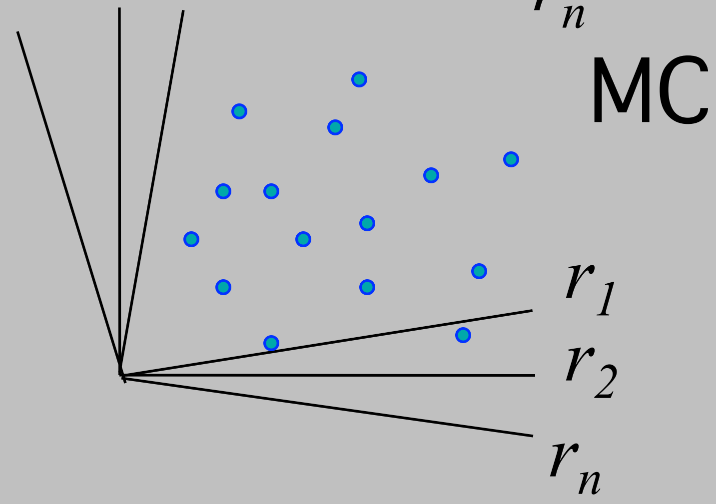
Introduction
Statistical Thermodynamics

Molecular Simulations

- Molecular dynamics: solve equations of motion



- Monte Carlo: importance sampling



Algorithm 1 (Basic Metropolis Algorithm)

```
 PROGRAM mc                          basic Metropolis algorithm

 do icycl=1,ncycl                    perform ncycl MC cycles
   call mcmove                       displace a particle
   if (mod(icycl,nsamp).eq.0)
+    call sample                     sample averages
 enddo
 end
```

Comments to this algorithm:

1. *Subroutine* `mcmove` *attempts to displace a randomly selected particle (see Algorithm 2).*
2. *Subroutine* `sample` *samples quantities every* `nsamp`*th cycle.*

Algorithm 2 (Attempt to Displace a Particle)

```
 SUBROUTINE mcmove                attempts to displace a particle

 o=int(ranf()*npart)+1            select a particle at random
 call ener(x(o),eno)              energy old configuration
 xn=x(o)+(ranf()-0.5)*delx        give particle random displacement
 call ener(xn,enn)                energy new configuration
 if (ranf().lt.exp(-beta          acceptance rule (3.2.1)
+    *(enn-eno)) x(o)=xn          accepted: replace x(o) by xn
 return
 end
```

Comments to this algorithm:

1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

Questions

Questions

- How can we prove that this scheme generates the desired distribution of configurations?

Questions

- How can we prove that this scheme generates the desired distribution of configurations?
- Why make a random selection of the particle to be displaced?

Questions

- How can we prove that this scheme generates the desired distribution of configurations?
- Why make a random selection of the particle to be displaced?
- Why do we need to take the old configuration again?

Questions

- How can we prove that this scheme generates the desired distribution of configurations?
- Why make a random selection of the particle to be displaced?
- Why do we need to take the old configuration again?
- How large should we take: `delx`?

Questions

What is the desired distribution?

- How can we prove that this scheme generates the desired distribution of configurations?
- Why make a random selection of the particle to be displaced?
- Why do we need to take the old configuration again?
- How large should we take: `delx`?

Outline

Outline

Rewrite History

- Atoms first! Thermodynamics last!

Outline

Rewrite History

- Atoms first! Thermodynamics last!

Thermodynamics

- First law: conservation of energy
- Second law: in a closed system entropy increase and takes its maximum value at equilibrium

Outline

Rewrite History

- Atoms first! Thermodynamics last!

Thermodynamics

- First law: conservation of energy
- Second law: in a closed system entropy increase and takes its maximum value at equilibrium

System at constant temperature and volume

- Helmholtz free energy decrease and takes its minimum value at equilibrium

Outline

Rewrite History

- Atoms first! Thermodynamics last!

Thermodynamics

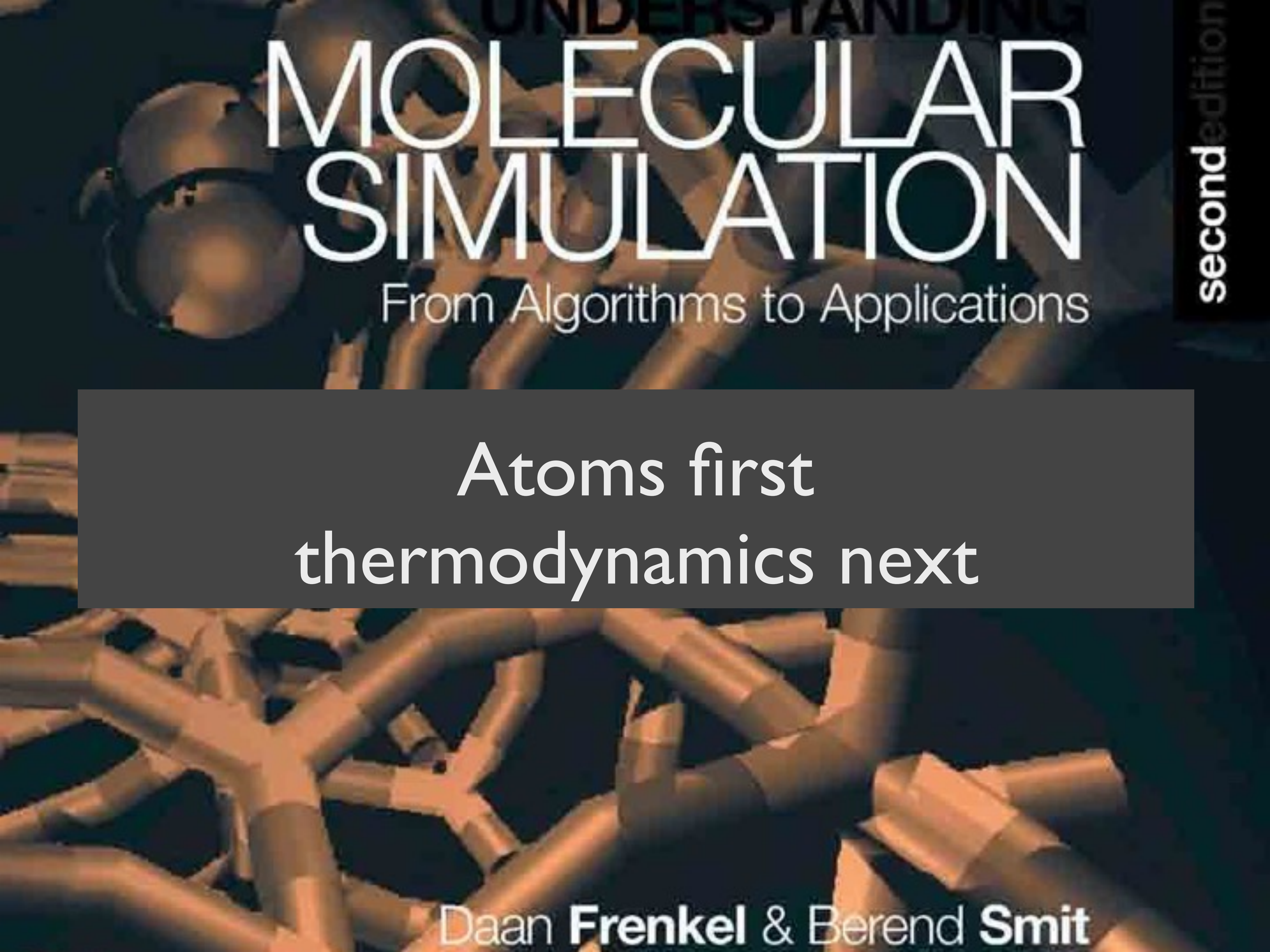
- First law: conservation of energy
- Second law: in a closed system entropy increase and takes its maximum value at equilibrium

System at constant temperature and volume

- Helmholtz free energy decrease and takes its minimum value at equilibrium

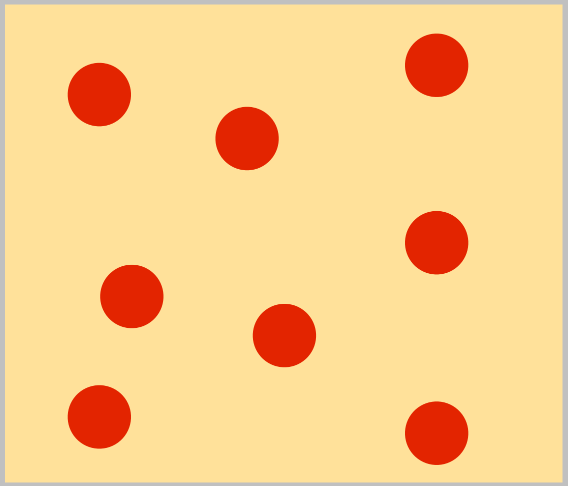
Other ensembles:

- Constant pressure
- grand-canonical ensemble

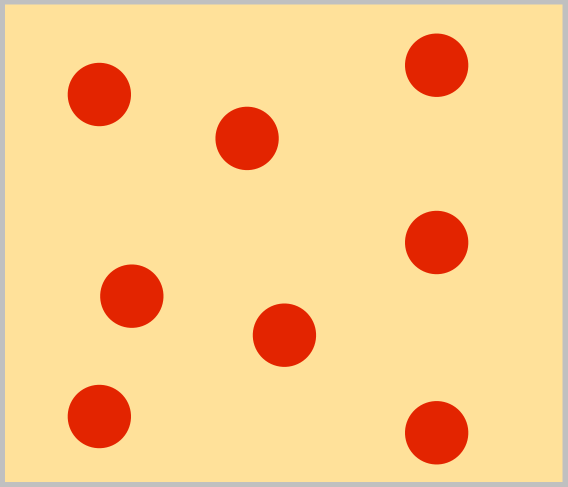


Atoms first
thermodynamics next

A box of particles

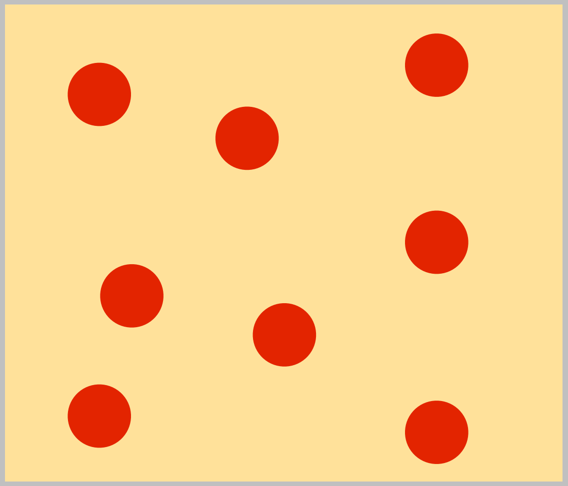


A box of particles



We have given the particles an intermolecular potential

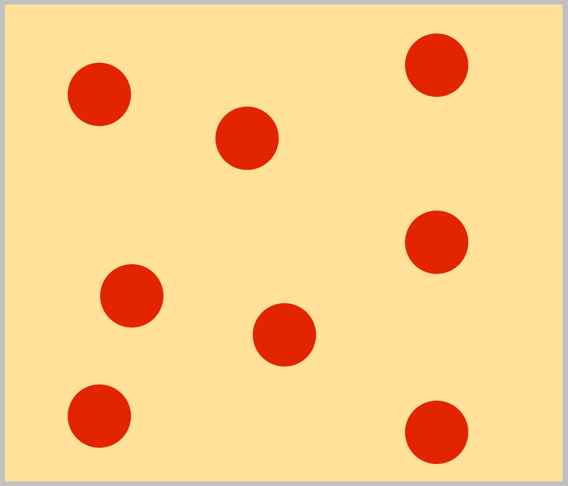
A box of particles



We have given the particles an intermolecular potential

Newton: equations of motion

A box of particles

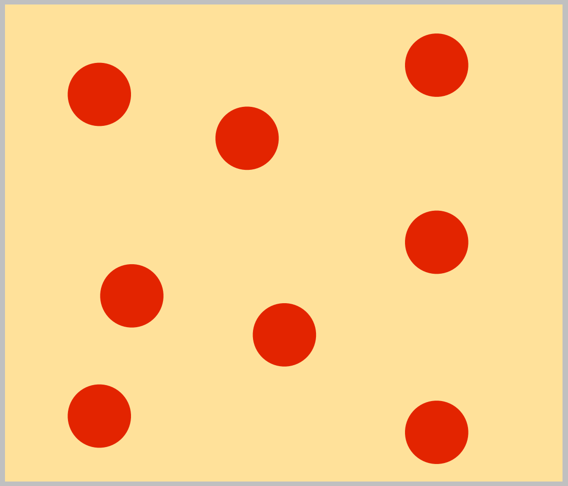


We have given the particles an intermolecular potential

Newton: equations of motion

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

A box of particles



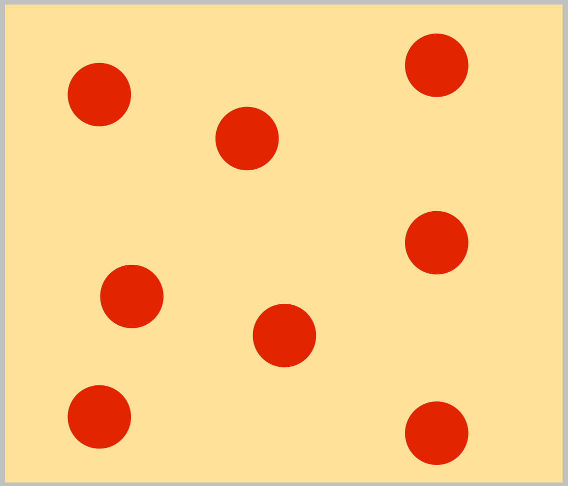
We have given the particles an intermolecular potential

Newton: equations of motion

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

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

A box of particles



We have given the particles an intermolecular potential

Newton: equations of motion

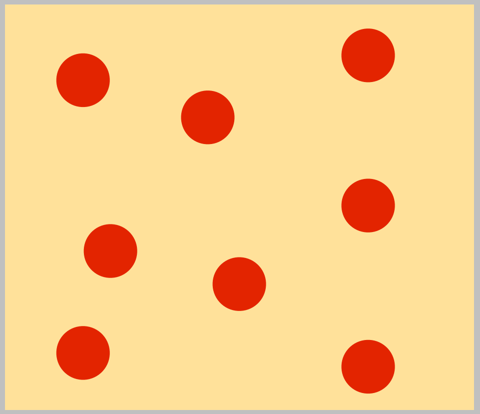
$$\mathbf{F}(r) = -\nabla u(r)$$

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

Conservation of total energy

Phase space

Thermodynamics: N,V,E

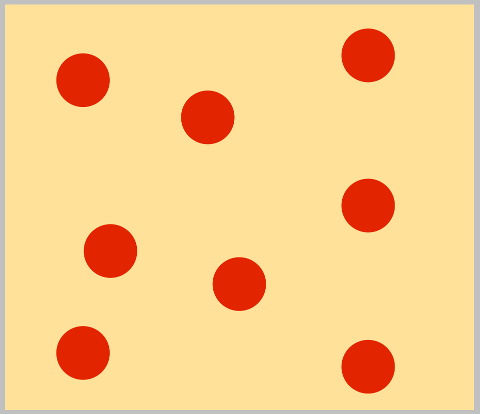


Phase space

Thermodynamics: N,V,E

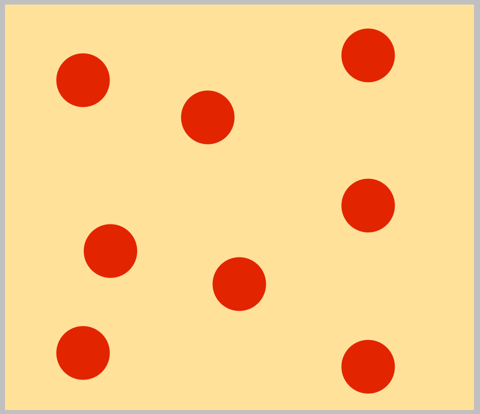
Molecular:

$$\Gamma^N = \left\{ \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N \right\}$$



Phase space

Thermodynamics: N,V,E



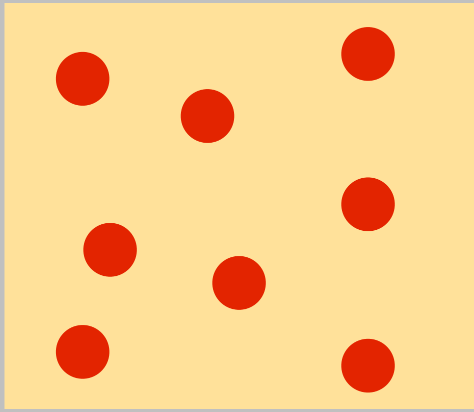
Molecular:

$$\Gamma^N = \left\{ \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N \right\}$$

point in phase space

Phase space

Thermodynamics: N,V,E

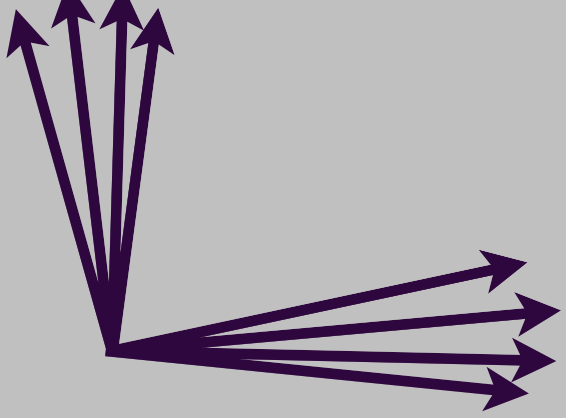


Molecular:

$$\Gamma^N = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N\}$$

point in phase space

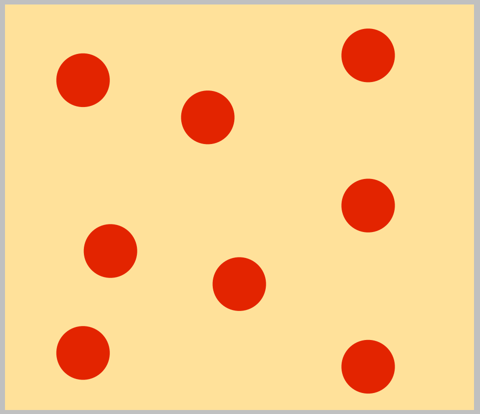
$$\{\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N\}$$



$$\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$$

Phase space

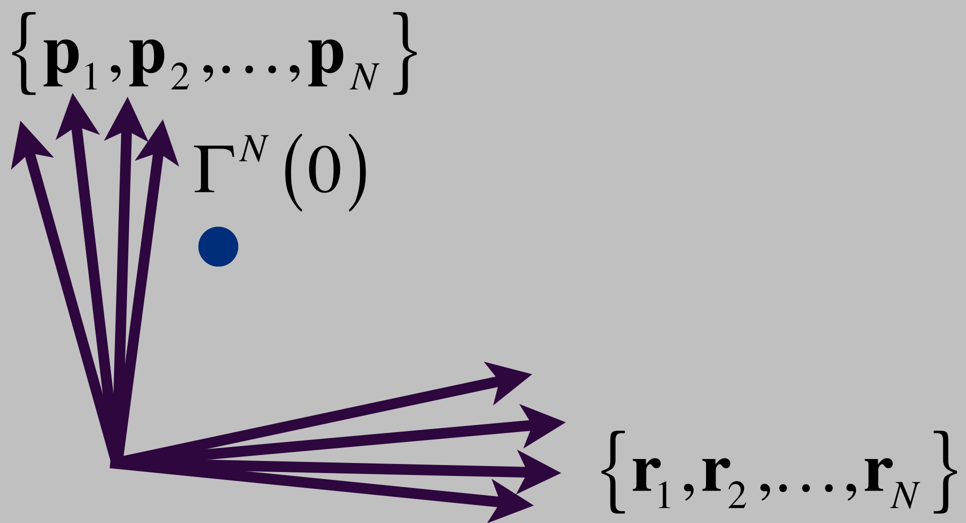
Thermodynamics: N,V,E



Molecular:

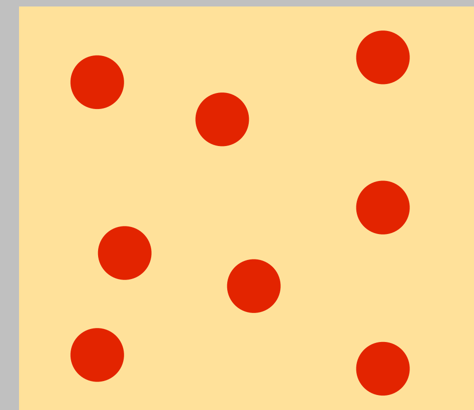
$$\Gamma^N = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N\}$$

point in phase space



Phase space

Thermodynamics: N,V,E



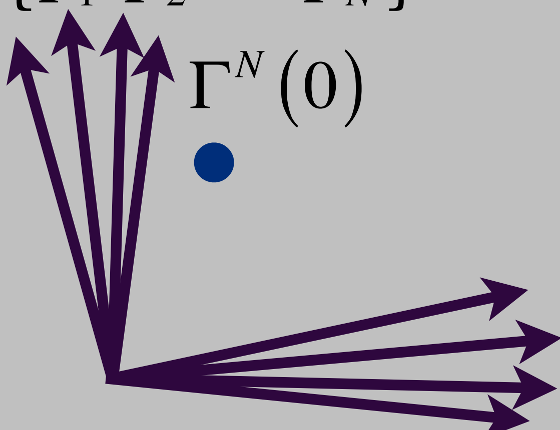
Molecular:

$$\Gamma^N = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N\}$$

point in phase space

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

$$\Gamma^N(0)$$

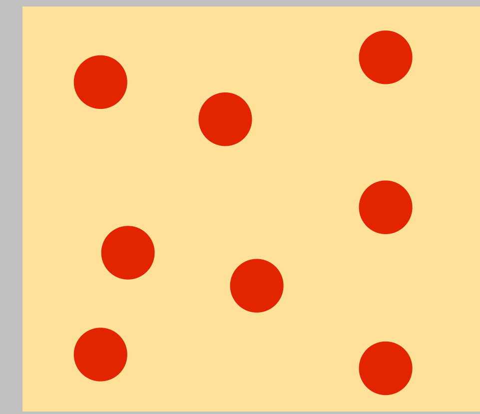


trajectory: classical mechanics

$$\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$$

Phase space

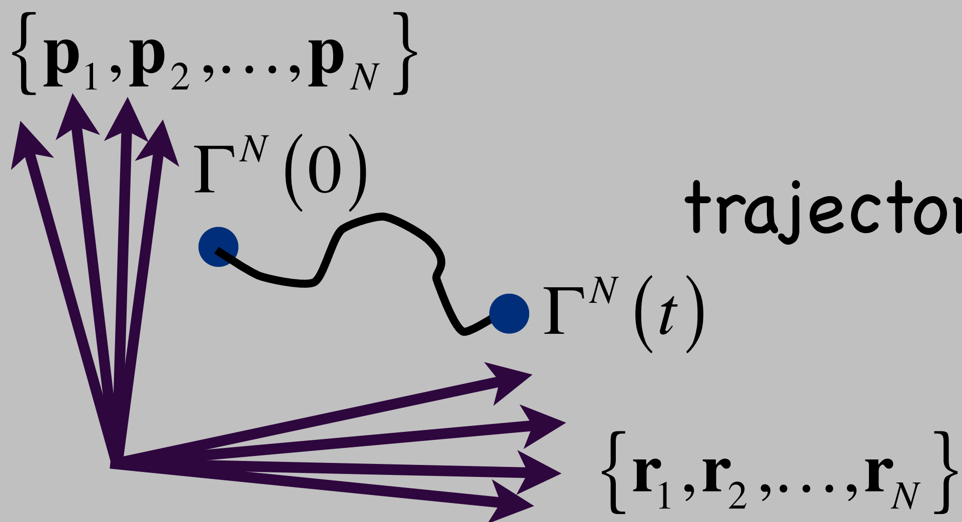
Thermodynamics: N,V,E



Molecular:

$$\Gamma^N = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N\}$$

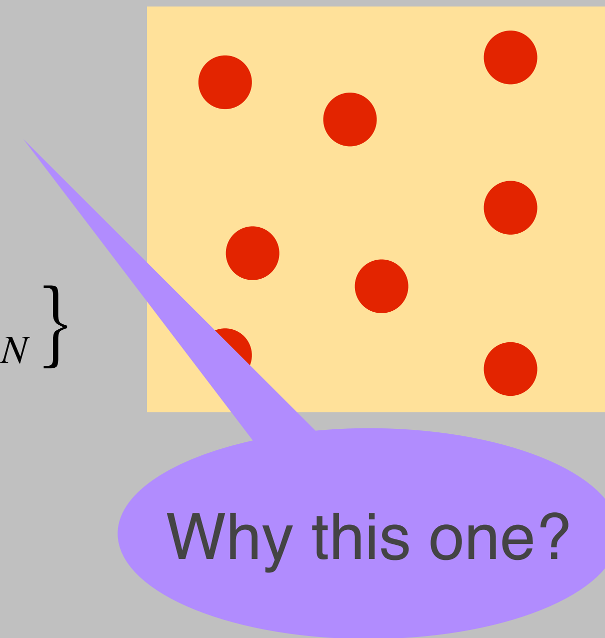
point in phase space



trajectory: classical mechanics

Phase space

Thermodynamics: N,V,E

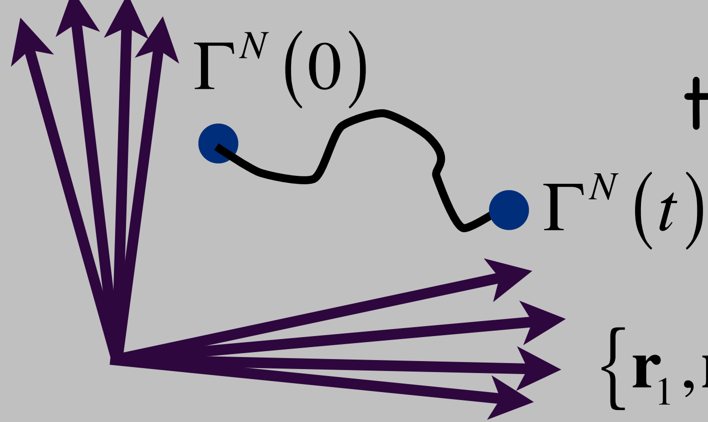


Molecular:

$$\Gamma^N = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N\}$$

point in phase space

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

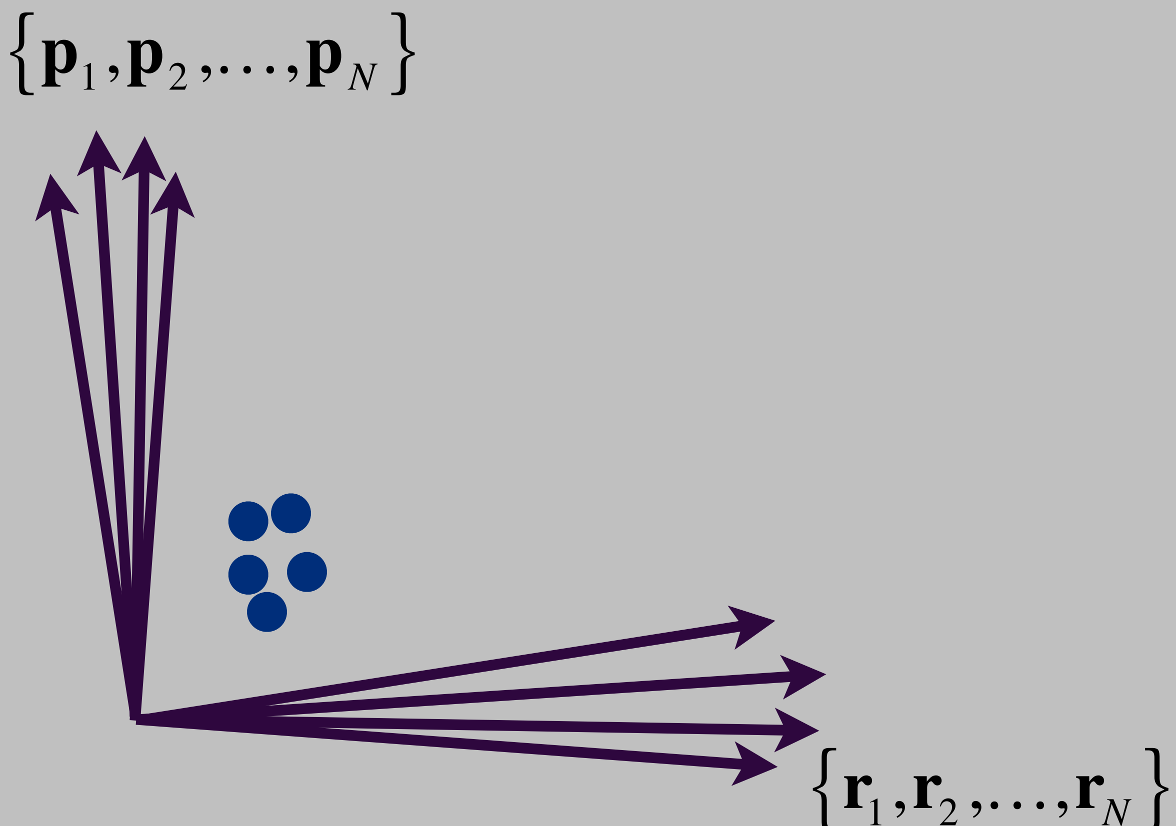


trajectory: classical mechanics

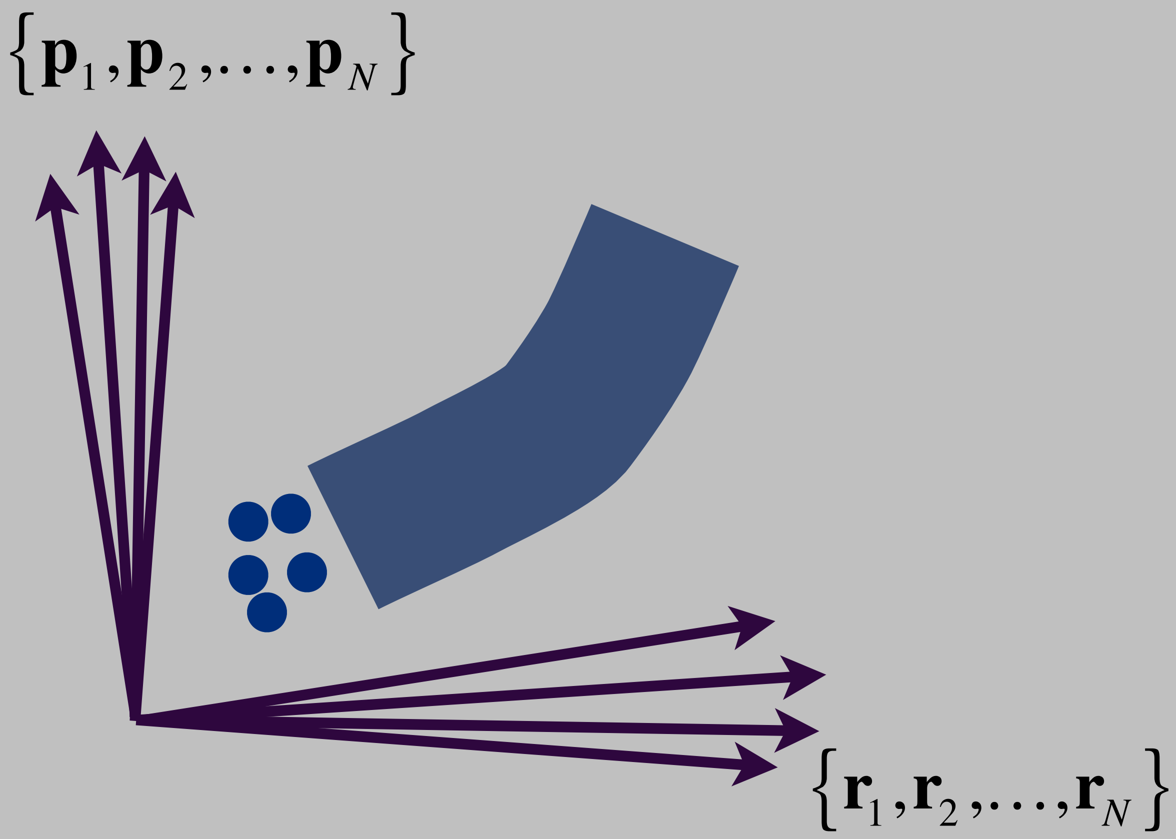
$\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$

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

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

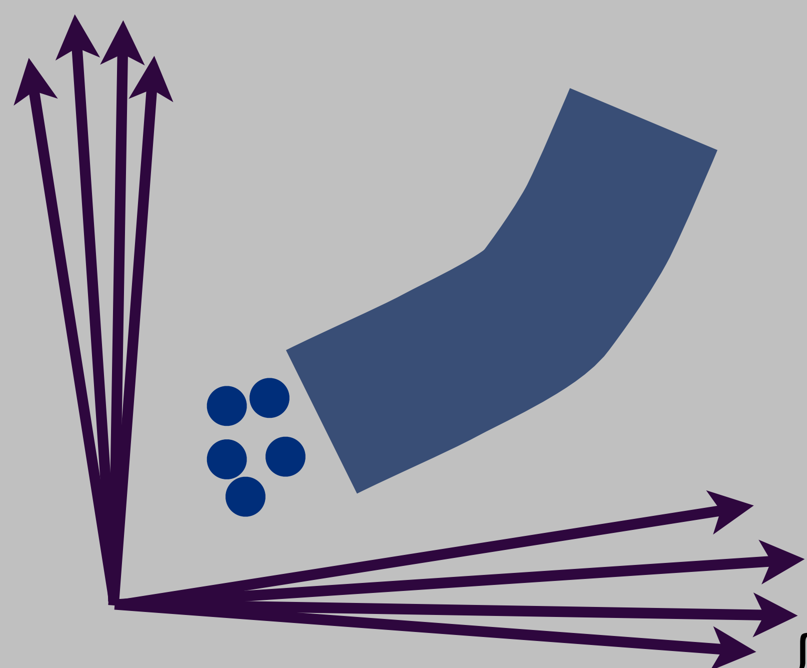


All trajectories with the same initial total energy should describe the same thermodynamic state



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

These trajectories define a probability density in phase space



Intermezzo 1: phase rule

Intermezzo 1: phase rule

- Question: explain the phase rule?

Intermezzo 1: phase rule

- Question: explain the phase rule?
- Phase rule: $F=2-P+C$

Intermezzo 1: phase rule

- Question: explain the phase rule?
- Phase rule: F=2-P+C
  - F: degrees of freedom

Intermezzo 1: phase rule

- Question: explain the phase rule?
- Phase rule: $F=2-P+C$
  - F: degrees of freedom
  - P: number of phases

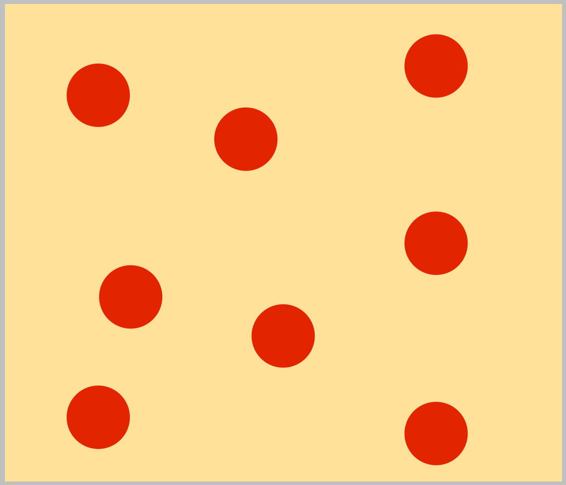
Intermezzo 1: phase rule

- Question: explain the phase rule?
- Phase rule: F=2-P+C
  - F: degrees of freedom
  - P: number of phases
  - C: number of components

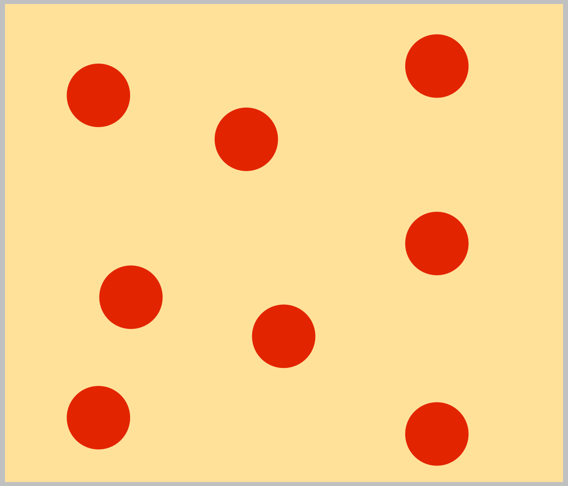
Intermezzo 1: phase rule

- Question: explain the phase rule?
- Phase rule: F=2-P+C
  - F: degrees of freedom
  - P: number of phases
  - C: number of components
- Why the 2?

Making a gas

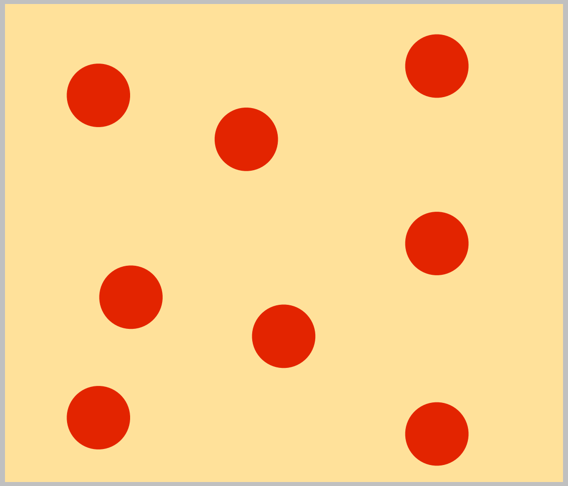


Making a gas



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

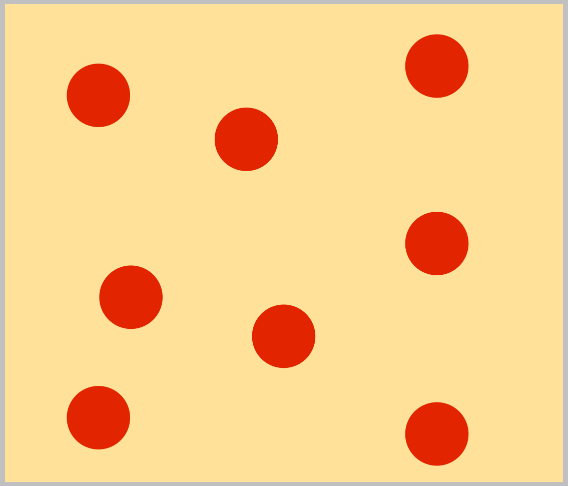
Making a gas



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

1. Specify the volume V

Making a gas

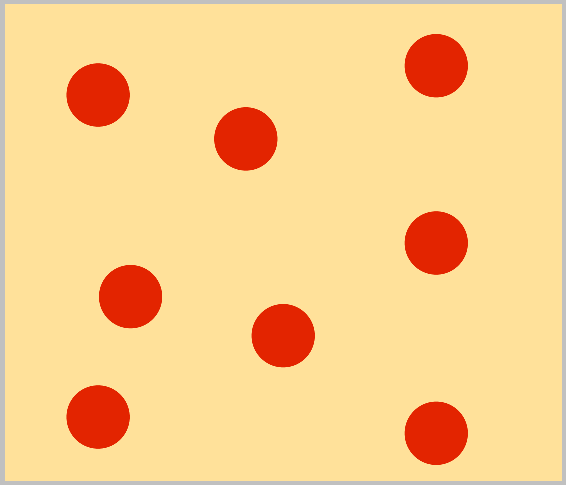


What do we need to specify to fully define a thermodynamic system?

1. Specify the volume V

2. Specify the number of particles N

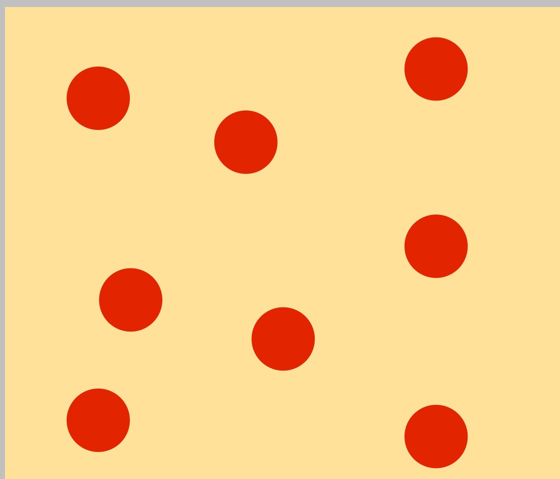
Making a gas



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

Making a gas

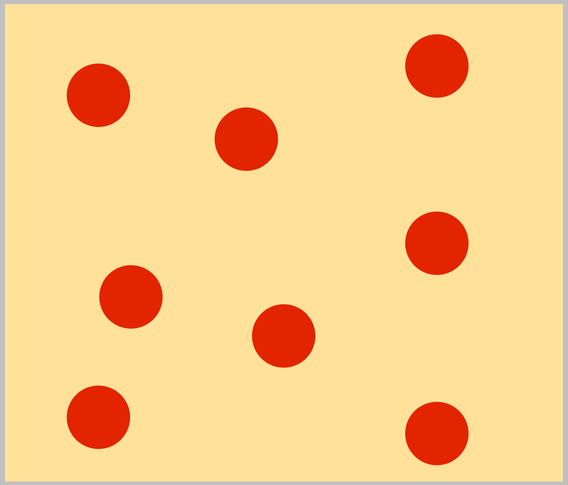


What do we need to specify to fully define a thermodynamic system?

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!

Making a gas



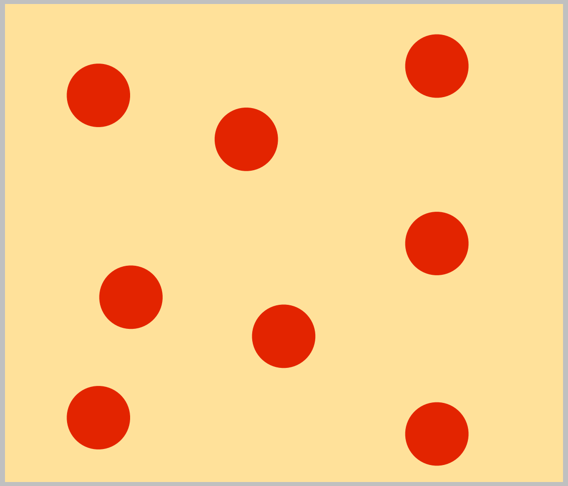
What do we need to specify to fully define a thermodynamic system?

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:

Making a gas



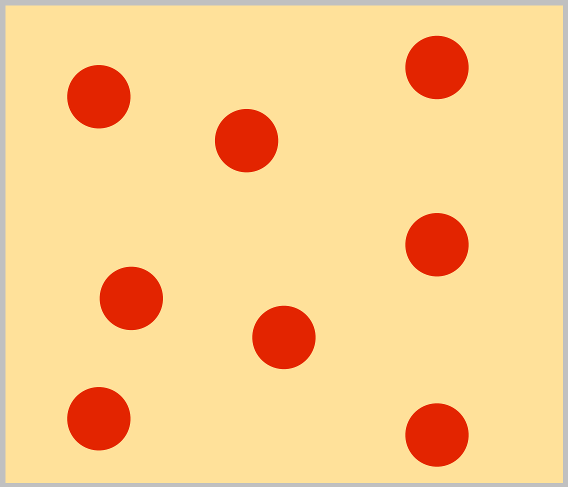
What do we need to specify to fully define a thermodynamic system?

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

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

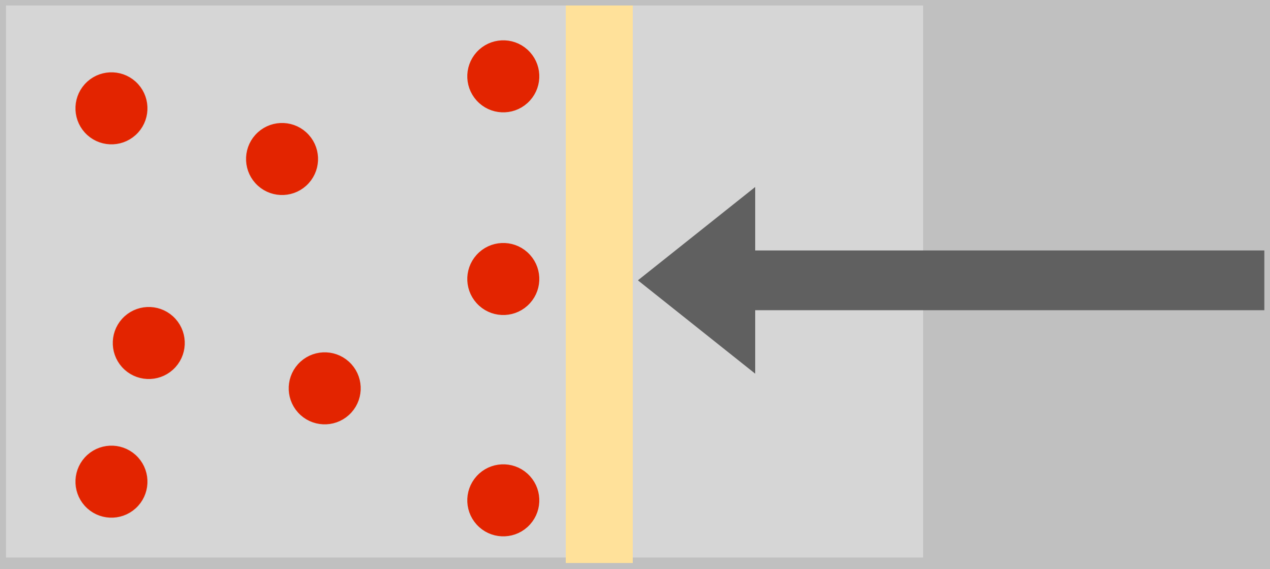
More we cannot do: Newton takes over!

System will be at constant: N,V,E

(micro-canonical ensemble)

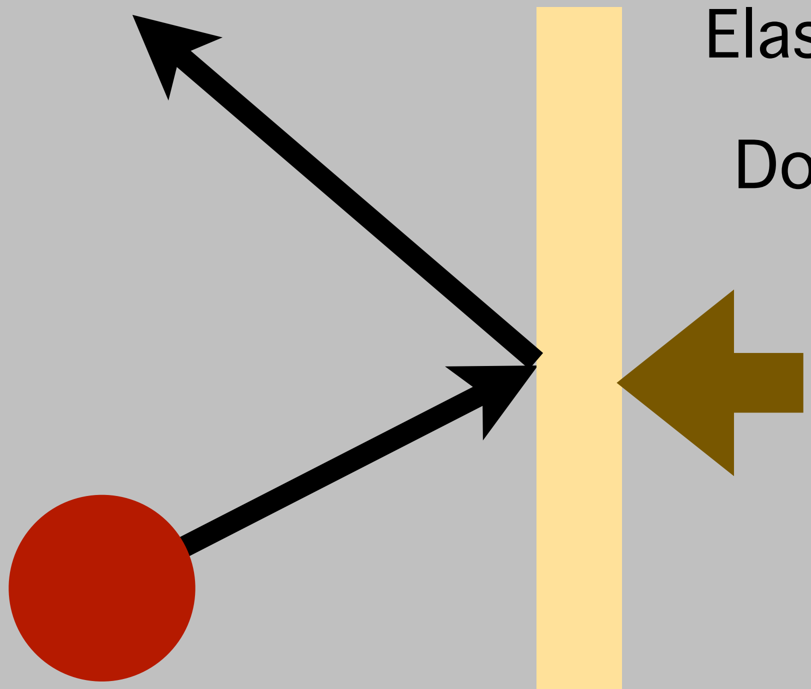
Pressure

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



How much work I do?

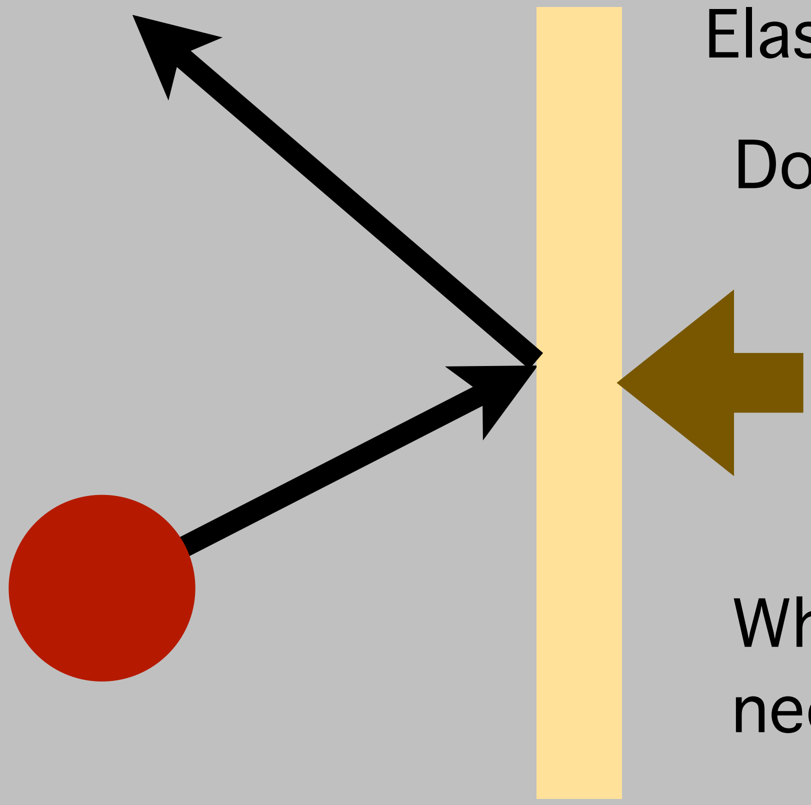
Collision with a wall



Elastic collisions:

Does the energy change?

Collision with a wall



Elastic collisions:

Does the energy change?

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

Pressure

Pressure

- one particle: 2 m v_x

Pressure

- one particle: 2 m v_x
- # particles: $\rho A v_x$

Pressure

- one particle: 2 m v_x
- # particles: ρ A v_x
- 50% is the positive directions: 0.5

Pressure

- one particle: $2\ m\ v_x$
- # particles: $\rho\ A\ v_x$
- 50% is the positive directions: 0.5
- $P\ A = F = \rho\ A\ m\ v_x^2$

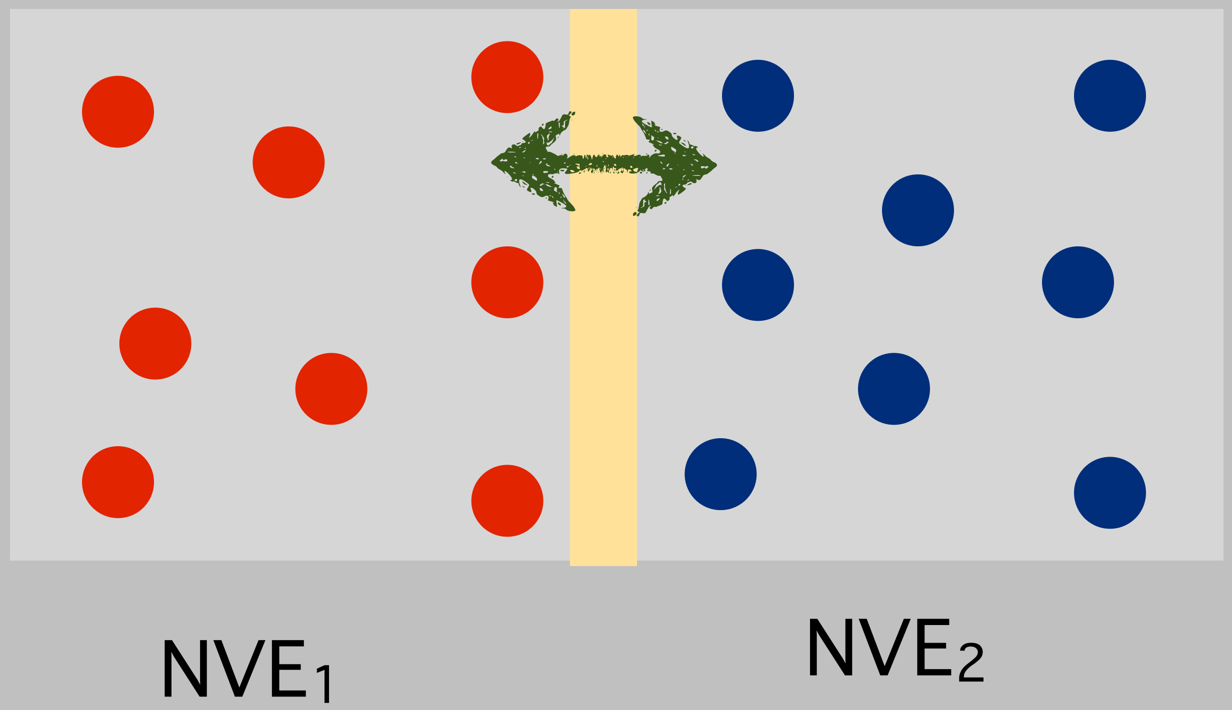
Pressure

- one particle: 2 m v_x
- # particles: ρ A v_x
- 50% is the positive directions: 0.5
- $P A = F = \rho A m v_x^2$
- Kinetic energy: $U_K = \frac{1}{2} m v^2 = \frac{3}{2} k_B T$
  - (we define temperature)

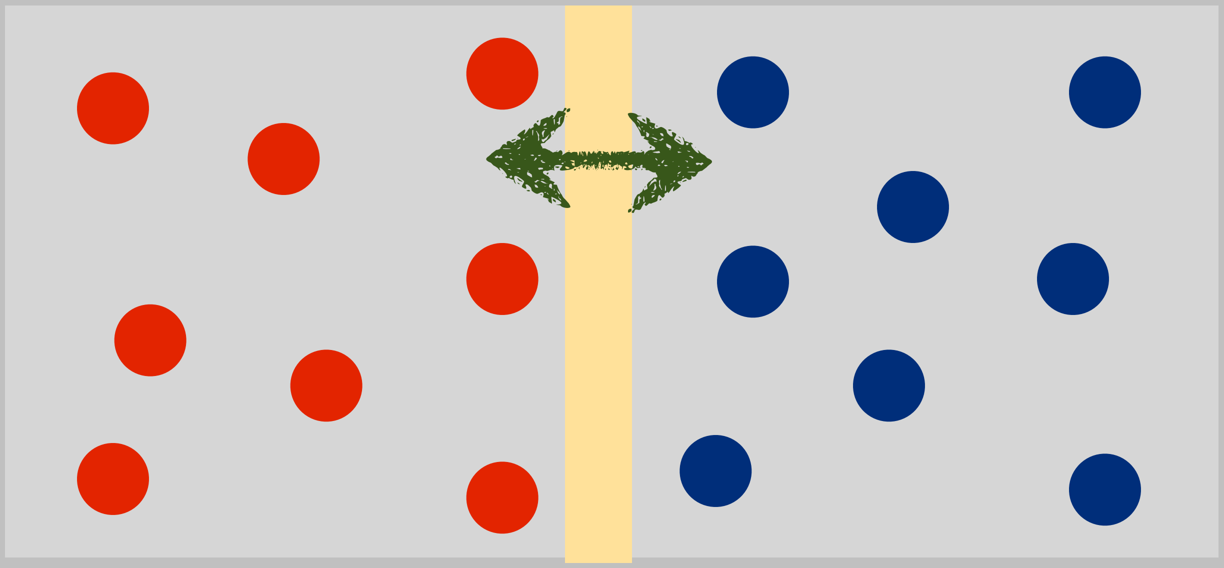
Pressure

- one particle: 2 m v_x
- # particles: ρ A v_x
- 50% is the positive directions: 0.5
- $P A = F = \rho A m v_x^2$
- Kinetic energy: $U_K = ½ m v^2 = ³⁄₂ k_B T$
    - (we define temperature)
- Pressure: $P V = N k_B T$

Experiment (1)

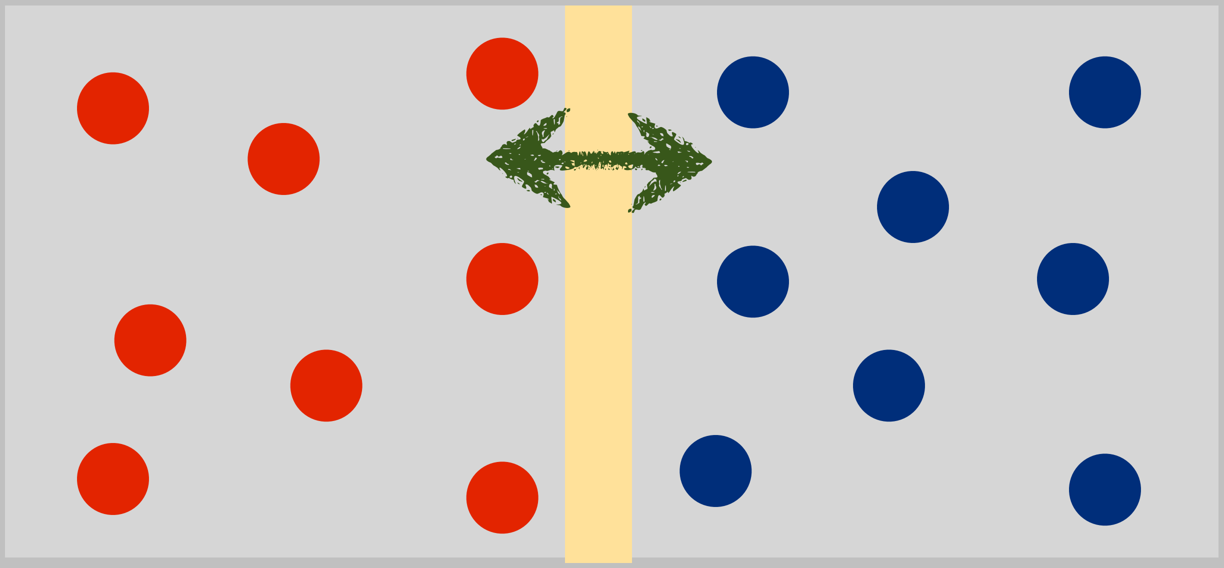


Experiment (1)



NVE_1 NVE_2 $E_1 > E_2$

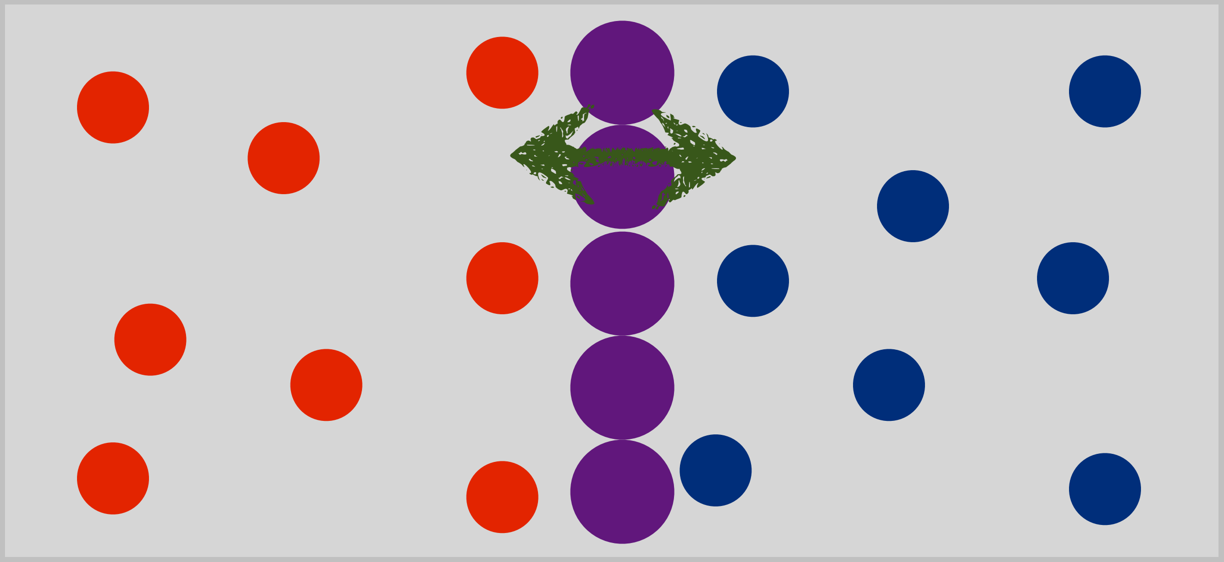
Experiment (1)



NVE_1 NVE_2 $E_1 > E_2$

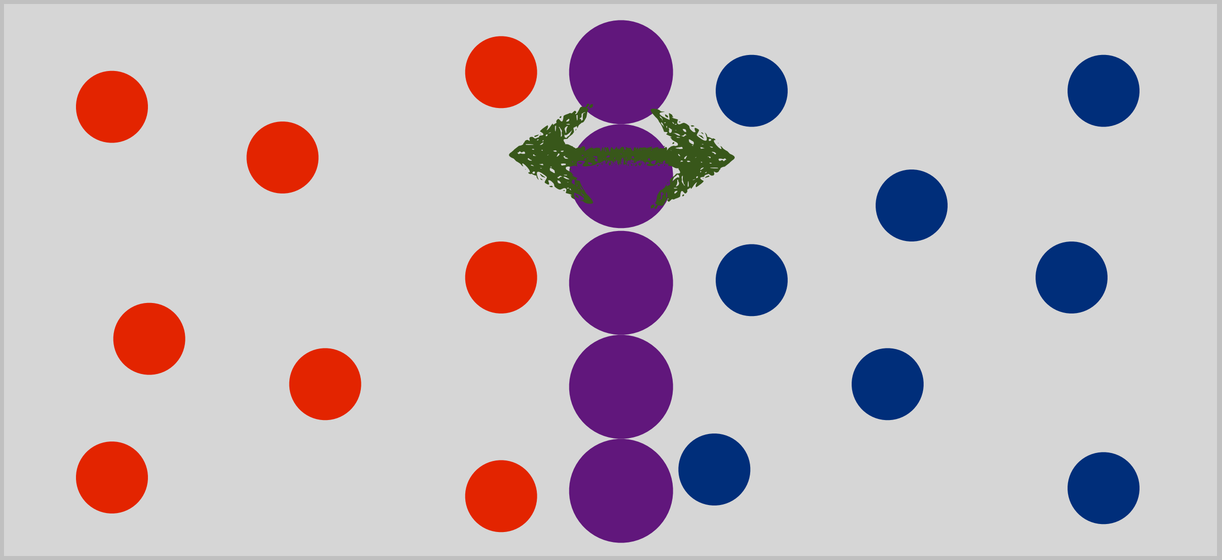
What will the moveable wall do?

Experiment (2)



NVE_1 NVE_2 $E_1 > E_2$

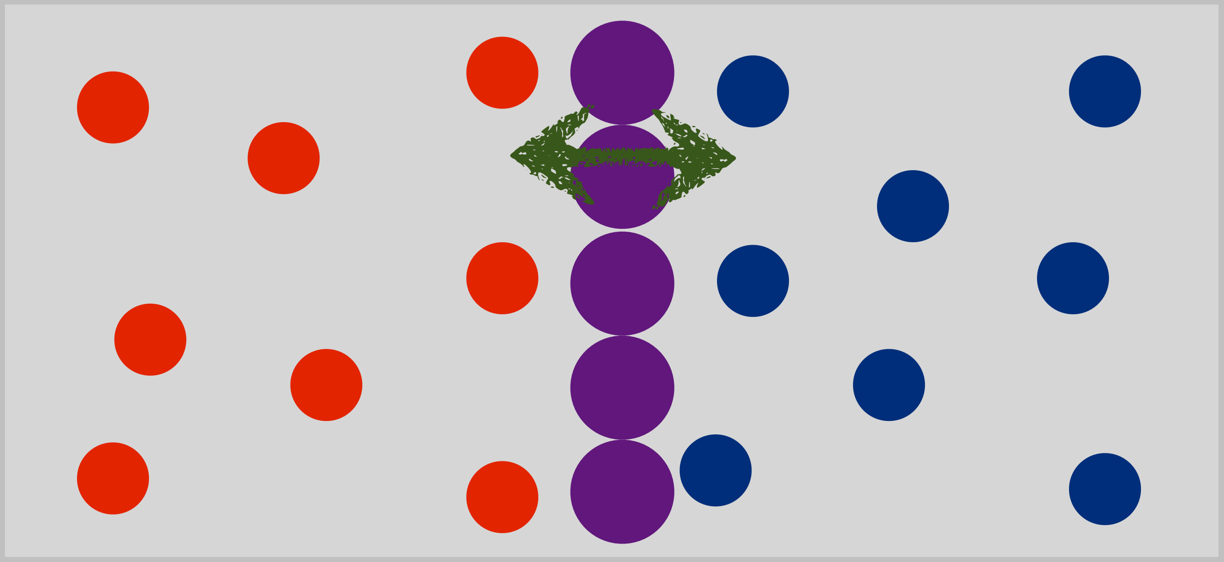
Experiment (2)



NVE_1 NVE_2 $E_1 > E_2$

Now the wall are heavy molecules

Experiment (2)



NVE$_1$ NVE$_2$ $E_1 > E_2$

Now the wall are heavy molecules

What will the moveable wall do?

Newton + atoms

Newton + atoms

- We have a natural formulation of the first law

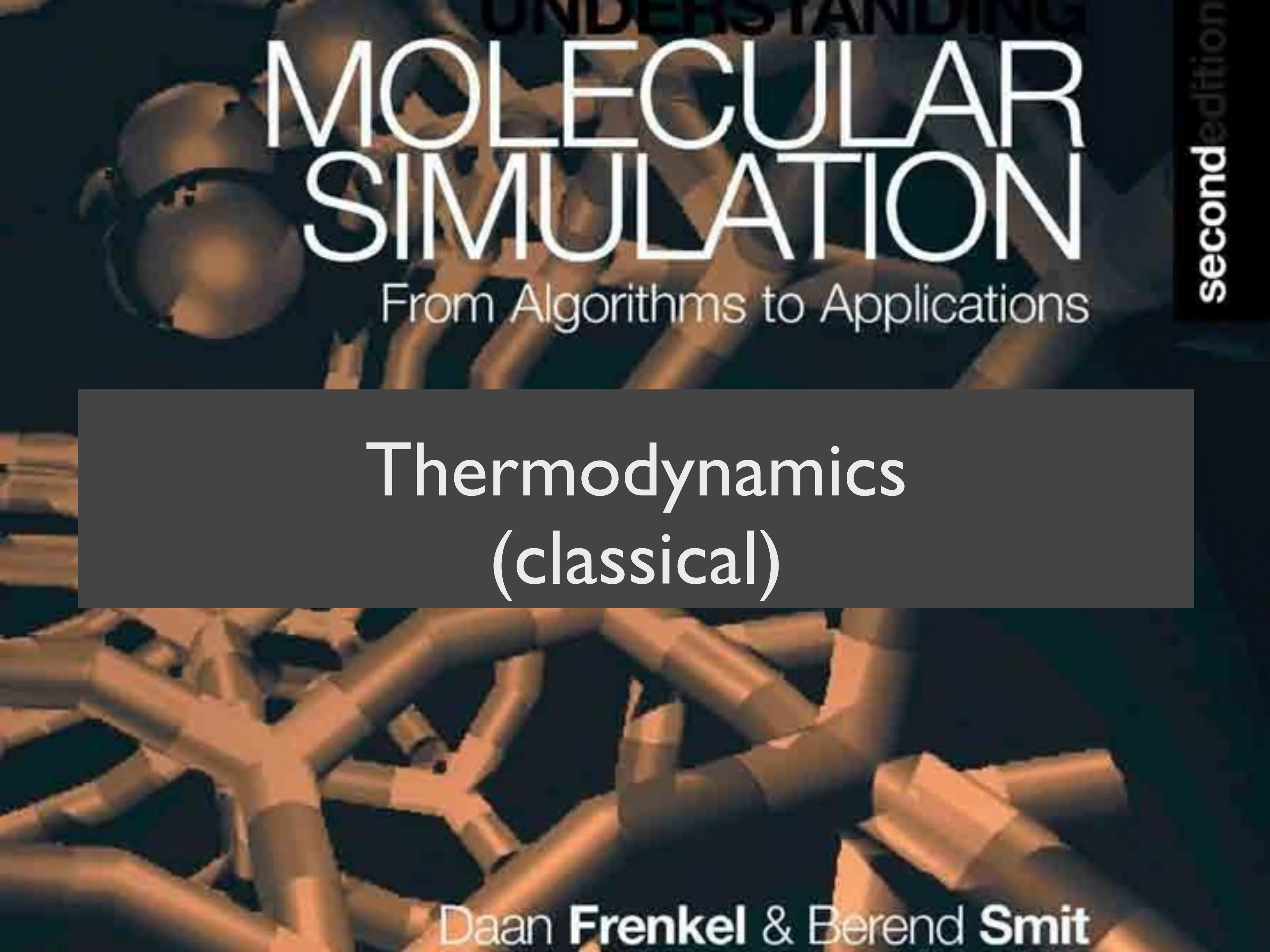
Newton + atoms

- We have a natural formulation of the first law
- We have discovered pressure

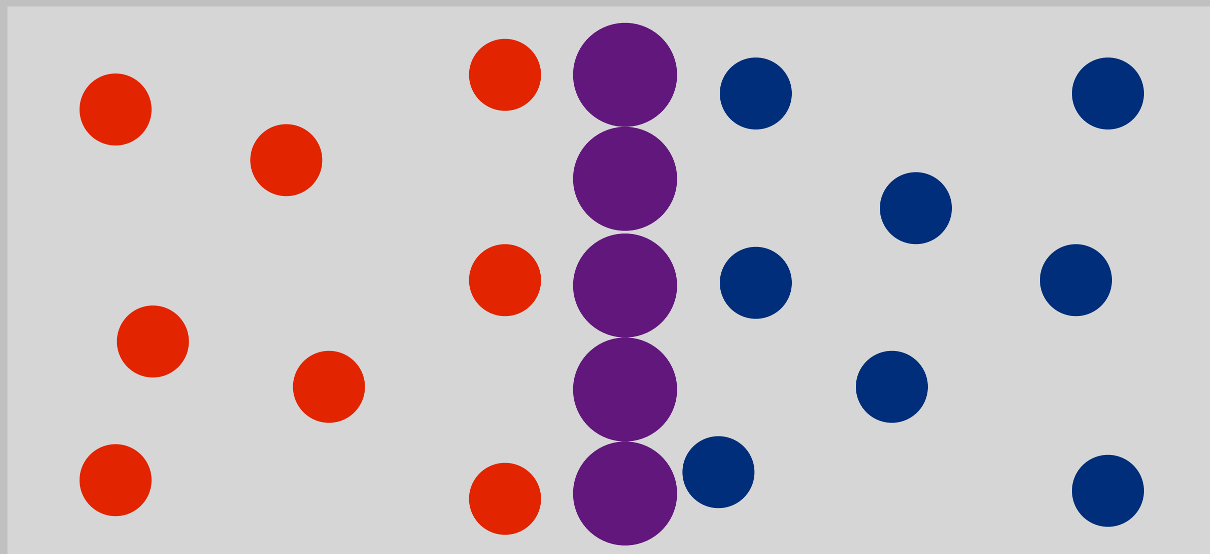
Newton + atoms

- 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

Thermodynamics (classical)

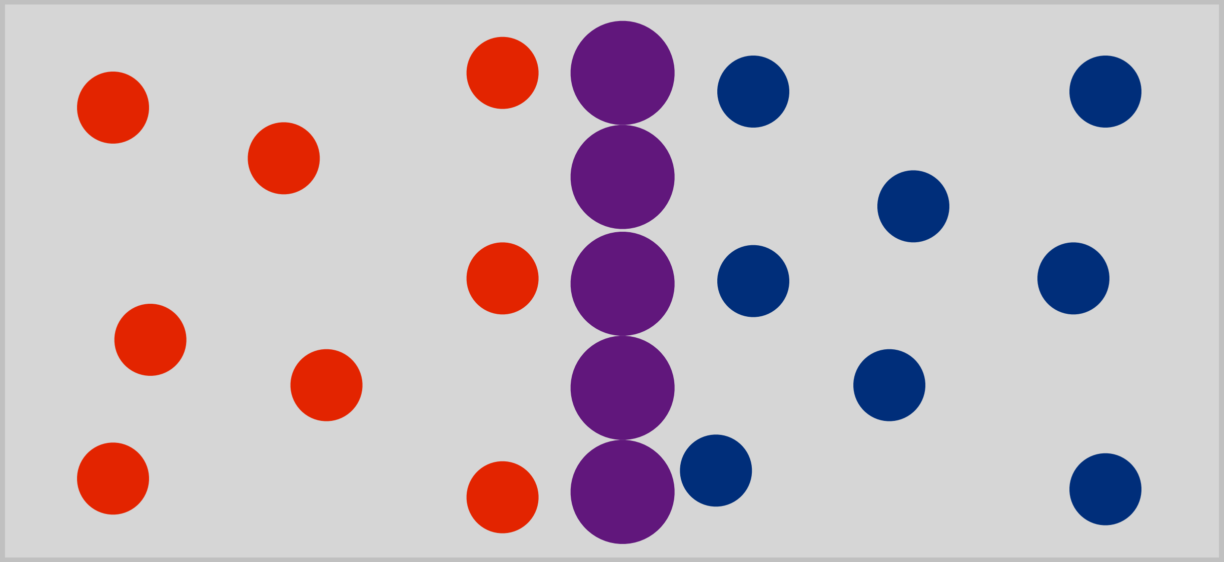


Experiment



NVE_1 NVE_2 $E_1 > E_2$

Experiment



NVE_1 NVE_2 $E_1 > E_2$

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

Classical Thermodynamics

Classical Thermodynamics

- 1st law of Thermodynamics
  - Energy is conserved

Classical Thermodynamics

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

Classical Thermodynamics

Classical Thermodynamics

Carnot: Entropy difference between two states:

Classical Thermodynamics

Carnot: Entropy difference between two states:

$$\Delta S = S_{B} - S_{A} = \int_{A}^{B} \frac{dQ_{rev}}{T}$$

Classical Thermodynamics

Carnot: Entropy difference between two states:

$$\Delta S = S_{\mathrm{B}} - S_{\mathrm{A}} = \int_{\mathrm{A}}^{\mathrm{B}} \frac{\mathrm{d}Q_{\mathrm{rev}}}{\mathrm{T}}$$

Using the first law we have:

Classical Thermodynamics

Carnot: Entropy difference between two states:

$$\Delta S = S_{\mathrm{B}} - S_{\mathrm{A}} = \int_{\mathrm{A}}^{\mathrm{B}} \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}$$

Using the first law we have:

Classical Thermodynamics

Carnot: Entropy difference between two states:

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

Using the first law we have:

$$\Delta U = Q + W$$

Classical Thermodynamics

Carnot: Entropy difference between two states:

$$\Delta S = S_{\mathrm{B}} - S_{\mathrm{A}} = \int_{\mathrm{A}}^{\mathrm{B}} \frac{\mathrm{dQ_{rev}}}{\mathrm{T}}$$

Using the first law we have:

$$\Delta \mathrm{U} = \mathrm{Q} + W$$

If we carry out a reversible process, we have for any point along the path

Classical Thermodynamics

Carnot: Entropy difference between two states:

$$\Delta S = S_{\mathrm{B}} - S_{\mathrm{A}} = \int_{\mathrm{A}}^{\mathrm{B}} \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}$$

Using the first law we have:

$$\Delta U = Q + W$$

If we carry out a reversible process, we have for any point along the path

$$dU = TdS + dW$$

Classical Thermodynamics

Carnot: Entropy difference between two states:

$$\Delta S = S_{\mathrm{B}} - S_{\mathrm{A}} = \int_{\mathrm{A}}^{\mathrm{B}} \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}$$

Using the first law we have:

$$\Delta U = Q + W$$

If we carry out a reversible process, we have for any point along the path

$$dU = TdS + dW$$

If we have work by a expansion of a fluid

Classical Thermodynamics

Carnot: Entropy difference between two states:

$$\Delta S = S_{\mathrm{B}} - S_{\mathrm{A}} = \int_{\mathrm{A}}^{\mathrm{B}} \frac{\mathrm{dQ}_{\mathrm{rev}}}{\mathrm{T}}$$

Using the first law we have:

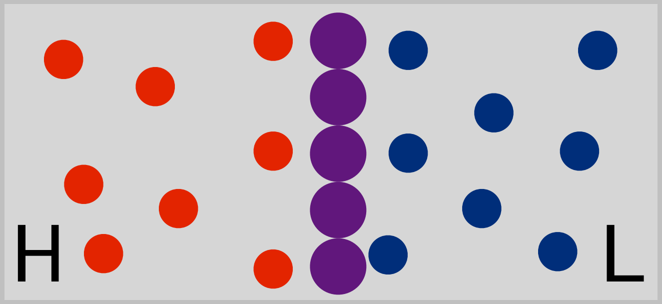
$$\Delta \mathrm{U} = \mathrm{Q} + W$$

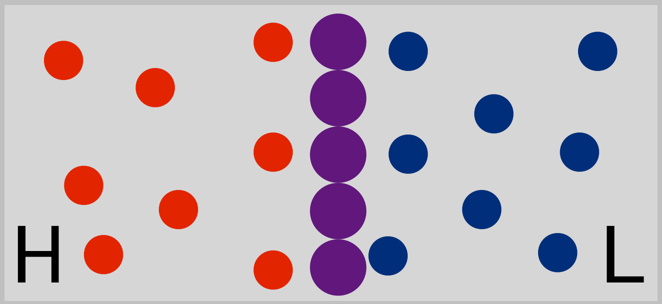
If we carry out a reversible process, we have for any point along the path

$$dU = TdS + dW$$

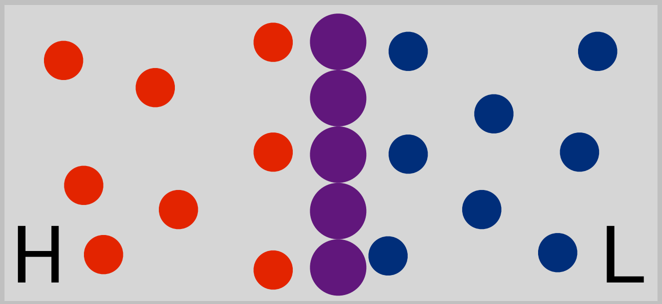
If we have work by a expansion of a fluid

$$\boxed{dU = TdS - pdV}$$


H
L

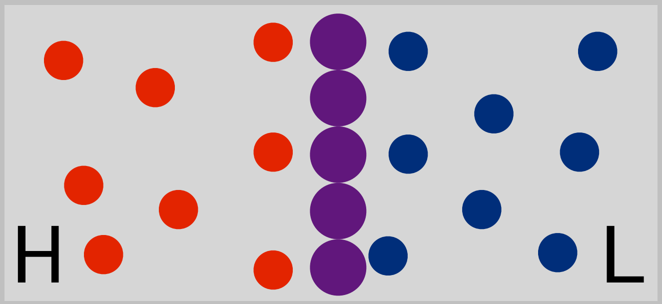


Let us look at the very initial stage



Let us look at the very initial stage

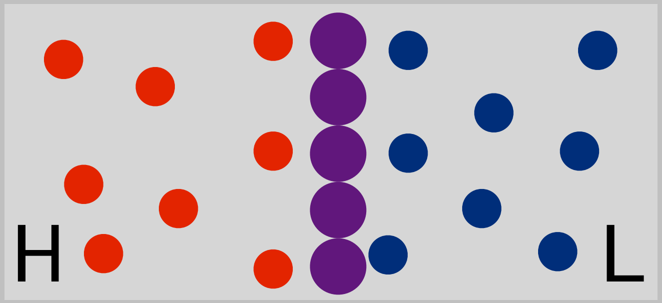
dq is so small that the temperatures of the two systems do not change



Let us look at the very initial stage

dq is so small that the temperatures of the two systems do not change

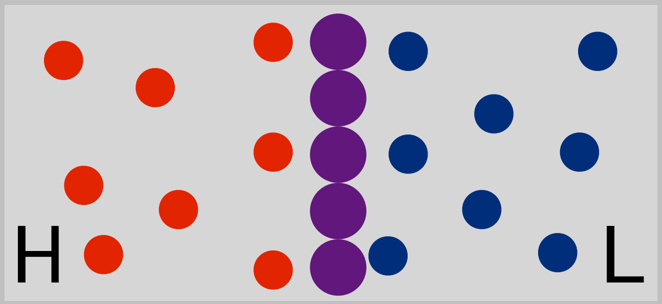
For system H



Let us look at the <u>very initial</u> stage

dq is so small that the temperatures of the two systems do not change

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

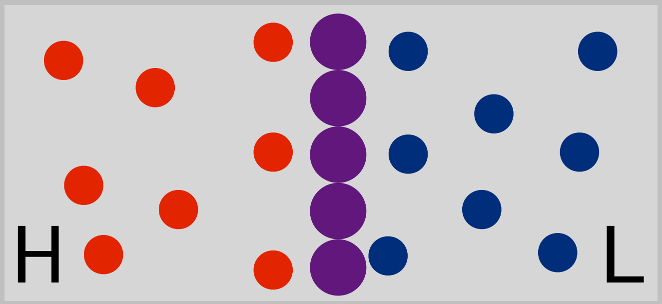


Let us look at the <u>very initial</u> stage

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

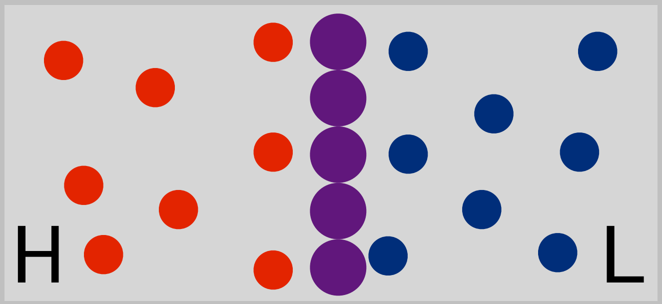


Let us look at the very initial stage

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
$$dS_L = \frac{dq}{T_L}$$



Let us look at the very initial stage

dq is so small that the temperatures of the two systems do not change

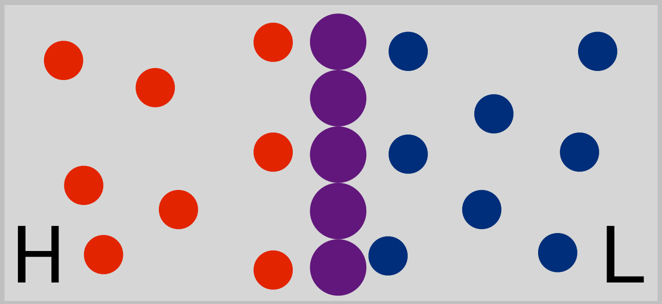
For system H

$$\mathrm{d}S_{\mathrm{H}} = -\frac{\mathrm{d}q}{T_{\mathrm{H}}}$$

For system L

$$\mathrm{d}S_{\mathrm{L}} = \frac{\mathrm{d}q}{T_{\mathrm{L}}}$$

Hence, for the total system



Let us look at the <u>very initial</u> stage

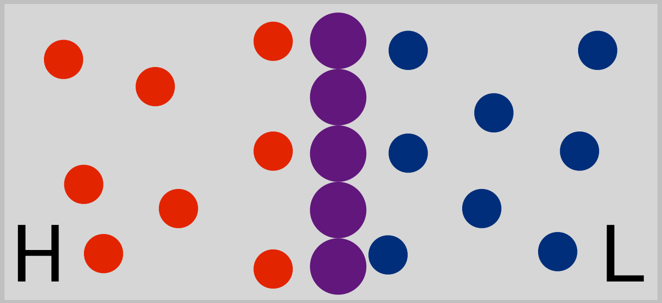
dq is so small that the temperatures of the two systems do not change

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

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

Hence, for the total system

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



Let us look at the very initial stage

dq is so small that the temperatures of the two systems do not change

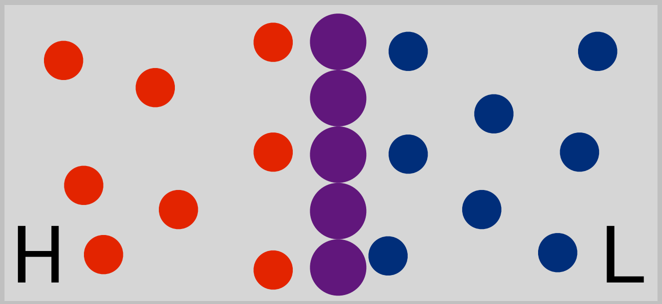
For system H $$dS_H = -\frac{dq}{T_H}$$

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

Hence, for the total system

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

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



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 $$dS_H = -\frac{dq}{T_H}$$

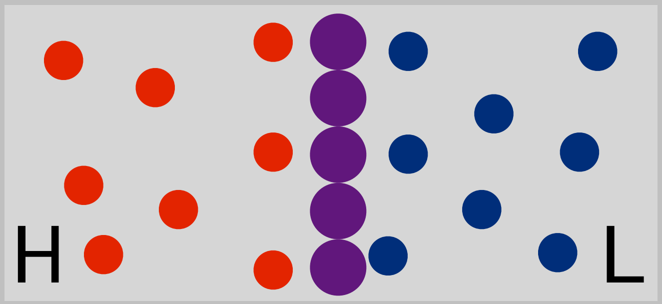
For system L $$dS_L = \frac{dq}{T_L}$$

Hence, for the total system

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

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

This gives for the entropy change: $dS > 0$



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

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

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

This gives for the entropy change: $dS > 0$

Hence, the entropy increases until the two temperatures are equal

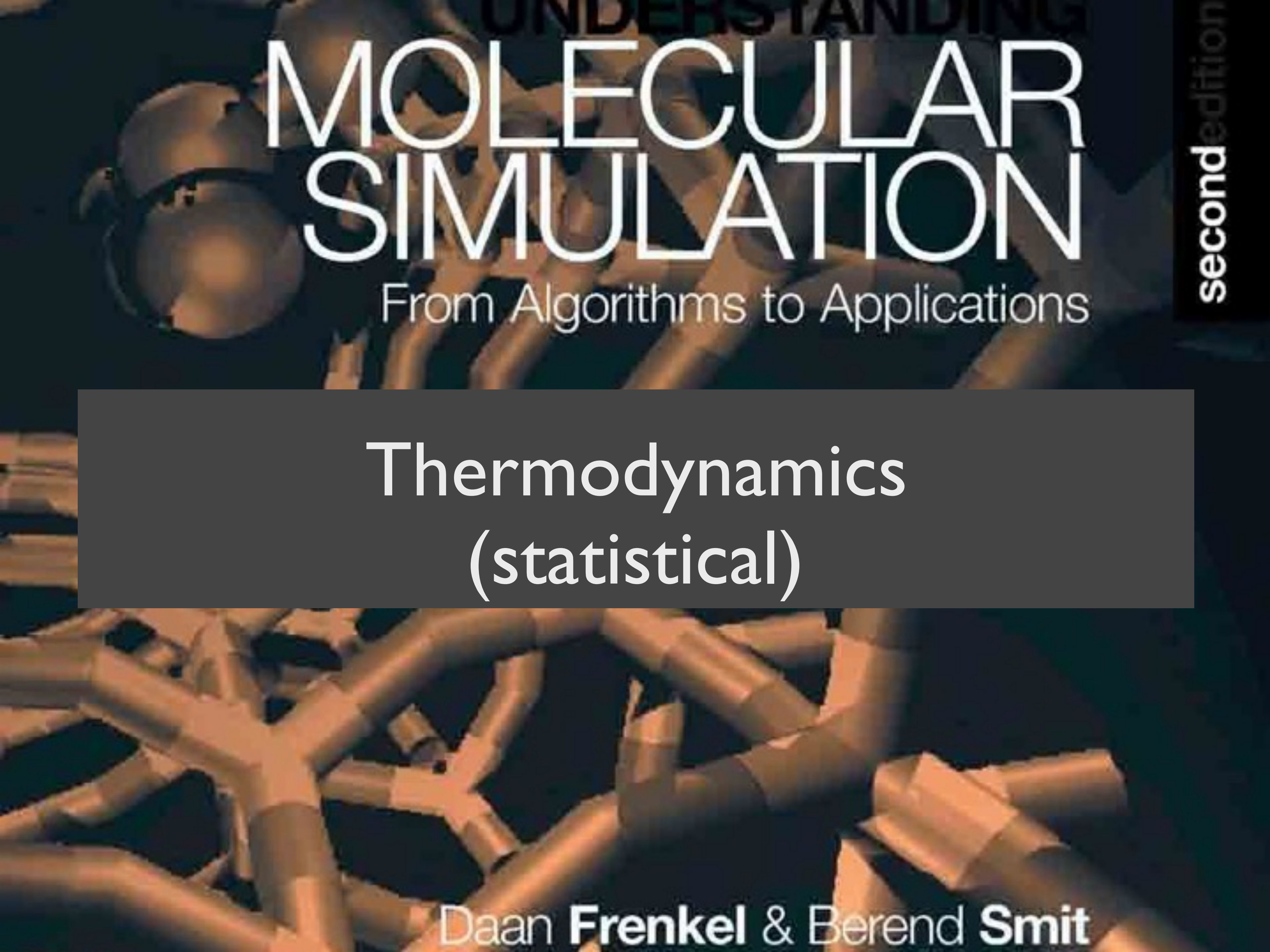
Question

Question

- Thermodynamics has a sense of time, but not Newton's dynamics
  - Look at a water atoms in reverse
  - Look at a movie in reverse

Question

- Thermodynamics has a sense of time, but not Newton's dynamics
  - Look at a water atoms in reverse
  - Look at a movie in reverse
- When do molecules know about the arrow of time?



Thermodynamics (statistical)

Statistical Thermodynamics

Statistical Thermodynamics

Basic assumption

Statistical Thermodynamics

Basic assumption

> For an isolated system any microscopic configuration is equally likely

Statistical Thermodynamics

Basic assumption

For an isolated system any microscopic configuration is equally likely

Consequence

Statistical Thermodynamics

Basic assumption

For an isolated system any microscopic configuration is equally likely

Consequence

All of statistical thermodynamics and equilibrium thermodynamics

Statistical The… …mics

Basic assumpti…

For c… …ic
co…

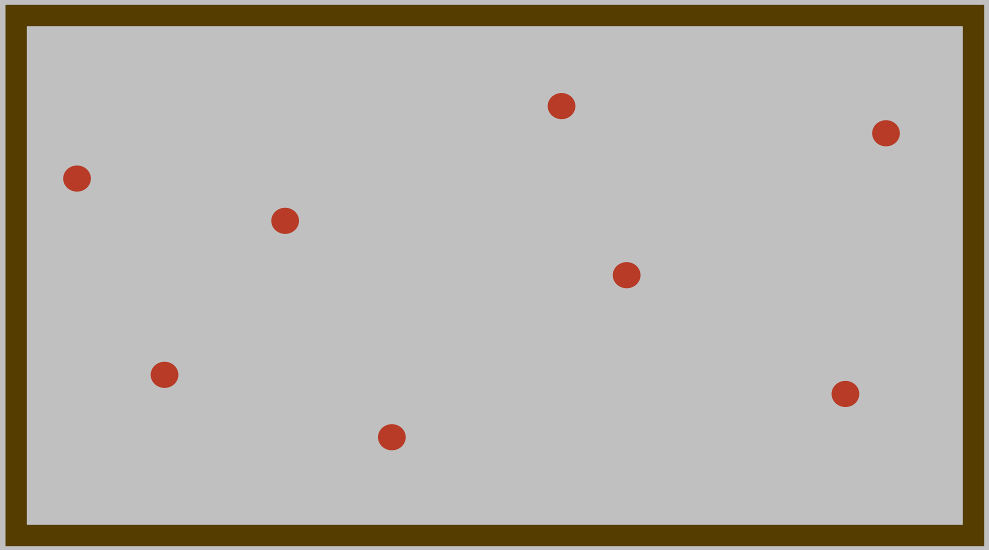
Co…

All … …modynamics and
equili… …dynamics

… but classical
thermodynamics
is based on laws

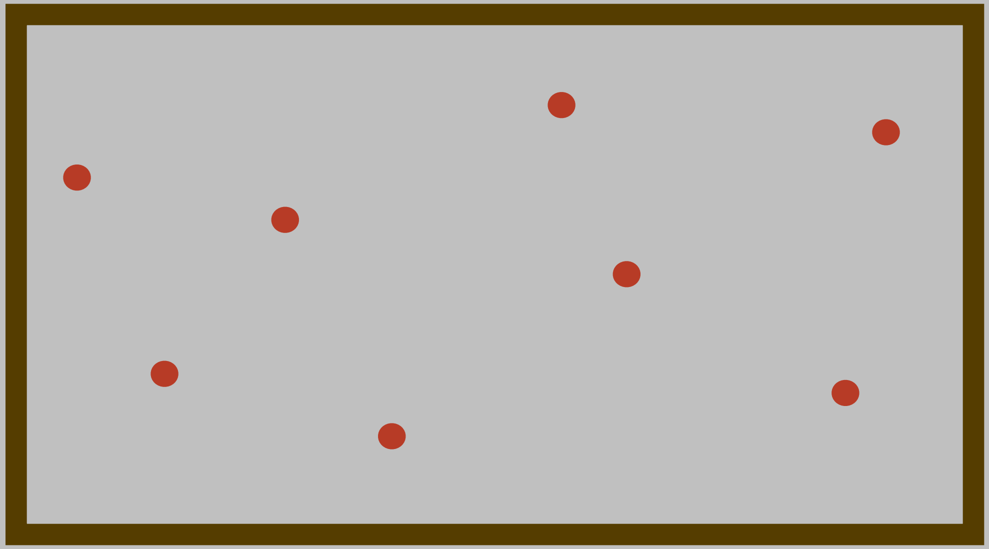
Ideal gas

Let us again make an ideal gas



Ideal gas

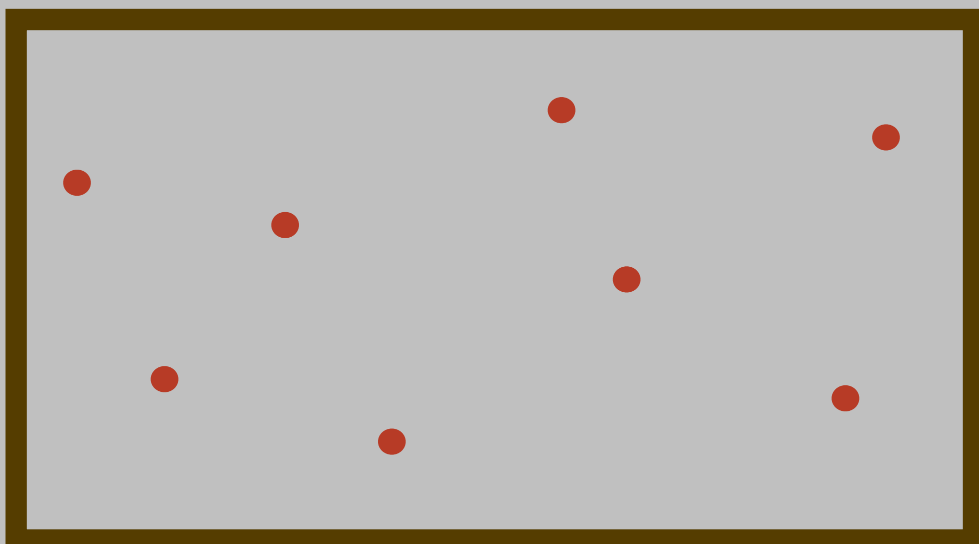
Let us again make an ideal gas



We select:

Ideal gas

Let us again make an ideal gas

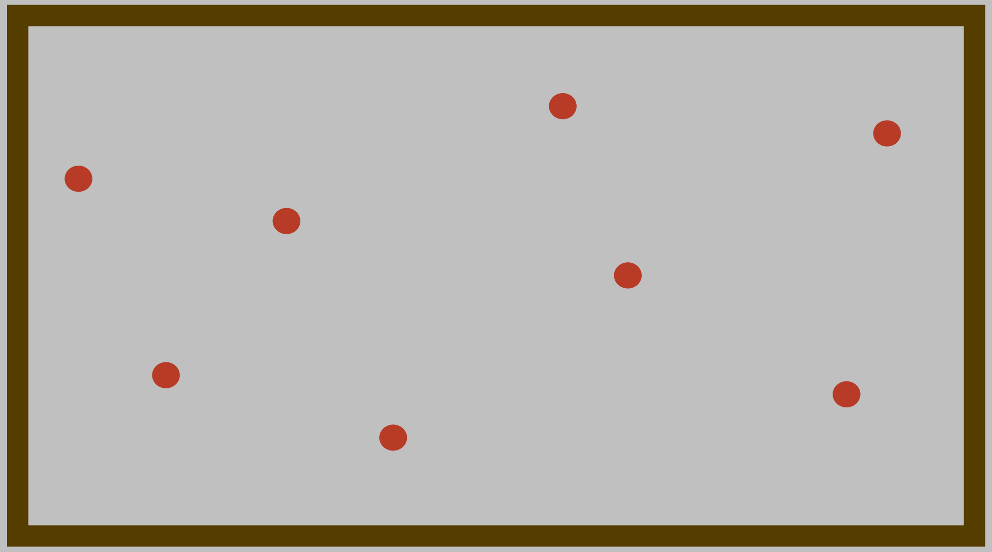


We select:

(1) N particles,

Ideal gas

Let us again make an ideal gas



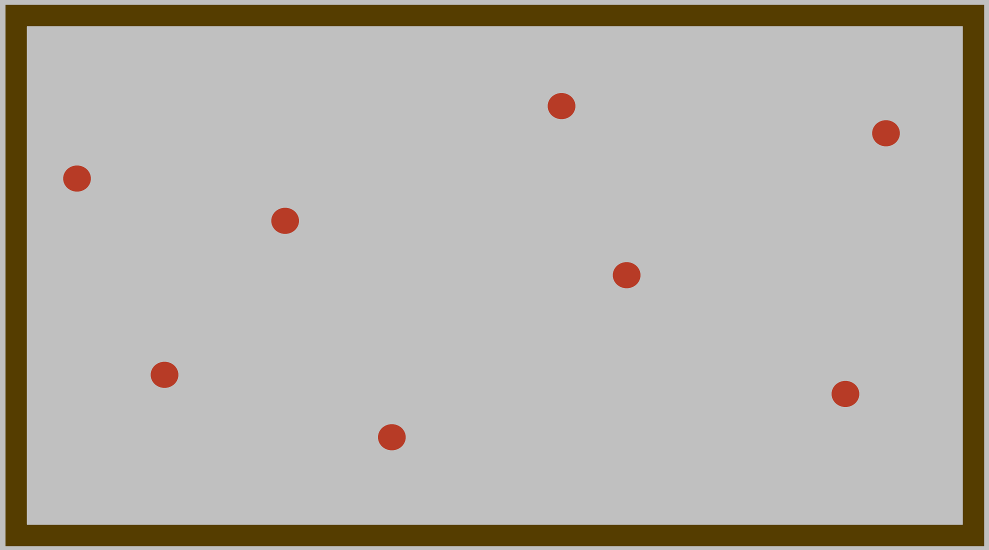
We select:

(1) N particles,

(2) Volume V,

Ideal gas

Let us again make an ideal gas

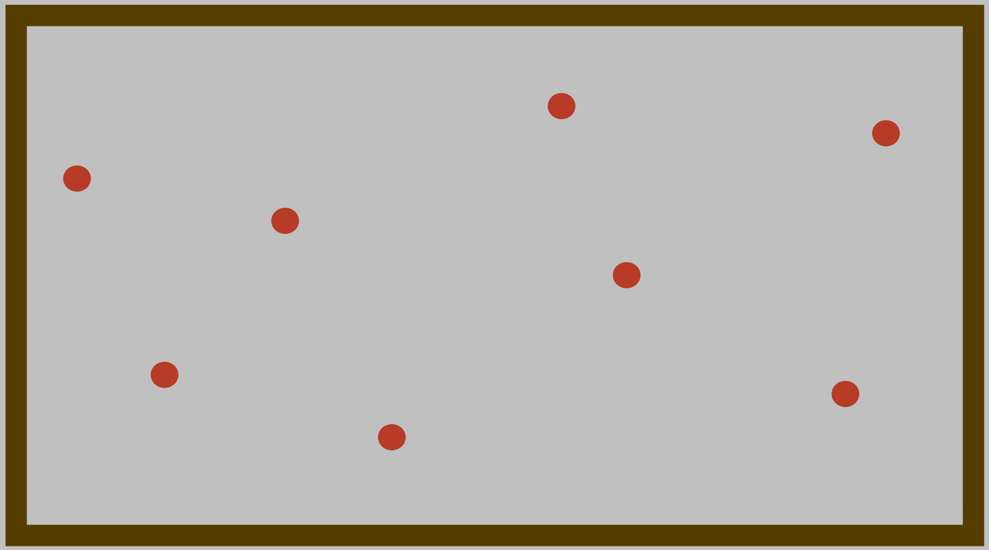


We select:

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

Ideal gas

Let us again make an ideal gas

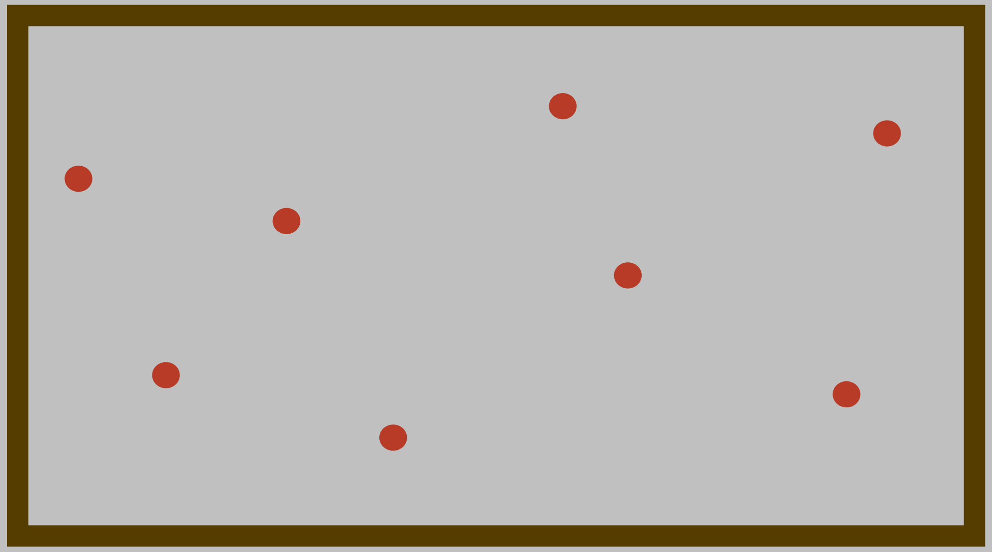


We select:

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

Ideal gas

Let us again make an ideal gas



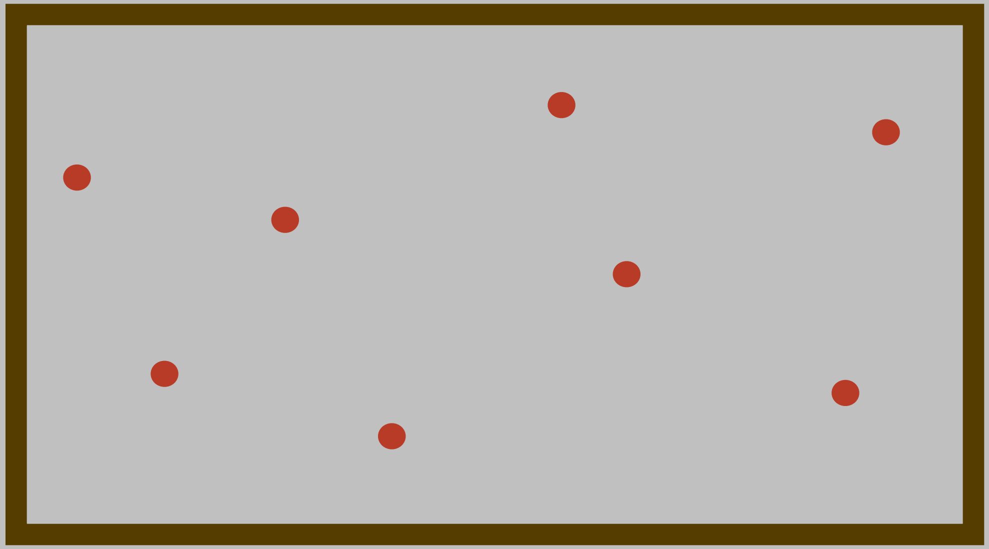
We select:

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

This fixes; V/n, U/n

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 any microscopic configuration is equally likely

What is the probability to find this configuration?

What is the probability to find this configuration?

The system has the same kinetic energy!!

What is the probability to find this configuration?

The system has the same kinetic energy!!

Our basic assumption must be seriously wrong!

What is the probability to find this configuration?

The system has the same kinetic energy!!

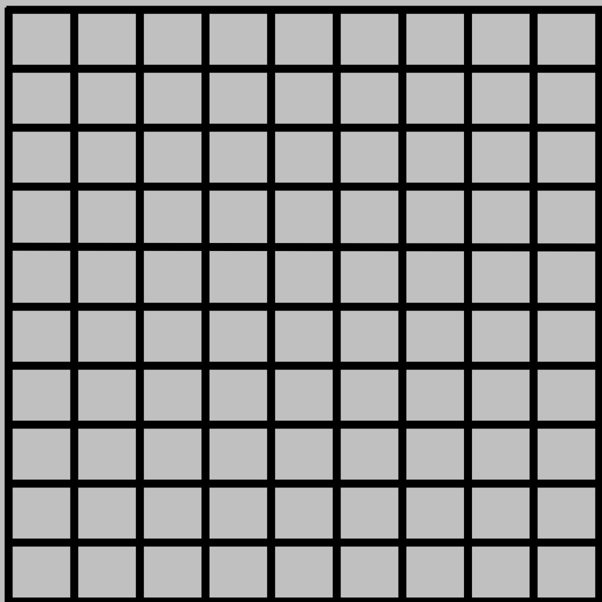
Our basic assumption must be seriously wrong!

... but are we doing the statistics correctly?

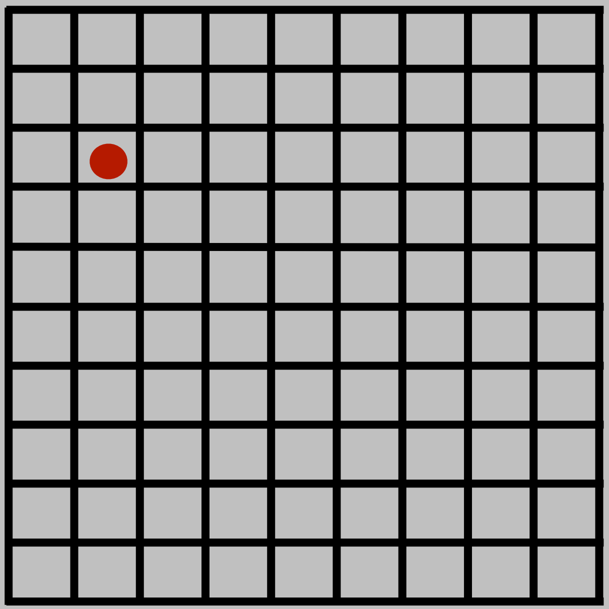
Question

- Is it safe to be in this room?

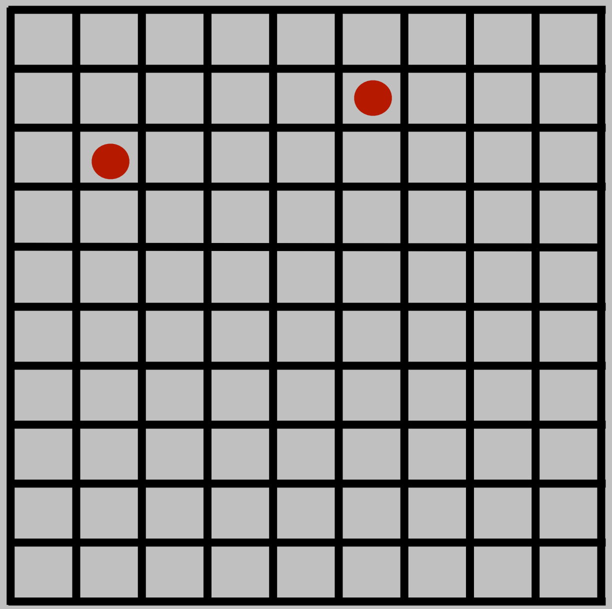
... lets look at our statistics correctly



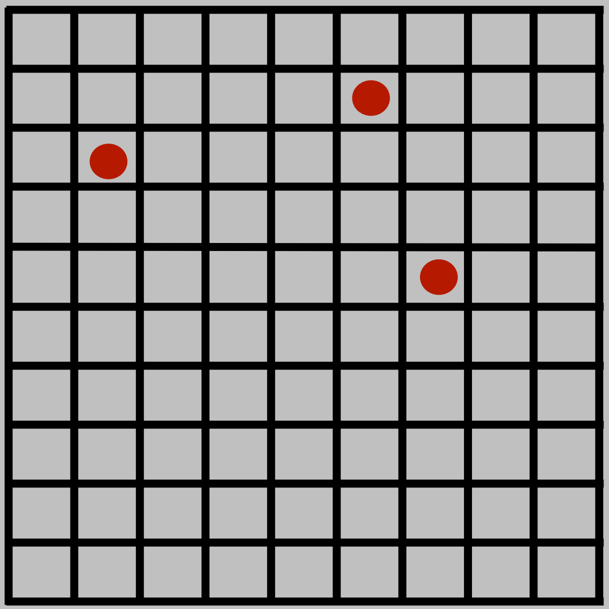
… lets look at our statistics correctly



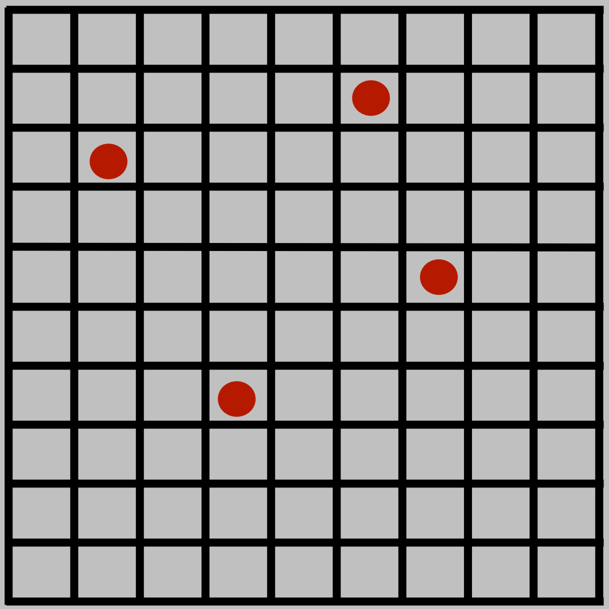
... lets look at our statistics correctly



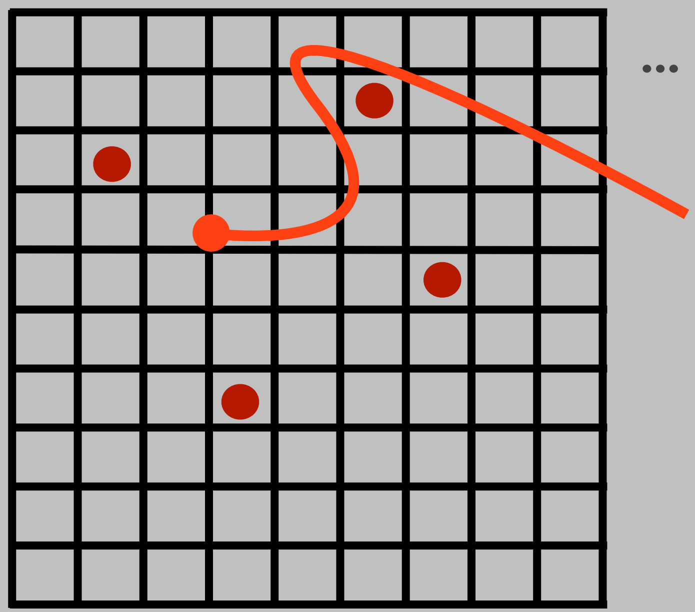
... lets look at our statistics correctly



… lets look at our statistics correctly

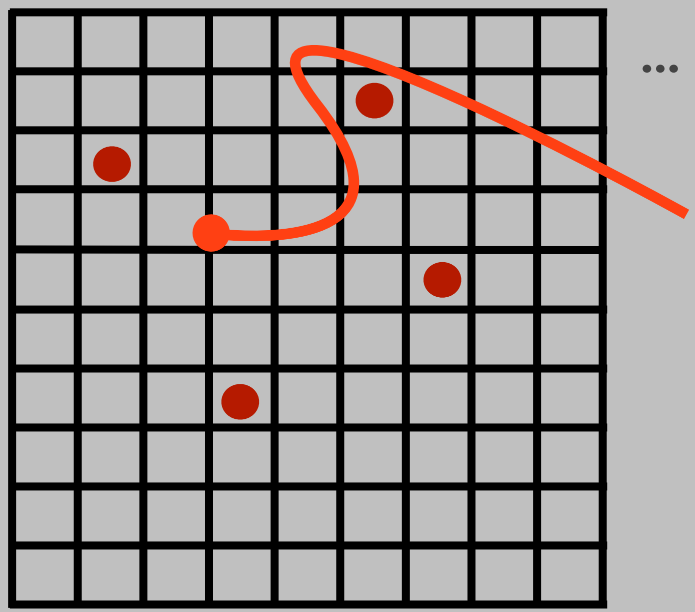


... lets look at our statistics correctly



… lets look at our statistics correctly

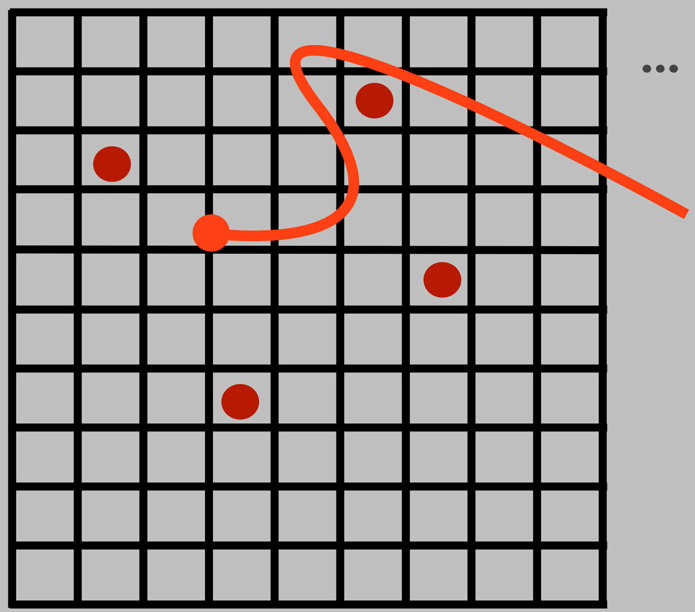
What is the probability to find this configuration?



... lets look at our statistics correctly

What is the probability to find this configuration?

Basic assumption:

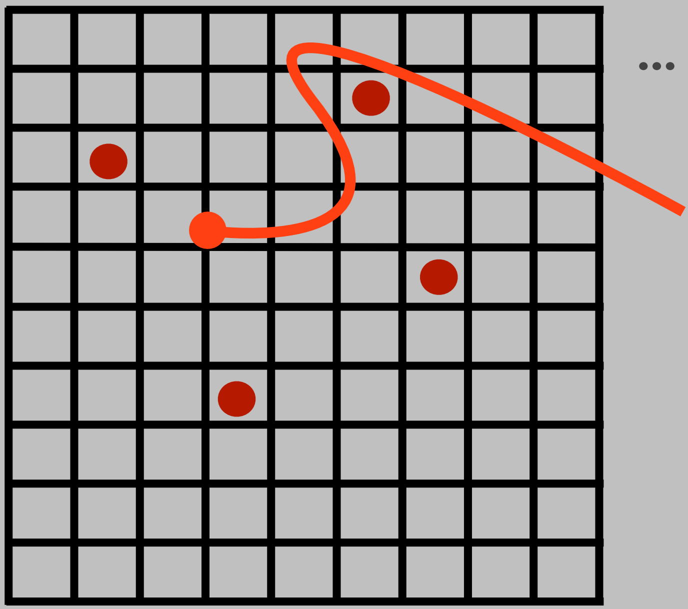


… lets look at our statistics correctly

What is the probability to find this configuration?

Basic assumption:

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



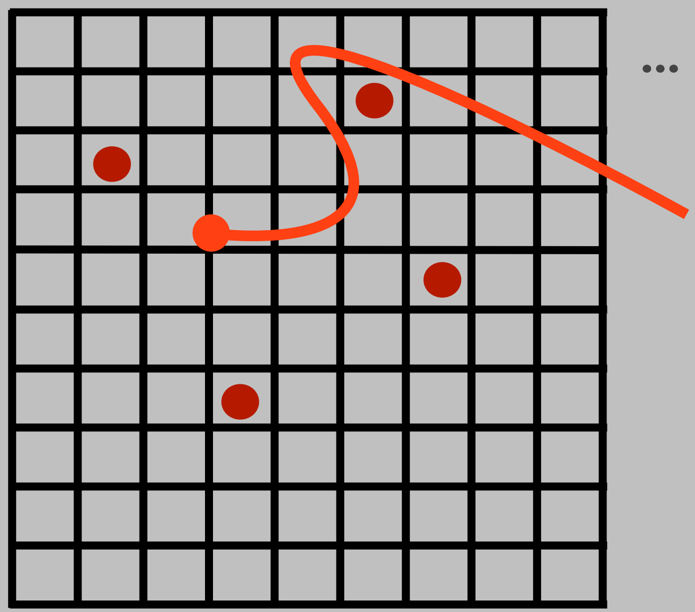
... lets look at our statistics correctly

What is the probability to find this configuration?

Basic assumption:

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

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



... lets look at our statistics correctly

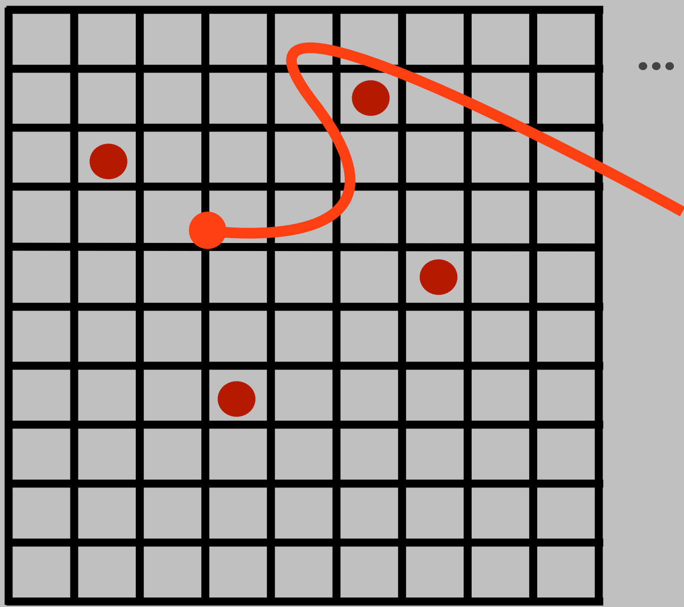
What is the probability to find this configuration?

Basic assumption:

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

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

Total number of configurations:



... lets look at our statistics correctly

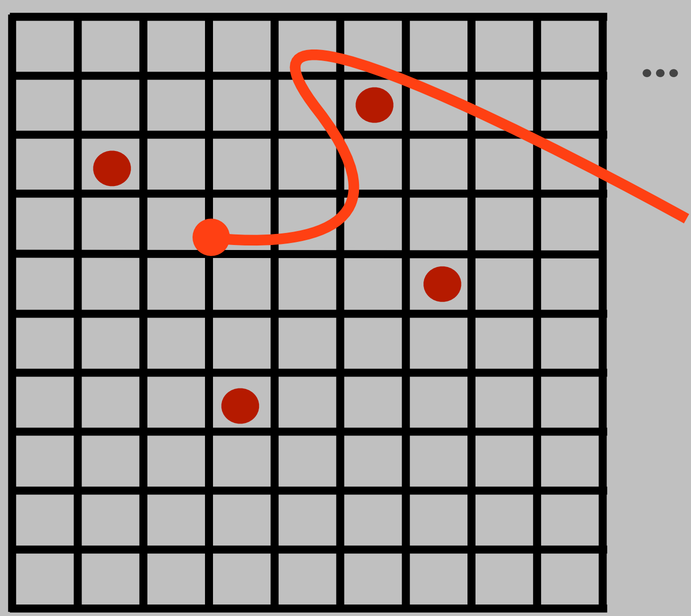
What is the probability to find this configuration?

Basic assumption:

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

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

Total number of configurations: M^N



... lets look at our statistics correctly

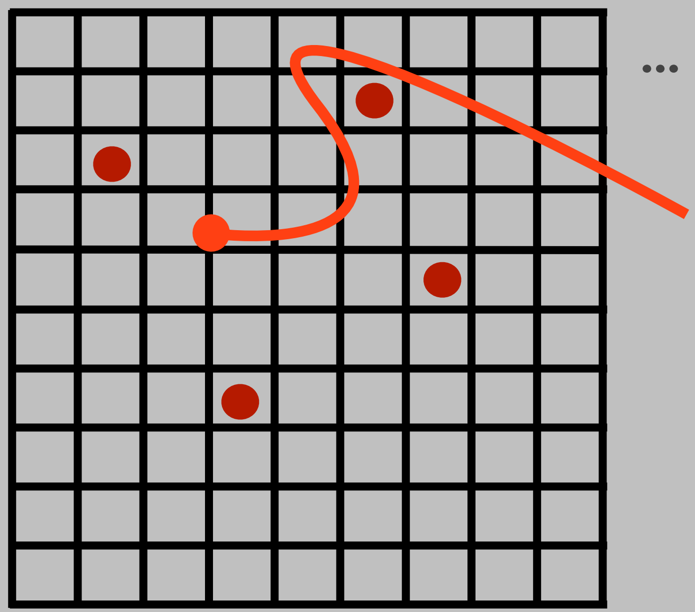
What is the probability to find this configuration?

Basic assumption:

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

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

Total number of configurations: M^{N} with $\mathrm{M} = \frac{\mathrm{V}}{\mathrm{d}\mathbf{r}}$



... lets look at our statistics correctly

What is the probability to find this configuration?

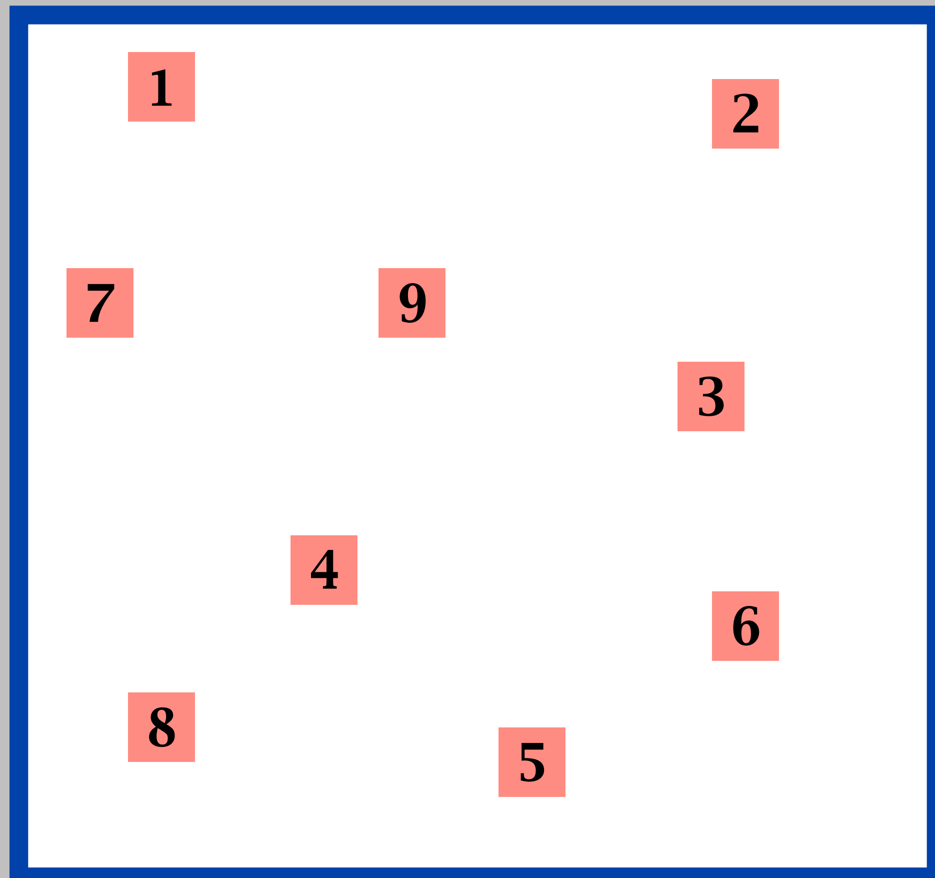
Basic assumption:

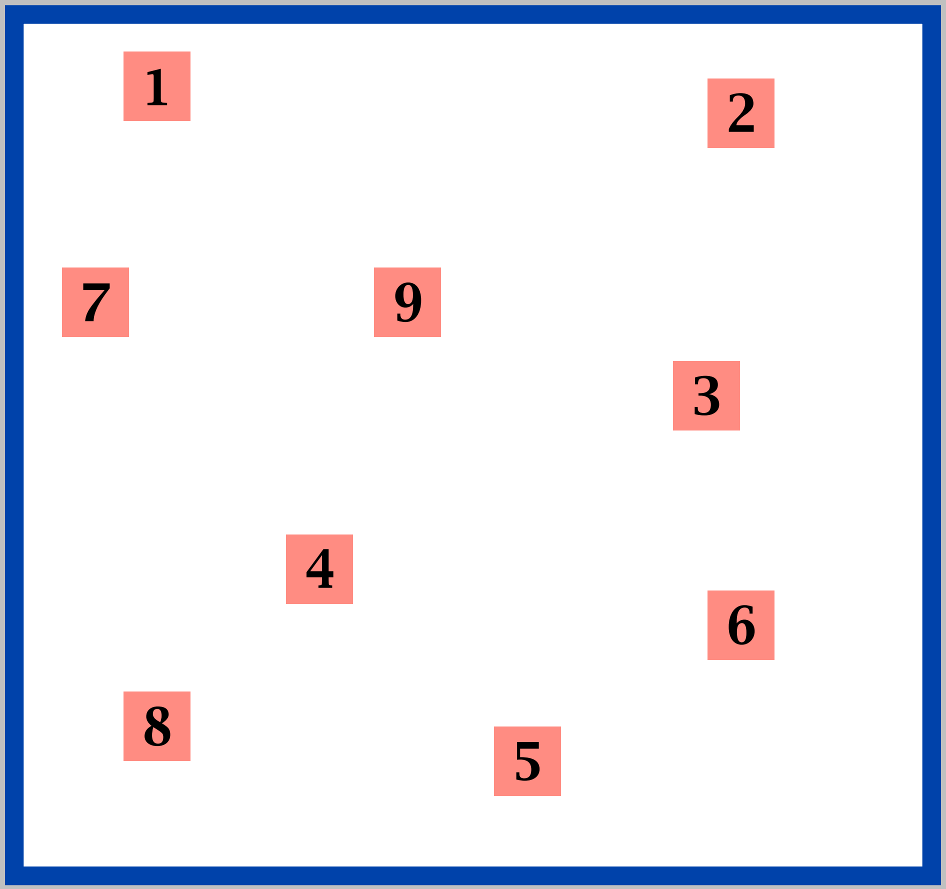
$$\mathcal{P} = \frac{1}{\text{total \# of configurations}}$$

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

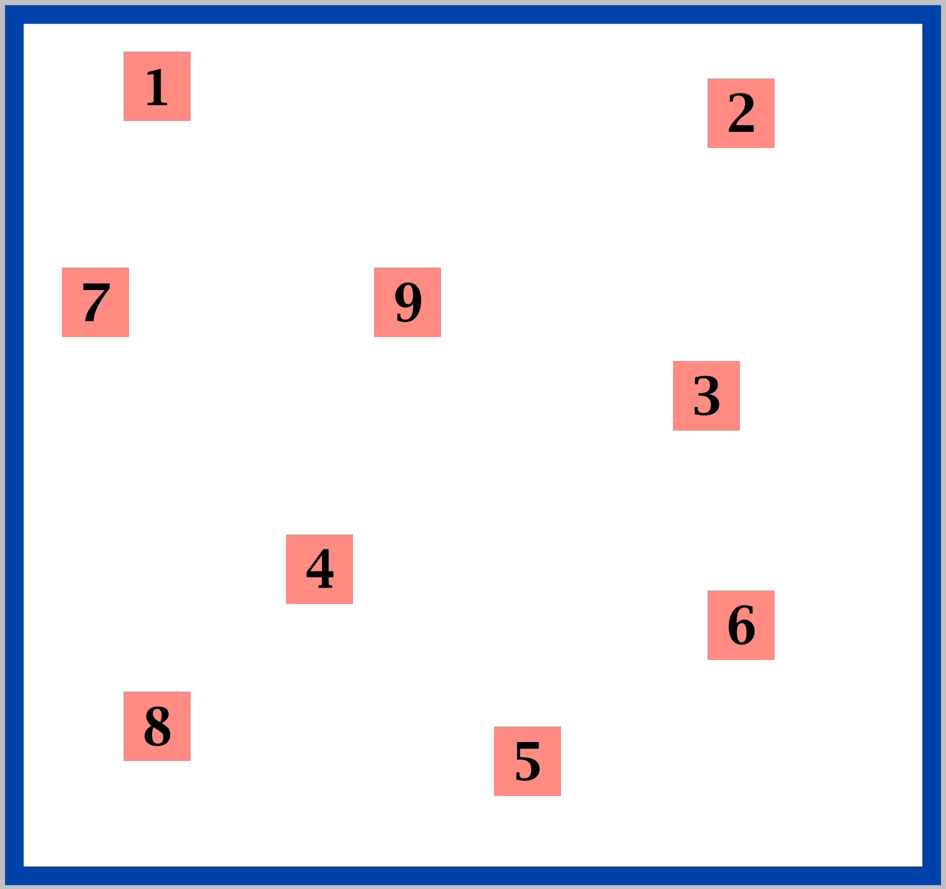
Total number of configurations: M^N with $M = \frac{V}{\mathrm{d}\mathbf{r}}$

the larger the volume of the gas the more configurations


1
2
7
9
3
4
6
8
5

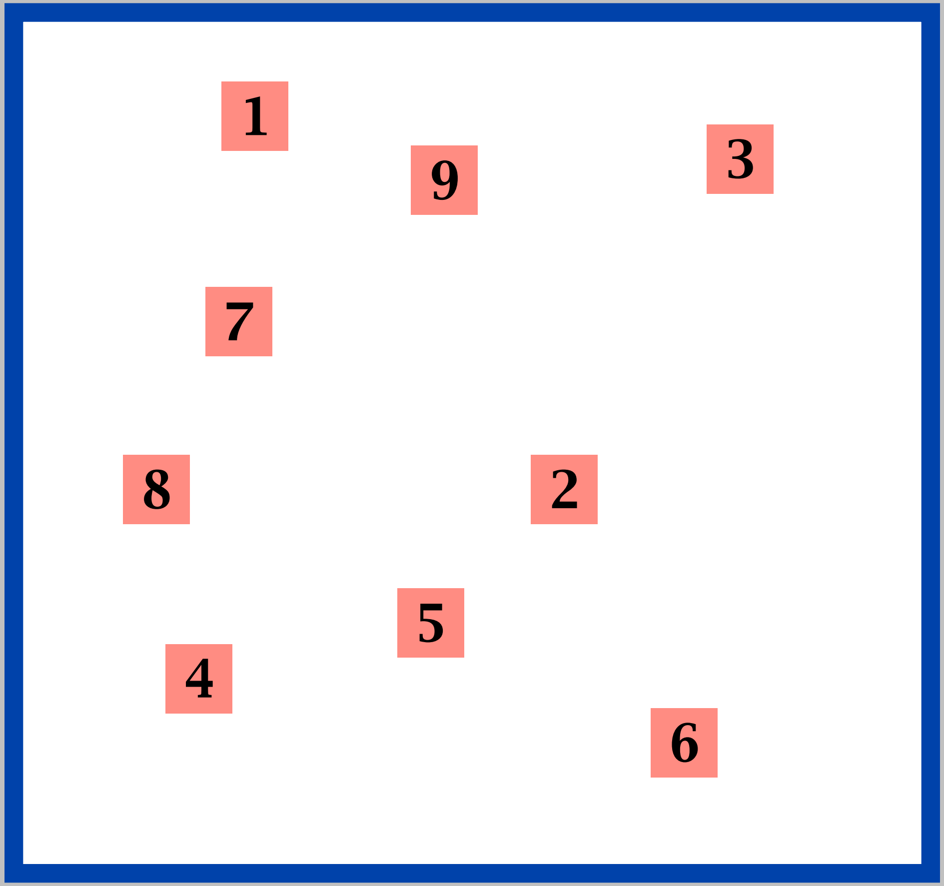


What is the probability to find the 9 molecules exactly at these 9 positions?

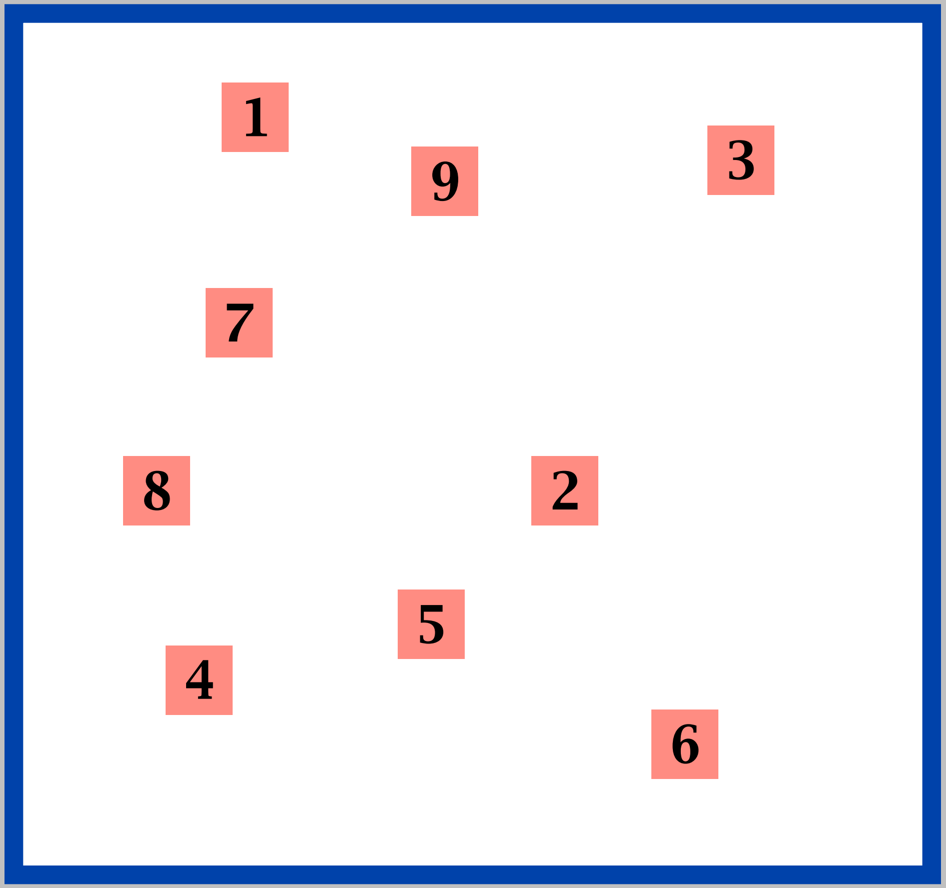


What is the probability to find the 9 molecules exactly at these 9 positions?

$$\left(\frac{\Delta V}{V}\right)^N$$

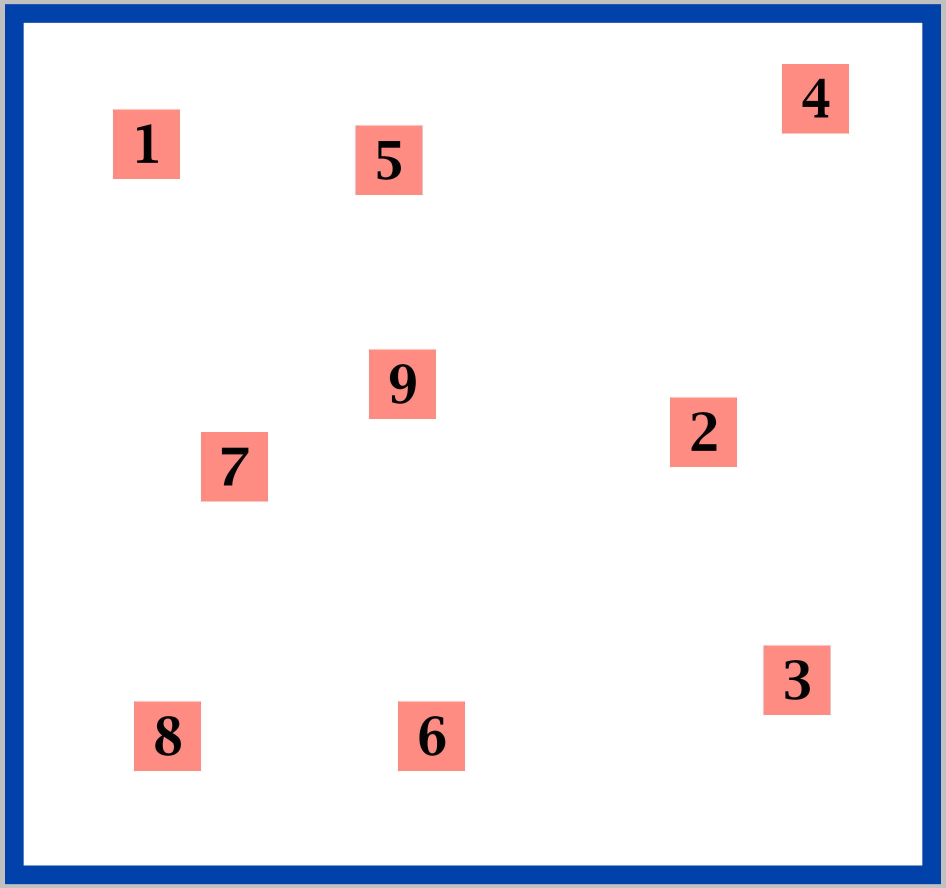


What is the probability to find the 9 molecules exactly at these 9 positions?

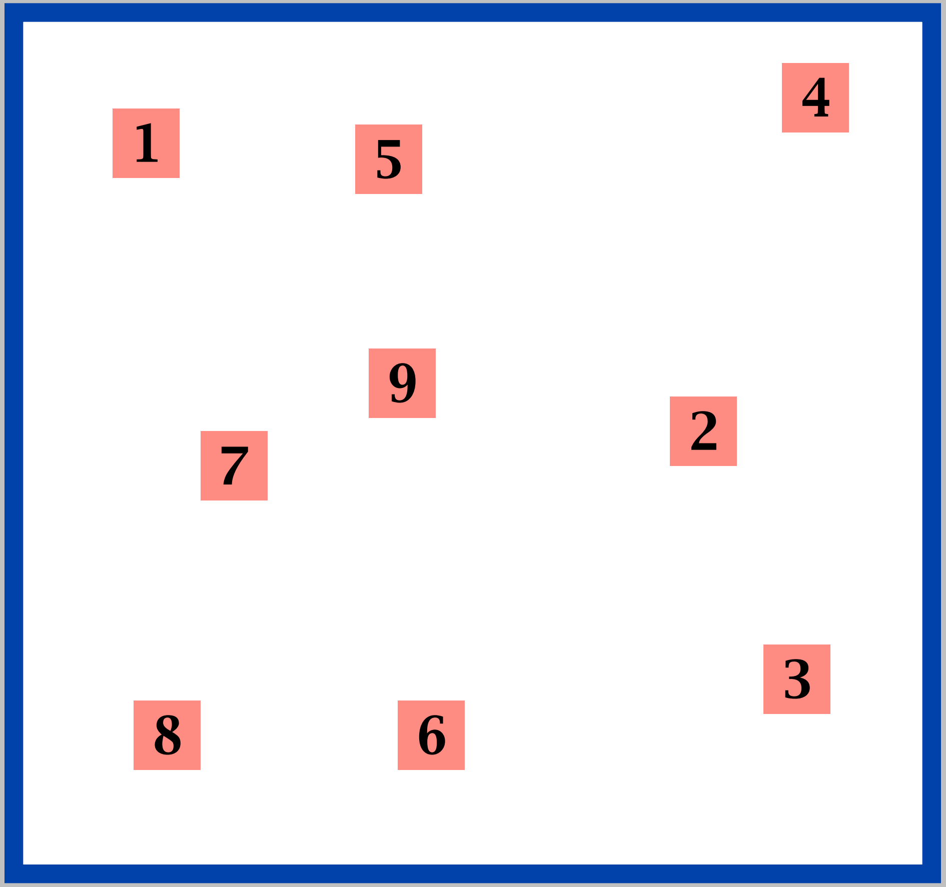


What is the probability to find the 9 molecules exactly at these 9 positions?

$$\left(\frac{\Delta V}{V}\right)^N$$

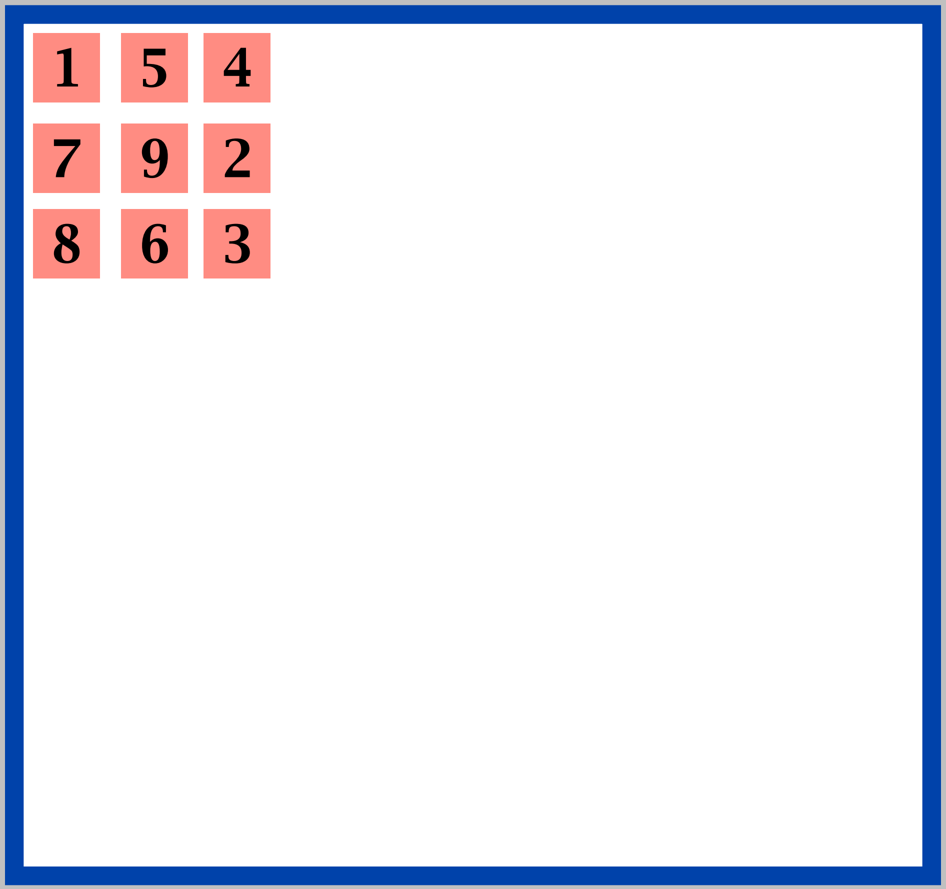


What is the probability to find the 9 molecules exactly at these 9 positions?

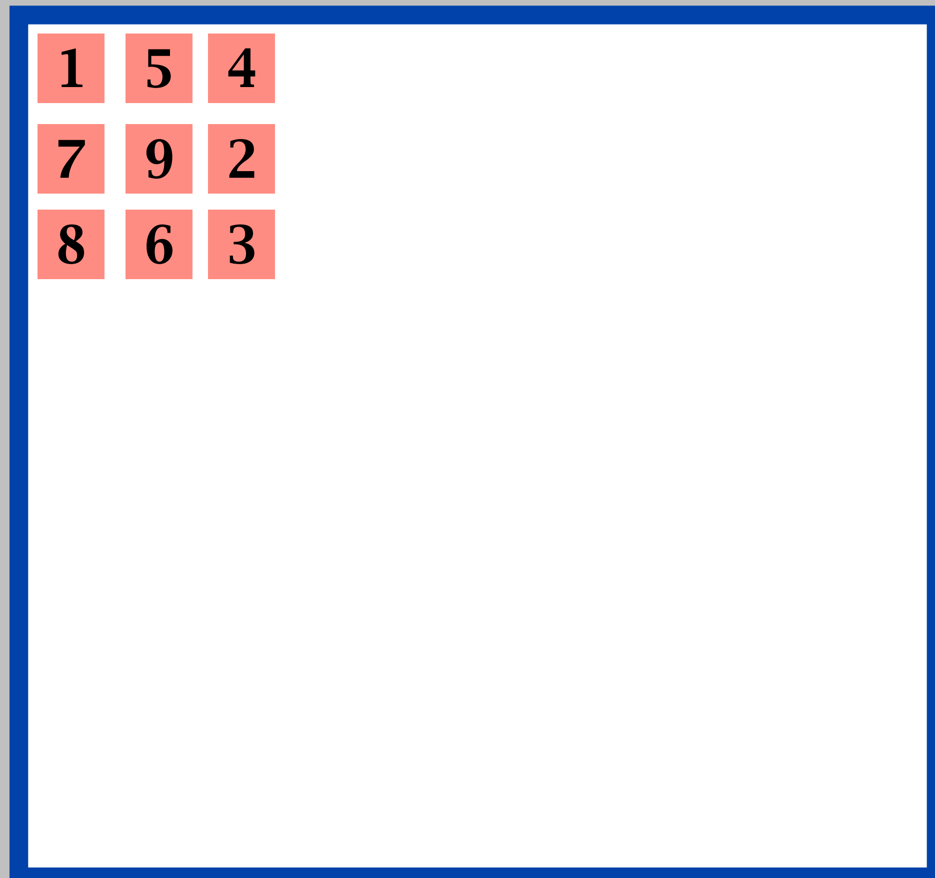


What is the probability to find the 9 molecules exactly at these 9 positions?

$$\left(\frac{\Delta V}{V}\right)^N$$

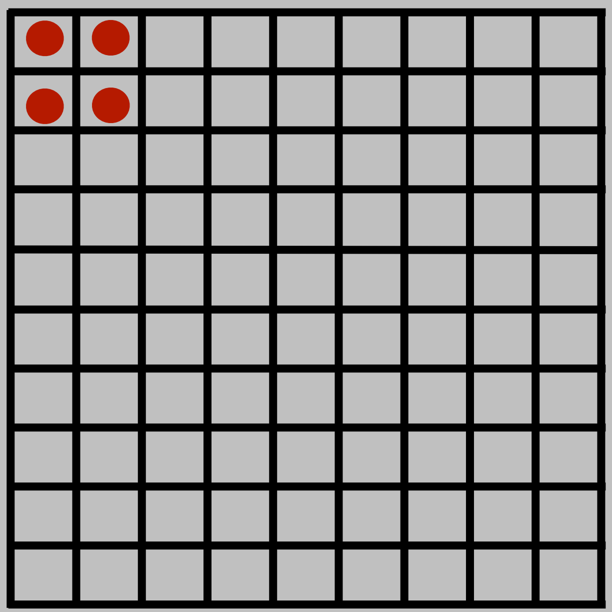


What is the probability to find the 9 molecules exactly at these 9 positions?

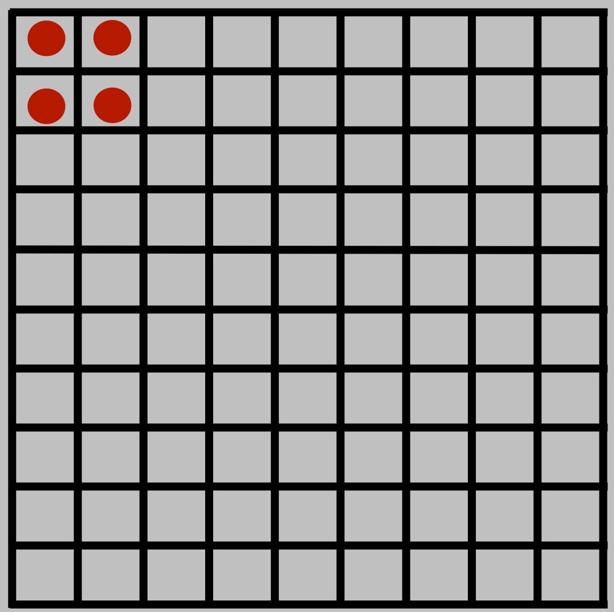


What is the probability to find the 9 molecules exactly at these 9 positions?

$$\left(\frac{\Delta V}{V}\right)^N$$

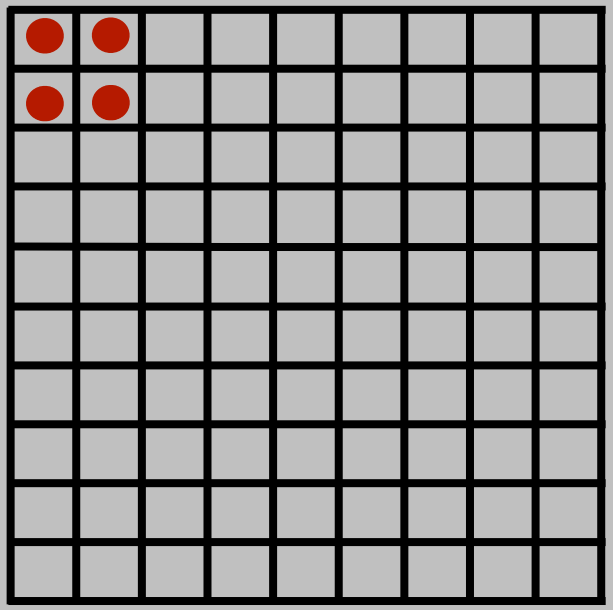


What is the probability to find this configuration?



What is the probability to find this configuration?

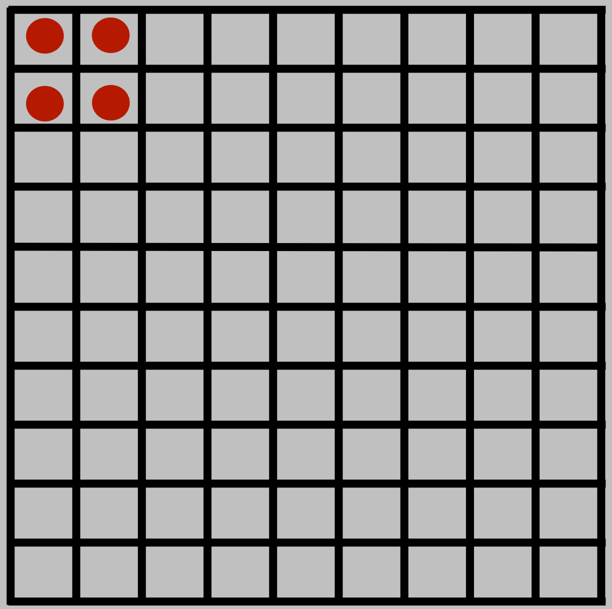
exactly equal as to any other configuration!!!!!!



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



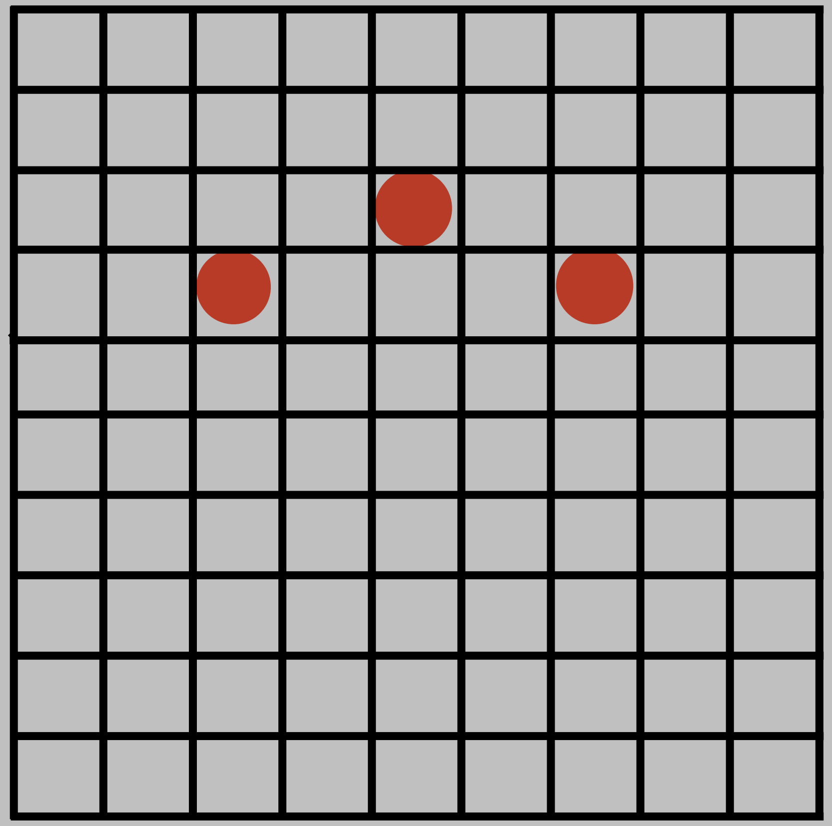
What is the probability to find this configuration?

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

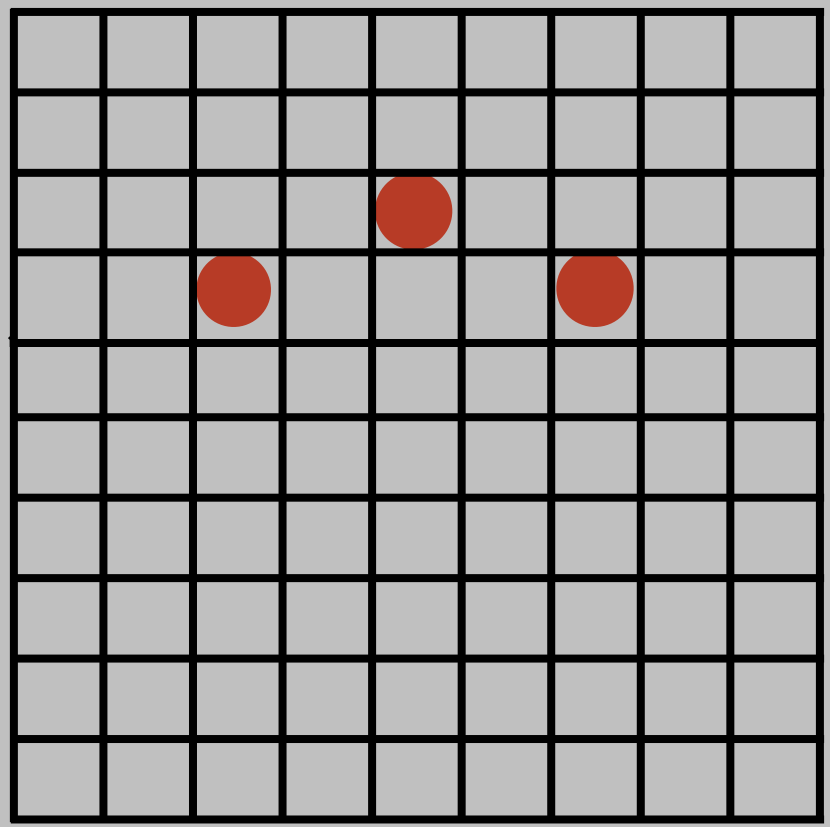
Are we asking the **right question**?

Are we asking the **right question**?



Are we asking the **right question**?

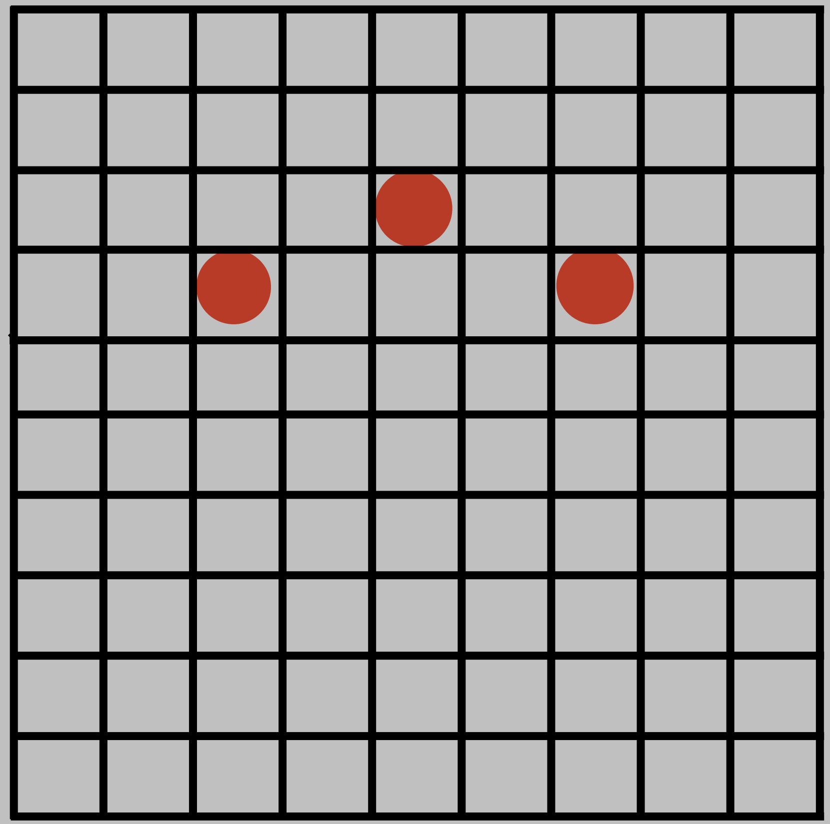
These are microscopic properties; **no irreversibility**



Are we asking the **right question**?

These are microscopic properties; **no irreversibility**

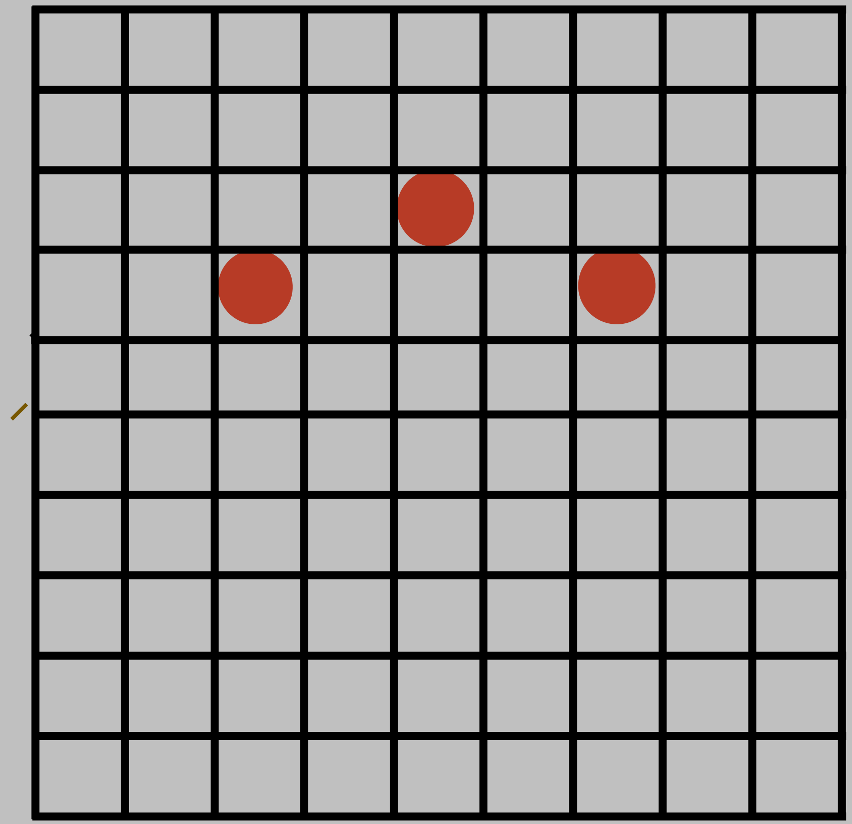
Thermodynamic is about macroscopic properties:



Are we asking the **right question**?

These are microscopic properties; **no irreversibility**

Thermodynamic is about macroscopic properties:

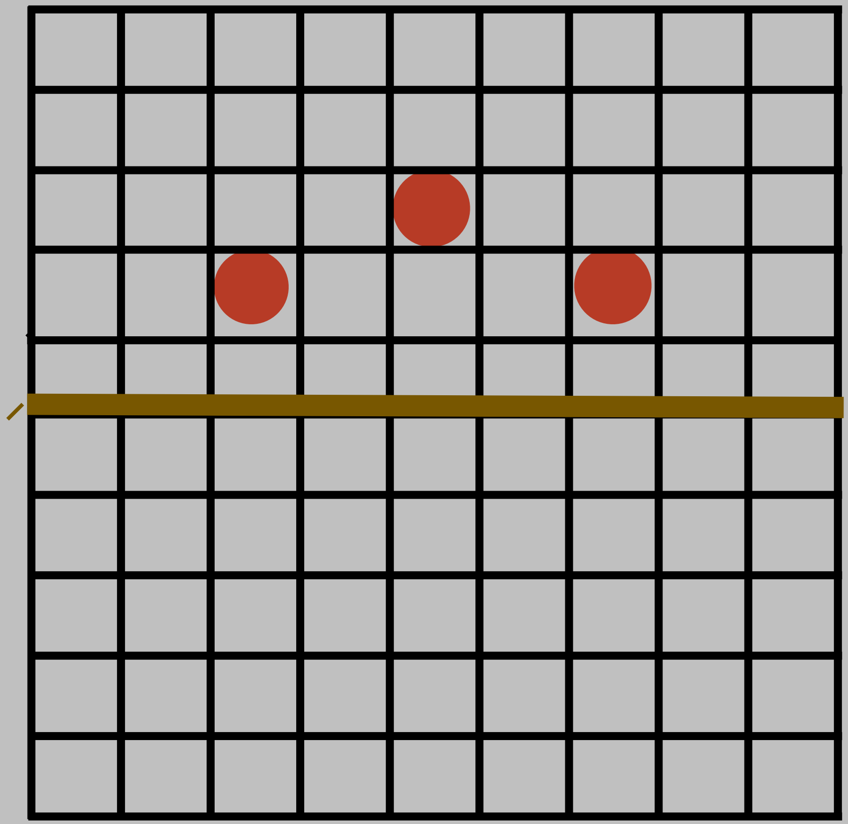


Measure densities: what is the probability that we have all our N gas particle in the upper half?

Are we asking the **right question**?

These are microscopic properties; **no irreversibility**

Thermodynamic is about macroscopic properties:

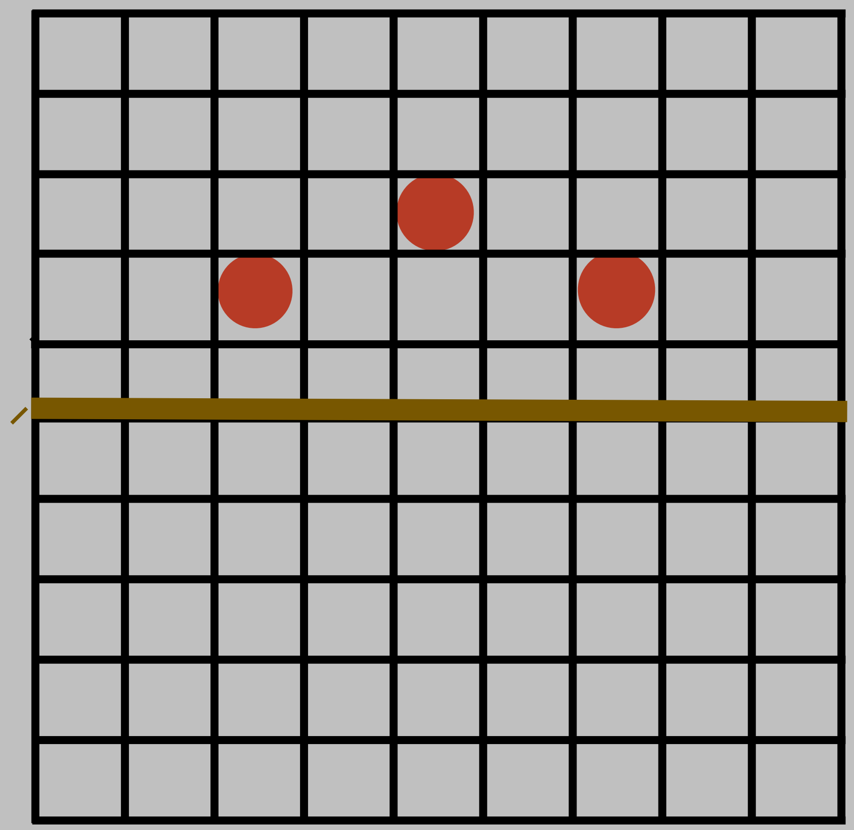


Measure densities: what is the probability that we have all our N gas particle in the upper half?

Are we asking the **right question**?

These are microscopic properties; **no irreversibility**

Thermodynamic is about macroscopic properties:



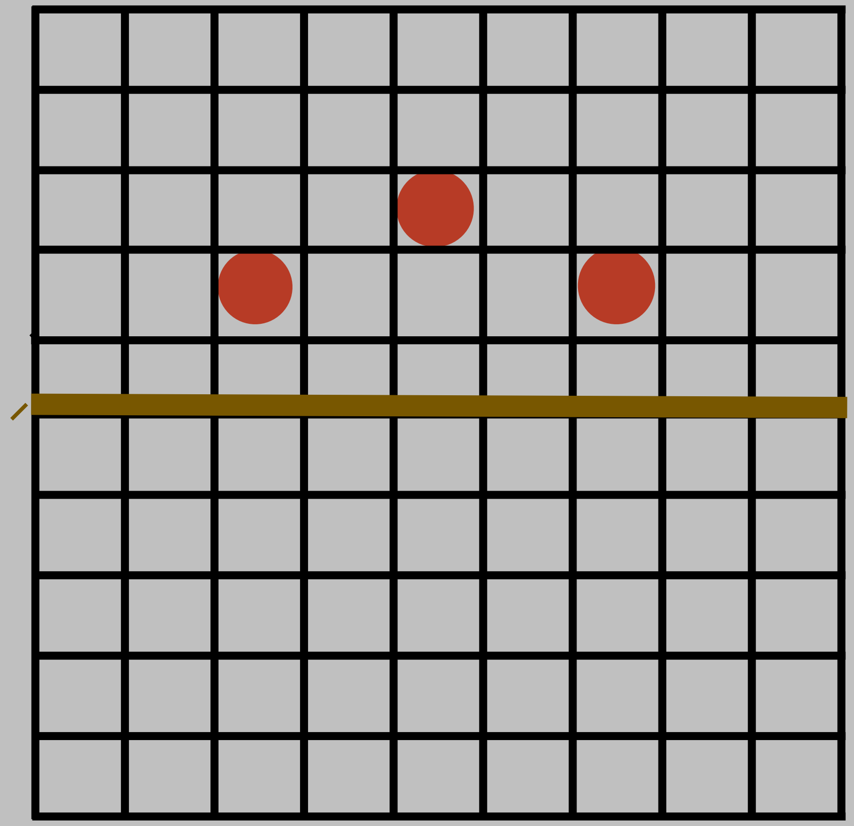
Measure densities: what is the probability that we have all our N gas particle in the upper half?

N	P(empty)

Are we asking the right question?

These are microscopic properties; **no irreversibility**

Thermodynamic is about macroscopic properties:



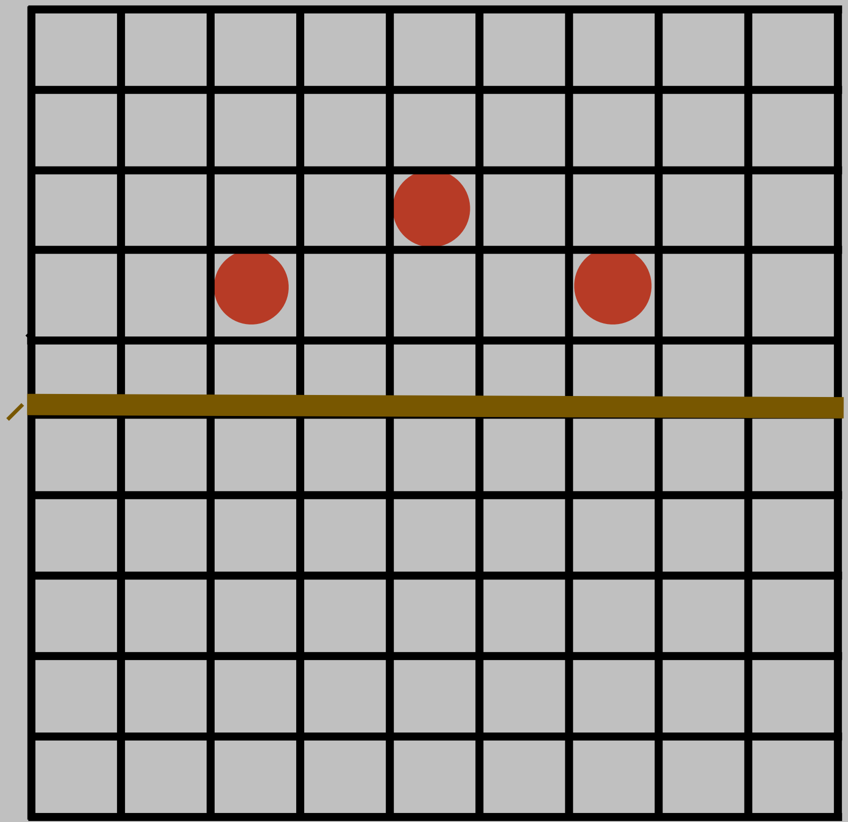
Measure densities: what is the probability that we have all our N gas particle in the upper half?

N	P(empty)
1	0.5

Are we asking the **right question**?

These are microscopic properties; **no irreversibility**

Thermodynamic is about macroscopic properties:



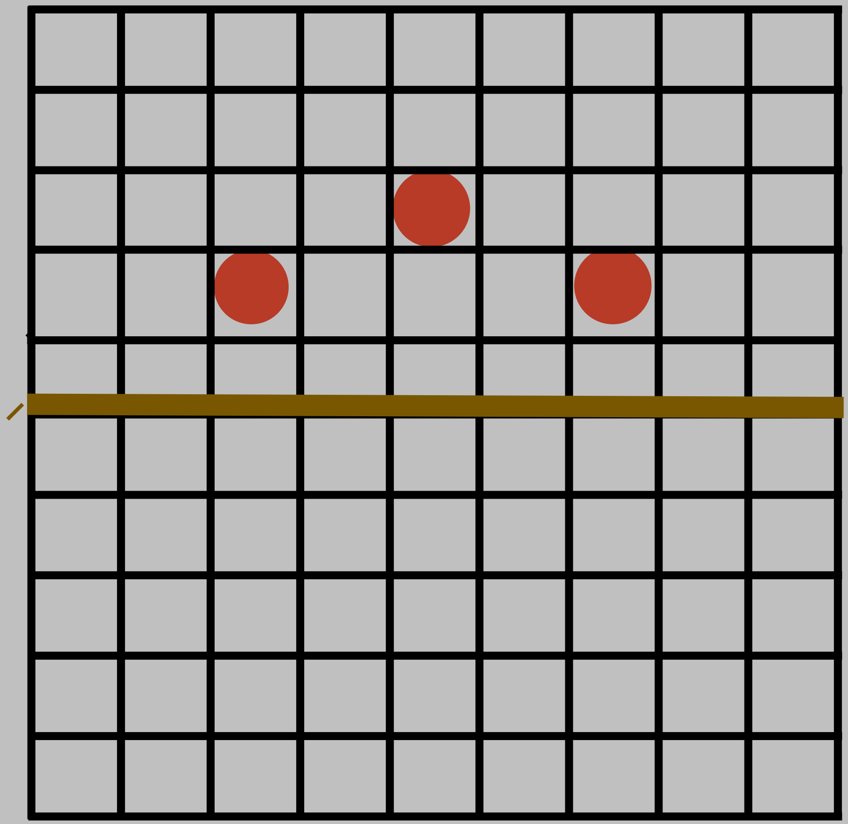
Measure densities: what is the probability that we have all our N gas particle in the upper half?

N	P(empty)
1	0.5
2	0.5 x 0.5

Are we asking the **right question**?

These are microscopic properties; **no irreversibility**

Thermodynamic is about macroscopic properties:



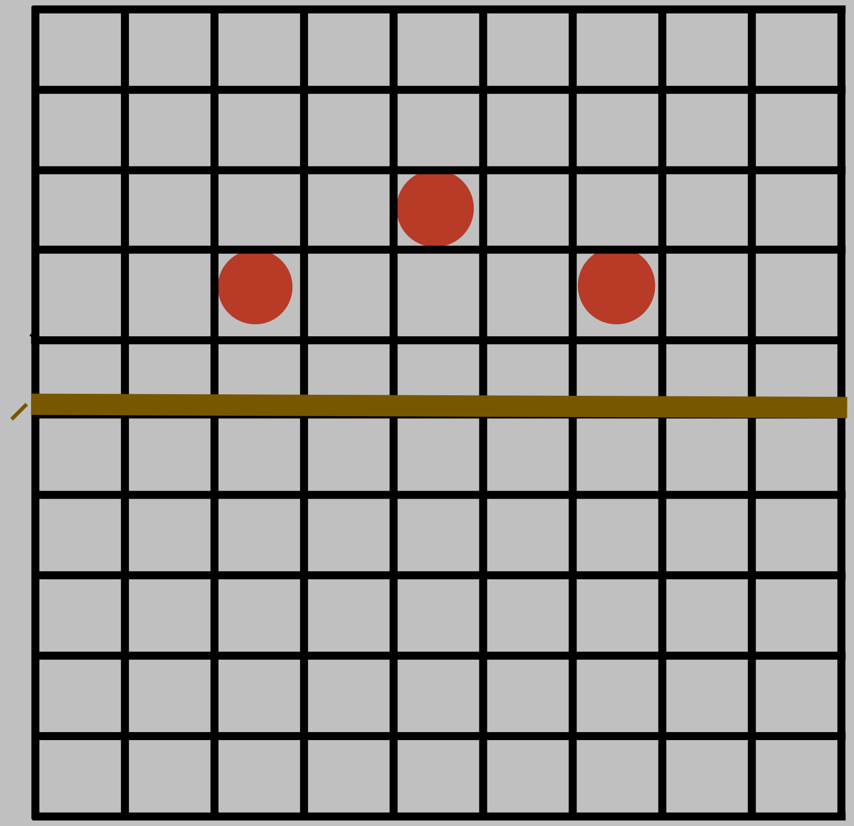
Measure densities: what is the probability that we have all our N gas particle in the upper half?

N	P(empty)
1	0.5
2	0.5 x 0.5
3	0.5 x 0.5 x 0.5

Are we asking the **right question**?

These are microscopic properties; **no irreversibility**

Thermodynamic is about macroscopic properties:



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 x 0.5
3	0.5 x 0.5 x 0.5
1000	10^{-301}

Summary

Summary

- On a microscopic level all configurations are equally likely

Summary

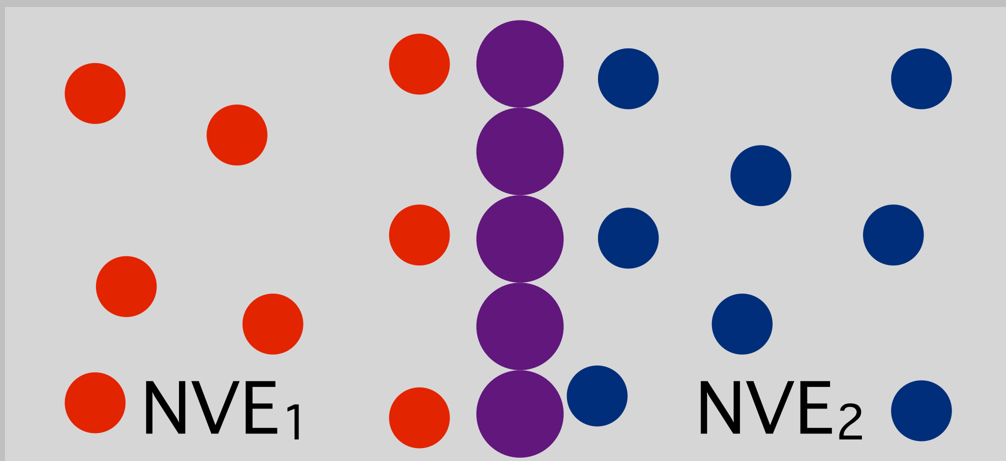
- On a microscopic level all configurations are equally likely
- On a macroscopic level; as the number of particles is extremely large, the probability that we have a fluctuation from the average value is extremely low

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 quantify these statements

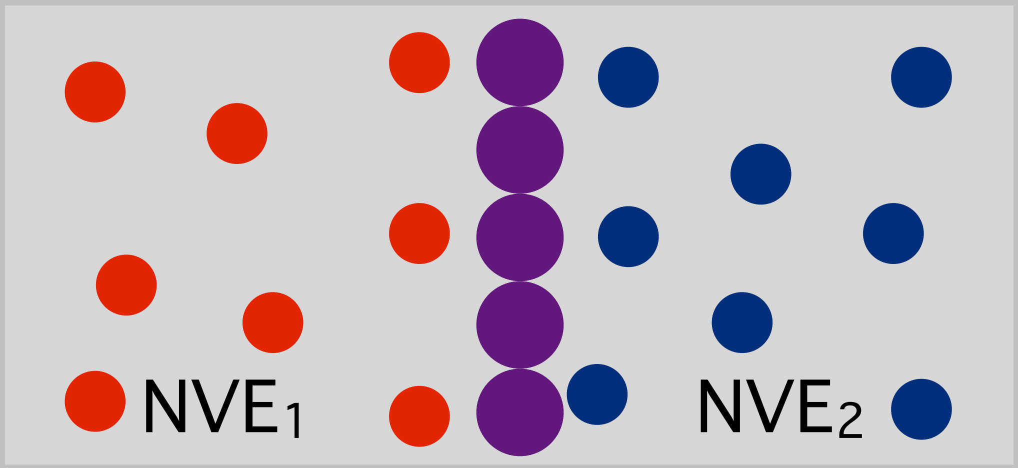
Basic assumption

$E_1 > E_2$



Basic assumption

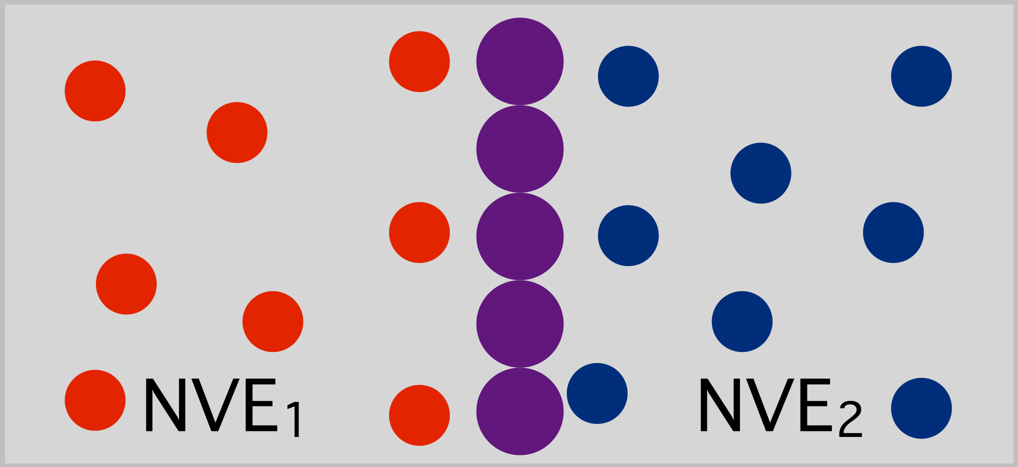
$E_1 > E_2$



Let us look at one of our examples; let us assume that the total system is isolate but heat can flow between 1 and 2.

Basic assumption

$E_1 > E_2$

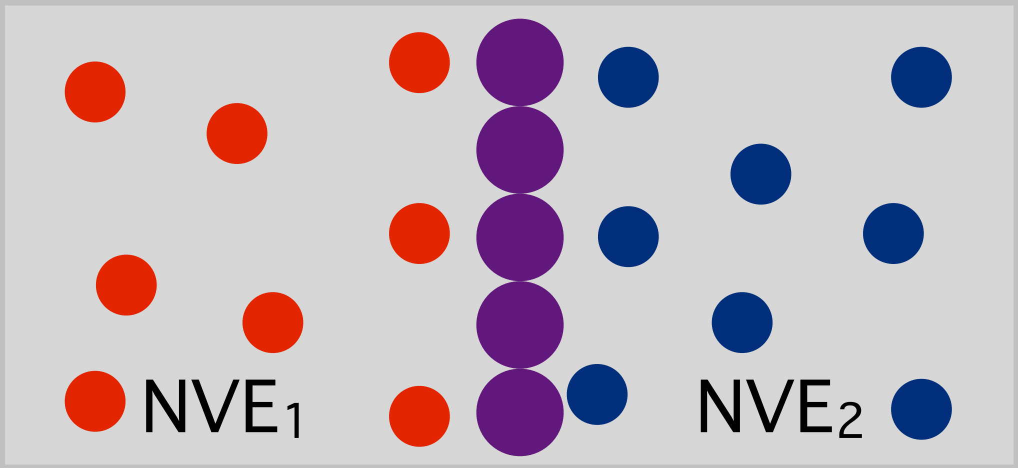


Let us look at one of our examples; let us assume that the total system is isolate but heat can flow between 1 and 2.

All micro states will be equally likely!

Basic assumption

$E_1 > E_2$



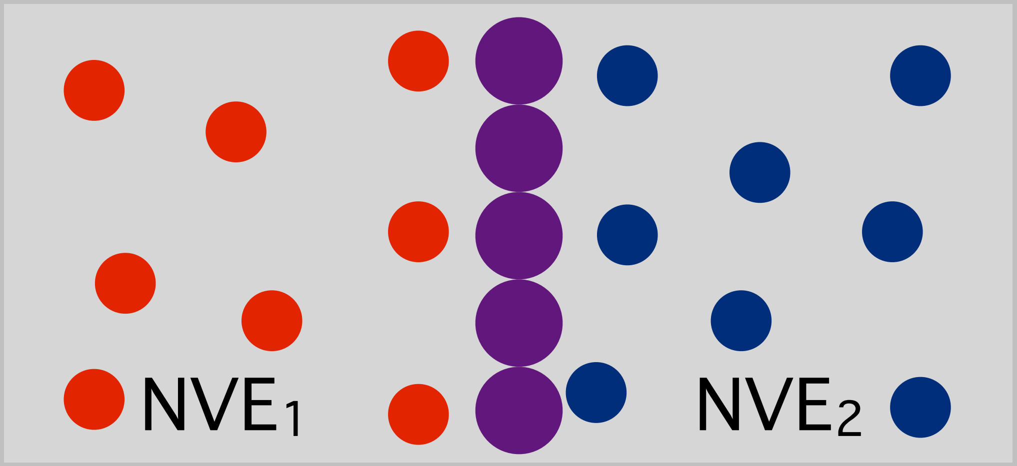
Let us look at one of our examples; let us assume that the total system is isolate but heat can flow between 1 and 2.

All micro states will be equally likely!

... but the number of micro states that give an particular energy distribution (E_1,$E-E_1$) not ...

Basic assumption

$E_1 > E_2$



Let us look at one of our examples; let us assume that the total system is isolate but heat can flow between 1 and 2.

All micro states will be equally likely!

... but the number of micro states that give an particular energy distribution (E_1,E-E_1) not ...

... so, we observe the <u>most likely</u> one ...

In a macroscopic system we will observe the most likely one

In a macroscopic system we will observe the most likely one

$$\mathcal{P}(E_1, E_2) = \frac{\mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}{\sum_{E_1=0}^{E_1=E} \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}$$

In a macroscopic system we will observe the most likely one

$$\mathcal{P}(E_1, E_2) = \frac{\mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}{\sum_{E_1=0}^{E_1=E} \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}$$

The summation only depends on the total energy:

In a macroscopic system we will observe the most likely one

$$\mathcal{P}(E_1, E_2) = \frac{\mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}{\sum_{E_1=0}^{E_1=E} \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}$$

The summation only depends on the total energy:

$$\mathcal{P}(E_1, E_2) = C \times \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)$$

In a macroscopic system we will observe the most likely one

$$\mathcal{P}(E_1, E_2) = \frac{\mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}{\sum_{E_1=0}^{E_1=E} \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}$$

The summation only depends on the total energy:

$$\mathcal{P}(E_1, E_2) = C \times \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)$$

$$\ln \mathcal{P}(E_1, E_2) = \ln C + \ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)$$

In a macroscopic system we will observe the most likely one

$$\mathcal{P}(E_1, E_2) = \frac{\mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}{\sum_{E_1=0}^{E_1=E} \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}$$

The summation only depends on the total energy:

$$\mathcal{P}(E_1, E_2) = C \times \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)$$

$$\ln \mathcal{P}(E_1, E_2) = \ln C + \ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)$$

We need to find the maximum

In a macroscopic system we will observe the most likely one

$$\mathcal{P}(E_1, E_2) = \frac{\mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}{\sum_{E_1=0}^{E_1=E} \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}$$

The summation only depends on the total energy:

$$\mathcal{P}(E_1, E_2) = C \times \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)$$

$$\ln \mathcal{P}(E_1, E_2) = \ln C + \ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)$$

We need to find the maximum

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

In a macroscopic system we will observe the most likely one

$$\mathcal{P}(E_1, E_2) = \frac{\mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}{\sum_{E_1=0}^{E_1=E} \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)}$$

The summation only depends on the total energy:

$$\mathcal{P}(E_1, E_2) = C \times \mathcal{N}_1(E_1) \times \mathcal{N}_2(E - E_1)$$

$$\ln \mathcal{P}(E_1, E_2) = \ln C + \ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)$$

We need to find the maximum

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

$$\frac{d \left[\ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)\right]}{dE_1} = 0$$

We need to find the maximum

$$\frac{d\left[\ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)\right]}{dE_1} = 0$$

We need to find the maximum

$$\frac{d\left[\ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)\right]}{dE_1} = 0$$

$$\frac{d \ln \mathcal{N}_1(E_1)}{dE_1} = -\frac{d \ln \mathcal{N}_2(E - E_1)}{dE_1}$$

We need to find the maximum

$$\frac{\mathrm{d}\left[\ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)\right]}{\mathrm{d}E_1} = 0$$

$$\frac{\mathrm{d}\ln \mathcal{N}_1(E_1)}{\mathrm{d}E_1} = -\frac{\mathrm{d}\ln \mathcal{N}_2(E - E_1)}{\mathrm{d}E_1}$$

As the total energy is constant

We need to find the maximum

$$\frac{d\left[\ln\mathcal{N}_1(E_1) + \ln\mathcal{N}_2(E - E_1)\right]}{dE_1} = 0$$

$$\frac{d\ln\mathcal{N}_1(E_1)}{dE_1} = -\frac{d\ln\mathcal{N}_2(E - E_1)}{dE_1}$$

As the total energy is constant

$$E_2 = E - E_1$$

We need to find the maximum

$$\frac{d\left[\ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)\right]}{dE_1} = 0$$

$$\frac{d \ln \mathcal{N}_1(E_1)}{dE_1} = -\frac{d \ln \mathcal{N}_2(E - E_1)}{dE_1}$$

As the total energy is constant

$$E_2 = E - E_1$$

$$dE_1 = -d(E - E_1) = -dE_2$$

We need to find the maximum

$$\frac{d\left[\ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)\right]}{dE_1} = 0$$

$$\frac{d \ln \mathcal{N}_1(E_1)}{dE_1} = -\frac{d \ln \mathcal{N}_2(E - E_1)}{dE_1}$$

As the total energy is constant

$$E_2 = E - E_1$$

$$dE_1 = -d(E - E_1) = -dE_2$$

Which gives as equilibrium condition:

We need to find the maximum

$$\frac{d\left[\ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)\right]}{dE_1} = 0$$

$$\frac{d \ln \mathcal{N}_1(E_1)}{dE_1} = -\frac{d \ln \mathcal{N}_2(E - E_1)}{dE_1}$$

As the total energy is constant

$$E_2 = E - E_1$$

$$dE_1 = -d(E - E_1) = -dE_2$$

Which gives as equilibrium condition:

$$\frac{d \ln \mathcal{N}_1(E_1)}{dE_1} = \frac{d \ln \mathcal{N}_2(E_2)}{dE_2}$$

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

$$S^{*} = \ln \mathfrak{N}(E)$$

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

$$S^* = \ln \mathfrak{N}(E)$$

Equilibrium if:

$$\frac{d \ln \mathfrak{N}_1(E_1)}{dE_1} = \frac{d \ln \mathfrak{N}_2(E_2)}{dE_2}$$

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

$$S^* = \ln \mathfrak{N}(E)$$

Equilibrium if:

$$\frac{d \ln \mathfrak{N}_1(E_1)}{dE_1} = \frac{d \ln \mathfrak{N}_2(E_2)}{dE_2}$$

or

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

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

$$S^* = \ln \mathfrak{N}(E)$$

Equilibrium if:

$$\frac{d \ln \mathfrak{N}_1(E_1)}{dE_1} = \frac{d \ln \mathfrak{N}_2(E_2)}{dE_2}$$

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:

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

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

$$S^* = \ln \mathfrak{N}(E)$$

Equilibrium if:

$$\frac{d \ln \mathfrak{N}_1(E_1)}{dE_1} = \frac{d \ln \mathfrak{N}_2(E_2)}{dE_2}$$

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 the S^* increases until it has reached its maximum value at equilibrium

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

$$S^* = \ln \mathfrak{N}(E)$$

Equilibrium if:

$$\frac{d \ln \mathfrak{N}_1(E_1)}{dE_1} = \frac{d \ln \mathfrak{N}_2(E_2)}{dE_2}$$

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 the 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):

$$
\begin{aligned}
S^*(E_1, E - E_1) &= \ln \aleph(E_1, E - E_1) \\
&= \ln \aleph_1(E_1) + \ln \aleph_2(E - E_1) \\
&= S_1^*(E_1) + S_2^*(E - E_1)
\end{aligned}
$$

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

$$S^*(E_1, E - E_1) = \ln \aleph(E_1, E - E_1)$$
$$= \ln \aleph_1(E_1) + \ln \aleph_2(E - E_1)$$
$$= S_1^*(E_1) + S_2^*(E - E_1)$$

Why is maximizing S* the same as maximizing N?

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

$$S^*(E_1, E - E_1) = \ln \aleph(E_1, E - E_1)$$
$$= \ln \aleph_1(E_1) + \ln \aleph_2(E - E_1)$$
$$= S_1^*(E_1) + S_2^*(E - E_1)$$

Why is maximizing S* the same as maximizing N?

The logarithm is a monotonically increasing function.

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

$$\begin{aligned} S^*(E_1, E - E_1) &= \ln \aleph(E_1, E - E_1) \\ &= \ln \aleph_1(E_1) + \ln \aleph_2(E - E_1) \\ &= S_1^*(E_1) + S_2^*(E - E_1) \end{aligned}$$

Why is maximizing S* the same as maximizing N?

The logarithm is a monotonically increasing function.

Why else is the logarithm a convenient function?

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

$$
\begin{aligned}
S^*(E_1, E - E_1) &= \ln \aleph(E_1, E - E_1) \\
&= \ln \aleph_1(E_1) + \ln \aleph_2(E - E_1) \\
&= S_1^*(E_1) + S_2^*(E - E_1)
\end{aligned}
$$

Why is maximizing S* the same as maximizing N?

The logarithm is a monotonically increasing function.

Why else is the logarithm a convenient function?

Makes S* additive! Leads to extensivity.

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

$$
\begin{aligned}
S^*(E_1, E - E_1) &= \ln \aleph(E_1, E - E_1) \\
&= \ln \aleph_1(E_1) + \ln \aleph_2(E - E_1) \\
&= S_1^*(E_1) + S_2^*(E - E_1)
\end{aligned}
$$

Why is maximizing S* the same as maximizing N?

The logarithm is a monotonically increasing function.

Why else is the logarithm a convenient function?

Makes S* additive! Leads to extensivity.

Why is S* not quite entropy?

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

$$\begin{aligned} S^*(E_1, E - E_1) &= \ln \aleph(E_1, E - E_1) \\ &= \ln \aleph_1(E_1) + \ln \aleph_2(E - E_1) \\ &= S_1^*(E_1) + S_2^*(E - E_1) \end{aligned}$$

Why is maximizing S* the same as maximizing N?

The logarithm is a monotonically increasing function.

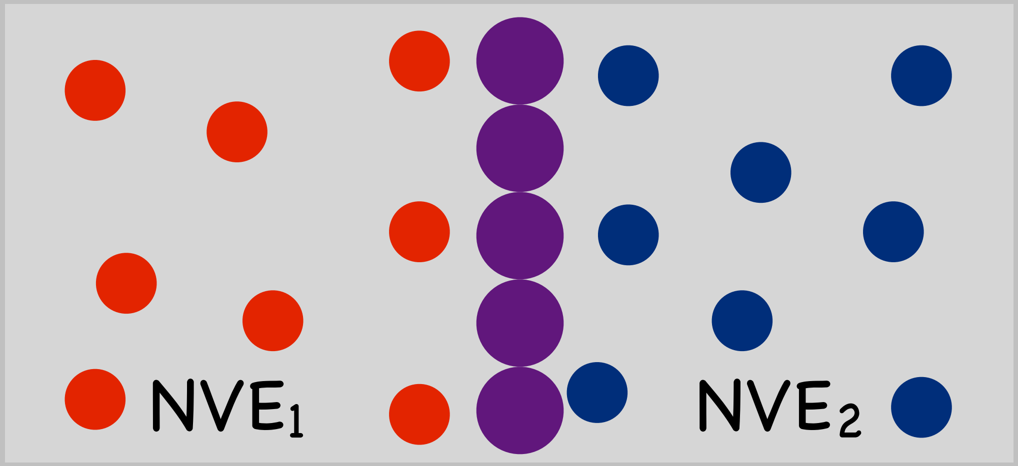
Why else is the logarithm a convenient function?

Makes S* additive! Leads to extensivity.

Why is S* not quite entropy?

Units! The logarithm is just a unitless quantity.

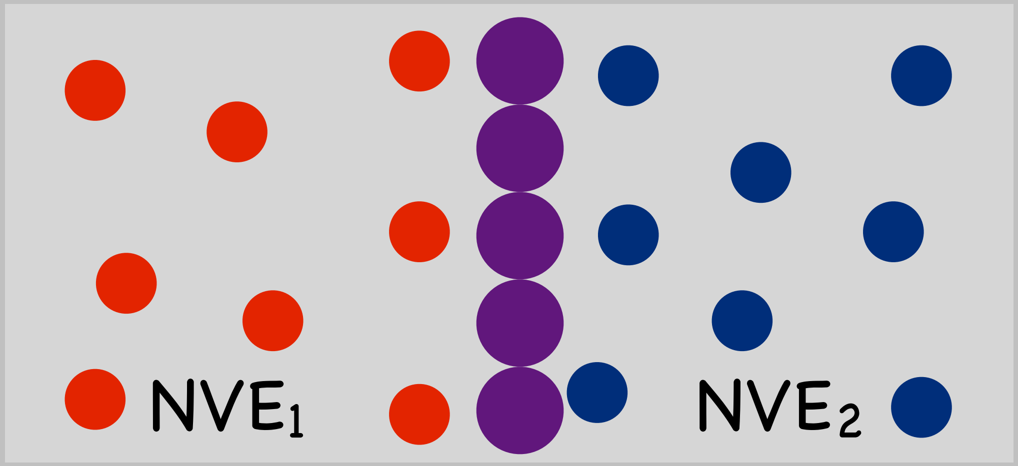
Thermal Equilibrium (Review)



$E_1 > E_2$

Isolated system that allows heat flow between 1 and 2.

Thermal Equilibrium (Review)

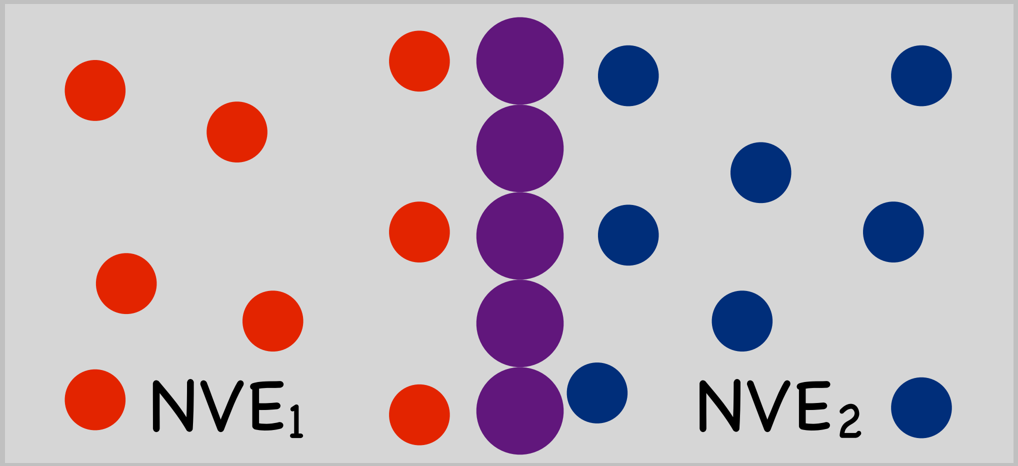


$E_1 > E_2$

Isolated system that allows heat flow between 1 and 2.

$$\aleph(E_1, E - E_1) = \aleph_1(E_1) \bullet \aleph_2(E - E_1)$$

Thermal Equilibrium (Review)



$E_1 > E_2$

Isolated system that allows heat flow between 1 and 2.

$$\aleph(E_1, E - E_1) = \aleph_1(E_1) \bullet \aleph_2(E - E_1)$$

Number of micro states that give an particular energy distribution (E_1,$E-E_1$) is maximized with respect to E_1.

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

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

For a partitioning of E between 1 and 2, the number of accessible states 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?

For a partitioning of E between 1 and 2, the number of accessible states 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?

Thermal equilibrium --> Temperature!

For a partitioning of E between 1 and 2, the number of accessible states 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?

Thermal equilibrium --> Temperature!

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \sum_{i=1}^{M} \mu_i \mathrm{d}N_i$$

For a partitioning of E between 1 and 2, the number of accessible states 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?

Thermal equilibrium --> Temperature!

$$\mathrm{d}E = T\mathrm{d}S\text{-}p\mathrm{d}V + \sum_{i=1}^{M} \mu_i \mathrm{d}N_i$$

Temperature

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

For a partitioning of E between 1 and 2, the number of accessible states 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?

Thermal equilibrium --> Temperature!

$$\mathrm{d}E = T\mathrm{d}S \text{-} p\mathrm{d}V + \sum_{i=1}^{M} \mu_i \mathrm{d}N_i$$

Temperature

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

Summary

- Statistical Mechanics:
  - basic assumption:
    - all microstates are equally likely
  - Applied to NVE
    - Definition of Entropy: $S = k_B \ln \Omega$
    - Equilibrium: equal temperatures

Question

Question

How large is Ω for a glass of water?

Question

How large is Ω for a glass of water?

- For macroscopic systems, super-astronomically large.

Question

How large is Ω for a glass of water?

- For macroscopic systems, super-astronomically large.
- For instance, for a glass of water at room temperature

Question

How large is Ω for a glass of water?

- For macroscopic systems, super-astronomically large.
- For instance, for a glass of water at room temperature

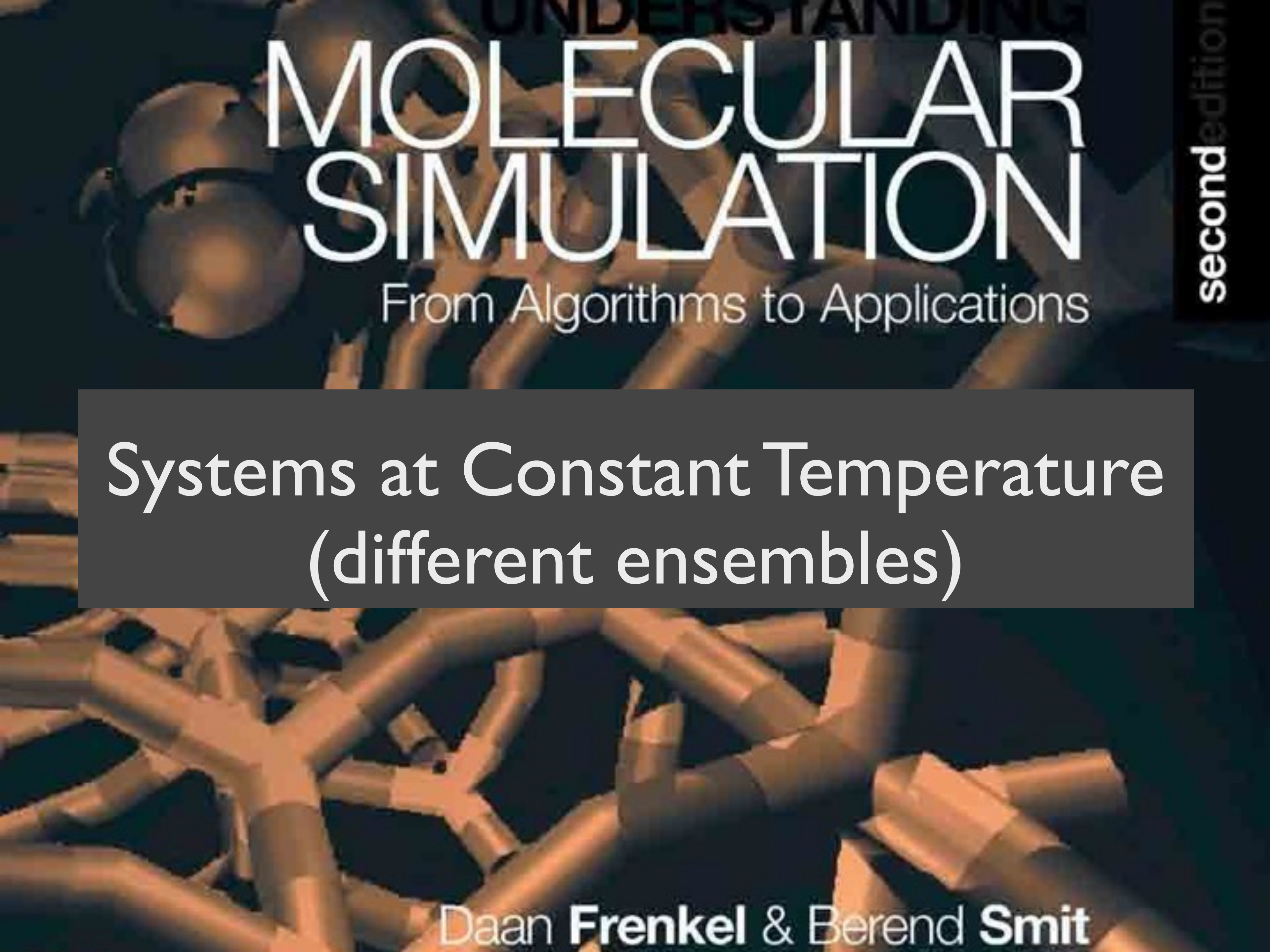
Question

How large is Ω for a glass of water?

- For macroscopic systems, super-astronomically large.
- For instance, for a glass of water at room temperature

$$\Omega \approx 10^{2\times 10^{25}}$$

- Macroscopic deviations from the second law of thermodynamics are not forbidden, but they are extremely unlikely.



Systems at Constant Temperature (different ensembles)

The 2^{nd} law

The 2nd law

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

The 2nd law

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

Most systems are at constant temperature and volume or pressure?

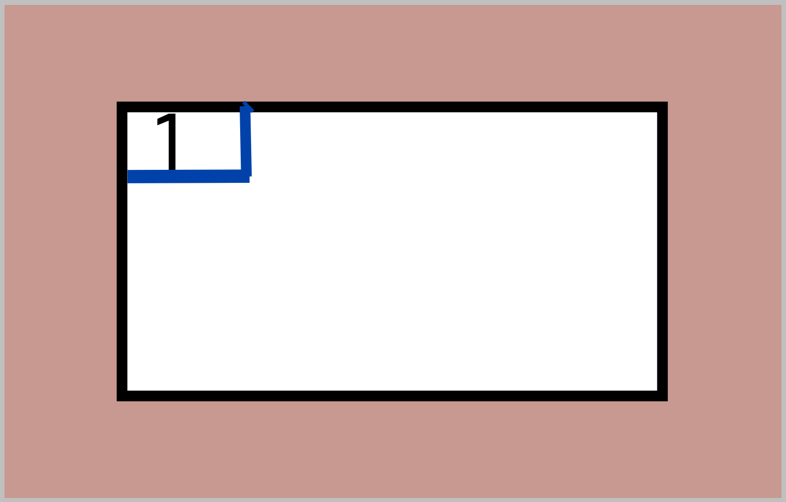
The 2^{nd} law

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

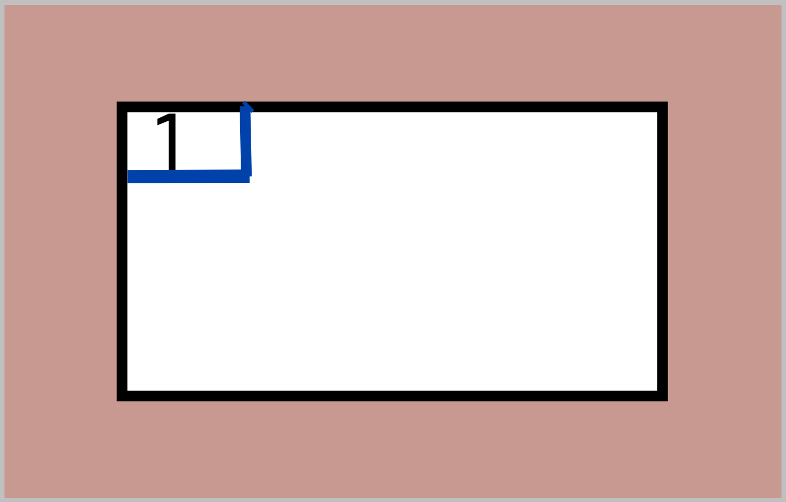
Most systems are at constant temperature and volume or pressure?

What is the formulation for these systems?

Constant T and V



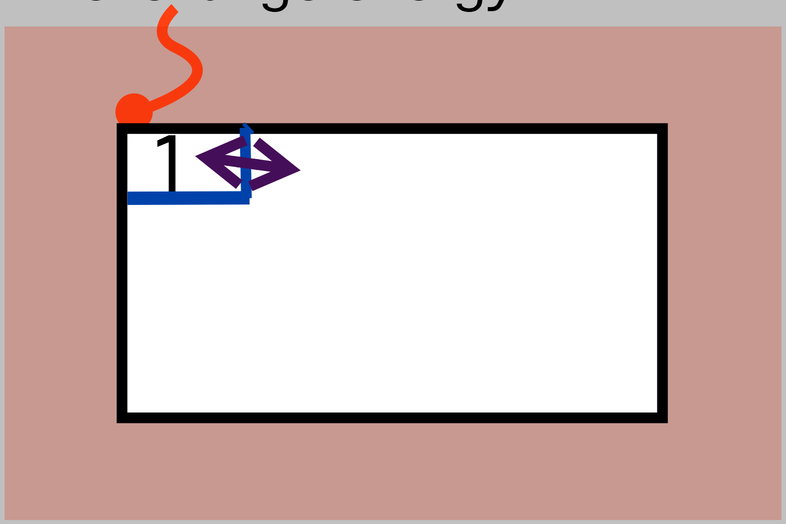
Constant T and V



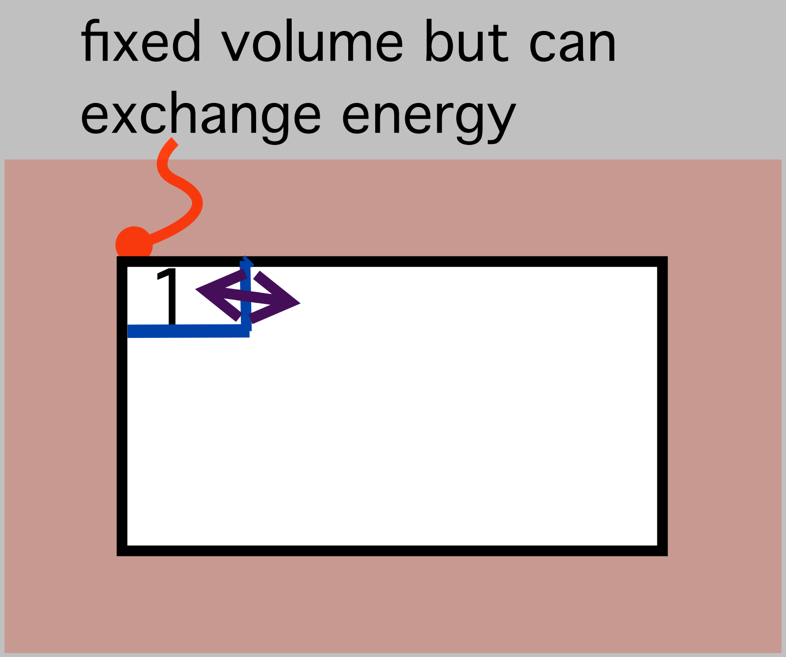
We have our box 1 and a bath

Constant T and V

fixed volume but can exchange energy



We have our box 1 and a bath

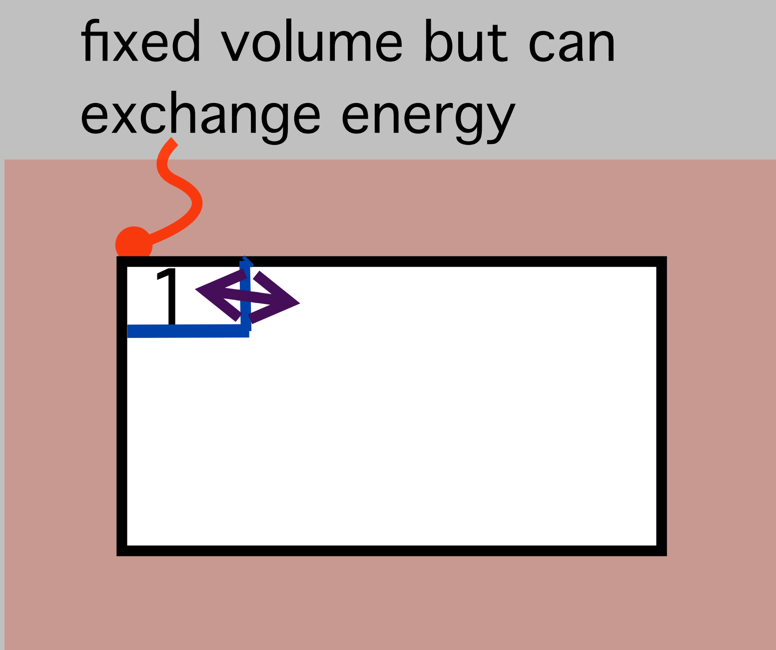


Constant T and V

We have our box 1 and a bath

Total system is isolated and the volume is constant

Constant T and V

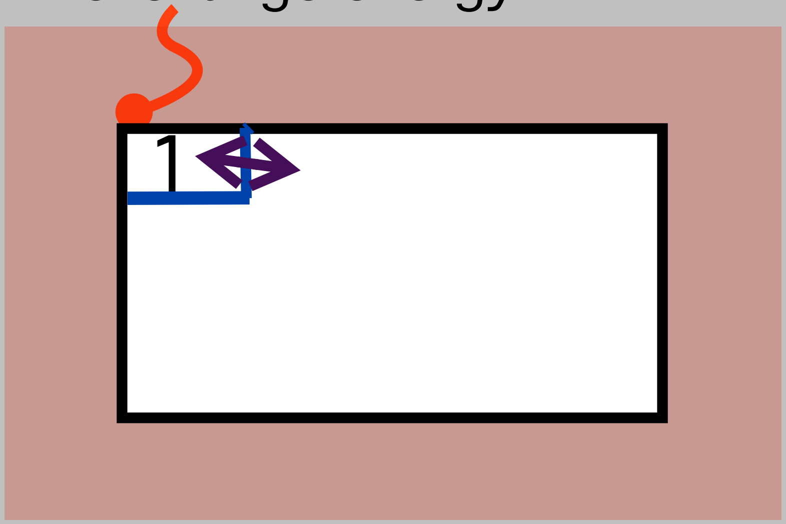


We have our box 1 and a bath

Total system is isolated and the volume is constant

First law

fixed volume but can exchange energy

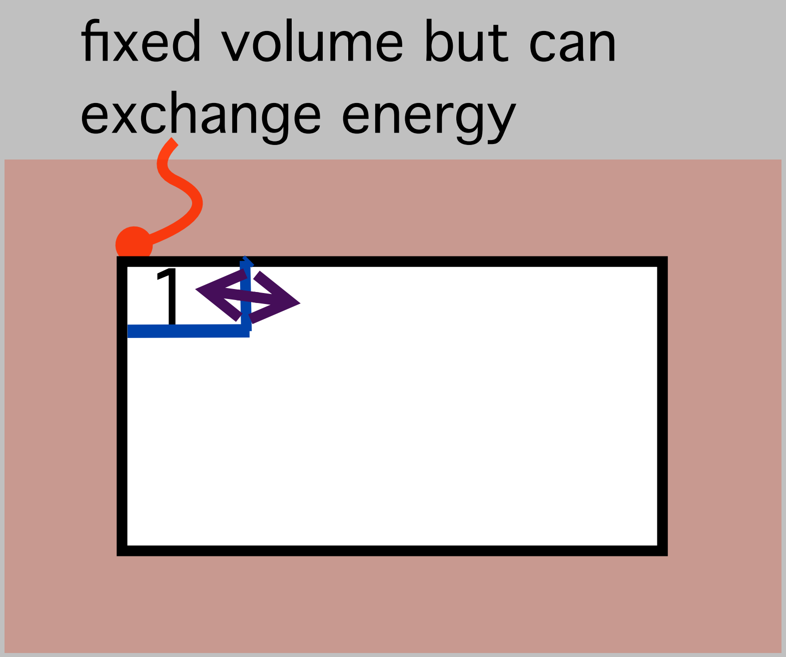


Constant T and V

We have our box 1 and a bath

Total system is isolated and the volume is constant

First law $dU = dq - pdV = 0$



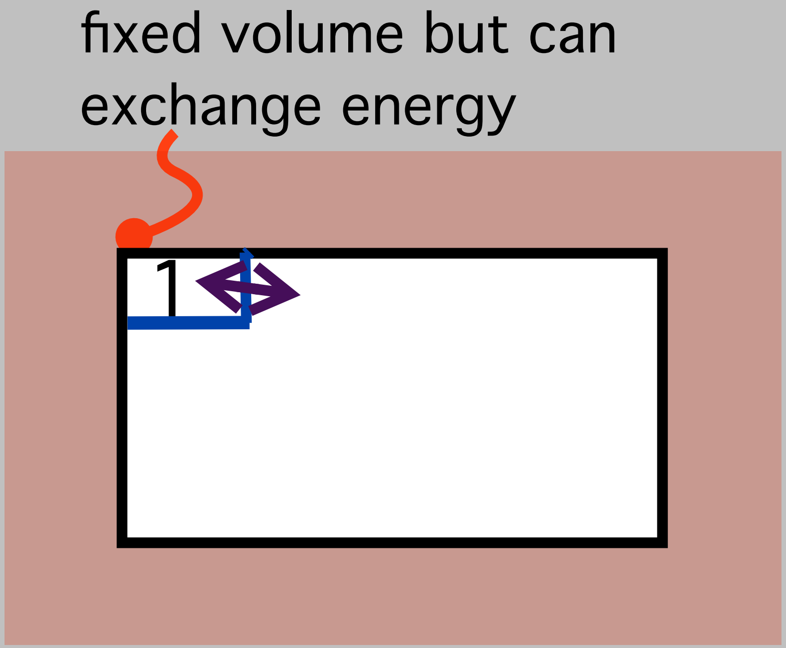
Constant T and V

We have our box 1 and a bath

Total system is isolated and the volume is constant

First law $$dU = dq - pdV = 0$$

Second law



Constant T and V

We have our box 1 and a bath

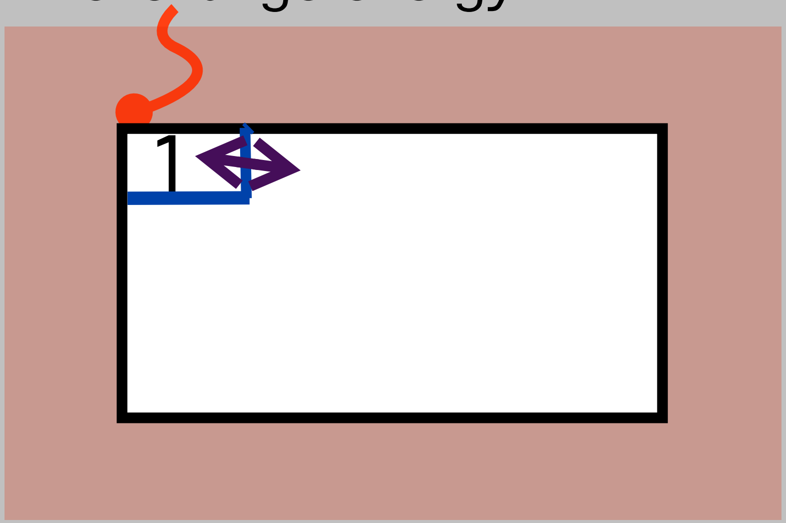
<u>Total system</u> is isolated and the volume is constant

First law $dU = dq - pdV = 0$

Second law $dS \geq 0$

Constant T and V

fixed volume but can exchange energy



We have our box 1 and a bath

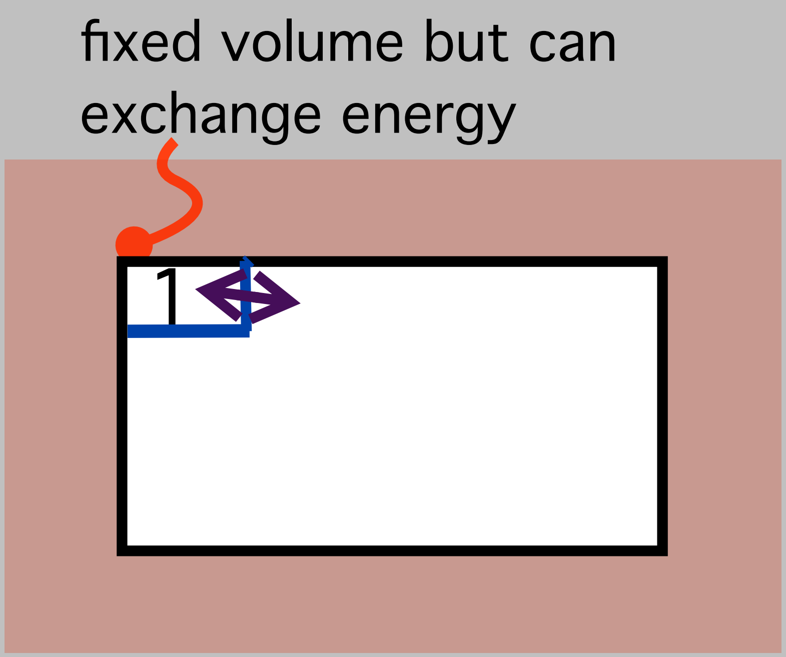
Total system is isolated and the volume is constant

First law $dU = dq - pdV = 0$

Second law $dS \geq 0$

Box 1: constant volume and temperature

Constant T and V



We have our box 1 and a bath

Total system is isolated and the volume is constant

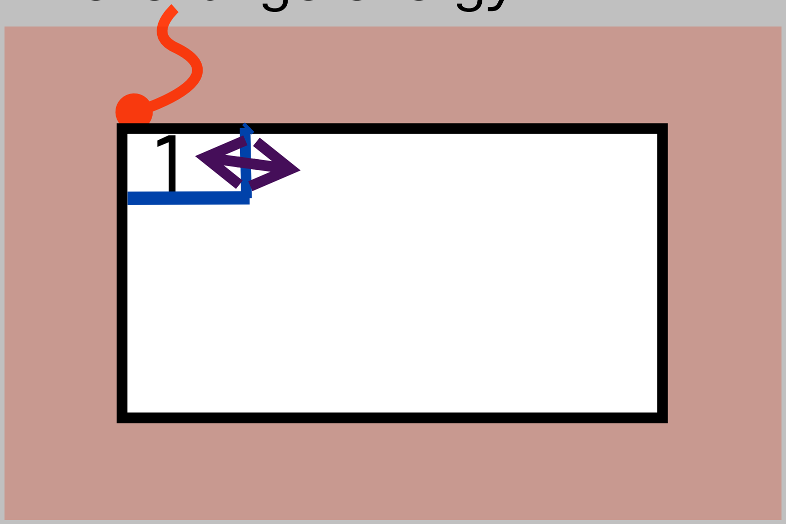
First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

Box 1: constant volume and temperature

1st law:

fixed volume but can exchange energy



Constant T and V

We have our box 1 and a bath

<u>Total system</u> is isolated and the volume is constant

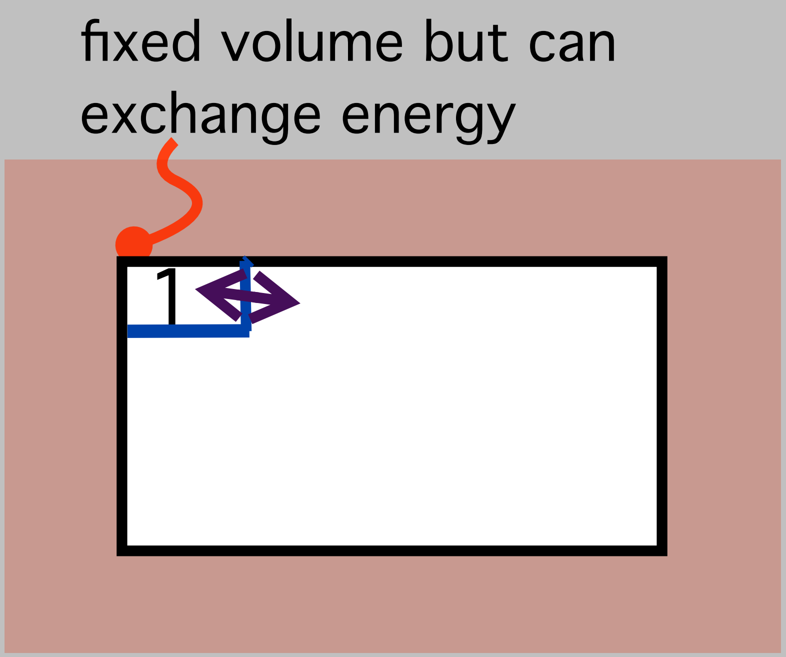
First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

<u>Box 1</u>: constant volume and temperature

1st law: $\mathrm{d}U_1 + \mathrm{d}U_b = 0$

Constant T and V



We have our box 1 and a bath

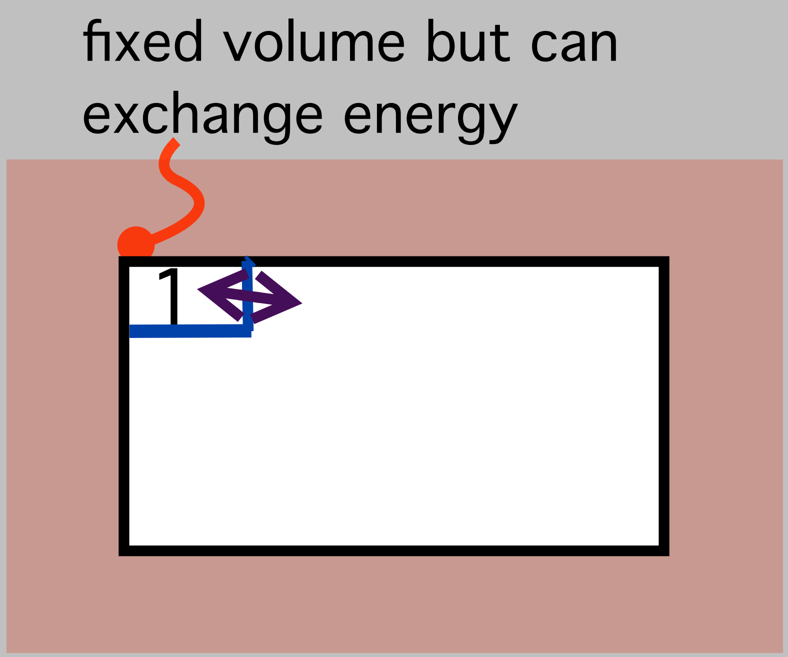
Total system is isolated and the volume is constant

First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

Box 1: constant volume and temperature

1st law: $\mathrm{d}U_1 + \mathrm{d}U_b = 0$ or



Constant T and V

We have our box 1 and a bath

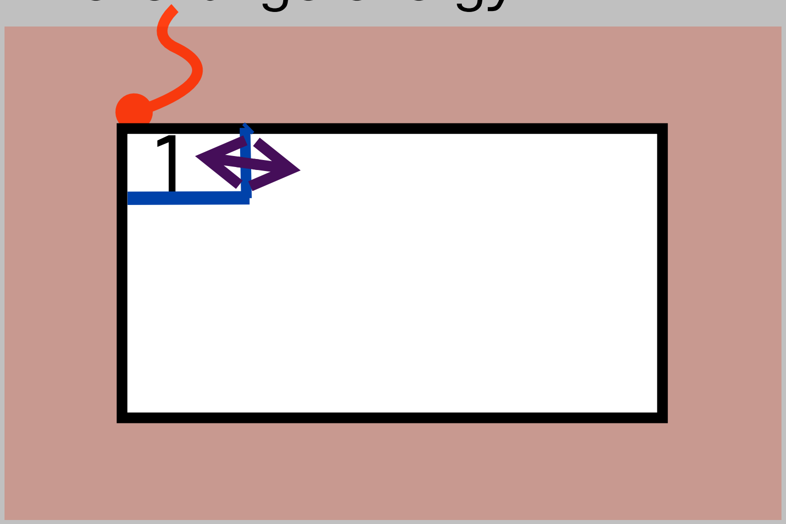
Total system is isolated and the volume is constant

First law $dU = dq - pdV = 0$

Second law $dS \geq 0$

Box 1: constant volume and temperature

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



Constant T and V

We have our box 1 and a bath

<u>Total system</u> is isolated and the volume is constant

First law $dU = dq - pdV = 0$

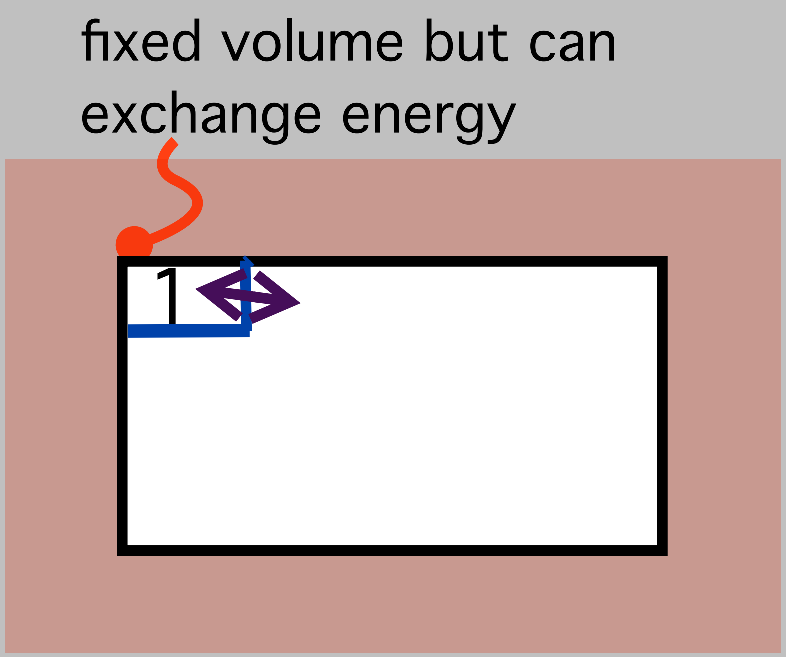
Second law $dS \geq 0$

<u>Box 1</u>: constant volume and temperature

1[st] law: $dU_1 + dU_b = 0$ 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

Constant T and V



We have our box 1 and a bath

<u>Total system</u> is isolated and the volume is constant

First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

<u>Box 1</u>: constant volume and temperature

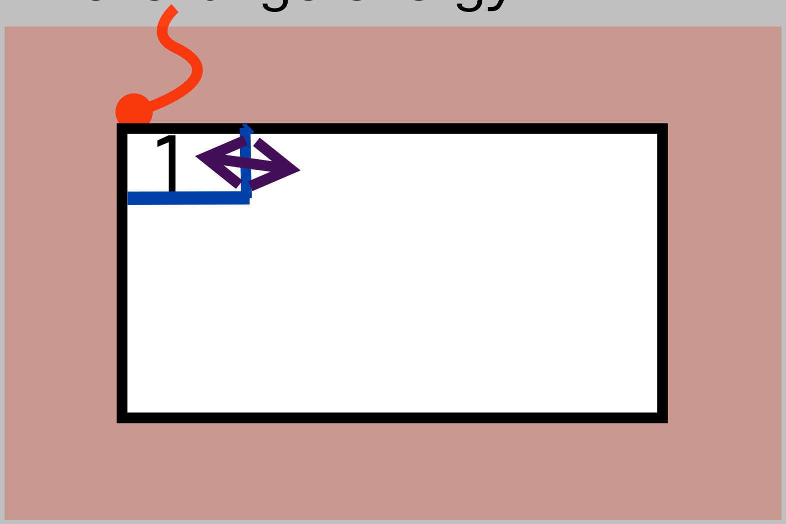
1st law: $\mathrm{d}U_1 + \mathrm{d}U_b = 0$ or $\mathrm{d}U_1 = -\mathrm{d}U_b$

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

2nd law:

Constant T and V

fixed volume but can exchange energy



We have our box 1 and a bath

Total system is isolated and the volume is constant

First law $dU = dq - pdV = 0$

Second law $dS \geq 0$

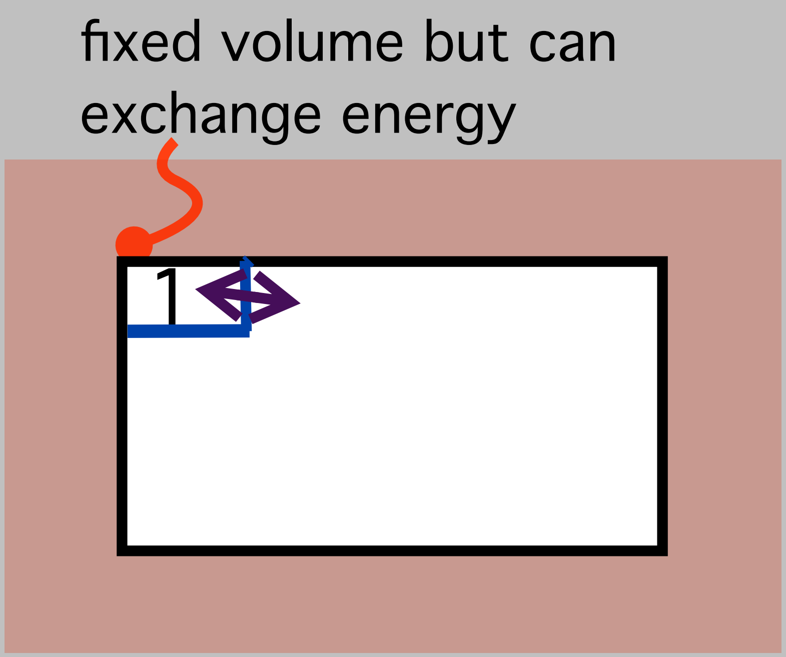
Box 1: constant volume and temperature

1st law: $dU_1 + dU_b = 0$ 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: $dS_1 + dS_b = dS_1 + \frac{dU_b}{T} \geq 0$

Constant T and V



We have our box 1 and a bath

Total system is isolated and the volume is constant

First law $dU = dq - pdV = 0$

Second law $dS \geq 0$

Box 1: constant volume and temperature

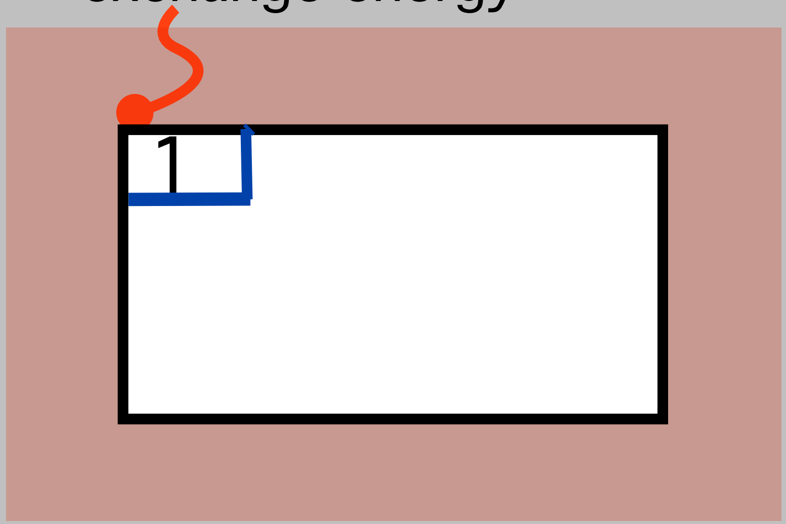
1st law: $dU_1 + dU_b = 0$ or $dU_1 = -dU_b$

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

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

$$TdS_1 - dU_1 \geq 0$$

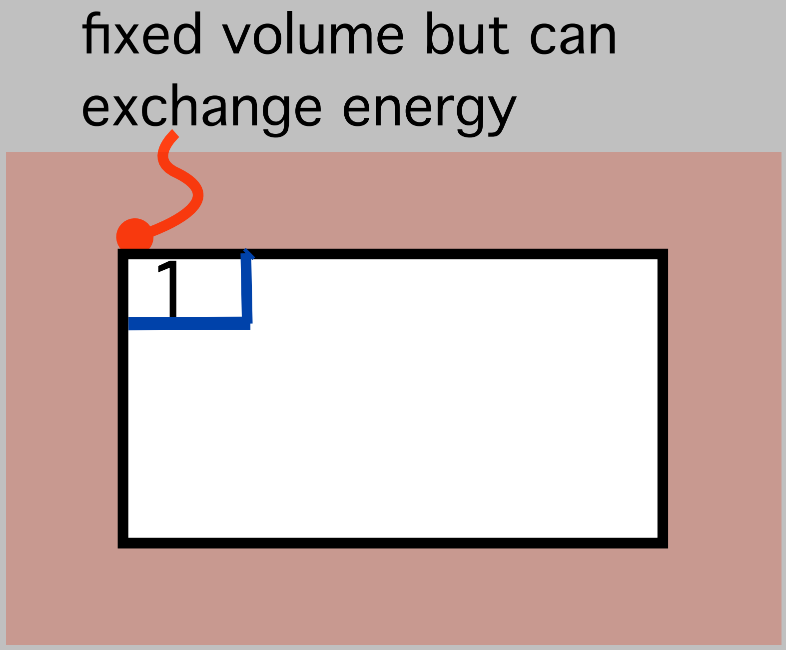
Constant T and V



Total system is isolated and the volume is constant

Box 1: constant volume and temperature

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



Constant T and V

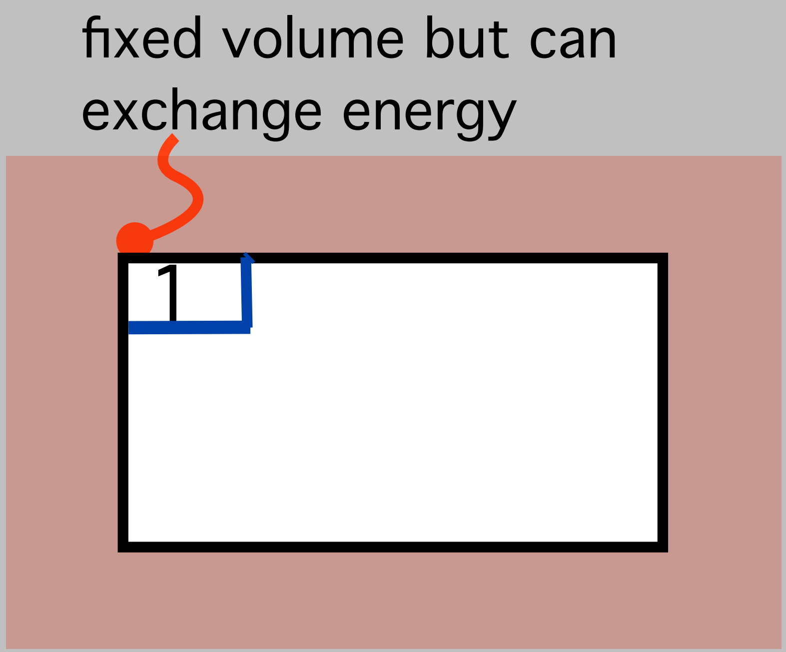
Total system is isolated and the volume is constant

Box 1: constant volume and temperature

2nd law: $T\mathrm{d}S_1 - \mathrm{d}U_1 \geq 0$

$$\mathrm{d}(U_1 - TS_1) \leq 0$$

Constant T and V



Total system is isolated and the volume is constant

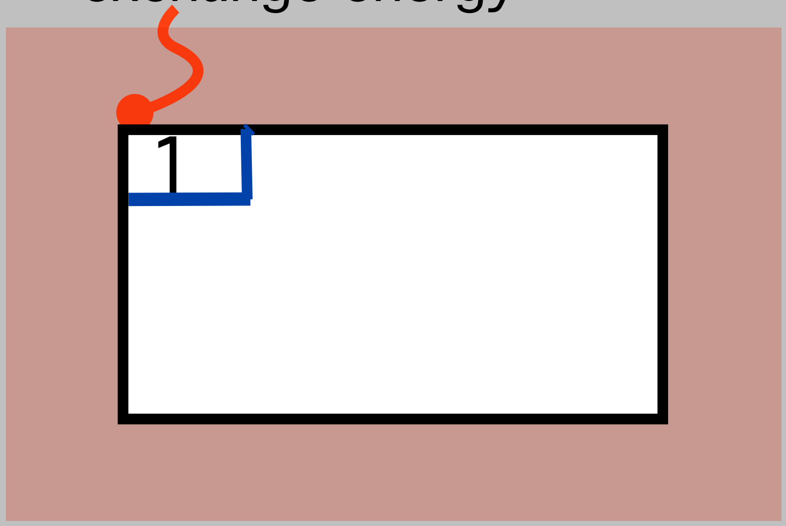
Box 1: constant volume and temperature

2nd law: $T\mathrm{d}S_1 - \mathrm{d}U_1 \geq 0$

$$\mathrm{d}(U_1 - TS_1) \leq 0$$

Let us define the Helmholtz free energy: A

Constant T and V



Total system is isolated and the volume is constant

Box 1: constant volume and temperature

2nd law: $T\mathrm{d}S_1 - \mathrm{d}U_1 \geq 0$

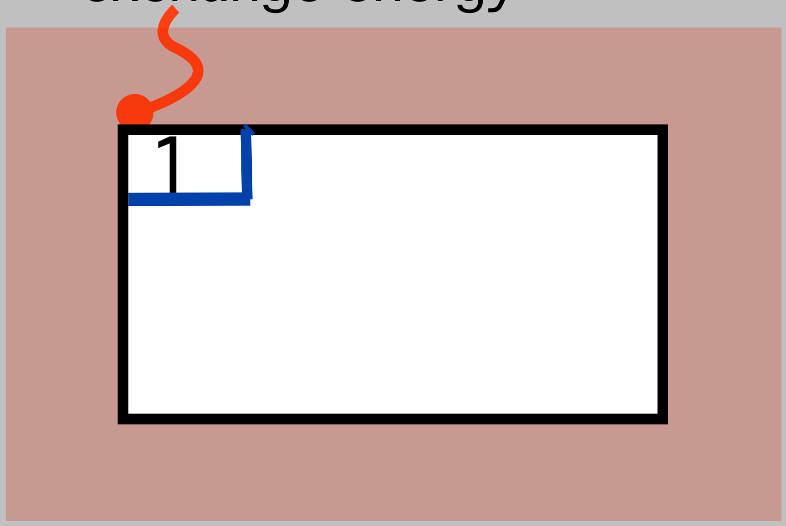
$$\mathrm{d}(U_1 - TS_1) \leq 0$$

Let us define the Helmholtz free energy: A

$$A \equiv U - TS$$

Constant T and V

fixed volume but can exchange energy



Total system is isolated and the volume is constant

Box 1: constant volume and temperature

2nd law: $$T dS_1 - dU_1 \geq 0$$

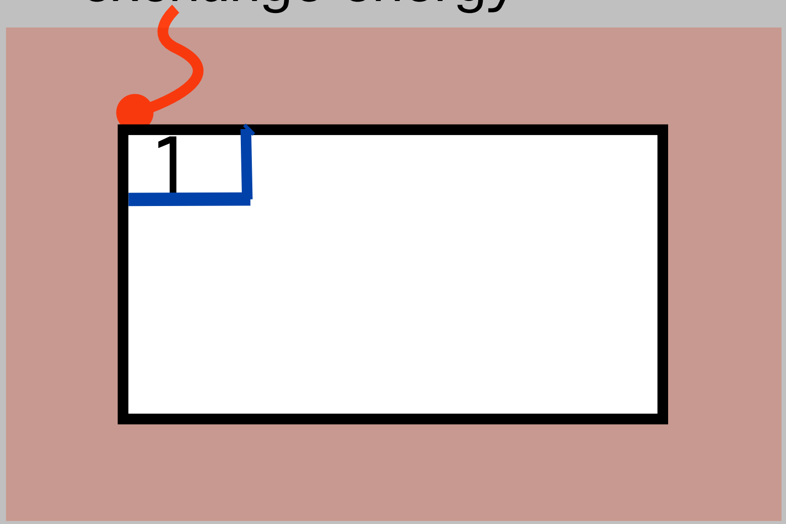
$$d(U_1 - TS_1) \leq 0$$

Let us define the Helmholtz free energy: A

$$A \equiv U - TS$$

For box 1 we can write

Constant T and V



<u>Total system</u> is isolated and the volume is constant

<u>Box 1</u>: constant volume and temperature

2nd law: $$T\mathrm{d}S_1 - \mathrm{d}U_1 \geq 0$$

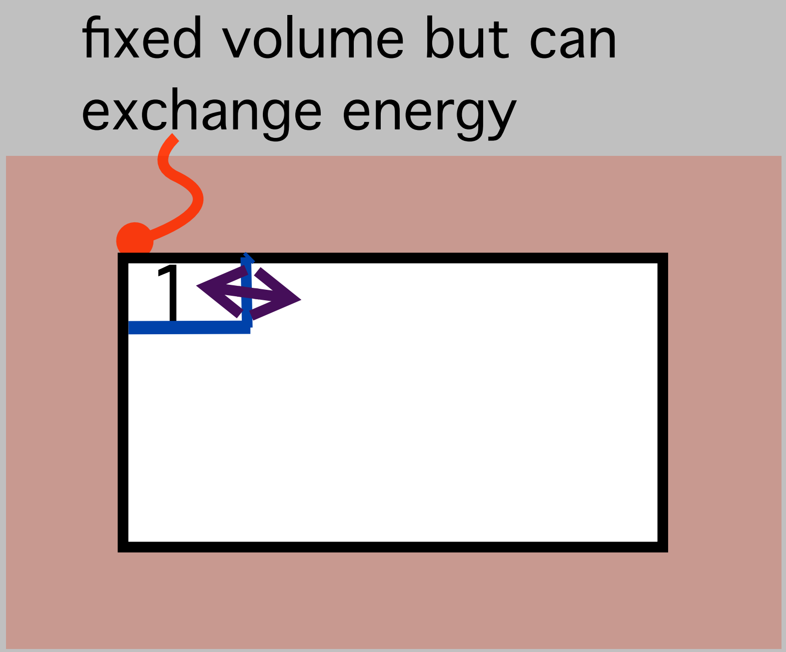
$$\mathrm{d}(U_1 - TS_1) \leq 0$$

Let us define the <u>Helmholtz free energy</u>: A

$$A \equiv U - TS$$

For box 1 we can write $\mathrm{d}A_1 \leq 0$

Constant T and V



Total system is isolated and the volume is constant

Box 1: constant volume and temperature

2nd law: $$T dS_1 - dU_1 \geq 0$$

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

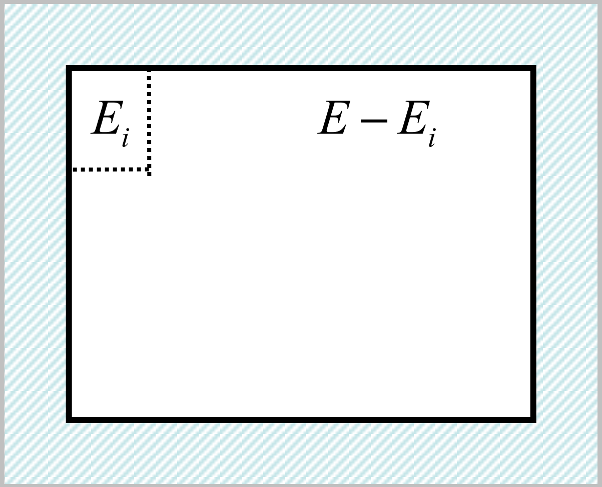
Let us define the Helmholtz free energy: A

$$A \equiv U - TS$$

For box 1 we can write $dA_1 \leq 0$

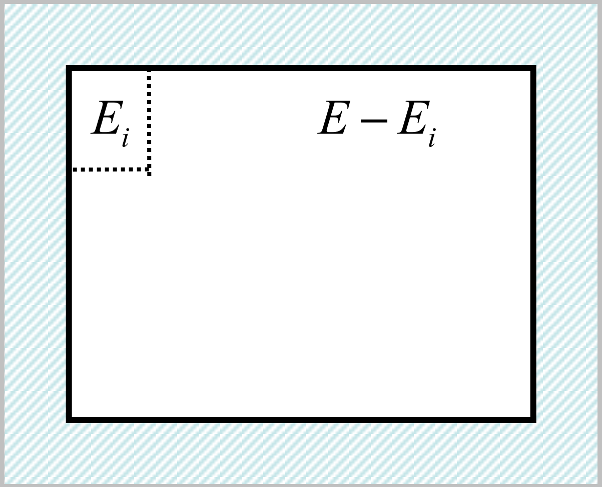
Hence, for a system at constant temperature and volume the Helmholtz free energy decreases and takes its minimum value at equilibrium

Canonical ensemble



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

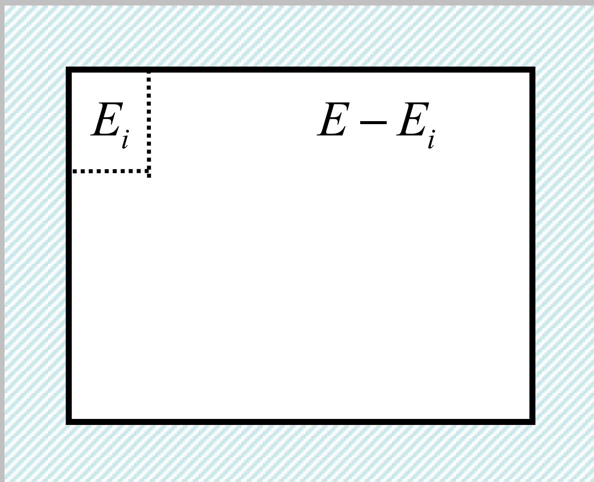
Canonical ensemble



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

$$\ln\Omega\left(E - E_i\right) = \ln\Omega\left(E\right) - \frac{\partial \ln\Omega}{\partial E} E_i + \cdots$$

Canonical ensemble

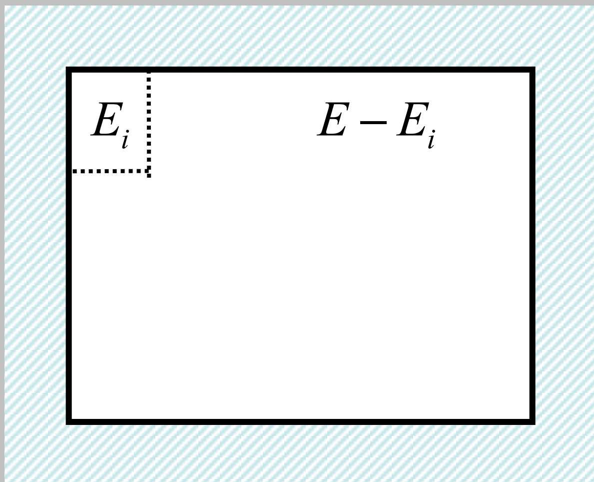


Consider a small system that can exchange heat with a big reservoir

$$\ln\Omega\left(E - E_i\right) = \ln\Omega\left(E\right) - \frac{\partial \ln\Omega}{\partial E} E_i + \cdots$$

$1/k_B T$

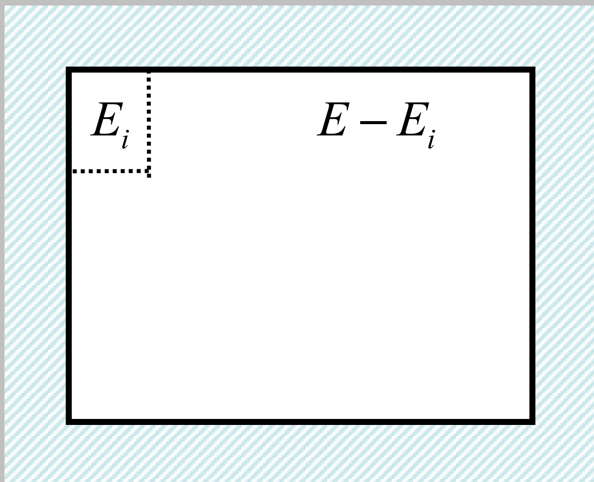
Canonical ensemble



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

$$\ln \Omega (E - E_i) = \ln \Omega (E) - \frac{\partial \ln \Omega}{\partial E} E_i + \cdots$$

Canonical ensemble

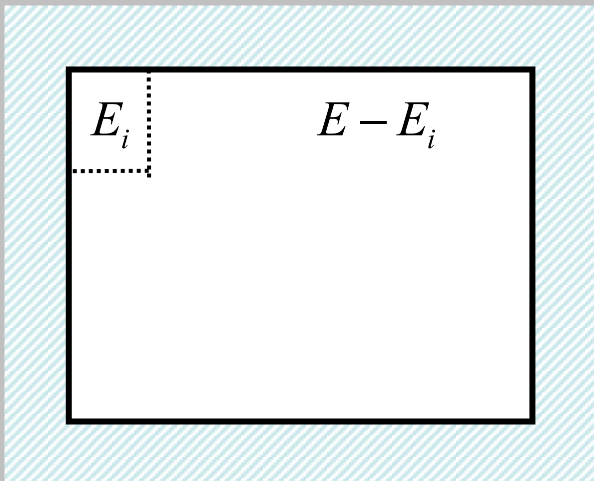


Consider a small system that can exchange heat with a big reservoir

$$\ln \Omega\left(E - E_i\right) = \ln \Omega\left(E\right) - \frac{\partial \ln \Omega}{\partial E} E_i + \cdots$$

$$\ln \frac{\Omega\left(E - E_i\right)}{\Omega\left(E\right)} = -\frac{E_i}{k_B T}$$

Canonical ensemble



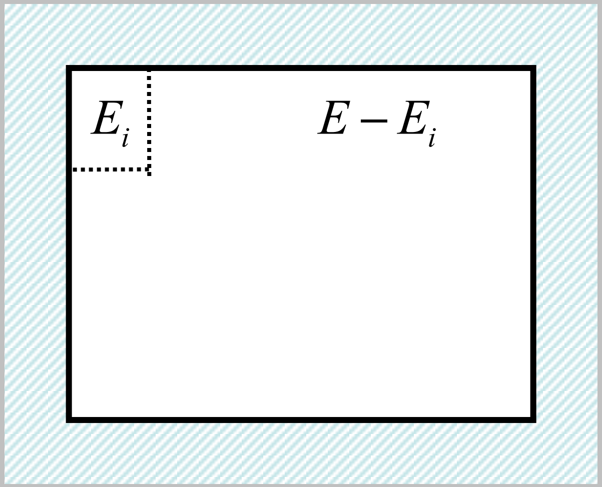
Consider a small system that can exchange heat with a big reservoir

$$\ln \Omega\left(E - E_i\right) = \ln \Omega\left(E\right) - \frac{\partial \ln \Omega}{\partial E} E_i + \cdots$$

$$\ln \frac{\Omega\left(E - E_i\right)}{\Omega\left(E\right)} = -\frac{E_i}{k_B T}$$

Hence, the probability to find E_i:

Canonical ensemble



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

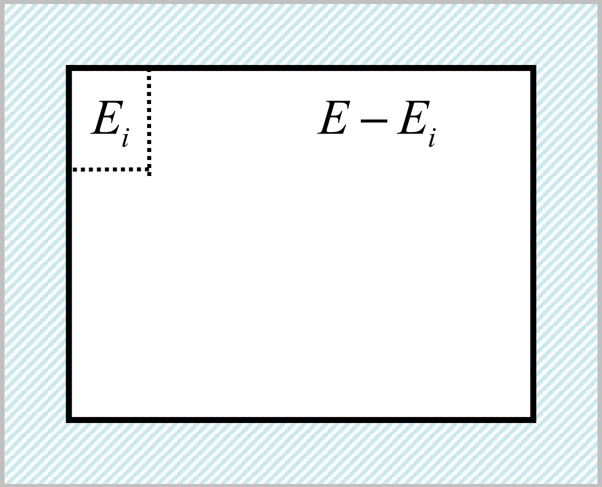
$$\ln \Omega(E - E_i) = \ln \Omega(E) - \frac{\partial \ln \Omega}{\partial E} E_i + \cdots$$

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

Hence, the probability to find E_i:

$$P(E_i) = \frac{\Omega(E - E_i)}{\sum_j \Omega(E - E_j)} = \frac{\exp(-E_i / k_B T)}{\sum_j \exp(-E_j / k_B T)}$$

Canonical ensemble



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

$$\ln \Omega (E - E_i) = \ln \Omega (E) - \frac{\partial \ln \Omega}{\partial E} E_i + \cdots$$

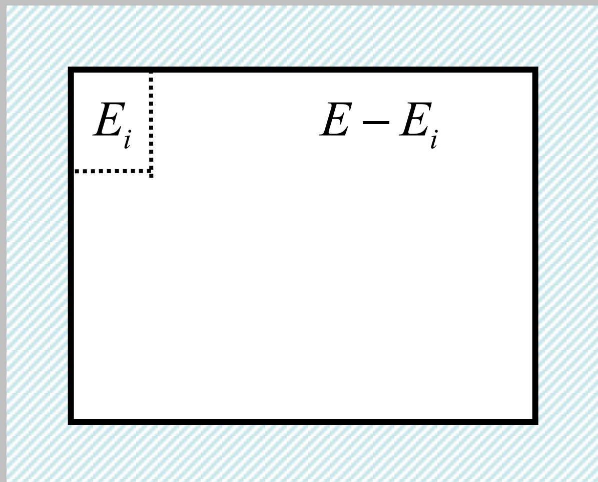
$$\ln \frac{\Omega (E - E_i)}{\Omega (E)} = -\frac{E_i}{k_B T}$$

Hence, the probability to find E_i:

$$P(E_i) = \frac{\Omega (E - E_i)}{\sum_j \Omega (E - E_j)} = \frac{\exp(-E_i / k_B T)}{\sum_j \exp(-E_j / k_B T)}$$

$$P(E_i) \propto \exp(-E_i / k_B T)$$

Canonical ensemble



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

$$\ln \Omega\left(E - E_i\right) = \ln \Omega\left(E\right) - \frac{\partial \ln \Omega}{\partial E} E_i + \cdots$$

$$\ln \frac{\Omega\left(E - E_i\right)}{\Omega\left(E\right)} = -\frac{E_i}{k_B T}$$

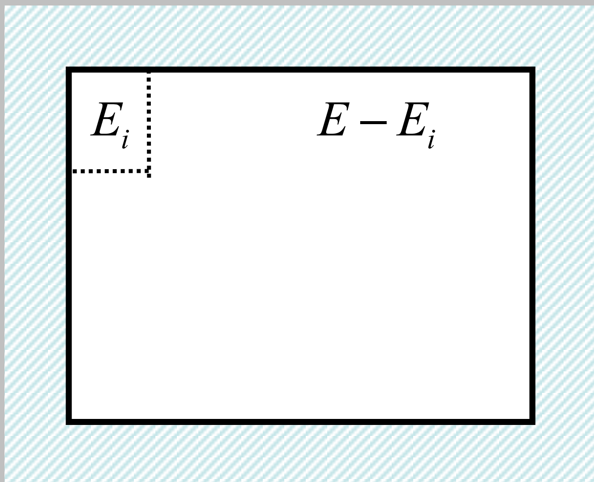
Hence, the probability to find E_i:

$$P\left(E_i\right) = \frac{\Omega\left(E - E_i\right)}{\sum_j \Omega\left(E - E_j\right)} = \frac{\exp\left(-E_i / k_B T\right)}{\sum_j \exp\left(-E_j / k_B T\right)}$$

$$P\left(E_i\right) \propto \exp\left(-E_i / k_B T\right)$$

Boltzmann distribution

Canonical ensemble



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

$$\ln \Omega(E - E_i) = \ln \Omega(E) - \frac{\partial \ln \Omega}{\partial E} E_i + \cdots$$

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

Hence, the probability to find E_i:

$$P(E_i) = \frac{\Omega(E - E_i)}{\sum_j \Omega(E - E_j)} = \frac{\exp(-E_i/k_B T)}{\sum_j \exp(-E_j/k_B T)}$$

$$P(E_i) \propto \exp(-E_i/k_B T)$$

Boltzmann distribution

Thermodynamics

What is the average energy of the system?

Thermodynamics

What is the average energy of the system?

$$\langle E \rangle \equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}$$

Thermodynamics

What is the average energy of the system?

$$\langle E \rangle \equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}$$

$$= -\frac{\partial \ln \sum_i \exp(-\beta E_i)}{\partial \beta}$$

Thermodynamics

What is the average energy of the system?

$$\langle E \rangle \equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}$$

$$= -\frac{\partial \ln \sum_i \exp(-\beta E_i)}{\partial \beta}$$

$$= -\frac{\partial \ln Q_{N,V,T}}{\partial \beta}$$

Thermodynamics

What is the average energy of the system?

$$\langle E \rangle \equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}$$

$$= -\frac{\partial \ln \sum_i \exp(-\beta E_i)}{\partial \beta}$$

$$= -\frac{\partial \ln Q_{N,V,T}}{\partial \beta}$$

Compare:

$$\left(\frac{\partial F/T}{\partial 1/T} \right) = E$$

Thermodynamics

First law of thermodynamics

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V$$

Thermodynamics

First law of thermodynamics

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V$$

Helmholtz Free energy:

Thermodynamics

First law of thermodynamics

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V$$

Helmholtz Free energy:

$$F \equiv E - TS$$

Thermodynamics

First law of thermodynamics

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V$$

Helmholtz Free energy:

$$F \equiv E - TS$$

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$$

Thermodynamics

First law of thermodynamics

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V$$

Helmholtz Free energy:

$$F \equiv E - TS$$

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$$

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

Thermodynamics

First law of thermodynamics

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V$$

Helmholtz Free energy:

$$F \equiv E - TS$$

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$$

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

$$= F + TS = E$$

What is the average energy of the system?

What is the average energy of the system?

$$\langle E \rangle \equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}$$

What is the average energy of the system?

$$\langle E \rangle \equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}$$

$$= -\frac{\partial \ln \sum_i \exp(-\beta E_i)}{\partial \beta}$$

What is the average energy of the system?

$$\langle E \rangle \equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}$$

$$= -\frac{\partial \ln \sum_i \exp(-\beta E_i)}{\partial \beta}$$

$$= -\frac{\partial \ln Q_{N,V,T}}{\partial \beta}$$

What is the average energy of the system?

$$\langle E \rangle \equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}$$

$$= -\frac{\partial \ln \sum_i \exp(-\beta E_i)}{\partial \beta}$$

$$= -\frac{\partial \ln Q_{N,V,T}}{\partial \beta}$$

Compare:

$$\left(\frac{\partial F/T}{\partial 1/T} \right) = E$$

What is the average energy of the system?

$$\langle E \rangle \equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}$$

$$= -\frac{\partial \ln \sum_i \exp(-\beta E_i)}{\partial \beta}$$

$$= -\frac{\partial \ln Q_{N,V,T}}{\partial \beta}$$

Compare:

$$\left(\frac{\partial F/T}{\partial 1/T}\right) = E$$

Hence:

$$\frac{F}{k_B T} = -\ln Q_{N,V,T}$$

Atoms?

We have assumed that we can count states

Atoms?

We have assumed that we can count states

- Quantum Mechanics: energy discreet

Atoms?

We have assumed that we can count states

- Quantum Mechanics: energy discreet
  - What to do for classical model such as an ideal gas, hard spheres, Lennard-Jones?

Atoms?

We have assumed that we can count states

Quantum Mechanics: energy discreet

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

Energy is continue:

- potential energy
- kinetic energy

Atoms?

We have assumed that we can count states

Quantum Mechanics: energy discreet

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

Energy is continue:

- potential energy
- kinetic energy

Particle in a box:

Atoms?

We have assumed that we can count states

Quantum Mechanics: energy discreet

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

Energy is continue:

- potential energy
- kinetic energy

Particle in a box:

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

Atoms?

We have assumed that we can count states

Quantum Mechanics: energy discreet

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

Energy is continue:
- potential energy
- kinetic energy

Particle in a box:

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

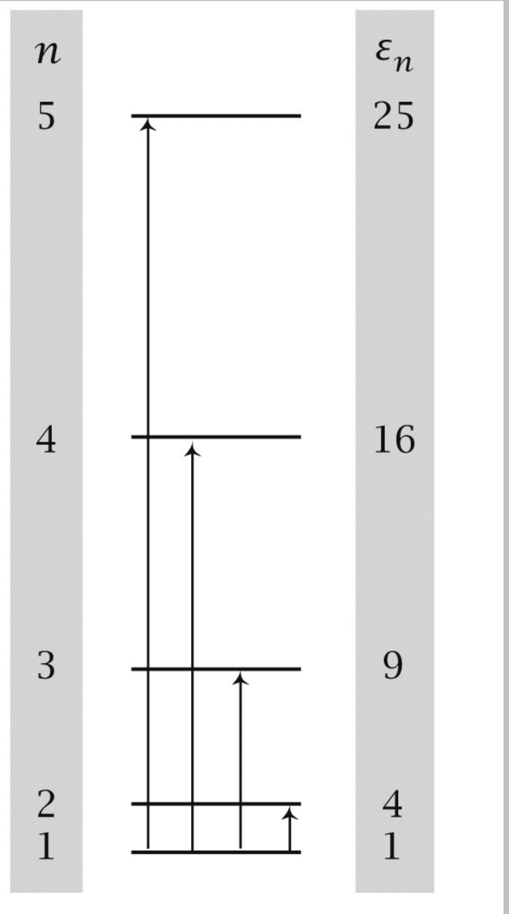


Figure 11.4 Molecular Driving Forces 2/e (© Garland Science 2011)

Atoms?

We have assumed that we can count states

Quantum Mechanics: energy discreet

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

Energy is continue:

- potential energy
- kinetic energy

Particle in a box:

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

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

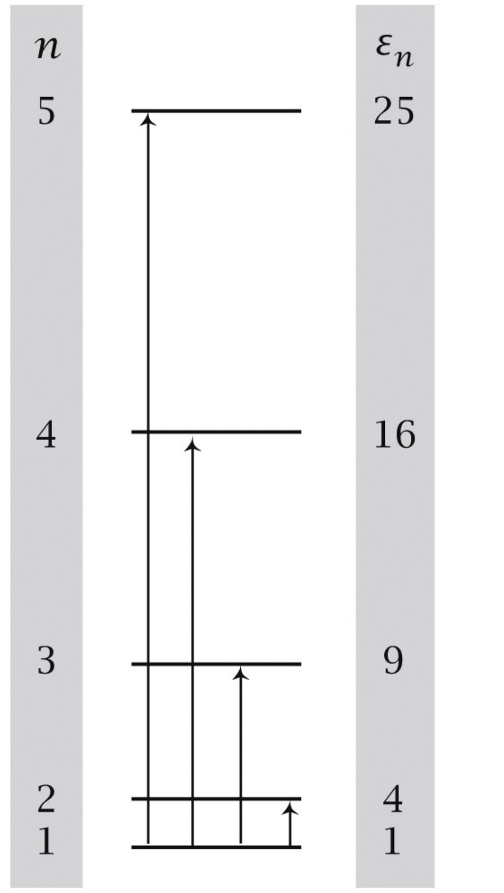


Figure 11.4 Molecular Driving Forces 2/e (© Garland Science 2011)

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

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

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

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

Argon: m=40 g/mol=6.63×10^{-26} kg

h=6.63×10^{-34} J s

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

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

Argon: m=40 g/mol=6.63×10^{-26} kg

h=6.63×10^{-34} J s

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

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

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

Argon: m=40 g/mol=6.63×10^{-26} kg

h=6.63×10^{-34} J s

$$\varepsilon_n = 5\times10^{-39} n^2 (J)$$

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

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

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

Argon: m=40 g/mol=6.63×10^{-26} kg

h=6.63×10^{-34} J s

$$\varepsilon_n = 5\times10^{-39} n^2 (J)$$

Kinetic energy of Ar at room temperature $\approx 4.14\times10^{-21}$ J

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

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

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

Argon: m=40 g/mol=6.63×10^{-26} kg
h=6.63×10^{-34} J s

$$\varepsilon_n = 5\times10^{-39} n^2 (J)$$

Kinetic energy of Ar at room temperature ≈4.14×10^{-21} J

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

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

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

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

Argon: m=40 g/mol=6.63×10^{-26} kg

h=6.63×10^{-34} J s

$$\varepsilon_n = 5\times10^{-39} n^2 (J)$$

Kinetic energy of Ar at room temperature ≈4.14×10^{-21} J

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

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

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

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

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

Argon: m=40 g/mol=6.63×10^{-26} kg
h=6.63×10^{-34} J s

$$\varepsilon_n = 5\times10^{-39} n^2 (J)$$

Kinetic energy of Ar at room temperature ≈4.14×10^{-21} J

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

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

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

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

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

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

Argon: m=40 g/mol=6.63×10^{-26} kg
h=6.63×10^{-34} J s

$$\varepsilon_n = 5\times10^{-39} n^2 (J)$$

Kinetic energy of Ar at room temperature ≈4.14×10^{-21} J

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

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

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

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

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

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

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

Argon: m=40 g/mol=6.63×10^{-26} kg
h=6.63×10^{-34} J s

$$\varepsilon_n = 5\times10^{-39} n^2 (J)$$

Kinetic energy of Ar at room temperature ≈4.14 × 10^{-21} J

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

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

$$q_{translational} = \int_0^{\infty} e^{-\frac{(nh)^2}{8mL^2k_BT}} dn \qquad q_{translational} = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{1}{2}} L$$

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

De Broglie wavelength

Partition function; $$q = \sum_{n=1}^{\infty} e^{-E_n} = \int e^{-E_n}\, dn$$

Partition function; $q = \sum_{n=1}^{\infty} e^{-E_n} = \int e^{-E_n} \, dn$

Hamiltonian: $H = U_{kin} + U_{pot} = \sum_i \frac{p_i^2}{2m_i} + U_{pot}\left(r^N\right)$

Partition function;

$$q = \sum_{n=1}^{\infty} e^{-E_n} = \int e^{-E_n}\, dn$$

Hamiltonian:

$$H = U_{kin} + U_{pot} = \sum_i \frac{p_i^2}{2m_i} + U_{pot}\left(r^N\right)$$

$$Z_{1,V,T} = C \int e^{-\frac{p^2}{2m\, k_B T}}\, dp^{3N} \int e^{-\frac{U_p(r)}{k_B T}}\, dr^{3N}$$

Partition function; $$q = \sum_{n=1}^{\infty} e^{-E_n} = \int e^{-E_n}\, dn$$

Hamiltonian: $$H = U_{kin} + U_{pot} = \sum_i \frac{p_i^2}{2m_i} + U_{pot}\left(r^N\right)$$

$$Z_{1,V,T} = C \int e^{-\frac{p^2}{2m\, k_B T}}\, dp^{3N} \int e^{-\frac{U_p(r)}{k_B T}}\, dr^{3N}$$

One ideal gas molecule: $U_p(r)=0$

Partition function;
$$q = \sum_{n=1}^{\infty} e^{-E_n} = \int e^{-E_n}\, dn$$

Hamiltonian:
$$H = U_{kin} + U_{pot} = \sum_i \frac{p_i^2}{2m_i} + U_{pot}\left(r^N\right)$$

$$Z_{1,V,T} = C \int e^{-\frac{p^2}{2m\, k_B T}}\, dp^{3N} \int e^{-\frac{U_p(r)}{k_B T}}\, dr^{3N}$$

One ideal gas molecule: $U_p(r)=0$
$$Z_{1,V,T}^{IG} = C \int e^{-\frac{p^2}{2m\, k_B T}}\, dp \int dr = CV\left(2\pi m k_B T\right)^{\frac{3}{2}}$$

Partition function; $$q = \sum_{n=1}^{\infty} e^{-E_n} = \int e^{-E_n}\, dn$$

Hamiltonian: $$H = U_{kin} + U_{pot} = \sum_i \frac{p_i^2}{2m_i} + U_{pot}\left(r^N\right)$$

$$Z_{1,V,T} = C \int e^{-\frac{p^2}{2m\ k_B T}}\, dp^{3N} \int e^{-\frac{U_p(r)}{k_B T}}\, dr^{3N}$$

One ideal gas molecule: $U_p(r)=0$

$$Z_{1,V,T}^{IG} = C \int e^{-\frac{p^2}{2m\ k_B T}}\, dp \int dr = CV\left(2\pi m k_B T\right)^{\frac{3}{2}}$$

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

Partition function; $$q = \sum_{n=1}^{\infty} e^{-E_n} = \int e^{-E_n}\, dn$$

Hamiltonian: $$H = U_{kin} + U_{pot} = \sum_i \frac{p_i^2}{2m_i} + U_{pot}\left(r^N\right)$$

$$Z_{1,V,T} = C \int e^{-\frac{p^2}{2m\, k_B T}}\, dp^{3N} \int e^{-\frac{U_p(r)}{k_B T}}\, dr^{3N}$$

One ideal gas molecule: $U_p(r)=0$

$$Z_{1,V,T}^{IG} = C \int e^{-\frac{p^2}{2m\, k_B T}}\, dp \int dr = CV\left(2\pi m k_B T\right)^{\frac{3}{2}}$$

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

$$Z_{1,V,T}^{IG} = CV\left(2\pi m k_B T\right)^{\frac{3}{2}} = \frac{V}{\Lambda^3}$$

N gas molecules:

$$Z_{N,V,T} = \frac{1}{h^{3N}} \int e^{-\frac{p^2}{2m\, k_B T}} \, dp^N \int e^{-\frac{U(r)}{k_B T}} \, dr^N$$

N gas molecules:

$$Z_{N,V,T} = \frac{1}{h^{3N}} \int e^{-\frac{p^2}{2m\, k_B T}} \, dp^N \int e^{-\frac{U(r)}{k_B T}} \, dr^N$$

WRONG!
Particles are indistinguishable

N gas molecules:

$$Z_{N,V,T} = \frac{1}{h^{3N}} \int e^{-\frac{p^2}{2m\, k_B T}}\, dp^N \int e^{-\frac{U(r)}{k_B T}}\, dr^N$$

WRONG!
Particles are
indistinguishable

$$Z_{N,V,T} = \frac{1}{h^{3N} N!} \int e^{-\frac{p^2}{2m\, k_B T}}\, dp^N \int e^{-\frac{U(r)}{k_B T}}\, dr^N$$

N gas molecules:

$$Z_{N,V,T} = \frac{1}{h^{3N}} \int e^{-\frac{p^2}{2m\, k_B T}} dp^N \int e^{-\frac{U(r)}{k_B T}} dr^N$$

WRONG!
Particles are
indistinguishable

$$Z_{N,V,T} = \frac{1}{h^{3N} N!} \int e^{-\frac{p^2}{2m\, k_B T}} dp^N \int e^{-\frac{U(r)}{k_B T}} dr^N$$

Configurational part of
the partition function:

N gas molecules:

$$Z_{N,V,T} = \frac{1}{h^{3N}} \int e^{-\frac{p^2}{2m\, k_B T}} dp^N \int e^{-\frac{U(r)}{k_B T}} dr^N$$

WRONG!
Particles are
indistinguishable

$$Z_{N,V,T} = \frac{1}{h^{3N} N!} \int e^{-\frac{p^2}{2m\, k_B T}} dp^N \int e^{-\frac{U(r)}{k_B T}} dr^N$$

Configurational part of
the partition function:

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

Question

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

ideal gas molecules:

$$Q_{N,V,T}^{IG} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

ideal gas molecules:

$$Q_{N,V,T}^{IG} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy:

ideal gas molecules:

$$Q_{N,V,T}^{IG} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy:

$$F^{IG} = -k_B T \ln Q_{N,V,T}^{IG} = k_B T N \left[\ln \Lambda^3 - \ln \left(V/N \right) \right]$$

ideal gas molecules: $$Q_{N,V,T}^{IG} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy: $$F^{IG} = -k_B T \ln Q_{N,V,T}^{IG} = k_B T N \left[\ln \Lambda^3 - \ln\left(V/N\right) \right]$$

$$F^{IG} = F^0 + k_B T N \ln \rho$$

ideal gas molecules:

$$Q_{N,V,T}^{IG} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy:

$$F^{IG} = -k_B T \ln Q_{N,V,T}^{IG} = k_B TN \left[\ln \Lambda^3 - \ln\left(V/N \right) \right]$$

$$F^{IG} = F^0 + k_B TN \ln \rho$$

Pressure:

ideal gas molecules:

$$Q_{N,V,T}^{IG} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy:

$$F^{IG} = -k_B T \ln Q_{N,V,T}^{IG} = k_B T N \left[\ln \Lambda^3 - \ln \left(V/N \right) \right]$$

$$F^{IG} = F^0 + k_B T N \ln \rho$$

Pressure:

$$p = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T N \frac{1}{V}$$

ideal gas molecules: $$Q_{N,V,T}^{IG} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy: $$F^{IG} = -k_B T \ln Q_{N,V,T}^{IG} = k_B T N \left[\ln \Lambda^3 - \ln\left(V/N \right) \right]$$

$$F^{IG} = F^0 + k_B T N \ln \rho$$

Pressure: $$p = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T N \frac{1}{V}$$

Energy:

ideal gas molecules:

$$Q_{N,V,T}^{IG} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy:

$$F^{IG} = -k_B T \ln Q_{N,V,T}^{IG} = k_B T N \left[\ln \Lambda^3 - \ln\left(V/N\right) \right]$$

$$F^{IG} = F^0 + k_B T N \ln \rho$$

Pressure:

$$p = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T N \frac{1}{V}$$

Energy:

$$E = \left(\frac{\partial F/T}{\partial 1/T} \right)_{V,N} = 3 k_B N \left(\frac{\partial \ln \Lambda}{\partial 1/T} \right)_{V,N}$$

ideal gas molecules:

$$Q_{N,V,T}^{IG} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy:

$$F^{IG} = -k_B T \ln Q_{N,V,T}^{IG} = k_B T N \left[\ln \Lambda^3 - \ln\left(V/N \right) \right]$$

$$F^{IG} = F^0 + k_B T N \ln \rho$$

Pressure:

$$p = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T N \frac{1}{V}$$

Energy:

$$E = \left(\frac{\partial F/T}{\partial 1/T} \right)_{V,N} = 3 k_B N \left(\frac{\partial \ln \Lambda}{\partial 1/T} \right)_{V,N}$$

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

ideal gas molecules:

$$Q^{IG}_{N,V,T} = \frac{V^N}{\Lambda^{3N} N!}$$

All thermodynamics follows from the partition function!

Free energy:

$$F^{IG} = -k_B T \ln Q^{IG}_{N,V,T} = k_B T N \left[\ln \Lambda^3 - \ln\left(V/N\right) \right]$$

$$F^{IG} = F^0 + k_B T N \ln \rho$$

Pressure:

$$p = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T N \frac{1}{V}$$

Energy:

$$E = \left(\frac{\partial F/T}{\partial 1/T} \right)_{V,N} = 3 k_B N \left(\frac{\partial \ln \Lambda}{\partial 1/T} \right)_{V,N}$$

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

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

Chemical potential: $\mu_\mathrm{i} = \left(\frac{\partial \mathrm{F}}{\partial N_i} \right)_{T,V,N_j}$

Chemical potential:

$$\mu_{\mathrm{i}} = \left(\frac{\partial \mathrm{F}}{\partial N_i} \right)_{T,V,N_j}$$

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

Chemical potential: $$\mu_{\mathrm{i}} = \left(\frac{\partial \mathrm{F}}{\partial N_i} \right)_{T,V,N_j}$$

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

$$\beta\mu = \ln \Lambda^3 + \ln \rho + 1$$

Chemical potential: $\mu_{\mathrm{i}} = \left(\frac{\partial \mathrm{F}}{\partial N_i} \right)_{T,V,N_j}$

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

$$\beta\mu = \ln \Lambda^3 + \ln \rho + 1$$

$$\beta\mu^{IG} = \beta\mu^0 + \ln \rho$$

Summary:
Canonical ensemble (N, V, T)

Summary:
Canonical ensemble (*N*, *V*, *T*)

Partition function:

$$Q(N,V,T)=\frac{1}{\Lambda^{3N}N!}\int \mathrm{d}\mathbf{r}^{N}\exp\left[-\beta U\left(r^{N}\right)\right]$$

Summary:
Canonical ensemble (*N*, *V*, *T*)

Partition function:

$$Q(N,V,T) = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N \exp\left[-\beta U\left(r^N\right)\right]$$

Probability to find a particular configuration

$$P(\Gamma) \propto \exp\left[-\beta U(\Gamma)\right]$$

Summary:
Canonical ensemble (N, V, T)

Partition function:

$$Q(N,V,T) = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N \exp\left[-\beta U\left(r^N\right)\right]$$

Probability to find a particular configuration

$$P(\Gamma) \propto \exp\left[-\beta U(\Gamma)\right]$$

Free energy

$$\beta F = -\ln Q_{N,V,T}$$

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

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

Partition function:

$$Q(N,V,E) = \frac{1}{h^{3N} N!} \iint \mathrm{d}\mathbf{p}^N \mathrm{d}\mathbf{r}^N \delta\left(H\left(\mathbf{p}^N, \mathbf{r}^N\right) - E\right)$$

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

Partition function:

$$Q(N,V,E)=\frac{1}{h^{3N}N!}\iint \mathrm{d}\mathbf{p}^N \mathrm{d}\mathbf{r}^N \delta\left(H\left(\mathbf{p}^N,\mathbf{r}^N\right)-E\right)$$

Probability to find a particular configuration

$$P(\Gamma)\propto 1$$

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

Partition function:

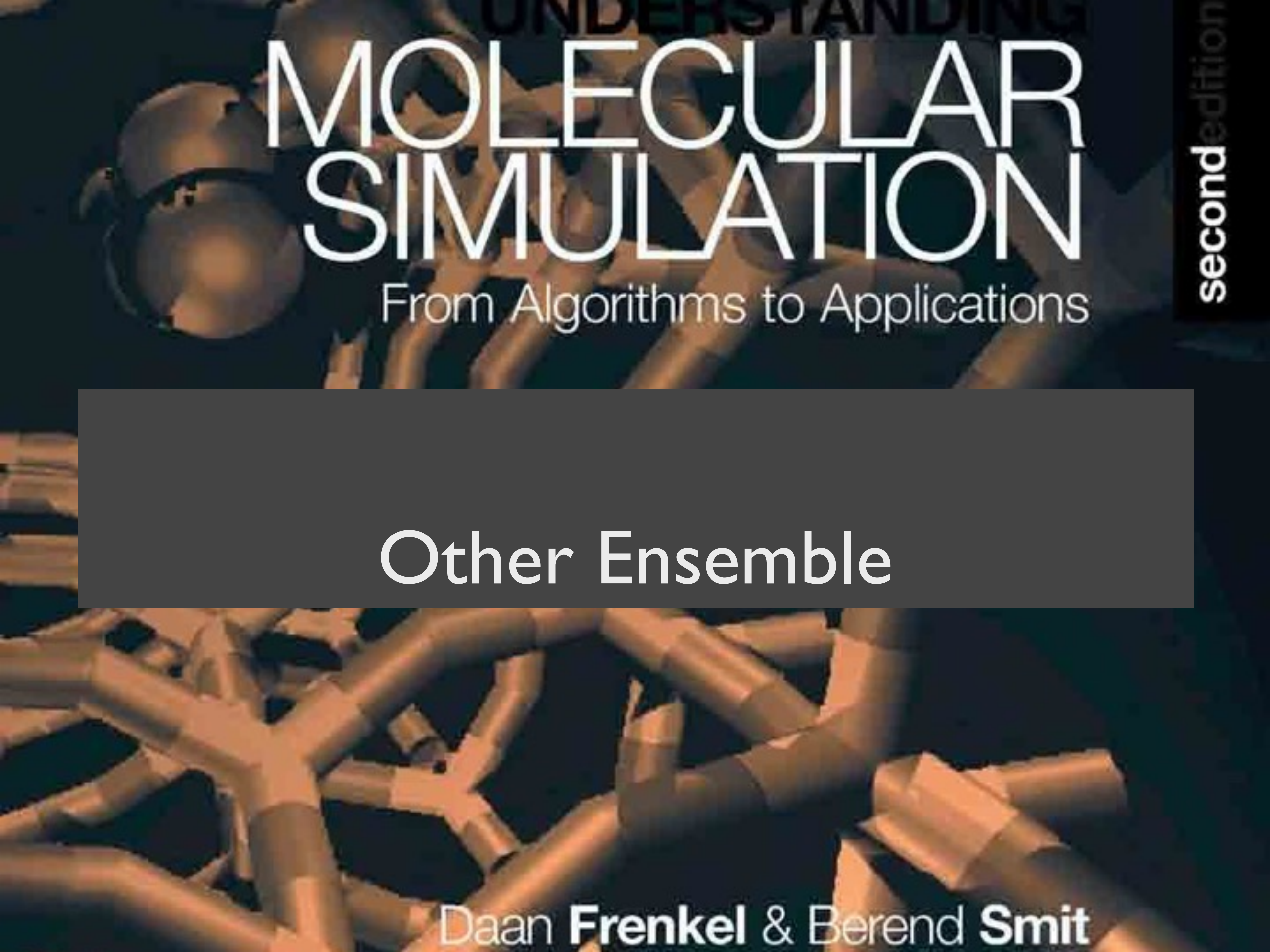
$$Q(N,V,E)=\frac{1}{h^{3N}N!}\iint d\mathbf{p}^N d\mathbf{r}^N \delta\left(H\left(\mathbf{p}^N,\mathbf{r}^N\right)-E\right)$$

Probability to find a particular configuration

$$P(\Gamma)\propto 1$$

Free energy

$$\beta S=\ln Q_{N,V,E}$$



Other Ensemble

Other ensembles?

Other ensembles?

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

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.

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.

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 wee need to know the Statistical Thermodynamics of the various ensembles.

Other ensembles?

In the thermodynamic limit the thermodynami
independent of the ensemble: so buy a bigger

COURSE:
MD and MC different
ensembles

However, it is most of the times much better to th 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 wee need to know the Statistical Thermodynamics of the various ensembles.

Other ensembles?

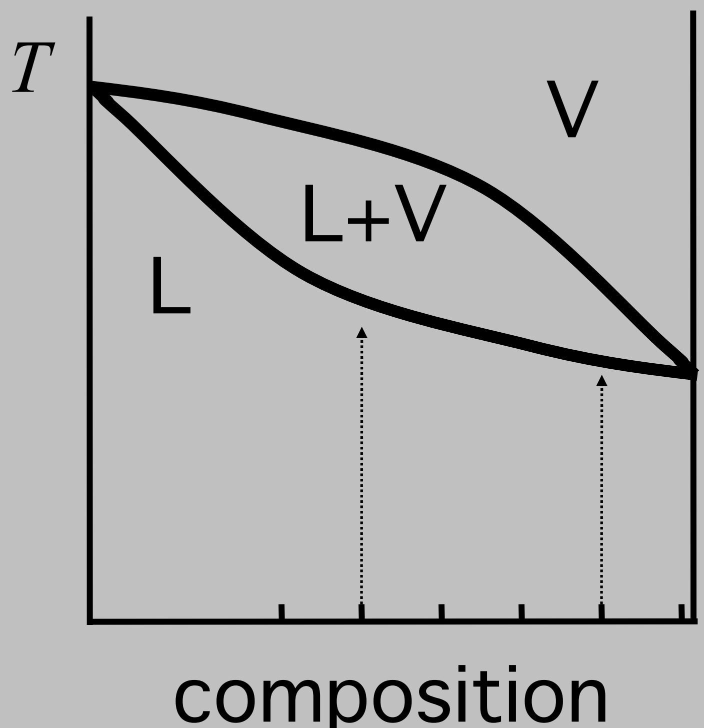
In the thermodynamic limit the thermodynamic properties are independent of the ensemble: so buy a bigger computer ···

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

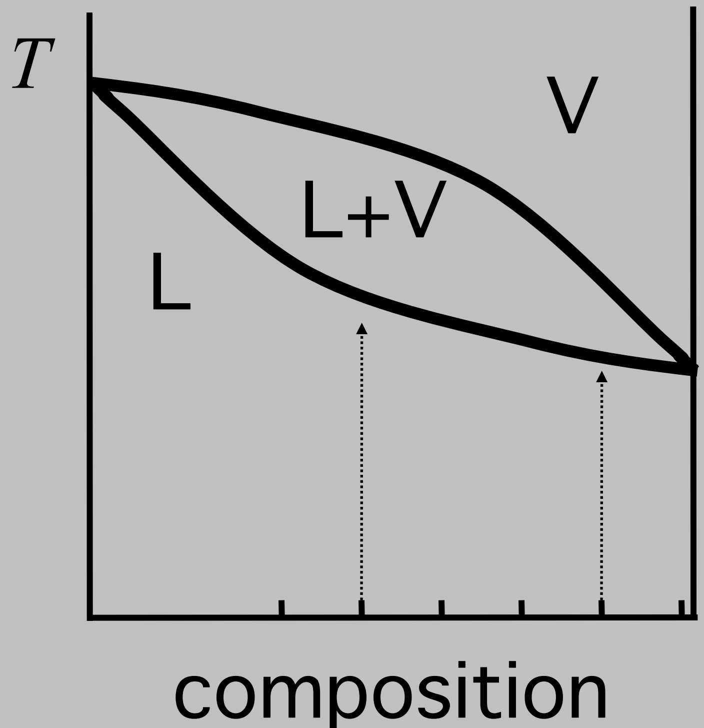
For this it is important to know how to simulate in the various ensembles.

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

Example (1): vapour-liquid equilibrium mixture

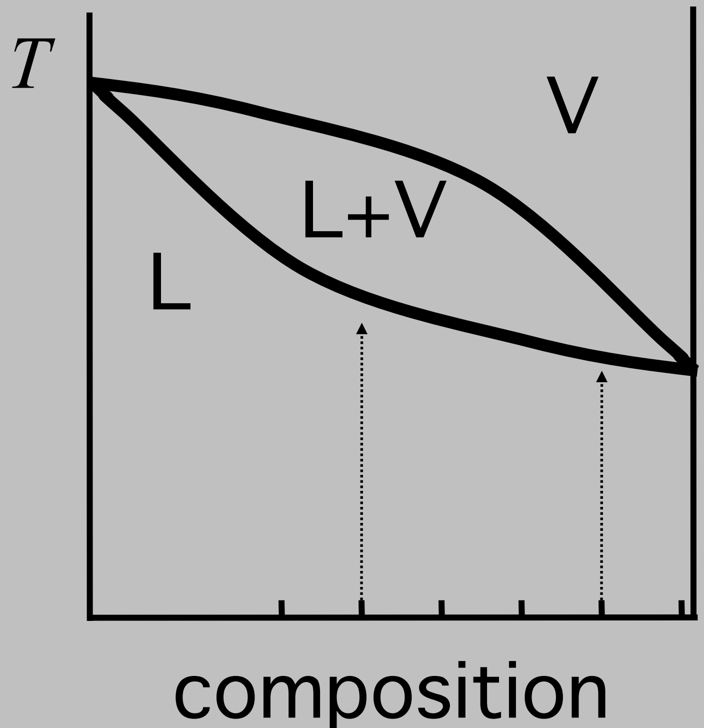


Example (1): vapour-liquid equilibrium mixture



Measure the composition of the coexisting vapour and liquid phases if we start with a homogeneous liquid of two different compositions:

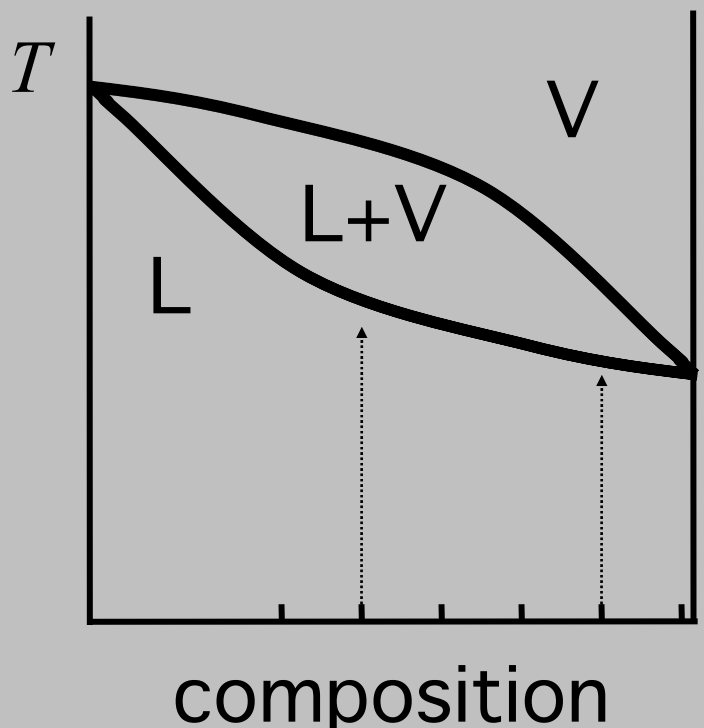
Example (1): vapour-liquid equilibrium mixture



Measure the composition of the coexisting vapour and liquid phases if we start with a homogeneous liquid of two different compositions:

- How to mimic this with the N,V,T ensemble?

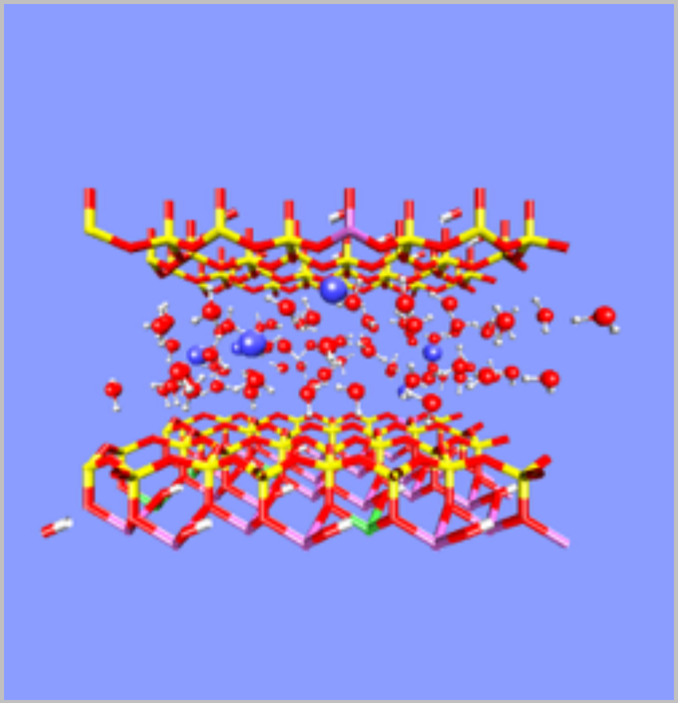
Example (1): vapour-liquid equilibrium mixture



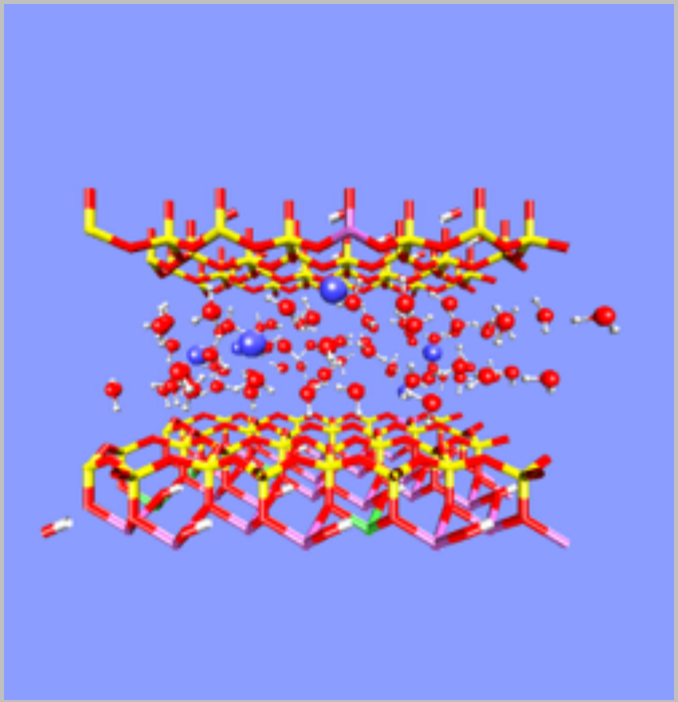
Measure the composition of the coexisting vapour and liquid phases if we start with a homogeneous liquid of two different compositions:

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

Example (2): swelling of clays



Example (2): swelling of clays



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

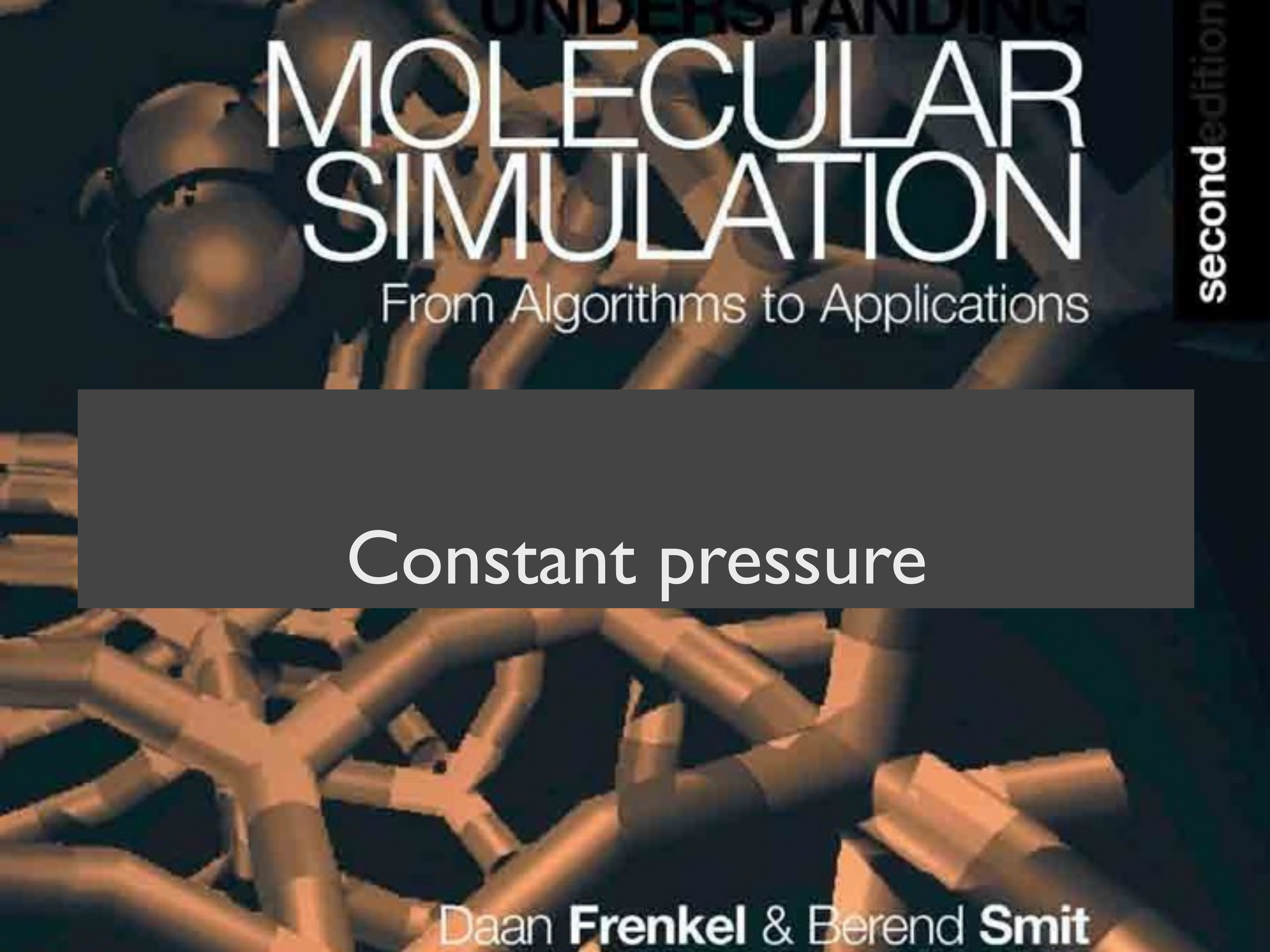
- How to mimic this in the N,V,T ensemble?
- What is a better ensemble to use?

Ensembles

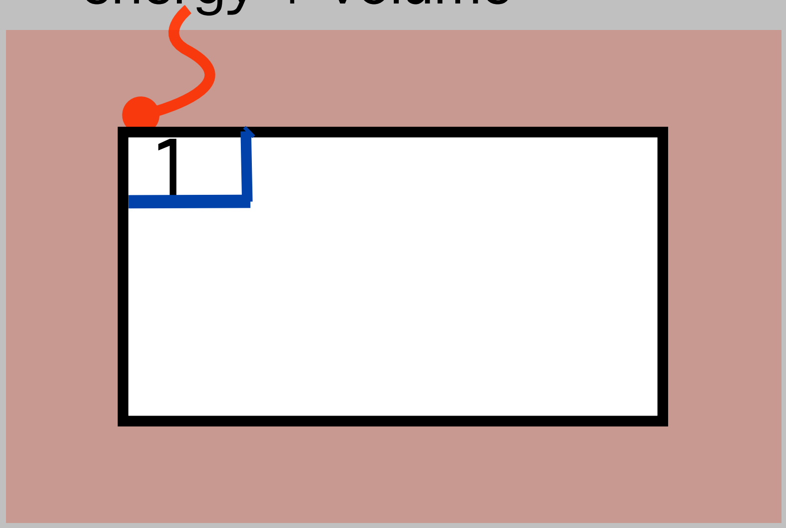
Ensembles

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

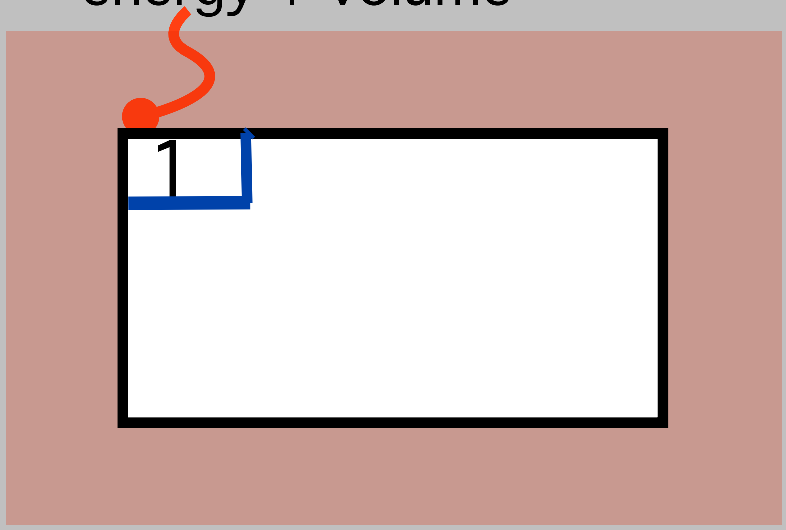
Constant pressure



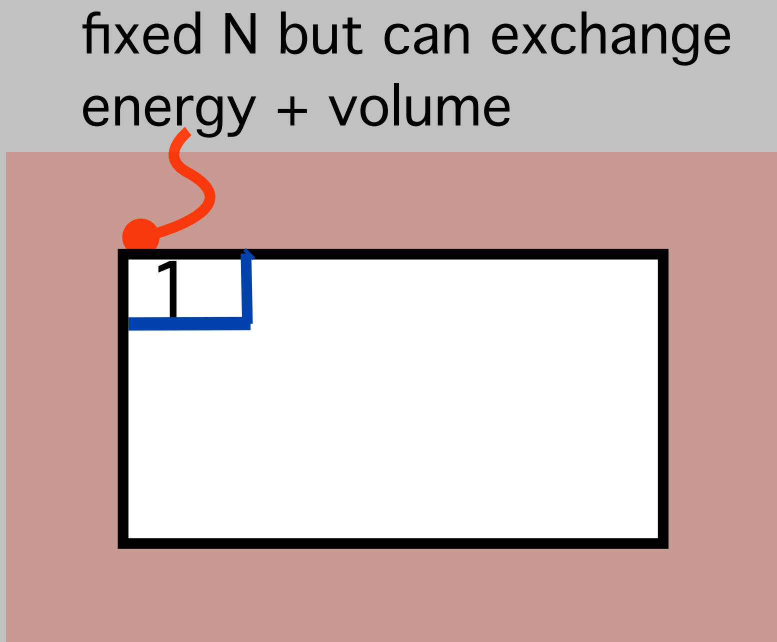
fixed N but can exchange
energy + volume



fixed N but can exchange energy + volume



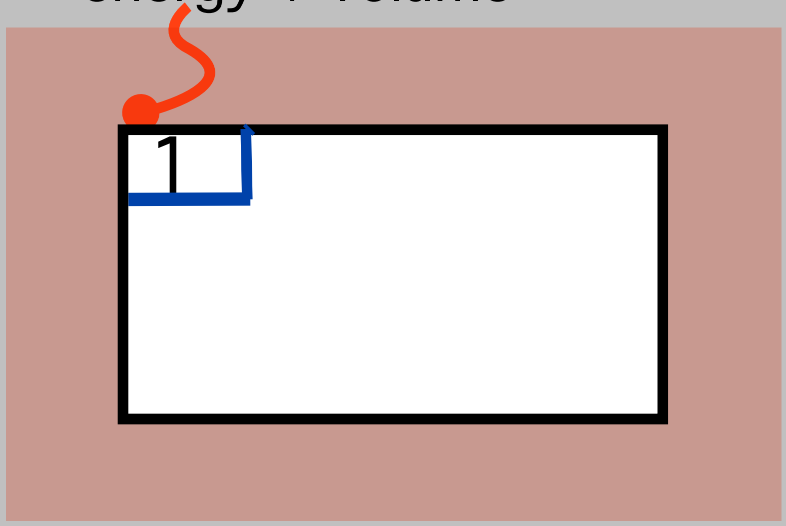
We have our box 1 and a bath



We have our box 1 and a bath

Total system is isolated and the volume is constant

fixed N but can exchange energy + volume

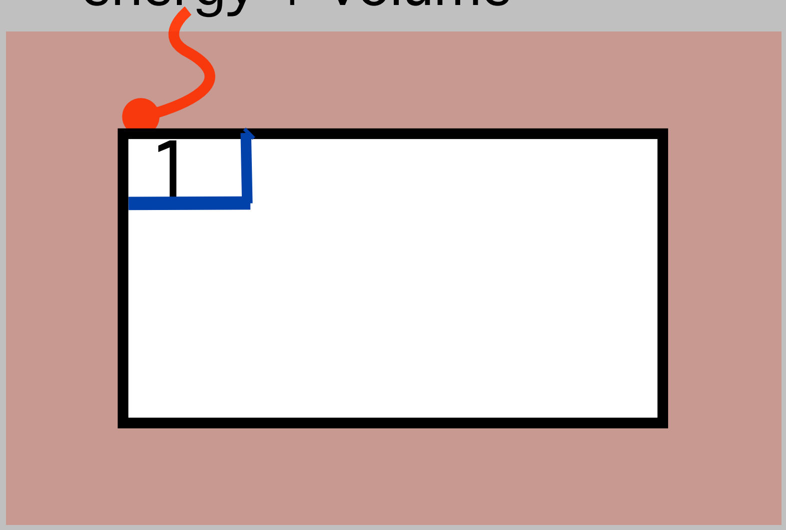


We have our box 1 and a bath

<u>Total system</u> is isolated and the volume is constant

First law

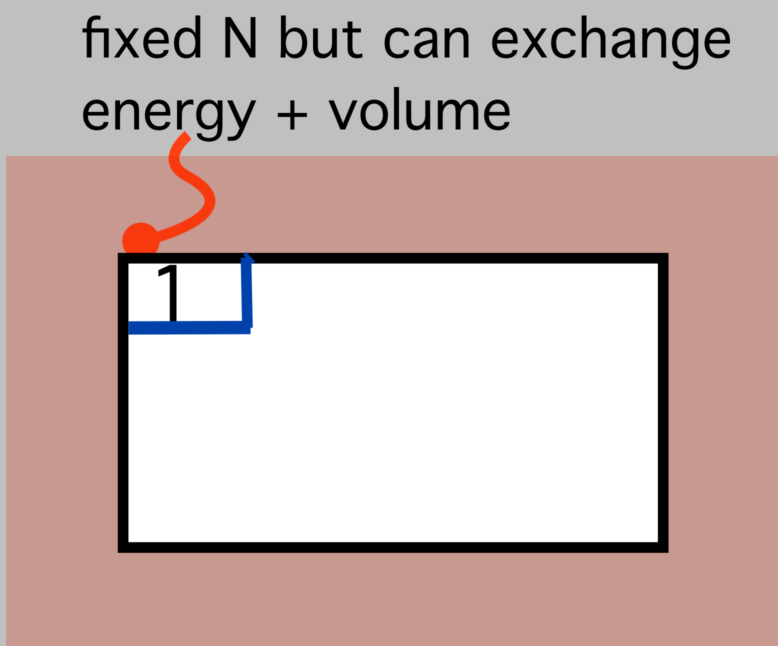
fixed N but can exchange energy + volume



We have our box 1 and a bath

Total system is isolated and the volume is constant

First law $dU = dq - pdV = 0$



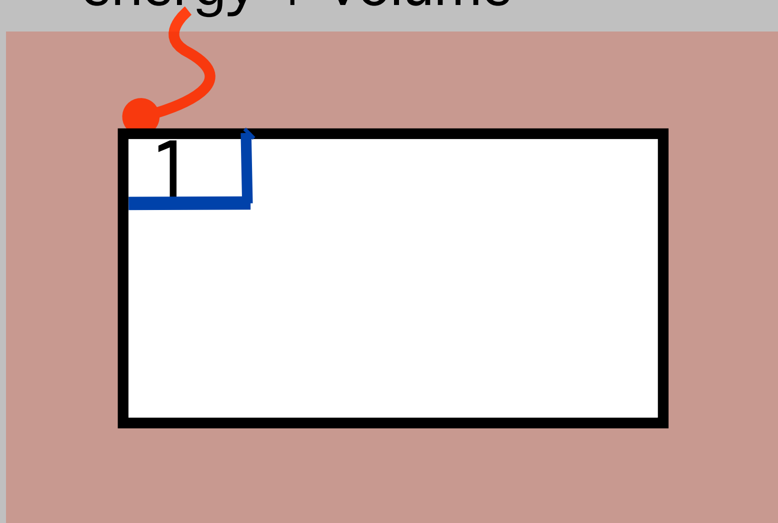
We have our box 1 and a bath

Total system is isolated and the volume is constant

First law $\mathrm{dU} = \mathrm{dq} - \mathrm{pdV} = 0$

Second law

fixed N but can exchange energy + volume



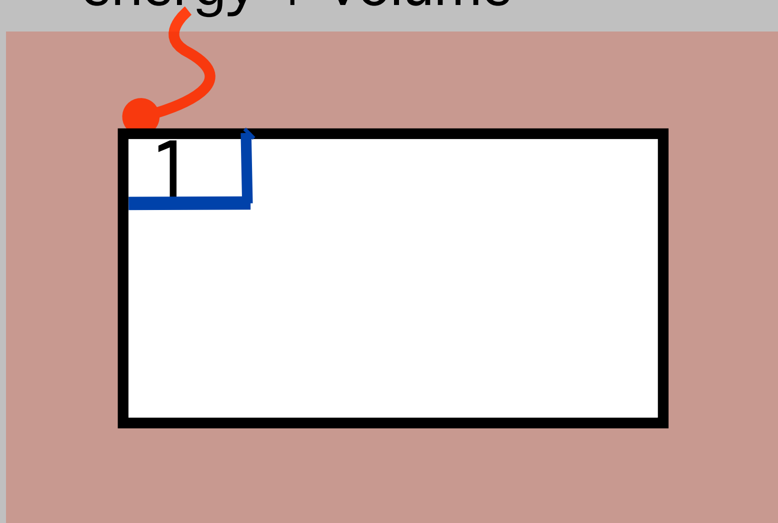
We have our box 1 and a bath

Total system is isolated and the volume is constant

First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

fixed N but can exchange energy + volume



We have our box 1 and a bath

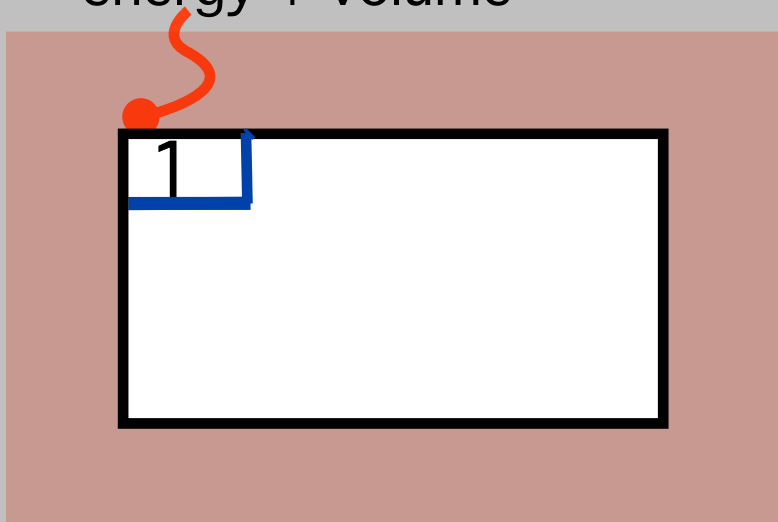
Total system is isolated and the volume is constant

First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

Box 1: constant pressure and temperature

fixed N but can exchange
energy + volume



We have our box 1 and a bath

Total system is isolated and the volume is constant

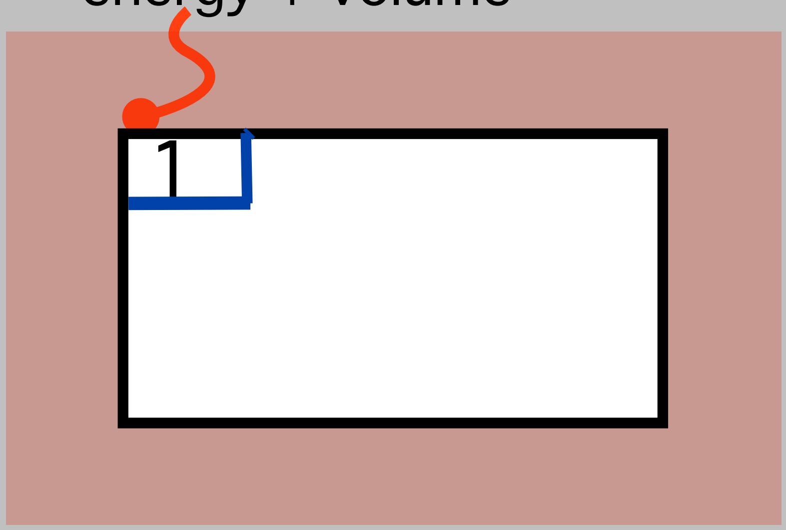
First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

Box 1: constant pressure and temperature

1^{st} law:

fixed N but can exchange
energy + volume



We have our box 1 and a bath

Total system is isolated and the volume is constant

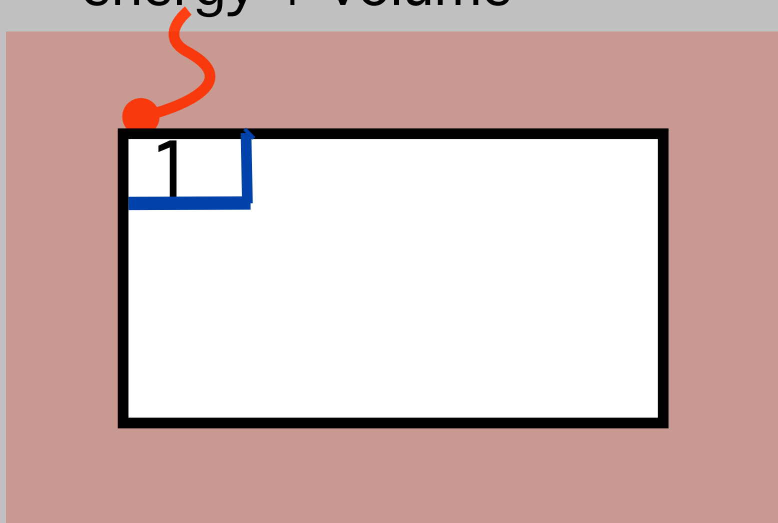
First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

Box 1: constant pressure and temperature

1st law: $\mathrm{d}U_1 + \mathrm{d}U_b = 0$

fixed N but can exchange
energy + volume



We have our box 1 and a bath

Total system is isolated and the volume is constant

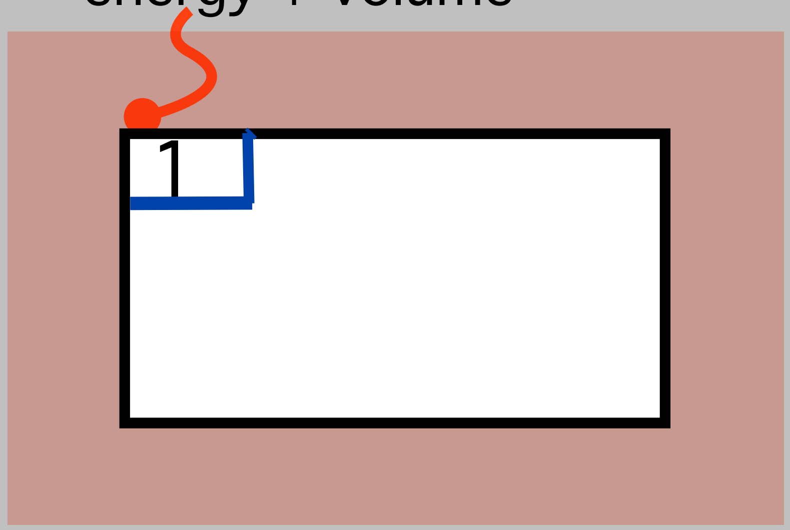
First law $dU = dq - pdV = 0$

Second law $dS \geq 0$

Box 1: constant pressure and temperature

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

fixed N but can exchange energy + volume



We have our box 1 and a bath

Total system is isolated and the volume is constant

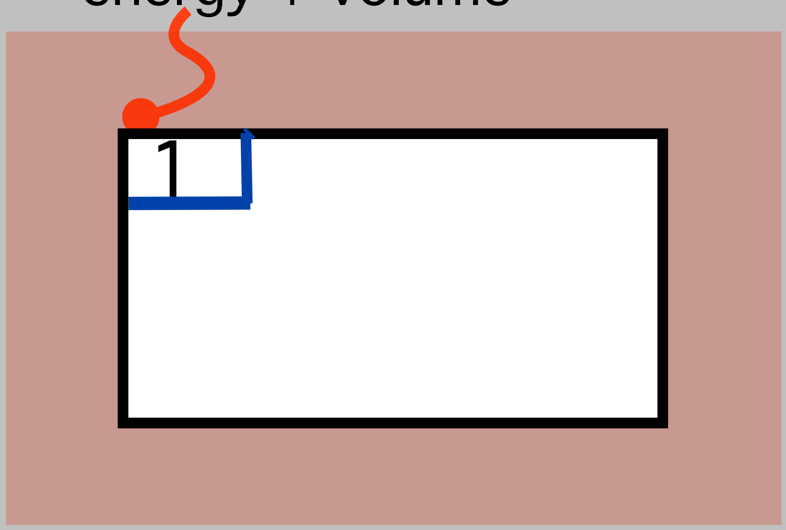
First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

Box 1: constant pressure and temperature

1st law: $\mathrm{d}U_1 + \mathrm{d}U_b = 0$ or $\mathrm{d}U_1 = -\mathrm{d}U_b$

fixed N but can exchange energy + volume



We have our box 1 and a bath

Total system is isolated and the volume is constant

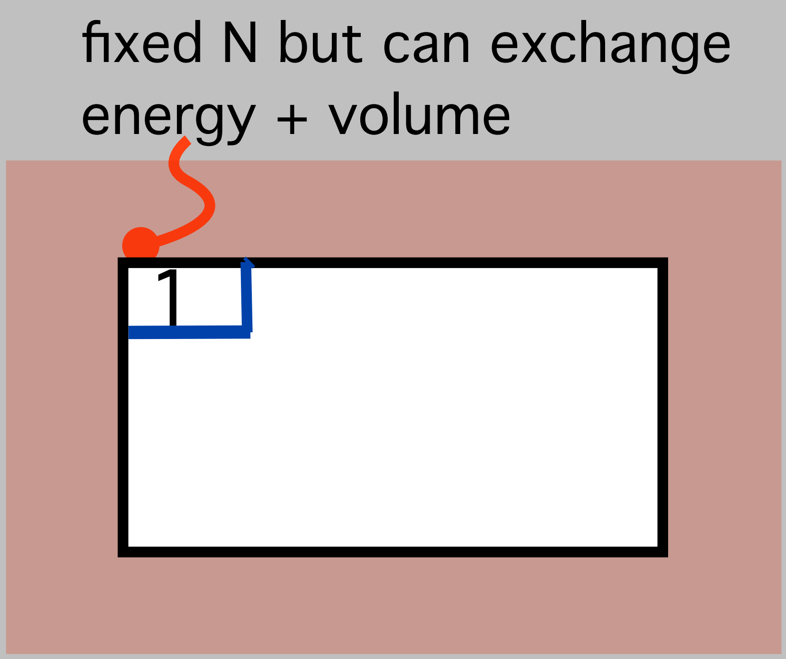
First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

Box 1: constant pressure and temperature

1st law: $\mathrm{d}U_1 + \mathrm{d}U_b = 0$ or $\mathrm{d}U_1 = -\mathrm{d}U_b$

$\mathrm{d}V_1 + \mathrm{d}V_b = 0$



We have our box 1 and a bath

<u>Total system</u> is isolated and the volume is constant

First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

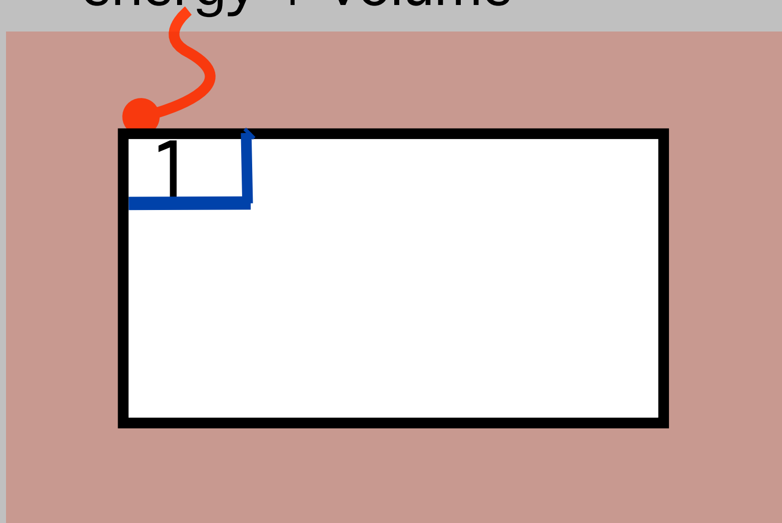
Second law $\mathrm{d}S \geq 0$

<u>Box 1</u>: constant pressure and temperature

1st law: $\mathrm{d}U_1 + \mathrm{d}U_b = 0$ or $\mathrm{d}U_1 = -\mathrm{d}U_b$

$\mathrm{d}V_1 + \mathrm{d}V_b = 0$ or

fixed N but can exchange energy + volume



We have our box 1 and a bath

<u>Total system</u> is isolated and the volume is constant

First law $dU = dq - pdV = 0$

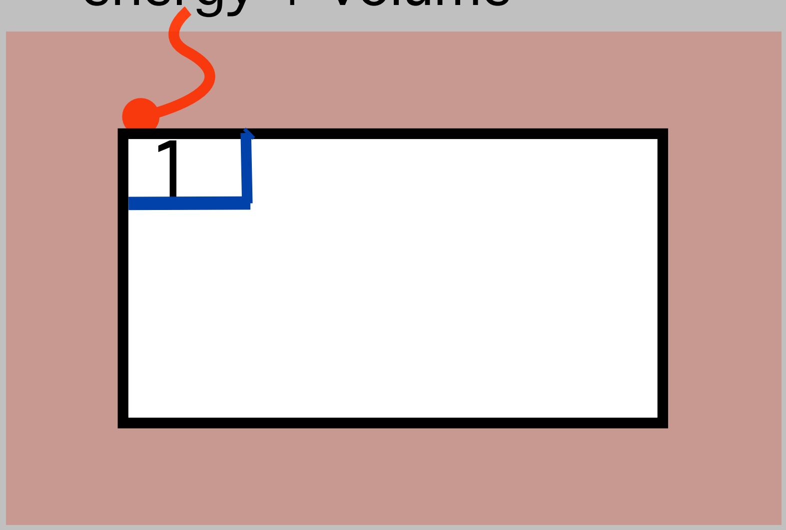
Second law $dS \geq 0$

<u>Box 1</u>: constant pressure and temperature

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

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

fixed N but can exchange energy + volume



We have our box 1 and a bath

<u>Total system</u> is isolated and the volume is constant

First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

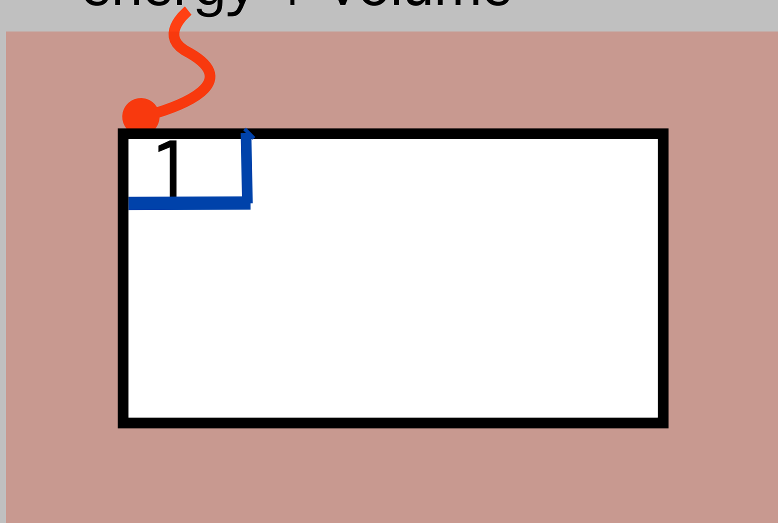
<u>Box 1</u>: constant pressure and temperature

1st law: $\mathrm{d}U_1 + \mathrm{d}U_b = 0$ or $\mathrm{d}U_1 = -\mathrm{d}U_b$

$\mathrm{d}V_1 + \mathrm{d}V_b = 0$ or $\mathrm{d}V_1 = -\mathrm{d}V_b$

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

fixed N but can exchange
energy + volume



We have our box 1 and a bath

<u>Total system</u> is isolated and the volume is constant

First law $\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V = 0$

Second law $\mathrm{d}S \geq 0$

<u>Box 1</u>: constant pressure and temperature

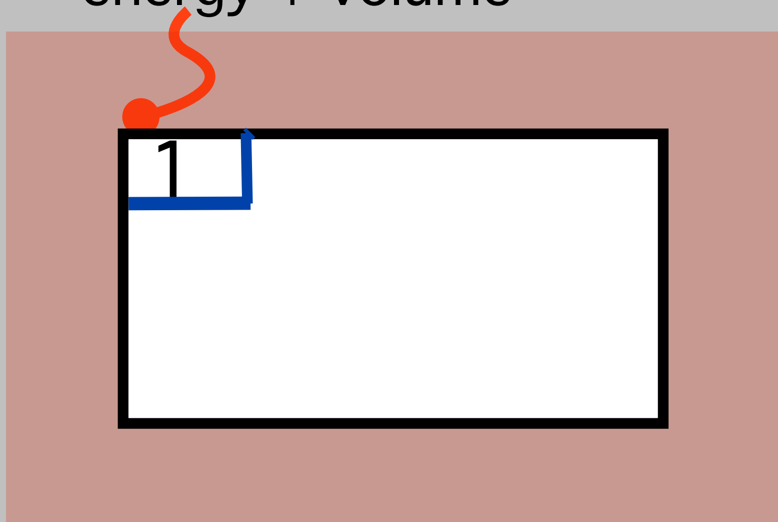
1st law: $\mathrm{d}U_1 + \mathrm{d}U_b = 0$ or $\mathrm{d}U_1 = -\mathrm{d}U_b$

$\mathrm{d}V_1 + \mathrm{d}V_b = 0$ or $\mathrm{d}V_1 = -\mathrm{d}V_b$

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

2nd law:

fixed N but can exchange energy + volume



We have our box 1 and a bath

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

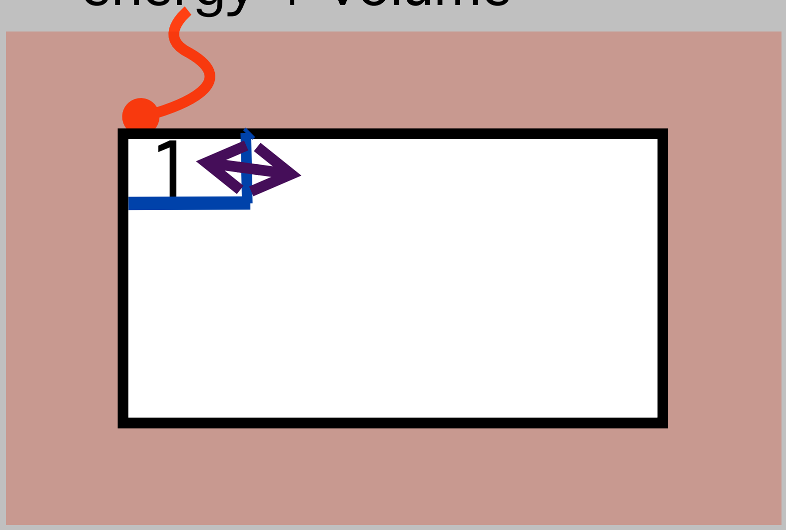
1st law: $dU_1 + dU_b = 0$ or $dU_1 = -dU_b$

$dV_1 + dV_b = 0$ 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: $$dS_1 + dS_b = dS_1 + \frac{dU_b}{T} + \frac{p}{T}dV_b \geq 0$$

fixed N but can exchange
energy + volume



We have our box 1 and a bath

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

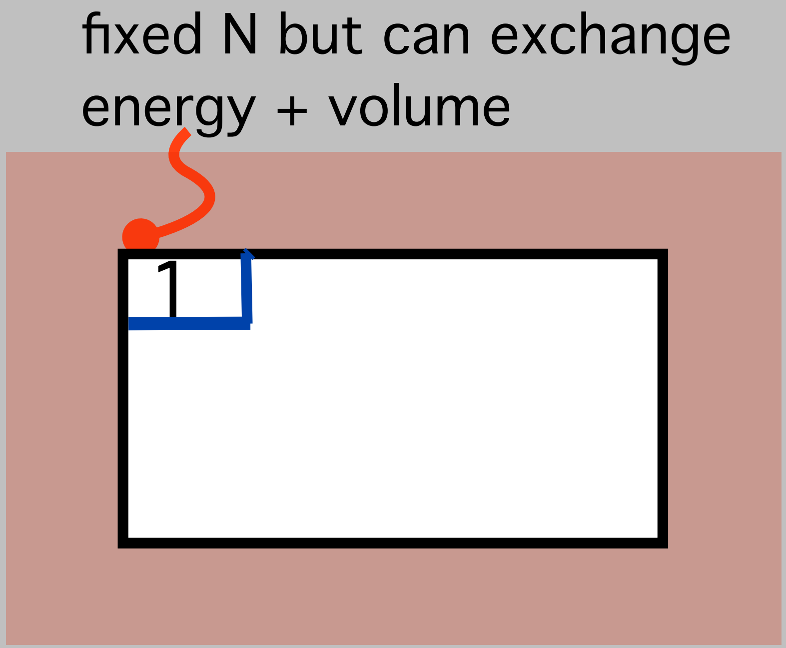
1st law: $dU_1 + dU_b = 0$ or $dU_1 = -dU_b$

$dV_1 + dV_b = 0$ 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: $dS_1 + dS_b = dS_1 + \frac{dU_b}{T} + \frac{p}{T}dV_b \geq 0$

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

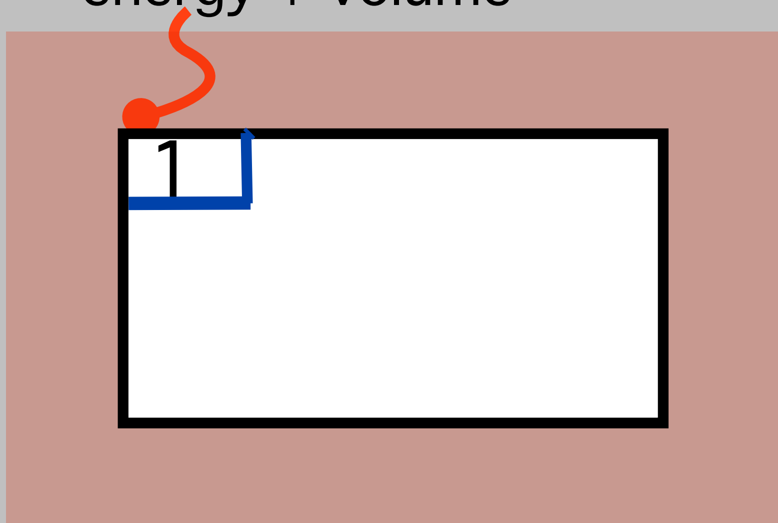


Total system is isolated and the volume is constant

Box 1: constant pressure and temperature

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

fixed N but can exchange energy + volume



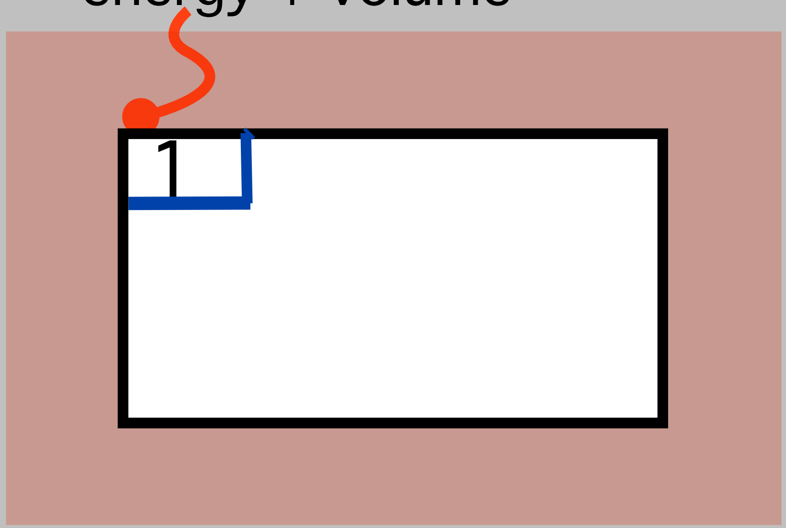
Total system is isolated and the volume is constant

Box 1: constant pressure and temperature

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

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

fixed N but can exchange
energy + volume



Total system is isolated and the volume is constant

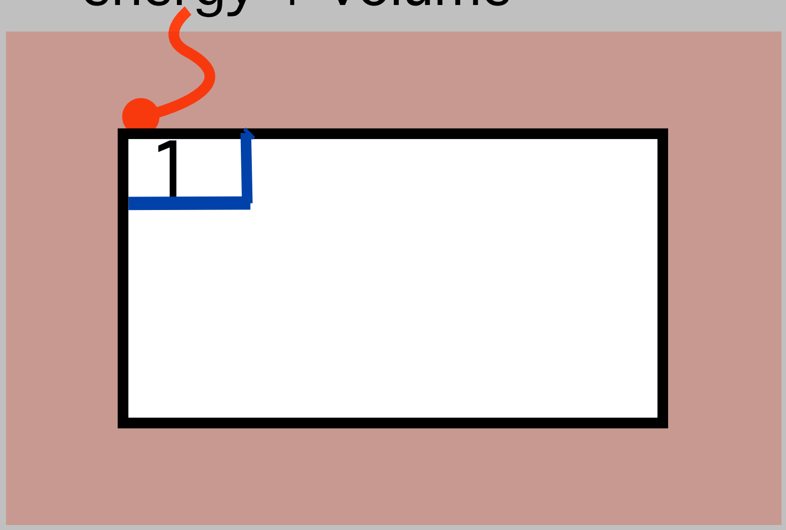
Box 1: constant pressure and temperature

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

fixed N but can exchange
energy + volume



Total system is isolated and the volume is constant

Box 1: constant pressure and temperature

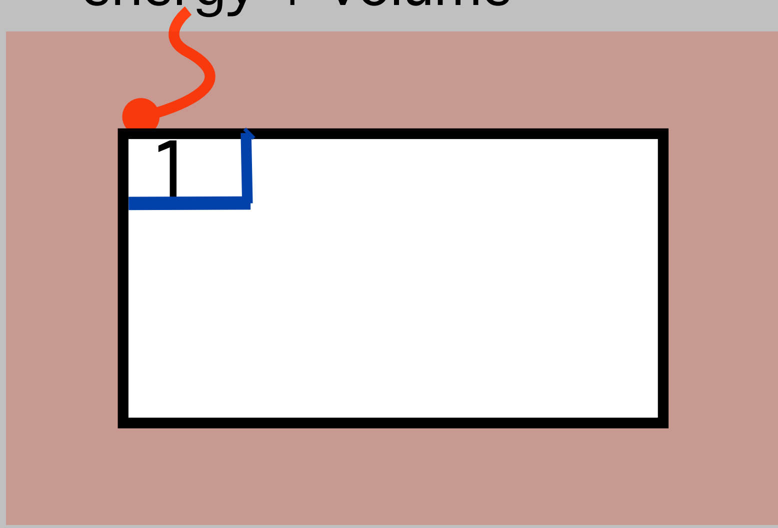
2nd law: $TdS_1 - dU_1 - pdV_1 \geq 0$

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

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

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

fixed N but can exchange energy + volume



<u>Total system</u> is isolated and the volume is constant

<u>Box 1</u>: constant pressure and temperature

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

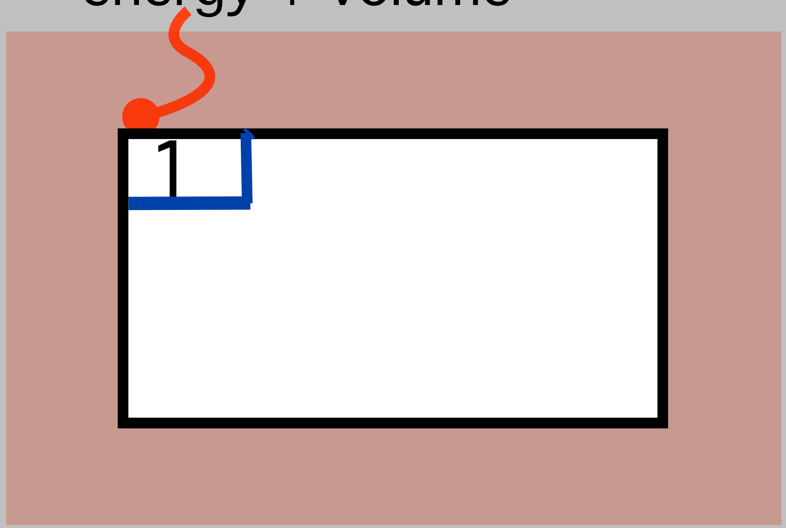
$$d(U_1 - TS_1 + pV_1) \leq 0$$

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

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

For box 1 we can write

fixed N but can exchange
energy + volume



<u>Total system</u> is isolated and the volume is constant

<u>Box 1</u>: constant pressure and temperature

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

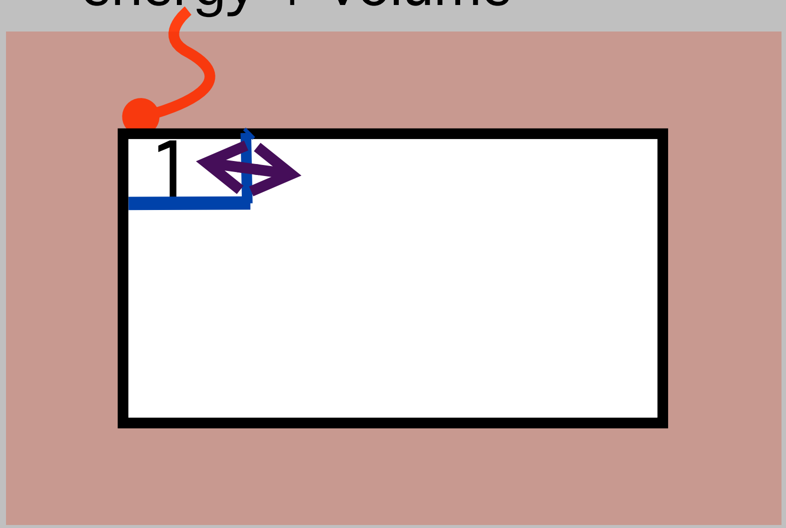
$$d(U_1 - TS_1 + pV_1) \leq 0$$

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

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

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

fixed N but can exchange energy + volume



Total system is isolated and the volume is constant

Box 1: constant pressure and temperature

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

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

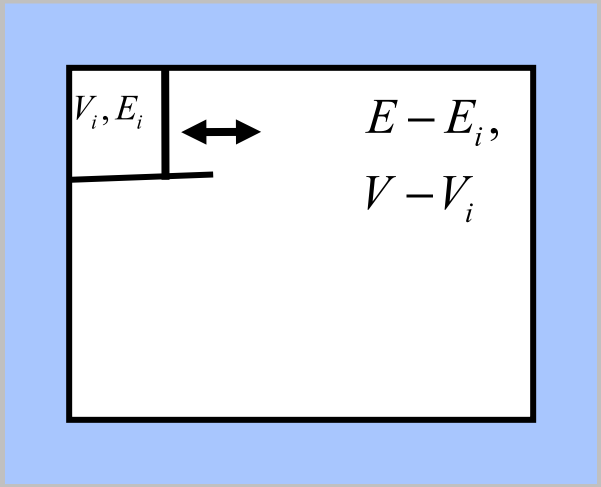
Let us define the **Gibbs free energy**: G

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

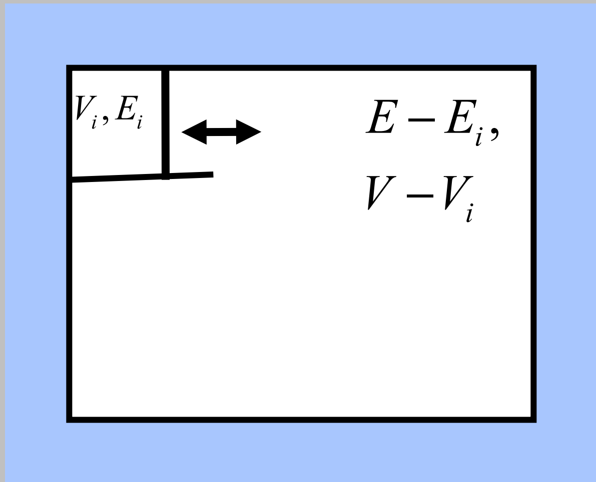
For box 1 we can write $dG_1 \leq 0$

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

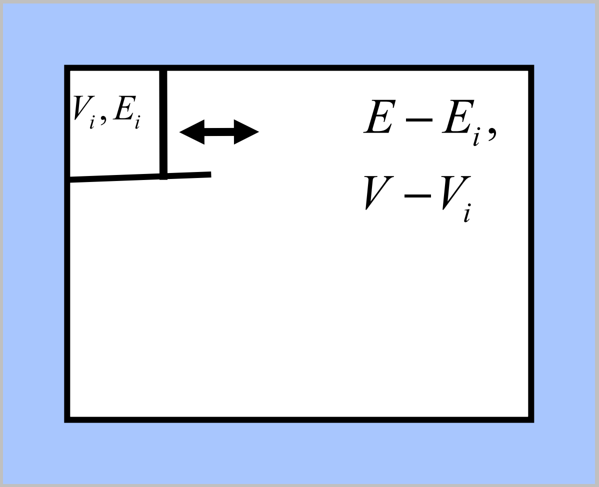


N,P,T ensemble

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

$$\ln\Omega\left(V - V_i, E - E_i\right) = \ln\Omega\left(V, E\right) - \left(\frac{\partial \ln\Omega}{\partial E}\right)_V E_i - \left(\frac{\partial \ln\Omega}{\partial V}\right)_E V_i + \cdots$$

N,P,T ensemble

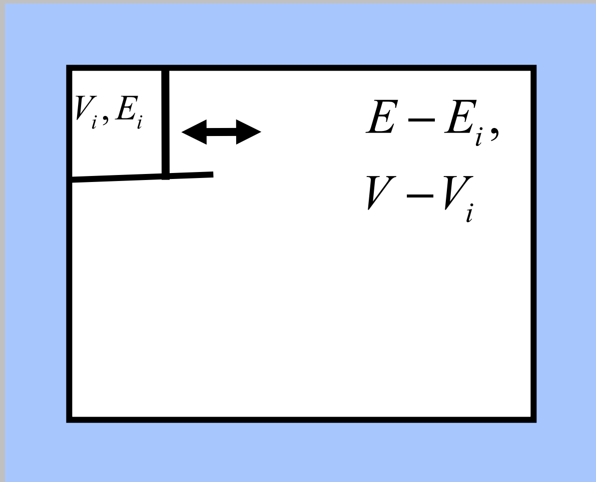


Consider a small system that can exchange volume and energy with a big reservoir

$$\ln \Omega\left(V - V_i, E - E_i\right) = \ln \Omega\left(V, E\right) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_V E_i - \left(\frac{\partial \ln \Omega}{\partial V}\right)_E V_i + \cdots$$

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

N,P,T ensemble



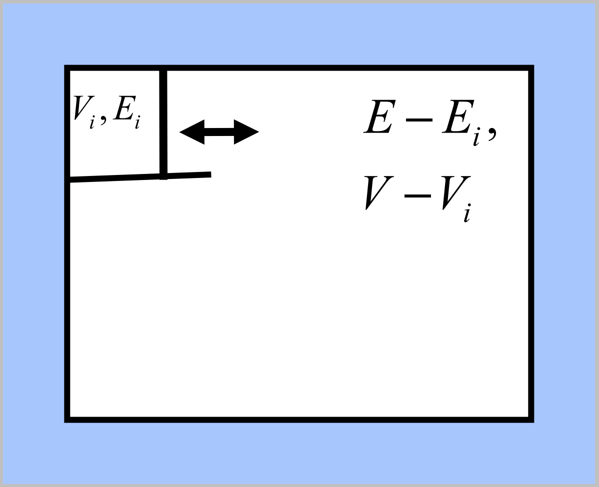
Consider a small system that can exchange volume and energy with a big reservoir

$$\ln\Omega\left(V - V_i, E - E_i\right) = \ln\Omega\left(V, E\right) - \left(\frac{\partial \ln\Omega}{\partial E}\right)_V E_i - \left(\frac{\partial \ln\Omega}{\partial V}\right)_E V_i + \cdots$$

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

$$S = k_B \ln\Omega$$

N,P,T ensemble



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

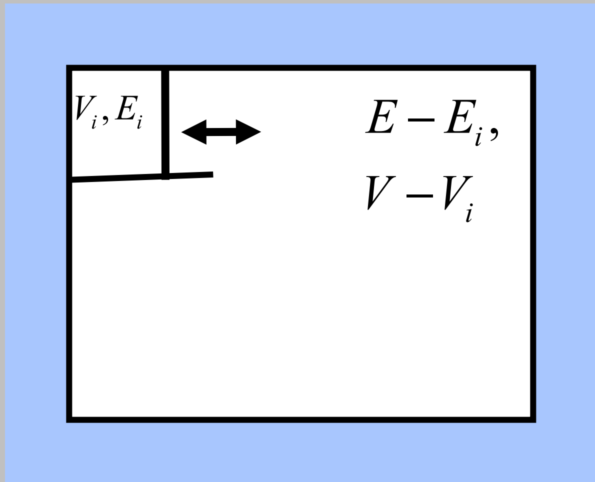
$$\ln \Omega\left(V - V_i, E - E_i\right) = \ln \Omega\left(V, E\right) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_V E_i - \left(\frac{\partial \ln \Omega}{\partial V}\right)_E V_i + \cdots$$

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

$$S = k_B \ln \Omega$$

We have:

N,P,T ensemble



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

$$\ln \Omega\left(V - V_{i,} E - E_i\right) = \ln \Omega\left(V, E\right) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_V E_i - \left(\frac{\partial \ln \Omega}{\partial V}\right)_E V_i + \cdots$$

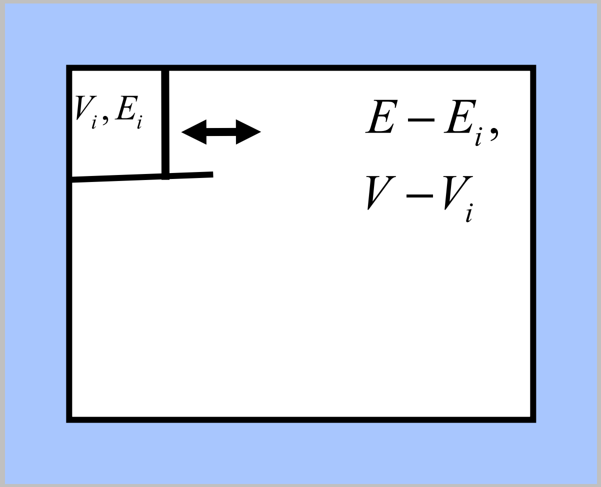
The terms in the expansion follow from the connection with Thermodynamics:

$$S = k_B \ln \Omega$$

We have:

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

N,P,T ensemble



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

$$\ln\Omega\left(V - V_i, E - E_i\right) = \ln\Omega\left(V, E\right) - \left(\frac{\partial \ln\Omega}{\partial E}\right)_V E_i - \left(\frac{\partial \ln\Omega}{\partial V}\right)_E V_i + \cdots$$

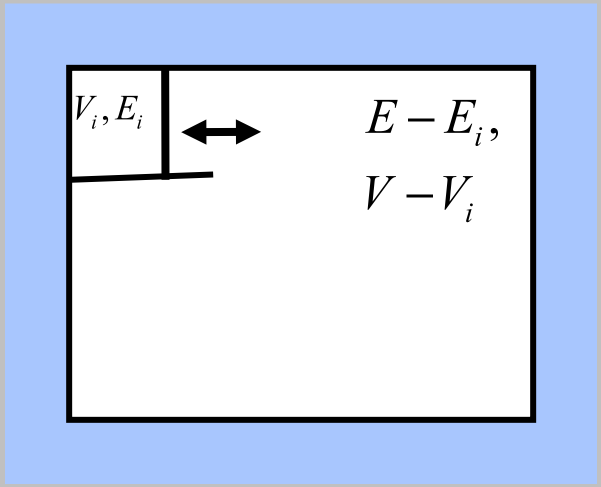
The terms in the expansion follow from the connection with Thermodynamics:

$$S = k_B \ln\Omega$$

We have:

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

$$\left(\frac{\partial S}{\partial U}\right)_{V,N_i} = \frac{1}{T}$$



N,P,T ensemble

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

$$\ln \Omega\left(V - V_i, E - E_i\right) = \ln \Omega\left(V, E\right) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_V E_i - \left(\frac{\partial \ln \Omega}{\partial V}\right)_E V_i + \cdots$$

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

$$S = k_B \ln \Omega$$

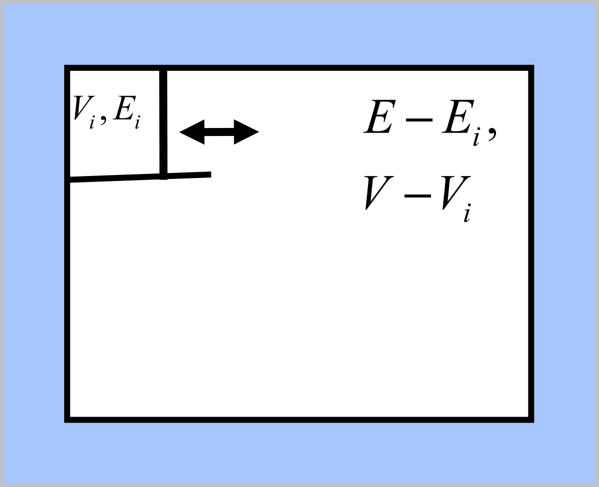
We have:

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

$$\left(\frac{\partial S}{\partial U}\right)_{V,N_i} = \frac{1}{T}$$

and

N,P,T ensemble



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

$$\ln\Omega\left(V - V_i, E - E_i\right) = \ln\Omega\left(V, E\right) - \left(\frac{\partial \ln\Omega}{\partial E}\right)_V E_i - \left(\frac{\partial \ln\Omega}{\partial V}\right)_E V_i + \cdots$$

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

$$S = k_B \ln\Omega$$

We have:

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

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

$$\ln\Omega\left(V-V_i,E-E_i\right)=\ln\Omega\left(V,E\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_{V,N}E_i-\left(\frac{\partial\ln\Omega}{\partial V}\right)_{E,N}V_i+\cdots$$

$$\ln\Omega\left(V-V_i,E-E_i\right)=\ln\Omega\left(V,E\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_{V,N}E_i-\left(\frac{\partial\ln\Omega}{\partial V}\right)_{E,N}V_i+\cdots$$

$$\ln\Omega\left(V-V_i,E-E_i\right)=\ln\Omega\left(V,E\right)-\frac{E_i}{k_BT}-\frac{p}{k_BT}V_i$$

$$\ln\Omega\left(V-V_i,E-E_i\right)=\ln\Omega\left(V,E\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_{V,N}E_i-\left(\frac{\partial\ln\Omega}{\partial V}\right)_{E,N}V_i+\cdots$$

$$\ln\Omega\left(V-V_i,E-E_i\right)=\ln\Omega\left(V,E\right)-\frac{E_i}{k_BT}-\frac{p}{k_BT}V_i$$

$$\ln\frac{\Omega\left(E-E_i,V-V_i\right)}{\Omega\left(E,V\right)}=-\frac{E_i}{k_BT}-\frac{pV_i}{k_BT}$$

$$\ln\Omega\left(V-V_i,E-E_i\right)=\ln\Omega\left(V,E\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_{V,N}E_i-\left(\frac{\partial\ln\Omega}{\partial V}\right)_{E,N}V_i+\cdots$$

$$\ln\Omega\left(V-V_i,E-E_i\right)=\ln\Omega\left(V,E\right)-\frac{E_i}{k_BT}-\frac{p}{k_BT}V_i$$

$$\ln\frac{\Omega\left(E-E_i,V-V_i\right)}{\Omega\left(E,V\right)}=-\frac{E_i}{k_BT}-\frac{pV_i}{k_BT}$$

Hence, the probability to find E_i,V_i:

$$\ln\Omega\left(V-V_i,E-E_i\right)=\ln\Omega\left(V,E\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_{V,N}E_i-\left(\frac{\partial\ln\Omega}{\partial V}\right)_{E,N}V_i+\cdots$$

$$\ln\Omega\left(V-V_i,E-E_i\right)=\ln\Omega\left(V,E\right)-\frac{E_i}{k_BT}-\frac{p}{k_BT}V_i$$

$$\ln\frac{\Omega\left(E-E_i,V-V_i\right)}{\Omega\left(E,V\right)}=-\frac{E_i}{k_BT}-\frac{pV_i}{k_BT}$$

Hence, the probability to find E_i,V_i:

$$P\left(E_i,V_i\right)=\frac{\Omega\left(E-E_i,V-V_i\right)}{\sum_{j,k}\Omega\left(E-E_j,V-V_k\right)}=\frac{\exp\left[-\beta\left(E_i+pV_i\right)\right]}{\sum_{j,k}\exp\left[-\beta\left(E_j+pV_k\right)\right]}$$

$$\propto\exp\left[-\beta\left(E_i+pV_i\right)\right]$$

Partition function:

Partition function:

$$\Delta(N,P,T) = \sum_{i,j} \exp\left[-\frac{E_i}{k_B T} - \frac{pV_j}{k_B T} \right]$$

Partition function:

$$\Delta(N,P,T)=\sum_{i,j}\exp\left[-\frac{E_i}{k_BT}-\frac{pV_j}{k_BT}\right]$$

Ensemble average:

Partition function:

$$\Delta(N,P,T)=\sum_{i,j}\exp\left[-\frac{E_i}{k_BT}-\frac{pV_j}{k_BT}\right]$$

Ensemble average:

$$\langle V\rangle=\frac{\sum_{i,j}V_j\exp\left[-\frac{E_i}{k_BT}-\frac{pV_j}{k_BT}\right]}{\Delta(N,p,T)}=-k_BT\left(\frac{\partial\ln\Delta}{\partial p}\right)_{T,N}$$

Partition function:

$$\Delta(N,P,T)=\sum_{i,j}\exp\left[-\frac{E_i}{k_BT}-\frac{pV_j}{k_BT}\right]$$

Ensemble average:

$$\langle V\rangle=\frac{\sum_{i,j}V_j\exp\left[-\frac{E_i}{k_BT}-\frac{pV_j}{k_BT}\right]}{\Delta(N,p,T)}=-k_BT\left(\frac{\partial\ln\Delta}{\partial p}\right)_{T,N}$$

Thermodynamics

Partition function:

$$\Delta(N,P,T) = \sum_{i,j} \exp\left[-\frac{E_i}{k_B T} - \frac{pV_j}{k_B T}\right]$$

Ensemble average:

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

Thermodynamics

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

Partition function:

$$\Delta(N,P,T)=\sum_{i,j}\exp\left[-\frac{E_i}{k_BT}-\frac{pV_j}{k_BT}\right]$$

Ensemble average:

$$\langle V\rangle=\frac{\sum_{i,j}V_j\exp\left[-\frac{E_i}{k_BT}-\frac{pV_j}{k_BT}\right]}{\Delta(N,p,T)}=-k_BT\left(\frac{\partial\ln\Delta}{\partial p}\right)_{T,N}$$

Thermodynamics

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

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

Partition function:

$$\Delta(N,P,T) = \sum_{i,j} \exp\left[-\frac{E_i}{k_B T} - \frac{pV_j}{k_B T}\right]$$

Ensemble average:

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

Thermodynamics

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

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

Hence:

Partition function:

$$\Delta(N,P,T) = \sum_{i,j} \exp\left[-\frac{E_i}{k_B T} - \frac{pV_j}{k_B T}\right]$$

Ensemble average:

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

Thermodynamics

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

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

Hence:

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

Summary

In the classical limit, the partition function becomes

Summary

In the classical limit, the partition function becomes

$$Q(N,P,T)=\frac{1}{\Lambda^{3N}N!}\int dV\,\exp(-\beta PV)\int \mathrm{d}\mathbf{r}^N\,\exp\left[-\beta U\left(r^N\right)\right]$$

Summary

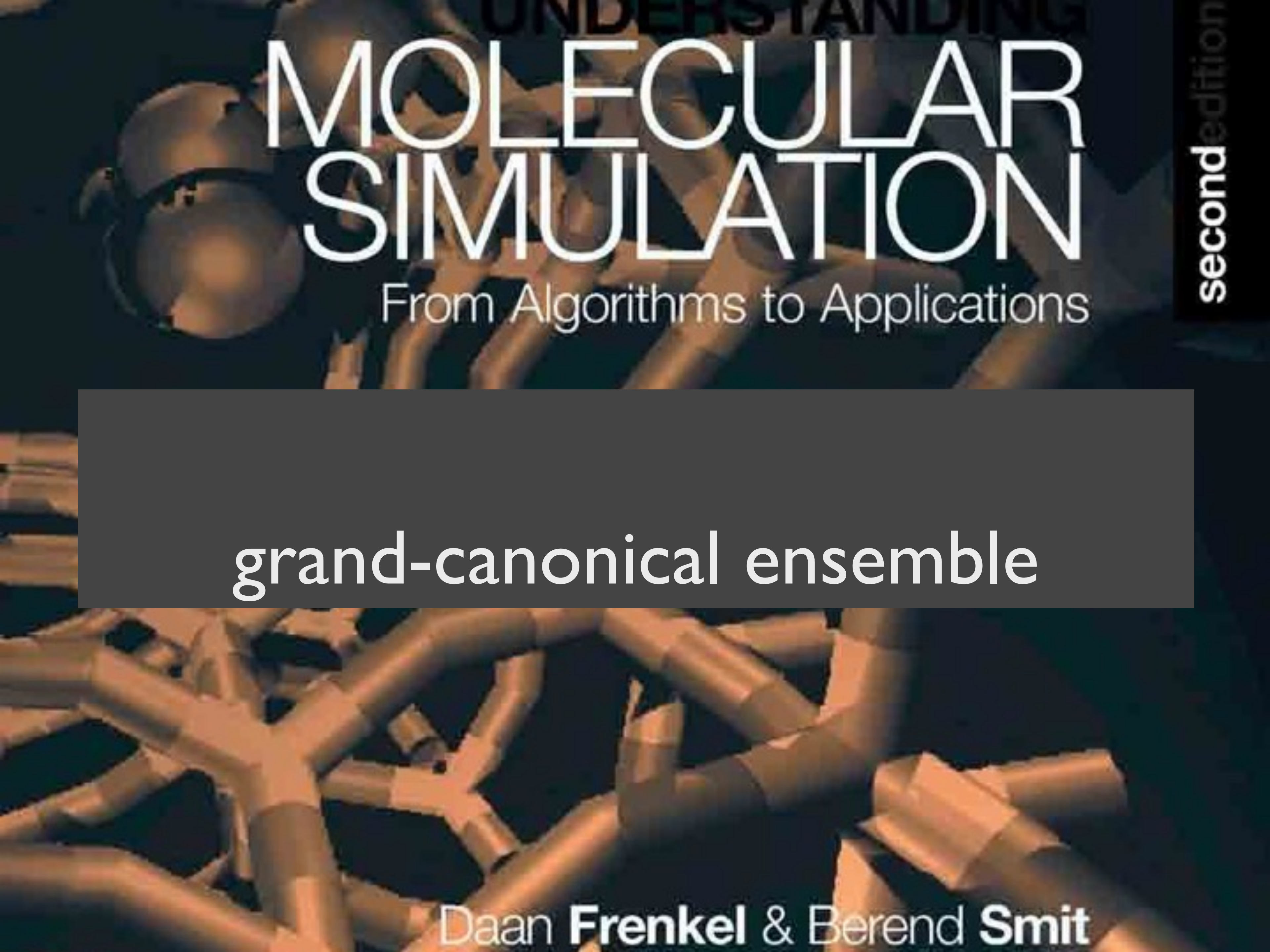
In the classical limit, the partition function becomes

$$Q(N,P,T) = \frac{1}{\Lambda^{3N} N!} \int dV \exp(-\beta PV) \int \mathrm{d}\mathbf{r}^N \exp\left[-\beta U\left(r^N\right)\right]$$

The probability to find a particular configuration:

$$\mathbf{r}^N, V$$

$$P\left(\mathbf{r}^N, V\right) \propto \exp\left[-\beta\left(PV + U\left(r^N\right)\right)\right]$$



grand-canonical ensemble

Grand-canonical ensemble

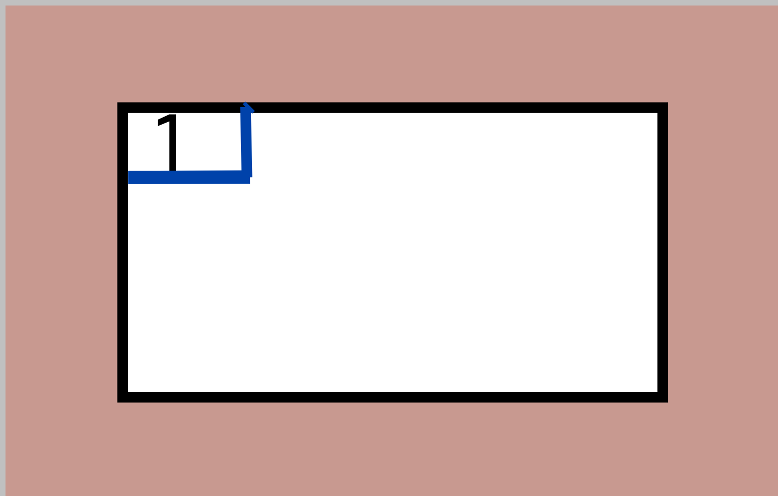
Classical

- A small system that can exchange heat and particles with a large bath

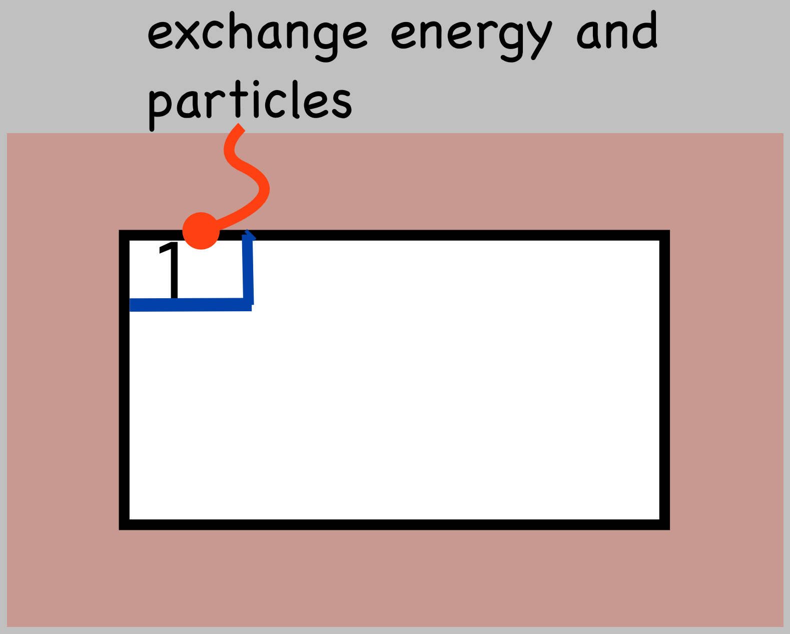
Statistical

- Taylor expansion of a small reservoir

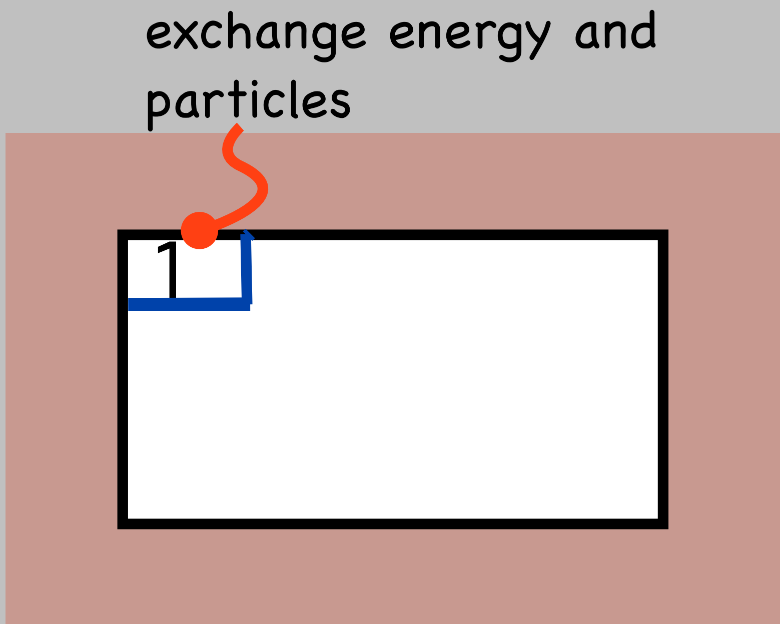
Constant T and μ



Constant T and μ

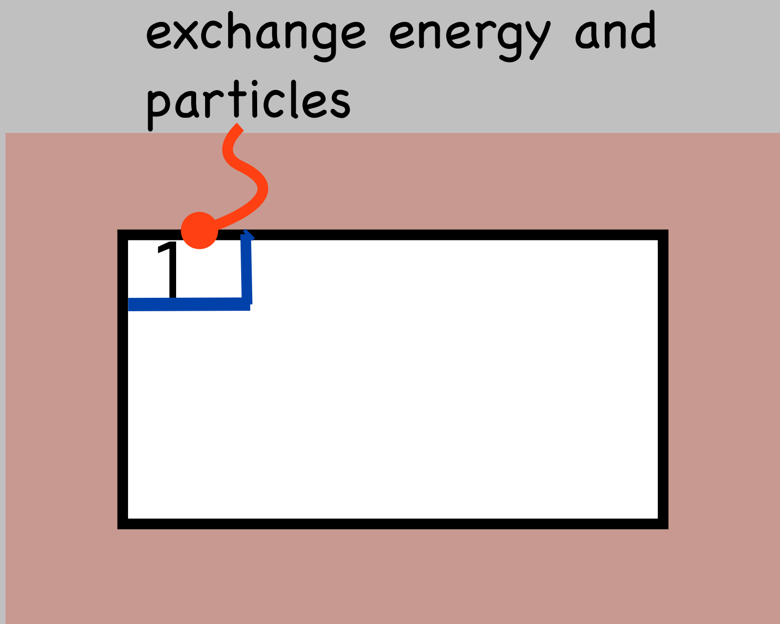


Constant T and μ



<u>Total system</u> is isolated
and the volume is constant

Constant T and μ

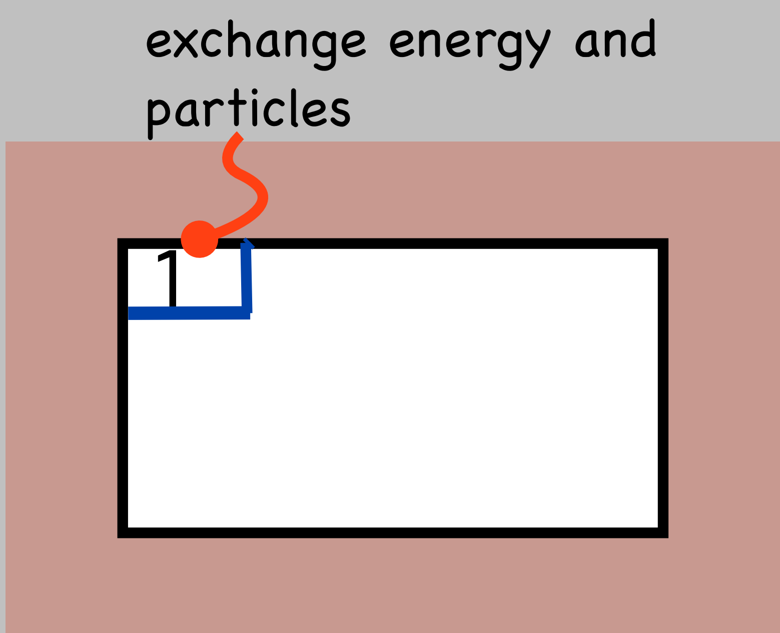


Total system is isolated
and the volume is constant

First law

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

Constant T and μ



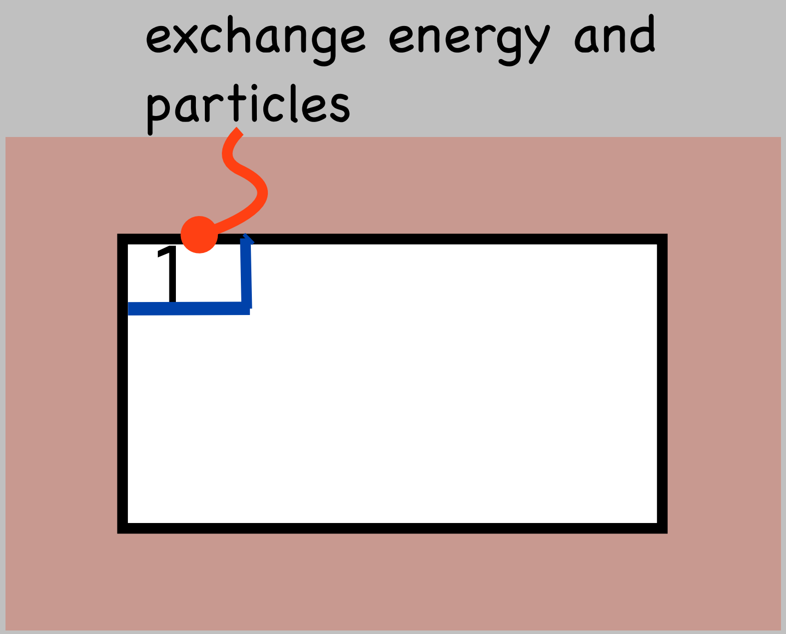
Total system is isolated
and the volume is constant

First law

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

Second law

Constant T and μ



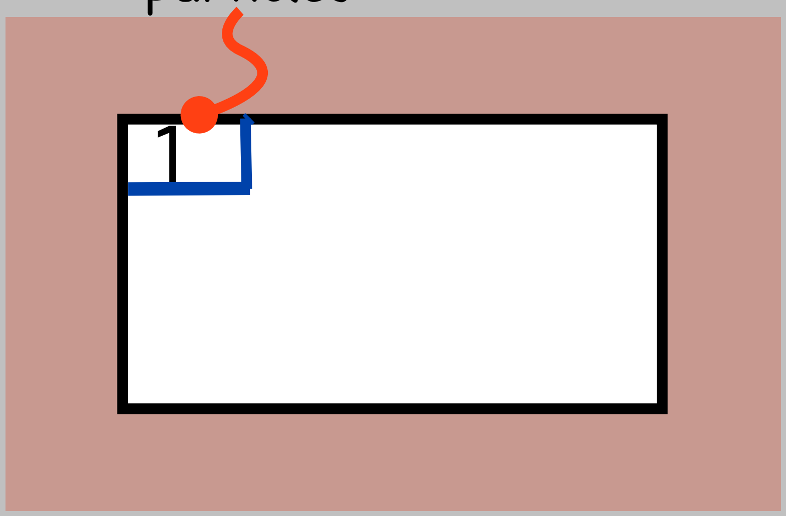
<u>Total system</u> is isolated and the volume is constant

First law

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

Second law $\mathrm{d}S \geq 0$

Constant T and μ



Total system is isolated and the volume is constant

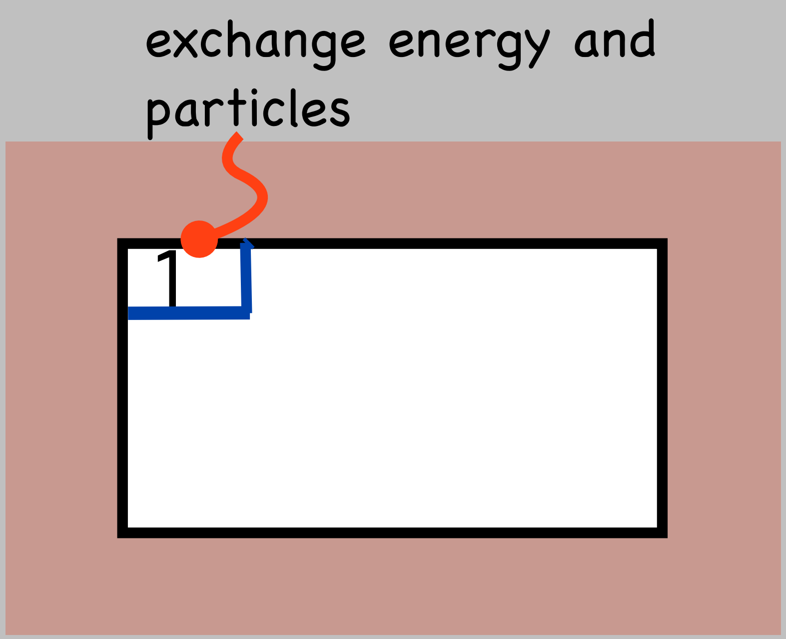
First law

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

Second law $dS \geq 0$

Box 1: constant chemical potential and temperature

Constant T and μ



Total system is isolated and the volume is constant

First law

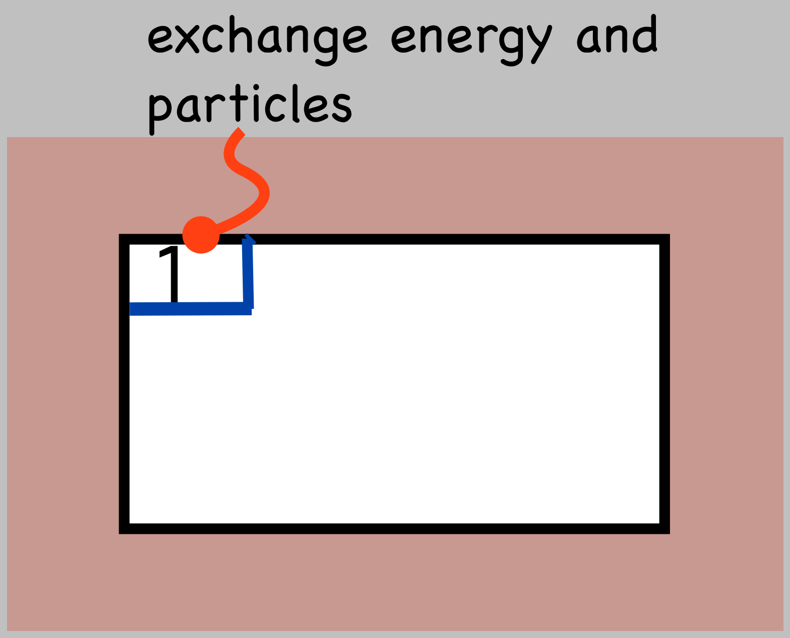
$$dU = TdS - pdV + \mu dN = 0$$

Second law $dS \geq 0$

Box 1: constant chemical potential and temperature

1^{st} law:

Constant T and μ



Total system is isolated and the volume is constant

First law

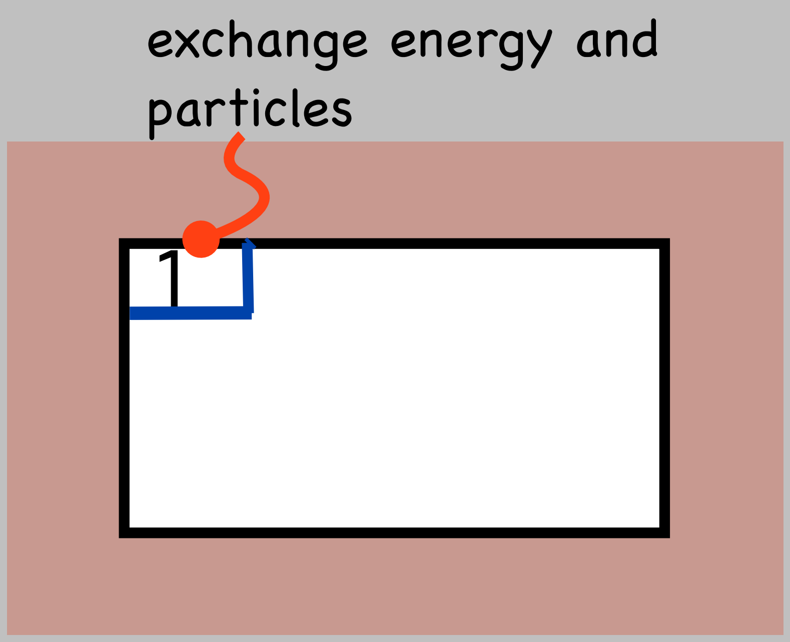
$$dU = TdS - pdV + \mu dN = 0$$

Second law $dS \geq 0$

Box 1: constant chemical potential and temperature

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

Constant T and μ



Total system is isolated
and the volume is constant

First law

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

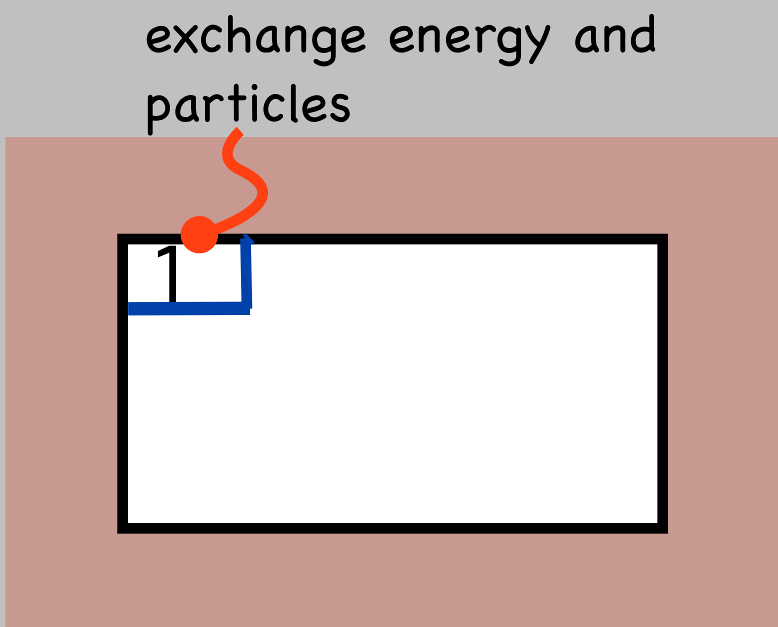
Second law $dS \geq 0$

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 $dN_b = -dN_1$

Constant T and μ



Total system is isolated and the volume is constant

First law

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

Second law $dS \geq 0$

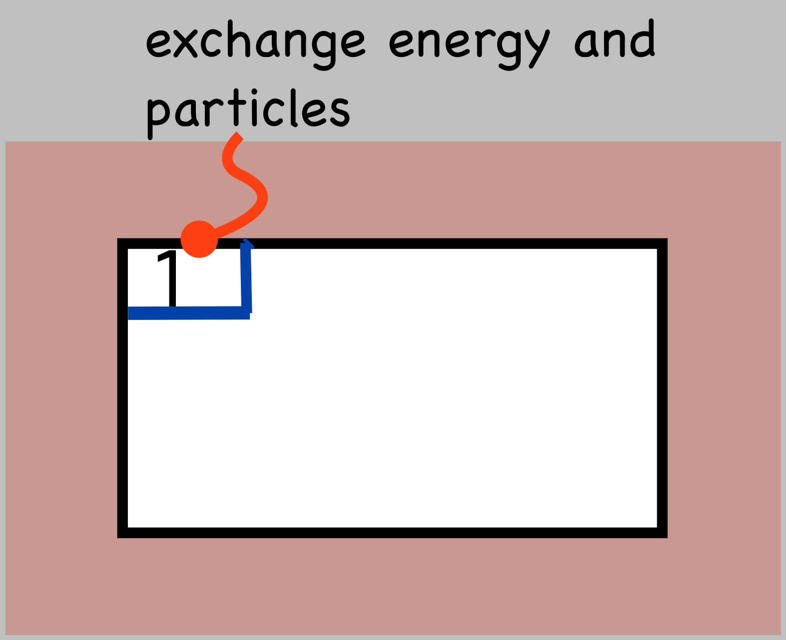
Box 1: constant chemical potential and temperature

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

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

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

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

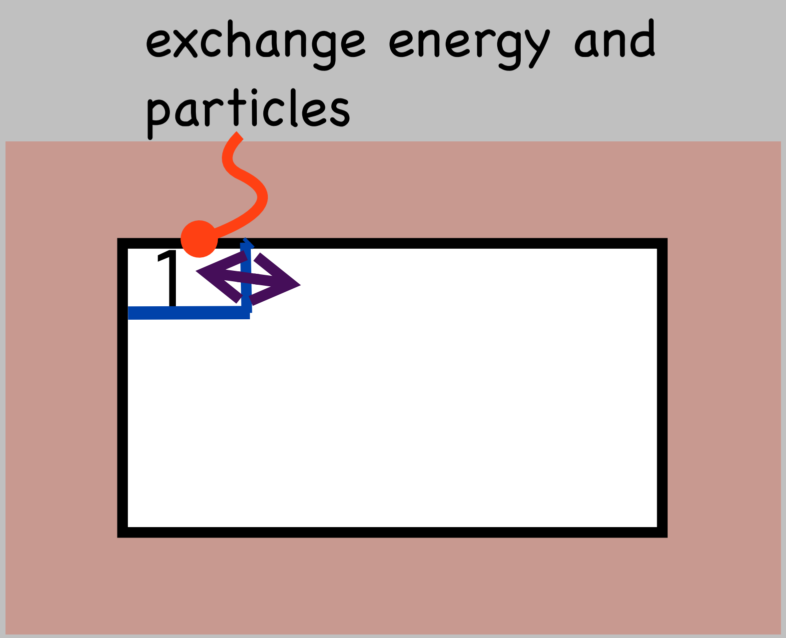
1st law: $dU_1 + dU_b = 0$ or $dU_1 = -dU_b$

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

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

2nd law:

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 $dN_b = -dN_1$

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

2nd law:

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0$$

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0 \qquad d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0 \qquad d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$d\left(U - TS - \mu N\right) \leq 0$$

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0 \qquad d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$d\left(U - TS - \mu N\right) \leq 0$$

For the Gibbs free energy we can write:

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0 \qquad d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$d\left(U - TS - \mu N\right) \leq 0$$

For the Gibbs free energy we can write:

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

$$G = \mu N$$

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0 \qquad d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$d\left(U - TS - \mu N\right) \leq 0$$

For the Gibbs free energy we can write:

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

or

$$-pV = U - TS - \mu N$$

$$G = \mu N$$

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0 \qquad d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$d\left(U - TS - \mu N\right) \leq 0$$

For the Gibbs free energy we can write:

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

or

$$-pV = U - TS - \mu N$$

$$G = \mu N$$

Giving:

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0 \qquad d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$d\left(U - TS - \mu N\right) \leq 0$$

For the Gibbs free energy we can write:

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

or

$$-pV = U - TS - \mu N$$

$$G = \mu N$$

Giving:

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

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0 \qquad d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$d\left(U - TS - \mu N\right) \leq 0$$

For the Gibbs free energy we can write:

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

$$G = \mu N$$

or

$$-pV = U - TS - \mu N$$

Giving:

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

or

$$d\left(pV\right) \geq 0$$

$$dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \geq 0$$

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

$$dS_1 - \frac{1}{T} dU_1 + \frac{\mu}{T} dN_1 \geq 0 \qquad d\left(TS_1 - U_1 + \mu N_1\right) \geq 0$$

$$d\left(U - TS - \mu N\right) \leq 0$$

For the Gibbs free energy we can write:

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

$$G = \mu N$$

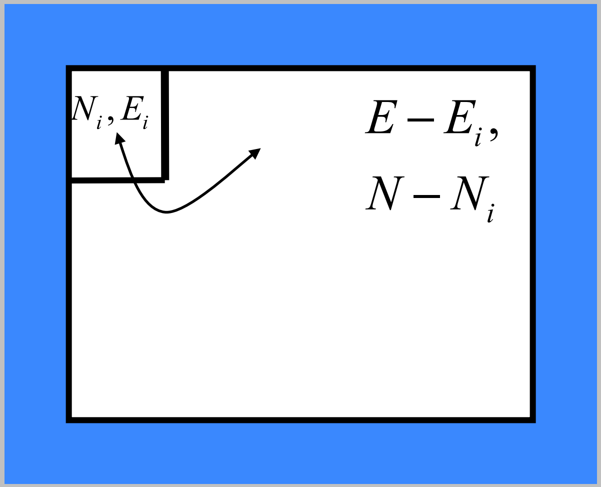
or

$$-pV = U - TS - \mu N$$

Giving:

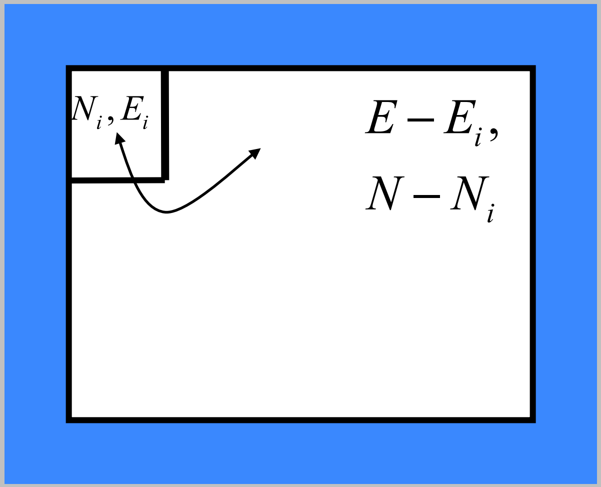
$$d\left(-pV\right) \leq 0 \qquad \text{or} \qquad d\left(pV\right) \geq 0$$

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



μ, V, T ensemble

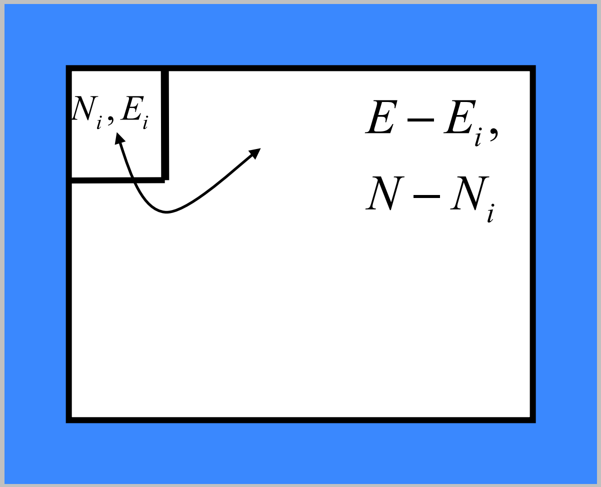
Consider a small system that can exchange particles and energy with a big reservoir



μ, V, T ensemble

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

$$\ln \Omega\left(E - E_i, N - N_j,\right) = \ln \Omega\left(E, N\right) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N} E_i - \left(\frac{\partial \ln \Omega}{\partial N}\right)_{E,V} N_j + \cdots$$

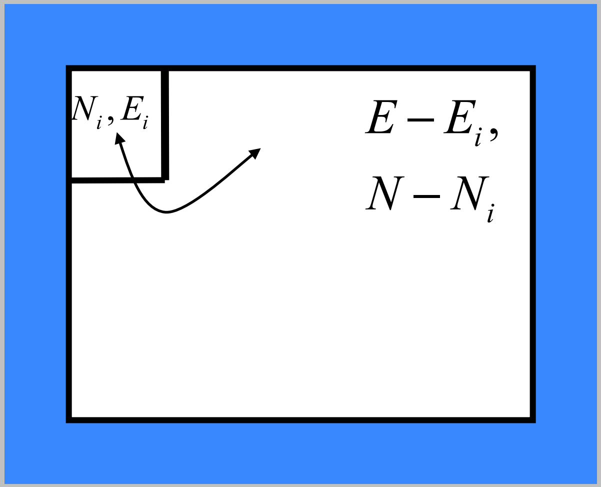


μ, V, T ensemble

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

$$\ln \Omega\left(E - E_i, N - N_j,\right) = \ln \Omega\left(E, N\right) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N} E_i - \left(\frac{\partial \ln \Omega}{\partial N}\right)_{E,V} N_j + \cdots$$

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

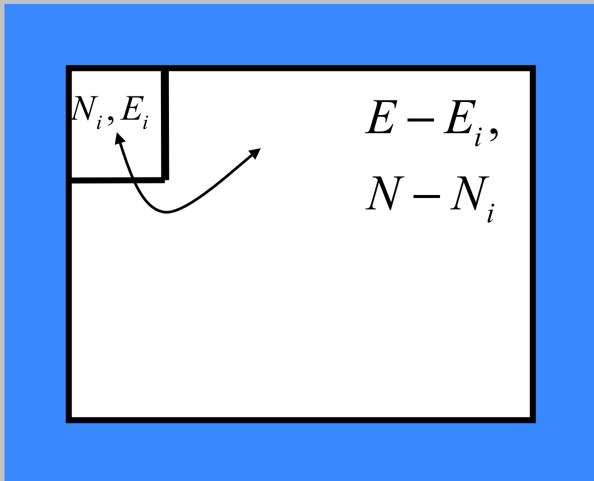


μ, V, T ensemble

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

$$\ln\Omega\left(E-E_i, N-N_j,\right) = \ln\Omega(E,N) - \left(\frac{\partial \ln\Omega}{\partial E}\right)_{V,N} E_i - \left(\frac{\partial \ln\Omega}{\partial N}\right)_{E,V} N_j + \cdots$$

The terms in the expansion follow from the connection with Thermodynamics: $S = k_B \ln\Omega$



μ, V, T ensemble

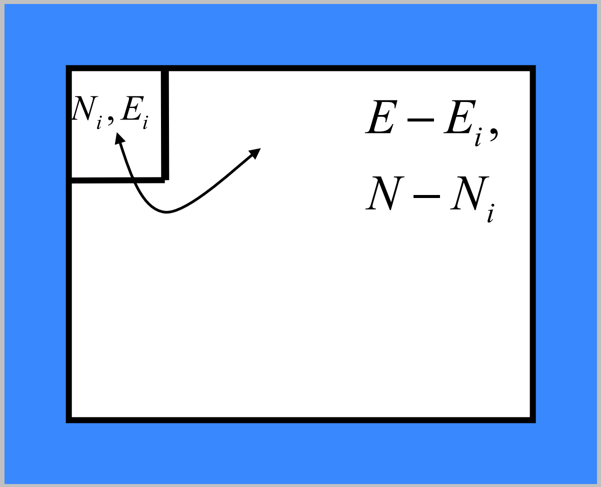
Consider a small system that can exchange particles and energy with a big reservoir

$$\ln\Omega\left(E - E_i, N - N_j,\right) = \ln\Omega(E,N) - \left(\frac{\partial \ln\Omega}{\partial E}\right)_{V,N} E_i - \left(\frac{\partial \ln\Omega}{\partial N}\right)_{E,V} N_j + \cdots$$

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

$$S = k_B \ln\Omega$$

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



μ, V, T ensemble

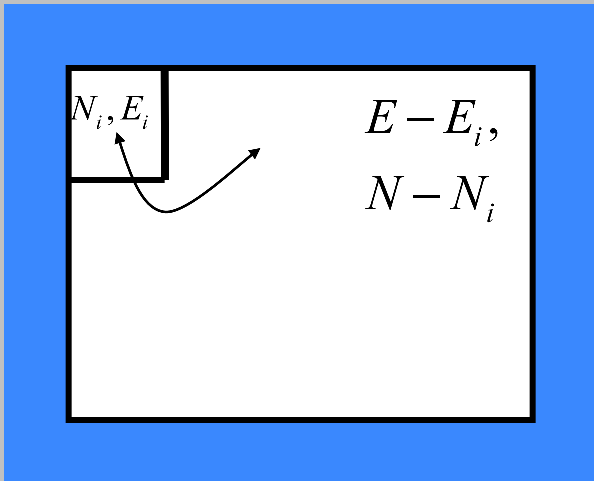
Consider a small system that can exchange particles and energy with a big reservoir

$$\ln\Omega\left(E - E_i, N - N_j,\right) = \ln\Omega(E,N) - \left(\frac{\partial \ln\Omega}{\partial E}\right)_{V,N} E_i - \left(\frac{\partial \ln\Omega}{\partial N}\right)_{E,V} N_j + \cdots$$

The terms in the expansion follow from the connection with Thermodynamics: $S = k_B \ln\Omega$

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

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$$



μ, V, T ensemble

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

$$\ln\Omega\left(E - E_i, N - N_j,\right) = \ln\Omega(E,N) - \left(\frac{\partial \ln\Omega}{\partial E}\right)_{V,N} E_i - \left(\frac{\partial \ln\Omega}{\partial N}\right)_{E,V} N_j + \cdots$$

The terms in the expansion follow from the connection with Thermodynamics: $S = k_B \ln\Omega$

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

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

$$\ln\Omega\left(E-E_i,N-N_j,\right)=\ln\Omega\left(E,N\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_{V,N}E_i-\left(\frac{\partial\ln\Omega}{\partial N}\right)_{E,V}N_j+\cdots$$

$$\ln\Omega\left(E - E_i, N - N_j,\right) = \ln\Omega\left(E, N\right) - \left(\frac{\partial \ln\Omega}{\partial E}\right)_{V,N} E_i - \left(\frac{\partial \ln\Omega}{\partial N}\right)_{E,V} N_j + \cdots$$

$$\ln\Omega\left(E - E_i, N - N_j\right) = \ln\Omega\left(E, N\right) - \frac{E_i}{k_B T} + \frac{\mu}{k_B T} N_j$$

$$\ln\Omega\left(E-E_i,N-N_j,\right)=\ln\Omega\left(E,N\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_{V,N}E_i-\left(\frac{\partial\ln\Omega}{\partial N}\right)_{E,V}N_j+\cdots$$

$$\ln\Omega\left(E-E_i,N-N_j\right)=\ln\Omega\left(E,N\right)-\frac{E_i}{k_BT}+\frac{\mu}{k_BT}N_j$$

$$\ln\frac{\Omega\left(E-E_i,N-N_j\right)}{\Omega\left(E,N\right)}=-\frac{E_i}{k_BT}+\frac{\mu}{k_BT}N_j$$

$$\ln\Omega\left(E-E_i,N-N_j,\right)=\ln\Omega\left(E,N\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_{V,N}E_i-\left(\frac{\partial\ln\Omega}{\partial N}\right)_{E,V}N_j+\cdots$$

$$\ln\Omega\left(E-E_i,N-N_j\right)=\ln\Omega\left(E,N\right)-\frac{E_i}{k_BT}+\frac{\mu}{k_BT}N_j$$

$$\ln\frac{\Omega\left(E-E_i,N-N_j\right)}{\Omega\left(E,N\right)}=-\frac{E_i}{k_BT}+\frac{\mu}{k_BT}N_j$$

Hence, the probability to find E_i,N_j:

$$\ln\Omega\left(E-E_i,N-N_j,\right)=\ln\Omega\left(E,N\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_{V,N}E_i-\left(\frac{\partial\ln\Omega}{\partial N}\right)_{E,V}N_j+\cdots$$

$$\ln\Omega\left(E-E_i,N-N_j\right)=\ln\Omega\left(E,N\right)-\frac{E_i}{k_BT}+\frac{\mu}{k_BT}N_j$$

$$\ln\frac{\Omega\left(E-E_i,N-N_j\right)}{\Omega\left(E,N\right)}=-\frac{E_i}{k_BT}+\frac{\mu}{k_BT}N_j$$

Hence, the probability to find E_i,N_j:

$$P\left(E_i,N_j\right)=\frac{\Omega\left(E-E_i,N-N_j\right)}{\sum_{k,l}\Omega\left(E-E_k,N-N_l\right)}\propto\exp\left[-\frac{E_i}{k_BT}+\frac{\mu N_i}{k_BT}\right]$$

μ,V,T ensemble (2)

In the classical limit, the partition function becomes

μ,V,T ensemble (2)

In the classical limit, the partition function becomes

$$Q(\mu, V, T) = \sum_{N=1}^{\infty} \frac{\exp(\beta\mu N)}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N \exp\left[-\beta U\left(r^N\right)\right]$$

μ,V,T ensemble (2)

In the classical limit, the partition function becomes

$$Q(\mu, V, T) = \sum_{N=1}^{\infty} \frac{\exp(\beta\mu N)}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N \exp\left[-\beta U(r^N)\right]$$

The probability to find a particular configuration: $N, \mathbf{r}^N$

$$P(N, \mathbf{r}^N) \propto \exp\left[\beta\mu N - \beta U(r^N)\right]$$