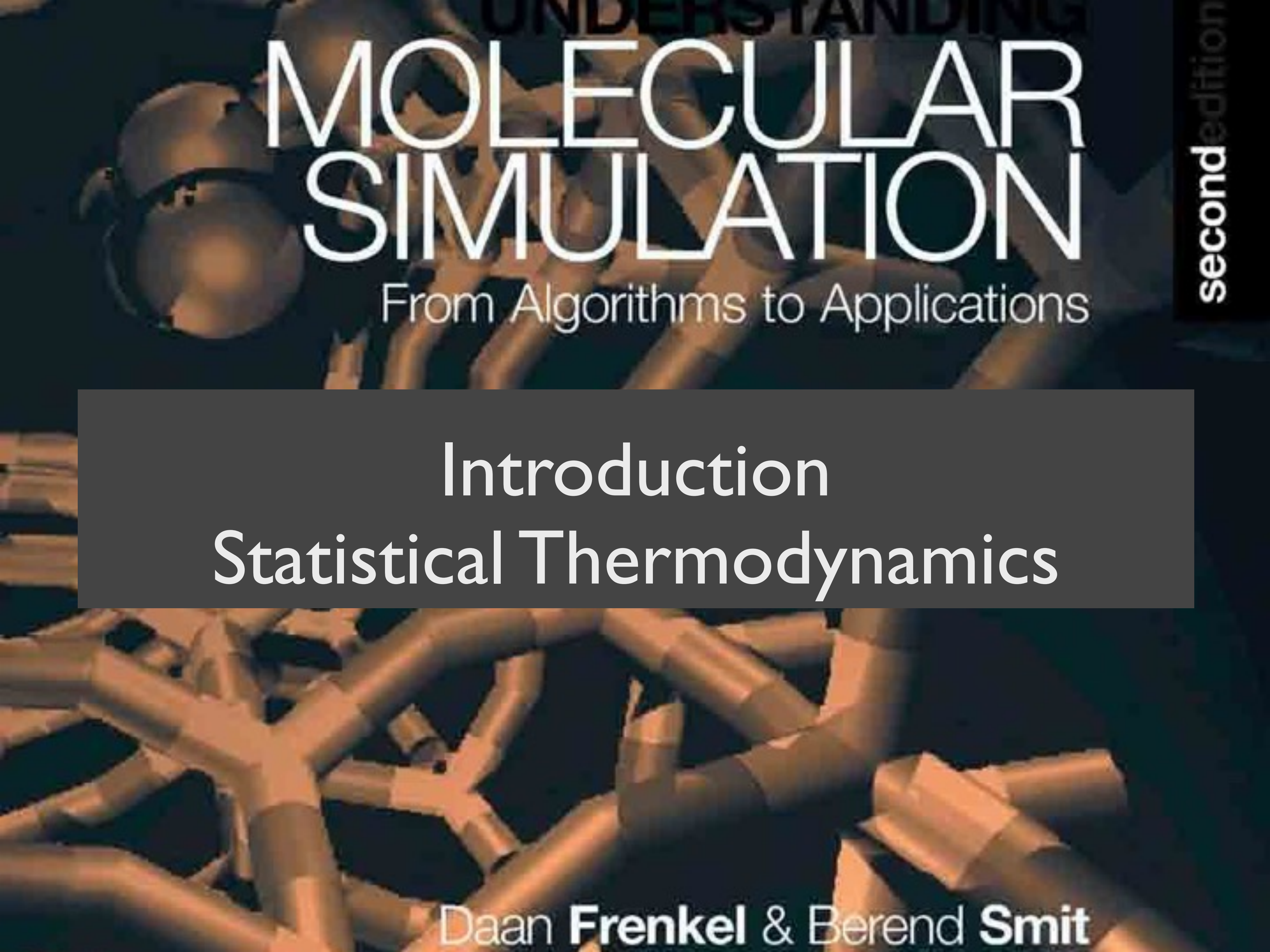
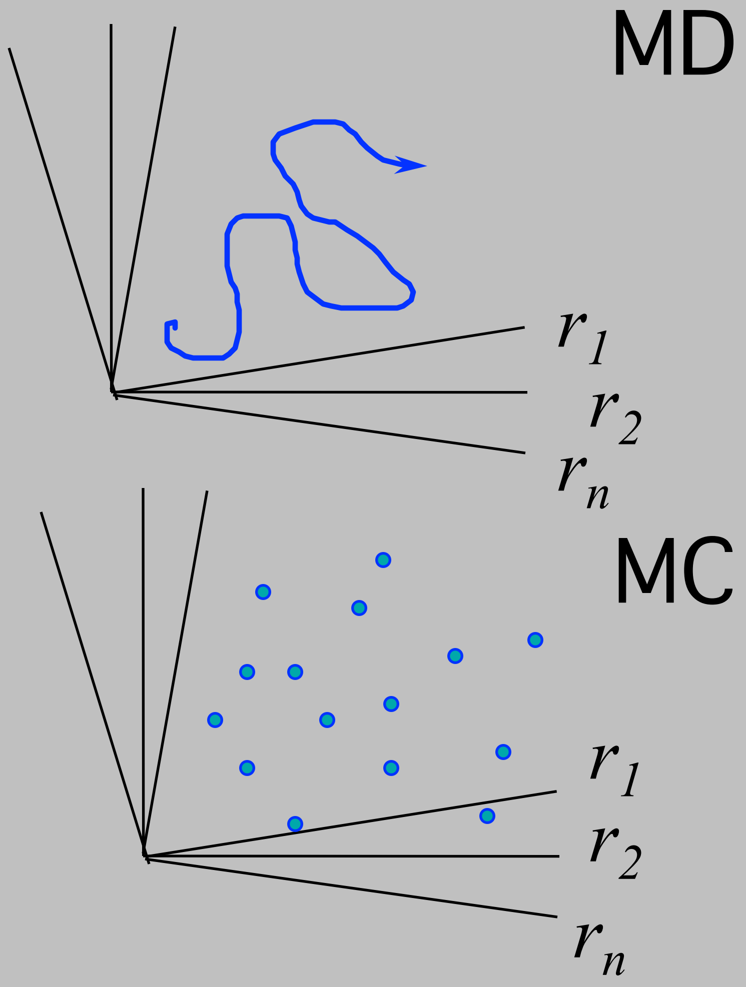


Introduction
Statistical Thermodynamics

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

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Outline

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Rewrite History

- Atoms first! Thermodynamics last!

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Thermodynamics

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

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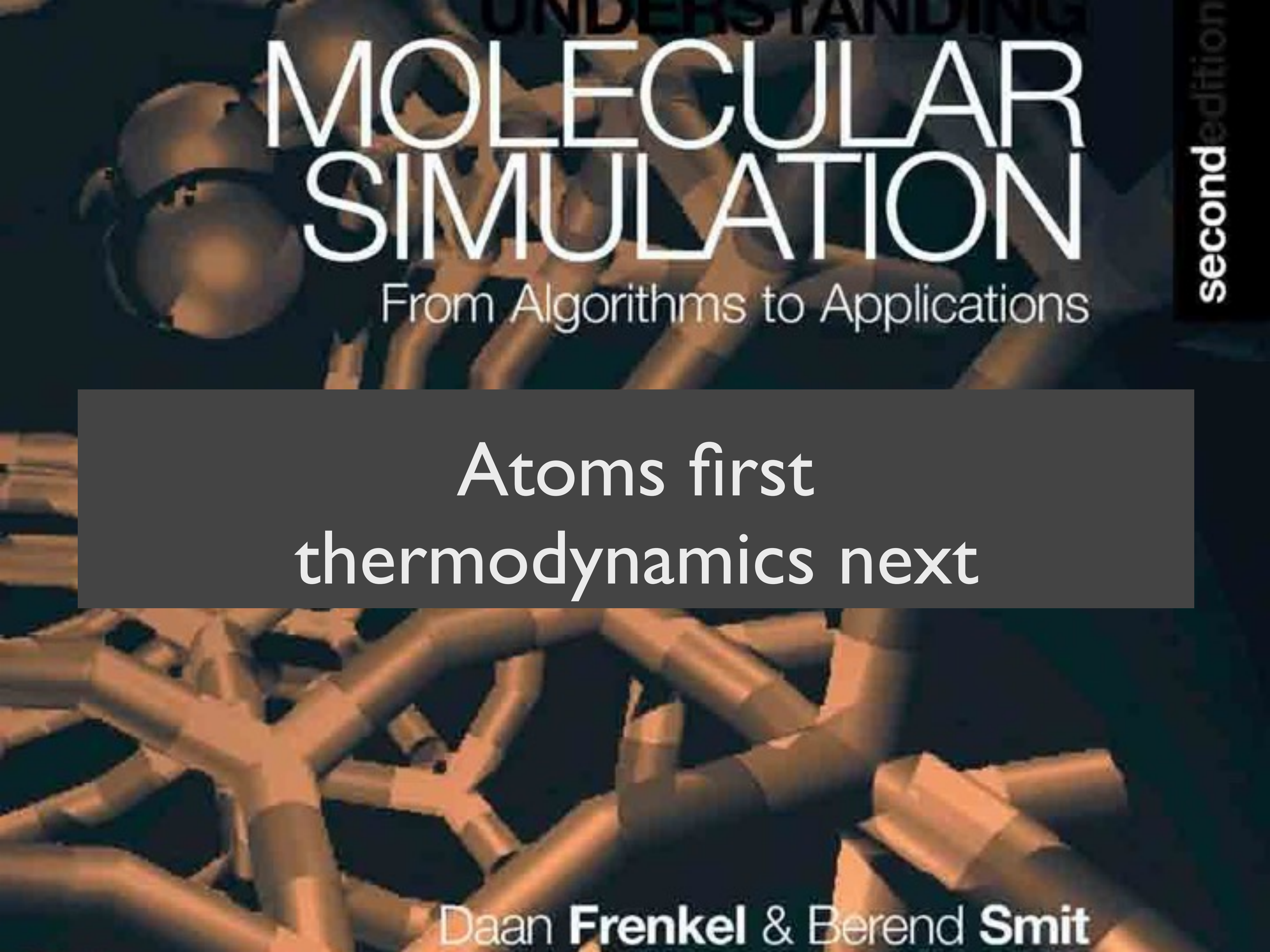
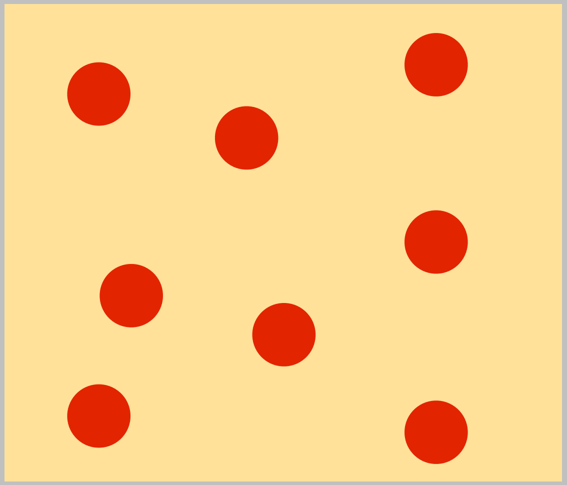
Other ensembles:

- Constant pressure
- grand-canonical ensemble



Atoms first thermodynamics next

A box of particles



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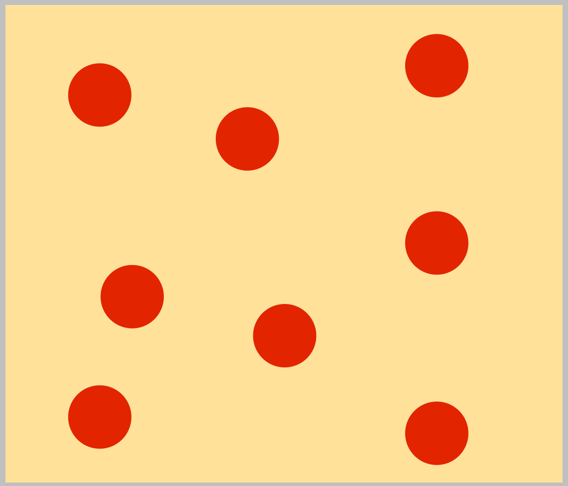

We have given the particles an intermolecular potential

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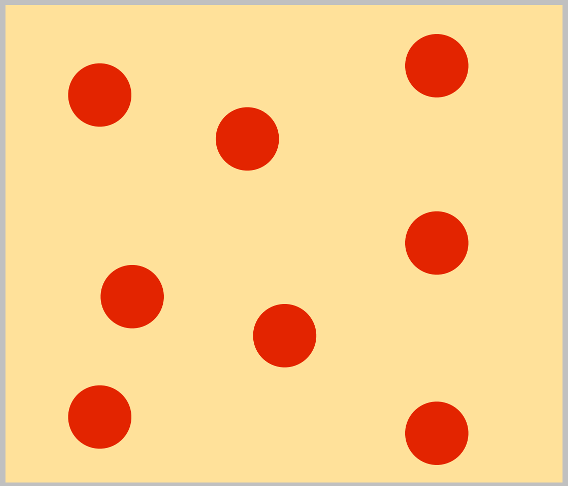

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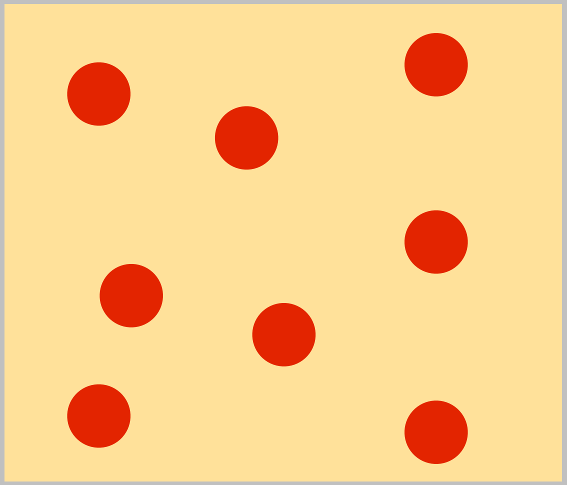

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$$\mathbf{F}(\mathrm{r}) = -\nabla \mathrm{u}(\mathrm{r})$$

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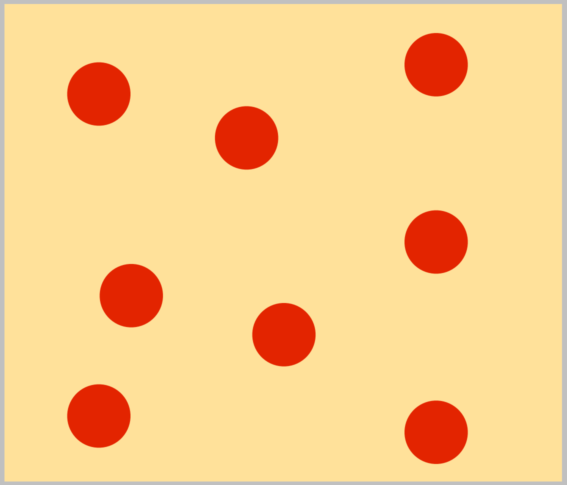

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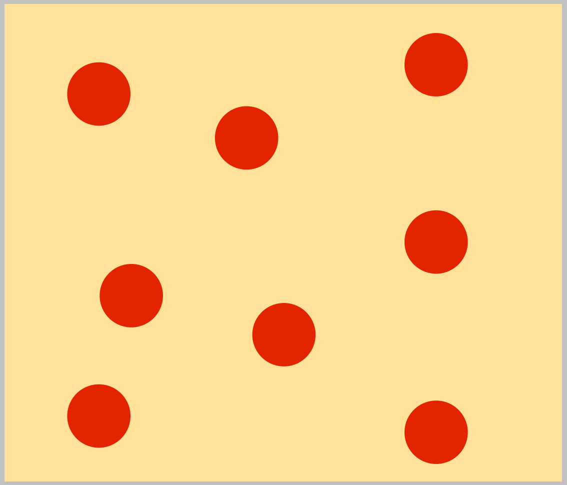

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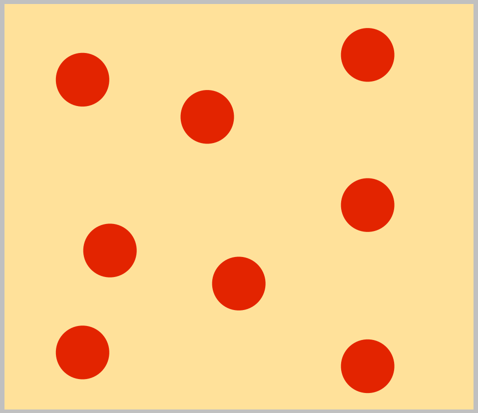
Conservation of total energy

Phase space

Thermodynamics: N,V,E



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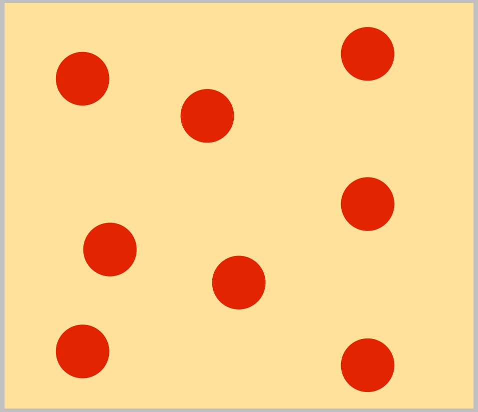

Molecular:

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

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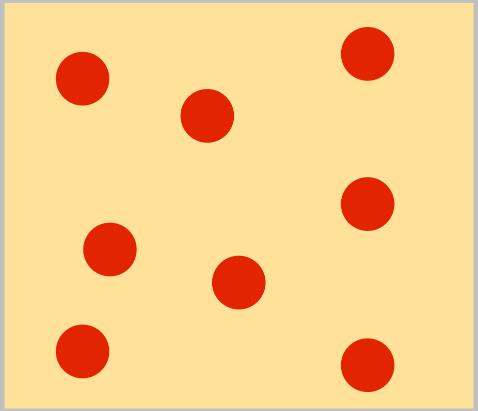

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point in <u>phase space</u>

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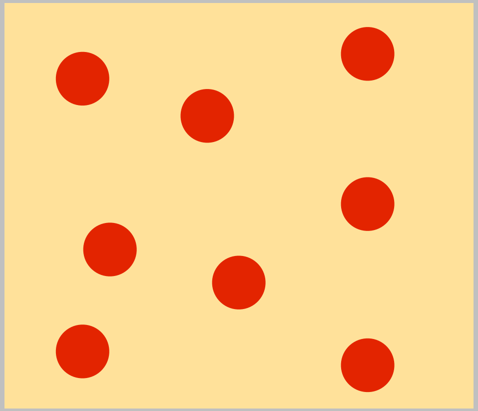

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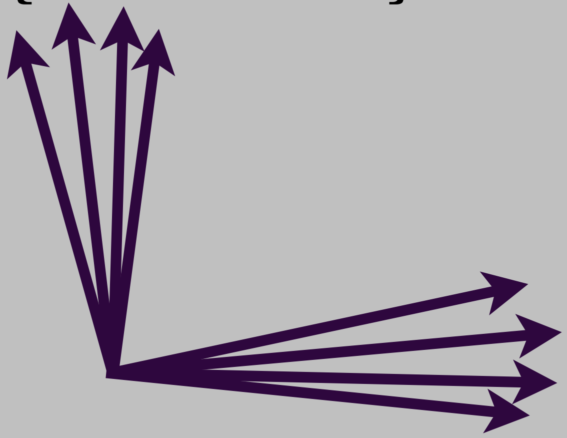

$$\left\{ \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N \right\}$$

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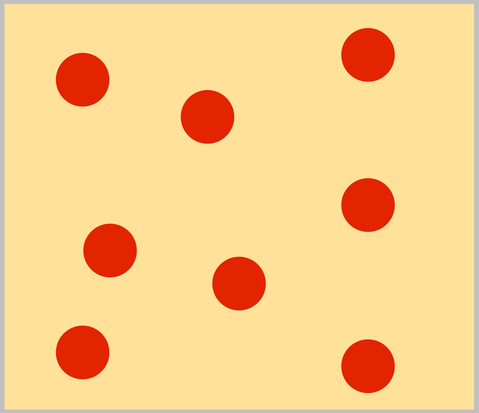
Phase space



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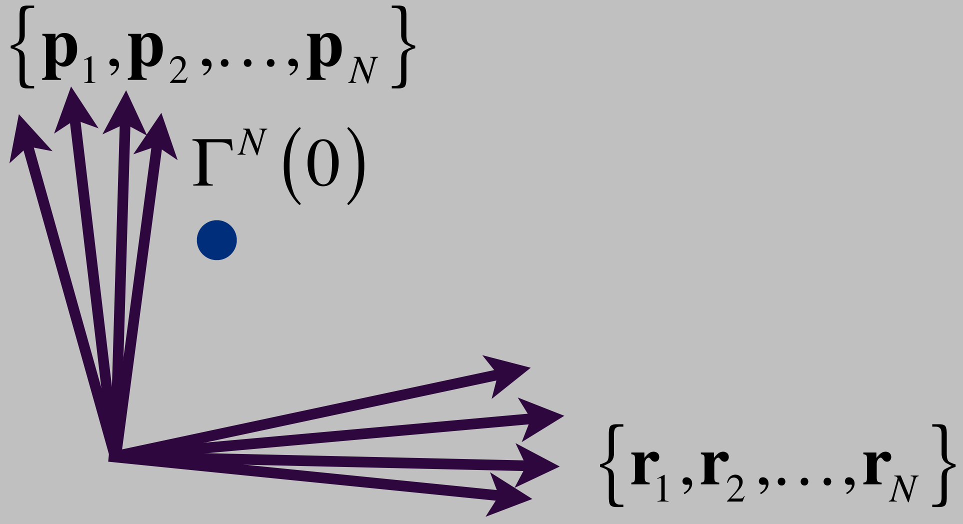

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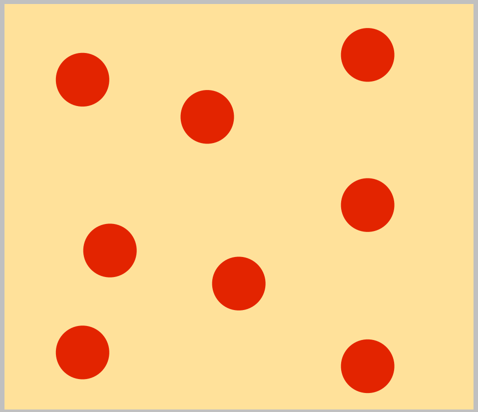

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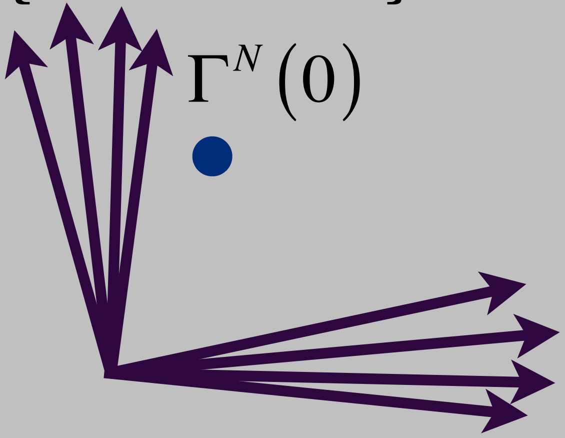


$\{\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N\}$

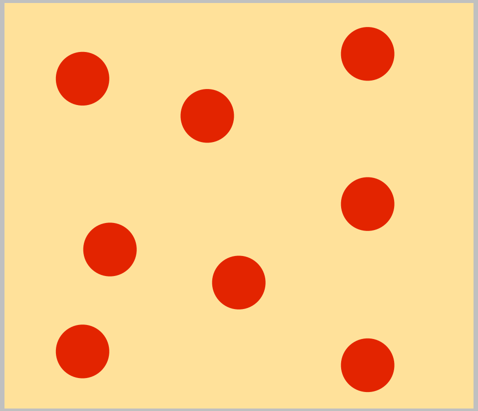
$\Gamma^N(0)$

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

trajectory: classical mechanics

Phase space

Thermodynamics: N,V,E



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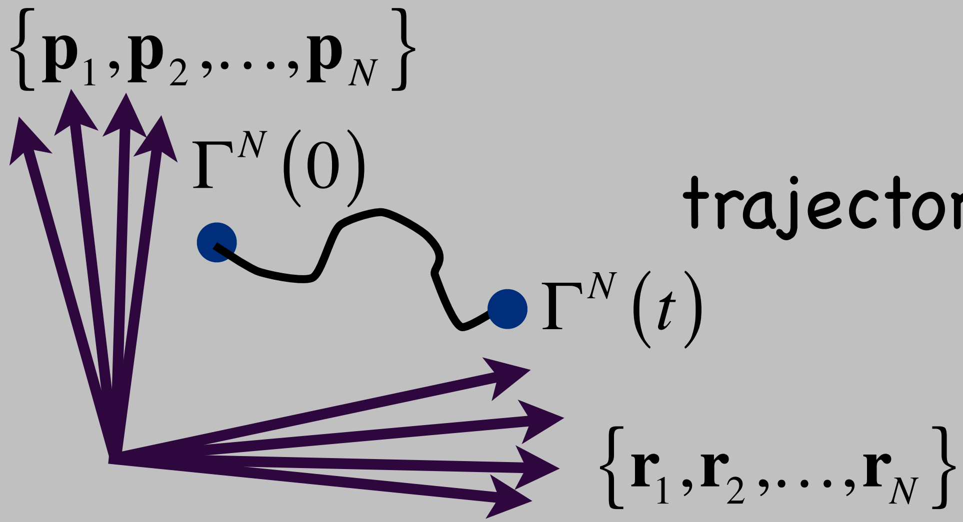

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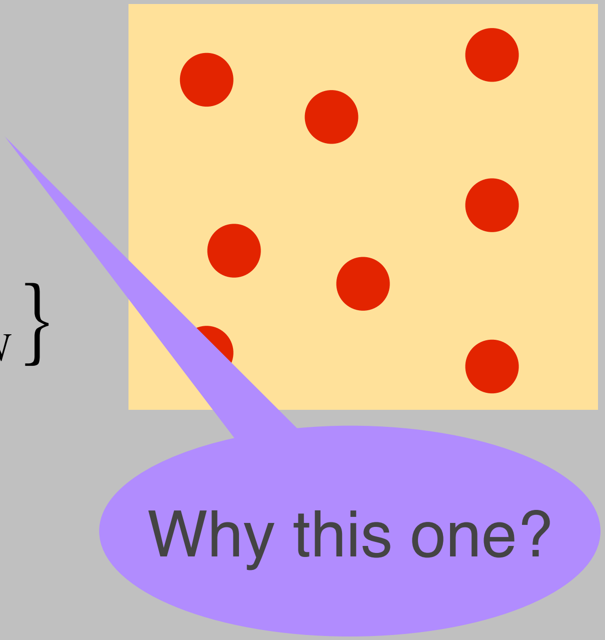

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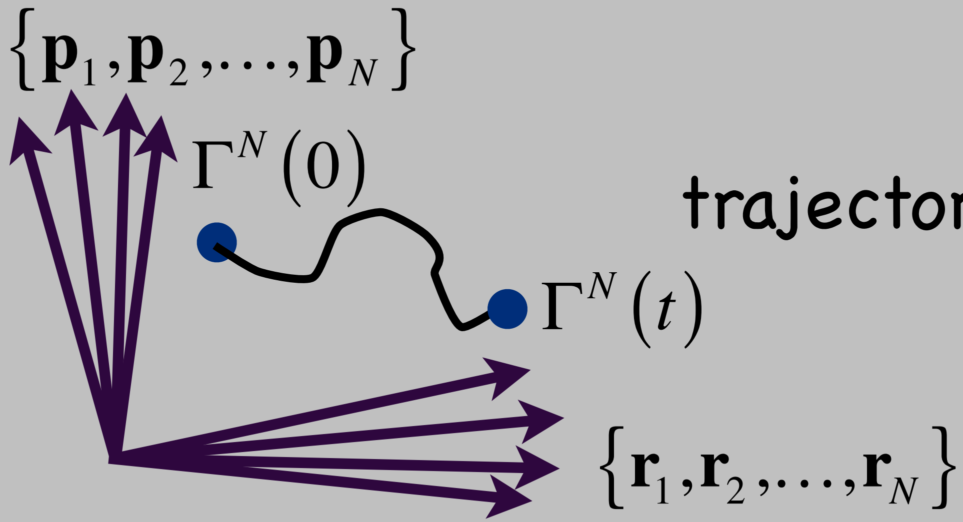

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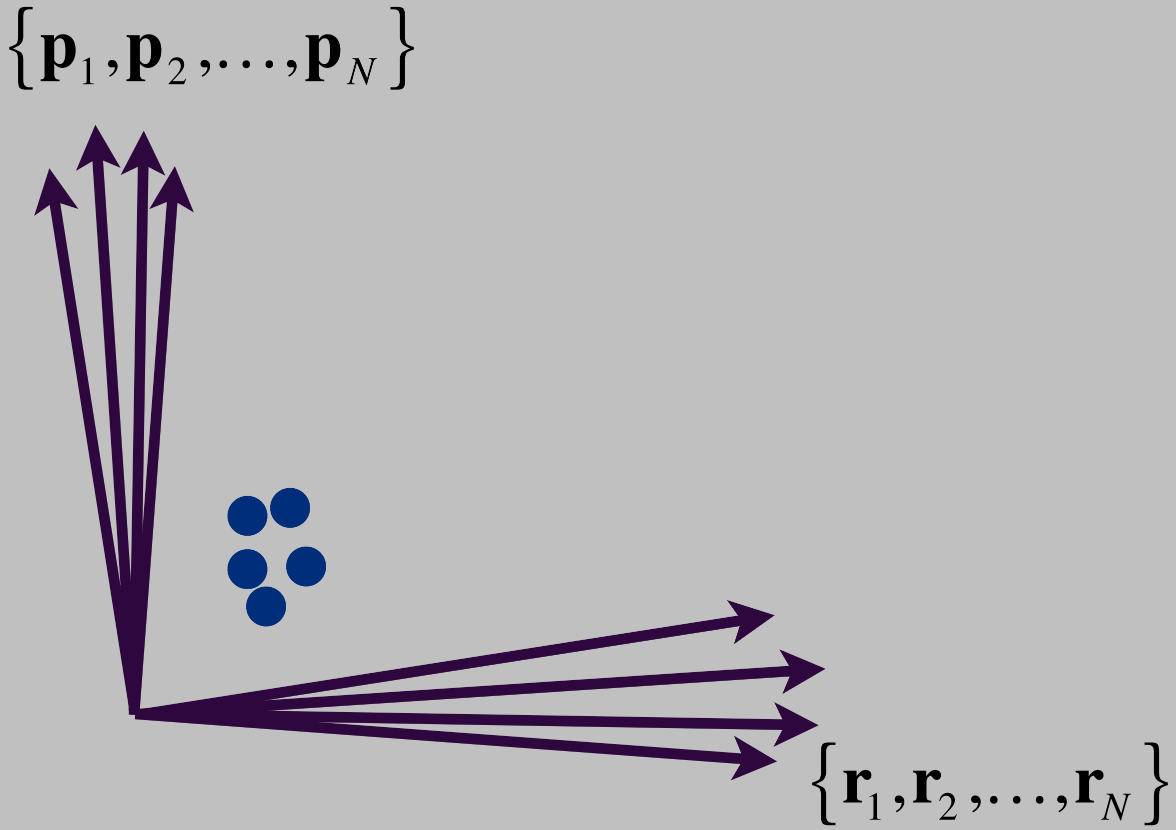

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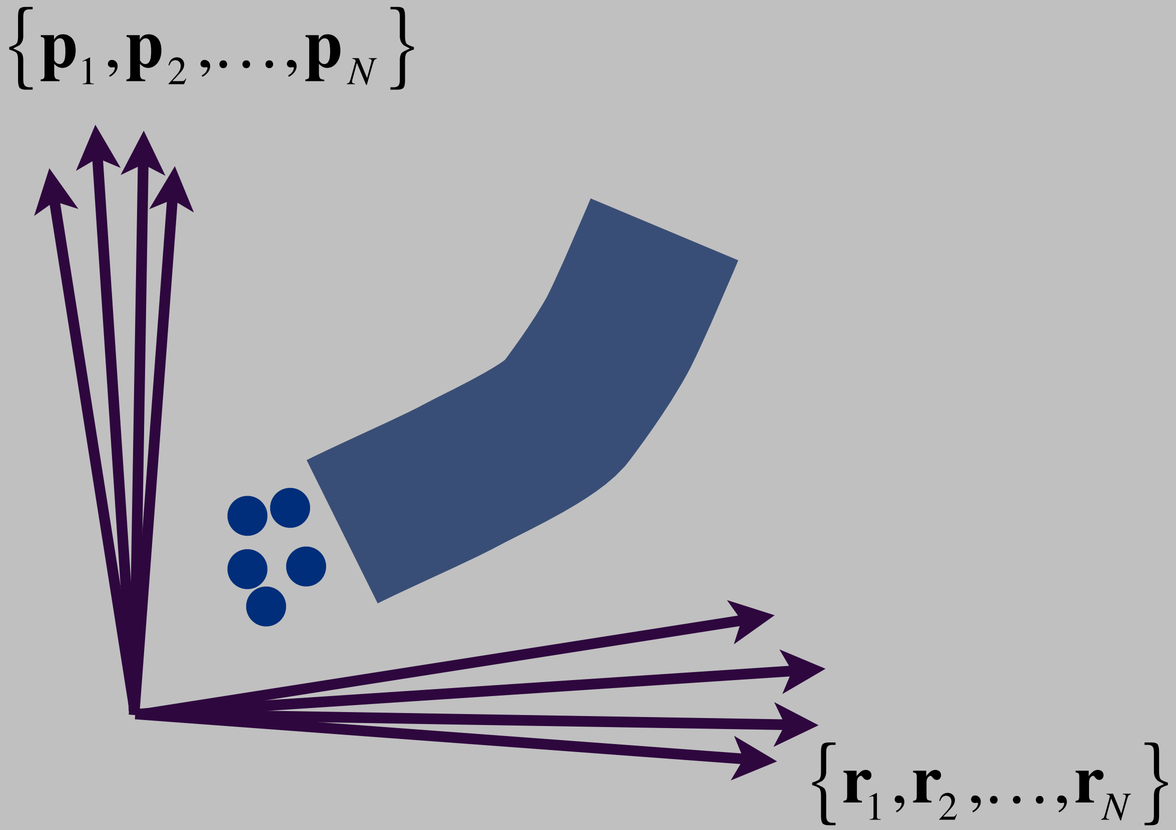

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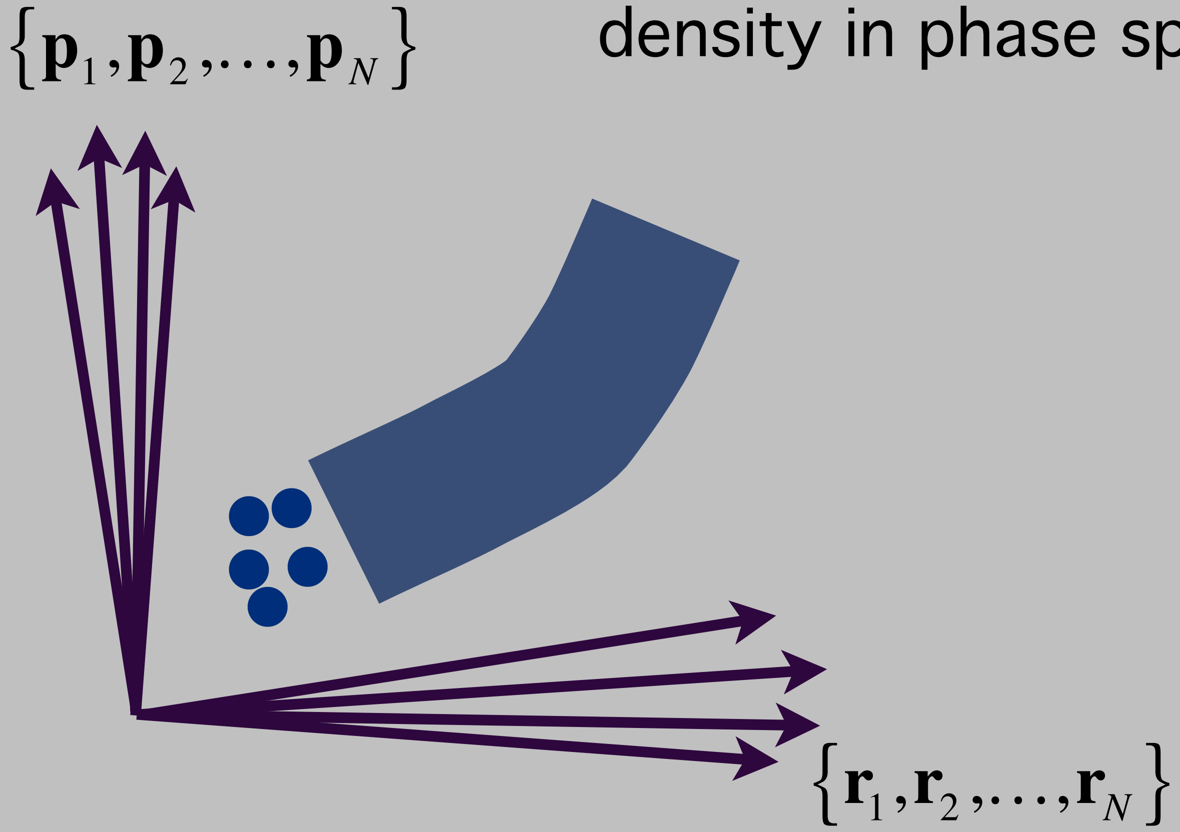
These trajectories define a probability density in phase space



Intermezzo 1: phase rule

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- Question: explain the phase rule?

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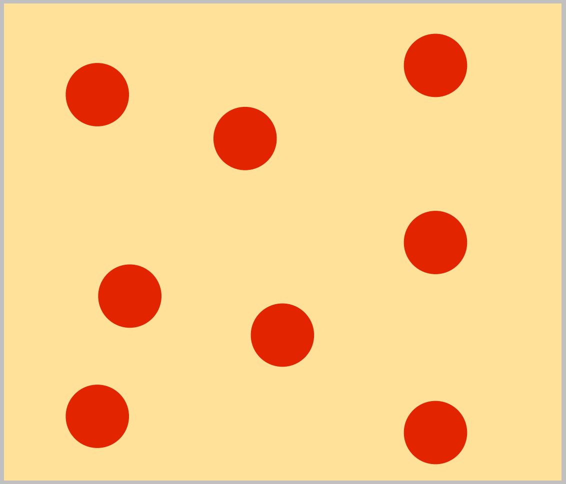
Making a gas



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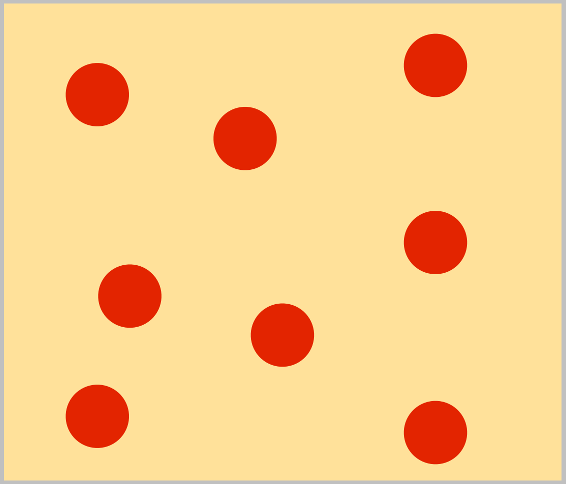
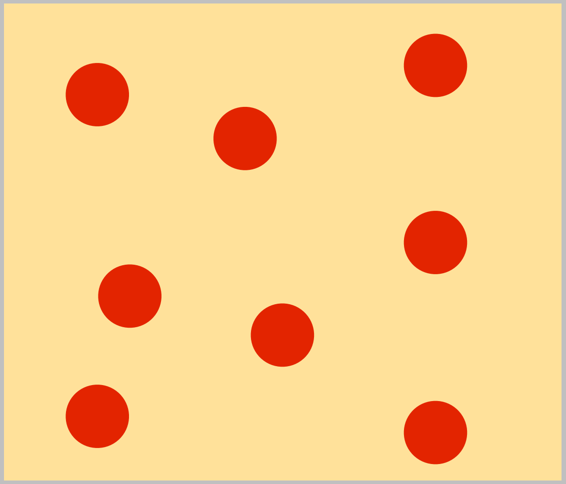


What do we need to specify to fully define a thermodynamic system?

Making a gas



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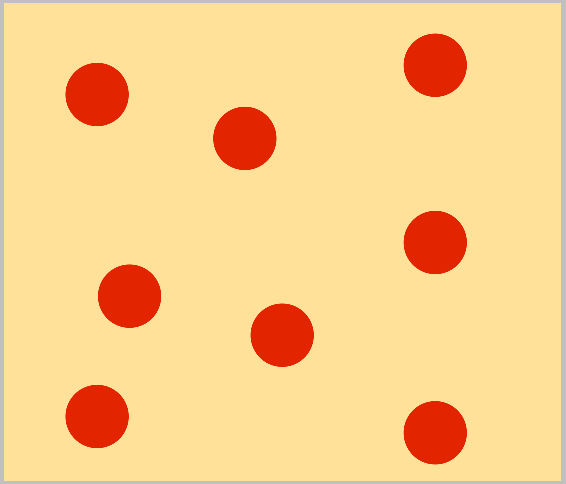
Making a gas



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

1. Specify the volume V
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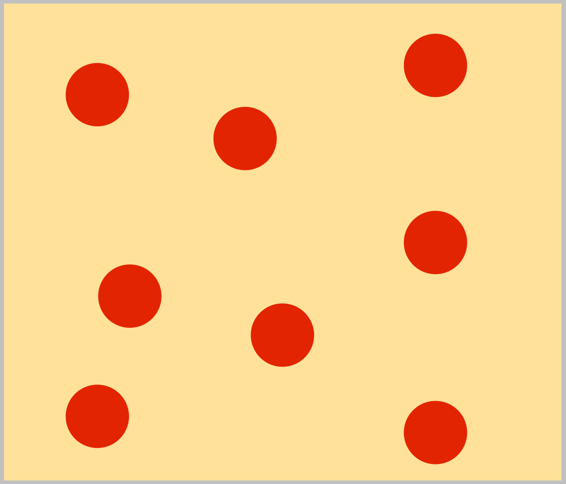
Making a gas



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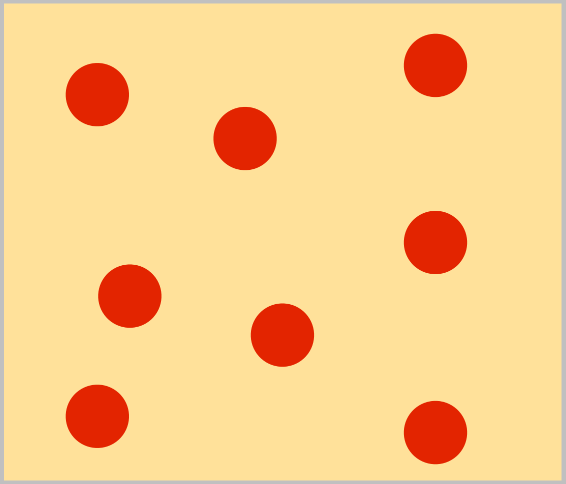

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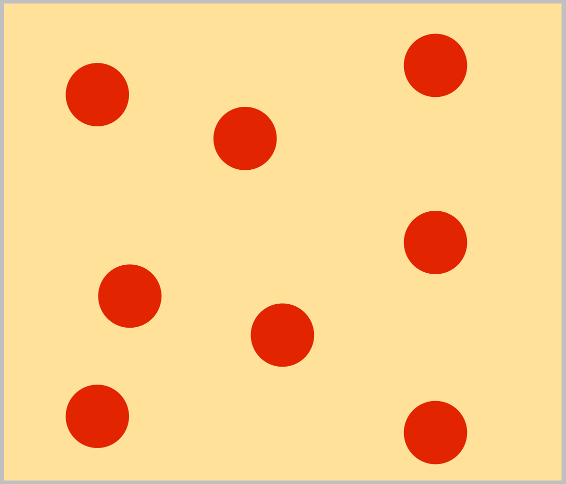

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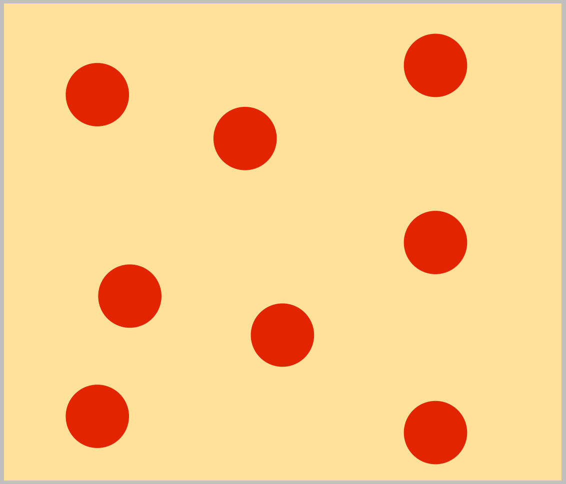

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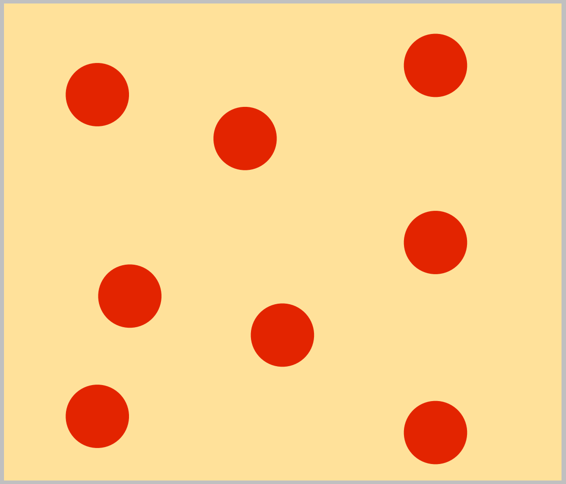

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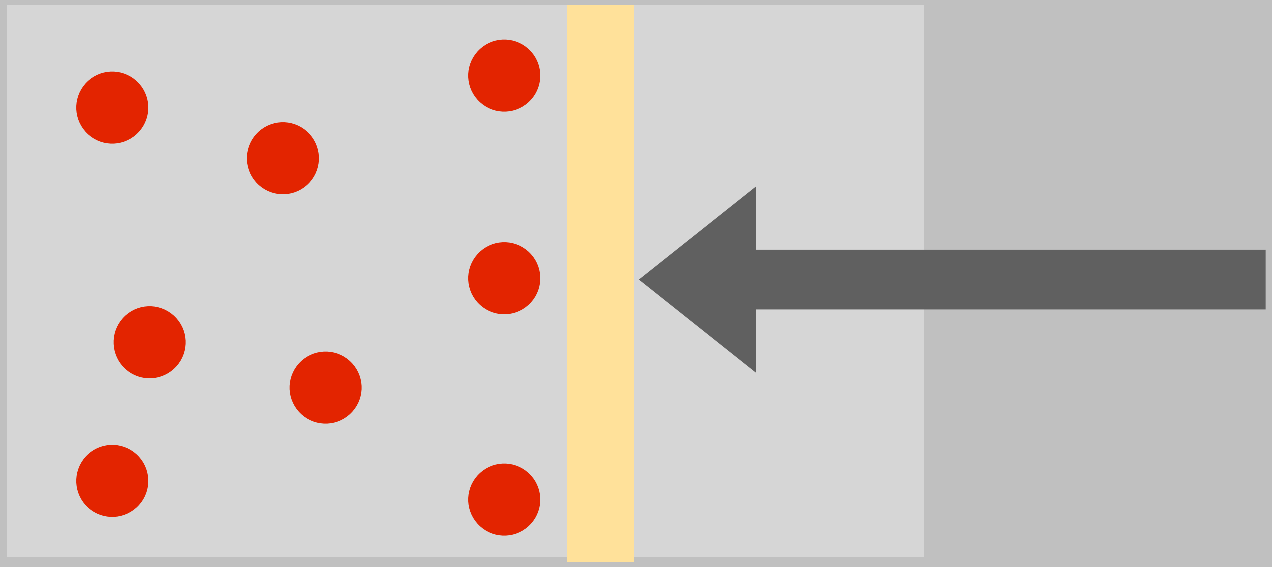
(micro-canonical ensemble)

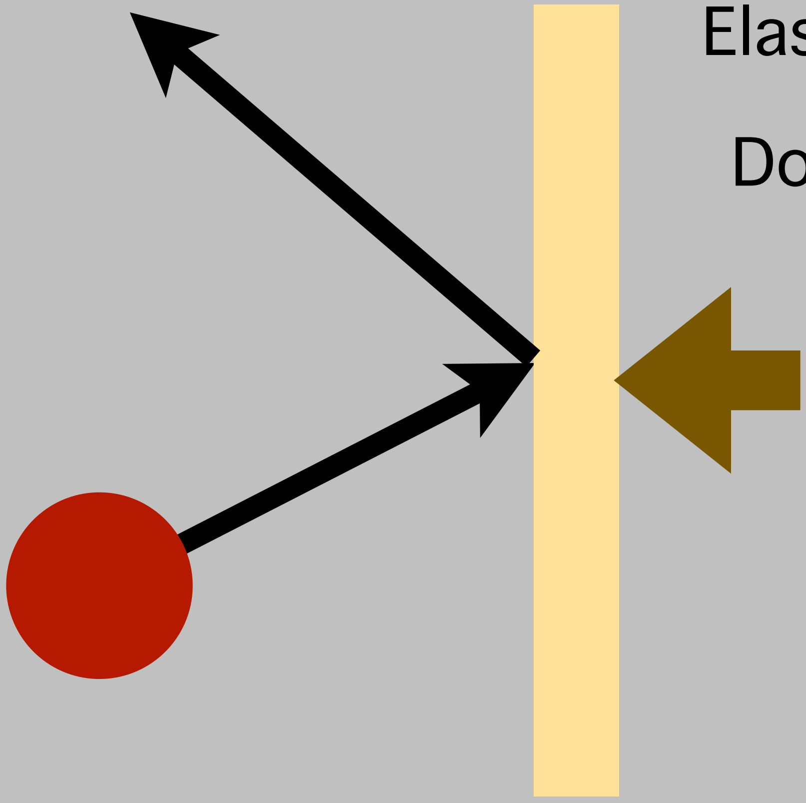
Pressure

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?

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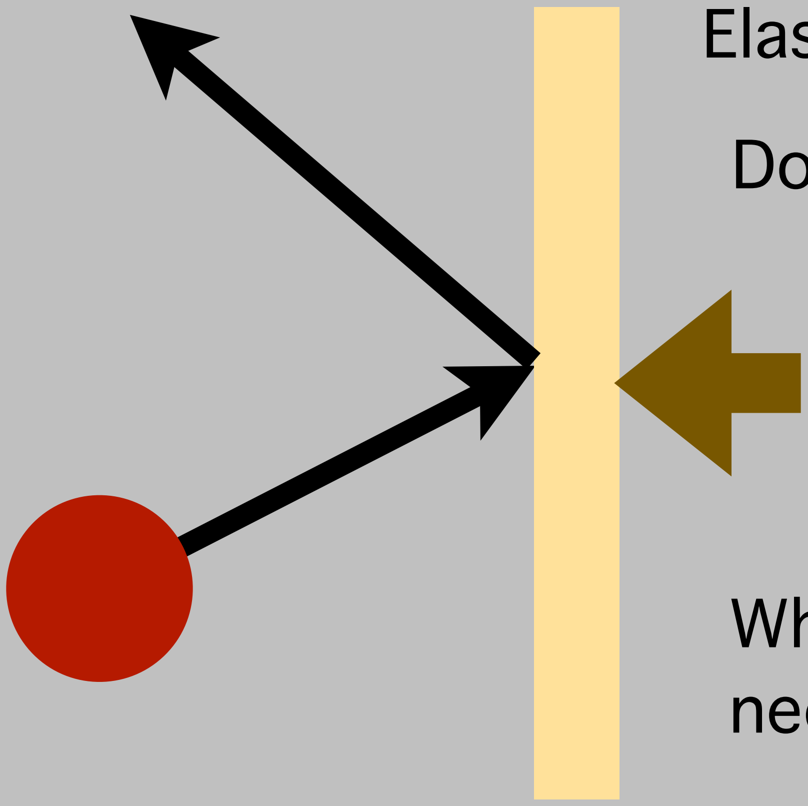

Elastic collisions:

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

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- # particles: $\rho\ A\ v_x$

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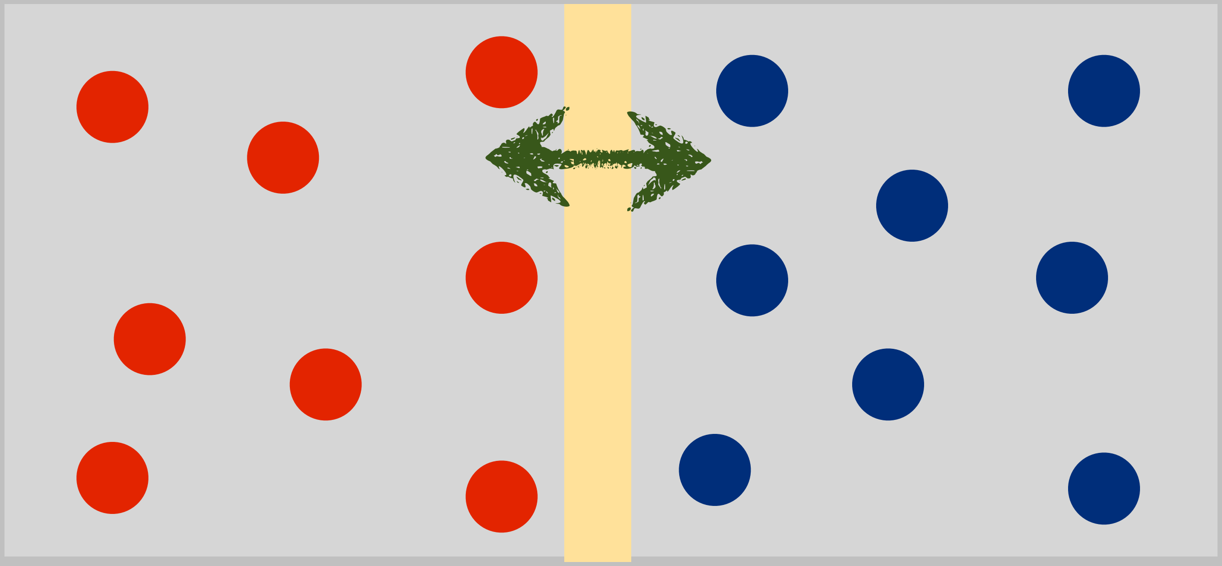
- Pressure: $P V = N k_B T$

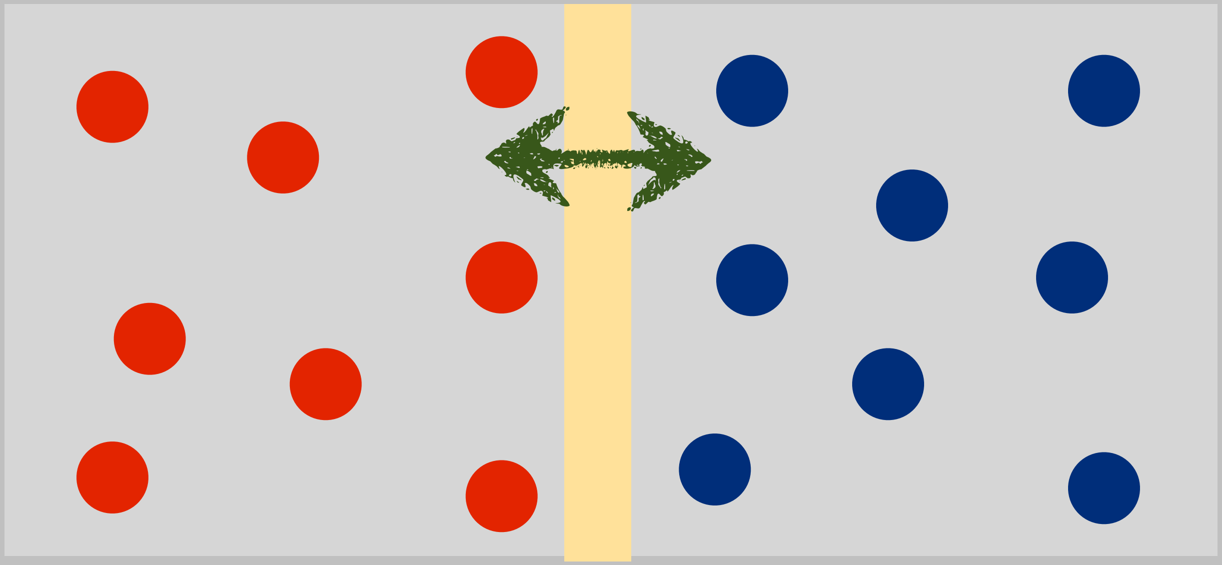
Experiment (1)



NVE_1

NVE_2

Experiment (1)



NVE_1

NVE_2

$E_1 > E_2$

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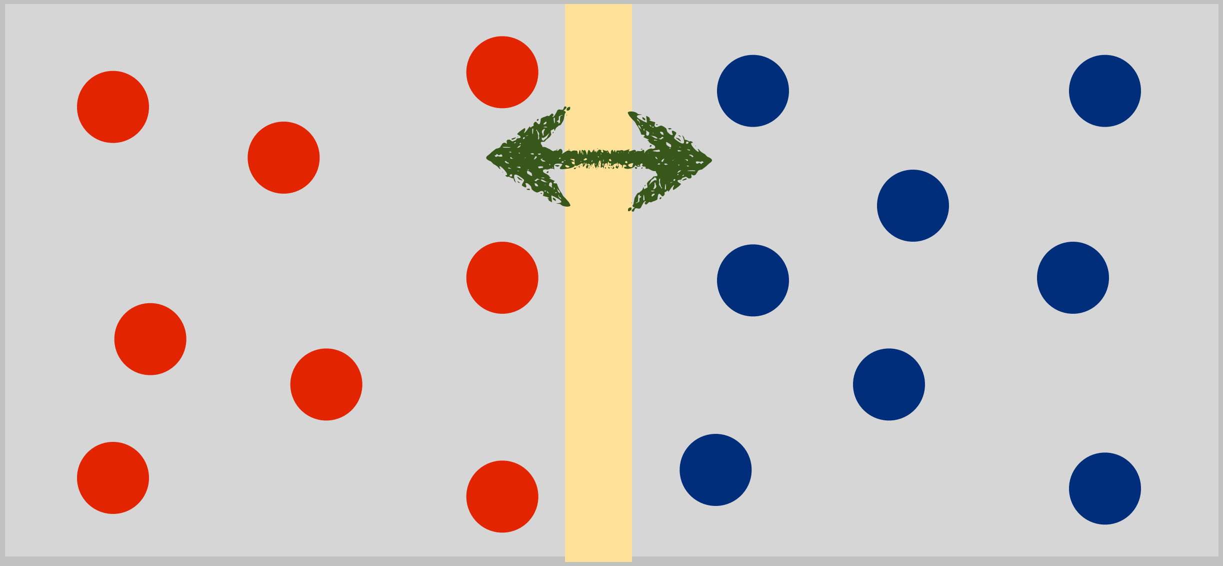
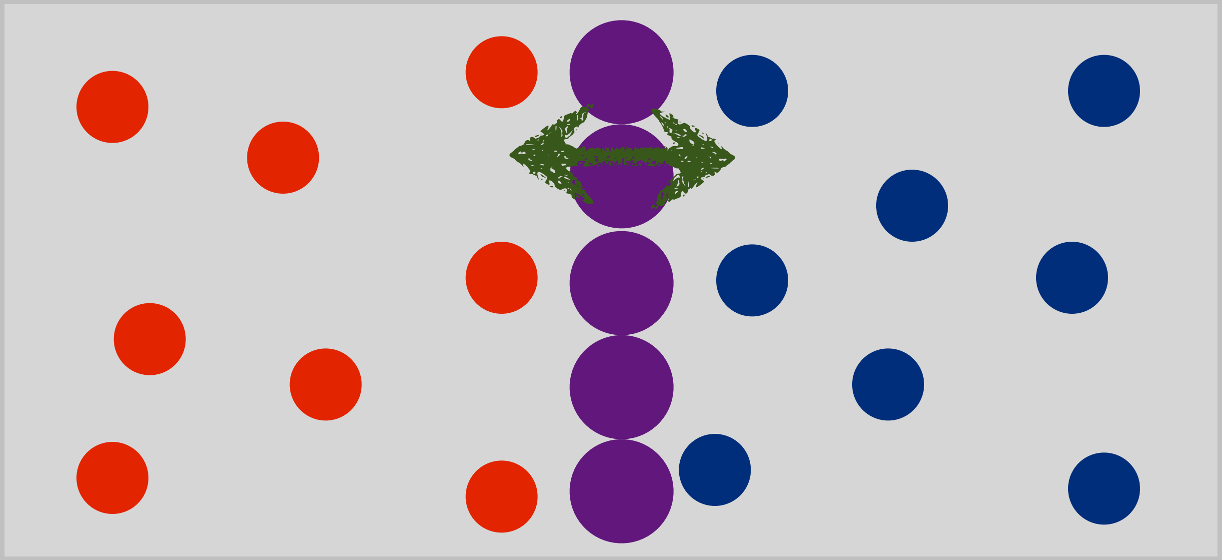


NVE_1 NVE_2 $E_1 > E_2$

What will the moveable wall do?

Experiment (2)



NVE$_1$

NVE$_2$

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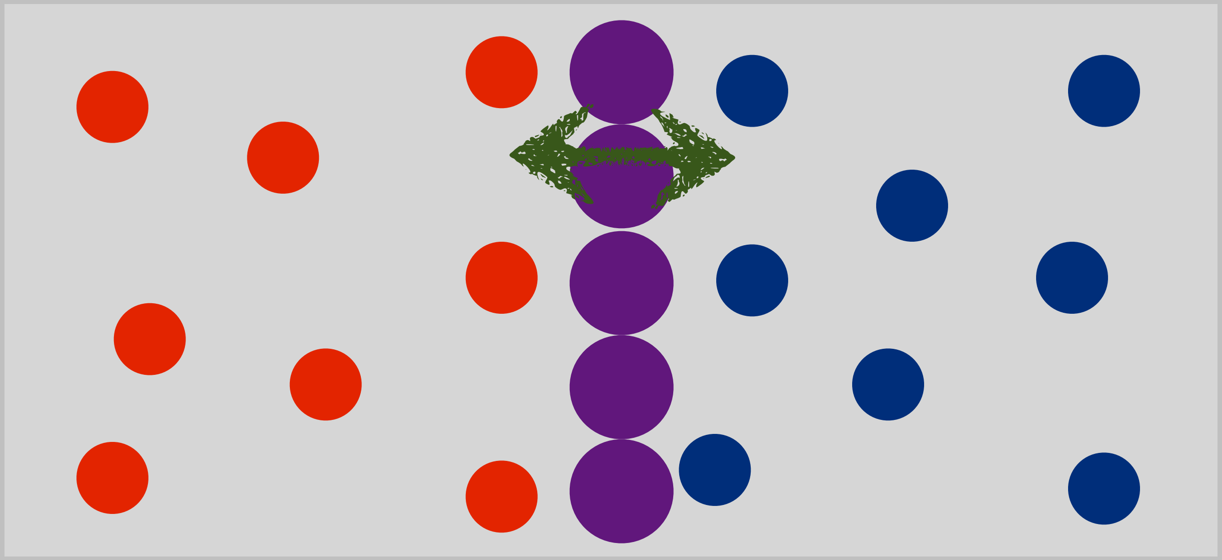
Experiment (2)



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

Now the wall are heavy molecules

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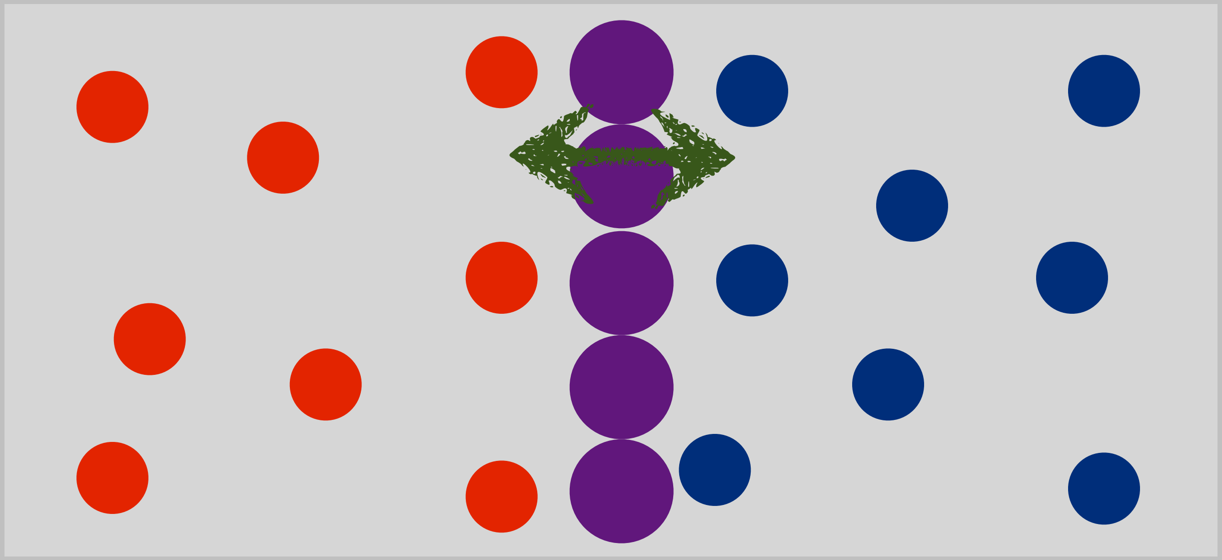

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Now the wall are heavy molecules

What will the moveable wall do?

Newton + atoms

Newton + atoms

- We have a natural formulation of the first law

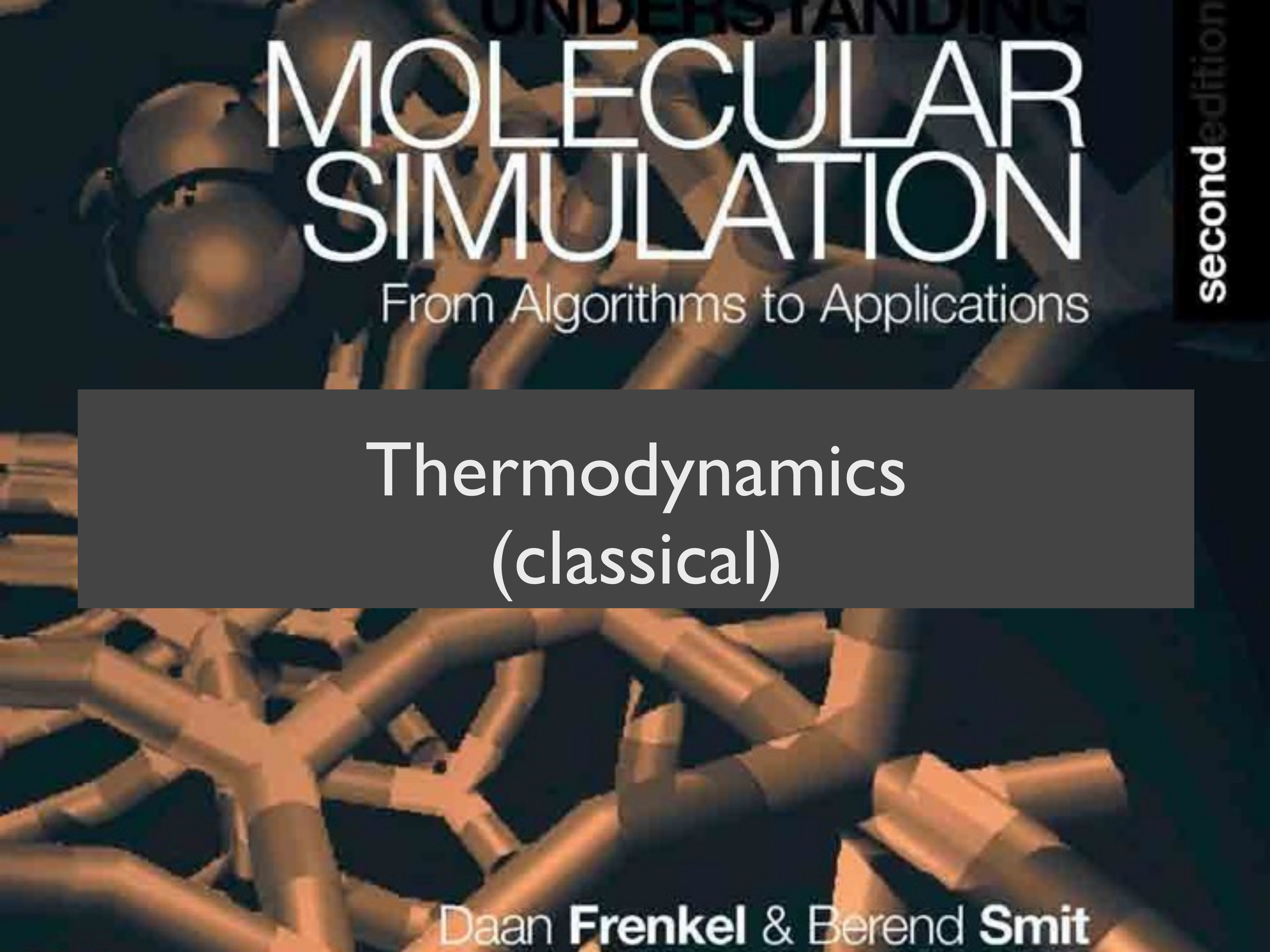
Newton + atoms

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

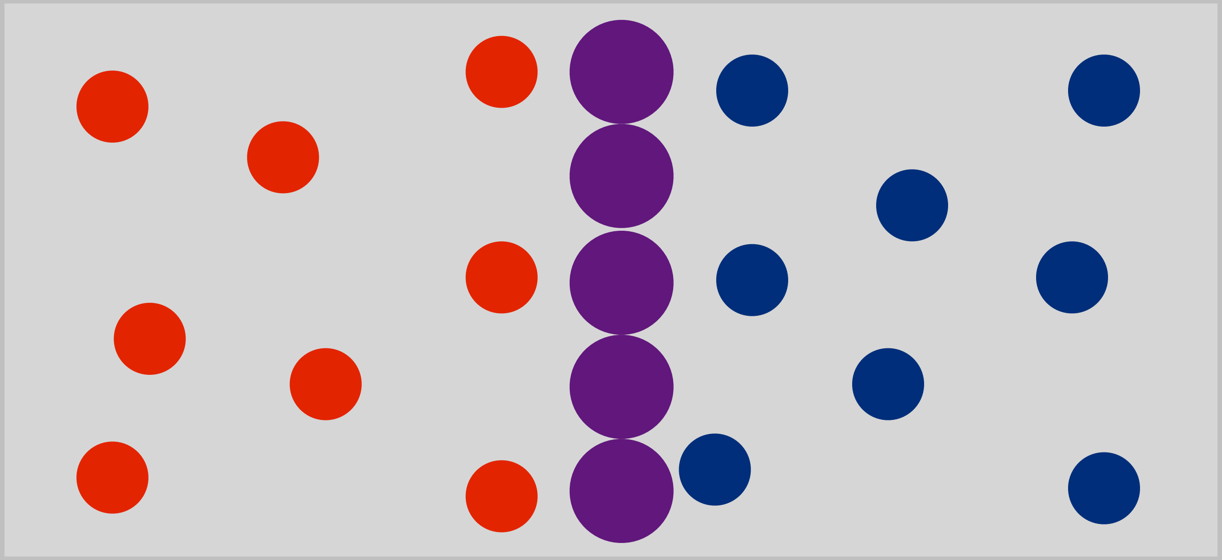
Newton + atoms

- 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$_2$ $E_1 > E_2$

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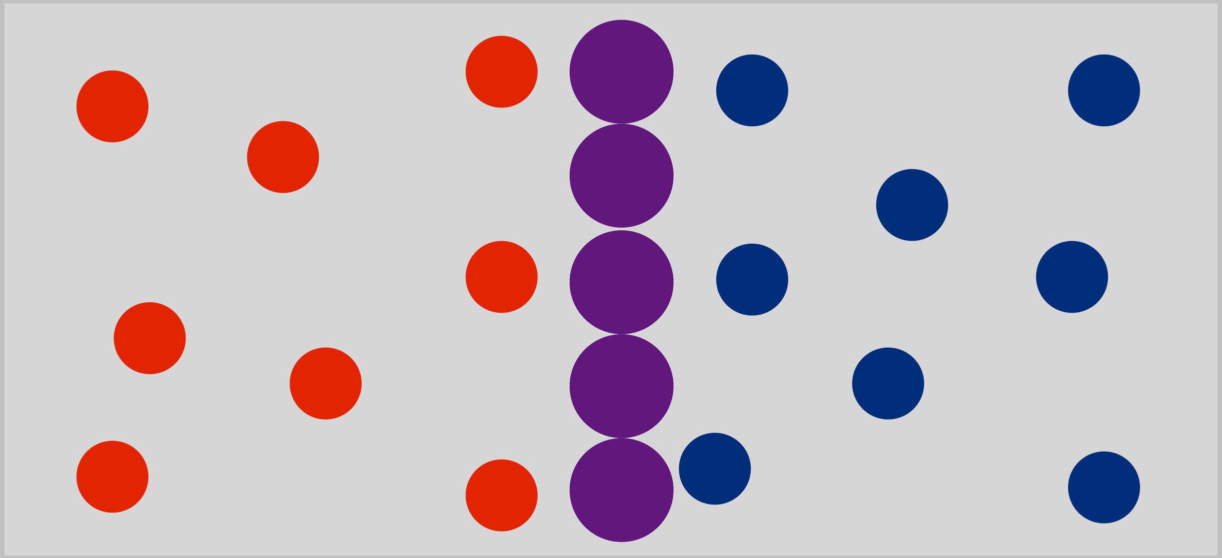

NVE_1 NVE_2 $E_1 > E_2$

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

Classical Thermodynamics

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- 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

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Carnot: Entropy difference between two states:

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

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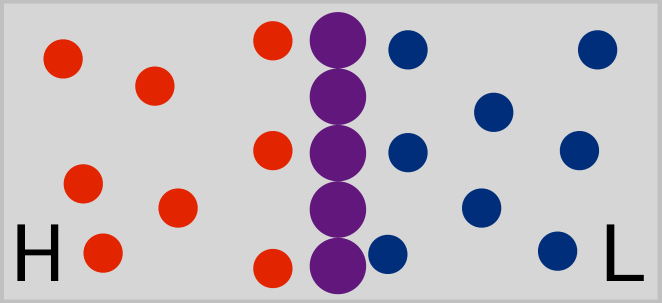
If we have work by a expansion of a fluid

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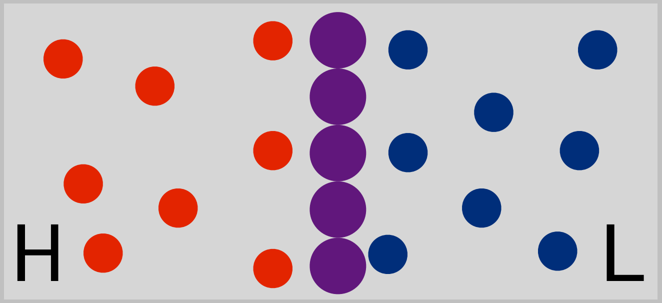
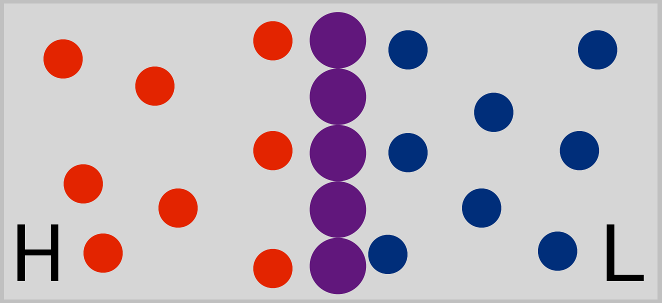


Let us look at the <u>very initial</u> stage



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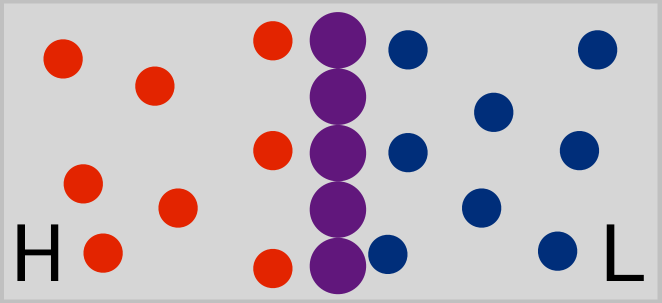
dq is so small that the temperatures of the two systems do not change



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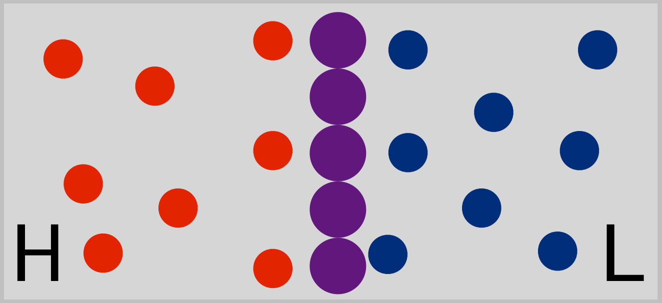

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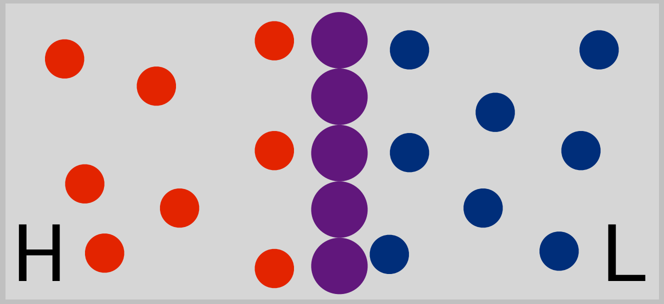

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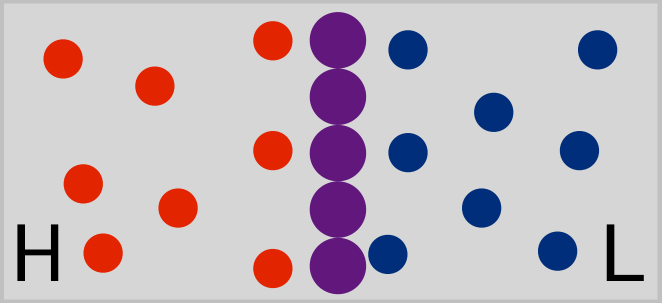

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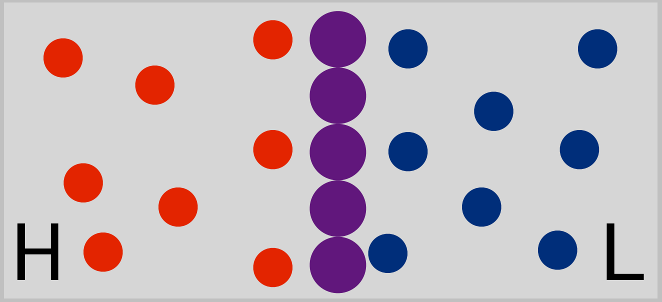

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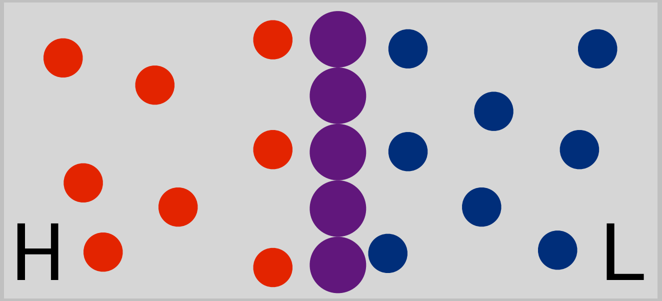

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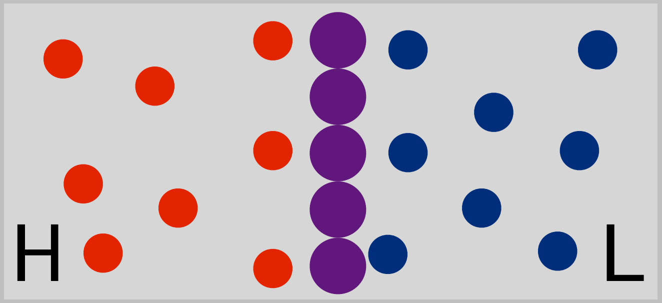

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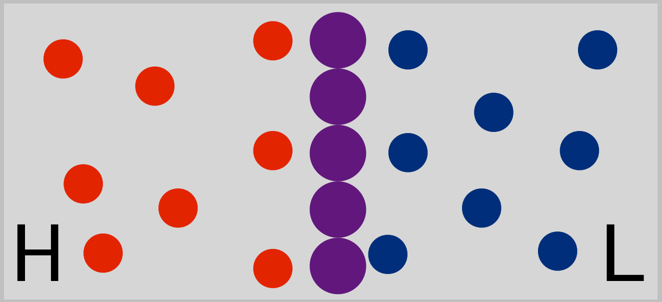

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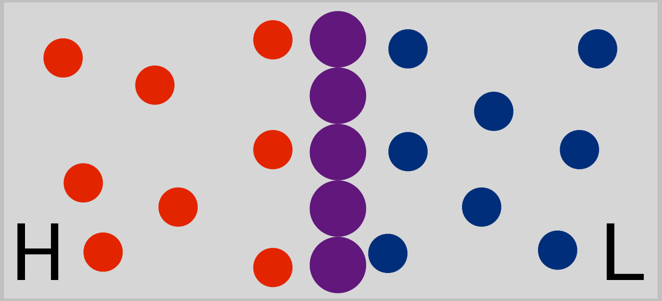

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This gives for the entropy change: $dS > 0$

Hence, the entropy increases until the two temperatures are equal

Question

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

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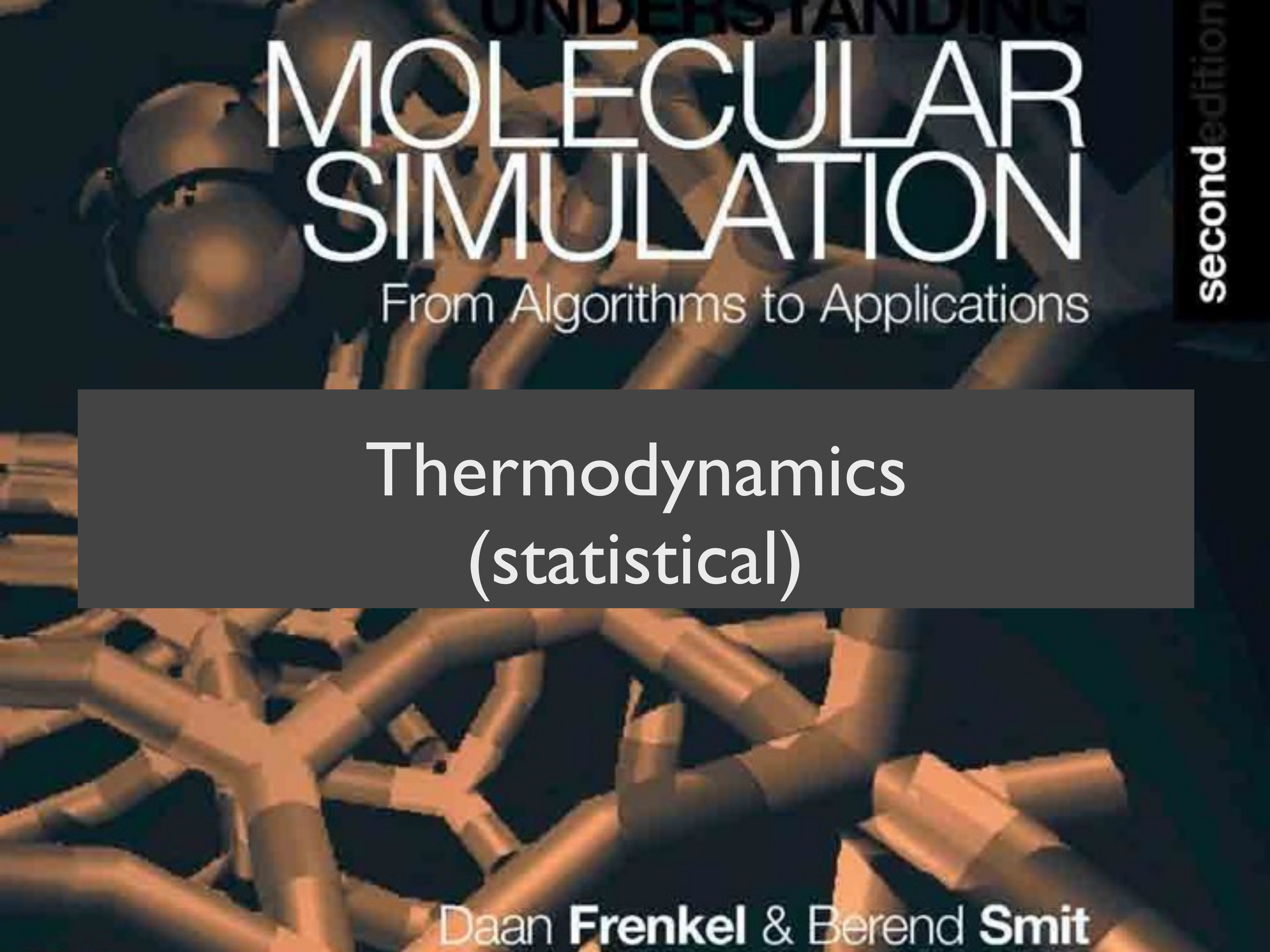
- Thermodynamics has a sense of time, but not Newton’s dynamics
  - Look at a water atoms in reverse
  - Look at a movie in reverse
- When do molecules know about the arrow of time?



Thermodynamics (statistical)

Statistical Thermodynamics

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All of statistical thermodynamics and equilibrium thermodynamics

Statistical The mics

Basic assumpti

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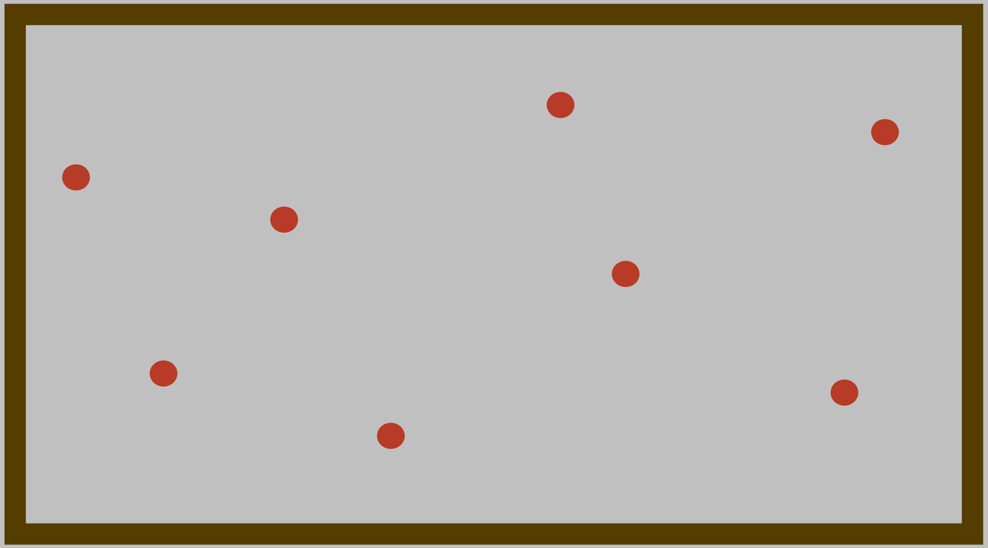
equili dynamics

··· but classical thermodynamics is based on laws

Ideal gas

Let us again make an ideal gas



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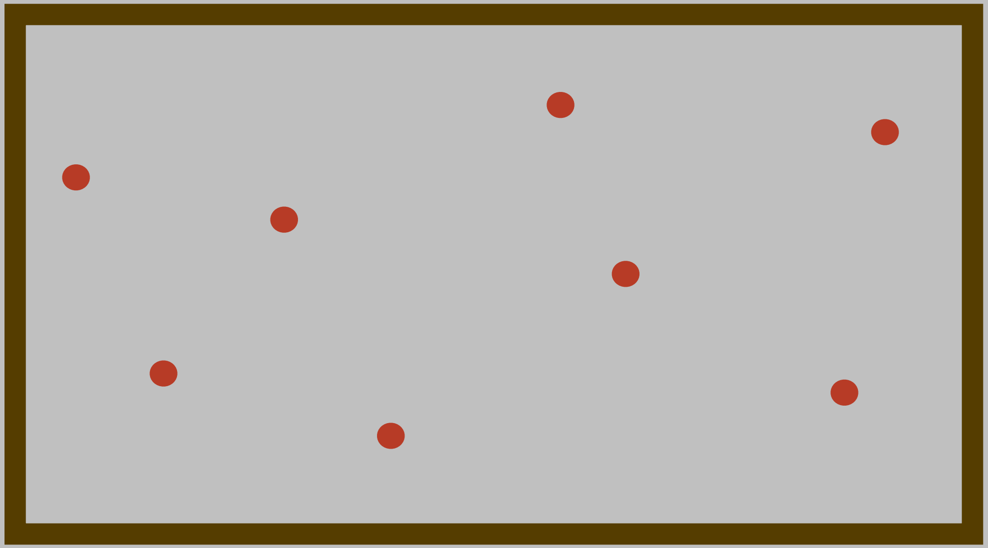

We select:

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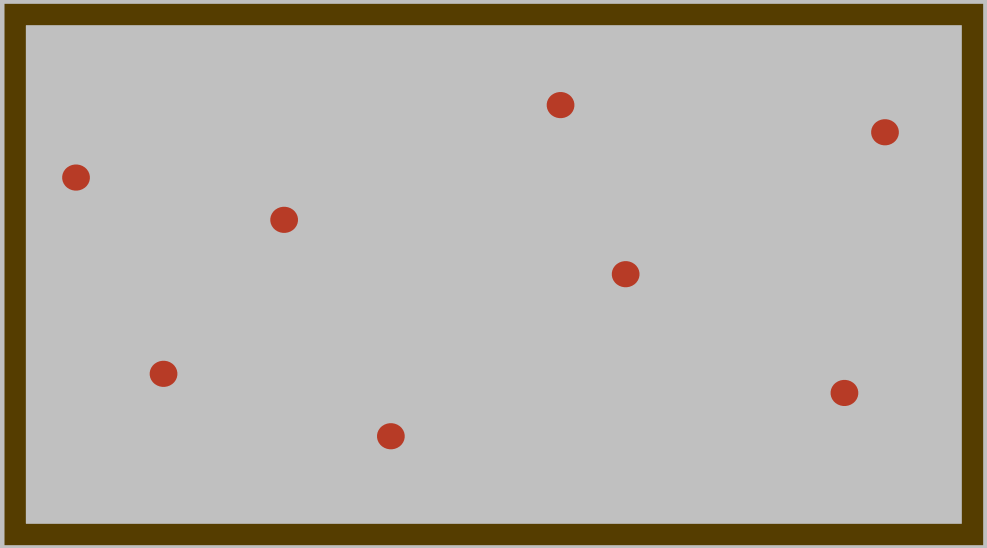

We select:

(1) N particles,

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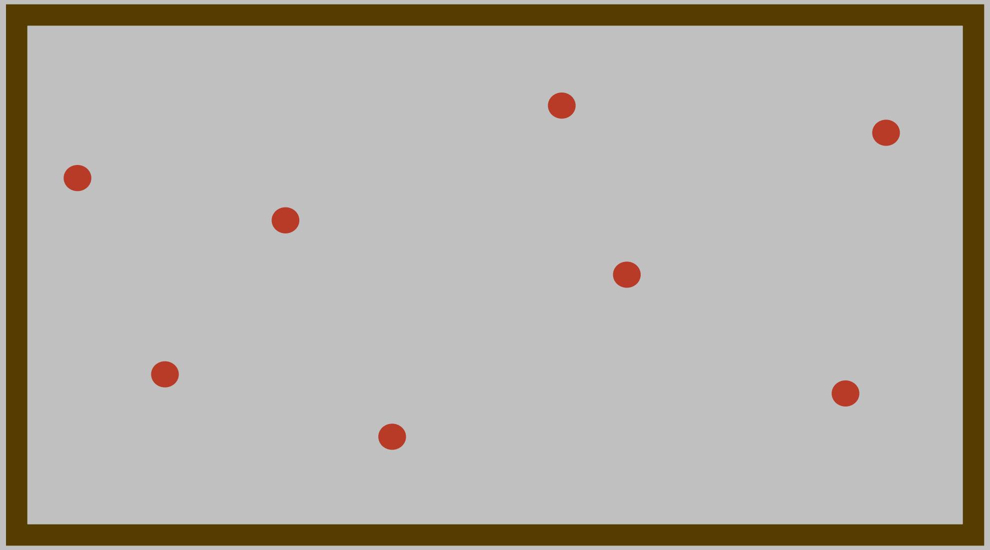

We select:
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(2) Volume V,

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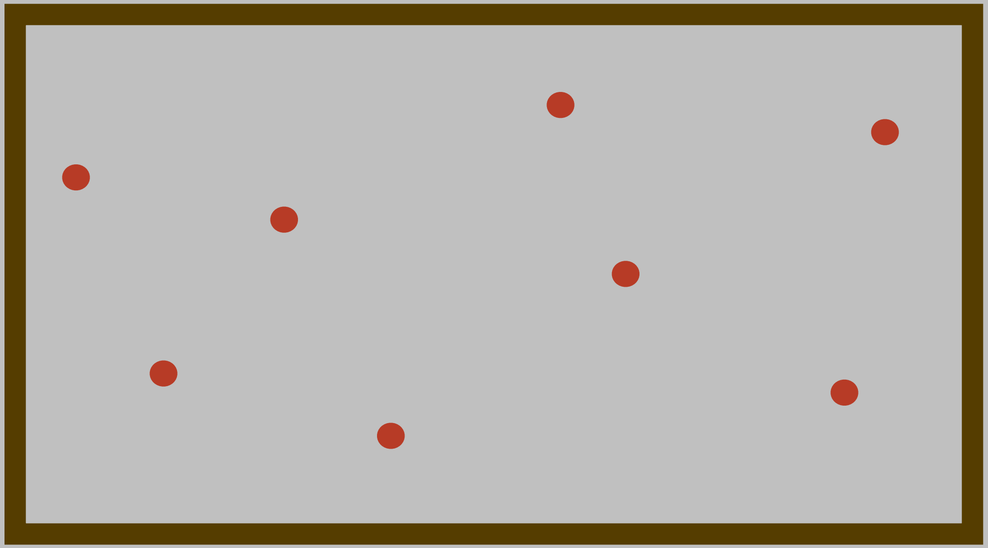

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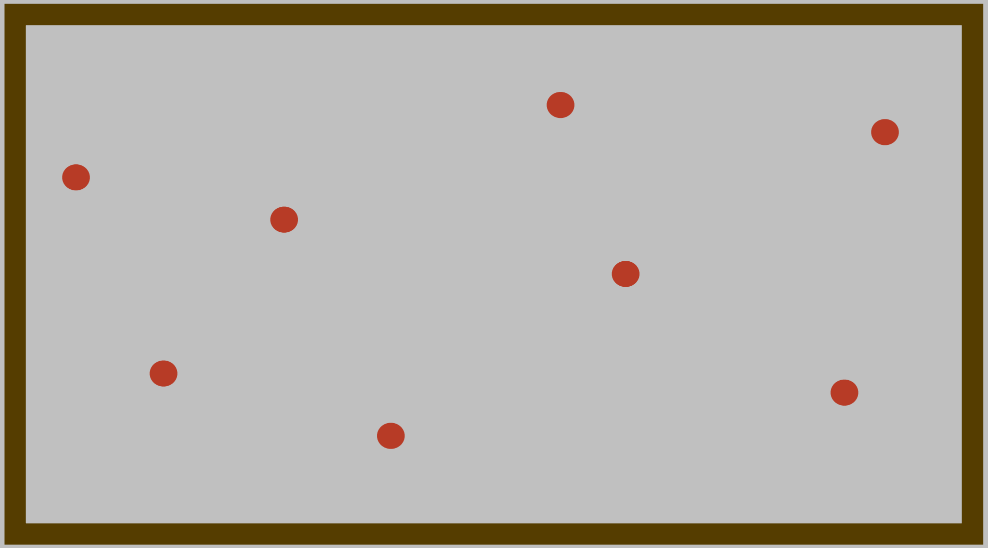

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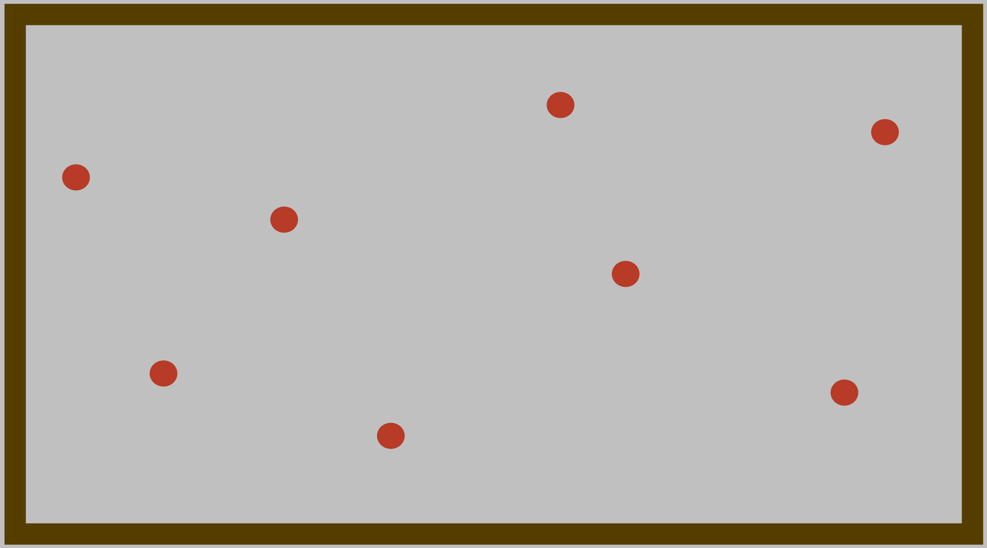

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This fixes; V/n, U/n

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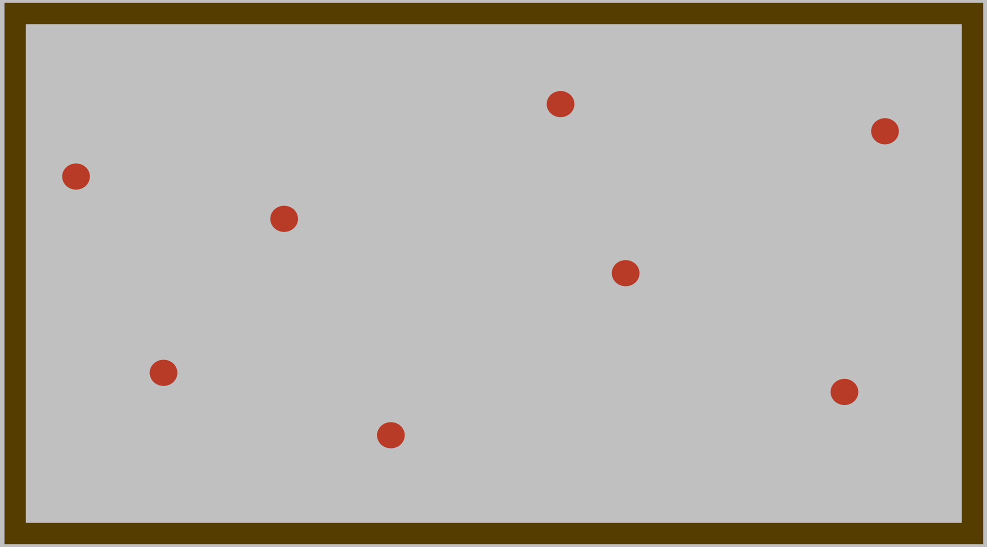

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Basic assumption

For an isolated system any microscopic configuration is equally likely

What is the probability to find this configuration?

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The system has the same kinetic energy!!

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Our basic assumption must be seriously wrong!

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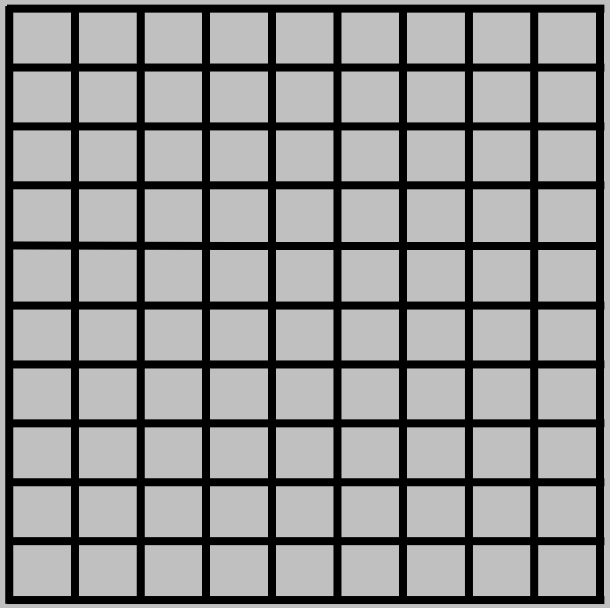
Our basic assumption must be seriously wrong!

... but are we doing the statistics correctly?

Question

- Is it safe to be in this room?

… lets look at our statistics correctly



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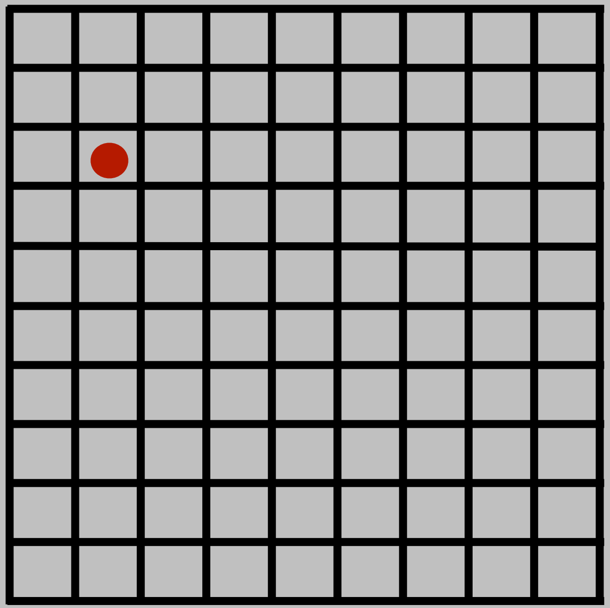

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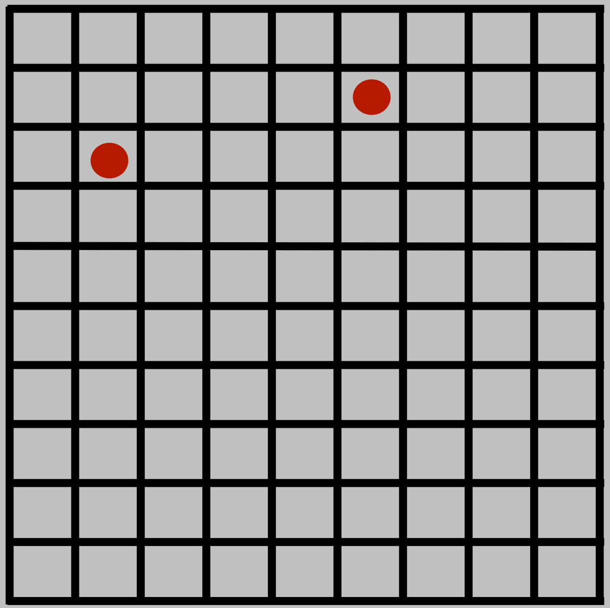

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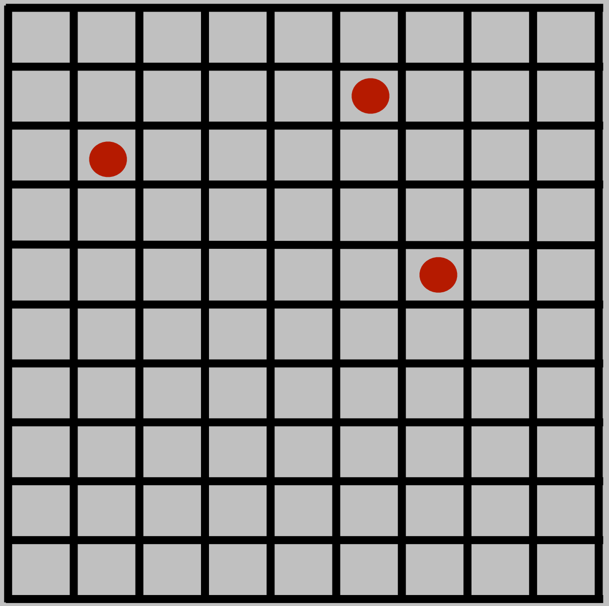

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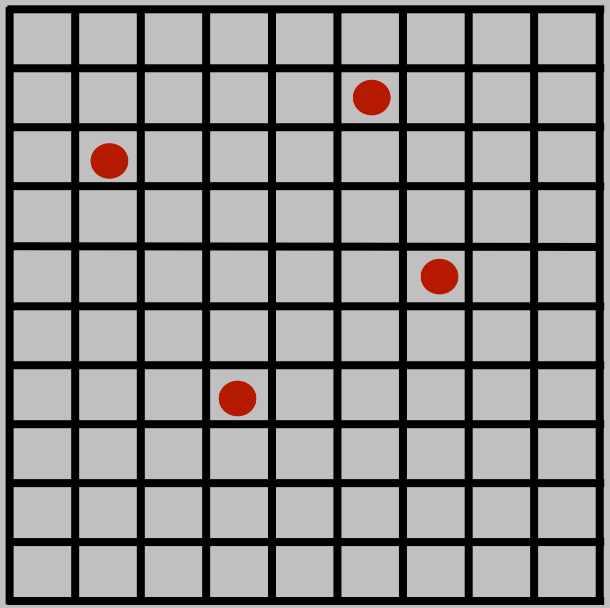

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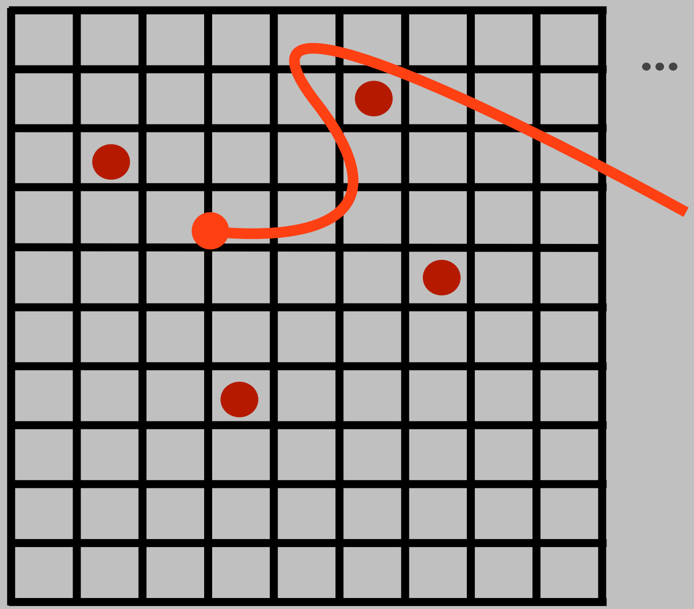

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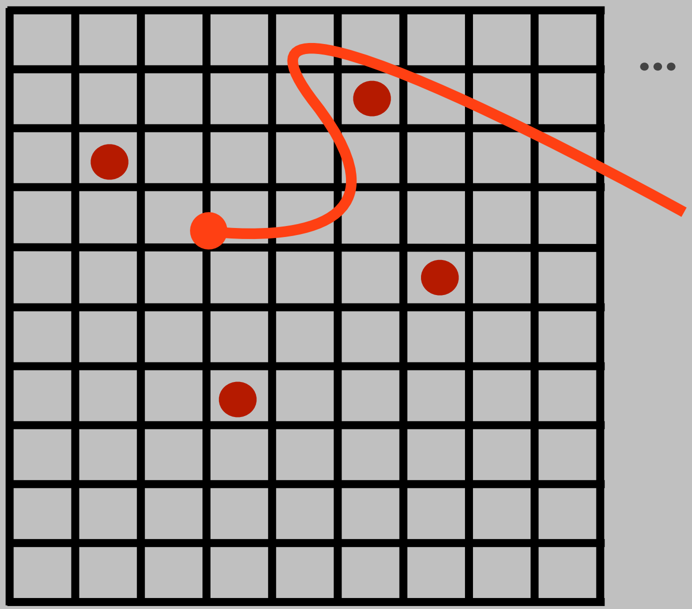

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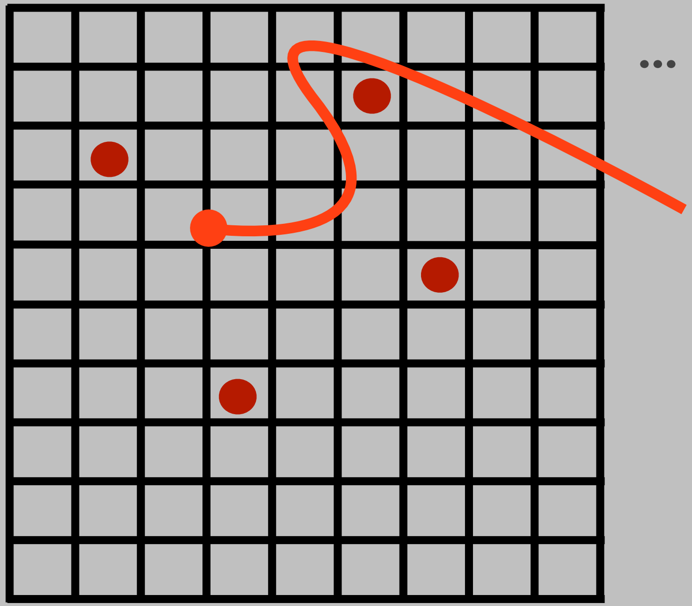

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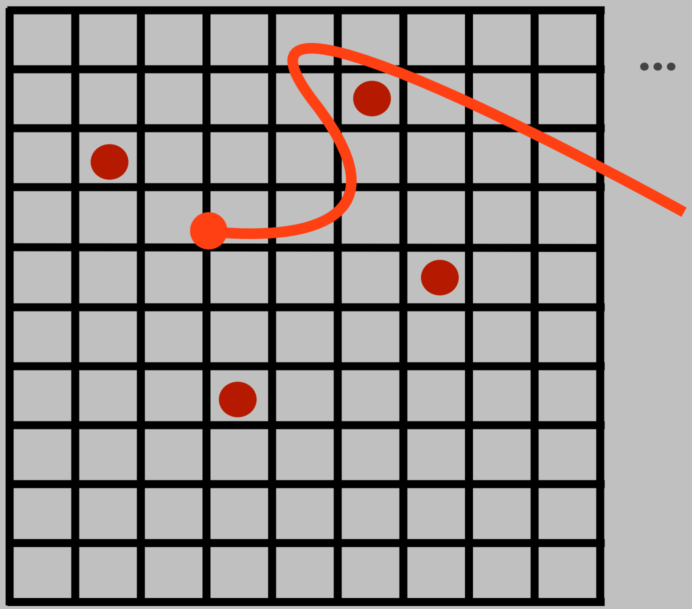

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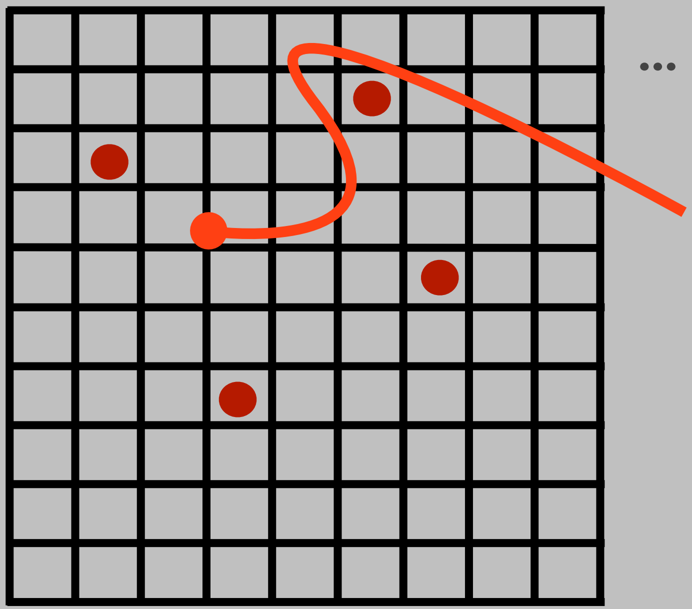

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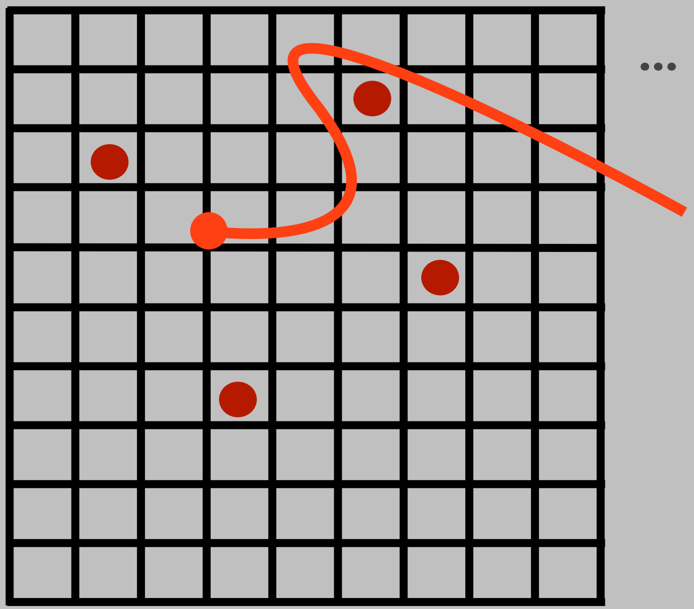

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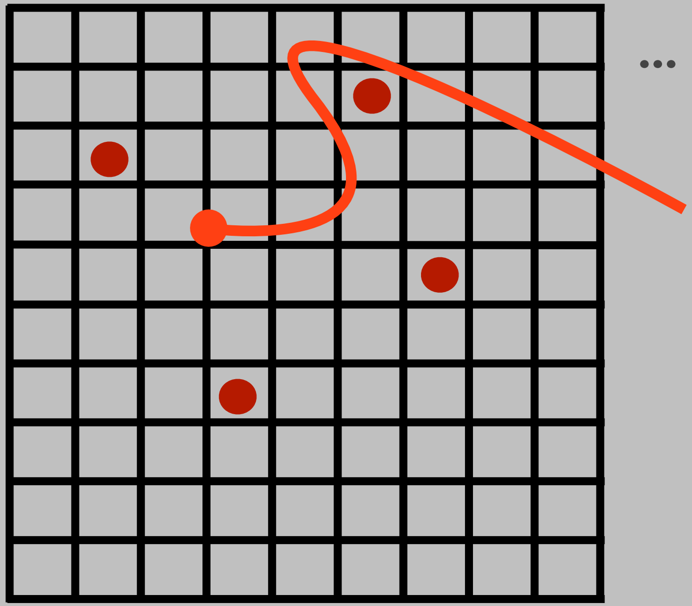

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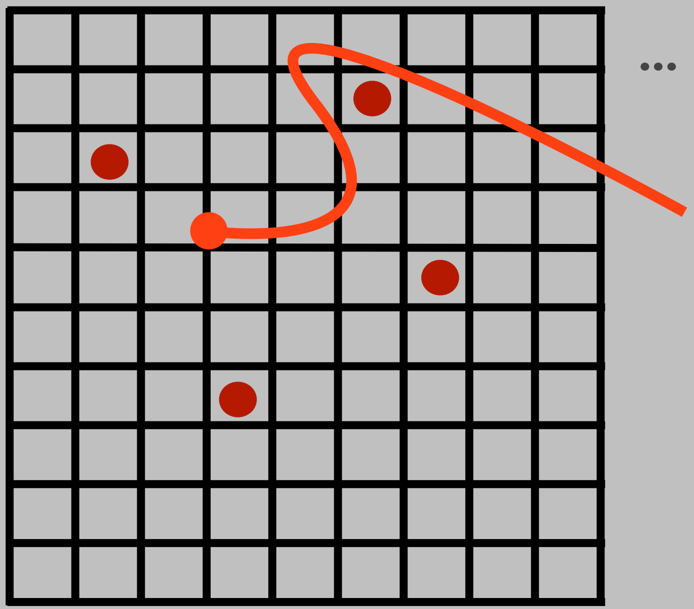

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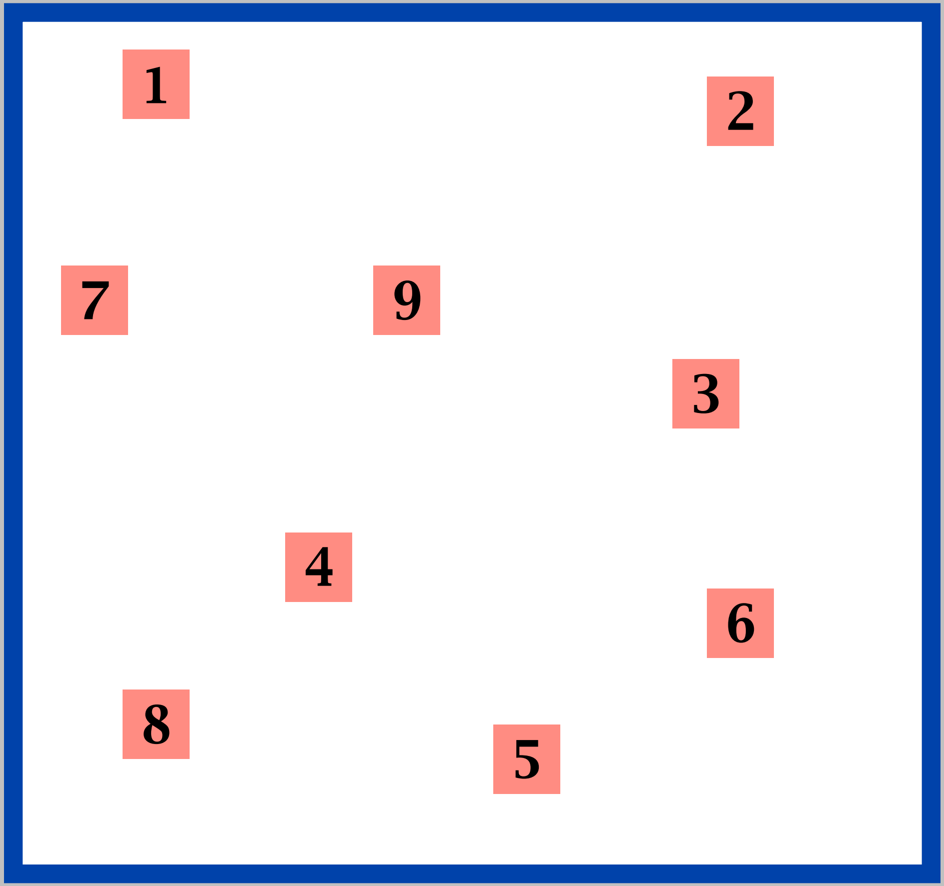
the larger the volume of the gas the more configurations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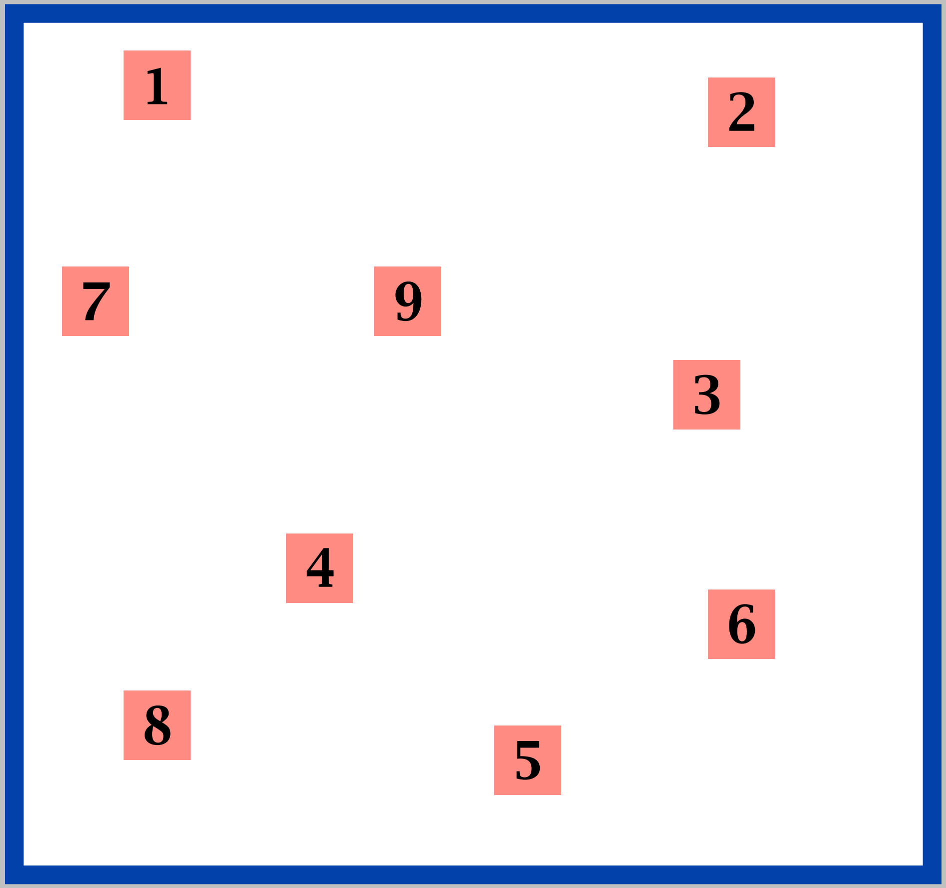
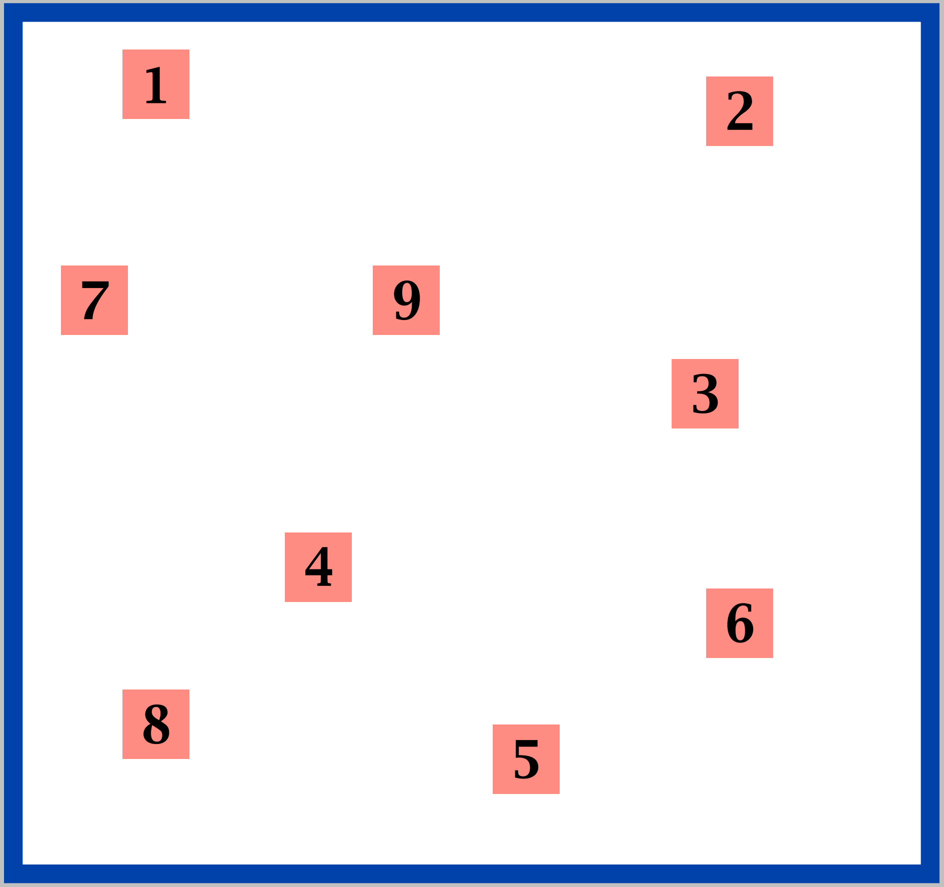


What is the probability to find the 9 molecules exactly at these 9 positions?



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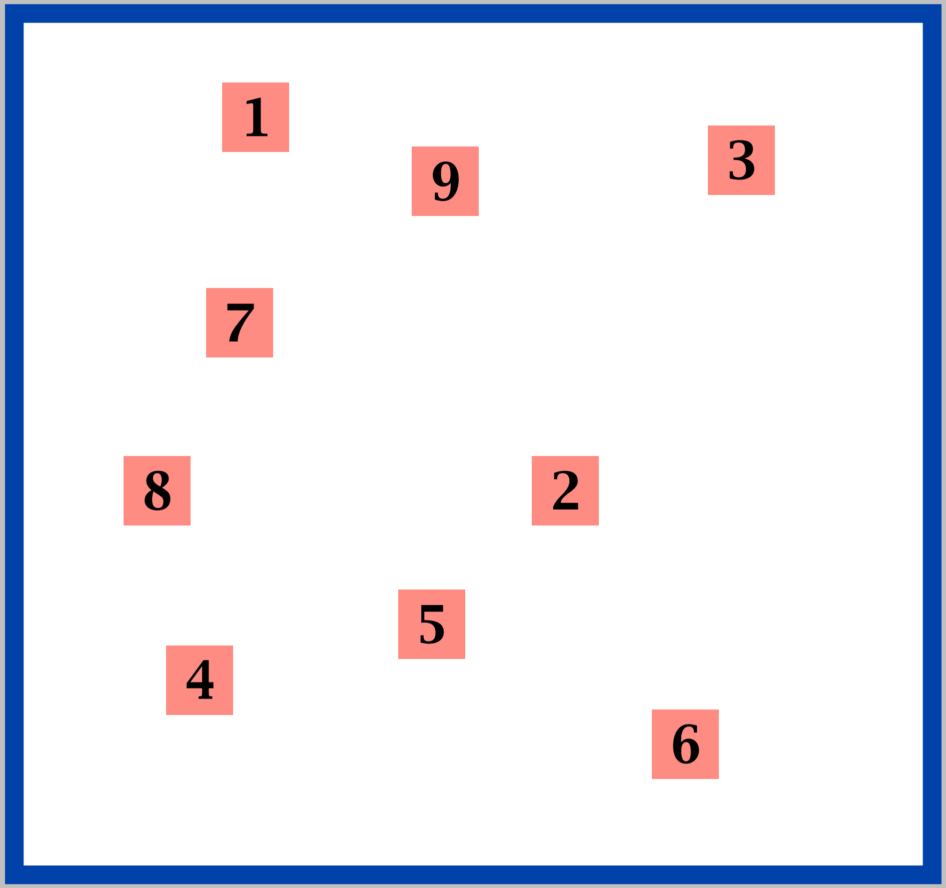

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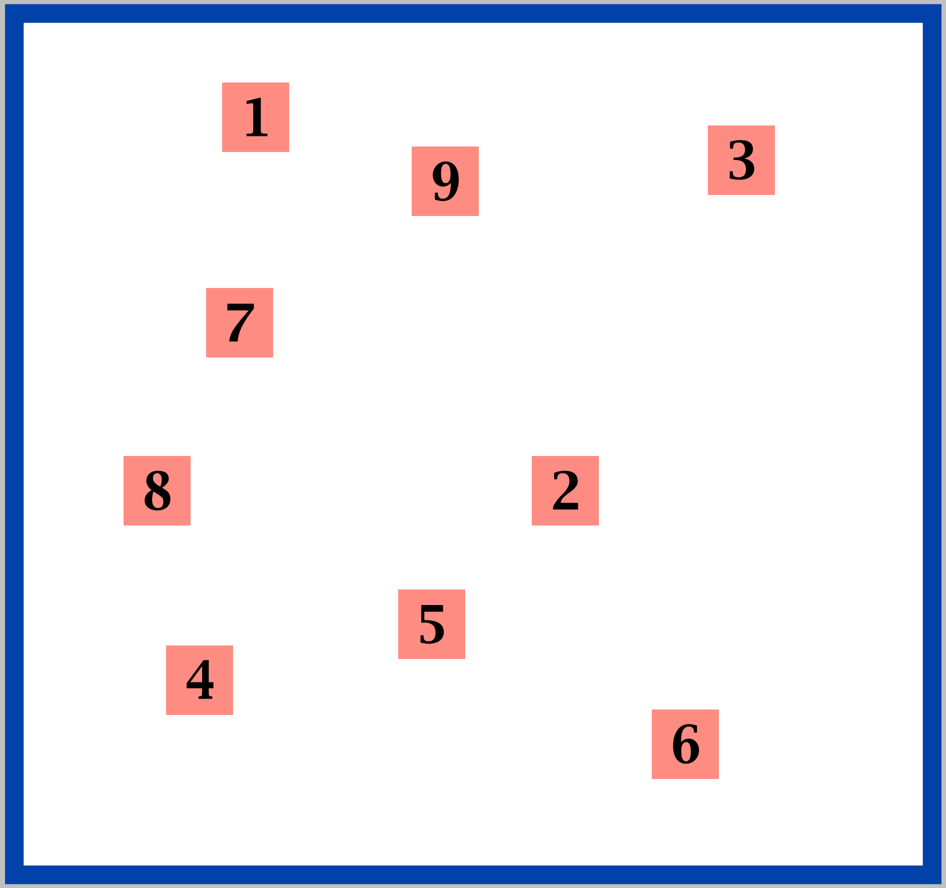

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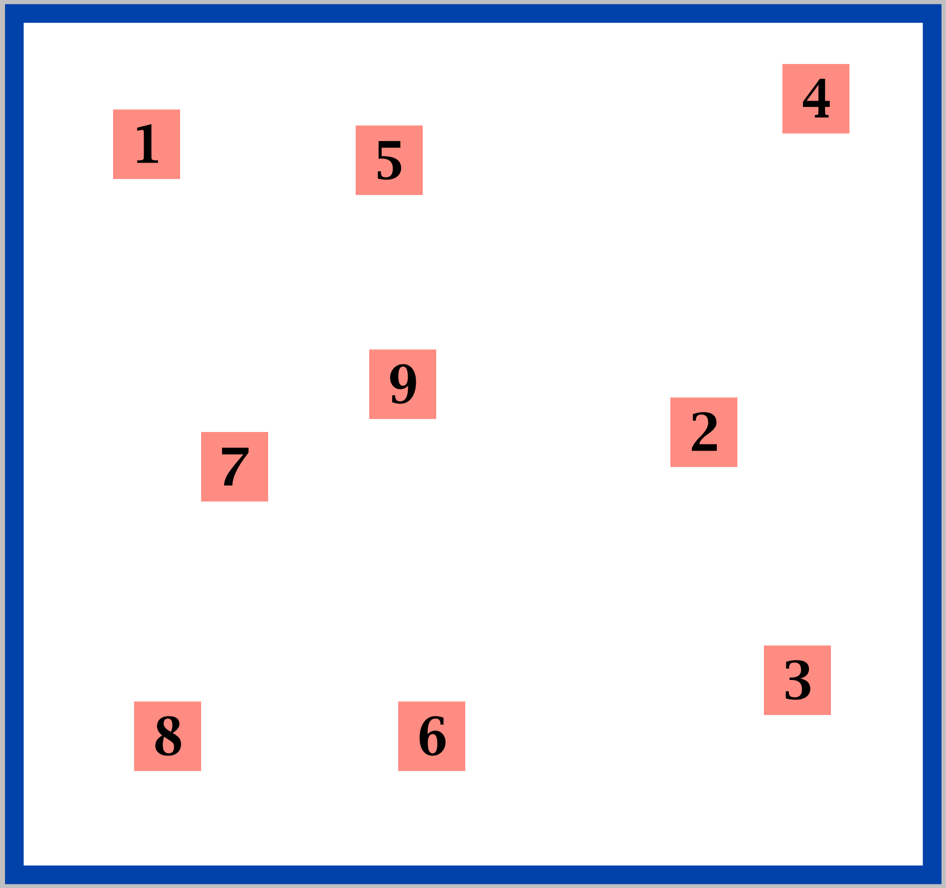

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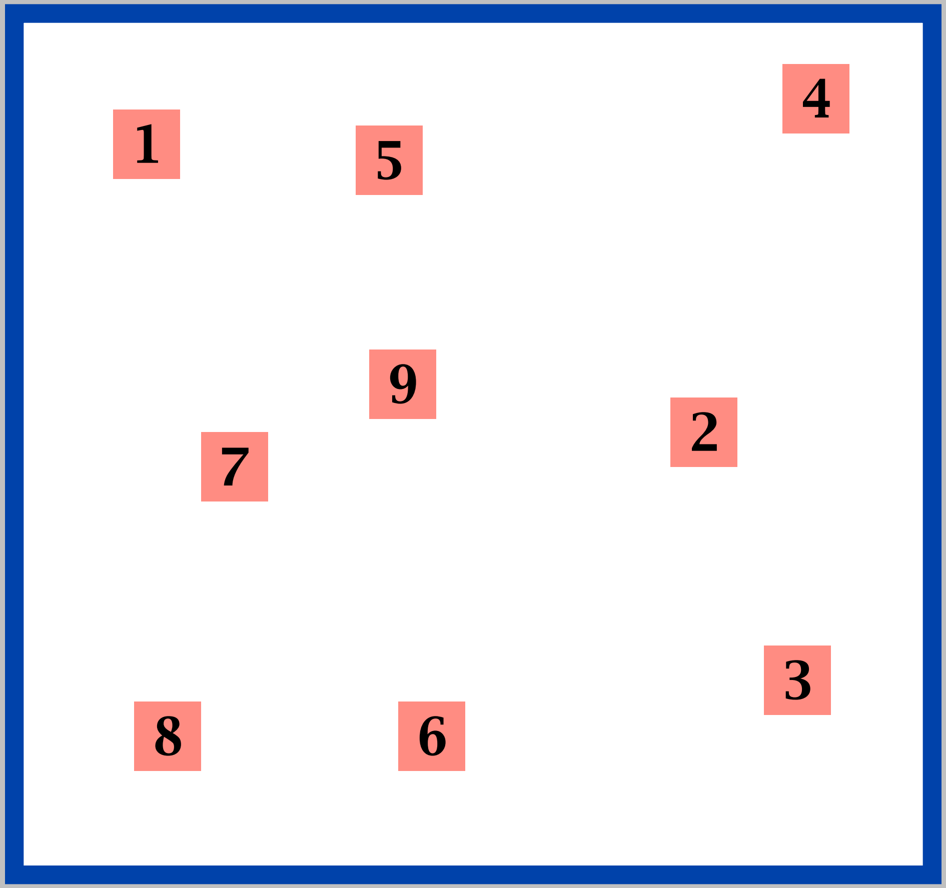

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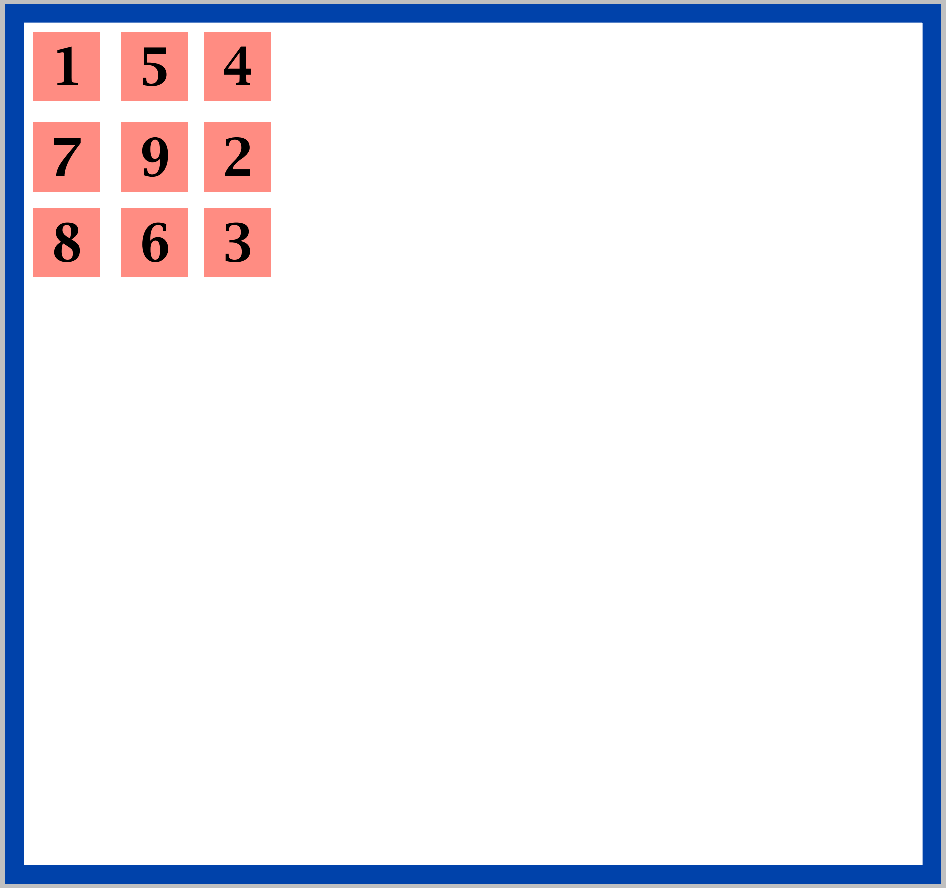

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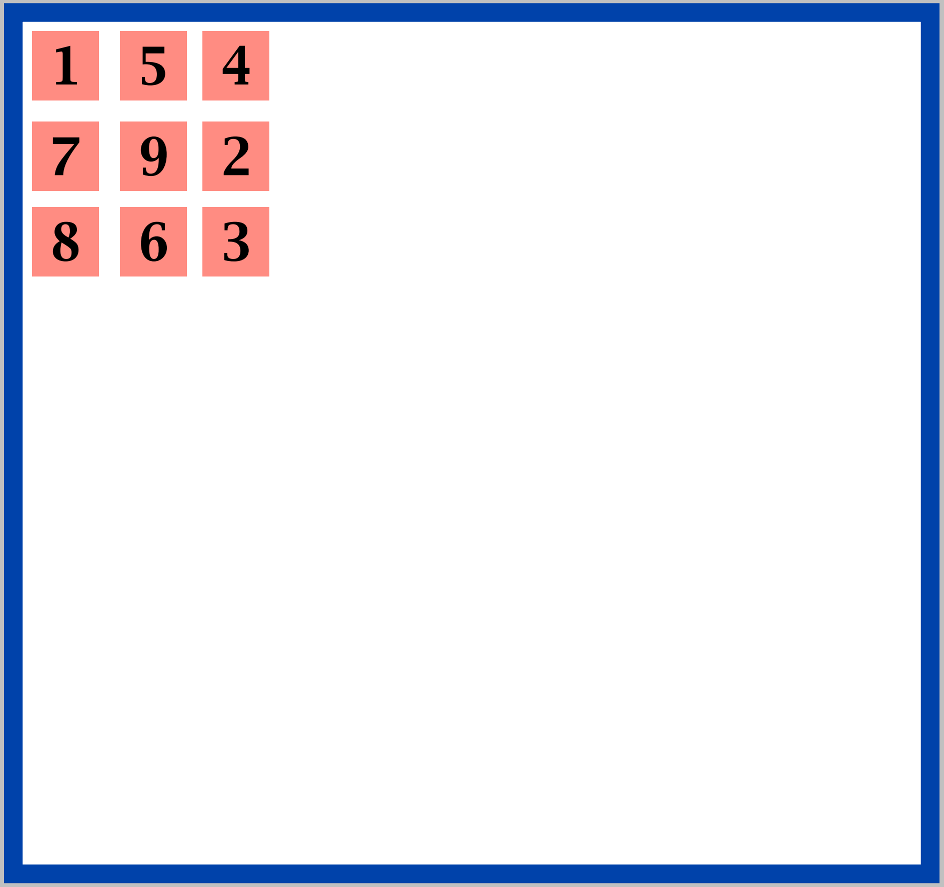

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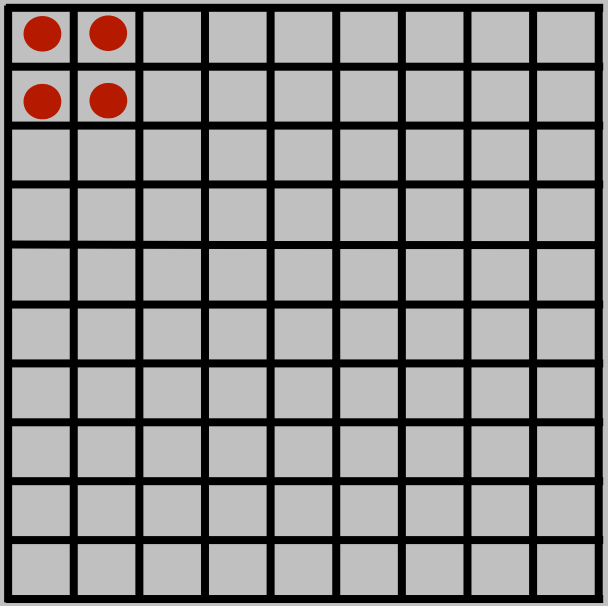
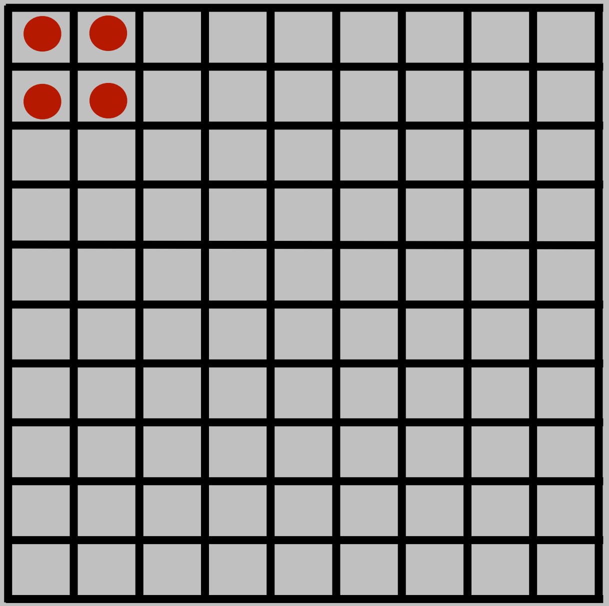
$$\boxed{\left(\frac{\Delta V}{V}\right)^{N}}$$



What is the probability to find this configuration?



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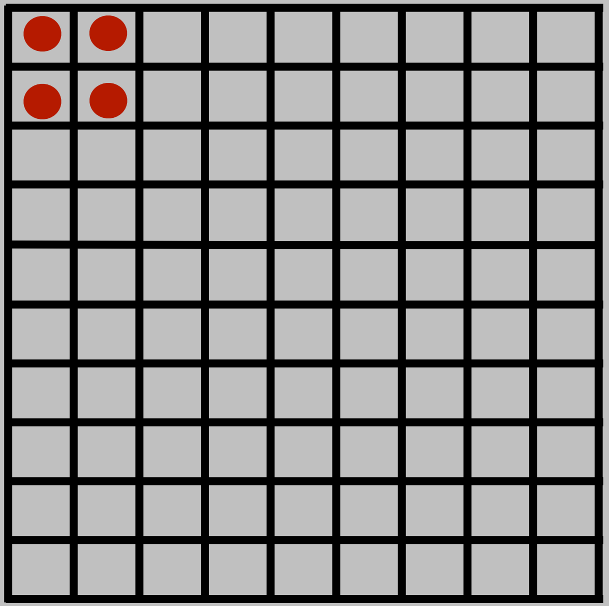

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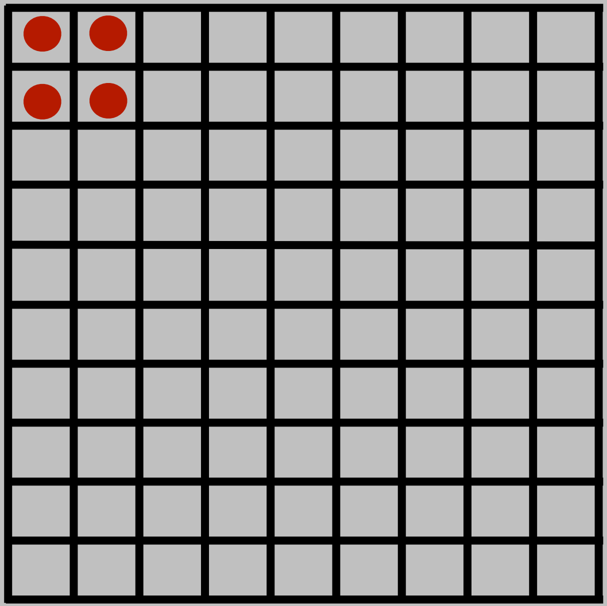

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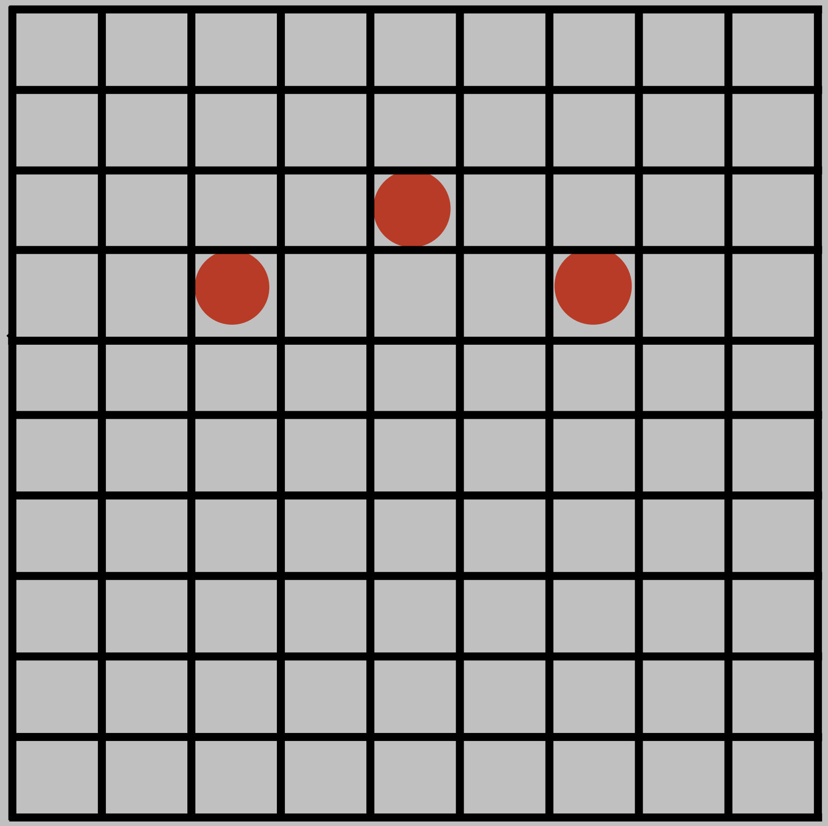

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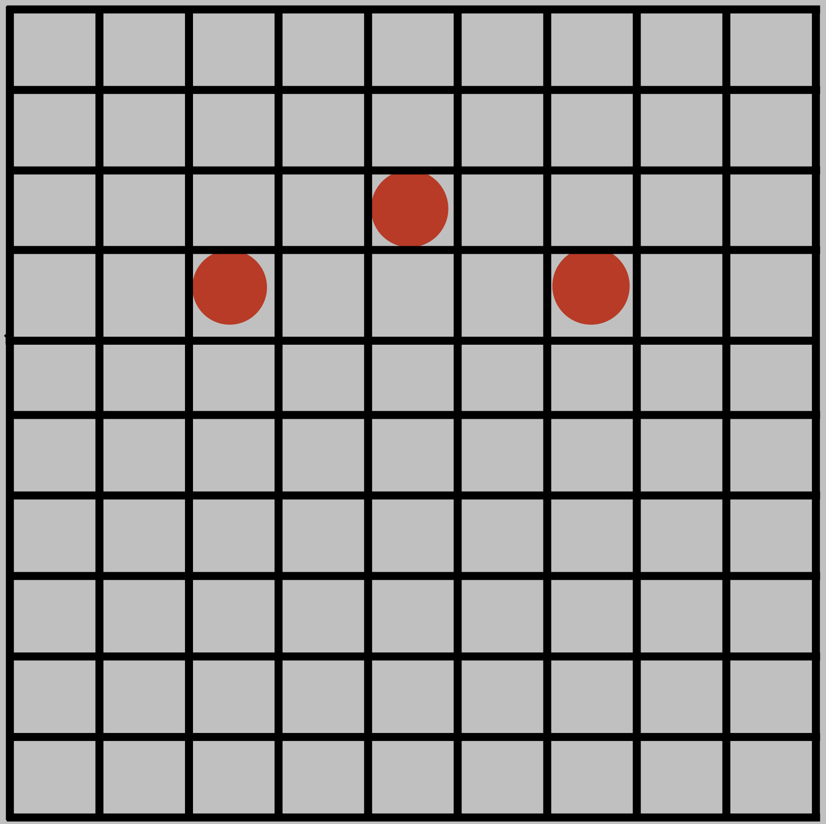

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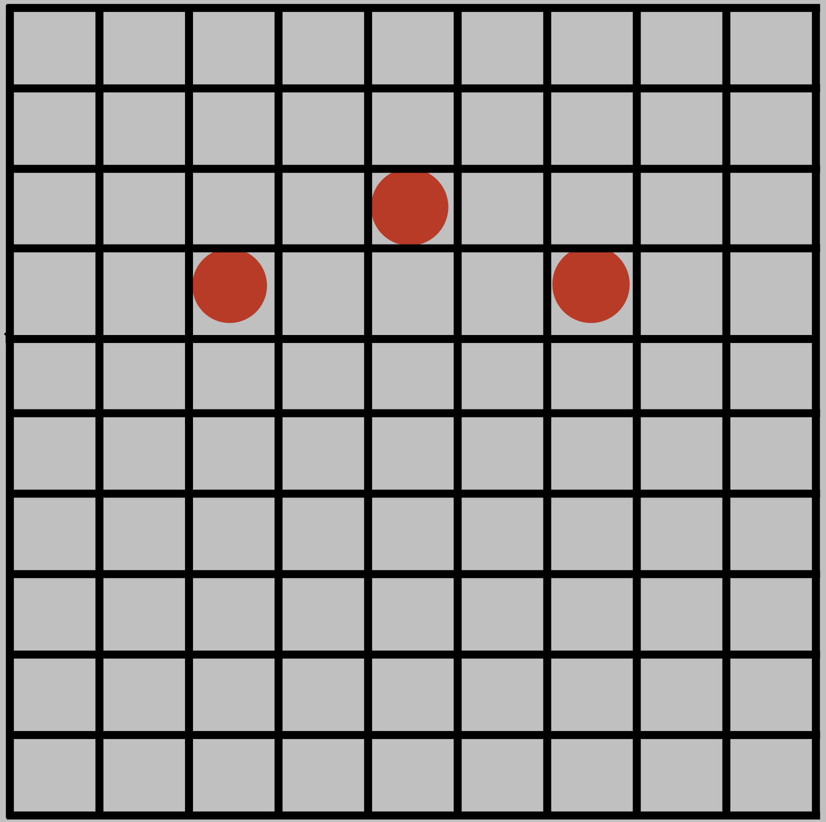

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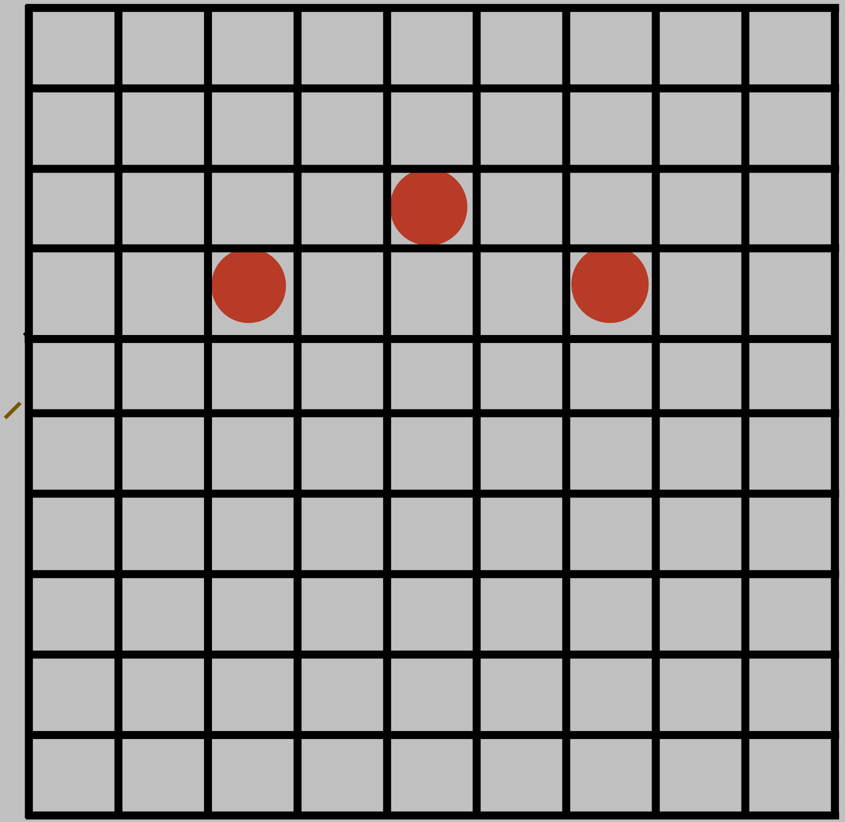

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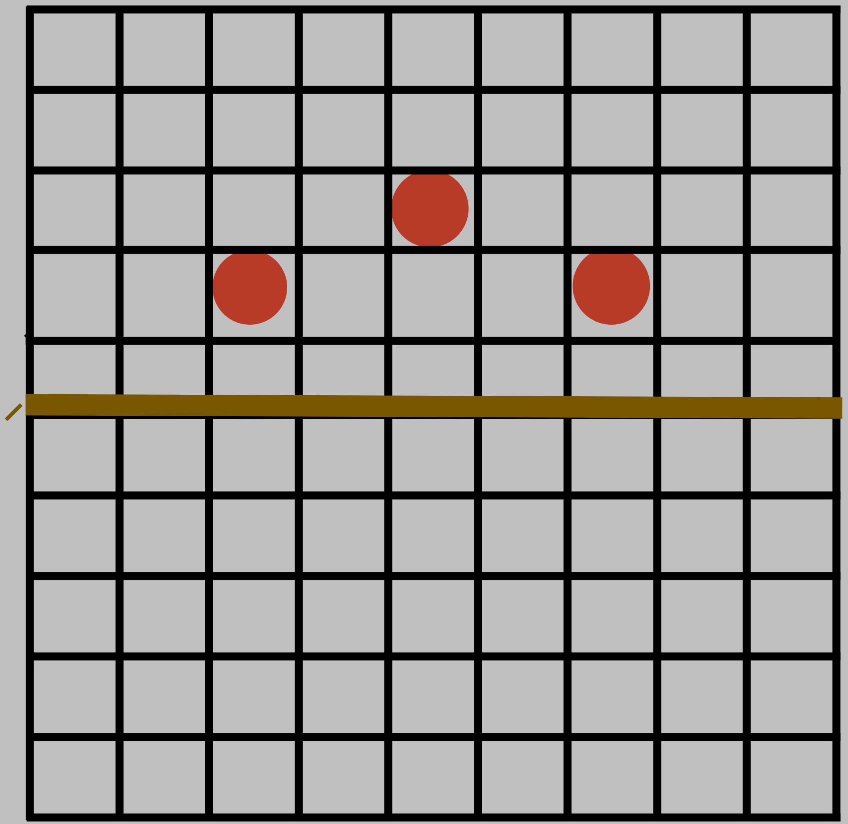

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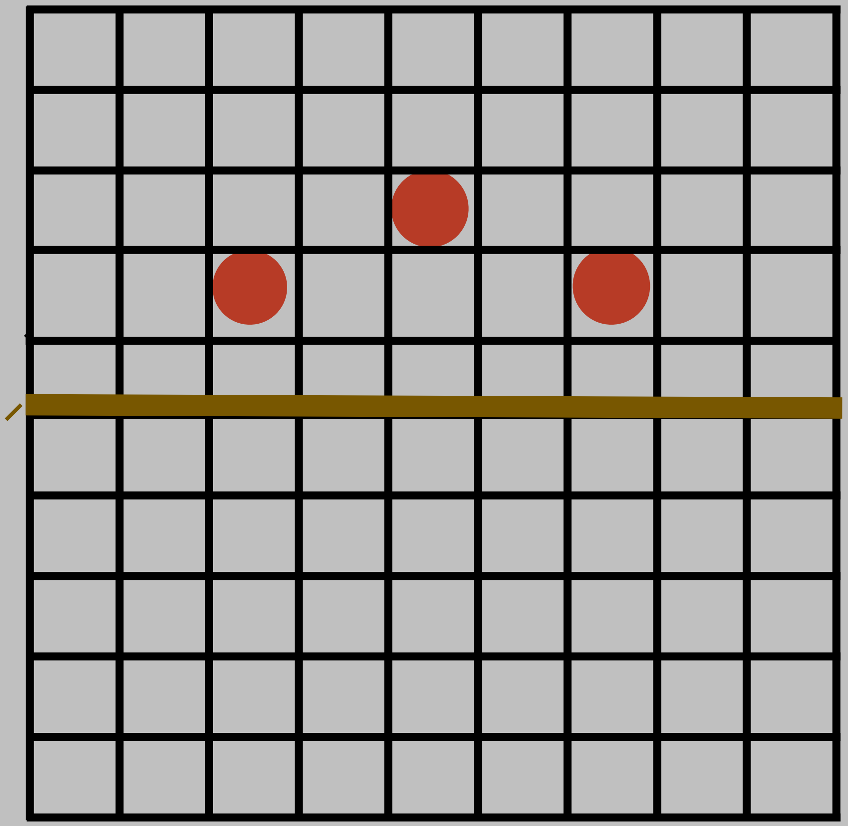

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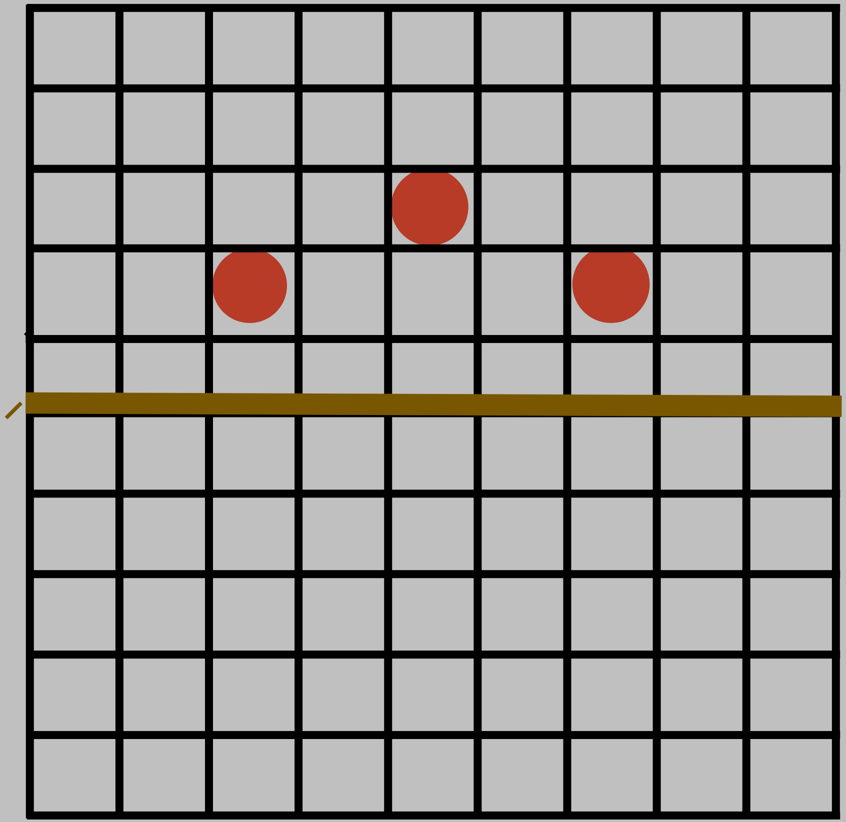

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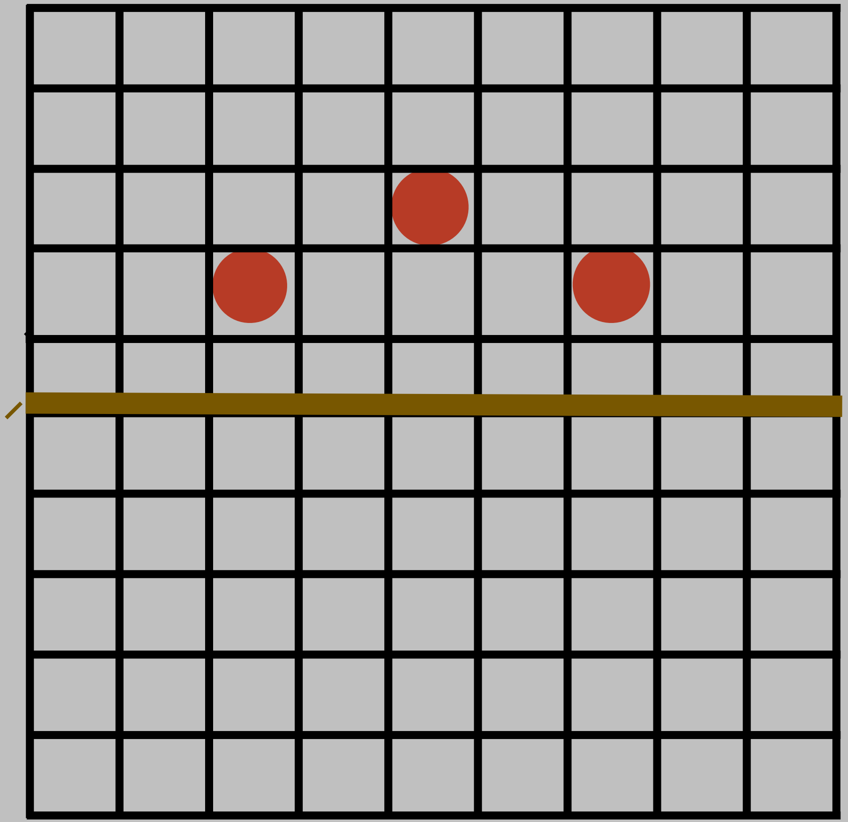

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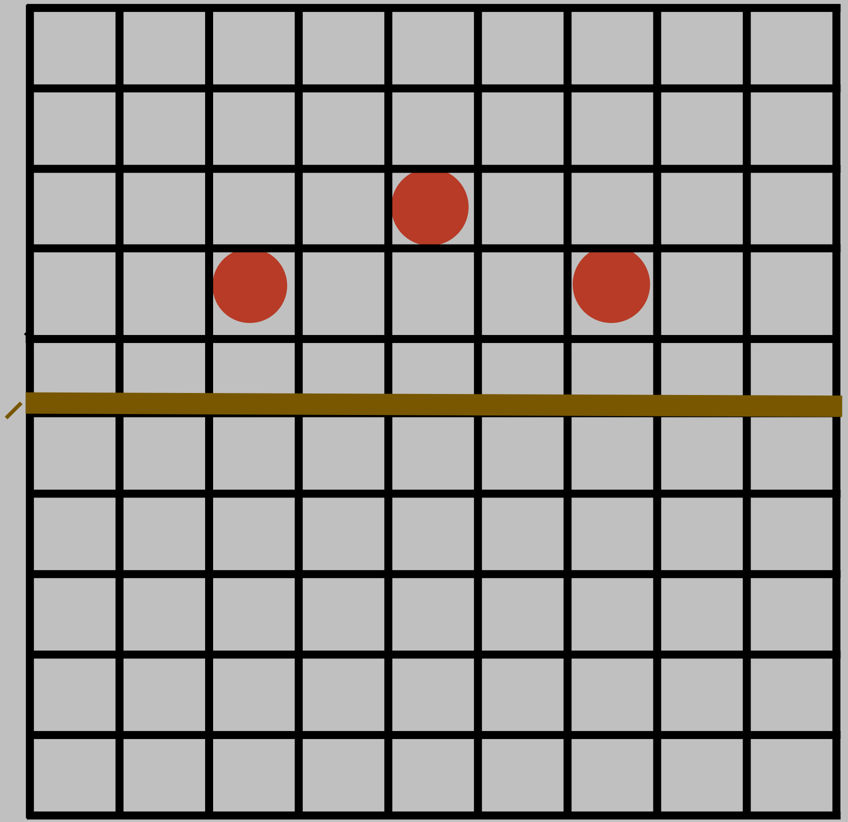

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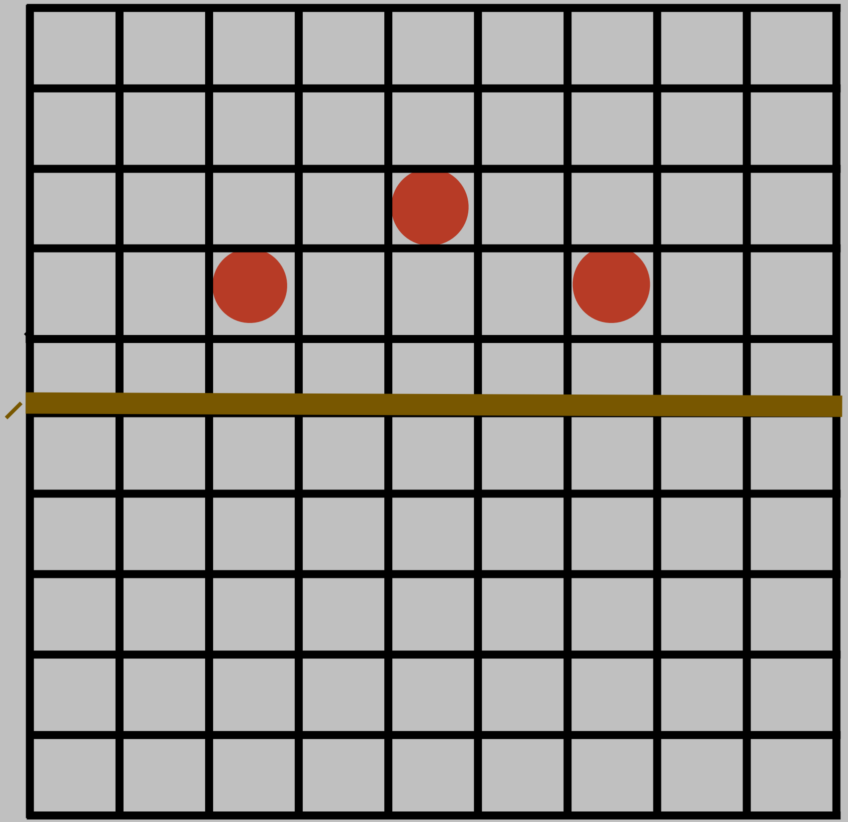

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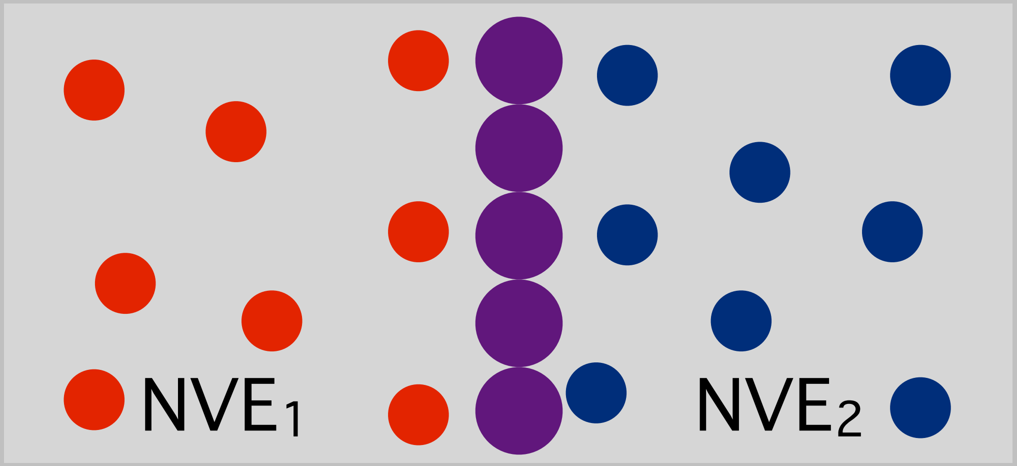

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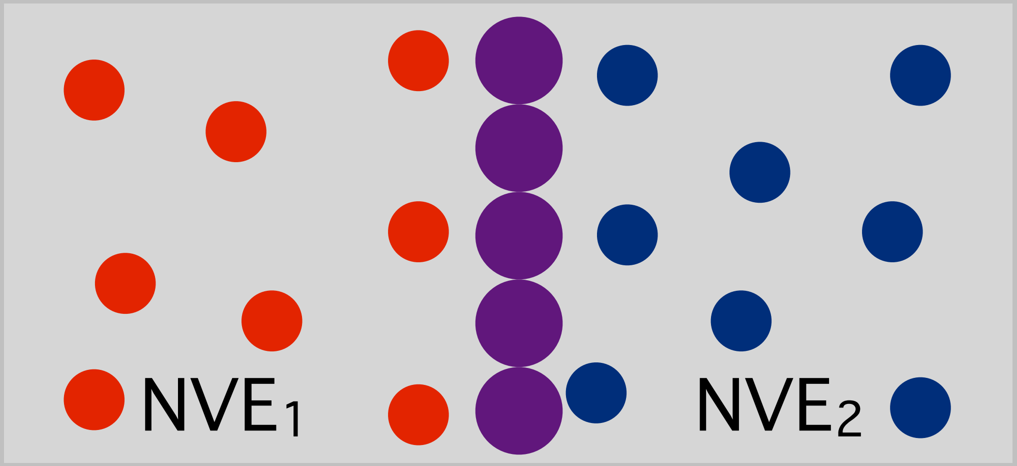

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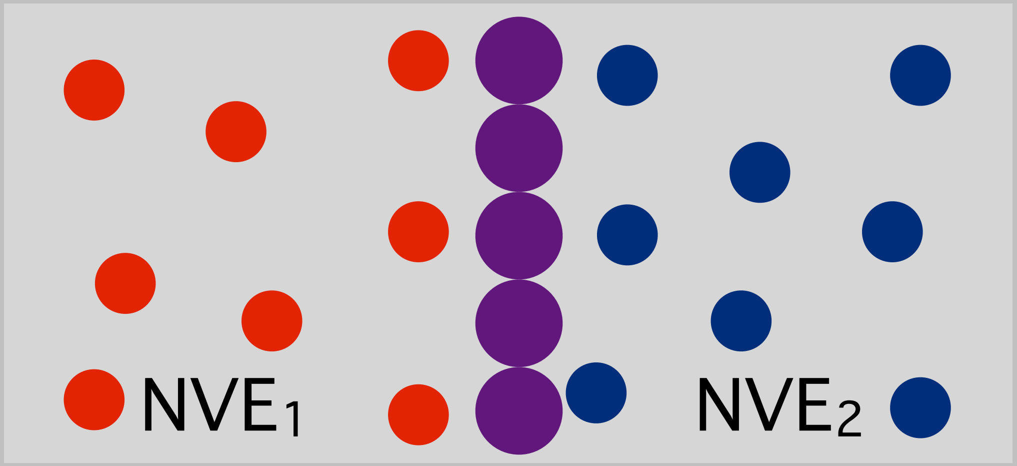

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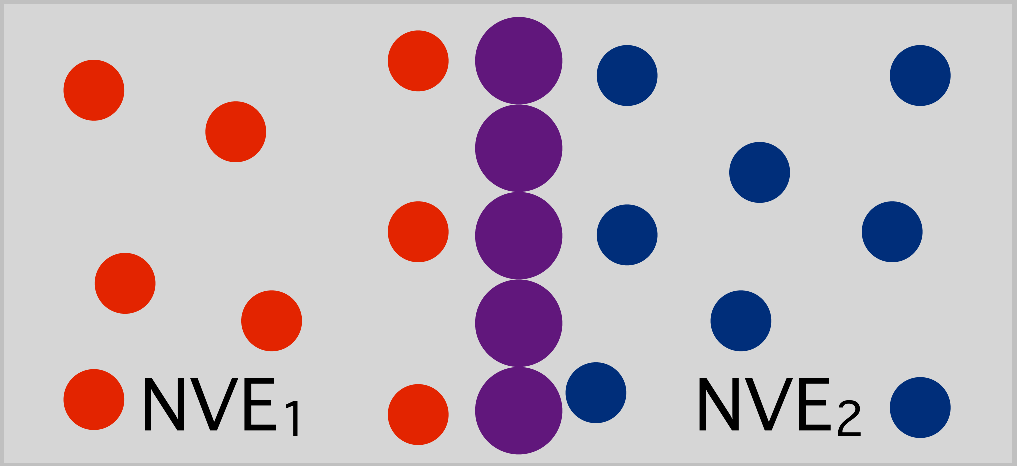

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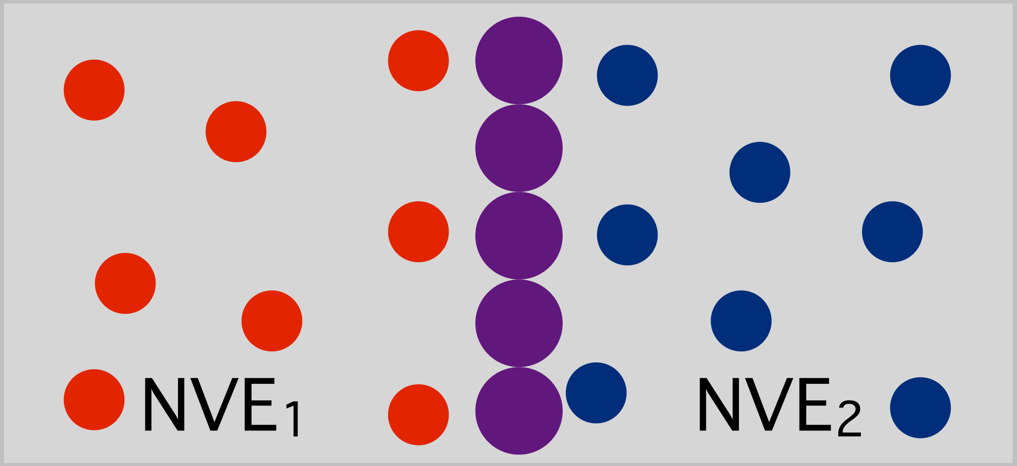

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What is this magic property S^*?

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

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

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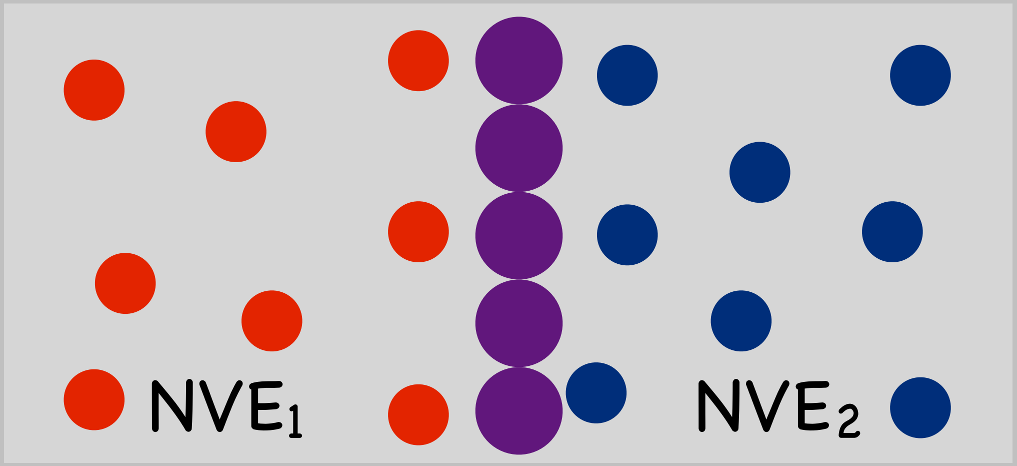
Units! The logarithm is just a unitless quantity.

Thermal Equilibrium (Review)



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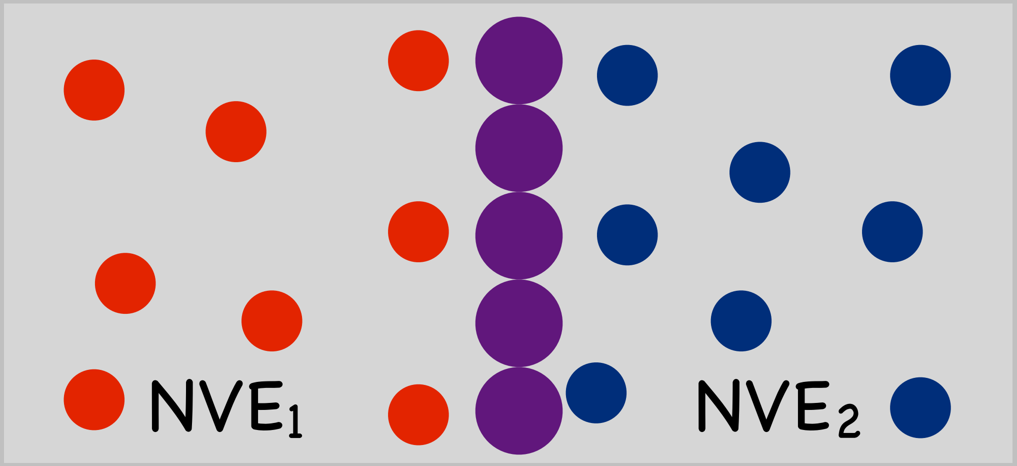

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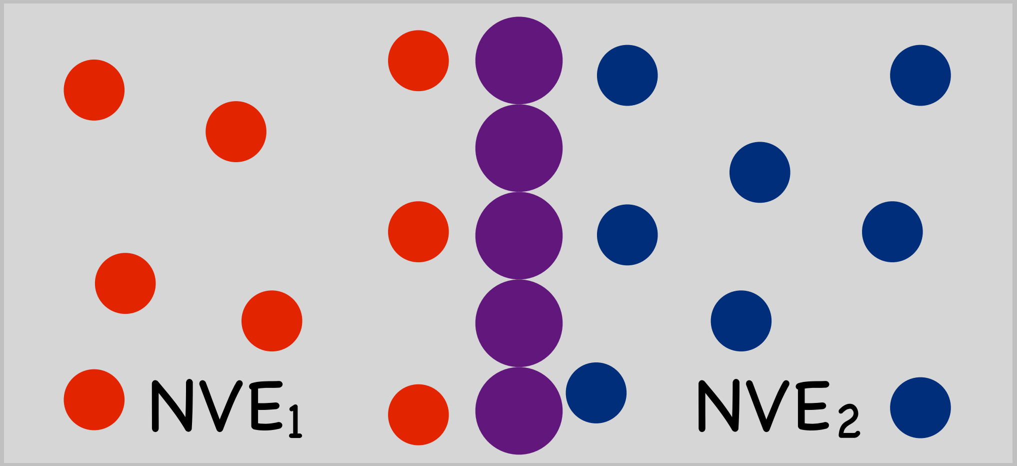

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Number of micro states that give an particular energy distribution (E_1,$E-E_1$) is maximized with respect to E_1.

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

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

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

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How large is Ω for a glass of water?

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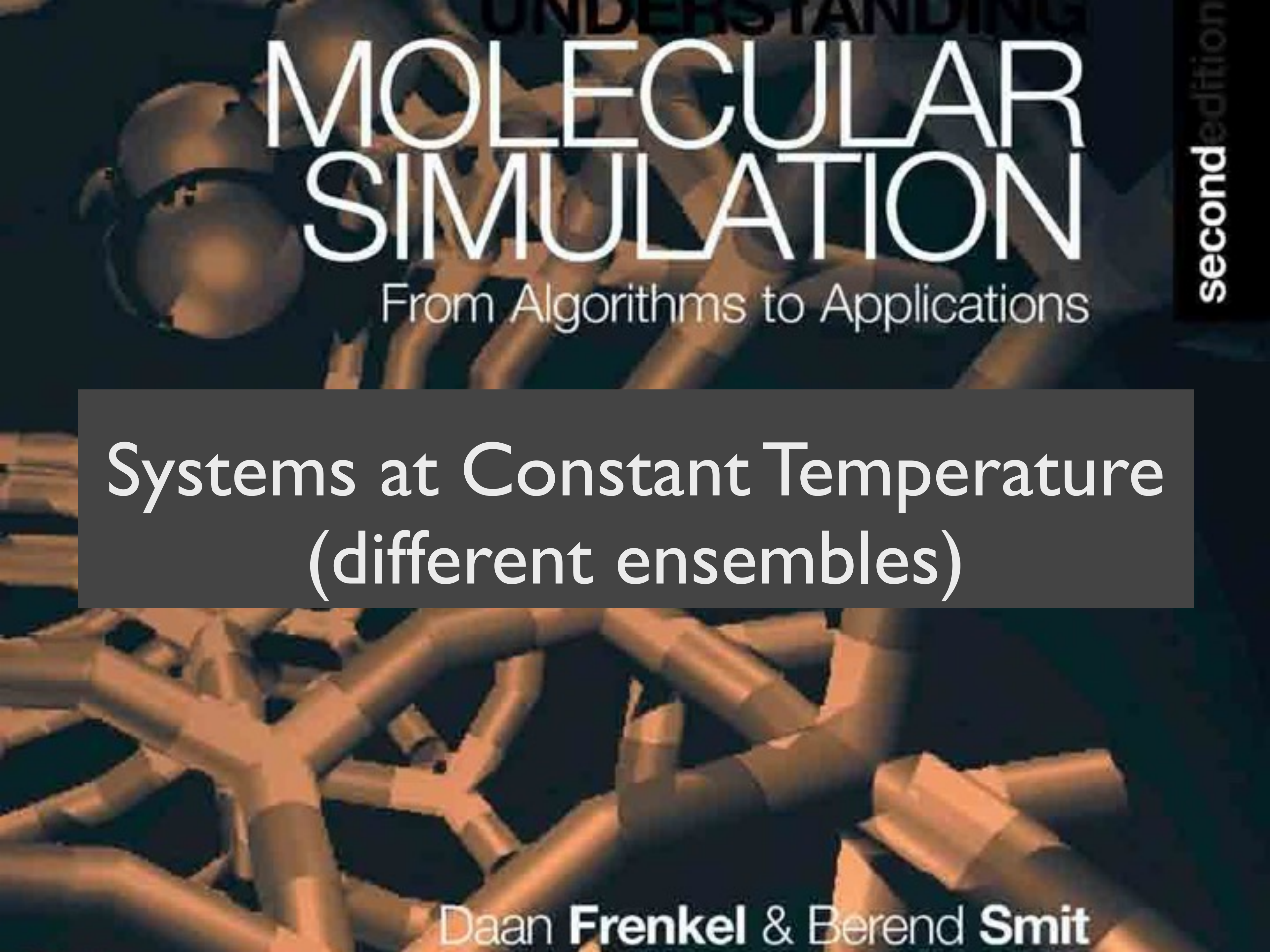
$$\Omega \approx 10^{2\times 10^{25}}$$

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

Systems at Constant Temperature (different ensembles)



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

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Most systems are at constant temperature and volume or pressure?

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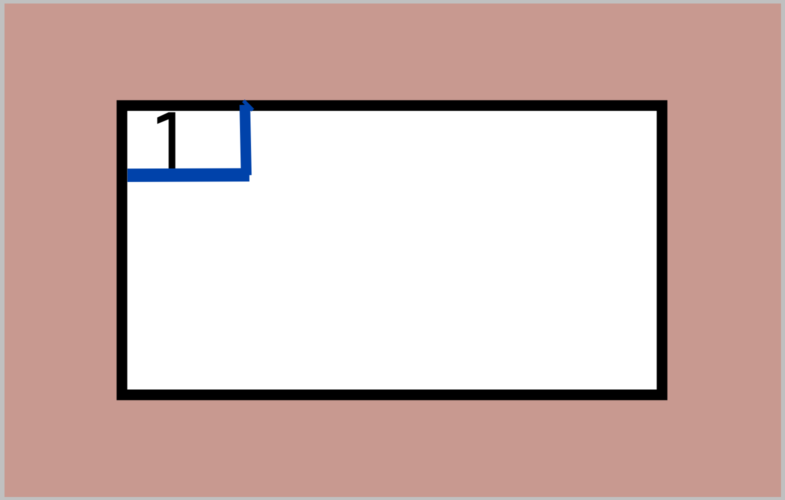
What is the formulation for these systems?

Constant T and V



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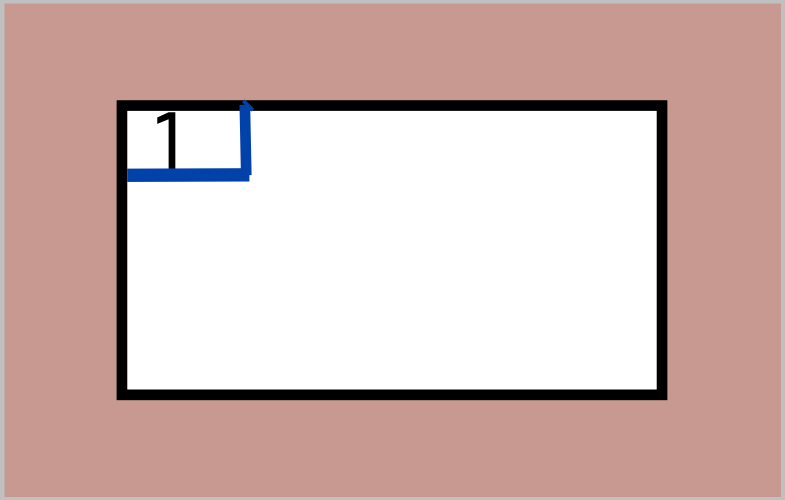
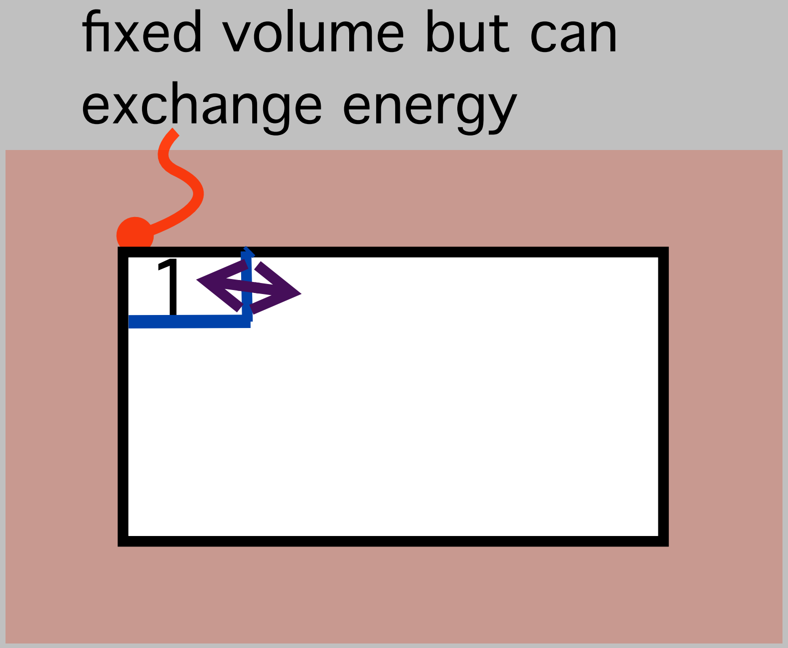


We have our box 1 and a bath

Constant T and V



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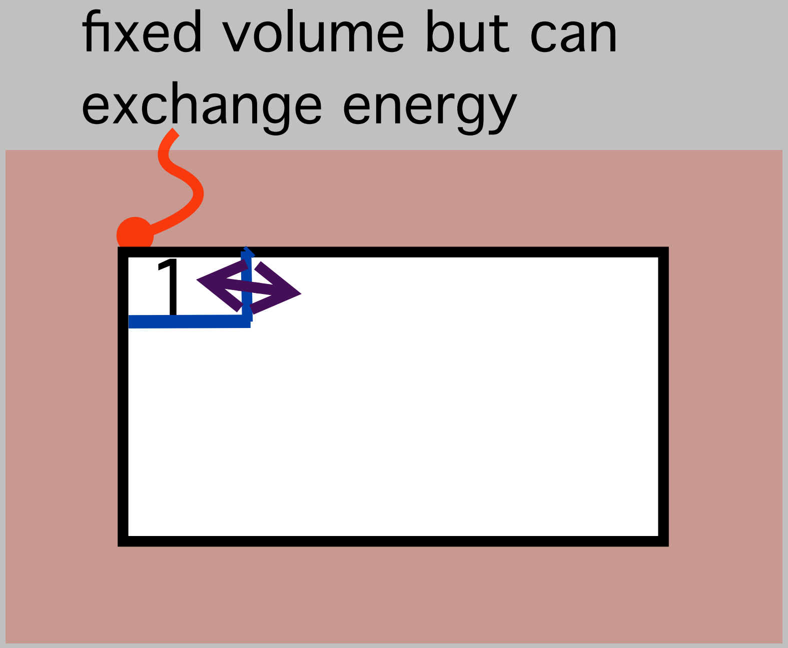

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Total system is isolated and the volume is constant

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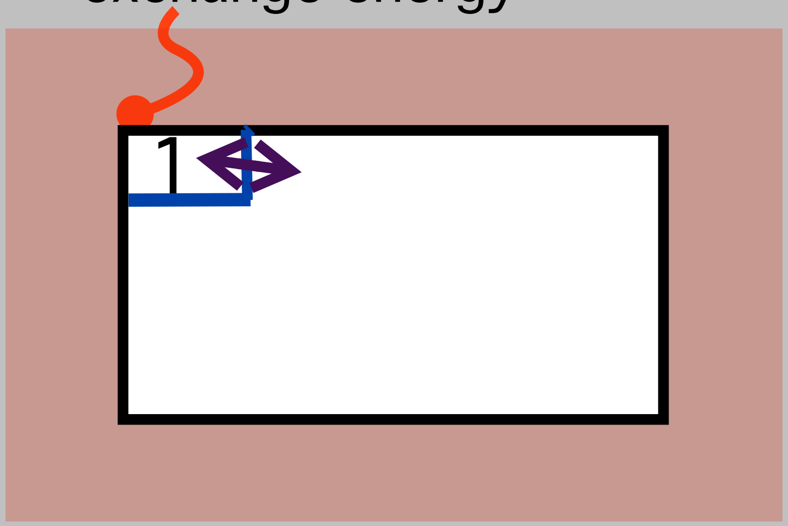

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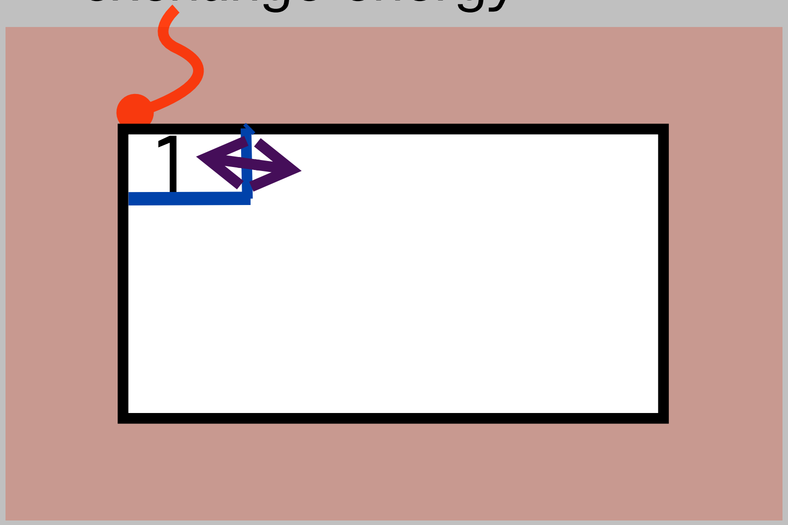
Total system is isolated and the volume is constant

First law

fixed volume but can
exchange energy



Constant T and V

We have our box 1 and a bath

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

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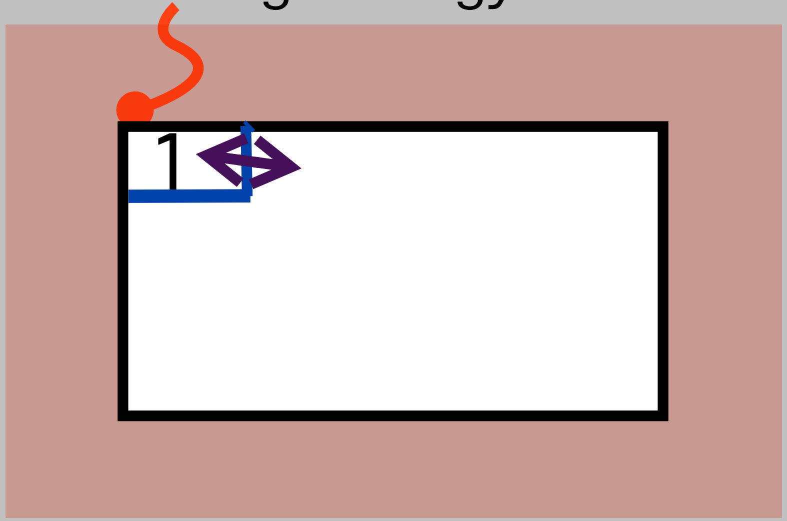
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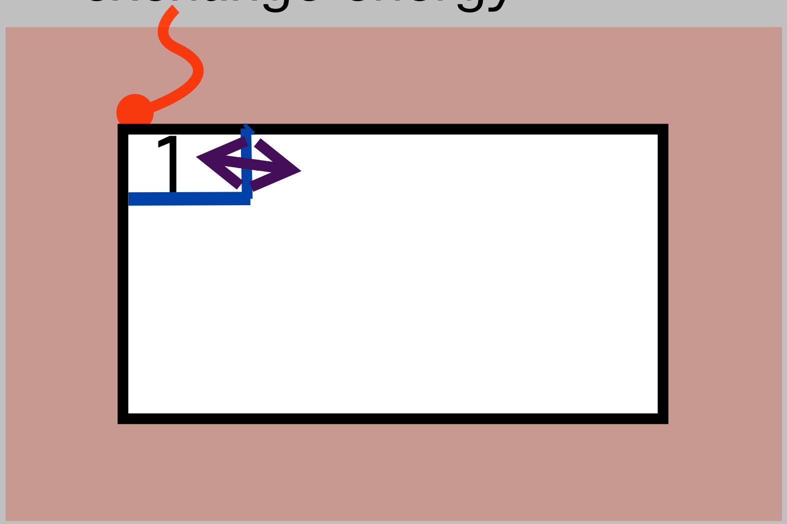
Second law

Constant T and V



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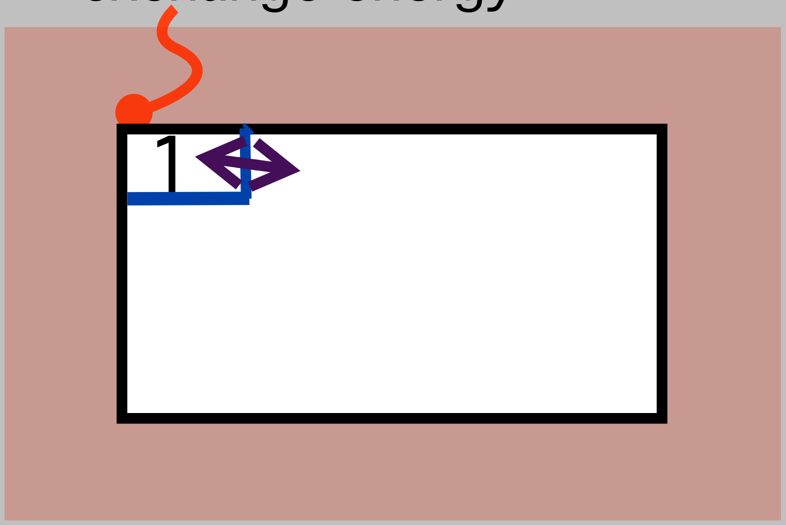

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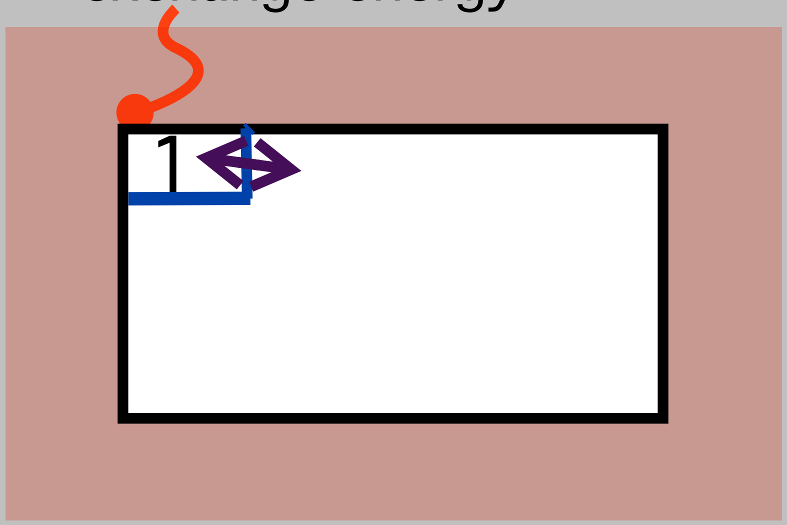

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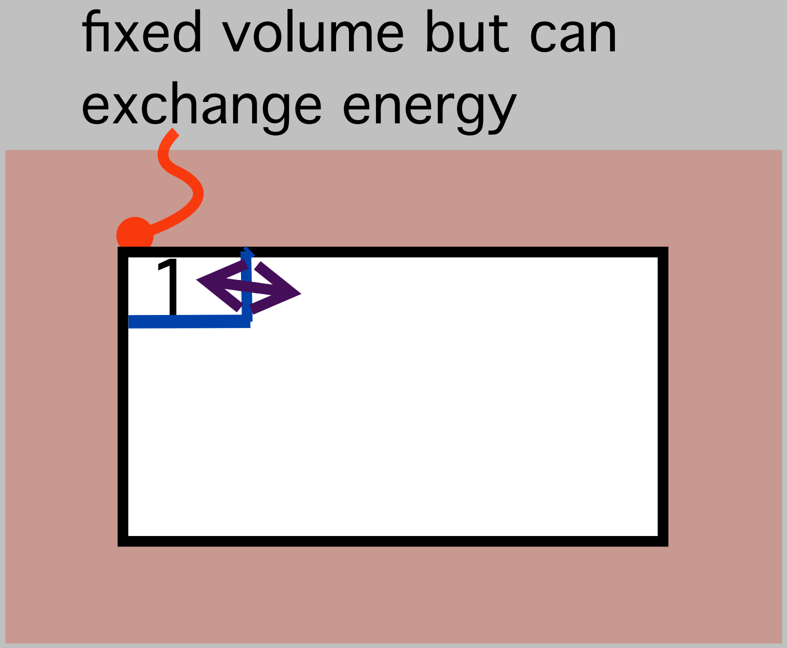

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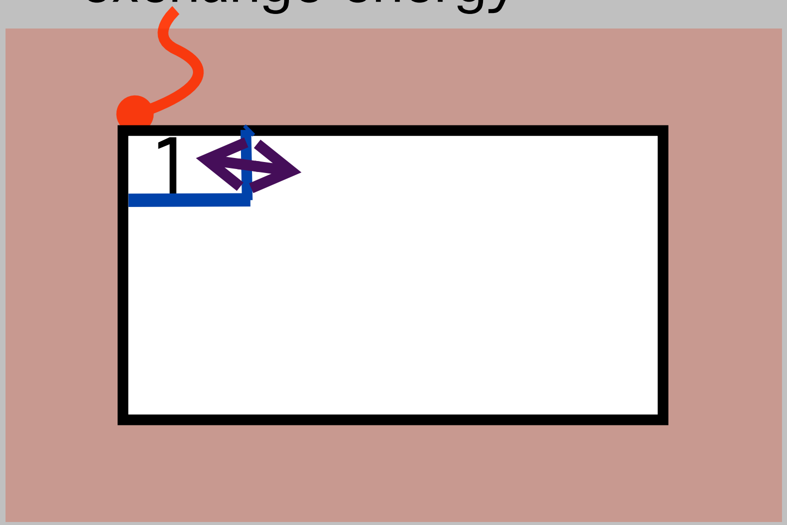

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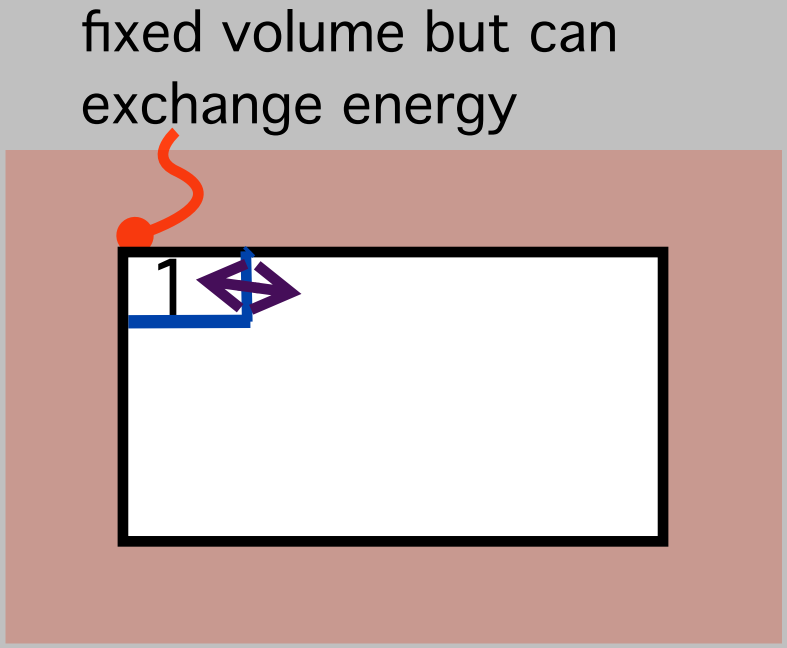

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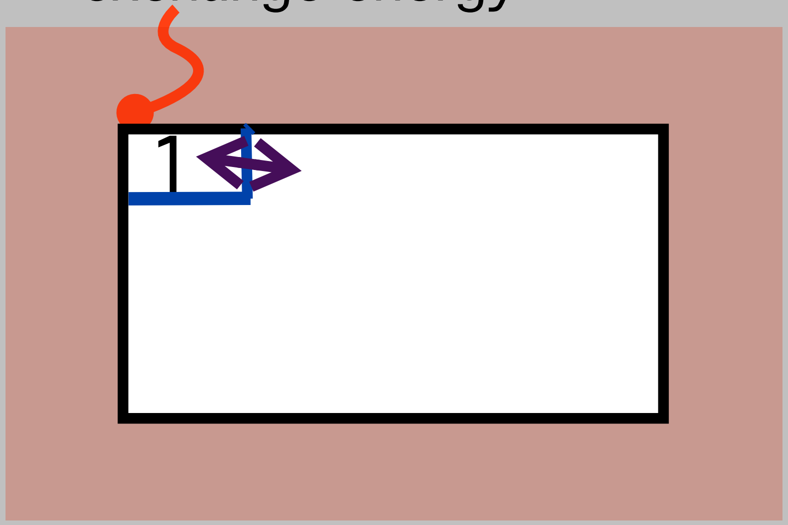
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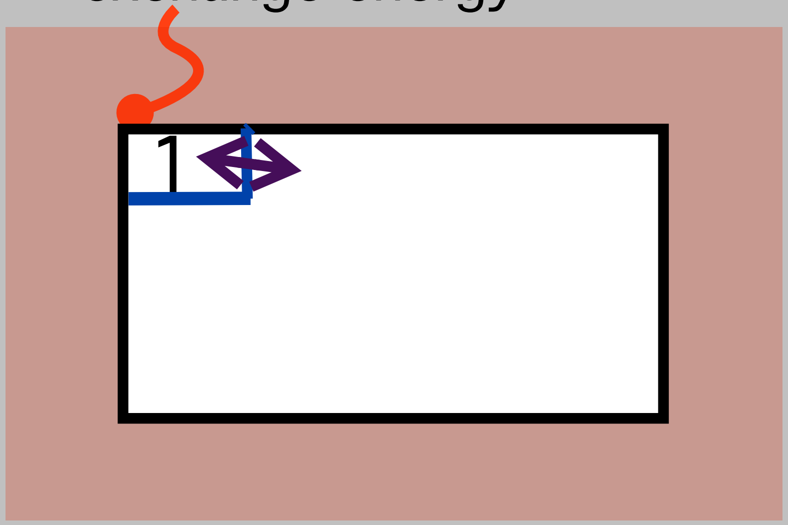

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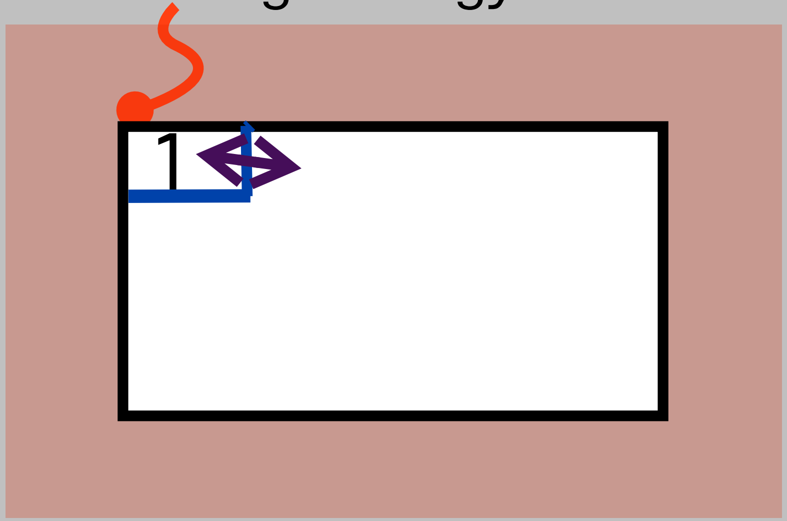

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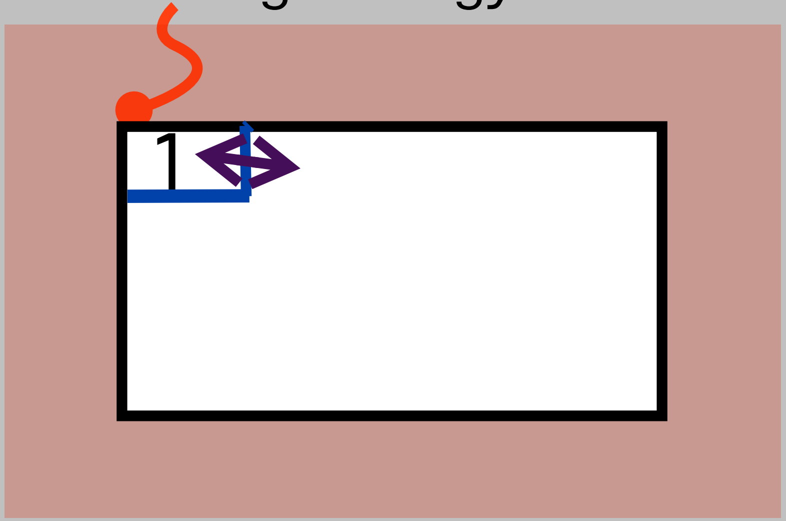

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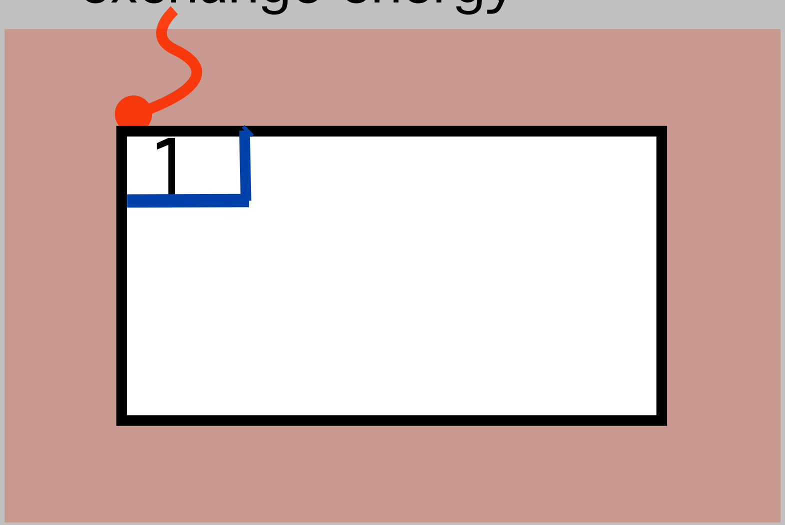
$$TdS_1 - dU_1 \geq 0$$

Constant T and V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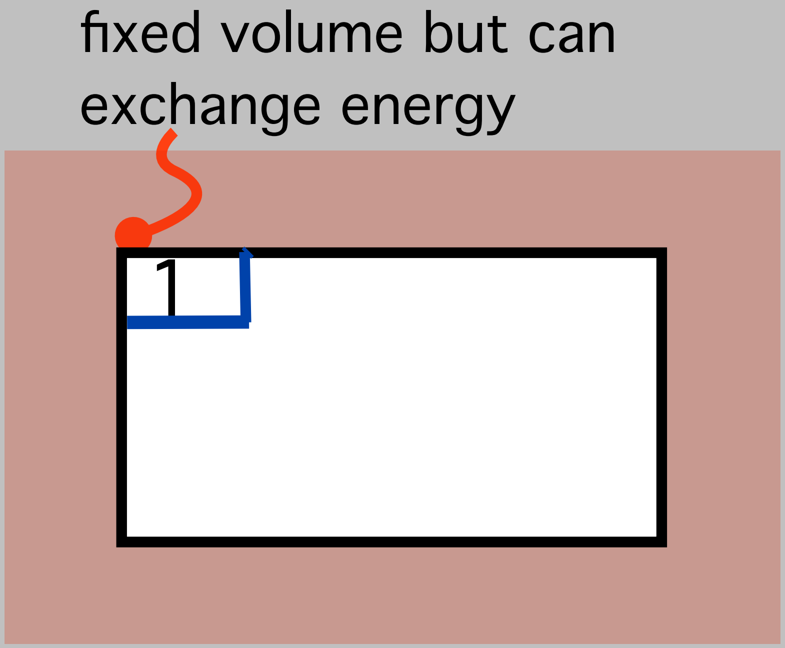

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Box 1: constant volume and temperature

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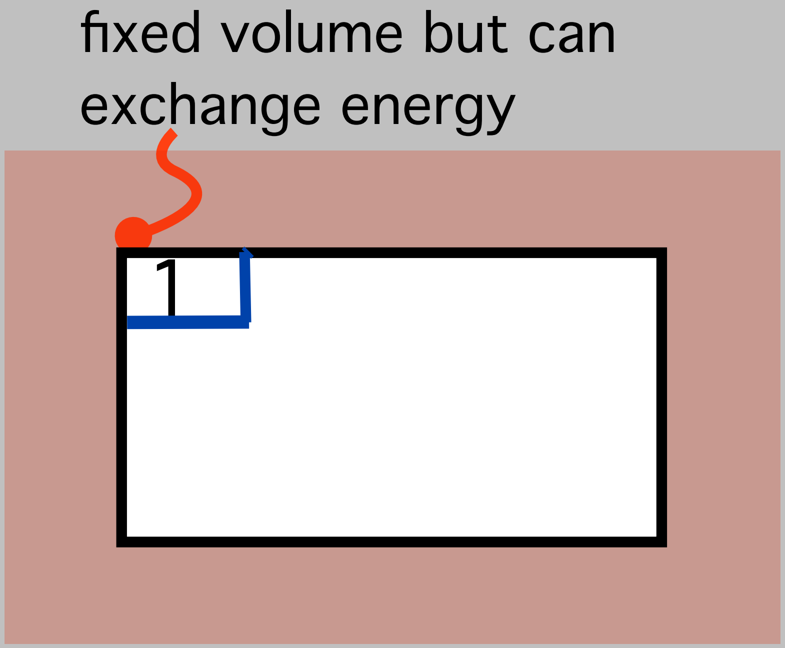

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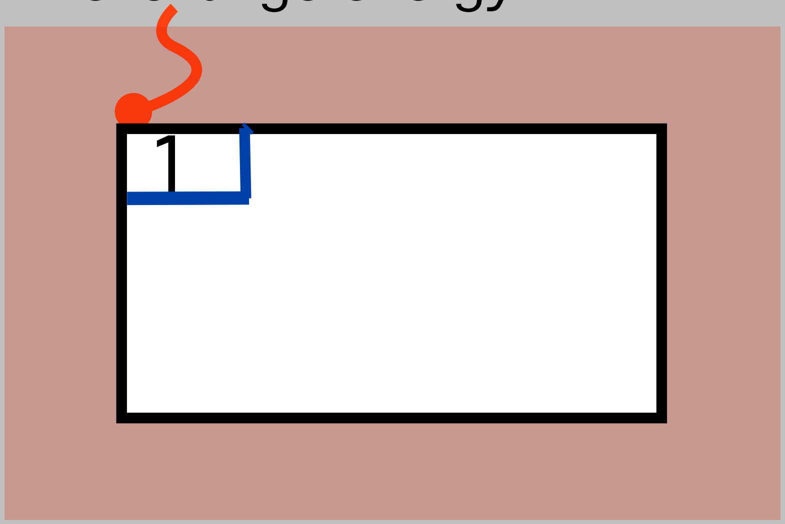
Let us define the Helmholtz free energy: A

Constant T and V



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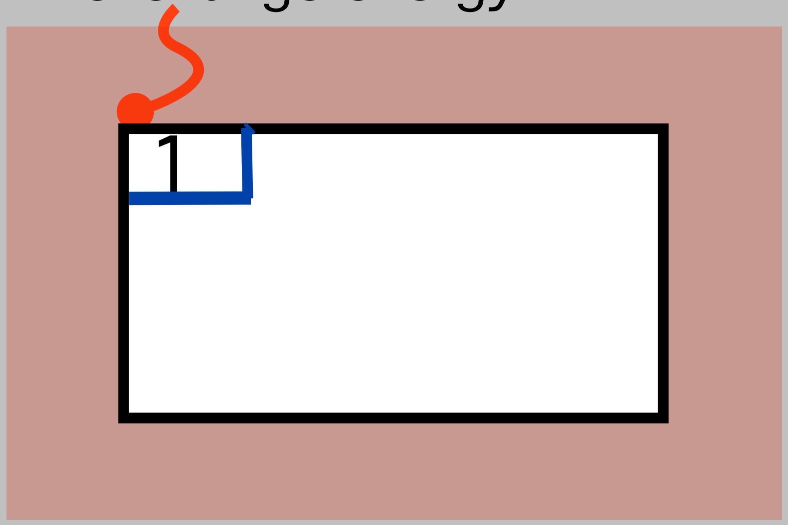
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Constant T and V

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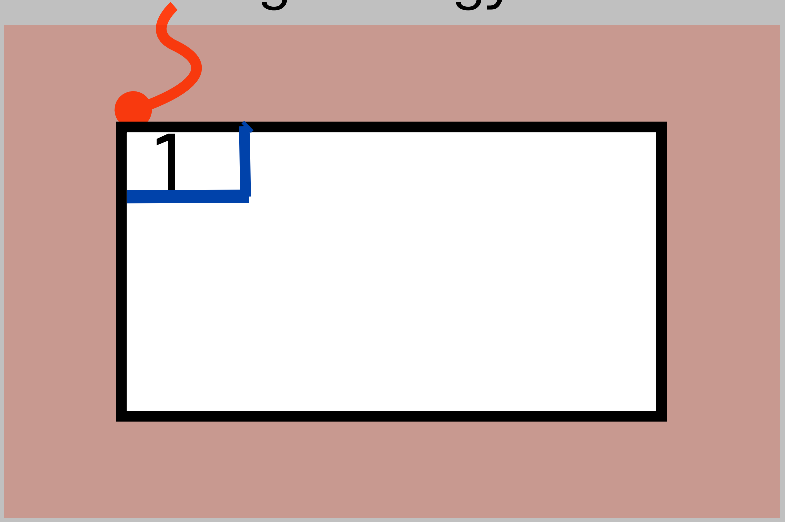

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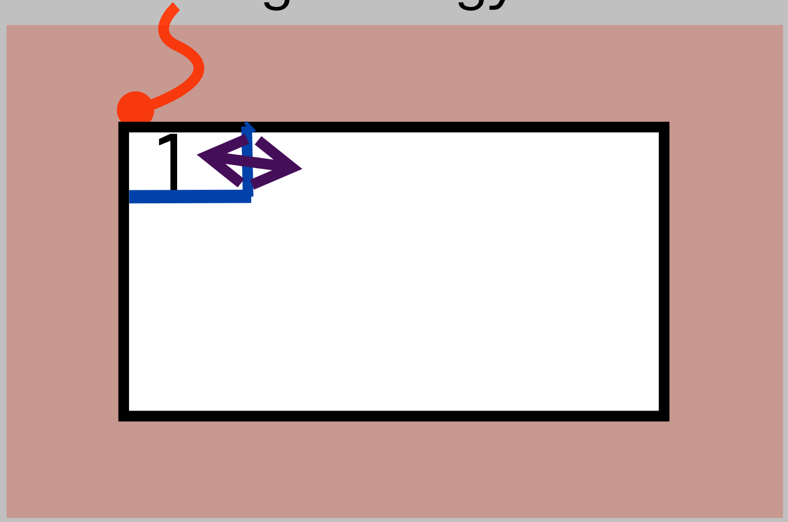

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2nd law: $$T dS_1 - dU_1 \geq 0$$

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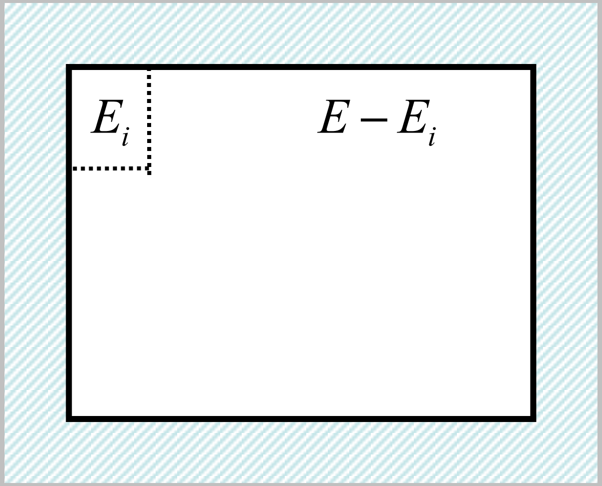
Let us define the Helmholtz free energy: A

$$A \equiv U - TS$$

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

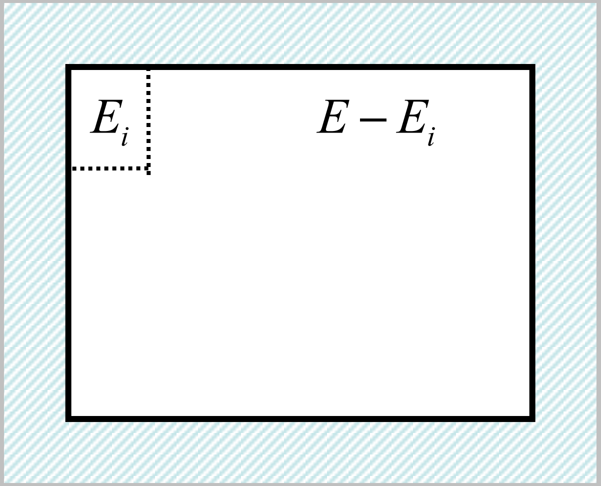
Hence, for a system at constant temperature and volume the Helmholtz free energy decreases and takes its minimum value at equilibrium

Canonical ensemble



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

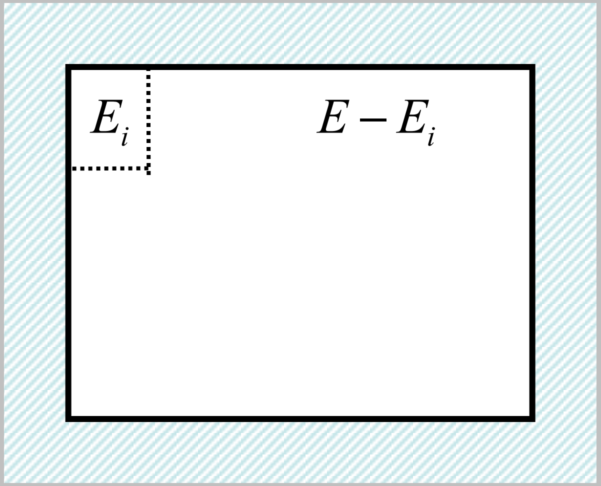
Canonical ensemble



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



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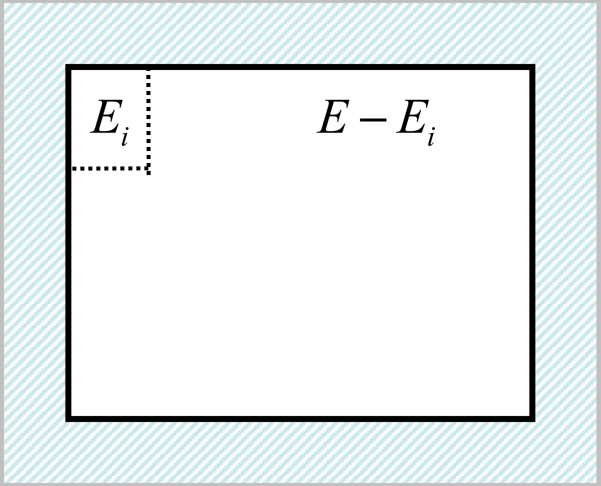
$1/k_BT$

Canonical ensemble



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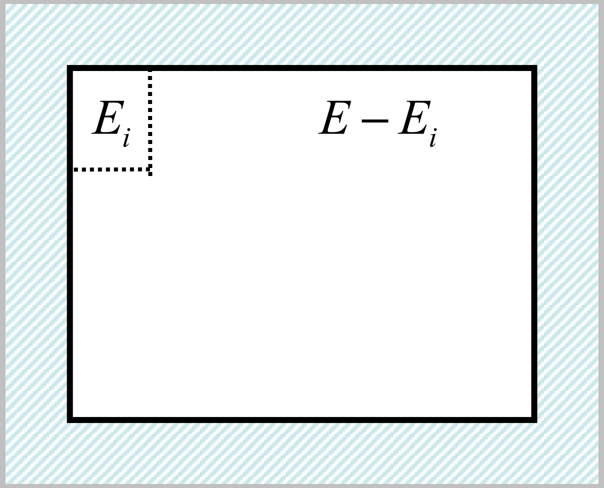

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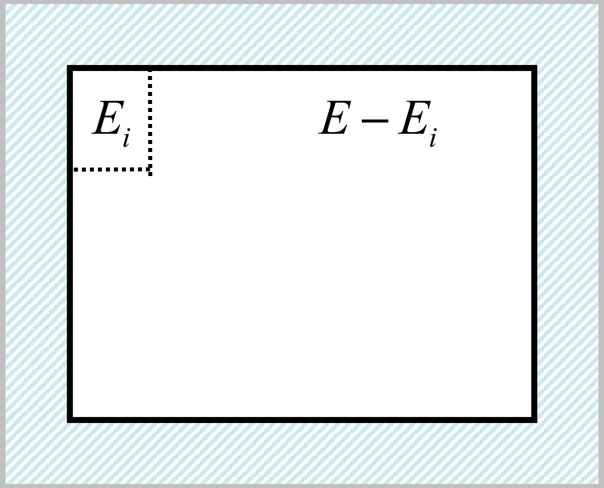
Canonical ensemble



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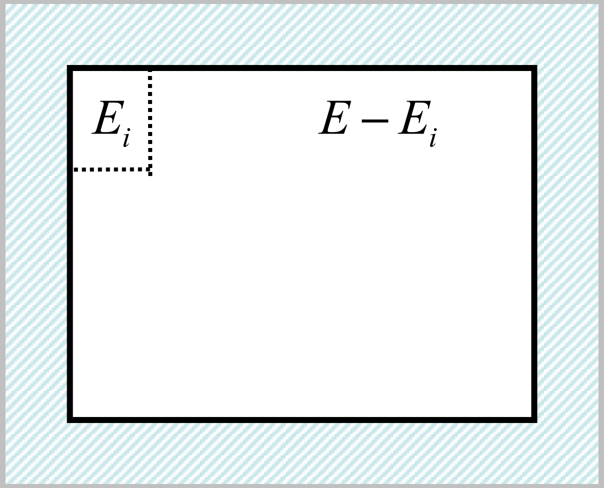
Hence, the probability to find E_i:

Canonical ensemble



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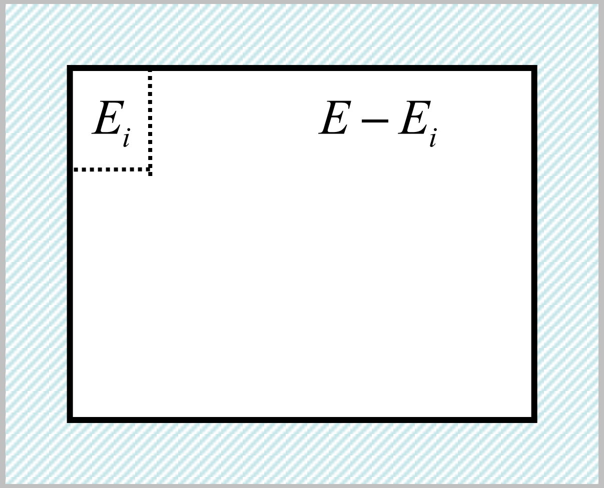
$$P\left(E_i\right) = \frac{\Omega\left(E - E_i\right)}{\sum_j \Omega\left(E - E_j\right)} = \frac{\exp\left(-E_i / k_B T\right)}{\sum_j \exp\left(-E_j / k_B T\right)}$$

Canonical ensemble



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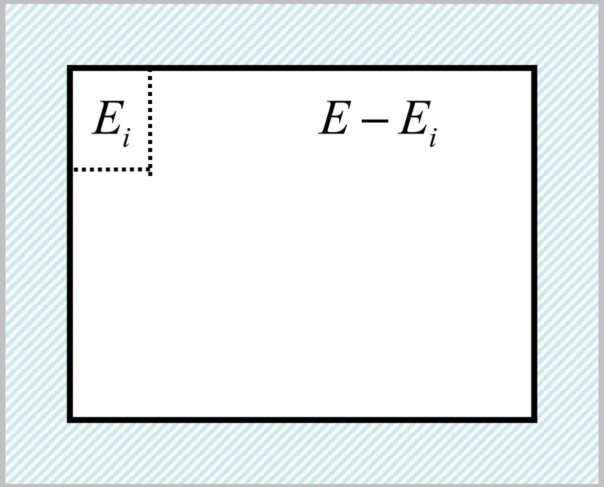

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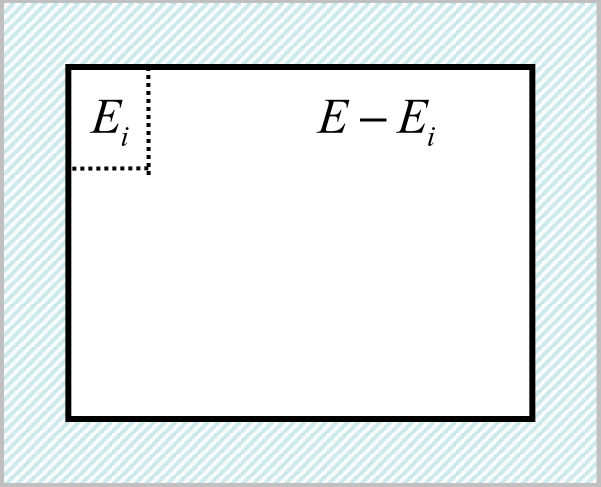
Boltzmann distribution

Canonical ensemble



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

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

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

Hence, the probability to find E_i:

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

$$\boxed{P\left(E_i\right)\propto\exp\left(-E_i/k_BT\right)}$$

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Compare:

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

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First law of thermodynamics

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

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Hence:

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

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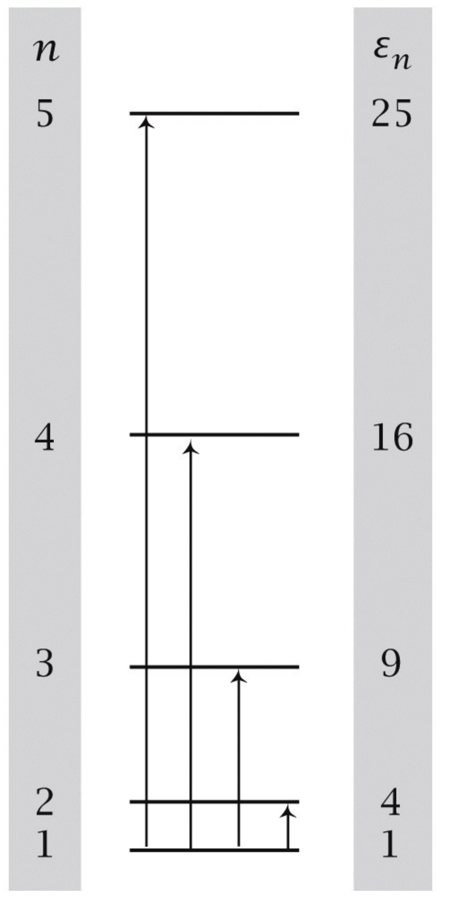

Figure 11.4 Molecular Driving Forces 2/e (© Garland Science 2011)

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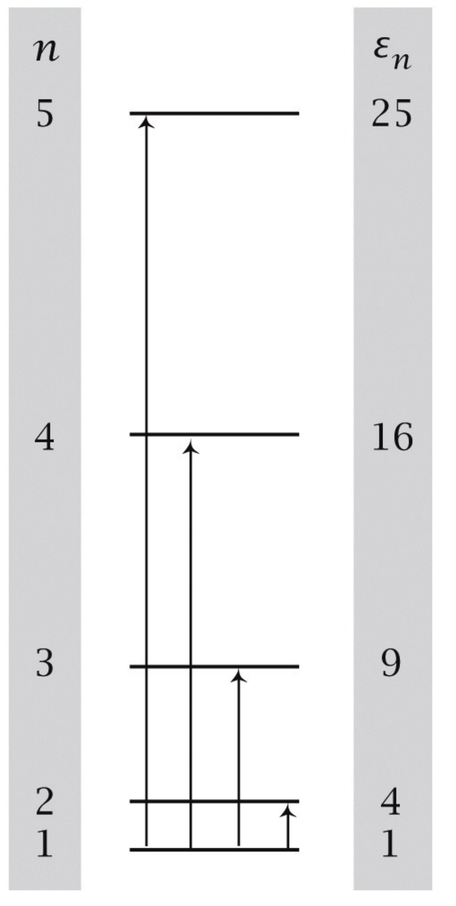

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$$\boxed{Q_{N,V,T} = \frac{1}{\Lambda^{3N} N!} \int e^{-\frac{U(r)}{k_B T}}\, dr^N}$$

Question

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

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

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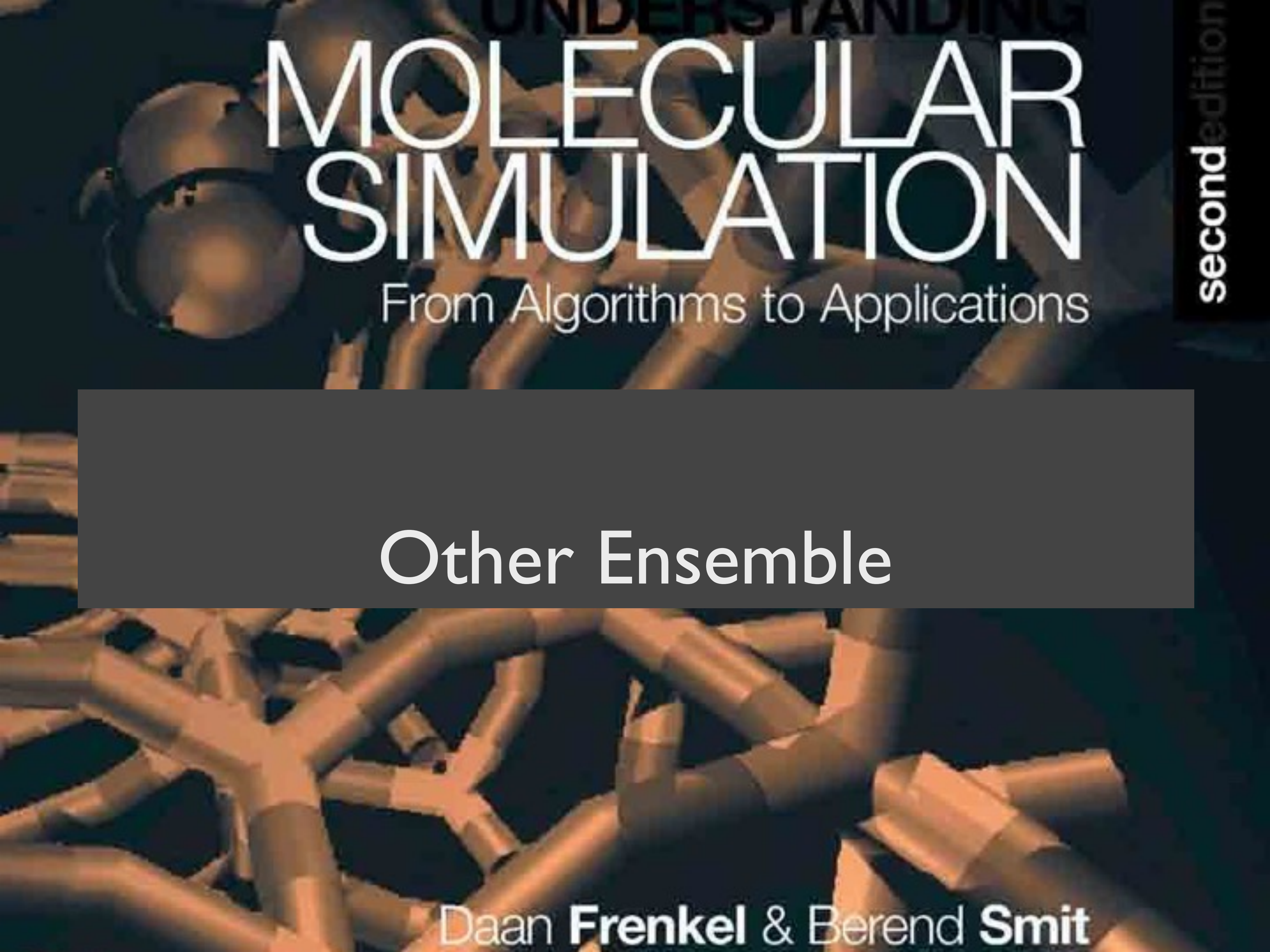

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COURSE:
MD and MC different
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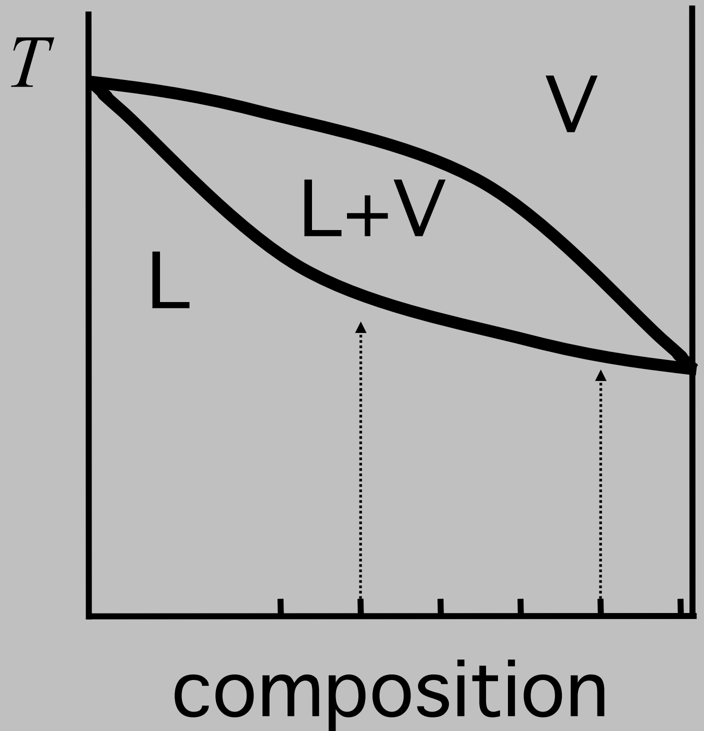
Example (1):
vapour-liquid equilibrium mixture



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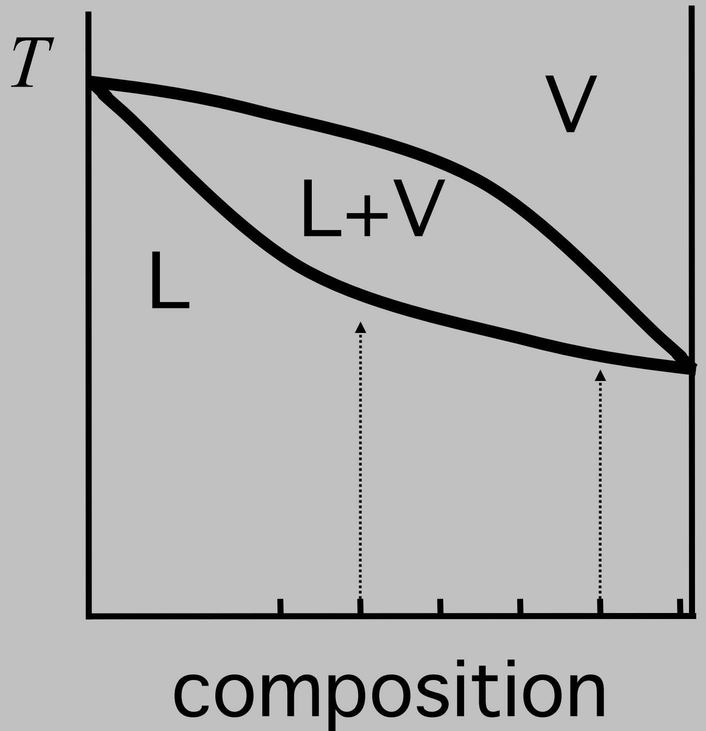

Measure the composition of the coexisting vapour and liquid phases if we start with a homogeneous liquid of two different compositions:

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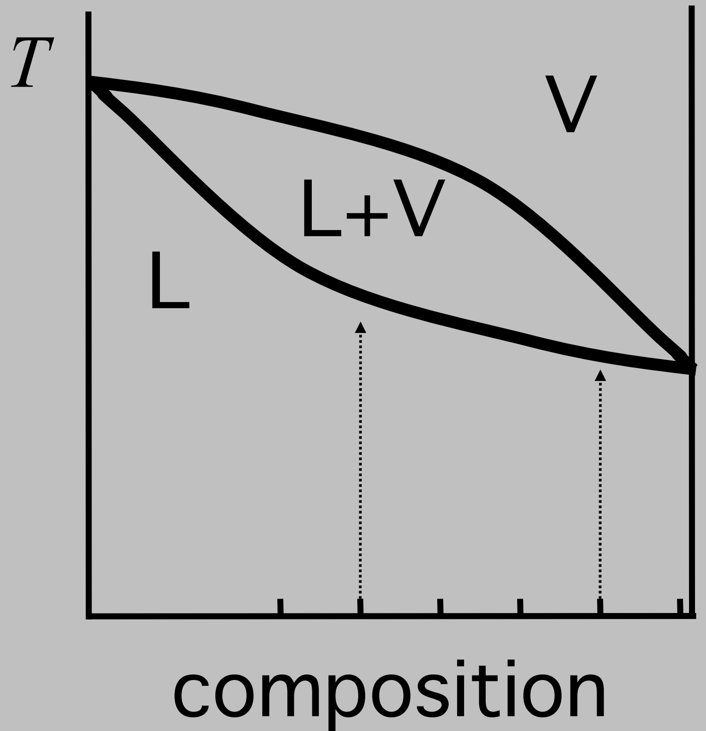

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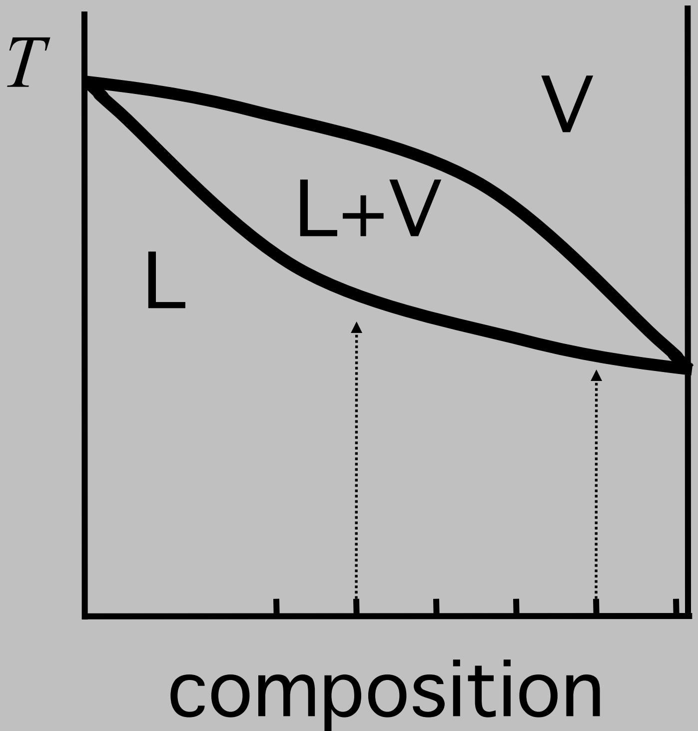

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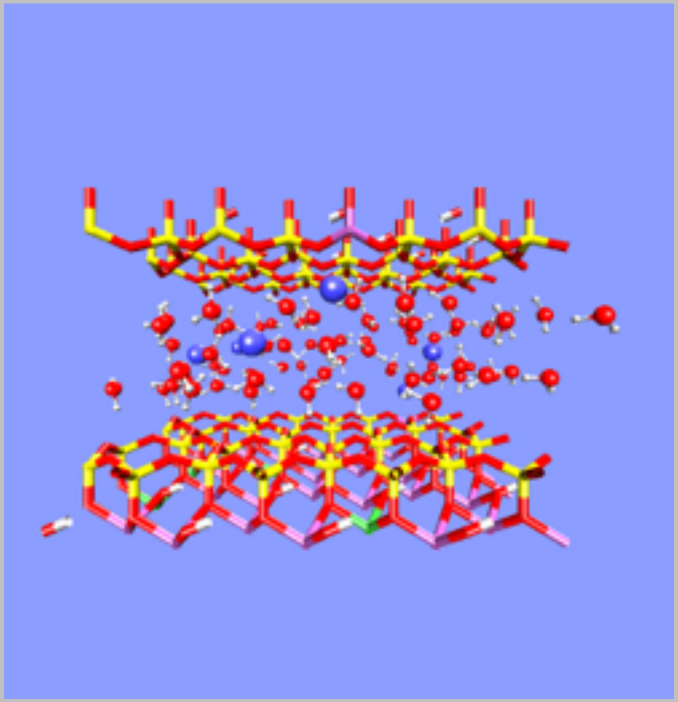
Example (2): swelling of clays



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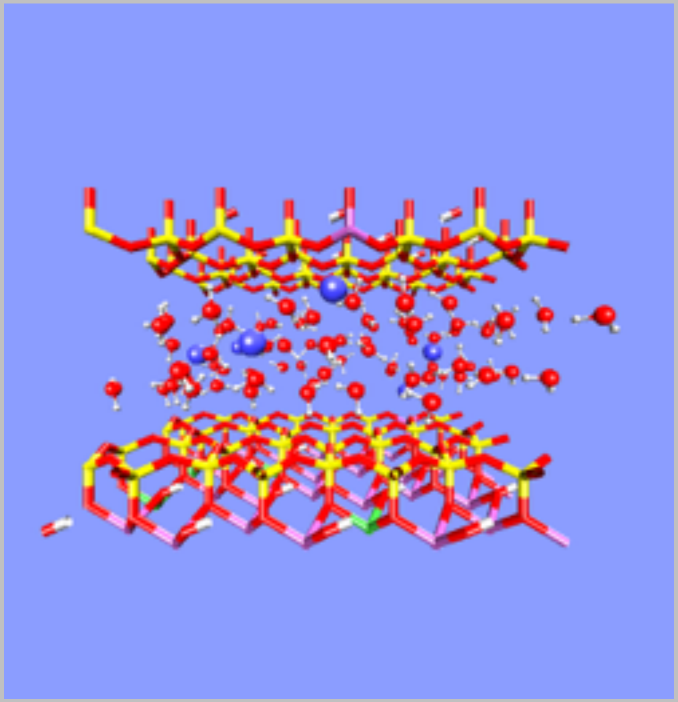


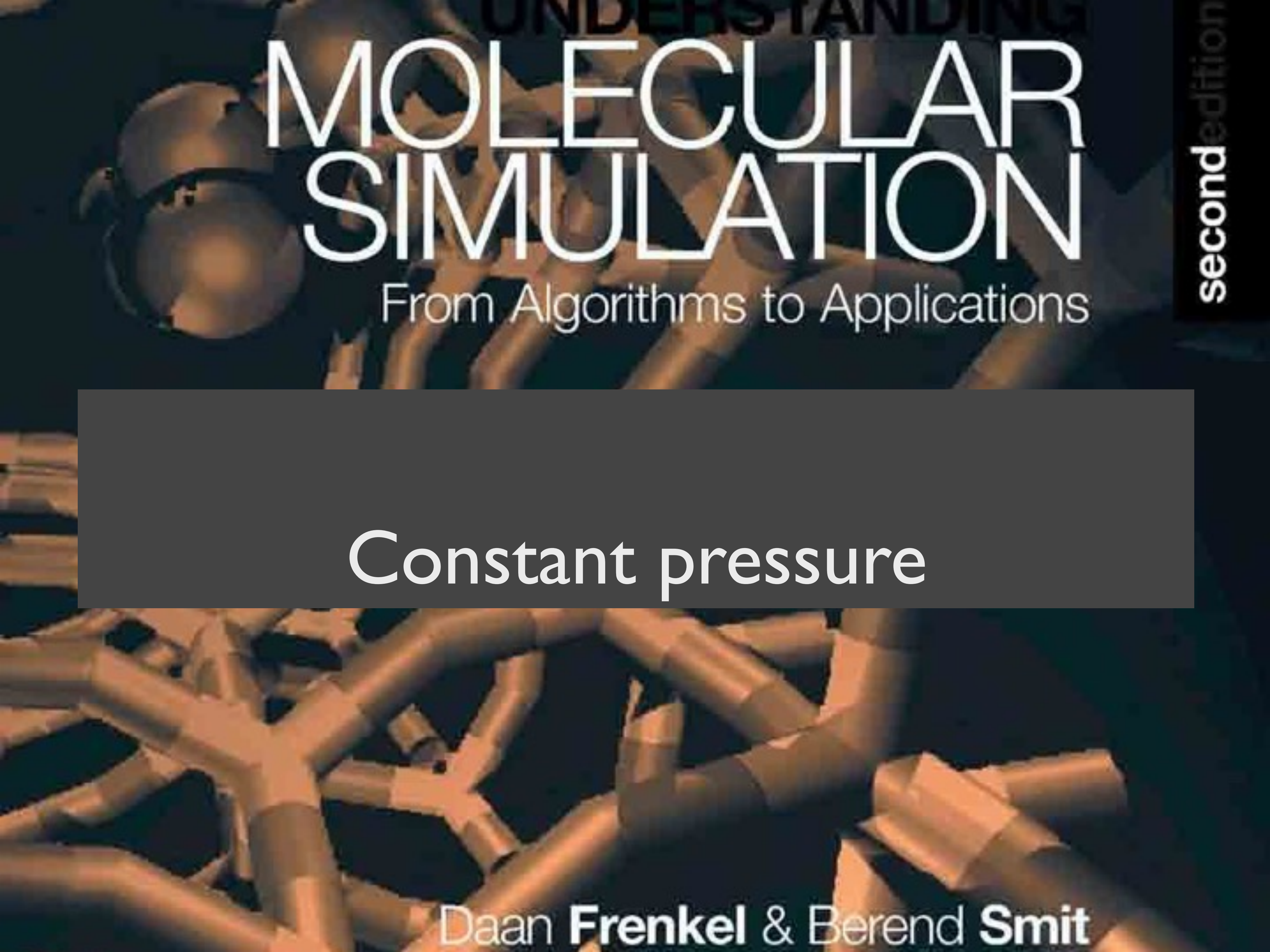
Deep in the earth clay layers can swell upon adsorption of water:

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

Ensembles

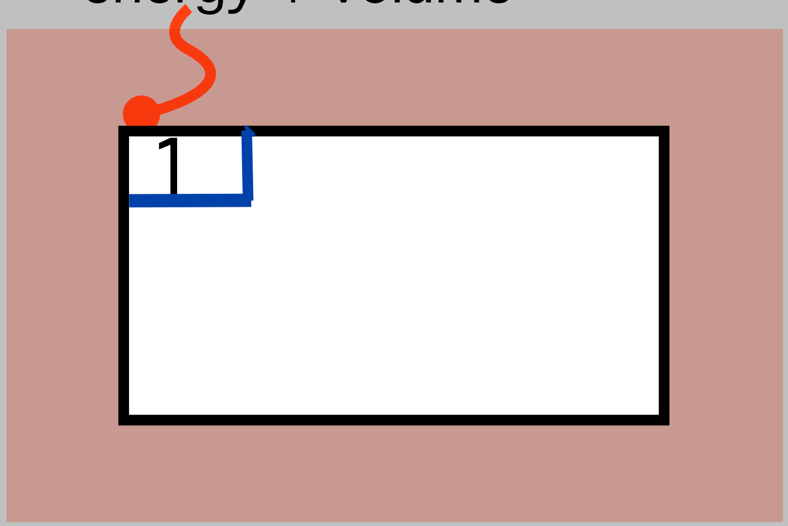
Ensembles

- 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



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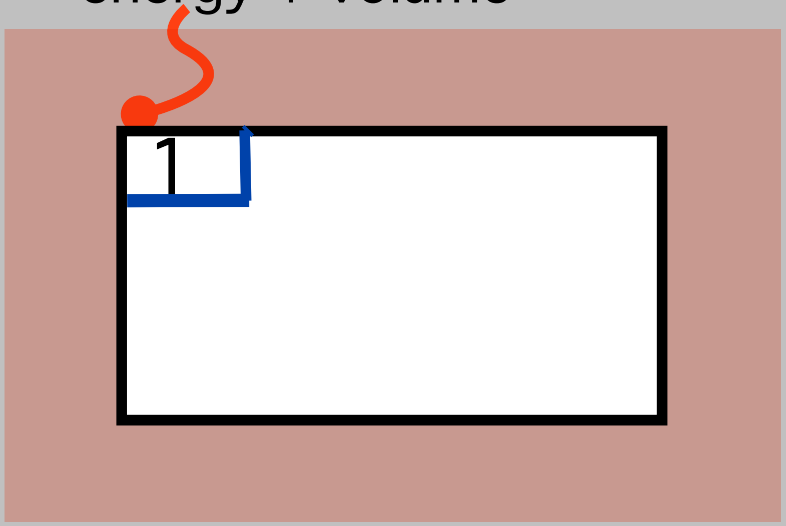
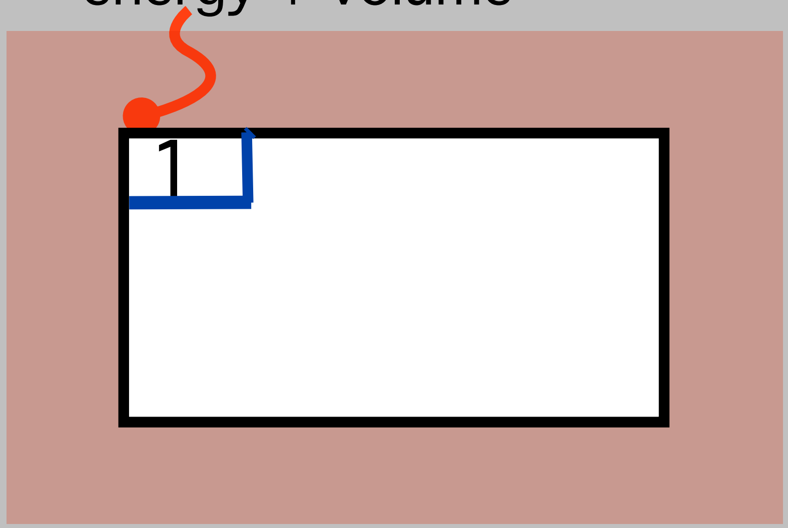


We have our box 1 and a bath



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We have our box 1 and a bath

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

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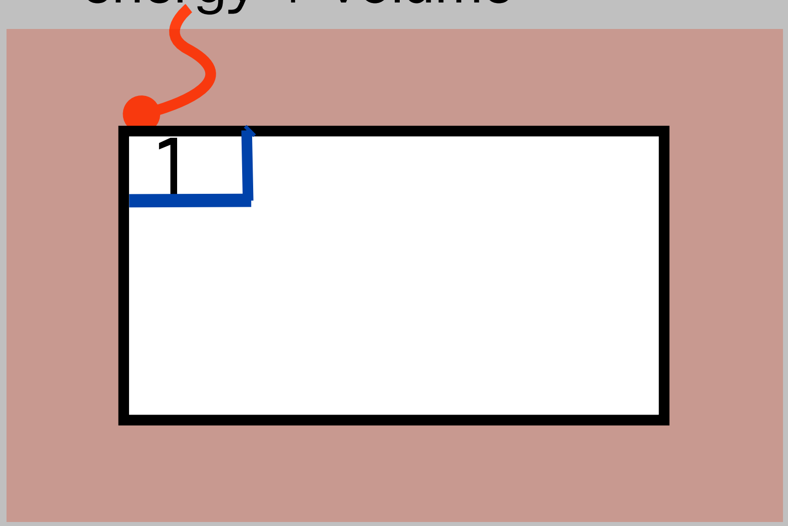

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First law

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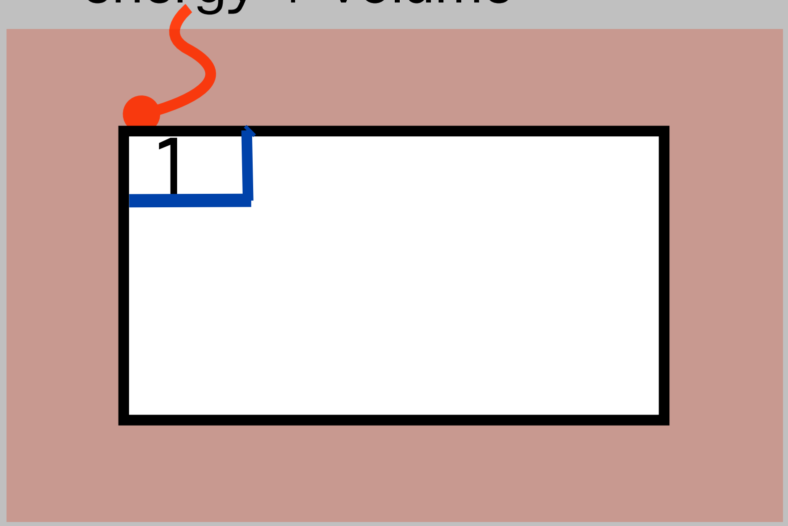

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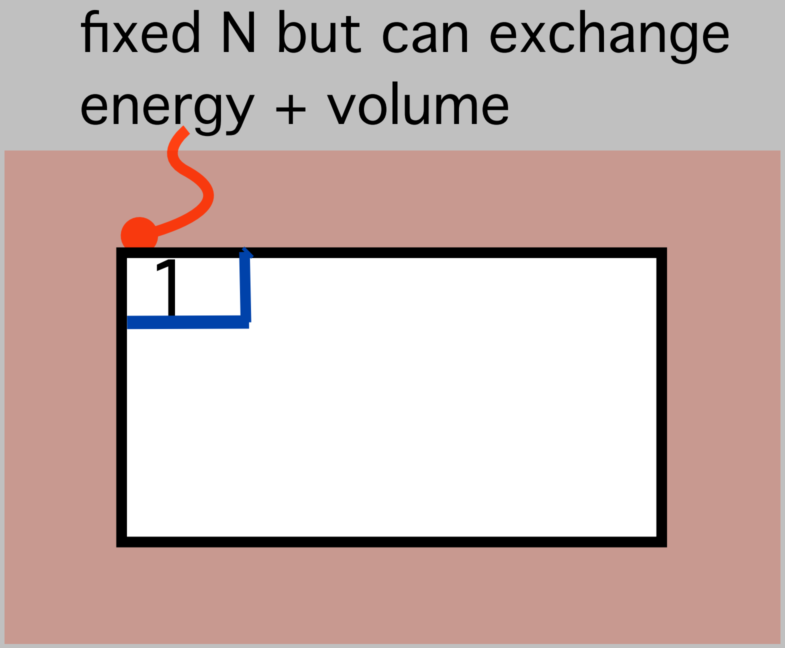

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Second law

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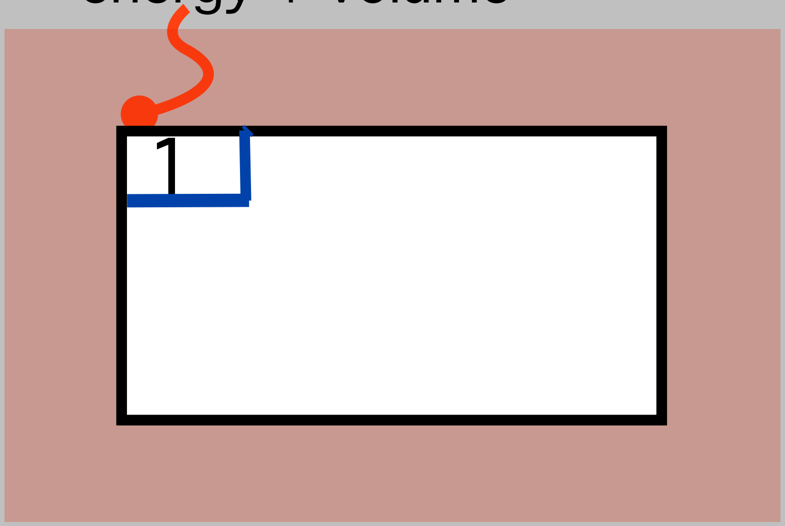

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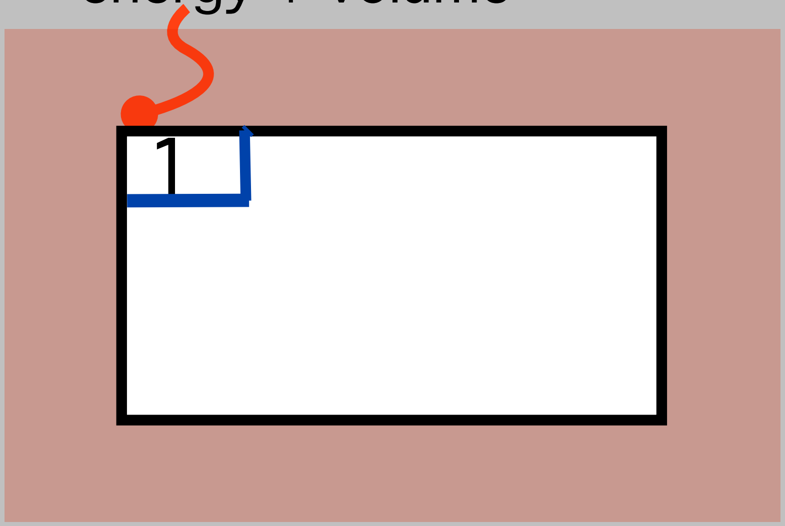

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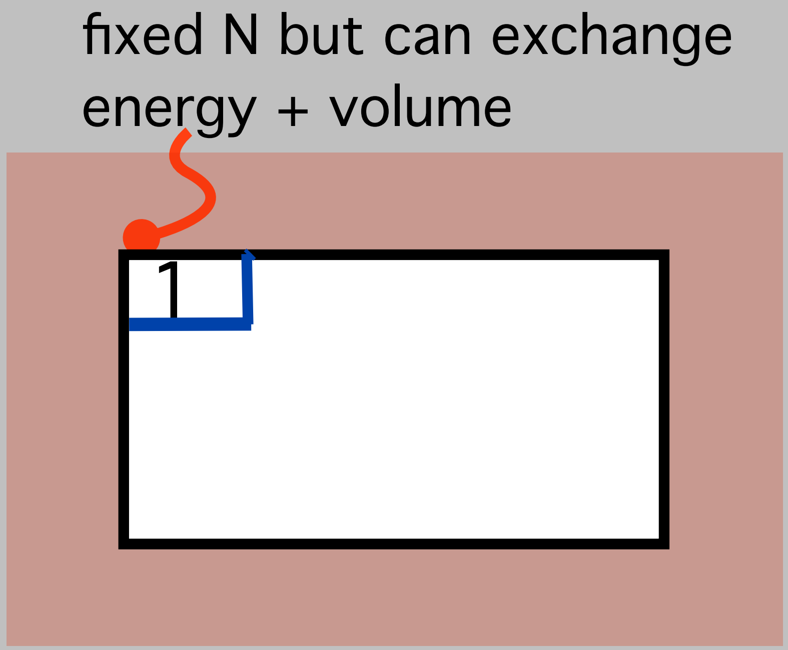

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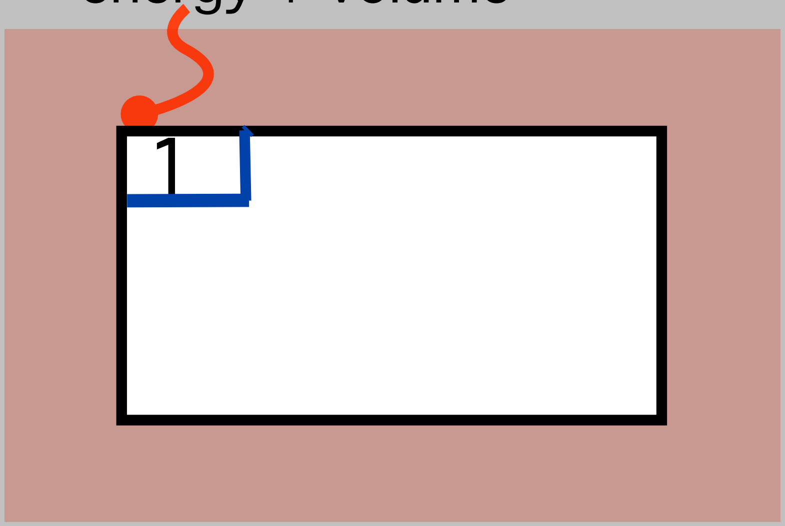

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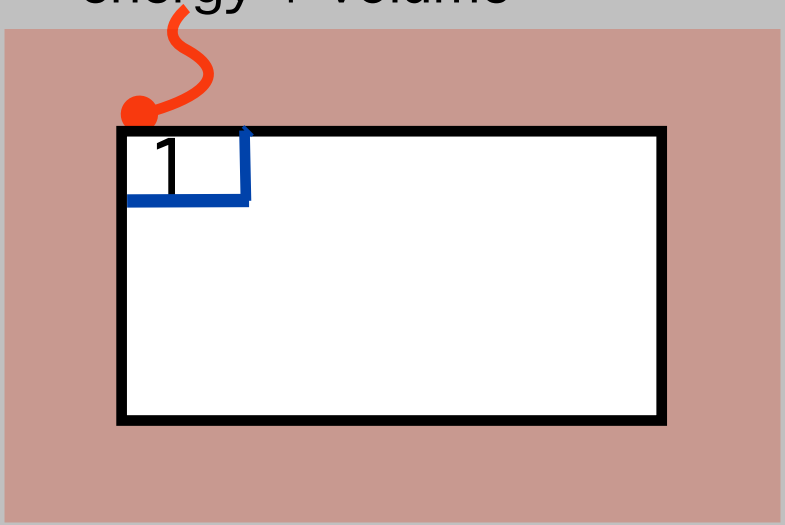

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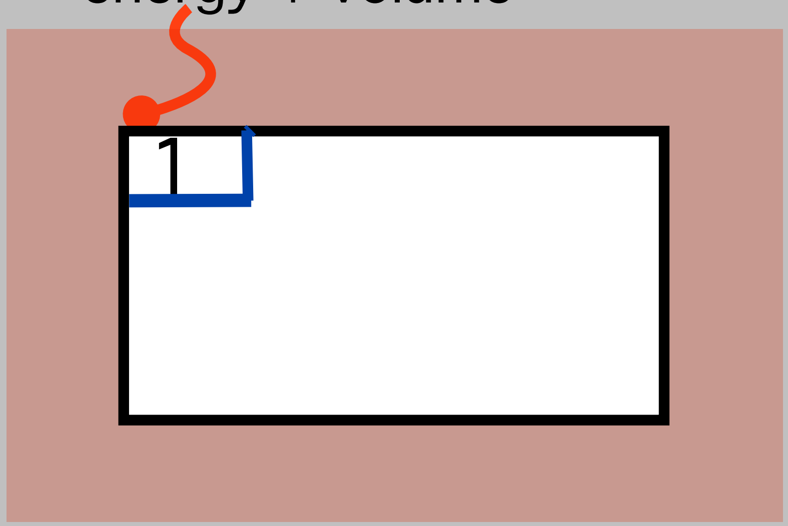

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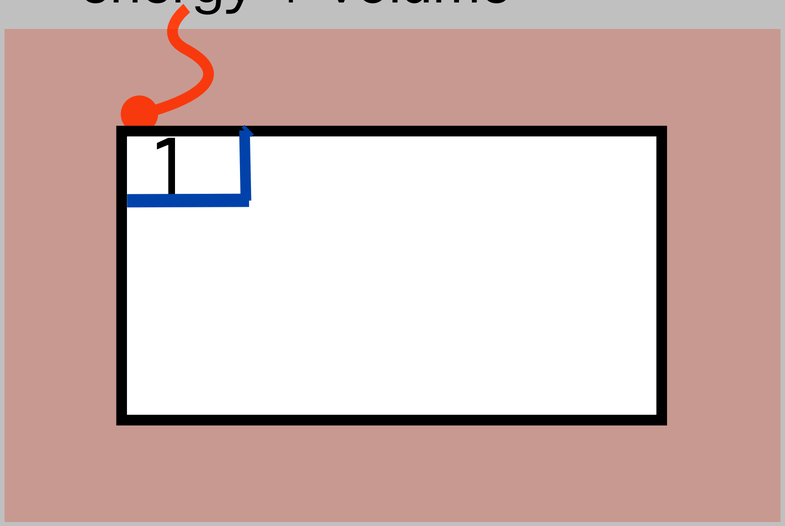

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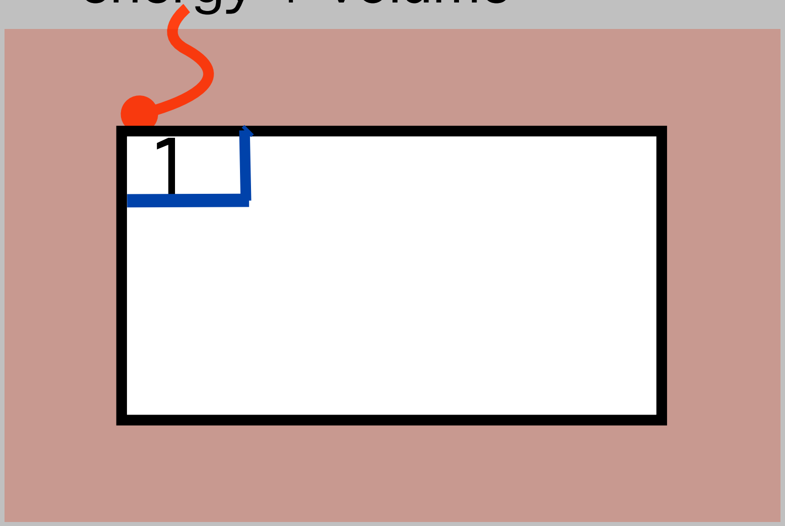

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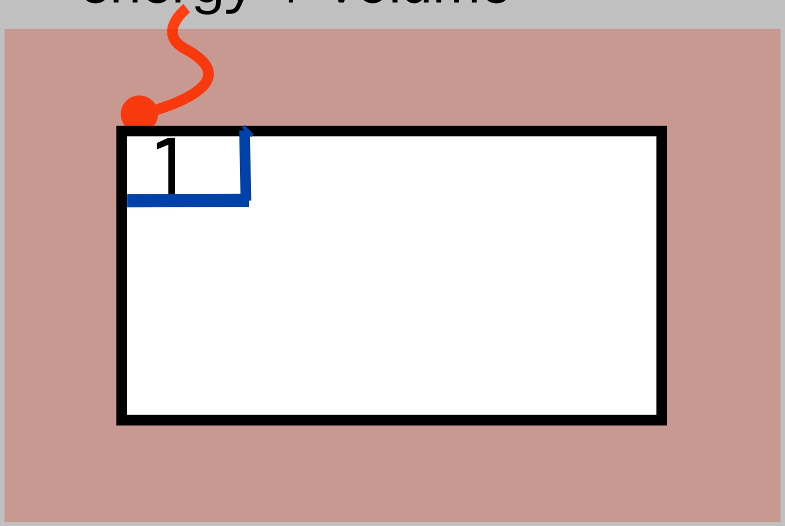

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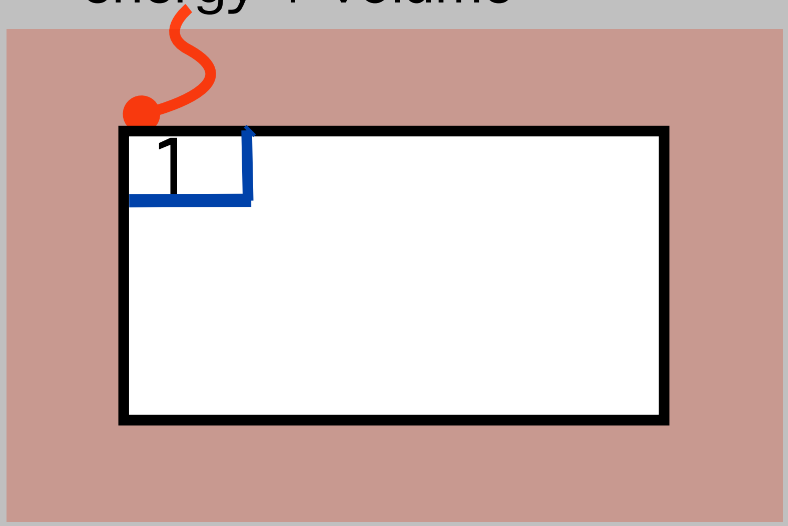

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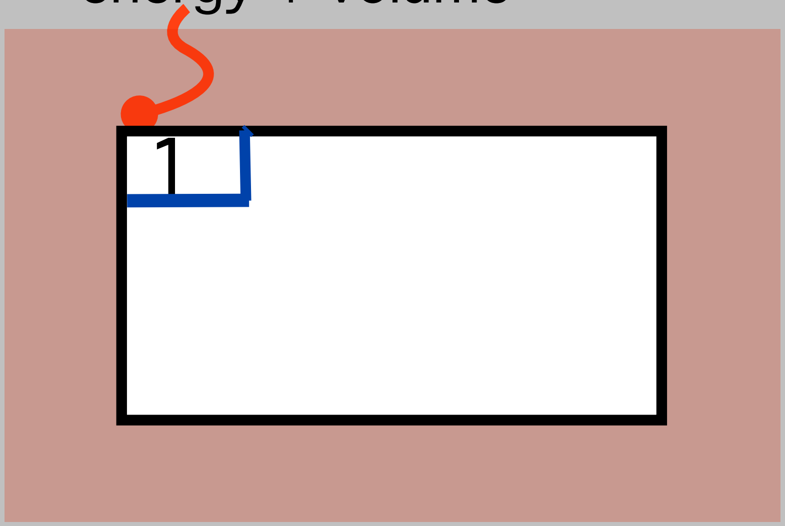

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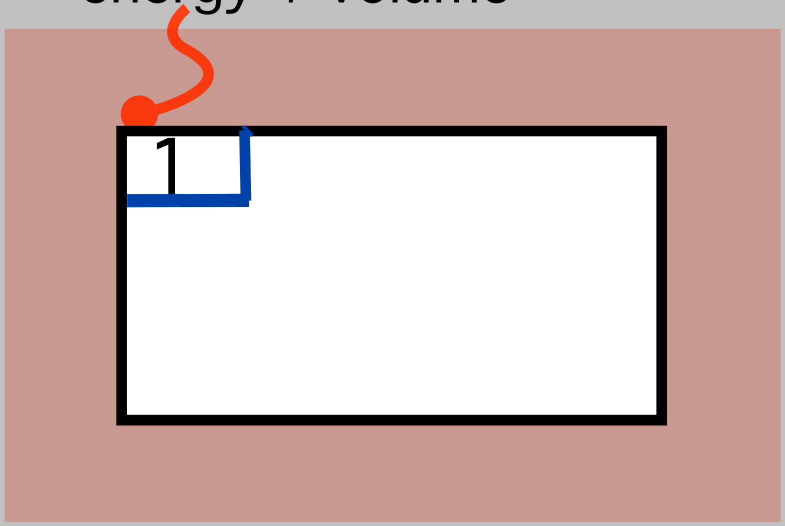

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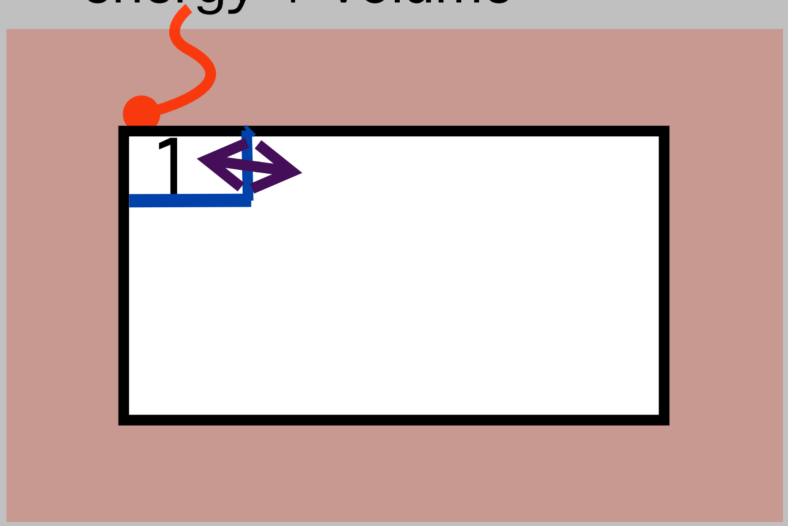

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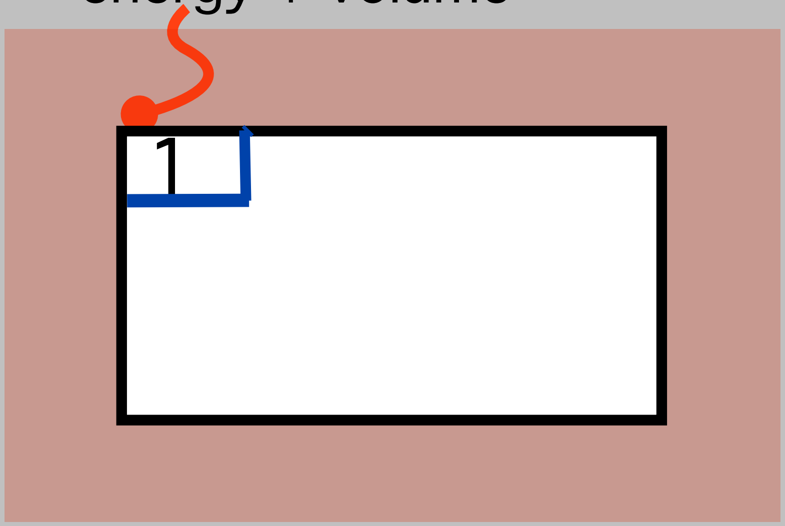
$$TdS_1 - dU_1 - pdV_1 \geq 0$$



fixed N but can exchange energy + volume

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Box 1: constant pressure and temperature

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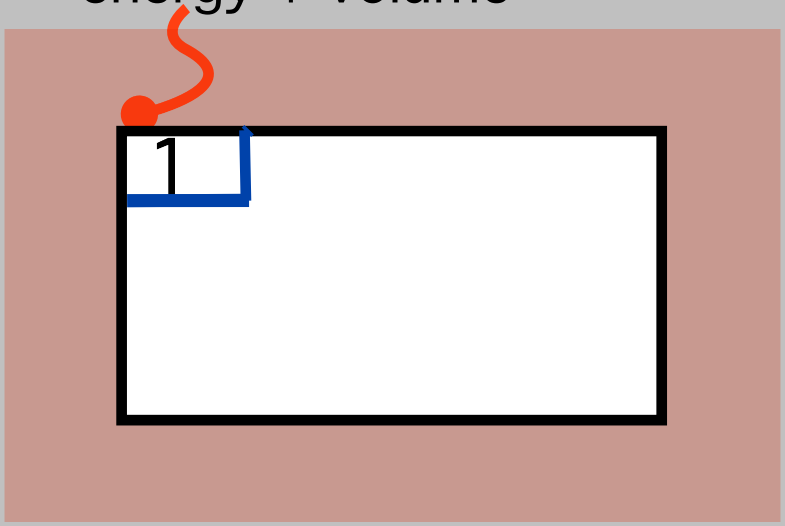

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2nd law: $\mathrm{T}\mathrm{d}S_1 - \mathrm{d}U_1 - p\,\mathrm{d}V_1 \geq 0$

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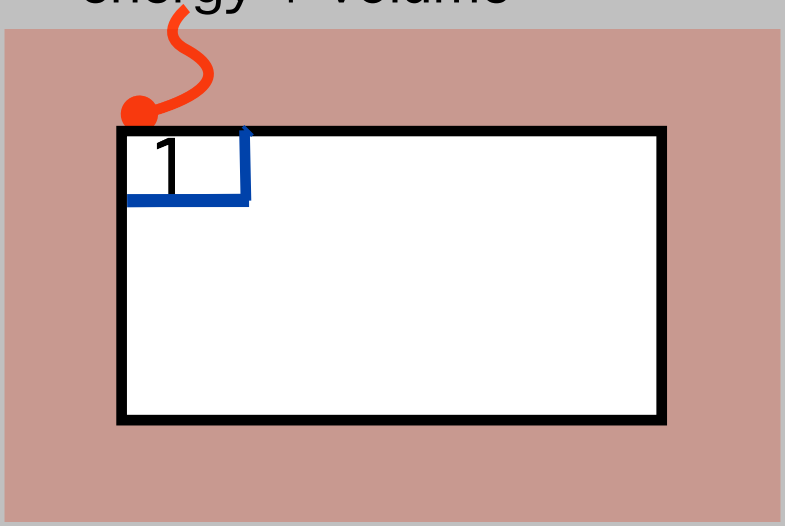

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Let us define the **Gibbs free energy**: G

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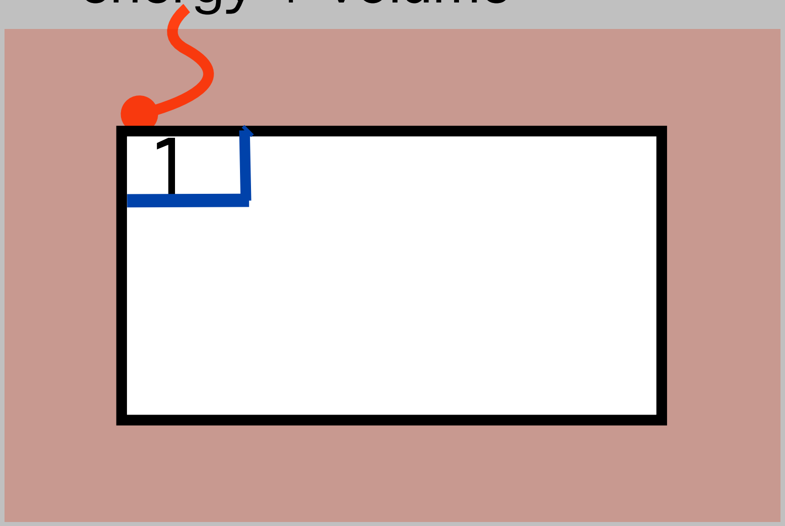

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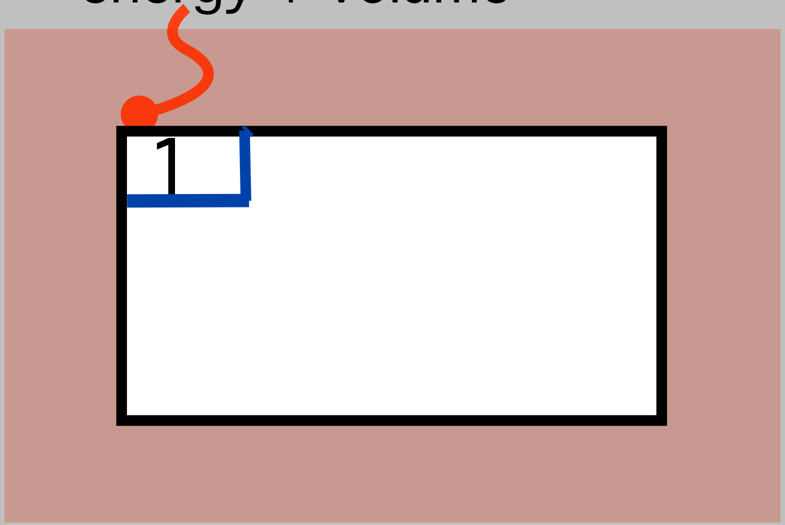

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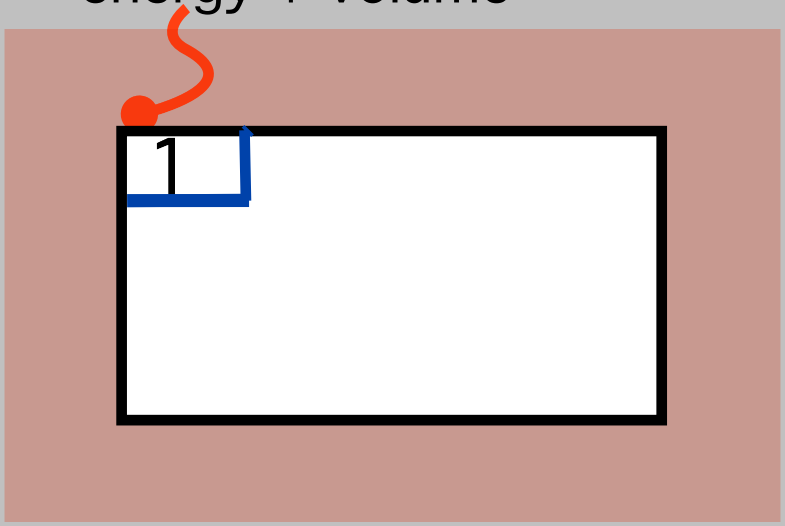

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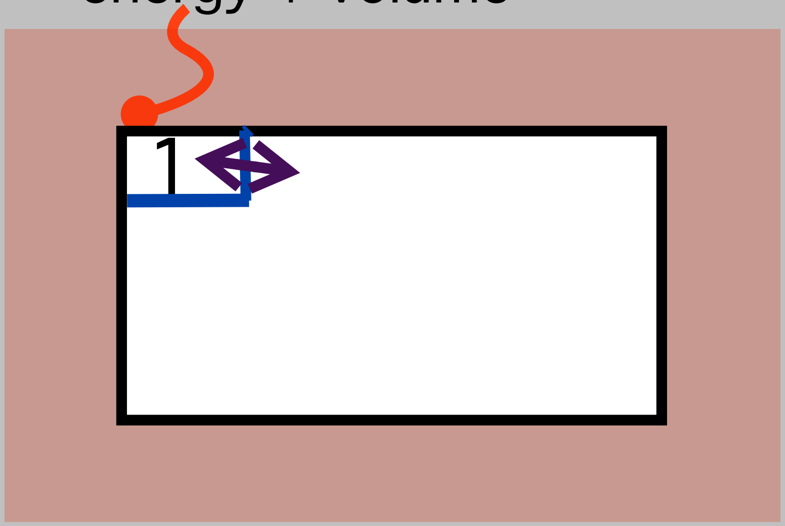

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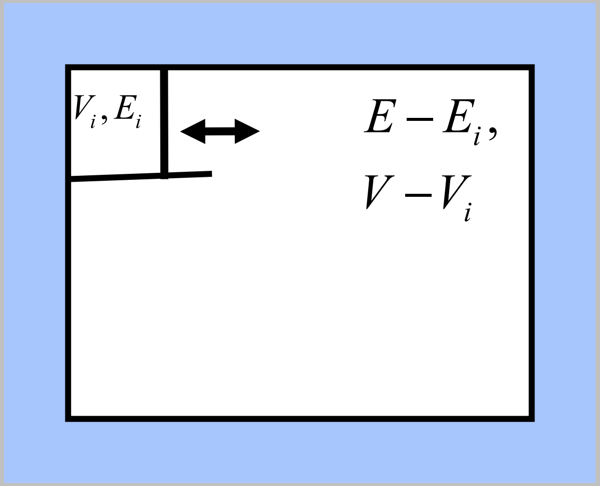
For box 1 we can write $\mathrm{dG_1 \leq 0}$

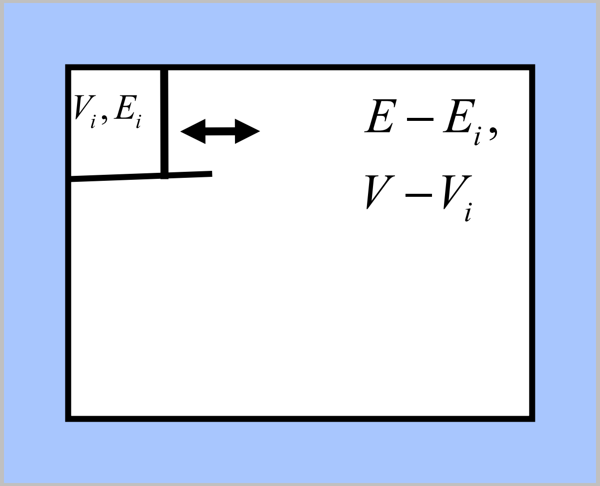
Hence, for a system at constant temperature and pressure the Gibbs free energy decreases and takes its minimum value at equilibrium



N,P,T ensemble

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

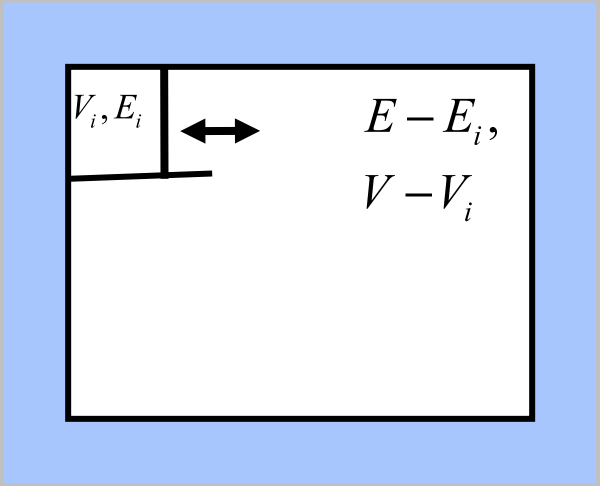
N,P,T ensemble



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

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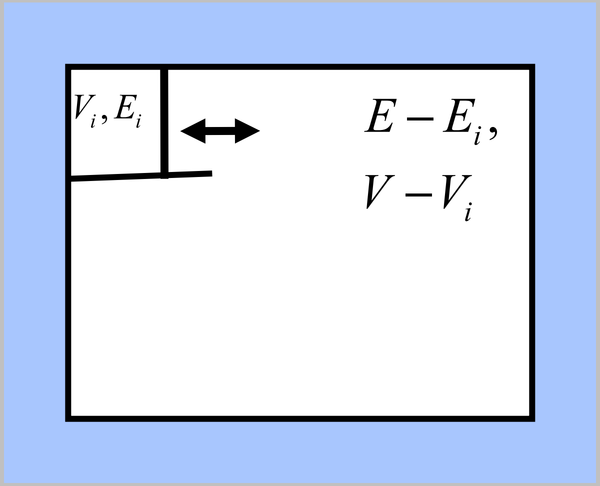

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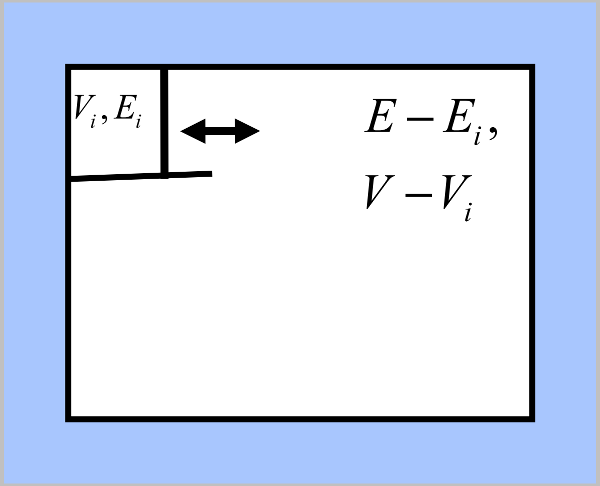

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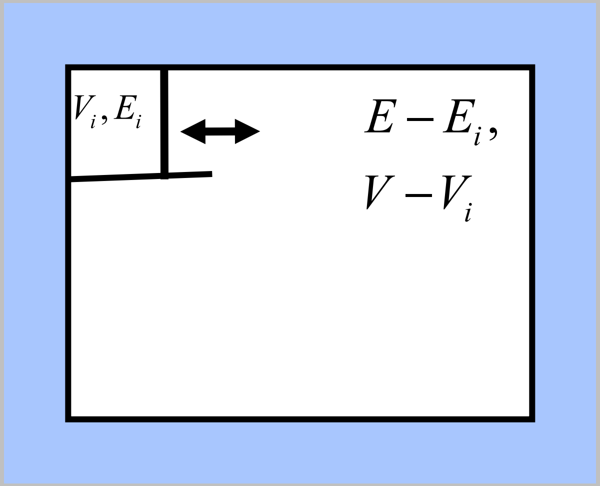

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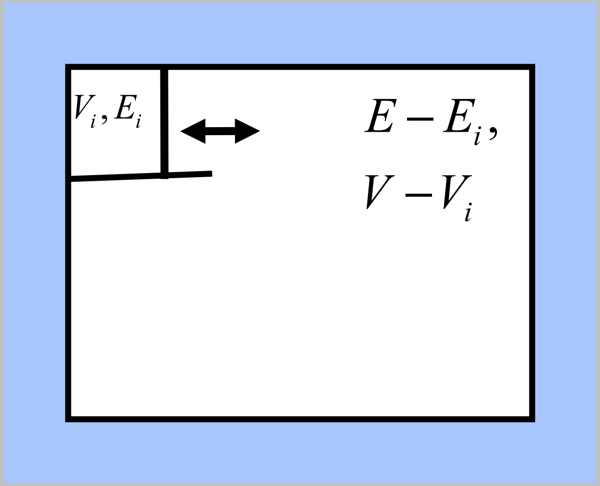

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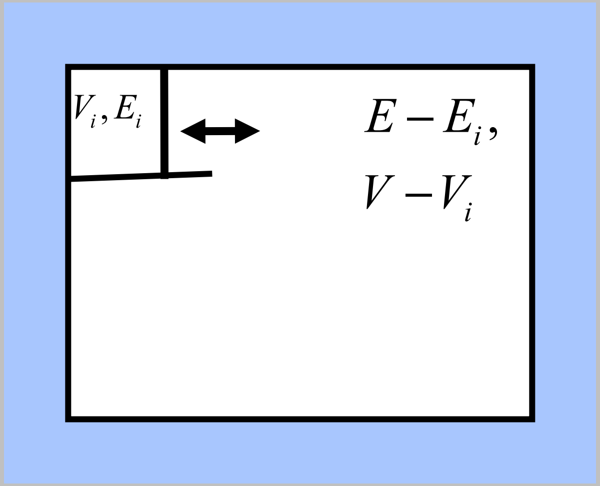

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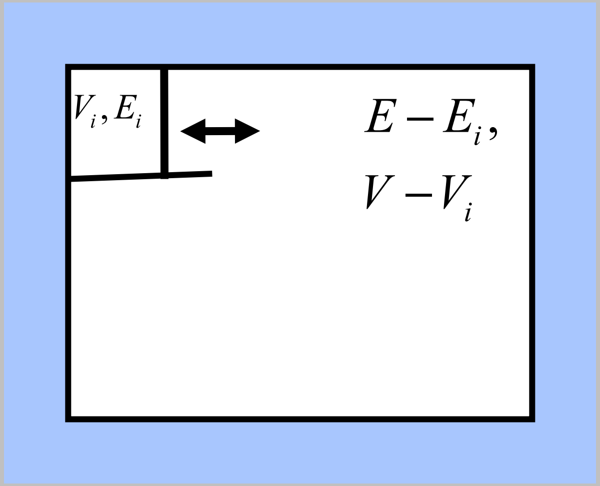

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$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum \frac{\mu_i}{T} dN_i$$

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

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

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

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

Hence, the probability to find E_i,V_i:

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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:

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Thermodynamics
$$dG = -SdT + Vdp + \sum \mu_i dN_i$$
$$V = \left(\frac{\partial G}{\partial p}\right)_{T,N}$$

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

Summary

In the classical limit, the partition function becomes

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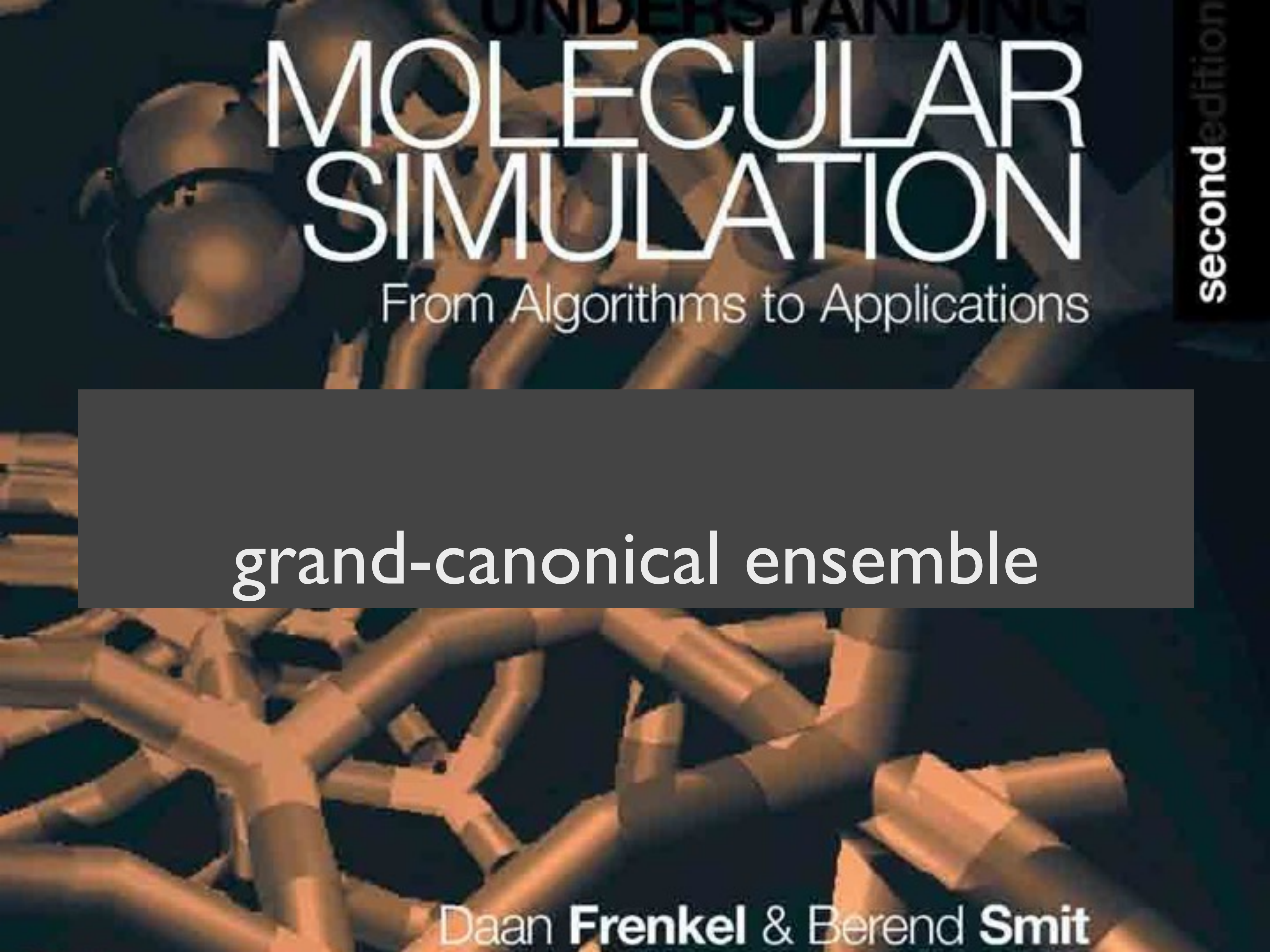
The probability to find a particular configuration:

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

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



grand-canonical ensemble

Grand-canonical ensemble

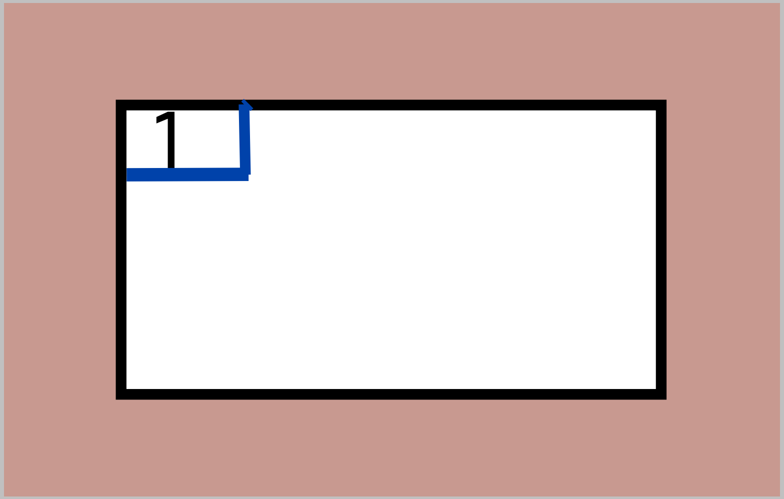
Classical

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

Statistical

- Taylor expansion of a small reservoir

Constant T and μ



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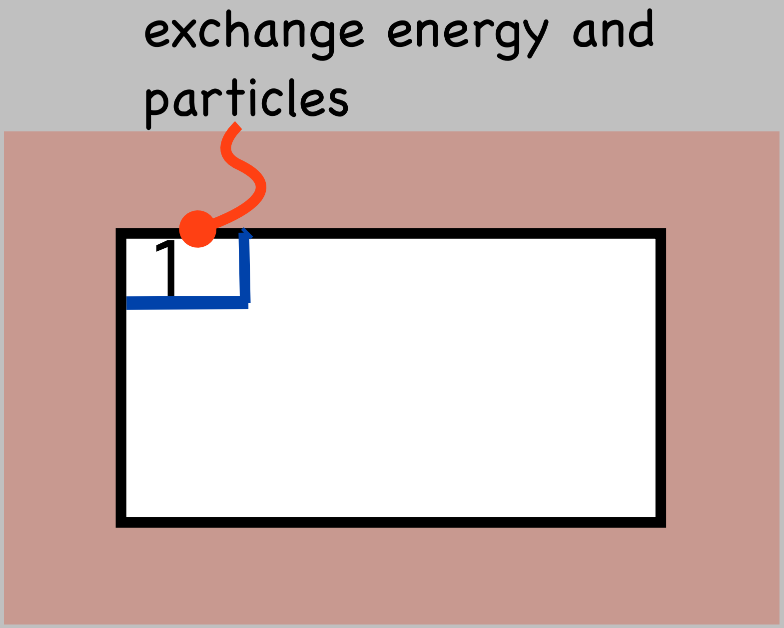

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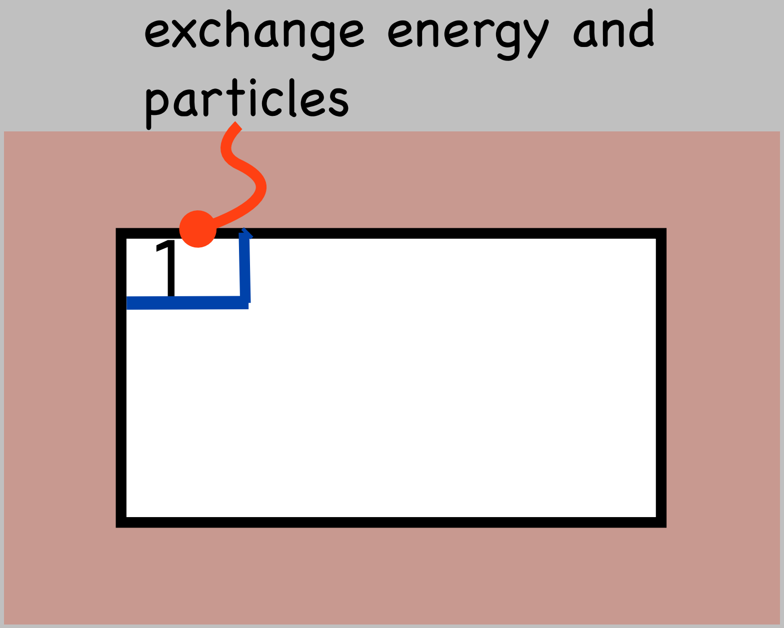

<u>Total system</u> is isolated
and the volume is constant

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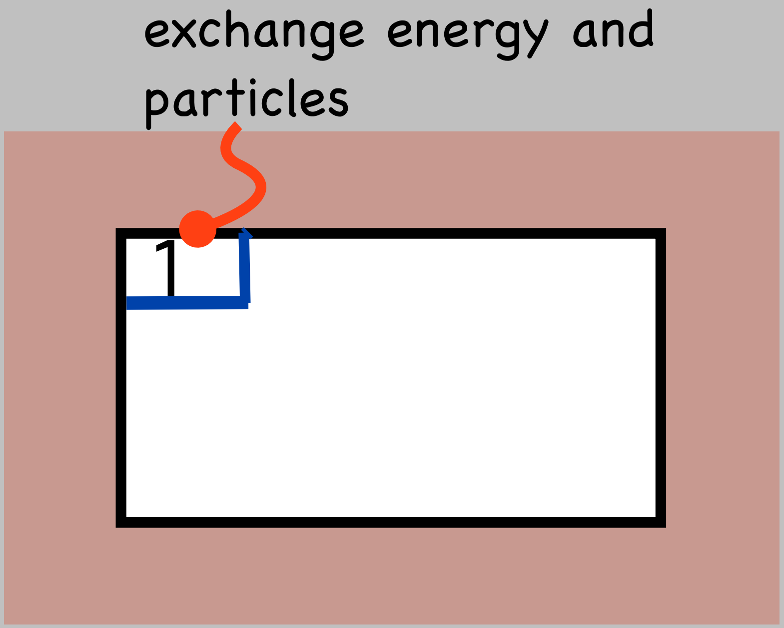

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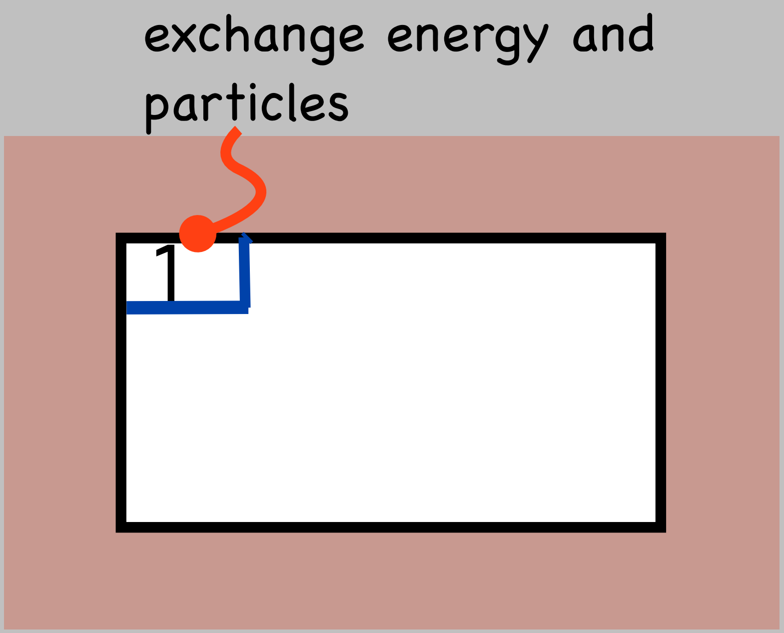

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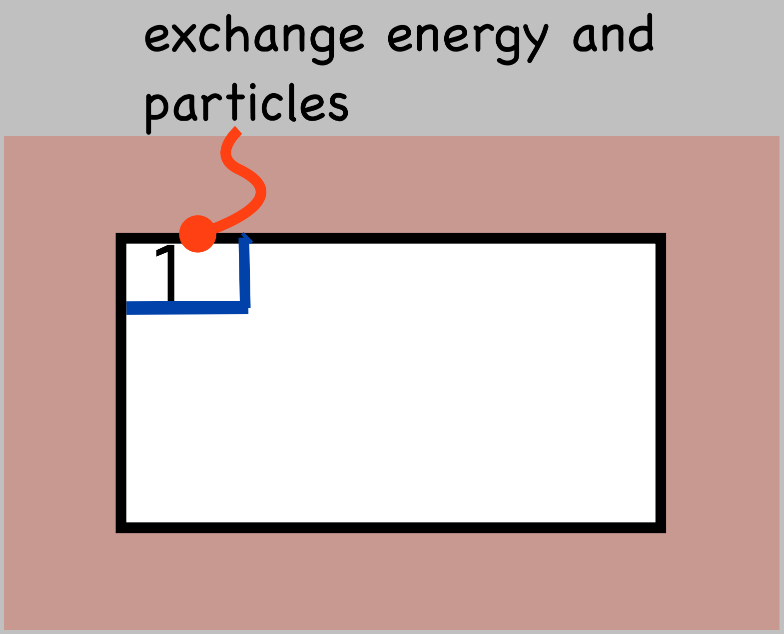

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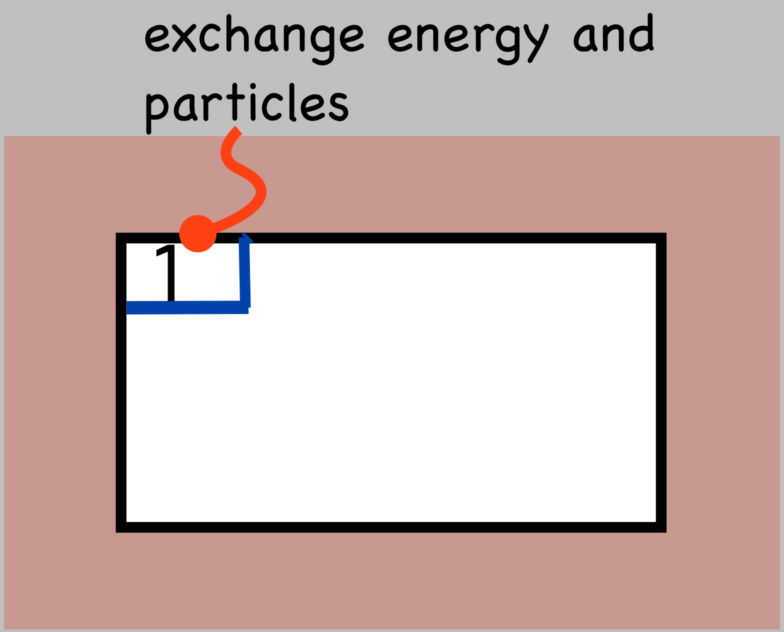

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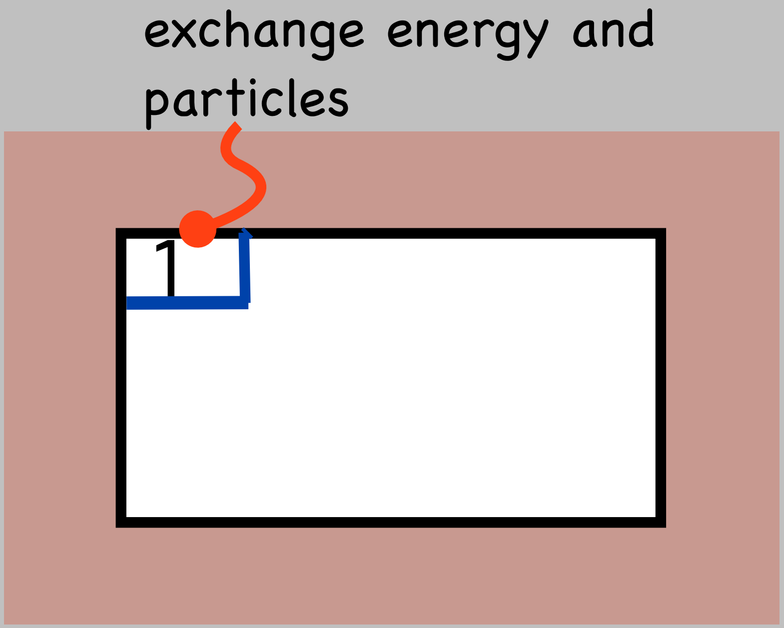

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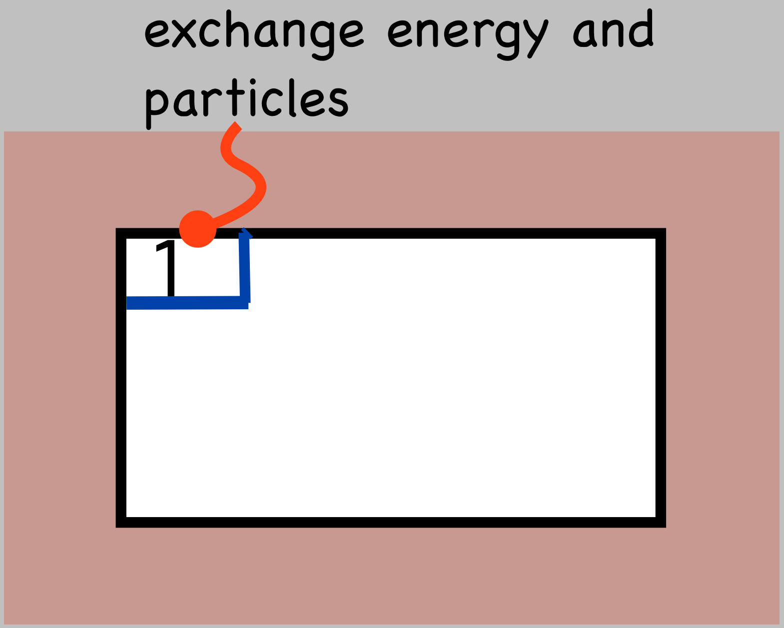

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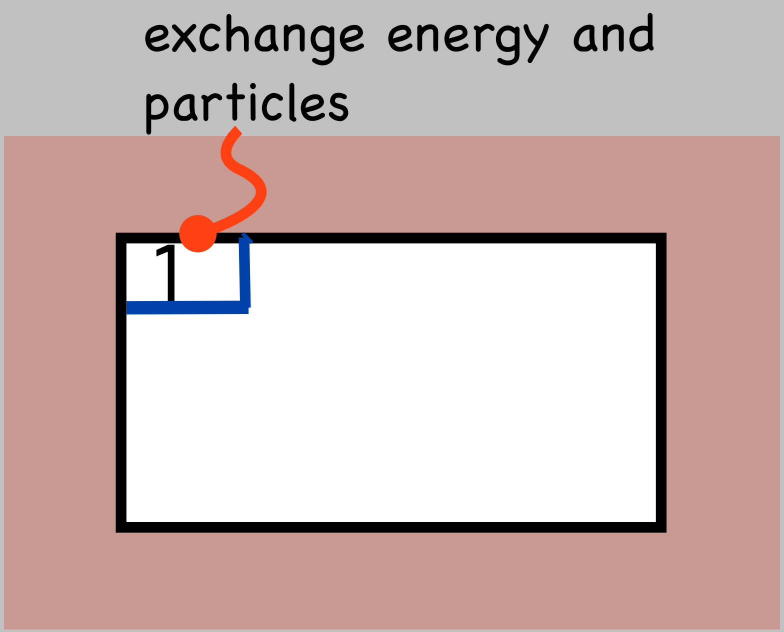

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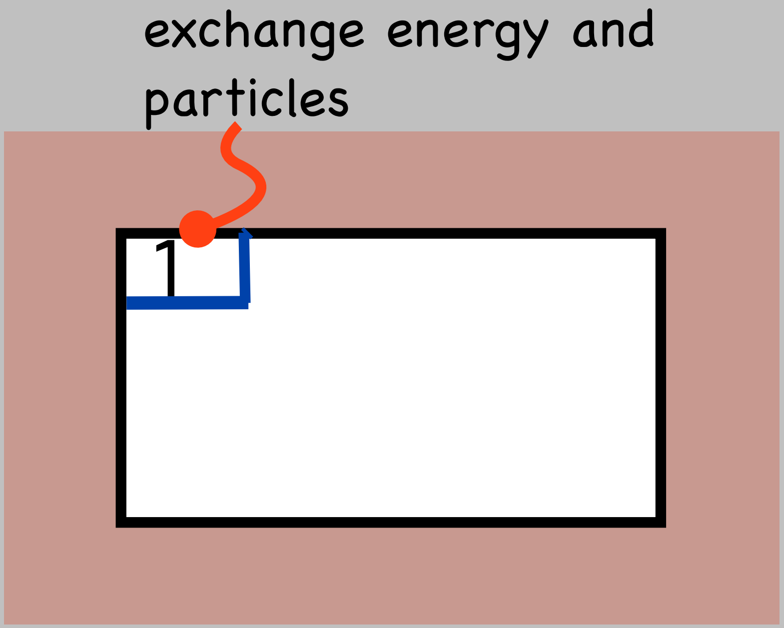

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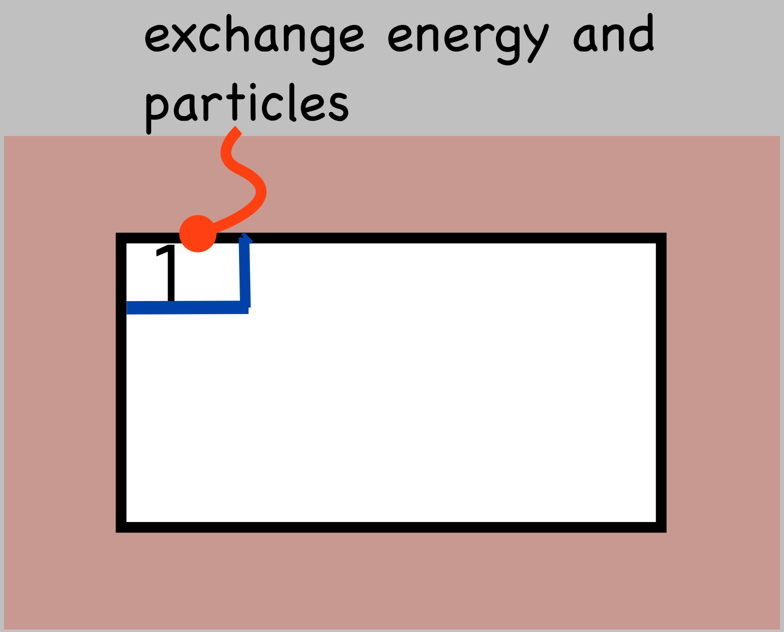

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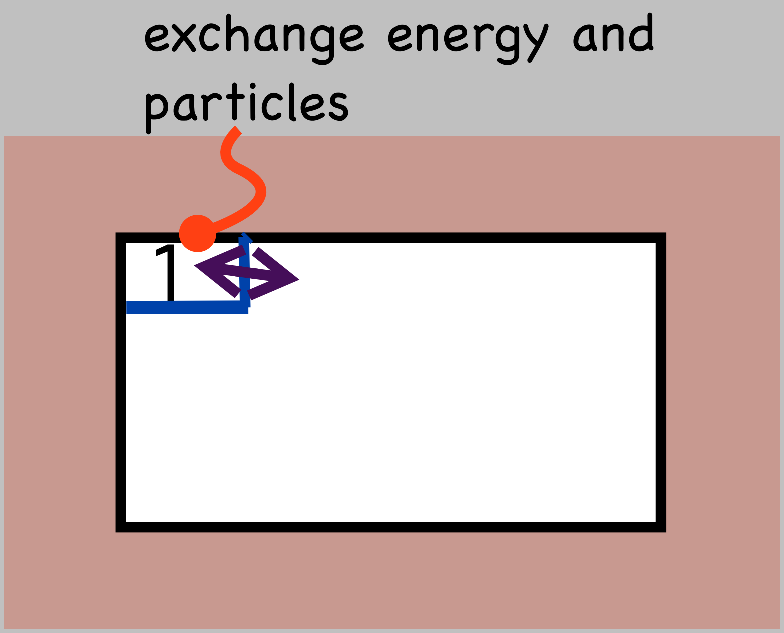
2nd law:

Constant T and μ



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

$$G = \mu N$$

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

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

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

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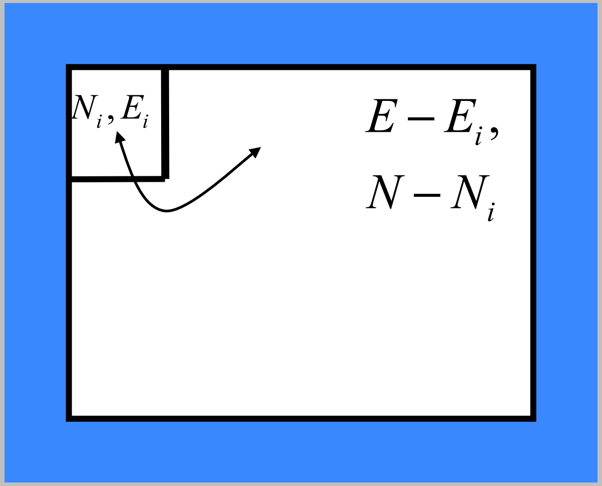
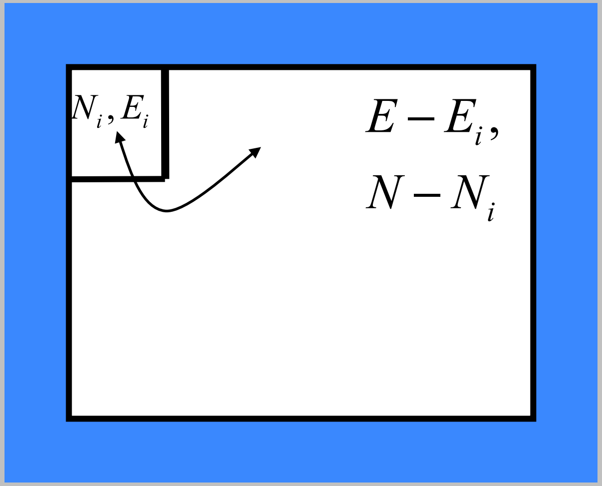
Hence, for a system at constant temperature and chemical potential pV increases and takes its maximum value at equilibrium

μ, V, T ensemble



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

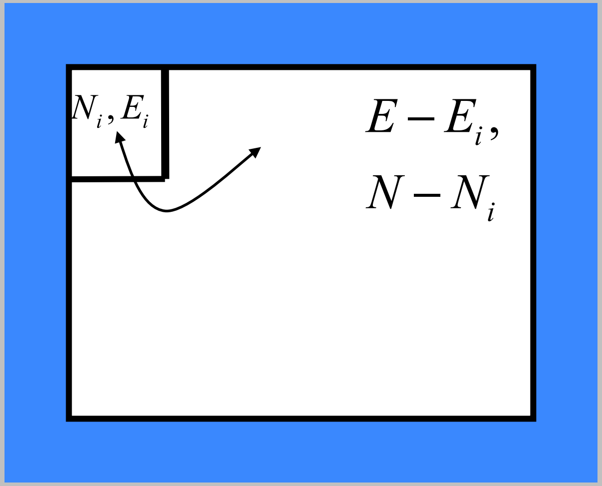
μ,*V*,*T* ensemble



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



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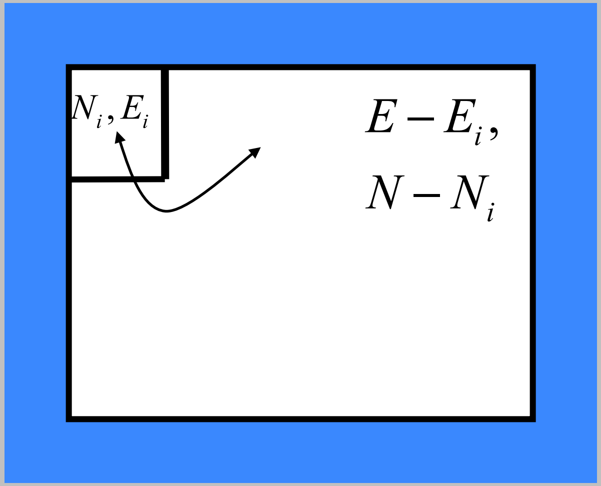
The terms in the expansion follow from the connection with Thermodynamics:



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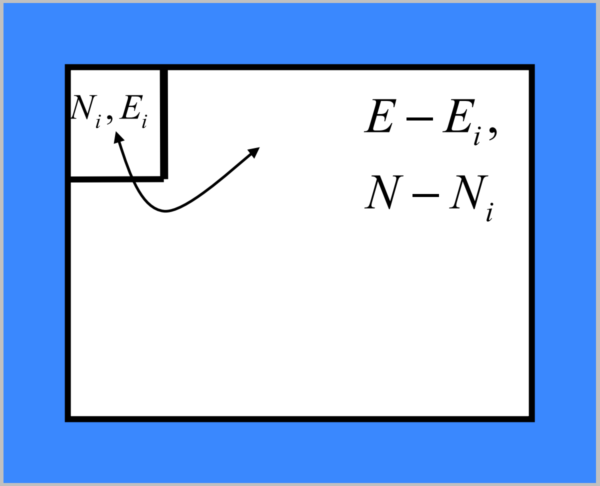
μ, V, T ensemble



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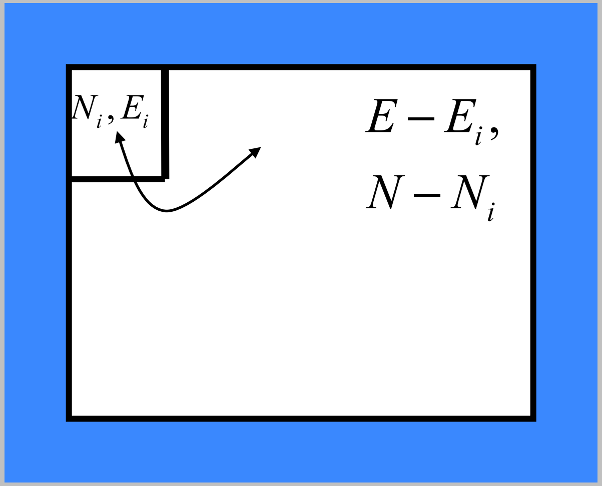
μ, V, T ensemble



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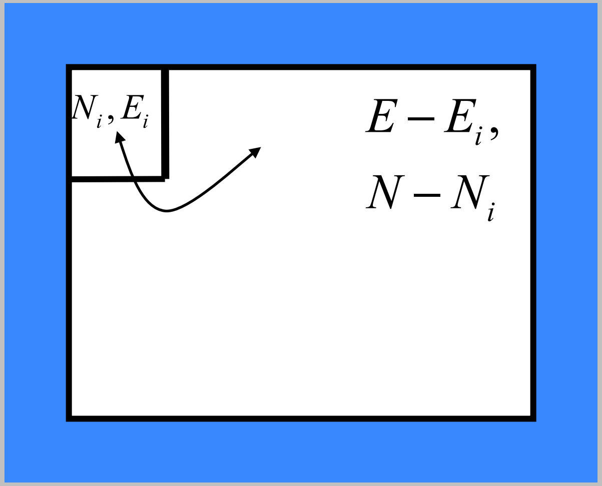

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$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN$$

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

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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

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The probability to find a particular configuration: $N,\mathbf{r}^N$

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