Statistical Mechanics & Simulations

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« Statistical Mechanics & Simulations »

I. Overview of Statistical Mechanics & Molecular Simulations

II. Molecular Dynamics Simulations

III. Monte Carlo methods

IV. « Outputs » : extracting properties from simulations

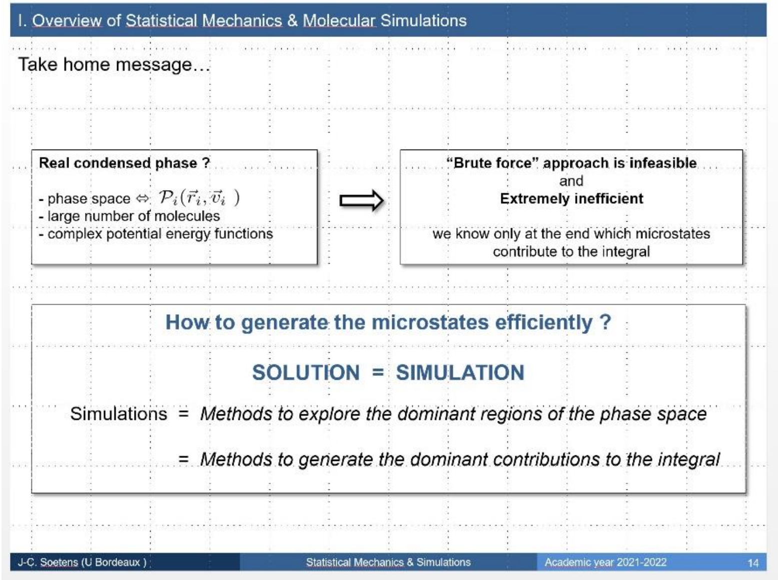
V. Initiation to statistical thermodynamics

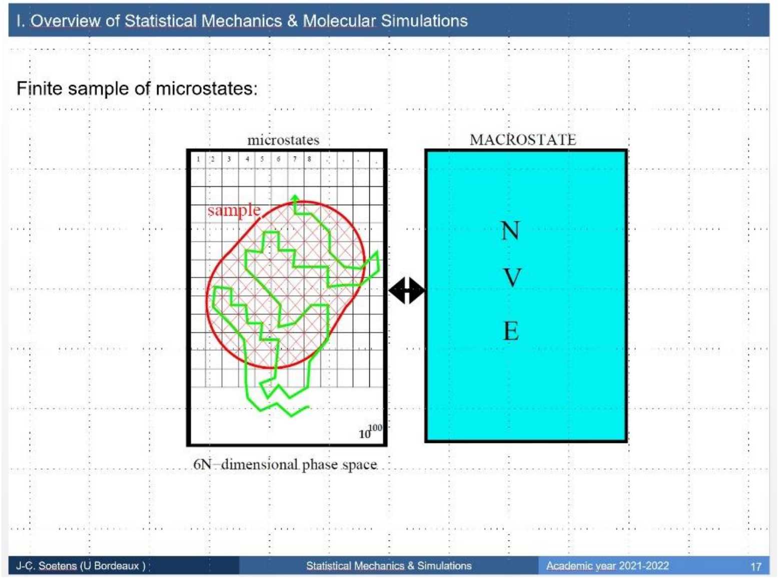
Goals :

- Come back to notions and ideas mentioned previously
- Make the link between microscopic and macroscopic properties of matter.

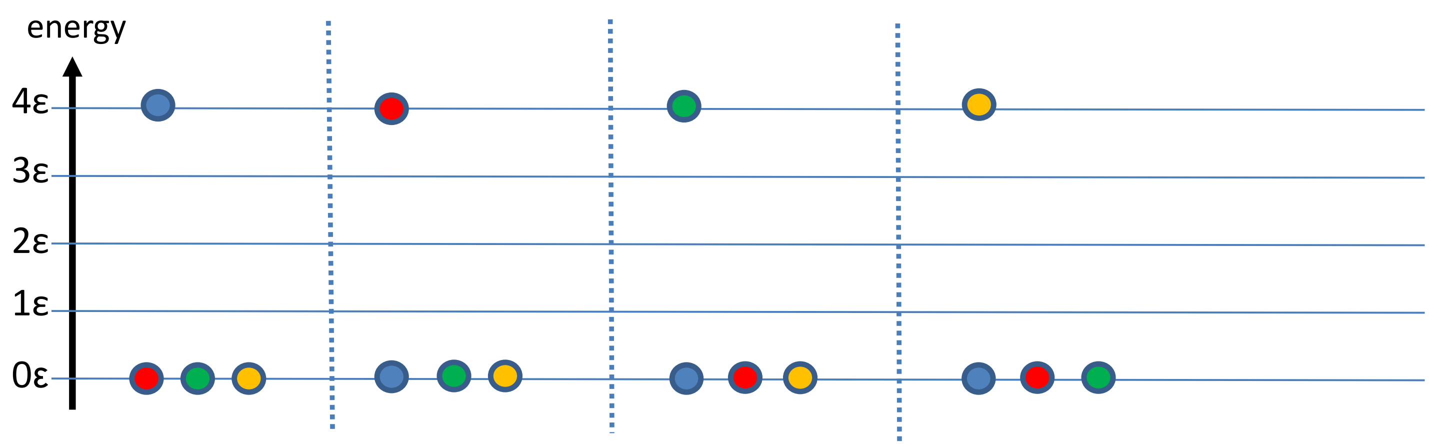
Key ideas :

- Levels of energy
- Populations of energy levels
- Configuration
- Weight of a configuration
- The partition function
- The Boltzmann distribution
- The canonical ensemble





Case 1 : system of N=4 distinguishable particules
5 levels of energy, 0ε, 1ε, 2ε, 3ε, 4ε
total energy of the macrostate E= 4ε



Configuration :	(3,0,0,0,1)	(3,0,0,0,1)	(3,0,0,0,1)	(3,0,0,0,1)
Total energy :	4ε	4ε	4ε	4ε

Number of microstates for this configuration (3,0,0,0,1) : 4

Case 1 : system of N=4 distinguishable particules
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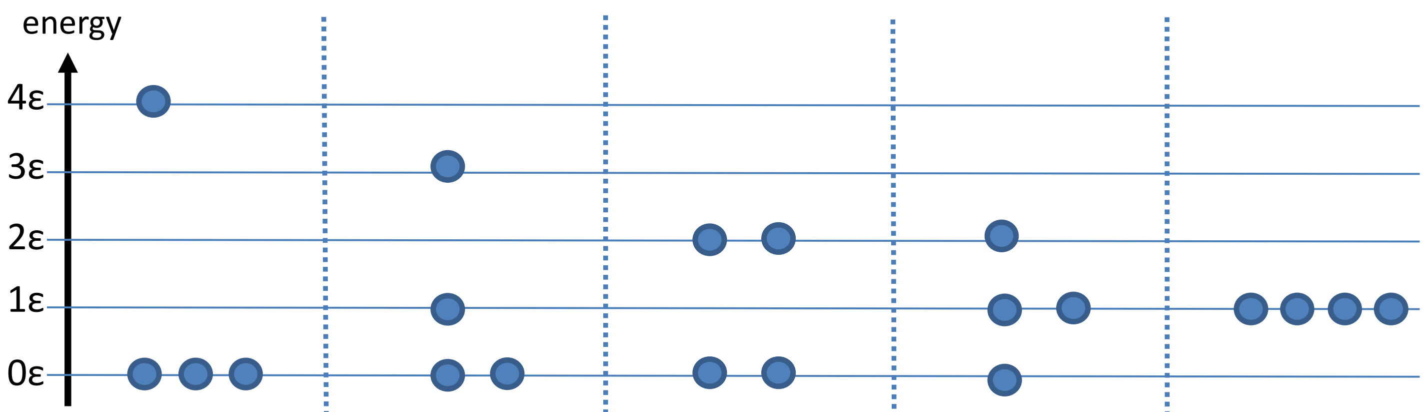
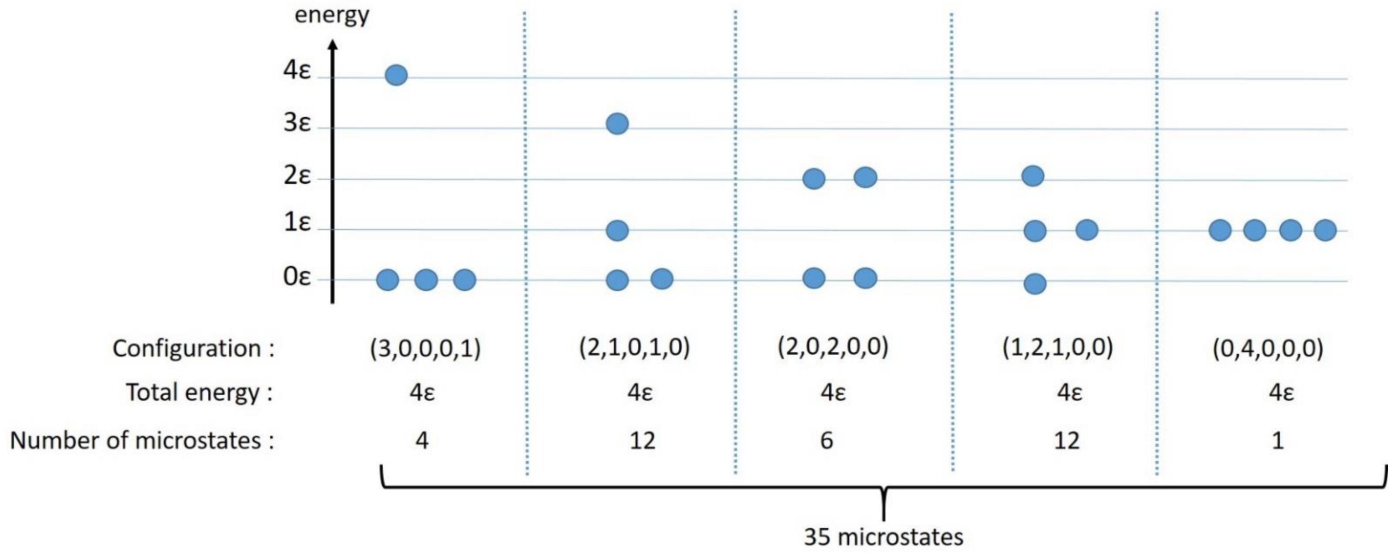
total energy of the macrostate E= 4ε



Configuration :	(3,0,0,0,1)	(2,1,0,1,0)	(2,0,2,0,0)	(1,2,1,0,0)	(0,4,0,0,0)
Total energy :	4ε	4ε	4ε	4ε	4ε
Number of microstates :	4	12	6	12	1

35 microstates



Remember

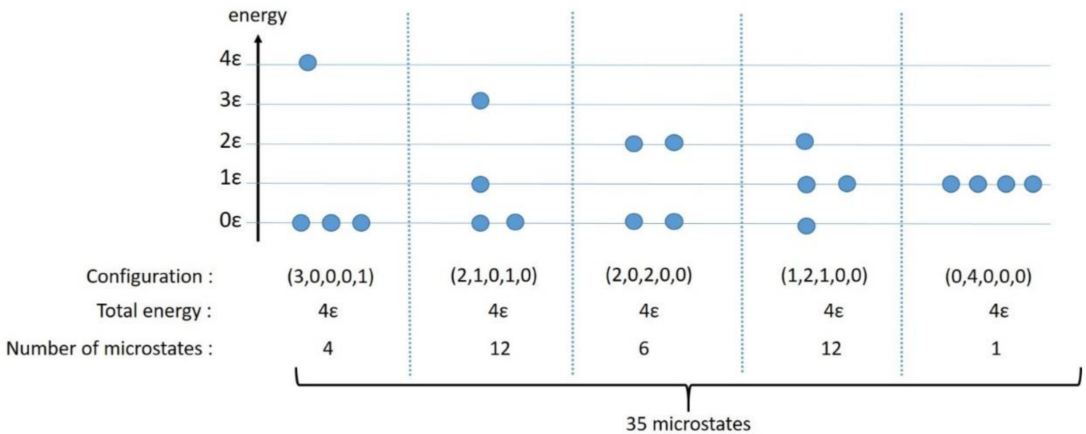
- Macrostate : 4 particules distributed on some energy levels with a total energy of 4ε.
- Microstate : a possible configuration. Here there are 35 microstates.

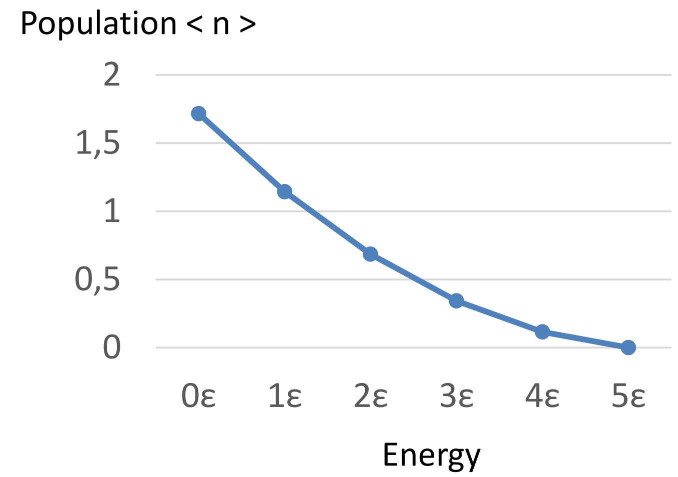
« Equal a priori probabilities »

At thermal equilibrium, in a given macrostate, the system can be in one of the microstates of equal probabilities.

So imagine the system constantly changing configuration among these 35 possibilities of the same energy and the same probability.

Some statistics :





Average number of particules (average population) for each energy level :

$e_4 = 4\varepsilon \quad < n_4 > = (\frac{4}{35})1 + (\frac{12}{35})0 + (\frac{6}{35})0 + (\frac{12}{35})0 + (\frac{1}{35})0 = 0.114$

$e_3 = 3\varepsilon \quad < n_3 > = (\frac{4}{35})0 + (\frac{12}{35})1 + (\frac{6}{35})0 + (\frac{12}{35})0 + (\frac{1}{35})0 = 0.343$

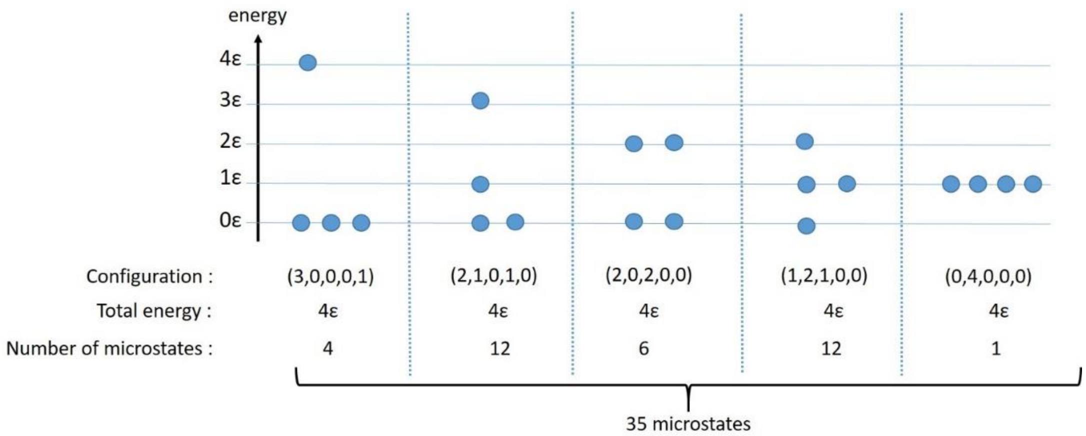
$e_2 = 2\varepsilon \quad < n_2 > = (\frac{4}{35})0 + (\frac{12}{35})0 + (\frac{6}{35})2 + (\frac{12}{35})1 + (\frac{1}{35})0 = 0.686$

$e_1 = 1\varepsilon \quad < n_1 > = (\frac{4}{35})0 + (\frac{12}{35})1 + (\frac{6}{35})0 + (\frac{12}{35})2 + (\frac{1}{35})4 = 1.143$

$e_0 = 0\varepsilon \quad < n_0 > = (\frac{4}{35})3 + (\frac{12}{35})2 + (\frac{6}{35})2 + (\frac{12}{35})1 + (\frac{1}{35})0 = 1.714$

$$\sum_{i=0}^{4} < n_i > \ e_i = \ 4\epsilon$$

$$\sum_{i=0}^{4} < n_i > = \ 4$$



Way to calculate the number of microstates for a given configuration (n_0, n_1, n_2, n_3, …) :

$$W = \frac{N!}{n_0!\ n_1!\ n_2!\ n_3!\ \ldots}$$

Examples :

(3,0,0,0,1) $$W = \frac{4!}{3!\ 0!\ 0!\ 0!\ 1!} = \frac{4!}{3!} = 4$$

(2,1,0,1,0) $$W = \frac{4!}{2!\ 1!\ 0!\ 1!\ 0!} = \frac{4!}{2!} = 12$$

Case 2 : system with a large number of particules N
3 levels of energy, 0ε, 1ε, 2ε
total energy E

Microstates : (n_0, n_1, n_2)

$$n_0 + n_1 + n_2 = N$$

$$n_0(0\epsilon) + n_1(1\epsilon) + n_2(2\epsilon) = n_1(1\epsilon) + n_2(2\epsilon) = E$$

Number of microstates :

$$W = \frac{N!}{n_0!\ n_1!\ n_2!}$$

with

$$\begin{cases} n_2 \\ n_1 = \frac{E}{\epsilon} - 2n_2 \\ n_0 = N - n_1 - n_2 = N - \frac{E}{\epsilon} + n_2 \end{cases}$$

$$W = \frac{N!}{(N - \frac{E}{\epsilon} + n_2)!\ (\frac{E}{\epsilon} - 2n_2)!\ n_2!}$$

For $E = N\epsilon$ or $\frac{E}{\epsilon} = N$

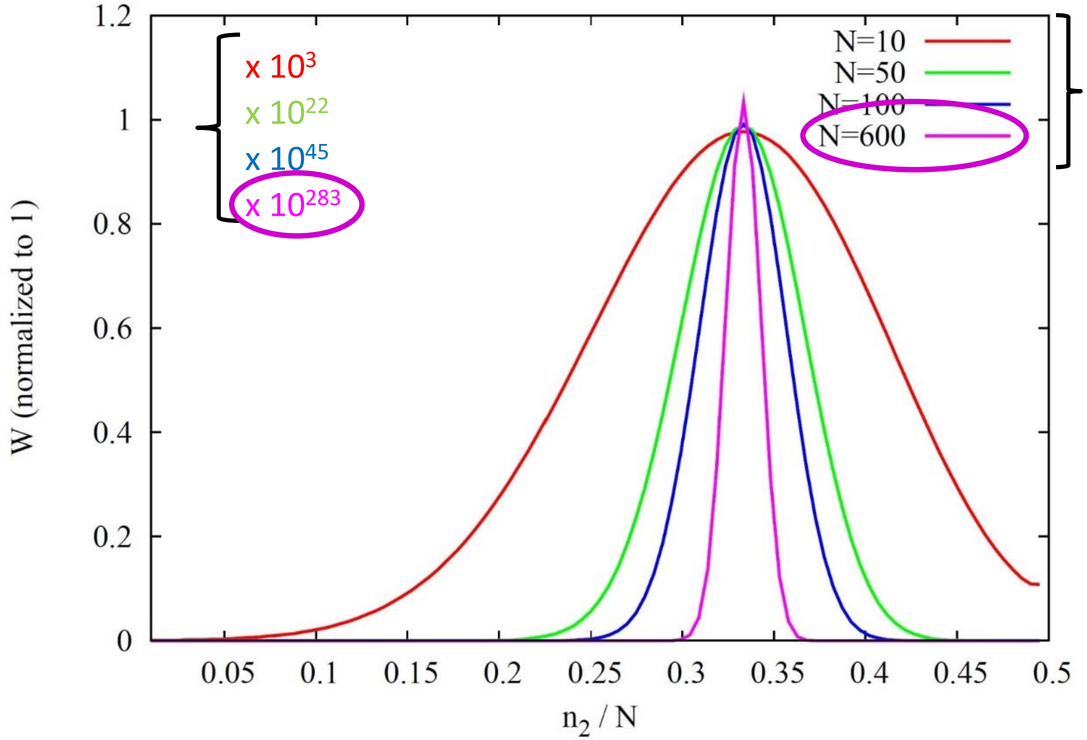
$$W = \frac{N!}{(n_2)!\ (N - 2n_2)!\ n_2!}$$

Evolution of W according to n_2 / N = a for different values of N ?

$\frac{n_2}{N} = a$ $\quad n_2 = aN$

$$W = \frac{N!}{(aN)!\ (N - 2aN)!\ (aN)!}$$

Results : $W = \frac{N!}{(aN)!\ (N-2aN)!\ (aN)!}$ with $a = \frac{n_2}{N}$



Number of particules

$\frac{\text{x } 10^{22}}{\text{x } 10^{3}} = 10^{19} \approx \frac{\text{earth – sun distance}}{\text{15 nanometer}}$

When the value of N increases, the system is only in a few configurations of infinitely large weight :

N = 600 => W = 10^{283} !!!!

Case 3 : **general case**, system with :
a very large number of particules N
a very large number of levels of energy
a total energy U

States	1	2	3	4	5	$\dots$
Levels of energy	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	$\dots$
Populations	n_1	n_2	n_3	n_4	n_5	$\dots$

Questions : What is the probability to observe a configuration $(n_1,\ n_2,\ n_3,\ n_4,\ n_5,\ \dots)$?

Is it necessary (if possible !) to find and to analyse all the possible configurations and microstates (*as for the case 1*) ???

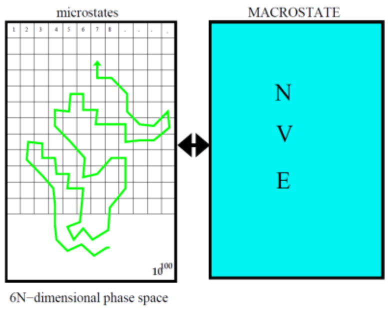
Case 3 : **general case**, system with :
a very large number of particules N
a very large number of levels of energy
a total energy U

States	1	2	3	4	5	$\dots$
Levels of energy	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	$\dots$
Populations	n_1	n_2	n_3	n_4	n_5	$\dots$

Some remarks :

- For a given energy U, there is a very large number of corresponding microstates, greater than N is great.

- **The first fundamental assumptions of statistical physics** consists to consider that a system in thermodynamic equilibrium, having a well-defined energy U, runs through all the microstates which are accessible to it, in a more or less long time **=>** ***A system verifying this property is said to be ergodic***.



- When a system is ergodic, we can look at its microstates from a point of probabilistic view only, without trying to know exactly how the system passes from one microstate to another.

- **The second fundamental assumptions of statistical physics is as follows**: all the microstates of a system with constant energy are equally likely, i.e. they have the same probability.

Idea of Ludwig Boltzmann (1844-1906) ?

M&M's did not exist in Mr. Boltzmann's time but to yours yes they do exist....

Shake your bag of M&M's and open it. What will you observe?

?

Idea of Ludwig Boltzmann (1844-1906) :

« *The probability to observe a configuration* $(n_1,\ n_2,\ n_3,\ n_4,\ n_5,\ ...)$ *depends on the number of possible combinations of this configuration.* »

By combinations, Ludwig Boltzmann means the number of permutations (ways of distributing) inside the configuration.

So… the permutability is a measure of the probability !

As the number of microstates for a given configuration is given by :

$$W = \frac{N!}{n_1!\ n_2!\ n_3!\ n_4!\ n_5!\ ...}$$

=> we have to look for the configuration $(n_1,\ n_2,\ n_3,\ n_4,\ n_5,\ ...)$ **that maximizes W .**

Number of microstates for a given configuration $(n_1,\ n_2,\ n_3,\ n_4,\ n_5,\ ...)$ **:**

$$W \;=\; \frac{N!}{n_1!\ n_2!\ n_3!\ n_4!\ n_5!\ ...}$$

=> we have to look for the configuration that maximizes W .

$$ln(W) = ln(N!) - ln(n_1!\ n_2!\ n_3!\ n_4!\ ...)$$

ln(W) is easier to handle than W

$$= ln(N!) - ln(n_1!) - ln(n_2!) - ln(n_3!) - ln(n_4!)...$$

$$= ln(N!) - \sum_j ln(n_j!)$$

If A is large : $ln(A!) = A\ ln(A) - A$

$$= (N ln(N) - N)\ -\ \sum_j (n_j\ ln(n_j) - n_j)$$

$$d(ln(W)) = -\sum_j (\ dn_j ln(n_j) + n_j (\frac{d(ln(n_j))}{dn_j}) dn_j - dn_j\ )$$

N is constant so dN=0

$$= -\sum_j (\ dn_j ln(n_j) + n_j \frac{1}{n_j} dn_j - dn_j\ )$$

$$= -\sum_j (\ dn_j ln(n_j)\ )$$

$$d(ln(W)) = -\sum_j (\ dn_j ln(n_j)\ ) = 0$$

There are constraints to satisfy :

$$\begin{cases} N = \sum_j n_j \\ U = \sum_j n_j\ \epsilon_j \end{cases} \quad => \quad \begin{cases} dN = \sum_j dn_j = 0 \\ dU = \sum_j dn_j\ \epsilon_j = 0 \end{cases}$$

The method of Lagrange multipliers (here α and β) allow to solve an equation under constraints :

$$L(n_j, \alpha, \beta) = -\sum_j (\ dn_j ln(n_j)\ ) + \alpha \sum_j dn_j + \beta \sum_j dn_j\ \epsilon_j = 0$$

$$=> -\sum_j\ (\ dn_j\ (ln(n_j) - \alpha - \beta\epsilon_j\ )\ ) = 0 \qquad \forall j$$

$$=> dn_j\ (ln(n_j) - \alpha - \beta\epsilon_j\ ) = 0 \qquad \forall dn_j$$

$$=> ln(n_j) - \alpha - \beta\epsilon_j = 0$$

$$=> n_j = e^{\alpha}\ e^{\beta\epsilon_j}$$

$$n_j = e^{\alpha}\ e^{\beta\epsilon_j}$$

Determination of the Lagrange multipliers thanks to the constraints : $\begin{cases} N = \sum_j n_j \\ U = \sum_j n_j\ \epsilon_j \end{cases}$

$$N = \sum_j n_j = \sum_j e^{\alpha}\ e^{\beta\epsilon_j} = e^{\alpha}\sum_j e^{\beta\epsilon_j} \quad \Rightarrow \quad e^{\alpha} = \frac{N}{\sum_j e^{\beta\epsilon_j}}$$

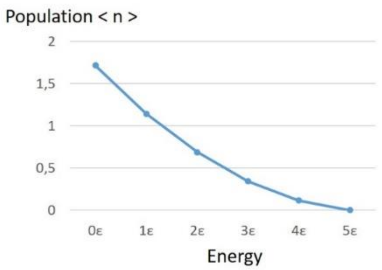
$$n_j = e^{\alpha}\ e^{\beta\epsilon_j} \quad \Rightarrow \quad n_j = \frac{N}{\sum_j e^{\beta\epsilon_j}}\ e^{\beta\epsilon_j}$$

$$\boxed{n_j = \frac{N}{Z}\ e^{\beta\epsilon_j} \quad \text{with} \quad Z = \sum_j e^{\beta\epsilon_j}}$$

Boltzmann distribution

Remember the « case 1 » : exponential decay of populations according to the energy => $\beta < 0$

β links the total energy of the system to the number of accessible microstates.



The relative populations of states do not depend of Z : $\frac{n_i}{n_j} = \frac{g_i}{g_j}\ e^{\beta(\epsilon_i - \epsilon_j)}$

with g_j the number of states at the energy ϵ_j (degeneracy)

Most of the accessible microstates belong to the most probable (mp) distribution :

Let's call the weight of this distribution W_{mp}

$$W_{mp} = \frac{N!}{n_1!\ n_2!\ n_3!\ n_4!\ n_5!\ \ldots}$$

$$\begin{aligned}
ln(W_{mp}) &= (Nln(N) - N) - \textstyle\sum_j (n_j\ ln(n_j) - n_j) \\
&= Nln(N) - \textstyle\sum_j (n_j\ ln(n_j)) \\
&= Nln(N) - \textstyle\sum_j (\frac{N}{Z}\ e^{\beta\epsilon_j}\ ln(\frac{N}{Z}\ e^{\beta\epsilon_j})) \\
&= Nln(N) - \textstyle\sum_j (\frac{N}{Z}\ e^{\beta\epsilon_j}\ ln(\frac{N}{Z}) + \frac{N}{Z} e^{\beta\epsilon_j} \beta\epsilon_j) \\
&= Nln(N) - \underbrace{\textstyle\sum_j (\frac{N}{Z}\ e^{\beta\epsilon_j}\ ln(\frac{N}{Z}))}_{\frac{N}{Z} Z ln(\frac{N}{Z})} - \underbrace{\textstyle\sum_j (\frac{N}{Z} e^{\beta\epsilon_j} \beta\epsilon_j)}_{\beta U}
\end{aligned}$$

$$N = \textstyle\sum_j n_j$$

$$n_j = \frac{N}{Z}\ e^{\beta\epsilon_j}$$

$$Z = \textstyle\sum_j e^{\beta\epsilon_j}$$

$$U = \textstyle\sum_j n_j\ \epsilon_j = \sum_j \frac{N}{Z}\ e^{\beta\epsilon_j} \epsilon_j$$

=> $$ln(W_{mp}) = Nln(Z) - \beta U$$

$$ln(W_{mp}) = Nln(Z) - \beta U$$

N (the number of particules or molecules) is a constant

$Z = \sum_j e^{\beta \epsilon_j}$, the partition function, is independant of U : $\frac{\partial ln(W_{mp})}{\partial U} = -\beta$

Analogy with thermodynamics : $dU = TdS - pdV$

V cst => $dU = TdS$

The relation between energy, temperature and entropy is thus : $\frac{\partial S}{\partial U} = \frac{1}{T}$ and $S = k_B ln(\Omega)$

$k_B \frac{\partial ln(\Omega)}{\partial U} = \frac{1}{T}$ => $\frac{\partial ln(\Omega)}{\partial U} = \frac{1}{k_B T}$

If we relate entropy to the number of accessible microstates, we deduce that : $\beta = -\frac{1}{k_B T}$

with k_B the Boltzmann constant.

The Boltzmann distribution :

The fraction of particules at the energy level i is : $\frac{n_i}{N} = \frac{e^{-\frac{\epsilon_i}{k_B T}}}{Z}$

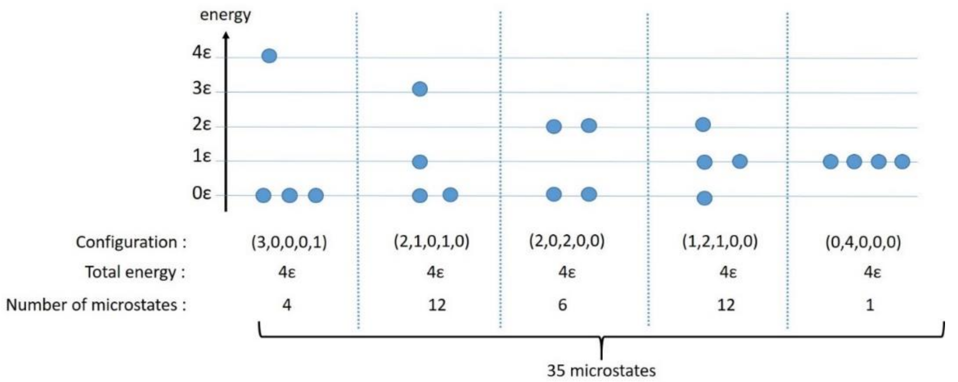
Z is the partition function : $Z = \sum_j e^{-\frac{\epsilon_j}{k_B T}}$

$k_B = 1.380649 \; 10^{-23} \quad J.K^{-1}$ is the Boltzmann constant.

The partition function gives an indication of the number of states that are thermally accessible to a particle (or molecule) at the temperature of the whole system.

Application of the Boltzmann distribution to the « case 1 »

Case 1 : system of N=4 distinguishable particules
5 levels of energy, 0ε, 1ε, 2ε, 3ε, 4ε
total energy of the macrostate E= 4ε

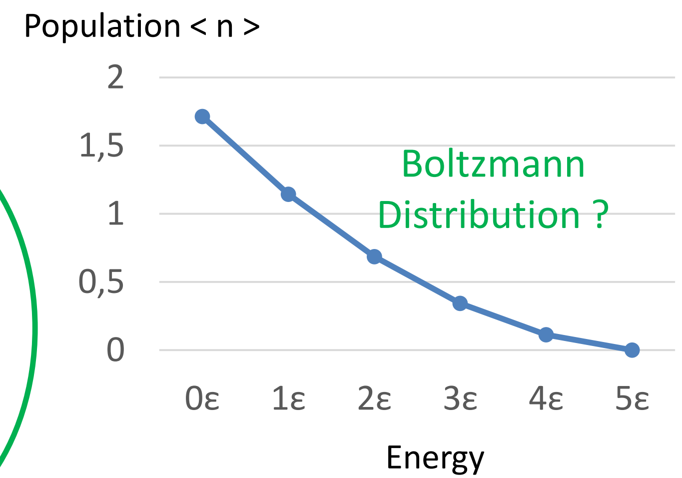


Work to do :

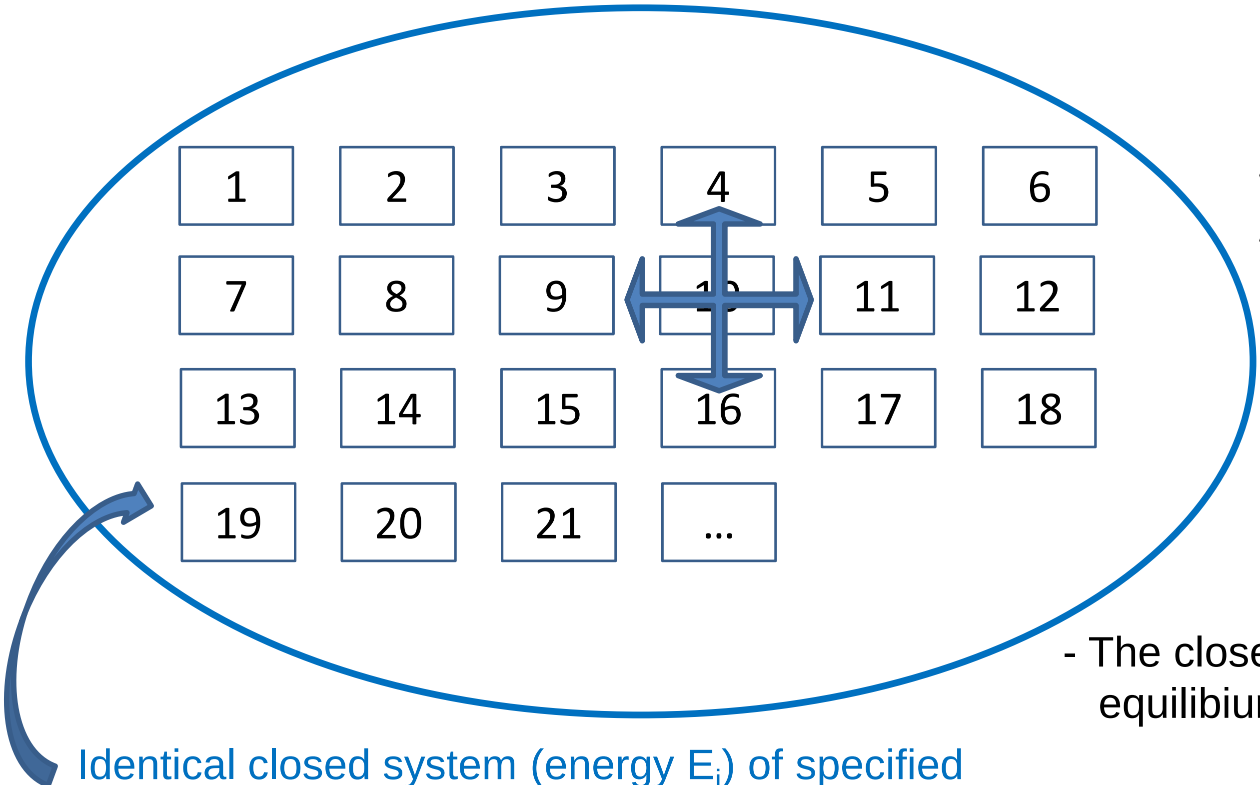
Calculate the populations of the energy levels making use of the Boltzmann distribution and compare with the previous results.

=> example of resolution with *excel*

CASE 1 : 4 particules, 5 levels of energy, Etot=4eps									kT (eps)	?
									Z=	?
			configurations							
Energies (eps)	C1	C2	C3	C4	C5		< ni >			< ni > boltzmann
4	1	0	0	0	0		0,11429			?
3	0	1	0	0	0		0,34286			?
2	0	0	2	1	0		0,68571			?
1	0	1	0	2	4		1,14286			?
0	3	2	2	1	0		1,71429			?
Nb particules	4	4	4	4	4		4,00000			?
Nb microstates	4	12	6	12	1	35				
Total energies	4	4	4	4	4		4,00000			?



The canonical ensemble = imaginary collection of replications of a system with a commun temperature



$\mathbb{E}$: total energy of all the systems

Identical closed system (energy E_i) of specified
N, number of molecules
V, volume
T, temperature
Replicated $\mathbb{N}$ times

- The closed systems are in thermal equilibium with one another.
- They can exchange energy.
- They have the same volume and composition so the energy levels accessible to the molecules are the same.

As previously, some of the configurations of the canonical ensemble will be very much more probable than others => there are dominating configurations.

$$\mathbb{W} = \frac{\mathbb{N}!}{N_1!\ N_2!\ N_3!\ \ldots}$$

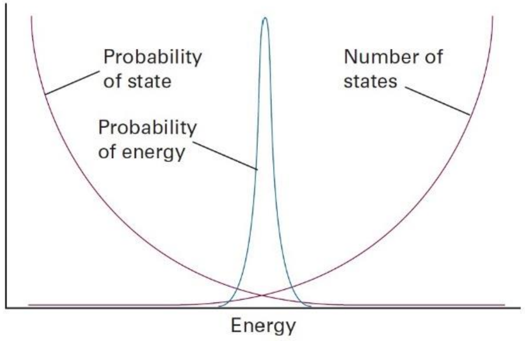
N_i Number of configurations at energy E_i

The configuration of greatest weight $(N_1, N_2, N_3, \ldots)$ is subject to the constraints that the total energy of the ensemble is constant at $\mathbb{E}$ and that the total number of members is fixed at $\mathbb{N}$, is given by the canonical distribution :

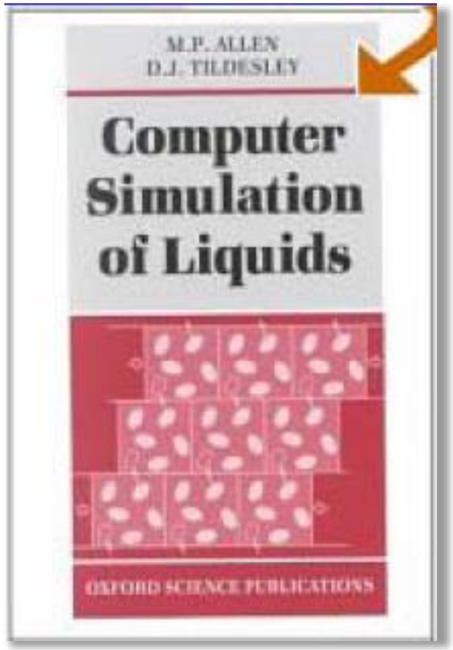
$$\frac{N_i}{\mathbb{N}} = \frac{e^{-\frac{E_i}{k_B T}}}{\mathbb{Z}}$$

$$\mathbb{Z} = \sum_j e^{-\frac{E_j}{k_B T}}$$

Canonical partition function



Distribution of members of a Canonical ensemble



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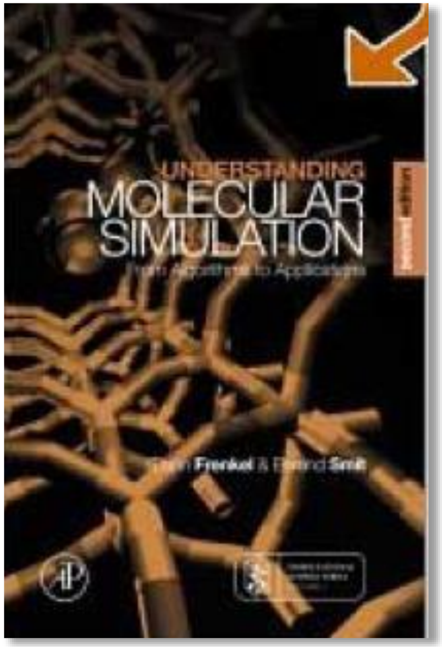

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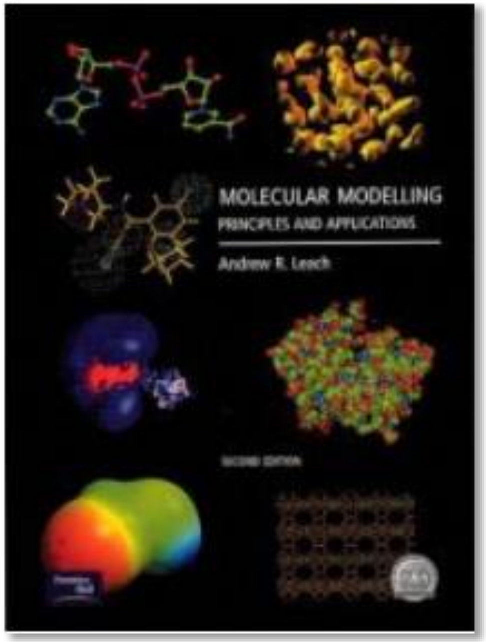

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