Seminar 2: Statistical thermodynamics

Biophysics

Course 2023-2024

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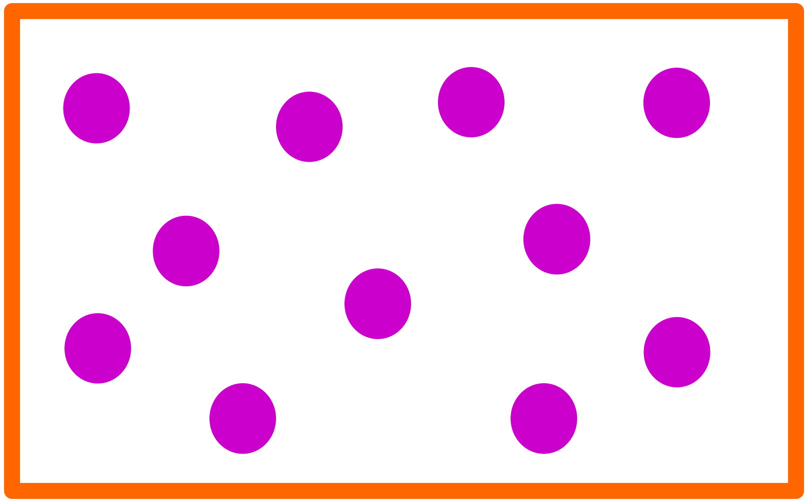
How energy is distributed between molecules?

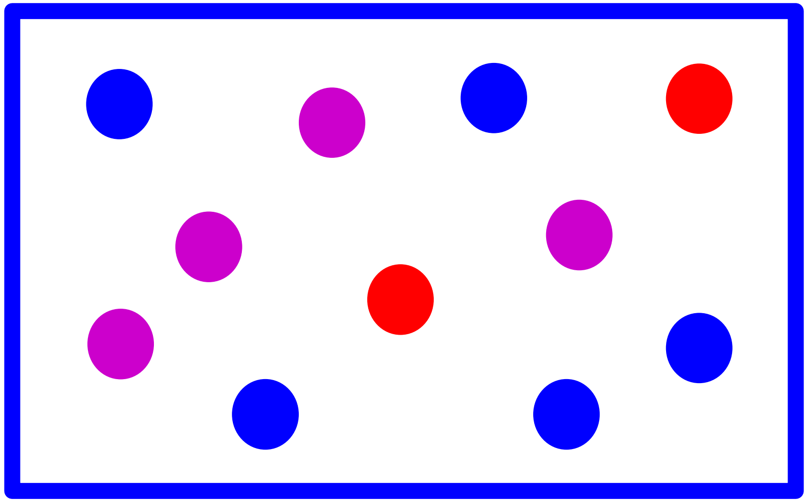
Right now, we are in a room full of gas at 298 K, and for simplicity we will assume that all gas molecules have the same mass

What of the two following scenarios do you think that represents what is happening in this room of gas at molecular level?

All molecules have the same kinetic energy



Molecules have different amounts of kinetic energy



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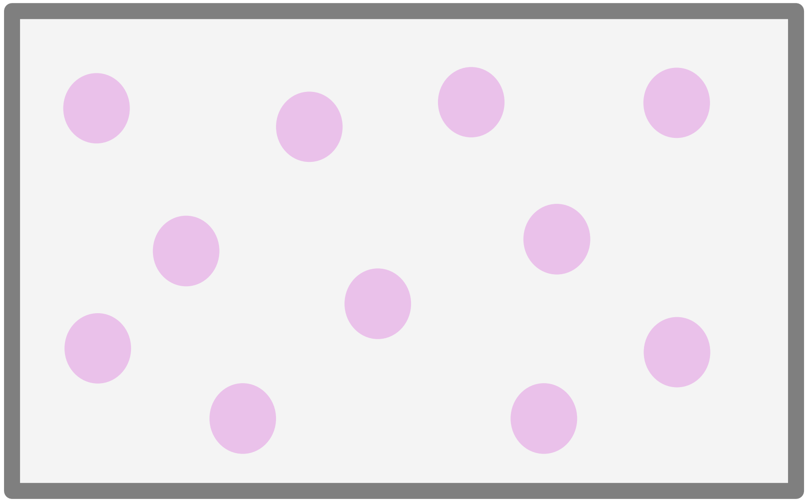

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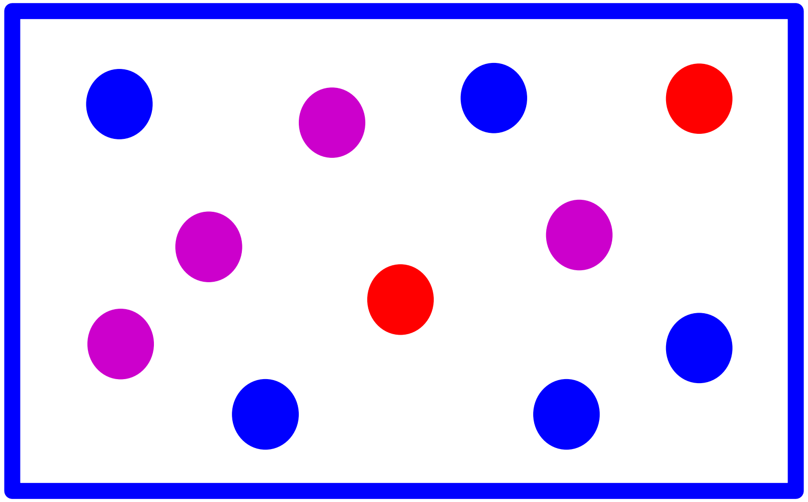
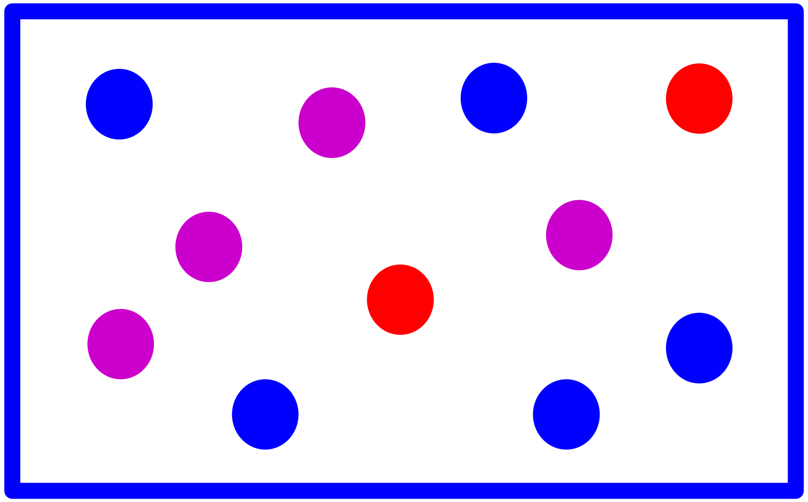


Molecular states

We classify molecules depending on their kinetic energy into molecular states

Molecular states are defined by two properties:

- The population of particles in that state (N_i)
- The energy of the particles in that state (E_i)



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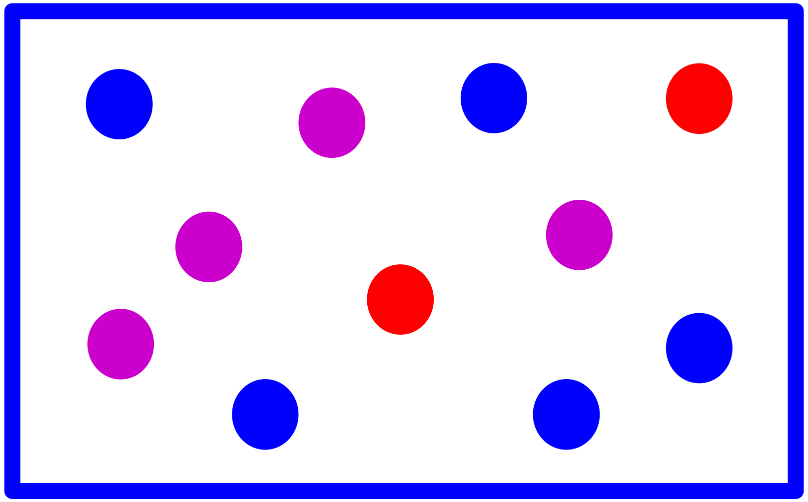


State 2: Population = 2; Energy = high

State 1: Population = 4; Energy = intermediate

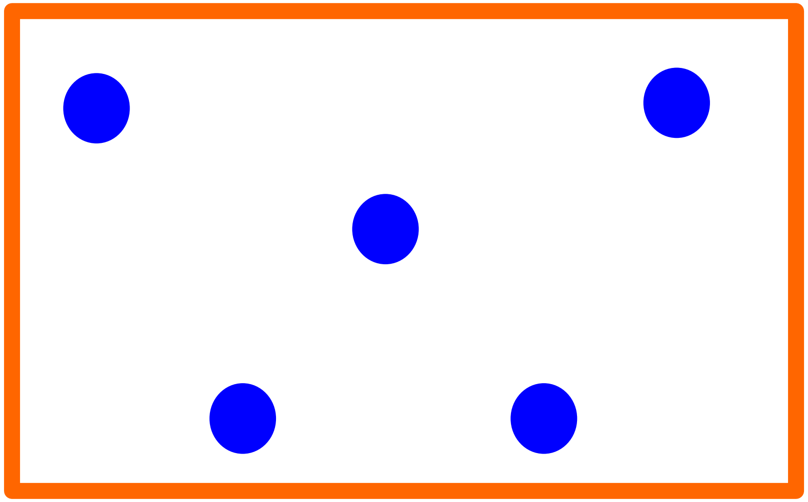
State 0: Population = 5; Energy = low

Configurations

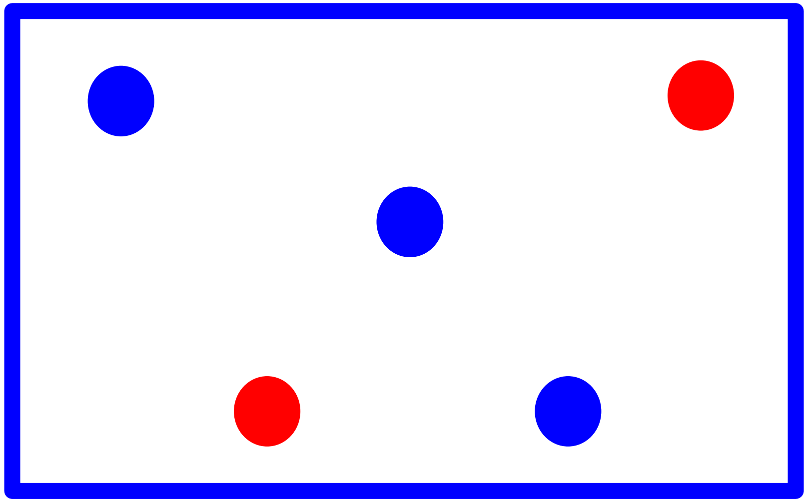
Imagine an isolated chemical system with two main properties:
A given number of molecules (N) and an amount of energy (E)

A configuration is one of the ways in which molecules in the system can be distributed among the different energy levels

Configuration 1



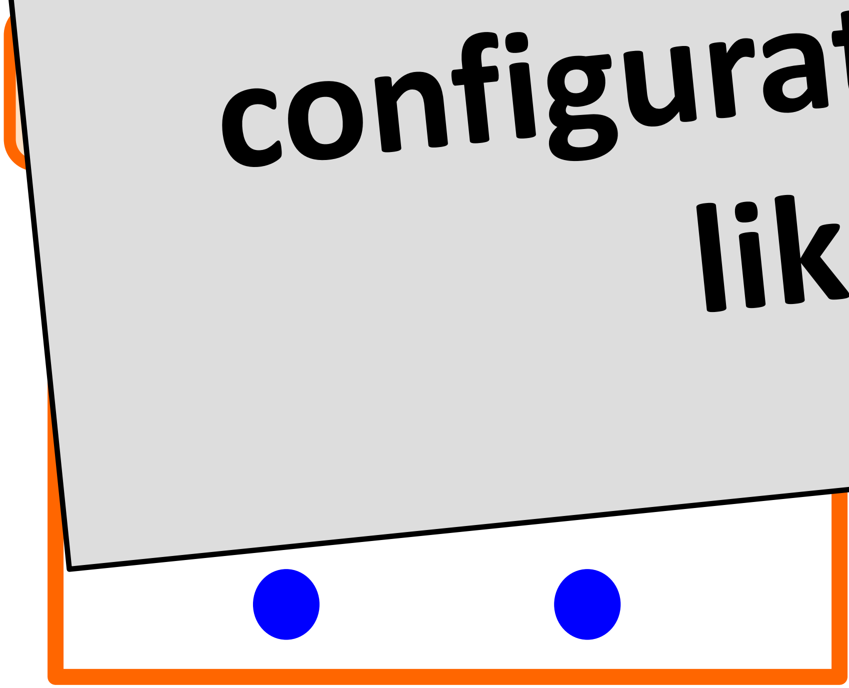
Configuration 2

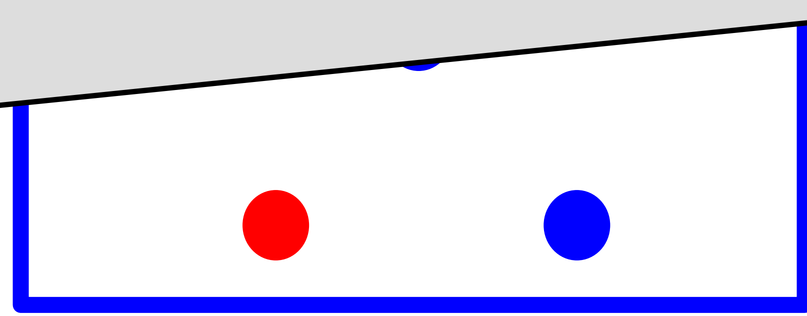


Configurations

Imagine an isolat…

Can we predict what configuration is more likely??



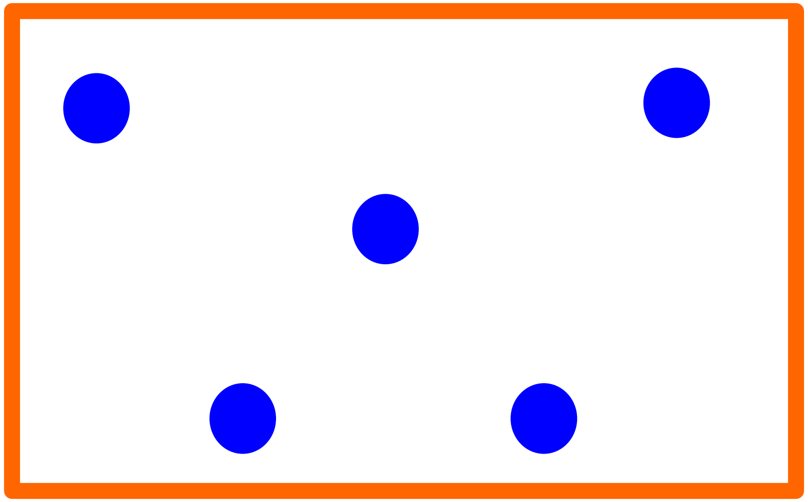


Configurations

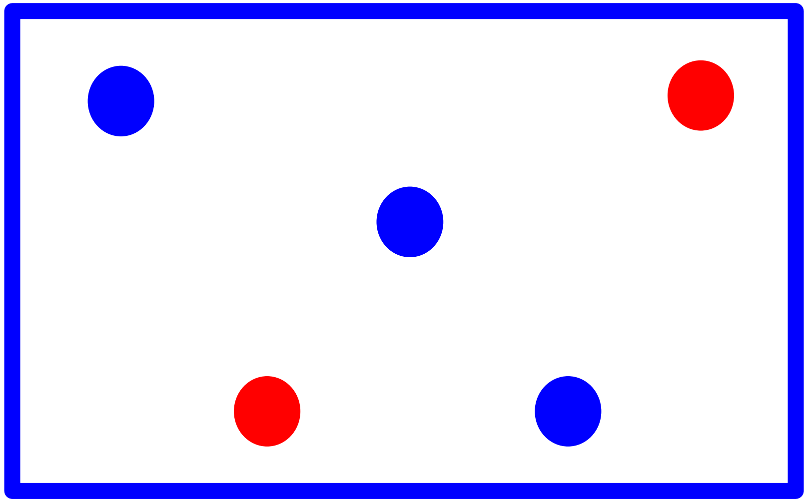
We can think of configurations as macrostates. Then, the configuration with more available microstates should be the most likely.

What configuration has more available microstates?
(Keep in mind that all microstates can happen with the same probability)

Configuration 1



Configuration 2



Configurations

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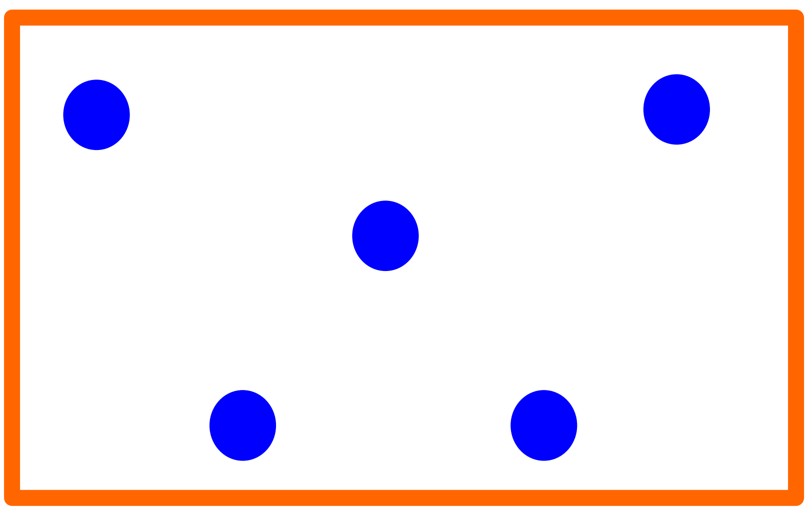
What configuration has more available microstates?

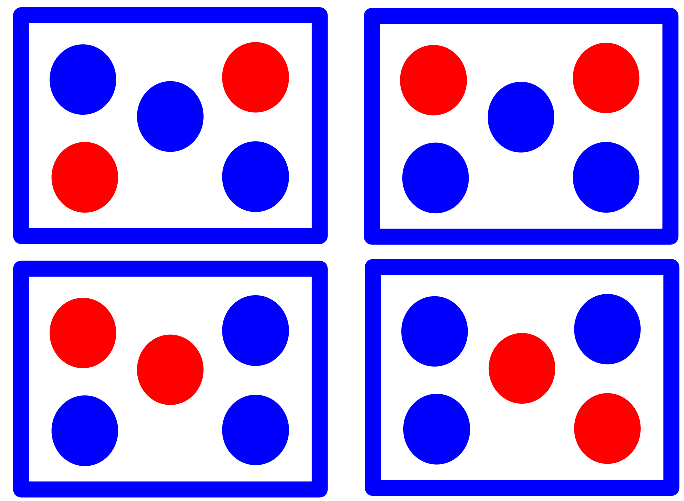
Configuration 1

1 microstate; P1 = 1/11



Configuration 2

10 microstates; P2 = 10/11



and so on and so forth...

Configurations

We can think of configurations as macrostates. Then, the configuration with more available microstates should be the most likely.

To calculate the microstates of a configuration we can use the following formula:

$$W = \frac{N!}{N_0!N_1!N_2!N_i!}$$

Where:

- N is the number of particles in the system
- N_0 is the number of particles in the molecular state 0
- N_1 is the number of particles in the molecular state 1
- N_2 is the number of particles in the molecular state 2
- N_i is the number of particles in the molecular state i

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Once you have the microstates available for a configuration you can calculate the entropy of that configuration with the following formula:

$$S = k \cdot \ln(W)$$

Configurations

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Configurations

Calculate the number of available microstates for the following configurations and their respective entropy:

C1: $\{N_0 = 20; N_1 = 0; N_2 = 0\}$

C2: $\{N_0 = 12; N_1 = 5; N_2 = 3\}$

C3: $\{N_0 = 7; N_1 = 7; N_2 = 7\}$

Keep in mind that energy from state 0 (E_0) is smaller than the one of state 1 (E_1), which is in turn smaller than the one from state 2 (E_2):

$$E_0 < E_1 < E_2$$

Configurations

We see that configurations that spread more their particles accross their molecular states have more microstates

Wait a minute, if configurations with particles in many different levels are the most likely, why there are systems (for example, ice at very low temperatures) where most particles are at the same level with very low energy?

Configurations

The energy of the configuration is the addition of the energy of its particles. If the configuration has more energy than the system it cannot happen.

Can you estimate the energy of the configurations of the previous exercise:

C1: $\{N_0 = 20; N_1 = 0; N_2 = 0\}$

C2: $\{N_0 = 12; N_1 = 5; N_2 = 3\}$

C3: $\{N_0 = 7; N_1 = 7; N_2 = 7\}$

Configurations

The energy of the configuration is the addition of the energy of its particles. If the configuration has more energy than the system, it cannot happen.

Can you estimate the energy of the configurations of the previous exercise:

C1: $\{N_0 = 20; N_1 = 0; N_2 = 0\}$

Low energy, available for all systems

C2: $\{N_0 = 12; N_1 = 5; N_2 = 3\}$

Medium energy, available for some

C3: $\{N_0 = 7; N_1 = 7; N_2 = 7\}$

Very high energy, available for almost no systems

Configurations

In this explanation, we are focusing in the kinetic energy of the particles

Can you think of any macroscopic property of a chemical system that is related to the kinetic energy of its particles?

Configurations

In this explanation, we are focusing in the kinetic energy of the particles (or thermal energy)

Can you think of any macroscopic property of a chemical system that is related to the kinetic energy of its particles?

TEMPERATURE

High temperature →	**High energy** →	**Many configurations available**
Medium temperature →	**Medium energy** →	**Some configurations available**
Low temperature →	**Low energy** →	**Few configurations available**

The Boltzmann distribution

The Boltzmann distribution explains the relation between populations in molecular states and temperature

$$\frac{N_i}{N} = \frac{e^{-E_i/kT}}{\sum_n e^{-E_n/kT}}$$

Where:

- N_i is the number of particles in a molecular state i
- N is the number of particles in the whole chemical system
- E_i is the energy in the molecular state i
- k is the Boltzmann constant
- T is temperature
- E_n represents the energy of all the molecular states in the system

The Boltzmann distribution

The Boltzmann distribution explains the relation between populations in molecular states and temperature

$$\frac{N_i}{N} = \frac{e^{-E_i/kT}}{\sum_n e^{-E_n/kT}}$$

The sum of the probability terms is called the **molecular partition function**. It is represented with a lower case q.

We will see how the value of the **molecular partition function** changes its value according with the temperature of the system:

- Being minimum at zero temperature
- Being maximum at infinite temperature

The Boltzmann distribution

We can relate what we already know about configurations with the use of the Boltzmann distribution

C3: $\{N_0 = 7; N_1 = 7; N_2 = 7\}$

The Boltzmann distribution

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C3: $\{N_0 = 7; N_1 = 7; N_2 = 7\}$ $\longrightarrow$ $N_2/N = 7/21 = 1/3$

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$$\frac{N_i}{N} = \frac{e^{-E_i/kT}}{\sum_n e^{-E_n/kT}}$$

$$\downarrow$$

$$\frac{N_2}{N} = \frac{e^{-E_2/kT}}{e^{-E_0/kT} + e^{-E_1/kT} + e^{-E_2/kT}}$$

The Boltzmann distribution

Assume that:

- $T = 298$ K (room temperature)
- $E0 = 0$ kJ/mol; $E1 = 2$ kJ/mol; $E2 = 4$ kJ/mol
- $k = 1.380649 \cdot 10^{-23}$ J/K

<u>Do you think configuration 3 is possible?</u>

C3: $\{N_0 = 7; N_1 = 7; N_2 = 7\} \longrightarrow N_2/N = 7/21 = 1/3$

$$\frac{N_2}{N} = \frac{e^{-E_2/kT}}{e^{-E_0/kT} + e^{-E_1/kT} + e^{-E_2/kT}}$$

The Boltzmann distribution

The population of one state is inversely proportional to the energy of the state. High energy states are unlikely.

High energy state

$$\downarrow\downarrow\frac{\boldsymbol{N_i}}{N} = \frac{e^{-\uparrow\uparrow \boldsymbol{E_i}/kT}}{\sum_n e^{-E_n/kT}}$$

Low energy state

$$\uparrow\uparrow\frac{\boldsymbol{N_i}}{N} = \frac{e^{-\downarrow\downarrow \boldsymbol{E_i}/kT}}{\sum_n e^{-E_n/kT}}$$

The Boltzmann distribution

As we decrease temperature, less states become available. At zero kelvin only one state is possible: the state of zero energy

Temperature = 0

$$\frac{N_i}{N} = \frac{e^{-E_i/k\mathbf{T}\downarrow\downarrow}}{\sum_n e^{-E_n/k\mathbf{T}\downarrow\downarrow}}$$

if $E_i > 0$ $\rightarrow$ $\lim_{T\to 0} \frac{E_i}{kT} = \infty$

if $E_i = 0$ $\rightarrow$ $\lim_{T\to 0} \frac{0}{kT} = 0$

The Boltzmann distribution

As we decrease temperature, less states become available. At zero kelvin only one state is possible: the state of zero energy

Temperature = 0

$$\frac{N_i}{N} = \frac{e^{-\infty}}{\sum_n e^{-\infty}} = \frac{0}{0+0+0+0\ldots}$$

The Boltzmann distribution

As we decrease temperature, less states become available. At zero kelvin only one state is possible: the state of zero energy

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$$\rightarrow \frac{N_i}{N} = \frac{e^{-\mathbf{0}}}{\sum_n e^{-\infty}} = \frac{1}{0+0+0+0+1\ldots}$$

The Boltzmann distribution

As we decrease temperature, less states become available. At zero kelvin only one state is possible: the state of zero energy

Temperature = 0

→ For any molecular state with Ei > 0:

$$\frac{N_i}{N} = \frac{e^{-\infty}}{\sum e^{-\infty}} = \frac{0}{1}$$

→ For the molecular state with E0 = 0:

$$\frac{N_i}{N} = \frac{e^{-0}}{\sum e^{-\infty}} = \frac{1}{1}$$

The Boltzmann distribution

As we increase temperature, more states become available. At infinite temperature all states become equally probable.

Temperature = ∞

$$\frac{N_i}{N} = \frac{e^{-E_i/k\boldsymbol{T}\uparrow\uparrow}}{\sum_n e^{-E_n/k\boldsymbol{T}\uparrow\uparrow}}$$

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$$\frac{N_i}{N} = \frac{e^{-E_i/k\boldsymbol{T}\uparrow\uparrow}}{\sum_n e^{-E_n/k\boldsymbol{T}\uparrow\uparrow}} \longrightarrow \frac{N_i}{N} = \frac{e^{\boldsymbol{-0}}}{\sum_n e^{\boldsymbol{-0}}}$$

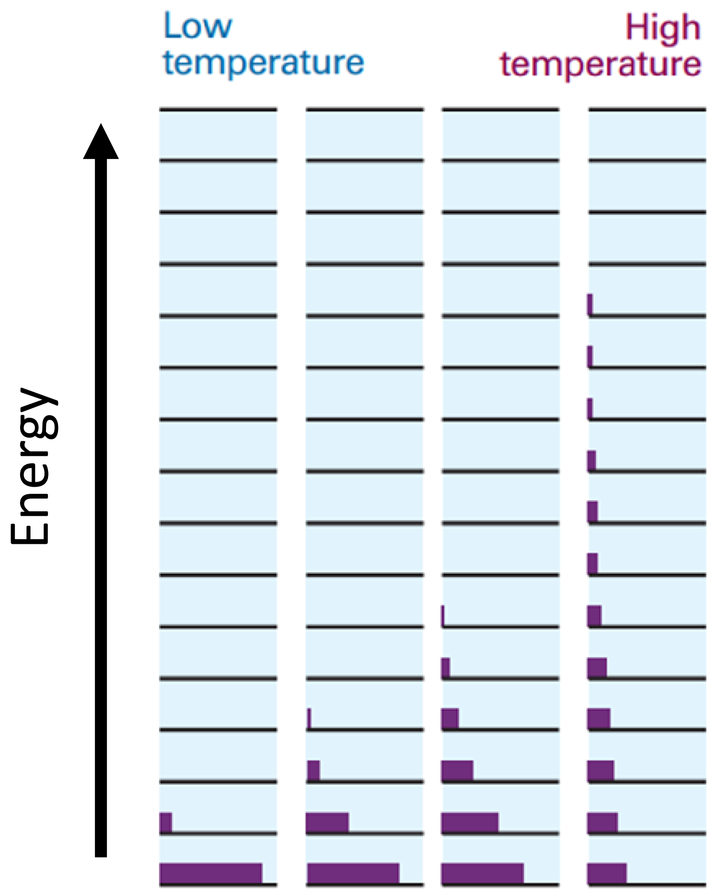
$$\frac{N_i}{N} = \frac{1}{1+1+1+1\ldots}$$

Temperature at microscopic scale

Besides being a measure of the average kinetic of particles, it can also be understood as a measure of molecule dispersion across molecular states

As you increase temperature, more molecular states are available, but you will always have most of your population in the low energy states.

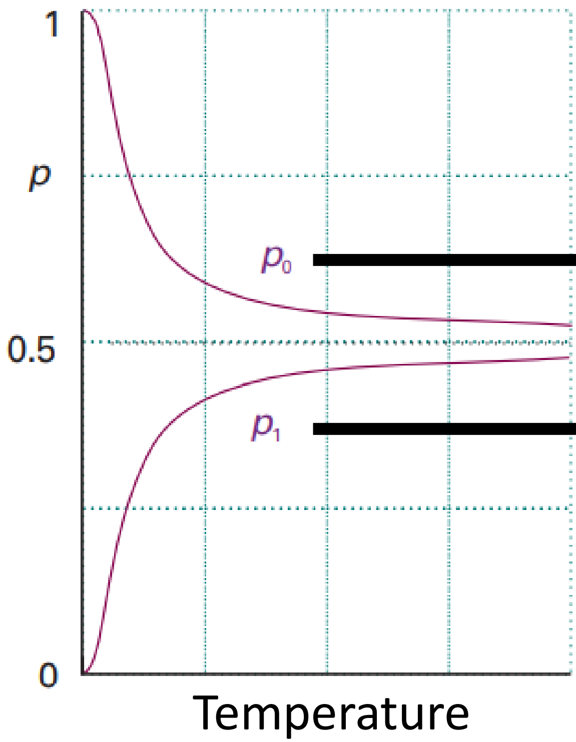
You can see this in the next plot, where each compartment represents a molecular state and purple bars represent how populated each state is.



Temperature at microscopic scale

If temperature is infinite you will still have molecules in your system with low energy, even with energy = 0

Imagine a system where only two states are possible, if temperature becomes infinite you will still have 50% of your molecules at low energy



P_0 is the population for the low energy state

P_1 is the population for the high energy state

The Boltzmann distribution

Try the following exercises:

1. A system has energy levels at $\varepsilon 0=0$, $\varepsilon 1=1.5$, $\varepsilon 2=2.2$ kJ/mol. a) Calculate the partition function and the relative population of the energy levels at a temperature of 300K. b) At what temperature is the population of the energy level at 1.5 kJ/mol equal to the population of the energy level at 2.2 kJ/mol .

2. It is observed that one drug could bind to its protein target in two different places (site A and site B). The energy associated to the binding of the drug when it is attached to site A is of -15.5 kJ/ mol, and when it is attached to the site B is of -13.7 kJ/mol. Determine at which temperature the population of the drug binding the site A is double than the population of the drug binding the site B.

The Boltzmann distribution

If you have a hard time doing Boltzmann distribution exercises, try to follow this tutorial:

https://www.youtube.com/watch?v=-tMW8iU0_ts

The Boltzmann distribution

Now that you know how to opperate with the Boltzmann distribution, create a script that:

- Takes as input the energies per mol for two molecular states (we assume a ground molecular state with energy 0 kJ/mol)

- Calculates the probabilities for each state at each temperature from 0 K to 3000 K in intervals of 10 K.

- Plots the values of these probabilities accross the different temperatures