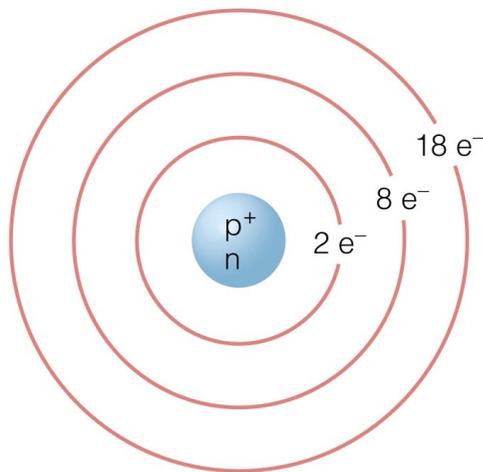


**MANY-PARTICLE SYSTEMS**  
**THE BOLTZMANN-**  
**DISTRIBUTION**

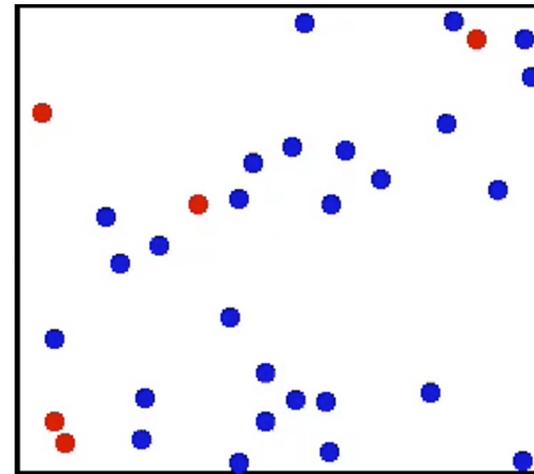
**MIKLÓS KELLERMAYER**

# From the atom to many-particle systems

Atom

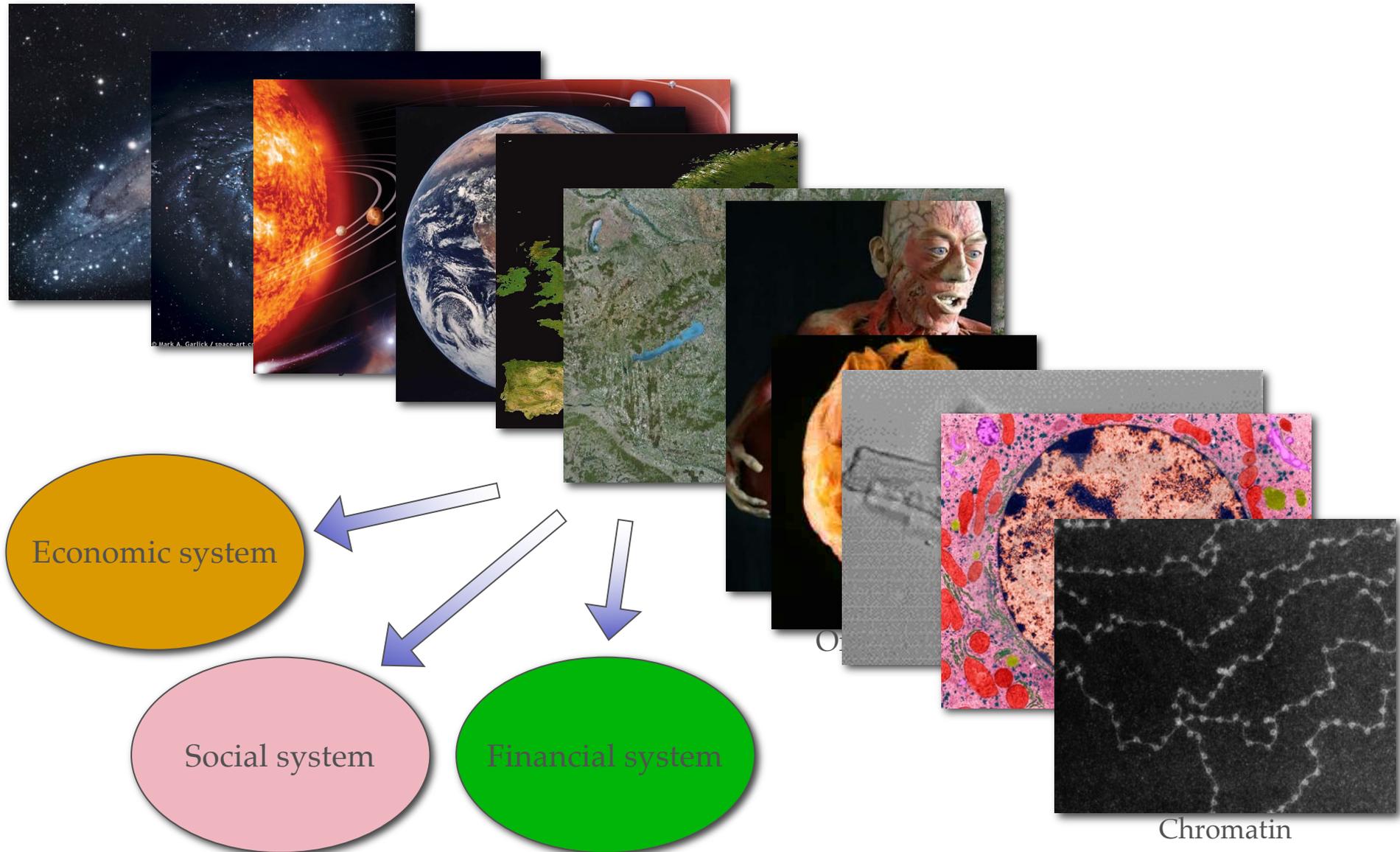


“Many-particle system”



- What is a system?
- How many particles are “many”?
- What is the internal “structure”?
- How do particles respond to forces (caused by potential differences)?

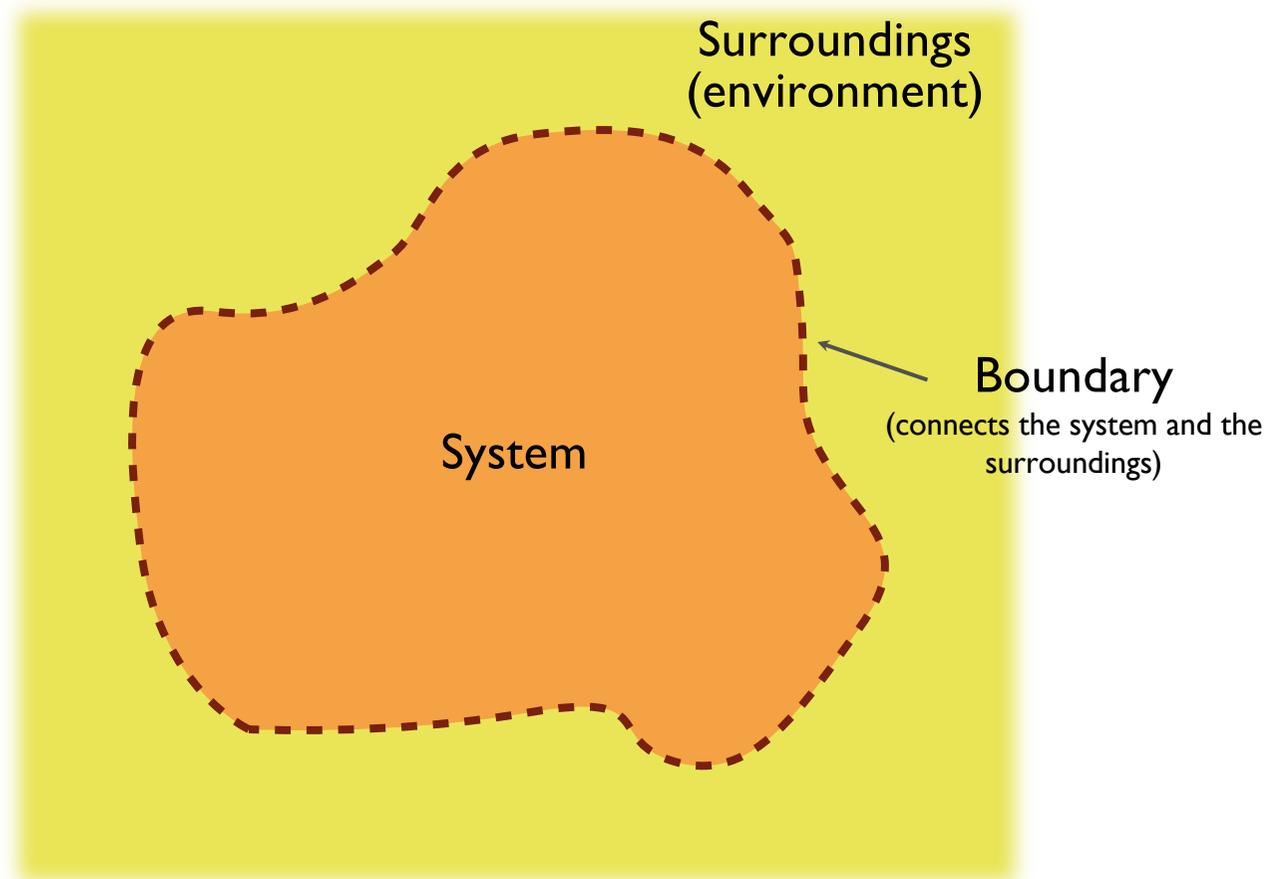
# What is a system?



# The system is an abstraction

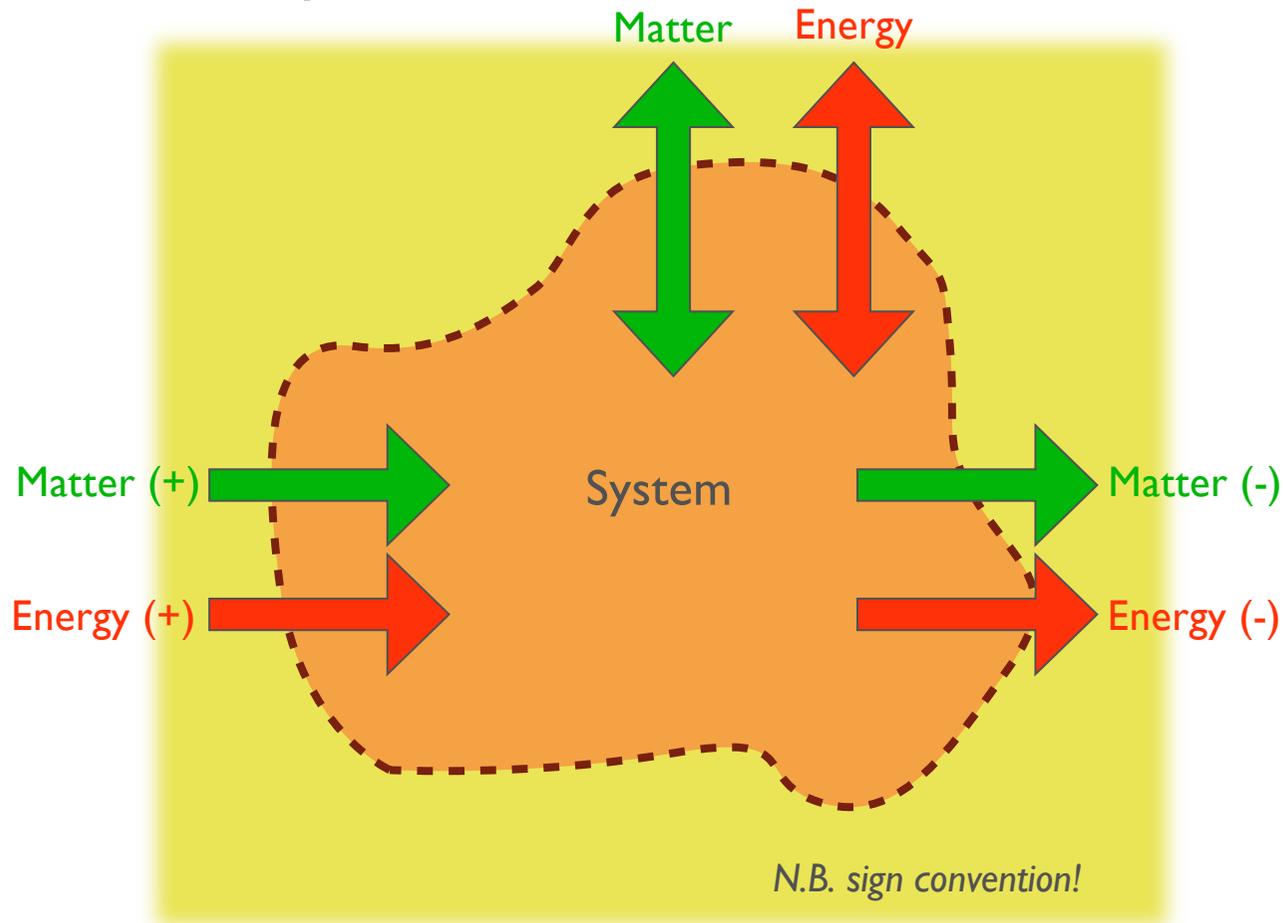
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*Definition:* the system is the part of nature under investigation.



# The system interacts with its surroundings

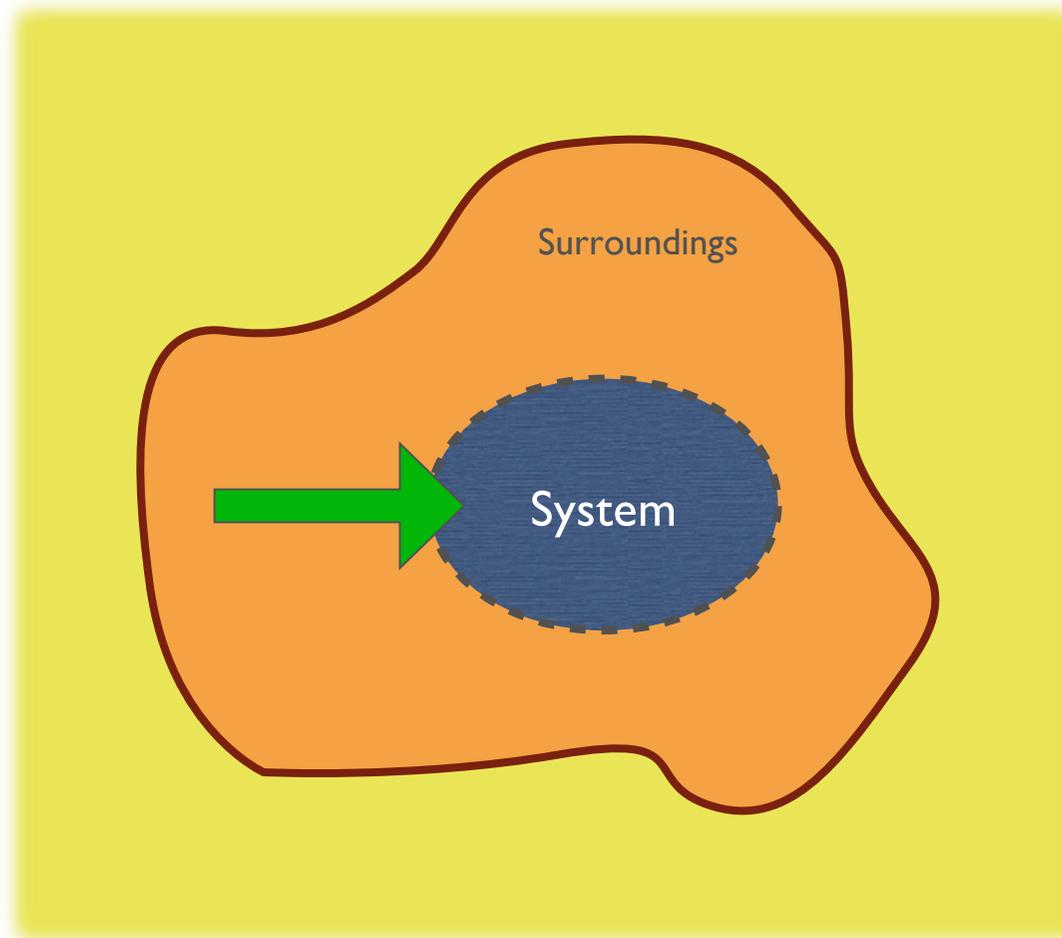
(But we ignore this fact for the time being... see thermodynamics)  
Exchange of matter and energy (“processes”) may take place across the boundary.



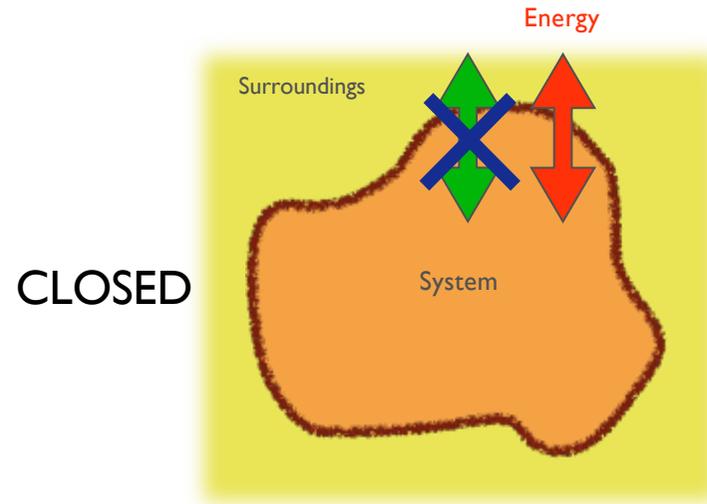
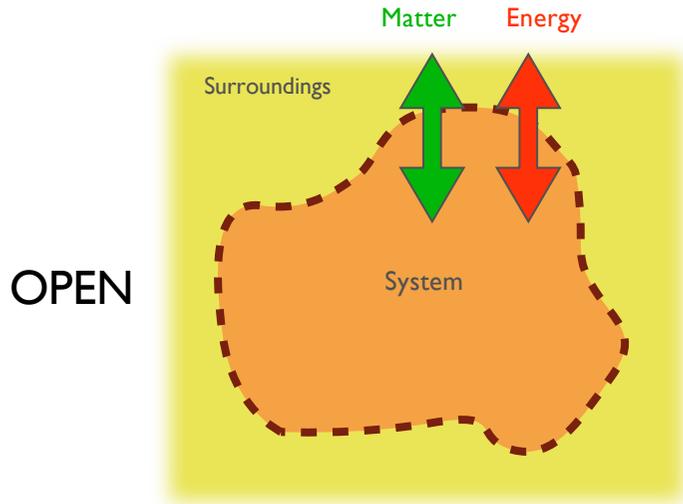
# Defining the system bears consequences

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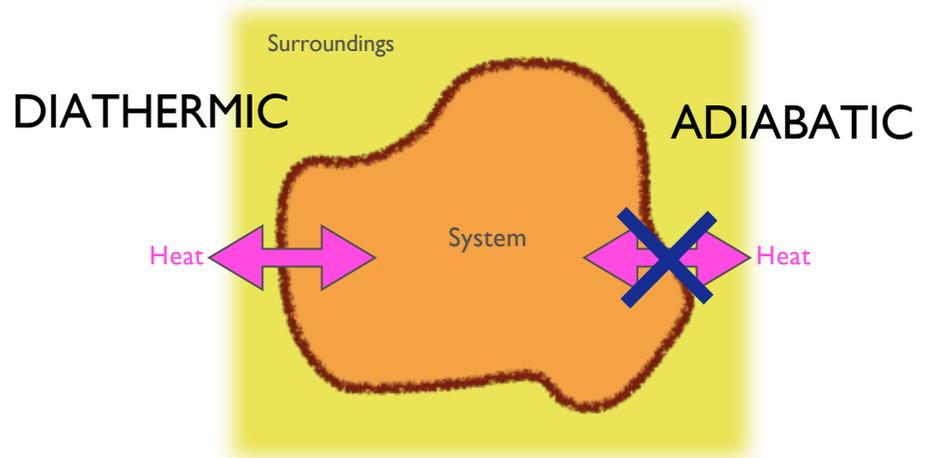
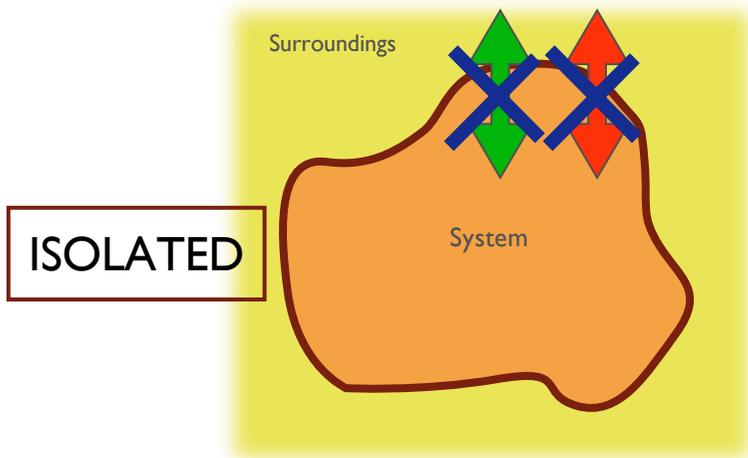
...for thermodynamic processes (see later)



# There are many Types of systems



...but for now we are interested in the **isolated** system.



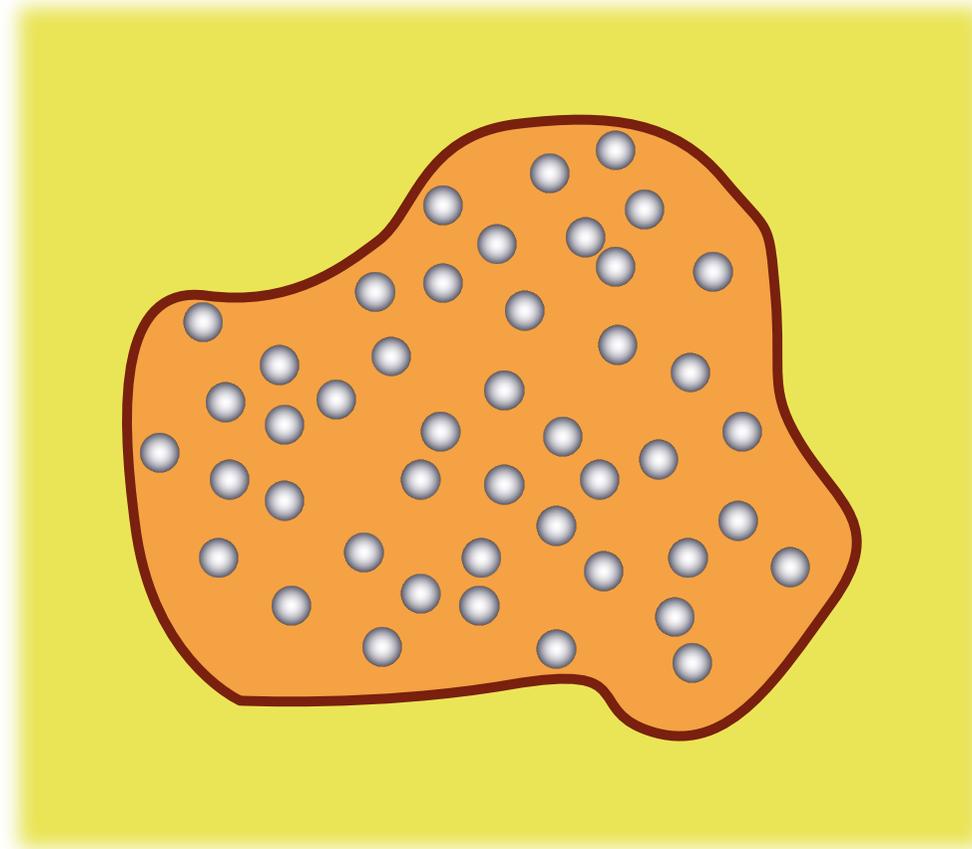
# the system may be characterized

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...macroscopically:

by state variables that explicitly determine the overall *state* of the system.

Pressure:  $p$   
Volume:  $V$   
Temperature:  $T$   
Concentration:  $c$   
(number of particles,  
 $N$  per unit volume  $V$ :  
 $N/V$ )



see universal gas law:  
 $pV=NkT$

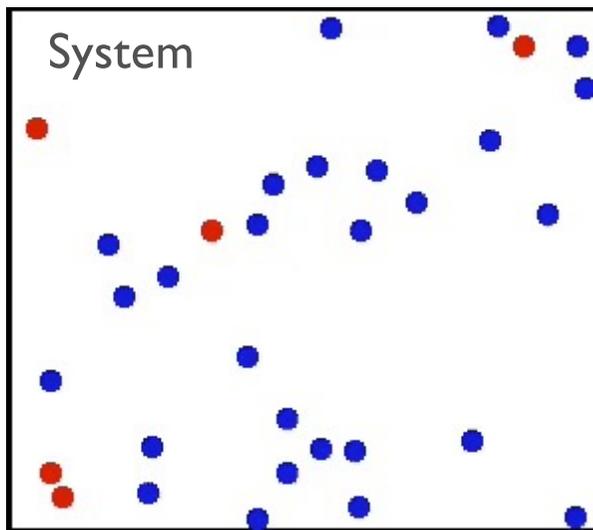
$k$ : Boltzmann's constant

# the system may be characterized

...microscopically:

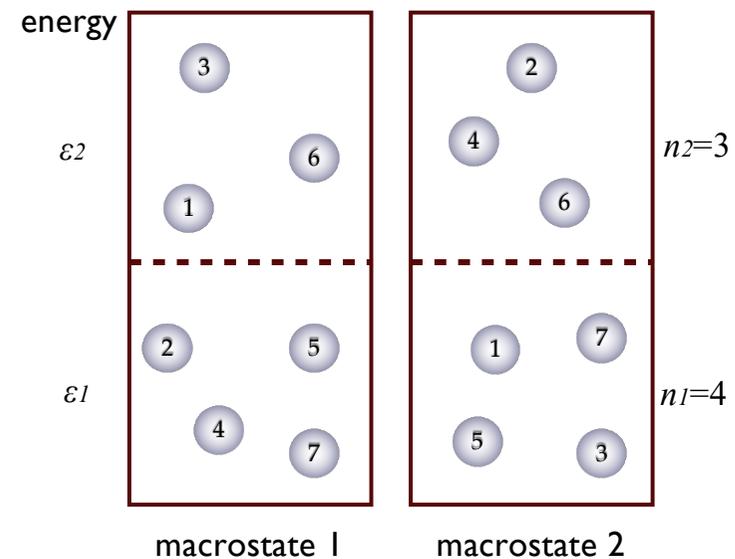
by describing the characteristics (e.g., energy) of each particle in the system

The energy of each particle in the system is different...

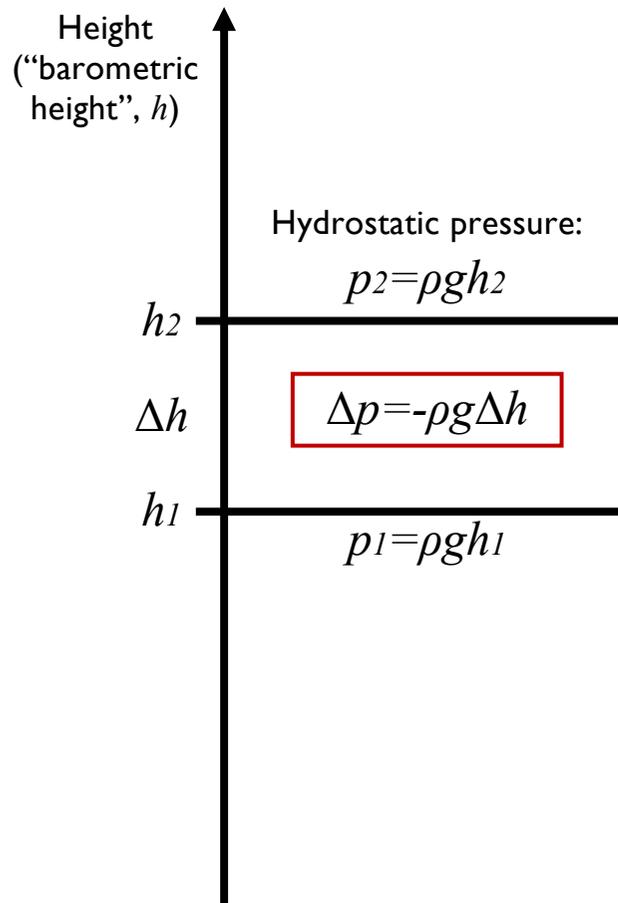


...but the average energy of every particle, for each degree of freedom, is  $1/2kT$  ("equipartition theorem").

Note: the **macrostates** (1 and 2) are identical (number of particles at given energies are same), but their **microstates** (arrangement of actual particles) differ:



# Macroscopic description of a system: distribution of pressure (gas density) in the atmosphere



$g$ : gravitational acceleration  
 $m$ : mass of a gas molecule

since gas density is proportional to pressure ( $\rho \sim p$ ):

$$\Delta\rho = \text{const}\Delta p$$

$$\Delta p = \Delta\rho / \text{const}$$

$$\Delta\rho / \text{const} = -\rho g \Delta h$$

$$\Delta\rho / \Delta h = -\text{const}\rho g$$

If a variable ( $\rho$ ) and its change ( $\Delta\rho$ ) are proportional, we obtain an exponential function:

$$\rho_h = \rho_0 \cdot e^{-\text{const} \cdot g \cdot h}$$

Considering the universal gas law ( $pV = NkT$ ), the definition of density ( $\rho = \frac{m \cdot N}{V}$ ), and that  $\rho = \text{const} \cdot p$ , "const" can be expressed as  $\frac{m}{k_B T}$

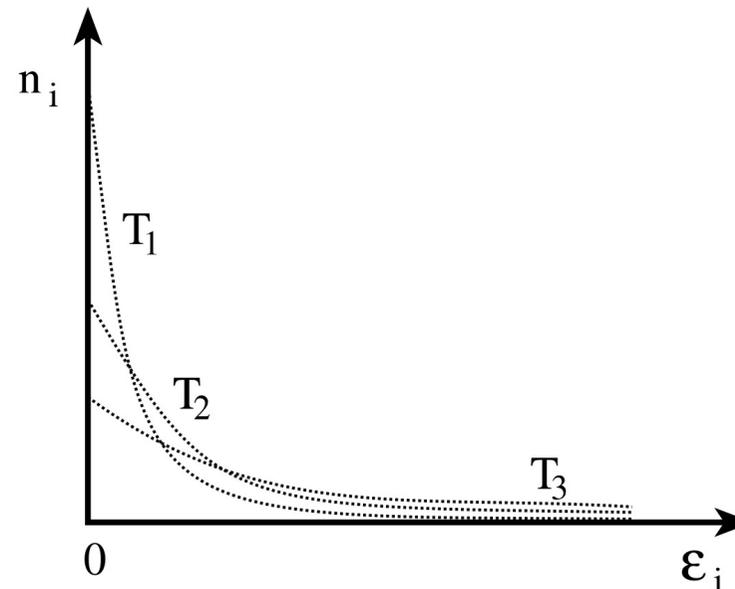
hence:

$$\rho_h = \rho_0 \cdot e^{-\frac{mgh}{k_B T}}$$

# Boltzmann's distribution is a universal organizing principle

- In a thermally equilibrated system the energy levels are populated according to an **exponential distribution**.
- Relative population is regulated by the ratio of the **energy difference** between the levels and the **thermal energy**.
- At higher temperatures higher energy levels are more populated.

$$\frac{n_i}{n_0} = e^{-\frac{\epsilon_i - \epsilon_0}{k_B T}}$$



# Boltzmann-distribution applications

## 1. Barometric height formula

Partial oxygen pressure progressively drops with the distance from the sea level: concentration (number of molecules in unit volume,  $n$ ) becomes progressively reduced

$$\left(\frac{p_h}{p_0}\right) \frac{n_h}{n_0} = e^{-\frac{mgh}{k_B T}}$$

$n_h$  : particle number at height  $h$   
 $n_0$  : particle number at the reference height  
 $mgh$  : potential energy

## 2. Thermal emission of metals

Upon thermal excitation, electrons leave the metal surface (e.g., x-ray tube, photoelectron multiplier tube)

$$\frac{N_i}{N_0} = e^{-\frac{W_a}{k_B T}}$$

$N_i$  : number of emitted electrons  
 $W_a$  : work function (work needed by the  $e^-$  to leave the atom)

# Boltzmann-distribution applications

## 3. Nernst equation

If, between two places ( $A$ ,  $B$ ), the concentration of charged particles ( $c_A$ ,  $c_B$ ) is different, then electrical voltage ( $U$ ) arises between these two places:

$$\frac{c_A}{c_B} = e^{-\frac{qU}{k_B T}} \quad U = \frac{k_B T}{q} \ln \frac{c_B}{c_A}$$

$q$ : elementary charge  
 $U$ : voltage between  $A$  and  $B$

Fundamental equation describing the behavior of concentration cells and the resting potential.

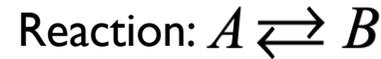
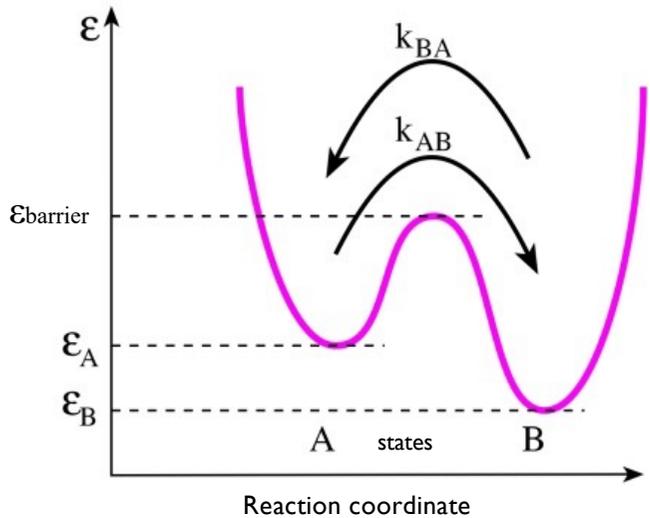


Walther Nernst (1864-1941)  
Nobel-prize (1920)

# Boltzmann-distribution applications

## 4. Reaction equilibrium, rate

The equilibrium (distribution among energy states) and rate (speed of transition between states) of a reaction are determined by relative differences between energy levels.



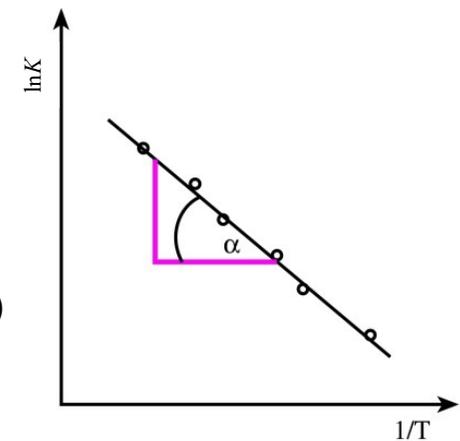
Equilibrium constant:  $K = \frac{n_A}{n_B} = e^{-\frac{\epsilon_A - \epsilon_B}{k_B T}}$

Rate constants:

$$k_{AB} = \omega e^{-\frac{\epsilon_{\text{barrier}} - \epsilon_A}{k_B T}} \quad k_{BA} = \omega e^{-\frac{\epsilon_{\text{barrier}} - \epsilon_B}{k_B T}} \quad \omega : \text{constant (s}^{-1}\text{)}$$

Ratio of rate constants = equilibrium constant:

$$k_{BA} / k_{AB} = e^{-\frac{\epsilon_{\text{barrier}} - \epsilon_B}{k_B T} + \frac{\epsilon_{\text{barrier}} - \epsilon_A}{k_B T}} = e^{-\frac{\epsilon_A - \epsilon_B}{k_B T}} = K$$



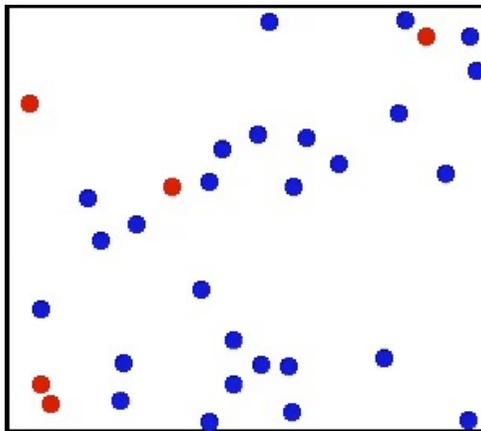
$$\ln K = -\frac{\epsilon_A - \epsilon_B}{k_B} \frac{1}{T}$$



Svante Arrhenius (1859-1927)  
Nobel-prize (1903)

# The ideal (perfect) gas

- Composed of a **large** number of identical particles (Avogadro number)
- Particles are **spherical**, their volume is **negligible**
- There is **no interaction** between the particles
- Collisions are **elastic** (sum of energies is constant)
- In the limiting case (point particles) collisions occur only with the wall of the container
- Particle motion follows the laws of classical (Newtonian) mechanics.



# Ideal gas relationships

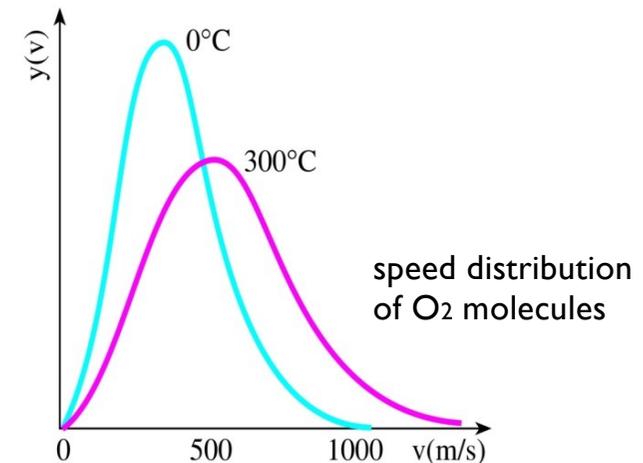
Average energy of a particle (equipartition theorem):  $\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$

Internal energy of a system containing  $N$  particles:  $E_b = \frac{3}{2} N k_B T$

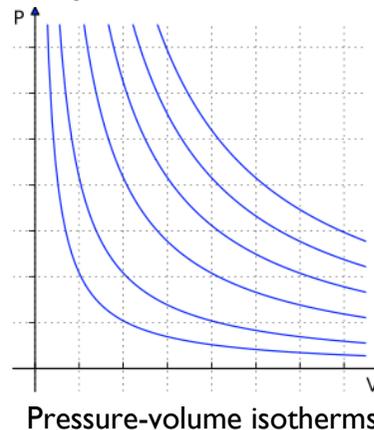
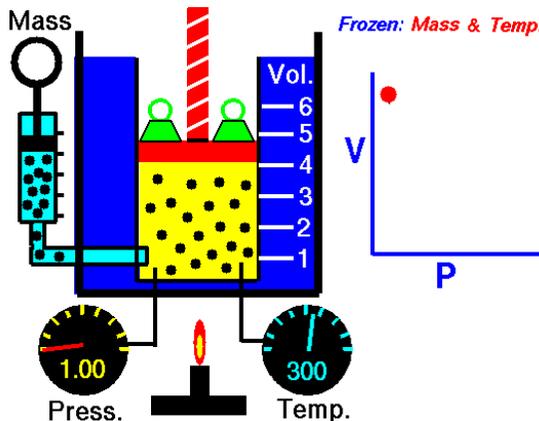
## Speed distribution - Maxwell distribution

Upon increasing temperature:

- the average of the absolute value of molecular speeds increases (see equipartition)
- the width of the distribution increases



**Universal gas law** (from the Clausius-Clapeyron, Boyle-Mariotte, Charles laws): relationship between the pressure, volume, temperature and matter content of the ideal gas (state equation).



$$PV = nRT$$

$$PV = Nk_B T$$

$P$  = pressure (Pa)  
 $V$  = volume (m<sup>3</sup>)  
 $n$  = amount of material (mol)  
 $R$  = gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>)  
 $T$  = absolute temperature (K)  
 $N$  = number of particles  
 $k_B$  = Boltzmann's constant

# The real gas

- Particles are not point-like, their volume ( $b$ ) is not negligible.  
Consequence: the volume available for motion =

$$V - Nb \quad N = \text{particle number}$$

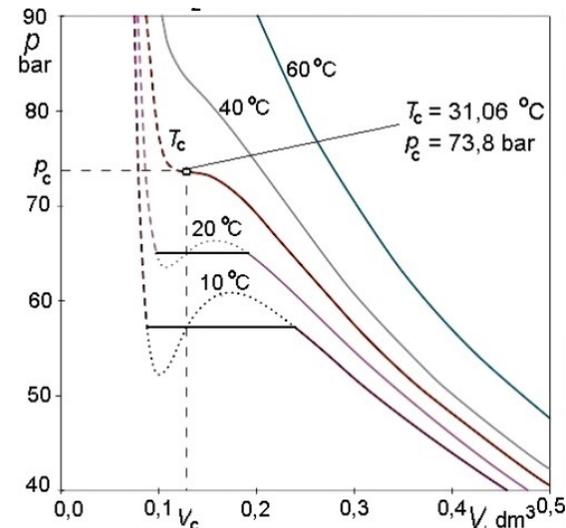
- Interactions ( $a$ ) arise between the particles.  
Consequence: pressure becomes reduced

$$p = \frac{Nk_B T}{V - Nb} - an^2 \quad n = \text{number of particles in unit volume } (N/V)$$

- Van der Waals state function:  $\left( p + a \frac{N^2}{V^2} \right) (V - Nb) = Nk_B T$

- Van der Waals isotherms:

Below a critical temperature ( $T_c$ ), at low pressures phase transition occurs (e.g., condensation)



Pressure-volume diagram of CO<sub>2</sub>