

MANY-PARTICLE SYSTEMS

THE BOLTZMANN-

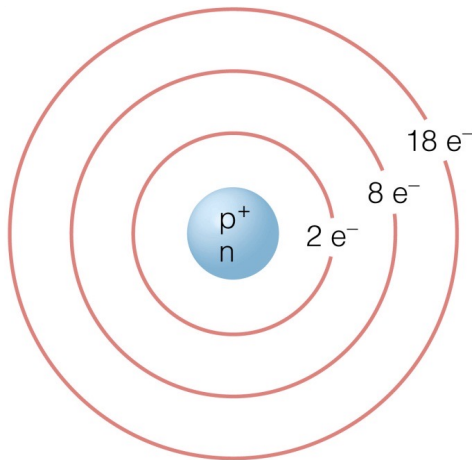
DISTRIBUTION

GASEOUS AND LIQUID STATES

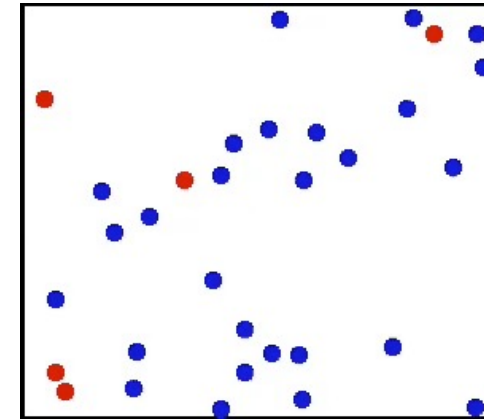
ZSOLT MÁRTONFALVI

# From the atom to many-particle systems

Atom



“Many-particle system”



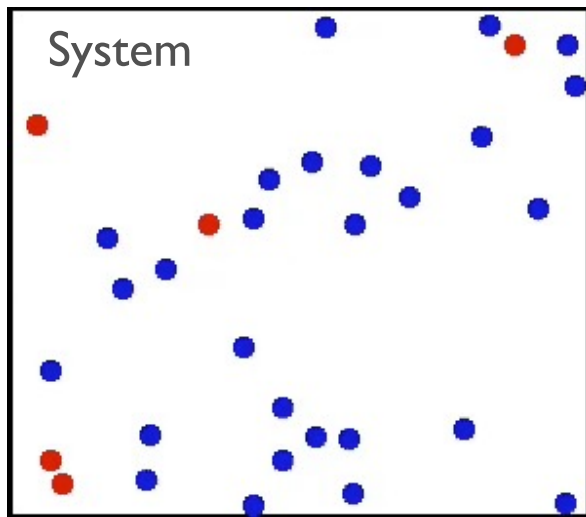
- What is a system?
- How many particles are “many”?
- What is the internal “structure”?
- How do particles respond to forces (caused by potential differences)?

# the system may be characterized

...microscopically:

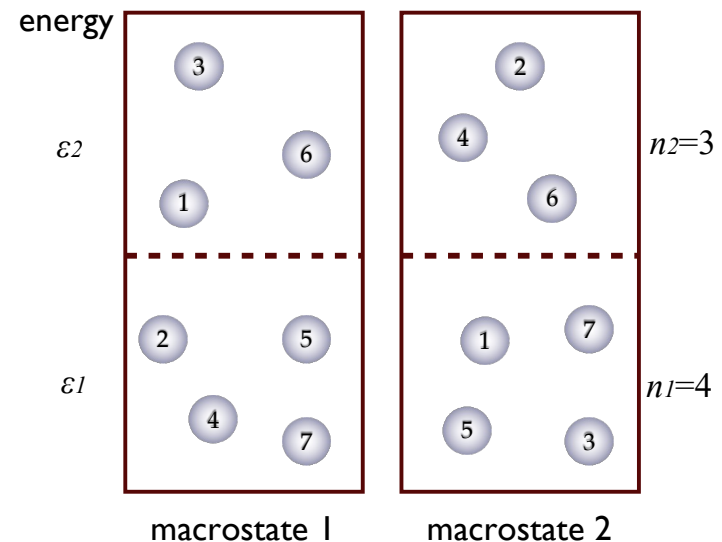
by describing the characteristics (e.g., energy) of each particle in the system

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

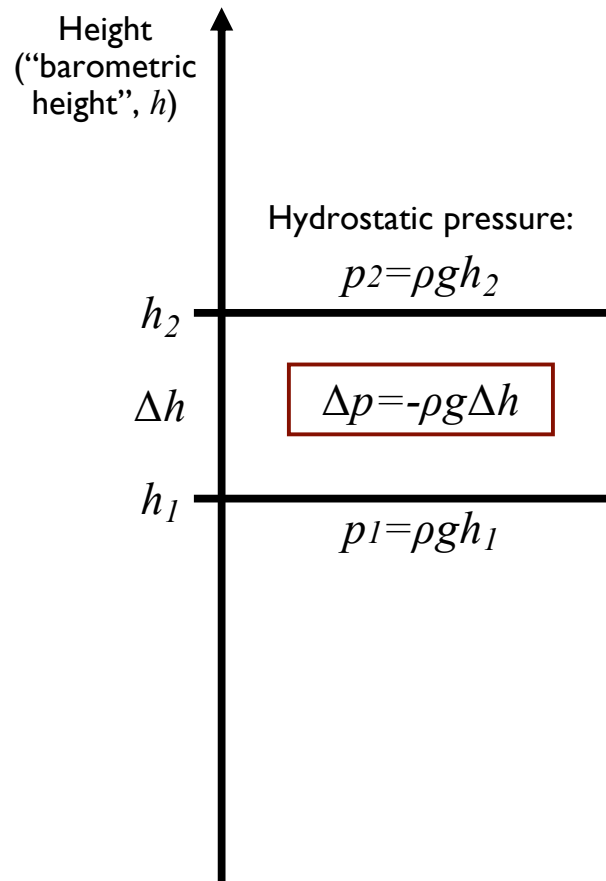


...but the average energy of every particle is proportional to  $kT$  ("equipartition theorem").

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:

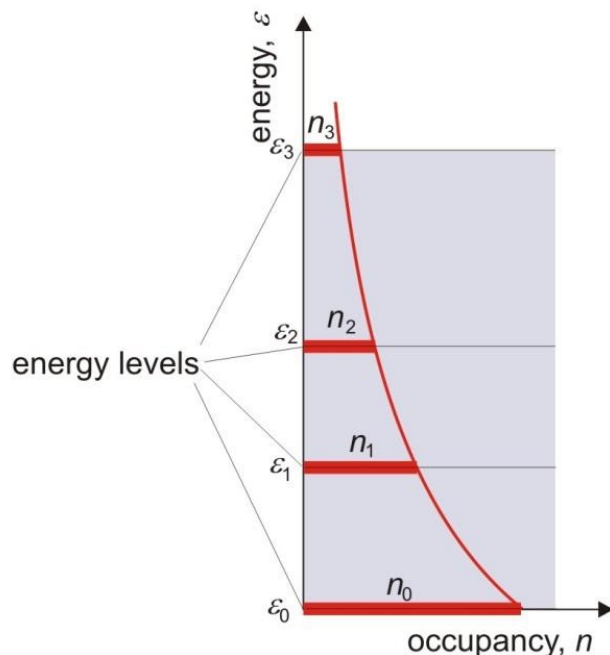
$$\rho_h = \rho_0 e^{-\text{const} g h}$$

Considering the universal gas law ( $pV = NkT$ ), the definition of density ( $\rho = mN/V$ ), and that  $\rho = \text{const} p$ , "const" can be expressed as  $m/kT$ , hence:

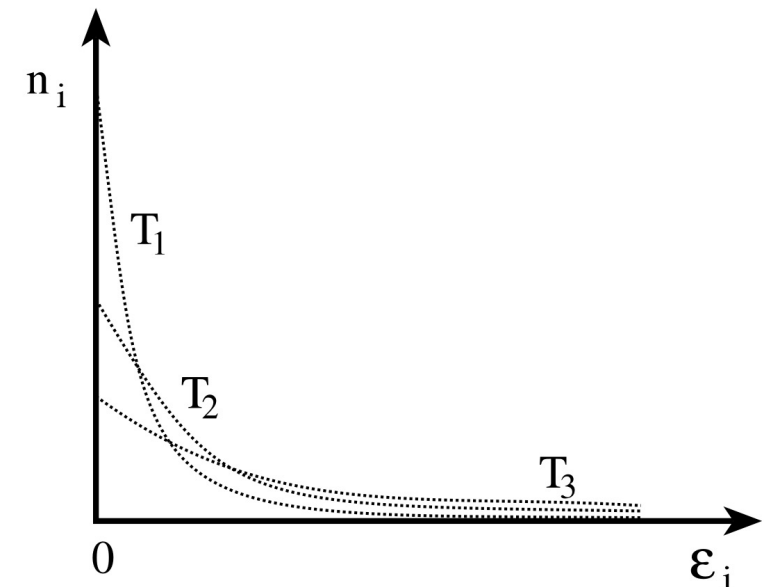
$$\rho_h = \rho_0 e^{-mgh/kT}$$

# 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

## I. 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

$$\frac{n_h}{n_0} = e^{-\frac{mgh}{k_B T}}$$

$n_h$  : concentration at height  $h$   
 $n_0$  : concentration 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)

$$\frac{N_l}{N} = e^{-\frac{W_a}{k_B T}}$$

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

# Boltzmann-distribution applications

## 3. Nernst equation

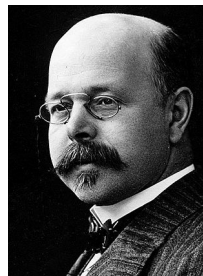
If, between two places ( $A$ ,  $B$ ), the concentration of charged particles ( $n_A$ ,  $n_B$ ) is different, then electrical voltage ( $U$ ) arises between these two places:

$$\frac{n_A}{n_B} = e^{-\frac{qU}{k_B T}}$$

$$U = \frac{k_B T}{q} \ln \frac{n_A}{n_B}$$

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

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

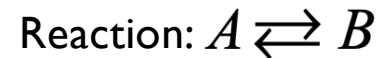
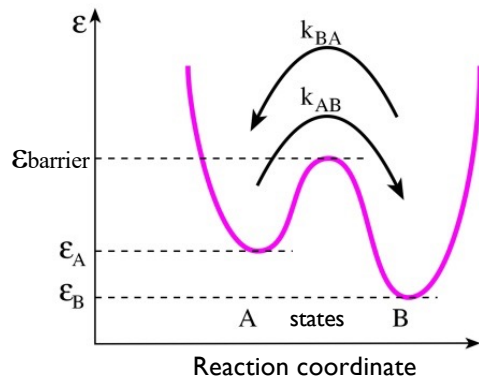


Walther Nernst (1864-1941)  
Nobel-prize (1920)

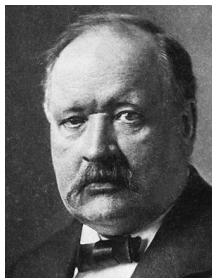
# Boltzmann-distribution applications

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



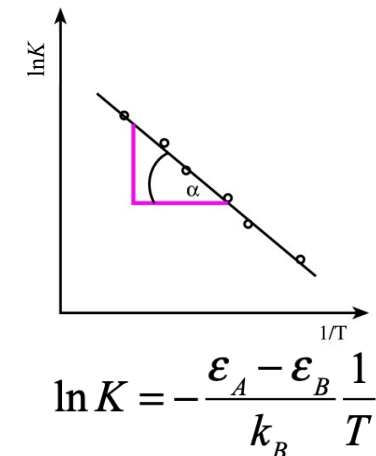
Svante Arrhenius (1859-1927)  
Nobel-prize (1903)

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:

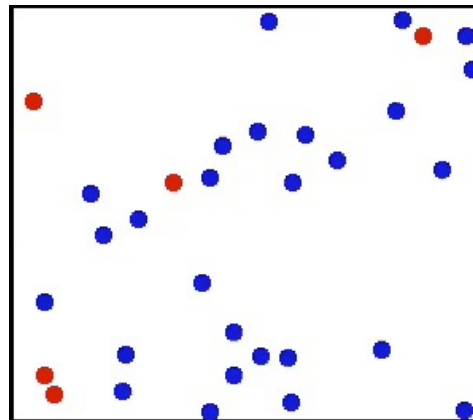
$$k_{BA}/k_{AB} = e^{-\frac{\epsilon_{\text{barrier}} - \epsilon_B}{k_B T} + \frac{\epsilon_{\text{barrier}} - \epsilon_A}{k_B T}} = e^{-\frac{\epsilon_A - \epsilon_B}{k_B T}} = K$$





# 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**):

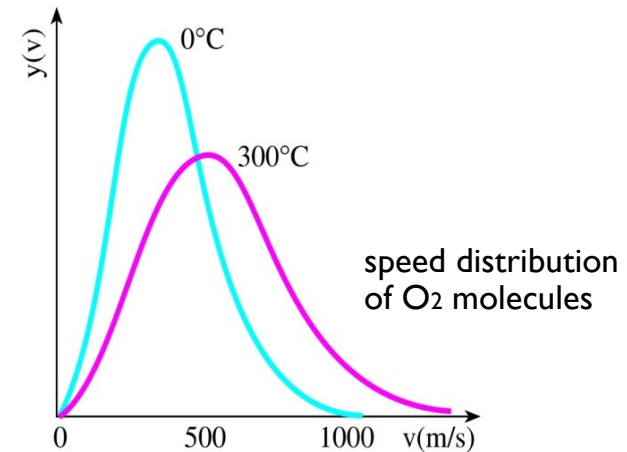
$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T$$

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

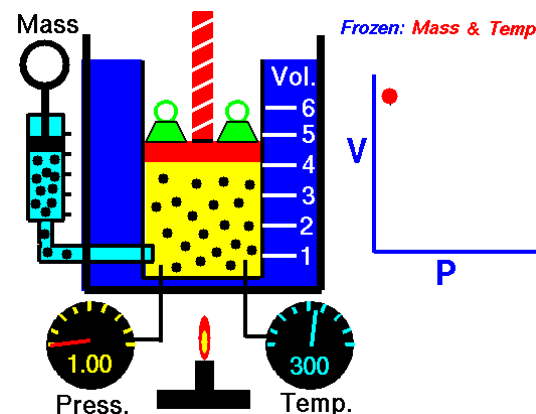
## Speed distribution - Maxwell distribution

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).



# Gas Laws

Boyle's Law

$$pV = \text{constant}_I$$

Charle's Law.

$$\frac{V}{T} = \text{constant}_{II}$$

Gay-Lussac's Law

$$\frac{p}{T} = \text{constant}_{III}$$

Avogadro's Law

$$\frac{V}{N} = \text{constant}_{IV}$$

$$\frac{p}{T} \cdot \frac{V}{N} = k_{III} \cdot k_{IV}$$

$$k_{III} \cdot k_{IV} = k_B = 1,38 \cdot 10^{-23} \text{ J/K}$$

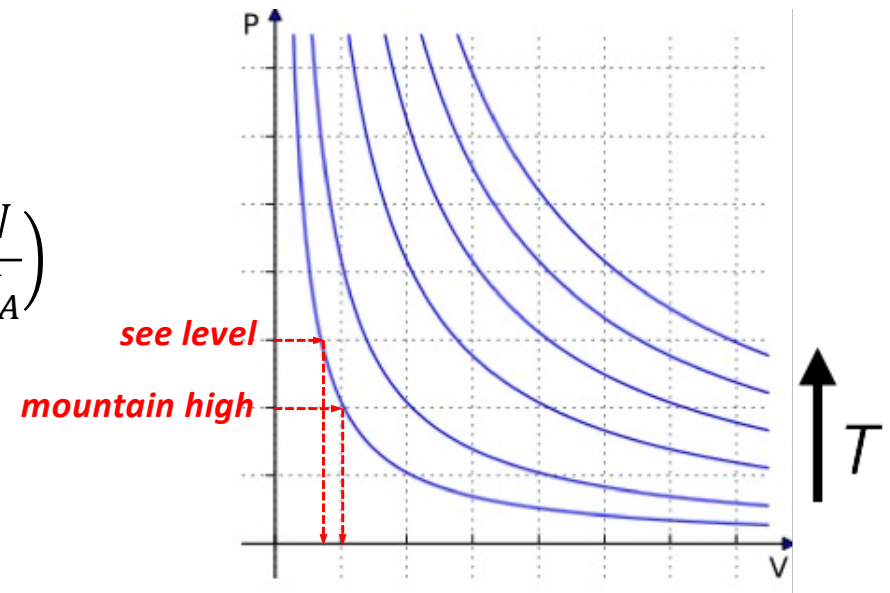
$$pV = Nk_B T$$

$$pV = \frac{N}{N_A} k_B N_A T$$

$$(k_B \cdot N_A = R) \quad \left( n = \frac{N}{N_A} \right)$$

$$pV = nRT$$

$P$  = pressure (Pa)  
 $V$  = volume ( $\text{m}^3$ )  
 $n$  = amount of material (mol)  
 $R$  = gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )  
 $T$  = 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 =

$$V - Nb$$

$N$  = particle number

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

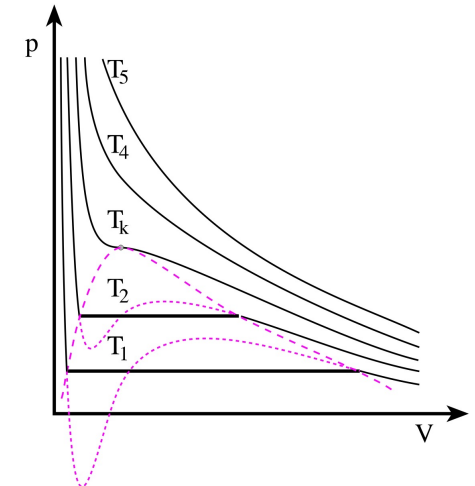
$$p = \frac{Nk_B T}{V - Nb} - an^2$$

$n$  = 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)



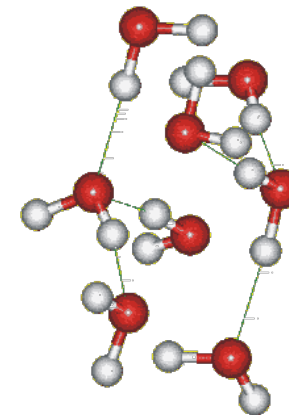
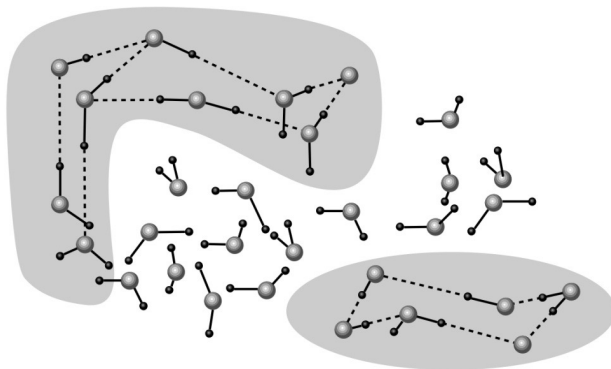
# Liquids

- Liquids have stable volume but no stable shape
- **Short range dynamic order**
- **Isotropic**: the physical properties have no directional dependence
- Physical quantities to describe the liquid state:

density (mass per volume)  $\left[\frac{kg}{m^3} \text{ or } \frac{g}{cm^3}\right]$

viscosity (resistance against flow)  $[Pa \cdot s]$

surface tension (energy required to increase interface)  $\left[\frac{J}{m^2} = \frac{N}{m}\right]$



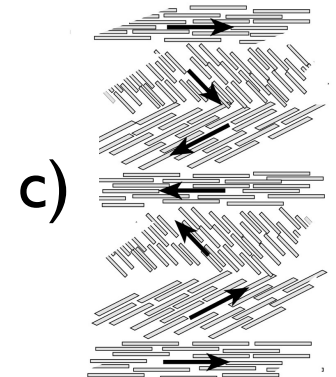
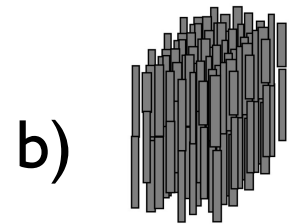
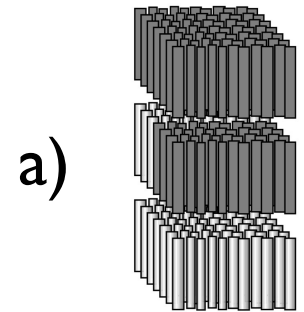
# Liquid crystals

- **Mesomorphic state**: anisotropic liquids (directional dependence)
- The molecules are **ordered**: 1) translational order 2) orientational order

Types: a) smectic (translational + orientational order)

b) nematic ( only orientational order)

c) cholesteric (twisted nematic)



**Thermotropic liquid crystals:**  
the order depends on  
temperature.

contact thermography



**Lyotropic liquid crystals:**  
the order depends on the  
concentration of molecules

phospholipids are lyotropic

