Many-particle systems
Boltzmann-distribution

Gases, Liquids and liquid crystals

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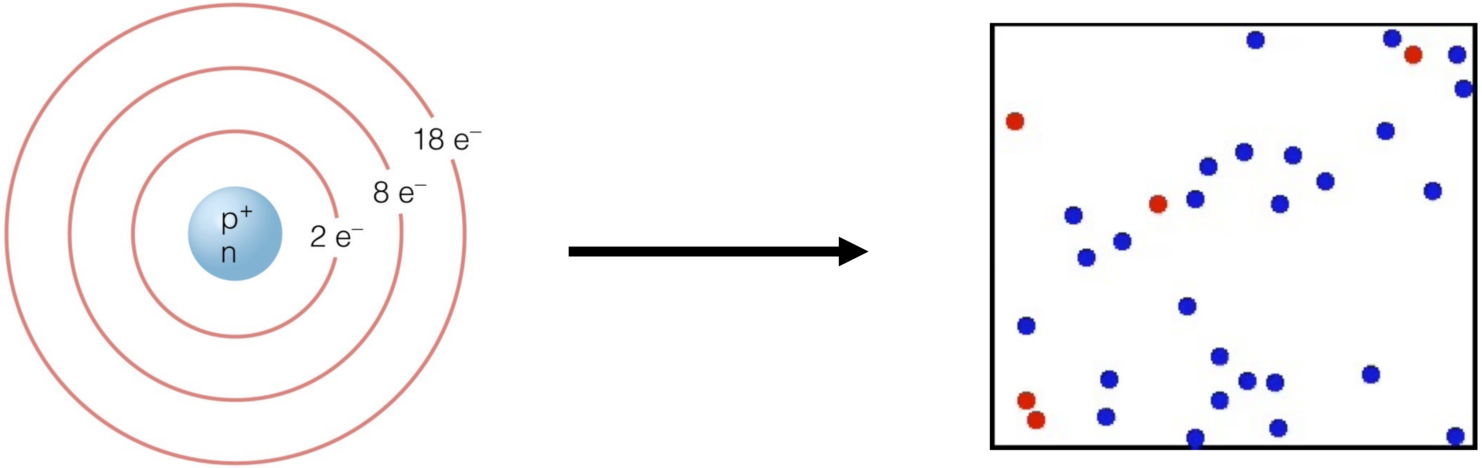
EGYETEM 1769

From atoms to many-particle systems


Atom

“Many-particle system”

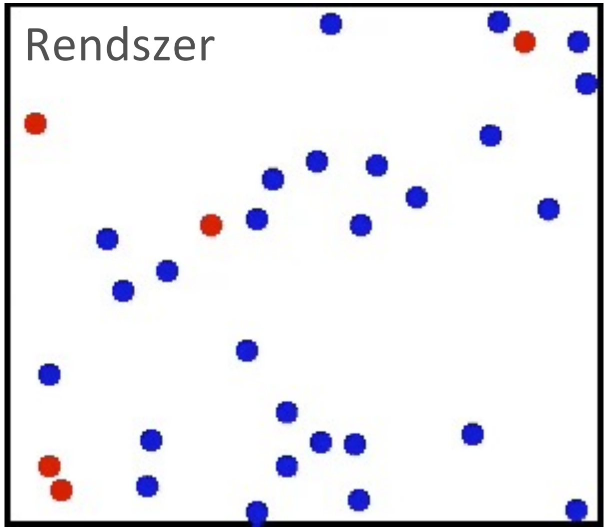
- What is a system?
- How many particles are „many”?
- What is the internal “structure” of the system?

A system may be characterized by

macrosopically (p, V, T, n) or **microscopically**:

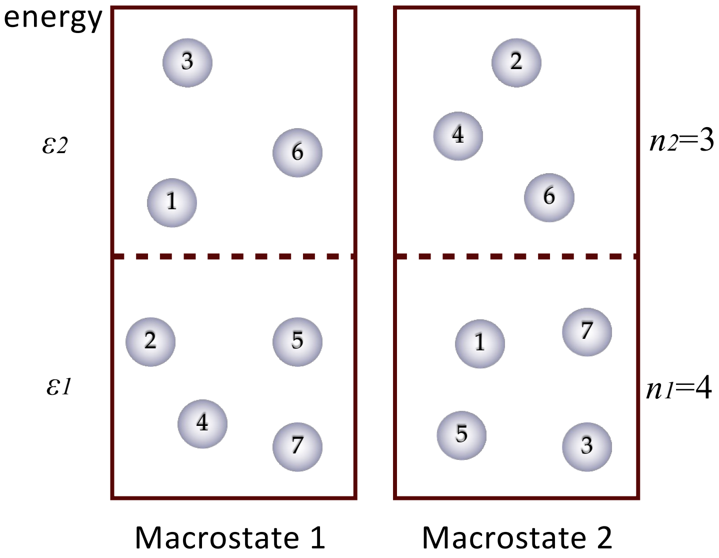
By describing of each particle in the system (i.e. energy)

The energy of each particle in the system is different…



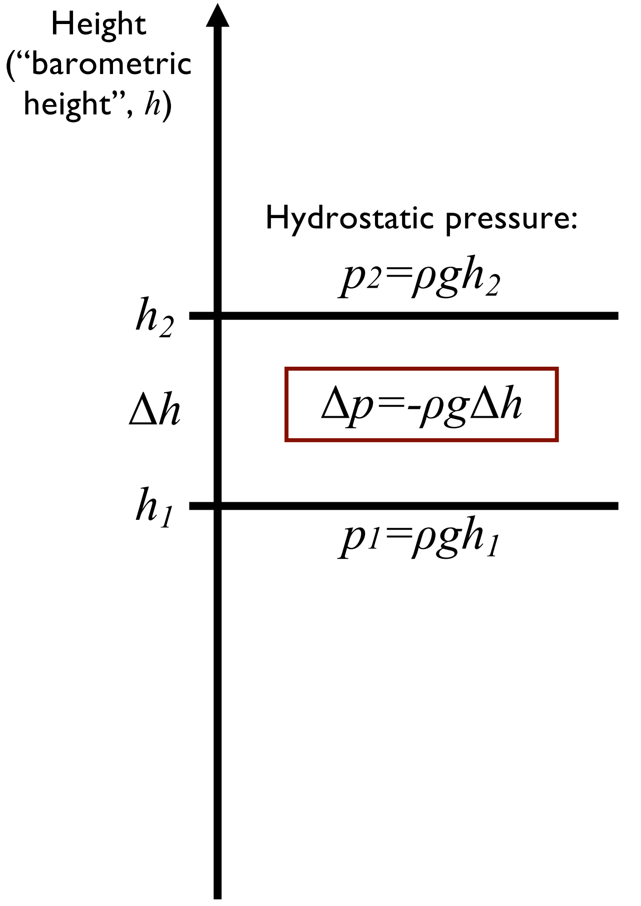
…but the average energy of every particle is proportional to kT ("equipartition theorem").

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



Macroscopic description of a system:

distribution of pressure (gas density) in the atmosphere



Hydrostatic pressure:

$p_2=\rho g h_2$

$\boxed{\Delta p=-\rho g \Delta h}$

$p_1=\rho g h_1$

g: gravitational acceleration
m: mass of a gas molecule

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

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

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

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

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

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

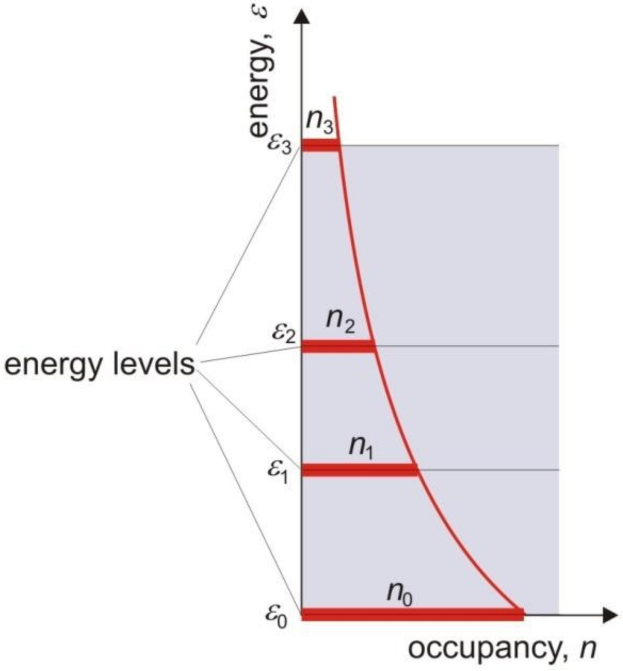
$$\boxed{\rho_h=\rho_0 e^{-\text{const}gh}}$$

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

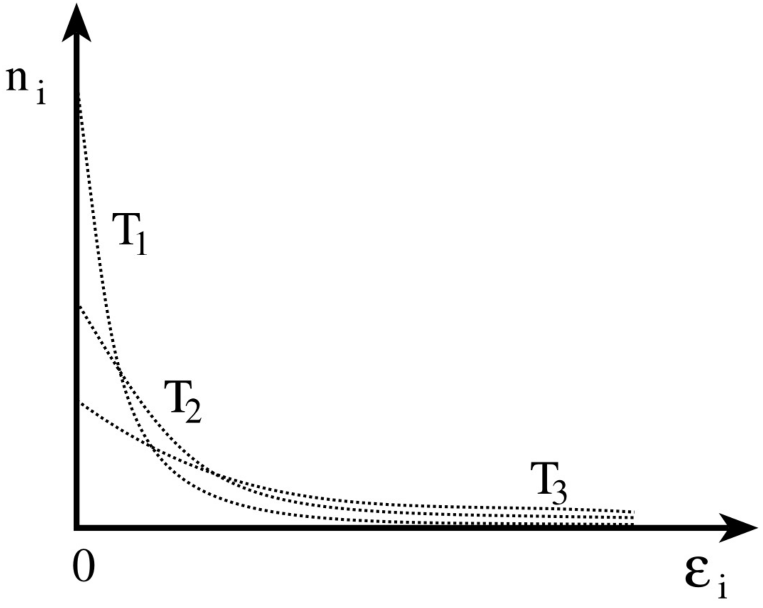
$$\boxed{\rho_h=\rho_0 e^{-mgh/kT}}$$

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.



$$\frac{n_i}{n_0} = e^{-\frac{\varepsilon_i - \varepsilon_0}{k_B T}}$$



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

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

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 fuction (work needed by the e^- to leave the atom)

Boltzmann-distribution applications

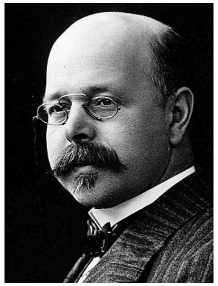
3. Nernst equation

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:

$$\frac{c_A}{c_B} = e^{-\frac{Uq}{k_b T}} \qquad \boxed{U = \frac{k_b T}{q} ln \frac{c_B}{c_A}} = \frac{RT}{zF} ln \frac{c_B}{c_A}$$

q : elementary charge
U : voltage between A and B

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

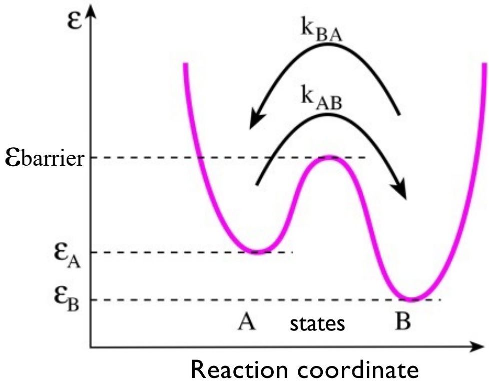


Walther Nernst (1864-1941)
Nobel-prize (1920)

Boltzmann-distribution applications

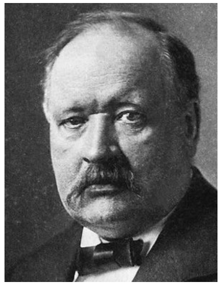
4. Reaction equilibrium, rate

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



Reaction: $A \rightleftarrows B$

Equilibrium constant: $K = \dfrac{n_A}{n_B} = e^{-\frac{\varepsilon_A - \varepsilon_B}{k_B T}}$



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

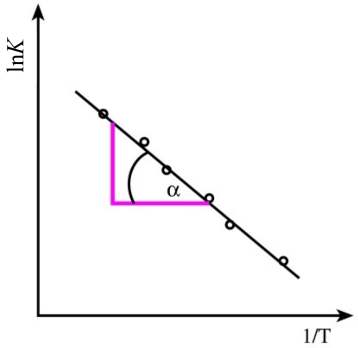
Rate constants:

$$k_{AB} = \omega e^{-\frac{\varepsilon_{barrier} - \varepsilon_A}{k_B T}} \qquad k_{BA} = \omega e^{-\frac{\varepsilon_{barrier} - \varepsilon_B}{k_B T}}$$

ω : constant (s^{-1})

Ratio of rate constants = equilibrium constant:

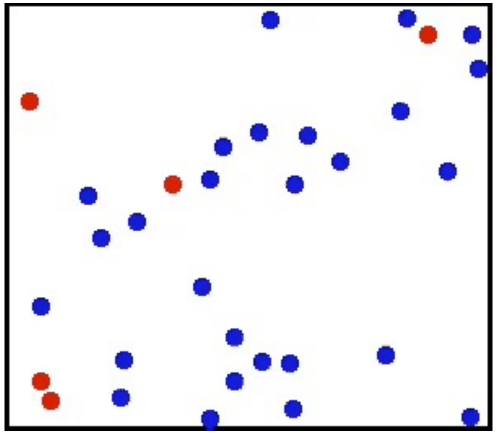
$$k_{BA} / k_{AB} = e^{-\frac{\varepsilon_{barrier} - \varepsilon_B}{k_B T} + \frac{\varepsilon_{barrier} - \varepsilon_A}{k_B T}} = e^{-\frac{\varepsilon_A - \varepsilon_B}{k_B T}} = K$$



$$\ln K = -\frac{\varepsilon_A - \varepsilon_B}{k_B} \frac{1}{T}$$

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

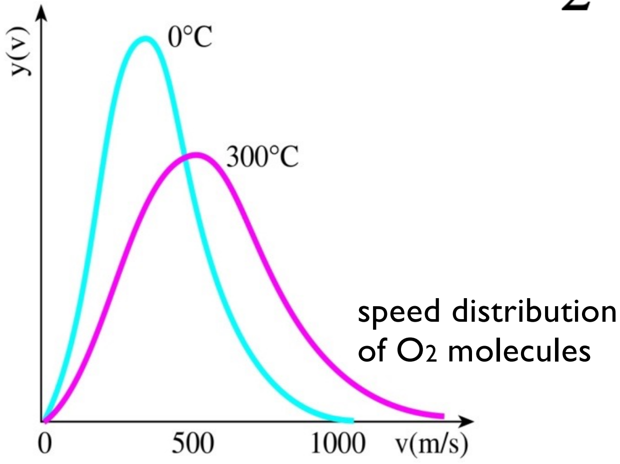
Average energy of a particle (**equipartition theorem**): $\boxed{\frac{1}{2}m\bar{v}^2 = \frac{3}{2}k_BT}$

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

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



speed distribution of O2 molecules

Universal gas law: relationship between the pressure, volume, temperature and matter content of the ideal gas (state equation).

Boyle's law $pV = constant_I$

Charles' law $\frac{V}{T} = constant_{II}$

Gay-Lussac's law $\frac{p}{T} = constant_{III}$

Avogadro's law $\frac{V}{N} = constant_{IV}$

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

$$pV = \frac{N}{N_A}k_BN_AT$$

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

$$(k_B\cdot N_A = R)$$

$$\left(n = \frac{N}{N_A}\right)$$

$$pV = Nk_BT$$

$$\boxed{pV = nRT}$$

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

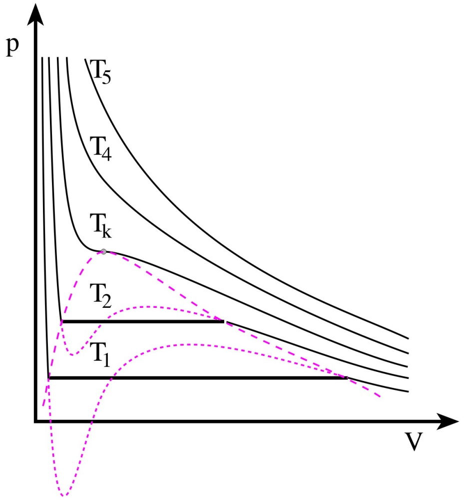
$$p = \frac{Nk_BT}{V - Nb} - an^2$$

n = number of particles in unit volume (N/V)

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

- Van der Waals isotherms:

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



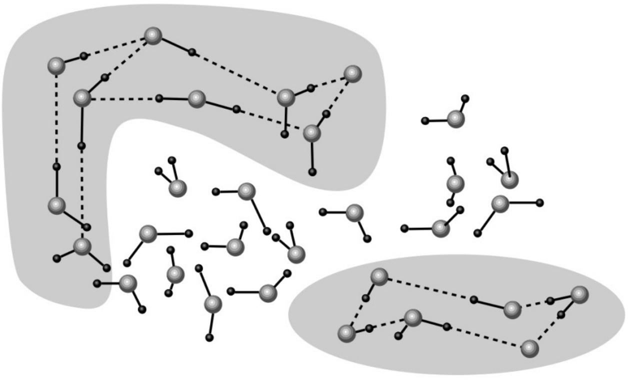
The liquid state

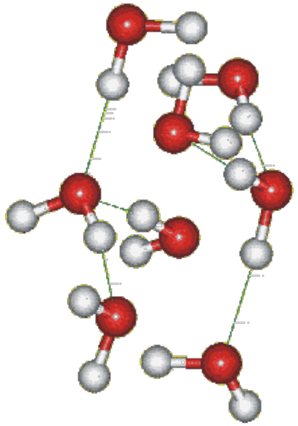
- Liquids have stable volume but no stable shape
- Short range dynamic order
- Isotropic: the physical properties have no directional dependence
- Physical quanites to describe the liquid state:

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

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

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



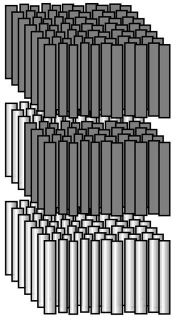


Lquid crystals

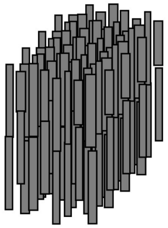
- Mesomorphic state: anisotropic liquids (directional dependence)
- The molecules are ordered: 1) translational order 2) orientational order

Types: a) smectic (translational + orientational order)
b) nematic (only orientational order)
c) cholesteric (twisted nematic)

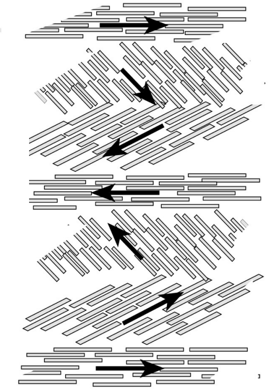
a)



b)



c)

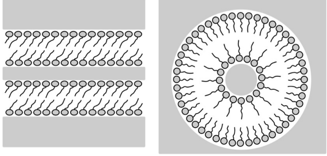


Thermotropic liquid crystals: the order depends on temperature.

contact thermography

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

phospholipids are lyotropic



Solid state

Has both stable volume and shape


Quartz (SiO_2)

CHRISTALLINE MATERIALS

- Long range spatial order
- **anisotropic:** the physical properties are direction dependent
- A lattice structure whose basic unit is the **unit cell**. Depending on the type of interactions, it can be an *atomic, ionic, metallic, or molecular lattice*. The crystalline order usually extends only over microscopic distances (microcrystalline material).
- i.e.: majority of metals, NaCl, $CaSO_4$, sugar, etc...

AMORPHOUS MATERIALS

- Short range spatial order
- **isotropic:** the physical properties are direction independent
- i.e.: glass


Obsidian: vulcanic glass (amorphous)

Comparing the properties of states

State		Order of particles	Movement of particles	Shape	Volume	Examples
1) Solid	*Crystalline*	Long range spatial order	Only vibrational motion around the lattice points	Has its own shape	Constant	Metals, ice, quartz
	Amorphous	Short range spatial order	Free sliding and flow are possible	Has its own shape	Constant	Glas, metallic glass
2) Liquid crystal	*smectic*	Long range dynamic order	Lateral diffusion	Takes the shape of the container	Constant	Phospholipid
	nematic					
	cholesteric					
3) Liquid		Short range dynamic order	articles roll over each other, flow	Takes the shape of the container	Constant	Water, alcohol, oil
4) Gas		Disordered, particles separated from each other	Free, straight-line motion with frequent collisions	Takes the shape of the container	Variable (fills the space)	Air, oxygen, carbon dioxide