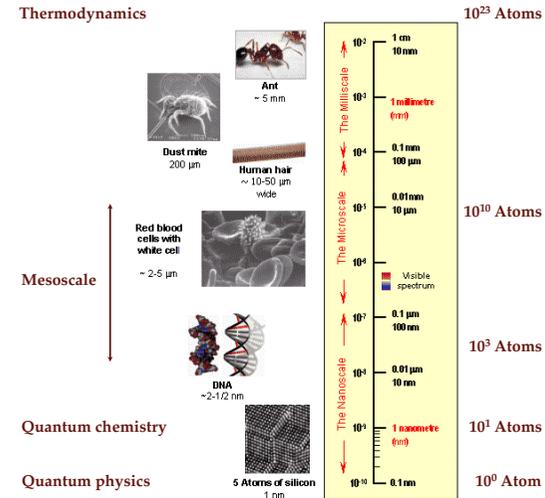


STRUCTURE OF MATTER, AFM

INTRODUCTION
MIKLÓS KELLERMAYER

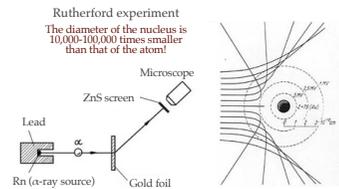
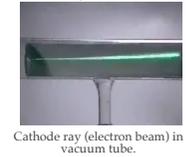
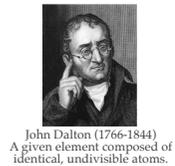
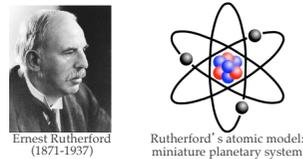
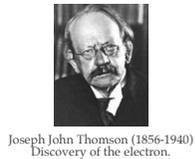
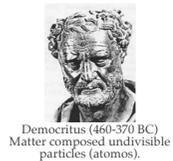
DIMENSIONS OF LIVING SYSTEMS



Richard P. Feynman (Nobel prize, 1965):

If, due to a disaster, the knowledge of humankind were destroyed, and only one sentence could be passed on to future generations, what would be the statement that best summarizes our knowledge? *Atomic theory:* The entire natural world is made up of particles that constantly move and attract or repel each other. The characteristics and processes of nature can be described through the atomic particles.

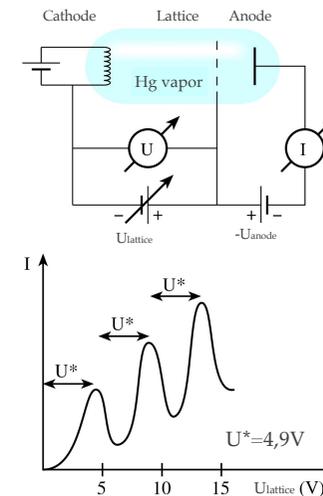
EARLY ATOMIC MODELS



Problem:
-unstable atom
-electrons: centripetal acceleration - light emission - energy loss - falling into the nucleus

ENERGY OF THE ATOM CHANGES IN DISCRETE STEPS

Franck-Hertz experiment (1914)

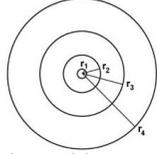


The electrons accelerated by the lattice voltage ($U_{lattice}$), upon inelastic collision with the Hg atoms, loose their energy in discrete packages ("quantum" - *sing.*, "quanta" - *pl.*).

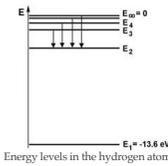
BOHR MODEL OF THE ATOM



Niels Bohr (1885-1962)



Bohr model of the hydrogen atom



Bohr's postulates

1. Quantum condition:

- The electrons of an atom are on given orbits.
- On the given orbit the electron does not emit, its energy is constant.
- The angular momentum (L) of the orbital electron is an integer multiple of $h/2\pi$:

$$L = mvr = n \frac{h}{2\pi}$$

n = principal quantum number. The radii of the orbits can be calculated. The radius of the first orbit is $r_1 = 5.3 \cdot 10^{-11}$ m ("Bohr-radius"). The radii of the further orbits are:

$$r_n = n^2 r_1$$

2. Frequency condition:

- The atom radiates (i.e., emits light) only if the electron "jumps" from one orbit to the other.
- Energy of the radiation is the difference between the orbit energies:

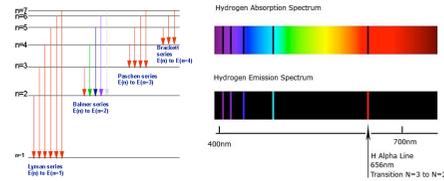
$$E_{\text{foton}} = h\nu = E_2 - E_1$$

The orbit energies can be calculated. Energy of the first orbit is $E_1 = -13.6$ eV. Further orbit energies are:

$$E_n = \frac{E_1}{n^2}$$

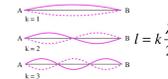
Significance

- The model explained the spectra of the hydrogen atom. But only that of the hydrogen atom.
- Absorption/emission spectroscopy
- Laser



THE ELECTRON AS A WAVE

Quantized behavior in the stationary waves of a stretched string

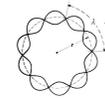


The electron as a wave



Louis V. de Broglie (1892-1978)

$$\lambda = \frac{h}{p} = \frac{h}{m_e v}$$



Atomic electron as a standing wave

$$\text{Quantum condition: } 2\pi r = n\lambda = n \frac{h}{m_e v}$$

Propagation law of electron waves



Erwin Schrödinger (1887-1961)

Ψ (psi) wavefunction:

- $|\Psi(x,t)|$: gives the amplitude of the electron wave as a function of position (x) and time (t).
- Ψ^2 : gives the probability of finding the electron.
- Ψ^2 : integrated across the entire space = 1 (i.e., the electron can be found somewhere).
- Ψ : with the help of Schrödinger's equation, allows calculation of electron energies.
- For a free electron Ψ is a sine wave: momentum is precisely known ($p=h/\lambda$), but position (x) entirely unknown (uncertainty principle)



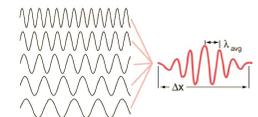
Wavefunction of freely moving particle (potential energy = 0)

Uncertainty principle



Werner Heisenberg (1901-1976)

To localize the wave, we need to superimpose waves of different wavelength (λ) (interference):



Upon spreading λ ($\Delta\lambda$), localization will be more certain (Δx decreases), but it also spreads the momentum values (Δp increases), thereby increasing the uncertainty of determining momentum:

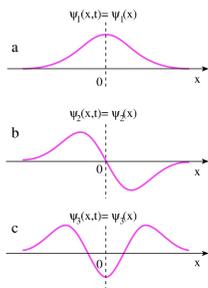
$$\Delta x \cdot \Delta p \geq \frac{h}{2\pi}$$

QUANTUM MECHANICAL ATOMIC MODEL

Within the atom every electron has a given state, and the probability of finding it around the nucleus has a specific shape.

Quantum mechanics:

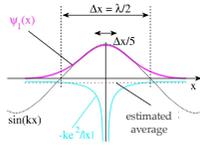
1. describes the states of the electron (one state \rightarrow one wavefunction, Ψ)



2. calculates the electron's most probable location (orbital, r) and energy (E)

$$E = E_{\text{kin}} + E_{\text{pot}} = \frac{mv^2}{2} - \frac{e^2}{r}$$

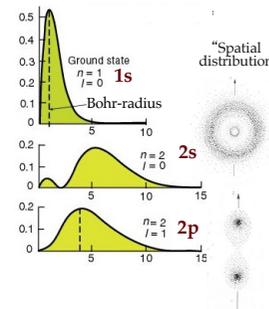
In the atom, Coulombic attraction determines the potential energy:



Simplified Schrödinger's equation:

$$\left(\frac{mv^2}{2} - \frac{e^2}{r} \right) \Psi = E\Psi$$

Probability of finding the electron in the atom:



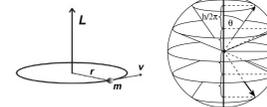
QUANTUM NUMBERS

The quantum numbers refer to *physical quantities* that describe the state of the electron:

1. Energy

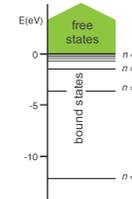
Energy of the electron in a given quantum state

2. Angular momentum



3. Spin

Intrinsic angular momentum and magnetic momentum



name	symbol	orbital meaning	range of values	value example
principal quantum number	n	shell	$1 \leq n$	$n = 1, 2, 3, \dots$
azimuthal quantum number (angular momentum)	ℓ	subshell	$(0 \leq \ell \leq n-1)$	for $n=3$: $\ell = 0, 1, 2$ (s, p, d)
magnetic quantum number, (projection of angular momentum)	m_ℓ	energy shift	$-\ell \leq m_\ell \leq \ell$	for $\ell=2$: $m_\ell = -2, -1, 0, 1, 2$
spin projection quantum number	m_s	spin	$-\frac{1}{2}, \frac{1}{2}$	for an electron, either: $-\frac{1}{2}, \frac{1}{2}$



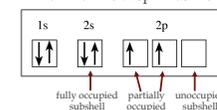
Wolfgang Pauli (1900-1958)

Pauli's exclusion principle:

- Each quantum state can be occupied by a single electron.
- Within an atom there cannot be two electrons for which all four quantum numbers are identical.

Hund principle:

- Order of filling up the quantum states.
- For a given electron configuration, the state with maximum total spin has the lowest energy.



Electron configuration of the C atom
s: "sharp", p: "principal", d: "determined"/"diffuse" (spectroscopic nomenclature)



Friedrich Hermann Hund (1896-1997)

THE SPIN QUANTUM NUMBER

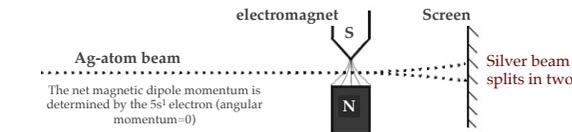
Stern-Gerlach experiment (1922)



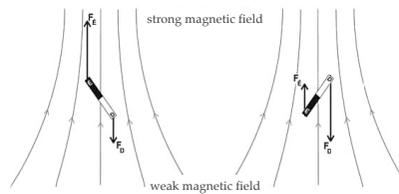
Otto Stern (1888-1969)



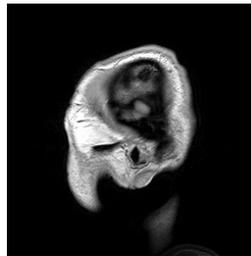
Walther Gerlach (1889-1979)



In an inhomogeneous magnetic field, in addition to torque, net force arises on the magnetic dipoles:



The spin magnetic moment may take on two values (+1/2, -1/2)

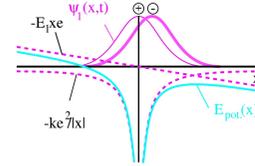


MRI

EFFECT OF EXTERNAL ELECTRIC FIELD ON THE BOUND ELECTRON

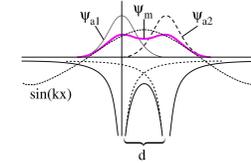
Weak external electric field (-E₁x):

- Ψ is deformed
- Atom becomes polarized



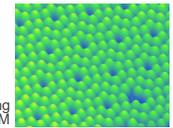
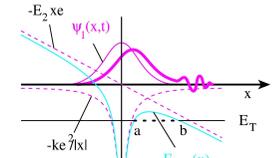
Upon the approach of another proton (nucleus):

- Intermediate Ψ is formed
- The electron belongs to both atoms
- formation of covalent bond



Strong external electric field (-E₂x):

- Ψ is deformed
- The electron may escape the atom without excitation
- Tunneling effect



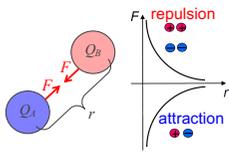
Scanning Tunneling Microscopy, STM

Si atoms

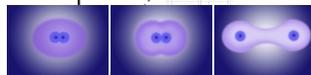
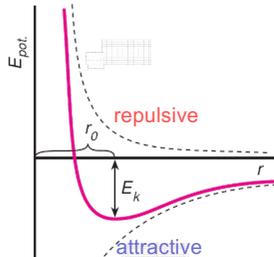
INTERACTIONS

Interaction type	Binding particle	Range (m)	Relative strength
gravitation	every particle	infinite ($\sim 1/r^2$)	10^{-40}
electrostatic (Coulomb)	charged particles	infinite ($\sim 1/r^2$)	10^{-2}
strong nuclear	nucleons	10^{-15}	1
weak nuclear	every particle	10^{-18}	10^{-13}

Coulomb-interaction



$$F_C \propto k \cdot \frac{Q_A \cdot Q_B}{r^2}$$



repulsion equilibrium attraction

$$E_{pot} \propto \begin{cases} E_{attraction} & \propto E_{repulsion} \\ \frac{A}{r^n} & \propto \frac{B}{r^m} \end{cases}$$

A, B: constants that depend on the interaction and the atoms
 n (attraction) < m (repulsion)

r_0 : binding distance
 E_k : binding energy

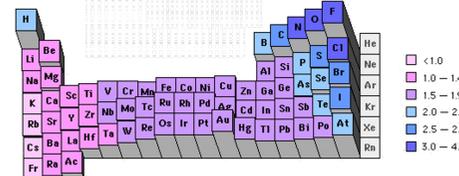
PRIMARY BONDS

intramolecular strong primary ↔ intermolecular weak secondary

- **covalent:** common electron state around the participating nuclei, strong: $E_b > 1\text{eV}$
- **metallic bond:** multi-atomic system, $E_b > 1\text{eV}$
- **ionic bond:** Coulomb-forces between ions, $E_b > 1\text{eV}$

type depends on electronegativity (EN)

EN: tendency of an atom to attract electrons



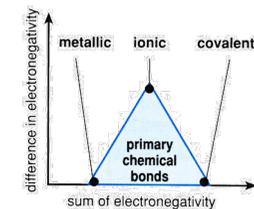
EN values according to Linus Pauling



Linus Pauling (1901-1994)

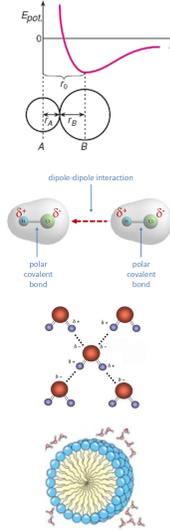
$$EN = |E_i| + |E_{ea}|$$

ionization energy electron affinity



SECONDARY BONDS

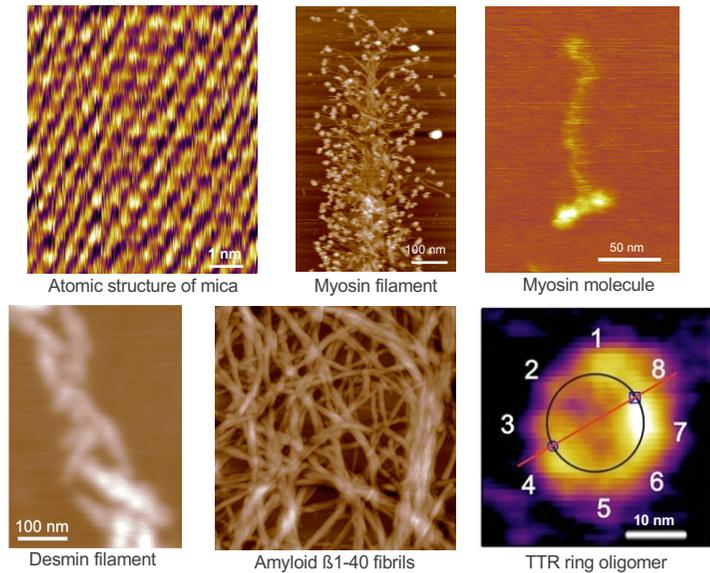
- Van der Waals:** between two apolar atoms (without permanent dipole moment) where a temporarily created dipole interacts with an apolar molecule or atom thus converting it into a dipole (induced dipole)
 - Van der Waals radius: $r_0=r_A+r_B$
 - Intermolecular or intramolecular
 - Important biological role: formation of organic structures
 - Weak: ($E_b \sim 0,02$ eV)
- Dipole-dipole interaction:** constant charge distribution is present in a (given part of a) molecule
 - partially (+) and (-) segments are held together by electrostatic interactions (Coulomb-forces)
 - intra-/intermolecular
 - weak interaction ($E_b = 0.003-0.02$ eV)
- H-bond:** H-atom interbridges two other atoms (F, O, N) of high electronegativity
 - $r \sim 0,23 - 0,35$ nm
 - $E \sim 0,2$ eV
- Hydrophobic interaction:** weak Van der Waals interaction ($E_b = 0.003 - 0.02$ eV), thermal motion ($kT \sim 0.025$ eV) could disrupt the system!
 - ordered water molecules exclude the apolar structures (contact surface can be minimized)



ATOMIC FORCE MICROSCOPY (AFM)

This block includes: 1) Portraits of Richard P. Feynman (1959), Gerd Binnig (Nobel-prize 1986), and Heinrich Rohrer (Nobel-prize 1986). 2) A diagram of AFM scanning showing a cantilever tip over a surface. 3) A graph of potential energy E_{pot} vs distance r with regions for 'contact' and 'non-contact or oscillating'. 4) A diagram of an oscillating driving signal and a detected signal. 5) Three AFM images: Height contrast, Amplitude contrast, and Phase contrast.

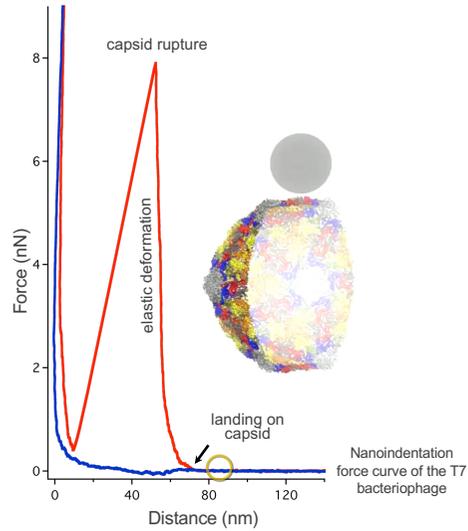
AFM IMAGES OF NANOSCALE STRUCTURES



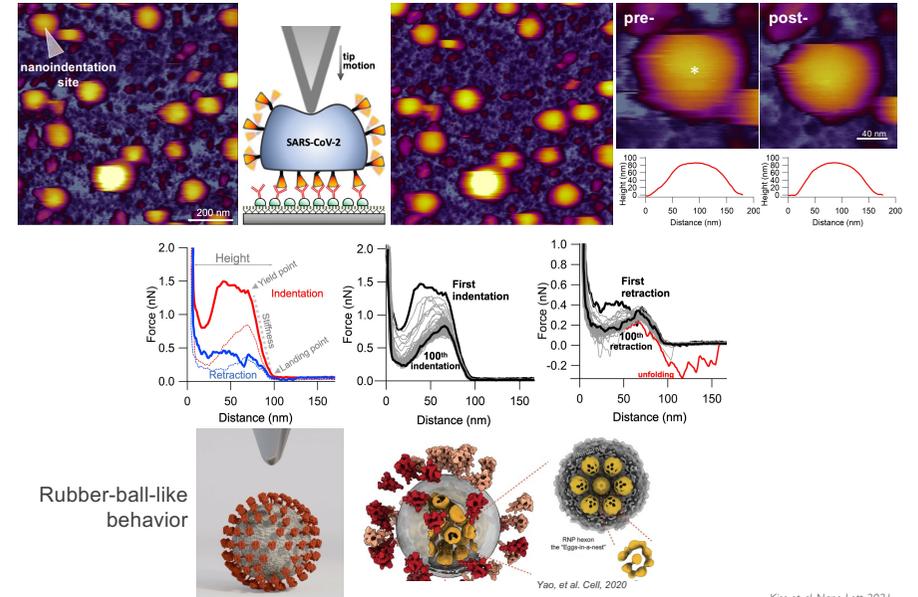
AFM IMAGE (AND SOUND...) OF THE CORONAVIRUS

This block includes: 1) Two AFM images of SARS-CoV-2 with 40 nm and 20 nm scale bars. 2) A schematic of the measurement setup showing a cantilever tip (stylus) moving over a SARS-CoV-2 particle on a surface, with labels for 'spike motion', 'apparent dynamic surface', and 'cantilever tip (stylus) movement'. 3) A histogram of virus height (nm) vs Frequency, comparing 'Native' (red bars) and 'Fixed' (grey bars) states. 4) A small image of a vinyl record player.

VIRUS MECHANICS EXPLORED WITH NANOINDENTATION



CORONAVIRUS NANOMECHANICS

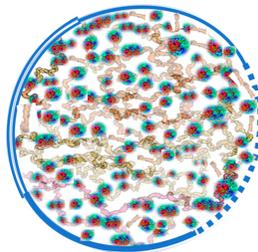
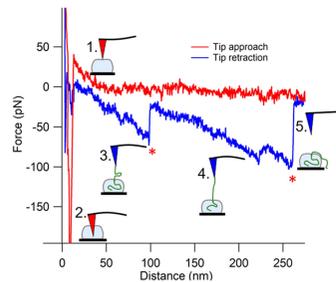
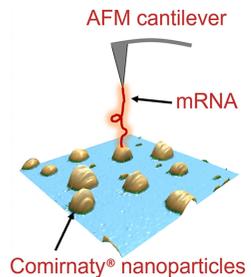


Kiss et al. Nano Lett 2021

NOBEL-PRIZE IN MEDICINE 2023

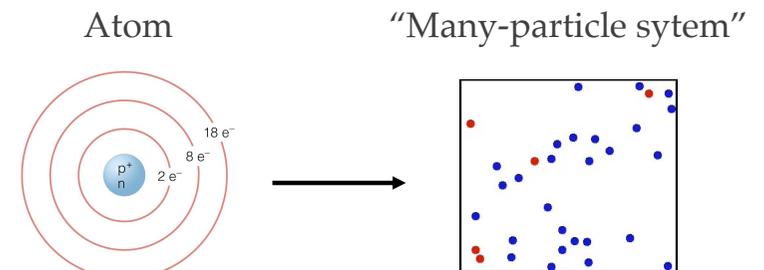


Drew Weissman and Katalin Karikó



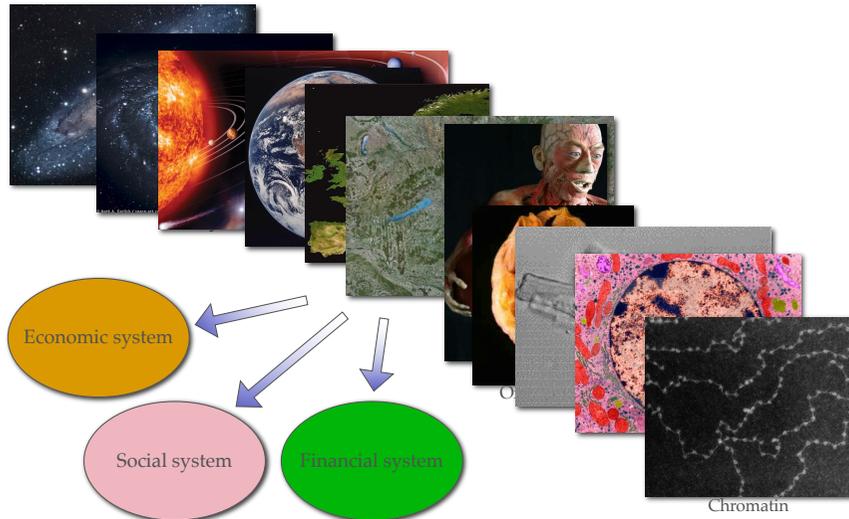
Szebeni et al. ACS Nano, 2023

FROM THE ATOM TO MANY-PARTICLE SYSTEMS



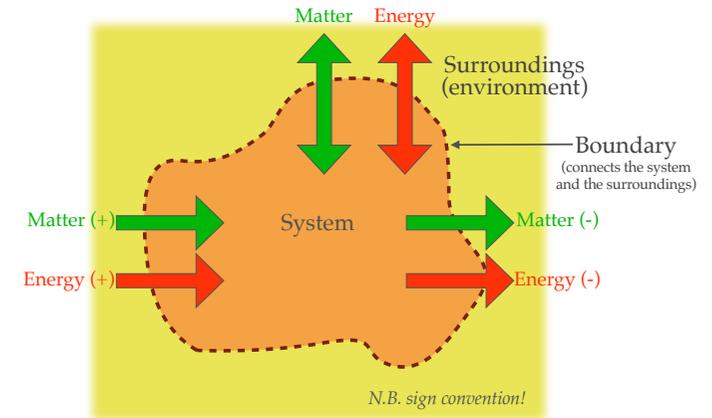
- What is a system?
- How many particles are "many"?
- What is the internal "structure"?
- How do particles respond to forces (caused by potential differences)?

WHAT IS A SYSTEM?



THE SYSTEM IS AN ABSTRACTION; IT INTERACTS WITH ITS SURROUNDINGS

Exchange of matter and energy ("processes") may take place across the boundary.

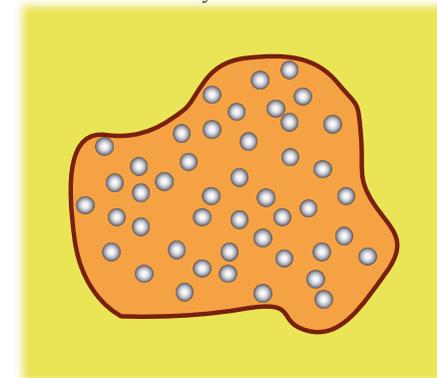


THERE ARE MANY TYPES OF SYSTEMS

THE SYSTEM MAY BE CHARACTERIZED

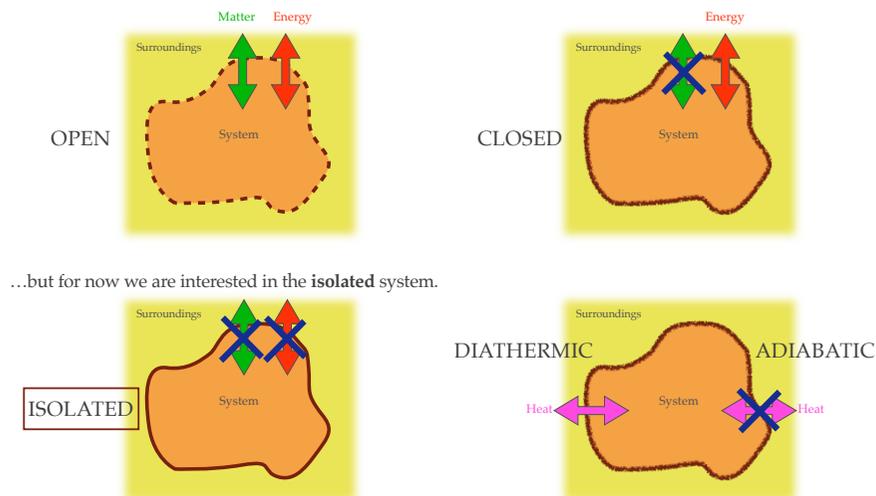
...macroscopically:

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



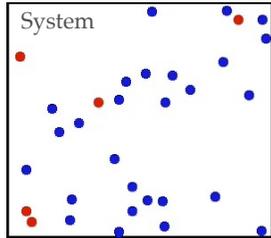
...but for now we are interested in the **isolated** system.

THE SYSTEM MAY BE CHARACTERIZED

...microscopically:

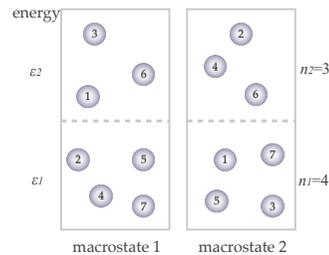
by describing the characteristics (e.g., energy) of each particle in the system

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").

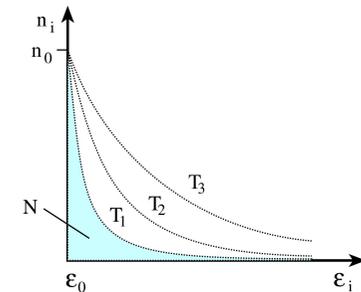
Note: the **macrostates** (1 and 2) are identical (number of particles at given energies are same), but their **microstates** (arrangement of actual particles) differ:



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

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

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:

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

q : elementary charge
 U : voltage between A and B

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



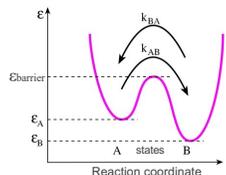
Walther Nernst (1864-1941)
Nobel-prize (1920)

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



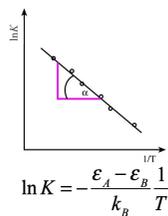
Svante Arrhenius (1859-1927)
Nobel-prize (1903)

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:

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



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

FEEDBACK



<https://feedback.semmelweis.hu/feedback/index.php?feedback-gr=KZJA3CSA2QIC48VC>