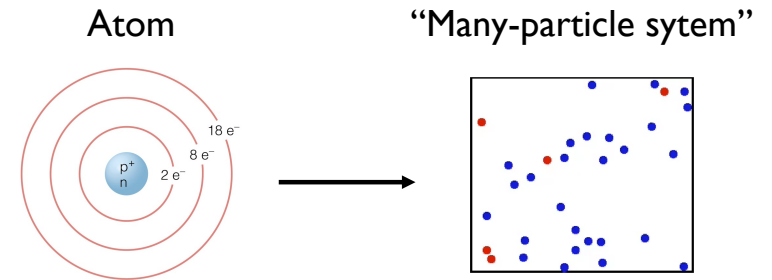


MANY-PARTICLE SYSTEMS THE BOLTZMANN- DISTRIBUTION

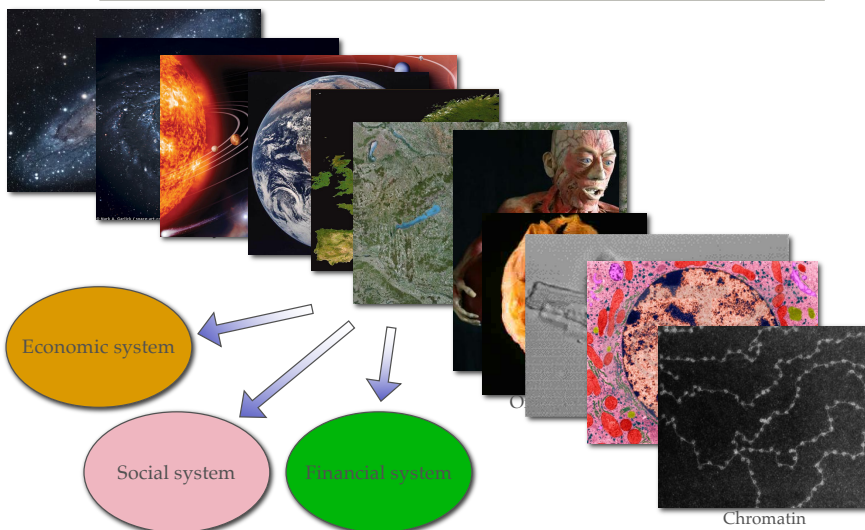
MIKLÓS KELLERMAYER

From the atom to many-particle systems



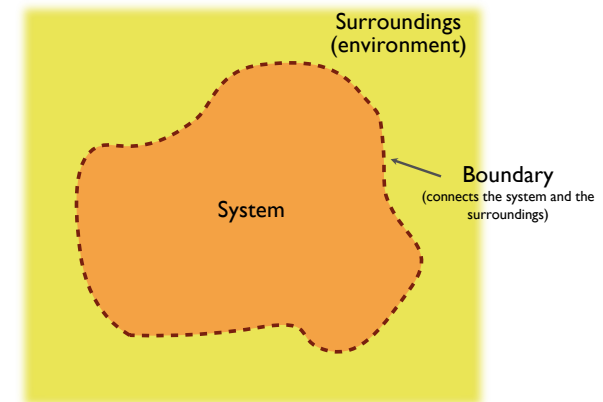
- What is a system?
- How many particles are “many”?
- What is the internal “structure”?
- How do particles respond to forces (caused by potential differences)?

What is a system?



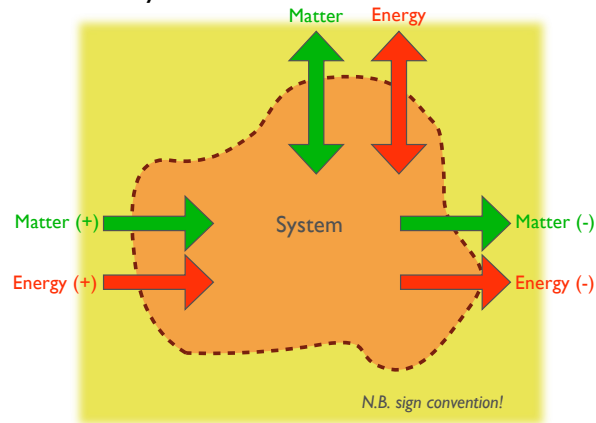
The system is an abstraction

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



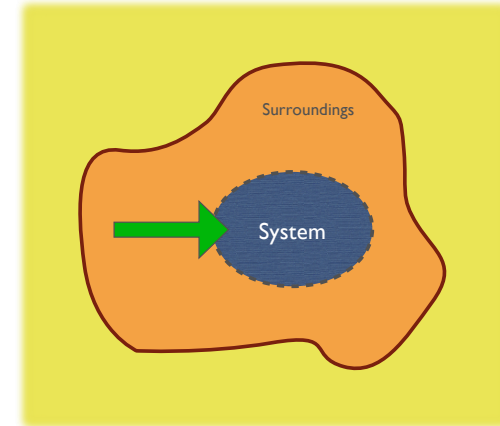
The system interacts with its surroundings

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

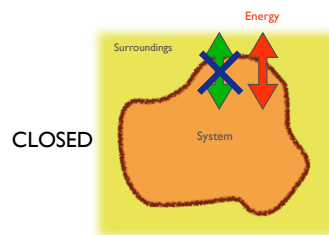
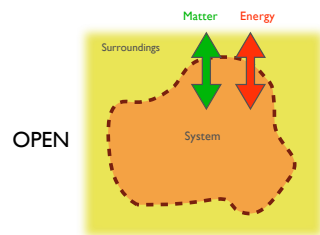


Defining the system bears consequences

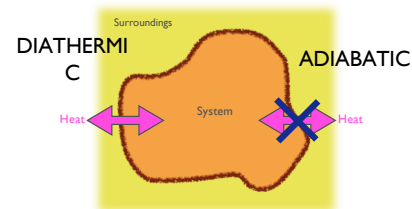
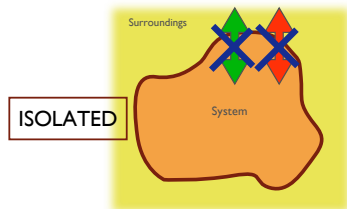
...for thermodynamic processes (see later)



There are many Types of systems



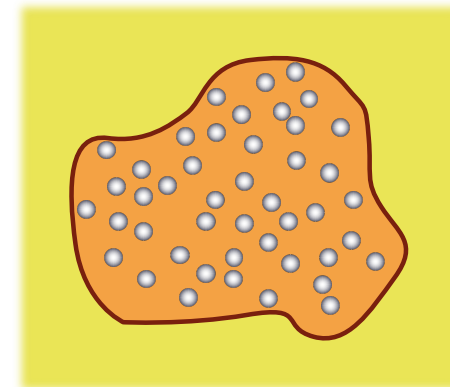
...but for now we are interested in the **isolated** system.



the system may be characterized

...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)



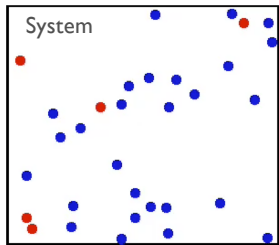
see universal gas law:
 $pV = NkT$
 k : Boltzmann's constant

the system may be characterized

...microscopically:

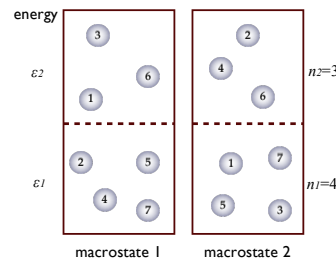
by describing the characteristics (e.g., energy) of each particle in the system

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

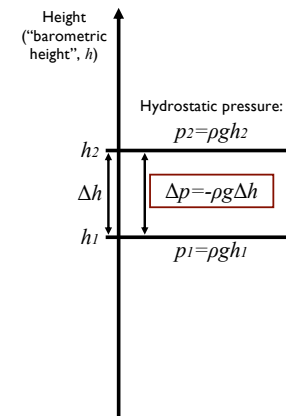


...but the average energy of every particle, for each degree of freedom, is $1/2kT$ ("equipartition theorem").

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 ($\rho \sim p$):

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

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

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

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

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

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

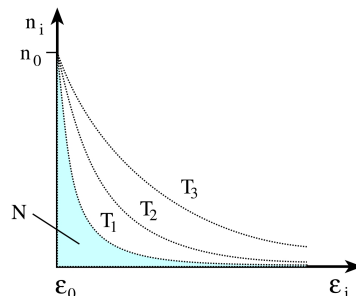
Considering the universal gas law ($pV = NkT$), the definition of density ($\rho = mN/V$), and that $\rho = \text{const} p$, "const" can be expressed as m/kT , hence:

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

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

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)

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.

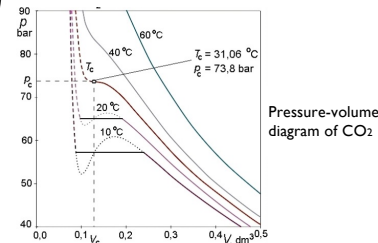
Consequence: pressure becomes reduced

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

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

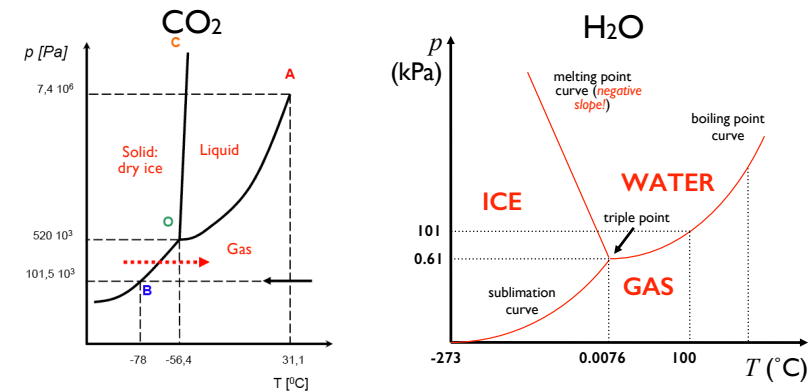
- Van der Waals isotherms:

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



Phase, phase transition

- Phases: regions of the material with identical chemical, but different physical properties
- Phase diagram: plot displaying the nature of phases as a function of thermodynamic variables (pressure, temperature)
- Phase curve: two phases are in equilibrium
- Area between phase curves: a single phase is present
- Intersection of phase curves: triple point



Feedback



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