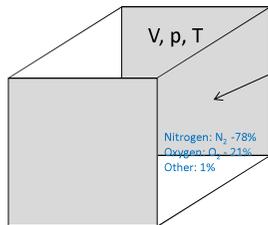


Describing many-particle systems

Prof. Judit Fidy
2018, October 17

- particle: - atom, atomic group
 - molecule
 - molecular complexes, macromolecules
 - etc.
- many: 6×10^{23}

Simple example



Air molecules in the room...
What do the particles „do“, when the macroscopic parameters are constant: V, p, T ?

Macrostate:

Described by parameters that characterize the whole system (p, V, T, N)

Microstate:

Given by a set of the parameters of all individual distinguishable particles in the system (position, velocity etc. for each)

One given macrostate can be realized by numerous varieties of microstates.



Ludwig Eduard Boltzmann
1844-1906, Austrian physicist



$\Omega \Leftrightarrow W$
Boltzmann's grave in Vienna

II. Law of Thermodynamics: in isolated systems, spontaneous processes driving toward equilibrium are of **- increasing Entropy**

No heat exchange
No particle exchange of **- increasing „probability“ ?**

„Equilibrium“ state: of highest **Entropy** or highest **„probability“**

L.E. Boltzmann defines the absolute value of Entropy „S“

Definition of „thermodynamic“ probability of a macrostate = number of ways how microstates can produce the same macrostate: Ω

$$S = k \ln \Omega$$

$k = 1.38 \times 10^{-23} \text{ J K}^{-1}$
Boltzmann constant

„ln“ logarithmus naturalis – e-based logarithm
„e“ natural base number: Euler-number / Napier constant
 $e = 2,718\ 281\ 828\ 459\ 045\ 235\ 360\ 287\ 471\ 35\dots$
 $e^{\ln \Omega} = \Omega \quad \ln x = \frac{\log x}{\log e} \quad \left(1 + \frac{1}{n}\right)^n \xrightarrow{n \rightarrow \infty} e$

Statistical definition of the absolute value of Entropy!

(The **change** of entropy in a reversible process is a measurable quantity! $\Delta S_{rev} = \frac{Q}{T}$)

III. Law of Thermodynamics

The **Entropy** of a chemically pure (of one component) crystalline (totally ordered) system is **zero at T=0 K**.

Direct consequence of Boltzmann's statistical definition of the Entropy:

$$S = k \ln \Omega$$

There is only **one** kind of microstate that results in a totally ordered, chemically pure system, and total order exists only at T=0 →

$$\text{if } \Omega = 1 \rightarrow S = 0 \quad (e^{\ln \Omega} = \Omega \quad \Omega = 1 \quad \ln \Omega = 0)$$

Boltzmann's distribution function

The system:

N distinguishable independent particles at thermal equilibrium at non-zero temperature, with E total energy and N total number of particles

ϵ_i : energy of one particle in the system (potential and kinetic)

n_j : number of particles with ϵ_j energy – **population** of state ϵ_j

$$N = \sum_j n_j \quad E = \sum_j n_j \epsilon_j$$

Macrostate: given by the **number of particles at each energy level:**

$$\{n_1, n_2, n_3, \dots, n_k, \dots\}$$

Microstate: **which** of the particles are at the individual levels

Boltzmann describes the probability of finding particles with ϵ_j energy in the system

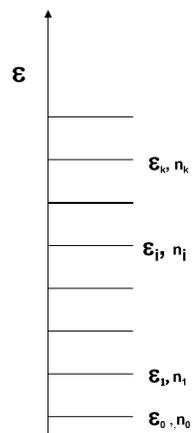
$$p(\epsilon_j) = \frac{n_j}{N} = \frac{1}{A} e^{-\frac{\epsilon_j}{kT}} \quad A = \sum_i e^{-\frac{\epsilon_i}{kT}} \text{ partition function}$$

Textbook p. 52 - 57

Boltzmann distribution function

yields the number of particles (n_j) with ϵ_j energy in a system of $E = \sum_j n_j \epsilon_j$ total energy.

In practice applications the relative probability is more interesting



$$\frac{p(\epsilon_k)}{p(\epsilon_j)} = \frac{\frac{n_k}{N}}{\frac{n_j}{N}} = \frac{1}{A} e^{-\frac{\epsilon_k}{kT}} \cdot \frac{A}{1} e^{\frac{\epsilon_j}{kT}} = \frac{n_k}{n_j} e^{-\frac{\epsilon_k - \epsilon_j}{kT}}$$

$$\frac{n_k}{n_j} = e^{-\frac{\epsilon_k - \epsilon_j}{kT}} = e^{-\frac{\Delta \epsilon}{kT}}$$

Boltzmann factor

Valid for any (j,k) combinations of energy levels

There is a strict order in the distribution of particles on the energy levels depending on the temperature

Textbook p. 52 - 57

Understanding the Boltzmann distribution function

$$E = \sum_j n_j \epsilon_j \quad N = \sum_j n_j \quad \frac{n_k}{n_j} = e^{-\frac{\epsilon_k - \epsilon_j}{kT}} = e^{-\frac{\Delta \epsilon}{kT}}$$

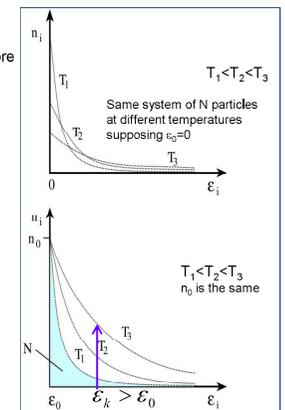
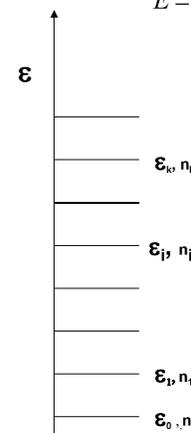
Populations of energy states

1. As the temperature is lowered, more and more particles are in the energy minimum state at T=0 all particles are there: $n_0=N, n_k=0$

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

2. At a given $\epsilon_k > \epsilon_0$ energy level, the relative population related to the energy minimum increases with the temperature

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



The B. distribution is in agreement with the concept of driving toward energy minimum

The relation of the equilibrium **macrostate** and the **microstates** in ideal gas.
Kinetic gas theory – Maxwell's – distribution function

Maxwell (1859) and Boltzmann (1868) describe the velocity distribution independently from each other, Gibbs completes the description with statistical physics based on kinetic gas theory (1902)

$$E_{total} = N \frac{1}{2} m \langle v^2 \rangle_{average} \quad \epsilon_1 = \frac{1}{2} m v_1^2 \quad \frac{1}{2} m \langle v^2 \rangle_{average} = \frac{3}{2} kT$$

$y(v) \Delta v$ – probability of finding particles with a velocity „v“ of an interval v to $v + \Delta v$ in the system (probability density function)

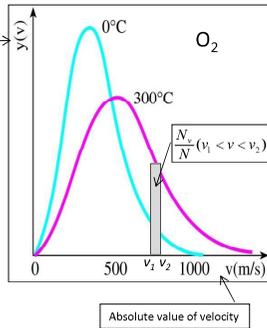
$$y(v) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

Graphical representation

$$\frac{N_v}{N} (v_1 < v < v_2) = y(\bar{v}_{1,2}) * (v_2 - v_1)$$

Relativ population of velocity v given by the formula

The velocity distribution function can be derived from Boltzmann's distribution as a special case – see t.b. p. 59
Maxwell-Boltzmann velocity distribution



James Clerk Maxwell
1831 – 1879



Josiah Willard Gibbs
1839 – 1903

Ideal gas - Real gas

Corrections: - the **volume** of the particles (b) is not negligible

- the **pressure** is decreased due to the non negligible attractive interaction between the particles

Maintained: the kinetic energy is related to the temperature

Internal energy $E \rightarrow E_{total} = E_{kin} + E_{interaction}$

Volume $V \rightarrow V - Nb \rightarrow$ gas Law $\rightarrow p(V - Nb) = NkT \rightarrow p = NkT / (V - Nb)$?

But pressure is also decreased $p \rightarrow NkT / (V - Nb) - a(N/V)^2 = p$
 characterizes the strength of interaction

Van der Waals – equation:
 one possible approach

$$\left(p + a \frac{N^2}{V^2} \right) (V - Nb) = NkT$$

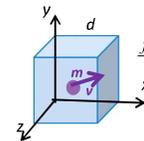
The ideal gas description is usually valid at higher temperatures

Repetition of high school knowledge

The model system of kinetic gas theory: **ideal gas**

1. Large number of point-like, independent particles in motion
2. The motion is arbitrary in direction and velocity, but obeys Newton's II. Law
3. The particles collide elastically with the wall of the container and with each other regulated by the conservation of energy and momentum
4. They interact with each other only in the instant of collision (short term), otherwise there is no interaction
5. The gas is chemically pure: the particles are identical

Concepts of kinetic gas theory



1. Definition of pressure p

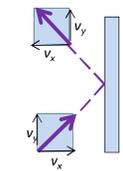
$$\text{force acting on a surface} / \text{area of surface} = \text{pressure} \left[\frac{N}{m^2} \right] = \frac{\sum -F_i}{d^2} = \frac{m \sum v_{ix}^2}{d^3} = \frac{m N \overline{v_x^2}}{V} = \frac{2}{3} \frac{N}{V} \left(\frac{1}{2} m \overline{v^2} \right) = p$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3} \overline{v^2}$$

Pressure is the function particle density and average kinetic energy

Elastic collision with the wall



$$F(\text{force}) = \frac{\Delta(m * v)}{\Delta t} = \frac{-m * v_x - (m * v_x)}{\Delta t} = \frac{-2m v_x}{2d / v_x} = -\frac{m v_x^2}{d}$$

Force acting on one particle during one collision. The force acting on the wall is (-1)-times this force. Newton II. and conservation Laws.

Kinetic Gas Theory + General Gas Law

$$pV = NkT = \frac{2}{3} N \left(\frac{1}{2} m \overline{v^2} \right)$$

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} kT$$

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} kT$$

3: degree of freedom

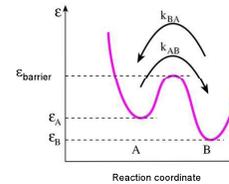
2. Definition of gas temperature: T is directly proportional to the average kinetic energy of the particles
3. Theory of equipartition

Boltzmann distribution - occurrence and validity in a wide range of phenomena - 5 examples

From textbook: 1. Thermal emission of electrons

2. Nernst equation

3. Temperature dependence of the rate of chemical reactions



Reaction: $A \rightleftharpoons B$

The k_{AB} and k_{BA} rates are proportional to the number of reactants which are of high enough energy to overcome the barrier

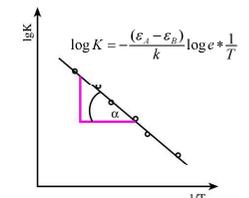
$$k_{AB} = \text{const} \times e^{-\frac{E_{barrier} - E_A}{kT}}$$

$$k_{BA} = \text{const} \times e^{-\frac{E_{barrier} - E_B}{kT}}$$

K: equilibrium reaction constant

$$K = \frac{k_{BA}}{k_{AB}} = e^{-\frac{E_B - E_A}{kT}}$$

Arrhenius plot



Experimental determination of the energy of activation

4. Barometric formula

Density of air in the atmosphere decreases with the altitude (h) by the formula:

$$\frac{\rho(h)}{\rho(0)} = e^{-\frac{mgh}{kT}}$$

Interpretation: the formula is direct consequence of Boltzmann distribution

$$\frac{n_h}{n_0} = e^{-\frac{\epsilon_h - \epsilon_0}{kT}} = e^{-\frac{mgh}{kT}}$$

m average mass of particles in the air
 g gravitational acceleration

$$\rho = \frac{n * m}{V}; \quad \epsilon = \epsilon_{pot} + \langle \epsilon_{kin} \rangle; \quad \langle \epsilon_{kin}(h) \rangle \approx \langle \epsilon_{kin}(h=0) \rangle$$

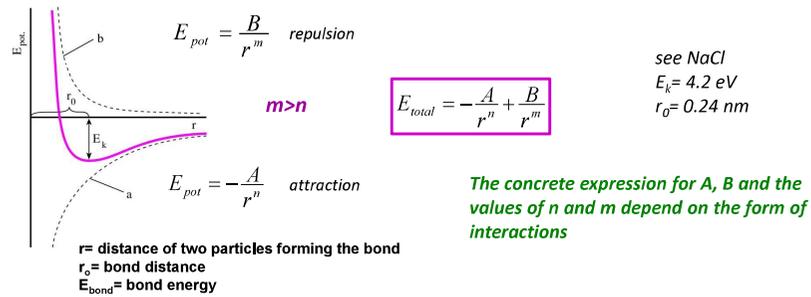
The change of T with altitude is neglected

5. Structural consequences of B. distribution in the classes of materials : gas – liquids – solids (crystals)

Concept of „structural order“: the interaction of particles within the system determines the spacial coordinates (relative position and orientation) of the particles.

- Lack of interaction → **disordered structure**: ideal gas
- Only a small fraction of particles are bound by interaction → **short range order**
- A large proportion of particles are in well defined position → **long range order**

Interactions lead to ordering → **bond** formation



Thank you for your attention!

