

$\sim 10^{22}$ molecules
Huge number of available states

1 litre
of gas

V, p, T

Mechanical properties of molecules

Position x_i, y_i, z_i
Momentum p_{xi}, p_{yi}, p_{zi}
Mass m_i

Kinetic energy E_{ki}
Potential energy U_{ij}

Thermodynamical properties of the system

Temperature T
Pressure p
Mass m

Entropy S
Internal energy U
Gibbsova energie G

STATISTICAL
MECHANICS

Calculates thermodynamical properties of the macroscopic system from the properties of individual molecules (structure of molecules, inter-molecular interactions).

Bridge between “classical” thermodynamics and molecular physics

Classical thermodynamics makes no assumption about the structure of the matter (existence of atoms/molecules is not required !).

Macroscopic (TD) properties must be determined by microscopic (molecular) properties

Example:

1 mL of Ar
(T, p)
 $\sim 10^{19}$ atoms

Quantum mechanical solution

- it is possible
- numerically too demanding (impossible)
- it is impractical (probabilistic character)

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

non-interacting
vs.
interacting

Classical description

- $\{q_i, p_i, t_0\}$ – complete system description
- computationally too demanding

\Rightarrow STATISTICAL METHODS

Limiting to typical/average behavior - getting a true average is still impractical !

Instead of average we should consider “only” THE MOST PROBABLE BEHAVIOR

\rightarrow It can be used only for sufficiently large system

STATISTICAL THEORMODYNAMICS

- *Logical consequence of atomistic theory*

1859 – Maxwell distribution law

1869 – Mendělejev

1871 – Boltzmann – generalization: Maxwell-Boltzmann distribution
- relationship between entropy and probability

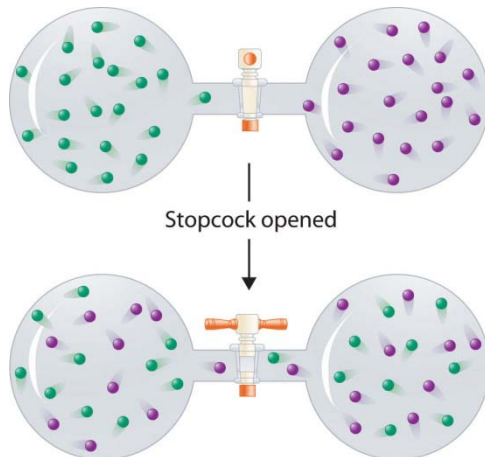
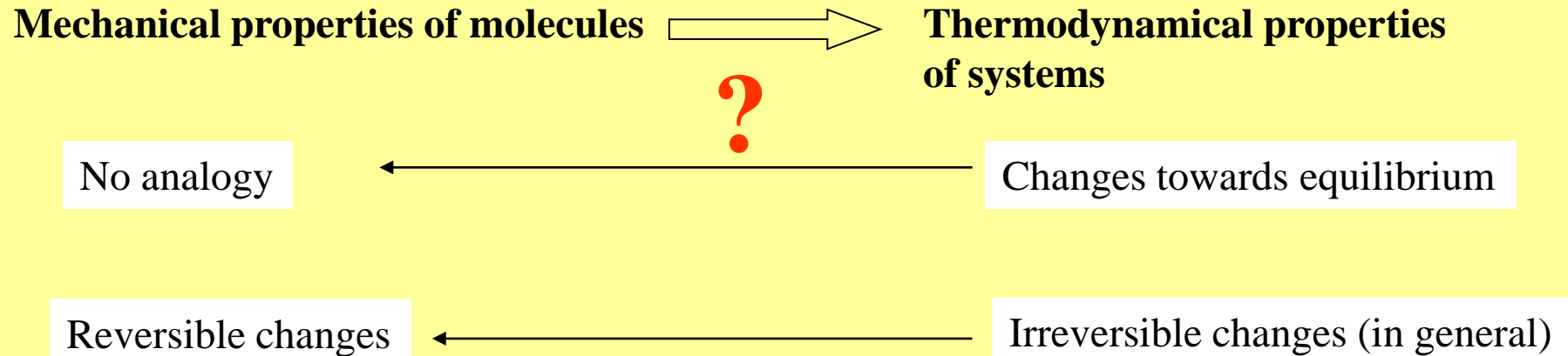
1895 – conference in Lübeck

1896 – Boltzmann $\Delta S = k \cdot \ln(W_2/W_1)$

1900 - Boltzmann, Gibbs – formulation of statistical theormodynamics



We have to give up on the detail description of mechanical variables of each molecule.
INSTEAD – analysis of possible values – finding the most probable values



System: spontaneous – irreversible – process
Individual molecules: they can always go back to its original position.

Ideal gas (no interactions between molecules):
Driving force for mixing must be entropy –
- Increase of entropy doesn't depend on individual molecules \Rightarrow the property of the system.

Entropy

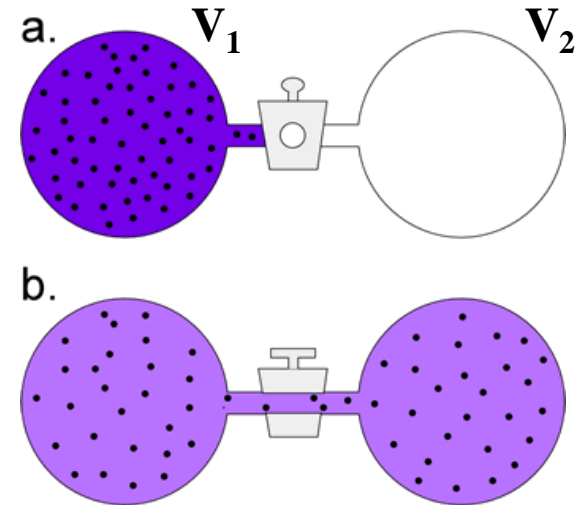
S ... **additive**

W ... Number of distinguishable states of the system ... **multiplicative**

$$\mathbf{S = a \ln W + b}$$

Ideal gas expansion from V_1 to V_2

$$\Delta S = S_2 - S_1 = nR \ln \frac{V_1 + V_2}{V_1} = k \cdot \ln \left(\frac{V_1}{V_1 + V_2} \right)^{-N}$$



All distribution of N molecules between V_1 and V_2 have the same energy

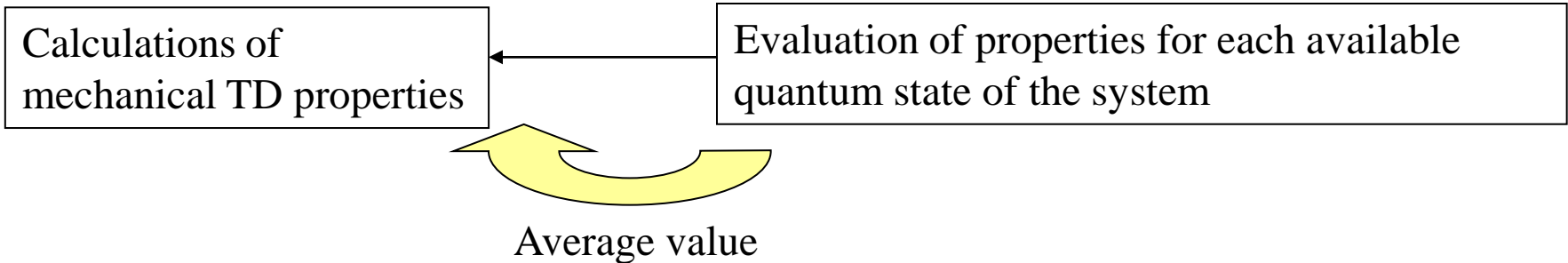
=> Entropy driven process – depends on number of possible states (probability – with respect to all possible states)

$$\Delta S = S_2 - S_1 = a \ln \frac{W_2}{W_1} = a \cdot \ln \left(\frac{V_1}{V_1 + V_2} \right)^{-N}$$

$$\Delta S = S_2 - S_1 = k \ln \frac{W_2}{W_1}$$

Boltzmann-Gibbs formulation of statistical thermodynamics (including quantum-mechanical description of the system)

System is in one of the available quantum states
(*originally: system is characterized by a point in a phase space*)



Mechanical vs. non-mechanical properties

Ensemble of systems

- Mental construction of large number of systems characterized by the same TD restrictions.

Microcanonical ensemble (N, V, E)

N, V E	N, V E	N, V E
N, V E	N, V E	N, V E
N, V E	N, V E	N, V E

Impermeable
adiabatic walls –
heat isolation

Rigid diathermic walls
- Allows for the heat transfer
- Molecules can go through

Canonical ensemble (N, V, T)

N, V T	N, V T	N, V T
N, V T	N, V T	N, V T
N, V T	N, V T	N, V T

POSTULATE ①. Ensemble average corresponds to TD average.

Mean value of arbitrary mechanical property M (in a real system it would be obtained by time averaging over the sufficiently long period of time) is equal to the mean value obtained for the ensemble; systems of this ensemble must reproduce TD state of real system. (Strictly speaking it holds only for $N \rightarrow \infty$)

POSTULATE ②. Principle of equal a priori probabilities.

For the ensemble representing isolated TD system (microcanonical ensemble) all the ensemble elements are distributed with the equal probability among all quantum states available for N, V, E .

Macroscopic system (N, V, E)

=> Microcanonical ensemble (N, V, E) consisting of \mathbb{A} systems

Available E_j are determined by N (number of molecules and their molecular properties) and by V

N, V E	N, V E	N, V E
N, V E	N, V E	N, V E
N, V E	N, V E	N, V E

Classical description: state of the system = point in the phase space

Ensemble – set of points in the phase space

Quantum mechanics: available/allowed states (energies)

\Rightarrow $E_j, \Omega(E_j)$

Individual systems – equivalent at the TD level
– different at the molecular level


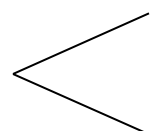
Degeneration – number of realization of system with the energy E_j

Postulate ② - each of $\Omega(E_j)$ states of the system is equally represented in the ensemble

=> $\mathbb{A} = n\Omega(E)$

\mathbb{A} can be arbitrarily large

Postulates ① a ② - ensemble average of mechanical properties ~ corresponding TD value

  Connection between molecular and macroscopic properties.
Totally impractical

Simple application – Boltzmann distribution law

Distribution of large number of molecules among available energy levels (regardless other characteristics)

N totally independent molecules (1 L of gas)

- ideal gas – *with respect to kinetic energy the potential energy can be neglected*
- equilibrium conditions
 - direct molecular collisions
 - collisions with the container wall

⇒ Canonical ensemble where systems are individual molecules

$N (=1), V, T$

Molecules are in the same container – same temperature

Each molecule can be in one of the i states characterized by ε_i

$\varepsilon_i \rightarrow N_i$... number of systems (molecules) with energy ε_i

Represents one member of microcanonical ensemble

V, N is known, E is determined by the temperature T

①+② mean values of system properties

Mean number of molecules N_i in the state i (energy ε_i) must be determined

⇒ *distribution* $\{N_i, \varepsilon_i\}$

N, V T	N, V T	N, V T
N, V T	N, V T	N, V T
N, V T	N, V T	N, V T

<table><tr><td>ε_1</td><td>ε_2</td><td>ε_3</td><td>ε_4</td></tr><tr><td>ε_1</td><td>ε_2</td><td>ε_3</td><td>ε_4</td></tr><tr><td>ε_1</td><td>ε_2</td><td>ε_3</td><td>ε_4</td></tr><tr><td>ε_1</td><td>ε_2</td><td>ε_3</td><td>ε_4</td></tr></table>	ε_1	ε_2	ε_3	ε_4	ε_1	ε_2	ε_3	ε_4	ε_1	ε_2	ε_3	ε_4	ε_1	ε_2	ε_3	ε_4	N, V E	N, V E
ε_1	ε_2	ε_3	ε_4															
ε_1	ε_2	ε_3	ε_4															
ε_1	ε_2	ε_3	ε_4															
ε_1	ε_2	ε_3	ε_4															
N, V E	N, V E	N, V E																
N, V E	N, V E	N, V E																

Schrödinger equation for particle in the 3-D box:

$$\psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi}{L_z} z\right)$$

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

1 L argon: m = 39.95 a.u.
 L_i = 0.1 m

$$E_{n_x, n_y, n_z} = 2 \times 10^{-1} \left(n_x^2 + n_y^2 + n_z^2 \right) \quad [\text{J.mol}^{-1}]$$

E(J)	nx	ny	nz	Lx	E(J/mol)
3.31E-39	1	0	0	0.1	1.99E-15
9.92E-39	1	1	1	0.1	5.97E-15
1.98E-38	2	1	1	0.1	1.19E-14
9.92E-37	10	10	10	0.1	5.97E-13
9.92E-35	100	100	100	0.1	5.97E-11

distribution of $\{N_i, \varepsilon_i\}$ – boundary conditions

$$\sum_i N_i = N$$

$$\sum_i \varepsilon_i N_i = E$$

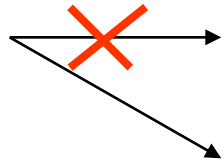
↓
Permutation within one energy level do not lead to a new distribution

$$W_n = \frac{N!}{N_1! N_2! \dots} = \frac{N!}{\prod_i N_i!}$$

$$W = \sum_n W_n = \sum_n \frac{N!}{\prod_i N_i!}$$

Total number of distinguishable states

Mean value of N_i



Averaging over all distributions

Using just N_i for the most probable distribution W_n

=> Search for the W_n maxima respecting the additional conditions

$$\delta W_n = 0$$

$$\delta \ln W_n = 0$$

$$W_n = \frac{N!}{\prod_i N_i!}$$

$$\ln W_n = \ln N! - \sum_i \ln N_i!$$

$$\sum_i \delta \ln N_i! = 0$$

Stirling formula: $\ln N! = N \ln N - N$

$$\delta \sum_i N_i \ln N_i - \delta \sum_i N_i = 0$$

$$\sum_i \ln N_i \delta N_i = 0$$

$$\sum_i N_i = N$$

$$\sum_i \delta N_i = 0$$

$$\sum_i \varepsilon_i N_i = E$$

$$\sum_i \varepsilon_i \delta N_i = 0$$

$$\sum_i \ln N_i \delta N_i + \sum_i \alpha \delta N_i + \sum_i \beta \varepsilon_i \delta N_i = 0$$

Independent variation of δN_i

$$\alpha + \beta \varepsilon_i + \ln N_i = 0$$

$$N_i = e^{-\alpha} e^{-\beta \varepsilon_i}$$

$$\sum_i N_i = N$$

$$N = e^{-\alpha} \sum_i e^{-\beta \varepsilon_i}$$

$$\frac{N_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}}$$

α

β

Can be determined by calculations of mean value of known molecular property of ideal gas:

=> Kinetic energy for one degree of freedom

$$\bar{\varepsilon} = \frac{1}{2} kT$$

$$\bar{\varepsilon} = \frac{\sum_i \varepsilon_i N_i}{\sum_i N_i} = \frac{\sum_i \varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}}$$

$$\varepsilon_i = \frac{p_{xi}^2}{2m}$$

$$\bar{\varepsilon} = \frac{\sum_i \frac{p_{xi}^2}{2m} e^{-\beta \frac{p_{xi}^2}{2m}}}{\sum_i e^{-\beta \frac{p_{xi}^2}{2m}}}$$

$$\bar{\varepsilon} = \frac{\int_{-\infty}^{+\infty} p_x^2 e^{-\beta \frac{p_x^2}{2m}} dp_x}{2m \int_{-\infty}^{+\infty} e^{-\beta \frac{p_x^2}{2m}} dp_x}$$

$$\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

$$\int_{-\infty}^{+\infty} x^2 e^{-ax^2} dx = \sqrt{\frac{\pi}{a^3}}$$

$$\bar{\varepsilon} = \frac{1}{2\beta}$$