Partition function ⟵ $\{E_j(N,V)\}$

From the Schrödinger eqution solution for N-particle system

Simplification (?)

$$H = \sum H_i \longrightarrow E = \sum E_i \longrightarrow \Psi = \prod \Psi_i$$

BOSONS – no restriction for the state occupation
FERMIONs – no particles can be in the same state

Examples:

Gas (low pressure) => *inter-molecular interactions neglected*
Polyatomic molecules – *separation of Hamiltonin*

1. **System of distinguishable particles**

$$H = \sum_i H_i \longrightarrow \left\{ \varepsilon_j^a \right\} \qquad \text{Energy level } j \text{ of particle } a.$$

$$Q(N,V,T) = \sum_j e^{-E_j(N,V)/kT} = \sum_{i,j,k,...} e^{-(\varepsilon_i^a + \varepsilon_j^b + \varepsilon_k^c + ...)/kT} = \sum_i e^{-\varepsilon_i^a/kT} \sum_j e^{-\varepsilon_j^b/kT} \sum_k e^{-\varepsilon_k^c/kT} \cdots = q_a q_b q_c \cdots$$

Molecular partition function $\quad q_x(V,T) = \sum_i e^{-\varepsilon_i^x/kT}$

$$Q(N,V,T) = q(V,T)^N$$

Independent
Distinguishable

For the same (distinguishble particles – allowed energy levels are the same:
=> Manybody probllem is reduced to single-particle terms
Example:

crystal

molecular partition function $\qquad q_{molecule} = q_{tr} q_{rot} q_{vib} q_{el}$
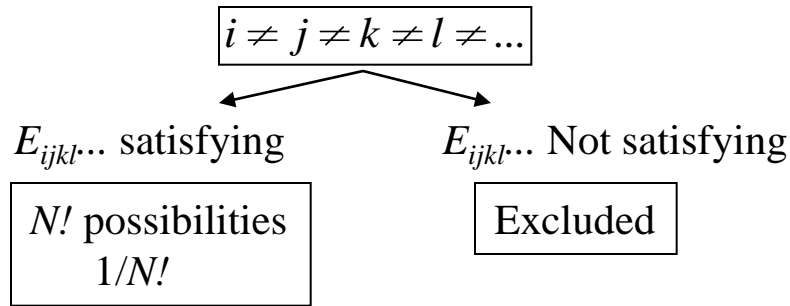
- additional simplifications

2. System of indistinguishable particles

$$E_{ijkl...} = \varepsilon_i + \varepsilon_j + \varepsilon_k + \varepsilon_l + \cdots \qquad \longleftarrow \qquad \{\varepsilon_j\}$$
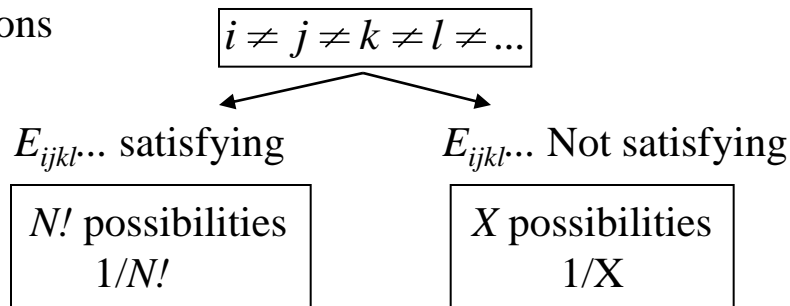
Energetická hladina j částice.

$$Q(N,V,T) = \sum_{i,j,k,l,...} e^{-(\varepsilon_i+\varepsilon_j+\varepsilon_k+\varepsilon_l+\cdots)/kT}$$

Summation indeces $i, j, k, ...$ are dependent
– summation cannot be broken into individual terms

Fermions: two fermions cannot be in the same (energy) state

$$i \ne j \ne k \ne l \ne ...$$

$E_{ijkl}...$ satisfying

N! possibilities
1/N!

$E_{ijkl}...$ Not satisfying

Excluded

Bosons: no restrictions

$$i \ne j \ne k \ne l \ne ...$$

$E_{ijkl}...$ satisfying

N! possibilities
1/N!

$E_{ijkl}...$ Not satisfying

X possibilities
1/X

Terms with two (or mor) indeces being equal are problematic!

$$\sum_{i,j,k,l,...} e^{-(\varepsilon_i+\varepsilon_j+\varepsilon_k+\varepsilon_l+\cdots)/kT}$$

Cannot be simplified!

Aproximative solution

If the number of allowed states is significantly larger than the number of praticles ➜ small probability that 2 (or more) particles will be at the same energy state. **Neglecting such situation**.

$$Q(N,V,T) = \frac{q^N}{N!}$$

Reduction of N-particla problem for   Indistinguishable particles

$$q(V,T) = \sum_i e^{-\varepsilon_i / kT}$$

Justification – particle in 3-D box
-Number of quantum states with energy $\leq \varepsilon$

$$\Phi(\varepsilon) = \frac{\pi}{6}\left(\frac{8ma^2\varepsilon}{h^2}\right)^{3/2}$$

$$m = 10^{-22}\,g$$
$$a = 10\,cm$$
$$T = 300^o\,K$$

$$\Phi(\varepsilon) \sim 10^{30}$$

Requirement of $\Phi(\varepsilon) \gg N$
In mjority of cases this is true:

$$\varepsilon = \frac{3}{2}kT$$

$$\frac{\pi}{6}\left(\frac{12mkT}{h^2}\right)^{3/2} \gg \frac{N}{V}$$

This holds in particular for large T, low density and heavy particles
BOLTZMANN STATISTICS

Problematic for light particles at low temperature

Table 4.1 – pge 72

Table 4–1. **The quantity** $(6N/\pi V)(h^2/12mkT)^{3/2}$ **for a number of simple systems***

	$T\,(°\text{K})$	$\dfrac{6N}{\pi V}\left(\dfrac{h^2}{12mkT}\right)^{3/2}$
liquid helium	4	1.6
gaseous helium	4	0.11
gaseous helium	20	2.0×10^{-3}
gaseous helium	100	3.5×10^{-5}
liquid neon	27	1.1×10^{-2}
gaseous neon	27	8.2×10^{-5}
gaseous neon	100	3.1×10^{-6}
liquid argon	86	5.1×10^{-4}
gaseous argon	86	1.6×10^{-6}
liquid krypton	127	5.4×10^{-5}
gaseous krypton	127	2.0×10^{-7}
electrons in metals (sodium)	300	1465

* This quantity must be much less than unity for Eq. (4–10) to be valid. The temperatures associated with the liquid states are the normal boiling points [*cf.* Eq. (4–11)].

BOLTZMANN STATISTICS

Approximation − holds better for higher temperatures

$$\overline{E} = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$Q(N,V,T) = \frac{q^N}{N!}$$

$$q(V,T) = \sum_i e^{-\varepsilon_i / kT}$$

$$\overline{E} = N \sum_j \varepsilon_j \frac{e^{-\varepsilon_j / kT}}{q} = N\overline{\varepsilon}$$

$\overline{\varepsilon}$ - Average energy of a particle

$$\pi_j = \frac{e^{-\varepsilon_j / kT}}{q}$$

Probabilisty that the molecule is in the state with the energy ε_j

The same result as obtained by Boltzmann

Gibbs approach is more rigorous

$$\delta W_n = 0$$

$$\delta \ln W_n = 0$$

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

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

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

Stirlingův vzorec: $\ln N! = N \ln N - N$

$$\sum_i N_i = N$$

$$\sum_i \varepsilon_i N_i = E$$

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

$$\sum_i \delta N_i = 0$$

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

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

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

Zcela nezávislé variace δN_i

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

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

$$\alpha$$

$$\sum_i N_i = N$$

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

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

BOLTZMANN STATISTICS

Approximation – holds better for higher temperatures

$$\overline{E} = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

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$$q(V,T) = \sum_i e^{-\varepsilon_i / kT}$$

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$\overline{\varepsilon}$ - Average energy of a particle

$$\pi_j = \frac{e^{-\varepsilon_j / kT}}{q}$$

Probabilisty that the molecule is in the state with the energy ε_j

Fluctuation in ε are of the same order as ε – distribution of energies of individual molecules is broad. An extremely narrow Gauss distribution of E (for large N) is a many-body effect!

Fermi-Dirac and Bose-Einstein statistics   Deduction based on GCE

ε_j ... Allowed quantum states of individual molecules
$E_j(N,V)$ ... Available energy states of an ensemble of N molecules
$n_k(E_j)$ ... Number of molecules in state ε_k in the system characterized by E_j
$\{n_k\}$ … describes the quantum state

$$E_j = \sum_k \varepsilon_k n_k$$

$$N = \sum_k n_k$$

$$\Xi\ V,T,\mu\ = \sum_{N=0}^{\infty} e^{\mu N/kT} Q(N,V,T) = \sum_{N=0}^{\infty} \lambda^N Q(N,V,T)$$

$$= \sum_{N=0}^{\infty} \lambda^N \sum_{(n_k)}{}^* e^{-\beta \sum_i \varepsilon_i n_i}$$

* Denotes that the sum runs only over the "allowed" states

$$= \sum_{N=0}^{\infty} \sum_{(n_k)}{}^* \lambda^{\sum_i n_i} e^{-\beta \sum_j \varepsilon_j n_j} = \sum_{N=0}^{\infty} \sum_{(n_k)}{}^* \prod_k \left(\lambda e^{-\beta \varepsilon_k}\right)^{n_k}$$

$$= \sum_{n_1=0}^{n_1 \max} \sum_{n_2=0}^{n_2 \max} \cdots \prod_k \left(\lambda e^{-\beta \varepsilon_k}\right)^{n_k} = \sum_{n_1=0}^{n_1 \max} \left(\lambda e^{-\beta \varepsilon_1}\right)^{n_1} \sum_{n_2=0}^{n_2 \max} \left(\lambda e^{-\beta \varepsilon_2}\right)^{n_2} \cdots = \prod_k \sum_{n_k=0}^{n_k \max} \left(\lambda e^{-\beta \varepsilon_k}\right)^{n_k}$$

Fermi-Dirac $n_i^{\max} = 1$ Bose-Einstein $n_i^{\max} = \infty$

$$\Xi_{FD} = \prod_k (1 + \lambda e^{-\beta \varepsilon_k})$$

$$\Xi_{BE} = \prod_k \sum_{n_k=0}^{\infty} \left(\lambda e^{-\beta \varepsilon_k}\right)^{n_k} = \prod_k (1 - \lambda e^{-\beta \varepsilon_k})^{-1}$$

Fermi-Dirac
$$\Xi_{FD} = \prod_k (1 + \lambda e^{-\beta \varepsilon_k})$$

$$\overline{N} = \sum_k \overline{n_k} = kT \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T} = \lambda \left(\frac{\partial \ln \Xi}{\partial \lambda} \right)_{V,T} = \sum_k \frac{\lambda e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}}$$

$$\overline{n_k} = \frac{\lambda e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}}$$

$$\overline{E} = \sum_k \overline{n_k} \varepsilon_k = \sum_k \frac{\lambda \varepsilon_k e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}}$$

$$pV = kT \sum_k \ln\, 1 + e^{-\beta \varepsilon_k} \quad \longleftarrow \quad pV = kT \ln \Xi \; V,T,\mu$$

Bose-Einstein
$$\Xi_{BE} = \prod_k (1 - \lambda e^{-\beta \varepsilon_k})^{-1}$$

Similar relationships, just "+" is replaced by "-"

Even if the inter-molecular interactions are neglected – individual particles are not independent in quantum statistics – follows from the requirement on wave function.
Molecular partition function q is not defined.

Both Fermi-Dirac and Bose-Einstein quantum statistics become equivalent with the classical Boltzmann statistics in the limit of high temperatures and low densities (number of allowed quantum states is significantly larger than the number of particles).

$$\overline{n_k} \to 0 \quad \longleftarrow \quad \lambda \to 0$$

From the TD point of view this means $\qquad \dfrac{N}{V} \to 0 \qquad$ or $\qquad T \to \infty$

$$\lambda \to 0: \qquad \overline{n_k} = \lambda e^{-\beta \varepsilon_k} \quad \longleftarrow \quad \overline{n_k} = \dfrac{\lambda e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}}$$

Summing over k and dividing both equations

$$\dfrac{\overline{n_k}}{N} = \dfrac{e^{-\beta \varepsilon_k}}{\sum_k e^{-\beta \varepsilon_k}} = \dfrac{e^{-\beta \varepsilon_k}}{q} \qquad \text{Boltzmann statistics}$$

Correspondence between Bose-Eisnstein and Fermi-Dirac statistics can be obtained in a similar way

Quantum statistics is necessary only in some "extreme" cases:
      electrons in metals
      liquid helium

Ideal monoatomic gas

Intermolecular interactions are neglected ($p < 1$ atm, $T > 300$ K).
Ideal gas – number of quantum states significantly larger than number of molecules:

$$Q(N,V,T) = \frac{q^N}{N!}$$

$$q(V,T) = q_{trans} q_{elect} q_{nucl}$$

Translation partition function

$$q_{trans} = \sum_{n_x,n_y,n_z=1}^{\infty} e^{-\beta\varepsilon_{n_x n_y n_z}}$$

$$\varepsilon_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$= \sum_{n_x=1}^{\infty}\exp\left(-\frac{\beta h^2 n_x^2}{8ma^2}\right)\sum_{n_y=1}^{\infty}\exp\left(-\frac{\beta h^2 n_y^2}{8ma^2}\right)\sum_{n_z=1}^{\infty}\exp\left(-\frac{\beta h^2 n_z^2}{8ma^2}\right)$$

$$= \left(\sum_{n=1}^{\infty}\exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right)\right)^3$$

$$q_{trans}(V,T) = \left(\int_0^{\infty} e^{-\beta h^2 n^2/8ma^2}\, dn\right)^3 = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$$\left(\frac{2\pi mkT}{h^2}\right)^{1/2} = \frac{1}{\Lambda}$$

Λ … thermal de Broglie wavelength

$$q_{trans} = \frac{V}{\Lambda^3}$$

Electronic partition function

$$q_{elect} = \sum_i \omega_{ei} e^{-\beta \varepsilon_i}$$

Energy of the ground state = 0

$$q_{elect} = \omega_{e1} + \omega_{e2} e^{-\beta \Delta \varepsilon_{12}}$$

Energy levels are well separated (in the most cases; radicals and unstable species are different). Degeneracy of the ground electronic state must be taken into consideration.

He – 1st excited state ~ 20 eV:
He (300 K) ... Population of 1st excited state ~ 10^{-334}
He (3000 K) …   ~ 10^{-33}

Atoms with low lying electronic excited states – several states should be considered in q_{elect}

Nuclear partition function

Even larger separation of energy levels– only the degeneracy of the ground state considered.

Table 5–1. **Atomic energy states**

atom	electron configuration	term symbol	degeneracy $g = 2J + 1$	energy (cm^{-1})	energy (eV)
H	$1s$	$^2S_{1/2}$	2	0	0
	$2p$	$^2P_{1/2}$	2	82258.907	10.20
	$2s$	$^2S_{1/2}$	2	82258.942	
	$2p$	$^2P_{3/2}$	4	82259.272	
He	$1s^2$	$^1S_0$	1	0	
	$1s2s$	$^3S_1$	3	159850.318	19.82
		$^1S_0$	1	166271.70	
Li	$1s^22s$	$^2S_{1/2}$	2	0	
	$1s^22p$	$^2P_{1/2}$	2	14903.66	1.85
		$^2P_{3/2}$	4	14904.00	
	$1s^23s$	$^2S_{1/2}$	2	27206.12	
O	$1s^22s^22p^4$	$^3P_2$	5	0	
		$^3P_1$	3	158.5	0.02
		$^3P_0$	1	226.5	0.03
		$^1D_2$	5	15867.7	1.97
		$^1S_0$	1	33792.4	4.19
F	$1s^22s^22p^5$	$^2P_{3/2}$	4	0	
		$^2P_{1/2}$	2	404.0	0.05
	$1s^22s^22p^43s$	$^4P_{5/2}$	6	102406.50	12.70
		$^4P_{3/2}$	4	102681.24	
		$^4P_{1/2}$	2	102841.20	
		$^2P_{3/2}$	4	104731.86	
		$^2P_{1/2}$	2	105057.10	

Source: C. E. Moore, "Atomic Energy States," *Natl. Bur. Standards, Circ.*, **1**, p. 467, 1949.

Partition function of ideal monoatomic gas

$$Q(N,V,T) = \frac{\left(q_{trans}q_{elec}q_{nucl}\right)^N}{N!}$$

$$q_{trans}(V,T) = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = \frac{V}{\Lambda}$$

$$q_{elect} = \omega_{e1} + \omega_{e2}e^{-\beta\Delta\varepsilon_{12}} + ...$$

$$q_{nucl} = \omega_{n1}$$

Only multiplication constant in Q
It can influence only S and A
It does not have to be considered in many cases

$$\overline{E} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3}{2}NkT + \frac{N\omega_{e2}\Delta\varepsilon_{12}e^{-\beta\Delta\varepsilon_{12}}}{q_{elec}} + ...$$

$$\overline{p} = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{NkT}{V}$$

$$S = \tfrac{3}{2}Nk + Nk \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve}{N}\right] + Nk \ln(\omega_{e1} + \omega_{e2}\,e^{-\beta\Delta\varepsilon_{12}})$$

$$+ \frac{Nk\omega_{e2}\,\beta\Delta\varepsilon_{12}\,e^{-\beta\Delta\varepsilon_{12}}}{q_{\text{elec}}} \quad (5\text{--}19)$$

$$= Nk \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right] + S_{\text{elec}} \quad (5\text{--}20)$$

In Eq. (5–20), S_{elect} denotes the last two terms of Eq. (5–19). Equation (5–20) is called the Sackur-Tetrode equation. Table 5–3 compares the results of this equation with experimental values for several monatomic gases.

Table 5–3. **Comparison of experimental entropies at 1 atm and $T = 298°K$ to those calculated from the statistical thermodynamical equation for the entropy of an ideal monatomic gas***

	exp. (e.u.)	calc. (e.u.)
He	30.13	30.11
Ne	34.95	34.94
Ar	36.98	36.97
Kr	39.19	39.18
Xe	40.53	40.52
C	37.76	37.76
Na	36.72	36.70
Al	39.30	39.36
Ag	41.32	41.31
Hg	41.8	41.78

* The experimental values have been corrected for any nonideal gas behavior.