Partition function $\{E_j(N,V)\}$

From the Schrödinger equation solution for $N$-particle system

Simplification (?)

\[ H = \sum H_i \quad \rightarrow \quad E = \sum E_i \quad \rightarrow \quad \Psi = \prod \Psi_i \]

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 Hamiltonian*
1. System of distinguishable particles

\[ H = \sum H_i \rightarrow \{ \varepsilon_j^a \} \]

Energy level \( j \) 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

\[
q_x(V, T) = \sum_i e^{-\varepsilon_i^x/kT}
\]

\[
Q(N, V, T) = q(V, T)^N
\]

For the same (distinguishable particles – allowed energy levels are the same):

\( \Rightarrow \) Manybody problem is reduced to single-particle terms

Example:

- crystal
- molecular partition function

\[ q_{molecule} = q_{tr} q_{rot} q_{vib} q_{el} \]

- additional simplifications
2. System of indistinguishable particles

\[ E_{ijkl...} = \varepsilon_i + \varepsilon_j + \varepsilon_k + \varepsilon_l + \cdots \]

\[ \{ \varepsilon_j \} \]

Energetická hladina j částice.

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

Summation indeces \( i, j, k, \ldots \) are dependent – summation cannot be broken into individual terms

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

\[ i \neq j \neq k \neq l \neq \ldots \]

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

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

Cannot be simplified!

Aproximative solution

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

Aproximative solution

Bosons: no restrictions

\[ i \neq j \neq k \neq l \neq \ldots \]

\[ N! \text{ possibilities} \]

\[ 1/N! \]

\[ E_{ijkl...} \text{ satisfying} \]

\[ E_{ijkl...} \text{ Not satisfying} \]

Excluded

\[ X \text{ possibilities} \]

\[ 1/X \]
If the number of allowed states is significantly larger than the number of particles $\Rightarrow$ 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-particle 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 $\leq \varepsilon$

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

\[
\begin{align*}
m &= 10^{-22} \text{ g} \\
a &= 10 \text{ cm} \\
T &= 300^\circ \text{ K}
\end{align*}
\]

\[\Phi(\varepsilon) \sim 10^{30}\]

Requirement of $\Phi(\varepsilon) \gg N$

In majority of cases this is true:

$$\varepsilon = \frac{3}{2} kT \quad \frac{\pi}{6} \left( \frac{12mkT}{\hbar^2} \right)^{3/2} \gg N \frac{V}{V}$$

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*

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>(6N/\pi V \left(\frac{h^2}{12mkT}\right)^{3/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquid helium</td>
<td>4</td>
<td>1.6</td>
</tr>
<tr>
<td>gaseous helium</td>
<td>4</td>
<td>0.11</td>
</tr>
<tr>
<td>gaseous helium</td>
<td>20</td>
<td>(2.0 \times 10^{-3})</td>
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<tr>
<td>gaseous helium</td>
<td>100</td>
<td>(3.5 \times 10^{-5})</td>
</tr>
<tr>
<td>liquid neon</td>
<td>27</td>
<td>(1.1 \times 10^{-2})</td>
</tr>
<tr>
<td>gaseous neon</td>
<td>27</td>
<td>(8.2 \times 10^{-5})</td>
</tr>
<tr>
<td>gaseous neon</td>
<td>100</td>
<td>(3.1 \times 10^{-6})</td>
</tr>
<tr>
<td>liquid argon</td>
<td>86</td>
<td>(5.1 \times 10^{-4})</td>
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<tr>
<td>gaseous argon</td>
<td>86</td>
<td>(1.6 \times 10^{-6})</td>
</tr>
<tr>
<td>liquid krypton</td>
<td>127</td>
<td>(5.4 \times 10^{-5})</td>
</tr>
<tr>
<td>gaseous krypton</td>
<td>127</td>
<td>(2.0 \times 10^{-7})</td>
</tr>
<tr>
<td>electrons in</td>
<td>300</td>
<td>1465</td>
</tr>
<tr>
<td>(sodium)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 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

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

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

\[ q(V,T) = \sum_i e^{-\epsilon_i/kT} \]

\[ \bar{E} = N \sum_j \bar{\epsilon}_j \frac{e^{-\epsilon_j/kT}}{q} = N \bar{\epsilon} \]

\[ \pi_j = \frac{e^{-\epsilon_j/kT}}{q} \]

\[ \bar{\epsilon} - \text{Average energy of a particle} \]

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: \[ \ln N! = N \ln N - N \]

\[ \sum_i N_i = N \]
\[ \sum_i \varepsilon_i N_i = E \]
\[ \sum_i \delta N_i = 0 \]
\[ \sum_i \varepsilon_i \delta N_i = 0 \]
\[ \delta \sum_i N_i \ln N_i - \delta \sum_i N_i = 0 \]
\[ \sum_i \ln N_i \delta N_i = 0 \]

\[ \sum_i \ln N_i \delta N_i + \sum_i \alpha \delta N_i + \sum_i \beta \varepsilon_i \delta N_i = 0 \]

Zcela nezávislé variace \( \delta N_i \)

\[ \alpha + \beta \varepsilon_i + \ln N_i = 0 \]
\[ N_i = e^{-\alpha} e^{-\beta \varepsilon_i} \]

\[ \sum_i N_i = N \]
\[ N = e^{-\alpha} \sum_i e^{-\beta \varepsilon_i} \]

\[ \frac{N_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}} \]
BOLTZMANN STATISTICS

Approximation – holds better for higher temperatures

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

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

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

\[\bar{E} = N \sum_j \varepsilon_j \frac{e^{-\varepsilon_j / kT}}{q} = N \bar{\varepsilon}\]

\[\bar{\varepsilon} \quad \text{- Average energy of a particle}\]

Probabilisty that the molecule is in the state with the energy \(\varepsilon_j\)

Fluctuation in \(\varepsilon\) are of the same order as \(\varepsilon\) – 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

\[ \varepsilon_j \quad \ldots \quad \text{Allowed quantum states of individual molecules} \]

\[ E_j(N,V) \quad \ldots \quad \text{Available energy states of an ensemble of N molecules} \]

\[ n_k(E_j) \quad \ldots \quad \text{Number of molecules in state } \varepsilon_k \text{ in the system characterized by } E_j \]

\[ \{n_k\} \quad \ldots \quad \text{describes the quantum state} \]

\[ E_j = \sum_k \varepsilon_k n_k \]

\[ N = \sum_k n_k \]

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

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

* Denotes that the sum runs only over the “allowed” states

\[ = \sum_{N=0}^{\infty} \lambda^N \sum_{(n_k)} \frac{\left(\sum_{j} n_j e^{-\beta \varepsilon_j}ight)^N}{\left(\sum_{j} e^{-\beta \varepsilon_j}\right)^N} \]

\[ = \sum_{n_1=0}^{n_1 \text{ max}} \sum_{n_2=0}^{n_2 \text{ max}} \cdots \prod_k \lambda e^{-\beta \varepsilon_k} n_k \]

\[ = \sum_{n_1=0}^{n_1 \text{ max}} \lambda e^{-\beta \varepsilon_1} \sum_{n_2=0}^{n_2 \text{ max}} \lambda e^{-\beta \varepsilon_2} \cdots = \prod_k \sum_{n_k=0}^{n_k \text{ max}} \lambda e^{-\beta \varepsilon_k} n_k \]

**Fermi-Dirac**

\[ n_i^{\text{max}} = 1 \]

\[ \Xi_{FD} = \prod_k \left(1 + \lambda e^{-\beta \varepsilon_k}\right) \]

**Bose-Einstein**

\[ n_i^{\text{max}} = \infty \]

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

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

\[ \bar{N} = \sum_k \bar{n}_k = kT \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V, T} = \lambda \left( \frac{\partial \ln \Xi}{\partial \lambda} \right)_{V, T} = \sum_k \frac{\lambda e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}} \]

\[ \bar{n}_k = \frac{\lambda e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}} \]

\[ \bar{E} = \sum_k \bar{n}_k \varepsilon_k = \sum_k \frac{\lambda \varepsilon_k e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}} \]

\[ pV = kT \sum_k \ln 1 + e^{-\beta \varepsilon_k} \]

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).

\[ \overline{n}_k \to 0 \quad \text{or} \quad \lambda \to 0 \]

From the TD point of view this means

\[ \frac{N}{V} \to 0 \quad \text{or} \quad T \to \infty \]

\[ \lambda \to 0: \quad \overline{n}_k = \lambda e^{-\beta \varepsilon_k} \quad \text{or} \quad \overline{n}_k = \frac{\lambda e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}} \]

Summing over \( k \) and dividing both equations

\[ \overline{n}_k \frac{e^{-\beta \varepsilon_k}}{N} = \sum_k e^{-\beta \varepsilon_k} = \frac{e^{-\beta \varepsilon_k}}{q} \]

Boltzmann statistics

Correspondence between Bose-Einstein 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:

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

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

**Translation partition function**

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

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

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

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

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

$$\Lambda \ldots \text{thermal de Broglie wavelength}$$

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

$$q_{\text{trans}} = \frac{V}{\Lambda^3}$$
Electronic partition function

\[ q_{\text{elect}} = \sum_i \omega_{ei} e^{-\beta \varepsilon_i} \]

Energy of the ground state = 0

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

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

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

Nuclear partition function

Even larger separation of energy levels– only the degeneracy of the ground state considered.
<table>
<thead>
<tr>
<th>atom</th>
<th>electron configuration</th>
<th>term symbol</th>
<th>degeneracy ( g = 2J + 1 )</th>
<th>energy (cm(^{-1}))</th>
<th>energy (eV)</th>
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</thead>
<tbody>
<tr>
<td>H</td>
<td>( 1s )</td>
<td>( ^2S_{1/2} )</td>
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<td>82258.942</td>
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<td></td>
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<td>0</td>
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<td>( 1s^23s )</td>
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<td>O</td>
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<td>2</td>
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</tbody>
</table>

Partition function of ideal monoatomic gas

\[ Q(N,V,T) = \frac{q_{\text{trans}} q_{\text{elec}} q_{\text{nucl}}}{N!} \]

\[ q_{\text{trans}}(V,T) = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V = \frac{V}{A} \]

\[ q_{\text{elec}} = \omega_{e1} + \omega_{e2} e^{-\beta \Delta \varepsilon_{12}} + \ldots \]

\[ q_{\text{nucl}} = \omega_{n1} \]

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

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

\[ \overline{p} = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} = \frac{NkT}{V} \]
\[ S = \frac{3}{2} Nk + Nk \ln \left[ \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \frac{Ve}{N} \right] + Nk \ln (\omega_{e1} + \omega_{e2} e^{-\beta \Delta \varepsilon_{12}}) \]

\[ + \frac{Nk \omega_{e2} \beta \Delta \varepsilon_{12} e^{-\beta \Delta \varepsilon_{12}}}{q_{\text{elec}}} \]  

(5-19)

\[ = Nk \ln \left[ \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \frac{Ve^{5/2}}{N} \right] + S_{\text{elec}} \]  

(5-20)

In Eq. (5-20), \( S_{\text{elec}} \) 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>
<thead>
<tr>
<th></th>
<th>exp. (e.u.)</th>
<th>calc. (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>30.13</td>
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<td>Ne</td>
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<td>Hg</td>
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</table>

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