Monatomic ideal gas: partition functions and equation of state.

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Systems of non-interacting particles

For non-interacting particles $a, b, c, d, \ldots$ we can decompose the system Hamiltonian to individual contributions:

$$\hat{H} \approx \hat{H}^a + \hat{H}^b + \hat{H}^c + \hat{H}^d + \ldots$$

Consequently, the energy is a sum of individual particle energies

$$E \approx \varepsilon^a + \varepsilon^b + \varepsilon^c + \varepsilon^d + \ldots$$

- Complex multi-body problem approximated as a superposition of simpler one- and two-body problems.
- Often encountered in Physics
- Allows for systematic corrections
- *e.g.* Separation of a single molecule Hamiltonian

$$\hat{H} \approx \hat{H}_{\text{translation}} + \hat{H}_{\text{rotation}} + \hat{H}_{\text{vibration}} + \hat{H}_{\text{electronic}} + \hat{H}_{\text{nuclear}} + \ldots$$

$$\varepsilon \approx \varepsilon_{\text{translation}} + \varepsilon_{\text{rotation}} + \varepsilon_{\text{vibration}} + \varepsilon_{\text{electronic}} + \varepsilon_{\text{nuclear}} + \ldots$$
Systems of non-interacting particles

Suppose we can decompose Hamiltonian to individual contributions. Non-interacting distinguishable particles $a, b, c, \ldots$:

$$Q(N, V, T) = \sum_j e^{-\beta E_j} = \sum_{k,l,m,\ldots} e^{-\beta (\epsilon_k^a + \epsilon_l^b + \epsilon_m^c + \ldots)}$$

$$= \left( \sum_k e^{-\beta \epsilon_k^a} \right) \left( \sum_l e^{-\beta \epsilon_l^b} \right) \left( \sum_m e^{-\beta \epsilon_m^c} \right) \cdots = q_a q_b q_c \cdots$$

where $k, l, m, \ldots$ are indices of quantum states of particles $a, b, c, \ldots$

Single-particle partition function:

$$q_i(V, T) = \sum_j e^{-\beta \epsilon_j^i}$$
Distinguishable vs. indistinguishable particles

- If all particles are the same but **distinguishable**, \( q_a = q_b = q_c = q \):
  \[
  Q(N, V, T) = \sum_{k,l,m,...} e^{-\beta(\varepsilon_k + \varepsilon_l + \varepsilon_m + \ldots)} = q_a q_b q_c \cdots = q^N(V, T)
  \]

- The \( N \)-body problem reduces to a one-body problem!
Distinguishable vs. indistinguishable particles

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  \]

- The \( N \)-body problem reduces to a one-body problem!
- But identical particles are **indistinguishable**:
  \[
  Q(N, V, T) = \sum_{k, l, m, \ldots} e^{-\beta(\epsilon_k + \epsilon_l + \epsilon_m + \ldots)}
  \]

- Permutation of \( k \) and \( l \) yields the same quantum state of the system.
- Correct for double-counting: \( N! \) permutations.
Indistinguishable particles

- For indistinguishable particles:

\[
Q(N, V, T) = \frac{q^N(V, T)}{N!} \quad \text{where} \quad q(V, T) = \sum_j e^{-\beta \varepsilon_j}
\]

We silently ignored multiply occupied states:

- Bosons: \( \psi \) symmetric with respect to permutation \( \Rightarrow \) any number of particles can occupy a given quantum state.
- Fermions: \( \psi \) antisymmetric with respect to permutation \( \Rightarrow \) two particles cannot occupy the same quantum state.

We will see that except for low temperatures or high densities the number of states \( N \gg N \).

Then multiply occupied states are rare and the equation above is an excellent approximation.
Indistinguishable particles

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

where

\[ q(V, T) = \sum_j e^{-\beta \varepsilon_j} \]

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- For indistinguishable particles:

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Indistinguishable particles

- For indistinguishable particles:
  \[ Q(N, V, T) = \frac{q^N(V, T)}{N!} \]
  where \[ q(V, T) = \sum_j e^{-\beta \epsilon_j} \]

- We silently ignored multiply occupied states: \( \epsilon_i = \epsilon_j \):
  - Bosons: \( \psi \) symmetric with respect to permutation
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- We will see that except for low temperatures or high densities the number of states \( \mathcal{N} \gg N \).
- Then multiply occupied states are rare and the equation above is an excellent approximation.
Some useful results from quantum mechanics (QM)

Time-independent Schrödinger equation:

\[ \hat{H} \psi = E \psi \]

Particle in a well of length \( a \):

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \]

\[ \varepsilon_n = \frac{\hbar^2 n^2}{2ma^2}, \quad n = 1, 2, \ldots \]

Number of states with \( \varepsilon_{n_x,n_y,n_z} < \varepsilon \):

\[ \Phi(\varepsilon) = \frac{1}{8} \left( \frac{4\pi R^3}{3} \right) \]

\[ \ldots = \frac{\pi}{6} \left( \frac{8ma^2 \varepsilon}{\hbar^2} \right)^{3/2} \]

Particle in a 3d box of length \( a \):

\[ \varepsilon_{n_x,n_y,n_z} = \frac{\hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2) \]
Degeneracy of translational energy levels

Density of energy levels from previous slide:

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

Number of levels between \( \varepsilon \) and \( (\varepsilon + \Delta\varepsilon) \):

\[ \omega(\varepsilon, \Delta\varepsilon) = \Phi(\varepsilon + \Delta\varepsilon) - \Phi(\varepsilon) = \frac{\pi}{4} \left( \frac{8ma^2}{h^2} \right)^{3/2} \varepsilon^{1/2} \Delta\varepsilon + \mathcal{O}\left((\Delta\varepsilon)^2\right) \]

Let's plug in some numbers:
\( \varepsilon = 3k_B T/2, \ T = 300 \text{ K}, \ m = 10^{-22} \text{ g}, \ a = 10 \text{ cm}, \ \Delta\varepsilon/\varepsilon = 0.01: \)

\[ \omega(\varepsilon, \Delta\varepsilon) \approx \mathcal{O}(10^{28}) \]

Degeneracy of translational energy levels far exceeds number of particles at sufficiently low density and high temperature.
Fermi-Dirac and Bose-Einstein statistics

- Sometimes we have to explicitly account for multiple occupancy of quantum states.

- At low T and high density.

- Partition function in terms of molecular energy levels (occupation numbers \( n_k \)):

\[
Q(N, V, T) = \sum_j e^{-\beta E_j} = \sum_{\{n_k\}}^* e^{-\beta \sum_i \epsilon_i n_i}
\]

*Constrained sum:

\[
N = \sum_k n_k
\]

\[
E_j = \sum_k \epsilon_k n_k
\]

- Evaluation of the restricted sum is awkward.

- Convenient solution: grandcanonical ensemble (GCE).
Fermi-Dirac and Bose-Einstein statistics

Formulation in GCE:

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

Absolute activity:

\[ \lambda = e^{\beta \mu} \]
\[ \mu = k_B T \ln \lambda \]

Rearrangements (* is the restricted sum from the previous slide):

\[ \Xi(\mu, V, T) = \sum_{N=0}^{\infty} \lambda^N \sum_{\{n_k\}}^* e^{-\beta \sum_i \varepsilon_i n_i} = \sum_{N=0}^{\infty} \sum_{\{n_k\}}^* \lambda \sum_i n_i e^{-\beta \sum_i \varepsilon_i n_i} \]

\[ = \sum_{N=0}^{\infty} \sum_{\{n_k\}}^* \prod_k \left( \lambda e^{-\beta \varepsilon_k} \right)^{n_k} \]

Crucial step (now each \( n_k \) ranges over all possible values):

\[ \Xi(\mu, V, T) = \sum_{n_1=0}^{n_1^{\text{max}}} \sum_{n_2=0}^{n_2^{\text{max}}} \cdots \prod_k \left( \lambda e^{-\beta \varepsilon_k} \right)^{n_k} \]
Fermi-Dirac and Bose-Einstein statistics

We continue rearranging

\[
\Xi(\mu, V, T) = \sum_{n_1=0}^{n_1^{\max}} \sum_{n_2=0}^{n_2^{\max}} \cdots \prod_k \left( \lambda e^{-\beta \varepsilon_k} \right)^{n_k}
\]

\[
= \sum_{n_1=0}^{n_1^{\max}} \left( \lambda e^{-\beta \varepsilon_1} \right)^{n_1} \sum_{n_2=0}^{n_2^{\max}} \left( \lambda e^{-\beta \varepsilon_2} \right)^{n_2}
\]

\[
= \prod_k \sum_{n_k=0}^{n_k^{\max}} \left( \lambda e^{-\beta \varepsilon_k} \right)^{n_k}
\]

Last equation is a general result. Special cases:
Fermions, \( n_k^{\max} = 1 \):

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

Bosons, \( n_k^{\max} = \infty \):

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

P. Košovan
Lecture 3: Monatomic ideal gas
Fermi-Dirac and Bose-Einstein statistics

Use \( \sum_{j=0}^{\infty} x^j = (1 - x)^{-1} \) for \( x < 1 \) to rewrite BE formula

\[
\Xi_{BE} = \prod_k \sum_{n_k=0}^{\infty} \left( \lambda e^{-\beta \epsilon_k} \right)^{n_k} = \prod_k \left( 1 - \lambda e^{-\beta \epsilon_k} \right)^{-1} \text{ for } \lambda e^{-\beta \epsilon_k} < 1
\]

and cast both FD and BE formula in the same form

\[
\Xi_{FD, BE} = \prod_k \left( 1 \pm \lambda e^{-\beta \epsilon_k} \right)^{\pm 1} \text{ for } \lambda e^{-\beta \epsilon_k} < 1
\]

- These are the only exact distributions in statmech.
- Low T and high density: FD or BE statistics apply, \( q(N, V, T) \) has no meaning (symmetry requirements of the wave function)
- High T and low density: both degenerate to Boltzmann statistics
Thermodynamic quantities from FD and BE statistics

Number of particles:

\[
\bar{N} = N = \sum_k \bar{n}_k = k_B T \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T} \]

\[
= \lambda \left( \frac{\partial \ln \Xi}{\partial \lambda} \right)_{V,T} = \sum_k \frac{\lambda e^{-\beta \epsilon_k}}{1 \pm \lambda e^{-\beta \epsilon_k}}
\]

Number of particles in state \( k \):

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

Energy \( E \) and average energy per particle, \( \bar{\epsilon} \):

\[
\overline{E} = N \overline{\epsilon} = \sum_k \bar{n}_k \epsilon_k = \sum_k \frac{\lambda \epsilon_k e^{-\beta \epsilon_k}}{1 \pm \lambda e^{-\beta \epsilon_k}}
\]

\[
pV = k_B T \ln \Xi = \pm k_B T \sum_k \ln \left( 1 \pm \lambda e^{-\beta \epsilon_k} \right)
\]
The limiting case of Boltzmann

For $\lambda \ll 1$ (equivalent $\beta \mu \ll 0$):

$$\bar{n}_k = \frac{\lambda e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}$$

we can write approximate relations

$$\bar{n}_k = \lambda e^{-\beta \varepsilon_k}, \quad N = \sum_k \bar{n}_k = \lambda \sum_k e^{-\beta \varepsilon_k}$$

and using $q(N, V, T) = \sum_k e^{-\beta \varepsilon_k}$

$$\frac{\bar{n}_k}{N} = \frac{e^{-\beta \varepsilon_k}}{\sum_k e^{-\beta \varepsilon_k}} = \frac{e^{-\beta \varepsilon_k}}{q(N, V, T)}$$

i.e. both FD and BE reduce to Boltzmann statistics.
The limiting case of Boltzmann

Similarly, for small $\lambda$ we obtain:

$$\bar{E} = \sum_k \frac{\lambda \varepsilon_k e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}} \rightarrow \sum_j \lambda \varepsilon_j e^{-\beta \varepsilon_j}, \quad \bar{\varepsilon} = \frac{\bar{E}}{\sum_k \bar{n}_k} \rightarrow \frac{\sum_j \varepsilon_j e^{-\beta \varepsilon_j}}{\sum_j e^{-\beta \varepsilon_j}}$$

Using $\ln(1 + x) \approx x$ for small $x$:

$$pV = k_B T \ln \Xi \rightarrow (\pm k_B T) \left( \pm \lambda \sum_j e^{-\beta \varepsilon_j} \right) = \lambda k_B T \sum_j e^{-\beta \varepsilon_j} = \lambda k_B T q$$

so that

$$\beta pV = \ln \Xi = \lambda q$$

$$\Xi = e^{\lambda q} = \sum_{N=0}^{\infty} \frac{(\lambda q)^N}{N!} = \sum_{N=0}^{\infty} \lambda^N Q(N, V, T), \text{ where } Q(N, V, T) = \frac{q^N}{N!}$$
Ideal monatomic gas

At high temperature and low pressure (Boltzmann limit):

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

Further decomposition of \( q \):

\[ q(V, T) = q_{tr} q_{el} q_{\text{nucl}} \]

Nuclear partition function:

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

Except for rare cases just a constant.
Ideal monatomic gas

At high temperature and low pressure (Boltzmann limit):

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

Further decomposition of \( q \):

\[ q(V, T) = q_{\text{tr}} q_{\text{el}} q_{\text{nucl}} \]

Electronic partition function:

\[ q_{\text{elec}} = \omega_{e1} + \omega_{e2} e^{-\beta \Delta \varepsilon_{1,2}} + \ldots \]

- Zero energy at electronic ground state
- Can be degenerate
- Higher excited states typically several eV
- At 300 K 1 eV \( \approx \) 40 \( k_B T \)
- First two or three terms usually suffice

Nuclear partition function:

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

Except for rare cases just a constant.
## Quantitative view of electronic levels

**Table 5–1. Atomic energy states**

<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>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1s</td>
<td>(^2S_{1/2})</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>(^2P_{1/2})</td>
<td>2</td>
<td>82258.907</td>
<td>10.20</td>
</tr>
<tr>
<td></td>
<td>2s</td>
<td>(^2S_{1/2})</td>
<td>2</td>
<td>82258.942</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>(^2P_{3/2})</td>
<td>4</td>
<td>82259.272</td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>1s(^2)</td>
<td>(^1S_{0})</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1s2s</td>
<td>(^3S_{1})</td>
<td>3</td>
<td>159850.318</td>
<td>19.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^1S_{0})</td>
<td>1</td>
<td>166271.70</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1s(^2)2s</td>
<td>(^2S_{1/2})</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1s(^2)2p</td>
<td>(^2P_{1/2})</td>
<td>2</td>
<td>14903.66</td>
<td>1.85</td>
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<tr>
<td></td>
<td></td>
<td>(^2P_{3/2})</td>
<td>4</td>
<td>14904.00</td>
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<tr>
<td></td>
<td>1s(^2)3s</td>
<td>(^2S_{1/2})</td>
<td>2</td>
<td>27206.12</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1s(^2)2s(^2)2p(^4)</td>
<td>(^3P_{2})</td>
<td>5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^3P_{1})</td>
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<td>158.5</td>
<td>0.02</td>
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<td>226.5</td>
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<td>(^1S_{0})</td>
<td>1</td>
<td>33792.4</td>
<td>4.19</td>
</tr>
<tr>
<td>F</td>
<td>1s(^2)2s(^2)2p(^5)</td>
<td>(^2P_{3/2})</td>
<td>4</td>
<td>0</td>
<td></td>
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<td>(^2P_{1/2})</td>
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<td></td>
<td></td>
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<td>4</td>
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<td></td>
<td>(^2P_{1/2})</td>
<td>2</td>
<td>105057.10</td>
<td></td>
</tr>
</tbody>
</table>


Table from McQuarrie, Statistical Mechanics, University Science Books (2000)
Quantitative view of electronic levels

Fraction of electrons in second excited state:

\[ f_2 = \frac{\omega e_2 e^{-\beta \Delta \varepsilon_{1,2}}}{\omega e_1 + \omega e_2 e^{-\beta \Delta \varepsilon_{1,2}} + \ldots} \]

Table 5-2. The fraction of fluorine atoms in the first excited electronic state as a function of temperature

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>( f_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.027</td>
</tr>
<tr>
<td>400</td>
<td>0.105</td>
</tr>
<tr>
<td>600</td>
<td>0.160</td>
</tr>
<tr>
<td>800</td>
<td>0.195</td>
</tr>
<tr>
<td>1000</td>
<td>0.219</td>
</tr>
<tr>
<td>1200</td>
<td>0.236</td>
</tr>
<tr>
<td>2000</td>
<td>0.272</td>
</tr>
</tbody>
</table>

Table from McQuarrie, Statistical Mechanics, University Science Books (2000)

Higher electronic states need to be considered at higher temperatures.
Translational partition function

Translational energy levels:

\[ \varepsilon_{n_x,n_y,n_z} = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2), \quad n_x, n_y, n_z = 1, 2, \ldots \]

\[ q_{tr} = \sum_{n_x,n_y,n_z=1}^{\infty} e^{-\beta \varepsilon_{n_x,n_y,n_z}} \]

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

\[ = \left( \sum_{n=1}^{\infty} \exp \left( -\frac{\beta \hbar^2 n^2}{8ma^2} \right) \right)^3 \approx \left( \int_{n=0}^{\infty} \exp \left( -\frac{\beta \hbar^2 n^2}{8ma^2} \right) dn \right)^3 \]

Alternative approach

\[ q_{tr} = \sum_{\varepsilon=0}^{\infty} \omega(\varepsilon) e^{-\beta \varepsilon} \approx \int_{\varepsilon=0}^{\infty} \omega(\varepsilon) e^{-\beta \varepsilon} d\varepsilon = \frac{\pi}{4} \left( \frac{8ma^2}{\hbar^2} \right)^{3/2} \int_{n=0}^{\infty} \varepsilon^{1/2} e^{-\beta \varepsilon} d\varepsilon \]
Translational partition function

We evaluate

\[ q_{tr} = \left( \int_{n=0}^{\infty} \exp\left( -\beta \frac{h^2 n^2}{8 m a^2} \right) \, dn \right)^3 = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V \]

and introduce thermal \textit{de Broglie} wavelength \( \Lambda \)

\[ \Lambda = \left( \frac{h^2}{2\pi m k_B T} \right)^{1/2} \]

such that \( q_{tr} = \frac{V}{\Lambda^3} \)

Translational energy and momentum per particle:

\[ \bar{\varepsilon}_{tr} = k_B T^2 \left( \frac{\partial \ln q_{tr}}{\partial T} \right) = \frac{3}{2} k_B T, \quad \overline{|\vec{p}|} = (3 m k_B T)^{1/2}, \quad \Lambda \approx \frac{h}{\overline{|\vec{p}|}} \]
Translational partition function

We evaluate

\[ q_{\text{tr}} = \left( \int_{n=0}^{\infty} \exp\left( -\frac{\beta \hbar^2 n^2}{8ma^2} \right) \, dn \right)^3 = \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} V \]

and introduce thermal de Broglie wavelength \( \Lambda \)

\[ \Lambda = \left( \frac{\hbar^2}{2\pi m k_B T} \right)^{1/2} \quad \text{such that} \quad q_{\text{tr}} = \frac{V}{\Lambda^3} \]

Translational energy and momentum per particle:

\[ \bar{\varepsilon}_{\text{tr}} = k_B T^2 \left( \frac{\partial \ln q_{\text{tr}}}{\partial T} \right) = \frac{3}{2} k_B T, \quad |\vec{p}| = (3m k_B T)^{1/2}, \quad \Lambda \approx \frac{h}{|\vec{p}|} \]

Boltzmann applies at \( \Lambda^3 \ll V \), i.e. when quantum effects diminish.
Summary – single-particle partition function

\[ q(V, T) = q_{\text{tr}} q_{\text{el}} q_{\text{nu}} \]

\[ q_{\text{tr}} = \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} V = \frac{V}{\lambda^3} \]

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

\[ q_{\text{nu}} = \omega_{n1} + \ldots \]

- The above holds for particles without internal structure (monatomic ideal gas)
- Vibrational and rotational terms arise for composite particles (next lecture)
Thermodynamic functions of an ideal monatomic gas

\[ A(N, V, T) = -k_B T \ln Q = k_B T \ln N! - Nk_B T \ln q(V, T) \]

\[ = -Nk_B T \ln \left[ \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \frac{V e}{N} \right] - Nk_B T \ln (\omega_{e,1} + \omega_{e,2} e^{-\beta \Delta \varepsilon_{1,2}}) \]

\[ E = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} = \frac{3}{2} Nk_B T + \frac{N \omega_{e,2} \Delta \varepsilon_{1,2}}{q_{el}} \]

In both above cases, the first term is dominant.

\[ p = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} = \frac{Nk_B T}{V} \]

Equation of state (EOS) of an ideal gas.
Thermodynamic functions of an ideal monatomic gas

Entropy:

\[ S = k_B T \left( \left. \frac{\partial \ln Q}{\partial T} \right|_{N,V} \right) + k_B \ln Q \]

\[ = \frac{3}{2} N k_B + N k_B \ln \left[ \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right] \]

\[ + \ N k_B \ln \left( \omega_{e,1} + \omega_{e,2} e^{-\beta \Delta \varepsilon_{1,2}} \right) + N k_B \left( \frac{\omega_{e,1} + \omega_{e,2} e^{-\beta \Delta \varepsilon_{1,2}}}{q_{el}} \right) \]

Sackur-Tetrode equation:

\[ S = \frac{3}{2} N k_B + N k_B \ln \left[ \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right] + S_{el} \]
Quantitative view of entropy

Sackur-Tetrode equation:

\[
S = \frac{3}{2} N k_B + N k_B \ln \left[ \left( \frac{2\pi m k_B T}{h^2} \right)^{2/2} \frac{V e^{5/2}}{N} \right] + S_{el}
\]

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*

<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>
<td>30.11</td>
</tr>
<tr>
<td>Ne</td>
<td>34.95</td>
<td>34.94</td>
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<tr>
<td>Ar</td>
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<td>36.97</td>
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<tr>
<td>Kr</td>
<td>39.19</td>
<td>39.18</td>
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<tr>
<td>Xe</td>
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<td>40.52</td>
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<tr>
<td>C</td>
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<td>36.70</td>
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<tr>
<td>Al</td>
<td>39.30</td>
<td>39.36</td>
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<tr>
<td>Ag</td>
<td>41.32</td>
<td>41.31</td>
</tr>
<tr>
<td>Hg</td>
<td>41.8</td>
<td>41.78</td>
</tr>
</tbody>
</table>

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

Table from McQuarrie, Statistical Mechanics, University Science Books (2000)

Higher electronic states have to be considered at higher temperatures.

P. Košovan

Lecture 3: Monatomic ideal gas
Chemical potential:

\[
\mu = -k_B T \left( \frac{\partial \ln Q}{\partial N} \right)_{T, V} = -k_B T \ln \frac{q}{N}
\]

\[
= -k_B T \ln \left[ \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \frac{V}{N} \right] - k_B T \ln q_{el} q_{nu}
\]

\[
= -k_B T \ln \left[ \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \frac{k_B T}{\rho^\Theta} \right] - k_B T \ln q_{el} q_{nu} + k_B T \ln \frac{\rho}{\rho^\Theta}
\]

\[
= \mu_0(T) + k_B T \ln \frac{\rho}{\rho^\Theta}
\]

where

\[
\mu_0(T) = -k_B T \ln \left[ \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \frac{k_B T}{\rho^\Theta} \right] - k_B T \ln q_{el} q_{nu}
\]
Summary

- Separation of different contributions to $\hat{H}, E, Q$ and $q$
- Fermi-Dirac and Bose-Einstein statistics
- Boltzmann as high-temperature and low-density limit
- Thermal wavelength
- EOS of an ideal gas from first principles (Boltzmann limit)
Summary

- Separation of different contributions to $\hat{H}$, $E$, $Q$ and $q$
- Fermi-Dirac and Bose-Einstein statistics
- Boltzmann as high-temperature and low-density limit
- Thermal wavelength
- EOS of an ideal gas from first principles (Boltzmann limit)

What comes next

- Polyatomic gas molecules – vibration and rotation
- Condensed matter – dense gases and liquids (classical limit)
- Distinguishable particles – crystals, magnets