You’ve learned about partition functions and some uses, now we’ll explore them in more depth using ideal monatomic, diatomic and polyatomic gases!

Before we start, remember:

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

What are N, V, and T?

We now apply this to the ideal gas where:

1. The molecules are independent.
2. The number of states greatly exceeds the number of molecules (assumption of low pressure).
Where can we put energy into a monatomic gas?

\[ \mathcal{E}_{\text{atomic}} = \mathcal{E}_{\text{trans}} + \mathcal{E}_{\text{elec}} \]

Only into translational and electronic modes! ☺

The total partition function is the product of the partition functions from each degree of freedom:

\[ q(V,T) = q_{\text{trans}}(V,T)q_{\text{elec}}(V,T) \]

We’ll consider both separately…
Translations of Ideal Gas: $q_{\text{trans}}(V, T)$

General form of partition function: 

$$q_{\text{trans}} = \sum_{\text{states}} e^{-\beta \varepsilon_{\text{trans}}}$$

Recall from QM slides...

$$\varepsilon_{\text{trans}} = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, \ldots, \infty$$

So what is $q_{\text{trans}}$?
Let’s simplify $q_{\text{trans}} \ldots$

$$q_{\text{trans}} = \sum_{n_x, n_y, n_z=1}^{\infty} e^{-\beta \varepsilon_{n_x, n_y, n_z}} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left[ -\frac{\beta \hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \right]$$

Recall: $e^{a+b+c} = e^a e^b e^c$

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

All three sums are the same because $n_x$, $n_y$, $n_z$ have same form!

We can simplify expression to:
\( q_{\text{trans}} \) is nearly continuous

We’d like to solve this expression, but there is no analytical solution for the sum!

\[
q_{\text{trans}}(V, T) = \left[ \sum_{n=1}^{\infty} \exp \left( -\frac{\beta \hbar^2 n^2}{8m a^2} \right) \right]^3
\]

No fears… there is something we can do!

Since translational energy levels are spaced very close together, the sum is nearly continuous function and we can approximate the sum as an integral… which we can solve!

\[
q_{\text{trans}}(V, T) = \left[ \int_0^{\infty} dn \exp \left( -\frac{\beta \hbar^2 n^2}{8m a^2} \right) \right]^3
\]

Note limit change … only way to solve but adds very little error to result

\[
q_{\text{trans}}(V, T) = \left( \frac{2\pi nk_B T}{h^2} \right)^{3/2}
\]
Translational energy, \( \langle \mathcal{E}_{\text{trans}} \rangle \)

With \( q \) we can calculate \textit{any} thermodynamic quantity!!

In Ch 17 (BZ notes) we showed this for the average energy ...

\[
\langle \mathcal{E}_{\text{trans}} \rangle = k_B T^2 \left( \frac{\partial \ln q_{\text{trans}}}{\partial T} \right)_V \quad \text{here... } q_{\text{trans}}(V, T) = \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} V
\]

\[
\langle \mathcal{E}_{\text{trans}} \rangle = k_B T^2 \left( \frac{\partial}{\partial T} \ln \left[ T^{3/2} \left( \frac{2\pi m k_B}{\hbar^2} \right)^{3/2} V \right] \right)_V
\]

As we found in BZ notes!
(Recall: this is \textit{per atom}.)

\( \mathcal{E}_{\text{trans}} \)
Next consider the electronic contribution to \( q \): \( q_{elec} \)

Again, start from the general form of \( q \), but this time sum over levels rather than states:

\[
q_{elec} = \sum_{levels} g_{ei} e^{-\beta \varepsilon_{ei}}
\]

We choose to set the lowest electronic energy state at zero, such that all higher energy states are *relative* to the ground state.

\[
\varepsilon_1 = 0
\]

For monatomic gases!
Can we simplify $q_{elec}$?

\[ q_{elec}(T) = g_{e1} + g_{e2}e^{-\beta \varepsilon_{e2}} + g_{e3}e^{-\beta \varepsilon_{e3}} + \ldots \]

Terms are getting small rapidly...

The electronic energy levels are spaced far apart, and therefore we typically only need to consider the first term or two in the series...

General rule of thumb: At 300 K, you only need to keep terms where $\varepsilon_{ej} < 10^3$ cm\(^{-1}\) ($e^{-\beta \varepsilon} > 0.008$)
A closer look at electronic levels…

\[ q_{\text{elec}}(T) = g_{e1} + g_{e2}e^{-\beta\varepsilon_{e2}} + g_{e3}e^{-\beta\varepsilon_{e3}} + \ldots \]

General trends,

1. Nobel gas atoms:
   \[ \varepsilon_{e2} = 10^5 \text{ cm}^{-1} \text{ (at 300K, keep \_\_\_ term(s))} \]

2. Alkali metal gas atoms:
   \[ \varepsilon_{e2} = 10^4 \text{ cm}^{-1} \text{ (at 300K, keep \_\_\_ term(s))} \]

3. Halogen gas atoms:
   \[ \varepsilon_{e2} = 10^2 \text{ cm}^{-1} \text{ (at 300K, keep \_\_\_ term(s))} \]

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### Table 4.1 (18.1)
Some atomic energy levels.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Electron configuration</th>
<th>Degeneracy ( g_e = 2J + 1 )</th>
<th>Energy/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>( 1s )</td>
<td>2</td>
<td>0.</td>
</tr>
<tr>
<td></td>
<td>( 2p )</td>
<td>2</td>
<td>82,258.907</td>
</tr>
<tr>
<td></td>
<td>( 2s )</td>
<td>2</td>
<td>82,258.942</td>
</tr>
<tr>
<td></td>
<td>( 2p )</td>
<td>4</td>
<td>82,259.272</td>
</tr>
<tr>
<td>He</td>
<td>( 1s^2 )</td>
<td>1</td>
<td>0.</td>
</tr>
<tr>
<td></td>
<td>( 1s2p )</td>
<td>3</td>
<td>159,850.318</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>166,271.70</td>
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<tr>
<td>Li</td>
<td>( 1s^22s )</td>
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<td>0.</td>
</tr>
<tr>
<td></td>
<td>( 1s^22p )</td>
<td>2</td>
<td>14,903.66</td>
</tr>
<tr>
<td></td>
<td>( 1s^23s )</td>
<td>4</td>
<td>14,904.00</td>
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<tr>
<td></td>
<td>( 1s^23p )</td>
<td>2</td>
<td>27,206.12</td>
</tr>
<tr>
<td>F</td>
<td>( 1s^22s^22p^5 )</td>
<td>4</td>
<td>0.</td>
</tr>
<tr>
<td></td>
<td>( 1s^22s^22p^43s )</td>
<td>6</td>
<td>102,406.50</td>
</tr>
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<td>4</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>105,057.10</td>
</tr>
</tbody>
</table>

In general it is sufficient to keep only the first two terms for $q_{elec}$

$$q_{elec}(T) \approx g_{e1} + g_{e2} e^{-\beta \varepsilon_{e2}}$$

However, you should always keep in mind that for very high temperatures (like on the sun) or smaller values of $\varepsilon_{ej}$ (like in F) that additional terms may contribute.

If you find that the second term is of reasonable magnitude (>1% of first term), then you must check to see that the third term can be neglected.
Finally… we can solve for $Q$!

For a *monatomic ideal gas* we have:

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

with

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

$$q_{elec}(T) \approx g_{e1} + g_{e2} e^{-\beta\varepsilon_{e2}}$$
We can now calculate the average energy, $U = \langle E \rangle$

$$U = \langle E \rangle = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V = N k_B T^2 \left( \frac{\partial \ln q}{\partial T} \right)_V = N k_B T^2 \left( \frac{\partial \ln q_{\text{trans}}}{\partial T} \right)_V$$

Plug in $q_{\text{trans}}$ and $q_{\text{elec}}$ ...

$$U = N k_B T^2 \left( \frac{\partial}{\partial T} \ln \left( \left( \frac{2 \pi m k_B T}{h^2} \right)^{3/2} V \left( g_{e_1} + g_{e_2} e^{-\beta \epsilon_{e_2}} \right) \right) \right)_V$$

$$U = \frac{3}{2} N k_B T + \frac{N g_{e_2} \epsilon_{e_2} e^{-\beta \epsilon_{e_2}}}{q_{\text{elec}}}$$

Electronic contribution typically small (i.e., negligible)

So ... $U \approx \bar{U}$ or $\bar{U} =$ molar energy
Molar heat capacity for a monatomic ideal gas:

\[ \overline{C_V} = \left( \frac{dU}{dT} \right)_{N,V} \]

\[ \overline{C_V} = \left( \frac{d \left( \frac{3}{2} RT \right)}{dT} \right)_{N,V} = \frac{3}{2} R \]

Could also find heat capacity:

\[ C_V = \frac{3}{2} Nk_B \]
Finding thermodynamic parameters…

\[ P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} = Nk_B T \left( \frac{\partial \ln q}{\partial V} \right)_T = Nk_B T \left( \frac{\partial \ln(q_{trans} q_{elec})}{\partial V} \right)_T \]

Plug in \( q_{trans} \) and \( q_{elec} \) …

\[ P = Nk_B T \left( \frac{\partial}{\partial V} \ln \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} V \left( g_{e_1} + g_{e_2} e^{-\beta \varepsilon_{e_2}} \right) \right)_T \]

Only function of \( V \)

So… \[ P = \quad \text{or} \quad \overline{P} = \]

Look familiar??

molar pressure
Ideal Monatomic Gas: A Summary

Partition Function:

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

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

\[ q_{\text{elec}}(T) \approx g_{e_1} + g_{e_2} e^{-\beta e_2} \]

From \( Q \) get:

Energy

\[ U \approx \frac{3}{2} N k_B T \]

(molar)

\[ \overline{U} = \frac{3}{2} RT \]

Heat Capacity

Pressure
In addition to trans. and elec. degrees of freedom, we need to consider:

1. Rotations
2. Vibrations

\[ \mathcal{E}_{\text{diatomic}} = \mathcal{E}_{\text{trans}} + \mathcal{E}_{\text{rot}} + \mathcal{E}_{\text{vib}} + \mathcal{E}_{\text{elec}} \]
Q. What will the form of the molecular diatomic partition function be given:
\[ E_{\text{diatomic}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} \]

Ans.

Q. How will this give us the diatomic partition function?

Ans.

Now all we need to know is the form of \( q_{\text{trans}}, q_{\text{rot}}, q_{\text{elec}}, \) and \( q_{\text{vib}} \).

Start with \( q_{\text{trans}} \): This is the same as in the monatomic case but with \( m = m_1 + m_2 \)!
We define the zero of the electronic energy to be separated atoms at rest in their ground electronic energy states.

With this definition,

$$\varepsilon_{e_1} = -D_e$$

And…

Note the slight difference in $q_{elec}$ between monatomic and diatomic gases!