Statistical Molecular Thermodynamics

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Video 4.1

Ideal Monatomic Gas: $q_{\text{trans}}$
Ideal Gas Partition Function

We have established that the partition function of a non-interacting system, \( Q(N,V,T) \), can be written in terms of individual atomic or molecular partition functions, \( q(V,T) \):

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

\( N \): number of particles
\( V \): volume
\( T \): temperature

We now apply this to an ideal gas where:

1) The molecules are indistinguishable

2) The number of states greatly exceeds the number of molecules (assumption of “low” pressure).
Monatomic Ideal Gas Partition Function

We consider each *degree of freedom* separately:

For an ideal *monatomic* gas the *only* degrees of freedom are translational and electronic (a significant simplification):

\[
\mathcal{E}_{\text{atomic}} = \mathcal{E}_{\text{trans}} + \mathcal{E}_{\text{elec}} \quad \text{(sum)}
\]

The total energy is the sum of the translational and electronic energy terms.
The atomic partition function is the product of the partition functions from each degree of freedom:

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

So, we must consider \( q_{\text{trans}}(V, T) \) and \( q_{\text{elec}}(T) \)
Given the general form of the partition function:

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

From QM, we have that for a cubic container with sides of length \( a \),

\[ \varepsilon_{\text{trans}} = \frac{h^2}{8ma^2} \left( n_x^2 + n_y^2 + n_z^2 \right) \quad \text{with} \quad n_x, n_y, n_z = 1, 2, \ldots \]

For this \( \varepsilon_{\text{trans}} \)

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

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

Or,

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

The three sums are all the same (only the index is different), so,

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

because of dependence on side length \(a\)
Dense Energy Levels

There is no simple, analytical expression for this sum:

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

However, since translational energy levels are spaced very densely, the sum is nearly a continuous function and we can approximate the sum as an integral,

\[ q_{\text{trans}}(V, T) = \left( \int_{1}^{\infty} dn e^{-\beta h^2 n^2 / 8ma^2} \right)^3 \]
Solving for $q_{\text{trans}}$

$$\int_{1}^{\infty} dn e^{-\beta h^2 n^2 / 8ma^2} \approx \int_{0}^{\infty} dn e^{-\beta h^2 n^2 / 8ma^2}$$

Integral table: $\int_{0}^{\infty} dn e^{-\alpha n^2} = \left( \frac{\pi}{4\alpha} \right)^{1/2} = \left( \frac{8\pi ma^2 k_B T}{4h^2} \right)^{1/2}$

$$q_{\text{trans}} (V, T) \approx \left( \int_{0}^{\infty} dn e^{-\beta h^2 n^2 / 8ma^2} \right)^3 = \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2} V$$

Consider methane (CH$_4$):

$m = 2.662 \times 10^{-26}$ kg, $V = 24.47$ dm$^3$, $T = 298.15$ K

$q_{\text{trans}} = 1.519 \times 10^{30}$

So, number of “accessible levels” vastly exceeds Avogadro’s number

choice of volume part of “standard-state” convention