# 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):

**The Energy:** $$\varepsilon_{\text{atomic}} = \varepsilon_{\text{trans}} + \varepsilon_{\text{elec}} \quad \text{(sum)}$$

- $\varepsilon_{\text{atomic}}$: total energy
- $\varepsilon_{\text{trans}}$: translational energy
- $\varepsilon_{\text{elec}}$: electronic energy

# Monatomic Ideal Gas Partition Function

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

**The Partition Function:**

$$q(V,T) = q_{\text{trans}}(V,T)\, q_{\text{elec}}(T) \qquad \text{(product)}$$

total atomic partition function

translational atomic partition function

electronic atomic partition function

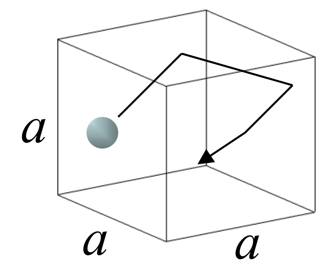
So, we must consider $q_{\text{trans}}(V,T)$ and $q_{\text{elec}}(T)$

# Translational Component

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 $a$,




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

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

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

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 $q_{\text{trans}}$

$$\int_1^\infty dn\, e^{-\beta h^2 n^2/8ma^2} \approx \int_0^\infty dn\, e^{-\beta h^2 n^2/8ma^2}$$

$$\alpha = \frac{h^2}{8ma^2 k_B T}$$

Integral table: $\int_0^\infty dn\, e^{-\alpha n^2} = \left(\frac{\pi}{4\alpha}\right)^{1/2}$ $= \left(\frac{8\pi m a^2 k_B T}{4h^2}\right)^{1/2}$

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

$a^3 = V$

*choice of volume part of "standard-state" convention*

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 Avogradro's number*