Deriving some partition functions from first principles or ab initio

Consider a monatomic gas

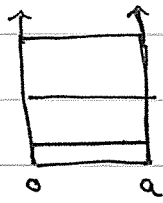
$\varepsilon_{atomic} = \varepsilon_{translation} + \varepsilon_{electronic}$ ← the only kinds of excitation available

$\therefore$

$q = q_{translation} \times q_{electronic}$

We've been using $q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$ but where does this come from?

Consider a particle in a 1-D box:



$\varepsilon_n = \frac{n^2 h^2}{8ma^2}$

$n = 1, 2, \ldots$

Or a particle in a 2-D square:

$$\varepsilon_{n_x n_y} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2\right)$$

Or a particle in a 3-D cube:

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

These energy expressions describe the quantum mechanical energy levels for <u>translation</u> for a particle of mass m in a box of length a on a side.

What happens when we make the box very large? Do the levels get closer in energy or farther apart?

Road map for finding q_{trans}

Energy levels in small box → q → Large box limit.

$$\varepsilon^{trans}_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$q_{trans} = \sum_{states} e^{-E_{state}/k_B T} = \sum_{n_x, n_y, n_z = 1}^{\infty} e^{-\frac{h^2}{8ma^2 kT}\left(n_x^2 + n_y^2 + n_z^2\right)}$$

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

Sum of products = product of sums

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

All 3 factors are the same

$$q_{trans} = \left(\sum_{n=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2} n^2}\right)^3$$

So how do we do this sum?

$$\sum_{n=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2} n^2} \approx \int_1^{\infty} e^{-\frac{\beta h^2}{8ma^2} n^2} dn \approx \int_0^{\infty} e^{-\frac{\beta h^2}{8ma^2} n^2} dn$$

OK if energy levels are close together

OK if 0 is ≈ 1 (actually OK if 1st level is close to 0)

This last integral is just a standard Gaussian integral:

$$\int_0^{\infty} e^{-\alpha n^2} dn = \sqrt{\frac{\pi}{4\alpha}}$$

$$\therefore \sum_{n=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2} n^2} \approx \sqrt{\frac{\pi\, 8ma^2}{4\beta h^2}} = \sqrt{\frac{2\pi m k_B T}{h^2}}\, a$$

Remember, we have 3 of these sums (one for each direction or side of the cube)

$$q_{trans} = \left(\sum_{n=1}^{\infty} e^{-(\beta h^2/8ma^2) n^2} \right)^3 \approx \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} a^3$$

a^3 ← Volume of the box!

$$\therefore \boxed{q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V}$$

$$\therefore q_{trans} = q_{trans}(V, T)$$

← translation is the only part of molecular partition function that depends on volume

Quick check of our previous result:

$$\langle \varepsilon_{trans} \rangle = -\left(\frac{\partial \ln q_{trans}}{\partial \beta} \right)$$

$$\ln q_{trans} = \frac{3}{2} \ln \frac{2\pi m}{\beta h^2} + \ln V$$

$$\therefore \langle \varepsilon_{trans} \rangle = -\frac{3}{2} \left(\frac{\beta h^2}{2\pi m} \right) \left(\frac{2\pi m}{h^2} \right) \left(\frac{-1}{\beta^2} \right)$$

$$= \frac{3}{2} \frac{1}{\beta} = \frac{3 k_B T}{2} \checkmark$$

For atoms, $\varepsilon = \varepsilon_{trans} + \varepsilon_{electronic}$

Electronic states are organized into levels

$n = 1 \longrightarrow 1s$

$n = 2 \longrightarrow 2s \quad 2p$

$n = 3 \longrightarrow 3s \quad 3p \quad 3d$

For Hydrogen all orbitals with same n have the same Energy

Hydrogenic atoms: $E_n = \dfrac{-m_e Z^2 e^4}{8\varepsilon_0^2 h^2 n^2}$ (Z: nuclear charge)

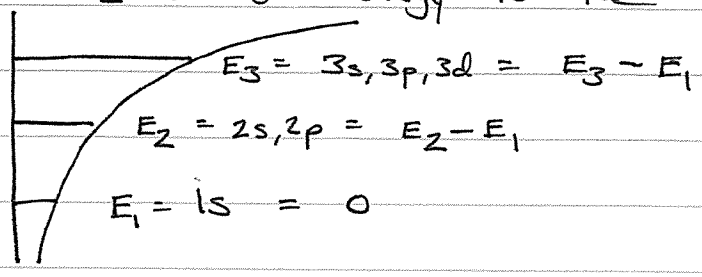
In general, it is most convenient to leave the electronic partition function in level form:

$$q_{electronic} = \sum_i g_i e^{-\beta\varepsilon_i}$$

ε_i = energy of level i

g_i = degeneracy of level i

If we set the zero of energy to the ground state:



Then we can write the partition function as:

$$q_{elect} = g_1 + g_2 e^{-\beta(E_2-E_1)} + g_3 e^{-\beta(E_3-E_1)} + \ldots.$$

g_1: Boltzmann factor for $n=1$

$g_2 e^{-\beta(E_2-E_1)}$: Boltzmann factor for $n=2$

$g_3 e^{-\beta(E_3-E_1)}$: Boltzmann factor for $n=3$

One thing we often want to know is the fraction of a population that's in an excited state

$$f_2(T) = \frac{g_2 e^{-\beta(E_2-E_1)}}{g_1 + g_2 e^{-\beta(E_2-E_1)} + g_3 e^{-\beta(E_3-E_1)}}$$

$f_2(T)$: Fraction in level 2 at temperature T

As an example, let's look at Fluorine:

$$f_2(T) = \frac{2e^{-\beta(E_2-E_1)}}{4 + 2e^{-\beta(E_2-E_1)} + 6e^{-\beta(E_3-E_1)}}$$

T	f_2	
300	0.0672	← unless we go to high T, the excited states don't play much of a role!
1000	0.219	
2000	0.272	

From Table 18.1

$E_2 - E_1 = 404.0\ cm^{-1}$

$E_3 - E_1 = 102406.50\ cm^{-1}$

$g_1 = 4$

$g_2 = 2$

$g_3 = 6$

for 300K:

$$\frac{2e^{-404.0\ cm^{-1}/(300\ K \cdot 0.695\ cm^{-1})}}{4 + 2e^{-404.0\ cm^{-1}/(300\ K \cdot 0.695\ cm^{-1})} + 6e^{-102406.50\ cm^{-1}/(300\ K \cdot 0.695\ cm^{-1})}}$$

$$= 0.0672$$