Translational partition function

Boltzmann statistics (corrected) $Q(N,V,T) = \frac{\left[q(N,V)\right]^N}{N!}$

$$q = \sum_i e^{-\varepsilon_i/kT} \quad \text{molecular partition function}$$

sum over single-molecule states

Separation of molecular partition function

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}} + \varepsilon_{\text{spin}} = \varepsilon_{\text{trans}} + \varepsilon_{\text{int}}$$

$$q = \sum_i e^{-\varepsilon_i/kT} = \sum_i e^{-\left(\varepsilon_{\text{trans}i} + \varepsilon_{\text{int}\,i}\right)/kT}$$

The sum includes every possible combination of translational and internal quantum numbers.

Consider the product

$$q_{\text{trans}} q_{\text{int}} = \sum_i e^{-\beta\varepsilon_{\text{trans}i}} \sum_i e^{-\beta\varepsilon_{\text{int}i}} = \left(e^{-\beta\varepsilon_{\text{trans}1}} + e^{-\beta\varepsilon_{\text{trans}2}} + e^{-\beta\varepsilon_{\text{trans}3}} + \cdots\right)\left(e^{-\beta\varepsilon_{\text{int}1}} + e^{-\beta\varepsilon_{\text{int}2}} + e^{-\beta\varepsilon_{\text{int}3}} + \cdots\right)$$

$$e^{-\beta\left(\varepsilon_{\text{trans}1} + \varepsilon_{\text{int}1}\right)} + e^{-\beta\left(\varepsilon_{\text{trans}1} + \varepsilon_{\text{int}2}\right)} + \cdots$$

The sum includes every possible combination of translational and internal quantum numbers!

The separation will be valid as long as the energies are simply additive.

Separation of thermodynamic contributions

We can write

$$Q = q^N/N! = Q_{\text{trans}} Q_{\text{int}} = \left(q_{\text{trans}}^N/N!\right) q_{\text{int}}^N$$

$$A = A_{\text{trans}} + A_{\text{int}} = \left(-NkT \ln q_{\text{trans}} + kT \ln N!\right) - NkT \ln q_{\text{int}}$$

Thermodynamic contributions are additive

Translational partition function

Translational energies are solutions to Schrödinger equation for particle in a box of dimension $a \times b \times c$

Quantum numbers n_x, n_y, n_z

$$\varepsilon(n_x, n_y, n_z) = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

$$q_{\text{trans}} = \sum_{n_x, n_y, n_z} e^{-\varepsilon(n_x, n_y, n_z)/kT} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left[-\frac{h^2}{8mkT}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)\right]$$
$$= \sum_{n_x=1}^{\infty} \exp\left(-\frac{h^2 n_x^2}{8mkTa^2}\right) \sum_{n_y=1}^{\infty} \exp\left(-\frac{h^2 n_y^2}{8mkTb^2}\right) \sum_{n_z=1}^{\infty} \exp\left(-\frac{h^2 n_z^2}{8mkTc^2}\right)$$

Need to solve sums

$$\sum_{n=1}^{\infty} \exp\left(-\frac{h^2 n^2}{8mkTa^2}\right) = \sum_{n=0}^{\infty} \exp\left(-\frac{h^2 n^2}{8mkTa^2}\right) - 1 \approx \sum_{n=0}^{\infty} \exp\left(-\frac{h^2 n^2}{8mkTa^2}\right)$$

Now approximate sum as integral:

$$\sum_{n=0}^{\infty} \exp\left(-\frac{h^2 n^2}{8mkTa^2}\right) \approx \int_0^{\infty} dn \exp\left(-\frac{h^2 n^2}{8mkTa^2}\right) = \left(\frac{2\pi mkTa^2}{h^2}\right)^{\frac{1}{2}}$$

$$\text{since } \int_0^{\infty} dn \exp\left(-g^2 n^2\right) = \frac{\sqrt{\pi}}{2g} \text{ with } g = \left(\frac{h^2}{8mkTa^2}\right)^{\frac{1}{2}}$$

So

$$q_{\text{trans}} = \left(\frac{2\pi mkTa^2}{h^2}\right)^{\frac{1}{2}} \left(\frac{2\pi mkTb^2}{h^2}\right)^{\frac{1}{2}} \left(\frac{2\pi mkTc^2}{h^2}\right)^{\frac{1}{2}} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} abc$$

$$\boxed{q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V}$$

where $V = abc$

We now have $q_{\text{trans}}(V,T)$ in terms of quantities that we know

Example: 1 mol N_2 at 1 atm, 273 K:

$$m = \frac{0.028\ \text{kg/mol}}{6x10^{23}\ \text{/mol}} = 4.7x10^{-26}\ \text{kg} \qquad V = 22.4\,\ell = 22.4x10^{-3}\ \text{m}^3$$

$$q_{\text{trans}} = \left[\frac{2\pi\left(4.7x10^{-26}\ \text{kg}\right)\left(1.38x10^{-23}\ \text{J/K}\right)\left(300\ \text{K}\right)}{\left(6.6x10^{-34}\ \text{J-s}\right)^2}\right]^{\frac{3}{2}}\left(22.4x10^{-3}\ \text{m}^3\right) = 3.3x10^{30}$$

$$\frac{N}{q_{\text{trans}}} = \frac{6x10^{23}}{3.3x10^{30}} = 1.8x10^{-7}$$

$\overline{n_i} = \dfrac{Ne^{-\beta\varepsilon_i}}{q} << 1$. Boltzmann statistics are fine for molecules at room T.

How about <u>electrons</u>? Assume gas of same density

$$m_e = 5x10^{-7}\ \text{kg/mol} \qquad \frac{q^{e}_{\text{trans}}}{q^{N_2}_{\text{trans}}} = \left(\frac{5x10^{-7}}{0.028}\right)^{\frac{3}{2}} = 7.5x10^{-8}$$

$$q^{e}_{\text{trans}} = q^{N_2}_{\text{trans}}\left(7.5x10^{-8}\right) = \left(3.3x10^{30}\right)\left(7.5x10^{-8}\right) = 2.5x10^{23} \qquad \frac{N}{q^{e}_{\text{trans}}} = \frac{6x10^{23}}{2.5x10^{23}} = 2.4$$

Definitely not <<1! Electrons must be treated with Fermi-Dirac statistics.

<u>Calculation of macroscopic thermodynamic properties</u> from microscopic energy levels: q_{trans}

$$q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V$$

$$Q_{\text{trans}} = \frac{q^{N}_{\text{trans}}}{N!} = \frac{1}{N!}\left[\frac{\left(2\pi mkT\right)^{\frac{3}{2}}}{h^3} V\right]^N$$

Translational contribution to energy

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$\ln Q_{\text{trans}} = -\ln N! + \frac{3}{2} N \ln T + N \ln \left[\frac{(2\pi mk)^{\frac{3}{2}}}{h^3} V \right]$$

$$\left(\frac{\partial \ln Q_{\text{trans}}}{\partial T} \right)_{N,V} = \frac{3}{2} \frac{N}{T}$$

$$E = kT^2 \left(\frac{3}{2} \frac{N}{T} \right)$$

$$\boxed{E = \frac{3}{2} NkT = \frac{3}{2} RT}$$ average translational energy per mole

$$\boxed{E = \frac{3}{2} kT}$$ average translational energy per molecule

Translational contribution to pressure

$$p = -\left(\frac{\partial A}{\partial V} \right)_{T,N} = kT \left(\frac{\partial \ln Q_{\text{trans}}}{\partial V} \right)_{T,N}$$

$$\ln Q_{\text{trans}} = -\ln N! + N \ln V + N \ln \left[\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \right]$$

$$\left(\frac{\partial \ln Q_{\text{trans}}}{\partial V} \right)_{N,V} = \frac{N}{V}$$

$$p = kT \frac{N}{V}$$

$$\boxed{pV = NkT = nRT}$$