Lecture 7: Monoatomic Partition Functions

Translational and Electronic Partition Functions

Monoatomic Ideal Gas

Last time:

$$q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vibr}} \cdot q_{\text{elec}}$$

Monoatomic Ideal Gas - no rotational or vibrational degrees of freedom:

$$\varepsilon_{total} = \varepsilon_{\text{trans}} + \varepsilon_{\text{elec}}$$

$$q = q_{\text{trans}} \cdot q_{\text{elec}}$$

Consider a system of N indistinguishable monoatomic molecules:

$$Q = \frac{q^N}{N!}$$

Translational Partition Function

Particle in a 3D box:

$$\varepsilon_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad n_x, n_y, n_z = 1, 2, 3, \ldots$$

Plug in and expand energy eigenvalues to q:

$$\begin{aligned} q_{\text{trans}} &= \sum_{n_x,n_y,n_z} e^{-\beta\varepsilon_{n_x,n_y,n_z}} \\ &= \sum_{n_x,n_y,n_z} \exp\left[-\beta\frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)\right] \\ &= \underbrace{\sum_{n_x}^{\infty} \exp\left(-\beta\frac{h^2}{8ma^2}n_x^2\right)}_{\text{x direction}} \cdot \underbrace{\sum_{n_y}^{\infty} \exp\left(-\beta\frac{h^2}{8ma^2}n_y^2\right)}_{\text{y direction}} \cdot \underbrace{\sum_{n_z}^{\infty} \exp\left(-\beta\frac{h^2}{8ma^2}n_z^2\right)}_{\text{z direction}} \end{aligned}$$

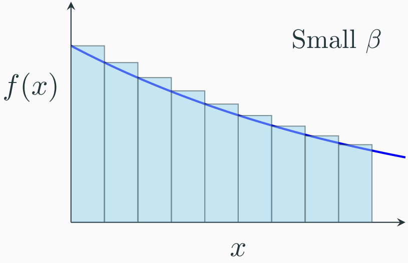
Translational Partition Function

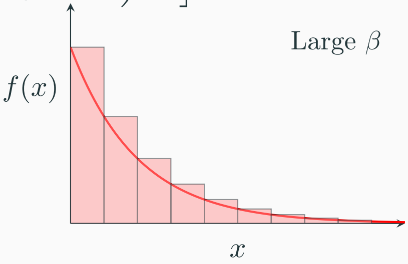
All 3 sums are equivalent:

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

Replace summation with integral since energies effectively a continuium:

$$q_{\text{trans}} \approx \left[\int_{0}^{\infty} \exp\left(-\beta \frac{h^2}{8ma^2} n^2\right) dn\right]^3$$





Translational Partition Function

$$q_{\text{trans}} = \left[\int_0^\infty \exp\left(-\frac{\beta h^2}{8ma^2}n^2\right)\, dn\right]^3$$

Gaussian integral:

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

Substitute $\alpha = \frac{\beta h^2}{8ma^2}$:

$$q_{\text{trans}} = \left[\sqrt{\frac{\pi}{4}\frac{8ma^2}{\beta h^2}}\right]^3 = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} a^3$$

For a 3D Particle in a box, $V = a^3$:

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

Connecting Q to q: 2 methods

Energy equation applies on molecular level as well:

$$\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} \implies \langle \varepsilon\rangle = -\left(\frac{\partial \ln q}{\partial \beta}\right)_{V}$$

Evaluate $\ln Q$

$$Q = \frac{q^N}{N!}$$

$$\ln Q = N\ln q - \ln N!$$

$$\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

$$= -N\left(\frac{\partial \ln q}{\partial \beta}\right)_{V}$$

$$= N\langle \varepsilon\rangle$$

Multiply by N

$$\langle \varepsilon\rangle = -\left(\frac{\partial \ln q}{\partial \beta}\right)_{V}$$

$$\langle E\rangle = \sum_i^N \langle \varepsilon_i\rangle$$

$$= N\langle \varepsilon\rangle$$

Energy of N particles

$$\langle E\rangle = N\langle \varepsilon\rangle$$

Distinguishability does not matter

Translational Energy Contribution

Translational Canonical Partition Function:

$$Q_{\text{trans}} = \frac{q_{\text{trans}}^N}{N!} = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2} V^N$$

Substitute q_{trans}:

$$\begin{aligned}\ln q_{\text{trans}} &= \ln\left(\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V\right) \\ &= \frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right) - \frac{3}{2}\ln\beta + \ln V \\ \langle\varepsilon_{\text{trans}}\rangle &= -\left(\frac{\partial \ln q_{\text{trans}}}{\partial\beta}\right)_V = \frac{3}{2\beta} = \frac{3}{2}k_{\text{B}}T\end{aligned}$$

$$\boxed{\frac{1}{2}k_B T \text{ for each translational degree of freedom}}$$

Occupancy at Room Temperature

Thermal energy is the energy of a system responsible for temperature $\propto k_B T$
Thermal energy at 298 K:

$$k_B T = 0.695\,\mathrm{cm}^{-1}\mathrm{K}^{-1} \cdot 298\,\mathrm{K} = 207\,\mathrm{cm}^{-1} \approx 200\,\mathrm{cm}^{-1}$$

Particle in a box energy spacing:

$$\varepsilon_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \implies \Delta\varepsilon \approx \frac{h^2}{8ma^2}$$

Plug in typical values:

$$\Delta\varepsilon = \frac{(6.626 \times 10^{-34}\ \mathrm{J\,s})^2}{8\,(3 \times 10^{-26}\ \mathrm{kg})\,(10^{-2}\ \mathrm{m})^2} \approx 1.83 \times 10^{-38}\ \mathrm{J} = 9.2 \times 10^{-16}\mathrm{cm}^{-1}$$

Translational motion behaves classically at room temperature, excited states occupied

Electronic Partition Function

Electronic Partition Function:

$$q_{\text{elec}} = \sum_{i,\text{levels}} g_i e^{-\beta\varepsilon_i}$$

where g_i is the degeneracy and ε_i is the energy of the ith electronic level

Define $\varepsilon_0 = 0$ as the ground electronic state to measure energies relative to it:

$$q_{\text{elec}} = g_0 + g_1 e^{-\beta\varepsilon_1} + g_2 e^{-\beta\varepsilon_2} + \dots$$

We will prove using relative energies is okay on our homework

UV–Vis for Electronic Transitions

$$\begin{aligned}\lambda &= 200 \text{ nm} \\ &= 2.0 \times 10^{-5} \text{ cm} \\ \tilde{\nu} &= \frac{1}{\lambda} \\ &= \frac{1}{2.0 \times 10^{-5} \text{ cm}} \\ &= 5.0 \times 10^{4} \text{ cm}^{-1}\end{aligned}$$

UV–Vis electronic transitions:

$$\begin{aligned}&\sim 200 - 800 \text{ nm} \\ &\sim 12{,}500 - 50{,}000 \text{ cm}^{-1}\end{aligned}$$

Example: Electronic Excited State Probability

For typical UV transition, excited state is much higher than $200\,\text{cm}^{-1}$:

$$\begin{array}{lllll} \varepsilon_0 & = & 0 & g_0 = 1 & \text{(ground state)} \\ \varepsilon_1 & = & 50{,}000\,\text{cm}^{-1} & g_1 = 3 & \text{(first excited electronic state)} \end{array}$$

Calculate q_{elec} at 298 K ($k_B T \approx 207$ cm^{-1}):

$$\begin{aligned} q_{\text{elec}} &= g_0 + g_1 e^{-\beta\varepsilon_1} = 1 + 3e^{-50{,}000/207} \\ &= 1 + 3e^{-241.5} \approx 1 \end{aligned}$$

Probability of being in the excited state:

$$\begin{aligned} P_1 &= \frac{g_1 e^{-\beta\varepsilon_1}}{q_{\text{elec}}} \approx \frac{3 \cdot 10^{-105}}{1} \\ &\approx 3 \cdot 10^{-105} \end{aligned}$$

Essentially all molecules remain in the ground electronic state at room temperature