Molecular partition functions

Independent, Distinguishable molecules

e.g. in a perfect crystal

$$E_l(N,V) = \varepsilon_i^a(V) + \varepsilon_j^b(V) + \varepsilon_k^c(V) + \cdots N\ terms$$

$$Q(N,V,T) = \sum_i e^{-\beta E_i} = \sum_{i,j,k\ldots} e^{-\beta\left(\varepsilon_i^a + \varepsilon_j^b + \varepsilon_k^c + \cdots\right)} = \sum_i e^{-\beta\varepsilon_i^a} \sum_j e^{-\beta\varepsilon_j^b} \sum_k e^{-\beta\varepsilon_k^c} \ldots$$

$$= q_a(V,T)q_b(V,T)q_c(V,T)\ldots$$

$$Q(N,V,T) = [q(V,T)]^N$$

$q(V,T)$ is called the *molecular partition function*.

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$$Q(N,V,T) = \sum_i e^{-\beta E_i} = \sum_{i,j,k\ldots} e^{-\beta\left(\varepsilon_i\ +\varepsilon_j\ +\varepsilon_k\ +\cdots\right)}$$

To avoid over-counting, use,

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

Decomposition of the molecular partition functions

For independent particles,

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = N k_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V = N \sum_i \varepsilon_i \frac{e^{-\varepsilon_i/k_B T}}{q(V,T)} = N\langle\varepsilon\rangle$$

Probability that a molecule is in its jth molecular energy state

$$\pi_j = \frac{e^{-\varepsilon_j/k_B T}}{q(V,T)} = \frac{e^{-\varepsilon_j/k_B T}}{\sum_j e^{-\varepsilon_j/k_B T}}$$

Energy of a molecule,

$$\varepsilon = \varepsilon_i^{trans} + \varepsilon_j^{rot} + \varepsilon_k^{vib} + \varepsilon_l^{elec}$$

All energy terms are distinguishable, so we can write, $q(V,T) = q_{trans}q_{rot}q_{vib}q_{elec}$

$$\pi_{ijkl} = \frac{e^{-\varepsilon_i^{trans}/k_B T}e^{-\varepsilon_j^{rot}/k_B T}e^{-\varepsilon_k^{vib}/k_B T}e^{-\varepsilon_l^{elec}/k_B T}}{q_{trans}q_{rot}q_{vib}q_{elec}}$$

If we sum over all other states, we get the probability that a molecule is in its kth vibrational state.

$$\pi_k^{vib} = \frac{\left(\sum_i e^{-\varepsilon_i^{trans}/k_B T}\right)\left(\sum_j e^{-\varepsilon_j^{rot}/k_B T}\right)\left(\sum_l e^{-\varepsilon_l^{elec}/k_B T}\right) e^{-\varepsilon_k^{vib}/k_B T}}{q_{trans} q_{rot} q_{vib} q_{elec}}$$

Also,

$$\langle \varepsilon^{vib} \rangle = \sum_k \varepsilon_k^{vib} \frac{e^{-\varepsilon_k^{vib}/k_B T}}{q(V,T)} = k_B T^2 \frac{\partial \ln q_{vib}}{\partial T} = -\frac{\partial q_{vib}}{\partial \beta}$$

Likewise for rotation and translation.

In case there is degeneracy, then we have g_j energy levels for the given energy state.

$$q(V,T) = \sum_{\substack{j \\ (levels)}} g_j e^{-\varepsilon_j/k_B T}$$

e.g. rotation, $q_{rot}(T) = \sum_{J=0}^{\infty}(2J+1)e^{-\hbar^2 J(J+1)/2Ik_B T}$

Molecular Partition Functions – Monatomic Ideal Gas

$$\varepsilon_{atomic} = \varepsilon_{trans} + \varepsilon_{elec} \quad \text{and} \quad q(V,T) = q_{trans}(V,T)q_{elec}(T)$$

Translational partition function

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

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

Each of the summations is

$$\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right) = e^{-\beta h^2/8ma^2} + e^{-4\beta h^2/8ma^2} + e^{-9\beta h^2/8ma^2} + \cdots$$

Thus,

$$q_{trans} = \left[\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right)\right]^3 = \left[\int_0^{\infty} e^{-\beta h^2 n^2/8ma^2} dn\right]^3 = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

$(\int_0^{\infty} e^{-\alpha x^2} dx = (\pi/4\alpha)^{1/2})$

$$\langle \varepsilon_{trans} \rangle = k_B T^2 \left(\frac{\partial \ln q_{trans}}{\partial T}\right)_V = k_B T^2 \left(\frac{\partial}{\partial T}\left[\frac{3}{2}\ln T + \text{terms independent of T}\right]\right)_V = \frac{3}{2} k_B T$$

Electronic partition function

Lets measure all electronic energies w.r.t. the G.S. i.e. $E_{GS} = \varepsilon_{e1} = 0$

$$q_{elec}(T) = g_{e1} + g_{e2}e^{-\beta\varepsilon_{e2}} + \cdots$$

These $\varepsilon's$ are typically ~ 10,000s cm^{-1}. Given, 1.986×10^{-23} J $= 1$ cm^{-1}, $k_B = 0.6950$ cm^{-1}.K^{-1}

Thus,

$$\beta\varepsilon_{elec} \approx \frac{10000 \text{ cm}^{-1}}{0.6950 \text{ cm}^{-1}.\text{K}^{-1}}\frac{1}{T} \approx \frac{10^4 \text{K}}{T} \sim 10 \text{ for } T = 1000 \text{ K}$$

$$e^{-\beta\varepsilon_{e2}} \sim 10^{-5}$$

$$q_{elec}(T) \sim g_{e1}$$