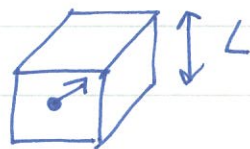# HH0062　Sackur-Tetrode Equation

Consider one atom in a 3D box.

$$\varepsilon_n = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

The partition function is the sum over all states (n_x, n_y, n_z):

$$Z_1 = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\varepsilon_n/\tau}$$

assume the high temperature limit,

$$= \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z\; e^{-\alpha^2(n_x^2+n_y^2+n_z^2)}, \qquad \alpha^2 = \frac{\pi^2\hbar^2}{2ML^2}.$$

$$= \frac{1}{\alpha^3}\left(\int_0^\infty dx\, e^{-x^2}\right)^3 = \left(\frac{\sqrt{\pi}}{2\alpha}\right)^3$$

Introduce the quantum concentration $n_Q \equiv \left(\frac{M\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}}$. The partition function can be expressed as

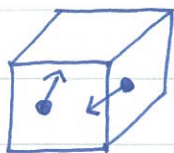$$\boxed{Z_1 = \frac{V}{(2\pi\hbar^2/M\tau)^{3/2}} = n_Q V = n_Q/n}$$

because $n = \frac{1}{V}$ ☺

We can compute the average energy of the one-atom gas.

$$U_1 = \tau^2\frac{\partial \log Z_1}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau}\left[\log n_Q - \log n\right] \qquad \text{independent of } \tau.$$

$$= \tau^2 \cdot \frac{1}{n_Q}\frac{dn_Q}{d\tau} = \frac{\tau^2}{n_Q}\cdot\frac{3}{2}\frac{n_Q}{\tau} \longrightarrow \boxed{U_1 = \frac{3}{2}\tau}$$

① Partition function of two independent systems.

Consider two atoms in a 3D box. Assuming there is no interaction between them.

$$\boxed{\varepsilon_S = \varepsilon_{S_1} + \varepsilon_{S_2}}$$

S_1, S_2 are quantum numbers for atom 1 and atom 2.

Note that $\sum_S = \sum_{S_1}\sum_{S_2}$ for sum over all possible states.

The partition function for the system is

$$Z = \sum_S e^{-\varepsilon_S/\tau} = \sum_{S_1}\sum_{S_2} e^{-(\varepsilon_{S_1}+\varepsilon_{S_2})/\tau} = \left(\sum_{S_1} e^{-\varepsilon_{S_1}/\tau}\right)\left(\sum_{S_2} e^{-\varepsilon_{S_2}/\tau}\right)$$

$$\longrightarrow \boxed{Z = Z_1 \cdot Z_2}$$ This argument can be easily generalized to N-atom system. Because all atoms are the same $Z_1 = Z_2 = \cdots$, the partition function is
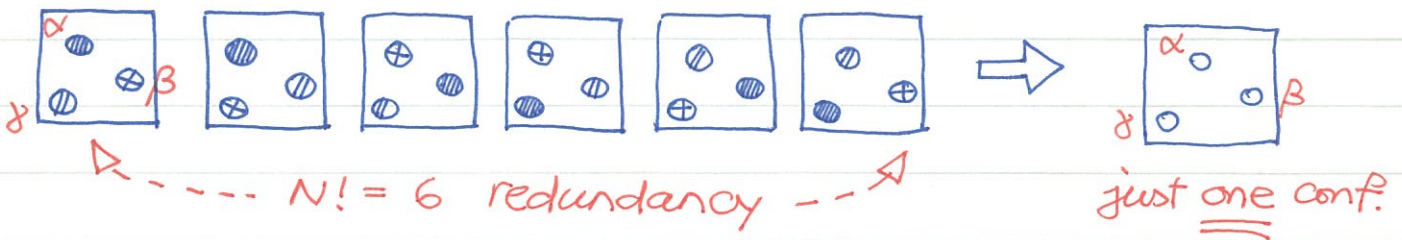
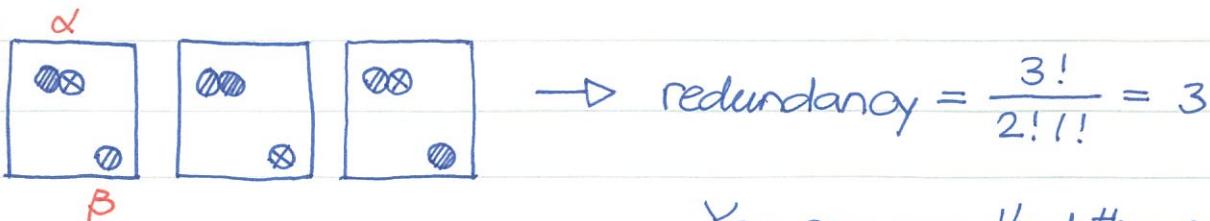$$Z = \underbrace{Z_1 \cdot Z_1 \cdots Z_1}_{N} = Z_1^N \longleftarrow$$ Unfortunately, this result is NOT quite right....

① Identical particles.

There is a problem when particles are identical...

N=3 case —

$\cdots\cdots$ N! = 6 redundancy $\cdots\cdots$ just one conf.

But not all states share the same redundancy (Woops...trouble!)

$$\longrightarrow \text{redundancy} = \frac{3!}{2!\,1!} = 3$$

no redundancy. ☺

You can see that the redundancy depends on how many different orbitals are occupied.

If the density is low $n \ll n_Q$, we can approximate all redundant factor by N!

$$Z_N = \frac{1}{N!}(Z_1 Z_1 \cdots Z_1) \longrightarrow \boxed{Z_N = \frac{Z_1^N}{N!}}$$

Let's compute the average energy,

$$U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \frac{3}{2}N\tau = NU_1 \quad \text{agrees with intuition.}$$

The Helmholtz free energy is

$$F = -\tau \log Z_N = -\tau \log Z_1^N + \tau \log N!$$

→ correction for redundancy.

$$= -N\tau \log(n_Q V) + \tau N \log N - \tau N, \qquad Z_1 = n_Q V.$$

$$\boxed{F = -N\tau \log\left(\frac{n_Q}{n}\right) - N\tau}$$

$F = N \cdot f$ is extensive. Good!

The pressure can be computed,

$$P = -\left(\frac{\partial F}{\partial V}\right)_\tau = -\frac{\partial}{\partial V}\left(-N\tau \log V + \text{other terms}\right)_{\text{const }\tau}$$

$$\rightarrow \quad P = \frac{N\tau}{V}$$

ideal-gas law again!

Here comes the most important result: Try to compute σ!

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = N\log\left(\frac{n_Q}{n}\right) + N\tau \cdot \frac{1}{n_Q/n} \cdot \frac{1}{n}\frac{dn_Q}{d\tau} + N$$

$\rightarrow \frac{3}{2}\frac{n_Q}{\tau}$

The entropy of the ideal gas is

$$\boxed{\sigma = N\left[\log\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right]}$$

Sackur-Tetrode equation

Holding N fixed ～

(1) At constant τ, expand from V_1 to V_2,

$$\Delta\sigma = \sigma(V_2) - \sigma(V_1) = N\log V_2 - N\log V_1 = N\log\left(\frac{V_2}{V_1}\right).$$
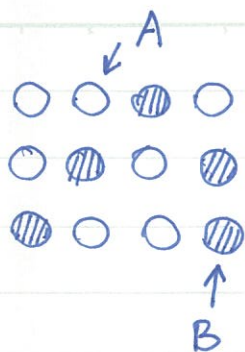
(2) At constant V, raise temperature from τ_1 to τ_2,

$$\Delta\sigma = \sigma(\tau_2) - \sigma(\tau_1) = N\log n_Q(\tau_2) - N\log n_Q(\tau_1) = \frac{3}{2}N\log\left(\frac{\tau_2}{\tau_1}\right)$$

① Entropy of mixing

Consider a mixture of N_A atom A and N_B atom B.

multiplicity $\qquad g = \dfrac{N!}{N_A! \, N_B!} \qquad N_A + N_B = N$

The entropy associated with these arrangements is

$$\sigma(x) = \log N! - \log N_A! - \log N_B! \quad , \quad x \equiv \frac{N_B}{N}$$

$$\cong -N_A \log(N_A/N) - N_B \log(N_B/N)$$

$$= N\left[-(1-x)\log(1-x) - x\log x\right]$$

It is easy to see that the mixing entropy can be understood in terms of Shannon entropy.

Suppose a strong repulsive energy exists for B atom to dissolve into A atoms. It is expected that $x \ll 1$.

$$F_L = U_L - \tau \sigma_L = N_B \cdot \Delta - \tau N\left[-(1-x)\log(1-x) - x\log x\right]$$

$$\approx N x \Delta - \tau N\left[-x\log x\right] = N\left[x\Delta + \tau x \log x\right].$$

Minimize the Landau free energy F_L.

$$\frac{\partial F_L}{\partial x} = 0 \quad \longrightarrow \quad \Delta + \tau \log x + \tau = 0, \qquad \boxed{\langle x \rangle = e^{-\frac{\Delta + \tau}{\tau}}}$$

The result indicates there is a natural impurity content in all crystals.

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