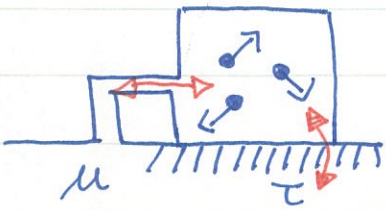
HH0068 Gibbs Sum

Consider a system in thermal and diffusive contacts with the reservoir. What is the probability to find the system in a particular state with energy ε_s and particle number N? According to the fundamental assumption of statistical physics, the probability $P(\varepsilon_s, N)$ is proportional to the number of accessible states in the reservoir;



$$P(N, \varepsilon_s) \propto g_R(N_0 - N, U_0 - \varepsilon_s) = e^{\sigma_R(N_0 - N,\, U_0 - \varepsilon_s)}$$

Expand the entropy σ_R in Taylor series and keep the lowest order terms,

$$\sigma_R(N_0 - N, U_0 - \varepsilon_s) \approx \sigma_R(N_0, U_0) - \frac{\partial \sigma_R}{\partial N_R} N - \frac{\partial \sigma_R}{\partial U_R} \varepsilon_s + \cdots$$

$$= \sigma_{R0} + \left(\frac{\mu}{\tau}\right) N - \left(\frac{1}{\tau}\right) \varepsilon_s + \cdots$$

Therefore, the probability $P(N, \varepsilon_s)$ for the state with N & ε_s is

$$\boxed{P(N, \varepsilon_s) \propto e^{(N\mu - \varepsilon_s)/\tau}}$$

← Gibbs factor, very similar to the Boltzmann factor.

Introduce the Gibbs sum (or the grand partition function)

$$\boxed{Z_G \equiv \sum_{N=0}^{\infty} \sum_{S(N)} e^{[N\mu - \varepsilon_{S(N)}]/\tau}} \longrightarrow P(N, \varepsilon_s) = \frac{1}{Z_G} e^{(N\mu - \varepsilon_s)/\tau}$$

One can obtain the average particle number from the grand partition function,

$$\frac{\partial Z_G}{\partial \mu} = \sum_{N=0}^{\infty} \sum_{S} \frac{N}{\tau} e^{(N\mu - \varepsilon_s)/\tau} = \frac{1}{\tau} Z_G \cdot \langle N \rangle$$

$$\longrightarrow \boxed{\langle N \rangle = \tau \cdot \frac{1}{Z_G} \frac{\partial Z_G}{\partial \mu} = \tau \frac{\partial}{\partial \mu} \log Z_G}$$

Sometimes, we employ the handy notation $\lambda \equiv e^{\mu/\tau}$ (the absolute activity) to simplify the calculations. It's easy to see

$$\boxed{\mathcal{Z}_G = \sum_N \lambda^N \sum_S e^{-\varepsilon_S/\tau} = \sum_{N=0}^{\infty} \lambda^N Z_N}$$

Z_N is the partition function ☺

⊘ Number fluctuations in ideal gas.

It is rather easy to compute the grand partition function for an ideal gas,

$$\mathcal{Z}_G = \sum_{N=0}^{\infty} \lambda^N \frac{Z_1^N}{N!} = e^{\lambda Z_1}, \quad Z_1 = n_Q V$$

We already know that $\langle N \rangle = \tau \frac{\partial}{\partial \mu} \log \mathcal{Z}_G$. Taking another derivative

$$\frac{\partial^2}{\partial \mu^2}(\log \mathcal{Z}_G) = \frac{\partial}{\partial \mu}\left[\frac{1}{\mathcal{Z}_G} \sum_{N,S} e^{(N\mu - \varepsilon_S)/\tau} \cdot \frac{N}{\tau}\right]$$

$$= \frac{1}{\mathcal{Z}_G} \sum_{N,S} \left(\frac{N}{\tau}\right)^2 e^{(N\mu-\varepsilon_S)/\tau} - \frac{1}{\mathcal{Z}_G^2} \frac{\partial \mathcal{Z}_G}{\partial \mu} \cdot \sum_{N,S} \left(\frac{N}{\tau}\right) e^{(N\mu - \varepsilon_S)/\tau}$$

$$= \frac{1}{\tau^2}\langle N^2 \rangle - \frac{1}{\tau^2}\langle N \rangle^2 \Longrightarrow \boxed{\langle N^2 \rangle - \langle N \rangle^2 = \tau^2 \frac{\partial^2}{\partial \mu^2} \log \mathcal{Z}_G}$$

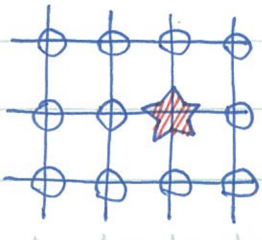
For ideal gas, $\log \mathcal{Z}_G = \lambda Z_1 = e^{\mu/\tau} \cdot n_Q V$. The fluctuations of particle number $\Delta N = \sqrt{\langle N^2 \rangle - \langle N \rangle^2}$ can be computed easily,

$$\Delta N = \sqrt{\tau^2 \cdot \frac{\partial^2}{\partial \mu^2}\left(e^{\mu/\tau} n_Q V\right)} = \sqrt{\cancel{\tau^2} \cdot \frac{1}{\cancel{\tau^2}} \cdot e^{\mu/\tau} \cdot n_Q V} = \sqrt{\langle n \rangle V} = \sqrt{\langle N \rangle}$$

Thus, if we measure ΔN, it is $\sqrt{N}$ and can be quite large. BUT! The density fluctuations are small,

$$\boxed{\frac{\Delta n}{\langle n \rangle} = \frac{\Delta N / V}{\langle N \rangle / V} = \frac{\Delta N}{\langle N \rangle} = \frac{1}{\sqrt{\langle N \rangle}}} \rightarrow 0 \text{ in thermodynamic limit}$$ ☺

⊘ Impurity ionization in semiconductor



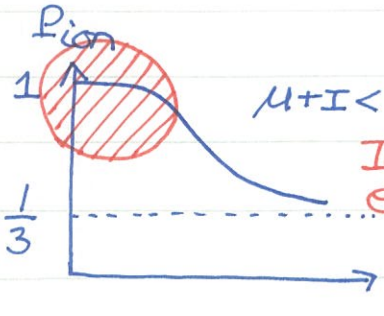
Three states for an impurity atom

$\lvert 0 \rangle$	$N = 0$,	$\varepsilon = 0$,	electron detached
$\lvert \uparrow \rangle$	$N = 1$,	$\varepsilon = -I$,	spin up electron attached
$\lvert \downarrow \rangle$	$N = 1$,	$\varepsilon = -I$	spin down electron attached

The Gibbs sum is simple $Z_G = 1 + 2e^{(\mu+I)/\tau}$. The ionized probability is

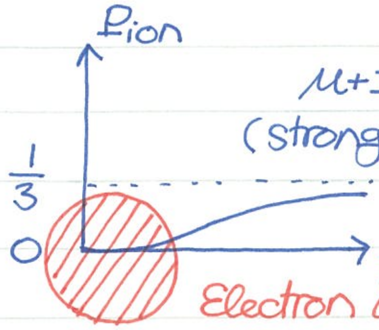
$$\boxed{P_{ion} = \frac{1}{Z_G} = \frac{1}{1+2e^{(\mu+I)/\tau}}}$$

The sign of $\mu+I$ is important.



$\mu+I<0$ (weak binding)

Ionization is easy at low τ.

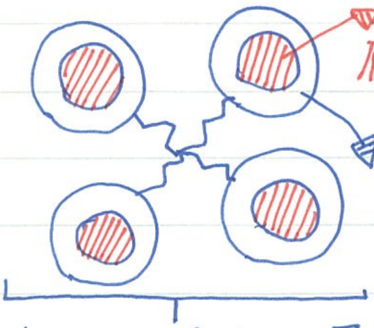


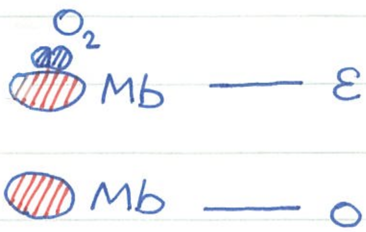
$\mu+I>0$ (strong binding)

Electron is attached at low τ.

⑩ Adsorption of O_2 by myoglobin

It is all about names....





Gibbs sum

$$\boxed{Z_G = 1 + \lambda e^{-\varepsilon/\tau}}$$

The O_2 molecules on hemes are in equilibrium with the O_2 in the surrounding liquid,

$$\mu(MbO_2) = \mu(O_2)$$

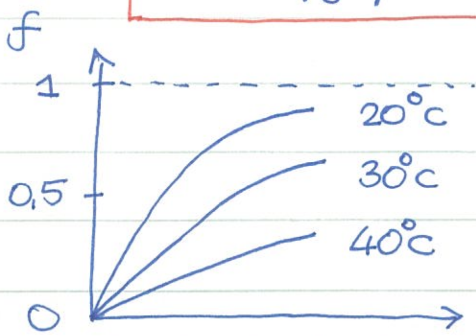
Assuming the O_2 in liquid can also be described by the ideal gas $\lambda = e^{\mu/\tau} = n/n_Q = P/\tau n_Q$

The fraction of Mb occupied by O_2 is found to be

$$f = \frac{1}{Z_G} \cdot \lambda e^{-\varepsilon/\tau} = \frac{\lambda e^{-\varepsilon/\tau}}{1+\lambda e^{-\varepsilon/\tau}} = \frac{P}{n_Q \tau e^{\varepsilon/\tau} + P}$$

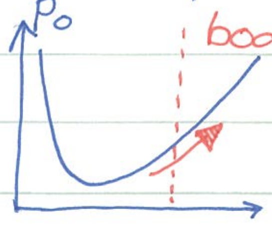
$$\rightarrow \boxed{f = \frac{P}{P_0 + P}, \text{ where } P_0 = n_Q \tau e^{\varepsilon/\tau}}$$

Langmuir adsorption isotherm

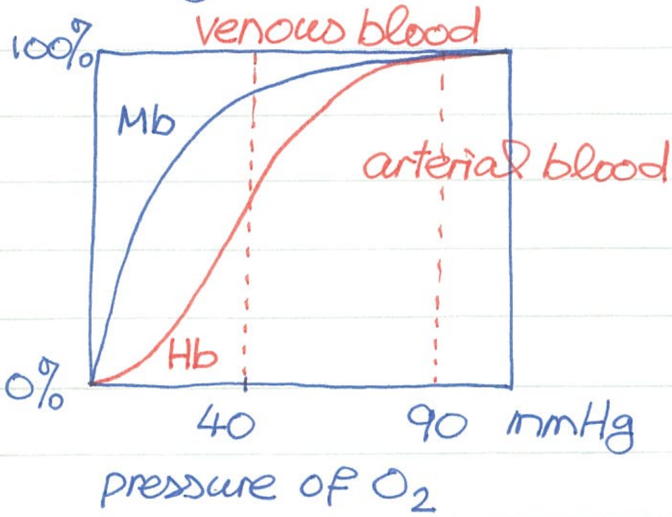


The occupation fraction depends on

$$P_0 \sim \tau^{5/2} e^{\varepsilon/\tau}$$



Saturation curves of O_2 bound to myoglobin (Mb) and hemoglobin (Hb) are different. The partial pressures of O_2



in arterial and venous bloods are about 90 mmHg and 40 mmHg. The O_2 occupation fractions of Mb do not change significantly within the pressure range.

But, the occupation fraction of Hb varies more significantly and is better for loading and/or unloading O_2 molecules in our bloods.

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