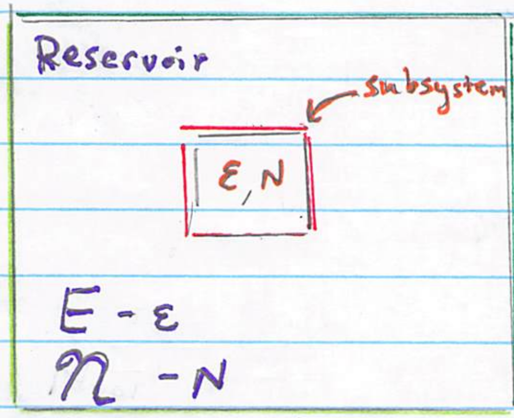
The Grand Canonical Ensemble



- Consider a small system exchanging energy and particles with a reservoir

- The total system (Reservoir + subsystem) has total energy E and total # of particles $\mathcal{N}$

- The number of States in the reservoir is $\Omega_R(E-\varepsilon, \mathcal{N}-N)$ and $S_R = k_B \ln \Omega_R$

- Let us require that the subsystem be in one microstate with energy ε and number N

$$\mathcal{P}(E-\varepsilon, \mathcal{N}-N; \varepsilon, N) \propto \Omega_R(E-\varepsilon, \mathcal{N}-N) \times 1$$

So

$$\ln \mathcal{P} = \underbrace{\ln \Omega_R(E-\varepsilon, \mathcal{N}-N)}_{\frac{S_R(E-\varepsilon, \mathcal{N}-N)}{k_B}} + \text{const}$$

So

- we expand using $(\partial S/\partial E)_N = 1/T$, and $(\partial S/\partial N)_E = \mu/T$

$$\frac{S_R}{k_B}(E-\varepsilon, \mathcal{N}-N) = \frac{S_R}{k_B}(E,\mathcal{N}) - \frac{1}{k_B T}\varepsilon + \frac{\mu}{k_B T} N$$

So re-exponentiating:

constant indep of ε, N

$$\ln \mathcal{P} = -\frac{(\varepsilon_s - \mu N)}{k_B T} + \text{const}$$

$$\boxed{\mathcal{P} = C e^{-(\varepsilon - \mu N)/k_B T}}$$

Summary:
The probability for the subsystem to have ε and number N is

$$P \propto e^{-(\varepsilon - \mu N)/kT}$$

- Then we may sum over all states and over all possible values of N

$$\sum_i \mathcal{P}_i = 1.$$

$$C \sum_i e^{-(\varepsilon_i - \mu N_i)/k_B T} = 1 \quad \text{or} \quad C = \frac{1}{\mathcal{Z}(T,\mu)}$$

where

script letter $\mathcal{Z}$ is a common notation. Book uses, Z.

$$\boxed{\mathcal{Z} = \sum_i e^{-(\varepsilon - \mu N_i)/k_B T}}$$

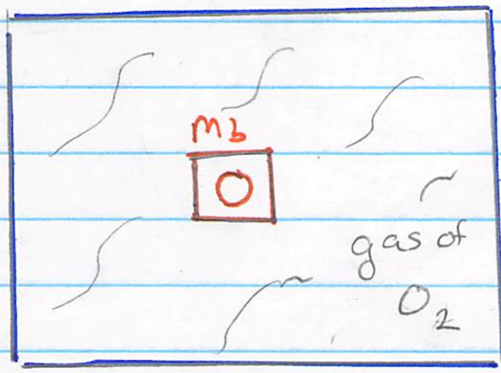
← This is known as the grand partition function

and

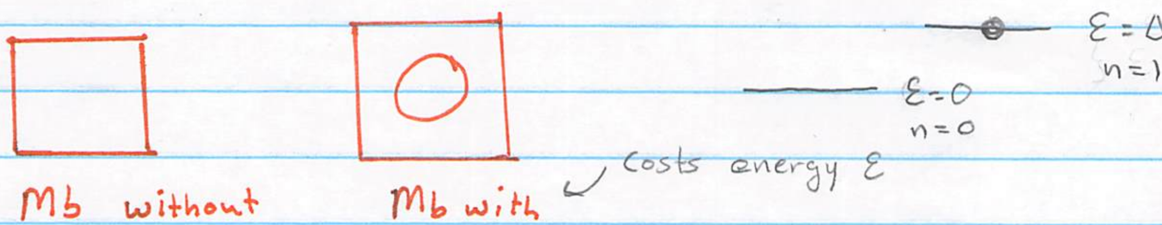
$$\boxed{\mathcal{P}_i = \frac{e^{-\beta(\varepsilon_i - \mu N_i)}}{\mathcal{Z}}}$$

Example : Occupied / Unoccupied (Adapted from Kittel + Kroemer)

- A protien myoglobin, Mb, can absorb O_2 from the surrounding gas raising its energy by ε Δ

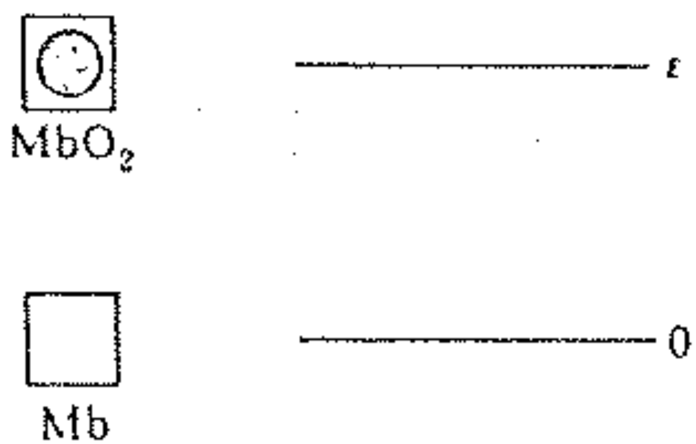


- Two states of Myoglobin without and with O_2



- Why do we need the chemical potential "nonsense"? Well clearly if the concentration of surrounding O_2 is low not much Myoglobin will be occupiend by O_2. If the concentration of O_2 is high but the temperature is low, again not much of the myoglobin will be absorbed. Equilibrium between the myoglobin and the surrounding gas is reached when the chemical potential of the surrounding gas and myoglobins are equal. In that sense the chemical potential is like the temperature, i.e. myoglobin and gas are in equilibrium at constant temperature

Occupied and Unoccupied: Absorption of O_2 by myoglobin



$$O_2 + Mb \leftrightarrow MbO_2$$

One myoglobin protein in a gas of O_2

- The Grand Partition function is

$$\mathcal{Z}_{mb} = e^{-\beta(0-\mu_0)} + e^{-\beta(\Delta-\mu)} = 1 +$$

So the probability to have absorbed O_2 is

$$\boxed{P_{absorb} = \frac{e^{-\beta(\Delta-\mu)}}{\mathcal{Z}} = \frac{e^{-\beta(\Delta-\mu)}}{(1 + e^{-\beta(\Delta-\mu)})}}$$

- So what is μ?

  - That is set by the properties of the surronnding gas. (The β is also set by the propenties of the surronnding gas.) From the ideal gas

density of O_2

$$\mu = k_B T \ln(n\lambda_{th}^3) \Rightarrow e^{\beta\mu} = n\lambda_{th}^3$$

And

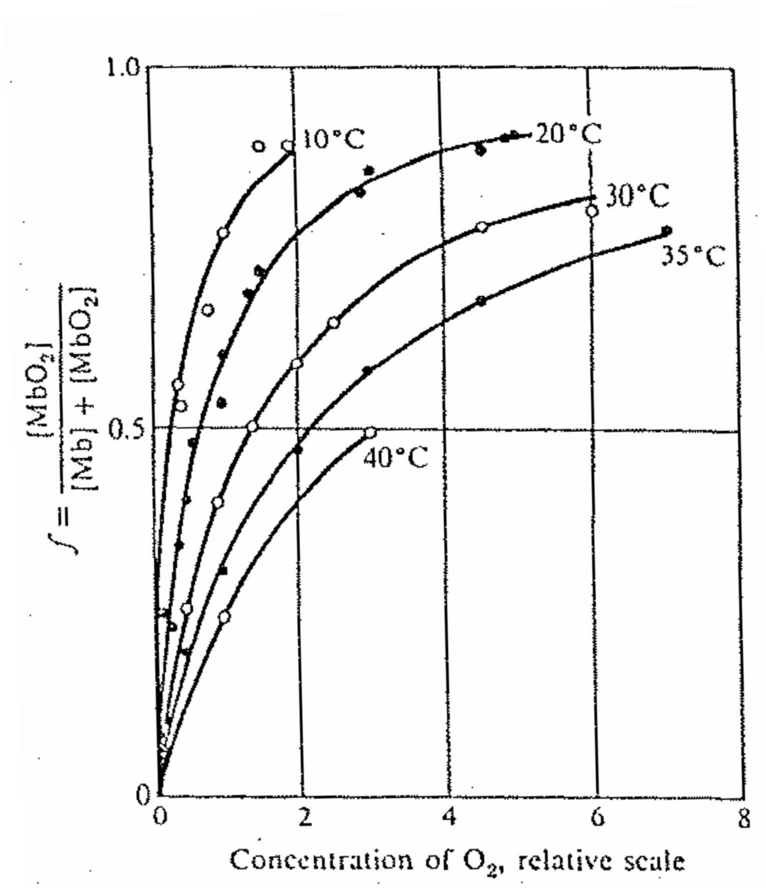
$$P_{absb} = \frac{e^{-\beta\Delta}\, n\lambda_{th}^3}{1 + e^{-\beta\Delta}\, n\lambda_{th}^3} = \frac{n}{e^{\beta\Delta}/\lambda_{th}^3 + n}$$

Calling $n_0 = e^{\beta\Delta}/\lambda_{th}^3$ we have

$$\boxed{P_{absb} = \frac{n}{n_0(T) + n}}$$

this prediction for the absorption fraction vs. the concentration of O_2 is shown on the next slide.

Fraction of Occupied Mb Protein



So How do we use The Grand Sum $\mathcal{Z}$?

- You use it like the partition function

$$\langle N \rangle = \sum_i N_i P_i = \frac{1}{\mathcal{Z}} \sum_i N_i e^{-(E_i - \mu N_i)/kT}$$

now

$$k_B T \left(\frac{\partial}{\partial \mu}\right)_T \left(e^{-(E_i - \mu N_i)/kT}\right) = N_i e^{-(E_i - \mu N_i)/kT}$$

So:

$$\boxed{\langle N \rangle = k_B T \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = k_B T \frac{\partial \ln \mathcal{Z}}{\partial \mu}}$$

Now similarly to the partition function

$$\langle E - \mu N \rangle = \sum_i (E_i - \mu N_i) P_i$$

$$= \frac{1}{\mathcal{Z}} \sum_i (E_i - \mu N_i) e^{-\beta(E_i - \mu N_i)}$$

Using

$$(E_i - \mu_i N_i) e^{-\beta(E_i - \mu N_i)} = -\frac{\partial}{\partial \beta} e^{-\beta(E_i - \mu N_i)}$$

So

$$\boxed{\langle E - \mu N \rangle = -\frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{\mu}}$$

or

$$\boxed{\langle E - \mu N \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}} \Rightarrow \langle E \rangle = \langle E - \mu N \rangle + \mu \langle N \rangle$$

Finally

$$S = -k_B \sum_i P_i \ln P_i \qquad P_i = \frac{e^{-\beta(\varepsilon_i - \mu N_i)}}{\mathcal{Z}}$$

like in Homework

$$= \frac{U - \mu N}{T} + k_B \ln \mathcal{Z}$$

Resuffling

$$k_B T \ln \mathcal{Z} = TS + \mu N - U$$

Gibbs Duhem

$$\boxed{k_B T \ln \mathcal{Z} = pV}$$

the book calls this $-\Phi_G$

So

$$\boxed{\mathcal{Z} = e^{-\beta \Phi_G} = e^{\beta p V}}$$

Φ_G is the "grand potential" i.e $-pV$

Deriving Everything else from Φ_G

- Once we know Φ_G we can derive everything else from it. It is analogous to the partition function and free energy

$$dU = T\,dS - p\,dV + \mu\,dN$$

$F \equiv U - TS$

$$dF = -S\,dT - p\,dV + \mu\,N$$

$\Phi_G = F - \mu N$

$$\boxed{d\Phi_G = -S\,dT - N\,d\mu - p\,dV}$$

From the Gibbs Duhem: $\Phi_G = -pV = U - TS - \mu N$

- From these derivatives we find several results

$$\boxed{\begin{aligned} S &= -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu, V} \\ N &= -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T, V} \\ p &= -\left(\frac{\partial \Phi}{\partial V}\right)_{T, \mu} \end{aligned}}$$