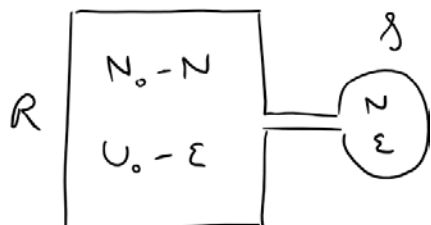## Lecture 12 – Grand canonical ensemble

PREVIOUSLY: In the canonical ensemble, system $\mathbb{S}$ is in thermal contact with reservoir $\mathcal{R}$ that maintains temperature T. We considered N to be fixed.

TODAY: We consider the grand canonical ensemble. $\mathcal{R}$ supplies both heat (to maintain temperature T) and particles to system $\mathbb{S}$ so N is not fixed.

The total system $\mathcal{R} + \mathbb{S}$ is closed so:
$$U_0 = U_{\mathcal{R}} + \varepsilon \text{ is fixed}$$
$$N_0 = N_{\mathcal{R}} + N \text{ is fixed}$$

What are the properties of the grand canonical ensemble?

KEY CONCEPT: the Gibbs or grand sum
If $\mathbb{S}$ is in a single microstate i with energy ε_i and N_i particles, what is the probability of being in that state?

From fundamental assumption, the probability is proportional to the multiplicity $\Omega_{\mathcal{R}+\mathbb{S}}$ of the combined system $\mathcal{R} + \mathbb{S}$

$$p(N_i,\varepsilon_i) = \frac{\Omega_{\mathcal{R}+\mathbb{S}}(N_i,\varepsilon_i)}{\displaystyle\sum_{\text{All } N_i,\,\varepsilon_i} \Omega_{\mathcal{R}+\mathbb{S}}(N_i,\varepsilon_i)}$$

but $\Omega_{\mathcal{R}+\mathbb{S}} = \Omega_{\mathcal{R}}(N_0 - N_i, U_0 - \varepsilon_i)\underbrace{\Omega_{\mathbb{S}}(N_i,\varepsilon_i)}_{1}$ since $\mathbb{S}$ is in a single state

Let's take the ratio of probs. for two systems in states 1 and 2 in equilibrium with $\mathcal{R}$

$$\frac{p(N_1,\varepsilon_1)}{p(N_2,\varepsilon_2)} = \frac{\Omega_{\mathcal{R}}(N_0-N_1,U_0-\varepsilon_1)}{\Omega_{\mathcal{R}}(N_0-N_2,U_0-\varepsilon_2)} = \frac{e^{S_{\mathcal{R}}(N_0-N_1,U_0-\varepsilon_1)/k_B}}{e^{S_{\mathcal{R}}(N_0-N_2,U_0-\varepsilon_2)/k_B}}$$
$$= \exp\left[S_{\mathcal{R}}(N_0-N_1,U_0-\varepsilon_1) - S_{\mathcal{R}}(N_0-N_2,U_0-\varepsilon_2)\right]/k_B$$

Now, we showed for a reservoir $\mathcal{R}$ that $U_0 \gg \varepsilon_1$ or ε_2 and $N_0 \gg N_1$ or N_2, so we can expand about U_0 and N_0

$$S_{\mathcal{R}}(N_0-N_i,U_0-\varepsilon_i) \approx S_{\mathcal{R}}(N_0,U_0) - \left.\frac{\partial S_{\mathcal{R}}}{\partial N}\right|_{N_0} N_i - \left.\frac{\partial S_{\mathcal{R}}}{\partial U}\right|_{U_0}\varepsilon_i = S_{\mathcal{R}}(N_0,U_0) + \frac{\mu}{T}N_i - \frac{\varepsilon_i}{T}$$

(Note that $T_{\mathcal{R}} = T_{\mathbb{S}} = T$ and $\mu_{\mathcal{R}} = \mu_{\mathbb{S}} = \mu$ at thermal and diffusive equilibrium)

It follows that:

$$\frac{p(N_1,\varepsilon_1)}{p(N_2,\varepsilon_2)} = \frac{e^{(\mu N_1 - \varepsilon_1)/k_B T}}{e^{(\mu N_2 - \varepsilon_2)/k_B T}}$$

To get $p(\varepsilon_i)$, we use the normalization condition for probabilities: $\sum_{N_i}\sum_{\varepsilon_i}p(N_i,\varepsilon_i)=1$:

$$p(N_i,\varepsilon_i)=\frac{e^{-(\varepsilon_i-\mu N_i)/k_BT}}{\sum_{N_j}\sum_{\varepsilon_j}e^{-(\varepsilon_j-\mu N_j)/k_BT}}$$

Each factor of the form $e^{-(\varepsilon_i-\mu N_i)/k_BT}$ is known as a <u>Gibbs factor</u>

It is also useful to define the <u>Gibbs (or grand) sum</u> $\mathcal{Z}(\mu,T)$:

$$\mathcal{Z}(\mu,T)=\sum_{N_j}\sum_{\varepsilon_j}e^{-(\varepsilon_j-\mu N_j)/k_BT}$$

As in partition function, the sum is taken over microstates of the <u>system $\mathcal{S}$ only</u> – states of the reservoir $\mathcal{R}$ don't factor at all.

We can relate $\mathcal{Z}(\mu,T)$ to the partition function $Z(T)$:

$$\mathcal{Z}(\mu,T)=\sum_{N}\sum_{\varepsilon(N)}e^{-(\varepsilon-\mu N)/k_BT}=\sum_{N}e^{\mu N/k_BT}\underbrace{\sum_{\varepsilon(N)}e^{-\varepsilon/k_BT}}_{Z(N,T)}$$

$$=\sum_{N}\lambda^N Z(N,T)$$

where $\lambda\equiv e^{\mu/k_BT}$ is called the "absolute activity". $Z(N,T)$ is the usual partition function for a system with N particles. Since N is no longer fixed, we have to sum over all possible N, weighted by the factors λ^N.

The particle number is now a statistical quantity with an average $\langle N\rangle$ given by:

$$\langle N\rangle=\frac{\sum_{N}\sum_{\varepsilon(N)}Ne^{-(\varepsilon-\mu N)/k_BT}}{\mathcal{Z}(\mu,T)}\quad\text{or}\quad=\frac{\sum_{N}\sum_{\varepsilon(N)}N\lambda^N e^{-\varepsilon/k_BT}}{\mathcal{Z}(\mu,T)}$$

$$=k_BT\frac{\partial}{\partial\mu}\ln\mathcal{Z}(\mu,T)\quad\text{or}\quad=\lambda\frac{\partial}{\partial\lambda}\ln\mathcal{Z}(\lambda,T)$$

Question 1: Write down an expression for the average energy in terms of derivatives of the Gibbs sum.

The definition of the average energy gives

$$U=\langle\varepsilon\rangle=\frac{\sum_{N}\sum_{\varepsilon(N)}\varepsilon e^{-(\varepsilon-\mu N)/k_BT}}{\mathcal{Z}(\mu,T)}$$
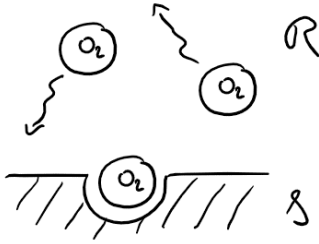
In analogy with the relationship $U=\langle\varepsilon\rangle=-\frac{\partial}{\partial\beta}\ln Z$ we can try $-\frac{\partial}{\partial\beta}\ln\mathcal{Z}$:

$$-\frac{\partial}{\partial\beta}\ln\mathcal{Z} = \frac{1}{\mathcal{Z}}\sum_{N}\sum_{\varepsilon(N)}(\varepsilon-\mu N)e^{-\beta(\varepsilon-\mu N)} = \langle\varepsilon\rangle - \mu\langle N\rangle$$
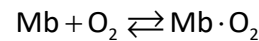
It follows that

$$U = \langle\varepsilon\rangle = \mu\langle N\rangle - \frac{\partial}{\partial\beta}\ln\mathcal{Z} = \frac{\mu}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z} - \frac{\partial}{\partial\beta}\ln\mathcal{Z}$$

Ex: myoglobin binding isotherm

Myoglobin (Mb) is a protein in our muscles that binds O_2:
$$Mb + O_2 \rightleftarrows Mb\cdot O_2$$

Model Mb as system $\mathcal{S}$ in contact with reservoir $\mathcal{R}$ of O_2.
\# of O_2 on Mb can be: 0 (with energy 0)
1 (with energy $\varepsilon_{O_2} < 0$)

Question 2: Write down an expression for a) the Gibbs sum for a single myoglobin and b) the probability that it has an O_2 molecule bound.

a) There are two microstates:
$$\mathcal{Z} = \sum_{N}\sum_{\varepsilon(N)}e^{-\beta(\varepsilon-\mu N)}$$
$$= \underbrace{e^{-\beta(0-\mu\cdot 0)}}_{\text{No }O_2} + \underbrace{e^{-\beta(\varepsilon_{O_2}-\mu\cdot 1)}}_{1\ O_2\ \text{bound}} = 1 + e^{-\beta(\varepsilon_{O_2}-\mu)}$$

b) Let f = probability to be in occupied state
$$f = \frac{e^{-\beta(\varepsilon_{O_2}-\mu)}}{1+e^{-\beta(\varepsilon_{O_2}-\mu)}} = \frac{1}{1+e^{\beta(\varepsilon_{O_2}-\mu)}} = \frac{1}{1+\lambda^{-1}e^{\varepsilon_{O_2}/k_B T}}$$

This is also the fraction of Mb that are bound to O_2.

O_2 is in equilibrium with $Mb\cdot O_2$. Treat O_2 as an ideal gas:
$$\mu(Mb\cdot O_2) = \mu(O_2) = k_B T\ln\left(\frac{n_{O_2}}{n_Q}\right) = k_B T\ln\left(\frac{p}{n_Q k_B T}\right)$$

where p is the partial pressure of O_2
Putting it all together gives the <u>Langmuir adsorption isotherm</u>:
$$f = \frac{p}{p+n_Q k_B T e^{+\varepsilon_{O_2}/k_B T}} = \frac{p}{p+p_{1/2}(T)}$$

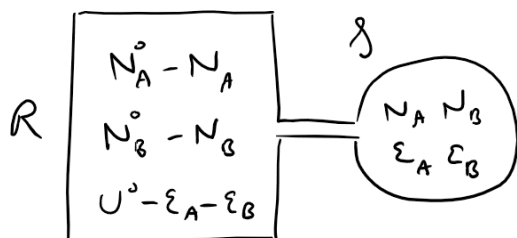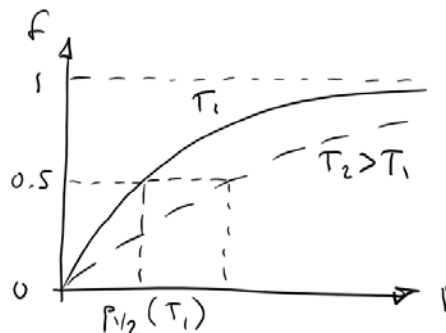$p_{1/2}$ is the pressure at which ½ of Mb are occupied

Putting in some numbers: $\varepsilon_{O_2} = -0.7$ eV

    $p(O_2)$ near lungs = 0.2 atm
    $\mu(O_2) = -0.6$ eV
    f = 98% almost all Mb are occupied

KEY CONCEPT: Grand canonical ensemble with multiple species

How do we deal with an ensemble with multiple species? Same line of reasoning as before, now with multiple chemical potentials μ_A, μ_B, …

$$\frac{p_1}{p_2} = \frac{\Omega_{\mathcal{R}}(N_A^0 - N_{A_1}, N_B^0 - N_{B_1}, U_0 - \varepsilon_{A_1} - \varepsilon_{B_1})}{\Omega_{\mathcal{R}}(N_A^0 - N_{A_2}, N_B^0 - N_{B_2}, U_0 - \varepsilon_{A_2} - \varepsilon_{B_2})} = \exp \Delta S_{\mathcal{R}}/k_B$$
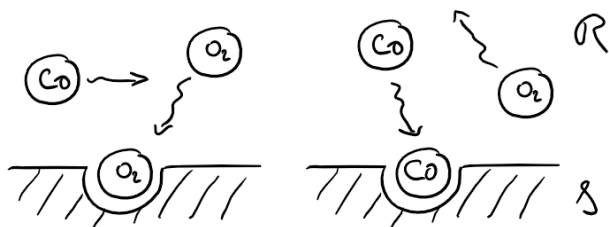
$$\Delta S_{\mathcal{R}} \approx \underbrace{-\left.\frac{\partial S_{\mathcal{R}}}{\partial N_A}\right|_{N_A^0}}_{-\frac{\mu_A}{T}} (N_{A_1} - N_{A_2}) \underbrace{-\left.\frac{\partial S_{\mathcal{R}}}{\partial N_B}\right|_{N_B^0}}_{-\frac{\mu_B}{T}} (N_{B_1} - N_{B_2}) \underbrace{-\left.\frac{\partial S_{\mathcal{R}}}{\partial U}\right|_{U_0}}_{\frac{1}{T}} \left[(\varepsilon_{A_1} + \varepsilon_{B_1}) - (\varepsilon_{A_2} + \varepsilon_{B_2})\right] \text{ etc.}$$

So

$$\mathcal{Z}(\mu, T) = \sum_{N_A, N_B \cdots} e^{(\mu_A N_A + \mu_B N_B + \cdots)/k_B T} \sum_{\varepsilon(N_A, N_B \cdots)} e^{-\varepsilon(N_A, N_B \cdots)/k_B T}$$

where $\varepsilon(N_A, N_B \cdots) = \varepsilon_A + \varepsilon_B + \cdots$

Ex: CO poisoning

Now Mb in equilibrium with 2 species of gas: O_2 and CO

Binding energy with $O_2 = \varepsilon_{O_2}$

        with CO = ε_{CO}

Each Mb only has one binding site

Question 3: Write down an expression for a) the Gibbs sum for a single myoglobin in O_2 and CO and b) the probability that it has O_2 bound

a) There are three microstates now:

$$\mathcal{Z} = \underbrace{e^{-\beta(0+0)}e^{\beta(\mu_{CO}\cdot 0+\mu_{O_2}\cdot 0)}}_{\text{No } O_2 \text{ or CO}} + \underbrace{e^{-\beta(0+\varepsilon_{O_2})}e^{\beta(\mu_{CO}\cdot 0+\mu_{O_2}\cdot 1)}}_{1\ O_2 \text{ bound}} + \underbrace{e^{-\beta(\varepsilon_{CO}+0)}e^{\beta(\mu_{CO}\cdot 1+\mu_{O_2}\cdot 0)}}_{1\ CO \text{ bound}}$$

$$= 1 + e^{-\beta(\varepsilon_{O_2}-\mu_{O_2})} + e^{-\beta(\varepsilon_{CO}-\mu_{CO})}$$

b) Now, if f = probability to be in O_2-bound state

$$f = \frac{e^{-\beta(\varepsilon_{O_2}-\mu_{O_2})}}{1 + e^{-\beta(\varepsilon_{O_2}-\mu_{O_2})} + e^{-\beta(\varepsilon_{CO}-\mu_{CO})}}$$

Treating O_2 and CO as ideal gases:

$$\mu_{O_2} = k_B T \ln\left(\frac{n_{O_2}}{n_Q(O_2)}\right) = k_B T \ln\left(\frac{p}{n_Q(O_2)k_B T}\right) \text{ and } \mu_{CO} = k_B T \ln\left(\frac{n_{CO}}{n_Q(CO)}\right) = k_B T \ln\left(\frac{p_{CO}}{n_Q(CO)k_B T}\right)$$

where p_{CO} is the partial pressure of CO.

Finally,

$$f = \frac{p/p_{1/2}}{1 + p/p_{1/2} + p_{CO}e^{-\beta\varepsilon_{CO}}/n_Q(CO)k_B T}$$

$$= \frac{p}{p + p_{1/2}(1 + p_{CO}/p')} \le \frac{p}{p + p_{1/2}}$$

$f(O_2$ with CO$) \le f(O_2$ without CO$)$

CO effectively increases the partial pressure at which ½ the Mb are occupied with O_2 – leads to less O_2 bound and asphyxiation. CO is called a <u>competitive inhibitor</u> of O_2

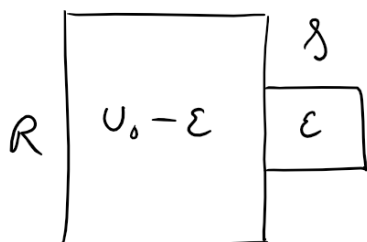Putting in some numbers:
   Assume p_{CO} 100× less than of O_2
   $\varepsilon_{CO} = -0.85$ eV   (CO is more tightly bound than O_2)
   $\mu(CO) = -0.72$ eV
   $f = 25\%$ (significant drop from 98%!)

Comparison of canonical and grand canonical ensembles:

Canonical	Grand canonical

Fixed in $\mathbb{S}$: T, N

Fixed in $\mathbb{S}$: T, μ

Not fixed: $U = \langle \varepsilon \rangle$

Not fixed: $U = \langle \varepsilon \rangle$, $\langle N \rangle$

Boltzmann factor:

$$p(\varepsilon_i) = \frac{e^{-\varepsilon_i/k_B T}}{Z(T)}$$

Gibbs factor:

$$p(N_i, \varepsilon_i) = \frac{e^{-(\varepsilon_i - \mu N_i)/k_B T}}{\mathcal{Z}(\mu, T)}$$

Partition function:

$$Z(T) = \sum_{\varepsilon_i} e^{-\varepsilon_i/k_B T}$$

Gibbs or grand sum:

$$\mathcal{Z}(\mu, T) = \sum_{N_i} \sum_{\varepsilon_i(N_i)} e^{-(\varepsilon_i - \mu N_i)/k_B T}$$

$$= \sum_{N_i} \lambda^{N_i} Z(N_i, T)$$

Mean values:

$$U = \langle \varepsilon \rangle = -\frac{\partial}{\partial \beta} \ln Z$$

Mean values:

$$U = \langle \varepsilon \rangle = \frac{\mu}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z} - \frac{\partial}{\partial \beta} \ln \mathcal{Z}$$

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z}(\mu, T)$$

Helmholtz free energy:

$$F \equiv U - TS$$
$$= -k_B T \ln Z$$

Grand potential:

$$\Phi \equiv U - TS - \mu \langle N \rangle$$
$$= -k_B T \ln \mathcal{Z}$$