

**Goal: Derive average fractional occupancy assuming a non-cooperative model.**

If we set up the hemoglobin so that we can exchange particles between the system and reservoir, the Boltzmann Factor becomes the Gibbs Factor.

$$e^{-\beta(E(s)-\mu N_s)}; \beta = \frac{1}{kT}$$

Where  $E$  is the energy of the system, defined by:

$$E = \varepsilon \sum_{\alpha=1}^4 \sigma_{\alpha}$$

$N_s$  is the number of particles in the state, and  $\mu$  is the chemical potential. Then we can use the Grand Partition Function:

$$\mathcal{Z} = \sum_s e^{-\beta(E(s)-\mu N_s)}$$

Which implies the probability of the state denoted by  $P(s)$  is:

$$P(s) = \frac{1}{\mathcal{Z}} e^{-\beta(E(s)-\mu N_s)}$$

Then the average fractional occupancy can be defined as follows:

$$\langle N \rangle = \sum_s (N_s) (P(s)) = \sum_s N_s \frac{e^{-\beta(E(s)-\mu N_s)}}{\mathcal{Z}}$$

Note that:

$$\frac{1}{\beta} \frac{\partial}{\partial \mu} [\ln \mathcal{Z}] = \frac{1}{\beta} \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \langle N \rangle$$

So:

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

The binding sites of hemoglobin has the following states, if we assume a non-cooperative model:

# Binding Sites	# Configurations	Configuration Notation
0	1	E
1	4	$O_1, O_2, O_3, O_4$
2	6	$T_1, T_2, T_3, T_4, T_5, T_6$
3	4	$H_1, H_2, H_3, H_4$
4	1	F

If we assume a non-cooperative model, then we only need to look at the states individually using the Grand Partition Function  $\mathcal{Z}$  (split on two lines for readability):

$$\begin{aligned}\mathcal{Z} &= \sum_s e^{-\beta(E(s) - \mu N_s)} \\ \mathcal{Z} &= e^{-\beta(E(\overline{E}) - \mu N_{\overline{E}})} + \sum_{i=1}^4 e^{-\beta(E(\overline{O}_i) - \mu N_{\overline{O}_i})} + \sum_{i=1}^6 e^{-\beta(E(\overline{T}_i) - \mu N_{\overline{T}_i})} \\ &\quad + \sum_{i=1}^4 e^{-\beta(E(\overline{H}_i) - \mu N_{\overline{H}_i})} + e^{-\beta(E(\overline{F}) - \mu N_{\overline{F}})}\end{aligned}$$

However, we know the values of  $E(s)$  and  $N_s$ .

State	$E(s)$	$N_s$
E	0	0
O	1	1
T	2	2
H	3	3
F	4	4

This means if we call the energy of the system  $\varepsilon$ , then State  $E(\overline{T}) = 2\varepsilon$ , for example. So we can simplify  $\mathcal{Z}$  to:

$$\begin{aligned}\mathcal{Z} &= 1 + 4e^{-\beta(\varepsilon - \mu)} + 6e^{-2\beta(\varepsilon - \mu)} + 4e^{-3\beta(\varepsilon - \mu)} + e^{-4\beta(\varepsilon - \mu)} \\ \frac{\partial \mathcal{Z}}{\partial \mu} &= \beta[4e^{-\beta(\varepsilon - \mu)} + 12e^{-2\beta(\varepsilon - \mu)} + 12e^{-3\beta(\varepsilon - \mu)} + 4e^{-4\beta(\varepsilon - \mu)}]\end{aligned}$$

Since we're given that:

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z} \Rightarrow \langle N \rangle = \frac{1}{\beta} \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu}$$

So:

$$\begin{aligned}\langle N \rangle &= \frac{1}{\beta} \frac{\beta[4e^{-\beta(\varepsilon - \mu)} + 12e^{-2\beta(\varepsilon - \mu)} + 12e^{-3\beta(\varepsilon - \mu)} + 4e^{-4\beta(\varepsilon - \mu)}]}{1 + 4e^{-\beta(\varepsilon - \mu)} + 6e^{-2\beta(\varepsilon - \mu)} + 4e^{-3\beta(\varepsilon - \mu)} + e^{-4\beta(\varepsilon - \mu)}} \\ \langle N \rangle &= \frac{4e^{-\beta(\varepsilon - \mu)} + 12e^{-2\beta(\varepsilon - \mu)} + 12e^{-3\beta(\varepsilon - \mu)} + 4e^{-4\beta(\varepsilon - \mu)}}{1 + 4e^{-\beta(\varepsilon - \mu)} + 6e^{-2\beta(\varepsilon - \mu)} + 4e^{-3\beta(\varepsilon - \mu)} + e^{-4\beta(\varepsilon - \mu)}}\end{aligned}$$

Note that this equation only holds for the non-cooperative model for hemoglobin (Assuming  $J = 0$ ).