PYP protein as an example of a thermodynamic engine

No light excitation: equilibrium

\[ E_1 \quad u_a \quad d_a \quad E_2 \quad u_b \quad d_b \quad E_3 \quad u_c \quad d_c \]

Excited state

Intermediate (may be more than one in reality)

[signaling state \( \Rightarrow \) transition \( 3 \rightarrow 1 \)]

\( \Rightarrow \) work \( \Rightarrow \) environment

\[ H_n = E_n + PV_n \]

\( u_a = e^{-\beta(H_2-H_1) - Win} \)

\( \frac{d_a}{u_a} = e^{\beta(H_2-H_1)} \)

\( W_{in} = \) represents work done on system by absorbing photon

\( W_{12} = Win \quad \text{where} \quad Win > 0 \)

\( W_{13} = W_{out} > 0 \quad \text{corresponding to} \quad 3 \rightarrow 1 \) transition.

\( W_{31} = -W_{out} \)

\[ [\text{Hence} \ 1 \rightarrow 3 \quad \text{corresponds to work} \ -W_{out}] \]
How is $W_{in}$ related to photon absorption / emission?

Let's say $u_a^0, d_a^0$ are up/down rates $1 \leftrightarrow 2$ due to just thermal fluctuations.

$$\frac{u_a^0}{d_a^0} = e^{-\beta (H_2 - H_1)}$$

Then

$$\frac{u_a}{d_a} = \frac{u_a^0 + \alpha}{d_a^0 + \gamma}$$

$$= \frac{u_a^0}{d_a^0} \frac{1 + \alpha/u_a^0}{1 + \gamma/d_a^0}$$

$$= e^{-\beta (H_2 - H_1 - W_{in})}$$

where $W_{in} = k_B T \ln \left( \frac{1 + \alpha/u_a^0}{1 + \gamma/d_a^0} \right)$

$\alpha = \text{rate of absorbing photon in } 1 \rightarrow 2$ transition

$\gamma = \text{rate of emitting a photon in } 2 \rightarrow 1$ transition

$\alpha \gg \gamma$

For biologically efficient photoreceptors, $\alpha \gg \gamma$ [high quantum yield]

Let's look at entropy equation:

$$\dot{S}(t) = \frac{1}{T} \left[ \dot{H}(t) + W(t) \right] + \dot{S}^i(t)$$

$$\dot{W}(t) = \langle W(t) \rangle = \frac{1}{\delta t} \sum_{m,n} P_{mn}(t) W_{mn}$$

$$= \frac{1}{\delta t} \left[ P_{21}(t)(-W_{in}) + P_{12}(t)W_{in} + P_{31}(t)(-W_{out}) + P_{13}(t)W_{out} \right]$$
Note: $P_{21} = \Omega_{21} P_1 \delta t$

$P_{12} = \Omega_{12} P_2 \delta t$

etc.

$W(t) = -J_{21}(t) W_{in} + J_{13}(t) W_{out}$

$J_{21}(t) = \Omega_{21} P_1(t) - \Omega_{12} P_2(t)$

= current from $1 \rightarrow 2$

$J_{13}(t) = \Omega_{13} P_3(t) - \Omega_{31} P_1(t)$

= current from $3 \rightarrow 1$

From master equation:

$$\frac{dp_n}{dt} = \sum_m \Omega_{nm} P_m(t) = \sum_{m \neq n} J_{nm}^{nm}(t)$$

Assume we reach a stationary state \[ p_n(t) = p_n^s \]

\[ \Rightarrow 0 = \sum_{m \neq n} J_{nm}^s \] for all $n$

\[ J_{21}^s = J \]

\[ J_{31}^s = J \]

\[ J_{32}^s = J \]

\[ J_{23}^s = J \]

\[ \Rightarrow J_{21}^s = J_{13}^s = J \text{ constant} \]

hence one current $J$ in the loop

(only possible outcome b/c of current conservation)

\[ J = 0 \text{ [equilibrium]} \]

\[ J \neq 0 \text{ [non-equilibrium]} \]
\[ \dot{W}(t) = J W_{\text{out}} - J W_{\text{in}} \]
\[ \equiv P_{\text{out}} - P_{\text{in}} \quad \text{(power out - power in)} \]

In stationary state:
\[ \dot{S} = \frac{1}{T} \left[ \dot{H}(t) + \dot{W}(t) \right] + \dot{S}^i(t) \]
\[ = \dot{Q}(t) \equiv \left< \dot{Q} \right>_t \quad \text{rate of heat into system} \]

note: \[ S(t) = -k_B \sum_n P_n(t) \ln P_n(t) \]

in stat. state \[ \dot{P}_n(t) = 0 \Rightarrow \dot{S}(t) = 0 \]

Similarly \[ \dot{H}(t) = \sum_n P_n(t) \left[ E_n + PV_n \right] \]

in stat. state \[ \dot{P}_n(t) = 0 \Rightarrow \dot{H}(t) = 0 \]

\[ 0 = \frac{1}{T} \dot{W}(t) + \dot{S}^i(t) \quad \text{in stat. state} \Rightarrow \dot{W} = -T \dot{S}^i \]

\[ J W_{\text{out}} = J W_{\text{in}} - T \dot{S}^i \]

\[ P_{\text{out}} = P_{\text{in}} - T \dot{S}^i \]

\[ P_{\text{out}} \leq P_{\text{in}} \quad \text{since} \quad \dot{S}^i \geq 0 \]

Perfect efficiency means \[ P_{\text{out}} = P_{\text{in}} \]
\[ \Rightarrow \dot{S}^i = 0 \Rightarrow J = 0 \quad [\text{equilibrium}] \]

Any non-zero output \[ P_{\text{out}} > 0 \] entails less than perfect efficiency \[ [\dot{S}^i > 0] \].

What happens to the difference in input and output power?
\[ \dot{S} = \frac{1}{T} \dot{Q}(t) + \dot{S}^i(t) \]

\[ \Rightarrow 0 = \frac{1}{T} \dot{Q} + \dot{S}^i \text{ in stat. state} \]

so \[ \dot{Q} = -T \dot{S}^i \] and \[ \dot{Q} = \dot{H} + \dot{W} \] from 1st law

\[ \leq 0 \]

\[ = \dot{W} = P_{\text{out}} - P_{\text{in}} \]

The excess energy is dissipated as heat into the environment (\( \dot{Q} \leq 0 \)).

The equation: \[ P_{\text{out}} = P_{\text{in}} - T \dot{S}^i \]

we can write as:

\[ P_{\text{out}} = P_{\text{in}} - P_{\text{diss}} \]

\[ \text{dissipated power} = 1 |\dot{Q}| = T \dot{S}^i \]

More complete analysis:

write down \( \Omega = \begin{pmatrix} -u_a - u_c & d_a & d_c \\ u_a & -d_a - d_b & u_b \\ u_c & d_b & -u_b - d_c \end{pmatrix} \)

Solve for \( p_n^s \) from:

\[ \Omega \begin{pmatrix} p_1^s \\ p_2^s \\ p_3^s \end{pmatrix} = 0 \text{ and } \sum_{n=1}^{3} p_n^s = 1 \]

\[ \Rightarrow \text{get equation for } J = J_{21}^s = u_a p_1^s - d_a p_2^s \]

\[ = \text{function (complicated)} \]

of \( W_{\text{in}} + W_{\text{out}} \)
General behavior of $P_{\text{out}} = J W_{\text{out}}$ and $P_{\text{in}} = J W_{\text{in}}$

![Graph](image)

\[ \text{diff} = P_{\text{diss}} = T S^i \]

fixed $W_{\text{out}}$, vary $W_{\text{in}}$

when $W_{\text{in}} / W_{\text{out}} = 1$

sweet spot: nearly maximal $P_{\text{out}}$ for given $W_{\text{out}}$; going any higher in $W_{\text{in}}$ will just generate more $P_{\text{diss}}$, w/o any big benefits in $P_{\text{out}}$

$J = 0$ [equil.]

$P_{\text{out}} = P_{\text{in}} = 0$

Notice that the sweet spot is still very dissipative: getting $P_{\text{out}} > 0$ always involves a waste of heat $P_{\text{diss}} > 0$. 