term 1 = \[ \sum_{m,n} p_{mn}(t) \ln p_n(t) - \sum_{m,n} p_{mn}(t) \ln p_{m(t+\Delta t)} \]

= \[ \sum_n p_n(t) \ln p_n(t) - \sum_m p_m(t+\Delta t) \ln p_m(t+\Delta t) \]

using fact that:
- \[ \sum_{m,n} p_{mn}(t) = p_n(t) \]
- \[ \sum_n p_{mn}(t) = p_m(t+\Delta t) \]

Define the "entropy" of the system:
- \[ S(t) \equiv -k_B \sum p_n(t) \ln p_n(t) \]

Note: \( S(t) \geq 0 \) since sum of negative terms times \(-k_B\) is always \(0\) for \(0 \leq p \leq 1\).
Physical meaning of entropy: \[ \text{[Gibbs/Shannon]} \]

\[ S(t) = -k_B \sum_n p_n(t) \ln p_n(t) \]

quantifies our degree of uncertainty about the state of the system at time \( t \).

Total certainty \( \Rightarrow \) \( p_n(t) = \begin{cases} 1 & \text{for } n = m \\ 0 & \text{for } n \neq m \end{cases} \)

(state is \( m \) at time \( t \))

\[ S(t) = 0 \quad (x \ln x \text{ as } x \to 0 \text{ is zero}) \]

Total uncertainty \( \Rightarrow \) \( p_n(t) = \frac{1}{N} \) for all \( n \)

(all states are equally likely at time \( t \))

where \( N = \# \text{ of states in system} \)

\[ S(t) = -k_B \sum_n \frac{1}{N} \ln \frac{1}{N} \]

\[ = -k_B N \frac{1}{N} \ln \frac{1}{N} \]

\[ = k_B \ln N \quad \text{[Boltzmann definition of entropy]} \]

In general, \( 0 \leq S(t) \leq k_B \ln N \)

minimum possible entropy

max. possible entropy
Sidenote: entropy as a measure of distribution "width"

\[ S = 0 \]

\[ P_n(t) = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases} \]

\[ S_{\text{max}} > S > 0 \]

\[ S = S_{\text{max}} \]

\[ \text{max. entropy} \]

\[ S_{\text{max}} = k_B \ln N \]
For term 2, we need DB condition:

\[
\frac{\Omega_{mn}}{\Omega_{nm}} = e^{-\beta \left( E_m - E_n + P(V_m - V_n) + W_{mn} \right)}
\]

- work done against water pressure \( P \)
- other work terms (included for generality)

\( Q_{mn} \)
- heat energy absorbed from environment in \( n \to m \) transition

\( E_m - E_n \)
- change in state energy

\( P(V_m - V_n) \)
- work against pressure

\( W_{mn} \)
- other work
note: work \( \Rightarrow \) system does work on environment
heat defined:
\[ Q_{mn} = E_m - E_n + P (V_m - V_n) + W_{mn} \]
\[ \Omega_{mn} = e^{-\beta Q_{mn}} \]
\[ \Omega_{nm} = \frac{\Omega_{mn}}{\Omega_{nm}} \]
\[ \text{term 2} = \sum_{m,n} P_{mn}(t) \ln \frac{\Omega_{mn}}{\Omega_{nm}} \]
\[ = -\frac{1}{k_B T} \sum_{m \neq n} P_{mn}(t) Q_{mn} \]
\[ = -\frac{1}{k_B T} \langle Q \rangle_t \]
\[ \text{where} \quad \langle Q \rangle_t = \text{mean heat absorbed by system in time interval} \quad t \rightarrow t + \delta t \]

Putting it all together:
\[ \langle I \rangle_t = \frac{1}{k_B} [S(t+\delta t) - S(t)] - \frac{1}{k_B T} \langle Q \rangle_t \]
\[ \Rightarrow S(t+\delta t) - S(t) = \frac{\langle Q \rangle_t + \langle I \rangle_t \cdot k_B}{T} \]

Compare to traditional definition of entropy change:
\[ dS = \frac{dQ}{T} \quad \text{for reversible process} \]
\[ dS > \frac{dQ}{T} \quad \text{otherwise} \]

We see our formulation perfectly replicates the traditional definition, since:
\[ \langle I \rangle_t = 0 \quad \text{for reversible process} \]
\[ \langle I \rangle_t > 0 \quad \text{otherwise} \]

Hence \( \langle I \rangle_t > 0 \) is indeed equivalent to traditional second law.

In more modern usage, we divide both sides of entropy equation by \( \delta t \):

\[ \frac{\dot{S}(t)}{\delta t} = \frac{\langle Q \rangle_t}{\delta t T} + \frac{\langle I \rangle_t k_B}{\delta t} \]

\[ \equiv \dot{S}^r(t) \quad \equiv \dot{S}^i(t) \]

\( \dot{S}^r(t) \) can be positive or negative, or zero and does not change the entropy budget of the universe. [since entropy production due to heat flowing into system is balanced by entropy destruction in environment of heat flowing out of the environment]

\[ \dot{S}^i(t) \propto \langle I \rangle_t \]

If \( \dot{S}^i(t) > 0 \) \( \Rightarrow \) entropy of universe increases.

Depending on size & sign of \( \dot{S}^r(t) \), the sum \( \dot{S}(t) = \dot{S}^r(t) + \dot{S}^i(t) \) can be positive or negative.
Recall first law + DB:

\[
\frac{\Omega_{mn}}{\Omega_{nm}} = e^{-\beta \left[ E_m - E_n + P(V_m - V_n) + W_{mn} \right]} \quad \text{heat}
\]

Define \( H_m = E_m + PV_m \) enthalpy of state \( m \).

Because we are working in aqueous environment \((P \neq 0)\) we will always use \( H_m \) in place of \( E_m \).

\[
Q_{mn} = H_m - H_n + W_{mn} \quad [1st \ text \ law]
\]

Let us decompose \( \dot{S}^r(t) = \frac{\langle Q \rangle_t}{\delta t} \)

\[
\Rightarrow = \frac{1}{\delta t T} \sum_{m \neq n} P_{mn}(t) \left[ H_m - H_n + W_{mn} \right]
\]

\[
= \frac{1}{\delta t T} \left[ \sum_{m \neq n} P_m(t + \delta t) H_m - \sum_n P_n(t) H_n \right.
\]

\[
\left. + \sum_{m \neq n} P_{mn}(t) W_{mn} \right]
\]

\[
= \frac{1}{T} \left[ \frac{\dot{H}(t + \delta t) - \dot{H}(t)}{\delta t} + \frac{\langle W \rangle_t}{\delta t} \right]
\]

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

mean rate of enthalpy change

mean rate of work done by system
Then
\[ \dot{S}(t) = \frac{1}{T} \left( \dot{H}(t) + \dot{W}(t) \right) + \dot{S^i}(t) \]

This is the entropy change equation, which together with \( \dot{S^i}(t) \geq 0 \) represents a combo of 1st and 2nd laws.

We can rewrite this using the definition:
\[ G(t) = \bar{H}(t) - TS(t) \equiv \text{Gibbs free energy} = \bar{E}(t) + PV(t) - TS(t) \]

\[ \Rightarrow \dot{G}(t) = -\dot{W}(t) - TS^i(t) \]

Simplest case: no ext. potential to do additional work \( \Rightarrow \dot{W}(t) = 0 \)

Then \( \dot{G}(t) = -TS^i(t) \leq 0 \)

\( G(t) \) is always decreasing (or constant)!

Since \( G(t) = \bar{H}(t) - TS(t) \)

and we know \( \bar{H}(t) \) is bounded from below by min. enthalpy among all states in the system,

\[ S(t) \leq S^{\text{max}} = k_B \ln N \]

\( \Rightarrow G(t) \) cannot decrease to \(-\infty\)!

Hence it must level off to a constant as \( t \to \infty \).

\[ \begin{array}{c}
\text{Graph:} \\
G(t) \\
G(0) \quad G(\infty) = G^{eq} \\
0 \quad t
\end{array} \]
How can this happen?

\[ \dot{G}(\infty) = -T \dot{S}^i(\infty) = 0 \]

hence \[ \dot{S}^i(\infty) = \frac{k_b \langle I \rangle_t}{\delta t} = 0 \]

But \( \langle I \rangle_t = 0 \) if and only if \( I_{mn}(t) = 0 \) for all \( m, n \)

\[ I_{mn}(t) = \ln \frac{P_{mn}(t)}{P_{nm}(t+\delta t)} \]

\[ = \begin{cases} \ln \frac{\Omega_{mn} \delta t \cdot P_{n}(t)}{\Omega_{nm} \delta t \cdot P_{m}(t+\delta t)} & m \neq n \\ \ln \frac{(\Omega_{nn} \delta t + 1) \cdot P_{n}(t)}{(\Omega_{nn} \delta t + 1) \cdot P_{m}(t+\delta t)} & m = n \end{cases} \]

This is zero when \( P_{n}(t) = P_n^s \)

\( P_{m}(t+\delta t) = P_m^s \)

and \( \frac{\Omega_{mn} P_n^s}{\Omega_{nm} P_m^s} = 1 \)

But this is just the definition of the equilibrium stationary state with no currents:

\[ J_{nm}^{eq} = \Omega_{mn} P_{n}^{eq} - \Omega_{nm} P_{m}^{eq} = 0 \]

Hence we see that:

\[ G(t) \xrightarrow{t \to \infty} G^{eq} \] (minimum free energy)

implies

\[ P_{n}(t) \xrightarrow{} P_{n}^{eq} \] (equilibrium stationary state)

\[ \langle I \rangle_t \xrightarrow{} 0 \]
In the absence of a persistent source of ext. work \([\dot{W}(t) = 0]\) any system must eventually reach an equilibrium with no currents, corresponding to a minimum \(G\).
In the most general case (no assumptions about \( W(t) \)):

\[
\dot{G}(t) = -\dot{W}(t) - T \dot{S}^i(t) \geq 0
\]

\[\Rightarrow \dot{W}(t) \leq -\dot{G}(t)\]

System can do work on environment (\( \dot{W} > 0 \)) by depleting \( G(t) \) \( [\dot{G}(t) \leq 0] \)

But then amount of work is always bounded by change in \( G \):

\[W(t + \delta t) - W(t) \leq G(t) - G(t + \delta t)\]

Hence "free energy" \( \Rightarrow \) energy available to do work

\[\text{[maximum conversion occurs only when } \dot{S}^i(t) = 0 \Rightarrow \text{equilibrium]}\]