\[ p_2(t) - p_2\left(\frac{T}{2}\right) = \frac{1}{3} = \tilde{\Psi}_a - \tilde{\Psi}_b \]
\[ \Rightarrow \tilde{\Psi}_a = \frac{1}{3}, \quad \tilde{\Psi}_b = 0, \quad \tilde{\Psi}_c = -\frac{1}{3} \]
\[ \Rightarrow \tilde{\Psi}_c^{tot} = \frac{1}{3} \frac{k_c^-}{k_c^+ + k_b^-} - \frac{1}{3} \leq 0 \]

Motor on average moves backwards (wheel rotates CW!)

Physical meaning:
\[ J_c(t) = \frac{\# 3 \rightarrow 1 \text{ jumps}}{\text{time}} - \frac{\# 1 \rightarrow 3 \text{ jumps}}{\text{time}} \]
on average
\[ \tilde{\Psi}_c^{tot} = \int_0^T J_c(t) \, dt = (\# 3 \rightarrow 1 \text{ jumps}) - (\# 1 \rightarrow 3 \text{ jumps}) \]
on average per cycle

2) Another way to drive the ratchet-pawl system: two simultaneous temp. reservoirs, instead of periodic "flashing."

[Diagram of a paddlewheel at \( T_2 > T_1 \) connected to a ratchet-pawl at temp. \( T_1 \)]

How do we generalize theory to multiple heat baths?

Total rate: \( k_a^+ = k_a^{(1)} + k_a^{(2)} \), etc.

Contribution from \( T_1 \) reservoir, from \( T_2 \) reservoir.
In our master equation:
\[ W_{nm} = W^{(1)}_{nm} + W^{(2)}_{nm} \]

where:
\[ \frac{W^{(1)}_{nm}}{W^{(2)}_{mn}} = e^{-\beta_j (E_n - E_m)} \]
\[ \beta_j = \frac{1}{k_B T_j} \]

satisfies detailed balance for jth reservoir.

Note that total \( \frac{W_{nm}}{W_{mn}} \) cannot satisfy detailed balance simultaneously for both reservoirs (unless \( T_1 = T_2 \)) \( \Rightarrow \) hence the stationary state for our master equation when \( T_1 \neq T_2 \) will not be equilibrium.

Current:
\[ J_{nm} = W_{nm} \, p_m - W_{mn} \, p_n \]
\[ = \left[ W^{(1)}_{nm} \, p_m - W^{(2)}_{mn} \, p_n \right] + \left[ W^{(2)}_{nm} \, p_m - W^{(2)}_{mn} \, p_n \right] \]
\[ = \{ J^{(1)}_{nm} \} + J^{(2)}_{nm} \]

Analogously:
\[ \dot{S}(t) = -k_B \sum_{(n,m)} J_{n,m} \ln \frac{p_n}{p_m} \]
\[ = -k_B \sum_{j=1}^{2} \sum_{(n,m)} J^{(j)}_{n,m} \ln \frac{W^{(j)}_{mn} \, p_n}{W^{(j)}_{nm} \, p_m} + k_B \sum_{j=1}^{2} J^{(j)}_{n,m} \ln \frac{W^{(j)}_{mn}}{W^{(j)}_{nm}} \]
\[ = \sum_{j=1}^{2} \dot{S}^{i(j)} + \sum_{j=1}^{2} \dot{S}^{e(j)} \]
\[ \dot{S}^{i} \quad \dot{S}^{e} \]
denote
\[ \dot{S}^e(j) = k_0 \sum_{(n,m)} J_{nm}^{(j)} \ln \frac{W_{nm}^{(j)}}{W_{mn}^{(j)}} \]

plug in detailed balance

\[ \dot{S}^e(j) = \frac{1}{T_j} \sum_{(n,m)} J_{nm}^{(j)} (E_n - E_m) \equiv \frac{\dot{Q}_j}{T_j} \]

\( \equiv \dot{Q}_j \)

heat flux from jth reservoir

entropy flow from jth reservoir

note:
\[ \dot{Q}_1 + \dot{Q}_2 = \sum_{(n,m)} J_{nm} (E_n - E_m) = \dot{E} \]

change in average energy

By same argument as before,
\[ S_i^{(j)} = 0 \] with \( S_i = 0 \) iff \[ W_{mn}^{(j)} P_n = W_{nm}^{(j)} P_m \]

\[ \Rightarrow \frac{P_n}{P_m} = e^{-\beta_j (E_m - E_n)} \]

For \( T_1 \neq T_2 \), a prob. distribution cannot simultaneously make all \( S_i^{(j)} = 0 \) \( \Rightarrow S^i > 0 \) always have entropy production.

which also entails that one or both of the currents \( J_{nm}^{(j)} \) for at least one \((n,m)\) must be nonzero [cannot have equilibrium]

As \( t \to \infty \) we reach a NESS with \( P_n(t) \to P_n^s \).

At this stationary state
\[ \dot{S}(t) = 0 = \dot{S}^i + \dot{S}^e \]

\[ \dot{E}(t) = 0 = \dot{Q}_1 + \dot{Q}_2 \Rightarrow \dot{Q}_1 = -\dot{Q}_2 \]

\[ \dot{S}^e = \frac{\dot{Q}_1}{T_1} + \frac{\dot{Q}_2}{T_2} = -\dot{S}^i < 0 \text{ if } T_1 \neq T_2 \]

\[ = \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \dot{Q}_2 \]

\( < 0 \text{ if } T_2 > T_1 \Rightarrow \dot{Q}_2 > 0 \) \( \dot{Q}_1 < 0 \)

\( > 0 \text{ if } T_1 > T_2 \Rightarrow \dot{Q}_2 < 0 \) \( \dot{Q}_1 > 0 \)
If $T_2 > T_1 \Rightarrow Q_2 > 0$ so system absorbs energy from hotter reservoir and $Q_1 < 0$ dumps energy in colder reservoir.

It drives current in the meantime.

If reservoirs are finite & not maintained at constant temps, this will eventually lead to equal temps for both reservoirs & equilibrium.

The typical assumption is that the reservoirs are large & maintained at constant temp, so the system persists in nonequilibrium stat. state.
Nature of interactions b/w system + its environment: heat vs. work

When part of the environment acts as a heat bath at temp. T_j, the underlying assumption (implicit in the math defining temperature + the canonical ensemble) is that the energy exchange interactions are random (uncorrelated over times greater than micro time scale δt) like fluid atoms hitting our ratchet wheel or Brownian particle, and hence

\[ W_{nm} = W_{nm}^{(1)} + W_{nm}^{(2)} \]

prob. of events leading to \( n \rightarrow m \) transition per unit time in each reservoir

\[ \text{sum of indep. events} \]

We defined entropy flow from bath j to system:

\[ \dot{S}^e(j) = k_B \sum_{n,m} J_{n,m}^{(j)} \ln \frac{W_{nm}^{(j)}}{W_{nm}} \]

Since this is a universal definition, we will use it to formally define heat flow from bath j to system:

\[ \dot{Q}_j = T_j \dot{S}^e(j) \]
For the special case of a simple heat bath:

\[ \dot{S}_e^{(j)} = \frac{1}{T_j} \sum_{(n,m)} J_{nm}^{(j)} (E_n - E_m) \]

because \( \frac{W_{mm}^{(j)}}{W_{nm}^{(j)}} = e^{-\beta (E_m - E_n)} \)

Hence \( \dot{Q}_j = \sum_{(n,m)} J_{nm}^{(j)} (E_n - E_m) \)

\( \Rightarrow \) heat is associated w/ prob. flows b/t states of system, leaving the energy levels of the states unchanged.

But there is another way a system can interact with environment: a nonrandom, sustained interaction (through some form of fixed or changing potential) \( \Rightarrow \) such interactions lead to idea of work.

1) Work resulting from external, time-independent potential interacting with the system.

Imagine a heat bath at temp \( T \) w/ additional nonrandom degrees of freedom coupled to a potential energy, such that:

- each \( m \rightarrow n \) jump involves the random (fluid) part of the bath donating energy
  \[ E_n - E_m + V_{nm} \]

\( \Delta x \) gravitational potential

\( + \) jump lowers potential energy by
\[ -mg \Delta x \]

\( \Delta x \) ever-jump raises it by
\[ +mg \Delta x \]
Detailed balance then reads:

\[
\frac{W_{nm}}{W_{mn}} = e^{-\beta (E_n - E_m + V_{nm})} \quad \text{note } V_{nm} = -V_{mn}
\]

In our example:

\[
V_{21} = V_{32} = V_{13} = -mg \Delta x
\]

\[
V_{12} = V_{23} = V_{31} = +mg \Delta x
\]

\[
\dot{Q} = T \dot{S}^e = \sum_{(n,m)} J_{nm} (E_n - E_m) + \sum_{(n,m)} J_{nm} \dot{V}_{nm}
\]

rate of "work" done by system on bath

\[
= -\dot{W}
\]

rate of work of bath on system

---

This depends on convention defining "system": if we include mass + earth's gravity as system, we could have absorbed \(V_{nm}\) into \(E_n - E_m\).

First law:

\[
\dot{E} = \dot{Q} + \dot{W}
\]

in general: \(\dot{W}\) is the contribution to \(\dot{E}\) that is not \(\dot{Q}\)

For only one heat bath:

\[
\dot{S} = \dot{S}^i + \dot{S}^e = \dot{S}^i + \frac{\dot{Q}}{T}
\]

In a stationary state \(\dot{S} = \dot{E} = 0\) hence

\[
\dot{Q} = -\dot{W}, \quad \dot{Q} = -T \dot{S}^i
\]

\[\Rightarrow \dot{W} = T \dot{S}^i \geq 0 \quad \text{b/c } \dot{S}^i \geq 0\]

Environment must do work on system, rather than the opposite. Can't extract heat from reservoir, \((\dot{Q} > 0)\), and have system do work \((\dot{W} < 0)\).
For our example in the stationary state:

\[ J^s_{21} = J^s_{32} = J^s_{13} = J^s \text{ constant} \]

\[ \dot{W} = -\sum_{(n,m)} J^s_{nm} V_{nm} \]

\[ = 3 J^s \text{ mg } \Delta x \]

\[ \dot{W} > 0 \Rightarrow J^s > 0 \] (mass cannot be lifted up)

In fact, using \[ J^s_{21} = J^s, J^s_{32} = J^s, J^s_{13} = J^s \]
and \[ p_1^s + p_2^s + p_3^s = 1 \] plus

det. balance \Rightarrow solve for \( J^s \)

we find: \[ J^s \propto 1 - e^{-3 \beta \text{ mg } \Delta x} \]

\[ > 0 \text{ for } m > 0 \]

---

Time-dependent bath potential energies:

\[ V_{nm}(t) \text{ [for example, change mass over time]} \]

\[ \Rightarrow \frac{W_{nm}(t)}{W_{mn}(t)} = e^{-\beta (E_n - E_m + V_{nm}(t))} \]

valid at each moment of time

only change is: \[ \dot{W} = -\sum_{(n,m)} J^s_{nm}(t) V_{nm}(t) \]

\[ \Rightarrow \text{ everything same as before} \]

If \[ V_{nm}(t+\tau) = V_{nm}(t) \] [periodic mass change]

\[ \Rightarrow W_{nm}(t+\tau) = W_{nm}(t) \]

\[ \Rightarrow \text{ as } t \to \infty, \text{ we have periodic state } p_n(t+\tau) = p_n(t) \]

[hot stationary] [see p. 74]
As a result:

\[ \bar{E}(t + \tau) = \bar{E}(t) \Rightarrow \int_t^{t+\tau} \dot{\bar{E}}(t') \, dt' = 0 \equiv \Delta \bar{E} \]

\[ \bar{S}(t + \tau) = \bar{S}(t) \Rightarrow \int_t^{t+\tau} \dot{\bar{S}}(t') \, dt' = 0 \equiv \Delta \bar{S} \]

\[ \bar{S} = \dot{\bar{S}}^i + \frac{\dot{\bar{Q}}}{T} \Rightarrow 0 = \Delta \bar{S}^i + \frac{\Delta \bar{Q}}{T} \]

\[ \bar{E} = \dot{\bar{Q}} + \dot{\bar{W}} \Rightarrow 0 = \Delta \bar{Q} + \Delta \bar{W} \]

\[ \Rightarrow \Delta \bar{W} = T \Delta \bar{S}^i \geq 0 \]

**Kelvin-Planck 2nd law**: Over one cycle, it is impossible to construct an engine that has no effect other than raising a weight (\(\Delta \bar{W} \leq 0\)) and cooling a single heat bath (\(\Delta \bar{Q} > 0\)), while operating over a cycle.