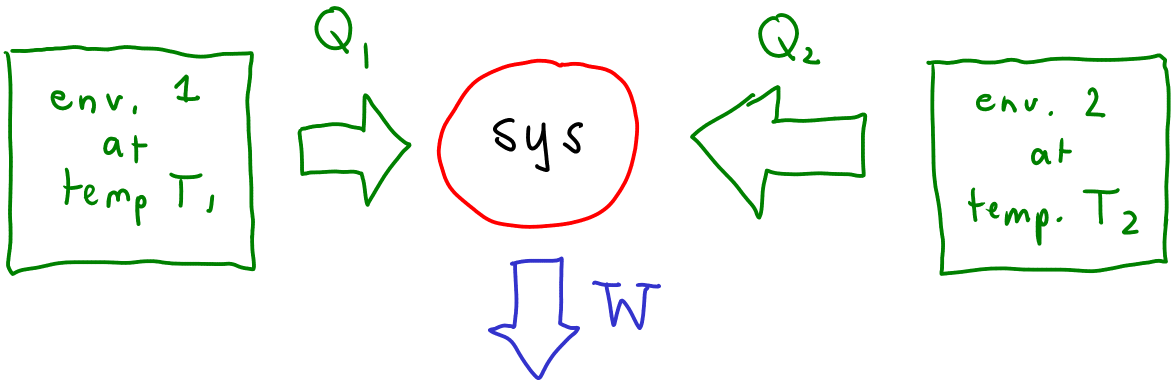
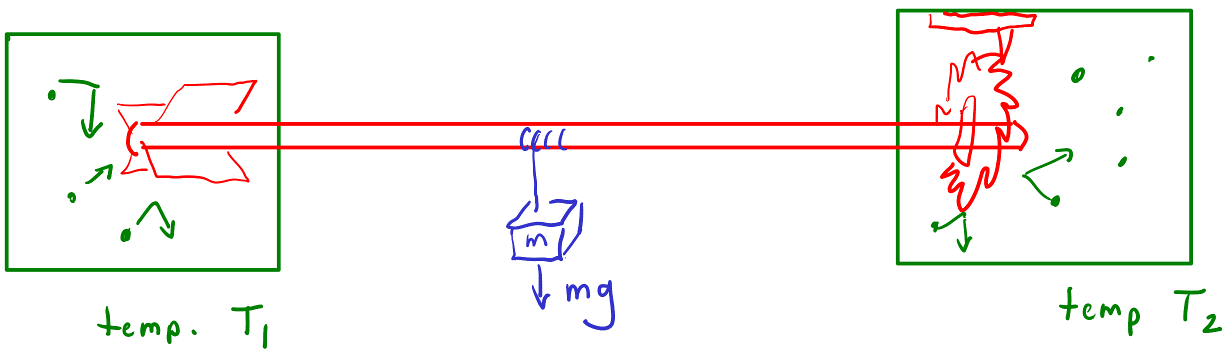
Systems coupled to multiple (2) temperatures:





two transition matrices
(for sys. connected to each env.)

$W_{nm}^{(1)}$ = prob. of $m \to n$ trans. due to exchange of energy w/ env. 1

$W_{nm}^{(2)}$ = " " " w/ env. 2

LDB: $\alpha = 1, 2$

$$\beta_\alpha = \frac{1}{k_B T_\alpha} \qquad \frac{W_{nm}^{(\alpha)}}{W_{mn}^{(\alpha)}} = e^{-\beta_\alpha (E_n - E_m + \omega_{nm})}$$

imagine that δt is small enough so that in each time step energy exchange happens w/ only one environment:

prob. of $m \to n$ trans. due to env. 1 alone

$$W^{(1)}_{nm}\left(1 - W^{(2)}_{nm}\right) \approx W^{(1)}_{nm} + \text{higher order terms}$$

(assuming W's are small for small δt)

traj. of system states:

$$\nu = (\underbrace{n_0, n_1}_{\substack{\alpha_0 \\ = \\ 1,2}}, \underbrace{\ \ , n_2}_{\substack{\alpha_1 \\ = \\ 1,2}}, \ldots, n_\tau)$$

env. labels

p_α = prob. that in a given time δt the transition occurs due to env. α

$$p_1 + p_2 = 1$$

$$I(\nu) = k_B \ln \frac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})}$$

$$\mathcal{P}(\nu) = p_{\alpha_{\tau-1}} W^{(\alpha_{\tau-1})}_{n_\tau n_{\tau-1}} \cdots \; p_{\alpha_0} W^{(\alpha_0)}_{n_1 n_0} P_{n_0}(t_0)$$

$$\tilde{\mathcal{P}}(\tilde{\nu}) = p_{\alpha_0} W^{(\alpha_0)}_{n_0 n_1} \cdots \; p_{\alpha_{\tau-1}} W^{(\alpha_{\tau-1})}_{n_{\tau-1} n_\tau} P_{n_\tau}(t_\tau)$$

$$I(\nu) = -k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t))$$
$$+ \; k_B \ln \frac{W^{(1)}_{\sim} \cdots W^{(1)}_{\sim}}{W^{(1)}_{\sim} \cdots W^{(1)}_{\sim}}$$
$$+ \; k_B \ln \frac{W^{(2)}_{\sim} \cdots W^{(2)}_{\sim}}{W^{(2)}_{\sim} \cdots W^{(2)}_{\sim}}$$

$$\frac{W^{(\alpha)}_{nm}}{W^{(\alpha)}_{mn}} = e^{-\beta_\alpha (E_n - E_m + \omega_{nm})}$$

$$\Rightarrow \quad I(\nu) = -k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t_0))$$
$$- \frac{1}{T_1}\left(\Delta E^{(1)}(\nu) + \mathcal{W}^{(1)}(\nu)\right)$$
$$- \frac{1}{T_2}\left(\Delta E^{(2)}(\nu) + \mathcal{W}^{(2)}(\nu)\right)$$

$\Delta E^{(\alpha)}(\nu)$ = sum of all energy diffs due to trans. w/ env. α

$\mathcal{W}^{(\alpha)}(\nu)$ = " work terms

" " "

define: $Q_\alpha(\nu) = \Delta E^{(\alpha)}(\nu) + \mathcal{W}^{(\alpha)}(\nu)$

= total heat energy into sys. from env. α during traj. ν

total for both env.

$$\begin{cases} \Delta E(\nu) = \Delta E^{(1)}(\nu) + \Delta E^{(2)}(\nu) \\ W(\nu) = W^{(1)}(\nu) + W^{(2)}(\nu) \end{cases}$$

$$\Rightarrow \quad I(\nu) = -k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t_0)) - \frac{1}{T_1} Q_1(\nu) - \frac{1}{T_2} Q_2(\nu)$$

take avg. over all traj

$$\boxed{I = \underbrace{\Delta S}_{S(t_\tau) - S(t_0)} - \frac{1}{T_1} Q_1 - \frac{1}{T_2} Q_2 \geq 0} \quad \text{2nd law}$$

$$\boxed{Q_1 + Q_2 = \Delta E + W} \quad \text{1st law}$$

Consider either:

- Stationary state $t \to \infty$ $(p_n(t) \to p_n^s)$
- periodic driving (cycle) ($p_n(t)$ becomes periodic as $t \to \infty$)

$$\Rightarrow \quad \Delta E = \Delta S = 0$$ in both cases

(2nd case, we consider traj. length = 1 period)

2nd: $I = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \geq 0$

1st: $Q_1 + Q_2 = W$

divide both laws by time $\Delta t = \begin{cases} \delta t & \text{stat. state} \\ \tau\, \delta t & \text{periodic case} \end{cases}$

where τ is period

$$\frac{I}{\Delta t} \equiv \sigma \quad \text{entropy production rate} \geq 0$$

$$\frac{Q_\alpha}{\Delta t} \equiv \dot{Q}_\alpha \quad \text{heat rate from env. } \alpha$$

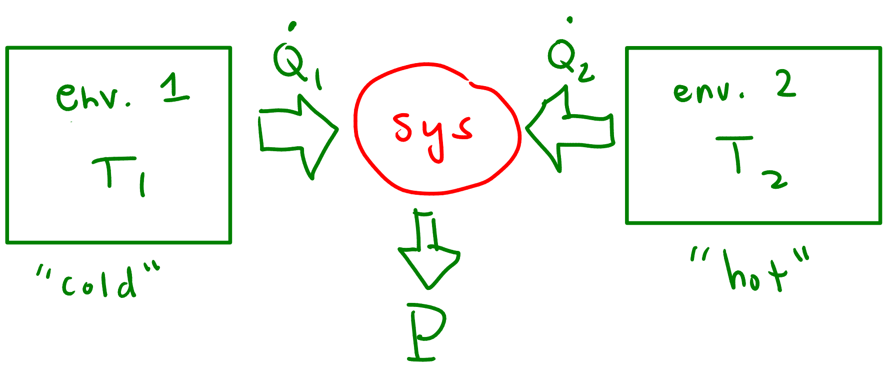
$$\frac{W}{\Delta t} = P \quad \text{net power output from sys.}$$

$$W = \underset{\substack{\text{output} \\ \text{work} \\ \text{(pos. terms)}}}{W_{out}} - \underset{\substack{\text{input work} \\ \text{(neg. terms)}}}{W_{in}}$$

$$P = P_{out} - P_{in}$$

$$\Rightarrow \quad \sigma = -\frac{\dot{Q}_1}{T_1} - \frac{\dot{Q}_2}{T_2} \geq 0$$

$$\dot{Q}_1 + \dot{Q}_2 = P$$



$T_1, T_2 > 0$

$T_2 \geq T_1$

case 1: $\dot{Q}_2 > 0$: hot env. donates energy to system ("heat engine")

$$\frac{\dot{Q}_1}{T_1} = \underbrace{-\frac{\dot{Q}_2}{T_2}}_{<0} \underbrace{-\,\dot{\sigma}}_{\leq 0} < 0 \Rightarrow \dot{Q}_1 < 0$$

heat is dumped into cold env.

$$\begin{aligned} P &= \dot{Q}_2 + \dot{Q}_1 \\ &= \dot{Q}_2 - |\dot{Q}_1| \\ &= \dot{Q}_2 - T_1\left(\frac{\dot{Q}_2}{T_2} + \dot{\sigma}\right) \\ &= \dot{Q}_2\left(1 - \frac{T_1}{T_2}\right) \underbrace{- T_1 \dot{\sigma}}_{\leq 0} \end{aligned}$$

$$P \leq \dot{Q}_2\left(1 - \frac{T_1}{T_2}\right)$$ upper bound on net power output

efficiency

$$\eta = \frac{P}{\dot{Q}_2} = \frac{\text{net power out}}{\text{heat input rate}}$$

$$\boxed{\eta \leq 1 - \frac{T_1}{T_2}}$$

Carnot efficiency bound on heat engines