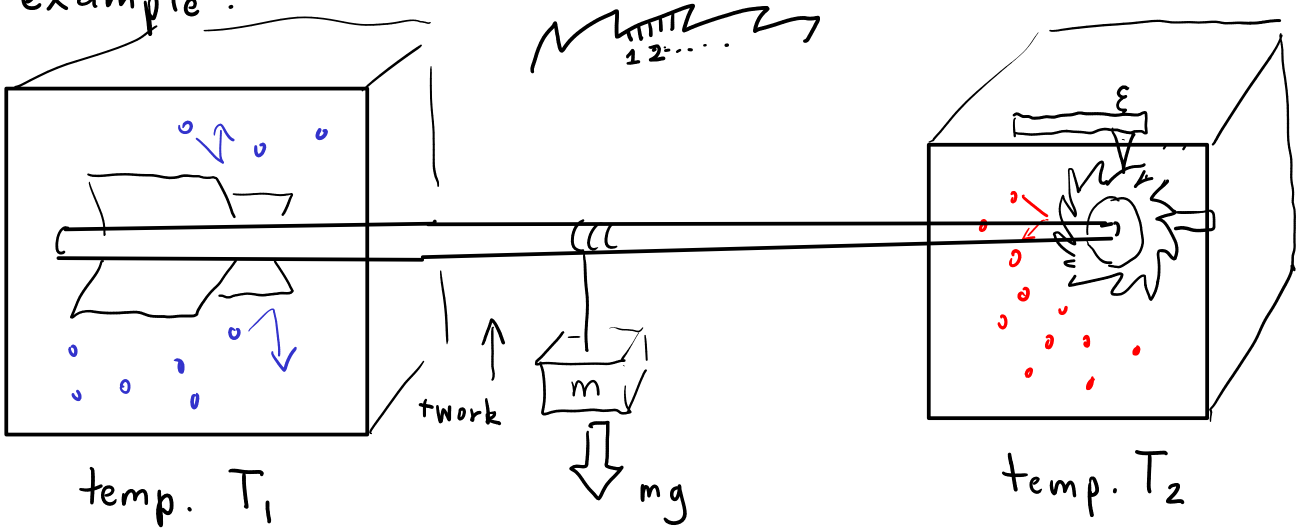
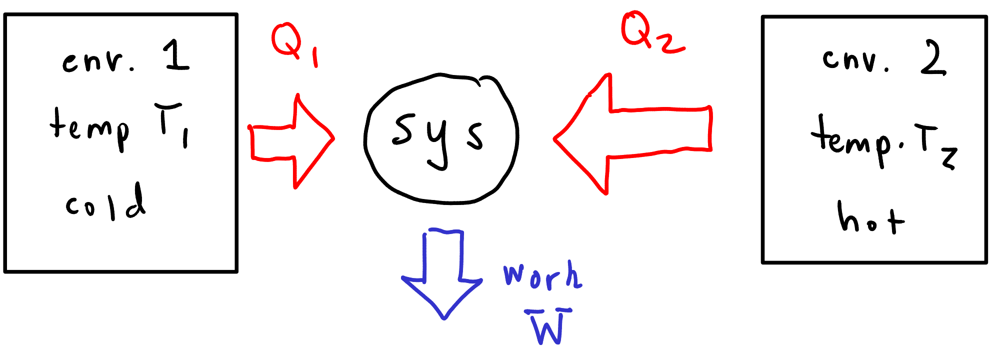
example:





$T_2 > T_1$

two transition matrices:

(one each for sys. connected to single env.)

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

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

$\alpha = 1, 2$:

LDB: $$\frac{W_{nm}^{(\alpha)}}{W_{mn}^{(\alpha)}} = e^{-\beta_\alpha (E_n - E_m + w_{nm})}$$

$$\beta_\alpha = \frac{1}{k_B T_\alpha}$$

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

p_α = prob. that in time step δt, the trans. occurs due to env. α

$$p_1 + p_2 = 1$$

traj. $\nu = (\underbrace{n_0, n_1}_{\alpha_0}, \underbrace{\ , \ -}_{\alpha_1} \cdots\cdots \underbrace{, n_\tau}_{\alpha_{\tau-1}})$

env. labels: $\alpha_0 = 1 \text{ or } 2$

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

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

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

p_α cancel out

$$= -k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t_0))$$

$$+ k_B \ln \frac{W^{(1)}_{\sim} W^{(1)}_{\sim} \cdots W^{(1)}_{\sim}}{W^{(1)}_{\sim} W^{(1)}_{\sim} \cdots W^{(1)}_{\sim}}$$

$$+ k_B \ln \frac{W^{(2)}_{\sim} \cdots\cdots W^{(2)}_{\sim}}{W^{(2)}_{\sim} \cdots\cdots W^{(2)}_{\sim}}$$

LDB

$$= -k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t_0))$$

$$- \frac{1}{T_1}\left(\Delta E^{(1)}(\nu) + \mathcal{W}^{(1)}(\nu)\right)$$

$$- \frac{1}{T_2}\left(\Delta E^{(2)}(\nu) + \mathcal{W}^{(2)}(\nu)\right)$$

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

$\bar{W}^{(\alpha)}(\nu)$ = " work terms " env. α

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

= total heat energy into sys from env. α

$\Delta E(\nu) = \Delta E^{(1)}(\nu) + \Delta E^{(2)}(\nu)$

= total sys. energy change

$\bar{W}(\nu) = \bar{W}^{(1)}(\nu) + \bar{W}^{(2)}(\nu)$

= total work done by sys.

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

take avg. on ν: $I = \underbrace{\Delta S}_{S(t_\tau) - S(t_0)} - \frac{1}{T_1} Q_1 - \frac{1}{T_2} Q_2 \geq 0$ 2nd law

$Q_1 + Q_2 = \Delta E + \bar{W}$ 1st law

Consider either: $\begin{cases} \text{• stationary state } (t \to \infty) \\ \text{• w/ periodic driving from ext. parameter (cycle time } \tau) \end{cases}$

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

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

1st: $Q_1 + Q_2 = \bar{W}$

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

$\frac{I}{\Delta t} \equiv \sigma$ entropy production rate ≥ 0

$\frac{Q_\alpha}{\Delta t} = \dot{Q}_\alpha$ heat rate from env. α

$\frac{W}{\Delta t} = P$ net power output of sys.

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

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

case 1: when $\dot{Q}_2 > 0$ hot env. donates energy to sys.

$T_1, T_2 > 0$

$T_2 \geq T_1$

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

heat is dumped into cold bath

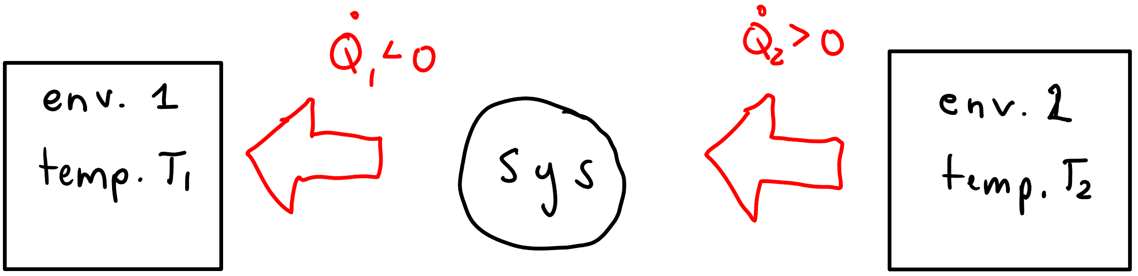
$$\begin{aligned} P &= \dot{Q}_2 + \dot{Q}_1 \\ &= \dot{Q}_2 - |\dot{Q}_1| \\ &= \dot{Q}_2 - T_1\left(\frac{\dot{Q}_2}{T_2} + \sigma\right) \\ &= \dot{Q}_2\left(1 - \frac{T_1}{T_2}\right) \underbrace{- T_1 \sigma}_{\leq 0} \end{aligned}$$

$$P \leq \dot{Q}_2\left(1 - \frac{T_1}{T_2}\right)$$

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

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

Carnot efficiency bound



"heat engine"
$\Downarrow$
converts temp. diff. to work

$$P = \dot{Q}_2\left(1 - \frac{T_1}{T_2}\right) - T_1 \sigma$$
$$\leq \dot{Q}_2\left(1 - \frac{T_1}{T_2}\right)$$