$\alpha = 1, 2$

$p_\alpha =$ prob. in a given time δt,

the trans. occurs due to

energy exchange w/ env. α

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

two diff. trans. matrices : $W^{(1)}_{nm}$ + $W^{(2)}_{nm}$

$$I(\nu) = k_B \ln \frac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})} \Rightarrow p_\alpha\text{'s cancel out}$$

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

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

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

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

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

LDB

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

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

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

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

$W^{(\alpha)}(\nu)$ = sum of work terms due to env. α

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

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

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

= total sys. energy change during ν

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

= total work done by sys.

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

take avg. over ν

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

2nd law

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

consider either: $\left\{ \begin{array}{l} \bullet \text{ stationary state } t \to \infty \\ \quad (p_n(t) \to p_n^s) \\ \bullet \text{ periodic driving (cycle)} \\ \quad (p_n(t) \text{ becomes periodic as } t \to \infty) \end{array} \right.$

$\Delta E = \Delta S = 0$ in both cases (over one period in cycle)

2nd: $\quad I = -\dfrac{Q_1}{T_1} - \dfrac{Q_2}{T_2} \geq 0 \qquad = 0 \text{ iff } I = 0$

1st: $\quad Q_1 + Q_2 = W$

divide both laws by time $\Delta t = \left\{ \begin{array}{ll} \delta t & \text{for stat. state} \\ \tau \delta t & \text{for periodic case w/ period } \tau \end{array} \right.$

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

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

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

$$W = W_{out} - W_{in}$$

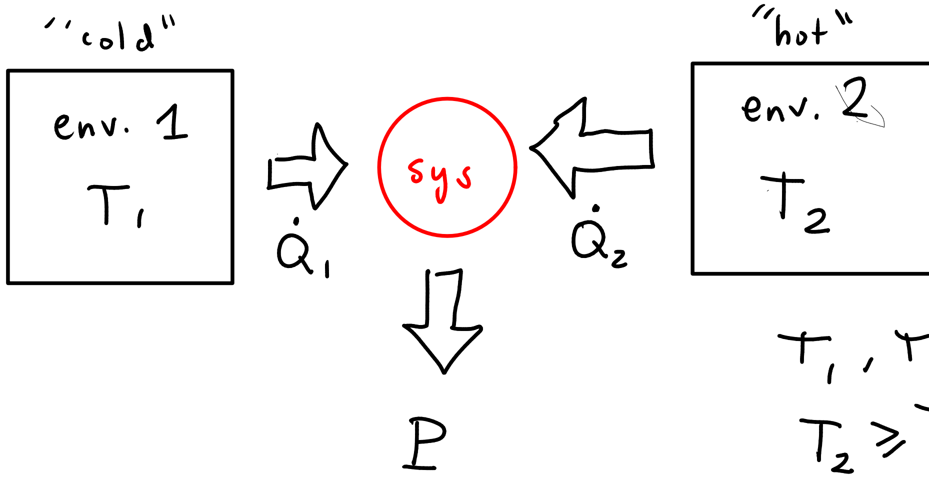
$$P = P_{out} - P_{in}$$

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

$P > 0 \Rightarrow$ net power done by sys.

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

$\dot{Q}_\alpha > 0 \Rightarrow$ heat <u>into</u> sys.



$T_1, T_2 > 0$

$T_2 \geq T_1$

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

heat engine

heat in $\Rightarrow$ power out

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

heat is dumped into cold bath

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

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

upper bound on net power output

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

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

Carnot bound on efficiency of "heat engines" (stat. states <u>or</u> cycles)

1) if $T_1 = T_2$: $\eta \leq 0$

(no net power output possible
$\Rightarrow$ no perpetual motion machines)

2) we assumed env >> sys so $\dot{Q}_1$ + $\dot{Q}_2$ do not change T_1 + T_2 over short time-scales $\Rightarrow$ but for huge times T_1 + T_2 also change

3) as we approach $\eta \to \eta_{max} = 1 - \dfrac{T_1}{T_2}$

what happens?

$$\sigma = \frac{I}{\Delta t} \to 0$$

two. options: • $I \to 0$ equilibrium

set $T_1 = T_2$ + let sys. equil. at one temp.

$$\eta = \eta_{max} = 1 - \frac{T_1}{T_2} = 0$$

• cycle $\Delta t \to \infty$ (infinitely long cycle period)

$$I \neq 0 \Rightarrow W = Q_1 + Q_2 > 0$$

power $\dfrac{W}{\Delta t} = P \to 0$ max. effic. but zero power

interesting question: What is efficiency at max. power?

$\Rightarrow$ no universal answer but we do know results under certain cases