Assumptions up to now:

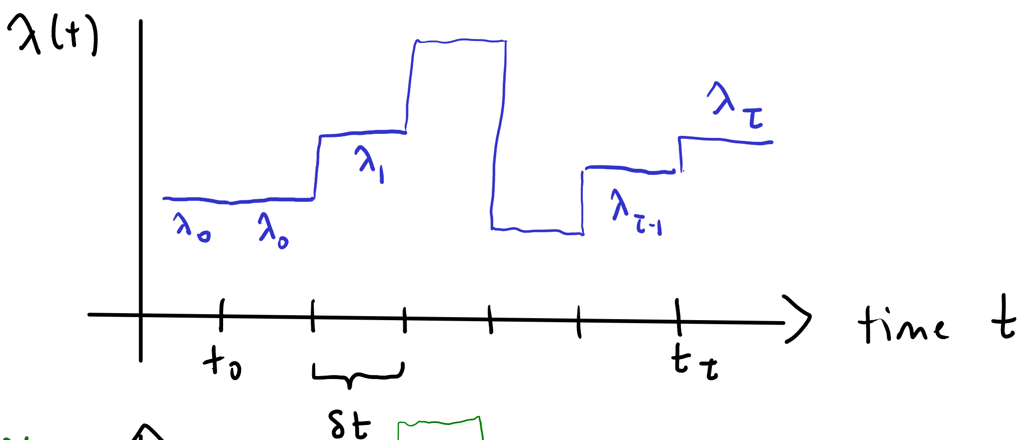
A) environment constant $\Rightarrow$ W_{nm} constant

B) single environ. w/ one temp. T

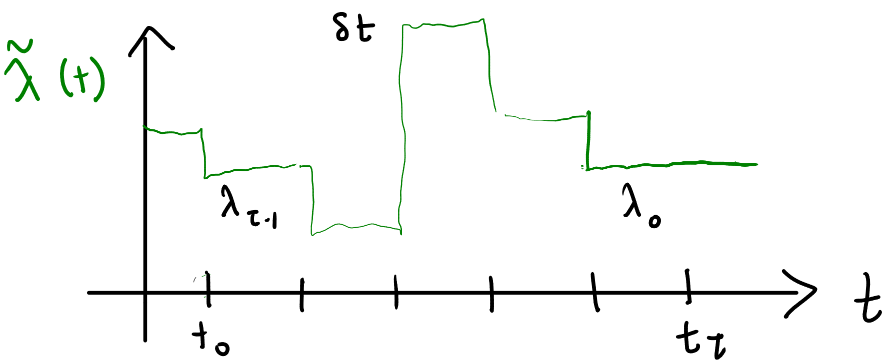
Relax assumpt. A: $W_{nm}(\lambda(t))$

$\lambda(t)$ = set of external parameters we control: temp, pressure, etc.

Control protocol: $\lambda(t)$ is known beforehand



"forward" control protocol (arbitrary)



"reverse" protocol

generalize def'n of irreversibility:

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

$\mathcal{P}(\nu)$ = prob. of forw. traj ν under forw. protocol

$\tilde{\mathcal{P}}(\tilde{\nu})$ = prob. of rev. traj. $\tilde{\nu}$ under rev. protocol

$$I(\nu) = k_B \ln \frac{W_{n_\tau n_{\tau-1}}(\lambda_{\tau-1}) \cdots\cdots W_{n_2 n_1}(\lambda_1) W_{n_1 n_0}(\lambda_0) p_{n_0}(t_0)}{W_{n_0 n_1}(\lambda_0) \cdots\cdots W_{n_{\tau-1} n_\tau}(\lambda_{\tau-1}) p_{n_\tau}(t_\tau)}$$

$$\nu = (n_0, n_1, \ldots, n_\tau) \qquad = \sum_{i=0}^{\tau-1} I(\mu_i) \qquad \mu_i = (n_i, n_{i+1})$$

$$I(\mu_i) = k_B \ln \frac{W_{n_{i+1} n_i}(\lambda_i) p_{n_i}(t_i)}{W_{n_i n_{i+1}}(\lambda_i) p_{n_{i+1}}(t_{i+1})}$$

every proof from before is same:

$$\text{IFT} \quad \langle e^{-I(\nu)/k_B} \rangle = 1$$

$$I = \langle I(\nu) \rangle \geq 0$$

$$= 0 \quad \text{iff}$$

$$P(\nu) = \tilde{P}(\tilde{\nu})$$

1st: $Q = \Delta E + W$

2nd: $I = -\frac{\Delta F}{T} - \frac{W}{T} \geq 0$

Special case: $\lambda(t)$ is periodic (i.e. engine cycle)

$$\lambda(t+\tau) = \lambda(t) \qquad \text{period } \tau$$

$$W(\lambda(t)) = W(\lambda(t+\tau))$$

PS # 2 proof: $t \to \infty$ you approach periodic state

$$p_n(t) = p_n(t+\tau)$$

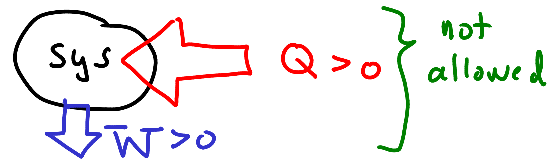
$$E(t) = \sum_n p_n(t) E_n \quad \text{is also periodic, etc.}$$

over one period: $\Delta E = E(\tau) - E(0) = 0$

$$\Delta F = F(\tau) - F(0) = 0$$

1st: $Q = W$

2nd: $W = -T\,I$



$$Q = W = -T\,I \leq 0 \quad \text{for pos. } T$$

Kelvin-Planck version of 2nd law:

You cannot create a cyclically driven system connected to env. at one temp. T that produces net work in the long term

$$W = W_{out} - W_{in} > 0$$

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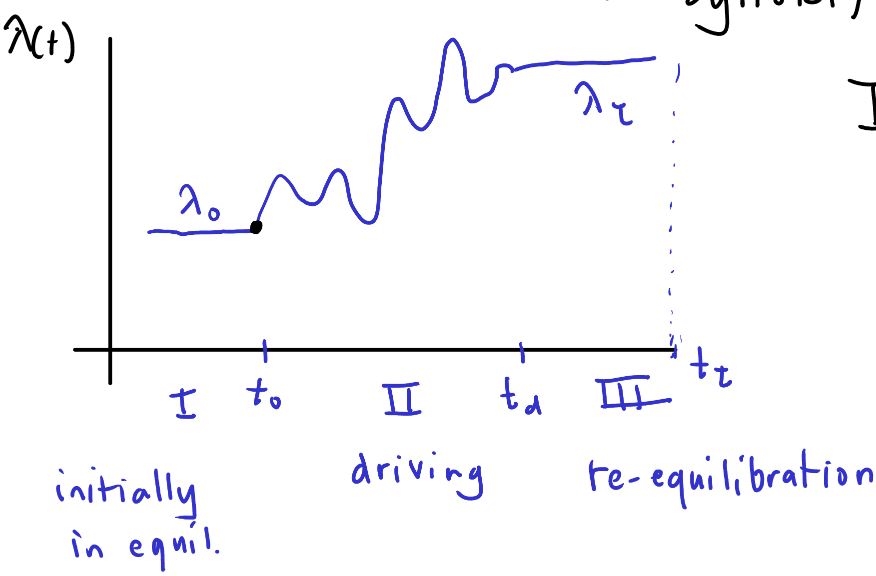
non-periodic $\lambda(t)$: case considered in late 1990's by Jarzynski, Crooks + others



I: before t_0 sys. has reached equil.

$$F(t_0) = F^{eq}(\lambda_0)$$
$$= -k_B T \ln Z(\lambda_0)$$

$$Z(\lambda_0) = \sum_n e^{-\beta E_n(\lambda_0)}$$

III: as $t \to \infty$, re-equilibrate to λ_τ

$$F(t_\tau) = F^{eq}(\lambda_\tau) \quad \text{for } t_\tau >> t_d$$

will prove: $W(\nu)$ = net work done by sys in traj. ν from t_0 to t_τ

$$\langle e^{\beta W(\nu)} \rangle = e^{-\beta \Delta F^{eq}}$$

Jarzynski equality

$$\Delta F^{eq} = F^{eq}(\lambda_\tau) - F^{eq}(\lambda_0)$$

related to noneq driving

related to equil. properties

PROOF:

start w/ IFT: $\langle e^{-I(\nu)/k_B} \rangle = 1$

$$I(\nu) = -k_B \left(\ln p_{n_\tau}(t_\tau) - \ln p_{n_0}(t_0) \right) - \frac{1}{T}\left(E_{n_\tau}(\lambda_\tau) - E_{n_0}(\lambda_0) \right) - \frac{1}{T} W(\nu)$$

$$\nu = (n_0, n_1, \ldots, n_\tau)$$
$$t_0 \longrightarrow t_\tau$$

at beg. + end we are at Boltzmann equ.

$$p_{n_\tau}(t_\tau) = p_{n_\tau}^{eq} = \frac{e^{-\beta E_{n_\tau}(\lambda_\tau)}}{Z(\lambda_\tau)}$$

$$p_{n_0}(t_0) = p_{n_0}^{eq} = \frac{e^{-\beta E_{n_0}(\lambda_0)}}{Z(\lambda_0)}$$

$$\Rightarrow \quad I(v) = k_B \ln Z(\lambda_\tau) - k_B \ln Z(\lambda_0) - \frac{1}{T}\overline{W}(v)$$

$$= -\frac{1}{T}\underbrace{\Delta F^{eq}}_{\text{same for each run}} - \frac{1}{T}\underbrace{\overline{W}(v)}_{\text{varies w/ each run}}$$

IFT: $$\left\langle e^{-I(v)/k_B} \right\rangle = 1$$

$$\left\langle e^{\beta \Delta F^{eq} + \beta \overline{W}(v)} \right\rangle = 1$$

$$e^{\beta \Delta F^{eq}} \left\langle e^{\beta \overline{W}(v)} \right\rangle = 1$$

$$\Rightarrow \quad \boxed{\left\langle e^{\beta \overline{W}(v)} \right\rangle = e^{-\beta \Delta F^{eq}}}$$