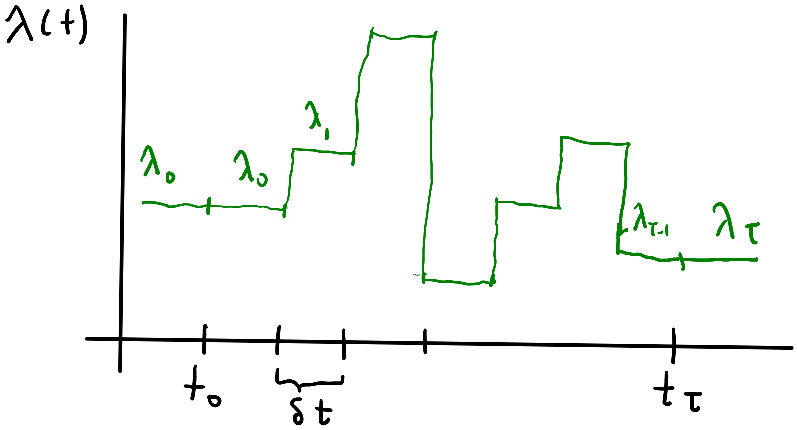
Two assumptions up to now:

A) const. transition matrix W_{nm}
(environ. conditions are const.)

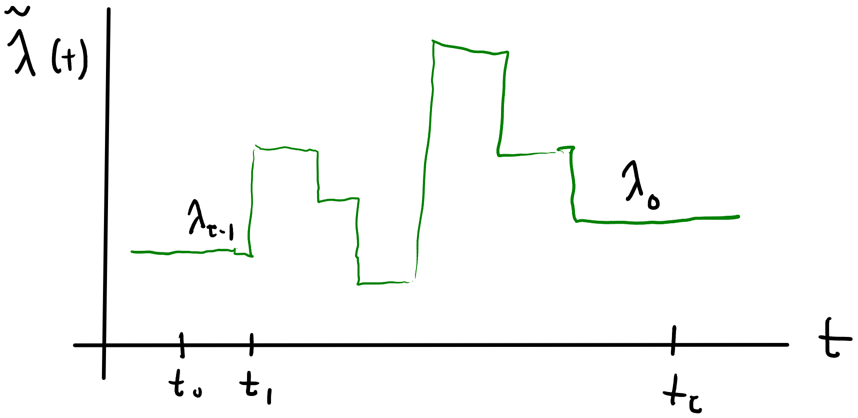
B) single environ. w/ one temp. T

Relax assumption A: $W_{nm}(\lambda(t))$
depends on time-varying parameters that we control: temp, pressure, etc.

control protocol: $\lambda(t)$ known beforehand



"forward" control protocol



"reverse" protocol

irreversibility: $I(\nu) = k_B \ln \dfrac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})}$

$$= k_B \ln \frac{\text{prob. of forw. traj. under forw. prot.}}{\text{prob. of rev. traj. under reverse prot.}}$$

(starting at final dist. of forw. case)

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

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

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

$$\begin{array}{c|c} & \begin{matrix} 3 & 5 \end{matrix} \\ \begin{matrix} 3 \\ 5 \end{matrix} & \begin{bmatrix} & \bullet \\ \bullet & \end{bmatrix} \end{array}$$

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

$\Rightarrow$ every proof is same: IFT $\langle e^{-I(\nu)/k_B} \rangle = 1$

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

$= 0$ iff $\mathcal{P}(\nu) = \tilde{\mathcal{P}}(\tilde{\nu})$ for all ν (if environ. is const.)

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

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

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

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

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

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

$$E(t) = \sum_n p_n(t) E_n \qquad p_n(t) = p_n(t+\tau)$$

look at one period: $\Delta E = E(t_\tau) - E(t_0) = 0$

$\Delta S = 0$, $\Delta F = 0$

$\Rightarrow$ 2nd: $\quad Q = \overline{W} = -TI \leq 0$
+ 1st

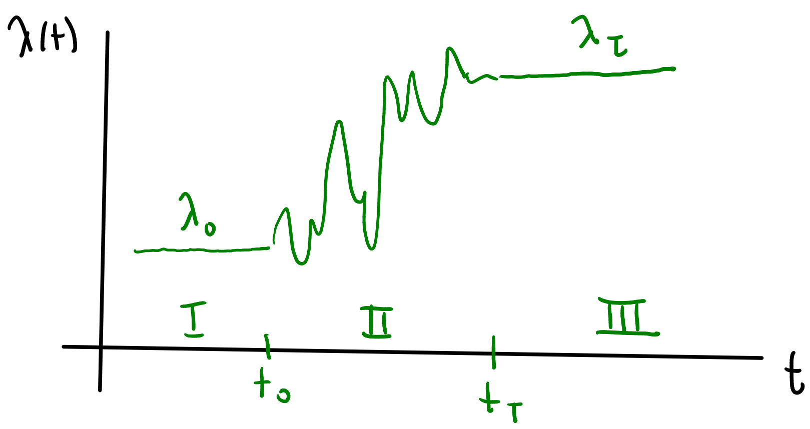
Kelvin-Planck statement of 2nd law:

you cannot create a cylically driven system connected to environ. at one temp. T that produces net work

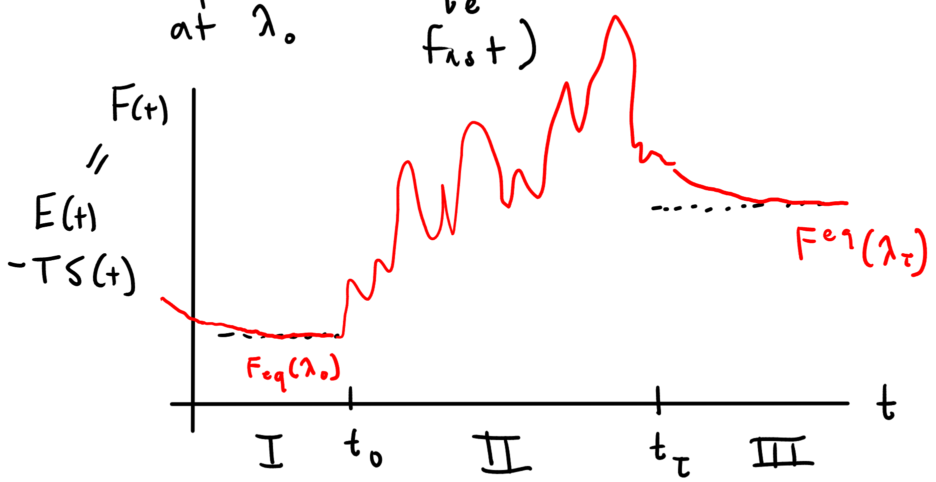
$$\overline{W} = \overline{W}_{out} - \overline{W}_{in} > 0 \quad \text{in the long run}$$

$\Rightarrow$ no perpetual motion!

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



initially in equil. at λ_0 | driving (could be fast) | re-equilibrate at λ_τ



$$\mathrm{I}: \; F(t) \to F^{eq}(\lambda_0) = -k_B T \ln Z(\lambda_0)$$

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

$$\mathrm{III}: \; F(t) \to F^{eq}(\lambda_\tau) = -k_B T \ln Z(\lambda_\tau)$$

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

will prove:

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

(diff. value for each exp. traj. ν)

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

Jarzynski equality