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

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

rev. traj. in rev. ensemble

define an avg. over all traj's in ensemble:

$$Q(\nu) = \text{traj. quantity}$$

$$Q \equiv \langle Q(\nu) \rangle = \underbrace{\sum_\nu}_{\sum_{n_0} \cdots \sum_{n_\tau}} \mathcal{P}(\nu)\, Q(\nu)$$

calculate the following average:

$$\langle e^{-I(\nu)/k_B} \rangle = \sum_\nu \mathcal{P}(\nu)\, e^{-I(\nu)/k_B}$$

$$= \sum_\nu \mathcal{P}(\nu) \frac{\tilde{\mathcal{P}}(\tilde{\nu})}{\mathcal{P}(\nu)}$$

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

$$= \sum_{\tilde{\nu}} \tilde{\mathcal{P}}(\tilde{\nu}) = 1$$

IFT:

integral fluctuation theorem

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

Seifert, PRL 040602 (2005)

precursors: 1990's

Consequences:

1) will prove: $\text{IFT} \Rightarrow \langle \mathcal{I}(\nu)\rangle = \mathcal{I} \geq 0$ always

proof:

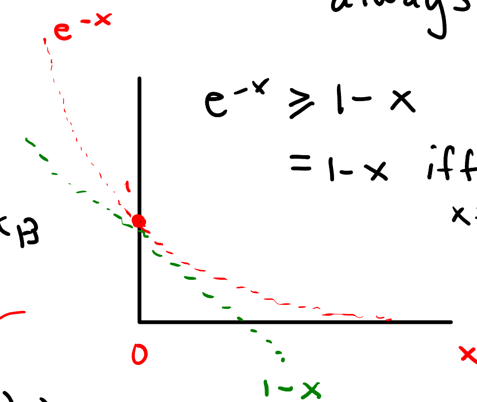
$$1 = \langle e^{-\mathcal{I}(\nu)/k_B}\rangle$$

$$= \sum_\nu \mathcal{P}(\nu)\, e^{-\mathcal{I}(\nu)/k_B}$$

$$\geq \sum_\nu \mathcal{P}(\nu)\left(1 - \frac{\mathcal{I}(\nu)}{k_B}\right)$$

$$= \sum_\nu \mathcal{P}(\nu) - \frac{1}{k_B}\sum_\nu \mathcal{P}(\nu)\,\mathcal{I}(\nu)$$

$$= 1 - \frac{1}{k_B}\mathcal{I}$$



$e^{-x} \geq 1-x$

$= 1-x$ iff $x=0$

$$\Rightarrow \quad 1 \geq 1 - \frac{\mathcal{I}}{k_B} \Rightarrow \boxed{\mathcal{I} \geq 0}$$

2) you can decompose $\mathcal{I}(\nu)$ into irreversibilities of single time step sub-trajectories:

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

$$= \underbrace{(n_0, n_1)}_{\mu_0} \oplus \overbrace{(n_1, n_2)}^{\mu_1} \oplus \cdots \oplus \underbrace{(n_{\tau-1}, n_\tau)}_{\mu_{\tau-1}}$$

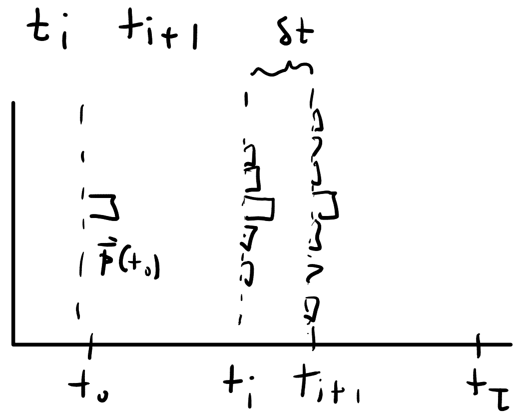
"concatenation"

$\mu_i = (n_i, n_{i+1})$

claim: $\underbrace{\mathcal{I}(\nu)}_{\text{LHS}} = \overbrace{\mathcal{I}(\mu_0) + \mathcal{I}(\mu_1) + \cdots + \mathcal{I}(\mu_{\tau-1})}^{\text{RHS}}$

$$I(\mu_i) = k_B \ln \frac{\mathcal{P}(\mu_i)}{\tilde{\mathcal{P}}(\tilde{\mu}_i)} = k_B \ln \frac{W_{n_{i+1} n_i}\, p_{n_i}(t_i)}{W_{n_i n_{i+1}}\, \underbrace{\tilde{p}_{n_{i+1}}(t_i)}_{p_{n_{i+1}}(t_{i+1})}}$$

$$\mu_i = (n_i, n_{i+1})$$



$$\vec{p}(t_{i+1}) = W \vec{p}(t_i)$$

$$\text{RHS} = \sum_{i=1}^{\tau-1} I(\mu_i) = k_B \ln \left[\frac{W_{n_1 n_0}\, p_{n_0}(t_0)}{W_{n_0 n_1}\, \cancel{p_{n_1}(t_1)}} \cdot \frac{W_{n_2 n_1}\, \cancel{p_{n_1}(t_1)}}{W_{n_1 n_2}\, \cancel{p_{n_2}(t_2)}} \; \cancel{\cdots} \; \frac{W_{n_\tau n_{\tau-1}}\, \cancel{p_{n_{\tau-1}}(t_{\tau-1})}}{W_{n_{\tau-1} n_\tau}\, p_{n_\tau}(t_\tau)} \right]$$

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

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

Let's use these results:

IFT $\Rightarrow$ $I \geq 0$ question: can $I = 0$?

focus on stationary state : $\vec{p}^{\,s}$

$$p_n(t_i) \rightarrow p_n^s$$

$$I(\mu_i) = k_B \ln \frac{W_{n_{i+1} n_i}\, p^s_{n_i}}{W_{n_i n_{i+1}}\, p^s_{n_{i+1}}}$$

imagine $I = \langle I(\nu) \rangle = 0 = \sum_i \langle I(\mu_i) \rangle$

we know $\langle I(\mu_i) \rangle \geq 0$

$\Rightarrow \langle I(\mu_i) \rangle = 0$

$\Rightarrow I(\mu_i) = 0$ for every possible μ_i

$\Leftrightarrow W_{n_{i+1} n_i}\, p^s_{n_i} = W_{n_i n_{i+1}}\, p^s_{n_{i+1}}$

LDB : $W_{ij}\, p_j^s = W_{ji}\, p_i^s$

if LDB true + we are at stationary state:

$I(\mu_i) = 0$ for every μ_i

$I(\nu) = \sum_i I(\mu_i) = 0$ for every traj. ν in stationary ensemble

$\Rightarrow \langle I(\nu) \rangle = 0$ as well

When $I(\nu) = 0$ for all ν in ensemble:

$\langle I(\nu) \rangle = 0$: equilibrium stationary state (ESS)

any stationary state where $\langle I(\nu) \rangle > 0$:

nonequilibrium stationary state