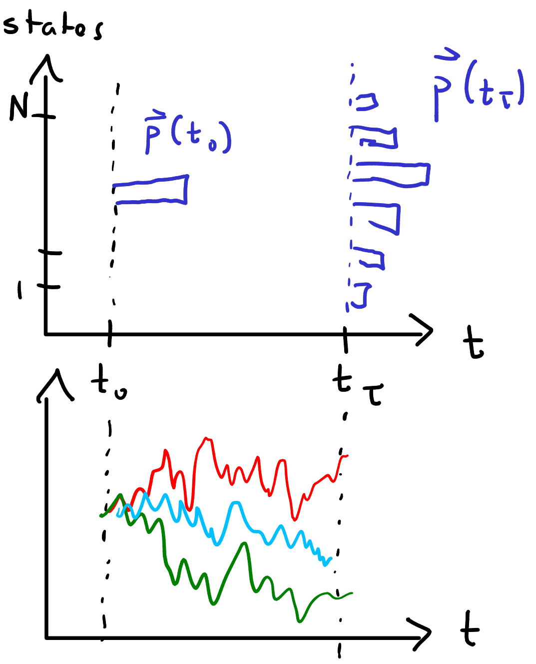
master eqn: $\vec{p}(t_\tau) = W\vec{p}(t_{\tau-1})$

$= \cdots\cdots = W^\tau \vec{p}(t_0)$




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

$\Rightarrow P(\nu)$ of the trajectory

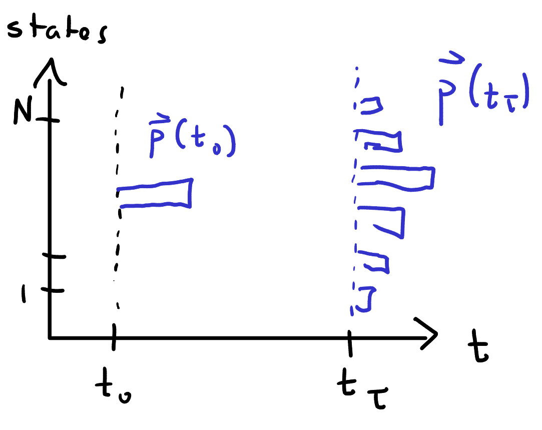
$= W_{n_\tau n_{\tau-1}} \cdots W_{n_1 n_0} P_{n_0}(t_0)$

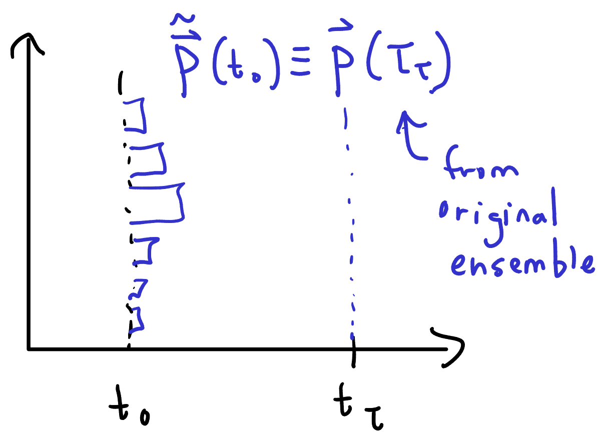
$$\sum_\nu P(\nu) = \sum_{n_\tau} \cdots \sum_{n_0} P(\nu) = 1$$

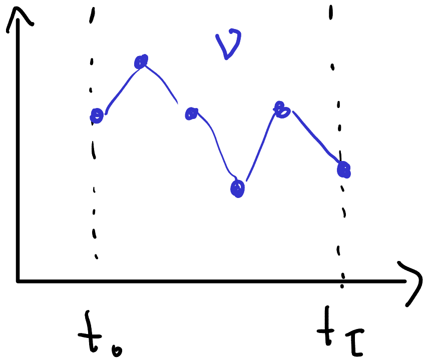
i) given a traj. $\nu$, define a reverse traj $\tilde{\nu}$ (going forward in time):

$$\tilde{\nu} = (\tilde{n}_0, \tilde{n}_1, \ldots, \tilde{n}_\tau)$$
$$\tilde{n}_0 = n_\tau,\quad \tilde{n}_1 = n_{\tau-1},\ \ldots,\ \tilde{n}_\tau = n_0$$

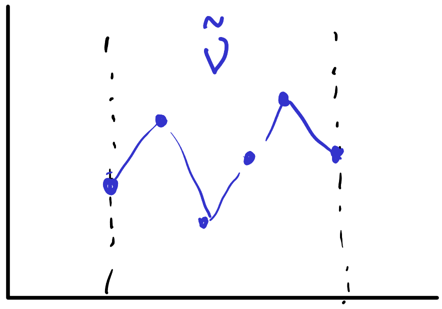
ii) reverse ensemble: initial distrib. of states is the final distrib. of our original ensemble






compare




prob. $\mathcal{P}(\nu)$ in forward ensemble

prob. $\tilde{\mathcal{P}}(\tilde{\nu})$ in reverse ensemble

b/c $W$ is ergodic + mixing $\Rightarrow$ LDB holds

if $W_{nm} \neq 0 \Rightarrow W_{mn} \neq 0$ (MR)

if $\mathcal{P}(\nu) \neq 0 \Rightarrow \tilde{\mathcal{P}}(\tilde{\nu}) \neq 0$

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

$|I(\nu)|$ is large when $\mathcal{P}(\nu) \gg \tilde{\mathcal{P}}(\tilde{\nu})$

or $\tilde{\mathcal{P}}(\tilde{\nu}) \gg \mathcal{P}(\nu)$

$I(\nu) = 0$ when $\mathcal{P}(\nu) = \tilde{\mathcal{P}}(\tilde{\nu})$

define an average over ensemble:

any quantity $Q(\nu)$ function of $\nu$

$$Q \equiv \langle Q(\nu) \rangle = \sum_\nu \mathcal{P}(\nu)\, Q(\nu)$$

universal relationship:

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

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

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

integral fluctuation theorem (IFT)

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

[Seifert, PRL 040602 (2005)]
precursors: 1990s (will see)

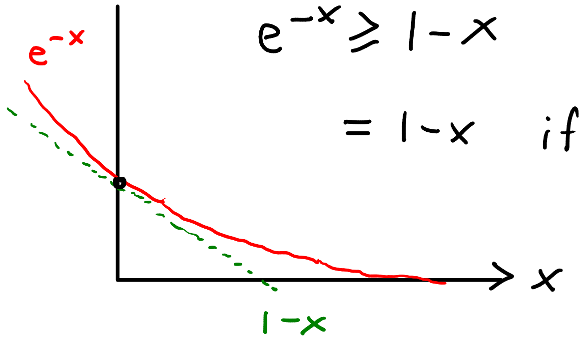
Consequences:

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

proof: $$1 = \left\langle e^{-I(\nu)/k_B} \right\rangle = \sum_\nu \mathcal{P}(\nu)\, e^{-I(\nu)/k_B}$$

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

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




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

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

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

Properties of $I(\nu)$:

decompose a traj. into individual "steps":

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

"concatenate"

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

$\mu_i \equiv$ traj. of length 1 step from $n_i$ to $n_{i+1}$

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

irrev. of each mini traj. $\mu_i$

$$I(\mu_0) + I(\mu_1) + \cdots + I(\mu_{\tau-1})$$

$$= k_B \ln \frac{W_{n_1 n_0}\, p_{n_0}(t_0)}{W_{n_0 n_1}\, \cancel{p_{n_1}(t_1)}} \frac{W_{n_2 n_1}\, \cancel{p_{n_1}(t_1)}}{W_{n_1 n_2}\, \cancel{p_{n_2}(t_2)}} \circ \circ \circ$$

$$\cdots \frac{W_{n_\tau n_{\tau-1}}\, \cancel{p_{n_{\tau-1}}(t_{\tau-1})}}{W_{n_{\tau-1} n_\tau}\, p_{n_\tau}(t_\tau)}$$

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

$= I(\nu)$ total irrev. for whole traj.

$\Rightarrow$ $I(\nu)$ is additive over concatenation of traj.