Markov Process $\dfrac{P(1\to 2)}{P(2\to 1)} = \dfrac{e^{-\beta E_2}}{e^{-\beta E_1}} = \dfrac{P(2)}{P(1)}$

Microscopic definition of work & heat

$$E = \sum P_i E_i$$

$$dE = \underbrace{\sum E_i \, dP_i}_{\substack{dQ \\ \text{heat}}} + \underbrace{\sum P_i \, dE_i}_{\substack{dW \\ \text{work}}}$$

$$\Delta E = \Delta Q + \Delta W$$

Assume Canonical Ensemble, Temp β

state specified by 2 indices $\to \begin{cases} i & \text{stochastic state index - can change during Markov step} \\ \lambda & \text{control parameter} \to \text{changed deterministically} \end{cases}$

energy of system $= \mathcal{E}(i_t, \lambda_t)$

where (i_t, λ_t) is state at time t.

The process we're studying is

$$i_0 \xrightarrow{\lambda_1} i_1 \xrightarrow{\lambda_2} i_2 \longrightarrow \cdots \xrightarrow{\lambda_\tau} i_\tau$$

start with system $\mathcal{E}(i_0, \lambda_0)$

change λ $\downarrow$ $\mathcal{E}(i_0, \lambda_1)$

Markov time step $\downarrow$ $\mathcal{E}(i_1, \lambda_1)$

initial state i_0, λ_0

final state i_τ, λ_τ τ is Time of Path.

$$\Delta E = \mathcal{E}(i_\tau, \lambda_\tau) - \mathcal{E}(i_0, \lambda_0)$$

$$W = [\mathcal{E}(i_0, \lambda_1) - \mathcal{E}(i_0, \lambda_0)] + [\mathcal{E}(i_1, \lambda_2) - \mathcal{E}(i_1, \lambda_1)] + \cdots + [\mathcal{E}(i_{\tau-1}, \lambda_\tau) - \mathcal{E}(i_{\tau-1}, \lambda_{\tau-1})]$$

$$= \sum_{t=0}^{\tau-1} [\mathcal{E}(i_t, \lambda_{t+1}) - \mathcal{E}(i_t, \lambda_t)] \quad \tau \text{ terms}$$

$$Q = [\mathcal{E}(i_1, \lambda_1) - \mathcal{E}(i_0, \lambda_1)] + \cdots + [\mathcal{E}(i_\tau, \lambda_\tau) - \mathcal{E}(i_{\tau-1}, \lambda_\tau)]$$

$$= \sum_{t=0}^{\tau-1} \mathcal{E}(i_{t+1}, \lambda_{t+1}) - \mathcal{E}(i_t, \lambda_{t+1})$$

$$W + Q = \sum_{t=0}^{\tau-1} \underbrace{\mathcal{E}(i_t, \lambda_{t+1}) - \mathcal{E}(i_t, \lambda_{t+1})}_{0} + \underbrace{\mathcal{E}(i_{t+1}, \lambda_{t+1}) - \mathcal{E}(i_t, \lambda_t)}_{\text{Telescopes}}$$

$$= \mathcal{E}(i_\tau, \lambda_\tau) - \mathcal{E}(i_0, \lambda_0) = \Delta E$$

Now consider $\dfrac{P(i_0 \xrightarrow{\lambda_1} i_1 \xrightarrow{\lambda_2} \cdots \xrightarrow{\lambda_\tau} i_\tau)}{P(i_\tau \xrightarrow{\lambda_\tau} i_{\tau-1} \cdots \xrightarrow{\lambda_1} i_0)} = \dfrac{P(i_0 \xrightarrow{\lambda_1} i_1)\, P(i_1 \xrightarrow{\lambda_2} i_2)}{P(i_\tau \xrightarrow{\lambda_\tau} i_{\tau-1})} \cdots \dfrac{P(i_{\tau-1} \xrightarrow{\lambda_\tau} i_\tau)}{P(i_1 \xrightarrow{\lambda_1} i_0)}$

But $\dfrac{P(i_0 \xrightarrow{\lambda_1} i_1)}{P(i_1 \xrightarrow{\lambda_1} i_0)} = \dfrac{e^{-\beta\mathcal{E}(i_1, \lambda_1)}}{e^{-\beta\mathcal{E}(i_0, \lambda_1)}}$

$$\boxed{\therefore \frac{P(\text{FORWARD PATH})}{P(\text{BACKWARD PATH})} = \exp[-\beta[\mathcal{E}(i_1, \lambda_1) - \mathcal{E}(i_0, \lambda_1) + \mathcal{E}(i_2, \lambda_2) - \mathcal{E}(i_1, \lambda_2) + \mathcal{E}(i_\tau, \lambda_\tau) - \mathcal{E}(i_{\tau-1}, \ldots}$$

$$\boxed{= e^{-\beta\Delta Q}}$$

TA DA!