$$\frac{W_{nm}}{W_{mn}} = e^{-\beta\underbrace{(E_n - E_m + \omega_{nm})}_{Q_{nm}}} \qquad \beta = \frac{1}{k_B T}$$

return to def'n of $I(\nu)$

$$\nu = (n_0, \ldots, n_\tau) \qquad \mu_i = (n_i, n_{i+1})$$

$$I(\nu) = k_B \ln \frac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})} = \sum_{i=1}^{\tau-1} I(\mu_i)$$

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

$$= -k_B \ln p_{n_{i+1}}(t_{i+1}) - (-k_B \ln p_{n_i}(t_i))$$
$$- \frac{1}{T}(E_{n_{i+1}} - E_{n_i}) - \frac{1}{T}\omega_{n_{i+1} n_i}$$

$$\Rightarrow I(\nu) = \underbrace{-k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t_0))}_{\equiv \Delta S(\nu)}$$

"change in entropy" in traj. ν

$$- \frac{1}{T}\underbrace{(E_{n_\tau} - E_{n_0})}_{\Delta E(\nu)}$$

"change in energy" in traj. ν

$$- \frac{1}{T}\sum_{i=0}^{\tau-1} \omega_{n_{i+1} n_i} \Big\} \; W(\nu)$$

"total work" done in traj. ν

$$I(\nu) = \Delta S(\nu) - \frac{1}{T}\Delta E(\nu) - \frac{1}{T}W(\nu)$$

notation: $\Delta A(\nu) = A_{n_\tau} - A_{n_0}$

diff in quantity A from initial to final state in ν

$$Q(\nu)$$

$$\langle Q(\nu) \rangle = Q$$

$$\langle \Delta A(\nu) \rangle = \Delta A$$

avg. over ensemble of traj:

$$\boxed{I = \Delta S - \frac{1}{T}\Delta E - \frac{1}{T}W \geq 0}$$

from earlier conseq. of IFT

Our version of 2nd law of thermodyn.

unpack $\Delta S(\nu) = -k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t_0))$

quantity associated w/ particular traj. ν, but it depends on knowing prob. dist. $\vec{p}(t)$ in whole ensemble

"Surprisal" $= -k_B \ln p_n(t_i)$

if small $p_n(t_i) \Rightarrow$ very surprised to observe state n at time t_i

$\Rightarrow$ high surprisal

if large $p_n(t_i) \Rightarrow$ not surprised

$\Rightarrow$ low surprisal

$\Delta S(\nu) =$ surprisal of n_τ at time t_τ

$-$ surprisal of n_0 at time t_0

$=$ "entropy diff. of a traj."

unpack work term:

$$W(\nu) = \sum_{i=0}^{\tau-1} \omega_{n_{i+1} n_i} \overset{?}{=} A_{n_\tau} - A_{n_0}$$

can we write?

$$= \Delta A(\nu)$$

if this is true: $W(\nu)$ corresponds to conservative work

traditional def'n in classical mech:

$\omega = \nabla U$ there exists a potential U

$$\Rightarrow \underbrace{\int_{path} \omega}_{\substack{\text{total work} \\ \text{done over path}}} = U(\text{end}) - U(\text{beginning})$$

compare: $$W(\nu) = A_{n_\tau} - A_{n_0}$$

if no such $A(\nu)$ exists $\Rightarrow$ $W(\nu)$ is <u>not</u> conservative

lastly: heat from environ. during $n_i \to n_{i+1}$ trans.

energy cons.

$$Q_{n_{i+1} n_i} = E_{n_{i+1}} - E_{n_i} + \omega_{n_{i+1} n_i}$$

total heat over traj.

$$Q(\nu) = \sum_{i=0}^{\tau-1} Q_{n_{i+1} n_i} = \Delta E(\nu) + W(\nu)$$

avg. over ensemble

$$\boxed{Q = \Delta E + W}$$

1st law of thermod.