traj. $\nu \Rightarrow I(\nu) = k_B \ln \dfrac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})} = \sum_{i=0}^{\tau-1} I(\mu_i)$

$\nu = (n_0, n_1, n_2, \ldots, n_\tau) \qquad \mu_i = (n_i, n_{i+1})$

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

IFT: $\langle e^{-I(\nu)/k_B} \rangle = 1 \Rightarrow \langle I(\nu) \rangle = \mathcal{I} \geq 0$

Can $\langle I(\nu) \rangle = 0$?

Focus on case where system is in stationary state $\vec{p}^{\,s}$: $p_n(t_i) \to p_n^s$

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

$$I(\mu_i) = 0 \Leftrightarrow W_{n_{i+1} n_i}\, p_{n_i}^s = W_{n_i n_{i+1}}\, p_{n_{i+1}}^s$$

same as LDB!

If LDB is valid & we have reached stationary state: $\boxed{I(\nu) = 0 \text{ for any } \nu}$

$\Rightarrow$ equilibrium stationary state (ESS)

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

If we are in a stationary state w/

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

(NESS)

So far we have only seen one stationary state (Boltzmann):

$$p_n^s = \frac{e^{-\beta E_n}}{Z} \quad \text{satisfies LDB}$$

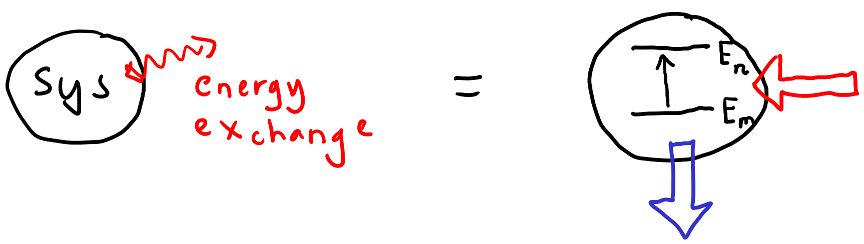
$\Rightarrow \langle I(v) \rangle = 0$ + we have an ESS

In order to get NESS, we need to describe system coupling to "work" $\Rightarrow$ modify LDB condition

up to now:

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

env. at temp. T



Q_{nm} = "heat" (energy from thermal env.) during $m \to n$ trans.

ω_{nm} = work done by system during $m \to n$ trans.

add work ω_{nm}:

$\omega_{nm} > 0$: by the sys

$\omega_{nm} < 0$: on the sys

$$Q_{nm} = E_n - E_m + \omega_{nm}$$

(need more heat if $\omega_{nm} > 0$)

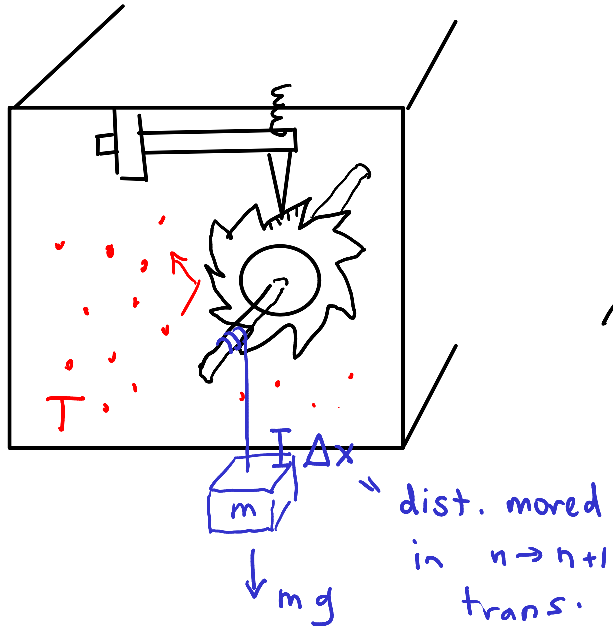
Proof of LDB just depends on energy diff's in your thermal environment:

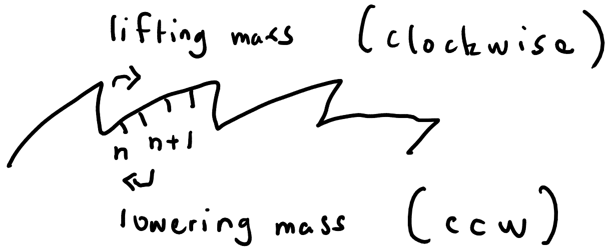
$\Rightarrow$ form always stays the same modified LDB

$$\frac{W_{nm}}{W_{mn}} = e^{-\beta Q_{nm}} = e^{-\beta(E_n - E_m + w_{nm})}$$

$$= \frac{\text{uphill}}{\text{downhill}} \qquad (\text{if } E_n > E_m)$$

$w_{nm} > 0 \Rightarrow$ makes it harder to go uphill





$$w_{n+1,n} = mg\Delta x$$

Question: can we set up a stationary state where the mass in on avg. lifted up continuously (i.e. perpetual motion)

Consequences of modified LDB:

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

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

$$- \frac{1}{T}(E_{n_{i+1}} - E_{n_i}) - \frac{1}{T} w_{n_{i+1} n_i}$$

$$\Rightarrow I(\nu) = \sum_{i=0}^{\tau-1} I(\mu_i) = \underbrace{-k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t_0))}_{\equiv \Delta S(\nu)}$$

"change of entropy" in traj. ν

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

change in energy in traj. ν

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

total work done in traj. ν

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

defined for each traj. ν

notation: $\Delta A(\nu) = A_{n_\tau} - A_{n_0}$ diff in quantity A from beg. of traj. to end

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

avg. over whole ensemble:

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

since $I \geq 0$

version of 2nd law of thermodyn.