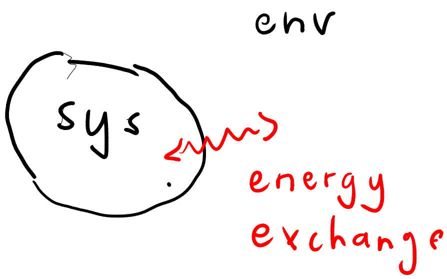
Modifying LDB condition:

up to now:

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



Q_{nm} = energy taken from therm. environment during $m \to n$ trans.

"heat"

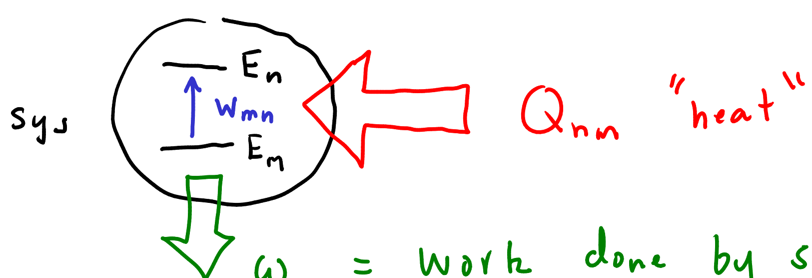
> 0 gain from env.

< 0 lost to env.

$\beta = \frac{1}{k_B T}$: characterizes "generosity" of env.

add a work term for $m \to n$ transition: ω_{nm}

$\omega_{nm} > 0$: sys. does work on something ext.



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

$\omega_{nm} < 0$: something does work on sys.

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

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

generalized version of LDB

$$\frac{W_{nm}}{W_{mn}} = e^{-\beta Q_{nm}}$$

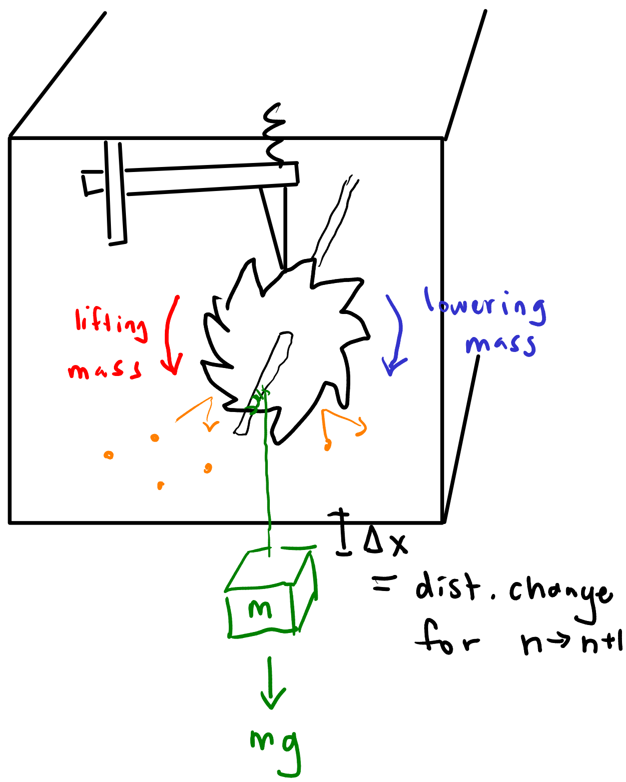
universal form

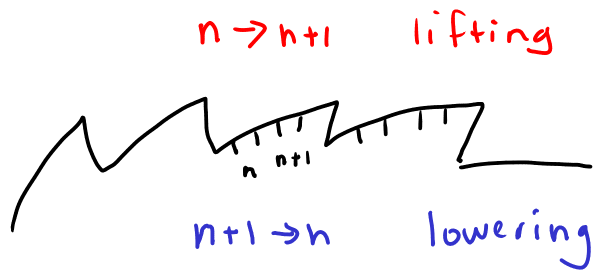
(just change Q_{nm} depending on physical model)

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

$\uparrow$ depends on trans. could be zero

if $\omega_{nm} > 0 \Rightarrow$ makes it harder to go uphill in energy





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

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

Question: can we set up a stationary state where mass is on avg. lifted up (i.e. perpetual motion machine) $\Rightarrow$ return to this later

Return to formalism: $\nu = (n_0, n_1, \ldots, n_\tau)$

$$I(\nu) = \sum_{i=1}^{\tau-1} I(\mu_i) \qquad \mu_i = (n_i, n_{i+1})$$

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

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

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

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

"change of entropy" in traj. ν

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

"change in energy" in traj. ν

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

"total work" done during traj. ν

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

defined for every ν

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

diff. in quantity A from initial to final state

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

$\langle \Delta A(\nu) \rangle = \Delta A$, etc.

avg. over ensemble of traj:

we showed $I \geq 0$ earlier

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

one version of 2nd law of thermodynamics

unpack $\Delta S(\nu) = -k_B \ln p_{n_T}(t_T) - (-k_B \ln p_{n_0}(t_0))$

depends on knowing prob's in entire ensemble

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

large $p_n(t_i) \Rightarrow$ not surprised to observe n at time t_i

$\Rightarrow$ low surprisal value

($\rightarrow 0$ as $p_n(t_i) \rightarrow 1$)

small $p_n(t_i) \Rightarrow$ very surprised to observe n

$\Rightarrow$ high surprisal

$$\Delta S(v) = \text{surprisal of } n_\tau \text{ at time } t_\tau$$
$$- \text{ surprisal of } n_0 \text{ at time } t_0$$
$$= \text{"entropy diff. of a traj."}$$