

LDB (local detailed balance)

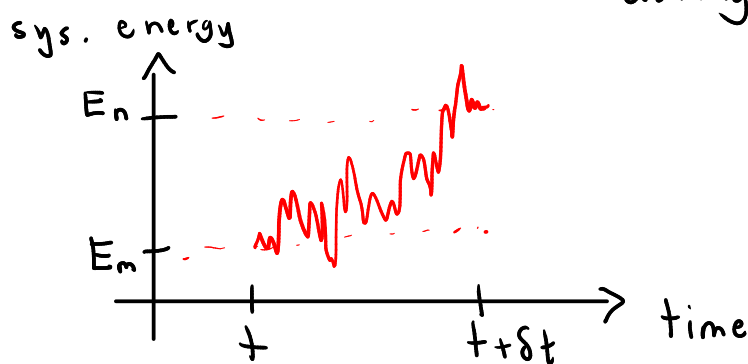
$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m)}$$

energy
exchange
w/ env.

$\Rightarrow$ ESS
(Boltzmann)

will argue: $\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m - \underbrace{W_{nm}}_{\text{"work" done during } m \rightarrow n \text{ trans.}})}$

recall:



$\Omega_{nm} \delta t \propto$
prob. env. takes
us from E_m
to E_n in δt
(donates $E_n - E_m$ energy)

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

$$= e^{-\frac{Q_{nm}}{k_B T}}$$

$$Q_{nm} = E_n - E_m$$

= how much energy
we need from env.
in $m \rightarrow n$ trans.

= "heat" needed from
env.

Imagine we have another source of energy
to system ("work") then the amount
of energy needed from env. is less:

$$Q_{nm} = E_n - E_m - \underbrace{W_{nm}}_{\text{work energy (other source)}}$$

$W_{nm} > 0 \Rightarrow$ help $\Rightarrow$ Q_{nm} decreases (need less
env. input)

$W_{nm} < 0 \Rightarrow$ hurts $\Rightarrow Q_{nm}$ increases

(b/c sys.

needs more
energy to do

work on outside)

energy needed
from env.

general LDB: $\frac{\Omega_{nm}}{\Omega_m} = e^{-\beta Q_{nm}}$

$$Q_{nm} = E_n - E_m - \underbrace{W_{nm}}_{\substack{\text{contrib.} \\ \text{from} \\ \text{multiple} \\ \text{sources}}}$$