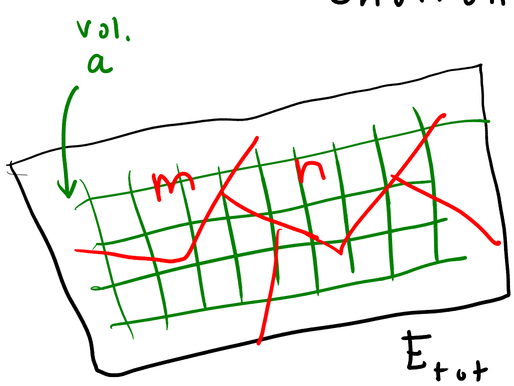
LDB: $W_{nm} p_m^s = W_{mn} p_n^s$

relates elements of W (relev. to transitions at all times) to elements of $\vec{p}^s$ ($t \to \infty$ limit)

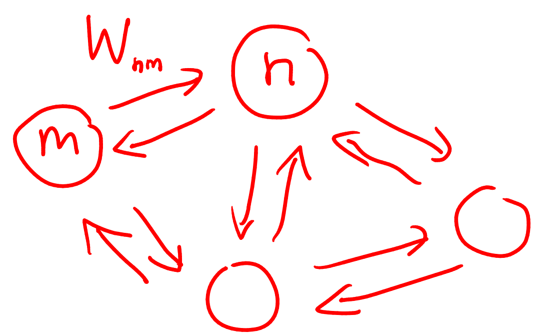
Zoom out:

1) isolated total (system + environment) w/ tot. energy E_{tot}. Assume total is ergodic + mixing.

2) divide up total into system + environment



$\Longleftrightarrow$



$p_n^s = \dfrac{\Theta_n}{\Theta_{tot}}$ ← boxes in n

↖ boxes on whole surface

$p_m^s = \dfrac{\Theta_m}{\Theta_{tot}}$

3) network of transitions w/ matrix W satisfies:

$W_{nm} p_m^s = W_{mn} p_n^s$ <u>LDB</u>

consequences of LDB + fact that components of $\vec{p}^s$ have to be nonzero for erg. + mixing systems:

if $W_{nm} \neq 0 \Rightarrow W_{mn} \neq 0$

if arrow in one direction

$\Rightarrow$ must be arrow in other

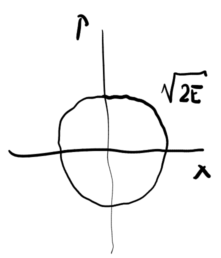
$\Rightarrow$ microscopic reversibility (MR)

$\Rightarrow$ get a unique stationary state

described by $p_n^s = \dfrac{\Theta_n}{\Theta_{tot}}$

Properties of this stationary state:

Θ_n = counts # of microstates (boxes) available to environment when sys. is in state n



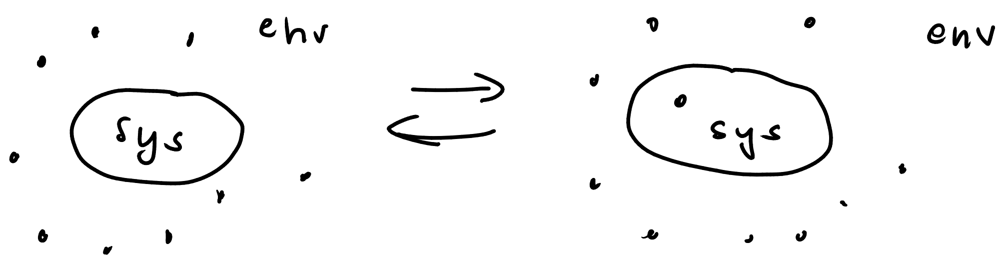
$\Rightarrow$ should depend on energy available to envir. when sys is in state n

(& any other conserved quantity b/t sys. & env.)

examples: energy $\underset{}{E_{tot}} = \underbrace{E_n}_{sys} + \underbrace{E_n^{env}}_{env.}$

$$E_n^{env} = E_{tot} - E_n$$

particles



$$N_{tot}^{part} = \underbrace{N_n^{part}}_{sys} + \underbrace{N_n^{part,env}}_{env.}$$

$$\Theta_n = \underbrace{\Theta}_{\substack{\text{some} \\ \text{function} \\ \text{(universal)}}}\Big(E_n^{env}, N_n^{part,env}, \underbrace{\ldots}_{\substack{\text{other} \\ \text{conserved} \\ \text{quantities}}}\Big)$$

focus: only energy is exchanged b/t sys. & environ.

$$\Theta_n = \Theta(E_n^{env})$$

$$W_{nm} \underset{\substack{\uparrow \\ \Theta_m/\Theta_{tot}}}{p_m^s} = W_{mn}^s \underset{\substack{\uparrow \\ \Theta_n/\Theta_{tot}}}{p_n^s} \Rightarrow \frac{W_{nm}}{W_{mn}} = \frac{\Theta_n}{\Theta_m} = \frac{\Theta(E_n^{env})}{\Theta(E_m^{env})}$$

$$\Rightarrow \quad \frac{W_{nm}}{W_{mn}} = \frac{\Theta(E_{tot}-E_n)}{\Theta(E_{tot}-E_m)}$$

assume:
env >> system
$E_{tot} \gg E_n$

$$\frac{W_{nm}}{W_{mn}} = \exp\left[\ln \Theta(E_{tot}-E_n) - \ln \Theta(E_{tot}-E_m)\right]$$

$$\ln \Theta(E_{tot}-E_n) \approx \ln \Theta(E_{tot}) - \overbrace{\left.\frac{\partial \ln \Theta}{\partial E}\right|_{E_{tot}}}^{\beta} E_n + \dots$$

$$\approx \ln \Theta(E_{tot}) - \beta E_n$$

$$\frac{W_{nm}}{W_{mn}} = \exp\left[-\beta(E_n - E_m) + \dots\right]$$

LDB in terms of energy for systems that only exchange energy w/ env.

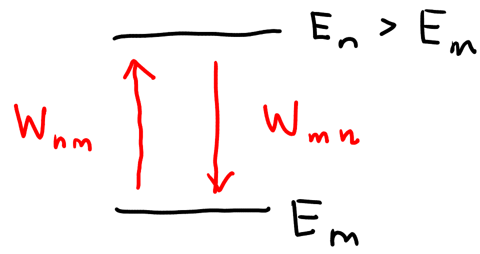
traditionally (def'n of temp.)

$$\beta = \frac{1}{k_B T} = \left.\frac{\partial \ln \Theta}{\partial E}\right|_{E_{tot}}$$

k_B = Boltzmann's const.
$= 1.38 \times 10^{-23}$ J/K

β = inverse energy = J^{-1}
T = units of Kelvin
$k_B T$ = units of J

$$\frac{W_{nm}}{W_{mn}} = \frac{\text{uphill trans.}}{\text{downhill trans.}} = e^{-\beta\underbrace{(E_n - E_m)}_{\substack{\text{energy diff. needed} \\ \text{from env. to} \\ \text{go } m\to n \\ \text{for sys.}}}}$$



$\beta > 0$

$\beta > 0$: uphill $<$ downhill

$W_{nm} < W_{mn}$

higher $\beta \Rightarrow$ harder to go uphill

(lower temp. T)