PHYS 320/420: Lecture 19

sys. described by $\frac{dp_n}{dt} = \sum_m \Omega_{nm} p_m$

where Ω matrix satisfies

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

(Boltzmann dist.)

$\Rightarrow$ there exists an ESS

solution $p_n(t) = p_n^s = \frac{e^{-\beta E_n}}{Z}$

$$\beta = \frac{1}{k_B T} \qquad Z = \sum_n e^{-\beta E_n}$$

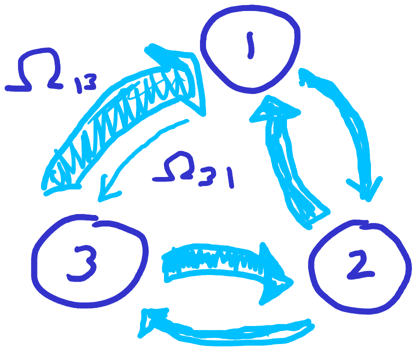
B/c this is an ESS, all currents

are zero: $J_{nm}^s = \Omega_{nm} p_m^s - \Omega_{mn} p_n^s$

$= 0$ for all

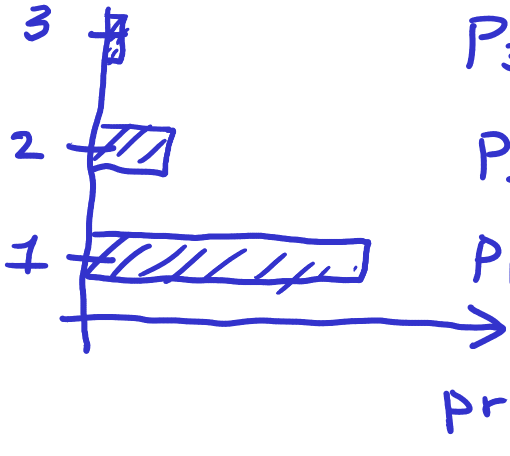
connected (n,m)

Look at Boltzmann dist. more concretely:



label states such that

$$E_1 < E_2 < E_3$$



$$P_3^s = e^{-\beta E_3}/Z$$

$$P_2^s = e^{-\beta E_2}/Z$$

$$P_1^s = \frac{e^{-\beta E_1}}{Z}$$

$$0 < T < \infty$$

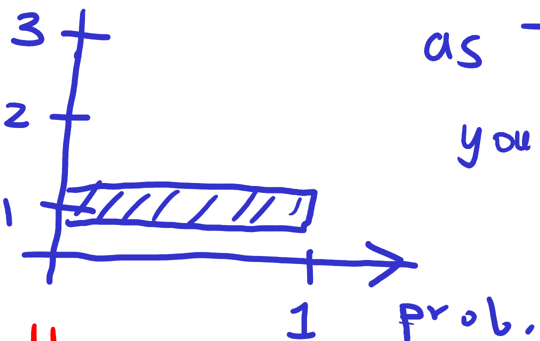
$$\infty > \beta > 0$$

$$J_{13}^s = \Omega_{13} P_3^s - \Omega_{31} P_1^s = 0$$

two limiting cases:

$T \to 0$

$\beta \to \infty$



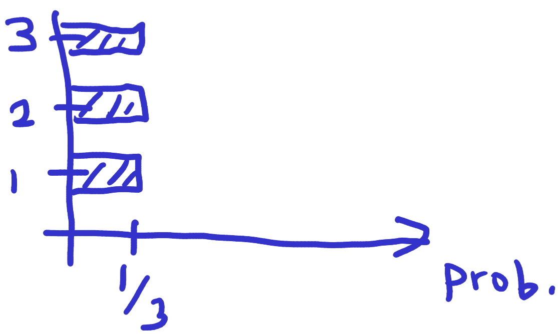
all prob. is in lowest energy state

as $T \to 0$ $(\beta \to \infty)$

you end up with a super greedy (never lends sys. energy) environment

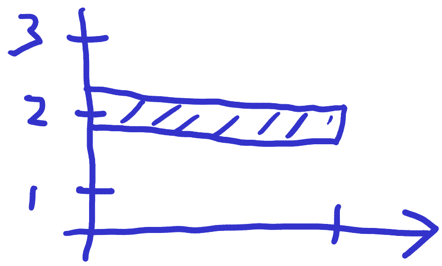
$T \to \infty$

$\beta \to 0$



$$P_n^s = \frac{1}{Z} = \frac{1}{N} = \frac{1}{3}$$

Is it always the case when Ω satisfies detailed balance that you will end in Boltzmann ESS as $t \to \infty$:



$t = 0$

$P_1(0) = 0$

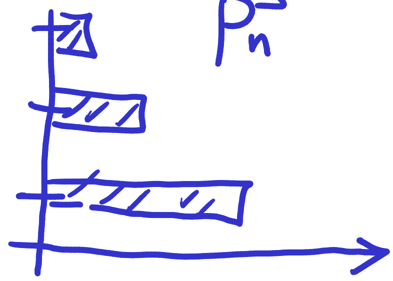
$P_2(0) = 1$

$P_3(0) = 0$

$\xrightarrow{t \to \infty}$

let time increase (run an ensemble of simulations)

Boltzmann P_n^s



Must this happen?

<u>**YES**</u>

eventually all currents in the sys. go to zero (DEATH)

<u>Next few lectures:</u>

we will prove that we always end up in ESS assuming detailed balance ("proof of death")

$\Longleftrightarrow$ statement of 2nd law of thermodynamics

To prove this, we need to introduce some terminology to describe quantities changing over time.

state n $\Rightarrow$ energy E_n

mean energy at time t $\quad \langle E \rangle_t = \sum_n p_n(t) E_n$

Simplify notation: $\quad E(t) \equiv \langle E \rangle_t$

no subscript: mean of a quantity

$$\frac{d}{dt} E(t) = \sum_n \underbrace{\frac{dp_n}{dt}}_{\sum_m \Omega_{nm} p_m(t) \; = \sum_m J_{nm}(t)} E_n$$

from master equ.

$$\frac{d}{dt} E(t) = \sum_{n,m} J_{nm}(t) E_n$$

$J_{13} = -J_{31}$

$J_{mn}(t)$

$= -J_{nm}(t)$

$$= \underbrace{\frac{1}{2}\sum_{nm} J_{nm}(t) E_n}_{} + \underbrace{\frac{1}{2}\sum_{nm} J_{mn}(t) E_m}_{}$$

$$\Rightarrow \frac{d}{dt} E(t) = \frac{1}{2}\sum_{nm} J_{nm}(t)\left(E_n - E_m\right)$$

"power" current $m \to n$ "pot. diff." from $m \to n$

$$\sum_{n=1}^{N}\sum_{m=1}^{N} J_{nm}(t) E_n$$

$$= \frac{1}{2}\left[\sum_{n=1}^{N}\sum_{m=1}^{N} J_{nm}(t) E_n + \sum_{i=1}^{N}\sum_{j=1}^{N} J_{ij}(t) E_i\right]$$

$$J_{ij}(t) = \Omega_{ij} p_j(t) - \Omega_{ji} p_i(t)$$

$$J_{ji}(t) = \Omega_{ji} p_i(t) - \Omega_{ij} p_j(t)$$

$$\Rightarrow J_{ij}(t) = -J_{ji}(t)$$

$$\cdots = \frac{1}{2}\left[\sum_{n,m} J_{nm}(t) E_n - \sum_{i,j} J_{ji}(t) E_i \right]$$

rename $(i,j) \to (m,n)$

$$= \frac{1}{2}\left[\sum_{nm} J_{nm}(t) E_n - \sum_{m,n} J_{nm}(t) E_m\right]$$

$$= \frac{1}{2} \sum_{nm} J_{nm} (E_n - E_m)$$

$$0 = \sum_{nm} J_{nm}(t) = \sum_{nm} J_{mn}(t)$$

$$J_{12} + J_{21} = -\sum_{nm} J_{nm}(t)$$

$$+ J_{13} + J_{31}$$

$$+ \cdots$$

$$J_{12} E_1 + J_{21} E_2$$