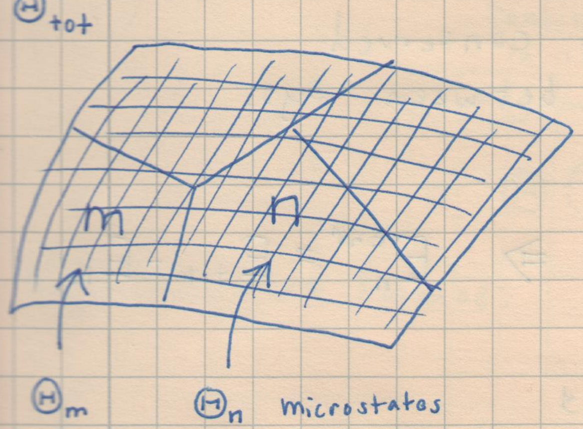
Zooming out: the big picture up to now in the course

Recipe for our theory:

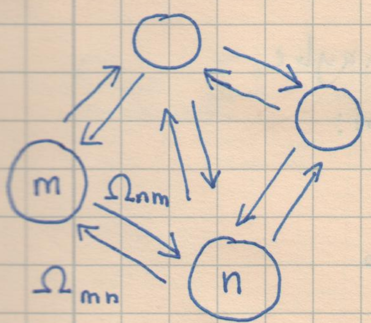
1) isolated Hamiltonian system w/ tot. energy E_{tot} ; ergodic + mixing



2) divide into "system" + environment

Θ_n = # environmental microstates in system state n

||



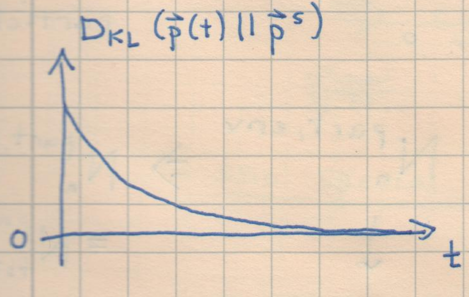
3) gives us Markovian dynamics with transition matrix Ω :

$$\dot{p}_n(t) = \sum_m \Omega_{nm} \, p_m(t)$$

where $$\frac{\Omega_{nm}}{\Omega_{mn}} = \frac{\Theta_n}{\Theta_m}$$ detailed balance $(n \neq m)$

4) because system is ergodic + microscopically reversible (no one way arrows) $\Rightarrow$ stationary state is unique

$$p_n^s = \frac{\Theta_n}{\Theta_{tot}}$$



$\vec{p}(t)$ "distance" to $\vec{p}^s$: $D_{KL}(\vec{p}(t) \| \vec{p}^s)$

$$= \sum_n p_n(t) \ln \frac{p_n(t)}{p_n^s} \geq 0$$

$$\frac{d}{dt} D_{KL}(\vec{p}(t) \| \vec{p}^s) < 0$$ and $\rightarrow 0$ as $\vec{p}(t) \rightarrow \vec{p}^s$

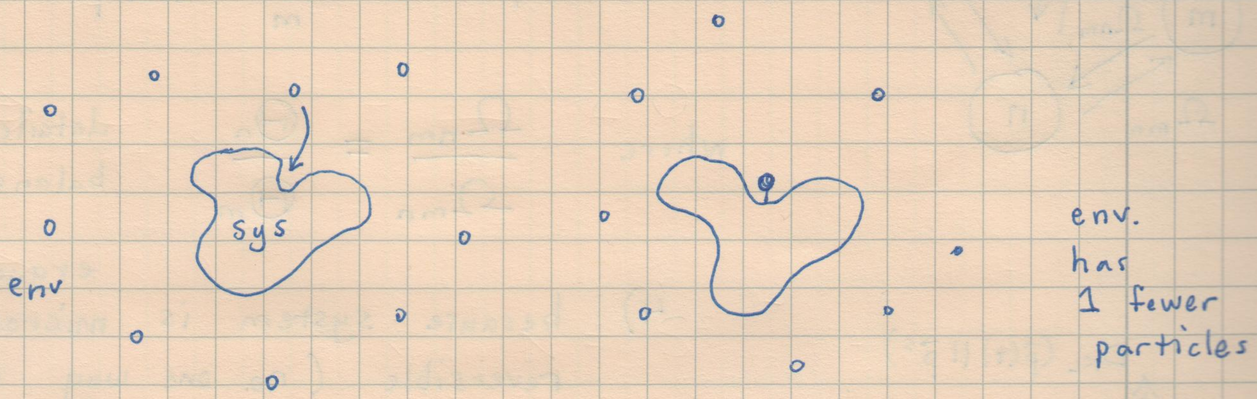
To go further, we need some physical intuition into $\vec{p}^{\,s}$, or equivalently $\textcircled{H}_n$

$\textcircled{H}_n$ depends on the microstates available to environment when system is in state n

$\Rightarrow$ hence depends on conserved quantities shared between sys. + env.

i.e.
$$\underset{\substack{\uparrow \\ \text{constant}}}{E_{tot}} = \underset{\substack{\uparrow \\ \text{energy} \\ \text{of} \\ \text{sys. in} \\ \text{state } n}}{E_n} + \underset{\substack{\uparrow \\ \text{energy} \\ \text{of} \\ \text{environ.} \\ \text{in} \\ \text{state } n}}{E_n^{env}} \Rightarrow E_n^{env} = E_{tot} - E_n$$

If environment is a gas / fluid, maybe can exchange particles w/ system:



$$\underset{\substack{\downarrow \\ \text{tot. \# particles} \\ = \text{const.}}}{N_{tot}^{part}} = \underset{\substack{\downarrow \\ \text{\# part.} \\ \text{adsorbed by} \\ \text{system}}}{N_n^{part}} + \underset{\substack{\downarrow \\ \text{\# part. in} \\ \text{environment}}}{N_n^{part,env}} \Rightarrow N_n^{part,env} = N_{tot}^{part} - N$$

Can have separate conservation for diff. particle types, etc.

Physical assumption:

$$\Theta_n = \underset{\substack{\downarrow \\ \text{Some} \\ \text{function} \\ \text{continuous} \\ \text{in its} \\ \text{arguments}}}{\Theta} \Big(\underbrace{E_n^{env}, N_n^{part,env}, \ldots}_{\substack{\text{physical quantities} \\ \text{characterizing env.} \\ \text{when sys. is in state} \\ n}} \Big)$$

$$= \Theta\left(E_{tot} - E_n, N_{tot}^{part} - N_n, \ldots\right)$$

DB detailed balance: $$\frac{\Omega_{nm}}{\Omega_{mn}} = \frac{\Theta\left(E_{tot} - E_n, N_{tot}^{part} - N_n^{part}, \ldots\right)}{\Theta\left(E_{tot} - E_m, N_{tot}^{part} - N_m^{part}, \ldots\right)}$$

Different thermodynamic "laws" will arise based on diff. assumptions about DB expression:

Case I: all system energy states equal $E_n = E$ for all n

$\Rightarrow$ hence in transition $n \rightarrow m$ no net exchange of energy with environment (for simplicity assume no net exchange of anything)

~~$\Rightarrow$ system is effectively~~

~~Θ~~

one special case: when system = total

system states n = microstates ν

$\Theta_n = 1$ for all n

In general for this case I:

$$\frac{\Omega_{nm}}{\Omega_{mn}} = \frac{\Theta\left(E_{tot} - E, \ldots\right)}{\Theta\left(E_{tot} - E, \ldots\right)} = 1$$

stationary state

$$p_n^s = \frac{\Theta_n}{\Theta_{tot}} = \frac{1}{N}$$

since all Θ_n for all N sys. states are equal

$$D_{KL}(\vec{p}(t)\,||\,\vec{p}^s) = \sum_n p_n(t) \ln \frac{p_n(t)}{p_n^s}$$

$$= \sum_n p_n(t) \ln p_n(t) + \underbrace{\sum_n p_n(t) \ln N}_{\ln N}$$

$$= -\frac{S(t)}{k_B} + \ln N \geq 0$$ by prop. of D_{KL}

by convention

where $S(t) \equiv -k_B \sum_n p_n(t) \ln p_n(t)$ ≡ "thermodynamic" entropy

$\leq k_B \ln N \equiv S^s$ entropy in stat. state $p_n^s = \frac{1}{N}$

$$\frac{d}{dt} D_{KL}(\vec{p}(t)\,||\,\vec{p}^s) < 0 \quad \text{for } \vec{p}(t) \neq \vec{p}^s$$

$$\Rightarrow \frac{d}{dt}\left(\ln N - \frac{S(t)}{k_B}\right) < 0$$

⇒ $S(t)$ increases monotonically until it reaches $k_B \ln N = S^s$ stat. state entropy

≡ Boltzmann entropy

first (of many) faces of the

<u>2nd law of thermodynamics</u>

What is physical interpretation of entropy?

- "counting states of system"

  $S^s = k_B \ln N$ valid only in <u>stationary</u> <u>state</u> (equilibrium)

  max. entropy possible

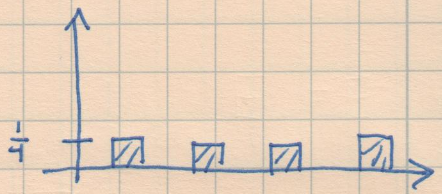
- $S(t) = -k_B \sum_n' p_n(t) \ln p_n(t)$ more general

$$S^s - S(t) = k_B D_{KL}(\vec{p}(t) \,||\, \vec{p}^s)$$

quantifies how "far" away we are from stationarity at time t

- $S(t)$ quantifies "width" + hence "uncertainty" about states

N=4



$p_n(t) = \delta_{1,n}$

$S(t) = 0$

no uncertainty b/c we are definitely in state 1

$p_n(t) = \frac{1}{N} = \frac{1}{4}$

$S(t) = k_B \ln 4$

max. uncertainty b/c all states equally likely

flip side of uncertainty is <u>information</u>:

$\vec{p}(t)$ contains potential information about state of the system

How much? Can we make it more quantitative?