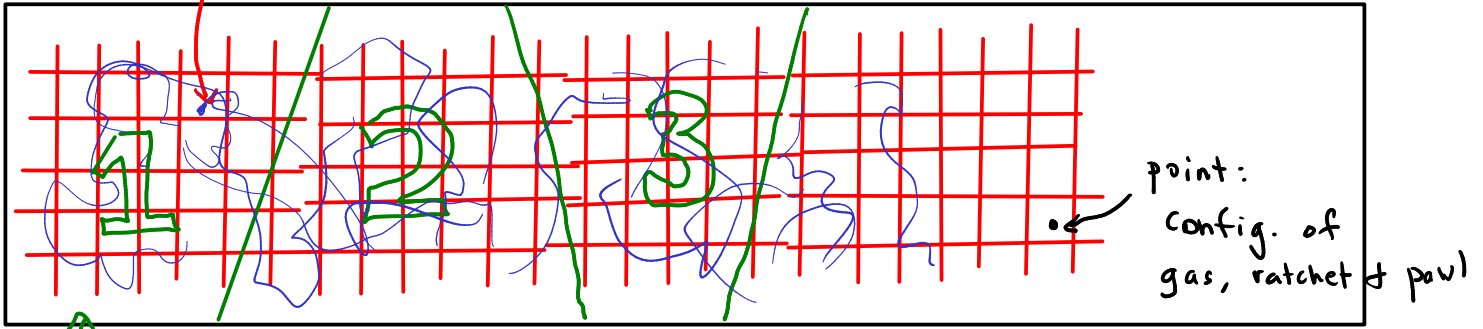


box: "microstate": μ
group of similar configs.



each "country" \equiv macrostate: all configs of total where system is in state n

entire phase for const tot. energy E_{tot}

total is ergodic + mixing:

$$P_{\mu}(t) \xrightarrow{t \rightarrow \infty} \frac{1}{\Theta(E_{tot})} \equiv \frac{1}{\Theta_{tot}}$$

prob. to be in microstate μ (small box)

each μ has the same volume of phase space α by construction

$\Theta_n = \#$ of microstates in macrostate n

\Rightarrow could be diff. between diff. n

b/c E_n^{env} env. energy varies w/ n

assumptions:

- envir. has many more degrees of freedom than sys:

$$\Theta_{tot} = \sum_{i=1}^N \Theta_n$$

\uparrow
tot # of microstates

$$\Theta_n \gg N$$

$$\Theta_{tot} \gg N$$

$N = \#$ of macrostates

- mixing is fast

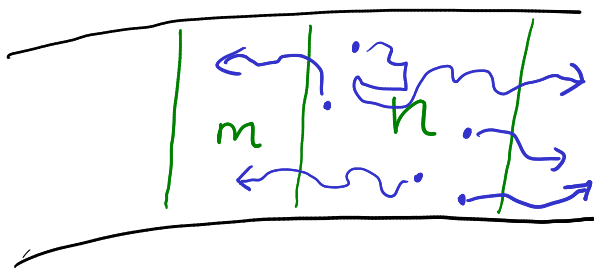
- dynamics of exploring within a macrostate happens faster than

transitions b/t macrostates

⇒ prob. of next macrostate visited depends at most on the current one (lose "memory" of deeper past b/c chaotic mixing dynamics)

transition matrix

W_{mn} = prob. to go from macrostate $n \rightarrow m$ in time interval δt , given we are currently in n



= # traj. that in start in n + end up in m after time δt

$P_n(t_i)$ = prob. of macrostate n at time t_i

traj. " " " in n + end up anywhere after time δt

$\vec{P}(t_{i+1}) = W \vec{P}(t_i)$ DTDS master eqn.

W must have this stationary state!

also know: $t \rightarrow \infty$ $P_m(t) \rightarrow \frac{1}{\Omega_{tot}}$

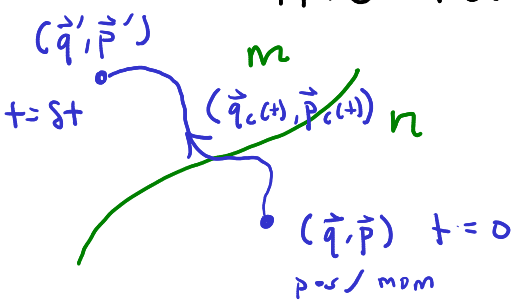
↓ What does this say about W?

$P_n(t) \rightarrow \frac{\Omega_n}{\Omega_{tot}} \equiv P_n^s$ stationary state

stationary state

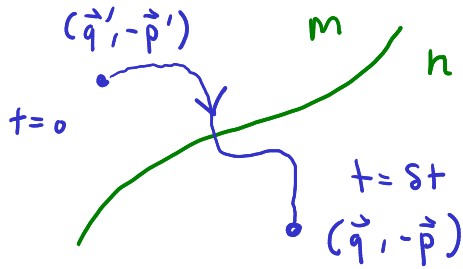
use a property of classical mechanics: time reversal symmetry

$m \neq n$



traj. satisfies Hamilton's eqn's:

$\frac{d\vec{q}_c}{dt} = \frac{\partial H}{\partial \vec{p}_c}$ $\frac{d\vec{p}_c}{dt} = -\frac{\partial H}{\partial \vec{q}_c}$



claim: another "reversed" sol'n must also exist:

$$\vec{q}_r(\tilde{t}) \equiv \vec{q}_c(t-\tilde{t})$$

$$\vec{p}_r(\tilde{t}) = -\vec{p}_c(t-\tilde{t})$$

Proof: $\frac{d\vec{q}_c}{dt} = \frac{\partial H}{\partial \vec{p}_c} \Rightarrow -\frac{d\vec{q}_r}{d\tilde{t}} = -\frac{\partial H}{\partial \vec{p}_r}$ ✓

$$\frac{d\vec{q}_c(t-\tilde{t})}{d\tilde{t}} = -\frac{d\vec{q}_c(t-\tilde{t})}{d\tilde{t}} = -\frac{d\vec{q}_r}{d\tilde{t}}$$

$$\frac{d\vec{p}_c}{dt} = -\frac{\partial H}{\partial \vec{q}_c} \Rightarrow \frac{d\vec{p}_r}{d\tilde{t}} = -\frac{\partial H}{\partial \vec{q}_r}$$
 ✓

as $t \rightarrow \infty$ we approach stationary state where all microstates are equally likely

\Rightarrow equally likely to start at (\vec{q}, \vec{p}) as $(\vec{q}', -\vec{p}')$

\Rightarrow equally likely to be observe original + reversed trajectories

\Rightarrow prob. of observing $m \rightarrow n$ trans. = prob. of observing $n \rightarrow m$ trans.

local detailed balance (LDB)

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

\uparrow prob. to observe $m \rightarrow n$ trans. given start in m
 prob. to be in m in stat. state
 " "

prob. to observe $m \rightarrow n$ trans.

tells us something about the elements of W matrix