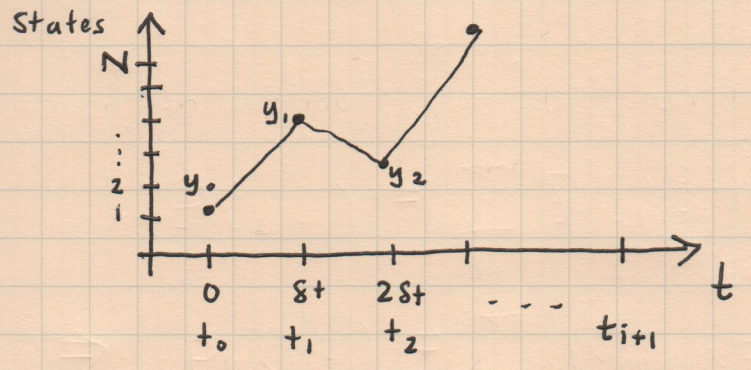
Spring 2017

PHYS 414 notes

trajectory $\nu = (y_0, y_1, \ldots, y_{i+1})$



Key approximation (encapsulates the "randomization" due to environment which causes system to lose dependence on distant past):

Markovian assumption:

$$\mathcal{P}(y_{i+1} \mid y_0, y_1, \ldots, y_i) = \mathcal{P}(y_{i+1} \mid y_i)$$

indep. of $y_0, \ldots, y_{i-1}$

dependent only on y_i

Generally one can choose δt large enough such that this is approx. true.

Rewrite:

$$\frac{\mathcal{P}(y_0, y_1, \ldots, y_{i+1})}{\mathcal{P}(y_0, y_1, \ldots, y_i)} = \mathcal{P}(y_{i+1} \mid y_i)$$

$$\Rightarrow \mathcal{P}(y_0, y_1, \ldots, y_{i+1}) = \mathcal{P}(y_{i+1} \mid y_i)\,\mathcal{P}(y_0, y_1, \ldots, y_i)$$

sum over all $y_0, y_1, \ldots, y_i$ on both sides:

$$\sum_{y_0=1}^{N} \sum_{y_1=1}^{N} \cdots \sum_{y_i=1}^{N} \mathcal{P}(y_0, y_1, \ldots, y_i, y_{i+1})$$

$$= \sum_{y_0} \sum_{y_1}' \cdots \sum_{y_i}' \mathcal{P}(y_{i+1}|y_i)\,\mathcal{P}(y_0, y_1, \ldots, y_i)$$

$$\Rightarrow \quad \mathcal{P}(y_{i+1}) = \sum_{y_i} \mathcal{P}(y_{i+1}|y_i)\,\mathcal{P}(y_i)$$

consistent with building up the prob. of the trajectory iteratively:

$$\mathcal{P}(y_0, \ldots, y_i, y_{i+1}) = \mathcal{P}(y_{i+1}|y_i)\,\mathcal{P}(y_0, \ldots, y_i)$$

$$= \mathcal{P}(y_{i+1}|y_i)\,\mathcal{P}(y_i|y_{i-1})\,\mathcal{P}(y_0, \ldots, y_{i-1})$$

$$= \cdots$$

$$= \left[\prod_{j=0}^{i} \mathcal{P}(y_{j+1}|y_j)\right] \mathcal{P}(y_0)$$

↓ initial distrib. of states

Key quantity: conditional prob. of state update during time t_i to t_{i+1}

~~$\mathcal{P}(y_i)$~~ $\mathcal{P}(y_{i+1}|y_i) \Rightarrow N \times N$ matrix

since $y_{i+1} = 1, \ldots, N$

$y_i = 1, \ldots, N$

Define: $\mathcal{P}(y_{i+1} = n \mid y_i = m)$

$$= \underbrace{W_{nm}(t_i)}\,\delta t$$

prob. per unit time (or prob. rate) to transition from $m \to n$ between t_i and $t_{i+1} = t_i + \delta t$.

$W(t)$ matrix is determined by environment. In many cases $W(t) = W$ (no time dependence) if environmental parameters (temp, pressure, etc.) stay same.

properties of W: $\sum_{y_{i+1}} \mathcal{P}(y_{i+1} \mid y_i) = 1$

$$\Rightarrow \sum_n \delta t W_{nm}(t_i) = 1$$

$\delta t \times$ (sum of a column) $= 1$

Our equation above can be written:

$$\mathcal{P}(y_{i+1}) = \sum_{y_i} \mathcal{P}(y_{i+1} \mid y_i)\, \mathcal{P}(y_i)$$

$$\Rightarrow \quad p_n(t_{i+1}) = \sum_m W_{nm}(t_i)\, p_m(t_i)\, \delta t$$

vector form

$$\vec{p}(t_{i+1}) = W(t_i)\, \vec{p}(t_i)\, \delta t$$

$\Rightarrow$ <u>discrete time master equation</u>

can iterate matrix multiplication to get $\vec{p}(t_{i+1})$ assuming some initial $\vec{p}(t_0)$.

<u>Kinetic network</u>: every W matrix can be visualized as a graph, with each element $\Rightarrow$ directed arrow

Example: $W(t) = W =$

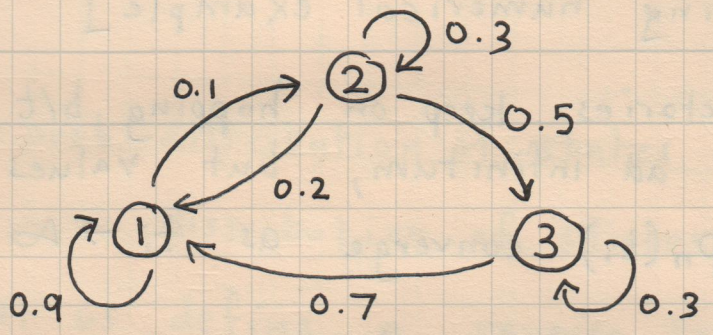
	1	2	3
1	0.9	0.2	0.7
2	0.1	0.3	0
3	0	0.5	0.3
	1	1	1

[units: s^{-1}]

columns sum to 1

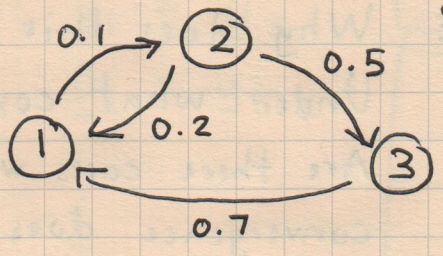
$\delta t = 1\,s$

network:



typical drawing convention: leave out self-arrows, since these are understood to exist in order to keep columns normalized

i.e.



Discrete master equation allows solving for

$$\vec{p}(t_{i+1}) \quad \text{or} \quad p_n(t_{i+1}) = \frac{\#\text{ of exper. runs with state } n \text{ at time } t_{i+1}}{\text{total } \#\text{ of exper. runs}}$$

How would you generate an "experimental" run on a computer?

algorithm: ~~do~~ ~~for~~ at every time step

```
r = random (0, 1)
if (state = 1) then {
    if ( r ≤ 0.1 δt) then  state = 2 }
if (state = 2) then {
    if (r ≤ 0.2 δt) then state = 1
    if (0.2 δt ≤ r ≤ (0.2+0.5)δt) then
                                state = 3 }
if (state = 3) then {
    if (r ≤ 0.7 δt) then state = 1 }
t = t + δt
```

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Note: in the example trajectories keep on hopping b/t states ad infinitum, but values of $p_n(t_i)$ converge as $t_i \to \infty$.

This convergence, when $p_n(t_i) \to p_n^s$ constant value as $t_i \to \infty$ is called a

<u>stationary state</u> of the system.

Big questions: Why does this happen?
Under what conditions?
Are there cases where this convergence does not occur?

Question #1: Does there exist at least one stationary solution?

discrete master equation

$$\vec{p}(t_{i+1}) = [W\,\delta t]\,\vec{p}(t_i)$$

stationary solution: $\vec{p}^{\,s}(t_{i+1}) = \vec{p}^{\,s}(t_i)$

$$\Rightarrow \vec{p}^{\,s} = [W\,\delta t]\,\vec{p}^{\,s} \Rightarrow \vec{p}^{\,s} \text{ is right e-vec w/ e-val } 1$$

[Assume W is time indep $\Rightarrow$ environmental parameters fixed]

Property of any real matrix M, i.e. $M = W\,\delta t$ (not necessarily symmetric $M \neq M^T$)

~~If there exists a left e-vec.~~

$\Rightarrow$ Eigenvalues of left and right e-vecs are the same.

Proof: Let $\vec{v}$ be ~~a right e-vec~~, left e-vec:

~~$M\vec{v} =$~~

$$\vec{v}^{\,T} M = \lambda \vec{v}^{\,T}$$

then $\vec{v}$ is also an ~~e~~ right e-vec of M^T:

$$M^T \vec{v} = \lambda \vec{v} \quad \text{(take transpose of both sides)}$$

so λ is a solution to:

$$\det(M^T - \lambda I) = 0$$

$$\Rightarrow \det((M - \lambda I)^T) = 0 \quad \text{since } I = I^T$$

$$\Rightarrow \det(M - \lambda I) = 0 \quad \text{since } \det A^T = \det A$$

hence λ is also a solution to the right e-vec equation of M, & there must exist a right e-vec

$$M\vec{u} = \lambda \vec{u}$$

(at least one such e-vec must exist)

If $M \neq M^T$, then $\vec{u}$ can be different than $\vec{v}$

For $M = W\delta t$, the vector $\vec{v}^T = (1, 1, 1, \ldots, 1)$ is a left e-vec w/ e-val $\lambda = 1$, because:

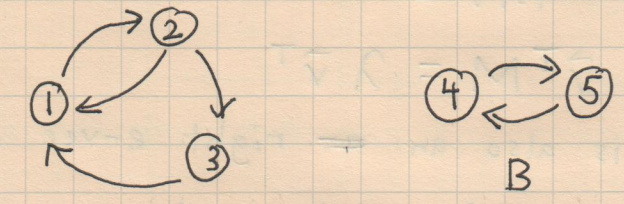
$$(\vec{v}^T M)_m = \sum_n v_n^T W_{nm} \delta t = \sum_n W_{nm} \delta t = 1 = (\vec{v}^T)_m$$

Hence $W\delta t$ must have <u>at least one</u> right e-vec w/ eigenvalue $1 \Rightarrow$ <u>true for any time-indep. W.</u>

<u>Question #2</u> Under what conditions is $\vec{p}^s$ a unique solution (only one right e-vec corresponding to $\lambda = 1$)?

We can easily find situations where $\vec{p}^s$ is <u>not</u> unique.

Consider a disconnected network w/ two connected pieces A and B.



A
matrix W^A

B
matrix W^B

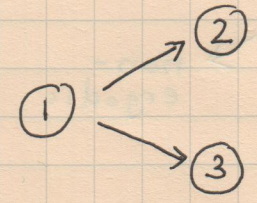
total has matrix $W = \begin{pmatrix} W^A & 0 \\ 0 & W^B \end{pmatrix}$ (rows/cols 1 2 3 | 4 5)

Let $\vec{p}_A^{\,s}$ be a stat. state of A (3 comp. vector)
and $\vec{p}_B^{\,s}$ be a stat. state of B (2 comp. vector)

then $\vec{p}^s = \begin{pmatrix} \vec{p}_A^{\,s} \\ 0 \\ 0 \end{pmatrix}$ and $\vec{p}^s = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vec{p}_B^{\,s} \end{pmatrix}$ are both stat. states of total

So we want the network to be connected as a necessary condition (but not sufficient) to have unique $\vec{p}^s$.

Even connected networks can have multiple $\vec{p}^s$:



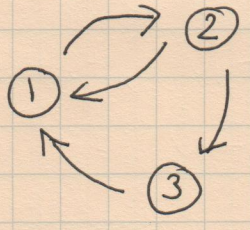
$$\vec{p}^s = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \vec{p}^s = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

are stat. states

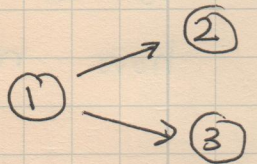
Thus we demand a network be strongly connected: you can reach any other state, starting from any state, following arrows.

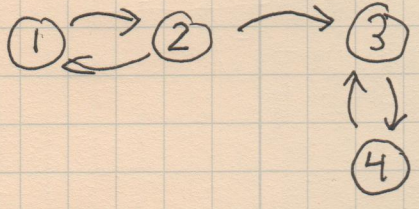
This is also called an ergodic network: if you wait long enough, every state will be visited during a trajectory (and you will return to each state ∞ times as $t \to \infty$).

ergodic network



non-ergodic:





For thermodynamics to make sense, we will demand an even stronger condition:

microscopic reversibility: if $W_{mn} \neq 0$, then $W_{nm} \neq 0$

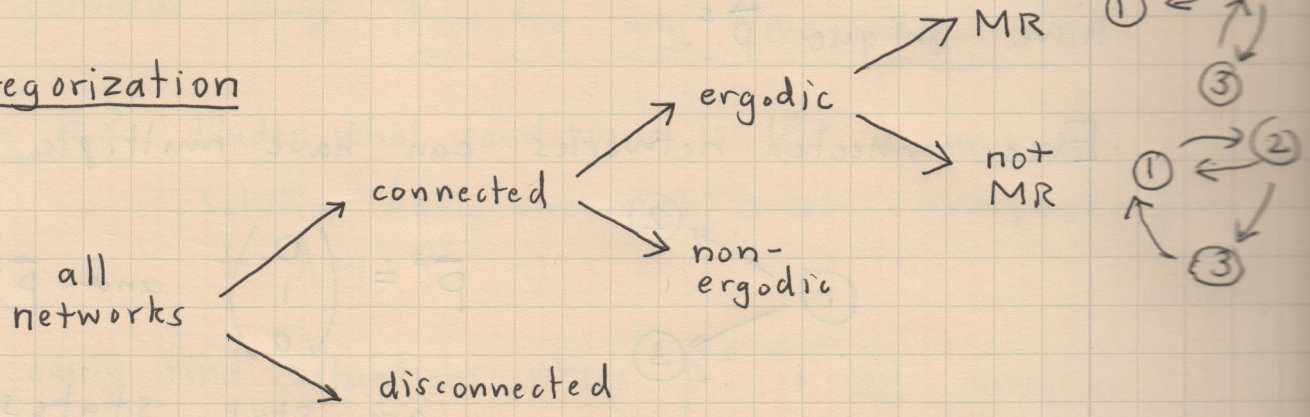
- (if two states are connected, arrows must go both ways)

(MR) Microscopic reversibility is a physical assumption, and we will return to its justification later.

In practice, if W_{nm} ($m \to n$ transition) is large, the reverse W_{mn} ($n \to m$) may be infinitesimally small (but still technically nonzero).

Without MR you cannot have a thermodynamic description of the system.

categorization



note: for ergodic network, vector $\vec{p}^{\,s}$ cannot have any zero elements (all states are visited)

But the question still remains:
even if we demand MR, is $\vec{p}^{\,s}$ unique?

To answer this, we define a measure of how reversible or irreversible a given trajectory is.