Introduction to Nonequilibrium Statistical Physics, C. Jarzynski, Spring 2020

Rate matrices, two examples.

$$\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = \mathcal{R}\mathbf{p} \quad , \quad \mathcal{R} = U\Lambda V^\dagger \quad , \quad \mathcal{T}(t) \equiv e^{\mathcal{R}t} = Ue^{\Lambda t}V^\dagger \tag{1}$$

Example 1.

$$\mathcal{R} = \begin{pmatrix} -1 & 0 & 1 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \end{pmatrix} = \frac{1}{3}\begin{pmatrix} 1 & 1 & 1 \\ 1 & -z & -z^* \\ 1 & -z^* & -z \end{pmatrix}\begin{pmatrix} 0 & & \\ & -1-z^* & \\ & & -1-z \end{pmatrix}\begin{pmatrix} 1 & 1 & 1 \\ 1 & -z^* & -z \\ 1 & -z & -z^* \end{pmatrix} \tag{2}$$

where

$$z = e^{i\phi} = \frac{1}{2} + i\frac{\sqrt{3}}{2} \quad , \quad z^* = e^{-i\phi} = \frac{1}{2} - i\frac{\sqrt{3}}{2} \quad , \quad \phi = \frac{\pi}{3} \quad . \tag{3}$$

Using this decomposition we get

$$\mathcal{T}(t) \equiv e^{\mathcal{R}t} = \frac{1}{3}\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} + \frac{2}{3}e^{-3t/2}\begin{pmatrix} \cos(\alpha t) & \cos(\alpha t - 4\phi) & \cos(\alpha t - 2\phi) \\ \cos(\alpha t - 2\phi) & \cos(\alpha t) & \cos(\alpha t - 4\phi) \\ \cos(\alpha t - 4\phi) & \cos(\alpha t - 2\phi) & \cos(\alpha t) \end{pmatrix} \tag{4}$$

where $\alpha = \sqrt{3}/2$. Note that $\mathcal{T}(0) = I$.

Example 2.

$$\mathcal{R} = \begin{pmatrix} -1 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -1 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & -1 \end{pmatrix} = \begin{pmatrix} \sqrt{1/3} & \sqrt{1/2} & \sqrt{1/6} \\ \sqrt{1/3} & 0 & -\sqrt{2/3} \\ \sqrt{1/3} & -\sqrt{1/2} & \sqrt{1/6} \end{pmatrix}\begin{pmatrix} 0 & & \\ & -\frac{3}{2} & \\ & & -\frac{3}{2} \end{pmatrix}\begin{pmatrix} \sqrt{1/3} & \sqrt{1/3} & \sqrt{1/3} \\ \sqrt{1/2} & 0 & -\sqrt{1/2} \\ \sqrt{1/6} & -\sqrt{2/3} & \sqrt{1/6} \end{pmatrix} \tag{5}$$

Using this decomposition we get

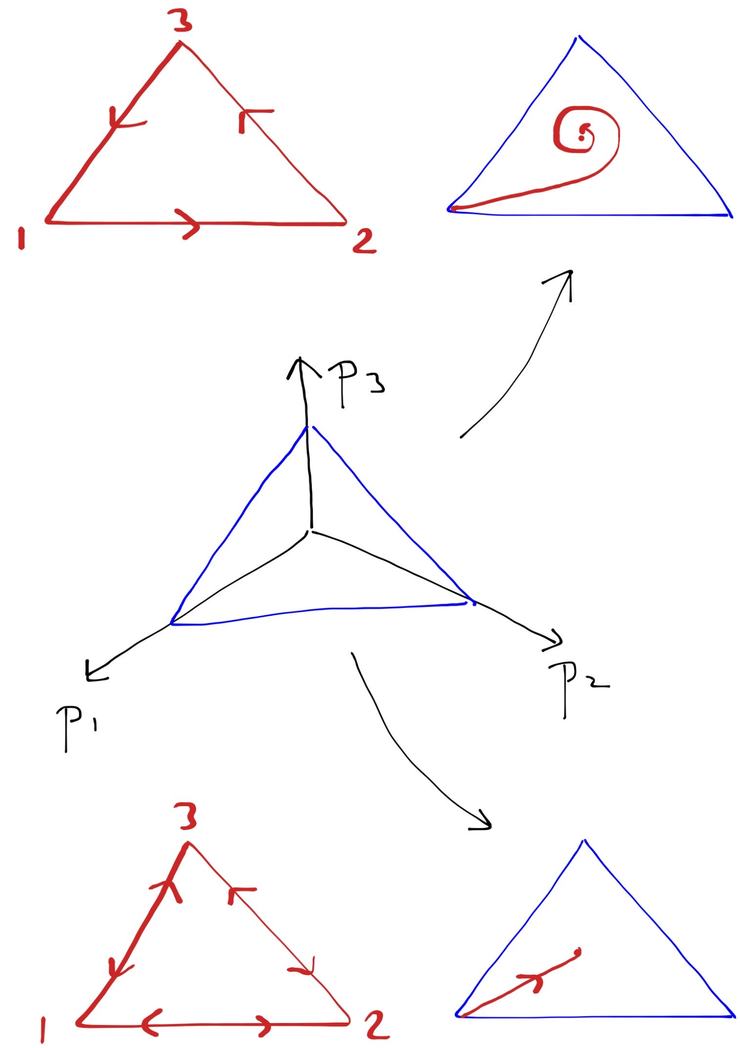
$$\mathcal{T}(t) \equiv e^{\mathcal{R}t} = \frac{1}{3}\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} + \frac{1}{3}e^{-3t/2}\begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} \quad . \tag{6}$$

Again, $\mathcal{T}(0) = I$.

Detailed Balance

(1)

$$\mathcal{R} = \begin{pmatrix} -1 & 0 & 1 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \end{pmatrix}$$



(2)

$$\mathcal{R} = \begin{pmatrix} -1 & 1/2 & 1/2 \\ 1/2 & -1 & 1/2 \\ 1/2 & 1/2 & -1 \end{pmatrix}$$

$\vec{\pi} = \begin{pmatrix} 1/3 \\ 1/3 \\ 1/3 \end{pmatrix}$ in both examples, but the <u>dynamics</u> differ significantly:

<u>Case 1</u>. Swarm of "particles" (realizations) distributed equally among the three sites, all jumping CCW

↳ counter-clockwise

Case 2. Similar swarm, but particles make both CW & CCW jumps, with equal frequencies.

Probability current: $J_{ij}(t) = R_{ij}\,p_j(t) - R_{ji}\,p_i(t)$

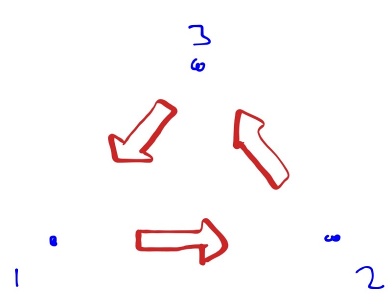
$= $ net flux from j to i

in stationary state: $J^s_{ij} = R_{ij}\pi_j - R_{ji}\pi_i$

master eqn: $\dfrac{dp_i}{dt} = \sum_{j\neq i} J_{ij}$

note that $J_{ij}(t) = -J_{ji}(t)$, by definition

Case 1 $\quad J^s_{21}\left(= -J^s_{12}\right) = \underbrace{R_{21}}_{1}\overset{1/3}{\pi_1} - \underbrace{R_{12}}_{0}\pi_2 = \frac{1}{3} = J^s_{32} = J^s_{13}$



CCW flux

Case 2. $J^s_{21} = \overset{1/2}{R_{21}}\,\underset{1/3}{\pi_1} - \overset{1/2}{R_{12}}\,\underset{1/3}{\pi_2} = 0$

$J^s_{ij} = 0$ for all i,j

(obvious by symmetry)

For a connected network,

If $J^s_{ij} = 0 \;\; \forall\, i,j$: dynamics satisfy detailed balance

If $J^s_{ij} \neq 0$ for some i,j : dynamics violate detailed balance

(Detailed balance can be violated even if all edges are undirected.)

Note: detailed balance is a property of the dynamics, rather than a property of the state of the system.

E.g. case 2: if $\vec{p}(0) = \begin{pmatrix}1\\0\\0\end{pmatrix}$ then $J_{21}(t) = \frac{1}{2} e^{-3t/2} \neq 0$

for all $t \geq 0$ (exercise: show this!)

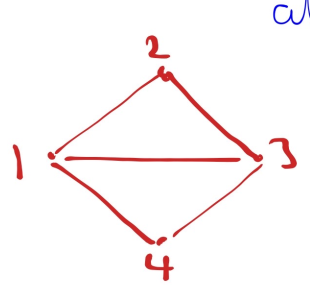
but the dynamics still satisfy D.B.

Detailed balance has an important physical interpretation in terms of the 2nd Law of thermo, but it is useful to examine it first from a mathematical perspective.

<u>graph</u> <u>topology</u> will play an important role.

terminology:

<u>path</u> = alternating sequence of nodes and edges, each one connected to the next, beginning & ending at nodes.



1-2-3-4 , 1-2-3-1-2,
3-2-3-4
(but <u>not</u> 1-2-4)

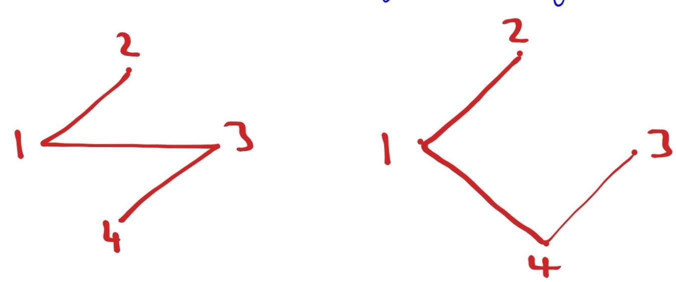
<u>cycle</u> = path that begins and ends in the same node.

1-2-3-4-1 , 1-2-3-1-2-3-1,
4-3-4

A path with no repeating nodes or edges is a <u>simple path</u> (1-2-3-4).

A cycle w/ no repeating nodes or edges except init'l & final nodes is a <u>simple cycle</u> (1-2-3-1, 4-3-2-1-4).

<u>tree graph</u> = connected graph containing no simple cycles.



For a transition rate matrix R, decribing transitions on a connected graph with no directed edges:

$$\boxed{\text{If } G \text{ is a tree graph, then the dynamics satisfy detailed balance.}}$$

(no currents in the stationary state)

intuitively obvious

If $G \neq$ tree, then D.B. might or might not be satisfied. See Cases 1 & 2 discussed earlier.

If $G =$ tree, it's easy to determine the stationary state from elements of R.

Define: $\gamma_1 = 1$

$$\gamma_n = \frac{R_{nm}}{R_{mn}} \cdot \frac{R_{ml}}{R_{lm}} \cdots \frac{R_{kj}}{R_{jk}} \cdot \frac{R_{j1}}{R_{1j}}$$

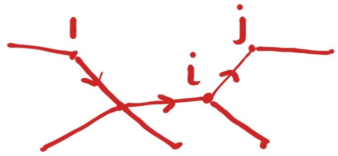
where $1jk\cdots lmn$ is the unique simple path from 1 to n.

$$(R\vec{\gamma})_i = \sum_j R_{ij}\gamma_j = \sum_{j\neq i}\left(R_{ij}\gamma_j - R_{ji}\gamma_i\right) \equiv \sum_{j\neq i} K_{ij}$$

Show that all $K_{ij} = 0$:

<u>Case 1</u>. i,j not connected: $R_{ij} = R_{ji} = 0 = K_{ij}$

<u>Case 2</u>. i,j connected & the simple path from 1 to j passes through i.
(j is "downstream" from i.)



$$\gamma_j = \frac{R_{ji}}{R_{ij}}\gamma_i$$

$$\therefore R_{ij}\gamma_j = R_{ji}\gamma_i$$

$$K_{ij} = 0$$

Identical logic applies if i is downstream.

$$\text{Hence } K_{ij} = 0 \quad \forall\ i,j$$

$$\therefore (\mathcal{R}\vec{\gamma})_i = \sum_{j \neq i} K_{ij} = 0$$

$$\text{i.e. } \mathcal{R}\vec{\gamma} = \vec{0}$$

$$\boxed{\vec{\pi} = \frac{\vec{\gamma}}{(\vec{1}^{+} \cdot \vec{\gamma})}}$$

This construction has a nice physical interp'n.

If we're modeling a physical system w/ state energies $E_1, \cdots, E_N$, & if $\vec{\pi}$ is an equil. dist'n. @ temp. β^{-1}, then

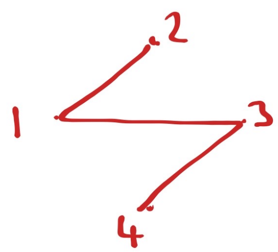
$$\frac{R_{ij}}{R_{ji}} = \frac{\pi_i}{\pi_j} = e^{-\beta(E_i - E_j)}$$

since $K_{ij} = 0$

(In physical situations, D.B. is often <u>defined</u> as the condition $\frac{R_{ij}}{R_{ji}} = e^{-\beta(E_i - E_j)}$.)

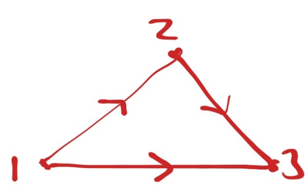
In other words, $-\beta^{-1}\ln\frac{R_{ij}}{R_{ji}} = E_i - E_j$

If we know (or fix) the energy of any specific node, e.g. E_1, then the energy of any other node can be determined summing contributions along a simple path



$$\begin{aligned} E_4 &= E_1 + (E_3 - E_1) + (E_4 - E_3) \\ &= E_1 - \beta^{-1}\ln\left(\frac{R_{31}}{R_{13}}\cdot\frac{R_{43}}{R_{34}}\right) \end{aligned}$$

If we attempt the same construction for $G \neq$ tree, then different paths might give different results:



$$\left.\begin{aligned} E_3 &= E_1 - \beta^{-1}\ln\frac{R_{31}}{R_{13}} \\ E_3 &= E_1 - \beta^{-1}\ln\frac{R_{21}}{R_{12}}\cdot\frac{R_{32}}{R_{23}} \end{aligned}\right\} \text{equal?}$$

We see that E_3 is well-defined by this construction iff

$$\frac{R_{31}}{R_{13}} = \frac{R_{21}}{R_{12}}\cdot\frac{R_{32}}{R_{23}} \quad \text{i.e.} \quad \frac{R_{21}}{R_{12}}\cdot\frac{R_{32}}{R_{23}}\cdot\frac{R_{13}}{R_{31}} = 1$$

In fact, this 3-state example illustrates the general condition that determines whether D.B. is satisfied.

Kolmogorov's condition (math) or Wegscheider's condition (chem. kinetics):

if $\dfrac{R_{in} R_{nm} \cdots R_{kj} R_{ji}}{R_{ni} R_{mn} \cdots R_{jk} R_{ij}} = 1$ for every simple cycle $ijk \cdots mni$ in G, the detailed balance is satisfied. Otherwise, D.B. is violated.

Proof left as exercise.

So, for a connected graph G w/no directed edges, and for a rate matrix R, three possibilities:

→ G = tree ⟹ D.B. is satisfied

→ $G \neq$ tree & Kolm's condition holds
⟹ D.B. is satisfied

→ $G \neq$ tree & Kolm's condition doesn't hold
⟹ D.B. is violated

If D.B. is satisfied & R models a physical system w/ states $1, \cdots N$, at temperature T, then we can use the elements of R to assign unique energies $E_1, \cdots E_N$ (apart from an over-all shift that amounts to setting the zero of the energy scale).