Network analysis of Kolmogorov's condition

For a given transition rate matrix R, we can determine whether K's cond'n holds, by examing fundamental cycles. These offer a kind of linear decomposition of a connected graph G. In a stationary state, once we specify the stationary current associated w/ each fundamental cycle, we can determine all the stationary currents J^s_{ij}.

see Schnakenberg, Rev Mod Phys, 1976 for more details.

N = # of nodes in G

E = # of edges

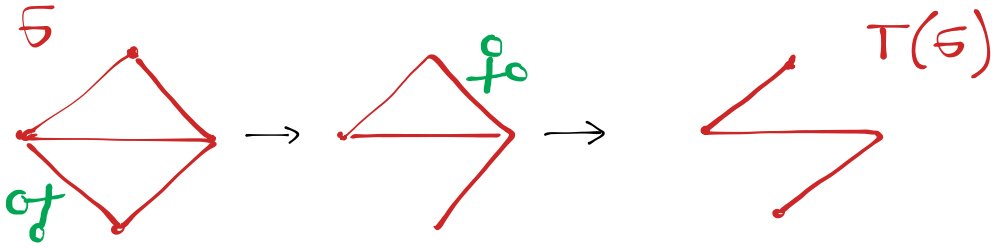
(= # of non-zero R_{ij}'s above diagonal)

then $C = E - N + 1$ = # of fund. cycles

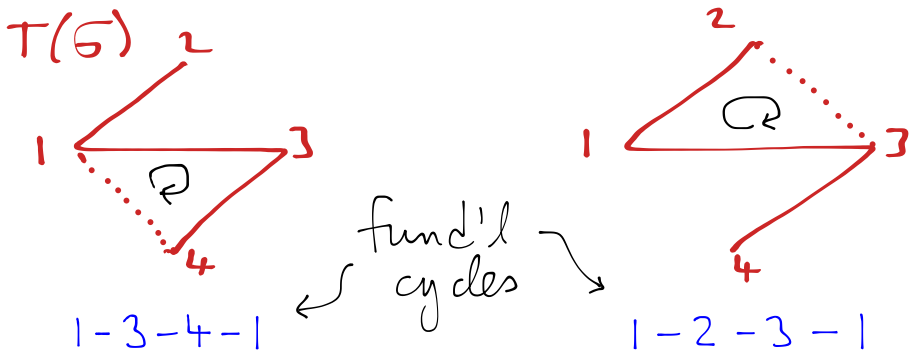
If $C=0$, then G = tree

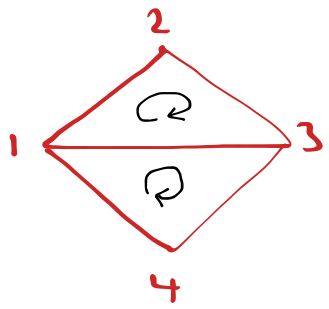
Let's assume $C>0$. Then there are 2 steps for constructing a set of fund'l cycles.

① Construct a <u>maximal tree</u> $T(G)$ by removing C edges from G, without breaking connectivity.

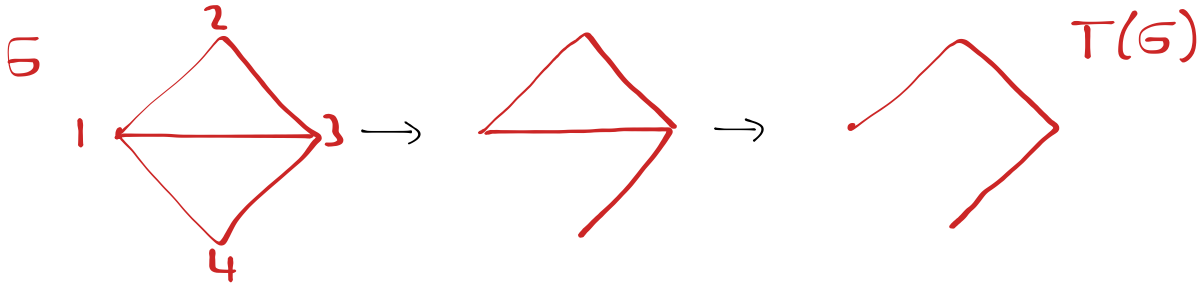


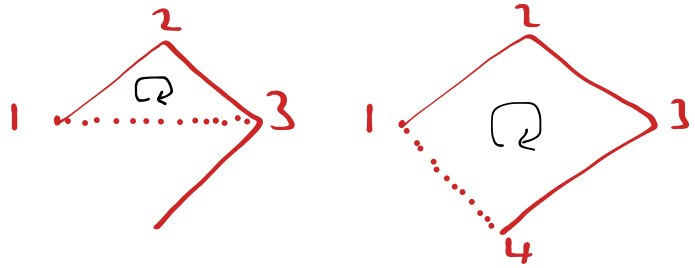
② For each edge removed, we obtain a fund'l cycle by replacing that edge only:

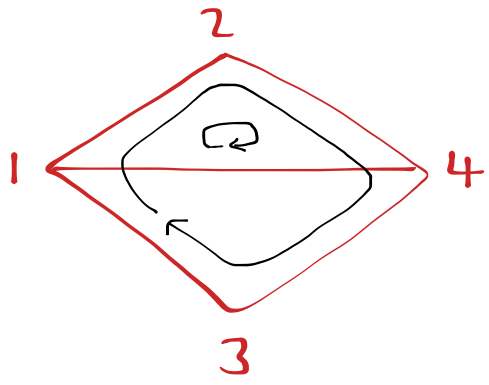




This construction is not unique: if we had chosen to remove edges 1-4 & 1-3 (instead of 1-4 & 2-3) then:







...but this G always has 2 fund. cycles.

To determine whether Kolmogorov's condition is satisfied, we first decompose G into $C = E - N + 1$ fund'l cycles.

The for each fund. cycle $c = i_1 - i_2 - \cdots i_M - i_{M+1} = i_1$, we determine the affinity

$$A_c = \sum_{k=1}^{M} \ln \frac{R_{i_{k+1} i_k}}{R_{i_k i_{k+1}}} \qquad (k_B T = 1)$$

> Kolmogorov's condition (& therefore det. bal.) is satisfied if and only if $A_c = 0$ for every fundamental cycle.

In other words: no need to check K's condition for every simple cycle in G, but only for a set of fundamental cycles.

If R satisfies detailed balance, then a system evolving under $\frac{d\vec{p}}{dt} = R\vec{p}$ relaxes to a stationary state $\vec{\pi}$ with no currents: $J^s_{ij} = 0 \quad \forall i,j$. If we are modeling a system in contact with a heat bath, then this stationary state is an equil state:

$$\pi_i = \frac{1}{Z} e^{-\beta E_i} \quad , \quad \beta^{-1} = k_B T$$

There are two ways of bringing nonequilibrium behavior into the picture:

(1) Consider a rate matrix R that violates det. bal., & study the non-equilibrium stationary state $\vec{\pi}$.

*(2) Consider time varying transition rates:

$$R = R(\lambda) \quad , \lambda = \lambda(t)$$

but assume $R(\lambda)$ satisfies det. bal. for all λ.

Assume $R(\lambda)$ satisfies det. bal. $\forall\ \lambda$,
& we are using R to model a system
in contact w/ a thermal reservoir.

Then $$\ln \frac{R_{ij}}{R_{ji}} = \frac{E_j - E_i}{k_B T} = \ln \frac{\pi_i}{\pi_j}$$

i.e. we can use $R(\lambda)$ to assign energies
$E_1(\lambda), \cdots, E_N(\lambda)$ to the discrete
states of the system. (Assume
the zero of energy is set by
the physical context.)

Now imagine a process during which
λ is varied with time, $0 \le t \le \tau$.

1 realization:

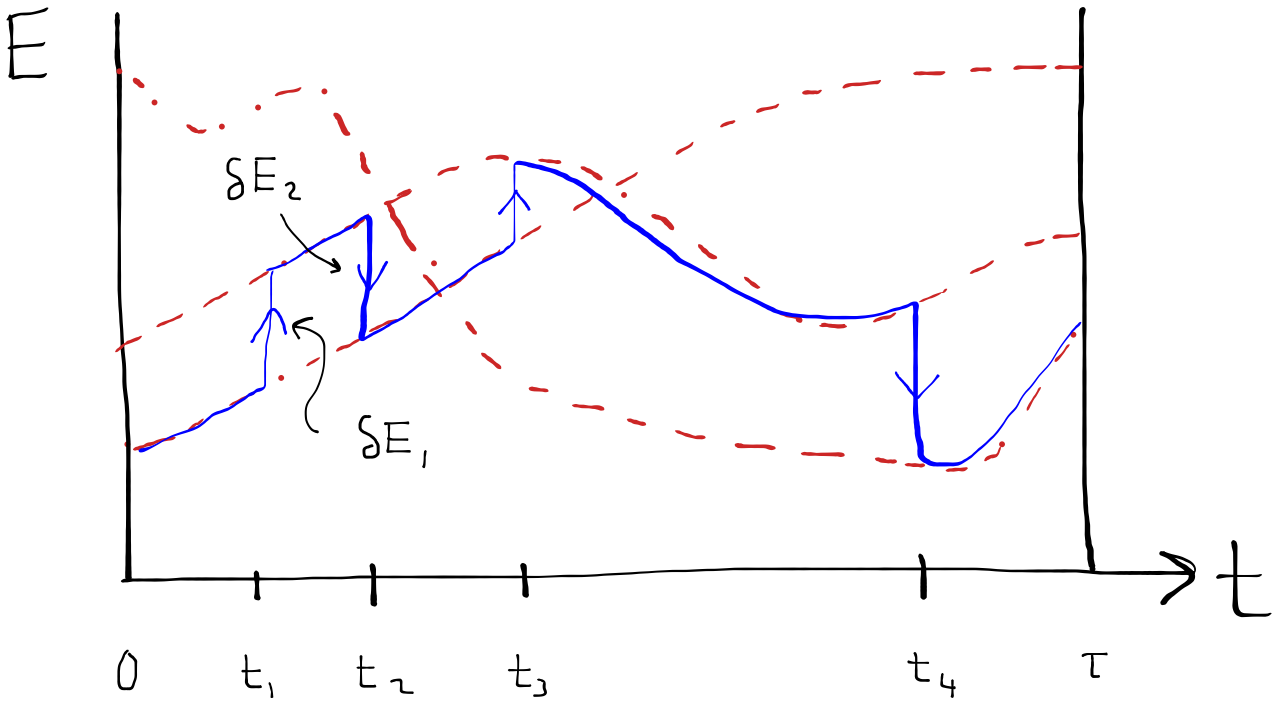
$$(t=0) \quad i_0 \xrightarrow{t_1} i_1 \xrightarrow{t_2} i_2 \cdots \xrightarrow{t_K} i_K \quad (t=\tau)$$

t_i = time of i^{th} transition.

K differs from 1 realizn to another.

Time-dependent energy: $E(t) = E_{i(t)}(\lambda(t))$

↑ microstate @ time t



dashed lines = $E_n(\lambda(t))$'s

solid line depicts trajectory i(t) (one realization)

E(t) changes w/time due to both:

- transitions from state to state
- the time-dependence of λ

$$\Delta E = E_{final} - E_{initial} = E(i_K, \lambda(\tau)) - E(i_0, \lambda(0))$$

$$= \underbrace{\sum_{k=1}^{K} \delta E_k}_{\text{interpret as heat}} + \underbrace{\int_0^\tau dt\ \dot{\lambda}(t)\ \frac{\partial E}{\partial \lambda}\left(i(t), \lambda(t)\right)}_{\text{interpret as work}}$$

$$= Q + W \qquad (1^{st}\ \text{Law})$$

Ensemble: $\langle E \rangle = \sum_i p_i(t)\ E_i(\lambda(t))$

$$\frac{d}{dt}\langle E \rangle = \sum_i \left(\dot{p}_i E_i + \dot{\lambda} p_i \frac{\partial E_i}{\partial \lambda} \right)$$

$$= \left(\sum_{ij} R_{ij} p_j E_i \right) + \left(\dot{\lambda} \sum_i p_i \frac{\partial E_i}{\partial \lambda} \right)$$

$$= \langle \dot{Q} \rangle + \langle \dot{W} \rangle$$

$$\frac{d}{dt}\langle Q \rangle_t \qquad \frac{d}{dt}\langle W \rangle_t$$

To get to the 2nd Law, let's first consider the case of fixed λ.

$\mathcal{D}(\vec{p}\,|\,\vec{\pi})$ = relative entropy of current state $\vec{p}$ w/ respect to equil. state $\vec{\pi}$.

$$= \sum_{i=1}^{N} p_i \ln \frac{p_i}{\pi_i} \geq 0$$

$$\frac{d}{dt}\mathcal{D} = \sum_i \left(\dot{p}_i \ln \frac{p_i}{\pi_i} + p_i \cdot \frac{1}{p_i} \dot{p}_i \right) \to 0$$

$$= \sum_{ij} R_{ij} p_j \ln \frac{p_i}{\pi_i}$$

$$= \sum_{i \neq j} \left(R_{ij} p_j - R_{ji} p_i \right) \ln \frac{p_i}{\pi_i}$$

$$= \frac{1}{2} \sum_{i \neq j} \left(R_{ij} p_j - R_{ji} p_i \right) \ln \frac{p_i}{\pi_i} + \frac{1}{2} \sum_{i \neq j} \left(R_{ji} p_i - R_{ij} p_j \right) \ln \frac{p_j}{\pi_j}$$

$i \leftrightarrow j$

$$= \frac{1}{2} \sum_{i \neq j} \left(R_{ij} p_j - R_{ji} p_i \right) \ln \left(\frac{p_i \pi_j}{\pi_i p_j} \right)$$

use det. bal.

$$= \sum_{i<j} \left(R_{ij} p_j - R_{ji} p_i \right) \ln \left(\frac{R_{ji} p_i}{R_{ij} p_j} \right)$$

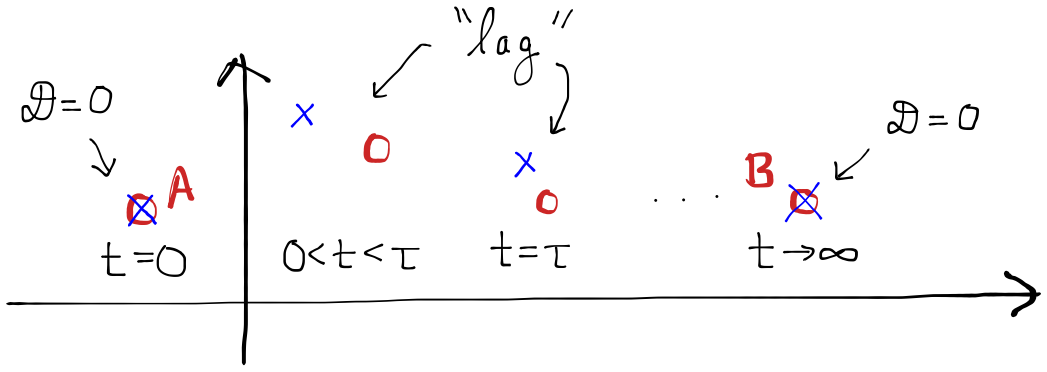
$$= -\sum_{ij} \underbrace{(a_{ij} - a_{ji})}_{+ \text{ or } -} \underbrace{\ln\left(\frac{a_{ij}}{a_{ji}}\right)}_{+ \text{ or } -} \qquad a_{ij} = R_{ij} p_j$$

$$\leq 0$$

As with diffusive processes, $\mathcal{D}(\vec{p}\,|\,\vec{\pi})$ provides a measure of "distance" from equilibrium. This distance decreases w/ time, when λ is held fixed.

Now consider the process:

1. Start in equil., $\lambda = A$: $\vec{p}(0) = \vec{\pi}_A$
2. $\lambda : A \to B$ as $t : 0 \to \tau$
3. Hold $\lambda = B$ fixed for $t > \tau$.
   $\vec{p}(t) \longrightarrow \vec{\pi}_B$ as $t \to \infty$.



- x = state of system, $\vec{p}(t)$
- o = equilibrium state, $\vec{\pi}_{\lambda(t)}$

Analysis similar to that in the diffusive case.

$$\pi_i(\lambda) = \frac{1}{Z} e^{-\beta E_i(\lambda)} = e^{\beta[F(\lambda) - E_i(\lambda)]}$$

$$\frac{d}{dt}\mathcal{D}\left(\vec{p}(t) \,\middle|\, \vec{\pi}(\lambda(t))\right) \leq \beta\dot{\lambda}\left[\left\langle \frac{\partial E}{\partial \lambda}\right\rangle - \frac{dF}{d\lambda}\right] \qquad \langle W \rangle$$

$$\hookrightarrow \sum_i p_i \frac{\partial E_i}{\partial \lambda}$$

(reduces to $\dot{\mathcal{D}} \leq 0$ when λ fixed)

Integrating both sides from $t=0$ to $t=\infty$:

$$\boxed{\langle W \rangle \geq \Delta F} = F_B - F_A$$

2nd Law / Clausius inequality

As in the diffusive case, the 2nd Law can be understood in terms of a system that tries to "keep up" with a changing equilibrium state $\vec{\pi}(\lambda(t))$ (moving target) but lags behind. The quantity $\beta(\langle W \rangle - \Delta F)$ provides a measure of the accumulated lag, over the duration of the process.

Now let's make a connection to entropy.

Start by assuming fixed λ, & take $\vec{p}(0) \neq \vec{\pi}$.

$$0 \leq -\frac{d}{dt} \mathcal{D}(\vec{p} \,|\, \vec{\pi})$$

$$= \sum_{i<j} (R_{ij} p_j - R_{ji} p_i) \ln \frac{R_{ij} p_j}{R_{ji} p_i}$$

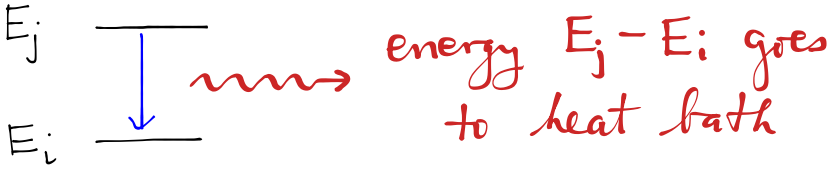
$$= \sum_{i<j} J_{ij} \ln \frac{R_{ij}}{R_{ji}} + \sum_{i<j} J_{ij} \ln \frac{p_j}{p_i}$$

show!

$$= \beta \sum_{i<j} J_{ij} (E_j - E_i) + \frac{d}{dt} \left[-\sum_i p_i \ln p_i \right]$$

$S(\vec{p})$, $k_B = 1$

J_{ij} = avg. rate of transitions $j \to i$



$\therefore \beta \sum_{i<j} J_{ij} (E_j - E_i) = \frac{1}{T} \times$ avg. rate of energy flow to reservoir

$$= -\frac{\langle \dot{Q} \rangle}{T} = \frac{dS_{res}}{dt}$$

Combining terms: $\boxed{0 \leq \frac{dS_{res}}{dt} + \frac{dS}{dt}}$ 2nd Law!

This derivation can be extended to processes during which λ varies with time.
We still get

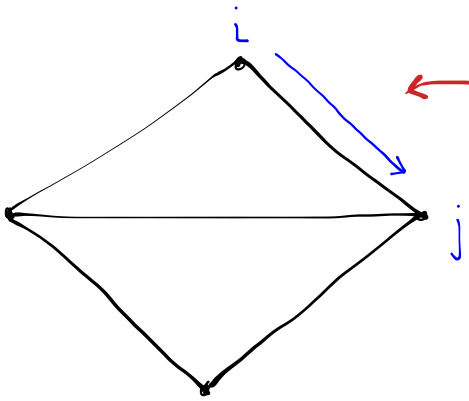
$$0 \leq -\frac{\langle \dot{Q} \rangle}{T} - \frac{d}{dt} \sum_i p_i \ln p_i = \frac{dS_{res}}{dt} + \frac{dS}{dt}$$

At the single trajectory level:

$$(t=0) \quad i_0 \xrightarrow{t_1} i_1 \xrightarrow{t_2} \cdots \xrightarrow{t_K} i_K \quad (t=\tau)$$

$$\Delta S_{res} = \frac{\text{energy absorbed by reservoir}}{T}$$

$$= \beta \sum_{\ell=1}^{K} \left[E(i_{\ell-1}) - E(i_\ell) \right] = \sum_{\ell=1}^{K} \ln \left(\frac{R_{i_\ell i_{\ell-1}}}{R_{i_{\ell-1} i_\ell}} \right)$$



$\leftarrow \delta S_{res} = \ln \frac{R_{ji}}{R_{ij}}$

When the system makes a transition $i \to j$, the change in the entropy of the reservoir is $\ln \frac{R_{ji}}{R_{ij}}$.

We have used detailed balance to derive

$$\Delta S_r = \sum_{l=1}^{K} \ln\left(\frac{\mathcal{R}_{i_l i_{l-1}}}{\mathcal{R}_{i_{l-1} i_l}}\right) \quad , \quad \delta S_r(i \to j) = \ln \frac{\mathcal{R}_{ji}}{\mathcal{R}_{ij}}$$

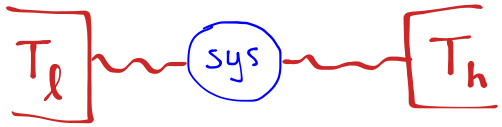
but the result remains valid even if $\mathcal{R}$ violates detailed balance. *

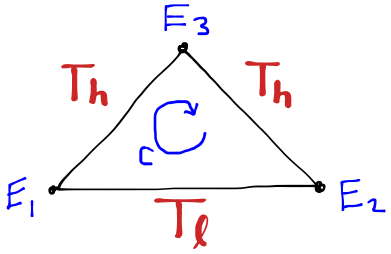
ΔS_r, δS_r = net change in entropy off all thermal surroundings (might include multiple reservoirs)

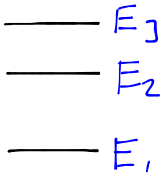
Instead of trying to justify this statement from microscopic principles, let's see how it works in two illustrative examples.

* This is a central principle of Stochastic Thermodynamics (Seifert, Rep. Prog. Phys. 2012)

Example 1 system + 2 heat baths







$$\frac{R_{31}}{R_{13}} = e^{-\beta_h (E_3 - E_1)}, \quad \frac{R_{23}}{R_{32}} = e^{-\beta_h (E_2 - E_3)}, \quad \frac{R_{12}}{R_{21}} = e^{-\beta_\ell (E_1 - E_2)}$$

$$A_c = \ln \left(\frac{R_{12}}{R_{21}} \cdot \frac{R_{23}}{R_{32}} \cdot \frac{R_{31}}{R_{13}} \right)$$

$$= -\beta_\ell (E_1 - E_2) - \beta_h (E_2 - E_3) - \beta_h (E_3 - E_1)$$

$$= (E_2 - E_1) \cdot \left(\frac{1}{T_\ell} - \frac{1}{T_h} \right) > 0$$

$$A_c = \Delta S_r (1 \to 3 \to 2 \to 1) > 0$$

... every time the system proceeds thru the cycle c, the net result is a transfer of energy $E_2 - E_1$ from the hot bath to the cold bath.

(In the stationary state, $J_{31} = J_{23} = J_{12} > 0$.
The temperature difference $T_h - T_\ell$ is like a force that drives a CW current.)