<u>Continuous time process</u> (but state space discrete)

$$M(c',c) = \delta_{c',c} + \Delta t\, \omega(c',c) + O(\Delta t^2)$$

$$\Rightarrow \quad P_{t+\Delta t}(c') = \sum_c M(c',c) P_t(c)$$

$$= \sum_c \left[\delta_{c',c} + \Delta t\, \omega(c',c) + \dots\right] P_t(c)$$

$$= P_t(c') + \Delta t \sum_c \omega(c',c) P_t(c) + O(\Delta t^2)$$

$$\Rightarrow \quad \frac{P_{t+\Delta t}(c') - P_t(c')}{\Delta t} = \sum_c \omega(c',c) P_t(c) + O(\Delta t)$$

in $\Delta t \to 0$ limit

$$\boxed{\frac{dP_t(c')}{dt} = \sum_c \omega(c',c) P_t(c)}$$

Master equation,
Pauli - M- equation,
Rate equation.

OR

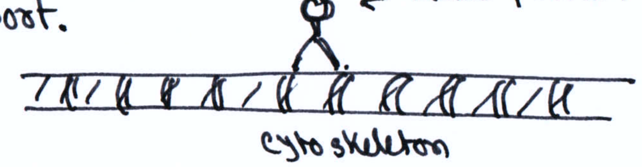
$$\boxed{\frac{d|P_t\rangle}{dt} = W |P_t\rangle}$$

<u>Remark</u>: $\omega(c',c)$ = is transition rate, therefore can be larger than 1.

$\Delta t \cdot \omega(c',c)$ gives the probability of a transition for small Δt.

<u>Remark</u>: $\omega(c',c)$ can be computed or measured ~~for a given~~ from the dynamics of a given system.

Example. Biological transport.



Example: chemical reactions

$$A + B \longrightarrow C$$

Example: transport of ion in hydrogen bonded network.

extra ion. (hydronium ion)

Grotthuss mechanism.

[TS. arXiv; 1009]

Example: Fermi's golden rule in QM.

time-dependent perturbation theory gives, ~~to~~.

$H_{system} + H_{extern}$ ← perturbation.

E_n are eigen states of H_{system}

$$w(n', n) = \frac{2\pi}{\hbar} \left| H_{Ext}(n', n) \right|^2 \rho(E_n)$$

matrix element in E_n basis.

density of states.

Remark: ① Spot the difference of $\frac{d|P_t\rangle}{dt} = W|P_t\rangle$ with Sch equation

$$i\hbar \frac{d}{dt}|\psi_t\rangle = H|\psi_t\rangle$$

② Compare with Boltzmann equation. See that B-equation is non-linear in phase space density, but M-equation is linear in P.

⊛ A conventional form of the M-equation.

$$\sum_{c'} M(c',c) = 1$$

$$\Rightarrow \quad 1 + \Delta t \sum_{c'} W(c',c) + \cdots = 1 \quad \Rightarrow \quad \boxed{\sum_{c'} W(c',c) = 0}$$

Column sum of W-matrix vanish.

A natural choice

$$W(c,c) = -\sum_{c' \neq c} W(c',c) \qquad \text{along the diagonal.}$$

$$W = \begin{pmatrix} \ddots & & w_1 & & \\ & \ddots & w_2 & & \\ & & -\sum w_i & & \\ & & w_N & \ddots & \\ & & \vdots & & \ddots \end{pmatrix}$$

Typically, this is incorporated in the M-equation by writing

$$\frac{d}{dt} P_t(c') = \sum_{c \neq c'} W(c',c)\, P_t(c) + W(c',c')\, P_t(c')$$

$$\downarrow$$

$$-\sum_{c'' \neq c'} W(c'',c')\, P_t(c')$$

$$\downarrow \quad c'' \text{ is dummy variable then, call it } c.$$

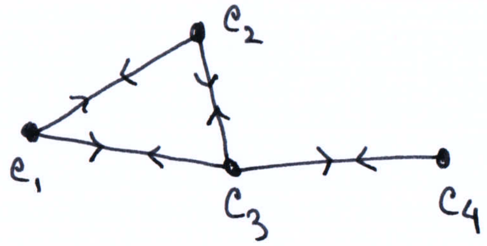
$$-\sum_{c \neq c'} W(c,c')\, P_t(c')$$

$$= \sum_{c \neq c'} \Big[\underbrace{W(c',c)\, P_t(c) - W(c,c')\, P_t(c')}_{\text{is zero.}} \Big]$$

↑ for $c = c'$, is zero. So we can write

$$\boxed{\frac{d}{dt} P_t(c') = \sum_{c} \Big[W(c',c)\, P_t(c) - W(c,c')\, P_t(c') \Big]}$$

Stationary state, equilibrium, and out-of equilibrium.



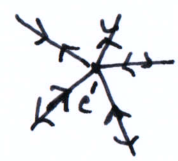
Stationary state:

$$\frac{d}{dt} P_{st}(c') = 0 \qquad \text{Prob does not change with time.}$$

$$\Rightarrow \sum_{c} \left[w(c',c) P_{st}(c) - w(c,c') P_{st}(c') \right] = 0$$

$$\Rightarrow \boxed{\sum_{c} w(c',c) P_{st}(c) = P_{st}(c') \sum_{c} w(c,c')}$$ "global balance"

incoming prob flux = Out going prob flux.



Equilibrium stationary state:

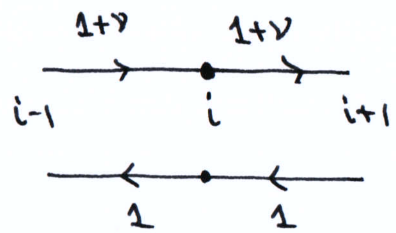
in flux = out flux for each edge.

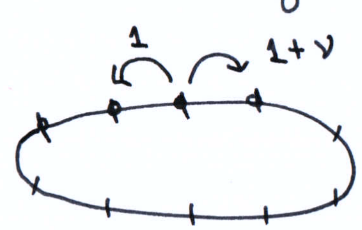
$$\boxed{w(c',c) P_{st}(c) = w(c,c') P_{st}(c')}$$ Detailed balance.

Out-of equilibrium:

Other wise

Example: biased random walk on a ring.





Pair wise cancellation

$$\left.\begin{aligned} &(1+\nu) P_{st}(i-1) = (1+\nu) P_{st}(i) \\ \text{and} \quad &1 \cdot P_{st}(i) = 1 \cdot P_{st}(i+1) \end{aligned}\right\} P_{st} = \text{uniform.}$$

For $\nu = 0$: detailed balance, P_{st} also uniform. But the state is in equilibrium.

Remark: ~~Markov~~ Event chain Monte Carlo. [Werner Krauth]

Remark: Stationary state does not mean that the system is frozen. Infact system is still exporing its config space, but in a way that $P(c)$ does not change with time.

Remark: System evolving towards an equilibrium stationary state is also out-of-equilibrium.

$$\begin{array}{ccc} & \text{Stationary state} & \\ \swarrow & & \searrow \\ \text{equilibrium stationary state} & & \text{non-equilibrium stationary state.} \end{array}$$

Few usefull facts about detailed balance.

① Detailed balance means $\longleftrightarrow$ zero probability current.

Also mean state is "statistically" time reverssible.
(See soon, what it means)

② Often, given an equilibrium state, one can construct rates such that the $P_{st} \equiv P_{eq}$. All that one needs is to satisfy detailed balance.

$$\frac{\omega(c',c)}{\omega(c,c')} = \frac{P_{eq}(c')}{P_{eq}(c)} = e^{-\beta[E(c')-E(c)]}$$

Central idea of Monte Carlo simulations!

A popular ~~exact~~ choice of such rates is

$$\omega(c',c) = \begin{cases} 1 & \text{if } E(c') \le E(c) \\ e^{-\beta(E(c')-E(c))} & \text{if } E(c') > E(c). \end{cases}$$

Metropolis filter.

Example: Glauber spin flip dynamics of Ising model.
or
Kawasaki spin-exchange

Remark: in these, the dynamics need not be physical, ~~because~~ as long as we are interested only in the one-time (static) properties in equilibrium.

Ref: Event chain Monte Carlo for 2-step melting in two dimensions.
[Etien Bernand & Werner Krauth]

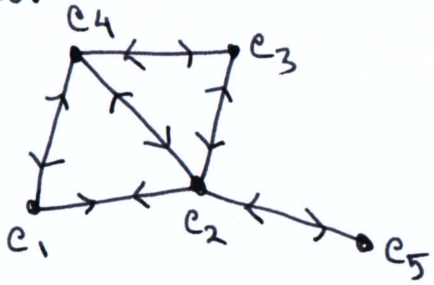
Remark: $P_{st}(c) = e^{-\beta E(c)}$ does not mean equilibrium!
The prob current needs to vanish.
[Katz-Spohn-Lebowitz model: Ising spin under driving field]

Exercise:

3 ~~for~~ Detailed balance is stated in terms of stationary prob.
Can one test detailed balance without knowing the $P_{st} = P_{eq}$?

Yes! by using Kolmogorov criteria.

You only need the rates ω.



If for all loops on config space product of rates in

clock wise = anti clock wise

then, it is a necessary and sufficient condition for detailed balance.

necessary condition:

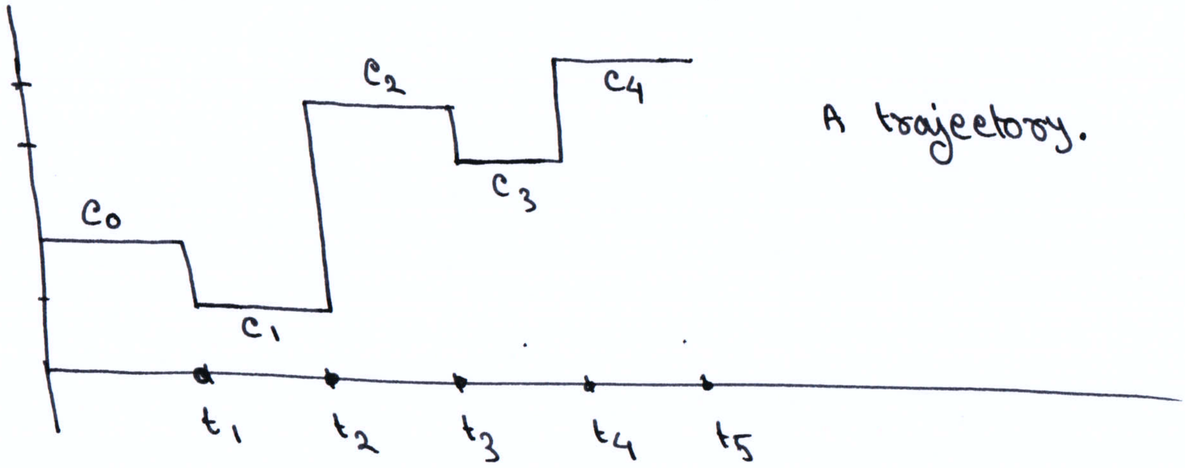
using detailed balance.

$$\frac{\omega(c_1, c_4)\,\omega(c_4, c_3)\,\omega(c_3, c_2)\,\omega(c_2, c_1)}{\omega(c_4, c_1)\,\omega(c_3, c_4)\,\omega(c_2, c_3)\,\omega(c_1, c_2)} = \frac{P(\cancel{c_1})}{P(\cancel{c_4})} \cdot \frac{P(\cancel{c_4})}{P(\cancel{c_3})} \cdot \frac{P(\cancel{c_3})}{P(\cancel{c_2})} \cdot \frac{P(\cancel{c_2})}{P(\cancel{c_1})}$$

$$= 1$$

Sufficient condition: See David Mukamel, ...

4 Time reversibility (stochastic): Onsager



A trajectory.

Prob to stay in a config(c) for time length t,

$$= \lim_{\Delta t\to 0}\left[1-\Delta t\sum_{c'\neq c}\omega(c',c)\right]^{t/\Delta t} = e^{-t\sum_{c'\neq c}\omega(c',c)} = e^{-t\,\omega(c,c)}$$

Prob for jump from $c\to c'$ is $\Delta t\cdot\omega(c',c)$

$$\Rightarrow \text{Prob}[c(t)] = P(c_0)\, e^{-t_1\omega(c_0,c_0)}\cdot \Delta t\,\omega(c_1,c_0)\cdot e^{-(t_2-t_1)\omega(c_1,c_1)} \cdots\cdots e^{-(t_5-t_4)\omega(c_4,c_4)}$$

Prob of time reversed trajectory

$$\text{Prob}[c^*(t)] = P(c_4)\, e^{-(t_5-t_4)\omega(c_4,c_4)}\cdot \Delta t\,\omega(c_3,c_4)\cdots\cdots e^{-t_1\omega(c_0,c_0)}$$

$$\Rightarrow \frac{\text{Prob}[c(t)]}{\text{Prob}[c^*(t)]} = \frac{P(c_0)\cdot \omega(c_1,c_0)\cdot \omega(c_2,c_1)\cdot \omega(c_3,c_2)\cdot \omega(c_4,c_3)}{P(c_4)\cdot \omega(c_3,c_4)\cdot \omega(c_2,c_3)\cdot \omega(c_1,c_2)\cdot \omega(c_0,c_1)}$$

$\big\downarrow$ detailed balance

$$= \frac{P(c_0)\cdot}{P(c_4)} \cdot \frac{P(c_1)}{P(c_0)} \cdot \frac{P(c_2)}{P(c_1)} \cdot \frac{P(c_3)}{P(c_1)} \cdot \frac{P(c_4)}{P(c_1)}$$

$$= 1$$

$\Rightarrow$ $\boxed{\text{Prob of a forward trajectory} = \text{Prob of a time reversed trajectory}}$

<u>A consequence</u>: In equilibrium, "the way" a fluctuation is spontaneously created, is "the same way" that fluctuation relaxes.

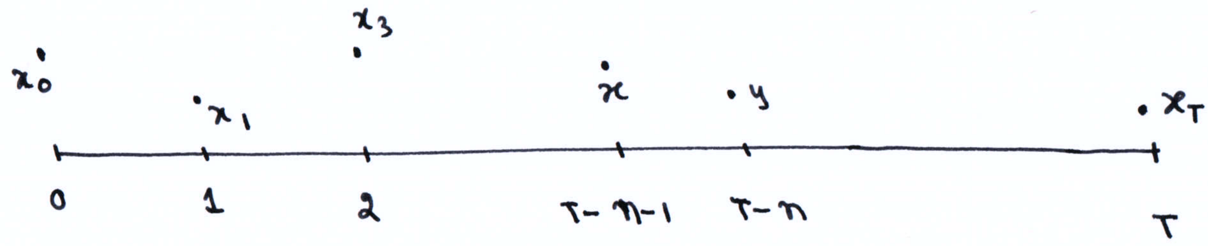
[Einstein, Onsager - Machlup]

<u>Remark</u>: Out-side equilibrium, this symmetry breaks down. But there is a more generalized symmetry. [Gallavotti - cohen fluctuation relations]

<u>Remark</u>: fluctuation-dissipation relation in linear response is a consequence of this symmetry.

Time-reversed process

[Book by Stroock
An Intro to Markov processes]



Forward evolution:

$$C(t) \equiv \{ c_0 = x_0, c_1 = x_1, \cdots\cdots, c_T = x_T \}$$

Prob evolves by $M(c', c)$

Time-reversed evolution:

$$c^*(t) = c(T-t)$$

$$c^*(t) = \{ c^*_0 = x_T, c^*_1 = x_{T-1}, \cdots\cdots, c^*_T = x_0 \}$$

Q: ~~How does~~ what dynamics describe $c^*(t)$?
Is it Markovian?

Answer:

$$P^*(c^*_{n+1} = x, c^*_n = y, \cdots, c^*_0 = x_T) = P(c_{T-n-1} = x, c_{T-n} = y, \cdots, c_T = x_T)$$

$$\Rightarrow M^*(c^*_{n+1} = x \mid c^*_n = y, \cdots, c^*_0 = x_T)\, P^*(c^*_n = y, \cdots, c^*_0 = x_T) = \cdots$$

Also

$$P^*(c^*_n = y, \cdots, c^*_0 = x_T) = P(c_{T-n} = y, \cdots, c_T = x_T)$$

- Taking ratio

$$M^*\left(C^*_{n+1}=x \,\middle|\, C^*_n=y,\cdots,C^*_0=x_T\right)$$

$$= \frac{P\left(C_{T-n-1}=x,\, C_{T-n}=y,\, \cdots,\, C_T=x_T\right)}{P\left(C_{T-n}=y,\, \cdots,\, C_T=x_T\right)}$$

$$= \frac{P\left(C_{T-n-1}=x\right) M(x\to y)\, \cancel{M(y\to x_{T-n+1})} \cdots \cancel{M(x_{T-1}\to x_T)}}{P\left(C_{T-n}=y\right) \cancel{M(y\to x_{T-n+1})} \cdots \cancel{M(x_{T-1}\to x_T)}}$$

$$= \frac{P\left(C_{T-n-1}=x\right)}{P\left(C_{T-n}=y\right)} M(y,x)$$

$[M(x\to y) \equiv M(y,x)]$

This means that the time reversed dynamics is also Markovian (because it only depends on y, and not on $C^*_{n-1}, C^*_{n-2}, \cdots, C^*_0$).

But $M^*(x,y)$ depends on time (n) $\Longrightarrow$ a time inhomogeneous process.

Remark: If the forward process has reached a stationary state, i.e. $P(C_n=x) = P_{st}(x)$, then

$$\boxed{M^*(x,y) = \frac{P_{st}(x)}{P_{st}(y)} M(y,x)}$$

time-homogeneous.
(Check: $\sum_x M^*(x,y) = 1$)

Remark: note, generally $M^*(x,y) \neq M(x,y)$. This equality happens only for equilibrium by detailed balance condition.

Remark: continuous time case can be obtained by

$$M^*(x,y) = \delta_{x,y} + \Delta t\, W^*(x,y) + \cdots = \frac{P(x)+\Delta t\, h(x)}{P(y)+\Delta t\, h(y)} \cdot \left(\delta_{y,x} + \Delta t\, W(y,x)\right)$$