LECTURE

Master equations

Example:
Death and Birth processes

Suggested Reading:
(1) Chapter 11 "Stochastic Methods" C. Gardiner
(2) Chapter Poly_copy P. Martin

Transition rates: Assume we have a system

$$W(n_1,n_2) = \lim_{t\to 0}\left(\frac{P(n_1,0\,|\,n_2,t)}{t}\right) = \frac{\partial}{\partial t}\left[P(n_1,0\,|\,n_2,t)\right]$$

Let use assume the transition probability:

$$P(n_1,0\,|\,n_2,t) = W(n_1,n_2)\cdot t + O(t^2)$$

Derive an Equation of motion for P:

$$P(n_1|n_2,\Delta t) = \begin{cases} n_1 = n_2 & \text{prob. } \underline{\text{stay}} \text{ in same state during } \Delta t \\ n_1 \neq n_2 & \text{prob. to } \underline{\text{arrive}} \text{ in state } n_2 \text{ during } \Delta t \end{cases}$$

Introduce $\boxed{a(n_1) = \sum_{n_1\neq n_2} W(n_1,n_2)}$ Transition rate out of state n_1

Derive equation of motion of $P(n_1|n_2,\Delta t)$

$$P(n_1|n_2,\Delta t) = \underbrace{(1-a(n_1)\Delta t)}_{\substack{\text{Probability to}\\ \text{stay in state } n_1=n_2}}\delta_{n_1,n_2} + \underbrace{(1-\delta_{n_1,n_2})W(n_1|n_2)\Delta t}_{\substack{\text{Probability to exit}\\ \text{if } n_1\neq n_2}}$$

For a Markov process the Chapman Kolmogorov equations give

$$P(n_1|n_3,t+\Delta t) = \sum_{n_2\in S} P(n_1|n_2,t)\,\underbrace{P(n_2,t\,|\,n_3,t+\Delta t)}_{= P(n_2|n_3+\Delta t)}$$

for a homogeneous process.

$$= \sum_{n_2} P(n_1|n_2,t)\left[(1-a(n_2)\Delta t)\delta_{n_2,n_3} + (1-\delta_{n_2,n_3})W(n_2|n_3)\Delta t\right]$$

$$P(u_1|u_3,t+\Delta t) = P(u_1|u_3,t) - P(u_1|u_3,t)\,a(u_3)\,\Delta t + \sum_{u_2} P(u_1|u_2,t)\,W(u_2|u_3)\,\Delta t \times (1-\delta_{u_2,u_3})$$

$$= P(u_1|u_3,t) - P(u_1|u_3,t)\,a(u_3)\Delta t + \sum_{\substack{u_2 \\ u_2\neq u_3}} P(u_1|u_2,t)\,W(u_2|u_3)\Delta t$$

$$= P(u_1|u_3,t) - P(u_1|u_3,t)\underbrace{\Big[\sum_{\substack{u_2\in S \\ u_2\neq u_3}} W(u_3|u_2)\Delta t\Big]}_{\hat{=}\, a(u_3)} + \sum_{\substack{u_2\in S \\ u_2\neq u_3}} P(u_1|u_2,t)\,W(u_2|u_3)\cdot\Delta$$

$\Leftrightarrow$

$$\lim_{\Delta t\to 0}\left(\frac{P(u_1|u_2,t+\Delta t)-P(u_1|u_3,t)}{\Delta t}\right) = \sum_{\substack{u_2\in S \\ u_2\neq u_3}} P(u_1|u_2,t)\,W(u_2|u_3) - P(u_1|u_3,t)\,W(u_3$$

Note that for $u_2 = u_3$:

$$P(u_1|u_2,t)\,W(u_2,u_2) - P(u_1|u_2,t)\,W(u_2|u_2) = 0$$

Mesoscopic Master Equation

$$\boxed{\frac{\partial}{\partial t} P(u,t) = \sum_{u'\in S} P(u',t)\,W(u'|u) - P(u,t)\,W(u|u')}$$

For a stationary process:

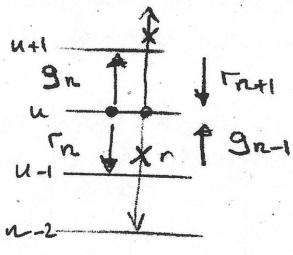
$$\begin{tikzcd} u \arrow[r, bend left, "W(u|u')"] & u' \arrow[l, bend left, "W(u'|u)"] \end{tikzcd}$$

$$\boxed{\sum_{u'\in S} p^s(u')\,W(u'|u) - p^s(u)\,W(u|u') = 0}$$

Birth and Death processes

$n \in \mathbb{N}_0$ e.g. number of particles (photons, atoms, animals etc)

We assume only transitions between states $n, n+1, n-1$



$$W(n|n+1) = g_n = g(n)$$

$$W(n|n-1) = r_n = r(n)$$

Thus:
$$\boxed{\frac{\partial}{\partial t} P_n(t) = g_{n-1} P_{n-1}(t) + r_{n+1} P_{n+1}(t) - (g_n + r_n) P_n(t)}$$

x: not allowed transitions

- Equation of motion for the average of $\langle n \rangle$:

$$\frac{d}{dt}\langle n \rangle = \frac{d}{dt} \sum_{n=0}^{\infty} n \cdot p_n(t)$$

$$= \sum_{n=0}^{\infty} n \left[g_{n-1} P_{n-1}(t) + r_{n+1} p_{n+1}(t) - (g_n + r_n) p_n(t) \right]$$

$$= \sum_{n=0}^{\infty} n g_{n-1} p_{n-1}(t) - \sum g_n p_n(t) n + \sum_{n=0}^{\infty} n \left(r_{n+1} p_{n+1}(t) - \sum r_n p_n(t) \right)$$

$n \to n+1$ $\qquad\qquad$ $n \to n-1$

$$= \sum_{n=0}^{\infty} (n+1) g_n p_n(t) - \sum_{n=0} g_n p_n(t) n + \sum_{n=0}^{\infty} (n-1) r_n p_n(t) - \sum_{n=0} r_n p_n(t) n$$

$$= \sum_{n=0}^{\infty} g_n p_n(t) - \underbrace{r_n p_n(t)}_{\hat{=} \langle r_n \rangle}.$$

$$\Leftrightarrow \boxed{\frac{d}{dt}\langle n \rangle = \langle g_n \rangle - \langle r_n \rangle}$$ Rate equation for the population.

- Most general solution in steady state:

call: $J(n) = r(n) P_s(n) - g(n-1) P_s(n-1) \Rightarrow \frac{\partial P_n}{\partial t} = J(n+1) - J(n) = 0 \quad (*)$

- There exists a lowest state $\Rightarrow r(0) = 0 \wedge P(n,t) = 0 \quad n < 0$
- $J(0) = r(0) P_s(0) - g(-1) P_s(-1) = r(0) p_s(0) = 0$ $\qquad$ Burgess 1954
- Sum over $(*)$ $\quad 0 = \sum_{n=0}^{n-1} J(n+1) - J(n) = J(n) - J(0) = J(n)$ $\quad$ But $J(0) = 0$

$\Rightarrow J(n) = 0 \quad \Rightarrow \quad \boxed{P_s(n) = \frac{g(n-1)}{r(n)} P_s(n-1) \qquad P_s(n) = P_s(0) \prod^{n} \frac{g(n-1)}{r(n)}}$

MASTER EQUATION

Applications: Radioactive decay.

Master equation for radio-active decay

TRANSITION PROBABILITY: Probability to transition in interval δt to new state. Transition rate depends on number of atoms n'

$$\delta t\, W(n,n') = \begin{cases} 0 = g_n & n > n' \\ r_{n'}\,\gamma\,\delta t & \text{for } n = n'-1 \\ \mathcal{O}(\delta t^2) & \text{for } n < n'-1 \end{cases}$$

$\uparrow$ final $\uparrow$ initial

$n+1$

$r_{n+1} = +\gamma(n+1)$

n

$r_n = \gamma(n)$

$n-1$

$$W(n,n') = n'\gamma\,\delta_{n,n'-1}$$ Transition rate (only transitions to adjacent levels are possible)

Thus:

$$\boxed{\partial_t p(n,t) = \sum_{n'} p(n',t)\underbrace{W(n',n)}_{n=n'-1} - p(n,t)\underbrace{W(n,n')}_{n'=n+1}}$$

since $n = n'-1$ i.e. $W(n-1,n) = \underbrace{(n+1)}_{=n'}\gamma$

yields:

$$\boxed{\dot p_n = (n+1)\gamma\, p_{n+1}(t) - n\gamma\, p_n(t)}$$

with initial condition $p_n(0) = n_0$

Hence the mean evolves according to / or solve with generating function (see Matic) $G(s,t) = \sum_n s^n p_n(t)$

$$N(t) = \langle n \rangle = \sum_n p_n(t)\, n$$

$$\frac{d}{dt}\langle n(t)\rangle = \sum_n n\cdot \dot p_n(t) = \gamma \sum_n (n)(n+1)\gamma\, p_{n+1}(t) - \sum_n n^2 p_n(t)$$

$$= \sum_{n-1} (n-1)n\, p_n(t) - \sum_n \gamma n^2 p_n = -\gamma \sum n\, p_n(t)$$

change indices $n \to n-1$

Thus $\underline{\langle n(t)\rangle = n_0\, e^{-\gamma t}}$ [note: steady state is $\langle \bar n\rangle = 0$!]

Deterministic part

We can also solve for the fluctuations.

$$N_2(t) = \langle n^2 \rangle = \sum_n n^2 p_n(t) \qquad \text{(variance)}$$

Thus:

$$\frac{d}{dt}\langle n^2(t)\rangle = \frac{d}{dt}\sum n^2 p_n = \gamma \sum n^2(n+1)\, p_{n+1}(t) - \gamma \sum n^3 p_n$$

$$= \gamma \sum (n-1)^2 n\, p_n - \gamma \sum n^3 p_n = \gamma \sum (n - 2n^2)\, p_n$$

thus $\underline{\frac{d}{dt}\langle n^2(t)\rangle = -2\gamma\langle n^2\rangle + \gamma\langle n\rangle}$ since for $t=0$ $N_2(0) = n_0^2 = \langle n^2(t=0)\rangle$

Thus

$$\boxed{\langle n^2(t)\rangle = n_0(n_0-1)\,e^{-2\gamma t} + n_0\, e^{-\gamma t}}$$

FLUCTUATIONS VERSUS TIME

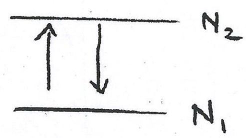
$$\Leftrightarrow \quad \langle \Delta n^2\rangle(t) = \left(n_0 e^{-2\gamma t} + n_0 e^{-\gamma t}\right)$$

Variance: $\langle \Delta n^2(t)\rangle = \langle (\langle n(t)\rangle - n(t))^2\rangle$

(i.e. two timescales)

Applications of Mesoscopic Master eqs: Photons

$$\left[\begin{array}{llll} g_n = \lambda(n+1) \text{ (spont. emiss.)} & \lambda = \gamma N_2 & \text{absorption} \\ r_n = \mu \cdot n \text{ (absorp.)} & \mu = \gamma N_1 & \text{\& emission} \\ & & \text{of photons} \end{array}\right]$$



$$\partial_t P_n(t) = \lambda n P_{n-1}(t) + \mu(n+1) P_{n+1}(t) - [(\mu+\lambda)n + \lambda] P_n(t)$$

$$\left[\Rightarrow \quad P_n^{(s)} = c\left(\frac{\lambda}{\mu}\right)^n \right] \qquad \text{(Burgess Solution)}$$

The distribution needs to satisfy Boltzmann statistics:

$$\left[\frac{\lambda}{\mu} = \frac{N_2}{N_1} = e^{-\beta(E_1-E_2)} = e^{-\hbar\omega\beta} \quad \wedge \quad \beta = (k_B T)^{-1} \right]$$

$\Rightarrow$ Normalization

$$P_n^{(s)} = c \cdot e^{-\beta\hbar\omega n} \qquad c = 1 - e^{-\beta\hbar\omega} \qquad \text{since } \sum_1^N \left(e^{-\beta\hbar\omega}\right)^n$$

$$= \frac{1+q^N}{1-q} \cong (1-q)^{-1}$$

$$\left[\boxed{P_n^{(s)} = \left(1 - e^{-\beta\hbar\omega}\right) e^{-\beta\hbar\omega n}} \right]$$

$$\langle n_s \rangle = \sum_{n=0}^{\infty} n \cdot p_n^{(s)} = \sum_{n=0}^{\infty} n \left(1 - e^{-\beta\hbar\omega}\right) e^{-\beta\hbar\omega n}$$

$$= \left(1 - e^{-\beta\hbar\omega}\right) \sum_n \frac{\partial}{\partial(-\beta\hbar\omega)} e^{-\beta\hbar\omega n} = \left(1 - e^{-\beta\hbar\omega}\right) \frac{\partial}{\partial(-\beta\hbar\omega)} \left[\left(1 - e^{-\beta\hbar\omega}\right)^{-1}\right]$$

$$\left[\boxed{\langle n_s \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}} \right] \qquad \text{BOSE DISTRIBUTION}$$

Chemical reaction Example:

$$X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A \qquad \text{with } A\text{: fixed}$$

$$g_n = k_2 A$$

$$r_n = k_1 X$$

CHEMICAL MASTER EQUATION:

$$\Rightarrow \boxed{\begin{aligned} \partial_t P(x,t) = {} & k_2 a P(x-1,t) + k_1(x+1) P(x+1,t) \\ & -(k_1 x + k_2 a) P(x,t) \end{aligned}}$$

Can be solved with generating Function $G(s,t) = \sum_{x=0}^{\infty} s^x P(x,t)$

$$\Rightarrow \quad \partial_t G(s,t) = k_2 a (s-1) G(s,t) - k_1 (s-1) \underbrace{\partial_s G(s,t)}_{\text{generates } P(x+1,t) \text{ Term}}$$

($\Rightarrow$ homework)

Mesoscopic Master Equation for a Chemical Reaction

$$\boxed{\begin{array}{l} A + 2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \\ A \underset{k_4}{\overset{k_3}{\rightleftharpoons}} X \end{array}}$$

/

A is a constant concentration.

Probability to enter: $g(x) = A\,x(x-1)\,k_1 + k_3 A$ (gain term)

$\Gamma(x) = k_2\, x(x-1)(x-2) + k_4 x$ (loss term)

This corresponds to

$$\boxed{\frac{dx}{dt} = g(x) - \Gamma(x) \cong -k_2 x^3 + k_1 A x^2 - k_4 x + k_3 A}$$

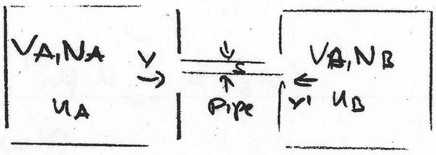
where we have assumed $x \gg 1 \wedge x(x-1)(x-2) \simeq x^3$

* Thermodynamics (supplement) *

Transits:

$\Delta N_A = n_A s v \Delta t$ (Molecules A to B)

$\Delta N_B = n_B s v \Delta t$ (" B to A)



Thus: $p(0) = 1 - \Delta N_{A,B}$ Probability of no molecules in pipe

$p(1) = \Delta N_{A,B}$ prob. of 1 molecule.

$$\Delta N_{A,B} = \frac{N_{A,B}}{V_{A,B}} s v \Delta t$$

Master Equation. $W_A(\delta N_A, N_A)$ transition probability of transferring δN_A molecules from V_A to V_B

$$\begin{aligned} P(N_A, t+\delta t) &= W_A(0, N_A) W_B(0, N_b) P(N_A, t) \\ &+ W_A(1, N_A+1) W_B(0, N_A-1) P(N_A+1, t) \\ &+ W_A(0, N_A-1) W_B(1, N_A+1) P(N_A-1, t) + \mathcal{O}(\delta t^2) \end{aligned}$$

$\Leftrightarrow$

$$\boxed{\begin{aligned} \frac{d}{dt} P(N_A, t) = \frac{sv}{a(1-a)V} \{ &(1-a)(N_A+1) P(N_A+1, t) - N_A P(N_A, t) \\ &+ a(N - N_A + 1) P(N_A - 1, t) - (N - N_A) P(N_A, t) \end{aligned}}$$

$V_B = (1-a)V$

VAN KAMPEN SIZE EXPANSION.

$$\boxed{N_A = \underbrace{V \cdot \varphi_A(t)}_{\text{macroscopic part}} + \underbrace{\sqrt{V}\, \xi(t)}_{\text{Fluctuations}}}$$

(e.g. see "Stochastic Processes and Non-Eq. Stat. Phys")

Lecture THE MASTER EQUATION PART II

Detailed Balance

$$\boxed{\sum_{u' \in \Sigma} \left(P_{u'}^{s} W(u'|u) - P_{u}^{s}(u|u')\right) = 0}$$

- Detailed Balance requires that each state is in equilibrium:

E_n: set of eigenenergies

$$\boxed{P_{u'}^{s} W(u'|u) = P_{u}^{s}(u|u')} \quad \forall u, u'$$

The stationary solution for a system in thermal equilibrium with a BATH @ Temp T satisfies:

Z: canonical ensemble
s: stationary
e: equilibrium
β: $1/k_BT$

$$P_n^s = P_n^e = Z^{-1} \cdot e^{-\beta E_n} \cdot d_n \qquad d_n\text{: degeneracy}$$

i.e. $$d_{u'} e^{-E_{u'}/k_BT} W_{u'u} = d_u e^{-E_u/k_BT} W_{uu'}$$

Hence for the simple case $d_{u'} = d_u$ we have:

$$\boxed{\frac{P_{u'}^{e}}{P_u^e} = \frac{W(u|u')}{W(u'|u)} = \frac{e^{-E_{u'}/k_BT}}{e^{-E_u/k_BT}} = e^{-\frac{1}{k_BT}(E_{u'}-E_u)}} \quad \text{EQUILIBRIUM } (*)$$

- Simulation of system fluctuations in thermal equilibrium:
  Algorithm Monte Carlo Metropolis

e.g. use function such that $(*)$ is always satisfied (i.e. ratio $\frac{W(u|u')}{W(u'|u)}$)

$$\boxed{F(x) = x F\left(\tfrac{1}{x}\right)} (*)_2 \quad \text{and} \quad \boxed{F\left(\frac{P^e_{u'}}{P^e_n}\right) \equiv W(n,u')} \quad \text{define our transition rates}$$

this implies that

$$\frac{W(u,u')}{W(u',u)} = \underbrace{\frac{F(P^e_{u'}/P^e_u)}{F(P^e_u/P^e_{u'})}}_{\text{note different argument}} = \frac{P^e_{u'}}{P^e_{u'}} \underbrace{\boxed{\frac{F(P^e_{u'}/P^e_n)}{F(P^e_n/P^e_{n'})}}}_{=1 \ (*)_2} = \frac{P^e_{n'}}{P^e_n} \Rightarrow \text{always satisfies Equilibrium relation.}$$

$$\downarrow \quad \hat{=} F\left(\frac{P^e_{n'}}{P^e_n}\right)$$

e.g. $F(x) = \min(x,1) \quad x > 0$
or $F = x/(1+x)$

Monte Carlo – Algorithm:

(i) choose a state (random or by prescription) u'. Choose u (or loop through the states)

(ii) Calculate $E_{n'} - E_u = \Delta E$

i.e.: $W_{uu'} = \min(1,x)$, $x = e^{-\Delta/k_BT}$

(iii) If $\Delta E < 0 \rightarrow W_{uu'} = 1$

$$W_{u,u'} = \begin{cases} 1 \\ e^{-\beta(E_{u'}-E_u)} \end{cases}$$

or If $\Delta E > 0 \quad W_{uu'} = e^{-\Delta E/k_BT}$ $\Big\{$ Compare to random number (0...1) if random number (R)

(iv) restart

acceptance if $R < e(-\Delta E/k_BT)$

In a simulation we can choose $W_{u,u'}$ at will as long as Equilibrium $(*)$ is satisfied i.e. $W(u,u')/W(u',u) = e^{-\Delta E\beta}$.

Historical Note: Metropolis 1933 → Manhattan Project (study of Neutron diffusion), Method to generate a sequence of random states.

⇒ Method is practical for systems where configuration state is very large. ⇐

Stat Phys IV Master Equation

Entropy out of Equilibrium:

$$S(t) = -k_B H(t) + S^{equil.}$$

and $$S^{equil} = -k_B \sum P_n^e \ln(P_n^e)$$

$$S(t) = -k_B\left(\sum P_n(t) \ln\left(\frac{P_n(t)}{P_n^e}\right)\right) + \sum P_n^e \ln(P_n^e)$$

Allows numerically computing entropy of system out of equilibrium (→ see eg CROOKS / JARZYNSKI EQUALITY).