Lecture 6 summary

2. Classical statistics in non-equilibrium

2.1 Master equation

- for a discrete state n (particle number)

$$\boxed{\frac{\partial}{\partial t} p_n(t) = \sum_{m \neq n} [\underbrace{W_{nm}\, p_m(t)}_{\substack{n \leftarrow m \\ \text{gain}}} - \underbrace{W_{mn}\, p_n(t)}_{\substack{m \leftarrow n \\ \text{loss}}}]}$$

- for one-step processes (birth-death): $W_{nn'} = \underbrace{r_{n'}}_{\text{recomb.}} \delta_{n,n'-1} + g_{n'} \delta_{n,n'+1}$

$$\boxed{\dot{p}_n = r_{n+1}\, p_{n+1} + g_{n-1}\, p_{n-1} - (r_n + g_n)\, p_n}$$

p_n – probability of finding the system in state n

g_n – generation rate (birth)

r_n – recombination rate (death)

Classification

(i) $r_n, g_n = \text{const}$ – random walk

(ii) r_n, g_n linear in n – random process

(iii) r_n, g_n nonlinear in n – bimolecular recomb.

Special case of (i): $g_n = g$, $r_n = 0$ – Poisson process

Stationary solution of master equation p_n^*

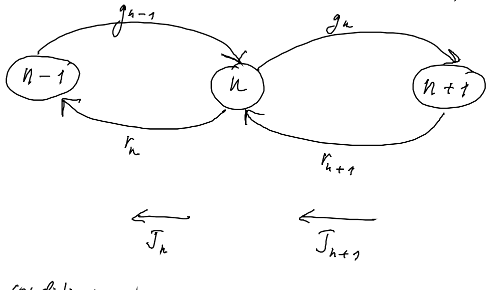
we can write the equation for the stationary solution p_n^* as

(1) $\boxed{0 = J_{n+1} - J_n}$ with

$J_n = r_n p_n^* - g_{n-1} p_{n-1}^*$

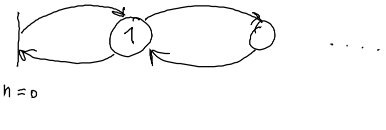
J_{n+1} – incoming probability flow in state n: $n+1 \to n$

J_n – outcoming probability flow in state n: $n \to n-1$



Boundary conditions $n=0$:

$r_n = 0$, $p_{n<0} = 0$



(no probability of an individual dying if there are none present; n is non-negative integer since we cannot have a negative number of individuals)

$J_0 = 0 \quad \left(J_0 = r_0 p_0^* - g_{0-1} p_{0-1}^* = 0 \right)$

We now sum (1) so

$$0 = \sum_{n'=0}^{n-1} \left(J_{n'+1} - J_{n'} \right) = J_n - \underbrace{J_0}_{=0}$$

$$\Rightarrow J_n = 0 \Rightarrow p_n^* = \frac{g_{n-1}}{r_n} p_{n-1}^* \qquad (*)$$

$$\boxed{p_n^* = p_0^* \prod_{n'=1}^{n} \frac{g_{n'-1}}{r_{n'}}} \quad \text{stationary solution}$$

<u>Detailed balance interpretation</u>

The condition $J_n = 0$ can be seen as a detailed balance requirement.

<u>Rate equations</u>

We notice that the mean of N satisfies

$$\frac{d}{dt}\langle N \rangle = \sum_{n=0}^{\infty} n \dot{p}_n = \sum_{n=0}^{\infty} n \left(\underbrace{r_{n+1}}_{\tilde{n}} \underbrace{p_{n+1}}_{\tilde{n}} - r_n p_n \right) + \sum_{n=0}^{\infty} n \left(\underbrace{g_{n-1}}_{\tilde{n}} \underbrace{p_{n-1}}_{\tilde{n}} - g_n p_n \right) =$$

$$= \sum_{\substack{\tilde{n}=\cancel{1} \\ 0 \text{ since } r_0 = 0}}^{\infty} (\tilde{n}-1) r_{\tilde{n}} p_{\tilde{n}} - \sum_{n=0}^{\infty} n r_n p_n + \sum_{\substack{\tilde{n}=\cancel{-1} \\ 0 \text{ since } \tilde{n}+1=0 \\ \text{for } \tilde{n}=-1}}^{\infty} (\tilde{n}+1) g_{\tilde{n}} p_{\tilde{n}} - \sum_{n=0}^{\infty} n g_n p_n =$$

$$= \sum_{n=0}^{\infty} g_n p_n - \sum_{n=0}^{\infty} r_n p_n$$

$$\boxed{\langle \dot{N} \rangle = \langle g_n \rangle - \langle r_n \rangle}$$

NB: for nonlinear processes this does not give a closed equation for mean values since $\langle N^2 \rangle \neq \langle N \rangle^2$, but a hierarchy for moments $\frac{d}{dt}\langle N^k \rangle$.

The corresponding <u>deterministic</u> equation is that which would be obtained by neglecting fluctuations:

$$\frac{dN}{dt} = g_n - r_n$$

Notice that a stationary state occurs deterministically when (no evolution in time):

$g_n = r_n$ Corresponding to this, notice that the maximum value of p_n^* occurs when:

$$\frac{p_n^*}{p_{n-1}^*} \simeq 1, \text{ which from } (*) \text{ corresponds to}$$

$$g_{n-1} = r_n$$

For sufficiently large N, $g_n = r_n$ and $g_{n-1} = r_n$ are essentially the same. Thus, the modal value of N, which corresponds to $g_{n-1} = r_n$, is the stationary stochastic analogue of the deterministic steady state that corresponds to $g_n = r_n$.

<u>Example</u> : chemical reaction $X \rightleftharpoons A$

We treat the case of a reaction $X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A$ in which it is assumed that A is a fixed concentration a (X plays a role of random variable $N(t)$). Therefore:

$$g_n = k_2 a$$

$$r_n = k_1 n$$

The Master equation takes form:

$$\boxed{\dot{p}_n = k_2 a\, p_{n-1} + k_1 (n+1)\, p_{n+1} - (k_1 n + k_2 a)\, p_n}$$

<u>generating function</u>

To solve the equation, we introduce the generating function

$$G(s,t) = \sum_{n=0}^{\infty} s^n p_n(t) \quad \text{so that}$$

$$\boxed{\frac{\partial}{\partial t} G(s,t) = k_2 a (s-1) G(s,t) - k_1 (s-1) \frac{\partial}{\partial s} G(s,t)} \qquad (**)$$

If we substitute $\varphi(s,t) = G(s,t)\, e^{\frac{-k_2 a s}{k_1}}$ the equation $(**)$ becomes

$$\partial_t \varphi(s,t) = k_1 (s-1)\, \partial_s \varphi(s,t)$$

$\Big|$ $\partial_t = \frac{\partial}{\partial t}$
$\exp = e$

The further substitution $s - 1 = e^z$,

$$\varphi(s,t) = \Psi(z,t) \quad \text{gives}$$

$$\partial_t \Psi(z,t) + k_1\, \partial_z \Psi(z,t) = 0$$

whose solution is an arbitrary function of $(k_1 t - z)$. For convenience write this as

$$\Psi(z,t) = F\left[\exp(-k_1 t + z)\right] e^{-\frac{k_2}{k_1} a} =$$

$$= F\left[(s-1)\, e^{-k_1 t}\right] e^{-\frac{k_2}{k_1} a} \quad \text{so} \Rightarrow$$

$$\Rightarrow \boxed{G(s,t) = F\left[(s-1)\, e^{-k_1 t}\right] \exp\left[(s-1)\frac{k_2}{k_1} a\right]}$$

Normalization requires $G(1,t) = 1$, and hence

$$F(0) = 1.$$

The initial conditions determine F $\Rightarrow$

I.C. $p_n(0) = \delta_{n,n_0} \Rightarrow G(s,0) = F(s-1)\, e^{(s-1)\frac{k_2 a}{k_1}}$

$$\Rightarrow \boxed{G(s,t) = \exp\left[\frac{k_2}{k_1} a (s-1)(1-e^{-k_1 t})\right]\left(1+(s-1)e^{-k_1 t}\right)^{n_0}}$$

From the generating function we can compute:

$$\langle N(t)\rangle = \partial_s G(s=1,t) = \frac{k_2}{k_1} a (1-e^{-k_1 t}) + n_0 e^{-k_1 t}$$

$$\langle N(t)^2\rangle = \underbrace{\partial_s^2 G(s=1,t)}_{\langle N(N-1)\rangle} + \langle N\rangle = \left(n_0 e^{-k_1 t} + \frac{k_2}{k_1} a\right)\left(1-e^{-k_1 t}\right)$$

$\partial_s^2 = \frac{\partial^2}{\partial s^2}$

Moment equations from the differential equation $\underset{\partial_t G(s,t)}{(**)}$

$k = 1,2,3\ldots$

$$\partial_t \left[\partial_s^k G(s,t)\right] = \Big\{ k\left[k_2 a\, \partial_s^{k-1} - k_1 \partial_s^k\right] + (s-1)\left[k_2 a\, \partial_s^k - k_1 \partial_s^{k+1}\right]\Big\} G(s,t)$$

setting $s=1$ and using

$\partial_s^k = \frac{\partial^k}{\partial s^k}$

$$\partial_s^k G(s,t)\Big|_{s=1} = \underset{\text{factorial moment}}{\langle N(t)^k\rangle_f} = \langle N(N-1)\ldots(N-k+1)\rangle$$

we find

$$\boxed{\frac{d}{dt}\langle N(t)^k\rangle_f = k\left[k_2 a \langle N(t)^{k-1}\rangle_f - k_1 \langle N(t)^k\rangle_f\right]}$$

and these equations form a closed hierarchy.