English Summary:

2. Classical statistics in nonequilibrium

2.1 Master eq.: discrete state n (particle number)

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

jump processes

Beispiel: Zerfall $\quad W_{nn'} = \gamma n' \delta_{n,n'-1}$

$$\dot{p}_n = \gamma [\underbrace{(n+1) p_{n+1}}_{n \leftarrow n+1} - \underbrace{n p_n}_{n-1 \leftarrow n}] \qquad \text{Anf. bed. } p_n(0) = \delta_{n,n_0}$$

Ableitung einer Rategl. (Mittelwertgl. $\langle N(t) \rangle = \sum_{n=0}^{\infty} n p_n(t)$)

$$\sum_{n=0}^{\infty} n \dot{p}_n = \gamma \sum_{n=0}^{\infty} [n \underbrace{(n+1)}_{\tilde{n}} p_{\underbrace{n+1}_{\tilde{n}}} - n^2 p_n]$$

$$= \gamma \left[\sum_{\tilde{n}=\cancel{1}\, 0}^{\infty} (\tilde{n}-1) \tilde{n} p_{\tilde{n}} - \sum_{n=0}^{\infty} n^2 p_n \right] = -\gamma \sum_{n=0}^{\infty} n p_n$$

0 weil $\tilde{n}=0$ keinen Beitrag gibt

$$\frac{d}{dt} \langle N(t) \rangle = -\gamma \langle N \rangle \quad \Rightarrow \quad \langle N(t) \rangle = n_0 e^{-\gamma t}$$

(funktioniert nur für lineare Prozesse!)

Ein-Schritt-Prozesse (birth-death processes)

(z.B. Population, chem. Reaktion, Absorption/Emission eines Photons, Anregung/Relaxation eines Atoms, Generation/Rekombination eines Elektrons im Halbleiter)

$$W_{nn'} = r_{n'} \delta_{n,n'-1} + g_{n'} \delta_{n,n'+1}$$

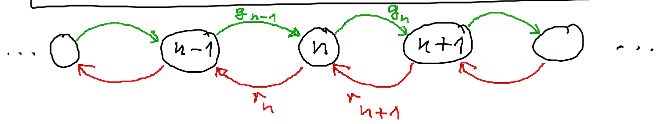
$n' \to n'-1$ (Rekomb.) $r_{n'}$

$n' \to n'+1$ (generation) $g_{n'}$

Übergangswahrscheinlichkeiten pro Zeiteinheit
(i.a. von n' abhängig!)

Mastergl.

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



Randeffekte ($n=0$): $\dot{p}_0 = r_1 p_1 - g_0 p_0$

Klassifikation:

(i) r_n, g_n = const. (unabh. v. n): random walk

(ii) r_n, g_n linear in n (z.B. Zerfallsprozess)

(iii) r_n, g_n nichtlinear in n (z.B. bimolekulare Rekombination, Auger-Prozesse)

Speziell (i) $r_n = 0$, $g_n = q$, $p_n(0) = \delta_{n,0}$ Poisson-Prozess

Mastergl. $\dot{p}_n = q(p_{n-1} - p_n)$ $(n \neq 0)$, Lösung $p_n(t) = \frac{(qt)^n}{n!} e^{-qt}$

$\langle n \rangle = qt$

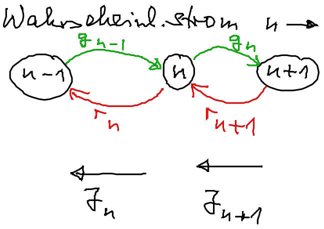
Stationäre Lösung der Mastergl. p_n^*

(1) $0 = J_{n+1} - J_n$ mit $J_n = r_n p_n^* - g_{n-1} p_{n-1}^*$

Einstrom- Ausstrom- Wahrscheinl.strom in Zustand n

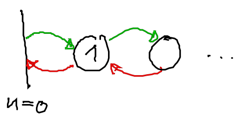
$n+1 \to n$ $\quad n \to n-1$

Wahrscheinl.strom $n \to n-1$



Randbed. bei $n=0$:

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

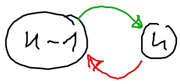


Gl. (1) aufsummiert: $0 \overset{!}{=} \sum_{n'=0}^{n-1} \left(J_{n'+1} - J_{n'}\right) = J_n - \underbrace{J_0}_{0}$ (Rand!)

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

rekursiv: $\boxed{p_n^* = p_0^* \prod_{n'=1}^{n} \frac{g_{n'-1}}{r_{n'}}}$

Detaillierte Bilanz (detailed balance): $J_n = 0$



für jeden einzelnen Schritt

Ratengl.

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

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

0, da $r_0 = 0$ 0, da $\tilde n + 1 = 0$ für $\tilde n = -1$

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

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

NB: Für nichtlineare Prozesse liefert dies keine geschlossene Gl. für Mittelwerte, weil $\langle N^2\rangle \neq \langle N\rangle^2$, sondern Hierarchie für Momente $\frac{d}{dt}\langle N^k\rangle$

Beispiel: Chem. Reaktion $X \underset{k_2}{\overset{k_1}{\rightleftarrows}} A$

$g_n = k_2 a$ X reagierende Spezies (Zufallsvar. $N(t)$)

$r_n = k_1 n$ A fest (Konzentration a)

Mastergl. $\dot p_n = k_2 a\, p_{n-1} + k_1 (n+1) p_{n+1} - (k_1 n + k_2 a) p_n$

Erzeugende Fkt. $G(s,t) = \sum_{n=0}^{\infty} s^n p_n(t)$

für $p_n(t) = n! \frac{\partial^n}{\partial s^n} G\Big|_{s=0}$

$$\Rightarrow \frac{\partial}{\partial t} G(s,t) = k_2 a \left[\sum_n s^n \underbrace{p_{n-1}}_{\tilde n} - \sum_n s^n p_n\right] + k_1 \left[\sum_n (n+1) s^n \underbrace{p_{n+1}}_{\tilde n} - \sum_n n s^n p_n\right]$$

$$= k_2 a (s-1)\sum_n s^n p_n - k_1 (s-1) \underbrace{\sum_n n s^{n-1} p_n}_{\frac{\partial}{\partial s}\sum_n s^n p_n}$$

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

Mit $\phi(s,t) := G(s,t)\, e^{-\frac{k_2}{k_1} a s}$

$$\frac{\partial}{\partial t}\phi(s,t) = -k_1 (s-1)\frac{\partial}{\partial s}\phi(s,t)$$

mit $s-1 = e^{z}$, $\phi(s,t) = \psi(z,t)$:

$$\frac{\partial}{\partial t}\psi(z,t) + k_1 \frac{\partial}{\partial z}\psi(z,t) = 0$$ Lös.: bel. Fkt. $F(k_1 t - z)$

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

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

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

Normierung: $G(1,t) = 1 \quad \Rightarrow \quad F(0) = 1$

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

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

$\Rightarrow p_n(t)$ durch Taylorentwicklung

Daraus

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

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

Hierarchie der Momentengln.:

$$\boxed{\frac{d}{dt}\langle N^k\rangle_f = k\left[k_2 a \langle N^{k-1}\rangle_f - k_1 \langle N^k\rangle_f\right]} \qquad k = 1, 2, 3, \ldots$$

folgt aus $\frac{\partial^k}{\partial s^k} G(s,t)\Big|_{s=1} = \langle N^k\rangle_f \equiv \langle N(N-1)\ldots(N-k+1)\rangle$

(factorial moment)