12. NOISE AND STOCHASTIC CHEMICAL KINETICS

12.1. FOUNDATIONS

Assumption: system is <u>well-mixed</u>, i.e.

(1) Prob. that a given pair of molecules reacts is independent of time

(2) A given molecule is equally likely to interact with every other molecule in the system.

Consider a system with two molecules A, B that react to form C:

$$A + B \xrightarrow{k} C$$

$k\,dt$: Prob. for reaction in $[t, t+dt)$

$f(t)$: Probability density for time of reaction if $t_0 = 0$

$F(t) = \int_0^t dt' f(t')$: cumulative prob. for reaction to occur at $T < t$.

$G(t) = 1 - F(t) = P(T > t)$: Prob. that reaction occurs at $T > t$

For well-mixed system (Markov assumption):

$P(T > t + \tau \mid T > \tau) = P(T > t)$: Memoryless!

(Def. of cond. prob. $P(A \mid B) = P(A \cap B)/P(B) \Rightarrow P(A \cap B) = P(A \mid B)\, P(B)$)

$$P(T > t+\tau \text{ AND } T > \tau) = P(T > t+\tau) \overset{\downarrow}{=} \underbrace{P(T > t+\tau \mid T > \tau)}_{P(T > t)} \cdot P(T > \tau)$$

$$\Rightarrow P(T > t+\tau) = P(T > t)\, P(t > \tau)$$

$$\Rightarrow G(t+\tau) = G(t)\, G(\tau)$$

$$\Rightarrow G(t) = e^{-\alpha t}, \quad F(t) = 1 - e^{-\alpha t}$$

$$F(dt) = 1 - e^{-\alpha dt} \cong 1 - (1 - \alpha dt) = \alpha dt \overset{!}{=} k\,dt$$

$$f(t) = \frac{d}{dt} F(t) = k e^{-kt}$$

12.2 CHEMICAL MASTER EQUATION

A, B, C SYSTEM: discrete state, continuous time Markov process

Two states:

STATE 1		STATE 2
A : 1		A : 0
B : 1	$\xrightarrow{k}$	B : 0
C : 0		C : 1

Probs. for states:

$$P_1(t) = e^{-kt} \qquad (= G(t))$$

$$P_2(t) = 1 - e^{-kt} \qquad (= F(t))$$

$$\dot{P}_1 = -k e^{-kt} = -k P_1(t)$$

$$\dot{P}_2 = +k e^{-kt} = +k P_2(t)$$

$$\dot{P} = \begin{pmatrix} \dot{P}_1 \\ \dot{P}_2 \end{pmatrix} = \begin{pmatrix} -k & 0 \\ +k & 0 \end{pmatrix} P$$ "Chemical master equation"

EXAMPLE 1: $A + B \xrightarrow{k} C$, 4A, 3B

$$\begin{bmatrix} A:4 \\ B:3 \\ C:0 \end{bmatrix} \xrightarrow{12k} \begin{bmatrix} A:3 \\ B:2 \\ C:1 \end{bmatrix} \xrightarrow{6k} \begin{bmatrix} A:2 \\ B:1 \\ C:2 \end{bmatrix} \xrightarrow{2k} \begin{bmatrix} A:1 \\ B:0 \\ C:3 \end{bmatrix}$$

$$\begin{pmatrix} \dot{P}_0 \\ \dot{P}_1 \\ \dot{P}_2 \\ \dot{P}_3 \end{pmatrix} = \begin{pmatrix} -12k & 0 & 0 & 0 \\ 12k & 6k & 0 & 0 \\ 0 & -6k & -2k & 0 \\ 0 & 0 & 2k & 0 \end{pmatrix} \begin{pmatrix} P_0 \\ P_1 \\ P_2 \\ P_3 \end{pmatrix}$$

$P_0(t=0) = 1$ $\quad P_0(t) = e^{-12kt}$

$P_1(t) = 2e^{-12kt}(e^{6kt} - 1)$

$\vdots$

$$\langle c \rangle = \sum_i i p_i = 3 - \frac{1}{5} e^{-12t} - e^{-6t} - \frac{9}{5} e^{-2t}$$ mean

$$\langle c^2 \rangle = \sum_i i^2 p_i = 9 - e^{-12t} + e^{-6t} - 9e^{-2t}$$

EXAMPLE 2: $\xrightarrow{k_1} m \xrightarrow{k_2} \phi$

STATES $m = 0, 1, 2, \ldots$

$\dot{P}_0 = -k_1 P_0 + k_2 P_1$

$\dot{P}_1 = +k_1 P_0 - (k_1 + k_2) P_1 + 2k_2 P_2$

$\dot{P}_2 = k_1 P_1 - (k_1 + 2k_2) P_2 + 3k_2 P_3$

$\vdots$

STEADY STATE:

$P_1^* = \frac{k_1}{k_2} P_0$

Adding the first two equations:

$0 = -k_1 P_1^* + 2k_2 P_2^* \implies P_2^* = \frac{k_1}{2k_2} P_1^* = \frac{k_1^2}{2k_2^2} P_0^*$

Adding the first n equations:

$$P_n^* = \frac{\alpha^n}{n!} P_0^* \qquad \alpha = k_1/k_2$$

What is P_0

$$\sum_{n=0}^{\infty} P_n^* = \sum_{n=0}^{\infty} \frac{\alpha_n}{n!} P_0 = 1$$

$$\Rightarrow P_0^{-1} = \sum_{n=0}^{\infty} \frac{\alpha_n}{n!} = e^{\alpha}$$

$$\Rightarrow P_0 = e^{-\alpha}, \quad P_n^* = \frac{\alpha^n}{n!} e^{-\alpha}$$

$$\langle m \rangle = \sum_{n=0}^{\infty} n P_n = \alpha = \frac{k_1}{k_2}$$

$$\langle m^2 \rangle = \sum n^2 P_n^* = \alpha + \alpha^2$$

STANDARD DEV: $\sqrt{\langle m^2 \rangle - \langle m \rangle^2} = \sqrt{\alpha} = \sqrt{k_1/k_2}$