Stochastic Master Equation

- the SME gives us a complete description of sys evolution
- it tells us, for every state S, how P(S,t) increases or decreases due to events

- $W_{S_1 \to S_2} = \sum_{k:\, R_k(S)=S_2} \omega_k(S_1)$

  total rate of all events take S_1 to S_2

- We can write the time evolution of **P**(s,t) in the form of a differential difference eq.

$$\frac{d\,P(S,t)}{dt} = \sum_{s' \in \Sigma} \Big(\underbrace{W_{s' \to s} P(s',t)}_{\text{gain/inflow}} - \underbrace{W_{s \to s'} P(s,t)}_{\text{loss out flow}} \Big)$$

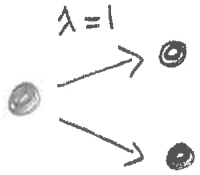
first-order differential eq in time
difference eq in state space

- complete probabilistic definition
- exact + fully charachterizes systems evolution

... often intractable + hard to numerically solve
ω very sparse

→ approx methods
→ coarse-graining → deterministic
→ gillespie → answers same q but in a way that lends it's self to be simulated.

Birth Process



State $\quad S = n \in \mathbb{N}$

Event $\quad \mathcal{E} = \{R\} \qquad R(n) = n+1$

rate $\quad \omega =$ n° particles × rate 1 particle

$\omega(n) = n\lambda$

$P_n(t) =$ Prob ∃ n particles at time t

$$\frac{dP_n(t)}{dt} = \text{gain into } S=n + \text{loss from } S=n$$

gain

can only come from

$$\sum_{s' \in S} W_{s' \to s} P(s', t) = \sum_{s' \in S} \sum_{k: R_k(s')=s} \omega_k(s')$$

only 1 reaction + one state

$$\omega(n-1) P_{n-1}(t) = (n-1)\lambda P_{n-1}(t)$$

loss

$$\omega(n) P_n(t)$$

Put together

$$\boxed{\frac{dP_n(t)}{dt} = (n-1)\lambda P_{n-1} - n\lambda P_n}$$

$\lambda = 1$ $\quad P_n(t=0) = \delta_{n,1}$ (one particle)

recursive approach

$$\dot{P}_n(t) = (n-1)P_{n-1}(t) - n P_n(t)$$

$$\Rightarrow \dot{P}_1(t) = -P_1(t) \longrightarrow \boxed{P_1(t) = P_1(t=0)\, e^{-t} = e^{-t}}$$

$$\Rightarrow \dot{P}_2(t) = P_1(t) - 2P_2(t)$$

$$\Rightarrow \left[\dot{P}_2 + 2P_2 = P_1 = e^{-t}\right] \times e^{\int 2\,dt} \quad e^{2t}$$

$$\Rightarrow \frac{d}{dt}\left[e^{2t} P_2(t)\right] = P_1 e^{2t} = e^{t}$$

Integrating factor

$$\left[\frac{dy}{dt} + P(t)y = q(t)\right] \times e^{\int P(t)dt}$$

$$\longrightarrow \frac{d}{dt}\left[\mu(t)y(t)\right] = \mu(t)\, q(t)$$

$$\frac{d}{dt}\left[\mu(t)y(t)\right] = \frac{d}{dt}\mu(t)\, y(t) + \mu(t)\frac{dy(t)}{dt}$$

if we choose $\frac{d\mu}{dt} = \mu(t)P(t)$

$\Rightarrow \mu(t) = e^{\int P(t)dt}$

then

$$\frac{d}{dt}\left[\mu(t)y(t)\right] = \mu(t)\frac{dy}{dt} + \mu(t)P(t)y$$

$P_2(t=0) = 0$

$$\longrightarrow e^{2t}P_2(t) = e^{t} + A$$

$$0 = 1 + A \Rightarrow A = -1$$

$$\longrightarrow \boxed{P_2(t) = e^{-t} - e^{-2t}}$$

∴ is there a better way?

yes $\longrightarrow$ generating function

generating function (encapsulation of sequence)

$$P(z) = \sum_{n=1}^{\infty} P_n(t)\, z^n$$

given a sequence $\{F_n\} = F_1, F_2, \dots$

$$F(z) = \sum_{n=0}^{\infty} F_n z^n$$

if we can solve $F(z)$ we know entire sequence

discrete version of laplace

z controls how far we look

generating function approach

$$P(z) = \sum_{n=1}^{\infty} P_n(t)\, z^n$$

$$\frac{\partial P}{\partial z} = \sum_{n=1}^{\infty} n P_n z^{n-1}$$

$$\frac{\partial P}{\partial t} = \sum_{n\geq 1} \dot{P}_n z^n$$

$$\sum_n \left[\dot{P}_n = (n-1) P_{n-1} - n P_n \right] \times z^n$$

$$\dot{P}(z) = \underbrace{\sum_{n\geq 1} (n-1) P_{n-1} z^n}_{①} - \underbrace{\sum_{n\geq 1} n P_n z^n}_{②}$$

$$= z^2 \frac{\partial P}{\partial z} - z \frac{\partial P}{\partial z}$$

$$\boxed{\dot{P}(z) = z(z-1)\frac{\partial P}{\partial z}}$$

1-dim wave eq from differential diff

① $\sum_{n\geq 1} (n-1) P_n z^n$

$$= z \sum_{n\geq 1} (n-1) P_{n-1} z^{n-1}$$

$$= z \left[0 + \sum_{n=2}^{\infty} (n-1) P_{n-1} z^{n-1} \right]$$

$$= z^2 \sum_{n=1}^{\infty} n P_n z^{n-1}$$

$$= z^2 \frac{\partial P}{\partial z}$$

Solve via method of charachteristics

* let us look for solutions along charachteristic $\bar{P}$ $(z(t), t)$ curve where P is constant

$$\frac{d}{dt} P(z(t), t) = 0 \Rightarrow \frac{\partial P}{\partial t} + \frac{\partial z}{\partial t}\frac{\partial P}{\partial z} = 0$$

$$\Rightarrow P(z(t), t) = f(y, t)$$

* compare with $\dfrac{\partial \dot{P}}{\partial t} + (-z(z-1))\dfrac{\partial P}{\partial z} = 0$

and IC $P(z, t=0) = \sum P_n(t=0) z^n = z$

solve $\dfrac{dz}{dt} = -z(z-1)$

$$\int \frac{dz}{z(z-1)} = -\int dt \rightarrow \int \left(\frac{1}{z} - \frac{1}{z-1} \right) dz = -\int dt \rightarrow \ln\left(\frac{z}{z-1}\right) = -t + C$$

$$\rightarrow \frac{z}{z-1} = A e^{t}$$

$$\rightarrow \boxed{A = \frac{z}{z-1} e^{-t}}$$

(2) Because P is constant along characteristics

$$P(z,t) = f\left(\frac{z}{z-1} e^{-t}\right)$$

at $t=0$ we know

$$P(z,t=0) = f\left(\frac{z}{z-1}\right) = z$$

↳ lets solve $f(\omega)$ | $\omega = \frac{z}{z-1} \Rightarrow z = \frac{\omega}{\omega-1}$

$\boxed{f(\omega) = z = \frac{\omega}{\omega-1}}$ functional form

$$\therefore \quad f\left(\frac{z}{z-1} e^{-t}\right) = \frac{\frac{z}{z-1} e^{-t}}{\frac{z}{z-1} e^{-t} - 1}$$

↳ simplify

$$\boxed{P(z,t) = \frac{z e^{-t}}{z e^{-t} - (z-1)} = \frac{z e^{-t}}{1 - z(1-e^{-t})}}$$

$z e^{-t} - z + 1$

$1 + z(e^{-t}-1)$

(3) Power series expansion | $P(z,t) = \sum_{n=1}^{\infty} P_n(t) z^n$

use $\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n \quad |x|<1$

$$P(z,t) = z e^{-t} \cdot \frac{1}{1-z(1-e^{-t})}$$

$$= z e^{-t} \sum_{n=0}^{\infty} z^n (1-e^{-t})^n$$

$$= \sum_{n=0}^{\infty} z^{n+1} \left(e^{-t}(1-e^{-t})^n\right)$$

$n' = n+1$

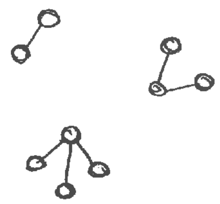
$$= \sum_{n'=1}^{\infty} z^{n'} \left[e^{-t}(1-e^{-t})^{n'-1}\right]$$

$$\boxed{P_n(t) = e^{-t}(1-e^{-t})^{n-1}}$$

observables + mean-field apprx

- SME often intractable
- for complex state spaces it is helpful to define an observable
- $f: \Sigma \to \mathbb{R}$ or $f: \Sigma \to \mathbb{R}^n$

ex/ S



$\longrightarrow$ $f(S) = \vec{n}$

$[n_1, n_2, n_3, n_4, \dots]$

$[0, 1, 1, 1, \dots]$

- We are now intrested in the time evolution of the expected value of this measure/observable

$$\bar{f}(t) = \langle f(S)\rangle(t) = \sum_S f(S)\,P(S,t)$$

(**) Heiristic + Broken down approach

**

① What happens when an event R_k occurs?

- state change $\quad S \to R_k(S)$
- measure $\quad f(S) \longrightarrow f(R_k(S))$
- net change $\quad \Delta_k f(S) = f(R_k(S)) - f(S)$

② How often does this event happen / what is the expected change in the observable due to one event?

- The process R_k has a rate $\omega_k(S)$ which gives the probability per unit time that it happens
- In a small time dt, the expected contribution of one process R_k:

$$\Delta_k f(S) \cdot \omega_k(S)\,dt$$

- This is still conditional on being in state S

③ Taking an average over all possible states + processes
(expected rate of change = average over all states)

- To find the overall expected change in f at time t, we average over all states + events

$$\frac{d}{dt}\langle f(S)\rangle(t) = \sum_k \overbrace{\sum_S \underbrace{\Delta_k f(S)}_{①} \cdot \underbrace{\omega_k(S)\, P(S,t)}_{②}}^{③}$$

1) change in observable due to each process
2) multiplied it by how likly that process is to happen at each state
3) Averaged over all possible states

$$\Rightarrow \frac{d}{dt}\langle f(S)\rangle(t) = \sum_k \langle \underbrace{\Delta_k f(S) \cdot \omega_k(S)}\rangle$$

this is the exact first-moment equation

Now the question becomes:

How does the expected value of $f(S)$, $\langle f(S) \rangle$, change over time

This can be calculated directly using the SHE (**) see notes for derivation

$$\frac{d}{dt}\langle f(S)\rangle(t) = \sum_{S\in\Sigma} f(S) \underbrace{\frac{d}{dt} P(S,t)}_{\text{Plug in}}$$

$$= \sum_{k} \langle \Delta_k f(S)\, \omega_k(S) \rangle$$

exact-first moment equation

$$\approx \sum_{k} \Delta_k f(\langle S \rangle)\, \omega_k(\langle S \rangle)$$

mean-field approx
assume weak correlations or small fluctuations

with $\Delta_k f(S) = f(R_k(S)) - f(S)$, which is the net change in the measurable when R_k happens $S \longrightarrow R_k(S)$ $f(S) \longrightarrow f(R_k(S))$

So here we have for each process R_k

(1) How much it changes the thing we are observing

(2) How often it happens, $\omega_k(\cdots)$

$\Rightarrow$ Multiply these together + average over all Possible states - or approximate using mean- and then sum over all events/Processes.

(**) **

Derivation from SHE

given $$\frac{d}{dt}\langle f(s)\rangle = \sum_{s\in\Sigma} f(s)\,\frac{d}{dt}P(s,t) \qquad (1)$$

we had from SHE

$$\frac{dp}{dt} = \sum_{s'}\Big[\underbrace{W_{s'\to s}\,P(s',t)}_{\text{gain}} - \underbrace{W_{s'\to s'}\,P(s,t)}_{\text{loss}}\Big]$$

with $$W_{s_1\to s_2} = \sum_{k:\,R_k(s_1)=s_2} \omega_k(s_1)$$

∴ the contribution to (1) from the $\boxed{\text{gain}}$

$$\sum_s f(s)\sum_{s'} W_{s'\to s}\,P(s',t)$$

$$\sum_{s_2}\sum_{k:\,R_k(s_1)=s_2} \Rightarrow \sum_k$$

$$= \sum_{s'}\sum_s f(s)\Big(\sum_{k:\,R_k(s')=s}\omega(s')\Big)P(s',t)$$

$s=R_k(s')$

$$\overset{R}{=} \sum_{s'} f(R_k(s'))\underbrace{\sum_s\sum_{k:\,R_k(s')=s}}_{\sum_k}\omega(s')\,P(s',t)$$

$$\boxed{= \sum_{s'}\sum_k f(R_k(s'))\,\omega_k(s')\,P(s',t)}$$

∴ contribution from $\boxed{\text{loss}}$

$$\sum_s f(s)\sum_{s'}W_{s\to s'}\,P(s,t) = \sum_s f(s)\underbrace{\sum_{s'}}_{\sum_k}\Big(\sum_{k:\,R_k(s)=s'}\omega_k(s)\Big)P(s,t)$$

$$= \sum_k\sum_s f(s)\,\omega_k(s)\,P(s,t)$$

$$\Rightarrow \frac{d}{dt}\langle f(s)\rangle = \sum_k\Big(\sum_s\big(f(R_k(s')) - f(s)\big)\,\omega_k(s)\,P(s,t)\Big)$$

$$= \sum_k\Big(\sum_s \Delta_k f(s)\,\omega_k(s)\,P(s)\Big)$$

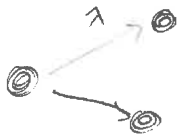
$$= \sum_k\langle \Delta_k f(s)\,\omega_k(s)\rangle$$

Birth Process revisted

$S = n \in \mathbb{N}$

$R: n \to n+1$

$\omega = n\lambda$



$$\frac{d\bar{f}(t)}{dt} = \sum_k \Delta_k f(\bar{S})\,\omega_k(\bar{S})$$

$f(n) = n$ (nº Particles)

$$\frac{d\bar{n}(t)}{dt} \approx \Delta f(\bar{n}) \cdot \omega(\bar{n})$$

- $\Delta f(\bar{n}) = (n+1) - n = \underline{1}$ w/ $\omega_k(n) = n$

$$\frac{dn}{dt} = \sum_k \Delta_k f(\langle S \rangle)\ \omega_k(\langle S \rangle)$$

$$= (1)(n)$$

---

solve $\dot{n}(t) = n(t)$ $\qquad n(t=0) = 1$

$$\Rightarrow \int \frac{dn}{n} = \int dt \longrightarrow \ln(n) = t + C \rightarrow n = Ae^{t}$$

$$\Rightarrow \boxed{n = e^{+t}}$$

Recall from SME

$$P_n(t) = e^{-t}(1-e^{-t})^{n-1}$$

$$\langle n \rangle = \sum_{n=0}^{\infty} n P_n(t)$$

$$= \sum_{n=1}^{\infty} n e^{-t}(1-e^{-t})^{n-1}$$

$$= e^{-t} \frac{\partial}{\partial a} \sum_{n=1}^{\infty} a^n$$

$$= e^{-t} \frac{\partial}{\partial a} a \sum_{n=1}^{\infty} a^{n-1}$$

$$= e^{-t} \frac{\partial}{\partial a} a \sum_{n=0}^{\infty} a^n$$

$$= e^{-t} \frac{\partial}{\partial a} \frac{a}{1-a}$$

$$= \frac{e^{-t}}{(1-a)^2} \overset{a=(1-e^{-t})}{=} \frac{e^{-t}}{e^{-2t}}$$

$$\boxed{\langle n \rangle = e^{t}} \longrightarrow \text{same solution}$$

$\frac{\partial}{\partial a}(a)^{n}$

$= n a^{n-1} \frac{\partial a}{\partial n}$

$a = (1-e^{-t})$

$\frac{1}{1-x} = \sum_{n=0} x^n \quad |x|<1$

$\frac{u'v - v'u}{v^2}$

$u = a \quad u' = 1$

$v = (1-a) \quad v' = -1$

$\frac{1-\cancel{a}+\cancel{a}}{(1-a)^2}$

$\frac{(1-e^{-t})^{2}}{1-2e^{-t}-e^{-2t}}$

Irriversible Aggregation

ex/ ① gravitational ecresion
② Blood coagulation
③ cloud formation
④ Polymirization

$$(i) + (j) \xrightarrow{K_{ij}} (i+j)$$

$$\bar{C}_k(t) = \frac{\bar{N}_k}{N} = \text{concentration of clusters of mass } k \text{ at time } t$$

Writting the master equation

- $S = (N_1, N_2, N_3, \ldots)$

$$\frac{d}{dt}\langle N_k\rangle(t)$$

- each aggregation event (i,j) $w_{ij} = K_{ij}$

$$A_i + A_j \xrightarrow{k_{ij}} A_{i+j}$$

So $R_{i,j}$

$N_i \to N_i - 1$
$N_j \to N_j - 1$
$N_{i+j} \to N_{i+j} + 1$

for identical particles

$$\binom{C_3}{2} = \frac{N_i(N_i-1)}{2} \approx \frac{1}{2}N_i^2$$

$$w_{ij}(S) = \begin{cases} k_{ij} N_i N_j & i \neq j \\ \frac{1}{2} k_{ii} N_i^2 & i = j \end{cases}$$

number of distinct pairs x rate per pair

- change in measure

$$\Delta_{ij} N_k = \begin{cases} +1 & \text{if } i+j=k \\ -1 & \text{if } i=k \text{ or } j=k \\ 0 & \text{otherwise} \end{cases}$$

$$\Rightarrow \frac{d}{dt} C_k = \frac{1}{2}\sum_{i,j}\left[K_{ij} N_i N_j\right]\left(\delta_{i+j,k} - \delta_{k,i} - \delta_{k,j}\right)$$

$$\boxed{\frac{d}{dt} C_k = \frac{1}{2}\sum_{i+j=k}\left[K_{ij} N_i N_j - N_k \sum_{i\geq 1} K_{ij} N_i\right.}$$

Smolukhowski Coagulation Eqn

Kernel ~ dependent only on mass

- encodes the physics
- in our case now assuming $N_{particles} \gg$ large, Shape + position dont matter

- 3 exactly soluble models

constant: $K_{ij} = \alpha$

sum: $K_{ij} = \beta(i+j)$

Product: $K_{ij} = \gamma ij$

Moments of $n_k(t)$ (help us capture shape)

$$M_n(t) = \sum_{k \geq 1} k^n n_k(t)$$

(decrease with time)

$M_0(t) = N_c(t) \longrightarrow$ Number of clusters / unit volume

$M_1(t) = N(t) \longrightarrow$ total mass (we expect this to be constant)
$= 1$

- $M_{n>1} \longrightarrow$ how mass is distributed across clusters
  - M_2 mass variance - grows over time as mass concentrates into larger clusters

* $M_1 / M_0 \equiv M/N$ gives average cluster mass

$M_{n+1} / M_n \equiv$ general

$\boxed{\text{Constant Kernel Aggregation}}$

lets for now take
$$C_k = \frac{N_k}{N}$$

$$K_{ij} = 2 \qquad C_k(t=0) = \delta_{k,0}$$

monomer only I.C.

$$\Rightarrow \boxed{\frac{d}{dt} C_k = \sum_{i+j=k} c_i c_j - 2 c_k \underbrace{\sum_i c_i}_{M_0(t)}}$$

Looking at the moments $\qquad M_n(t) = \sum_{k \geq 1} k^n c_k(t)$

typical mass $\quad M_{n+1}(t)/M_n(t)$

$$\dot{M}_n(t) = \sum_{k \geq 1} k^n \dot{c}_k(t)$$

$$= \underbrace{\sum_{k \geq 1} \sum_{i+j=k}}_{\text{unrestricted}} c_i c_j k^n - 2 \sum_{k \geq 1} c_k \sum_i c_i k^n$$

$$\boxed{\dot{M}_n(t) = \sum_{ij} (i+j)^n c_i c_j - 2 M_0(t) M_n(t)}$$

$\underline{\underline{n=0}}$ $\quad \dot{M}_0(t) = \sum_{ij} c_i c_j - 2 M_0^2 = -M_0^2 \xrightarrow{-\int \frac{1}{N^2} dN = dt} N_c(t) = \frac{1}{t+1}$

concentration decaying like $1/t$

$\underline{\underline{n=1}}$ $\quad \dot{M}_1(t) = \sum_{ij} (i+j) c_i c_j - 2 M_0 M_1 = 0 \longrightarrow N = \boxed{M_1(t) = 1}$

$\underline{\underline{n=2}}$ $\quad \dot{M}_2(t) = \sum_{ij} (i^2 + j^2 + 2ij) c_i c_j - 2 M_0 M_2 \longrightarrow \boxed{M_2(t) = 1 + 2t}$

$$= 2 \cancel{M_2 N} + 2 M_1^2 - 2 \cancel{M_2 M_0} = 2 M_1^2 = 2$$

(gives you an idea of typical cluster mass)

$\underline{\underline{n=3}}$

$$\dot{M}_3(t) = \sum_{ij} (i^3 + 3i^2 j + 3ij^2 + j^3) c_i c_j - 2 M_3 M_0 \longrightarrow \boxed{M_3(t) = 1 + 6t + 6t^2}$$

$$= 2 \cancel{M_3 N} + 2 \cdot 3 M_2 M_1 - 2 \cancel{M_3 M_0}$$

$$= 6 (1 + 2t)(1)$$

in general $\qquad M_n \simeq n!\, t^{n-1}$ as $t \to \infty$

Recursion Approach

$$\frac{dc_k}{dt} = \left\{ \sum_{i+j=k} c_i c_j \right\} - 2c_k \sum_{i=1}^{\infty} c_i \qquad N = \frac{1}{1+t}$$

$\underline{\underline{k=1}}$

$$\dot{c}_1 = -2c_1 M_0(t) = -\frac{2}{1+t} c_1$$

$c_1(0) = 1$

$$\longrightarrow \int \frac{1}{c_1} dc_1 = -2\int (1+t)^{-1} dt$$

$$\boxed{c_1 = (1+t)^{-2}}$$

$$\ln(c_1) = -2\ln(1+t) + C$$

exponentiate

$$c_1 = \cancel{A}^{1}(1+t)^{-2}$$

$\underline{\underline{k=2}}$

$$\dot{c}_2 = c_1^2 - 2c_2 M_0$$

$$= \frac{1}{(1+t)^4} - \frac{2c_2}{1+t}$$

Integrating factor $\mu(t)$

$$\left[\frac{dy}{dt} + p(t)y = q(t)\right] \times e^{\int p(t)dt}$$

$$\longrightarrow \frac{d}{dt}\left[\mu(t) C_2\right] = \mu(t) q(t)$$

$$\rightarrow \frac{d}{dt}c_2 + \frac{2}{1+t}c_2 = \frac{1}{(1+t)^4}$$

$$\mu(t) = e^{\int \frac{2}{1+t} dt} = e^{2\ln(1+t)} = (1+t)^2$$

$$\Rightarrow \frac{d}{dt}\left[(1+t)^2 c_2\right] = \frac{1}{(1+t)^2}$$

$$\Rightarrow (1+t)^2 c_2 = -\frac{1}{(1+t)} + A$$

$A = 1$

$$\Rightarrow \boxed{c_2 = t/(1+t)^3}$$

$\underline{\underline{k=3}}$

$$\dot{c}_3 = 2c_1c_2 - 2c_3 N$$

$$= 2t(1+t)^{-5} - 2(1+t)^{-1}c_3$$

$$\longrightarrow \boxed{c_3 = \frac{t^2}{(1+t)^4}}$$

$k=4$

$$\boxed{c_4 = \frac{t^3}{(1+t)^5}}$$

$k=5$

$$\boxed{c_5 = \frac{t^4}{(1+t)^{k+1}}}$$

general solution

$$\boxed{c_k(t) = \frac{t^{k-1}}{(1+t)^{k+1}}}$$

Alternative Approach : generating function

$$g(z,t) = \sum_{k=1}^{\infty} c_k(t) z^k$$

$$\frac{dc_k}{dt} = \underbrace{\sum_{i+j=k} c_i c_j}_{\text{convolution } ①} - \underbrace{2c_k \sum_{i=1}^{\infty} c_i}_{②}$$

$$\sum_k c_k = g(z=1,t)$$

$$= N(t)$$

$$g(z, t=0) = z$$

$$\sum_k ① \times z^k = \sum_i \sum_j c_i c_j z^i z^j = g(z,t)^2$$

$$\sum_k ② \times z^k = 2 \sum_k c_k z^k \cdot \underbrace{\sum_i c_i}_{k=1} = 2g(z,t)$$

$$\Rightarrow \boxed{\dot{g}(z,t) = g(z,t)^2 - 2g(1,t)\,g(z,t)}$$

because of the convolution structure we reduce

infinite ODE's $\longrightarrow$ single PDE !

$\dot{g}(z,t)$

$$g(1,t) = \sum c_k(t) = \mu_0$$

Solving the generating fonction

$$\boxed{\dot{g} = g^2 - 2gM_0} \quad - \quad \boxed{\dot{N} = -M_0^2}$$

$M_0 = \sum \sigma_k$
$= 1$
$g(z) = \sum c_k z^k$
$= z^1$

$$\dot{g} - \dot{N} = g^2 - 2gM_0 + M_0^2 = (g - M_0)^2$$

let $U = g - M_0$

$$\boxed{\dot{U} = U^2}$$

ricatti-equation

$$U(t=0) = \underbrace{g(z,0)}_{\sum n_k z^k} - M_0(0) = z - 1$$

$-\frac{1}{z-1} = 0 + A,$

$$\Rightarrow \quad -\frac{1}{U} = t + A = -\frac{1}{z-1}$$

$$\Rightarrow \quad \frac{1}{U} = \frac{t(z-1) - 1}{(z-1)} \rightarrow \boxed{U(z,t) = \frac{z-1}{1 - t(z-1)}}$$

$$M_0 = N_c = \frac{1}{1+t}$$

recovering $g = U + M_0$

$$g(z,t) = \frac{z-1}{1-t(z-1)} + \frac{1}{1+t}$$

$$= \frac{1}{1+t}\,\frac{z}{1-(z-1)t} = \frac{z}{(1+t)^2}\,\frac{1}{\left(1 - \frac{zt}{(1+t)}\right)}$$

$$g(z,t) = \sum_{k\geq 1} c_k(t) z^k$$

recovering power series form

$$g(z,t) = \sum_k z^k \frac{t^{k-1}}{(1+t)^{k+1}}$$

$$\boxed{c_k = \frac{t^{k-1}}{(1+t)^{k+1}}}$$

$$= \frac{z}{(1+t)^2} \sum_{k=0} z^k \frac{t^k}{(1+t)^k}$$

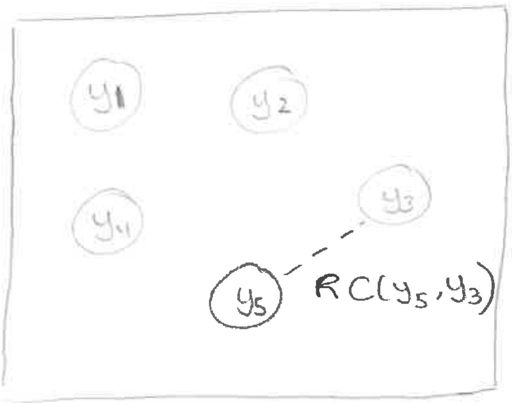
$$= \sum_{k=0} z^{k+1} \frac{t^k}{(1+t)^{k+2}}$$

$k' \to k+1$

$$= \sum_{k'=1} z^{k'} \frac{t^{k'-1}}{(1+t)^{k'+1}}$$

System: Link formation ; heterogeneous Network

Model Setup : Random Network with heterogeneity dependent rates



- N Labeled monomers
- $y_i \ \forall \ i \in [1, N]$ — $q(y)$: probabity distribution
- $(y_i) \ (y_j) \xrightarrow{C_{ij} R} (y_i)—(y_j)$

$$R_{ij} = C(y_i, y_j)$$

rate of link formation

Model Setup : State, event, rates

$$[i] + [j] \xrightarrow{K_{ij}} [i+j]$$

- State Network (N, E)

$\boxed{\text{measure } \cancel{\text{State}} \quad \hat{n}_k \equiv \text{connected components}}$

- Events $[i] + [j] \rightarrow [i+j]$

rates

- $K_{ij} = R \, F \, \underbrace{(i \cdot j)}_{①}$

① number of links that can form between

② Pair-wise interaction rate

③ $F \equiv$ mean field coalescence probability

$F \equiv$ average value for all

$$= \int_0^1 \int_0^1 C(y_i, y_j) \, q(y_i) \, q(y_j) \, dy_i \, dy_j$$

Master equation (mean-field)

I.C. $\boxed{n_k(t) = N \delta_{1k}}$

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} k_{ij} n_i n_j - n_k \sum_i K_{ik} n_i$$

$$= \left[\frac{\cancel{RF}}{2} \sum_{i+j=k} i j \, n_i n_j - k n_k \sum_i \cancel{k} i n_i \right] \times RF$$

Method of moments (Detection of critical time)

$$\boxed{M_n(t) = \sum_k k^n n_k(t)}$$

IC

$$\boxed{M_n(0) = N \quad \forall n}$$

Conservation of mass $\quad M_1(t) = N$

$$\dot{M}_1 = \sum_k k \dot{n}_k = RF\left(\frac{1}{2}\sum_i \sum_j (i+j) ij n_i n_j - \sum_k k^2 n_k \sum_i i n_i\right)$$

$$= RF\left(M_2(t) M_1(t) - M_2(t) M_1(t)\right) = 0$$

$$\xrightarrow{IC} = \boxed{M_1(t) = N}$$

Second moment + onset of gelation

$$\dot{M}_2(t) = \sum_k k^2 \dot{n}_k = RF\left(\frac{1}{2}\sum_i \sum_j (i+j)^2 ij n_i n_k - \sum_k k^3 n_k \sum_i i n_i\right)$$

$$= RF\left(\frac{1}{2}\sum_i \sum_j (\cancel{2i^3 j} + 2i^2 j^2) n_i n_k - \cancel{\sum_k k^3 n_k \sum_i i n_i}\right)$$

$$= RF\, M_2^2(t)$$

$$-\frac{1}{M_2} + \frac{1}{M_2(0)} = RFt$$

$$\xrightarrow{IC} \int \frac{1}{M_2^2} dM_2 = RF \int dt$$

$$\boxed{M_2(t) = N\left(1 - (RFN)t\right)^{-1} = N\left(1 - t/t_c\right)^{-1}}$$

when $\boxed{t = t_c = \frac{1}{RFN}}$ $\rightarrow$ $M_2(t)$ diverges $\rightarrow \infty$
typical cluster size $\sim \infty$

divergence in finite time

- Break down of mean-field description
- non-equilibrium phase transition : sudden apearance of a cluster (giant) $\sim N$, contains finite fraction of total system

higher order moments

ex/ $n=3$ $\dot{M}_3 = 3RF\, M_2(t)\, M_3(t)$

Solving with I.C $\boxed{M_3 = N\left(1 - t/t_c\right)^{-3}}$

- diverges at same point
- diverges faster

* One can show by induction $M_2(t)$ for $n \geq 2$ diverges at t_c

Gel Fraction and mass conservation beyond t_c

- Let us define $\boxed{g(t) \in [0,1]}$
- $$\boxed{M_1(t) = \begin{cases} N & t < t_c \\ N(1-g(t)) & t \geq t_c \end{cases}}$$

* this will be useful later

Zeroth moment and number of clusters $M_0 = \sum n_k(t)$

$$\dot{N}_c(t) = \dot{M}_0(t) = \sum \dot{n}_k(t)$$
$$= RF\left(\frac{1}{2}\sum_i\sum_j ij\, n_i n_j - \sum_k k n_k \sum_i i n_i\right)$$
$$= -\frac{RF}{2} M_1^2(t)$$

~~$t<t_c$~~ $\dot{N}_c = -\frac{RFN^2}{2} = -\frac{N}{2t_c} \Rightarrow \boxed{N_c = N\left(1 - \frac{1}{2}\frac{t}{t_c}\right)}$

linear decay

$t \geq t_c$ $\dot{N}_c = -\frac{RN}{2}(1-g(t))^2$

Generating function approach

- exponential generating Function $\quad D(x,t) = \sum_{k\geq 1} n_k e^{kx}$
- more convenient to work with derivative (will simplify analysis)

$$\mathcal{E}(x,t) = \frac{\partial}{\partial x} D(x,t) = \sum_{k\geq 1} k n_k e^{kx}$$

- At $x=0$ derivatives of generating functions are just the moments

$$M_n(x,t) = \frac{\partial^n}{\partial x^n} D(x,t)\Big|_{x=0} = \sum_{k\geq 1} k^n n_k(t)$$

$$\dot{\mathcal{E}}(x,t) = \sum_{k\geq 0} k \dot{n}_k e^{kx}$$

$$= RF\left(\frac{1}{2}\sum_i\sum_j (i+j) i j n_i n_j e^{ix} e^{jx} - \sum_k k^2 n_k e^{kx} \sum_i i n_i \right)$$

$$= RF\left(\sum i^2 n_i e^{ix} \sum j n_j e^{jx} - \sum k^2 n_k e^{kx} \underbrace{\sum i n_i}_{M_1(t)} \right)$$

$$= RF\left(\mathcal{E}'\mathcal{E} - \mathcal{E}' N \right) = -\frac{1}{N t_c}(N - \mathcal{E})\mathcal{E}'$$

$$\Rightarrow \quad \boxed{\dot{\mathcal{E}} + U(\mathcal{E})\mathcal{E}' = 0} \longrightarrow \text{invicid burgers equation}$$

$$\boxed{U(\mathcal{E}) = \frac{1}{N t_c}(N - \mathcal{E})}$$

Solving invicid burger's equation : method of characteristics

$$\dot{\mathcal{E}} + v(\mathcal{E})\,\mathcal{E}' = 0 \qquad v(\mathcal{E}) = \frac{1}{N t_c}(N-\mathcal{E})\mathcal{E}'$$

- method of charachteristics PDE $\to$ ODE
  'lets look only along the paths where $\mathcal{E}(x(t),t)$ is constant'

$$\frac{d}{dt}\left(\mathcal{E}(x(t),t)\right) = \frac{\partial \mathcal{E}}{\partial t} + \frac{dx}{dt}\frac{\partial \mathcal{E}}{\partial t} = 0$$

- $$\frac{dx}{dt} = V(\mathcal{E}(x,t)) = \frac{1}{t_c}\left(1 - \frac{\bar{\mathcal{E}}}{N}\right)$$

$$x(t) = \frac{1}{t_c}\left(1 - \frac{\bar{\mathcal{E}}}{N}\right)t + f(\mathcal{E})$$

- initial conditions

$$\mathcal{E}(x,0) = \sum_{k\geq 1} k n_k e^{kx} = N e^{x(t=0)}$$

$$\Rightarrow \bar{\mathcal{E}} = \mathcal{E}(x,0) = N e^{x(t=0)} \Rightarrow x(t=0) = \ln(\bar{\mathcal{E}}/N)$$

- In general we have the implicit solution

$$x(t) = \left(1 - \frac{1}{N}\mathcal{E}(x,t)\right)\frac{t}{t_c} + \ln\left(\frac{1}{N}\mathcal{E}(x,t)\right)$$

$$\Rightarrow \boxed{e^{x - t/t_c} = \frac{\mathcal{E}}{N} e^{-\mathcal{E}/N \, t/t_c}}$$

Dynamics of cluster size distribution : lagrange inversion

$$e^{x-t/t_c} = \frac{\mathcal{E}}{N} e^{-\mathcal{E}/N \, t/c}$$

- invert this and get series expansion of $\mathcal{E}(x,t)$

Lagrange inversion

- Suppose you have a function implicity defined

$$X = f(Y) = Ye^{-Y}$$

- known result (series expansion of tree function)

Inverse function $\quad Y(X) = \sum_{k\geq 1} \frac{k^{k-1}}{k!} X^k$

- we have

$$\frac{t}{t_c} e^{x-t/t_c} = \frac{t}{t_c}\frac{\mathcal{E}}{N} e^{-\mathcal{E}/N \, t/t_c}$$

$$\Rightarrow \quad X = t/t_c \, e^{x-t/t_c} \qquad Y = t/t_c \frac{\mathcal{E}}{N}$$

$$\Rightarrow \frac{t}{Nt_c}\mathcal{E}(x,t) = \sum_{k\geq 1} \frac{k^{k-1}}{k!} \left(\frac{t}{t_c}\right)^k (e^{xk})(e^{-t/t_c k})$$

$$\mathcal{E}(x,t) = \sum_{k\geq 1} \left[k e^{xk}\right] \underbrace{\left[\frac{k^{k-2}}{k!}\left(\frac{t}{t_c}\right)^{k-1} e^{-k t/t_c}\right]}_{n_k(t)}$$

$$\boxed{n_k(t) = N \left(\frac{k^{k-2}}{k!}\right)\left(\frac{t}{t_c}\right)^{k-1} e^{-k\, t/t_c}}$$

Looking at the cluster size distribution

monomers $n_1(t) = N \left(\frac{k}{1}\right)\left(\frac{t}{t_c}\right)^0 e^{-t/t_c}$

$$\boxed{n_1(t) = N e^{-t/t_c}}$$

$n_k(t)$ for $k \gg 1$

$$k! \approx \sqrt{2\pi k}\left(\frac{k^k}{e^k}\right)$$ Stirling apprx

$$\left(t/t_c\right)^{k-1} = \exp((k-1)\ln(t/t_c))$$
$$\approx \exp(k\ln(t/t_c))$$

$$\to n_k(t) \approx N \left(\frac{\cancel{k^{k-2}}\ k^{-2}}{\sqrt{2\pi}\cancel{k}\,k^{1/2}}\right)\left(\frac{e^k}{\cancel{k^k}}\right) e^{(k-1)\ln(t/t_c)}\, e^{-k(t/t_c)}$$

$$\approx \frac{N}{\sqrt{2\pi}}\left(k^{-5/2}\right)\exp\left[-k\left(t/t_c - \ln(t/t_c) - 1\right)\right]$$

when $t \approx t_c \Rightarrow t/t_c \approx 1 \Rightarrow$

$\longrightarrow \alpha - \ln(\alpha) - 1 \approx \frac{1}{2}(\alpha-1)^2$

$f(\alpha) = f(1) + f'(1)(\alpha-1) + \frac{1}{2}f''(1)(\alpha-1)^2$ $\quad f'(\alpha) = 1 - 1/\alpha$
$\approx 0 + 0 + \frac{1}{2}(\alpha-1)^2$ $\quad f''(\alpha) = 1/\alpha^2$

$$\Rightarrow \boxed{n_k(t) = \frac{N}{\sqrt{2\pi}} k^{-5/2} e^{-\frac{k}{2}(1 - t/t_c)^2}}$$

$n_k(t = t_c)$

$$\boxed{n_k(t=t_c) = \frac{N}{\sqrt{2\pi}} k^{-5/2}}$$

Power law w/ exponent -2.5

Dynamics of gel ($g(t)$: gel fraction)

- $M_1(t) = \begin{cases} N & t < t_c \\ N(1-g(t)) & t < t_c \end{cases}$

- Notice $\quad \mathcal{E}(x=0,t) = M_1(t) = \sum k n_k = N(1-g(t))$

- recall implicit solution

$$e^{x - t/t_c} = \frac{\mathcal{E}}{N} e^{-\mathcal{E}/N \, t/t_c}$$

Set $x=0$

$$e^{-t/t_c} = \frac{N}{N}(1-g(t)) e^{-(1-g(t)) t/t_c}$$

$ye^y = x$

$$\Rightarrow \quad -(1-g(t))\frac{t}{t_c} e^{-(1-g(t)) t/t_c} = -\frac{t}{t_c} e^{-t/t_c}$$

- Lambert-W functions
  - given $\quad ye^y = x \quad \Rightarrow \quad y = W_k(x)$ — solution can be expressed
    ↳ multi valued function

- for real y & x only two branches
  ↳ $W_0(x)$: principle branch $\quad x \geq -1/e$
  ↳ $W_1(x)$: lower branch $\quad -\frac{1}{e} \leq x < 0$

- $$-(1-g(t))\frac{t}{t_c} = W_k\left(-\frac{t}{t_c} e^{-t/t_c}\right)$$

$$\Rightarrow \quad \boxed{g(t) = 1 + \frac{W_0(-t/t_c \, e^{-t/t_c})}{t/t_c}}$$

✱ only W_0 branch gives physical solutions $g(t) \in [0,1]$