Sid Redner, Lecture 12

Aggregation kinetics

$$\boxed{K_{ij} = K_{ji}}$$

"kernel"

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

irreversible reaction

We want $C_k(t) \equiv$ concentr'n of clusters of mass k @ time t (in units of monomer mass)

Master Eq'n $\dot{C}_k = \frac{1}{2} \sum'_{\substack{i,j \\ i+j=k}} C_i C_j K_{ij} - \sum_{i=1}^{\infty} K_{ik} C_i C_k$

restricted sum; gain term

$\frac{1}{2}$: avoid overcounting

$\sum_{i=1}^{\infty} K_{ik} C_i C_k$: loss term

no fragmentation, loss term due to "k" lumping w/ other things

✓ gain term:

$k=5$; sum over (1,4) (2,3) (3,2) (4,1):

$K_{14} C_1 C_4 + K_{23} C_2 C_3$

$\underline{k=6}$;

$K_{15} C_1 C_5 + K_{24} C_2 C_4 + \frac{1}{2} K_{33} (C_3^2)$

$\frac{N_3 (N_3 - 1)}{2} \approx \frac{N_3^2}{2}$ ← relative fraction of mass 3 pairs

$$\dot{C}_k = \frac{1}{2} \sum_{i,j \geq 1} K_{ij} C_i C_j [\delta_{i+j,k} - \delta_{i,k} - \delta_{j,k}]$$

Analogously, $\frac{\partial C(x,t)}{\partial t} = \frac{1}{2} \int_0^{x} C(x-y,t) \times C(y,t) K(x-y,y) dy - \int_0^{\infty} C(y,t) C(x,t) \times K(x,y) dy$

- mean-field
- no fluctuations → thermodynamic limit
- no cluster shape effects
- bimolecular (low density, no 3-part. collisions)
- spatial homogeneity

✓ Loss term:

note that we have $K_{kk} C_k C_k$ (no $\frac{1}{2}$!) since 2 clusters of size k disappear

—o—

Note that

$\underbrace{M(t)}_{\text{mass density}} = \sum_{k \geq 1} k C_k(t)$ is conserved

$\frac{dM}{dt} = \sum k \frac{dC_k}{dt} = \emptyset$

Rate $\underline{K_{ij}}$:

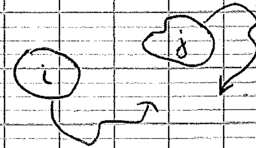
– exactly soluble models:

$K_{ij} = \text{const}$, ← focus on this

$K_{ij} = i + j$ (i, j are cluster masses)

$K_{ij} = i\,j$

– Brownian kernel



$K_{ij} \sim (R_i + R_j)(D_i + D_j) \sim$

R: radius; D: diff'n const

$$\sim (i^{1/3} + j^{1/3})(i^{-1/3} + j^{-1/3}) = 2 + \underbrace{\left(\frac{i}{j}\right)^{1/3} + \left(\frac{j}{i}\right)^{1/3}}_{}$$

$i^{1/3}, j^{1/3}$: masses

$O(1)$ argument for $i/j, j/i$ "does not work", these ratios diverge

so $K_{ij} = 2$ let's consider as an example

$D = \frac{k_B T}{6\pi\eta R} \rightarrow D \sim \frac{1}{R_i} \sim \frac{1}{i^{1/3}}$

Ways to "solve" master eq'n

Ø. Power counting

$s \equiv$ typical cluster mass "after a while"

$$\frac{\Delta s}{\Delta t} \sim \frac{s}{1/\rho} \sim 1 \Rightarrow s \sim t,$$ clusters grow w/time (infinite system!)

Focus on $K_{ij} = \text{const} = 2$ for convenience

1. Moments $M_n(t) = \sum_{k=1}^{\infty} k^n c_k(t)$

restricted sum

$$\dot{c}_k = \sum_{\substack{i,j \\ i+j=k}}{}' c_i c_j - \underset{K_{ij}}{2} \sum_{i=1}^{\infty} c_i c_k \quad (*)$$

$\dot{M}_n = \sum_{k\geq 1} k^n \dot{c}_k = \sum_{k\geq1} k^n \left[\sum_{i+j=k} c_i c_j - 2c_k \sum_{i\geq1} c_i\right] = \sum_{i,j}(i+j)^n c_i c_j - 2M_n M_0$

$t=0 \Rightarrow M_0^{(0)}=1$ ("concentr'n is set to 1")

$$\dot{M}_0 = M_0^2 - 2M_0^2 = -M_0^2 \Rightarrow M_0 = \frac{1}{1+t}$$

$$\dot{M}_1 = \sum_{k=1}^{\infty} k\dot{c}_k = \sum_{i,j}(i+j)c_i c_j - 2\sum_{i,k} k c_i c_k =$$

$$= 2M_0M_1 - 2M_0M_1 = 0. \quad M_1 = 1$$

total mass is conserved (initial cond.)

$$\dot{M}_2 = \sum_{k=1}^{\infty} k^2 \dot{c}_k = \sum_{i,j}(i+j)^2 c_i c_j - 2\sum_{i,k} c_i c_k k^2 =$$

$$= 2M_1^2 \qquad M_1 = 1 \text{ (init. cond.)}$$

Note that $M_n(0) = \sum_{k\geq1} k^n \underbrace{c_k(0)}_{\delta_{k,1}} = 1$ monomers only

$$\dot{M}_2 = 2t+1 \sim t$$ as in power counting

$t\to\infty$: $M_n(t) \sim n!\, t^{n-1}$

2. Solve (*) directly: $\frac{dc_k}{dt} = \sum_{i+j=k} c_i c_j - 2c_k \underbrace{\sum_{i\geq1} c_i}$

Recursive solution $\Rightarrow$

$\dot{c}_1 = -2\sum c_1 c_i = -2c_1 M_0 \equiv -2c_1 N$ $\quad N(t)$ = total concentr'n of clusters

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

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

$\to c_2(t) = t(1+t)^{-3}$

$\dot{M}_0 = -M_0^2$

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

$\dot{c}_3 = 2c_1c_2 - 2c_3M_0$

$\to \ldots$

$\dot{c}_4 = 2c_1c_3 + c_2^2 - 2c_4 M_0$

$\vdots$

generally

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

$c_k(0) = \delta_{k,1}$ monomers only

$\sim e^{-k\log}$

$\sim e^{-k}$

3. Generating f'n solution:

Ex.: solve Fibonacci series by generating f's

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

$$\sum_{k=1}^{\infty}\left[\dot{c}_k = \sum_{\substack{i,j\\ i+j=k}}{}' c_i c_j - 2\sum_i c_i c_k\right] z^k$$

$i+j=k$

$$\sum_{k=1}^{\infty}\sum_{i,j}{}' = \sum_{i,j} c_i c_j z^i z^j$$ (no restriction)

a hile" · ono · inite · stem!) · $\Rightarrow M_0^{(0)}=1$ ("concentr'n is set to 1") · $C_k =$ total mass is conserved · $M_1 = 1$ (initial cond.) · $C_k k^2 =$ · cond.) · er · inting · $\sum C_i$ · $N(t)$ = total concentr'n of clusters · M_0^2 · $\frac{1}{1+t}$ · $\delta_{k,1}$ · mers only · $i+j=k$ · $i \geq j$ · iction)

We get $\dot g(z,t) = g^2(z,t) - 2\overbrace{g(1,t)}^{N(t)\equiv g_1(t)}\, g(z,t)$

$$\dot g = g^2 - 2gg_1 \to h = g - g_1$$

$$\dot g_1 = -g_1^2 \Longrightarrow g_1 = \frac{1}{1+t} \qquad g_1 = M_0 = N$$

Then $\dot h = g^2 - 2gg_1 + g_1^2 = h^2$ ($\dot h = \dot g + g_1^2$)

$$\left(\frac{1}{h}\right)^{\cdot} = -1 \qquad \frac{1}{h} - \frac{1}{h(t=0)} = -t$$

$$\frac{1}{h} = \frac{1}{h(t=0)} - t = \frac{1}{z-1} - t$$

$$h = \frac{z-1}{1-(z-1)t} \qquad h(t=0) = \sum_k \overbrace{C_k^{(0)}}^{\delta_{k,1}}(z^k - 1) = z-1$$

$$g_{(z,t)} = \frac{z-1}{1-(z-1)t} + \frac{1}{1+t} = \frac{z}{(1+t)(1-(z-1)t)} = \sum_{k\geq 1} z^k \frac{t^{k-1}}{(1+t)^{k+1}}$$

From this, $C_k(t) = \frac{1}{(1+t)^2}\left(\frac{t}{1+t}\right)^{k-1}$.

[note that $g(z,t=0) = \sum \underbrace{C_k(t=0)}_{\delta_{k,1}} z^k = z$

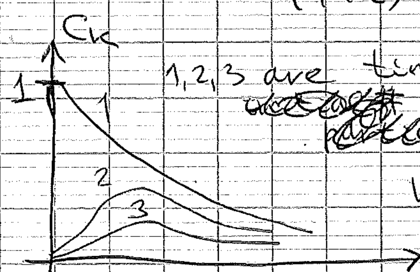
@ $t=0$: $h = g - g_1 = z - 1$]

Now, $C_k = \frac{1}{(1+t)^2}\underbrace{\left(\frac{t}{1+t}\right)^{k-1}}_{\approx (1+\frac{1}{t})^{-k}} \xrightarrow[\substack{k \text{ fixed} \\ t\to\infty}]{\text{large}} \frac{1}{t^2}e^{-k/t}$ ///

$\sim e^{-k\log(1+\frac{1}{t})} \sim$

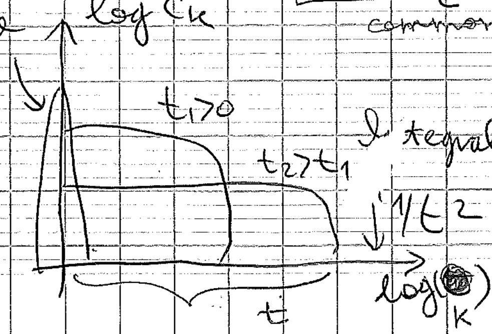
$\sim e^{-k/t}$

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



1,2,3 are time-dependence curves for monomers, dimers, trimers

common dependence $\sim \frac{1}{t^2}$ when $k \ll t$



integral $= \frac{1}{t^2} \times t \sim \frac{1}{t}$

clusters $\sim 1/t$

$1/t^2$ since $e^{-k/t} \simeq 1$ when $k \ll t$

x - cluster mass
S(t) - typical mass @ t
reaction rate:
C(x,t) - concentr'n of clusters of mass x @ t

4. Scaling theory

from conserv'n of total mass; $\int dx\, x\, c(x,t) \overset{2}{=} 1$ (conserved total mass) $\rightarrow$

$u \rightarrow s^{-2}$ prefactor

$\int d\left(\frac{x}{s}\right)\left(\frac{x}{s}\right) s^2 s^{-2} f\left(\frac{x}{s}\right) = \int du\, u f(u)$.

$$C(x,t) \rightarrow s^{-2} f(x/s)$$

$$K(ax,ay) = a^{\lambda} K(x,y)$$

λ – homogeneity exponent (or index)

Use these to "solve" the ME

$$\frac{\partial c(x,t)}{\partial t} = \int_0^x K(x-y,y)\, c(x-y,t)\, c(y,t)\, dy - \int_0^\infty K(x,y)\, c(x,t)\, c(y,t)\, dy$$

First, solve the diff'n eq'n:

$$C(x,t) \rightarrow s^{-1} f(x/s) \quad s \text{ - "characteristic scale"}$$

From $\int dx\, c(x,t) = 1 \rightarrow s^{-1}$ prefactor

$\int du\, f(u) = \int d\left(\frac{x}{s}\right) s\, s^{-1} f\left(\frac{x}{s}\right)$ # particles conserv'n

$C_t = D\, C_{xx}$, or

$$C_t = -\frac{1}{s^2}\dot{s} f(u) + \frac{1}{s} f'(u)\left(-\frac{x}{s^2}\dot{s}\right) =$$

$u = x/s$

$$= -\frac{\dot{s}}{s^2}\left[f(u) + u f'(u)\right]$$

$$C_{xx} = \frac{1}{s^3} f''(u)$$

$$-\frac{\dot{s}}{s^2}(uf)' = \frac{D}{s^3} f''(u),$$

$$\dot{s} s = -D\frac{f''(u)}{(uf)'} \equiv \lambda \text{ (const)} \quad \text{(separation of variables)}$$

$$s = \sqrt{2\lambda t} \Leftarrow \dot{s} s = \frac{1}{\sqrt{2\lambda t}} \frac{1}{2}(2\lambda)\sqrt{2\lambda t} = \lambda$$

$$f' = -\frac{\lambda}{D}(uf) + \text{const}$$

const – init. cond's

$$f \sim e^{-\lambda u^2/2D} = e^{-x^2/4Dt}$$

"correct prefactors can be restored"

$$\frac{\lambda u^2}{2D} = \frac{\lambda}{2D}\left(\frac{x}{s}\right)^2 = \frac{\lambda x^2}{2D(2\lambda t)} = \frac{x^2}{4Dt}$$

Finally, $c(x,t) \sim \frac{1}{\sqrt{t}} e^{-\frac{x^2}{4Dt}}$.

Back to the aggreg'n theory:

$$C_t = -2\frac{\dot{S}}{S^3} f(u) + S^{-2} f'(u)\left(-\frac{x}{S^2}\right) =$$

$$= -\frac{\dot{S}}{S^3}(2f + uf') \qquad u = \frac{x}{S}$$

Now, the 1st term on RHS is:

$$\int_0^u \frac{1}{S^2} f\Big(\underbrace{\frac{y}{S}}_{v}\Big) \frac{1}{S^2} f\Big(\underbrace{\frac{x-y}{S}}_{u-v}\Big) \underbrace{K(S(u-v), Sv)}_{S^\lambda K(u-v,v)} S\,dv =$$

$$= \frac{1}{S^{3-\lambda}} \int_0^u f(v) f(u-v) K(u-v, v)\,dv$$

2nd term: $\displaystyle \frac{1}{S^{3-\lambda}} \int_0^\infty f(u) f(v) K(u,v)\,dv$

same scaling as 1st term

So, $\displaystyle -\frac{\dot{S}}{S^3}(2f+uf') = \frac{1}{S^{3-\lambda}} \underbrace{H(u)}_{\text{some complicated f'n of } u}$, or

$$\underbrace{\dot{S} S^{-\lambda}}_{\text{time}} = \underbrace{-\frac{H(u)}{(2f+uf')}}_{\text{f'n of } u} = \Lambda \quad \text{(separ'n of variables)}$$

Consider $\displaystyle \frac{\dot{S}}{S^\lambda} = \Lambda$

S – typical mass $\Rightarrow$
$\Rightarrow S^{-1}$ – typical density
Δt – time when all clusters react: $\Delta S \sim S$

$\Delta t \sim \frac{1}{\text{rate}}$, rate $\sim \frac{1}{S} K(S,S) \sim \frac{S^\lambda}{S}$ (conc'n)

$\frac{\Delta S}{\Delta t} \sim \frac{S S^\lambda}{S}$

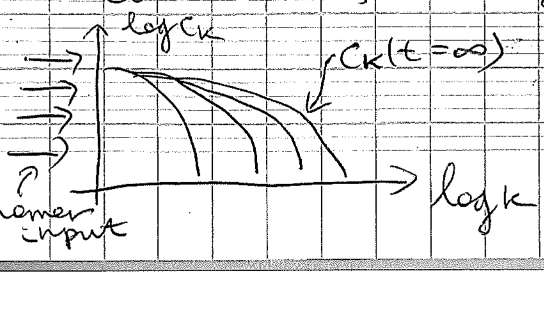
Time dependence of a typical mass affected by λ (only)

$$S(t) \sim \begin{cases} t^{\frac{1}{1-\lambda}}, & \lambda < 1 \\ e^{\Lambda t}, & \lambda = 1 \\ \dfrac{1}{(t_g - t)^{\frac{1}{\lambda - 1}}}, & 1 < \lambda \leq 2 \end{cases}$$

t_g – const, called "gelation time"

$\lambda > 2$ – "pathological case", instantaneous gelation (needs more analysis)

Consider now aggregation w/input
(adding monomers @ const rate to the infinite system)



We have $\left[\begin{array}{c}\text{use}\\ K_{ij}=2 \text{ again}\end{array}\right]$

$$\dot{C}_k = \sum{}' c_i c_j - 2C_k \underbrace{\sum C_i}_{N(t)} + \delta_{k,1}$$

$C_k(0)=0$ (initially empty system)

$$\hookrightarrow \dot{N} = -N^2+1 \underset{t\to\infty}{\approx} 1$$

$$N(t) = \tanh(t) \underset{t\to 0}{\approx} t$$

Generating f'n:

$$\sum_{k=1}^{\infty}\left[\dot{C}_k = \sum{}' c_i c_j - 2C_k \sum C_i + \delta_{k,1}\right] z^k$$

Look for SS solution:

$$\emptyset = \dot{g} = g^2 - 2g\overbrace{g(1)}^{N(t)\to 1 \text{ as } t\to\infty} + z$$

$$g(1) \underset{t\to\infty}{=} 1 \Rightarrow g^2 - 2g + z = \emptyset$$

$$\text{So, } g(z) = 1 - \sqrt{1-z} = \sum_{k=1}^{\infty} C_k z^k$$

How to get C_k?

recall that $\Gamma(k) = (k-1)!$

$$\frac{\Gamma(k+a)}{\Gamma(a)} = (k+a-1)(k+a-2)\dots(a+1)a$$

Then

$$(1+(-z))^{1/2} \overset{\text{Taylor expansion}}{=} 1 + \frac{1}{2}(-z) + \frac{1}{2}\left(-\frac{1}{2}\right)(-z)^2\frac{1}{2!} +$$

$$+ \frac{1}{2}\left(-\frac{1}{2}\right)\left(-\frac{3}{2}\right)(-z)^3\frac{1}{3!} + \dots =$$

$$= 1 - \frac{1}{2}\sum_{k=1}^{\infty}\frac{\Gamma(k-\frac{1}{2})}{\Gamma(\frac{1}{2})}\frac{1}{\Gamma(k+1)} z^k$$

$$\text{So, } C_k = \frac{1}{2}\frac{\Gamma(k-\frac{1}{2})}{\underbrace{\Gamma(\frac{1}{2})}_{\sqrt{\pi}}}\frac{1}{\Gamma(k+1)}$$

Stirling appr'n:

$$\lim_{k\to\infty}\frac{\Gamma(k+a)}{\Gamma(k+b)} \sim k^{a-b}$$

$$C_k \sim \frac{1}{\sqrt{4\pi}} k^{-3/2} \quad \text{asymptotically}$$

↑
SS profile