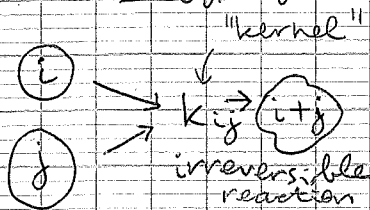


Sid Redner, Lecture 12

Aggregation kinetics

$$K_{ij} = K_{ji}$$



We want

in units of mass

$C_k(t) \equiv$ concentration of clusters of mass k

@ time t

Master Eq'n

$$\dot{C}_k = \frac{1}{2} \sum_{i+j=k} C_i C_j K_{ij} - \dots$$

↑ $i+j=k$
avoid overcounting

Gain term:

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

$$K_{14} C_1 C_4 + K_{23} C_2 C_3 - \sum_{i=1} K_{ik} C_i C_k$$

↑ loss term

no fragmentation, loss term due to "k"

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

$$\dot{C}_k = \frac{1}{2} \sum_{i+j=k} K_{ij} C_i C_j - \dots$$

lumping w/ other thing

$$\frac{N_3(N_3-1)}{2} \approx \frac{N_3^2}{2}$$

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

relative fraction of mass 3 pairs

$$\times K(x,y) dy$$

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

Loss term:

note that we have $K_{11} C_1 C_1$ (no 2.1) since 2 clusters of size disappear

Rate K_{ij} :

of size disappear

exactly soluble models:

$K_{ij} = \text{const}$, ← focus on this
 $K_{ij} = i+j$ (i, j are cluster masses)
 $K_{ij} = i \cdot j$

Note that

$$M(t) = \sum_{k>1} k C_k(t)$$

mass density is conserved

$$\frac{dM}{dt} = \sum_k k \frac{dC_k}{dt} = 0$$

Brownian kernel

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

↑ radius ↑ diff'n const

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

↑ masses

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

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

$\Theta(1)$ argument for $i, j \rightarrow 1$ "does not work", these ratios diverge

Ways to "solve" master eq'n

1. Power counting

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

$$\frac{\Delta S}{\Delta t} \sim \frac{S}{1/\beta} \sim 1 \rightarrow S \sim t, \text{ clusters grow w/ time (infinite system?)}$$

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

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

$$\dot{C}_k = \sum_{\substack{i,j \\ i+j=k}} C_i C_j - 2 \sum_{i=1}^{\infty} C_i C_{k-i} \quad (*)$$

$$\begin{aligned} \dot{M}_n &= \sum_{k=1}^{\infty} k^n \dot{C}_k \\ &= \sum_{k=1}^{\infty} k^n \left[\sum_{\substack{i,j \\ i+j=k}} C_i C_j - 2 \sum_{i=1}^{\infty} C_i C_{k-i} \right] \\ &= \sum_{i,j} (i+j)^n C_i C_j - 2 M_n M_0 \end{aligned}$$

$$M_0 = M_0^2 - 2 M_0^2 = -M_0^2 \Rightarrow M_0 = \frac{1}{1+t} \quad \begin{matrix} t=0 \Rightarrow M_0=1 \\ \downarrow \text{"concentration is set to 1"} \end{matrix}$$

$$M_1 = \sum_{k=1}^{\infty} k \dot{C}_k = \sum_{i,j} (i+j) C_i C_j - 2 \sum_{i,k} k C_i C_k = 2 M_0 M_1 - 2 M_0 M_1 = 0 \Rightarrow M_1 = 1 \quad \begin{matrix} \text{total mass is conserved} \\ \text{initial cond.} \end{matrix}$$

$$M_2 = \sum_{k=1}^{\infty} k^2 \dot{C}_k = \sum_{i,j} (i+j)^2 C_i C_j - 2 \sum_{i,k} k^2 C_i C_k = 2 M_1^2 - 2 M_1^2 = 0 \Rightarrow M_2 = 2t + 1$$

Note that

$$M_n(0) = \sum_{k=1}^{\infty} k^n C_k(0) = 1 \quad \begin{matrix} \text{monomers only} \\ \delta_{k,1} \end{matrix}$$

$M_2 = 2t + 1 \sim t$ as in power counting

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

2. Solve (*) directly: $\frac{dC_k}{dt} = \sum_{i+j=k} C_i C_j - 2 C_k \sum_{i=1}^{\infty} C_i$

Recursive solution \Rightarrow

$$\begin{aligned} \dot{C}_1 &= -2 \sum C_1 C_i = -2 C_1 M_0 = -2 C_1 N \quad \begin{matrix} N(t) = \text{total} \\ \text{concentration} \\ \text{of clusters} \end{matrix} \\ &\rightarrow C_1(t) = (1+t)^{-2} \\ \dot{C}_2 &= C_1^2 - 2 C_2 M_0 = N^2 - 2 C_2 N \\ &\rightarrow C_2(t) = t(1+t)^{-3} \\ \dot{C}_3 &= 2 C_1 C_2 - 2 C_3 M_0 \\ &\rightarrow C_3(t) = \frac{1}{2} t^2 (1+t)^{-4} \\ \dot{C}_4 &= 2 C_1 C_3 + C_2^2 - 2 C_4 M_0 \\ &\vdots \end{aligned}$$

$$\begin{aligned} M_0 &= -M_0^2 \\ M_0 &= \frac{1}{1+t} \end{aligned}$$

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

generally \rightarrow

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

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

3. Generating f'n solution:

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

$$\sum_{k=1}^{\infty} \left[\dot{C}_k = \sum_{\substack{i,j \\ i+j=k}} C_i C_j - 2 \sum_{i=1}^{\infty} C_i C_k \right] z^k$$

$$\sum_{k=1}^{\infty} \sum_{i,j} C_i C_j z^i z^j - 2 \sum_{k=1}^{\infty} \sum_{i=1}^{\infty} C_i C_k z^i z^k = \sum_{i,j} C_i C_j z^i z^j \quad \begin{matrix} \text{(no restriction)} \\ \downarrow i+j=k \end{matrix}$$

Ex.: solve Fibonacci series by generating f'n

2)

a hole
one
finite
system?

we get $g(z,t) = g^2(z,t) - 2g_1(t)g(z,t)$
 $g = g^2 - 2gg_1 \rightarrow h = g - g_1$
 $g_1 = -g^2 \Rightarrow g_1 = \frac{1}{1+t}$ $g_1 = M_0 = N$

Then $h = g^2 - 2gg_1 + g_1^2 = h^2$
 $\left(\frac{1}{h}\right) = -1 \quad \frac{1}{h} - \frac{1}{h(t=0)} = -t$

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

$h = \frac{z-1}{1-(z-1)t}$ $h(t=0) = \sum_k c_k^{(0)} (z^k - 1) = z-1$

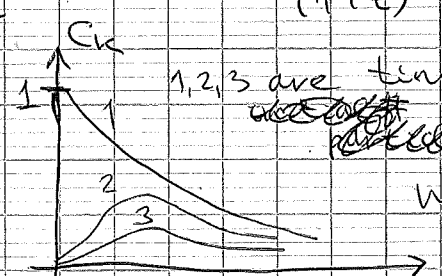
$g(z,t) = \frac{z-1}{1-(z-1)t} + \frac{1}{1+t} = \frac{z}{(1+t)(1-(z-1)t)}$
 $= \sum_{k \geq 1} z^k \frac{1+t}{(1+t)^{k+1}}$

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

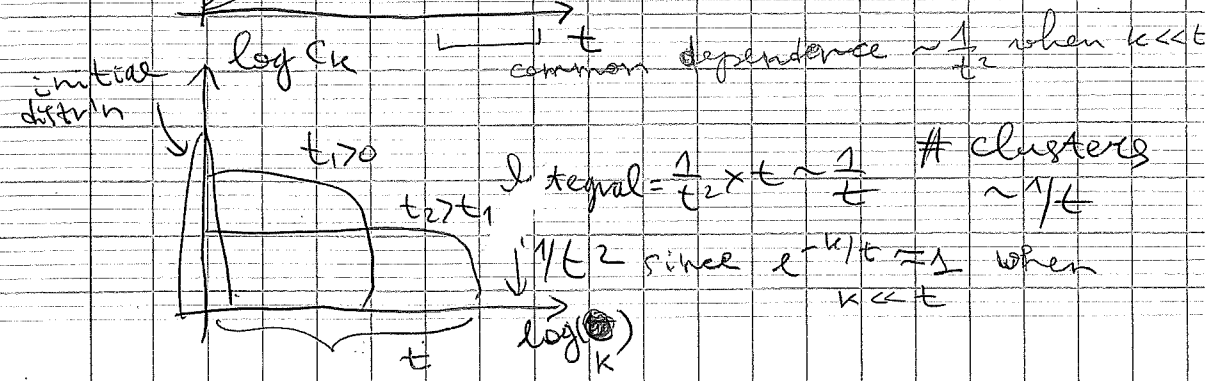
[note that $g(z,t=0) = \sum_k c_k(t=0) z^k = z$
 @ $t=0$: $h = g - g_1 = z - 1$]

Now, $c_k = \frac{1}{(1+t)^2} \left(\frac{t}{1+t}\right)^{k-1} \Rightarrow \frac{1}{5^2} e^{-k/5}$
 (large k \rightarrow fixed $1/5$)

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



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



$M_0 = 1$
 ("concentration is set to 1")

$c_k =$
 total mass is conserved
 $1 = 1$
 initial cond.)
 $c_k k^2 =$

cond.)
 er
 mting

$\sum_{k=1}^{\infty} c_k$
 $N(t) =$ total concentration of clusters
 $M_0 = 2$ clusters
 1
 $1+t$

$k, 1$
 mers only

$i+j = k$
 z^k
 ction)

4. Scaling theory \swarrow from conserve'n of total mass; $\int dx x c(x,t) = \text{const}$ \rightarrow s^{-2} prefactor

x -cluster mass $S(t)$ - typical mass @ t

reaction rate: $K(ax, ay) = a^\alpha K(x, y)$ homogeneity exponent (or index)

$C(x,t)$ - concentration of clusters of mass x @ t

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:

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

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

$\int dx x C(x,t) = \int dx x S^{-1} f(x/S) = \int du u f(u) = \int du u f(u)$ # particles conserved

$C_t = D C_{xx}$, or

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

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

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

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

$$S = \sqrt{2\lambda t} \leftarrow \dot{S} S = \frac{1}{\sqrt{2\lambda t}} \cdot \frac{1}{2} (2\lambda) \sqrt{2\lambda t} = \lambda$$

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

init. cond's

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

"correct prefactors can be restored"

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

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