Physics 210 B

→ Aggregation, cont'd → Gelation

Recall – aggregation → application of Master Eqn.

General form:

$$\frac{d}{dt} c_k = \underbrace{\frac{1}{2} \sum_{i+j=k} k_{ij}(c)\, c_i c_j}_{\substack{\text{birth} \\ \text{(emission into)}}} - \underbrace{c_{j,k} \sum_{i\geq 1} k_{i,j}(c)\, c_i}_{\substack{\text{death,} \\ \text{(emission from)}}}$$

and simplified form for Smoluchowski colloidal aggregation:

$$\boxed{\frac{d\nu_k}{d\tau} = \sum_{i+j} \nu_i \nu_j - 2\nu_k \sum_{j=1}^{\infty} \nu_j} \qquad k = 1, \ldots$$

$\tau = 4\pi D R t$ ⇔ rescale.

and can solve, exploiting evolution

$\sum_{k=1}^{\infty} \nu_k$, can solve.

→ Mass conservation also useful

The Key to Dynamics: $K_{ij}(c)$

⇒ Gelation (example — Krapivsky, DeGennes "Scaling Concepts in Polymer Physics")

- structure K_{ij} s/t condense to a single cluster — Jello — in finite time → gelation time τ_g. Contrast Schmoluchowski

After gelation time τ_g:

2 phases: gel → infinite cluster; sol → finite cluster (mass ↓)

- similar → finite time singularity (turbulence)

$$\epsilon = \frac{v(\ell)^3}{\ell} \rightarrow \frac{v(\ell)}{\ell} \uparrow \text{ as } \ell \downarrow$$

dissipation / turnover rate increasing.

Consider:

- monomers : f-function reactive group

  i.e. $f = 3$  monomer

- dimer

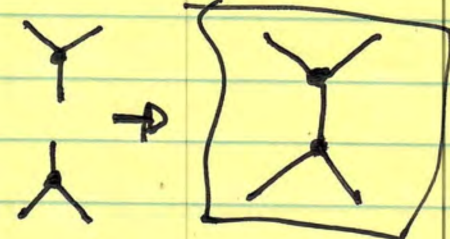
trimer

etc

f = # functional reactive end groups

- mergers? – Aggregation!

2 monomers → dimer



$2f-2$ reactive endgroups (4)

trimer : $3f-4$ (see above)

and

- k-mer: $kf - 2(k-1) = (f-2)k + 2$

$\downarrow$

endgroups for k-mer

The point: $\rightarrow$ # reactive groups increases with k (size)

$\Downarrow$

key $\rightarrow$ big clusters more reactive

Then, for aggregation

$$K_{ij} = [\#\text{ endgroup } i][\#\text{ endgroup } j]$$

$\S$

Merger i,j rate coeff

so

$$K_{ij} = [(f-2)i+2][(f-2)j+2]$$

$$= (f-2)^2 ij + 2(f-2)ij + 4$$

N.B. — $f = 2$ ⇒ linear polymers

$K_{ij} = 4$ (à la Schmoluchowski)

— $f > 2$ ⇒ kernel is linear combo of const, sum, product

$$\sim a f^2 + b f + c$$

So

⇒ natural model to explore is product kernel — (related to Erdos-Renyi rndm graph).

⇒ So write model Master Eqn.:

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{\substack{i,j \\ i+j=k}} ij\, c_i c_j - k c_k \sum_{i \geq 1} i c_i$$

normalizing $\sum_i i c_i = M$

so $$\boxed{\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} ij\, c_i c_j - k c_k}$$

→ will ultimately condense to giant gel cluster(s), of entire system

Solving:

- Gel → accumulation
- detect by moments
  → finite system
  → initial mass $\mathcal{M}$

∴ gel → cluster with $g\mathcal{M}$ $(g \to 1)$

concen $1/\mathcal{M}$

so decompose moments:

$$M_n = \sum_{k \geq 1} k^n c_k$$

$$M_n = \underbrace{\sum_{sol} k^n c_k}_{\text{finite}} + \underbrace{(k^n c_k)_{gel}}_{\text{infinite}}$$

so

$$M_0 = \sum_{sol} c_k$$

$$M_1 = \sum_{sol} k c_k + g$$

$$M_2 = \sum_{sol} k^2 c_k + g^2 \mathcal{M}$$

$$M_3 = \sum_{sol} k^3 c_k + g^3 \mathcal{M}^2$$

→ $M_2, M_3 \ldots$ diverge in thermodynamic limit (i.e. $\mathcal{M} \uparrow$)

→ prior to gelation ($t < t_g$)

$g(t) = 0$, so all M_n finite.

∴ to look at gelation, examine 2nd moment

→ minimal interesting moment.

so

$$\frac{d}{dt} M_2 = \sum_{k \geq 1} k^2 \frac{dc_k}{dt}$$

$$= \frac{1}{2} \sum_{i \geq 1} \sum_{j \geq 1} (i+j)^2 \, i c_i \, j c_j$$

$$- \sum k^3 c_k$$

Now $(i+j)^2 = k^2 \rightarrow ij$

$$\frac{dM_2}{dt} = \sum_{i \geq 1} \sum_{j \geq 1} (i^2 c_i)(j^2 c_j) = M_2^2$$

[using $\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} ij \, c_i c_j - k c_k \sum_i i c_i$

$= \frac{1}{2} \sum_{i+j=k} ij \, c_i c_j - k c_k$]

so $M_2 \to \infty$ at $t_g = 1$

$\left(M_2 \sim 1/1-t \right)$

[Gelation as divergence of 2^{nd} moment

Higher moments slower...

Another approach: Generating Fctn.

(recall random walks)

Define:

$$\mathcal{E}(y,t) = \sum_{k \geq 1} k\, c_k e^{yk}$$

gen fctn.

so $k e^{yk} \left(\frac{dc_k}{dt} \text{ eqn} \right)$ gives:

$$\frac{d\mathcal{E}}{dt} = \frac{1}{2} \sum_{i \geq 1} \sum_{j \geq 1} (i+j)\, ij\, c_i c_j e^{yk}$$

$$- \sum_{k \geq 1} k^2 c_k e^{yk}$$

(eq. 6)

$$\frac{d\mathcal{E}}{dt} = \frac{1}{2}\left(\sum_{i\geq 1} i^2 c_i e^{yi}\right)\left(\sum_{j\geq 1} j c_j e^{yj}\right)$$

$$+ \frac{1}{2}\left(\sum_{i\geq 1} i c_i e^{yi}\right)\left(\sum_{j\geq 1} j^2 e^{yj} c_j\right)$$

$$- \sum_{k\geq 1} k^2 c_k e^{yk}$$

$$= (\mathcal{E} - 1)\frac{\partial \mathcal{E}}{\partial y}$$

$\Rightarrow$

$$\frac{\partial \mathcal{E}}{\partial t} + \frac{\partial \mathcal{E}}{\partial y} - \mathcal{E}\frac{\partial \mathcal{E}}{\partial y} = 0$$

$$\mathcal{E} \to -\mathcal{E}$$

$$\frac{\partial(-\mathcal{E})}{\partial t} + \frac{\partial}{\partial y}(-\mathcal{E}) + \mathcal{E}\frac{\partial}{\partial y}(-\mathcal{E}) = 0$$

$$\boxed{\frac{\partial \mathcal{E}}{\partial t} + \frac{\partial \mathcal{E}}{\partial y} + \mathcal{E}\,\partial_y \mathcal{E} = 0}$$

and recall:

$$\partial_t v + v\partial_x v - \nu\,\partial_x^2 v = 0$$

$$\Updownarrow$$

Burgers $\Rightarrow$ shock solutions

(1D Hydro) $\Downarrow$

Gelation $\longrightarrow$ finite time singularity (if $\nu \to 0$)

then

$$\frac{\partial \varepsilon}{\partial t} = (\varepsilon - 1)\frac{\partial \varepsilon}{\partial y}$$

$$\frac{\partial \varepsilon}{\partial t} - (\varepsilon - 1)\frac{\partial \varepsilon}{\partial y} = 0$$

Char. $\quad \frac{d\varepsilon}{dt} = 0 \quad$ along $\quad \frac{\partial y}{\partial t} = 1 - \varepsilon$

$\Rightarrow \quad \varepsilon = \text{const}$ along $y_t = 1 - \varepsilon$

f(ε) from initial condition, $y = f(\varepsilon) + (1-\varepsilon)t$

For monomer only i.c.

$$\mathcal{E}(t=0) = \sum k c_k e^{yk}\Big|_{t=0} = e^y$$

$$y(t=0) = \ln \mathcal{E}$$

$$\Rightarrow \boxed{-\ln \mathcal{E} = (1-\mathcal{E})\,t}$$ implicit soln.

etc. See Krapivsky for more...

Key Points:

→ gel as finite time divergence of large cluster.

→ gel via K increasing with ij

Contrast Schmoluchowski $\frac{1}{0}$.