210 B

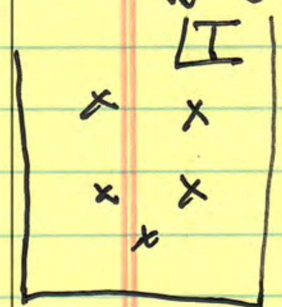
Aggregation – An Application of the Master Equation

(cf: Chandra Review, Krapivsky)
(Smoluchowski)

Recall Master Eqn:

$$\frac{d}{dt} P_n = \sum_{n'} \left(W_{n,n'} P_{n'} - W_{n',n} P_n \right)$$

Now 'Aggregation': $D \sim T/\beta$

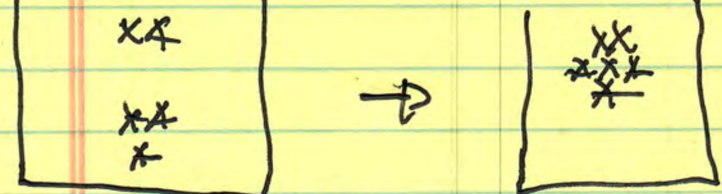


$\Rightarrow$ system of (charged) colloidal particles, walking randomly

charge colloid in electrolyte

t_1

Particles stick when interact closely $\Rightarrow$ 'sticky' collisions



t_2 $\qquad$ t_3

N.B. - each particle has 'sphere of influence'. Spheres touch $\Rightarrow$ merge

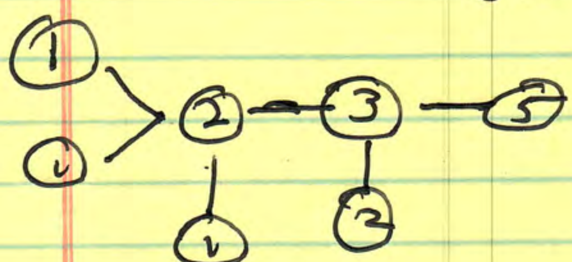
- $R_{SI} \sim \lambda_D$

- Motion $\Rightarrow$ random walk
  $\Leftrightarrow$ diffusion

Then, expect:

- evolution

$$1+1 \rightarrow 2$$
$$2+1 \rightarrow 3$$
$$3+2 \rightarrow 5$$



no breakup
$\rightarrow$ once stuck, remains so.

- so have simultaneous evolution of $f_n \Rightarrow$ probability of n-tuple cluster

- idea then is to model 'birth' and 'death' of n-tuple cluster by interactions of/with other clusters.

so, might have: $\quad \nu \equiv$ popln. density

$$\frac{d}{dt}\nu_2 = \underset{1+1}{\text{in}} - \underset{2+1,\,2,\,3,\,4,\,\ldots}{\text{out}}$$

$$\frac{d}{dt}\nu_3 = \underset{2+1}{\text{in}} - \underset{3+1,\,2,\,\ldots}{\text{out}}$$

etc. $\quad$ to ν_4

in general,

rate coeff

rate production of n-particle $\cong \sum_{p,q} \left(\# \underbrace{\nu_p \nu_q}_{p+q=n} \right)$

joint popln/prob. $p+q$

rate destruction of n-particle $\cong \sum_{i=1}^{N} \# \nu_n \nu_i$

i.e. n-particle + any other.

So, have:

- classic input-output / birth and death model for populations

- system of coupled Master Eqns!

i.e. birth → merger of smaller

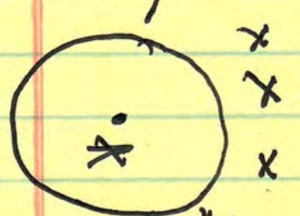
$$\frac{d}{dt}\nu_n = \sum_{\substack{i,j \\ i+j=n}} C_{ij}\,\nu_i\nu_j - \sum_{i=1}^{N} C_{in}\,\nu_n\nu_i$$

death → absorption to larger

What are the rate coefficients?

→ Rate of interaction ⇒ diffusion!

→ density diffuses – consider rate at which sphere R sweeps fluid



$n = \text{const}, \quad t = 0$

$|r| > R$

R_{si}

$$\frac{\partial n}{\partial t} = D\nabla^2 n$$

$n = 0, \quad |r| = R \qquad t > 0$
absorbing bndry

Heuristically, since particles diffuse together

$$\underbrace{\frac{\partial}{\partial t}\nu}_{\#} \sim \underbrace{4\pi R^2}_{\text{Area of Influence Sphere}} \underbrace{\left(+D \frac{\partial n}{\partial r}\Big|_R \right)}_{\text{Flux thru surface of sphere}}$$

$\rightsquigarrow$

$$\frac{\partial}{\partial t}\nu \sim 4\pi D \; R^2 D \frac{\partial \nu}{\partial r} \text{ [redacted]}$$

$$\sim 4\pi D \; R^{\cancel{2}} D \frac{\nu}{\cancel{R}} \sim 4\pi \underbrace{D R}_{\substack{\text{basic} \\ c_{ij}}} \nu$$

N.B.

$$\frac{\partial n}{\partial t} = D \nabla^2 n$$

symmetry $\rightarrow$

$$\partial_t (rn) = D \frac{\partial^2}{\partial r^2} (nr)$$

$x = rn, \quad x\Big|_{t \to \infty} = a + br$

$$n = r\left[1 - \frac{R}{r} + \frac{2R}{r\sqrt{\pi}} \int_0^{(r-R)/(2Dt)^{1/2}} e^{-x^2}\, dx\right]$$

$\Rightarrow$

$$\underset{\text{swept}}{\text{rate}} = 4\pi D R r \left(1 + R\right)(\pi D t)^{1/2}$$

Now, rate for mergers:

i sweeps k

$$J_{ik}\, dt = 4\pi D_{ik} r_i r_k \, dt$$

$$D_{i,k} = D_i + D_k$$

$\rightarrow$ independent diffusion

$\rightarrow$ mean square step adds (quadratures)

$\Rightarrow$

to avoid double counting

in

$$\frac{d}{dt} \nu_k = 4\pi \left(\frac{1}{2} \sum_{\substack{i,j \\ i+j=k}} \nu_i \nu_j D_{j,i} R_{ij} \right.$$

out

$$\left. - \nu_k \sum_{j=1}^{\infty} \nu_j D_{k,j} R_{k,j} \right)$$

- Master Eqn. for k-tuple (Really N)

Now, simplifying approximations:

→ $R_i = R_k = R$ single scale

→ $D_j = D$ all same

→ $D_i R_i = DR$ "

→ $D_{in} R_{in} = 2DR$ D's add

So have much simpler :

$$\frac{d}{dt} \nu_k = 8\pi DR \left(\frac{1}{2} \sum_{\substack{i+j \\ =k}} \nu_i \nu_j - \nu_k \sum_{j=1} \nu_j \right)$$

rate

$$\boxed{\tau = 4\pi DR t}$$

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

→ reduced Master Equation

→ specifies population evolution for clusters.

then, to solve:

$$\sum_k \qquad \Rightarrow$$

$$\frac{d}{dt}\left(\sum_{k=1}^{\infty} \nu_k\right) = \sum_{i}^{\infty} \sum_{j}^{\infty} \nu_i \nu_j - 2\sum_{k=1}^{\infty} \sum_{j=1}^{\infty} \nu_k \nu_j$$

release sum constr

$$= -\left(\sum_{k=1}^{\infty} \nu_k\right)^2$$

∞ $\quad \frac{dx}{dt} = -x^2 \quad \rightarrow \quad 1/x = t + c$

$$\boxed{\sum_{k=1}^{\infty} \nu_k = \nu_0 / 1 + \nu_0 T}$$

sum of popl'ns decays → cluster into 1.

And can solve for populations:

$$\frac{d}{dt}\nu_1 = -2\nu_1 \sum_{k\geq 1}^{\infty} \nu_k$$

$$= -2\nu_1 \sum \nu_k$$

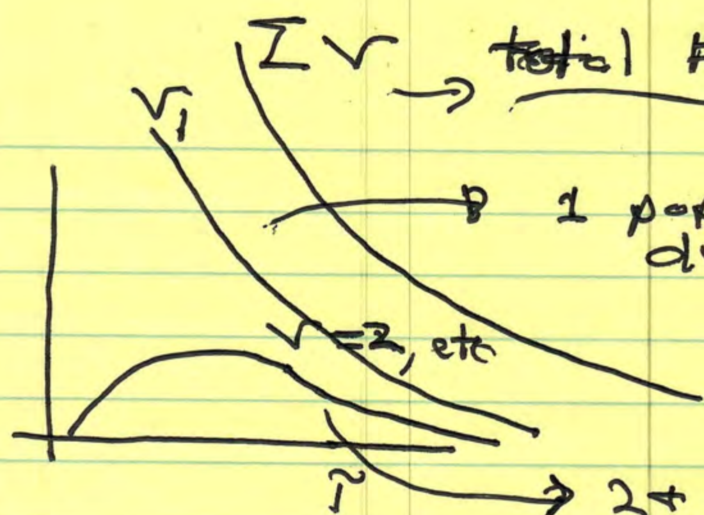
$$= -2\nu_1 \nu_0 / 1 + T\nu_0$$

$$\boxed{\nu_1 = \nu_0 / (1 + T\nu_0)^2}$$

and

$$\boxed{\nu_k = \nu_0 \, (\nu_0 T)^{k-1} / (1 + \nu_0 T)^{k+1}}$$

$k = 1, 2, 3 \ldots$



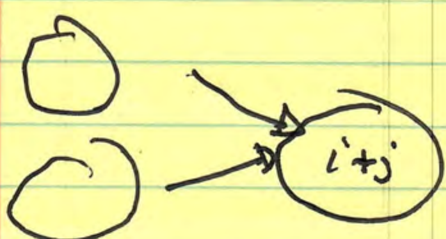
$\Sigma \nu$ → ~~total~~ # drops

1 population drops due mergers

2+ up first rise due mergers, then decline, as absorbed.

N.B:

- typical of aggregation problems



clusters join (irreversibly) when meet

e.g. { milk curdling
blood coagulation
planet formation

[1 way flow → larger scale]

- basic description is system of Master Eqns

$$\frac{d}{dt} c_k = \overbrace{\frac{1}{2} \sum_{i+j=k} K_{ij}\, c_i c_j}^{\text{in}} - \overbrace{c_k \sum_{i \geq 1} K_{ik}\, c_i}^{\text{out}}$$

couplings are the key!

$\Rightarrow$ rate

$\Rightarrow$ time to form large (∞) cluster finite, infinite

[finite time singularity ?!]

- Typical of 'inverse cascade'.

- Many approaches to solution

  - exact → some simple cases
  - moments
  - recursion

see Krapivsky

→ Constraint: "Basic Equation" conserves mass.

i.e. nothing lost enroute to N cluster.

$c \to f$

$M \to \sum k c$

$$M(t) = \sum_{k \geq 1} k\, c_k(t)$$

Now

$$\frac{dM}{dt} = \sum_k k \frac{dc_k}{dt}$$

$$= \sum_k \sum_{\substack{i,j \\ i+j=k}} \frac{1}{2} K_{ij} \overbrace{(i+j)}^{k} c_i c_j - \sum_k \sum_i K_{ik}\, k\, c_i c_k$$

$i+j=k$

$$= \sum_k \sum_i \frac{1}{2}(2) K_{i,k} k c_i c_j - \sum_k \sum_i K_{ik}\, k\, c_i c_k = 0$$

so, Mass conserved. (plausible).

this brings us to Gelation

$\Rightarrow$

Gelation = Aggregation with rate
increasing with cluster mass

(i.e. more interesting 'coeffs').