Aggregation - An Application of the Master Equation

(c.f. Chandrasekhar, Kramersky)

Recall Master Eqn:

\[ \frac{d P_n}{dt} = \sum_{n'} (W_{n'n} P_{n'} - W_{n'n} P_n) \]

Now Aggregation:

\[ \Phi - T/\alpha \]

\( \{ \begin{array}{c} x \quad x \quad x \\ x \quad x \\ \_ \end{array} \) \rightarrow \text{system of (charged) colloid particles, walking randomly}

\text{charge colloid on electric field}

Particles which interact closely \( \rightarrow \) sticky collisions

\( \{ \begin{array}{c} x \quad x \\ x \quad x \\ x \quad x \end{array} \) \rightarrow \quad \{ \begin{array}{c} * \quad * \\ x \quad x \\ \_ \end{array} \}

\[ t_2 \rightarrow t_3 \]
N.B. - each particle has "sphere of influence". Spheres touch $\rightarrow$ merge

- $R_{50} \sim \lambda_0$

- Motion $\rightarrow$ random walk $\rightarrow$ diffusion

Then, expect:

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

- have simultaneous evolution of

- idea then is to model "birth" and "death" of $n$-tuple cluster by interactions of/with other clusters.
So, might have:

\[ \frac{d}{dt} V_2 = \text{in} - \text{out} \]

\[ 1 + 2 \rightarrow 3 + 4 \rightarrow \cdots \]

\[ \frac{d}{dt} V_3 = \text{in} - \text{out} \]

\[ 2 + 4 \rightarrow 5 + 3 \rightarrow \cdots \]

e tc.

to \( V_4 \)

In general,

\[ \text{Rate coefficient} \]

\[ \text{Rate production of } n\text{-particle} = \sum_{BE} \left( \frac{V_{P} V_{2}}{p + 2} \right) \]

\[ \text{Rate destruction of } n\text{-particle} = \sum_{c=1}^{N} \# V_n V_c \]

i.e. \( n\text{-particle} \) and any other
So, have:

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

- system of coupled Master Eqns

\[ \frac{d}{dt} n_i = \sum_{j=1}^{N} C_{ij} v_j n_j = \sum_{i=1}^{n} C_{i} v_i n_i v_i = \]

birth \( \rightarrow \) merger of smaller

What are the rate coefficients?

\( \Rightarrow \) rate of interaction \( \rightarrow \) diffusion

\( \Rightarrow \) density, diffuses \( \rightarrow \) consider rate at which sphere \( R \) sweeps fluid

\[ \frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \]

\( n = \text{const}, \quad t = 0 \)

\[ 1/s > \frac{R}{S} \]

\( R \rightarrow \)
\[ n = 0, \quad W_1 = R > 0 \]

absorbing body

Heuristically, since particles diffuse together:

\[ \frac{\partial \rho}{\partial t} = 4\pi R^2 \left( \frac{\partial}{\partial r} \left( \frac{1}{r} \right) \right) \]

# Area of Influence Sphere

Flux thru Surface of Sphere

\[ \frac{\partial}{\partial t} \left( \int R^2 \right) \]

\[ \sim 4\pi D R^2 \frac{\partial V}{\partial R} \]

\[ \sim 4\pi D \frac{\partial V}{\partial R} \]

N.B.

\[ \frac{\partial n}{\partial t} = D A^2 \frac{n}{\partial R} \]

symmetry $\rightarrow$
\[ a_{\frac{d^2}{dr^2} \varphi} = 0 \]

\[ x = r \cos \theta, \quad x_l = a + b r \to \infty \]

\[ n = \sqrt{1 - \frac{R}{r} + \frac{2R}{r^3} \int_{r_0}^{r_{\infty}} e^{-x^2/(2a + r)^2} \, dx} \]

\[ \text{rate} = 4\pi R \sqrt{a(1 + R)(\varphi dt)^{3/2}} \]

Now, rate for mergers:

\[ \int_{\infty}^{\infty} dt = 4\pi D_i \varphi_i \varphi_f \, dt \]

\[ D_{i,f} = D_i + D_f \quad \to \quad \text{independent diffusion} \]

\[ \varphi \text{ mean square step adds} \quad \text{(quadratures)} \]
\[
\frac{d}{dt} V_k = -4\pi \left( \frac{1}{2} \sum_{i \neq k} V_i V_j D_{ij} \cdot R_{ij} \right)
\]

- Master Eqn. for \( V \)-triple (Really \( N \))

Now, simplifying approximations:

1. \( R_i = R_k = R \) single scale
2. \( D_{ij} = D \) all same
3. \( Q_i R_i = D R \) ""
4. \( D \cdot R_{in} = 2 \cdot DR \) D's edge
So have much simpler:

\[
\frac{d}{dt} \frac{V_i}{V_i} = 8\pi D R \left( \frac{1}{4} \sum_{j} \frac{\nu_j}{\nu_i} - \nu_i \sum_{j=1} \nu_j \right)
\]

\[
\gamma = \frac{4\pi D R^2}{4}
\]

\[
\frac{d}{dt} \frac{V_i}{V_i} = \sum_{i,j} \frac{\nu_i \nu_j}{\nu_i} - 2\nu_i \sum_{j=1} \nu_j
\]

\[\Rightarrow \text{reduced Master Equation}\]

\[\Rightarrow \text{specific population evolution for clusters.}\]

then, to solve:

\[
\sum_{i=1}^{N} \frac{d}{dt} \left( \sum_{i=1}^{N} \nu_i \right) = \sum_{i=1}^{N} \sum_{j} \nu_i \nu_j - 2 \sum_{i=1}^{N} \nu_i \sum_{j=1}^{N} \nu_j
\]
\frac{dx}{dt} = -x^2 \quad \rightarrow \quad \sqrt{x} = t + C

\sum_{i=1}^{n} V_i = \frac{V_0}{1 + x_0 T}

Sum of phons decays to cluster into 1.

And can solve for populations:
\begin{align*}
\frac{d}{dt} V_i &= -2x_i \sum_{j=1}^{n} V_j \\
&= -2x_i \sum_{j=1}^{n} V_j \\
&= -2V_i V_0 / (1 + T V_0)
\end{align*}

\begin{align*}
V_i &= \frac{V_0}{(1 + T V_0)^2} \\
\text{and} \\
V_i &= \frac{V_0}{(V_0 T)^{4i-1} / (1 + V_0 T)^{4i+1}}
\end{align*}

n = 1, 2, 3 \ldots
1. $\Sigma V \rightarrow$ total # drops

2. $\rightarrow 1$ population drops due to mergers

3. $\rightarrow 2$ up first rise due to mergers, then declining, as observed

N.B.:
- typical of aggregation problems

- cheaters join (irreversibly) when meet

eg. milk curdling
- blood coagulation
- planet formation

\[ \text{[1 way flow $\rightarrow$ longer scale]} \]
- basic description is system of Master Eqns

\[
\frac{d}{dt} C_k = \frac{4}{z} \sum_{i+j=k} k_{ij} c_i c_j - c_{in} \sum_{i=1}^{c_{in}} k_{in} c_i
\]

couplings are the key!

a rate

a time to form large (\(\infty\))
cluster finite, infinite
[finite time one clarity?]

- Typical of (inverse cascade).

- Many approaches to solution

  - exact \(\rightarrow\) some simple cases
  - moments
  - recursion
  
  see Krapivsky
Constraint: "Basic Equation conserves mass."

\[ M \rightarrow \sum k_i c_i \]

\[ M(t) = \sum_{i \geq 1} k_i c_i(t) \]

Now

\[ \frac{dM}{dt} = \sum_k \frac{k}{n} \frac{dC_k}{dt} \]

\[ = \sum_k \sum_{i \neq k} \left( \frac{1}{2} k_{ij} c_i(t) c_j(t) \right) \]

\[ - \sum_k \sum_{i} k_{ik} \frac{1}{2} c_i(t) c_i(t) \]

\[ = \sum \sum \frac{1}{2} (2) k_{ik} n k_c c_i c_j \]

\[ - \sum k_{ik} n k_c c_i c_i \]
so Mass conserved, (plausible).

This brings us to Gelation

\[ \text{Gelation} = \text{Aggregation with rate increasing with cluster mass} \]

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