Oscillatory kinetics in cluster-cluster aggregation

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Aggregation phenomena: motivation

Many particles of one material dispersed in another.

Transport is diffusive or advective.

Particles stick together on contact.

**Applications**: surface physics, colloids, atmospheric science, earth sciences, polymers, cloud physics.

This talk:

Today we will focus on simple theoretical models of the statistical dynamics of such systems.
Simplest model of clustering: coalescing random walks

- Particles perform random walks on a lattice.
- Multiple occupancy of lattice sites is allowed.
- Particles on the same site merge with probability rate $k$: $A + A \rightarrow A$.
- A source of particles may or may not be present.
- No equilibrium - lack of detailed balance.

Cartoon of dynamics in 1-D with $k \rightarrow \infty$. 

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Mean field description

Equation for the average density, $N(x, t)$, of particles:

$$\partial_t N = D \Delta N - k N^{(2)} + J$$

$k$ - reaction rate, $D$ - diffusion rate, $J$ - injection rate, $N^{(2)}$ - density of same-site pairs.

Mean field assumption:
- No correlations between particles: $N^{(2)} \sim \frac{1}{2} N^2$
- Spatially homogeneous case, $N(x, t) = N(t)$.

Mean field rate equation:

$$\frac{dN}{dt} = -\frac{1}{2} k N^2 + J \quad N(0) = N_0$$

$$J = 0 : \quad N(t) = \frac{2 N_0}{2 + k N_0 t} \sim \frac{1}{k t} \quad \text{as } t \to \infty$$

$$J \neq 0 : \quad N(t) \sim \sqrt{\frac{2 J}{k}} \quad \text{as } t \to \infty$$

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A more sophisticated model of clustering: size-dependent coalescence

A better model would track the sizes distribution of the clusters:

\[ A_{m_1} + A_{m_2} \rightarrow A_{m_1 + m_2}. \]

- Probability rate of particles sticking should be a function, \( K(m_1, m_2) \), of the particle sizes (bigger particles typically have a bigger collision cross-section).
- Micro-physics of different applications is encoded in \( K(m_1, m_2) \).
- Given the kernel, objective is to determine the cluster size distribution, \( N_m(t) \), which describes the average number of clusters of size \( m \) as a function of time.
Mean-field theory of irreversible coagulation

Assume the system is statistically homogeneous and well-mixed so that there are no spatial correlations. Particle size distribution, \( N_m(t) \), satisfies the kinetic equation:

\[
\partial_t N_m(t) = \frac{1}{2} \int_0^m dm_1 K(m_1, m - m_1) N_{m_1}(t) N_{m-m_1}(t) \\
- \quad N_m(t) \int_0^M dm_1 K(m, m_1) N_{m_1}(t) \\
+ \quad J \delta(m - m_0)
\]

Smoluchowski equation:

Microphysics is encoded in the coagulation kernel, \( K(m_1, m_2) \).

- Source: particles of size \( m_0 \) are continuously added to the system at rate \( J \).
- Sink: particles larger than cut-off, \( M \), are removed from the system.
Notation: In many applications kernel is homogeneous:

\[ K(a m_1, a m_2) = a^\lambda K(m_1, m_2) \]

\[ K(m_1, m_2) \sim m_1^\mu m_2^\nu \quad m_1 \ll m_2. \]

Clearly \( \lambda = \mu + \nu \).

Examples:
Brownian coagulation of spherical droplets \((\nu = \frac{1}{3}, \mu = -\frac{1}{3})\):

\[ K(m_1, m_2) = \left( \frac{m_1}{m_2} \right)^{\frac{1}{3}} + \left( \frac{m_2}{m_1} \right)^{\frac{1}{3}} + 2 \]

Gravitational settling of spherical droplets in laminar flow \((\nu = \frac{4}{3}, \mu = 0)\):

\[ K(m_1, m_2) = \left( m_1^3 + m_2^3 \right)^2 \left| m_1^2 - m_2^2 \right| \]
Self-similar solutions of Smoluchowski equation

For homogeneous kernels, cluster size distribution often self-similar. Without source:

\[ N_m(t) \sim s(t)^{-2} F(z) \quad z = \frac{m}{s(t)} \]

\( s(t) \) is the typical cluster size. The scaling function, \( F(z) \), determining the shape of the cluster size distribution, satisfies:

\[
-2F(z) + z \frac{dF(z)}{dz} = \frac{1}{2} \int_0^z dz_1 K(z_1, z - z_1) F(z_1) F(z - z_1) - F(z) \int_0^\infty dz_1 K(z, z_1) F(z_1).
\]
Stationary solutions of the Smoluchowski equation with a source and sink

- Add monomers at rate, $J$.
- Remove those with $m > M$.
- Stationary state is obtained for large $t$ which balances injection and removal.
- Constant mass flux in range $[m_0, M]$.
- Model kernel:
  \[ K(m_1, m_2) = \frac{1}{2} (m_1^\mu m_2^\nu + m_1^\nu m_2^\mu) \]

Stationary state for $t \to \infty$, $m_0 \ll m \ll M$ (Hayakawa 1987):

\[ N_m = \sqrt{\frac{J (1 - (\nu - \mu)^2) \cos((\nu - \mu) \pi/2)}{2\pi}} m^{-\nu+\mu+3/2}. \]

Require mass flux to be local: $|\mu - \nu| < 1$. But what if it isn’t?
Asymptotic solution of the nonlocal case

Nonlocal stationary state is \textit{not} like the Hayakawa solution:

- Stationary state has the asymptotic form for $M \gg 1$:
  \[ N_m = \frac{\sqrt{2J\gamma} \log M}{M} M^{m^{-\gamma}} m^{-\nu}. \]
  \[ \gamma = \nu - \mu - 1. \]
- Stretched exponential for small $m$, power law for large $m$.
- Agrees well with numerics without any adjustable parameters.

Note: the stationary state \textbf{vanishes} as $M \to \infty$. What happens to the mass flux?

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Hopf bifurcation of stationary state as $M$ increased

- We did a (semi-analytic) linear stability analysis of the exact stationary state.
- Concluded that the nonlocal stationary state is linearly unstable for large enough $M$.
- Constant mass flux is replaced by time-periodic pulses.
- Oscillatory behaviour due to an attracting limit cycle embedded in this very high-dimensional dynamical system.

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Oscillations are a sequence of "resets" of self-similar pulses:

\[ N_m(t) = s(t)^a F(\xi) \quad \text{with} \quad \xi = \frac{m}{s(t)}, \]

where

\[ a = -\frac{\nu + \mu + 3}{2} \]

\[ s(t) \sim t^{\frac{2}{1-\nu-\mu}}. \]

Period estimated as the time, \( \tau_M \), required for \( s(\tau_M) \approx M \). Amplitude, \( A_M \), estimated as the mass supplied in time \( \tau_M \):

\[ \tau_M \sim M^{\frac{1-\nu-\mu}{2}} \quad A_M \sim J M^{\frac{1-\nu-\mu}{2}}. \]
Other examples: collisional evaporation / fragmentation models

- With probability $\lambda \ll 1$, collisions result in:
  - evaporation (both particles removed) with $J$ fixed.
  - complete fragmentation (both particles converted to monomers) with $J = 0$

- Rate equations are almost the same (except for equation for monomer density in fragmentation case):

$$\frac{\partial N_m(t)}{\partial t} = \frac{1}{2} \sum_{m_1=1}^{m} K_{m-m_1,m_1} N_{m-m_1} N_{m_1} - (1 + \lambda) N_m \sum_{m_1=1}^{\infty} K_{m,m_1} N_{m_1} + J \delta_{m,1}$$

Keep the model kernel $K(m_1, m_2) = \frac{1}{2} (m_1^\mu m_2^\nu + m_1^\nu m_2^\mu)$.


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Oscillatory regime observed for both models when $\lambda \ll 1$ (for certain kernels).

Oscillations in collisional evaporation / fragmentation models

Oscillations are not a result of "hard" cut-off.

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Conclusions and open questions

Summary:
- Stationary solution of Smoluchowski equation with source investigated in regime $|\nu - \mu| > 1$.
- Size distribution can be calculated asymptotically and has a novel functional form.
- Amplitude of state vanishes as the dissipation scale grows.
- Stationary state can become unstable so the long-time behaviour of the cascade dynamics is oscillatory.

Questions:
- Do any physical systems really behave like this?
- What happens in spatially extended systems?
- Other examples of oscillatory kinetics? Eg in wave turbulence?
Violation of mass conservation: the gelation transition

Microscopic dynamics conserve mass: \( A_{m_1} + A_{m_2} \rightarrow A_{m_1+m_2} \).

- Smoluchowski equation formally conserves the total mass,
  \[ M_1(t) = \int_0^\infty m \, N(m, t) \, dm. \]
- However for \( \lambda > 1 \):
  \[ M_1(t) < \int_0^\infty m \, N(m, 0) \, dm \, t > t^*. \]
  (Lushnikov [1977], Ziff [1980])
- Mean field theory violates mass conservation!!!

Best studied by introducing cut-off, \( M \), and studying limit \( M \rightarrow \infty \). (Laurencot [2004])

Physical interpretation? Intermediate asymptotics...

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Asymptotic behaviour of the kernel controls the aggregation of small clusters and large:

\[ K(m_1, m_2) \sim m_1^\mu m_2^\nu \quad m_1 \ll m_2. \]

\( \mu + \nu = \lambda \) so that gelation always occurs if \( \nu \) is big enough.

**Instantaneous Gelation**

- If \( \nu > 1 \) then \( t^* = 0. \) (Van Dongen & Ernst [1987])
- Worse: gelation is complete: \( M_1(t) = 0 \) for \( t > 0. \)

Instantaneously gelling kernels cannot describe even the intermediate asymptotics of any physical problem. Mathematically pathological?
The process of gravitational settling is important in the evolution of the droplet size distribution in clouds and the onset of precipitation.

Droplets are in the Stokes regime $\rightarrow$ larger droplets fall faster merging with slower droplets below them.

Some elementary calculations give the collision kernel

$$K(m_1, m_2) \propto (m_1^{\frac{1}{3}} + m_2^{\frac{1}{3}})^2 \left| m_1^{\frac{2}{3}} - m_2^{\frac{2}{3}} \right|$$

$\nu = 4/3$ suggesting instantaneous gelation but model seems reasonable in practice. How is this possible?
Instantaneous gelation in the presence of a cut-off

With cut-off, $M$, regularized gelation time, $t^*_M$, is clearly identifiable.

$t^*_M$ decreases as $M$ increases.

Van Dongen & Ernst recovered in limit $M \to \infty$.

Decrease of $t^*_M$ as $M$ is very slow. Numerics and heuristics suggest:

$$t^*_M \sim \frac{1}{\sqrt{\log M}}.$$

This suggests such models are physically reasonable.

Consistent with related results of Krapivsky and Ben-Naim and Krapivsky [2003] on exchange-driven growth.