Instantaneous gelation in Smoluchowski’s coagulation equation revisited

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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, bio-physics, cloud physics.

**This talk**: Today we will focus on mean field models of the statistical dynamics of such systems.
Wish to 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 $K(m_1, m_2)$ - the collision kernel - which is often a homogeneous function:

$$K(\alpha m_1, \alpha m_2) = \alpha^\lambda K(m_1, m_2)$$

- 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.

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The Smoluchowski equation

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

$$\frac{\partial N_m(t)}{\partial t} = \int_0^\infty dm_1 dm_2 K(m_1, m_2) N_{m_1} N_{m_2} \delta(m - m_1 - m_2)$$
$$- 2 \int_0^\infty dm_1 dm_2 K(m, m_1) N_m N_{m_1} \delta(m_2 - m - m_1)$$
$$+ J \delta(m - m_0)$$

**Notation:** In many applications kernel is homogeneous:

$$K(am_1, am_2) = a^\lambda K(m_1, m_2)$$

$$K(m_1, m_2) \sim m_1^\mu m_2^\nu \quad m_1 \ll m_2.$$
Some example kernels

Brownian coagulation of spherical droplets ($\nu = \frac{1}{3}, \mu = -\frac{1}{2}$):

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

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

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

Differential rotation driven coalescence (Saturn’s rings) ($\nu = \frac{2}{3}, \mu = -\frac{1}{2}$):

$$K(m_1, m_2) = \left( m_1^{\frac{1}{3}} + m_2^{\frac{1}{3}} \right)^2 \sqrt{m_1^{-1} + m_2^{-1}}$$
Self-similar Solutions of the Smoluchowski equation

In many applications kernel is a homogeneous function:

\[ K(am_1, am_2) = a^\lambda K(m_1, m_2) \]

Resulting cluster size distributions often exhibit self-similarity.

Self-similar solutions have the form

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

where \( s(t) \) is the typical cluster size. The scaling function, \( F(z) \), determines the shape of the cluster size distribution.
Stationary solutions of the Smoluchowski equation with a source of monomers

- 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):

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

Require mass flux to be local: $|\mu - \nu| < 1$. 

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])

What is the physical interpretation?

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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?
Droplet coagulation by gravitational settling: a puzzle

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 → larger droplets fall faster merging with slower droplets below them.

Some elementary calculations give the collision kernel

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

$$\nu = \frac{4}{3}$$ suggesting instantaneous gelation but model seems reasonable in practice. How is this possible?

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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 Ben-Naim and Krapivsky [2003] on exchange-driven growth.
A stationary state is reached in the regularised system if a source of monomers is present (Horvai et al [2007]).

- Stationary state has the asymptotic form for $M \gg 1$:
  \[ N_m = \frac{\sqrt{J \log M^{\nu-1}}}{M} M^{1-\nu} m^{-\nu}. \]

- Stretched exponential for small $m$, power law for large $m$.

- Stationary particle density:
  \[
  N = \frac{\sqrt{J \left( M - M^{M^{1-\nu}} \right)}}{M \sqrt{\log M^{\nu-1}}} \sim \sqrt{\frac{J}{\log M^{\nu-1}}} \quad \text{as} \ M \to \infty.
  \]
Collective oscillations: a surprise from dynamics

- Numerics indicate that dynamics are non-trivial.
- Stationary state can be unstable for $|\nu - \mu| > 1$ (nonlocal). Includes instantaneous gelation cases but gelation is not necessary.
- Observe collective oscillations of the total density of clusters.
- Heuristic explanation in terms of “reset” mechanism.

$K(m_1, m_2) = m_1^{1+\epsilon} + m_2^{1+\epsilon}.$

$\nu = 3/4, \mu = -3/4, M = 10^4.$

Instability has a nontrivial dependence on parameters. Linear stability analysis (semi-analytic) of the stationary state for $\nu > 1$ reveals presence of a Hopf bifurcation as $M$ is increased. Contrary to intuition, dependence of the growth rate on the exponent $\nu$ is non-monotonic. Oscillatory behaviour seemingly due to an attracting limit cycle embedded in this very high-dimensional dynamical system.
Aggregation phenomena exhibit a rich variety of non-equilibrium statistical dynamics.

If the aggregation rate of large clusters increases quickly enough as a function of cluster size, clusters of arbitrarily large size can be generated in finite time (gelation).

Kernels with $\nu > 1$ which, mathematically speaking, undergo complete instantaneous gelation still make sense as physical models provided a cut-off is included since the approach to the singularity is logarithmically slow as the cut-off is removed.

Stationary state for regularised system with a source of monomers seems to be unstable when $|\nu - \mu| > 1$ giving rise to persistent oscillatory kinetics.
References


