Instantaneous gelation in Smoluchowski's coagulation equation revisited

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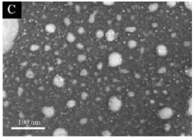
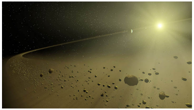
Aggregation phenomena : motivation





- 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.

Mass action kinetics for size-dependent coalescence

Wish to track the sizes distribution of the clusters:

$$A_{m_1} + A_{m_2} \to A_{m_1+m_2}.$$

- 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:

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

- 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 :

Smoluchowski equation :

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

Notation: In many applications kernel is homogeneous:

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

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

Clearly $\lambda = \mu + \nu$.

Some example kernels

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

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

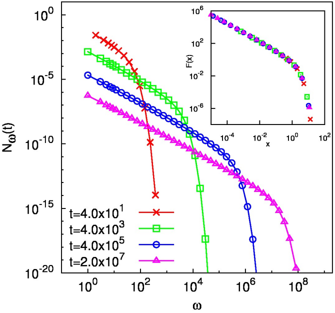
Gravitational settling of spherical droplets in laminar flow ($\nu = \frac{4}{3}$, $\mu = 0$) :

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

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

$$N_m(t) \sim s(t)^{-2} F(z) \qquad z = \frac{m}{s(t)}$$

where $s(t)$ is the typical cluster size. The scaling function, $F(z)$, determines the shape of the cluster size distribution.

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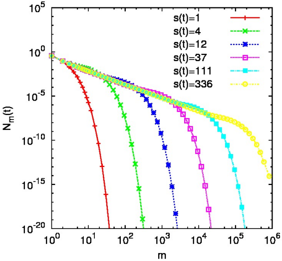
Stationary solutions of the Smoluchowski equation with a source of monomers



- 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):

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

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

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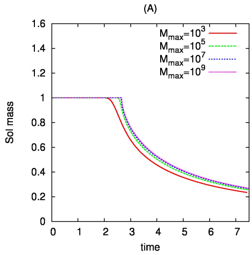
Violation of mass conservation: the gelation transition

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



$M_1(t)$ for $K(m_1, m_2) = (m_1 m_2)^{3/4}$.

- Smoluchowski equation formally conserves the total mass, $M_1(t) = \int_0^\infty m\, N(m,t)\, dm$.
- However for $\lambda > 1$:

  $$M_1(t) < \int_0^\infty m\, N(m,0)\, dm \quad t > t^*.$$

  (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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Instantaneous gelation

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 ν 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?

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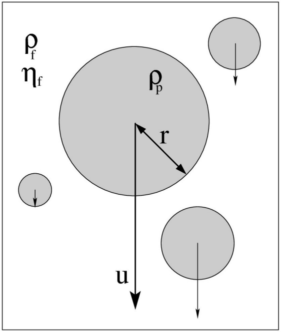
Droplet coagulation by gravitational settling: a puzzle



- 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 $\rightarrow$ 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?

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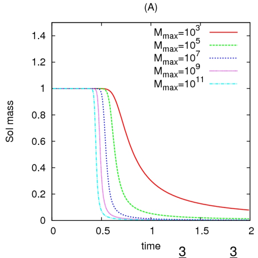
Instantaneous gelation in the presence of a cut-off



$M(t)$ for $K(m_1, m_2) = m_1^{\frac{3}{2}} + m_2^{\frac{3}{2}}$.

- With cut-off, M, regularized gelation time, t_M^*, is clearly identifiable.
- t_M^* *decreases* as M increases.
- Van Dongen & Ernst recovered in limit $M \to \infty$.

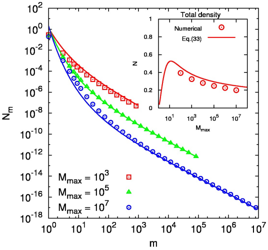
- Decrease of t_M^* as M is very slow. Numerics and heuristics suggest:

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

  This suggests such models are physically reasonable.
- Consistent with related results of Ben-Naim and Krapivsky [2003] on exchange-driven growth.

"Instantaneous" gelation with a source of monomers

A stationary state is reached in the regularised system if a source of monomers is present (Horvai et al [2007]).



Stationary state (theory vs numerics)

for $\nu = 3/2$.

- Stationary state has the asymptotic form for $M \gg 1$:

$$N_m = \frac{\sqrt{J \log M^{\nu-1}}}{M} M^{m^{1-\nu}} m^{-\nu}.$$

- Stretched exponential for small m, power law for large m.
- Stationary particle density:

$$N = \frac{\sqrt{J}\left(M - M^{M^{1-\nu}}\right)}{M\sqrt{\log M^{\nu-1}}} \sim \sqrt{\frac{J}{\log M^{\nu-1}}} \text{ as } M \to \infty.$$

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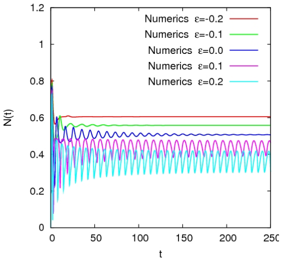
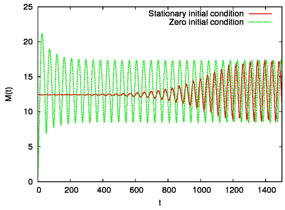
Collective oscillations: a surprise from dynamics



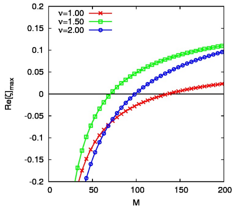
Total density vs time for $K(m_1, m_2) = m_1^{1+\epsilon} + m_2^{1+\epsilon}$.



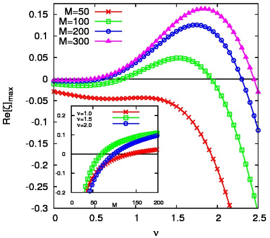
$\nu = 3/4$, $\mu = -3/4$, $M = 10^4$.

- 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.

Instability has a nontrivial dependence on parameters



Instability growth rate vs *M*



Instability growth rate vs ν.

- 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 ν is non-monotonic.
- Oscillatory behaviour seemingly due to an attracting limit cycle embedded in this very high-dimensional dynamical system.

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Summary and conclusions

- 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.

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