Oscillatory kinetics in cluster-cluster aggregation

Colm Connaughton

Mathematics Institute and Centre for Complexity Science,
University of Warwick, UK

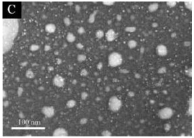
London Mathematical Laboratory,
14 Buckingham St, London WC2N 6DF

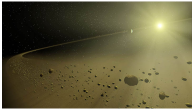
Collaborators: R. Ball (Warwick), A. Dutta (Chennai), P.P. Jones (Warwick), R. Rajesh (Chennai), O. Zaboronski (Warwick).

WCPM MIRaW Day
University of Warwick
12 June 2017

PRL 109, 168304 (2012); EPL 117(1):10002 (2017)

Aggregation phenomena : motivation





- Many particles of one material dispersed in another.
- Transport is diffusive or advective.
- Particles stick together on contact.

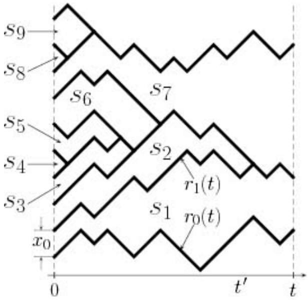
Applications: surface physics, colloids, atmospheric science, earth sciences, polymers, cloud physics.

This talk:

Today we will focus on simple theoretical models of the statistical dynamics of such systems.

THE UNIVERSITY OF WARWICK

Simplest model of clustering: coalescing random walks



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

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

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:

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

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

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

A more sophisticated model of clustering: size-dependent coalescence

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

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

- 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 $K(m_1, m_2)$
- 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 :

Smoluchowski equation :

$$
\begin{aligned}
\partial_t N_m(t) &= \frac{1}{2}\int_0^m dm_1\, K(m_1, m-m_1)\, N_{m_1}(t)\, N_{m-m_1}(t) \\
&- N_m(t)\int_0^M dm_1\, K(m, m_1)\, N_{m_1}(t) \\
&+ J\,\delta(m-m_0)
\end{aligned}
$$

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.

Scale-invariant coagulation kernels

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 $\lambda = \mu + \nu$.

Examples:

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

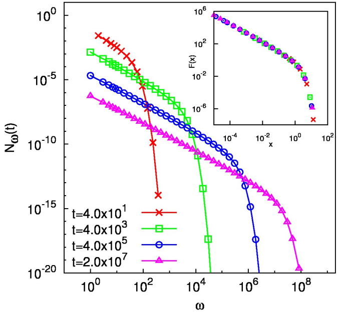
$$K(m_1, m_2) = \left(\frac{m_1}{m_2}\right)^{\frac{1}{3}} + \left(\frac{m_2}{m_1}\right)^{\frac{1}{3}} + 2$$

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

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

THE UNIVERSITY OF WARWICK

Self-similar solutions of Smoluchowski equation



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

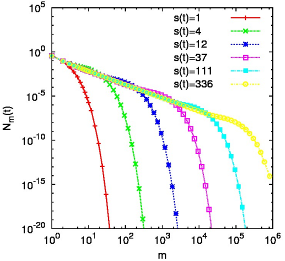
$$N_m(t) \sim s(t)^{-2}\, F(z) \quad z = \frac{m}{s(t)}$$

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

$$\begin{aligned} -2F(z) + z\frac{dF(z)}{dz} &= \frac{1}{2}\int_0^z dz_1 K(z_1, z - z_1) F(z_1) F(z - z_1) \\ &- F(z) \int_0^\infty dz_1 K(z, z_1) F(z_1). \end{aligned}$$

THE UNIVERSITY OF WARWICK

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:

$$K(m_1, m_2) = \frac{1}{2}(m_1^{\mu} m_2^{\nu} + m_1^{\nu} m_2^{\mu})$$

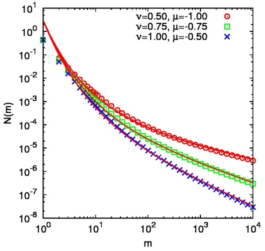
Stationary state for $t \to \infty$, $m_0 \ll m \ll M$ (Hayakawa 1987):

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

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 *not* like the Hayakawa solution:



Stationary state (theory vs numerics).

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

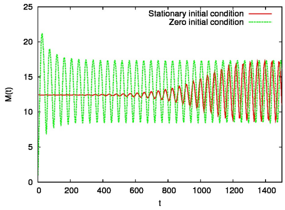
$$N_m = \frac{\sqrt{2J\gamma \log M}}{M} M^{m^{-\gamma}} m^{-\nu}.$$

$$\gamma = \nu - \mu - 1.$$

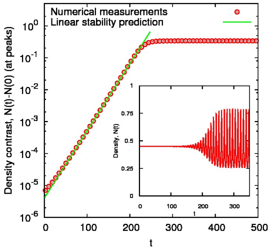
- Stretched exponential for small m, power law for large m.
- Agrees well with numerics without any adjustable parameters.

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

Hopf bifurcation of stationary state as *M* increased



Total density, $N(t)$, vs time for $\nu = \frac{3}{2}$, $\mu = -\frac{3}{2}$.

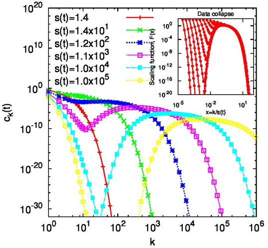


Linear stability analysis

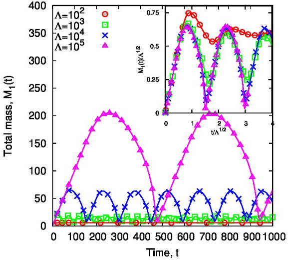
- We did a (semi-analytic) linear stability analysis of the exact stationary state.
- Concluded that the nonlocal stationary state is linearly unstable for large enough *M*.
- Constant mass flux is replaced by time-periodic pulses.
- Oscillatory behaviour due to an attracting limit cycle embedded in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

THE UNIVERSITY OF WARWICK

Scaling of period and amplitude of oscillation with M



Self-simliarity of mass pulse



Oscillations for different M

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

$$N_m(t) = s(t)^a \, F(\xi) \qquad \text{with } \xi = \frac{m}{s(t)},$$

where

$$a = -\frac{\nu + \mu + 3}{2} \qquad s(t) \sim t^{\frac{2}{1-\nu-\mu}}.$$

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

$$\tau_M \sim M^{\frac{1-\nu-\mu}{2}} \qquad A_M \sim J\, M^{\frac{1-\nu-\mu}{2}}.$$

Other examples: collisional evaporation / fragmentation models

- With probabilty $\lambda \ll 1$, 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):

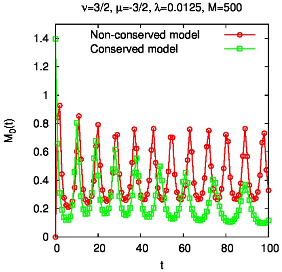
$$\frac{\partial N_m(t)}{\partial t} = \frac{1}{2}\sum_{m_1=1}^{m} K_{m-m_1,m_1} N_{m-m_1} N_{m_1} - (1+\lambda) N_m \sum_{m_1=1}^{\infty} K_{m,m_1} N_{m_1} + J\,\delta_{m,1}$$

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

C. Connaughton, A. Dutta, R. Rajesh, and O. Zaboronski. Universality properties of steady driven coagulation with collisional evaporation. EPL Europhys. Lett., 117(1):10002, 2017

Oscillatory kinetics for collisional evaporation / fragmentation model

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.

Conclusions and open questions

Summary:

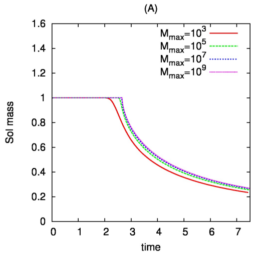
- Stationary solution of Smoluchowski equation with source investigated in regime $|\nu - \mu| > 1$.
- Size distribution can be calculated asymptotically and has a novel functional form.
- Amplitude of state vanishes as the dissipation scale grows.
- Stationary state can become unstable so the long-time 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: $A_{m_1} + A_{m_2} \to A_{m_1+m_2}$.



$M_1(t)$ 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 $M \to \infty$. (Laurencot [2004])

Physical interpretation? Intermediate asymptotics...

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.

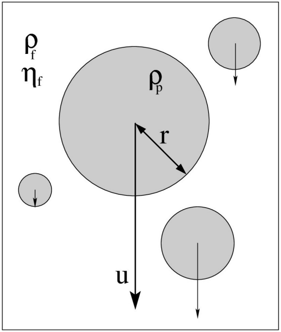
Instantaneous Gelation

- 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?

THE UNIVERSITY OF WARWICK

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.

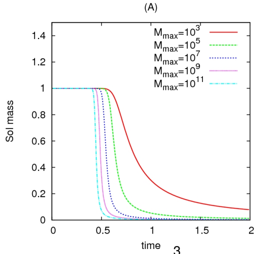
Some elementary calculations give the collision kernel

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

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

THE UNIVERSITY OF WARWICK

Instantaneous gelation in the presence of a cut-off



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

- 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 Krapivsky and Ben-Naim and Krapivsky [2003] on exchange-driven growth.

THE UNIVERSITY OF WARWICK