On Smoluchowski's classical model for aggregation phenomena

Barbara Niethammer

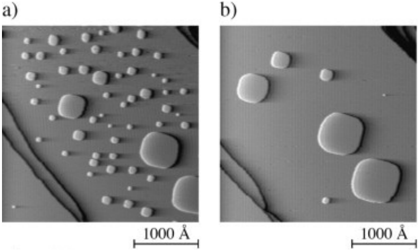
Institut für Angewandte Mathematik
Universität Bonn

based on joint work with
M. Bonacini, M. Herrmann and J. Velázquez

Mass aggregation phenomena

Stars

Smog formation



Nanostructures

Smoluchowski's mean-field model

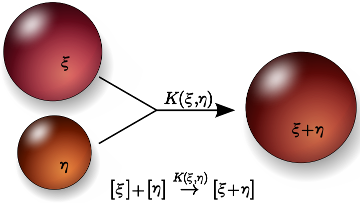
Motivation: (Smoluchowski, Z. phys. Chemie, 1917)
Coagulation in homogeneous colloidal gold solution

Setting

- Uniformly distributed particles
- $\xi \in (0, \infty)$: particle size
- $g(\xi)$: number density of ξ-clusters

Assumptions

- binary coagulation
- Coagulation rate
  $K(\xi, \eta)g(\xi)g(\eta)$
  with rate kernel K



Smoluchowski's coagulation equation

Rate equation:

$$\partial_t g(t,\xi) = \frac{1}{2}\int_0^{\xi} K(\xi-\eta,\eta)g(\xi-\eta)g(\eta)\,d\eta - g(\xi)\int_0^{\infty} K(\xi,\eta)g(\eta)\,d\eta$$

Smoluchowski (1917): $K \equiv \mathit{const}.$: explicit solutions; comparison with experiment "essentially satisfactory"

Smoluchowski's classical kernel

Assumptions

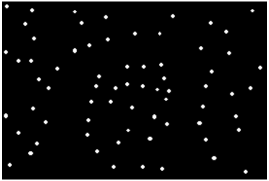
- Clusters move independently by Brownian motion
- Adsorption if clusters come close

$$K(\xi,\eta) = \left(\xi^{1/3} + \eta^{1/3}\right)\left(\xi^{-1/3} + \eta^{-1/3}\right)$$

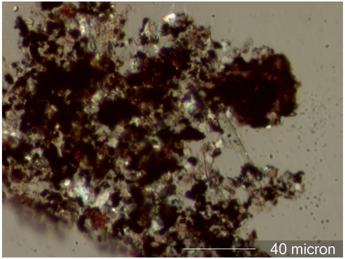
where

$\xi^{1/3} \sim$ Cluster radius

$\xi^{-1/3} \sim$ Diffusion constant



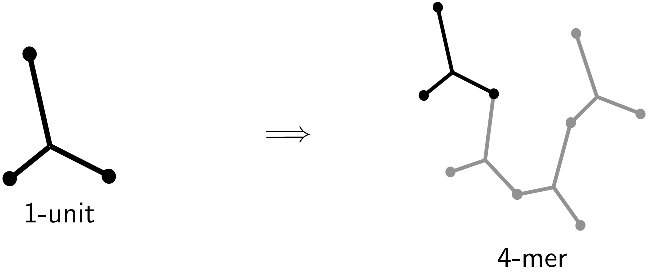
Further examples: soot agglomeration



$$K(\xi,\eta) = \left(\xi^{1/3} + \eta^{1/3}\right)^2 \left(\xi^{-1} + \eta^{-1}\right)^{1/2}$$

free molecular kernel (Mulholland et al '88)

Polymers (Flory & Stockmayer)

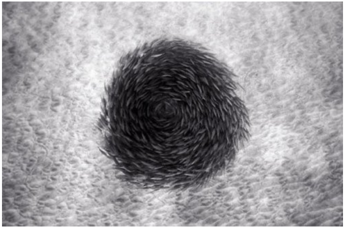


Rate kernel

- ξ-mer has $\xi + 2$ free A-atoms
- η-mer has $(\xi + 2)(\eta + 2)$ possibilites to join ξ-mer

$$K(\xi, \eta) = (\xi + 2)(\eta + 2) \sim \xi\eta$$

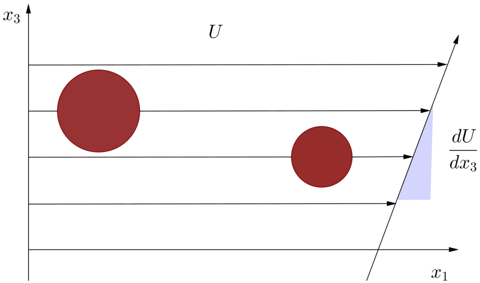
Example: schooling of fish



$$K(\xi, \eta) = \xi \eta e^{1/\xi} e^{1/\eta}$$

(Niwa '98)

Example: particles in a shear flow



$$K(\xi, \eta) = U\left(\xi^{1/3} + \eta^{1/3}\right)^3$$

Extensions

- Fragmentation (linear or nonlinear)
- Diffusion of clusters
- Transport (e.g. particles in a flow)
- Kinetic coalescence
  (additional characterization by momentum)
- Condensation; evaporation
- Friction
- Maximal admissible mass
- .....

Today:

- only pure coagulation

Well-posedness of the initial value problem

$$\partial_t g(t,\xi) = \frac{1}{2}\int_0^\xi K(\xi-\eta,\eta)g(t,\eta)g(t,\xi-\eta)\,d\eta \\ \qquad - g(t,\xi)\int_0^\infty K(\xi,\eta)g(t,\eta)\,d\eta$$

$$g(0,\xi) = g_0(\xi)$$

Goal:

- Given $g_0 \geq 0$, $g_0 \in L^1(0,\infty)$ there exists a unique nonnegative solution for all times

Bounded Kernels:

- follows via standard fixed point argument

Well-posedness for unbounded kernels

Problem:

- Integral operators do not map subsets of spaces into itself, e.g. if $g(t,\cdot) \in L^1(0,\infty)$ then in general $K(\xi,\cdot)g(t,\cdot) \notin L^1(0,\infty)$

Strategy: [White '80, Ball & Carr '92, Norris '01, Laurençot & Mischler '02, Fournier & Laurençot '06]

- For cut-off kernel K^n obtain solutions g^n
- Derive uniform moment and equiintegrability estimates for g^n
  $\Rightarrow$ subsequence converges weakly in L^1
- pass to limit in the equation
- Uniqueness via contraction argument for integrated density

Further properties of solutions

Moment identity

$$\frac{d}{dt}\int_0^\infty \psi(\xi)g(t,\xi)\,d\xi$$
$$= \tfrac{1}{2}\int_0^\infty\int_0^\infty K(\xi,\eta)g(\xi)g(\eta)\big[\psi(\xi+\eta)-\psi(\xi)-\psi(\eta)\big]\,d\xi\,d\eta$$

(Formal) consequence

$$M_1(t) = \int_0^\infty \xi g(t,\xi)\,d\xi = M_1(0)$$

However: e.g. $K(\xi,\eta)=\xi\eta$, assume $M_1(t)=1$, then

$$\frac{d}{dt}M_0(t) = -\frac{1}{2} \qquad \Rightarrow M_0(t) < 0 \ \text{ for } t > 2M_0(0)$$

Something must be wrong!

Failure of mass conservation: Gelation

Superlinear growth:

If K grows sufficiently fast, e.g. if K is homogeneneous of degree $\gamma > 1$, then mass is not conserved for all times, i.e. $\exists t_* < \infty$ with

$$\int_0^\infty \xi g(t,\xi)\, d\xi = \int_0^\infty \xi g(0,\xi)\, d\xi \qquad \text{for } t \in [0, t_*]$$

$$\int_0^\infty \xi g(t,\xi)\, d\xi \qquad \text{strictly decreases for } t > t_*$$

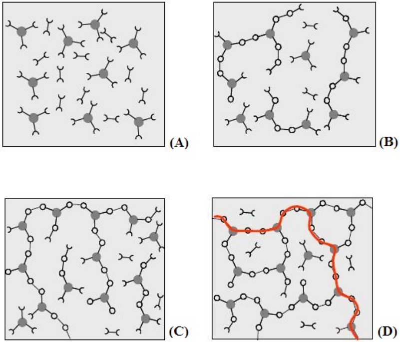
i.e. clusters of infinite size are created in finite time

(McLeod '62, Leyvraz & Tschudi '81, Carr & Da Costa '92, Jeon '98, Norris '00, Escobedo & Mischler & Perthame '03)

Gelation in polymers

Polymer chemistry

- Gelation: change from sol to gel
- typically abrupt change in viscosity $\Rightarrow$ gelation point



Mass conservation

Suppose K homogeneous of degree $\gamma \in \mathbb{R}$, i.e.

$$K(c\xi, c\eta) = c^\gamma K(\xi, \eta) \qquad \text{for all } c, \xi, \eta > 0$$

Mass conservation

If $\gamma \leq 1$ and $\int_0^\infty \xi g_0(\xi)\, d\xi < \infty$ then

$$\int_0^\infty \xi g(t, \xi)\, d\xi = \int_0^\infty \xi g_0(\xi)\, d\xi \qquad \text{for all } t > 0$$

(Ball & Carr '90, Laurençot & Mischler '02)

From now on: K homogeneous with degree $\gamma \leq 1$

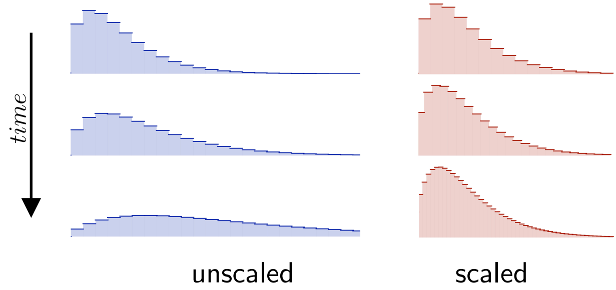
Scaling

Main aspects

- Mass goes into larger and larger clusters
- Entirely dynamical problem, no equilibrium

Question

- Is there a dynamic equilibrium, i.e. a solution that becomes stationary after a similarity transformation?



In other words

Expectation

- There exist self-similar solutions of the form

$$g(t,\xi) = s(t)^{-\alpha} f\Big(\frac{\xi}{s(t)}\Big)$$

  for a scaling $s(t)$ and a self-similar profile f
- Convergence to self-similar form

$$s(t)^{\alpha} g(t, s(t)x) \to f(x) \qquad \text{as } t \to \infty$$

Questions

- Do such solutions exist?
- Are they stable? What are their domains of attraction?

Solvable kernels

Scaling hypothesis well understood for

- The constant kernel
$$K(\xi, \eta) \equiv 2$$
- The additive kernel
$$K(\xi, \eta) = \xi + \eta$$
- The multiplicative kernel
$$K(\xi, \eta) = \xi\eta$$

Today exclusively

- solutions with finite mass

The constant kernel $K \equiv 2$

Explicit self-similar solution

$$f(x) = e^{-x}$$

Domains of attraction (Menon & Pego '04)

There exists a scaling function $s(t)$ such that the rescaled solution to the coagulation equation converges to f if and only if the data $g(0,\cdot)$ satisfy

$$\int_0^x y g(0,y)\,dy \sim L(x) \qquad \text{for a slowly varying } L.$$

Remarks:

- $L(x) \to \infty$ as $x \to \infty$ possible, e.g. $L(x) = \ln x$
- Proof based on Laplace transform

Non-solvable kernels

The case $\gamma < 1$:

- Existence and properties of self-similar profile with finite mass (Fournier-Laurençot '05,'06; Escobedo-Mischler-Ricard '05,'06; Mischler-Canizo '11, N.-Velázquez '11)

Recent progress:

- Uniqueness for $K(\xi, \eta) = (\xi\eta)^{-\alpha}$ (Laurençot '18)
- Uniqueness for kernels close to constant (N.-Throm-Vel. '15)
- Domains of attraction for diagonal kernel (Laurençot-N.-Vel. '18)

Open:

- General uniqueness
- Domains of attraction of self-similar profiles

The case $\gamma = 1$:

- Only the case $K(\xi, \eta) = \xi + \eta$ has been considered

The borderline case: $\gamma = 1$:

Two different cases

(van-Dongen & Ernst '88)

Class II:

$$\lim_{\xi \to 0} K(\xi, 1) = 1$$

Examples:

$$K(\xi, \eta) = \xi + \eta$$
$$K(\xi, \eta) = \left(\xi^{1/3} + \eta^{1/3}\right)^3$$

Class I:

$$\lim_{\xi \to 0} K(\xi, 1) = 0$$

Examples:

$$K(\xi, \eta) = (\xi\eta)^{1/2}$$
$$K(\xi, \eta) = \xi^2 \delta_{\xi - \eta}$$

A change of variables

Original equation: conservative form

$$\partial_t\big(\xi g(t,\xi)\big) = -\partial_\xi\Big(\int_0^\xi \int_{\xi-\eta}^\infty K(\eta,\zeta)\eta g(t,\eta) g(t,\zeta)\, d\zeta\, d\eta\Big)\,.$$

New variables

$$\xi = e^x\,, \qquad u(t,x) = \xi^2 g(t,\xi)$$

Equation in new variables

$$\partial_t u = -\partial_x\Big(\int_{-\infty}^x \int_{x+\log(1-e^{y-x})}^\infty K(e^{y-z},1) u(t,y) u(t,z)\, dz\, dy\Big)$$

Note:

$$M := \int_0^\infty \xi g(t,\xi)\, d\xi = \int_{-\infty}^\infty u(t,x)\, dx = \text{const.}$$

Special solutions

Ansatz: $u(t,x) = G(x - bt)$

$$
\begin{aligned}
bG(x) &= \int_{-\infty}^{x} \int_{x+\ln(1-e^{y-x})}^{\infty} K(e^{y-z},1) G(y) G(z)\, dz\, dy \\
&= \int_{-\infty}^{0} \int_{\ln(1-e^{y})} K(e^{y-z},1) G(x+y) G(x+z)\, dz\, dy
\end{aligned}
$$

Hence:

- Self-similar solutions in variable ξ with finite mass correspond to traveling waves in variable x with finite integral

Formal considerations

Note

$$\int_{-\infty}^{0}\int_{\ln(1-e^y)}^{\infty} K(e^{y-z},1)\,dz\,dy \begin{cases} =\infty & \text{Class II} \\ <\infty & \text{Class I} \end{cases}$$

First conclusions:

- Class II: self-similar solutions with finite mass can exist (Bonacini-N.-Velázquez '17)
- Class I: Formal asymptotics

$$G(x) \to G_{-\infty} > 0 \qquad \text{as } x \to -\infty \quad \Rightarrow \quad \int_{-\infty}^{\infty} G(x)\,dx = \infty$$

Consequence: Solutions with finite mass cannot exist.

What happens for solutions with integrable data in the long-time limit?

Long-time behaviour

Recall evolution equation

$$\partial_t u = -\partial_x \Big(\int_{-\infty}^{0} \int_{\log(1-e^y)}^{\infty} K(e^{y-z}, 1) u(t, y+x) u(t, z+x)\, dz\, dy \Big)$$

and

$$\int_{-\infty}^{\infty} u(t,x)\, dx = \text{const.}$$

Rescaling:

$$u_\varepsilon(\tau, \tilde{x}) = \frac{1}{\varepsilon} u\Big(\frac{\tau}{\varepsilon^2}, \frac{\tilde{x}}{\varepsilon}\Big)$$

Result:

$$\partial_\tau u_\varepsilon = -\partial_{\tilde{x}} \Big(\int_{-\infty}^{0} \int_{\varepsilon \ln \left(1-e^{\frac{y}{\varepsilon}}\right)}^{\infty} \frac{K\left(e^{\frac{y-z}{\varepsilon}}, 1\right)}{\varepsilon^2} u_\varepsilon(\tilde{x}+y) u_\varepsilon(\tilde{x}+z)\, dz\, dy \Big)$$

$$\approx -c_0 \partial_{\tilde{x}} \left(u_\varepsilon(\tilde{x})^2 \right),$$

The inviscid Burgers equation

Burgers equation; positive data with finite mass

$$\partial_t u + \partial_x\Big(\frac{u^2}{2}\Big) = 0 \qquad \text{and} \qquad \int_{\mathbb{R}} u(0,x)\,dx = M$$

If $u(0,\cdot) \geq 0$, then u converges to the N-wave

$$u(t,x) \sim \tfrac{1}{\sqrt{t}} N\big(\tfrac{x}{\sqrt{t}}; M\big) \qquad \text{with} \qquad N(x;M) = \frac{x}{2}\chi_{[0,2\sqrt{M}]}(x)$$

Riemann data: convergence to a traveling wave

Conjecture:

- Solutions to coagulation equation display the same long-time behaviour

Special case: $K(\xi,\eta)=\xi^2\delta_{\xi-\eta}$

Equation:

$$\partial_t u(t,x) = u(t,x-1)^2 - u(t,x)^2$$

Consider first:

$$\dot u_j(t) = u_{j-1}^2 - u_j^2\,, \qquad j\in\mathbb{Z}$$

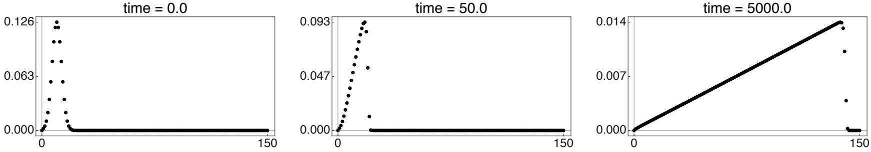
Integrable data: If $u_j^0 \geq 0$ and $\sum_j u_j^0 = M$, then

$$\sum_j \left| u_j(t) - \frac{1}{\sqrt{t}} N\left(\tfrac{j}{\sqrt{t}}; M\right)\right| \to 0$$

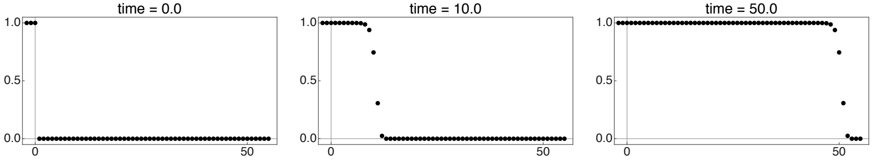
as $t\to\infty$, with the N-wave $N(x;M) = \frac{x}{2}\chi_{[0,2\sqrt{M}]}(x)$

Numerical simulations for diagonal kernel

Integrable data



Riemann data



Family of lattices

Equation with diagonal kernel

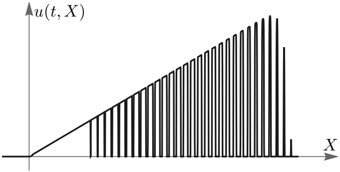
$$\partial_t u(t,x) = u(t,x-1)^2 - u(t,x)^2$$

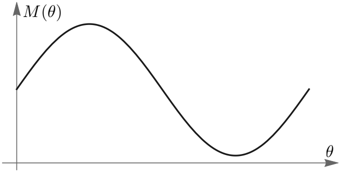
Reduction: suffices to study $u(t,n+\theta)$ with $\theta \in [0,1)$

We have

$$u(t,n+\theta) \sim \frac{1}{\sqrt{t}} N\Big(\frac{n+\theta}{\sqrt{t}}; M(\theta)\Big)$$

$\Rightarrow$ oscillatory behaviour for nonconstant $M(\theta)$:





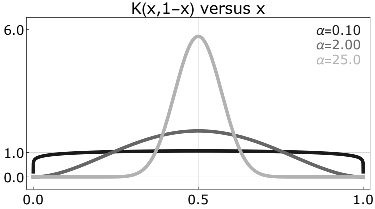
A family of Class I kernels

Family of kernels:

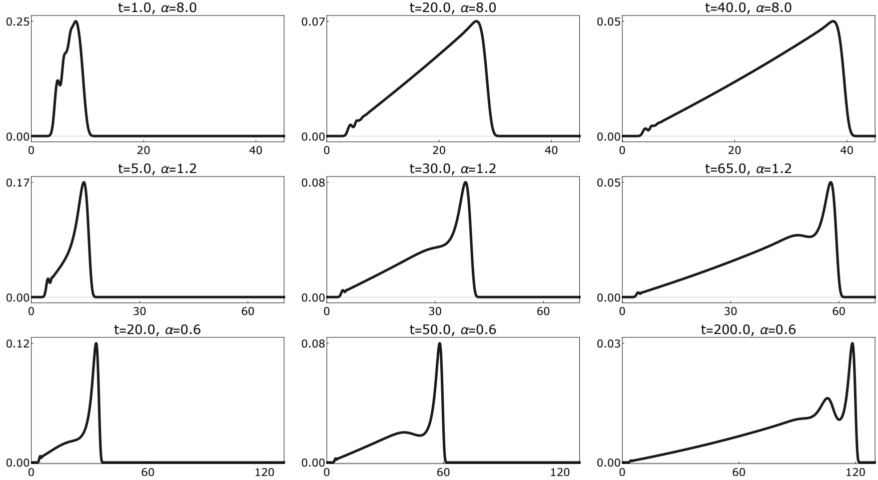
$$K_\alpha(\xi,\eta) = c_\alpha \xi^\alpha \eta^\alpha (\xi+\eta)^{1-2\alpha}\,, \qquad \alpha > 0$$

Simulations

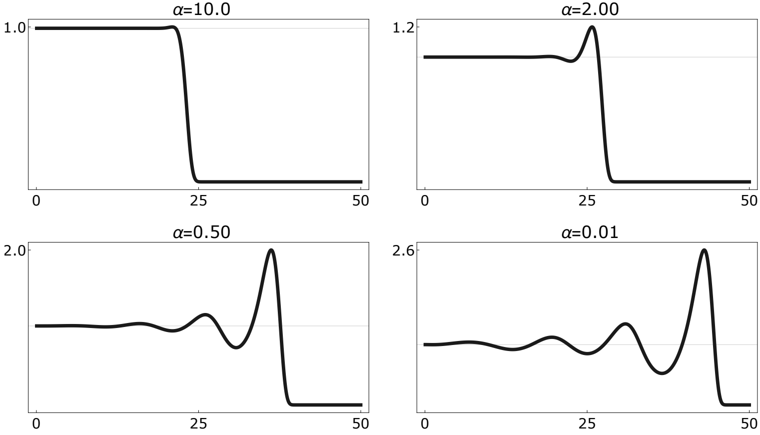
- initial data: smooth with compact support
- Snapshots of the evolution for different values of α



Results of simulations: small and moderate α



Traveling waves



- Detailed asymptotics of waves (N.-Velázquez '18)

First conclusions

Formal asymptotics and simulations suggest

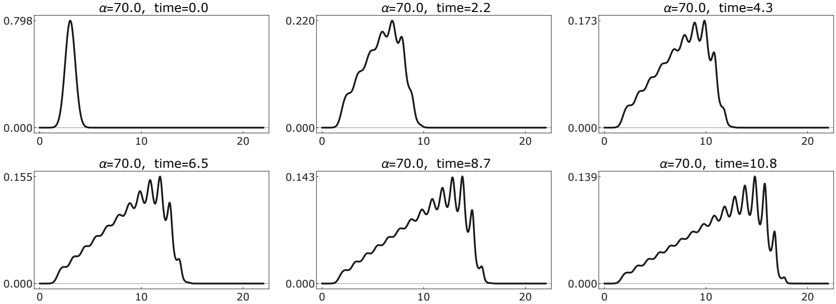
Oscillations

- For small α there are traveling waves with oscillations in front of the shock
- For moderate α, there are monotone traveling waves
- For kernels with very large α: unclear

Instabilities

- For small α the constant solution (and probably the traveling wave) is linearly stable
- For large α the constant solution (and probably the traveling wave) is unstable

Instabilities for kernels close to diagonal



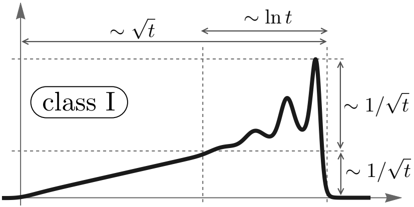
Conjecture:

- Evolutions towards peak solutions

Summary on Class I kernels

Conjectures

- Integrable data; α not too large $\Rightarrow$ Convergence to *N*-wave
- For small α profile governed by oscillating traveling wave



- Instability of constant solutions for large α suggests that in this case there is no convergence to *N*-wave
- Simulations suggest evolution into peaks
- Corresponding result for $\gamma < 1$ is work in progress

Summary

Smoluchowski's coagulation equation

- Mass conservation vs gelation

Self-similar long-time behaviour

- Solvable kernels understood
- Mostly open for all other kernels

General expectation:

- convergence to self-similar form

Our conjecture:

- In general not true if the kernel concentrates on the diagonal