Instantaneous gelation and explosive condensation in non-equilibrium cluster growth

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Non-equilibrium statistical physics
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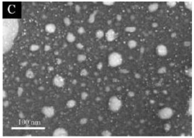
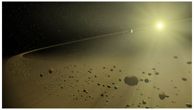
Kinetics of non-equilibrium particle growth : motivation





- Many particles of one material dispersed in another.
- Transport is diffusive or advective.
- Particles grow upon contact.

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

Growth mechanisms:

- Aggregation
- Exchange-driven growth
- Ostwald ripening

Exchange-driven growth

Upon interaction clusters exchange a single monomer:

$$(i,j) \overset{K(i,j)}{\to} (i \pm 1, j \mp 1)$$

The interaction kernel, $K(i,j)$, gives the rate of exchange which typically depends on the sizes of the interacting particles.
Mean field rate equations for $c_k(t)$ - density of particles of size k:

$$\frac{dc_k}{dt} = \sum_{i,j} K(i,j)\, c_i\, c_j \, \left[\delta_{k,i+1} + \delta_{k,i-1} - 2\delta_{k,i}\right] \tag{1}$$

Monodisperse initial condition $c_k(0) = \delta_{k,1}$.
Single conserved quantity, $M_1 = \sum_{k=1}^{\infty} k\, c_k(t)$, total mass.

E. Ben-Naim and P. Krapivsky, Phys. Rev. E, 68:031104, (2003)

Irreversible aggregation

Upon interaction clusters merge:

$$(i,j) \overset{K(i,j)}{\to} (i+j).$$

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 interaction kernels

Notation:In many applications kernel is homogeneous:

$$K(am_1, am_2) = a^{2\gamma} K(m_1, m_2)$$
$$K(m_1, m_2) \sim m_1^{\mu} m_2^{\nu} \quad m_1 \ll m_2.$$

Clearly $2\gamma = \mu + \nu$.

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 ($\nu = \frac{4}{3}$, $\mu = 0$) :

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

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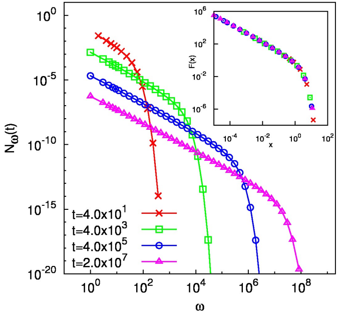
Self-similar evolution of particle size distribution



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:

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

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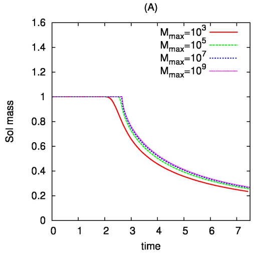
Violation of mass conservation: the gelation transition

Microscopic dynamics conserve mass: $c_{m_1} + c_{m_2} \to c_{m_1+m_2}$.



$M_1(t)$ 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 $2\gamma > 1$:

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

(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...

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Instantaneous gelation

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

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

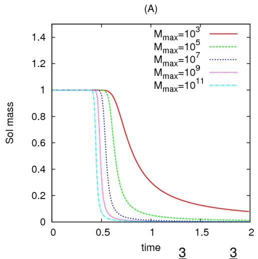
$\mu + \nu = 2\gamma$ so that gelation always occurs if ν is big enough.

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?

Instantaneous gelation in 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 that for $\nu > 1$:

$$t^*_M \sim \log M^{-\alpha} \qquad \alpha = \nu - 1?$$

This suggests such models are physically reasonable.

Gelation transition in exchange-driven growth

Similar phenomenology applies to the mean-field theory of exchange-driven growth (Ben-Naim & Krapivsky, PRE, (2003)).

For $K(i,j) = (ij)^\gamma$, there are 3 regimes based, on the value of γ and the growth of the typical cluster size, $m(t)$,:

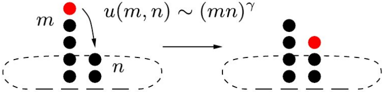
No gelation	$m(t) \sim t^{\frac{1}{3-2\gamma}}$	$0 < \gamma < \frac{3}{2}$
Regular gelation	$m(t) \sim (t^* - t)^{\frac{1}{3-2\gamma}}$	$\frac{3}{2} < \gamma < 2$
Instantaneous gelation	$m(t) = \infty$	$\gamma > 2$

Gelation is "harder" to achieve for exchange-driven growth than for irreversible aggregation (the critical value of γ is higher) since dynamics allows particles to shrink as well as grow. For finite systems of size N, heuristic argument gives the gelation time

$$T_N^* \sim (\log N)^{-(\gamma-2)} \quad \text{as } N \to \infty.$$

Spatially extended models of non-equilibrium growth

We now consider an class of spatially extended models which generalise the Zero-Range Process.



Lattice of size L: Λ_L (in our case a ring).
Configurations: $\boldsymbol{\eta} = \{\eta_x : x \in \Lambda_L\}$ (η_x is # particles at site x).
Particles jump from site x to site y with rate:

$$c(\boldsymbol{\eta}, x, y) = p(x, y)\, u(\eta_x, \eta_y)$$

Symmetric transport: $p(x, y) = \frac{1}{2}\delta_{y,x+1} + \frac{1}{2}\delta_{y,x-1}$.
Asymmetric transport: $p(x, y) = \delta_{y,x+1}$.

Exchange-driven growth is an analogue at mean field level.

Stationary state distribution

We consider the product form for the jump rates:

$$u(n,m) = n^{\gamma}\ (d + m^{\gamma}) \qquad \text{with } \gamma > 1 \text{ and } d > 0. \qquad (2)$$

One of a class of models [M. Evans, S. Majumdar & R. Zia, J. Phys. A, 37(25):L275, (2004)] with factorised stationary state :

$$\mathbb{P}^L_\phi(\boldsymbol{\eta}) = \prod_{x\in\Lambda_L} p_\phi(\eta_x) = \prod_{x\in\Lambda_L} \frac{1}{z(\phi)}\, w(\eta_x)\, \phi^{\eta_x}.$$

Here the stationary weights are

$$w(n) = \prod_{k=1}^{n} \frac{(k-1)^{\gamma} + d}{k^{\gamma}} \sim n^{-\gamma} \qquad \text{as } n \to \infty,$$

and the single site partition function is

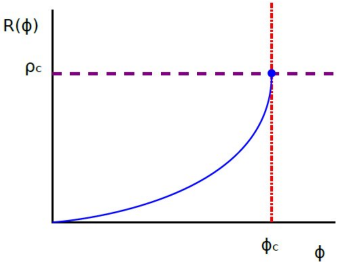
$$z(\phi) = \sum_{k=0}^{\infty} w(k)\, \phi^k.$$

Condensation transition

The parameter ϕ controls the average particle density:

$$R(\phi) = \langle \eta_x \rangle_\phi = \phi\, \partial_\phi \log z(\phi).$$

$R(\phi)$ increases monotonically from $R(0) = 0$ to $\rho_c = R(1)$:

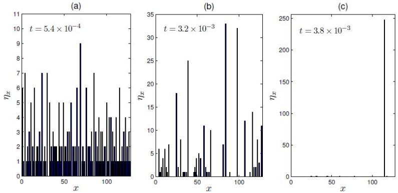


Key observation: $\rho_c < \infty$ when $\gamma > 2$. If the initial density exceeds ρ_c, the excess particles concentrate on a single site.

This phenomenon is referred to as the *condensation transition*: in the limit $L \to \infty$, a finite fraction of the total mass in the stationary state is found on a single site.

Kinetics of the condensation transition

Knowledge of the stationary state does not tell us anything about the dynamics



Snapshots of configurations of Zero Range Process, $u(n, m) = 1 + \gamma/n$, with $\gamma = 5$, $L = 128$ and $\rho = 2 > \rho_c$.

(from Y.-X. Chau, PhD thesis, Univ. of Warwick (2015))

In particular, we would like to know what is the characteristic time to reach the stationary state as a function of the system size, L? If, $\gamma > 2$ and $\rho > \rho$ what is the time, T_{ss}, until the condensate forms? Mean field model doesn't help: $T_{ss} = 0$!

[movie for ZRP with $\gamma = 3$ - from B. Waclaw & M. Evans, PRL (2012)]

Explosive condensation for asymmetric transport

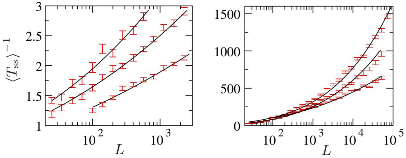
B. Waclaw and M. R. Evans. Phys. Rev. Lett., 108(7):070601 (2012) studied the following model:

$$u(n,m) = ((n+d)^\gamma - d^\gamma)\,(d+m)^\gamma \quad \text{with } \gamma > 1 \text{ and } d > 0. \tag{3}$$

with totally asymmetric transport. They found that for $\gamma > 2$:

$$\langle T_{SS} \rangle \sim (\log L)^{1-\gamma} \quad \text{as } L \to \infty.$$

Condensation is instantaneous as $L \to \infty$: *explosive condensation*.



[movie for Model 3 with $\gamma = 3$ - from B. Waclaw & M. Evans, PRL (2012)]

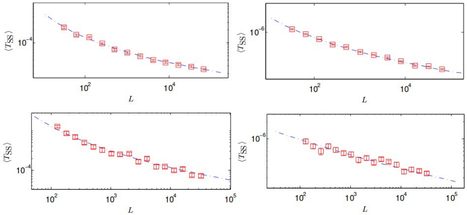
Explosive condensation for symmetric transport

Is the asymmetric dynamics required for explosive condensation? We considered the simpler rates

$$u(n,m) = n^{\gamma}\ (d + m^{\gamma}) \qquad \text{with } \gamma > 2 \text{ and } d > 0.$$

with totally symmetric hopping rates. We find that explosive condensation is delayed to $\gamma > 3$. Thereafter

$$\langle T_{SS} \rangle \sim (\log L)^{3-\gamma} \quad \text{as } L \to \infty.$$



T_{SS} vs L for above rates with $\gamma = 5$ (left) and $\gamma = 7$ (right) and values of $d = 0.1$ (top) and $d = 1.0$ (bottom).

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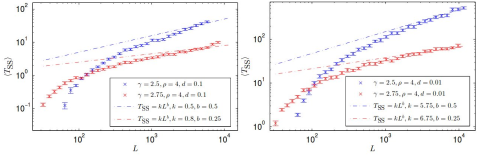
Coarsening: a regime dominated by spatial correlations

In the range $2 < \gamma < 3$ (for which the asymmetric model exhibits explosive condensation), the symmetric model exhibits condensate growth by coarsening. This leads to a condensate size growing algebraically in time and $\langle T_{SS} \rangle$ increases with the system size:

$$\langle T_{SS} \rangle \sim L^{3-\gamma} \quad \text{as } L \to \infty.$$



T_{SS} vs L in coarsening regime for $\gamma = 2.5$ (blue) and $\gamma = 2.75$ (red) and $d = 0.1$ (left) and $d = 0.01$ (right).

Mixing is too weak to overcome spatial correlations generated by interactions.

The mechanism of explosive condensation

The average cluster size is dominated by the growth of the largest cluster. A cluster of size m gains mass at a rate $D(m)/m$ where $D(m)$ is the hopping rate. A heuristic argument suggests

$$D(m) \sim m^{\gamma-1}.$$

Then for $\gamma > 3$, the largest cluster grows according to

$$\frac{dm}{dt} = c\, m^{\gamma-2} \Rightarrow m(t) = c\,(t^* - t)^{-\frac{1}{\gamma-3}}$$

where $t^* = c^{-1}\, m(0)^{3-\gamma}$. The initial condition $m(0)$ comes from initial fluctuations in site occupancy. For Poisson initial conditions, these fluctuations are of order $\log L$.
This gives a time to formation of the condensate,
$t^* \sim (\log L)^{3-\gamma}$.

Summary

- Instantaneous gelation is a physically relevant phenomenon rather than a mathematical curiosity but it must be interpreted carefully via regularisation.
- The slow dependence of the regularised gelation time on the regularisation parameter may make it difficult to observe in practice.
- Explosive condensation can be thought of as a spatially extended example although the analogy is closer with exchange-driven growth than with aggregation.
- Explosive condensation can occur in models with symmetric dynamics although its onset is delayed ($\gamma > 3$) compared to the asymmetric and mean field cases ($\gamma > 2$).

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