Phase separation and oscillations in cluster growth models

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November 18 2020

Outline

- Introduction and motivation on growth mechanisms
- Longtime behaviour under detailed balance
- Self-similar behavior without detailed balance
- Oscillatory behavior under suitable forcing

Introduction and Motivation

Models of nucleation and condensation

Nucleation of oversaturated vapor:

- Only monomers move
- no collisions between clusters
- clusters grow/shrink by one monomer

Applications:

- polymerization
- cloud and galaxy formation mechanism

[Smoluchowski 1916, Becker–Döring 1935]

[Tanaka et al J. Chem. Phys. 2011]

Models of nucleation and condensation

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[Smoluchowski 1916, Becker–Döring 1935]

Clustering of granular gases:

- Single beads hop to neighboring cells
- hopping rate depends on cell filling
- phases: frozen, clustering, gaseous

Applications:

- migration, population dynamics
- wealth exchange

[Spitzer 1970 zero-range process]

[S Dorbolo et al 2011 Eur. J. Phys. 32]

Goal: Dynamic of cluster population.

Longtime behavior of the exchange-driven growth model

[S. J Nonlinear Sci '19]

Exchange driven growth model (EDG)

Previous models evolve size distribution $(X_k)_{k\geq 0}$ in a population of clusters as

$$X_{k-1} + X_l \underset{K(k,l-1)}{\overset{K(l,k-1)}{\rightleftharpoons}} X_k + X_{l-1} \ , \qquad \text{for} \quad k,l \geq 1 \ .$$

- $K(l,k-1)$ rate kernel: jump of monomer from l to $k-1$ cluster
- rate equation is a countable set of nonlinear coupled ODEs:

$$\begin{aligned} \dot{c}_k \quad &= \quad \sum_{l\geq 1} K(l,k-1)c_l c_{k-1} - \sum_{l\geq 1} K(k,l-1)c_k c_{l-1} \\ &\quad - \sum_{l\geq 1} K(l,k)c_l c_k + \sum_{l\geq 1} K(k+1,l-1)c_{k+1}c_{l-1}. \end{aligned} \tag{EDG}$$

- two conservation laws:

$$1 = \sum_{k\geq 0} c_k \qquad \text{and} \qquad \varrho = \sum_{k\geq 1} k c_k$$

Theorem (Well posedness [S. J Nonlinear Sci '19])

If the kernel K has at most linear growth $K(k,l) \leq C\,k\,l$, then the solution to (EDG) is a semigroup on $\mathcal{P}^\varrho = \{c \in \ell^1(\mathbb{N}_0) \ : \ c_k \geq 0 \ , \ \sum_{l\geq 0} c_k = 1 \ , \ \sum_{l\geq 1} l\, c_k = \varrho\}$.

Equilibria - longtime behavior - phase separation

If the kernel is curl-free

$$X_{k-1} + X_l + X_0 \underset{K(k,l-1)}{\overset{K(l,k-1)}{\rightleftharpoons}} X_k + X_{l-1} + X_0$$

$$X_{k-1} + X_l + X_0 \underset{K(1,l-1)}{\overset{K(l,0)}{\rightleftharpoons}} X_{k-1} + X_{l-1} + X_1 \underset{K(k,0)}{\overset{K(1,k-1)}{\rightleftharpoons}} X_k + X_{l-1} + X_0$$

$$\iff \quad K(k,l-1)\,K(l,0)\,K(1,k-1) = K(l,k-1)\,K(k,0)\,K(1,l-1)$$

then there exists a chemical potential and (formal) equilibria

$$Q_0 = 1, \quad Q_l = \prod_{k=1}^{l} \frac{K(1,k-1)}{K(k,0)} \quad \text{and} \quad \omega_l(\phi) = \frac{\phi^l\, Q_l}{Z(\phi)} \quad \text{with} \quad Z(\phi) = \sum_{l\geq 0} \phi^l Q_l$$

These equilibria have a critical mass density $\varrho_c \in [0,\infty]$

$$\varrho_c = \limsup_{\phi\uparrow\phi_c} \sum_{l\geq 1} l\omega_l(\phi) \qquad \text{with} \qquad \phi_c = \lim_{k\to\infty} \frac{K(k,0)}{K(1,k-1)} \in (0,\infty].$$

$\Rightarrow$ Free energy functional (gradient flow, Lyapunov function)

$$\mathcal{F}[c] = \sum_{k\geq 0} c_k \log \frac{c_k}{Q_k}$$

Longtime behavior and phase separation

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Theorem [S. J Nonlinear Sci ’19]

Let K be curl-free, sublinear, sufficiently regular with $\phi_c \in (0,\infty)$.
Then for any $\varrho \in (0,\infty)$ and any $c(0) \in \mathcal{P}^\varrho$, the solution c of (EDG) satisfies $\forall \varepsilon > 0$

1. If $\varrho \le \varrho_c$: Then $\mathcal{F}[c(t)] \to \mathcal{F}[\omega^\varrho]$ and $\displaystyle\sum_{l\ge 0}(l+1)|c_l(t) - \omega_l^\varrho| \to 0$ as $t \to \infty$.
2. If $\varrho > \varrho_c$: Then $\mathcal{F}[c(t)] \to \mathcal{F}[\omega^{\varrho_c}] + (\varrho - \varrho_c)\log\phi_c$ and $c_l(t) \to \omega_l^{\varrho_c}$ as $t \to \infty$.
   In particular, excess mass $\varrho - \varrho_c$ vanishes!

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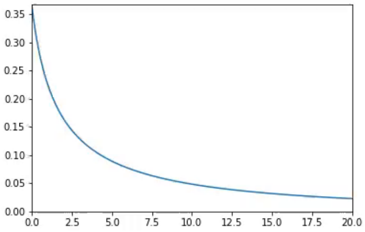
1



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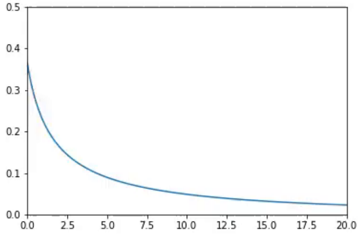

Self-similar behavior of the exchange-driven growth model

[Eichenberg-S. arXiv:2005.11980]

Special class of kernels

Product kernel: for $\lambda \in [0,2)$

$$K(k,l) = K_\lambda(k,l) = a_\lambda(k)a_\lambda(l)$$

$$\text{with} \quad a_\lambda(k) = \begin{cases} k^\lambda, & \lambda > 0, \\ 1 - \delta_{k,0}, & \lambda = 0, \end{cases}$$

- $K_\lambda(k,0) = 0$ for all $k \geq 1$ $\Rightarrow$ no formation of new clusters
- Homogeneity and symmetry simplify (EDG) through moments

$$M_\kappa[c] = \sum_{l\geq 1} l^\kappa \, c_l$$

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$$\begin{cases} \dot{c}_0 = M_\lambda[c]\, c_1, \\ \dot{c}_1 = M_\lambda[c]\left(-2c_1 + 2^\lambda c_2\right), \\ \dot{c}_k = M_\lambda[c]\left((k-1)^\lambda c_{k-1} - 2k^\lambda c_k + (k+1)^\lambda c_{k+1}\right). \end{cases} \qquad (\mathrm{EDG}_\lambda)$$

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$$M_\kappa[c] = \sum_{l\geq 1} l^\kappa\, c_l$$

- Average cluster size

$$\ell(t) = \frac{1}{1-c_0(t)} \sum_{k=1}^{\infty} k\, c_k(t) = \frac{\rho}{M_0[c]},$$

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Theorem (Coarsening rate)

$$\ell(t) \propto \begin{cases} t^\beta, & \text{if } 0 \le \lambda < 3/2, \\ \exp(Ct), & \text{if } \lambda = 3/2, \\ (t_{\mathrm{gel}} - t)^\beta, & \text{if } 3/2 < \lambda < 2, \end{cases}$$

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- Coarsening exponent

$$\beta = \frac{1}{3-2\lambda}.$$

Self-similar behavior

Behave solutions dynamical self-similar?

$$c_k(t) \propto \rho\, s(t)^{-2} g_\lambda\big(s(t)^{-1} k\big) \qquad \text{for } t \gg 1?$$

for the explicit profile

$$g_\lambda(x) = \frac{1}{Z_\lambda} \frac{x^{1-\lambda}}{2-\lambda} \exp\left(-\frac{x^{2-\lambda}}{(2-\lambda)^2}\right),$$

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Measure-valued formulation

$$\mu_c(t) = s(t)\sum_{k\geq 1} c_k(t)\delta_{s(t)^{-1}k}.$$

Number of clusters

$$M_0[c] = 1 - c_0 = s^{-1}(t)\int_0^\infty \mathrm{d}\mu_c.$$

Total mass density

$$M_1[c] = \int_0^\infty \mathrm{d}\mu_c.$$

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$$g_\lambda(x) = \frac{1}{Z_\lambda}\frac{x^{1-\lambda}}{2-\lambda}\exp\Big(-\frac{x^{2-\lambda}}{(2-\lambda)^2}\Big),$$

Theorem (Self-similar behavior)

1. For $0 \le \lambda < 3/2$ there exists $C = C(\lambda,\rho) > 0$ and
$$s(t) = Ct^\beta \qquad \text{with } \beta = (3-2\lambda)^{-1},$$
such that every global solution c to (EDG$_\lambda$) satisfies
$$\mu_c(t) \rightharpoonup \rho\, g_\lambda \qquad \text{as } t \to \infty.$$
2. For $\lambda = 3/2$ …
3. For $3/2 < \lambda < 2$ and t_{gel} as before there exists $C = C(\lambda,\rho) > 0$ and
$$s(t) = C(t_{\text{gel}} - t)^\beta \qquad \text{with } \beta = (3-2\lambda)^{-1},$$
such that every solution c to (EDG$_\lambda$) existing on $[0, t_{\text{gel}})$ satisfies $\qquad \mu_c(t) \rightharpoonup \rho\, g_\lambda \qquad \text{as } t \to t_{\text{gel}}.$

Measure-valued formulation

$$\mu_c(t) = s(t)\sum_{k\ge1} c_k(t)\delta_{s(t)^{-1}k}.$$

Number of clusters

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Total mass density

$$M_1[c] = \int_0^\infty \mathrm{d}\mu_c.$$

Some ingredients for the proof

Time-change

$$\tau(t) = \int_0^t M_\lambda[c](s)\,\mathrm{d}s.$$

Discrete weighted Lapplacian:

$$\begin{cases} \partial_\tau u = \Delta_{\mathbb{N}}(a_\lambda u), & k \geq 1, \\ u(\tau, 0) = 0, & \tau \geq 0. \end{cases}.$$

Tail-distribution: $U(t,k) = \sum_{l \geq k} u(t,l)$

$$\begin{cases} \partial_t U(k) = \partial^-(a_\lambda \partial^+ U)(k), \\ \partial^+ U(t,0) = 0. \end{cases}.$$

Proposition (Discrete Nash-inequality)

$$\|U\|_2^2 \lesssim \|U\|_1^{\frac{2(2-\lambda)}{3-\lambda}} E_\lambda(U)^{\frac{1}{3-\lambda}},$$

Dirichlet form: $E_\lambda(U) = \sum_{k \geq 1} k^\lambda |\partial^+ U(k)|^2$.

$\Rightarrow$ Nash-continuity, decay, moment bounds, ...

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Continuous solution:

$$\begin{cases} \partial_t \varphi = \partial_x(a_\lambda \partial_x \varphi) = \mathcal{L}_\lambda \varphi, & (t,x) \in \mathbb{R}_+^2, \\ a_\lambda \partial_x \varphi|_{x=0} = 0, & t \in \mathbb{R}_+, \\ \varphi(0,\cdot) = \varphi_0, & x \in \mathbb{R}_+. \end{cases}$$

Discrete-to-continuum interpolation:

$$\mathcal{U}_\varepsilon(t,x) = (\iota_\varepsilon U)(\varepsilon^{-1}t, x) = \varepsilon^{-\alpha} U(\varepsilon^{-1}t, \lfloor \varepsilon^{-\alpha} x \rfloor + 1).$$

parabolic scaling: $k \propto t^\alpha$ with $\alpha = \frac{1}{2-\lambda} \in \left[\frac{1}{2}, \infty\right)$

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Theorem

It holds $\mathcal{U}_\varepsilon \to \mathcal{U}$ solution to (NP').

Proof: Replacement lemma, compactness

Note: For $t = 1$, we get

$$\varepsilon^{-\alpha} U(\varepsilon^{-1}, \lfloor \varepsilon^{-\alpha} x \rfloor + 1) \to \rho\, \mathcal{G}_\lambda(x).$$

$\Rightarrow$ Obtain long-time behavior by setting $t = \varepsilon^{-1}$.

Oscillations in a Becker–Döring model with injection and depletion

[Niethammer-Pego-S.-Velazquez WIP '20]

From the Morgan reaction to the Bubbleator

Morgan reaction[†] describes the oscillatory release of gas CO during dehydration of formic acid in concentrated sulfuric acid

$$\mathrm{HCOOH(soln)} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{CO\,(g)} + \mathrm{H_2O(soln)}$$

SNB[♭] separated reaction into reversible and irreversible parts

$$\mathrm{HCOOH(soln)} \underset{}{\overset{\mathrm{H_2SO_4}}{\rightleftarrows}} \mathrm{CO(soln)} + \mathrm{H_2O(soln)} \qquad \{C\}$$
$$\mathrm{CO(soln)} \longrightarrow \mathrm{CO(g)} \qquad \{P\}$$

Process {P} is separated into a growth process of CO-bubbles

$$\mathrm{CO(soln)} \rightleftarrows \mathrm{CO(nuclei)} \qquad \{P_1\}$$
$$\mathrm{CO(nuclei)} + \mathrm{CO(soln)} \rightleftarrows 2\,\mathrm{CO(bubbles)} \qquad \{P_2\}$$
$$\mathrm{CO(bubbles)} \longrightarrow \mathrm{CO(g)} \qquad \{P_3\}$$

Goal: Minimal models for $\{P_1–P_3\}$ showing oscillations.

† [Morgan, J. S. *J. Chem. Soc., Trans.* 1916, 109, 274-83.]
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[Kunz, H.; Johannesmeyer , F.; Oetken , M.: Das „pulsierende Sektglas“, CHEMKON 7 (2000) 30-31]

Modeling of the Bubbleator

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Ingredients for oscillations in chemical reaction networks:

- open system
- no detailed balance
- feed-back loop (nonlinear)
- multiple stationary points

Bubbleator is a physical-chemical system:[1]

Chemical: reaction provides a constant source of microbubbles

Physical: diffusion of microbubbles into bubbles describes the formation of larger bubbles

Oscillations are caused by the growth process of the bubbles.

Goal: Oscillatory growth model for the statistics of bubble sizes with constant source.

[1] Bowers, P. G.; Noyes, R. M.: *Chapter 13: Gas Evolution Oscillators.* Wiley, New York (1985) 473-492.

Becker-Döring equation – derivation

Model [Becker–Döring '35] for coagulation and fragmentation of clusters consisting of identical monomers (microbubbles)

$$X_1 + X_{l-1} \underset{b_l}{\overset{a_{l-1}}{\rightleftharpoons}} X_l, \qquad l = 2, 3, \dots$$

under the assumption of conservation of the total mass density

$$\sum_{l=1}^{\infty} l\, n_l(t) = \sum_{l=1}^{\infty} l\, n_l(0) = \rho_0.$$

Let J_l be the net-flux from $l-1$ to l-clusters

$$\dot{n}_l(t) = J_{l-1}(t) - J_l(t) \qquad l = 2, 3 \dots .$$

Mass conversation implies

$$\dot{n}_1(t) = -\sum_{l=1}^{\infty} J_l(t) - J_1(t) =: J_0(t) - J_1(t).$$

The (net) flux is determined from mass-action-kinetics

$$J_l(t) = a_l n_1(t) n_l(t) - b_{l+1} n_{l+1}(t), \qquad l = 1, 2, \dots .$$

Becker-Döring equation – stationary states and rates

Stationary states are characterized by the detailed balance condition $J_l = 0$

$$a_l \omega_1 \omega_l = b_{l+1} \omega_{l+1} \quad \Rightarrow \quad \omega_l(z) = z^l Q_l \quad \text{with } Q_1 = 1 \text{ and } Q_l = \frac{a_{l-1} \cdots a_1}{b_l \cdots b_2}, l \geq 2.$$

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Has $\omega(z)$ finite mass?

Assumption: Series $z \mapsto \sum_{l=1}^{\infty} l\omega_l(z)$ has finite radius of convergence $z_s < \infty$ with finite value $\rho_s := \sum_{l=1}^{\infty} l\omega_l(z_s) < \infty$.

Concrete (physical) rates: For $\alpha \in [0,1)$, $\gamma \in (0,1)$ and $z_s, q > 0$

$$a_l := l^\alpha \qquad \text{and} \qquad b_l := l^\alpha\left(z_s + q l^{-\gamma}\right).$$

Example: Exponents 3-dim balls (diffusion-controlled growth): $\alpha = \gamma = \frac{1}{3}$

Stationary state for $l \gg 1$

$$\omega_l(z) \simeq \exp\left(l \log\left(\frac{z}{z_s}\right) - \frac{q}{1-\gamma} l^{1-\gamma}\right).$$

Define $z(\rho_0)$ such that $\sum l\omega_l(z) = \rho_0$ for $\rho_0 \leq \rho_s$ and set $z(\rho_0) = z_s$ for $\rho_0 > \rho_s$.

Becker-Döring equation – long-time behavior

Consider free energy

$$\mathcal{F}(n) := \mathcal{H}(n|\omega(z)) := \sum_{l=1}^{\infty} \omega_l \eta\left(\frac{n_l}{\omega_l}\right) \qquad \text{with} \qquad \eta(x) = x \log x - x + 1.$$

Then

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}(n) = -\sum_{l=1}^{\infty}(a_l n_1 n_l - b_{l+1}n_{l+1})(\log a_l n_1 n_l - \log b_{l+1}n_{l+1}) \le 0$$

Long-time behavior [Ball, Carr, Penrose '89]

- For $z = z(\rho_0)$ as before holds $\mathcal{F}(n) \to 0$ as $t \to \infty$.
- In the case $\rho_0 > \rho_s$ holds $n(t) \overset{*}{\rightharpoonup} \omega(z_s)$ in ℓ^1 as $t \to \infty$.
  In particular $\rho_0 = \sum_l l n_l(t) \not\to \sum_l l\omega_l(z_s) = \rho_s$.
  Moreover, the infimum

$$\inf_{n \in \mathcal{M}(\rho_0)} \mathcal{F}(n) = \mathcal{F}(\omega(z_s)) \qquad \text{is not attained!}$$

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[Niethammer '03, S. '19] find a nonlocal conservation law (LSW) for the excess mass.

The Becker-Döring-Bubbleator: Model

BD-bubbleator: source $S > 0$ and depletion $r > 0$

$$\emptyset \xrightarrow{S} X_1$$

$$X_1 + X_k \underset{b_{k+1}}{\overset{a_k}{\rightleftharpoons}} X_{k+1}\,, \qquad k = 1, 2, 3, \ldots$$

$$X_k \xrightarrow{rk^b} \emptyset, \qquad k = 2, 3, \ldots$$

Reaction rate ODE system

$$\dot{n}_1 = -J_1[n] - \sum_{k=1}^{\infty} J_k[n] + S$$

$$J_k[n] = a_k\, n_1\, n_k - b_{k+1}\, n_{k+1}\,, \qquad k = 2, 3, \ldots$$

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The Becker-Döring-Bubbleator: Model

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Assumptions and regime:

Physical rates (surface area, Gibbs-Thompson):

$$a_k = k^\alpha \quad \text{and} \quad b_k = a_k\left(1 + \frac{q}{k^\gamma}\right).$$

Stationary distribution ($S = 0, r = 0$): $n_1 = 1$

$$\omega_l(n_1) \simeq \exp\left(l \log(n_1) - \frac{q}{1-\gamma} l^{1-\gamma}\right).$$

Let $n_1 = 1 + \varepsilon > 1$: critical radius $k_{\text{crit}}(n_1)$ is

$$a_{k_{\text{crit}}} n_1 - b_{k_{\text{crit}}} = 0 \quad \Leftrightarrow \quad k_{\text{crit}} = \left(\frac{q}{\varepsilon}\right)^{\frac{1}{\gamma}}.$$

Second order expansion: excess defect u

$$n_1 = 1 + \varepsilon + \left(\frac{\varepsilon}{q}\right)^{\frac{1}{\gamma}} u = 1 + \varepsilon + \frac{u}{k_{\text{crit}}}.$$

Constant flux steady states: Nucleation flux

Recall: Zero flux steady states are characterized by the detailed balance condition $J_l = 0$

$$a_l \omega_1 \omega_l = b_{l+1} \omega_{l+1}$$

$$\Rightarrow \quad \omega_l(z) = z^l Q_l$$

with $Q_1 = 1$ and $Q_l = \frac{a_{l-1} \cdots a_1}{b_l \cdots b_2}$.

Constant flux steady states: Nucleation flux

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Now: Constant flux steady states $\{f_k\}_{k\geq 1}$ solve $J_k[f] = J(\bar{n}_1) \neq 0$

$$a_k \bar{n}_1 f_k(\bar{n}_1) - b_{k+1} f_{k+1}(\bar{n}_1) = J_k[f] = J(\bar{n}_1)\,, \qquad l \geq 2\,,$$

$f_1(\bar{n}_1) = \bar{n}_1$ and such that $f_k(\bar{n}_1)$ is bounded as $k \to \infty$.

$$\Rightarrow \qquad f_k(\bar{n}_1) = J(\bar{n}_1) Q_k \bar{n}_1^k \sum_{l=k}^{\infty} \frac{1}{a_l Q_l \bar{n}_1^{l+1}}$$

where
$$\frac{1}{J(\bar{n}_1)} = \sum_{l=1}^{\infty} \frac{1}{a_l Q_l \bar{n}_1^{l+1}}\,.$$

By Laplace asymptotics follows for $n_1 = 1 + \varepsilon + \left(\frac{\varepsilon}{\gamma}\right)^{\frac{1}{\gamma}} u$

$$J(n_1) \simeq J_\infty e^u \qquad \text{with } J_\infty = \sqrt{\frac{\gamma}{2\pi q^{\frac{1}{\gamma}}}}\, \varepsilon^{\frac{\gamma+1}{2\gamma}} \exp\left(-\frac{\gamma}{1-\gamma} q^{\frac{1}{\gamma}} \varepsilon^{-\frac{1-\gamma}{\gamma}}\right).$$

and
$$f_k(\bar{n}_1) \simeq \frac{J(\bar{n}_1)}{\varepsilon a_k} = \frac{J(\bar{n}_1)}{\varepsilon k^\alpha} \qquad \text{for } k \gg k_{\text{crit}}\,.$$

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Quasistationary approximation

Transport approximation of large clusters:

For the flux for cluster much larger the critical radius $k \gg R \gg k_{\mathrm{crit}}$ holds

$$J_k = a_k\big(n_1 - 1\big)n_k - \tfrac{a_k q}{k^\gamma} n_k + b_k n_k - b_{k+1} n_{k+1} \simeq a_k \varepsilon n_k.$$

$\Rightarrow$ transport equation on macroscopic scale: Set $f(k,t) = n_k(t)$

$$\partial_t f(y,t) + \varepsilon \partial_y \big(y^\alpha f(y,t)\big) = -r y^b f(y,t).$$

coupled through boundary layer

$$f(y,t) \simeq J(n_1)\frac{1}{\varepsilon\, y^\alpha} \simeq J_\infty e^u \frac{1}{\varepsilon\, y^\alpha} \qquad \text{for } k_{\mathrm{crit}} \ll y \ll R.$$

Exponential monomer excess:

Introduce cut-off $L \ll 1$ of sub- and supercritical clusters:

$$\frac{\partial_t u}{k_{\mathrm{crit}}} = -\big(L k_{\mathrm{crit}} + 1\big) J(n_1) - \varepsilon \int_{L k_{\mathrm{crit}}+1}^{\infty} f(y,t) y^\alpha \, dy + S.$$

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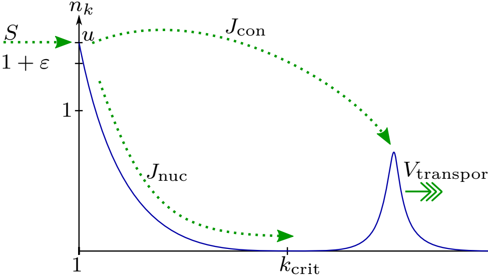

Quasistationary approximation

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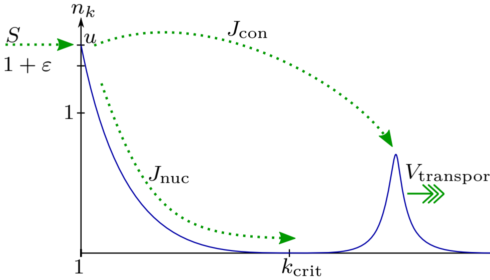

Identification of scales:

- $J_{\text{nuc}} \approx J_{\text{con}} \approx 1 \quad \Rightarrow$ fixes time and length-scale
- S such that $u = O(1) \quad \Rightarrow$ fixes $S > 0$

Limit model and Hopf bifurcation

Model after setting the scales (R, T, S):

Evolution of exponential monomer excess:

$$\partial_\tau u = 1 - \int_0^\infty g(x,\tau) x^\alpha dx$$

Evolution of supercritical cluster density for $x = R^{-1}y > 0$:

$$\partial_\tau g(x,\tau) + \partial_x \big(x^\alpha g(x,\tau)\big) = -\big(TR^b r\big) x^b g(x,\tau)$$

Boundary behavior: $g(x,\tau) \simeq \frac{e^u}{x^\alpha}$ for $x \to 0$

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Change of variable: $\nu = \frac{\alpha}{1-\alpha}$, $\beta = \frac{b}{1-\alpha}$

Limit model

$$\partial_\tau u = 1 - \int_0^\infty h(z,\tau) z^\nu \, dz \,,$$

$$\partial_\tau h(z,\tau) + \partial_z h(z,\tau) = -\theta z^\beta h(z,\tau) \,, \quad z > 0$$

$$h(0,\tau) = e^{u(\tau)} \,,$$

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$$h(0,\tau) = e^{u(\tau)} \,,$$

Integration of characteristics:

$$h(z,\tau) = \exp(u(\tau - z)) \exp\left(-\frac{\theta}{\beta+1} z^{\beta+1}\right)$$

gives in the equation of the monomer excess:

$$\partial_\tau u = 1 - \int_0^\infty e^{u(\tau-z)} \exp\left(-\frac{\theta}{\beta+1} z^{\beta+1}\right) z^\nu dz$$

Constant stationary solution: For any $\theta > 0$

$$1 = e^{u_0} \int_0^\infty \exp\left(-\frac{\theta}{\beta+1} z^{\beta+1}\right) z^\nu dz \,.$$

Limit model and Hopf bifurcation

Model after setting the scales (R, T, S):

Evolution of exponential monomer excess:

$$\partial_\tau u = 1 - \int_0^\infty g(x,\tau) x^\alpha dx$$

Evolution of supercritical cluster density for $x = R^{-1} y > 0$:

$$\partial_\tau g(x,\tau) + \partial_x \left(x^\alpha g(x,\tau)\right) = -\left(T R^b r\right) x^b g(x,\tau)$$

Boundary behavior: $g(x,\tau) \simeq \frac{e^u}{x^\alpha}$ for $x \to 0$

Change of variable: $\nu = \frac{\alpha}{1-\alpha}$, $\beta = \frac{b}{1-\alpha}$

Limit model

$$\partial_\tau u = 1 - \int_0^\infty h(z,\tau) z^\nu \, dz \,,$$

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$$1 = e^{u_0} \int_0^\infty \exp\left(-\frac{\theta}{\beta+1} z^{\beta+1}\right) z^\nu dz \,.$$

Starting point for Hopf analysis:

- Linearization around constant solution
  $$u(\tau) = A + U\left(\frac{\tau}{\sigma}\right), \qquad s = \frac{\tau}{\sigma}.$$
- Find pure imaginary eigenvalues $\Rightarrow$ critical θ^*
- Prove transversality condition: critical eigenvalues get positive real part for $\theta < \theta^*$

  $\Rightarrow$ second order expansion of U.
- β odd has infinitely many bifurcations

Hopf-Bifurcation of the limit model

Parameters: $\theta = 0.1$, $n = 2$, $\beta = 1$

The Becker-Döring-Bubbleator: Model II

Consider the truncated Becker-Döring model on $\{1, 2, \ldots, M\}$

$$X_1 + X_k \rightleftharpoons X_{k+1}\,, \qquad k = 1, \ldots, M-1$$

with constant source $S > 0$ of monomers:

$$\begin{aligned}
\dot{n}_1 &= -J_1[n] - \sum_{k=1}^{M-1} J_k[n] - J_M^{\text{out}}[n] + S \\
J_k[n] &= a_k\, n_1\, n_k - b_{k+1}\, n_{k+1}\,, && \text{for} \quad k = 2, \ldots, M-1 \\
\dot{n}_k &= J_{k-1}[n] - J_k[n] && \text{for} \quad k = 2, \ldots, M-1 \\
\dot{n}_M &= J_{M-1}[n] - J_M^{\text{out}}[n] && \text{with} \quad J_M^{\text{out}}[n] = a_M\, n_1\, n_M\,.
\end{aligned}$$

Oscillations can be observed for the rates:

- strong dissipative dynamic of small clusters $k = 1, \ldots, K$
- transport/hyperbolic dominated dynamic of large clusters $k = K+1, \ldots, M$

$$\begin{aligned}
a_l &= A\,, \quad l = 1, \ldots, K-1 && \text{and} \quad a_l = 1\,, \quad l = K, \ldots, M \\
b_l &= A\,, \quad l = 2, \ldots, K && \text{and} \quad b_l = 0\,, \quad l = K+1, \ldots, M
\end{aligned}$$

Hopf-Bifurcation in $M = 500, K = 15$

Unstable stationary state $M = 500, K = 30$

The Becker-Döring-Bubbleator: Stationary states

$$
\begin{aligned}
\partial_t n_1 &= -A\left[(n_1)^2 - n_2 + \sum_{\ell=1}^{K-1}(n_1 n_\ell - n_{\ell+1})\right] - n_1 \sum_{\ell=K}^{M} n_\ell + S \\
\partial_t n_\ell &= A\left[(n_1 n_{\ell-1} - n_\ell) - (n_1 n_\ell - n_{\ell+1})\right] \quad , \quad 2 \le \ell \le K-1 \\
\partial_t n_K &= A\,(n_1 n_{K-1} - n_K) - n_1 n_K \\
\partial_t n_\ell &= n_1\,(n_{\ell-1} - n_\ell) \quad , \quad K+1 \le \ell \le M
\end{aligned}
$$

Constant flux stationary state is explicit given by

$$
\frac{S}{M+1} = n_1^{K+1} \frac{1-n_1}{1-\left(1-\frac{1}{A}\right)n_1 - \frac{n_1^K}{A}}
$$

$$
\begin{aligned}
n_l &= n_1^l - \frac{S}{M+1}\frac{1-n_1^{l-1}}{1-n_1}\,, && \text{for } l = 2,\dots,K \\
n_l &= n_K\,, && \text{for } l = K+1,\dots,M\,.
\end{aligned}
$$

Quasi-stationary approximation $A \to \infty$

Small clusters become quasistationary in the limit $A \to \infty$

$$n_l = n_1^l \qquad \text{for } l = 2, \dots, K$$

Allows to arrive at simplified systems, after deriving equation for n_1

$$\partial_t n_1 = \frac{S - n_1 \Phi - (n_1)^{K+1}}{\sum_{\ell=1}^{K} \ell^2 (n_1)^{\ell-1}} \qquad \text{with} \quad \Phi = \sum_{\ell=K}^{M} n_\ell$$

$$\partial_t n_\ell = n_1 (n_{\ell-1} - n_\ell) \,, \qquad K + 1 \leq \ell \leq M$$

$$n_K = (n_1)^K$$

which has a constant flux stationary state given by

$$N_1 = \left(\frac{S}{M - K + 2} \right)^{\frac{1}{K+1}} \qquad \text{and} \qquad N_l = N_1^K \quad \text{for } l = K, \dots, M \,.$$

Linearization in the regime $M \gg 1$ shows a Hopf-birfurcation in the parameter K.
Eigenvalues for $M \gg 1$ solve approximately

$$\frac{1}{K} \left(\alpha z^2 + z \right) + \left(1 - e^{-z} \right) = 0 \qquad \text{with} \qquad \alpha = \frac{1}{M^2} \sum^{K-1} (K - m)^2 (N_1)^{-m}$$