From Becker-Doring to Lifshitz-Slyozov: deriving the boundary condition

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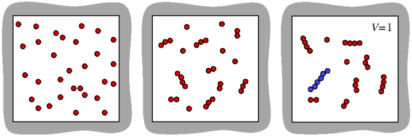
Becker-Döring model for Nucleation

Reversible one-step agregation

$$C_i + C_1 \underset{b_{i+1}}{\overset{a_i}{\rightleftharpoons}} C_{i+1} \qquad (1)$$



$t=0$ $\quad 0<t<t^*$ $\quad t=t^*$

où $C_i = \sharp\{\text{agregates of size i}\}$.

The **nucleation time** is given by the following waiting time,

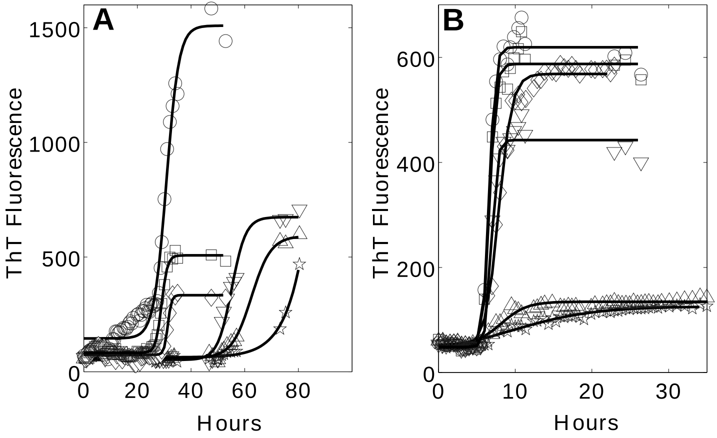
$$t^* = \inf\{t \geqslant 0 : C_N(t) = 1 \mid (C_i(0))_{i\geqslant 1}\}, \qquad (2)$$

Typical initial condition $C_i(t=0) = M\delta_{i=1}$.
N is a size of the nucleus : it's a parameter of the model (with M,a_i, b_i).

Remark

$$C_1(t) + \sum_i iC_i(t) \equiv M\,.$$

This model is used to understand spontaneous protein poylmerization experiments



“Large number limit” of the nucleation time

What are the dependencies of the nucleation time with respect to the model parameters ?
Analytical approximation and numerical simulations showed (R.Y., Maria R. D’Orsogna, Tom Chou, J. Chem. Phys. 2012) :

- non-monotone behavior with respect to the detachment rate b
- complex depencies with respect to the total mass M ($\log t^*$ is not proportional to $\log M$)
- discrete size effect due to specific configuration that are “traps”.

Here, we ask : what is the nucleation time for very large nucleus

$$\lim_{N \to \infty} t^* \tag{3}$$

Choose a fix state space

With $\varepsilon = \dfrac{1}{N} \to 0$, we obtain a fix state space by studying (for appropriately rescaled C_i^ε)

$$\mu_t^\varepsilon(.) = \sum_{i \geqslant 2} C_i^\varepsilon(t)\delta_{i\varepsilon}(.) \ \in \mathcal{M}_b(\mathbb{R}^+) \tag{4}$$

The nucleation time is thus

$$t_\varepsilon^* = \inf\{t \geqslant 0 : \mu_t^\varepsilon(\{1\}) > 0 \mid \mu_0^\varepsilon\}, \tag{5}$$

Based on the flux at size i, for C_i^ε,

$$C_{i-1}^\varepsilon \underset{}{\overset{J_{i-1}^\varepsilon}{\rightleftharpoons}} C_i^\varepsilon \overset{J_i^\varepsilon}{\rightleftharpoons} C_{i+1}^\varepsilon, \tag{6}$$

if

$$J_i^\varepsilon = \frac{1}{\varepsilon}\Big(a_i^\varepsilon C_1^\varepsilon C_i^\varepsilon - b_{i+1}^\varepsilon C_{i+1}^\varepsilon\Big), \tag{7}$$

We will get for the limit $\mu = \lim\limits_{\varepsilon\to 0} \sum\limits_{i\geqslant \mathbf{2}} C_i^\varepsilon(t)\delta_{i\varepsilon}$

a **Lifhsitz-Slyozov equation** (in weak form)

$$\frac{\partial \mu_t}{\partial t} + \frac{\partial\Big(J(x, C_1)\mu_t\Big)}{\partial x} = 0 \Leftrightarrow \frac{d\langle \mu_t, \varphi\rangle}{dt} = \int_0^\infty \varphi'(x) J(x, C_1)\mu_t(dx)\,. \tag{8}$$

with $\varphi \in \mathcal{C}_c(\mathbb{R}_*^+)$ and

$$J(x, C_1) = a(x)C_1 - b(x) \text{ and } C_1(t) + \int_0^\infty x\mu_t(dx) = m\,.$$

References : Laurençot and Mischler 2002 J. Stat. Phys., Collet et al 2002 SIAM J. Appl. Math.

The limit is deterministic, finite or infinite

The nucleation time, for this limiting model

$$\frac{\partial \mu_t}{\partial t} + \frac{\partial\Big((a(x)C_1 - b(x))\mu_t\Big)}{\partial x} = 0\,,$$

is

$$t^* = \inf\{t \geqslant 0 : \mu_t(\{1\}) > 0 \mid \mu_0\}, \tag{9}$$

which can be finite or infinite (but is "easier" to compute, at least numerically).

However for typical initial condition $\mu_0 = 0$, we need $a(0)C_1 - b(0) > 0$ and then a **boundary condition**!

Strategy of proof

To prove a convergence result, the strategy is the following

- Write down equation on μ^ε
- Prove compactness of $((\mu_t^\varepsilon)_{t\leqslant T})_{\varepsilon>0}$ (**“choose” the right scaling for that**)
- Take a convergence subsequence of μ^ε, and prove that all terms in the equation on μ^ε do converge (and find their limit)
- Prove a uniqueness result fot the limit equation.

First problem : Topology !

Compacts of $\mathcal{M}_b(\mathbb{R})$ are not so easy to handle in strong topology, so we use a weak-$*$ topology.
Test functions : $\varphi \in \mathcal{C}_b(\mathbb{R}^+)$ to capture the boundary (**and NOT** $\varphi \in \mathcal{C}_c(\mathbb{R}^+_*)$).
The **mass balance** property $C_1(t) + \sum_i C_i(t) \equiv M$ will translate into

$$C_1^\varepsilon(t) + \int_0^\infty x\mu_t^\varepsilon(dx) \equiv M^\varepsilon. \tag{10}$$

so we actually need to take test functions of the form

$$(1+x)\varphi \text{ with } \varphi \in \mathcal{C}_b(\mathbb{R}^+).$$

(Long calculations...)

With the appropriate scaling, and within the weak topology on

$$(\mathcal{M}_b, (1+x)dx),$$

Proposition

$((\mu_t^\varepsilon)_{t \leqslant T})_{\varepsilon > 0}$ *is compact in* $\mathcal{D}(\mathbb{R}^+, (\mathcal{M}_b, (1+x)dx))$.

GREAT BUT IT'S NOT FINISHED !

Rescaled Equation (1)

So Let's look at the equation on μ^ε, in a weak form,

$$
\begin{aligned}
\langle \mu_t^\varepsilon, \varphi \rangle = \langle \mu_{\mathrm{in}}^\varepsilon, \varphi \rangle + \mathcal{O}_t^{\varepsilon,\varphi} \\
& \int_0^t \varphi(2\varepsilon) \left[a_1^\varepsilon (C_1^\varepsilon(s))^2 - b_2^\varepsilon \langle \mu_s^\varepsilon, 1_{2\varepsilon} \rangle \right] ds \\
& + \int_0^t \int \Delta_\varepsilon(\varphi) a^\varepsilon(x) C_1^\varepsilon(s) \mu_s^\varepsilon(dx)\, ds \\
& - \int_0^t \int \Delta_\varepsilon(\varphi)(x) b^\varepsilon(x) \mu_s^\varepsilon(dx)\, ds\,.
\end{aligned} \tag{11}
$$

Remark

Large monomer number / Slow-down agregation rates / speed up depolymerization rate / **specific scaling for boundary terms $a_1^\varepsilon, b_2^\varepsilon$.**

Rescaled Equation (2)

By compactness, everything converge nicely except the red term !

$$\langle \mu_t^\varepsilon, \varphi \rangle = \langle \mu_{\mathrm{in}}^\varepsilon, \varphi \rangle + \mathcal{O}_t^{\varepsilon,\varphi}$$
$$\int_0^t \varphi(2\varepsilon) \left[a_1^\varepsilon (C_1^\varepsilon(s))^2 - b_2^\varepsilon \langle \mu_s^\varepsilon, 1_{2\varepsilon} \rangle \right] ds$$
$$+ \int_0^t \int_0^{+\infty} \Delta_\varepsilon(\varphi) a^\varepsilon(x) C_1^\varepsilon(s) \mu_s^\varepsilon(dx)\, ds$$
$$- \int_0^t \int_0^{+\infty} \Delta_\varepsilon(\varphi)(x) b^\varepsilon(x) \mu_s^\varepsilon(dx)\, ds\,. \quad (12)$$

We need to look at the term $\langle \mu_s^\varepsilon, 1_{2\varepsilon} \rangle = \ldots = C_2^\varepsilon$!

Fast variable

The equations on C_2^ε involves C_3^ε, which involves C_4^ε and so on...and there are **fast variables**.

$$C_{i-1}^\varepsilon \underset{\frac{1}{\varepsilon} b^\varepsilon(\varepsilon i) C_i^\varepsilon}{\overset{\frac{1}{\varepsilon} a^\varepsilon(\varepsilon(i-1)) C_1^\varepsilon C_{i-1}^\varepsilon}{\rightleftharpoons}} C_i^\varepsilon \underset{\frac{1}{\varepsilon} b^\varepsilon(\varepsilon(i+1)) C_{i+1}^\varepsilon}{\overset{\frac{1}{\varepsilon} a^\varepsilon(\varepsilon i) C_1^\varepsilon C_i^\varepsilon}{\rightleftharpoons}} C_{i+1}^\varepsilon,$$

We cannot hope a convergence in a standard function space. We need a functional space that do not see the fast variations, such as $\mathcal{M}(\mathbb{R}^+, l_1(\mathbb{R}^+))$, (with respect to the weak topology) for the occupation measure, defined by, for measurable sets U of l^1,

$$\Gamma^\varepsilon\Big([0, T] \times U\Big) := \int_0^t \mathbf{1}_{\{(C_i^\varepsilon(s))_i \in U\}} ds$$

Parenthesis (Kurtz' averaging theorem (1992))

Let $\{(X_n, Y_n)\}$ a family of stochastic process, with **suitable compactness conditions**, such that for **suitable test functions** f, g,

$$\begin{aligned} f(X_n(t)) &= \int_0^t Af(X_n(s), Y_n(s))ds + \varepsilon_n^{1,f}(t) + M_t^{1,f,n}, \\ g(Y_n(t)) &= \int_0^t \alpha_n Bg(X_n(s), Y_n(s))ds + \varepsilon_n^{2,g}(t) + M_t^{2,g,n}, \end{aligned}$$

where $M_t^{1,f,n}, M_t^{2,g,n}$ are martingales, $\alpha_n \to \infty$ and

$$\begin{aligned} \lim_{n\to\infty} \mathbb{E}\big[\sup_{t\leqslant T} \mid \varepsilon_n^{1,f}(t) \mid \big] &= 0, \\ \lim_{n\to\infty} \mathbb{E}\big[\sup_{t\leqslant T} \beta_n^{-1} \mid \varepsilon_n^{2,g}(t) \mid \big] &= 0. \end{aligned}$$

Assume that the operator $B_x : \mathcal{D}(B) \to C_b(E_2)$, $B_x g(y) = Bg(x, y)$, has a unique stationary distribution π_x. Then any limiting point X of X_n is solution of the martingale problem for

$$Cf(x) = \int Af(x, y)\pi_x(dy)$$

Theorem

(Under some conditions...) $(\mu^\varepsilon, (C_i^\varepsilon))$ *converges in* $\mathcal{D}(\mathbb{R}^+, (\mathcal{M}, (1+x)dx)) \times \mathcal{M}(\mathbb{R}^+, l_1(\mathbb{R}^+))$ *towards*

$$\begin{aligned}
\langle \mu_t, \varphi \rangle &= \langle \mu_{\text{in}}, \varphi \rangle + \int_0^t \varphi(0) \left[a_1 (C_1(s))^2 - b_2 C_2(s) \right] \\
&\quad + \int_0^t \int_0^{+\infty} \varphi'(x)(a(x) C_1(s) - b(x)) \mu_s(dx)\, ds \,. \\
\langle \mu_t, \mathrm{id} \rangle + C_1(t) &= m := \langle \mu_0, \mathrm{id} \rangle + C_1(0)
\end{aligned}$$

And $(C_i(t))_{i \geqslant 2}$ *is a stationary solution in* l_1 *of the following deterministic Becker-Döring system (***for constant*** $C_1 = C_1(t)$*)*

$$\begin{aligned}
\dot{C}_2 = 0 &= -\Big(\overline{a}_2 C_1 C_2 - \overline{b}_3 C_3 \Big), \\
\dot{C}_i = 0 &= \Big(\overline{a}_{i-1} C_1 C_{i-1} - \overline{b}_i C_i \Big) - \Big(\overline{a}_i C_1 C_i - \overline{b}_{i+1} C_{i+1} \Big) \,.
\end{aligned}$$

where $\overline{a}_i$, $\overline{b}_i$ *depends on the behavior of* a, b *at* 0

For $a(x) = \bar{a}x^r + o(x)$, $b(x) = \bar{b}x^r + o(x)$, $r < 1$, the above equation reduces to, for $C_1(t) \leqslant \frac{\bar{b}}{\bar{a}}$,

$$\begin{aligned}
\langle \mu_t, \varphi \rangle &= \langle \mu_{\mathrm{in}}, \varphi \rangle \\
&\quad + \int_0^t \int_0^{+\infty} \varphi'(x)(a(x)C_1(s) - b(x))\mu_s(dx)\, ds\,. \\
\langle \mu_t, \mathrm{id} \rangle + C_1(t) &= m := \langle \mu_0, \mathrm{id} \rangle + C_1(0)
\end{aligned}$$

and to, for $C_1(t) > \frac{\bar{b}}{\bar{a}}$,

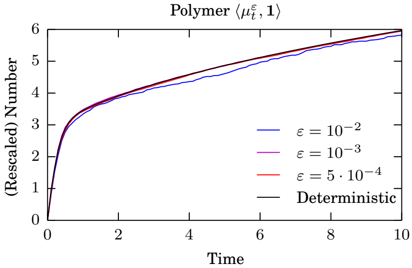
$$\begin{aligned}
\langle \mu_t, \varphi \rangle &= \langle \mu_{\mathrm{in}}, \varphi \rangle + \int_0^t \varphi(0) a_1 (C_1(s))^2 \\
&\quad + \int_0^t \int_0^{+\infty} \varphi'(x)(a(x)C_1(s) - b(x))\mu_s(dx)\, ds\,. \\
\langle \mu_t, \mathrm{id} \rangle + C_1(t) &= m := \langle \mu_0, \mathrm{id} \rangle + C_1(0)
\end{aligned}$$

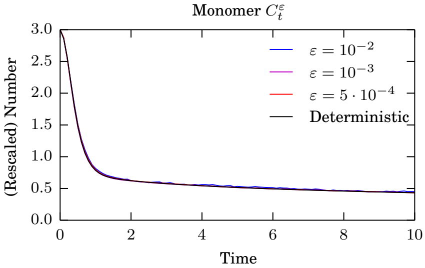
Remark

The boundary condition is : flux at 0 = dimerization rate

Numerical illustration

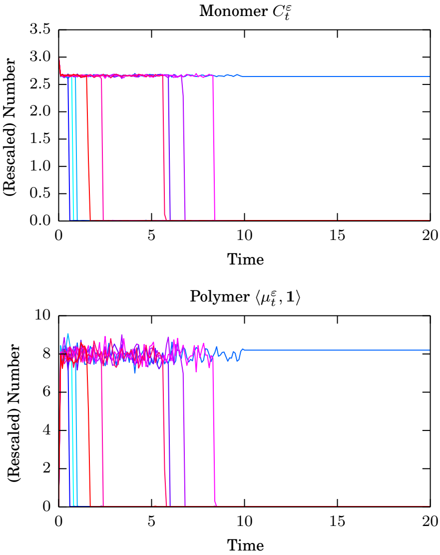
- $a(x) \equiv 1$,
  $b(x) = x$,
- Incoming charcateristics.
- Video





Numerical illustration and further work

- $a(x) \equiv x$,
  $b(x) = 1$,
- outgoing charcateristics.
- Video : **Metastability**



Obrigado !

- *First passage times in homogeneous nucleation and self-assembly*, R.Y., Maria D'Orsogna and Tom Chou (Journal of Chemical Physics (2012) 137 :244107)
- *From a stochastic Becker-Döring model to the Lifschitz-Slyozov equation with boundary value*, Julien Deschamps, Erwan Hingant and R.Y., arXiv :1412.5025 (2014)

Consider a sequence of $(\tilde{a}_i^\varepsilon)$, $(\tilde{b}_i^\varepsilon)$, $(\tilde{C}_i^\varepsilon(0))$, $(\tilde{M}^\varepsilon)$. Let $(\tilde{C}_i^\varepsilon(t))$ be the corresponding solution and define (suppose $a_1^\varepsilon, b_2^\varepsilon, a^\varepsilon, b^\varepsilon$ and $C_1^\varepsilon(0), \mu^\varepsilon(0, dx)$ converges in an appropriate sense)

$$
\begin{aligned}
a_i^\varepsilon &:= \varepsilon^A \tilde{a}_i^\varepsilon , \quad \forall i \geqslant 2 , \\
b_i^\varepsilon &:= \varepsilon^B \tilde{b}_i^\varepsilon , \quad \forall i \geqslant 3 , \\
a_1^\varepsilon &:= \varepsilon^{A_1} \tilde{a}_1^\varepsilon , \\
b_2^\varepsilon &:= \varepsilon^{B_1} \tilde{b}_2^\varepsilon .
\end{aligned}
\qquad
\begin{aligned}
\chi_i^\varepsilon &:= \mathbf{1}_{[(i-1/2)\varepsilon^\beta, (i+1/2)\varepsilon)} , \\
a^\varepsilon(x) &:= \sum_{i \geqslant 2} a_i^\varepsilon \chi_i^\varepsilon(x) , \\
b^\varepsilon(x) &:= \sum_{i \geqslant 3} b_i^\varepsilon \chi_i^\varepsilon(x) .
\end{aligned}
$$

We then define the variables

$$
\begin{aligned}
C_i^\varepsilon &= \varepsilon^\alpha \tilde{C}_i^\varepsilon , \forall i \geqslant 2 , \\
C_1^\varepsilon &= \varepsilon^\theta \tilde{C}_1^\varepsilon .
\end{aligned}
\qquad
\begin{aligned}
\mu^\varepsilon(t, dx) &= \sum_{i \geqslant 2} C_i^\varepsilon(t) \delta_{i\varepsilon^\beta}(dx) , \\
M^\varepsilon &= \varepsilon^{\alpha+\beta} \tilde{M}^\varepsilon .
\end{aligned}
$$

The above results hold with the following choices

$$
\begin{aligned}
\theta &= \alpha + \beta , \\
A &= -\alpha , \\
B &= \beta ,
\end{aligned}
\qquad
\begin{aligned}
A_1 &= -\alpha - 2\beta , \\
B_1 &= 0 ,
\end{aligned}
\qquad
\begin{aligned}
a_i^\varepsilon &\sim \overline{a}_i \varepsilon^{r_a \beta}, \ \forall i \geqslant 2 \\
b_i^\varepsilon &\sim \overline{b}_i \varepsilon^{r_b \beta}, \ \forall i \geqslant 2 , \\
0 &\leqslant \min(r_a, r_b) < 1 .
\end{aligned}
$$

Concrete Example

Consider a sequence of $(\tilde{a}_i^\varepsilon)$, $(\tilde{b}_i^\varepsilon)$, $(\tilde{C}_i^\varepsilon(0))$, $(\tilde{M}^\varepsilon)$. Let $(\tilde{C}_i^\varepsilon(t))$ be the corresponding solution and define (suppose $a_1^\varepsilon, b_2^\varepsilon, a^\varepsilon, b^\varepsilon$ and $C_1^\varepsilon(0), \mu^\varepsilon(0, dx)$ converges in an appropriate sense)

$$\begin{aligned} a^\varepsilon(x) &:= \frac{1}{\varepsilon} \sum_{i \geqslant 2} \tilde{a}_i^\varepsilon \chi_i^\varepsilon(x)\,, \\ b^\varepsilon(x) &:= \varepsilon \sum_{i \geqslant 3} \tilde{b}_i^\varepsilon \chi_i^\varepsilon(x)\,. \end{aligned}$$

$$\begin{aligned} a_1^\varepsilon &:= \frac{1}{\varepsilon^3} \tilde{a}_1^\varepsilon\,, \\ b_2^\varepsilon &:= \tilde{b}_2^\varepsilon\,, \\ \tilde{a}_i^\varepsilon &\sim \overline{a}_i \varepsilon^{1+r_a}, \\ \tilde{b}_i^\varepsilon &\sim \overline{b}_i \varepsilon^{r_b - 1}, \ \min(r_a, r_b) < 1\,. \end{aligned}$$

We then define the variables

$$C_1^\varepsilon = \varepsilon^2 \tilde{C}_1^\varepsilon\,, \qquad \mu^\varepsilon(t, dx) = \varepsilon \sum_{i \geqslant 2} \tilde{C}_i^\varepsilon(t) \delta_{i\varepsilon^\beta}(dx)\,.$$