Nucleation Time in Coagulation-Fragmentation models

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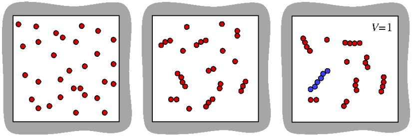
Becker-Döring model for Nucleation

Reversible one-step agregation

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



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

The **nucleation time** is given by the following First Passage Time,

$$T_{1,0}^{N,M} := \inf\{t \geqslant 0 : C_N(t) = 1 \mid C_i(t=0) = M\delta_{i=1}\}\,. \qquad (2)$$

More generally, we can look at

$$T_{\rho,h}^{N,M} := \inf\{t \geqslant 0 : C_N(t) \geqslant \rho M^h \mid C_i(t=0) = M\delta_{i=1}\}\,. \qquad (3)$$

for given positive constant ρ and $0 \leqslant h \leqslant 1$.

Remark

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

“Large number limit” of the nucleation time

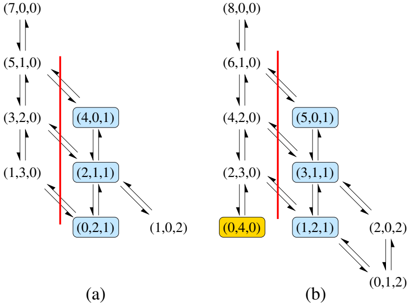
What are the dependencies of the nucleation time with respect to the model parameters ?
Here, we ask : what is the **nucleation time for very large initial quantity M and nucleus size N** ?

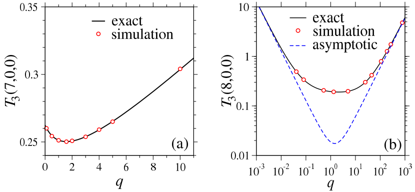
$$\lim_{M,N\to\infty} T_{\rho,h}^{N,M} \tag{4}$$

Première approche "standard"

"petits M, N"

on peut décrire l'ensemble du système, écrire la matrice de passage entre les états et résoudre l'équation linéaire correspondante.





Dimension du système

$$\sharp\{\text{config. } \{C\}, \sum_{i=1}^{N} iC_i = M\} \approx \frac{M^N}{N!}$$

Simplified model 1) Constant Monomer formulation

The model with **Constant** C_1 is Linear, we have 'exact' solution

Proposition

$$\mathbb{E}\big[T_{\rho,h}^{N,M}\big] \sim_{M\to\infty} \frac{C^{te}(a,N)}{M}\frac{1}{M^{(1-h)/(N-1)}} \tag{5}$$

where $C^{te}(a,n)$ is a constant that depends on $a(i), i \leqslant N$ and N.

$(C_i)_i$ follows a Poisson distribution of mean the solution of a linear ODE (constant monomer original Becker-Döring formulation)

$$\begin{aligned} \frac{d\mathbf{c}}{dt} &= \mathbf{A}\mathbf{c} + \mathbf{B}, \\ \frac{dc_n}{dt} &= c_1 c_{n-1}, \end{aligned} \tag{6}$$

for which we can show

$$c_N(t) \approx \Big(\prod_{k=1}^{N-1} a(k)\Big) C_1^N \frac{t^{N-1}}{(N-1)!},$$

Simplified model 2) Single-cluster formulation

If we suppose that a single cluster can be present at a time, then the model is one-dimensional, 'exact' solution and classical FPT theory gives (it's a 1D discrete random walk)

Proposition

$$\mathbb{E}\big[T_{1,0}^{N,M}\big] = \sum_{i=1}^{N-1}\sum_{j=1}^{i}\frac{b_i b_{i-1}\dots b_{j+1}}{a_i a_{i-1}\dots a_j}\frac{1}{(M-i)\dots(M-j)M^{\delta_{j=1}}}$$

Remark

Similar results with "Pre-equilibrium" hypothesis when $b \to \infty$.

General idea : rescaling strategy

Consider the deterministic irreversible aggregation model

$$\begin{aligned} \frac{dc_i}{dt} &= a_i c_1 (c_{i-1} - c_i), \\ c_1 + \sum_i i c_i &= m, \\ t^* &= \inf\{t \geqslant 0 : c_N(t) = \rho m \mid c_1(0) = m\} \end{aligned}$$

Then with $c_i' = \frac{c_i}{m}$, $\tau = mt$,

$$\begin{aligned} \frac{dc_i'}{d\tau} &= a_i c_1' (c_{i-1}' - c_i'), \\ c_1' + \sum_i i c_i' &= 1, \\ \tau^* &= \inf\{t \geqslant 0 : c_N'(t) = \rho \mid c_1'(0) = 1\} \end{aligned}$$

This strategy shows that

$$t^* = \frac{C^{te}}{m}.$$

Asymptotic for finite N

The same results holds

Proposition

$$\mathbb{E}\left[T_{\rho,h}^{N,M}\right] \sim_{M\to\infty} \frac{C^{te}(a,N)}{M}\frac{1}{M^{(1-h)/(N-1)}} \tag{7}$$

where $C^{te}(a,n)$ is a constant that depends on $a(i), i \leqslant N$ and N.

Indeed, $\frac{C_i(Mt)}{M}$ is "close" to the solution of the SDE

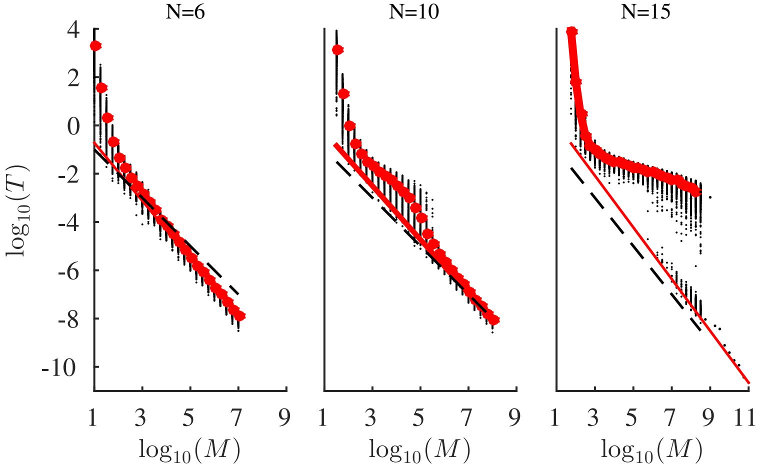
$$d\mathbf{c}^{\varepsilon} = J(c_1)\mathbf{c}dt + \sqrt{\varepsilon}B(c_1)\mathbf{c}d\mathbf{w}_t \tag{8}$$

where the variance is of order $\varepsilon = \frac{1}{M}$ and the nucleation time can be comuted by

$$T_{\rho,h}^{N,M} \equiv \inf\{\tau \geqslant 0 : c_N^{\varepsilon}(\tau) = \rho\varepsilon^{1-h} \mid c_i(\tau = 0) = 1\delta_{i=1}\}. \tag{9}$$

But ! There are complex behavior for 'intermediate' M. Indeed $T_{1,0}^{N,M}$ may be

- bimodal
- nearly independent of M over several log.



Asymptotic for large N

Wa want to prove behavior like

$$T_{1,0}^{\sqrt{M},M} = \inf\{t \geqslant 0 : C_{\sqrt{M}}(t) = 1 \mid C_i(t=0) = M\delta_{i=1}\} \\ \sim_{M\to\infty} \sqrt{M}\,. \quad (10)$$

We need a limit theorem when $N, M \to \infty$...

Choose a fix state space

With $\varepsilon = \frac{1}{N} = \frac{1}{\sqrt{M}} \to 0$, we obtain a fix state space by looking at

$$\mu_t^\varepsilon(.) = \sum_{i \geqslant 2} \varepsilon^\alpha C_i^\varepsilon(\varepsilon^\gamma t)\delta_{i\varepsilon}(.) \ \in \mathcal{M}_b(\mathbb{R}^+) \tag{11}$$

The nucleation time is thus

$$T_{1,0}^{\sqrt{M},M} = \inf\{t \geqslant 0 : \mu_t^\varepsilon(\{1\}) = \varepsilon^\alpha > 0 \mid \mu_0^\varepsilon = 0\}, \tag{12}$$

The scaling exponents α, γ need to be adjusted in order to obtain a non-trivial limit (and according to other scaling hypotheses on a, b...).

Rescaled Equation (1)

$$
\begin{aligned}
\sum_i \varphi(i\varepsilon) C_i(t) \quad &= \quad \sum_i \varphi(i\varepsilon) C_i(0) + \mathcal{O}_t^{\varphi} \\
&+ \quad \int_0^t \varphi(2\varepsilon) \left[a_1 (C_1(s))^2 - b_2 C_2(s) \right] \, ds \\
&+ \quad \int_0^t \sum_i (\varphi(i\varepsilon + \varepsilon) - \varphi(i\varepsilon)) a_i C_1(s) C_i(s) \, ds \\
&+ \quad \int_0^t \sum_i (\varphi(i\varepsilon - \varepsilon) - \varphi(i\varepsilon)) b_i C_i(s) \, .
\end{aligned}
$$

$$
\begin{aligned}
\langle \mu_t^{\varepsilon}, \varphi \rangle = \langle \mu_{\mathrm{in}}^{\varepsilon}, \varphi \rangle + \mathcal{O}_t^{\varepsilon,\varphi} \\
\int_0^t \varphi(2\varepsilon) \left[a_1^{\varepsilon} (C_1^{\varepsilon}(s))^2 - b_2^{\varepsilon} C_2^{\varepsilon}(s) \right] \, ds \\
+ \varepsilon \int_0^t \int \Delta_{\varepsilon}(\varphi) (a^{\varepsilon}(x) C_1^{\varepsilon}(s) - b^{\varepsilon}(x)) \mu_s^{\varepsilon}(dx) \, ds \quad (13)
\end{aligned}
$$

Rescaled Equation (2)

Hence, if the flux $(a^\varepsilon(x)C_1^\varepsilon(s) - b^\varepsilon(x))$ is of order ε^{-1}), we may expect everything to converge nicely, except the red term !

$$\langle \mu_t^\varepsilon, \varphi \rangle = \langle \mu_{\mathrm{in}}^\varepsilon, \varphi \rangle + \mathcal{O}_t^{\varepsilon,\varphi}$$

$$\int_0^t \varphi(2\varepsilon) \left[a_1^\varepsilon (C_1^\varepsilon(s))^2 - b_2^\varepsilon C_2^\varepsilon(s) \right] ds$$

$$+ \int_0^t \int_0^{+\infty} \Delta_\varepsilon(\varphi)(a^\varepsilon(x)C_1^\varepsilon(s) - b^\varepsilon(x))\mu_s^\varepsilon(dx)\, ds \quad (14)$$

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

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,

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

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*

$$\begin{aligned} \langle \mu_t, \varphi \rangle &= \langle \mu_{\rm in}, \varphi \rangle + \int_0^t \varphi(0)\left[a_1(c_1(s))^2 - b_2 c_2(s)\right] \\ &\quad + \int_0^t \int_0^{+\infty} \varphi'(x)(a(x)c_1(s) - b(x))\mu_s(dx)\, ds\,. \\ \langle \mu_t, {\rm id} \rangle + c_1(t) &= m := \langle \mu_0, {\rm id} \rangle + c_1(0) \end{aligned}$$

And $(c_i(t))_{i\geqslant 2}$ *is a stationary solution in* l_1 *of the following deterministic constant-monomer Becker-Döring system (***for 'freezed'*** $c_1 = c_1(t)$*)*

$$\begin{aligned} \dot{c}_2 = 0 &= -\left(\overline{a}_2 c_1 c_2 - \overline{b}_3 c_3\right), \\ \dot{c}_i = 0 &= \left(\overline{a}_{i-1} c_1 c_{i-1} - \overline{b}_i c_i\right) - \left(\overline{a}_i c_1 c_i - \overline{b}_{i+1} c_{i+1}\right). \end{aligned}$$

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

For $a(x) = \overline{a}x^r + o(x)$, $b(x) = \overline{b}x^r + o(x)$, $r < 1$, the above equation reduces to, for $c_1(t) > \frac{\overline{b}}{\overline{a}}$,

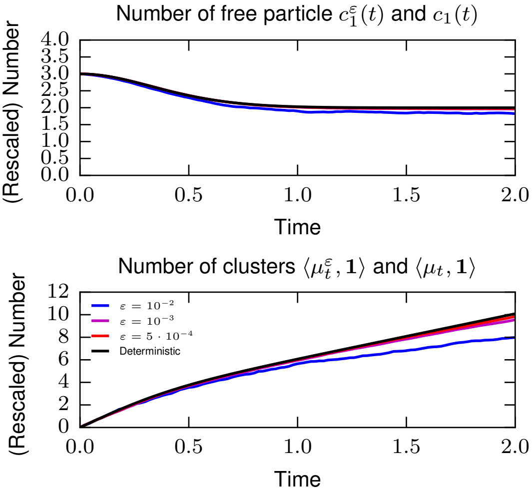
$$\begin{aligned}
\langle \mu_t, \varphi \rangle &= \langle \mu_{\mathrm{in}}, \varphi \rangle + \int_0^t \varphi(0) a_1 (c_1(s))^2 \\
&\quad + \int_0^t \int_0^{+\infty} \varphi'(x)(a(x)c_1(s) - b(x))\mu_s(dx)\, ds\,. \\
\langle \mu_t, \mathrm{id} \rangle + c_1(t) &= m := \langle \mu_0, \mathrm{id} \rangle + c_1(0)
\end{aligned}$$

Remark

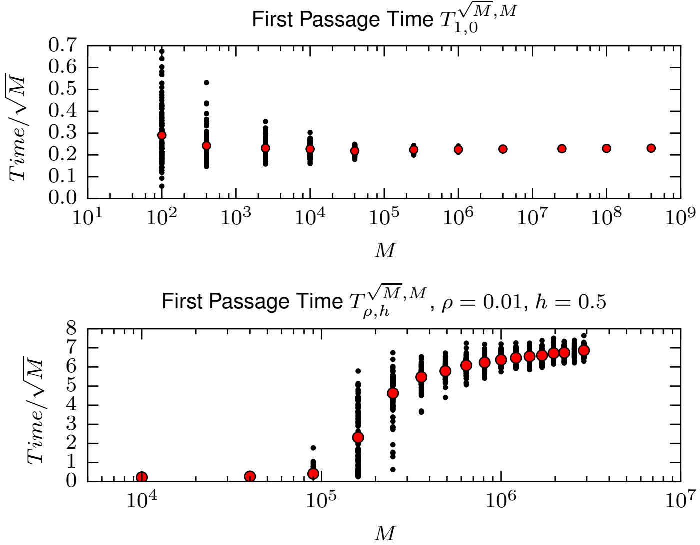
The boundary condition is : flux at 0 = dimerization rate

Numerical illustration : SBD to LS

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

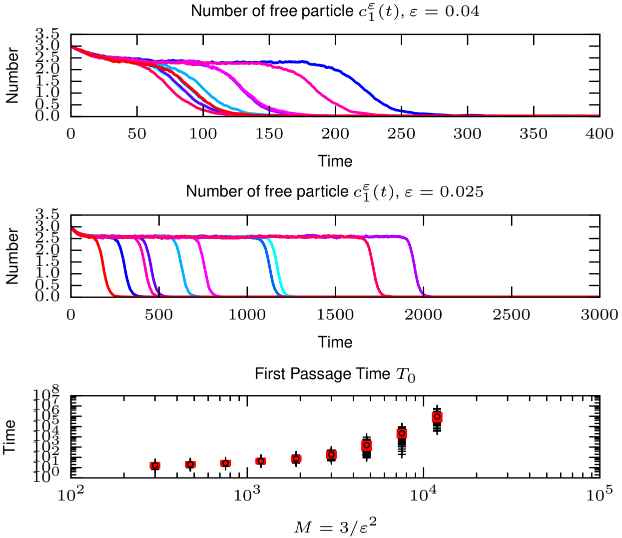


Numerical illustration : verifying the time-scale



Numerical illustration and further work

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



Merci !

- *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)

$$\begin{aligned} a_i^\varepsilon &:= \varepsilon^A \tilde{a}_i^\varepsilon\,, \quad \forall i \geqslant 2\,, \\ b_i^\varepsilon &:= \varepsilon^B \tilde{b}_i^\varepsilon\,, \quad \forall i \geqslant 3\,, \\ a_1^\varepsilon &:= \varepsilon^{A_1} \tilde{a}_1^\varepsilon\,, \\ b_2^\varepsilon &:= \varepsilon^{B_1} \tilde{b}_2^\varepsilon\,. \end{aligned}$$

$$\begin{aligned} \chi_i^\varepsilon &:= \mathbf{1}_{[(i-1/2)\varepsilon^\beta, (i+1/2)\varepsilon)}\,, \\ a^\varepsilon(x) &:= \sum_{i\geqslant 2} a_i^\varepsilon \chi_i^\varepsilon(x)\,, \\ b^\varepsilon(x) &:= \sum_{i\geqslant 3} b_i^\varepsilon \chi_i^\varepsilon(x)\,. \end{aligned}$$

We then define the variables

$$\begin{aligned} C_i^\varepsilon &= \varepsilon^\alpha \tilde{C}_i^\varepsilon\,, \forall i \geqslant 2\,, \\ C_1^\varepsilon &= \varepsilon^\theta \tilde{C}_1^\varepsilon\,. \end{aligned}$$

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

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

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