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Nucleation Time in Coagulation-Fragmentation models

Romain Yvinec¹, **Julien Deschamps**² and **Erwan Hingant**³

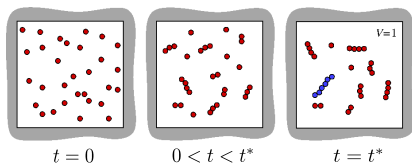
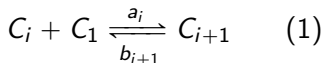
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Becker-Döring model for Nucleation

Reversible one-step aggregation



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

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

More generally, we can look at

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

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

Remark

$$C_1(t) + \sum_i i C_i(t) \equiv M.$$

“Large number limit” of the nucleation time

What are the dependencies of the nucleation time with respect to the model parameters?

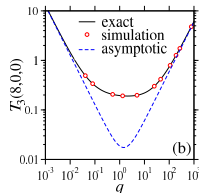
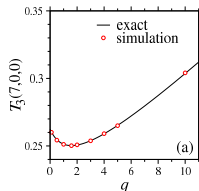
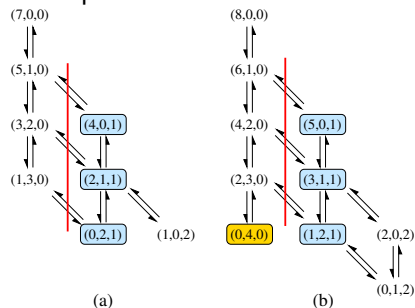
Here, we ask : what is the **nucleation time for very large initial quantity M and nucleus size N** ?

$$\lim_{M, N \rightarrow \infty} T_{\rho, h}^{N, M} \quad (4)$$

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

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

$$\frac{M^N}{N!}$$

Simplified model 1) Constant Monomer formulation

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

Proposition

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

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

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

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

for which we can show

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

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

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

Remark

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

General idea : rescaling strategy

Consider the deterministic irreversible aggregation model

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

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

$$\begin{aligned}\frac{dc'_i}{d\tau} &= a_i c'_1 (c'_{i-1} - c'_i), \\ c'_1 + \sum_i i c'_i &= 1, \\ \tau^* &= \inf\{t \geq 0 : c'_N(t) = \rho \mid c'_1(0) = 1\}\end{aligned}$$

This strategy shows that

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

Asymptotic for finite N

The same results holds

Proposition

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

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

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

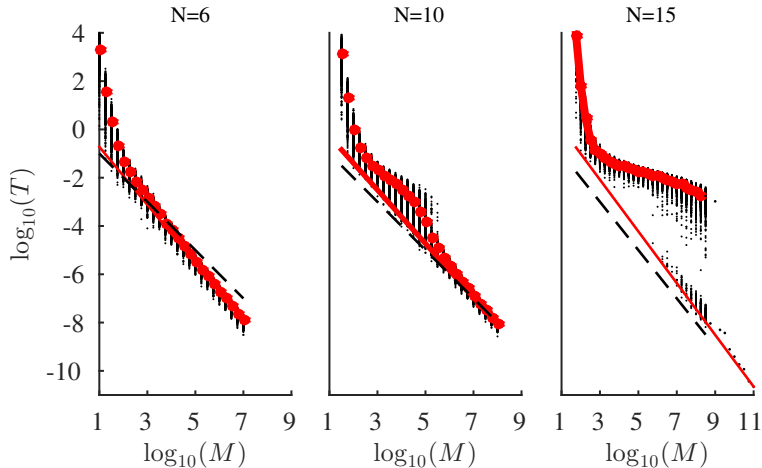
$$d\mathbf{c}^\varepsilon = J(c_1)\mathbf{c}dt + \sqrt{\varepsilon}B(c_1)\mathbf{c}d\mathbf{w}_t \quad (8)$$

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

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

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

We want to prove behavior like

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

We need a limit theorem when $N, M \rightarrow \infty \dots$

Choose a fix state space

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

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

The nucleation time is thus

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

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

Rescaled Equation (1)

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

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

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!

$$\begin{aligned}\langle \mu_t^\varepsilon, \varphi \rangle &= \langle \mu_{\text{in}}^\varepsilon, \varphi \rangle + \mathcal{O}_t^{\varepsilon, \varphi} \\ &\quad \int_0^t \varphi(2\varepsilon) [a_1^\varepsilon(C_1^\varepsilon(s))^2 - b_2^\varepsilon C_2^\varepsilon(s)] ds \\ &\quad + \int_0^t \int_0^{+\infty} \Delta_\varepsilon(\varphi)(a^\varepsilon(x)C_1^\varepsilon(s) - b^\varepsilon(x))\mu_s^\varepsilon(dx) ds \quad (14)\end{aligned}$$

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**.

$$C_{i-1}^\varepsilon \xrightleftharpoons[\frac{1}{\varepsilon} b^\varepsilon(\varepsilon i) C_i^\varepsilon]{\frac{1}{\varepsilon} a^\varepsilon(\varepsilon(i-1)) C_1^\varepsilon C_{i-1}^\varepsilon} C_i^\varepsilon \xrightleftharpoons[\frac{1}{\varepsilon} b^\varepsilon(\varepsilon(i+1)) C_{i+1}^\varepsilon]{\frac{1}{\varepsilon} a^\varepsilon(\varepsilon i) C_1^\varepsilon C_i^\varepsilon} C_{i+1}^\varepsilon,$$

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 ,

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

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

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

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

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

where \bar{a}_i, \bar{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 $c_1(t) > \frac{\bar{b}}{\bar{a}}$,

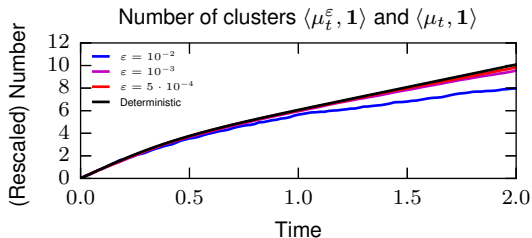
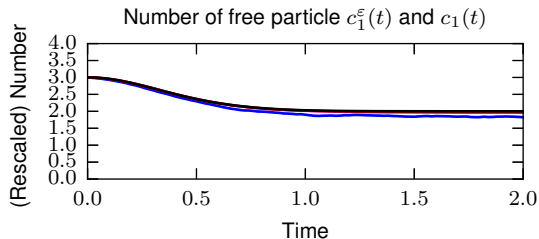
$$\begin{aligned} \langle \mu_t, \varphi \rangle &= \langle \mu_{\text{in}}, \varphi \rangle + \int_0^t \varphi(0) a_1(c_1(s))^2 \\ &\quad + \int_0^t \int_0^{+\infty} \varphi'(x) (a(x)c_1(s) - b(x)) \mu_s(dx) ds. \\ \langle \mu_t, id \rangle + c_1(t) &= m := \langle \mu_0, id \rangle + c_1(0) \end{aligned}$$

Remark

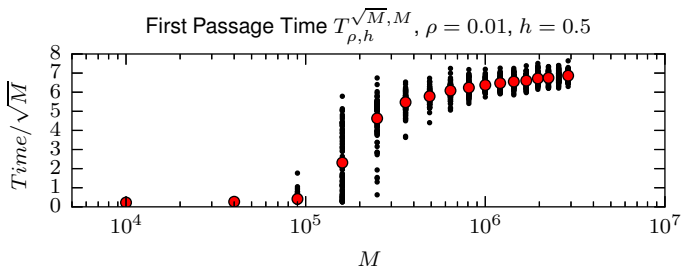
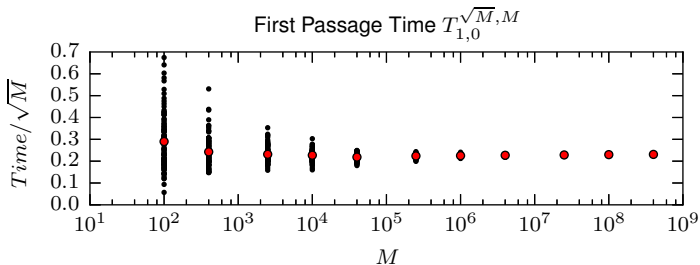
The boundary condition is : flux at 0 = dimerization rate

Numerical illustration : SBD to LS

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

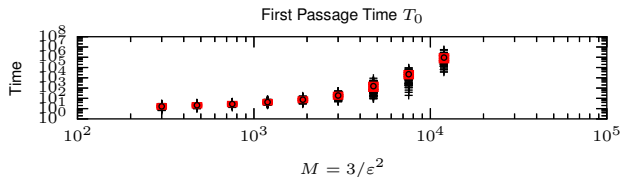
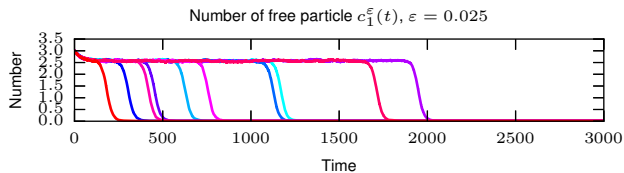
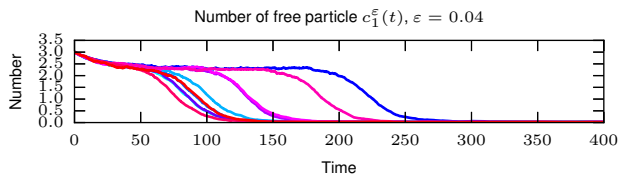


Numerical illustration : verifying the time-scale



Numerical illustration and further work

- ▶ $a(x) \equiv x$,
 $b(x) = 1$,
- ▶ outgoing characteristics.
- ▶ 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}^ε) . 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)

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

We then define the variables

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

The above results hold with the following choices

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

Concrete Example

Consider a sequence of $(\tilde{a}_i^\varepsilon)$, $(\tilde{b}_i^\varepsilon)$, $(\tilde{C}_i^\varepsilon(0))$, (\tilde{M}^ε) . 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)

$$\begin{aligned} a^\varepsilon(x) &:= \frac{1}{\varepsilon} \sum_{i \geq 2} \tilde{a}_i^\varepsilon \chi_i^\varepsilon(x), & a_1^\varepsilon &:= \frac{1}{\varepsilon^3} \tilde{a}_1^\varepsilon, \\ b^\varepsilon(x) &:= \varepsilon \sum_{i \geq 3} \tilde{b}_i^\varepsilon \chi_i^\varepsilon(x). & b_2^\varepsilon &:= \tilde{b}_2^\varepsilon, \\ & & \tilde{a}_i^\varepsilon &\sim \bar{a}_i \varepsilon^{1+r_a}, \\ & & \tilde{b}_i^\varepsilon &\sim \bar{b}_i \varepsilon^{r_b-1}, \quad \min(r_a, r_b) < 1. \end{aligned}$$

We then define the variables

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