Gold! $$$

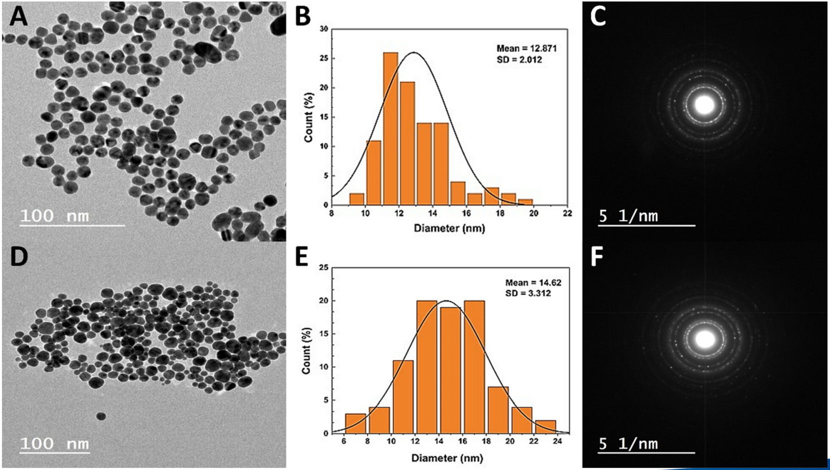
Enrico Bibbona, DISMA, Politecnico di Torino, Italy

joint work with

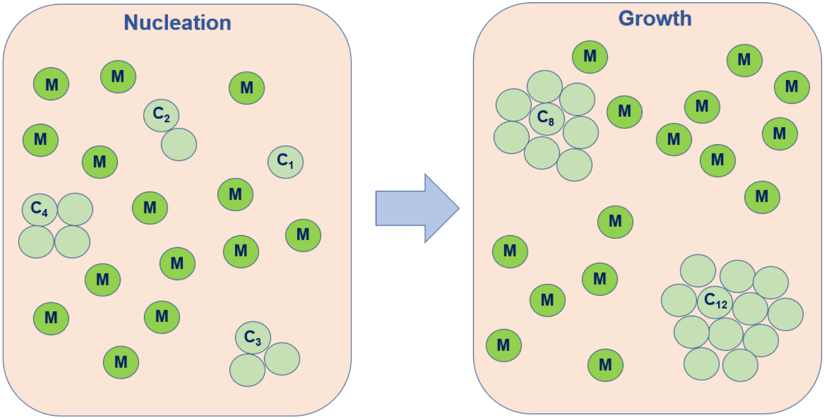
Rebeka Szabo, Gabor Lente, Elena Sabbioni, Anderson M. Hernandez, Paola Siri, Daniele Cappelletti

Gold nanoparticles

Gold nanoparticles have unique chemical properties (cathalist in CO_2 capture, vehicles for drugs...). They are formed by aggregation of small precursors, and their final size distribution determines such properties



Mechanisms of nanoparticle formation and growth



A stochastic model of nanoparticle formation and growth

The model can be written as the following CRN

$$\begin{cases} nM \xrightarrow{\nu'} C_n, \\ M + C_i \xrightarrow{\gamma'} C_{i+1}, i \in \{1, \cdots, N\} \end{cases}$$

The state vector is

$$X^N(t) = \{C_1^N(t), \cdots, C_N^N(t)\}.$$

rates are

$$\lambda_0^N = \nu' \frac{M(t)!}{(M(t)-m)!} \qquad \text{nucleation}$$

$$\lambda_i^N = \gamma' C_i^N(t) M(t). \qquad \text{growths}$$

Monomers can be derived by conservation of mass as

$$M(t) = M(0) - \sum_i C_i^N(t)$$

Initially $M(0) = N$, $C_i(0) = 0$ for all i. Trivial limit cases...

Deterministic limit under the classical scaling

Under the classical scaling

$$X(0) \sim (N, 0, \dots, 0), \qquad \nu' = \frac{\nu}{N^{n-1}}, \qquad \gamma' = \frac{\gamma}{N}.$$

and initially the nucleation rate dominates the growth, and they equilibrate only when the number of created particles is of order N. The quantities $\frac{X(t)}{N}$ converge to the solution of an infinite ode system (BD)

$$\frac{d}{dt}m(t) = -\nu(m(t))^n - \gamma m(t)\sum_i c_i(t) \qquad m(0) = 1$$

$$\frac{d}{dt}c_n(t) = \nu(m(t))^n - \gamma m(t) c_{i+1}(t), \qquad c_n(0) = 0$$

$$\dots$$

$$\frac{d}{dt}c_i(t) = \gamma m(t)(c_{i-1}(t) - c_{i+1}(t)), \qquad c_i(0) = 0, \forall i > n$$

$$\dots$$

Coarsening

Some autors proved that if the space of the sizes is mapped to the continuous (so-called coarsening) this equations are well approximated by the solutions of Lifshitz-Slyozov trasport PDE

$$\frac{\partial}{\partial t} f(x,t) + \gamma m(t) \frac{\partial}{\partial x} f(x,t) = \delta(x) \gamma m^n(t)$$

with suitable initial and boundary conditions (e.g. Hingant, Yvinec. Deterministic and stochastic Becker-Döring equations: Past and recent mathematical developments. Stochastic Processes, Multiscale Modeling, and Numerical Methods for Computational Cellular Biology, Editions Springer, pp.175-204, 2016,).

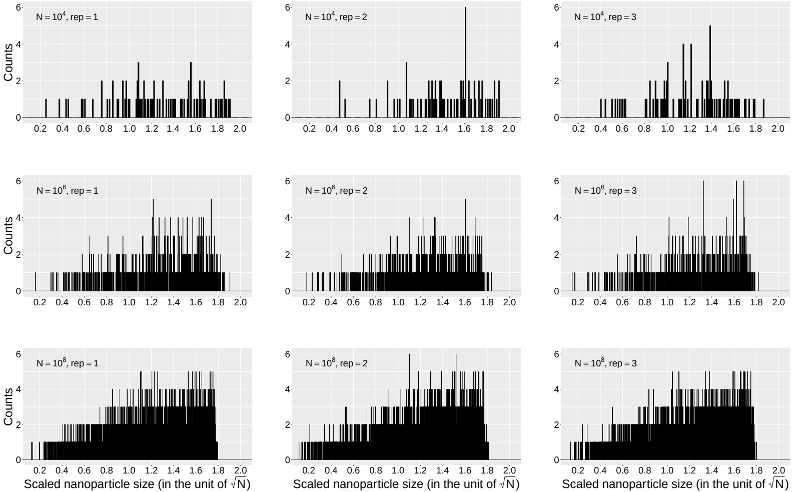
Simulations - 0

We first tried simulating the process in a different parameter range

$$X(0) \sim (N, 0, \dots, 0), \qquad \nu' = \frac{\nu}{N^{n-1}}, \qquad \gamma' = \gamma \sim 1.$$

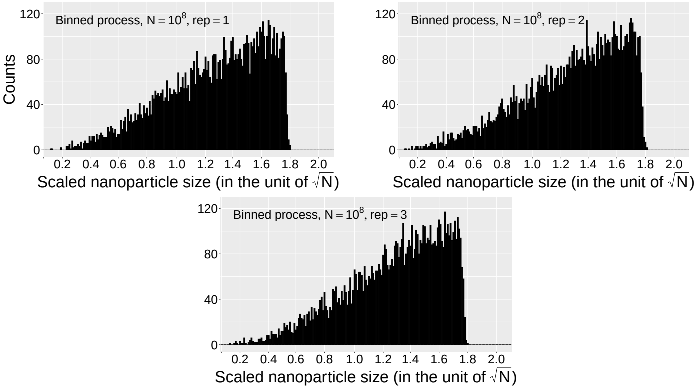
such that the rates of nucleation and growth are equilibrated at the very initial moment when the first particle is nucleated.

Simulations - 1

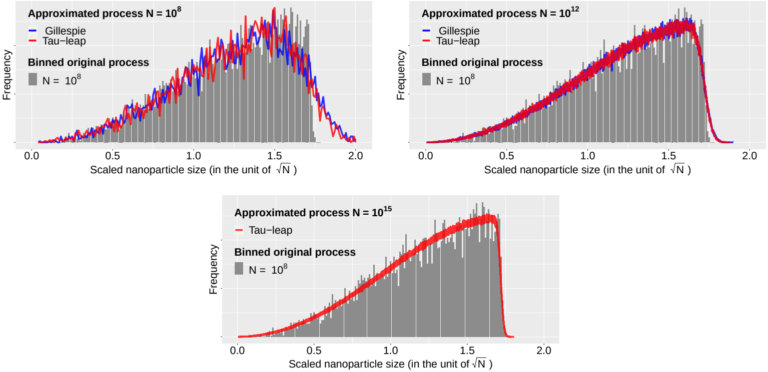


Simulations - 2

After some binning



Simulations + a guess for an approximated process



Sabbioni E, Szabó R, Siri P, Cappelletti D, Lente G, Bibbona E. *Final nanoparticle size distribution under unusual parameter regimes.* doi:10.26434/chemrxiv-2024-wh3jv To appear in J. Chem. Phys.

Main statement

The state vector of the population is $X^N(t) = \{C_1^N(t), \cdots, C_N^N(t)\}$. For every t (including when $t \to \infty$), and for every $0 < \beta \leq 1$ ($\beta = 1$ being the CS)

$$\frac{\displaystyle\sum_{i \in N^{1-\beta}[a,b]} C_i^N(N^{\beta-1}t)}{\displaystyle\sum_i C_i^N(N^{\beta-1}t)} \xrightarrow{\mathbb{P}} \frac{\int_a^b f(x,t)\,dx}{\int_0^\infty f(x,t)\,dx}$$

where $f(x,t)$ is a generalized function that satisfies the weak form of the Lifshitz-Slyozov equation

$$\frac{\partial}{\partial t} f(x,t) + \gamma m(t) \frac{\partial}{\partial x} f(x,t) = \delta(x) \gamma m^n(t)$$

where $m(t)$ is the (explicit) solution of

$$\frac{d}{dt} m(t) = -\gamma m(t) c(t) \qquad m(0) = 1;$$
$$\frac{d}{dt} c(t) = \nu (m(t))^n, \qquad c(0) = 0.$$

Step 1: simplified model, ode limit

Let's introduce the total number of particles $C^N(t) = \sum_{i=n}^{N} C_i^N(t)$. Growth reactions do not modify $C^N(t)$:

$$\begin{cases} nM \xrightarrow{\nu'} C & \lambda_0^N = \nu' \frac{M(t)!}{(M(t)-n)!} \\ M + C \xrightarrow{\gamma'} C & \lambda_1^N = \gamma' C^N(t) M(t). \end{cases}$$

and scaling the model so that for any $0 < \beta \leq 1$

$$\overline{M}^N(t) := \frac{M^N(N^\alpha t)}{N}, \quad \overline{C}^N(t) := \frac{C^N(N^\alpha t)}{N^\beta}, \quad \gamma' = \gamma N^\theta, \quad \nu' = \nu N^{1-n}$$

Note that if $\beta = 1$, $\alpha = 0$ and $\theta = -1$ we are in the classical scaling (covered), and if $\beta = 1/2$, $\alpha = 1/2$ and $\theta = 0$ we are in the regime of the simulations above.

Step 1: simplified model, ode limit

We get that if $\theta = 1 - 2\beta$ and $\alpha = \beta - 1$, then

$$\mathbb{P}\left(\lim_{N\to\infty}\sup_{t\in[0,T]}\left|\overline{M}^N(t) - m(t)\right| > \varepsilon\right) = 0, \quad \mathbb{P}\left(\lim_{N\to\infty}\sup_{t\in[0,T]}\left|\overline{C}^N(t) - c(t)\right| > \varepsilon\right) = 0$$

where $m(t), c(t)$ can be computed in an explicit form by solving the following ode

$$\frac{d}{dt}m(t) = -\gamma m(t)c(t) \qquad m(0) = 1;$$
$$\frac{d}{dt}c(t) = \nu(m(t))^n, \qquad c(0) = 0.$$

and the solution is available in an explicit form

Step 2: Individual particle models

At most we can nucleate $\lfloor \frac{N}{n} \rfloor$ particles For all $j \in 1, \ldots, \lfloor \frac{N}{n} \rfloor$ the scaled size of the j-th particle is

$$\frac{S_j^N(t)}{N^{1-\beta}} = \frac{n}{N^{1-\beta}} Y_{j0} \left(\int_0^t \nu' \frac{M^N(s)! \mathbb{1}_{\{S_j^N(s)=0\}}}{(M^N(s)-n)!\,(N-C^N(s))} ds \right) + \frac{1}{N^{1-\beta}} \sum_{i=n}^{N-1} Y_{ji} \left(\gamma' \int_0^t M^N(s) \mathbb{1}_{\{S_j^N(s)=i\}} ds \right)$$

that after applying the above scalings can be approximated by

$$\frac{S_j^N(t)}{N^{1-\beta}} \approx \frac{n}{N^{1-\beta}} Y_{j0} \left(N^{\beta-1} \nu \int_0^t m^n(s) \mathbb{1}_{\{S_j^N(s)=0\}} ds \right) + \gamma \int_0^t m(s) \mathbb{1}_{\{S_j^N(s)>0\}} ds$$

Step 2: Individual particle models

In other words, when N is large, scaled particles sizes become independent and equal to

$$\frac{S_j^N(t)}{N^{1-\beta}} \approx \begin{cases} 0 & \text{if } t < \sigma_j^N \\ \gamma \int_{\tau_j^N}^t m(s)ds = s_t(\tau_j^N) & \text{if } t \geq \sigma_j^N \end{cases}$$

where σ_j^N is the time of the first jump of the inhomogeneous Poisson process $Y_{j0}\left(N^{\beta-1}\nu \int_0^t m^n(s)ds\right)$. Its distribution is then

$$\mathbb{P}(\{\sigma_j^N \leq t\}) = N^{\beta-1}\nu \int_0^t m^n(s)ds$$

meaning that with probability $1 - N^{\beta-1}\nu \int_0^\infty m^n(s)ds$ the particle will not be created in finite time.

Step 2: Individual particle models

Step 2: Individual particle models

Therefore the probability "*density*" of the scaled size is the following generalized function

$$N^{\beta-1} f(x,t) = \int_0^t \delta(x - s_t(u)) f_\tau(u) du.$$

where

$$f_\tau(u) = \nu m^n(u)$$

which can be verified to solve the weak form

$$\frac{\partial}{\partial t} \int_0^\infty \varphi(x) f(x,t) dx + \gamma m(t) \int_0^\infty \varphi(x) \frac{\partial f(x,t)}{\partial x} dx = \varphi(0) f_\tau(t)$$

of the the Lifshitz-Slyozov transport PDE, for all
$\varphi \in C^1([0,+\infty)) \cap L^1(([0,+\infty)).$

Step 3: LLN

Putting all together we have

$$\frac{\sum_{i\in N^{1-\beta}[a,b]} C_i^N(N^{\beta-1}t)}{\sum_{i=n}^{\lfloor \frac{N}{n} \rfloor} C_i^N(N^{\beta-1}t)} = \frac{\sum_{j=1}^{\lfloor \frac{N}{n} \rfloor} \mathbb{1}_{\left\{\frac{S_j^N(N^\alpha t)}{N^{1-\beta}}\in[a,b]\right\}}}{\sum_{j=1}^{\lfloor \frac{N}{n} \rfloor} \mathbb{1}_{\left\{\frac{S_j^N(N^\alpha t)}{N^{1-\beta}}\in(0,\infty]\right\}}}$$

which, by the law of large numbers for i.i.d. variables tends to

$$\frac{\int_a^b f(x,t)\,dx}{\int_0^\infty f(x,t)\,dx} = \frac{\int_{s_t^{-1}(b)}^{s_t^{-1}(a)} f_\tau(w)dw}{\int_0^\infty f_\tau(w)dw}$$

Open questions

- What if

$$\begin{cases} nM \xrightarrow{\nu'} C_n, \\ M + C_i \xrightarrow{\gamma_i'} C_{i+1}, i \in \{1, \cdots, N\} \end{cases}$$

- Better simulation methods? Tau-leap kind?

Thank you for the attention

POLITECNICO
DI TORINO