

Stochastic numerics for the gas-phase synthesis of nanoparticles

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 - Motivation
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- What are nanoparticles? Why are they important?
 - Particles sized between 1-100 nm.
 - Both inorganic and organic nanoparticles find wide applications in various fields.
- Why model nanoparticle systems?
 - To optimise industrial operations and to obtain products of highly specific properties for sensitive applications.
 - To understand the molecular level properties that are difficult to be observed experimentally.

Salient features of the current model:

- Fully-coupled multidimensional stochastic population balance model.
- Describing various properties of nanoparticles at an unprecedented level of detail.
- Tracking properties not only at macroscopic level but also at a molecular level.

Applications of silica nanoparticles

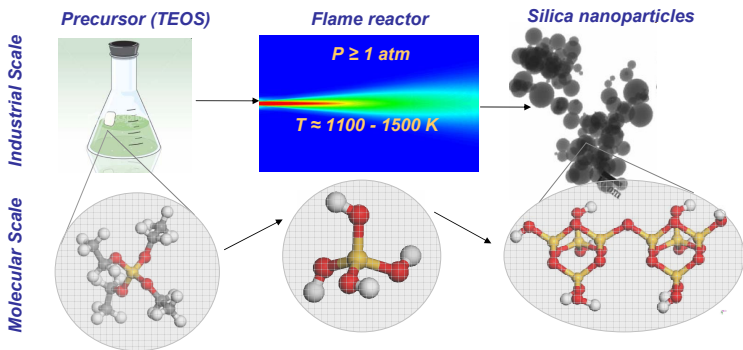
Silica nanoparticles are amorphous and have $\text{Si}:\text{O} = 1:2$.

Their applications include:

- Catalysis
- Bio-medical applications
- Support material for functional nanoparticles
- Fillers/Binders
- Optics

Physical system

To describe the system at a macroscopic level it is essential to understand it at a molecular level.



Type space I

- Each particle is represented as:

$$P_q = P_q(p_1, \dots, p_{n(P_q)}, \mathbf{C}).$$

- Particle P_q consists of $n(P_q)$ primary particles p_i with $i \in \{1, \dots, n(P_q)\}$ and $q \in \{1, \dots, N\}$, where N is the total number of particles in the system.

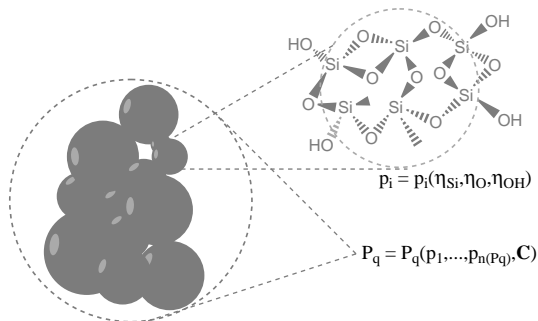


Figure: Type Space.

- Each primary particle p_i is represented as:

$$p_i = p_i(\eta_{\text{Si}}, \eta_{\text{O}}, \eta_{\text{OH}})$$

where η_x ($\eta_x \in \mathbb{Z}$ with $\eta_x \geq 0$) is the number of chemical units of type $x \in \{\text{Si}, \text{O}, \text{OH}\}$.

Type space III

\mathbf{C} is a lower diagonal matrix of dimension $n(P_q) \times n(P_q)$ storing the common surface between two primary particles:

$$\mathbf{C}(P_q) = \begin{pmatrix} 0 & \dots & 0 & \dots & 0 \\ C_{21} & \ddots & 0 & \dots & 0 \\ \vdots & \ddots & \ddots & \dots & \vdots \\ C_{i1} & \dots & C_{ij} & \ddots & \vdots \\ \vdots & \dots & \vdots & \dots & \vdots \end{pmatrix}.$$

The element C_{ij} of matrix \mathbf{C} has the following property:

$$C_{ij} = \begin{cases} 0, & \text{if } p_i \text{ and } p_j \text{ are non-neighbouring,} \\ C_{ij} > 0, & \text{if } p_i \text{ and } p_j \text{ are neighbouring.} \end{cases}$$

Particles are transformed by the following processes:

- Inception
- Surface reaction
- Coagulation
- Sintering
- Intra-particle reaction

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- Two molecules in gas phase collide to form a particle consisting of one primary.

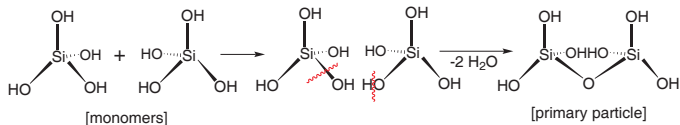


Figure: Inception of primary particles from gas-phase monomers.

- An inception event increases the number of particles in the system



$$\mathbf{C} = \mathbf{0}.$$

- Initial state of primary p_1 given by:

$$p_1 = p_1(\eta_{\text{Si}} = 2, \eta_{\text{O}} = 1, \eta_{\text{OH}} = 6),$$

- Inception rate for each particle (P_q) calculated using the free molecular kernel:

$$R_{\text{inc}}(P_q) = \frac{1}{2} K^{\text{fm}} N_A^2 C_g^2,$$

N_A is Avogadro's constant, C_g is the gas-phase concentration of the incepting species ($\text{Si}(\text{OH})_4$),

$$K^{\text{fm}} = 4 \sqrt{\frac{\pi k_B T}{m_g}} (d_g^2),$$

k_B is the Boltzmann constant, T is the system temperature, m_g and d_g are the mass and diameter respectively of the gas-phase molecule $\text{Si}(\text{OH})_4$.

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Surface reaction

- Dehydration reaction between gas-phase monomer and particle surface:

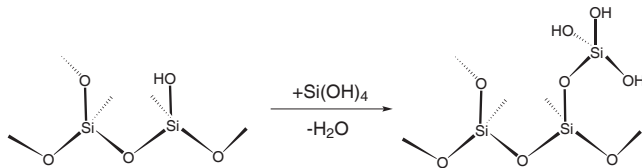
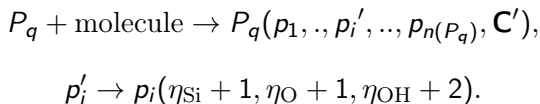


Figure: Surface reaction between a particle and a gas-phase molecule.

- Surface reaction transforms particle as:



Particle rounding due to surface reaction

- Surface reaction also alters the common surface ($\mathbf{C} \rightarrow \mathbf{C}'$).
- Net common surface area of p_i changes due to volume addition:

$$\Delta s(p_i) = (v(p_i') - v(p_i)) \frac{2\sigma}{d_p(p_i)},$$

where σ is the surface smoothing factor ($0 \leq \sigma \leq 2$).

- \mathbf{C}' is given by:

$$C'_{ij} = \begin{cases} 0, & \text{if } p_i \text{ and } p_j \text{ are non-neighbouring,} \\ C_{ij} + \Delta s(p_i), & \text{if } p_i \text{ and } p_j \text{ are neighbouring.} \end{cases}$$

- Surface reaction rate calculated using equation of Arrhenius form:

$$R_{\text{surf}}(P_q) = A_{\text{surf}} \exp\left(-\frac{E_a}{RT}\right) \eta_{\text{OH}}(P_q) N_A C_g,$$

A_{surf} is pre-exponential factor (obtained from collision theory),

E_a is activation energy,

$\eta_{\text{OH}}(P_q)$ is the total number of $-\text{OH}$ sites on particle P_q .

Particles are transformed by the following processes:

- Inception
- Surface reaction
- **Coagulation**
- Sintering
- Intra-particle reaction

- Two particles collide and stick to each other:

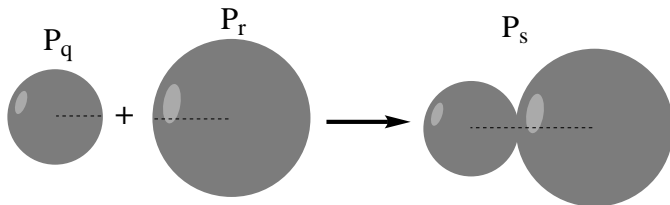


Figure: Coagulation between two particles.

- Coagulation of particles P_q and P_r forms new particle P_s as:

$$P_q + P_r \rightarrow P_s(p_1, \dots, p_{n(P_q)}, p_{(n(P_q)+1)}, \dots, p_{n(P_q)+n(P_r)}, \mathbf{C}).$$

Coagulation II

- Primary p_i from particle P_q and primary p_j from P_r are assumed to be in point contact.
- The matrix $\mathbf{C}(P_s)$ is calculated as:

$$\mathbf{C}(P_s) = \begin{pmatrix} & & & \vdots & & \\ & \mathbf{C}(P_q) & \cdots & C_{ij} & \cdots & \\ & \vdots & & \vdots & & \\ \cdots & C_{ji} & \cdots & \mathbf{C}(P_r) & & \\ & \vdots & & & & \end{pmatrix}$$

and has dimension $n(P_s) \times n(P_s)$, where $n(P_s) = n(P_q) + n(P_r)$.

Coagulation rate

- Coagulation rate between P_q and P_r calculated using transition coagulation kernel:

$$K^{\text{tr}}(P_q, P_r) = \frac{K^{\text{sf}}(P_q, P_r)K^{\text{fm}}(P_q, P_r)}{K^{\text{sf}}(P_q, P_r) + K^{\text{fm}}(P_q, P_r)},$$

where the slip-flow kernel is:

$$K^{\text{sf}}(P_q, P_r) = \frac{2k_B T}{3\mu} \left(\frac{1 + 1.257Kn(P_q)}{d_c(P_q)} + \frac{1 + 1.257Kn(P_r)}{d_c(P_r)} \right) \times (d_c(P_q) + d_c(P_r)),$$

and the free molecular collision kernel is:

$$K^{\text{fm}}(P_q, P_r) = 2.2 \sqrt{\frac{\pi k_B T}{2}} \left(\frac{1}{m(P_q)} + \frac{1}{m(P_r)} \right)^{\frac{1}{2}} (d_c(P_q) + d_c(P_r))^2$$

Particles are transformed by the following processes:

- Inception
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- **Sintering**
- Intra-particle reaction

- Sintering described using viscous-flow model.

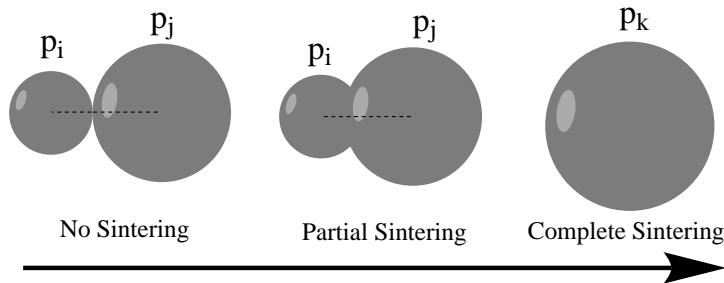


Figure: Evolution of sintering process with time.

- Sintering between p_i and p_j of a single particle P_q calculated on a primary particle-level.

- Sintering level defined to represent degree of sintering between p_i and p_j :

$$s(p_i, p_j) = \frac{\frac{S_{\text{sph}}(p_i, p_j)}{C_{ij}} - 2^{\frac{1}{3}}}{1 - 2^{\frac{1}{3}}}.$$

$S_{\text{sph}}(p_i, p_j)$ is the surface area of a sphere with the same volume as the two primaries.

- P_q conditionally changes depending on the sintering level $s(p_i, p_j)$.
- Two types are defined depending upon a threshold (95%):

Partial sintering $s(p_i, p_j) < 0.95$

Complete sintering $s(p_i, p_j) \geq 0.95$

Partial sintering

- Surface areas of primaries are reduced by a finite amount.
- -OH sites at contact surface react to form Si-O-Si bonds:

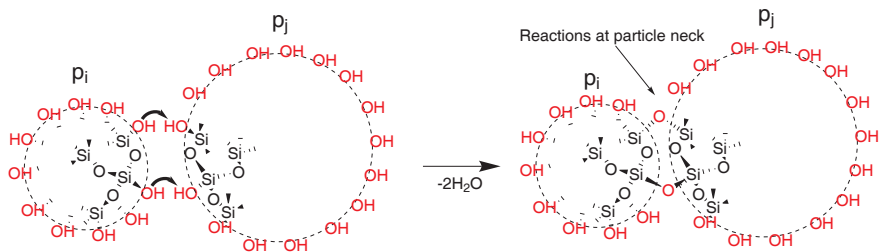


Figure: Dehydration reaction due to sintering.

- Surface density of $-OH$ sites assumed constant throughout sintering.
- The change in the internal variables of primaries p_i and p_j given by:

$$\Delta\eta_{OH}(p_i) = \Delta\eta_{OH}(p_j) = \rho_s(P_q)\Delta C_{ij}/2,$$

$$\Delta\eta_O(p_i) = \Delta\eta_O(p_j) = -0.5 \times \Delta\eta_{OH}(p_i),$$

$$\Delta\eta_{Si}(p_i) = \Delta\eta_{Si}(p_j) = 0.$$

- Particle continuously transforms due to partial sintering as:

$$P_q(p_1, \dots, p_{n(P_q)}, \mathbf{C}) \rightarrow P_q(p_1, \dots, p'_i, p'_j, \dots, p_{n(P_q)}, \mathbf{C}')$$

where,

$$p'_i = p_i(\eta_{Si}, \eta_O - \Delta\eta_O(p_i), \eta_{OH} - \Delta\eta_{OH}(p_i)),$$

$$p'_j = p_j(\eta_{Si}, \eta_O - \Delta\eta_O(p_j), \eta_{OH} - \Delta\eta_{OH}(p_j)).$$

- Element of \mathbf{C}' given by:

$$C'_{ij} = C_{ij} - \frac{\Delta t}{\tau(p_i, p_j)} (C_{ij} - S_{\text{sph}}(p_i, p_j)),$$

where Δt is a time interval.

Complete sintering

- p_i and p_j replaced by new primary p_k'' .
- Particle transforms due to complete sintering as:

$$P_q(p_1, \dots, p_{n(P_q)}, \mathbf{C}) \rightarrow P_q(p_1, \dots, p_k'', \dots, p_{n(P_q)}, \mathbf{C}''),$$

where new primary:

$$p_k'' = p_k'' (\eta_{\text{Si}}(p_i) + \eta_{\text{Si}}(p_j), \eta_{\text{O}}(p_i) + \eta_{\text{O}}(p_j), \eta_{\text{OH}}(p_i) + \eta_{\text{OH}}(p_j)).$$

- C is changed by removing columns and rows i and j and adding new column and row k :

$$C'' = \begin{pmatrix} 0 & \cdots & 0 & \cdots & 0 \\ \vdots & \ddots & \vdots & \vdots & \vdots \\ C''_{k1} & \cdots & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ C_{(n(P_q)-1)1} & \cdots & C''_{(n(P_q)-1)k} & \cdots & 0 \end{pmatrix}.$$

- Sintering rate between p_i and p_j equivalent to rate of change of their common surface ΔC_{ij} in time Δt :

$$\frac{\Delta C_{ij}}{\Delta t} = -\frac{1}{\tau(p_i, p_j)} (C_{ij} - S_{\text{sph}}(p_i, p_j)),$$

$S_{\text{sph}}(p_i, p_j)$ is the surface area of a sphere with the same volume as the two primaries.

- Characteristic sintering time of p_i and p_j is:

$$\tau(p_i, p_j) = A_s \times d_p(p_i, p_j) \times \exp\left(\frac{E_s}{T} \left(1 - \frac{d_{p,\text{crit}}}{d_p(p_i, p_j)}\right)\right),$$

where $d_p(p_i, p_j)$ is the minimum diameter of p_i and p_j , and A_s , E_s and $d_{p,\text{crit}}$ are sintering parameters.

Particles are transformed by the following processes:

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Intra-particle reaction

- Reaction of two adjacent -OH sites on one particle:

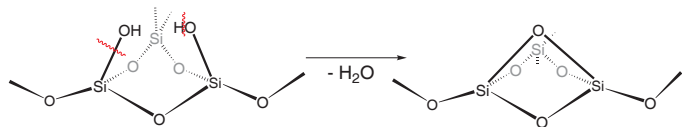


Figure: Intra-particle reaction.

- Intra-particle reaction transforms particle as:

$$P_q(p_1, \dots, p_i, \dots, p_{n(P_q)}, \mathbf{C}) \rightarrow P_q(p_1, \dots, p'_i, \dots, p_{n(P_q)}, \mathbf{C}),$$

where

$$p'_i \rightarrow p_i(\eta_{\text{Si}}, \eta_{\text{O}} + 1, \eta_{\text{OH}} - 2).$$

- Deduce rate of intra-particle reaction from surface reaction rate and average sintering rate such that Si/O ratio of 1/2 is attained:

$$R_{\text{int}}(P_q) = A_{\text{surf}} \exp\left(-\frac{E_a}{RT}\right) \eta_{\text{OH}}(P_q) N_A C_g - \frac{\rho_s(P_q)}{2} \left[\sum_{i,j=1}^{n(P_q)} \frac{C_{ij} - S_{\text{sph}}(p_i, p_j)}{\tau(p_i, p_j)} \right],$$

where $\rho_s(P_q) = \eta_{\text{OH}}(P_q)/S(P_q)$ is the surface density of active sites.

Algorithm

Input: State of the system Q_0 at initial time t_0 and final time t_f .

Output: State of the system Q at final time t_f .

$t \leftarrow t_0, Q \leftarrow Q_0;$

while $t < t_f$ **do**

 Calculate an exponentially distributed waiting time τ with parameter;

$$R_{\text{tot}}(Q) = R_{\text{inc}}(Q) + R_{\text{coag}}(Q) + R_{\text{surf}}(Q) + R_{\text{int}}(Q).$$

 Choose a process m according to the probability

$$P(m) = \frac{R_m(Q)}{R_{\text{tot}}(Q)},$$

 where R_m is the rate of the process $m \in \{\text{inc}, \text{coag}, \text{surf}, \text{int}\};$

 Perform process $m;$

 Update sintering level of all particles;

 Increment $t \leftarrow t + \tau;$

end

- For a given property of the system ξ calculated using N_{sp} computational particles and L number of independent runs, the empirical mean is:

$$\mu_1^{(N_{\text{sp}},L)}(t) = \frac{1}{L} \sum_{l=1}^L \xi^{(N_{\text{sp}},l)}(t).$$

- The empirical variance is:

$$\mu_2^{(N_{\text{sp}},L)}(t) = \frac{1}{L} \sum_{l=1}^L \xi^{(N_{\text{sp}},l)}(t)^2 - \mu_1^{(N_{\text{sp}},L)}(t)^2.$$

- The confidence interval I_P within which there is a probability P of finding the true solution is then given by:

$$I_P = \left[\mu_1^{(N_{\text{SP}}, L)}(t) - c_P, \mu_1^{(N_{\text{SP}}, L)}(t) + c_P \right].$$

$$c_P = a_P \sqrt{\frac{\mu_2^{(N_{\text{SP}}, L)}(t)}{L}}.$$

- We use $a_P = 3.29$ which corresponds to $P = 0.999(99.9\%)$

- The error e is:

$$e^{(N_{\text{sp}}, L)}(t) = \left| \mu_1^{(N_{\text{sp}}, L)}(t) - \zeta^\infty(t) \right|,$$

- $\zeta^\infty(t)$ is an approximation for the true solution which is obtained from a "high-precision calculation" with a very large number of particles.
- The average error over the entire simulation time is:

$$\bar{e}(N_{\text{sp}}, L) = \frac{1}{M} \sum_{j=1}^M e^{(N_{\text{sp}}, L)}(t_j),$$

where the M time steps t_j are equidistant.

- The zeroth moment is the particle number density:

$$M_0(t) = \frac{N(t)}{V_{\text{simpl}}}$$

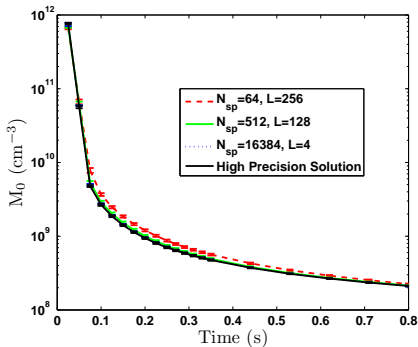
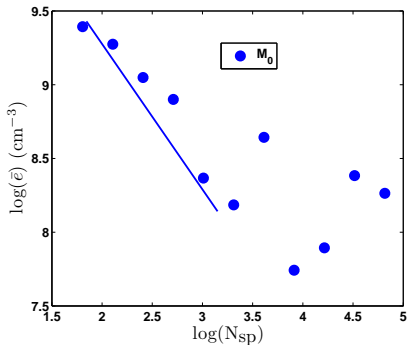


Figure: Convergence of zeroth moment ($N_{\text{sp}} \times L = 65536$). Solid line indicates slope of -1.

Volume

- The average particle volume:

$$V(t) = \frac{1}{N(t)} \sum_{q=1}^{N(t)} V(P_q(t))$$

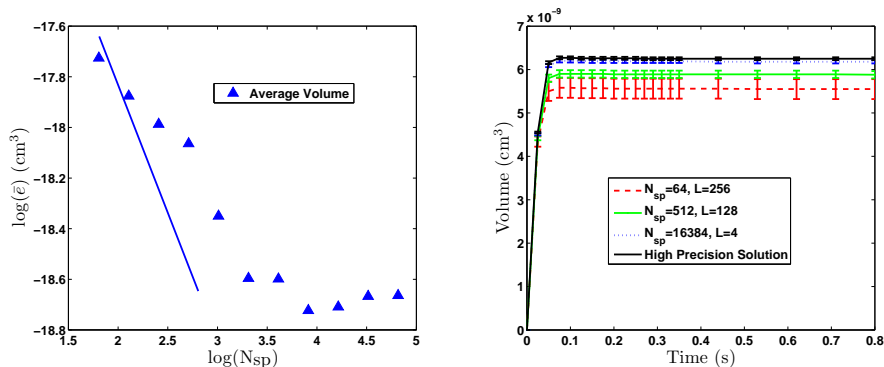


Figure: Convergence of average volume ($N_{sp} \times L = 65536$). Solid line indicates slope of -1.

Collision diameter

- The average collision diameter of a particle:

$$D_c(t) = \frac{1}{N(t)} \sum_{q=1}^{N(t)} d_c(P_q(t))$$

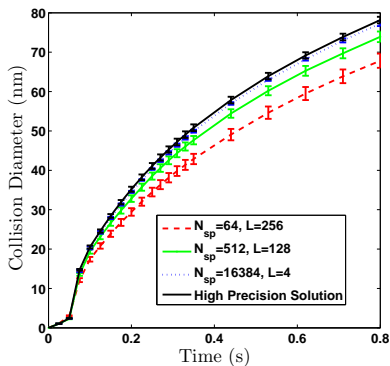
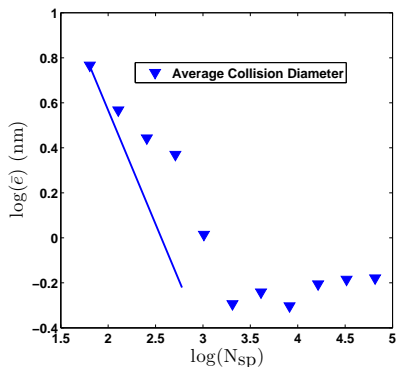


Figure: Convergence of average average collision diameter ($N_{sp} \times L = 65536$). Solid line indicates slope of -1.

Computational time

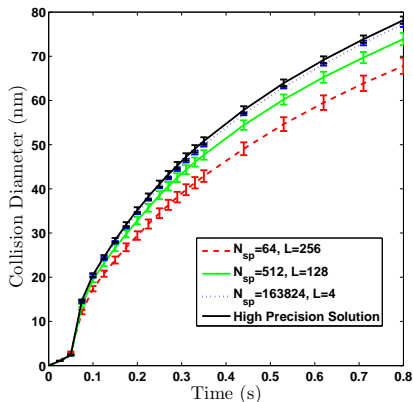
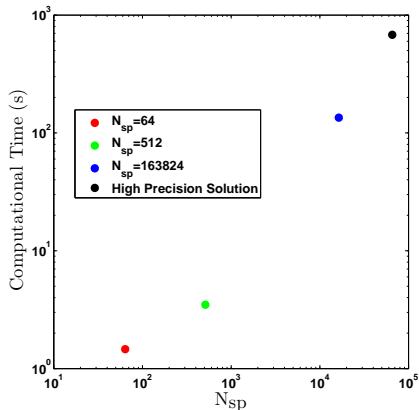


Figure: Computational time for different N_{sp} .

Computer-generated TEM

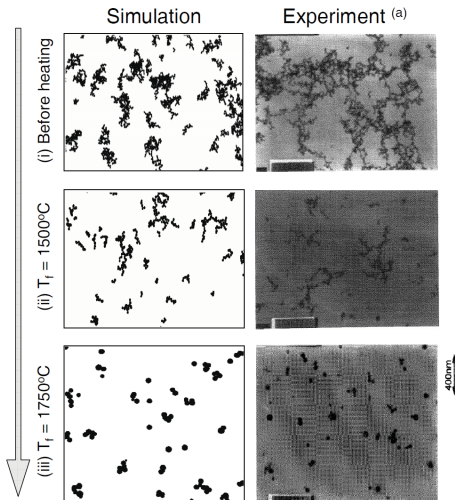


Figure: TEM images generated by projecting particles onto a plane. Experimental values from Seto *et al.* (1995).

Conclusion

- Description of a detailed population balance model.
- Numerical studies performed.
- Demonstrated feasibility of using first-principles to model complex nanoparticle synthesis processes.

Thank You!



```
function collision_occurred  
    compute_rates(CurrentCell, FieldParticleIndex  
    Phi_future(CurrentCell)=Phi_future(CurrentCell)  
    Phi_future(CurrentCell) * exp(-Delta_t * Phi_future
```

Welcome from the CoMo Group!



Welcome to the website of the Computational Modelling Group! We develop and apply modern numerical methods to problems arising in Chemical Engineering. The overall aim is to shorten the development period from research bench to the industrial production stage by providing insight into the underlying physics and supporting the scale-up of processes to industrial level.

The [group](#) currently consists of 25 members from various backgrounds. We are keen to collaborate with people from both within industry and academia, so please [get in touch](#) if you think you have common interests.

The group's [research](#) divides naturally into two inter-related branches. The first of these is research into mathematical [methods](#), which consists of the development of stochastic particle methods, computational fluid dynamics and quantum chemistry. The other branch consists of research into [applications](#), using the methods we have developed in addition to well established techniques. The main application areas are reactive flow, combustion, engine modelling, extraction, nano particle synthesis and dynamics. This research is [sponsored](#) on various levels by the [UK](#), [EU](#), and industry.



Markus Kraft - Head of the CoMo Group