Parameter estimation and statistical analysis of a new model for silicon nanoparticle synthesis

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Contents

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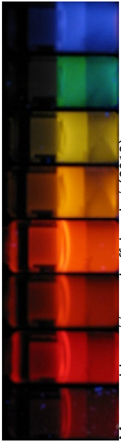
Introduction: significance of Si nanoparticles

- Si nanoparticles are usually obtained from the thermal decomposition of silane

$$SiH_4 \rightarrow Si + 2H_2$$

- Are used for mainly research purposes
  - Medical imaging (as quantum dots)
  - Printable semiconductor inks
  - Future touchscreen devices
- Properties of Si nanoparticles are strongly dependent on size and morphology



May et al http://www.buffalo.edu/ (2012)

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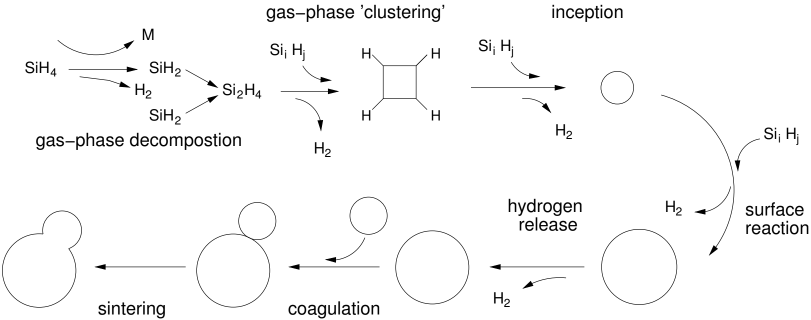
Introduction: particle synthesis

- Particles grow through complex physiochemical pathways



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Introduction: parameter estimation

- Particle synthesis models may have unknown/uncertain parameters
- **Inverse problem**: How do we choose these parameters?
- How do we solve this problem for a complex non-linear model?
- Which parameters are actually important?

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Introduction: key aims

1. Present model for silicon nanoparticle synthesis
   - Gas-phase kinetic model
   - Particle population balance
2. Discuss parameter estimation efforts
   - How do we estimate the parameters?
   - Which parameters is the model most sensitive to?

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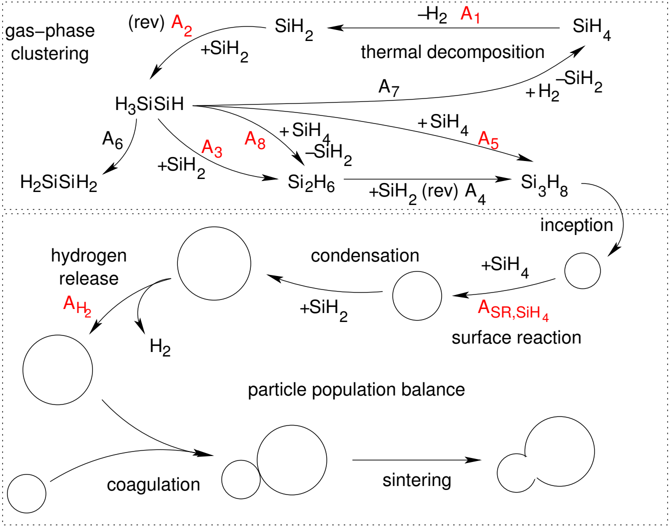
Model: fully-coupled model

- The model consists of a gas-phase kinetic model fully-coupled with a **particle population balance**



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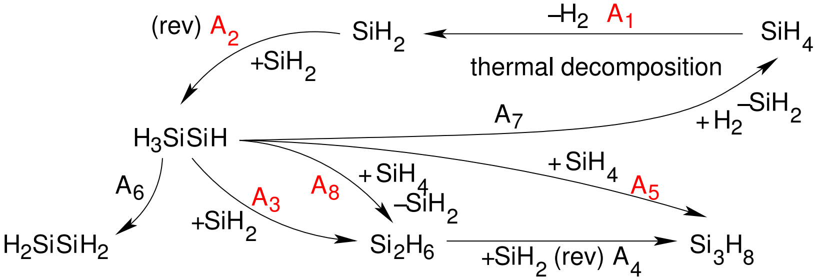
Model: gas-phase

- The gas-phase model contains 8 reactions and 11 species
- This system of ODEs is solved with a conventional solver



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Model: particle type-space

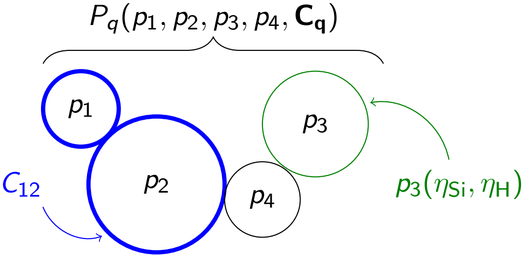
- Each particle P_q is represented as

$$P_q = P_q\left(p_1, \ldots, p_{n_q}, \mathbf{C}\right)$$

- Primaries are described by the number of silicon (η_{Si}) and hydrogen (η_{H}) units

$$p_x = p_x\left(\eta_{\mathrm{Si}}, \eta_{\mathrm{H}}\right)$$

- E.g., a particle with 4 primaries



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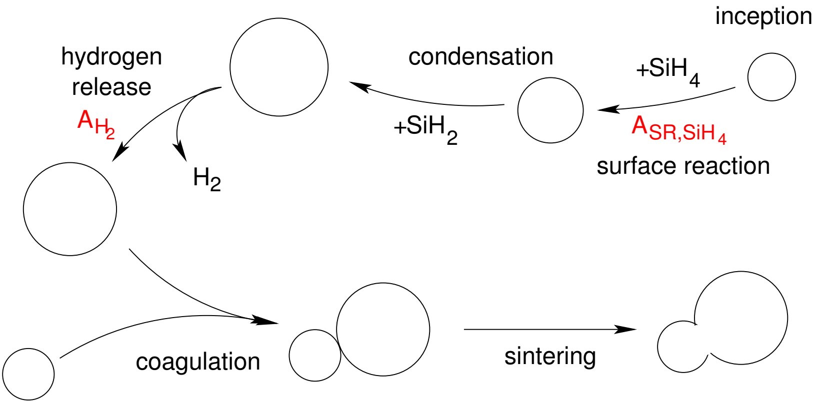
Model: particle population balance

- The particle population balance includes terms for inception, heterogeneous growth, coagulation and sintering



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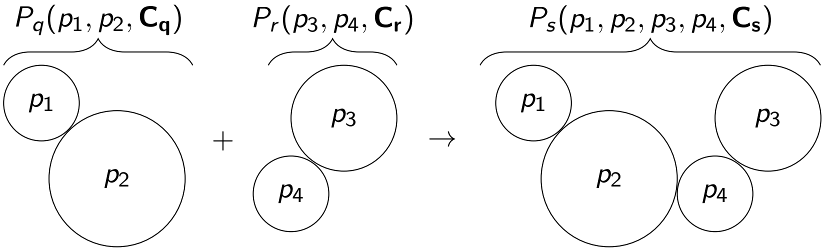
Model: type-space and coagulation

- The particle model is needed to capture process details
- For example, coagulation joins the particle tree structures



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Model: population balance solver

- A stochastic solver is used
- Enables use of the detailed particle model
- Takes advantage of a number of developments
  1. LPDA: accelerates surface reaction processes
  2. Binary tree: reduces summation time over the ensemble
  3. Majorant rates and fictitious jumps

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Parameter estimation: the adjusted parameters

- Previous studies and preliminary work identified two areas with significant uncertainty
  - gas-phase rates ($A_{1,\mathrm{LP}},\ A_{2,\mathrm{LP}},\ A_{3,\mathrm{LP}},\ A_{5,\mathrm{LP}},\ A_{8,\mathrm{rev}}$)
  - heterogeneous growth rates ($A_{\mathrm{SR,SiH_4}},\ A_{\mathrm{H_2}}$)
- Seven parameters were adjusted, giving parameter vector **x**

$$\mathbf{x} = (A_{1,\mathrm{LP}},\ A_{2,\mathrm{LP}},\ A_{3,\mathrm{LP}},\ A_{5,\mathrm{LP}},\ A_{8,\mathrm{rev}},\ A_{\mathrm{SR,SiH_4}},\ A_{\mathrm{H_2}})$$

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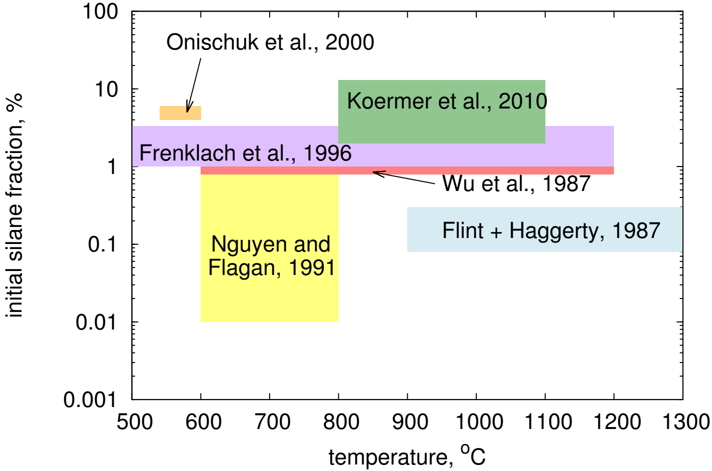
Parameter estimation: case studies

- The model was tested against a range of experimental studies



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Parameter estimation: objective function

- The objective function for this system was defined as

$$\Phi(\mathbf{x}) = \sum_{i=1}^{N_{\text{exp}}} \left(\phi_i^{\text{exp}} - \phi_i^{\text{sim}}(\mathbf{x})\right)^2$$

- where ϕ_i represents one of the N_{exp} experimental datasets used for fitting
- We considered two forms of ϕ_i:

ϕ_i^{μ} : mean or mode of a particle size distribution
ϕ_i^{σ} : geometric standard deviation of a PSD

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Parameter estimation: initial optimisation

1. Locate parameter sets near the minimum of $\Phi(\mathbf{x})$ using low discrepancy (Sobol) sequences
2. Refine initial guess using SPSA algorithm
3. Select optimal parameter set $\mathbf{x}^*$
4. Construct a response surface (surrogate model) around $\mathbf{x}^*$
5. Conduct MCMC sampling to estimate the posterior distribution of parameters
6. Obtain confidence intervals for parameters
7. Evaluate model at mode of confidence interval

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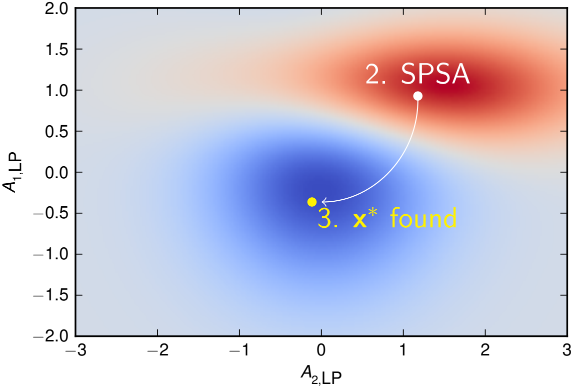
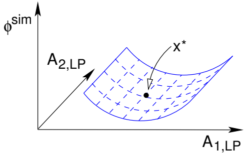
Parameter estimation: visualised

1. Low discrepancy sequence scan

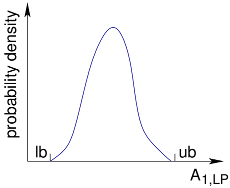


4. Make response surface



5. MCMC sampling of surface

6. Obtain parameter CIs



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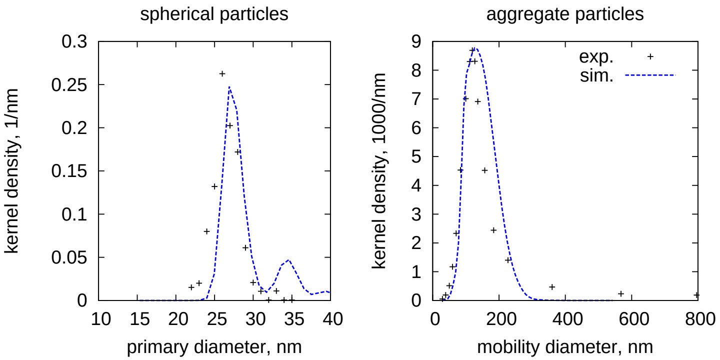
Parameter estimation: model results

7. Evaluated model at mode of parameter confidence intervals
   - Generally good agreement with experimental measurements



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Parameter estimation: HDMR response surfaces

- The global sensitivities can be determined from a High Dimensional Model Representation (HDMR)
- Decomposes a response ϕ^{sim} into a function of the parameters x_i

$$\phi^{\text{sim}} \approx f(\mathbf{x}) = f_0 + \underbrace{\sum^{N_{\text{param}}} f_i(x_i)}_{\text{first-order terms}} + \underbrace{\sum_{i=1}^{N_{\text{param}}} \sum_{j=i+1}^{N_{\text{param}}} f_{ij}(x_i, x_j)}_{\text{second-order terms}}$$

- We truncate $f(x)$ to second-order terms

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Parameter estimation: HDMR sensitivities

- The first-order absolute sensitivity is given by the variance of the response function $f(x_i)$ integrated over specified upper- and lower-bounds

$$S^*_{\phi^{\text{sim}}}(x_i) = \int_{\text{l.b.}}^{\text{u.b.}} f_i^2(x_i)\mathrm{d}x_i$$

- These tell us how much variance in output response ϕ^{sim} can be achieved by adjusting the parameter x_i

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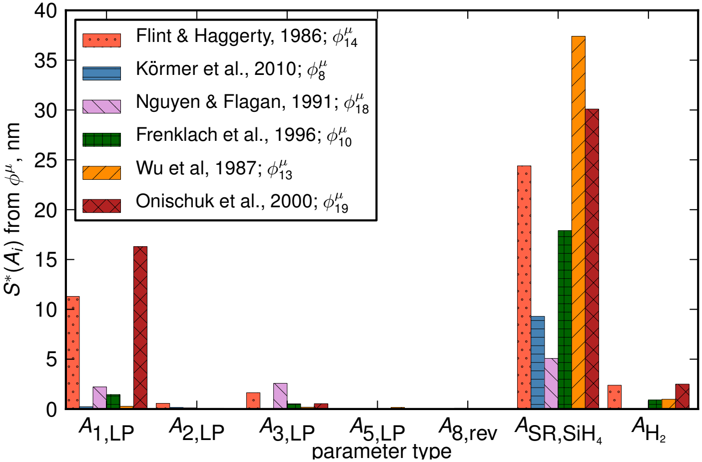
Parameter estimation: sensitivity analysis

- First-order sensitivities for the PSD mode objective function



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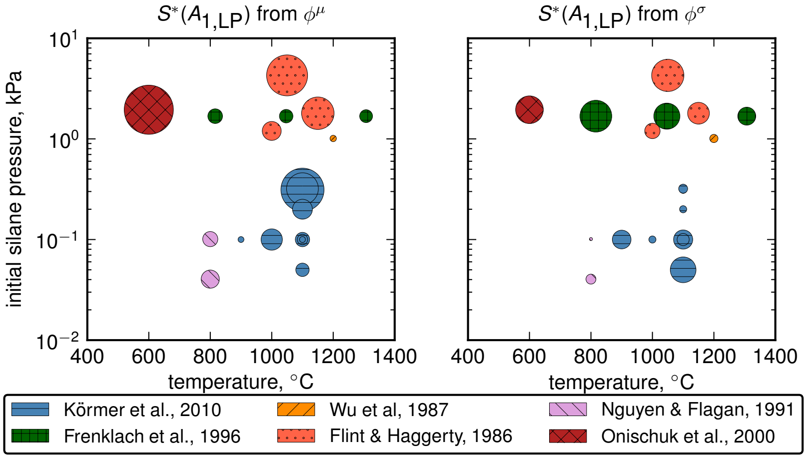
Parameter estimation: bubble plots (1)

- Global sensitivities of the initial decomposition step pre-exponential ($A_{1,\mathrm{LP}}$) to different experimental cases



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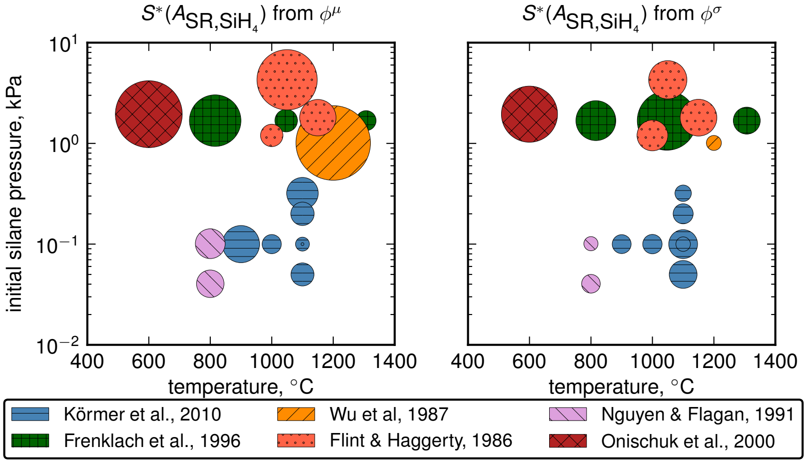
Parameter estimation: bubble plots (2)

- Global sensitivities of the surface reaction pre-exponential (A_{SR,SiH_4}) to different experimental cases



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Parameter estimation: next steps

- Bar chart indicated that $A_{1,\mathrm{LP}}$, $A_{3,\mathrm{LP}}$ and $A_{\mathrm{SR},\mathrm{SiH}_4}$ are the most important parameters
  - ▷ Can we use fewer parameters for the parameter estimation?
- Bubble plots tell us which parameters influence which experiments
  - ▷ Which experiments pull optimals in which directions?
  - ▷ Which experiments (or their model representation) are poor?
- Answering these questions embarks us on a **model and experimental discrimination** pathway

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Conclusions

- Parameter estimation for a detailed model is challenging!
- For models with many parameters, a systematic estimation procedure is necessary
- Global sensitivities from HDMR can potentially yield physical insight about the model
- These tools will be used for model and experimental discrimination

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