OTTO VON GUERICKE UNIVERSITÄT MAGDEBURG

VST FACULTY OF PROCESS AND SYSTEMS ENGINEERING

Monte Carlo simulation of shape evolution in solutions
A model study of BaSO4 precipitation

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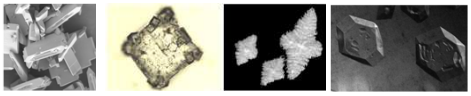
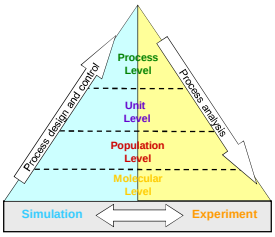
Motivation

Crystallization is an established industrial production and separation technology for bulk chemicals, pharmaceuticals or agrochemicals. Specific control of crystal size and **crystal shape**, plays an important role in achieving a high product quality in crystallization. A detailed understanding of the fundamental phenomena driving crystal growth is therefore crucial to design a tailor-made process environment where **control of the crystal shape** can be maintained with a desired accuracy. This requires an understanding of all different aspects from the atomic and molecular scales up to the process system level. **Molecular modelling** is therefore a major important part toward the completion of a multi scale process engineering methodology.



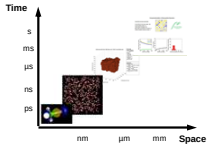
Systems Approach

Our multi level systems approach connects the different levels of a technical application from the top process level down to the molecular scale. We combine the system simulation based on a variety of models at process, unit, population and the **molecular scale** with well-designed experiments. The combination of data from simulation and experiment validates these models, enhances our understanding and generates new design pathways.

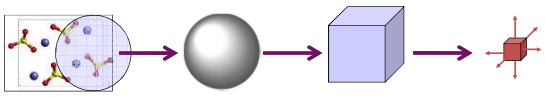


Molecular Modeling

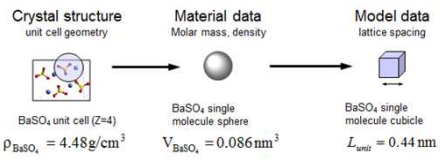
The time evolution of a crystal shape is driven by several phenomena. Convection and diffusion of molecules leads to transport in solution. This motion will lead to collision and binding of molecules to one another, the primary step for nucleation. Additional solute molecules will attach to the surfaces of such a nucleus in successive growth steps. This leads to **face growth** which depends on site binding energy as well as on the surface motion of molecules. The dynamical interplay of diffusion, nucleation and growth is key in understanding the dynamics of the **crystal shape evolution** in solution.



Simulation basics



Approximation from complex molecular level to simplified mesoscale stochastic diffusion



Molecular and material data of Barium sulfate for estimation of scale

- Solving **time-independent** Schrödinger equation
- Apply **approximations** like Born-Oppenheimer (mass difference)
- Use **simplifications** like Hartree-Fock
- Compare with experiments like attosecond laser pulse technology (COLTRIMS)

- Limited to
  - simple structures
  - small molecules
  - ground states
  - stationary states

- Use QM parameterized force fields
- Solving complex systems of **equations of motion**
- Apply **Newton's force law**
- Chose approximated **potentials** like Lennard Jones
- Check **simplifications** to convert complex molecules into single beads
- Compare with dynamic experiment like surface growth AFM

- Limited to
  - small time and length scales
  - available force fields
  - clean systems

- Using parameterized probabilities from MD
- Evolving discrete entity systems with **Monte Carlo simulation**
- Use **random number generators**
- Use **event probabilities** for case differentiation i.e. face growth
- Apply **Boltzmann factors** for event selection rules
- Compare to dynamic experiments with real-time data

- Limited to
  - mesoscale length and times
  - available MD input data
  - coarse-grained systems

- Motion of $BaSO_4$ depends on molecule size r, viscosity η and temperature T via the Einstein-Smoluchowski diffusion constant D
- Crystal growth of $BaSO_4$ depends on (i j k)-surface properties
- Free molecules attach to a crystal nucleus at different faces with different probability p
- Monte-Carlo move probability p_{move} relates the energy difference ΔE between surface-free/surface-surface sites as a function of temperature T
- Step-wise simulation of free diffusion, attachment and surface relocation for every molecule in a selected system box

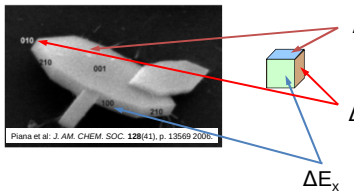


TABLE 23: Surface Energies of Barite–Water Interfaces at 298 K, Which Were Calculated from 80-ps MD Simulations with FF Developed to Fit to Higher-Level QM (BSLYP/LACVP**++)

surface	(210)	(001)	(010)	(100)
E(composite) (kcal/mol)[a]	−19575	−19550	−19525	−19549
$\Delta E/2$ (kcal/mol)[a]	89	102	114	102
surface area (Å^2)	198	194	246	160
surface energy (mJ/m^2)	311	364	321	443

[a] E(reference system) = E(bulk water) + E(bulk barite) = −19753 ± 6 kcal/mol.

Jang et al: J. Phys. Chem. B 106, p. 9951 2002.

$$D = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot r}$$

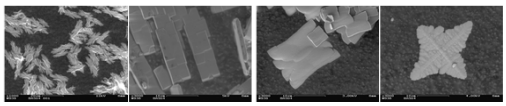
$$p_{move} = e^{\frac{\Delta E}{k_B \cdot T}}$$

$BaSO_4$ molecule diffusion constant … D ≈ 10^{-9} m^2/s
- $BaSO_4$ radius … $r \approx 0.2nm$, viscosity of water … $\eta \approx 1cP$
- Temperature … $T \approx 300K$, Boltzmann constant … $k_B = 1.38 \cdot 10^{-23} J/K$

Experiment vs. Simulation

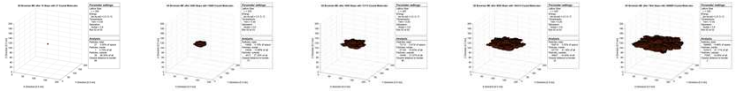
Reactive crystallization experiments in a CSTR

- Mixing of water based $BaCl_2$ and Na_2SO_4 solutions
- Variation of process conditions like temperature, concentration, feed policy and stoichiometry
- Concentration between 0.01M and 0.3 M
- Temperatures between 300K and 340K
- Feed policy $BaCl_2 \rightarrow Na_2SO_4$ or $Na_2SO_4 \rightarrow BaCl_2$
- Stoichiometry of 1:1 or 1:10 or 10:1
- Observation of crystals with REM microscopy



Monte Carlo simulation in closed box systems

- 3D cubic lattice basis or 3D hexagonal lattice basis with box size up to 500^3
- Variation of concentration with number of molecules inside box up to 1.000.000
- Observation of short and long time evolutions up to 1.000.000 steps



- Variation of temperature by change of k_BT
- Variation of shape anisotropy with relation $\Delta E_z/\Delta E_x$ between 1 and 0.1
- Variation of initial nucleation shape from cubic to plate to hexagonal