OTTO VON GUERICKE UNIVERSITÄT MAGDEBURG

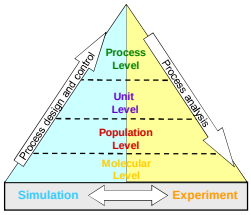
VST FAKULTÄT FÜR VERFAHRENS- UND SYSTEMTECHNIK

Molecular Modeling of Crystal Shape Evolution in Solutions

Dr. Andreas Voigt and Prof. Kai Sundmacher , Chair of Process Systems Engineering
Contact: andreas.voigt@ovgu.de , +49-391-6751435, Carnot-Gebäude 25, Raum 313
Mail: OvGU, FVST/IVT/SVT, Universitätsplatz 2, 39106 Magdeburg, Germany

Motivation

Crystallization from solution is an important industrial process in many applications ranging from bulk materials, pharmaceuticals, to catalysts and nanoparticles. Nowadays not only the size of the crystal but also its specific and well-defined shape needs to be maintained and controlled. A tailored production process can only be established with the appropriate knowledge of the underlying phenomena and principles in crystal generation. In this specific research area molecular modeling has become an important theoretical approach in the more general engineering process development.



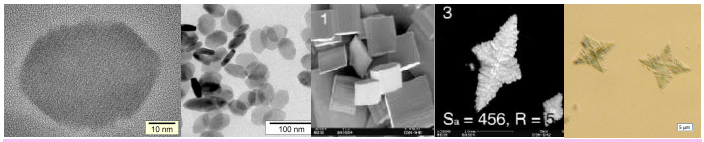
Modeling

From the molecular perspective the evolution of a crystal shape is driven by a number of important phenomena. Convection and diffusion of molecules leads to transport in solution. This molecular movement will in turn lead to collision and binding of molecules to one another, building the primary step in a nucleation event. Additional solute molecules will attach to the surfaces of such a nucleus in successive growth steps. The attachment of molecules onto the crystal structure at different crystal faces will depend on a corresponding energy barrier and also after the attachment molecules are still changing their position on the surfaces by surface diffusion. The dynamical interplay of all phenomena (diffusion, nucleation and growth) will be of importance in modeling and simulating the dynamics of the shape evolution of crystals in solution. Understanding the driving forces will help in finding the corresponding material and process conditions in a tailored engineering process application.

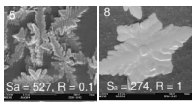
Results

Here we will present a molecular modeling approach as a combination of molecular dynamics (MD) and Monte Carlo (MC) simulation methods. The molecule movement in solution and at surfaces with MD can offer insight into the specific differences of binding at certain crystal faces. This information can be passed on to MC models where the mesoscale evolution of the crystal shape can be studied. Model simulations will be compared to specific experimental data like REM pictures of precipitated $BaSO_4$ crystals or AFM pictures of Na_2CO_3 surface growth in solution. Change in certain process conditions like concentration, feeding schedule or temperature lead to different shape evolution scenarios in the experiments. The corresponding simulations of these model systems will provide a deeper insight into the driving phenomena and will help to improve our understanding of the crystallization process as a whole.

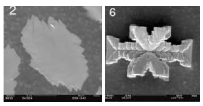
Barium Sulfate Precipitation



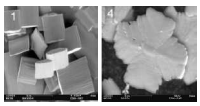
Different evolution stages of $BaSO_4$ by HRTEM, TEM, REM (2x) and optical microscopy



Low/High concentration

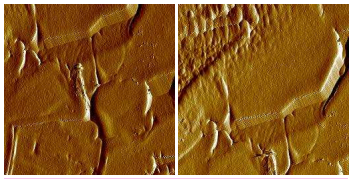


Change feed direction

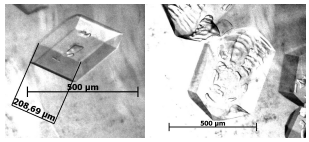


Slow/Fast feed

Sodium Carbonate Crystallization



Time-dependent AFM pictures of Na_2CO_3

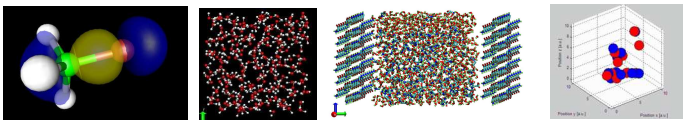


Time-dependent optical microscopy of Na_2CO_3

- Observation of growth on different faces
- Anisotropic growth leads to different shapes
- Understand shape evolution – Design crystal size **and** shape

- A.Voigt, D. Adityawarman and K. Sundmacher, *Size and distribution prediction for nanoparticles produced by microemulsion precipitation: A Monte-Carlo Simulation study",* Nanotechnology **16**, p.429-434 (2005).
- Niemann, B., Veit, P. and Sundmacher, K., *Nanoparticle Precipitation in Reverse Microemulsions: Particle Formation Dynamics and Tailoring of Particle Size Distributions*, Langmuir **24** p.4320-4328 (2008) .
- C. Steyer and K. Sundmacher, *Impact of feeding policy and ion excess on particle shape in semi-batch precipitation of barium sulfate*, Journal of Crystal Growth **311**, p.2702-2708 (2009).
- C. Borchert, N. Nere, D. Ramkrishna, A. Voigt and K. Sundmacher, *On the prediction of crystal shape distributions in a steady-state continuous crystallizer,* Chemical Engineering Science **64**, p.686-696 (2009).
- Heineken, W., Voigt, A., Flockerzi, W., and Sundmacher, K., *Dimension reduction of bivariate population balances using the quadrature method of moments,* Computers and Chemical Engineering **35**, p.50-62 (2011).

Molecular Dynamics



Scaling the complexity from quantum stage up to bead-and-spring models

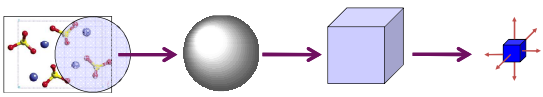
- Solving **time-independent** Schrödinger equation
- Apply **approximations** like Born-Oppenheimer (mass difference)
- Use **simplifications** like Hartree-Fock
- Compare with experiments like attosecond laser pulse technology (COLTRIMS)

- Limited to
  - simple structures
  - small(er) molecules
  - ground states
  - stationary states

- Using parameterized force fields from QM
- Solving systems of **equation of motion**
- Use **Newton's force law**
- Use different **potential approximation** like Lennard-Jones
- Apply **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

Kinetic Monte Carlo



Approximation from complex molecular level to simplified mesoscale stochastic diffusion

- 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