Analysis of Anisotropic Crystal Growth in Solution using Molecular Modeling Methods

Andreas Voigt[a] and Kai Sundmacher[a,b]

[a] Process Systems Engineering, Otto-von-Guericke University Magdeburg, Germany

[b] Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany

Motivation

- Improve the control of size and shape of crystal particles in industrial production processes
- Enhance the understanding of nucleation and initial growth of crystals from solution at the molecular scale
- Extract microscopic driving forces for specific and anisotropic crystal shape growth
- Connect driving micromechanics to macroscopic process conditions for production control of crystal shape
- Develop appropriate molecular modeling approaches to bridge the gap between lab theory and real-world production environment

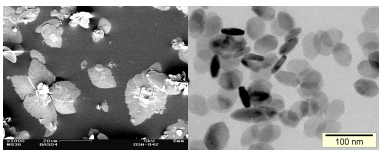


Figure 1: Left) Different sizes and shapes of a $BaSO_4$ crystal products in an "uncontrolled" production (bulk system);
Right) Regular size and shape in a "controlled" production (microemulsion system)

Modeling Approach

- *Dynamic Monte Carlo* (DMC) simulations are based on a discretization in space and time
- Time discretization is based on different event steps: free Brownian diffusion, surface attachment and surface relocation based on surface energy change
- Space discretization is based on a basic building block, a crystal growth unit moving in a "hidden" solution
- Random numbers are used to carry out different events with different units with a certain probability
- Check of random number generation, proof of statistical evidence and appropriate finite size scaling tests are key to successful Monte Carlo simulations

DMC Procedure

1. Brownian diffusion step with all free crystal growth units
2. Check for surface attachment of growth units with solute-surface energy $\Delta E_{sol\text{-}surf}$
3. Attempt relocation step of surface crystal units with surface-surface energy $\Delta E_{surf\text{-}surf}$
4. Consider anisotropy of different crystal faces in energy calculation

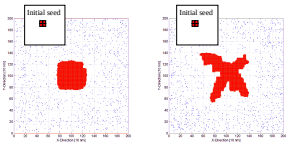
$$D = \frac{k_B \cdot T}{3 \cdot \pi \cdot \eta_{solute} \cdot d_{growth\ unit}}$$

$$rand() < p_{attach} = e^{-\frac{\Delta E_{sol-surf}}{k_B \cdot T}}$$

$$rand() < p_{reloc} = e^{-\frac{\Delta E_{surf-surf}}{k_B \cdot T}}$$

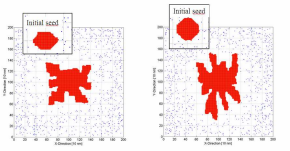
Two-dimensional Systems – 2D

Space discretization with square lattice for 2D DMC:
a) Free Brownian diffusion step
b) Lattice relocation to nearest neighbor place
c) Lattice relocation to next-nearest neighbor place



- Left: Less attachment probability and more relocation probability lead to simple square unit growth.
- Right: Enhanced attachment probability and less relocation probability lead to dendritic growth in fractal fashion – Star-Shape.

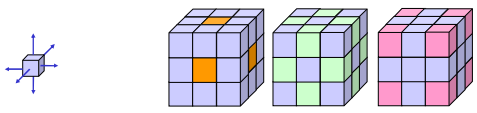
Figure 2: Results for isotropic 2D growth from a simple square seed: Left high temperature, right low temperature.



- Left: Hexagon seed leads to 6-Star shape.
- Right: Octagon seed leads to 8-Star shape

Figure 3: Results for isotropic 2D growth from hexagon and octagon seeds under low temperature conditions

Three-dimensional Systems – 3D



Space discretization with square lattice for 3D DMC:
a) Free lattice diffusion step
b) Lattice relocation to nearest neighbor place
c) Lattice relocation to next-nearest neighbor place
d) Lattice relocation to next-next nearest neighbor place

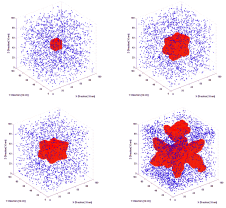


Figure 4: Results for isotropic 3D growth from a cubic seed unit under different growth conditions
Left: high temperature,
Right: low temperature,
Upper: low concentration,
Lower: high concentration.

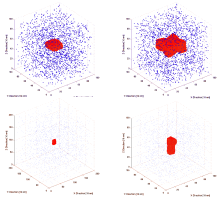


Figure 5: Results for anisotropic 3D growth from a cubic seed unit under different growth conditions:
Left: high temperature,
Right: low temperature,
Upper: $E_{xy} = 2\ E_z$,
Lower: $E_{xy} = 1/2\ E_z$.

Future Directions

- Refine the model parameters to realistic production process conditions
- Extend model variety and lattice geometries to include specific crystal structure growth units
- Specify the surface-energy related steps including results from *ab initio* and *Molecular Dynamics* data
- Compare with experimental data from meso and nano scale crystal growth (AFM)

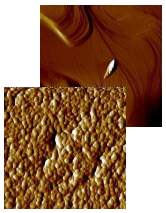


Figure 6: AFM pictures of surface crystal growth in solution for different crystals.