09AIChE
Annual Meeting, Nashville, TN

Simulating the Shape Evolution of Crystals with Monte Carlo Methods

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MAX-PLANCK-INSTITUT
DYNAMIK KOMPLEXER
TECHNISCHER SYSTEME
MAGDEBURG

Outline

- Motivation

  Crystal shape – Modelling the Evolution – Design this Property

- Experimental observation

  Crystal shape images of model system $BaSO_4$

  Influence of macroscopic process conditions on shape evolution

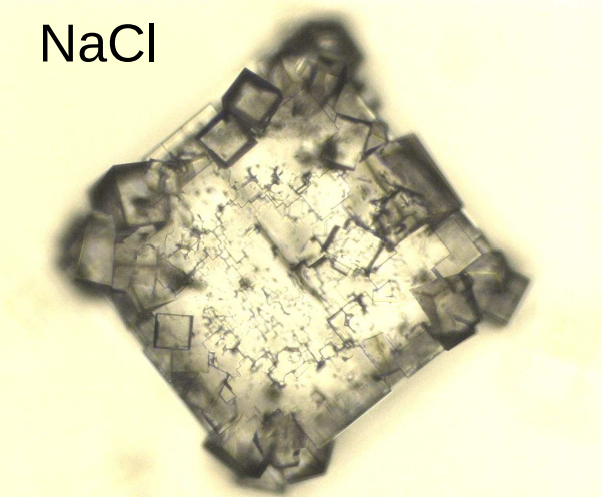
- Modelling the shape evolution

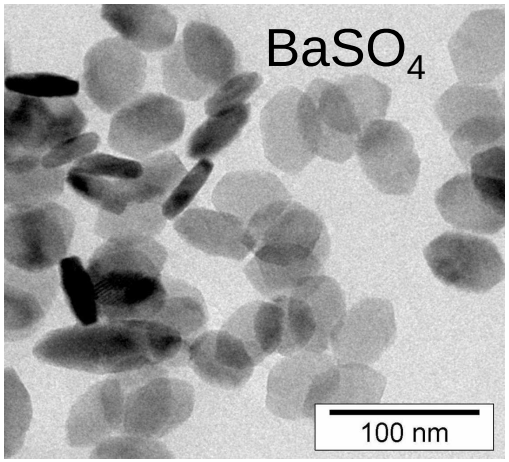
  Basic principles of kinetic Monte Carlo simulation

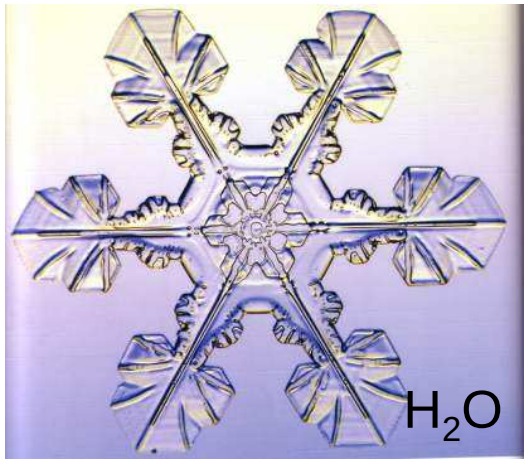
  Comparison of simulation and experiments

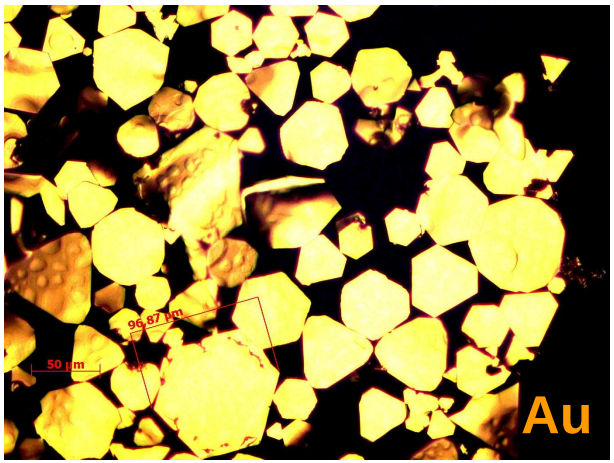
- Summary and Outlook

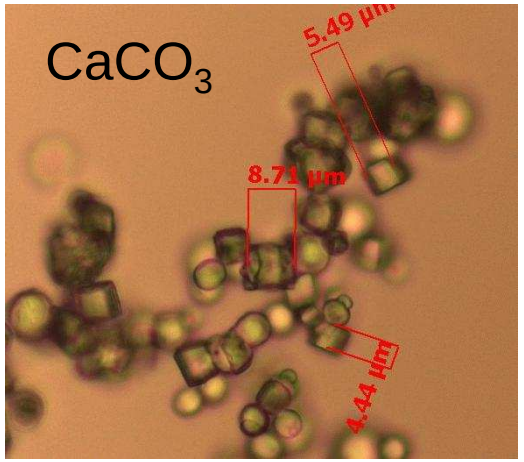
Crystal Shape Variations











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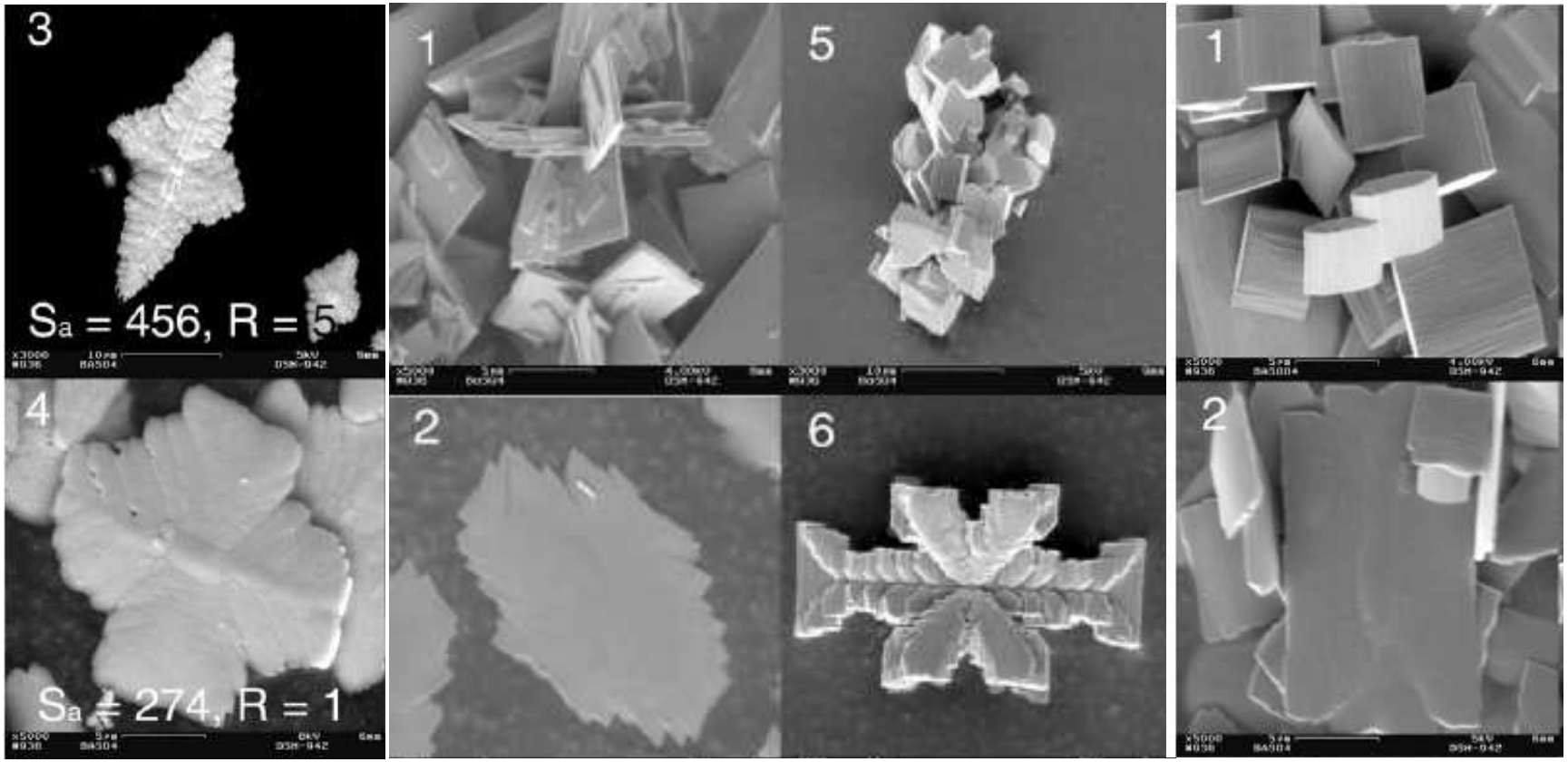
Motivation

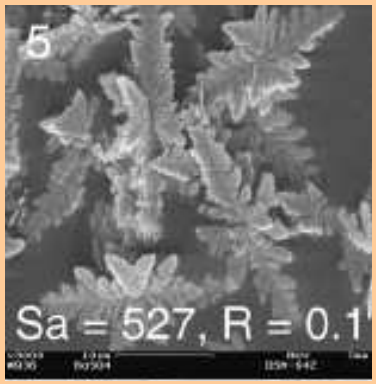
Current Research on Model System Barium Sulfate – $BaSO_4$

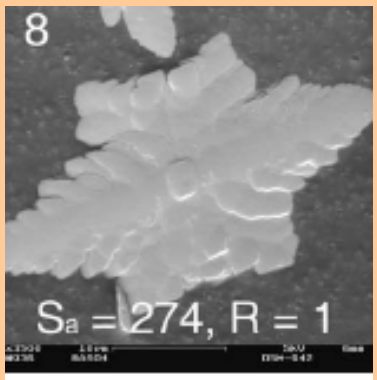


C. Steyer and K. Sundmacher (2009): *Impact of feeding policy and ion excess on particle shape in semi-batch precipitation of barium sulfate*, Journal of Crystal Growth **311** , p.2702-2708.

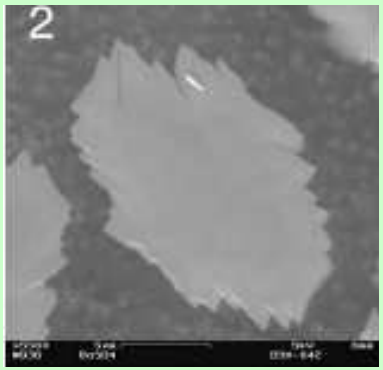
Change of Shape due to Process Variation

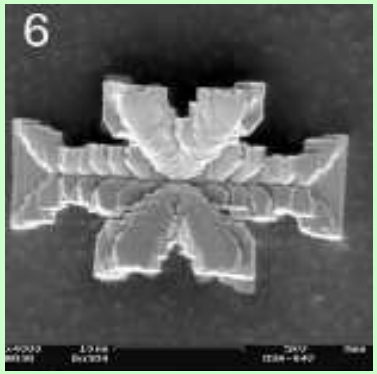
- Experiments in a isothermal semi-batch CSTR with $BaCl_2$ and K_2SO_4 feed



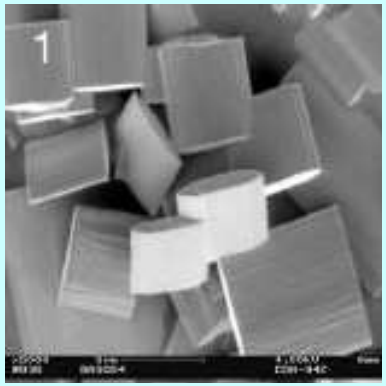


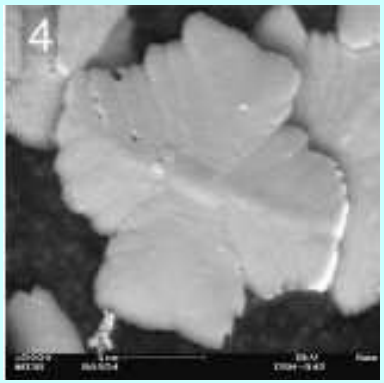
Change in total Concentration:
High and low





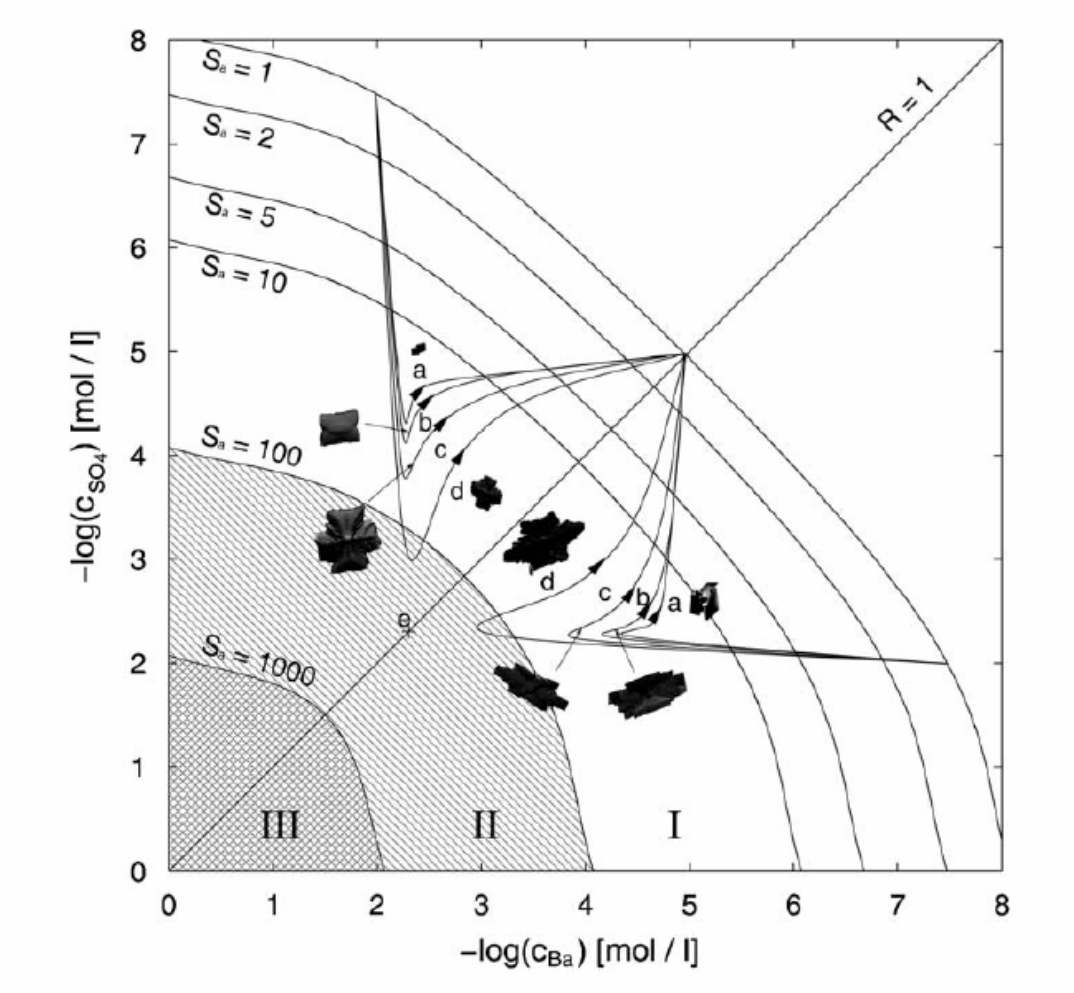
Change in Feed Direction:
A→B or B→A





Change in Feed Rate:
Slow and fast

Summary of Experiment



Crystal Shape Variations

- Dependence on total concentration
  For higher Concentration
  → Star-like shape
- Dependence on concentration ratio
  For higher concentration ratio
  → Compact shape
- Dependence on initial concentration
  For excess of certain ions
  → 2D or 3D shape

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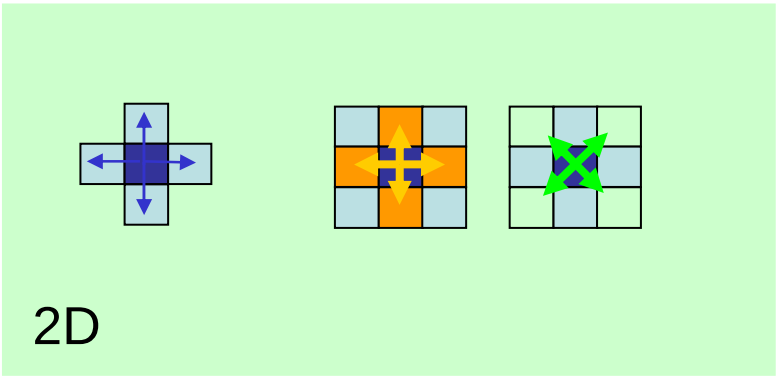
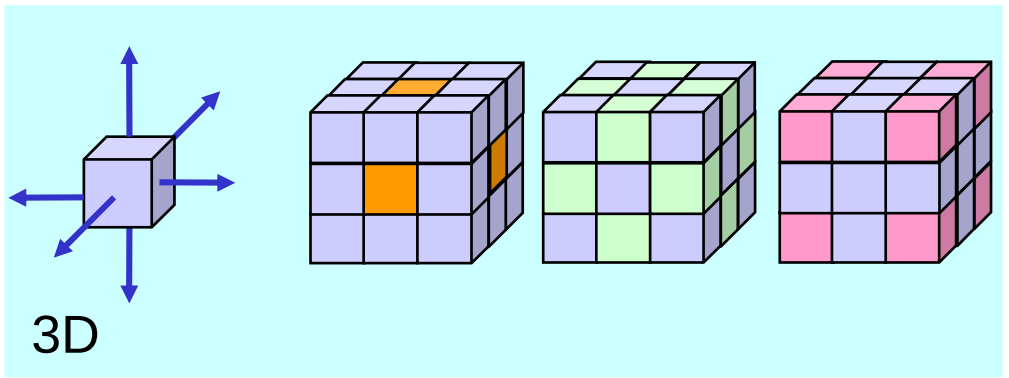
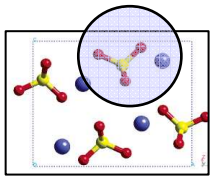
Lattice Monte-Carlo Simulation in 2D/3D

- Simple square/cubic lattice for molecule movements





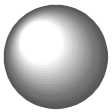
Crystal structure
unit cell geometry



$BaSO_4$ unit cell (Z=4)

$$\rho_{BaSO_4} = 4.48\,g/cm^3$$

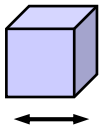
Material data
Molar mass, density



$BaSO_4$ single molecule sphere

$$V_{BaSO_4} = 0.086\,nm^3$$

Model data
lattice spacing

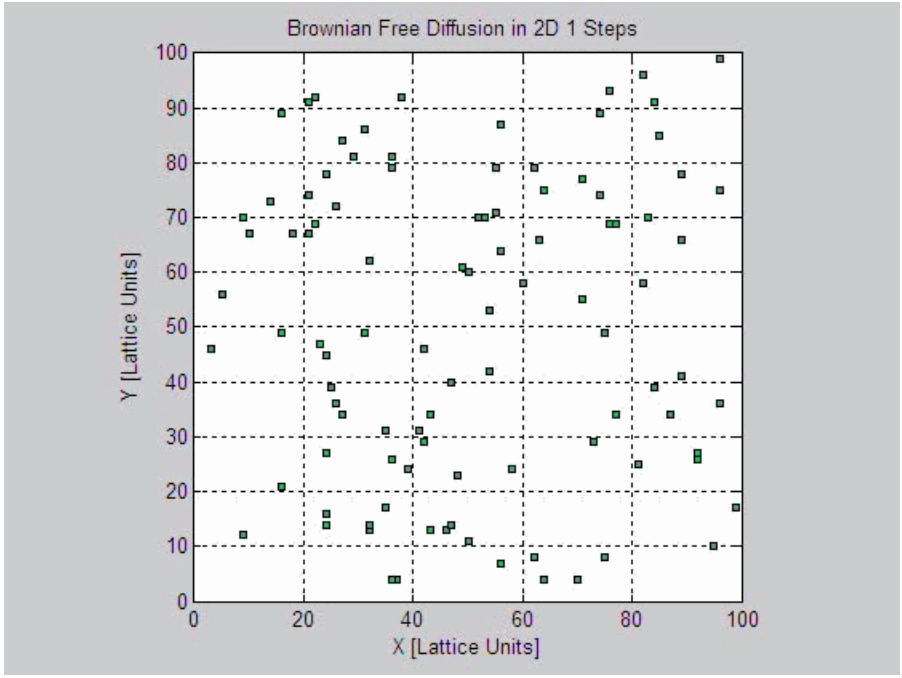


$BaSO_4$ single molecule cubicle

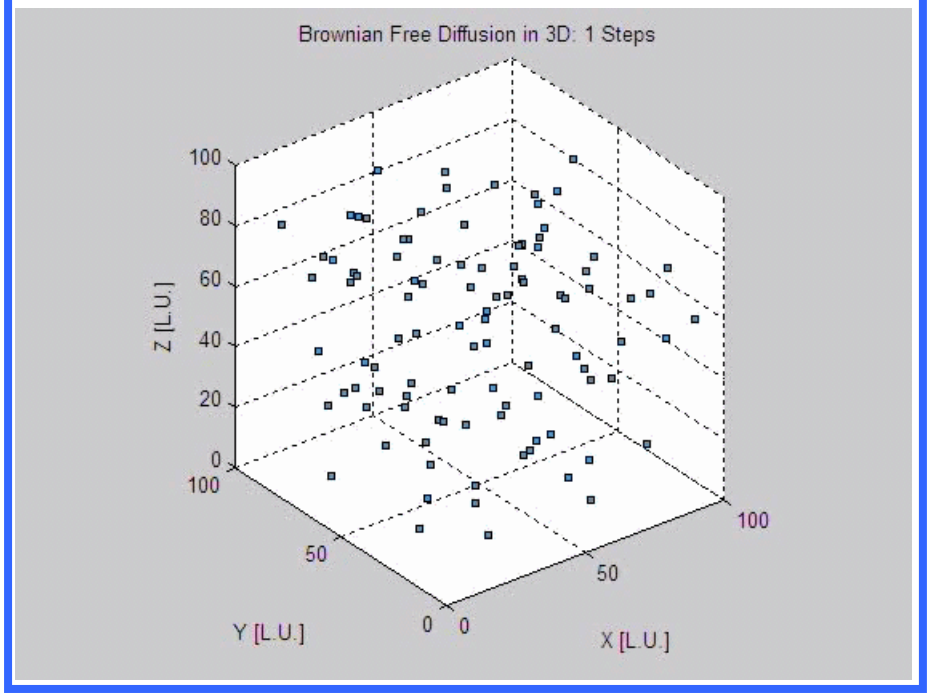
$$L_{unit} = 0.44\,nm$$

Movies of Free Diffusion 2D/3D

2D System - Free Diffusion

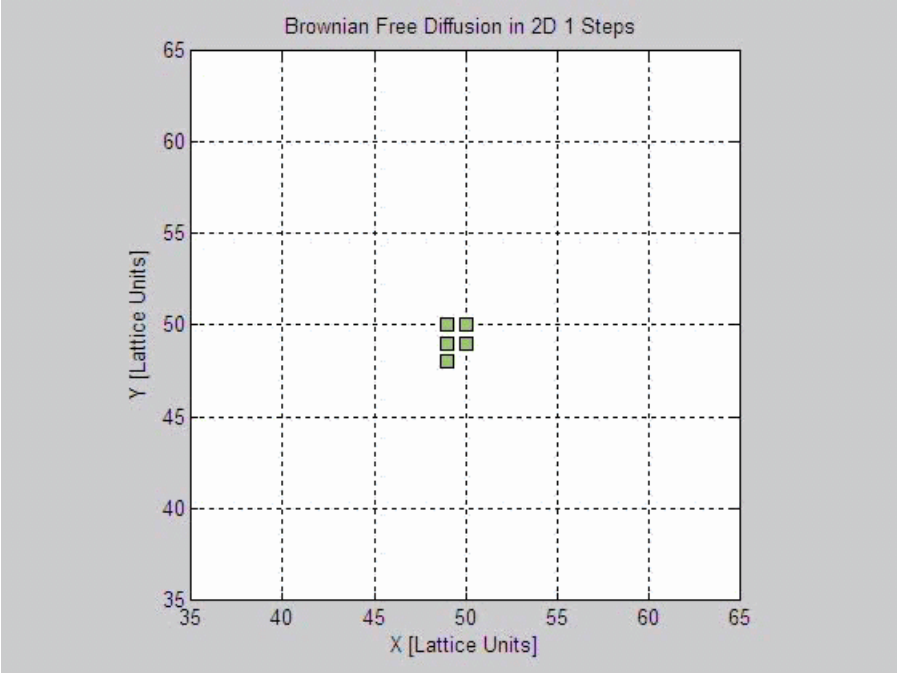


3D System - Free Diffusion

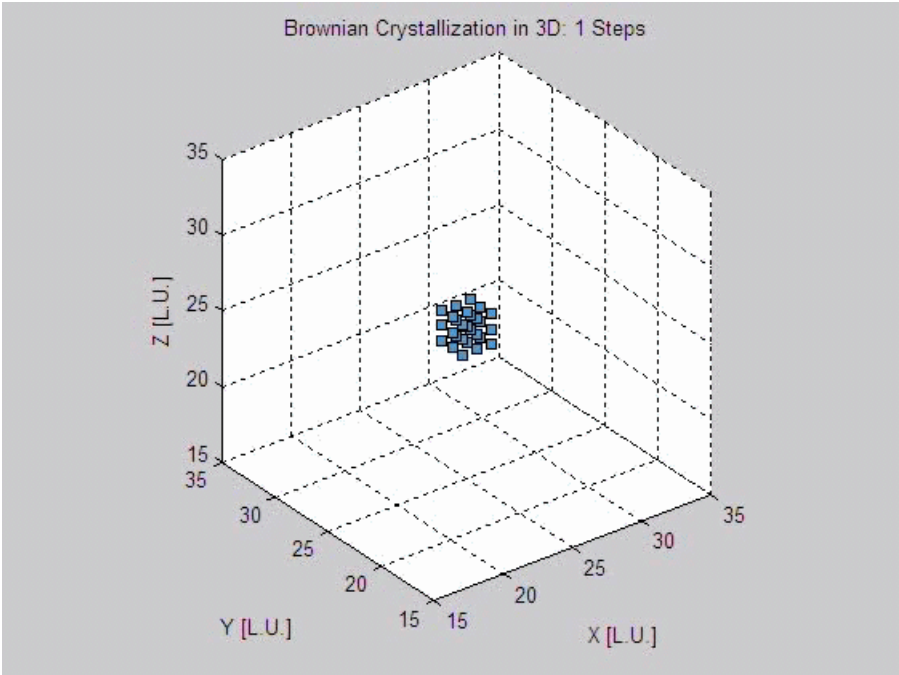


Unit Movement at the surface

2D System – NN and NNN Moves

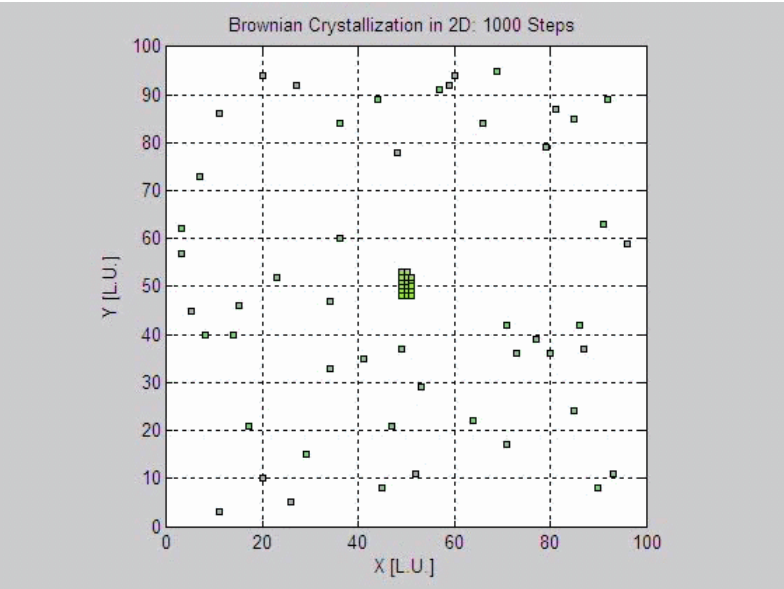


3D System – NN, NNN and NNNN Moves

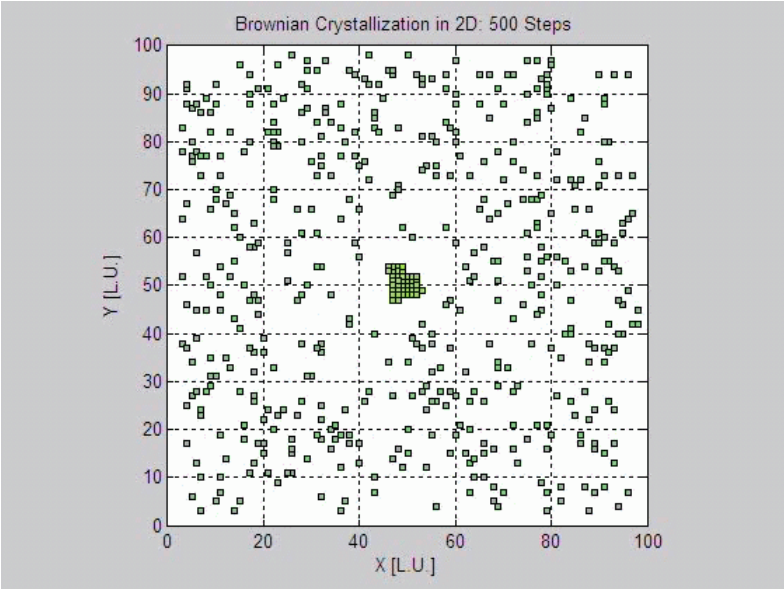


Isotropic Growth Mode in 2D

Low Concentration of Molecules



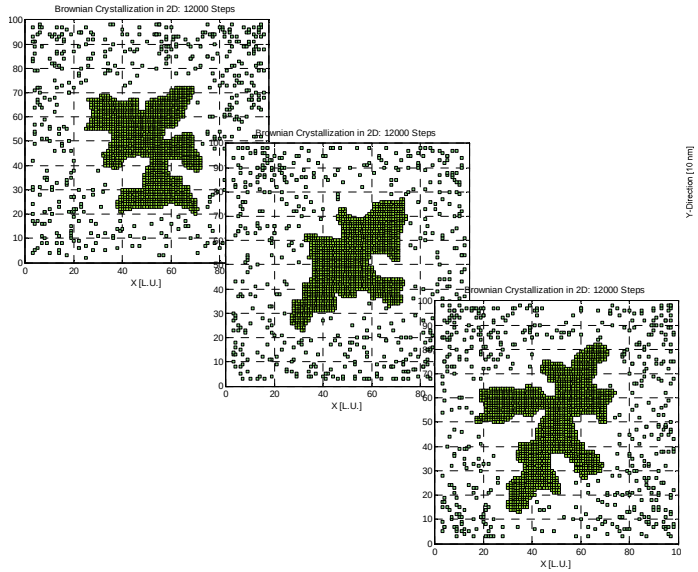
High Concentration of Molecules

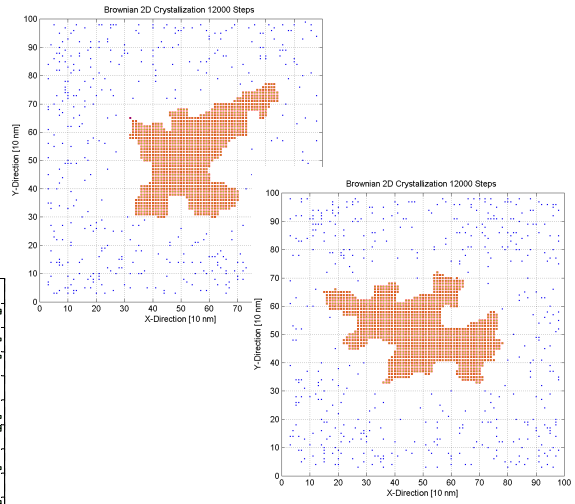


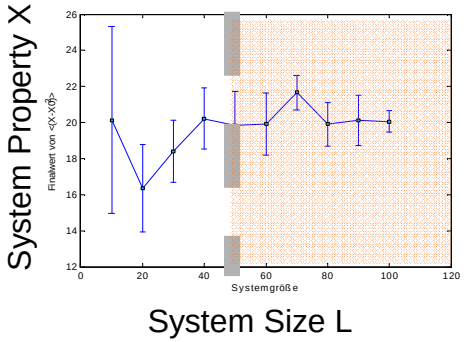
Statistical Analysis of Results

1. Proof of statistical evidence
2. Check of random number generation
3. Appropriate finite size scaling tests

Keys to a successful Monte Carlo simulation







System Size L

Calculate meaningful and measurable properties for statistics

Test different RNGs

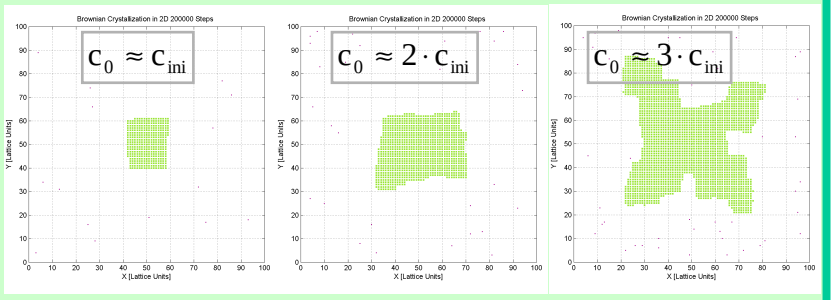
- Mersenne – ‚twister‘
- Marsaglia – ‚state‘
- Congruential – ‚seed‘

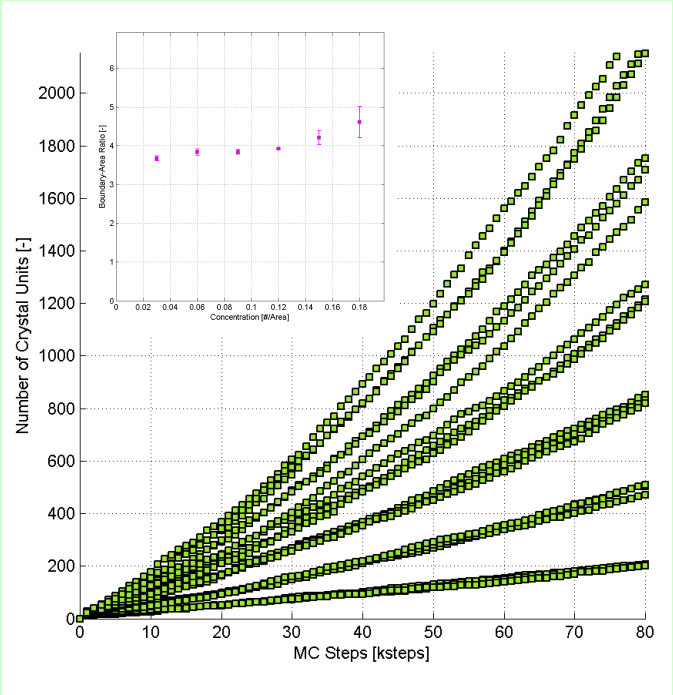
Finite-size scaling test

Here finite system, but check the influence of simulation box boundary

Simulation Variations in 2D

Variation of Concentration

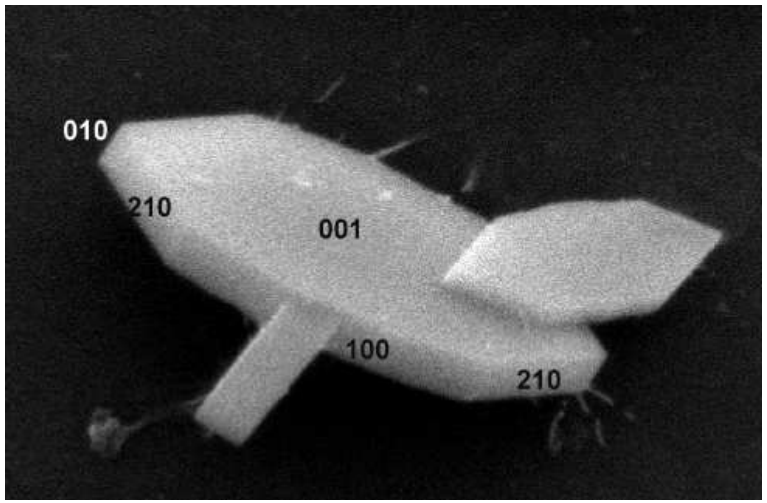




Crystal Shape Variations by concentration variation

- Change of shape from square to star-like
- Change of size from small to larger
- Change in attachment rate from low to high
- Change in ratio of boundary to area (from two-dimensional to fractal)

Surface-Energy related Crystal Growth in 2D/3D Simulation



Piana et al: *J. AM. CHEM. SOC.* **128**(41), p. 13569 2006.

Lattice Monte-Carlo Simulation in 3D

- Crystal growth of $BaSO_4$ depends on (i j k)-surface
- Free molecules attach to a crystal nucleus at different faces with different probability
- Monte-Carlo move probability p_{move} relates the energy difference ΔE between surface-free/surface-surface site and Boltzmann temperature

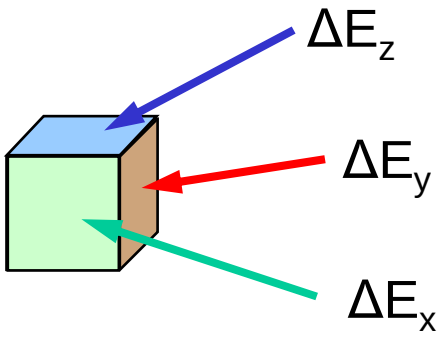
$$p_{move} = e^{-\frac{\Delta E}{k_B \cdot T}}$$

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 (B3LYP/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.

Jones et al: *J. Phys. Chem. B* **110**(14), p. 7418 2006.



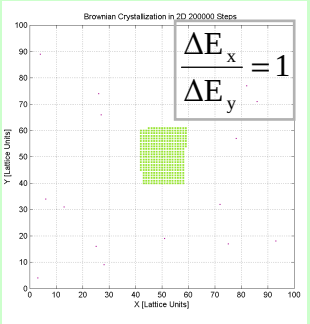
Model Assumption:
$\Delta E_x = \Delta E_{ys} \neq \Delta E_z$

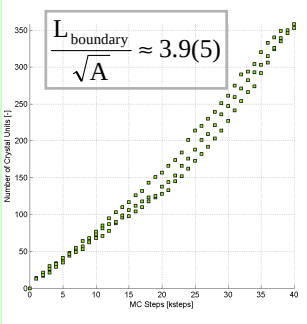
Anisotropy parameter

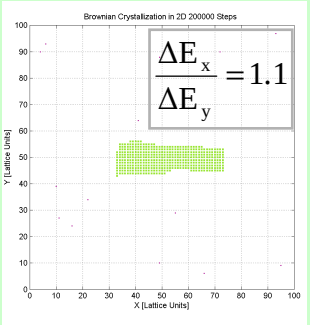
$$\frac{\Delta E_{x,y}}{\Delta E_z}$$

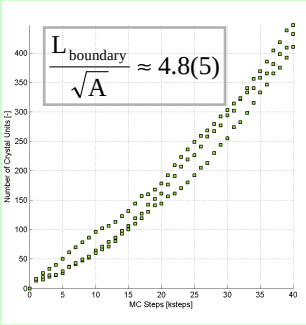
Simulation Variations in 2D

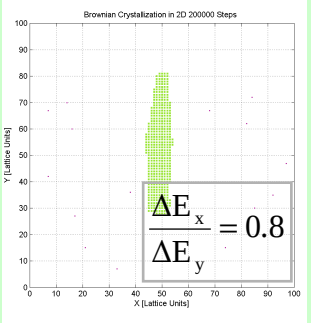
Variation of Anisotropy

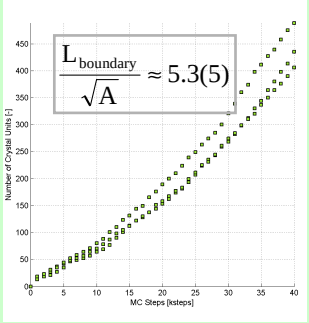












Crystal Shape Variations by anisotropy variation

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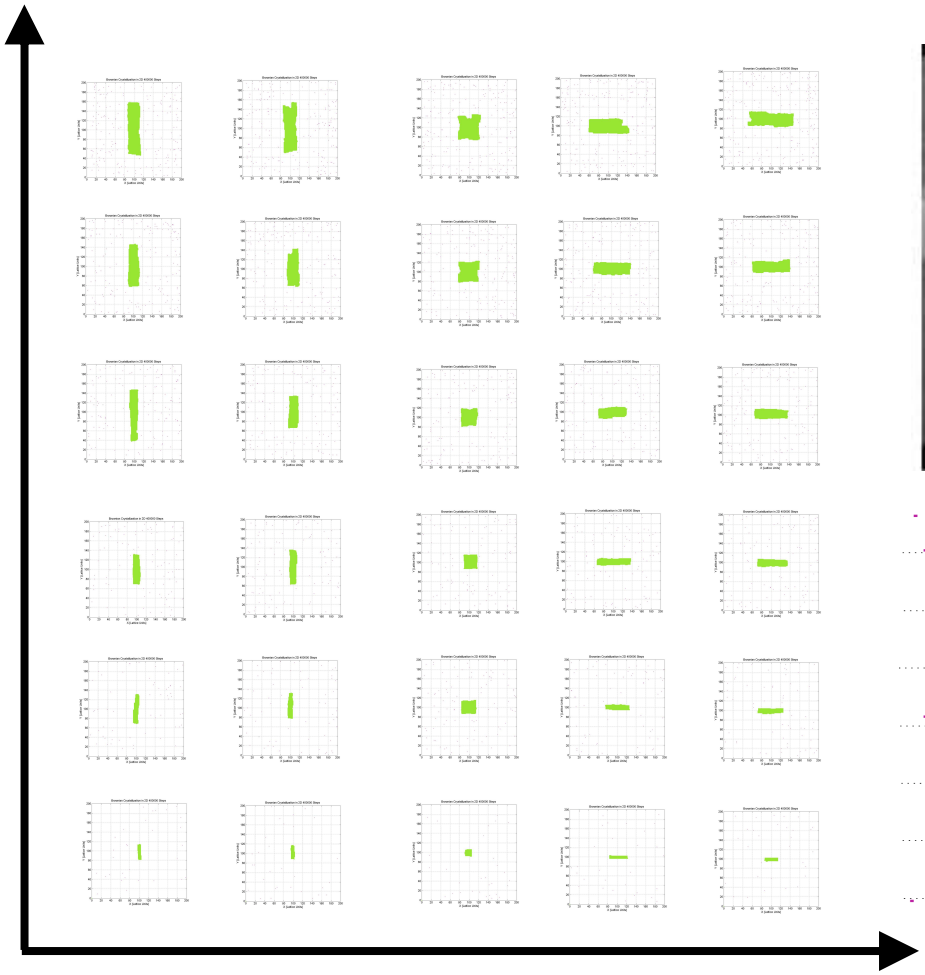
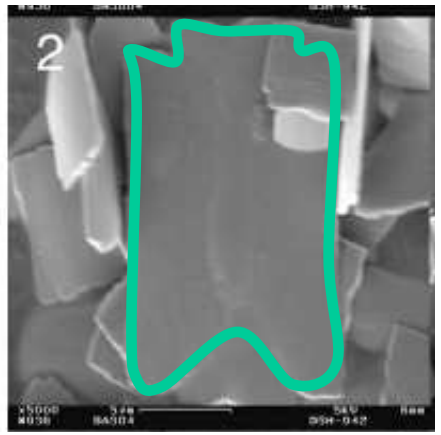
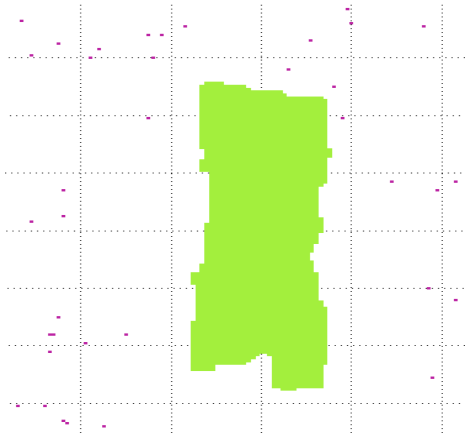
- Change in ratio of boundary to area (from two-dimensional to one-dimensional)

Phase Diagram of Anisotropic 2D Growth

Concentration

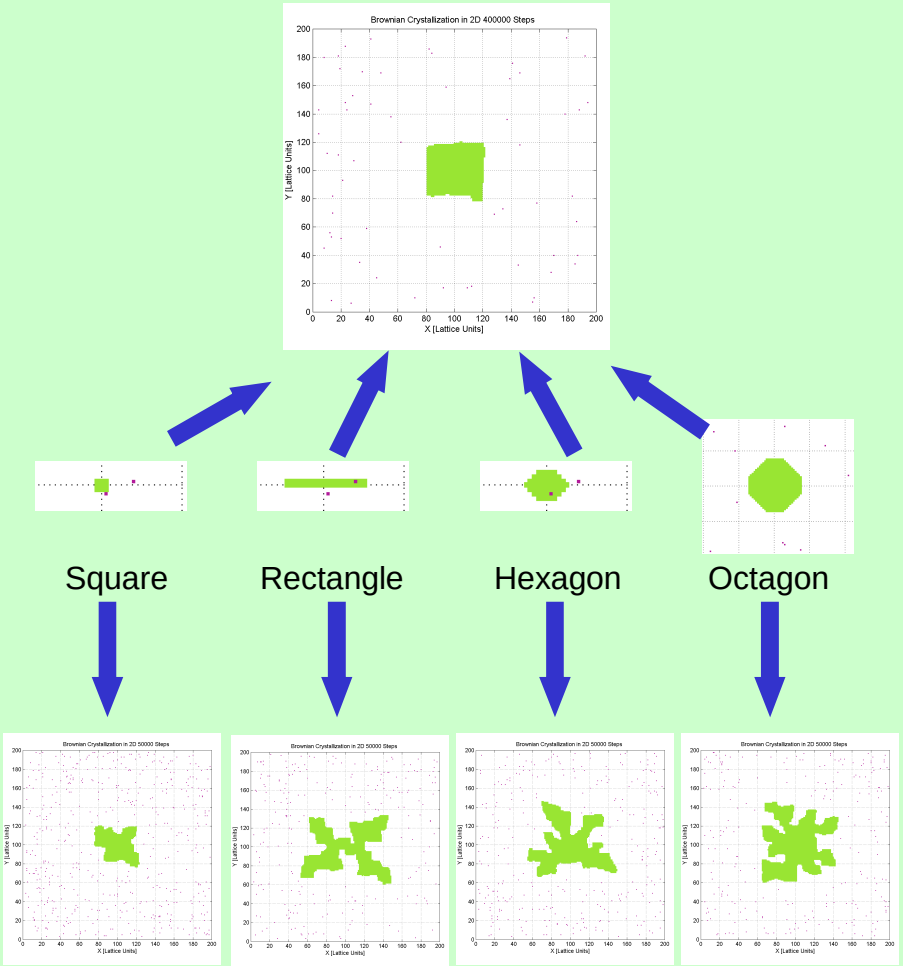






Simulation Variations in 2D

Variation of Seed Shape



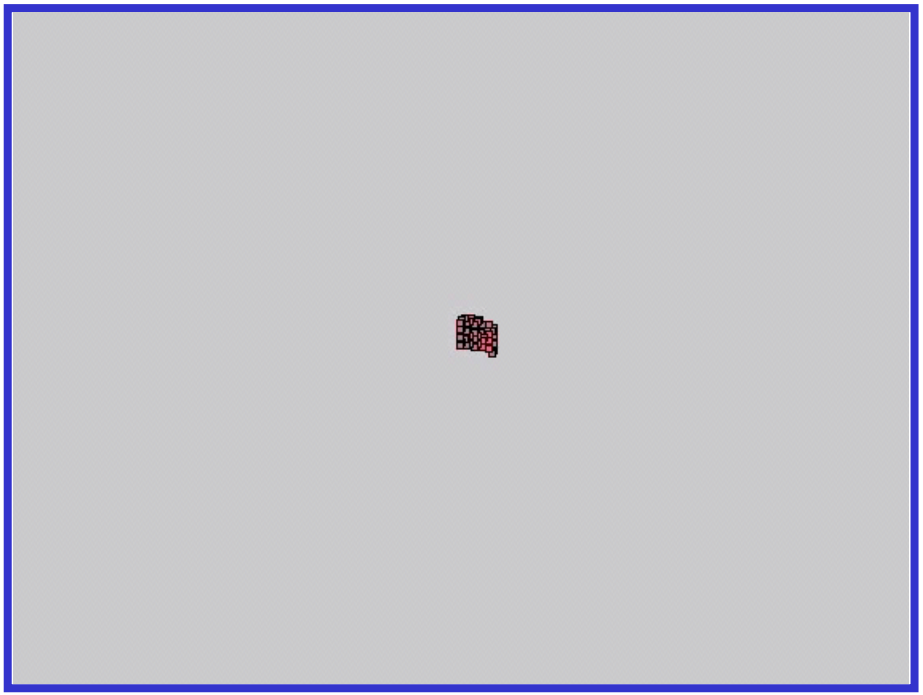
Crystal Shape Variations by seed shape variation

- At **low** concentration growth is dictated by anisotropy of attachment energy
- Crystal forgets its past – no memory

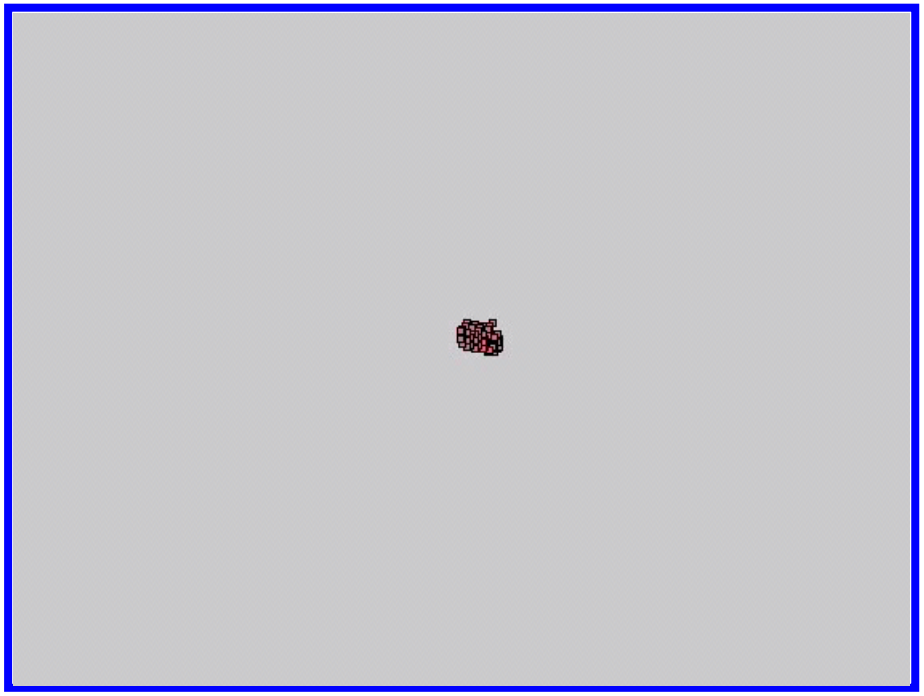
- At **high** concentration growth follows dendritic pattern
- Number of arms defined by number of edges (4-fold, 6-fold, 8-fold etc.)
- Growth of dendritic substructures

First Results of Simulations in 3D

Low Concentration

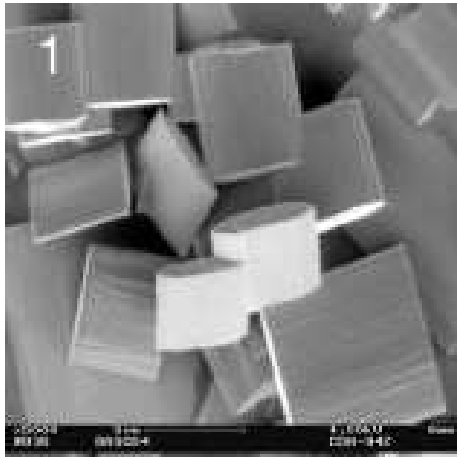


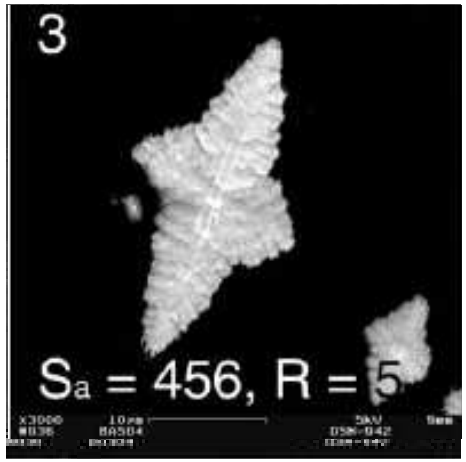
High Concentration



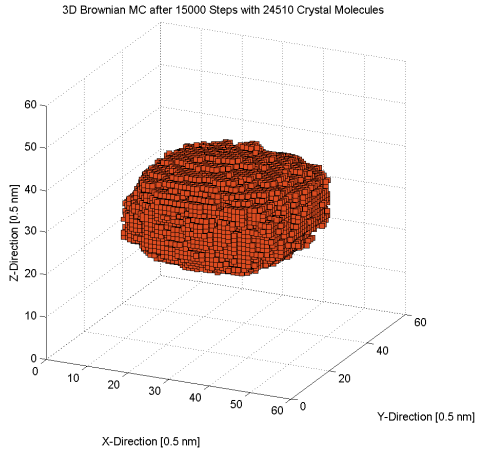
Comparison of Experiment and Simulations

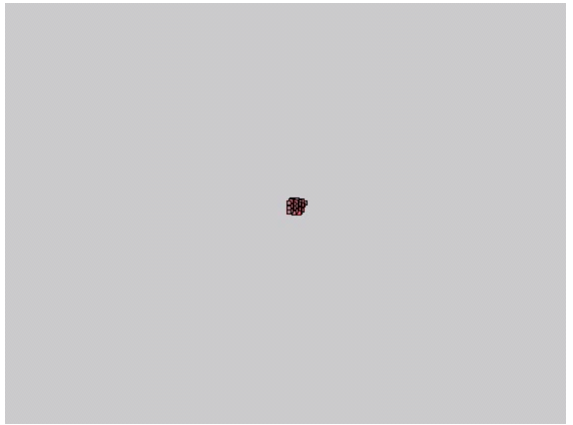
Experiment





Simulation





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- Summary and Outlook

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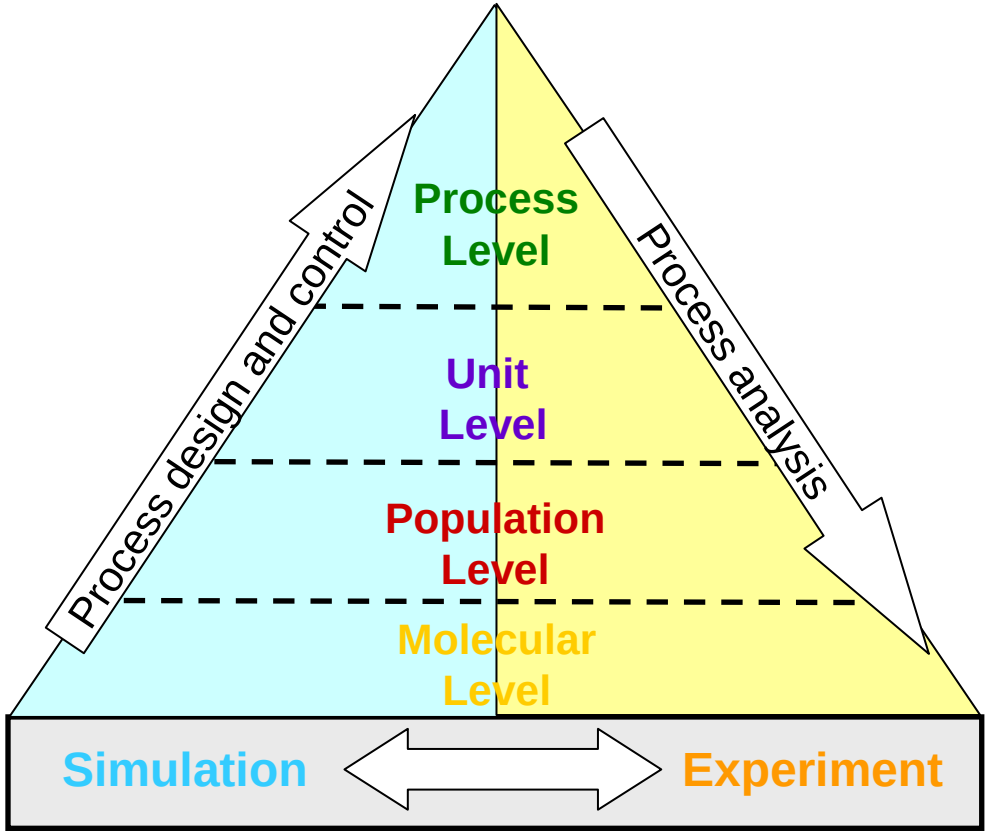
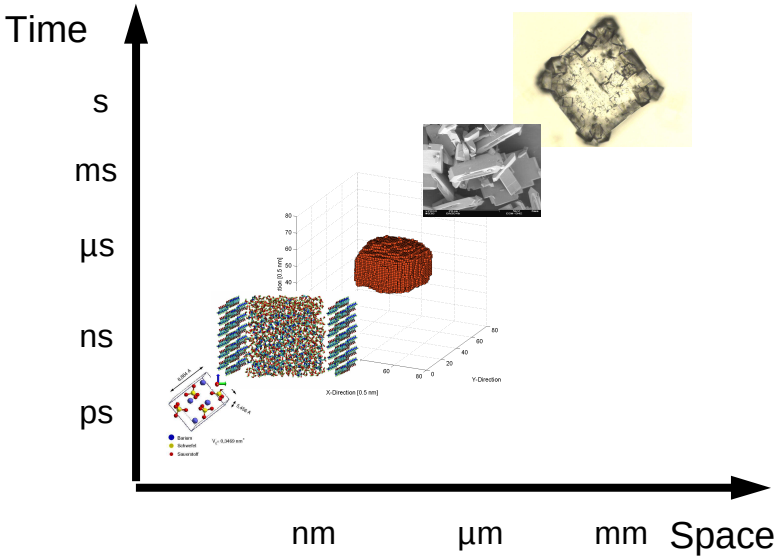
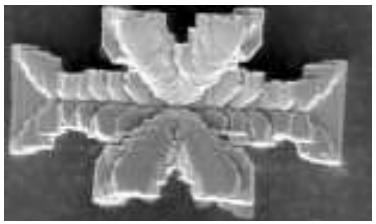




- Model the **crystal shape evolution** at different scales
- Combine molecular level data with mesoscale level **Monte Carlo simulation**
- Use modeling tools for process design and control for tailor-made crystal shape

Thank you for your attention.



Questions?