10 AIChE
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Modeling Solution Crystallization – Small steps and big leaps towards an improved understanding

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Introduction

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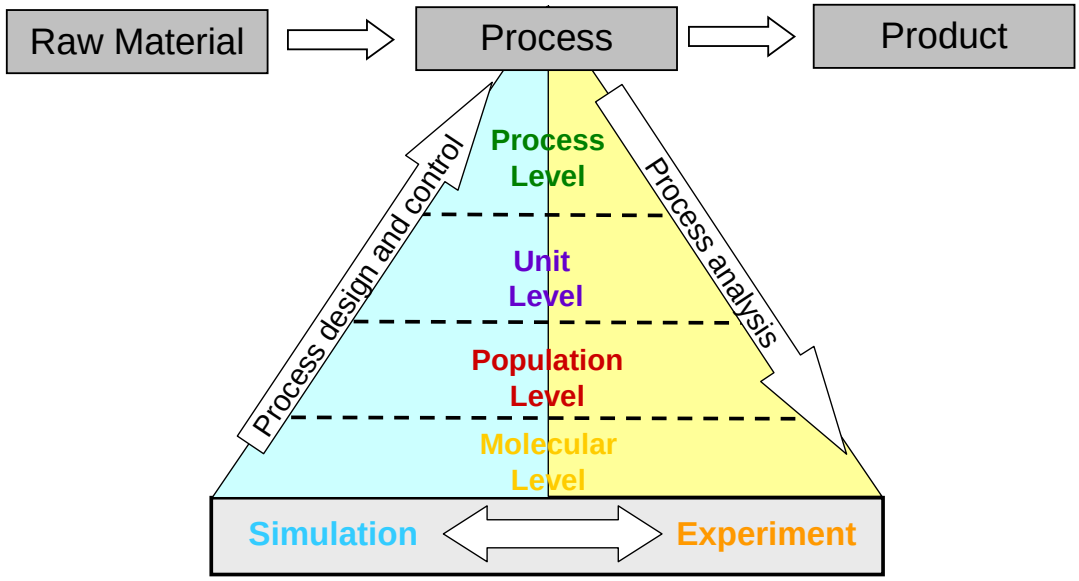
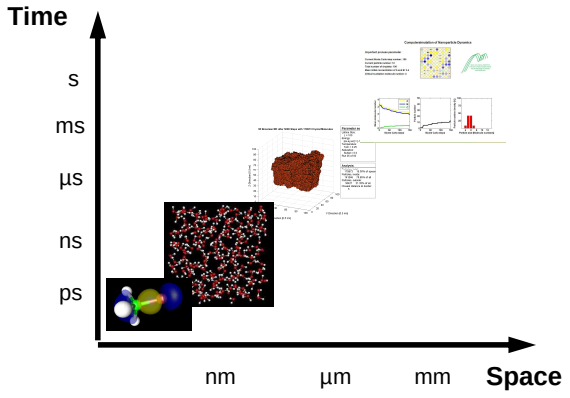


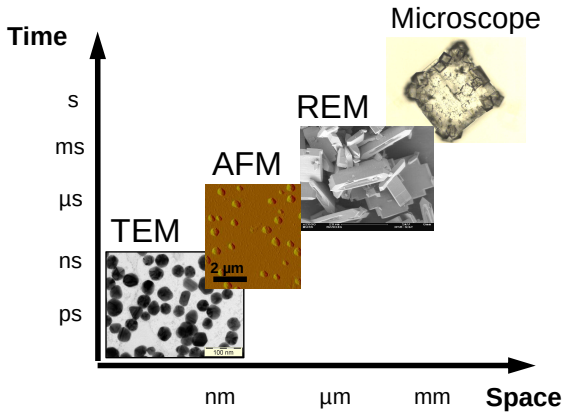
- Model the dynamical evolution of **crystal size** and **shape**
- Combine atomic, molecular, mesoscale and macroscopic level in **experiment** & **simulation**
- Use modeling approaches for process **design** and **control** of tailor-made crystals

Crystals from Solution

Simulation



Experiment



- Established **experimental set-up** - small-scale reactor with wet solution chemistry
- Development of **product analysis procedures**: TEM, AFM, REM, XRD, UV-Vis, microscopy ..
- **Simulations** - Use of established tools and development of new simulators

Outline

- **Motivation**

  Evolution stages of crystal production: Solution - Nucleation – Growth

- **Simulation Approaches**

  Electronic details between solute and solvent molecules – Quantum Mechanics

  Molecular motion of molecules and clusters – Molecular Dynamics

  Brownian diffusion of crystals and agglomerates – Monte Carlo

- **Modeling and validation – Experimental possibilities and limitations**

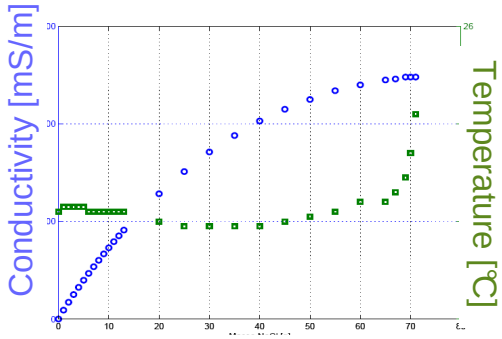
  Short time dynamics and small box simulation – Small steps

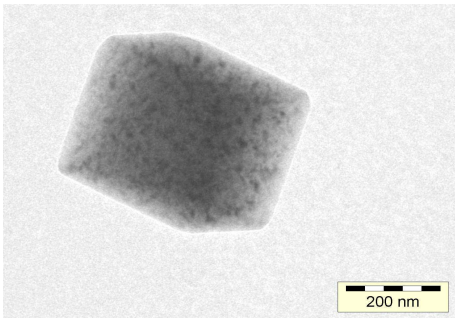
  Mesoscale experiments and modeling – Big leaps

- **Summary and Outlook**

Solution

- Solubility depends on:
  - temperature
  - solute properties
  - solvents and additives
  - …
- Solubility can be measured:
  - conductivity
  - turbidity
  - UV-Vis
  - …
- Solubility is crucial for:
  - pre- and postprocessing
  - chemical reaction pathways
  - crystallization dynamics

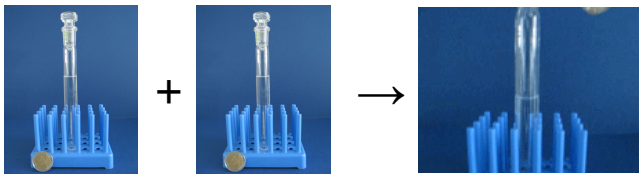




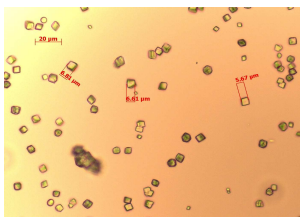
Nanocrystals in “solution” matrix

Nucleation

- Reactive crystallization:
  - reaction of two or more educts (almost) insoluble product
  - solid phase precipitation



- Supersaturation driven crystallization:
  - change of supersaturation by cooling or evaporation
  - solid phase appearance by homogeneous or heterogeneous nucleation

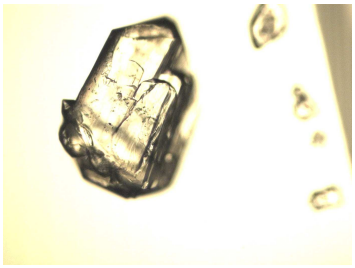


- Emulsion crystallization:
  - Emulsion droplets as reactor units
  - Droplets as templates for crystals
  - Droplets dynamics defines nucleation

Growth

- Nanoscale growth:
  - diffusion
  - attachment/detachment
  - solute-solvent interaction
- Mesoscale growth:
  - steps, kinks, edges
  - terraces and spirals
  - face growth
- Macroscale growth:
  - convection
  - agglomeration
  - imperfections

- AFM in solution to measure surface changes
- Obtain growth patterns on different faces to see **shape** evolution



- Microscopic pictures of face growth
- Obtain face growth rate for different faces to model **shapes**

See also paper 533d on Wednesday at 3:55PM in 250F by Christian Borchert:
Image-based experimental investigation of crystal aggregation in pipe-flow

Simulation Approaches

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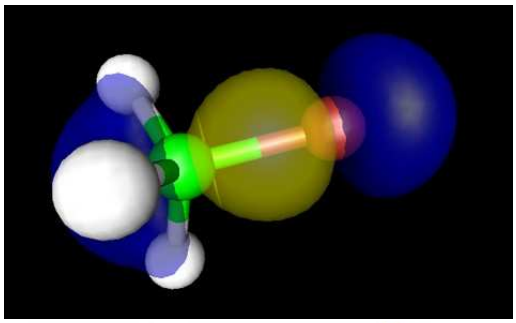
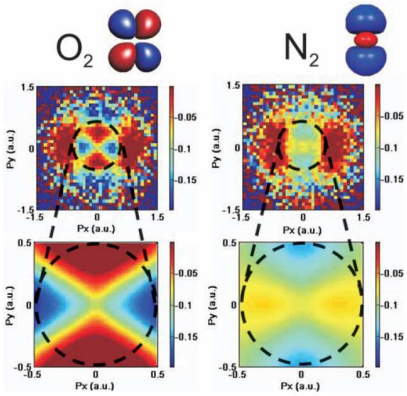
Molecular Structure



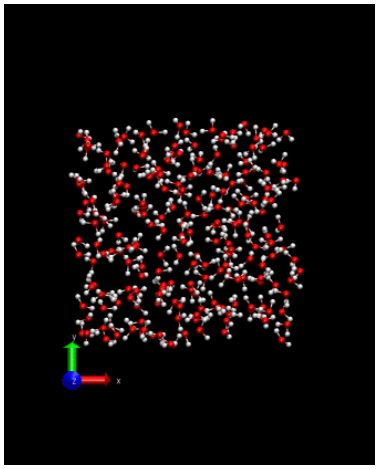


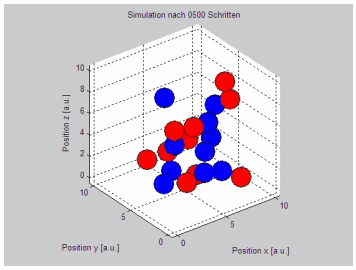
From: Meckel et al., Science 320, 2008.

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

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

Molecular Dynamics

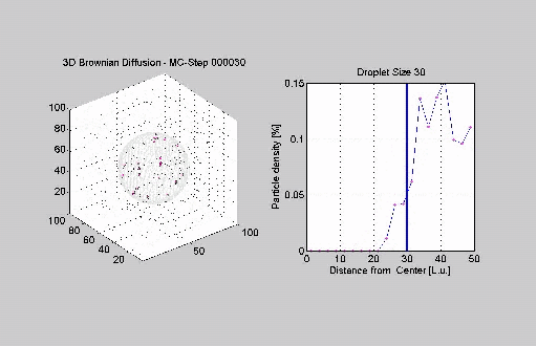


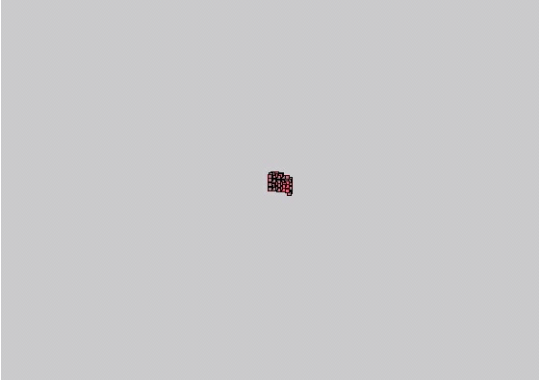


- Using parametrized force fields from QM
- Solving systems of **equation of motion**
- Use **Newtons force law**
- Use different **potential approximation** like Lennard-Jones
- Apply **simplifications** to convert complex molecules into single beads
- Compare with dynamic experiment like surface growth AFM

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

Diffusion Monte Carlo

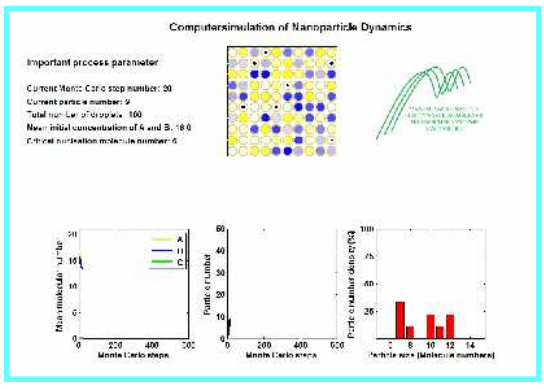




- Using parametrized probabilities from MD
- Evolving discrete entity systems with **Monte Carlo simulation**
- Use **random number generators**
- Use **event probabilities** for case differention i.e. face growth
- Apply **Boltzmann factors** for event selection rules
- Compare to dynamic experiments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

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

Population Monte Carlo



- Simulate dynamics of **high-dimensional** property distributed systems
- Use of **random number generators**
- Application of **rate probabilities** for dynamic changes
- Observe system size limits with **finite size scaling** rules
- Compare to final state observations and dynamic experiments

- Limited to
  - discretized systems
  - approximated dynamics
  - larger scales in size and time
  - proper statistics and repetition

Modeling and Validation

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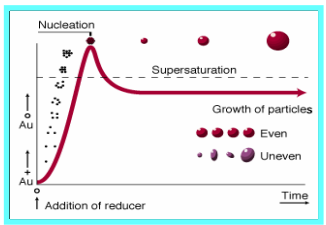
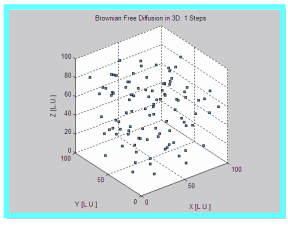
- **Summary and Outlook**

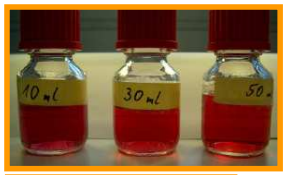
Small steps with big impacts

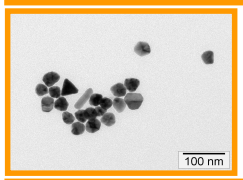
Start of model experiment due to company request:
Scale-up issues with batch production?!

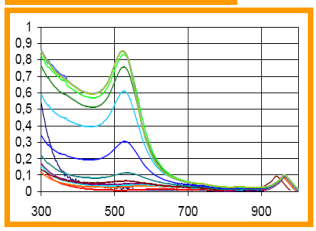




- Modeling the gold cluster formation
- Cluster diffusion with temperature dependence
- Modeling nucleation clusters and counting



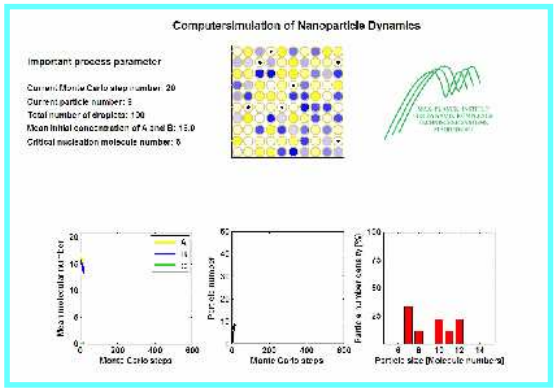




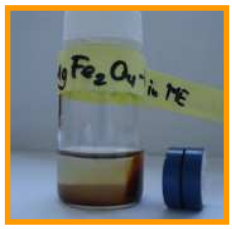
- Colored nanogold dispersions from **reactive crystallization**
- Change in product quality with **shape**
- Analysis with **TEM** pictures
- Use dynamics of **UV-Vis** signals for simple control of production process

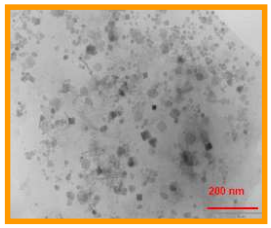
Solution:
1. Fix mixing issues!
2. Provide constant temperature

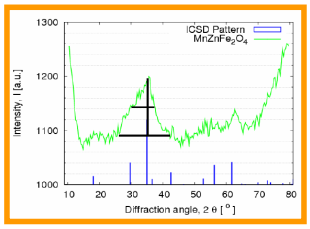
Bigg(er) steps in little droplets



- Discrete population model of droplet dynamic exchange and reaction
- Modeling the dynamical evolution including solution, nucleation and growth within emulsion droplets lead to predictions for mean size and size distribution







- Polydispers magnetic nanocrystals from **microemulsion precipitation**
- Change in superpara-magnetism with **size**
- Obtain morphology from **XRD** data
- Calculate particle size from XRD line broading (applying Scherer formula)

Conclusion

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- **Theoretical Approaches**

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- **Summary and Outlook**

Summary and Outlook

- **Different time and length scales are important for crystallization in solution**
  - Solution – Atomic & Molecular scale / Nucleation – Molecular scale / Growth – Mesoscale
- **Modeling complements experimental observations**
  - All models rely on observable experimental data due to many approximations
  - Advanced computer power is available to many
- **Modeling and experimental possibilities should go hand in hand**
  - Newly developed measurement techniques open exciting possibilities
  - Model simulations help to plan and design valuable experiments

Acknowledgment

- **Collaborators**
  - Soumik Banerjee (now UMich, Ann Arbor) and Heiko Briesen (TU Munich)
  - Petra Pulisova and Pavel Raschman (TUKE Kosice, Slovakia)
- **Motivated and enthusiastic undergraduate students**
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  - Crystal growth & AFM: Sophia Bongart, Janine Matschek, Matthias Karl
  - Modeling and simulation: Uwe Lelke
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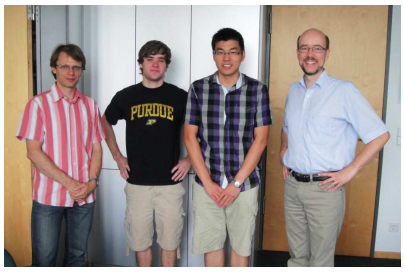
- **Company support**
  - Sasol GmbH (Surfactant supplies)
  - Human GmbH Magdeburg (Nanogold investigations)



Every (big) journey starts with the first (little) step.