Pathways to Crystal Nucleation and Growth

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Presentation Overview

• Motivation

• Part 1: Model Particles
  – Simulations
  – Comparison with colloidal experiments

• Part 2: Real Molecules
  – Initial seeded simulations
Motivation for Project

• Organic crystals are found in everyday products and structure is critical to their usefulness

• Many molecules can form two or more solid structures (polymorphs)

• Polymorphs can have different properties (solubility, strength, etc.)

• Nucleation is the initial stage of polymorph formation
  – Polymorph development not always determined by seed*

• Most nucleation is heterogeneous
  – What is learned in homogeneous nucleation can be applied to heterogeneous nucleation

• Explore nucleation using
  – Simulations

Part 1: Model Particles

• Hard-core screened coulomb pair potential

\[
\frac{u}{\varepsilon} = \begin{cases} 
\exp[-K\sigma(r/\sigma - 1)] & \text{if } r > \sigma \\
\infty & \text{if } r < \sigma
\end{cases}
\]

– Spherically symmetric

• Molecular dynamics simulations
  – Seeded initial conditions
  – Unseeded, homogenous nucleated simulations

• Direct comparison with experimental data (Weitz & coworkers)
Model particle parameter space

Coulomb limit

Experimental conditions

Simulation Details

• Molecular dynamics simulations
  – NVT ensemble
  – 10717 to 32000 particles
• Seeded initial conditions
  – FCC or BCC polymorph
  – Spherical shape
  – Variable seed size
  – Structure of particles after box is fully crystalline is compared to structure of the seed
  – Results of simulations that are homogenously nucleated from fully random initial condition are shown later
Seed Evolution

Fluid

FCC

BCC

packing fraction ($\eta$) vs. screening length ($1/\kappa\sigma$)
Seed Evolution

- Packing fraction ($\eta$)
- Screening length ($1/\kappa\sigma$)

Fluid

- FCC seed-FCC crystal

FCC

BCC
Seed Evolution

- Screen length ($1/\kappa\sigma$)
- Packing fraction ($\eta$)

Graph showing:
- BCC Seed-BCC crystal
- FCC seed-FCC crystal

Fluid phase transition points:
- BCC
- FCC
Seed Evolution

- Packing fraction ($\eta$)
- Screening length ($1/\kappa\sigma$)

Fluid

- BCC Seed-BCC crystal
- BCC Seed-FCC crystal
- FCC seed-FCC crystal

Graph showing the relationship between packing fraction ($\eta$) and screening length ($1/\kappa\sigma$) for different crystal structures.
Seed Evolution - Low Temperature

$T^* = 0.05$

- BCC Seed-BCC crystal
- BCC Seed-FCC crystal
- FCC seed-FCC crystal

Fluid

BCC

FCC

screening length ($1/\kappa \sigma$)

packing fraction ($\eta$)
Effect of Undercooling

Screening length = 0.1

Dimensionless Temperature ($T^*$) vs. packing fraction ($\eta$)

- BCC Seed-FCC crystal
- BCC Seed-BCC crystal
- FCC Seed-FCC crystal

Melting line

Fluid

FCC
Initial Conclusions

- BCC can transform into FCC during crystal evolution
- FCC not observed to transform into BCC
- Undercooling can effect how polymorph develops
  - Seeding desired polymorph does not guarantee growing desired polymorph
  - Consistent with Yu’s observation of D-mannitol and D-sorbitol
Comparison with Experiments

- Nucleation of colloidal particles observed by Weitz & coworkers using laser scanning confocal microscopy
  - Melting and freezing packing fractions comparable at $T^*=0.125$ and screening length=0.05
- Same simulation procedure as in previous work but without seeding- homogenous nucleation
- Can compare simulations and experiments
  - Shape
  - Size
  - Structure
Model particle parameter space

Experimental conditions

Comparison with Experiments

Nucleus 1
Side view
Top view

Nucleus 2

Nucleus 3

Nucleus 4
Comparison with Experiments

Nuclei from Weitz et. al. experiments

FCC/HCP structure

Nuclei from simulation

FCC/HCP structure

Results of Comparison with Experiments

- Particles in nuclei are primarily FCC coordinated
- No spherical nuclei observed
  - More elliptical in shape
- Nuclei have rough surface
- Minimum size for growth between 60 and 135 particles
  - Agrees with experimental result of between 60 and 160 particles
- Findings agree with experiments
Part 1: Future Plans

- Surface stress and surface energy calculation
- Develop predictive simulations for colloidal experiments
- Explore the effect of seed size on polymorph selection
- Improved model for crystal nucleation useful in process and product design
  - Be able to select and control the polymorph that is formed
Part 2: Real Molecules

- Same techniques developed for particle study can be applied to molecular study
- First system studied is stearic acid in hexane
- Stearic acid has 4 polymorphs (A,B,C,E)
- System exhibits a change in stable polymorph
  - C above 32°C, B below
  - Change yields many conditions (temperature and concentration) of interest for polymorph selection

Form C in hexane

Polymorph C: Crystal Description

Long Axis View
6 molecules in form of
2 - complete bilayers, 2 - \( \frac{1}{2} \) bilayers

Perpendicular view
6 and 12 molecules in other directions
Simulation Details

- Molecular dynamics simulations
  - NPT ensemble
  - Gromacs software
- Explicit hexane solvent
- United atom model
  - CH$_3$, CH$_2$ groups
  - Individual atoms in carboxylic acid group
- Current running conditions
  - 33 ºC
  - 0.073 mole fraction (128 g/L)
    - Solubility of polymorph C at 47 ºC
  - Seed size 2 bilayers, 10 and 11 molecules in other directions
    - ~400 stearic acid molecules
Initial Condition
Initial Condition - Seed

128°
Seed after 1.5 ns
Part 2: Future Plans

• Questions raised by initial simulation
  – What is the minimum seed size that does not dissolve?
  – How does shape effect the minimum seed size?
  – What does structure change indicate?
    • Possible transition to another polymorph

• Future work
  – Smaller and larger seeds of different shapes
  – Higher concentrations or lower temperatures
  – Compare with polymorph B seeds
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