A Multiscale Simulation Model to Simulate Crystal Growth

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POPULATION BALANCE SYSTEMS

Motivation

- Correct prediction of crystal habit, growth rates and polymorphism is important.
- Multiscale molecular simulations can provide a fundamental insight on the dynamics of crystal growth.

Objective

- Numerical investigation of **Glycine (NH_2CH_2COOH)** as a model compound.
- Characterization of the growth rate and crystal habit for solution crystallization of glycine.

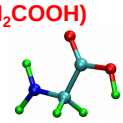


Figure 1: Structure of a single Glycine molecule.

Multiscale Approach*

- *Molecular Dynamics* (MD) simulations provide the transition rates for incorporation of solute at various surface sites.
- Transition rates thus obtained can be used as input to kinetic *Monte Carlo* simulations.
- Much larger simulation times (of the order of microseconds) can thus be achieved.

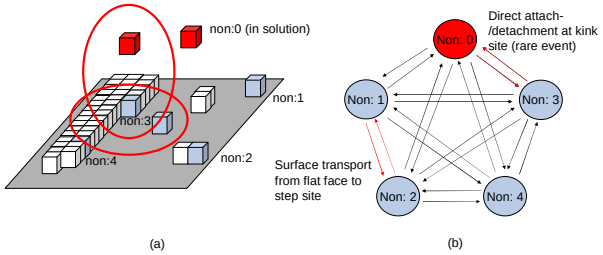


Figure 2: (a) Scheme illustrating typical transitions on the crystal surface, and (b) all possible transitions.

Module I: Molecular Dynamics

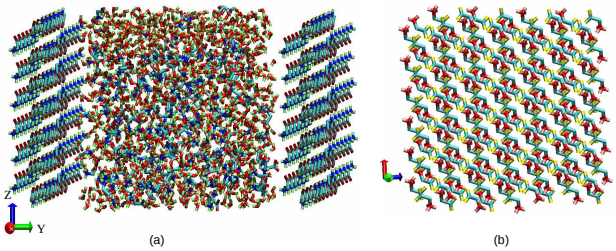


Figure 3: (a) Glycine crystal surrounded by a solution of glycine in water (b) Structure of α-Glycine crystal.

Parallelized MD simulations using GROMACS

- Intermolecular forces are obtained from the GROMOS96 force field which is realistic for prediction of crystallization of complex organic molecules.
  - Typical simulation time: 40 ns.
  - For each of the 20 × 10^6 steps one has to
    - calculate the force field,
    - solve the equation of motion.
  - In MD simulations, transitions between all the states can be counted.

Results†

- Density distribution normal to crystal surface is useful for growth characterization:
  - The first four peaks are the crystal seeds.
  - The peaks move towards the ends of the simulation domain, signifying dissolution.

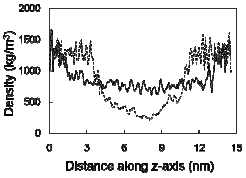


Figure 4: Density distribution of Glycine along the Z-axis (as illustrated in Fig 3a) at the initial stages (dotted line) and final stages (firm line) of a MD simulation.

*Piana, S., Reyhani, M., and Gale, J.D., "Simulation micrometre-scale crystal growth from solution," Nature, 438(7064), 70 (2005).

†Banerjee, S., and Briesen, H., "Molecular dynamics simulations of glycine crystal-solution interface," *submitted*, (2009).

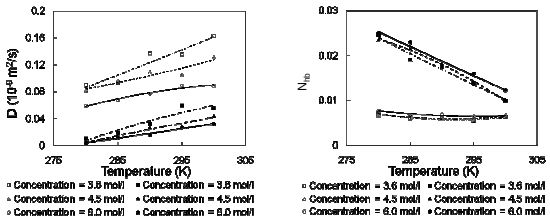


Figure 5: (a) Diffusion coefficient and (b) normalized number of hydrogen bonds at various conditions (Filled and open markers indicate the interface and bulk).

- Diffusion coefficient increases with temperature and decreases with concentration.
- The number of hydrogen bonds formed follows an opposite trend with higher number of bonds formed at the interface than in the bulk solution.

- Transition rates can be calculated from the counted number of transitions:

$$k_{a-b} = \frac{\langle n_{a-b} \rangle}{\Delta t \langle a \rangle}$$

where, k_{a-b} is the transition rate from state *a* to *b*, $\langle n_{a-b} \rangle$ is the average number of events in time Δt, and $\langle a \rangle$ is the average number of molecules in state *a*.

Module II: Kinetic Monte Carlo

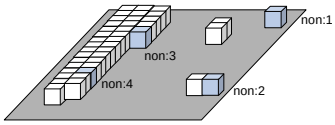


Figure 6: Crystal surface for the Kinetic Monte Carlo simulations. The various coordination states are characterized by the number of neighboring (non) molecules. The molecules can essentially be represented by blocks for the purpose of these simulations.

Kinetic Monte-Carlo simulations using MONTY

- Kinetic Monte Carlo simulations use the transition rates for events to set up probability charts for each event.
- Random events are generated by defining cumulative functions involving transition rates.
- Random number picked from a uniform distribution decides which event occurs and this process is repeated to obtain a time evolving process.

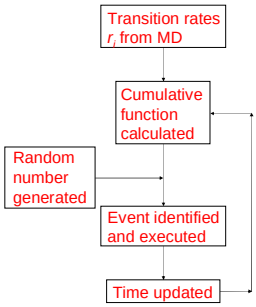
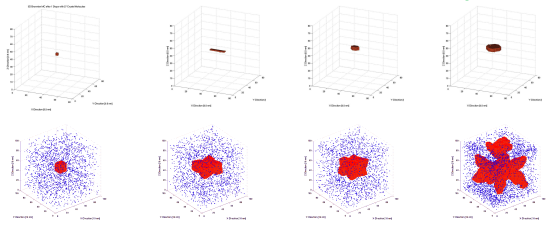


Figure 7: Schematic description of Kinetic Monte Carlo algorithm.



Future Directions

- Combine MD kinetics and MC step rates
- Include energy considerations for different surface geometries
- Extend model variety to include anisotropy and lattice geometry of specific model systems
- Compare with experimental data from meso and nano scale crystal growth (AFM)

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