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Crystallization of *trans*-stilbene derivatives via bound-sphere kinetic Monte Carlo in SPPARKS (Stochastic Parallel PARticle Kinetic Simulator)

Tesia Janicki, Christine Roberts, Helen Cleaves, Christopher Brotherton, Rekha Rao, Theron Rodgers
Sandia National Laboratories

Background

Resveratrol is widely used in medical treatments due to its antioxidant properties. *trans*-resveratrol has a stilbene derivative structure and is commonly isolated by recrystallization from solution. The mechanism of recrystallization has not been widely explored and is expected to proceed via non-classical crystallization pathways.

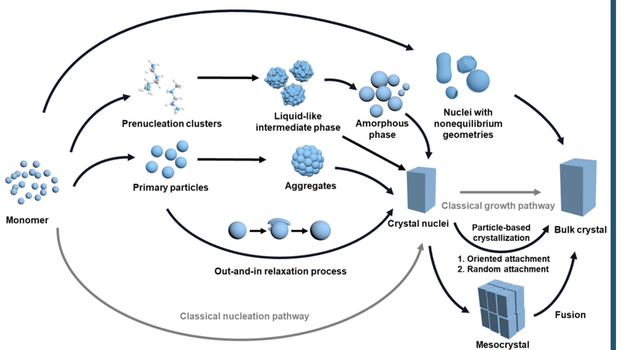


Fig. 1: Non-classical crystallization pathways. Reproduced with permission from [1] Copyright 2022 American Chemical Society.

We interrogate this mechanism in a multiscale approach, combining experiment, meso-scale, and kinetic Monte Carlo (kMC) models. Initial measurements of as-delivered resveratrol crystals reveal preferential, rod-like orientations (Fig. 2) which may form single-crystal aggregates prior to nucleation "events" upon recrystallization.

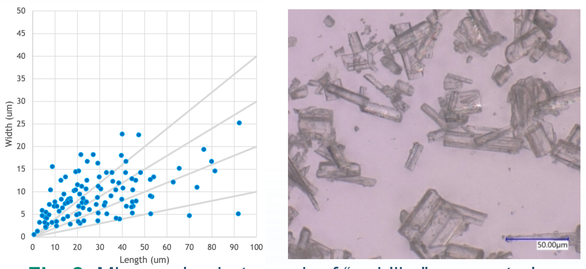


Fig. 2: Microscale photograph of "rod-like" resveratrol crystals and measurement of length/width profile.

The present work focuses on kMC approaches to determine growth rates of single crystals which will inform mesoscale growth models. Goals of this work are to:
1. Develop a kMC theoretical model which reasonably coarse-grains the molecular system for on-lattice simulations.
2. Adapt our kMC platform (SPPARKS) to accommodate this model.
3. Apply electronic structure benchmark calculations for our crystallization deposition/diffusion event library.

Kinetic Monte Carlo (kMC) Approach

Bound-sphere approximation for on-lattice kMC

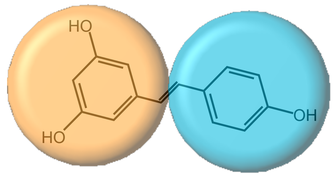


Fig. 3: We approximate resveratrol by coarse-graining into two bound spheres as coupled sites.

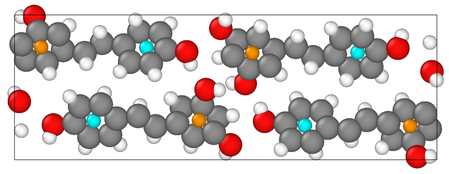


Fig 4: Each 28-atom molecule is reduced to 2 center-of-mass sites for facile on-lattice kMC implementation.

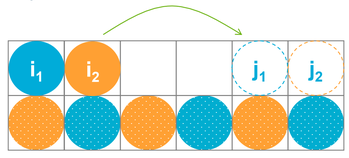


Fig 5: On-lattice models restrict possible positions of particles in deposition/diffusion events. For the sphere in site i_1 to move to site j_1, site j_2 must be available to accept i_2.

(1) $\Gamma_{ij} = \nu_0 \exp\left[-\frac{E_{ij}}{kT}\right]$

(2) $E_{ij} = 2\left(E_{j1+j2} - E_{i1+i2}\right) + E_{barrier}$

Eq 1: Rates of deposition/diffusion (Γ) are determined by relative energies between randomly chosen initial (i) and final (j) states. These energies are determined via DFT.
Eq 2: The bound-sphere model requires energy of both coupled sites in the possible move.

SPPARKS & modifications

https://spparks.sandia.gov

SPPARKS [2] is a modular, parallelized, open-source kMC platform with a range of MC solvers. The following modifications have been made to SPPARKS to enable bound-sphere models of trans-stilbenes:

1. "Bound-site" models
Standard on-lattice approaches in SPPARKS treat each site uniquely. To apply the bound-sphere problem, deposition and diffusion in SPPARKS have been adapted to couple sites as pairs. This impacts the physical structure of the lattice as well as energetic propensities, according to Eq. 1&2.

1. Non-orthogonal 3D simulation types
Resveratrol has a monoclinic unit cell ($P2_1/c$). Prior to this work, all simulations in SPPARKS were constrained to orthogonal shapes. By enabling non-orthogonal simulation cells in SPPARKS, a larger materials library can be more accurately modeled, including the present resveratrol system.

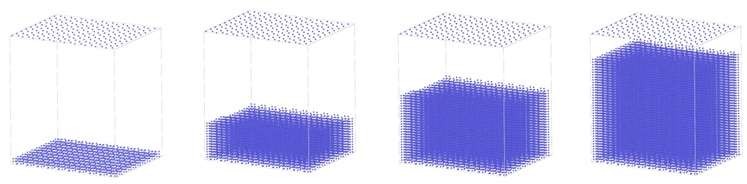
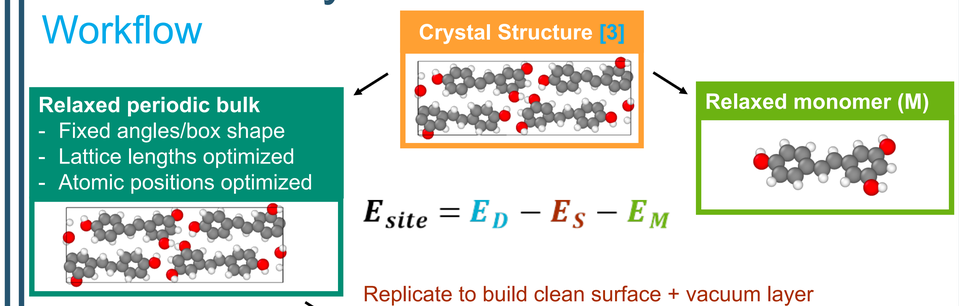


Fig. 6: Bound-sphere crystal growth with "toy" energies.

Event Library Characterization

Workflow



Schematic: The binding energy (E_{site}) of each site is determined from the difference in initial and final state energies.

Energies are computed for the all-atom system then tabulated in SPPARKS and indexed by coordination number of each site in the bound-sphere pair.

Computational Details

All electronic structure calculations are performed in FHI-aims [4] using "light" numerical settings and tier-1 basis functions. Perdew, Burke and Ernzerhof GGAs [5] are invoked for exchange-correlation interactions with a Tkatchenko-Scheffler Hirschfeld-partitioning vdW correction [6] and a Pulay DIIS mixing algorithm [7].
Periodic calculations invoke a 3x3x1 kpoint mesh. Geometric minimization is performed using a Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [8] with a trust radius of 0.01 eV/Å. SCF iterations are converged within 10^{-4} eV. Surfaces were created from 6x2x2 unit cell replications with an added >20 Å vacuum to omit periodic interactions between surfaces. Surface calculations constrain the bottom two monolayers (first unit cell) of molecules.

Ongoing Work

1. We have developed the infrastructure in SPPARKS to model trans-stilbenes as a bound-sphere approximation in on-lattice kMC.
2. Collection of energetic benchmarks from electronic structure is **ongoing**.
3. Once complete, rates extracted from our model will inform continuum- and meso-scale models for aggregate formation and other possible non-classical crystallization pathways.

References

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