Simulations of homopolymer collapse using forward-flux sampling.

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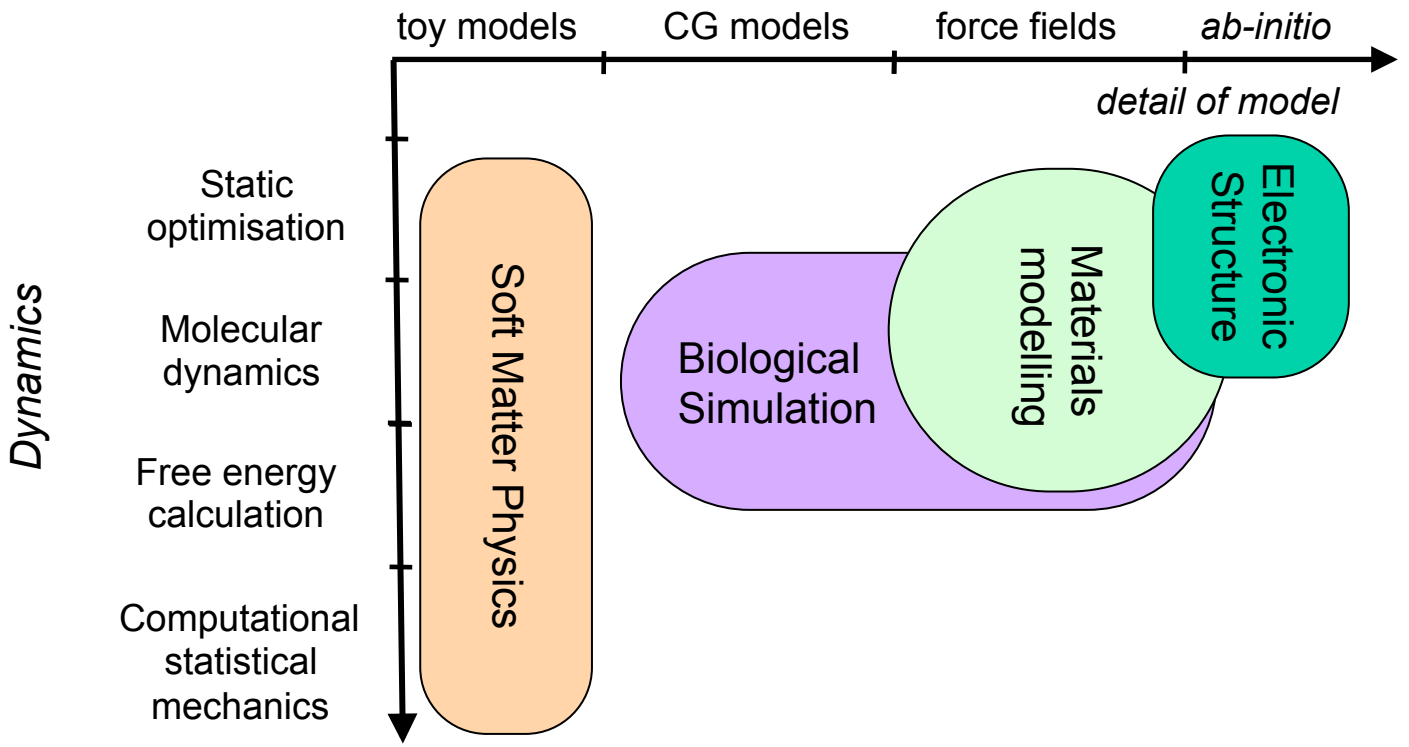
Third placed in recent QS World University Rankings
'Top 50 Under 50'

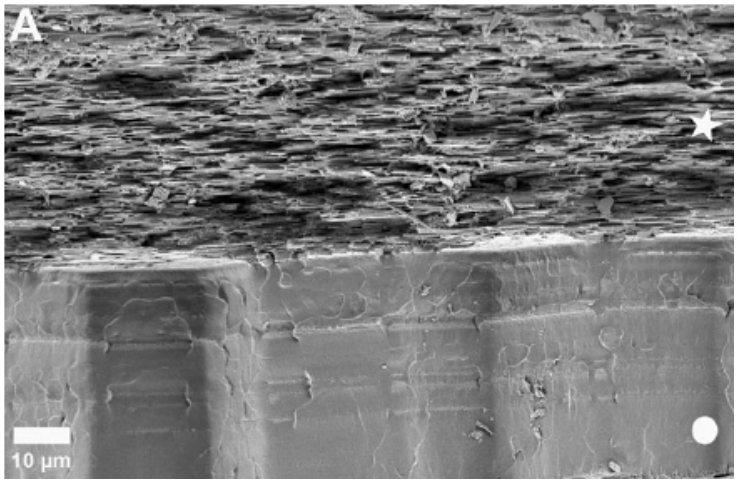
WARWICK

Atomic and molecular simulation

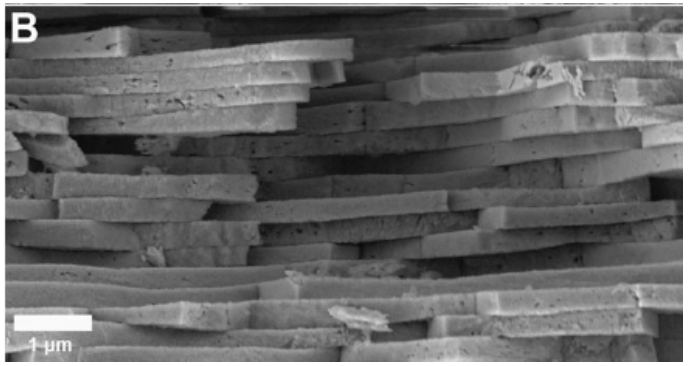
- *An attempt to visualise the field.*



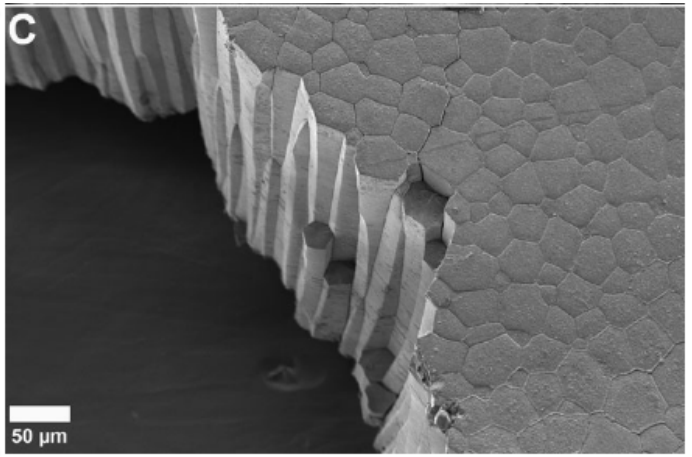
Motivation - biomineralisation



[Nudelman *et al Faraday Discuss*. ***136***, 9-25 (2007)]



Sheets of aragonite tablets



Columns of calcite

Control of morphology and assembly?

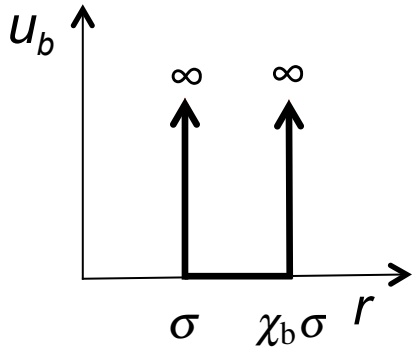
Control of polymorph selection?

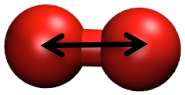
Control of orientation?

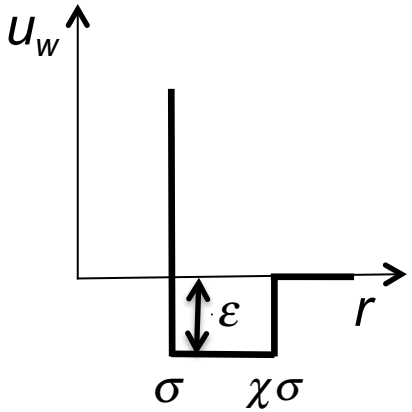
Overview

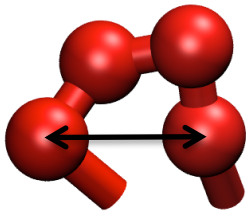
- Forward-flux sampling on a toy system
  - Freezing of a hard-sphere polymer chain.
  - Kinetics vs thermodynamics.
  - Breakdown of the two state assumption.
  - Improved reaction coordinate?

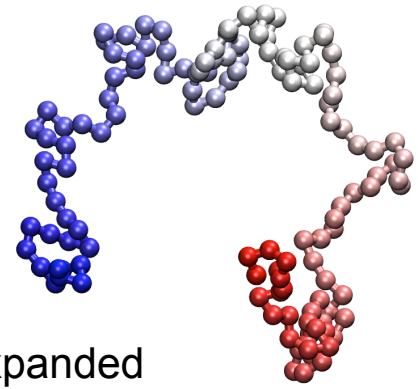
Attractive hard sphere chain



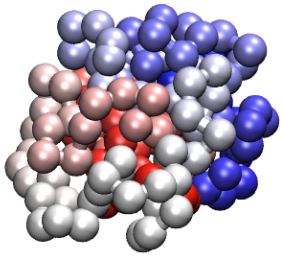




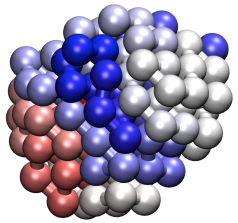




expanded



globule



crystal

Temperature

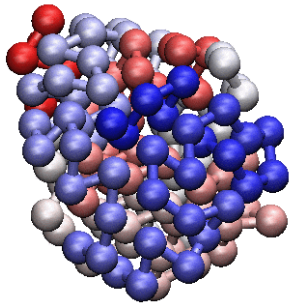
Attractive hard sphere chain

- Simulate with both Metropolis MC and collision dynamics (event driven molecular dynamics).

Monte-Carlo move set

- Crank shaft
- Pivot
- End-bridging
- Regrowth (Rosenbluth / CBMC)

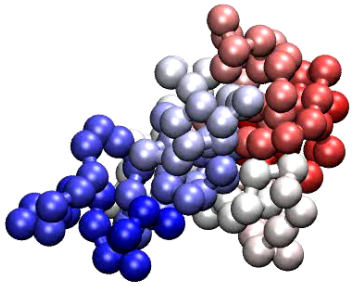
connectivity altering



Collision dynamics

- Ballistic between events
- Hard core collision
- Well capture and escape events
- Thermal ‘jolt’ events

connectivity constrained

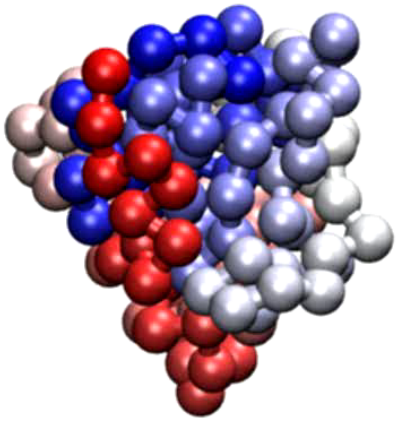


Properties

- Thermodynamics of system extensively studied previously.

  [Taylor, Paul and Binder. *Phys. Rev. E.* **79**, 050801 (2009)
  J. Chem. Phys. **131**, 114907 (2009)]

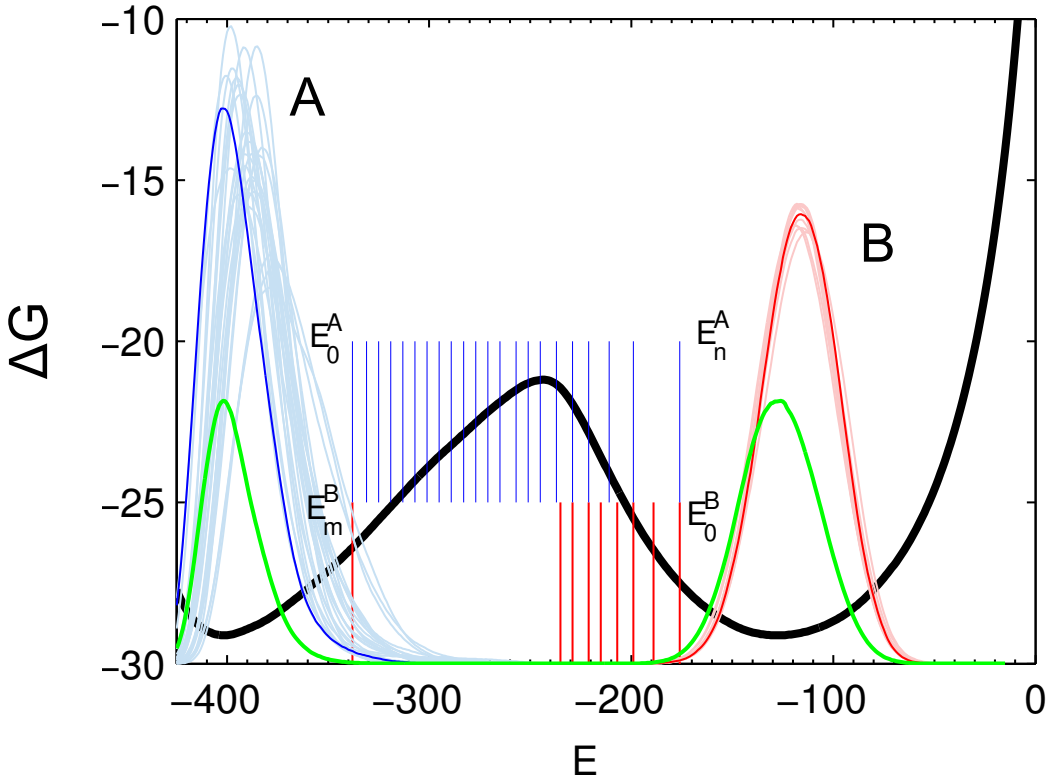
- Single stage “protein-like” collapse for $\chi \lesssim 1.06$
- We study globule-crystal transition for larger χ.
- Brute force sampling feasible for $\chi \geq 1.15$.
- Use Forward Flux Sampling (FFS) for smaller χ.
- FFS simulations use collision dynamics.
- Wang-Landau simulations use MC move set to locate thermodynamic transition temperature.



Brute force CD trajectory at transition temperature.

Sampling and FFS

- All globule states can be connected by short CD trajectories.
- Different realisations of the crystal state separated by high barriers.
- Breakdown of two-state assumption.



Free energy surface

P(E) at transition T

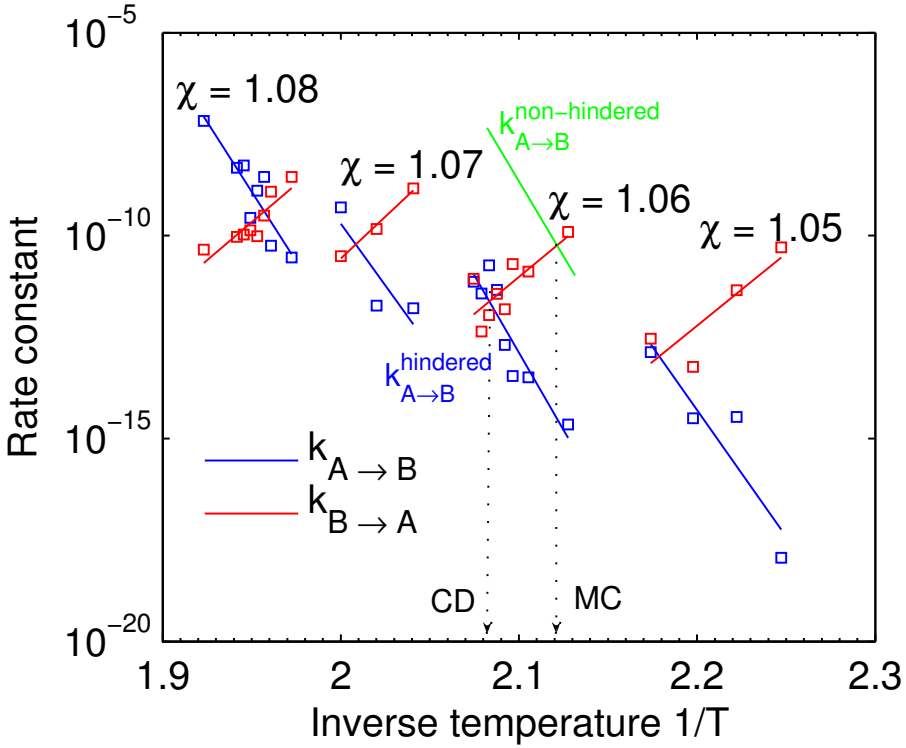
High T *P(E)*

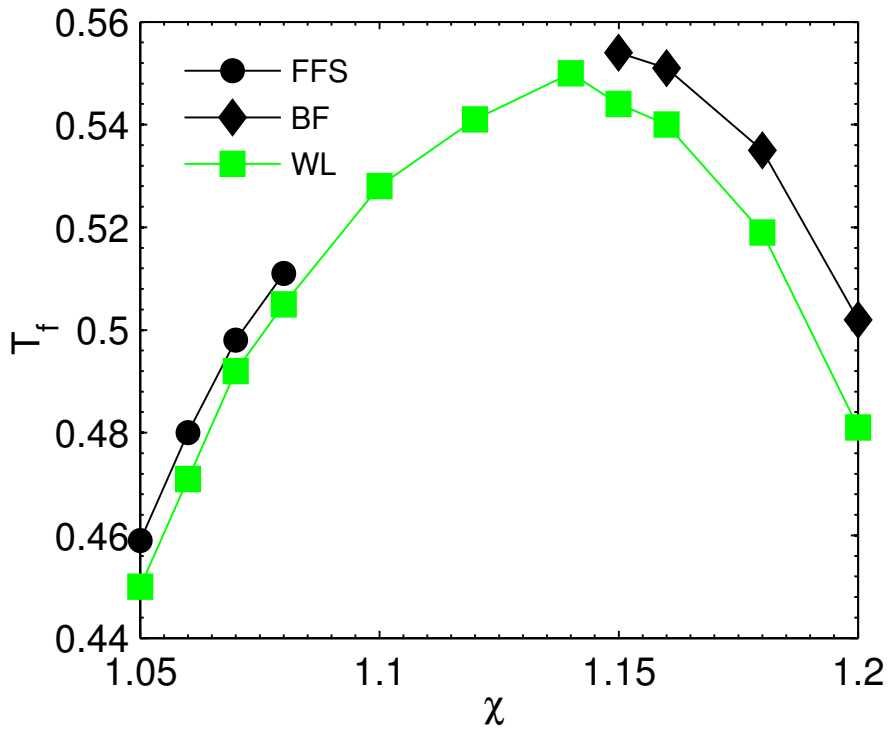
Low *T(E)*

8192 configurations at each FFS interface

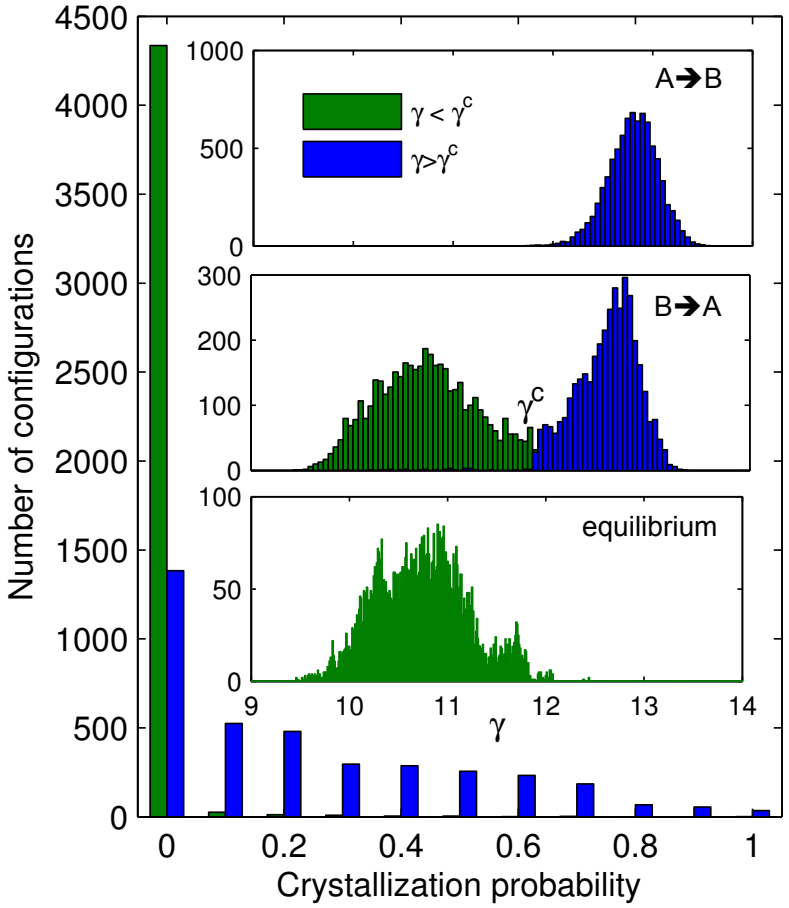
Transition temperature via kinetics

- Systematic upward shift of transition temperature vs Wang-Landau (WL) MC simulations.
- Attribute this to inability of CD to sample transitions between realisations of crystal.
  - Kinetic hindering of transitions in direction A➔B?





An improved reaction coordinate?



- Compute Laplacian matrix *G*

$$G_{ij} = \begin{cases} -1 & \text{if } |i-j| > 1 \text{ and } r_{ij} \le \chi\sigma, \\ 0 & \text{if } |i-j| > 1 \text{ and } r_{ij} > \chi\sigma, \\ 0 & \text{if } |i-j| = 1, \\ -\sum_{k,k\neq j} G_{kj} & \text{if } |i-j| = 0. \end{cases}$$

- γ is largest eigenvalue.
- *G* sometimes treated as analogue of Hessian.
- Related to SPRINT coordinate of Pietrucci & Andreoni, Phys. Rev. Lett. **107**, 085504 (2011).

Summary

- Studied a very simple model, amenable to extensive MC/MD sampling.
- Brute force rates can be computed in some parameter ranges.
- Computed both forward and backward rates with FFS;
  - as a function of temperature
  - as a function of model parameters
- Discrepancy between ‘kinetic’ and Wang-Landau transition temperature
  - small c.f. typical error bar in bulk FFS crystallisation studies, but annoying nonetheless.
  - breakdown of two-state assumption due to large barriers between crystalline states?
  - effect of thermalisation or non-statistical dynamics?
  - poor choice of reaction coordinate?
- Proposed alternative reaction coordinate for future study.

Thank You!

Ruzicka, S.; DQ & Allen, M.P.
Folding kinetics of a polymer.
Phys. Chem. Chem. Phys., **2012**, 14, 6044-6053.