Simulating crystallisation mechanisms with long timescale molecular dynamics.

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Metadynamics of ice and $CaCO_3$

Prof. P. Mark Rodger	(Warwick)
Prof. John Harding	(Sheffield)
Dr Colin Freeman	(Sheffield)
Dr Dorothy Duffy	(UCL)
A. Matt Bano	(Warwick)

Freezing of a hard-sphere polymer

Prof. M. P. Allen	(Warwick)
Stepan Ruzicka	(Warwick)

WARWICK

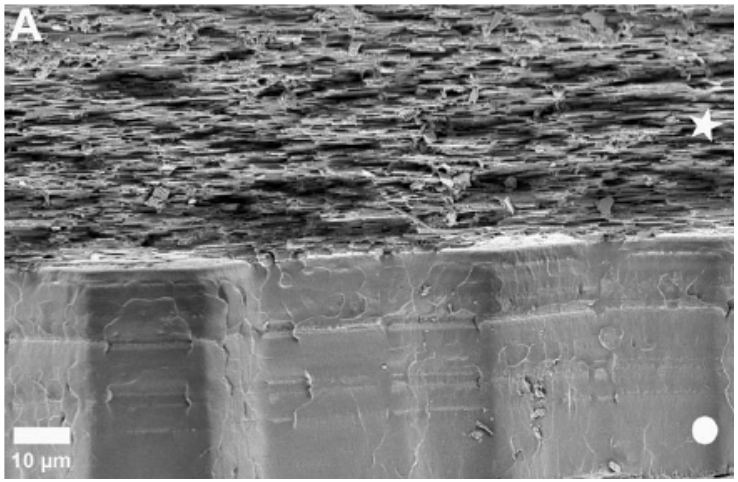
Overview

- Motivation
  - Understanding biomineralisation processes.
  - Crystal nucleation as a rare event.

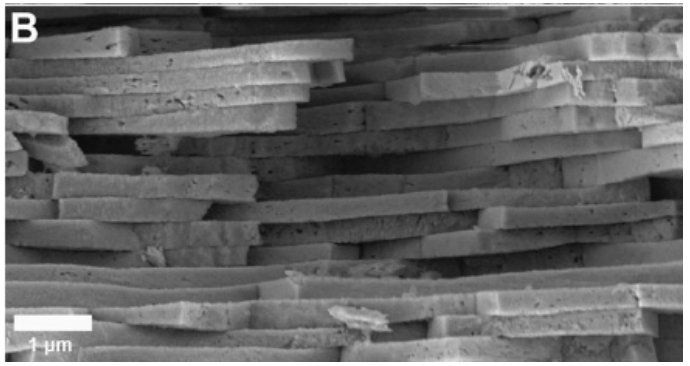
- Adventures with metadynamics
  - Adapting collective variables from previous MC studies.
  - Example - control of crystal orientation by self-assembled organic monolayers.
  - Problems going forward.

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

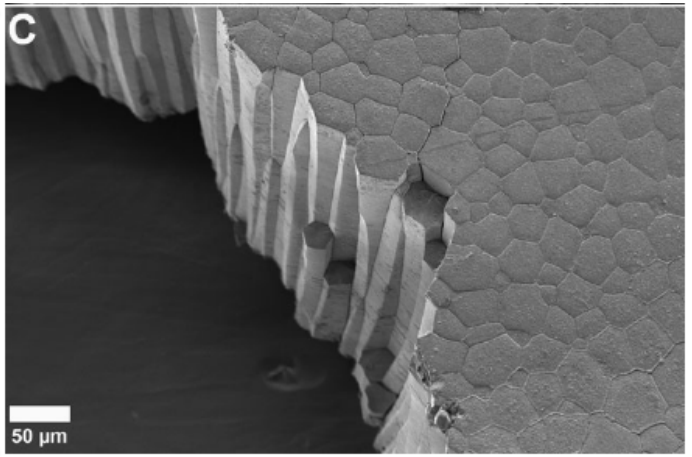
Motivation - biomineralisation



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



Sheets of aragonite tablets



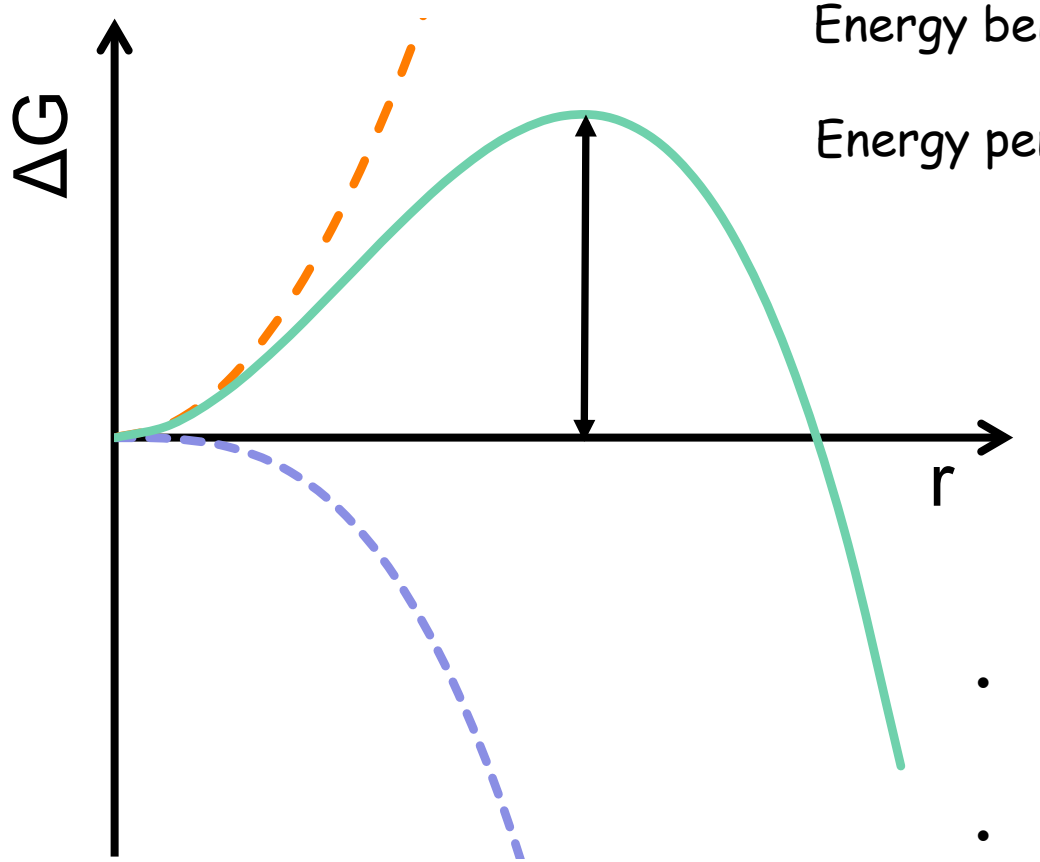
Columns of calcite

Control of morphology and assembly?

Control of polymorph selection?

Control of orientation?

Crystal nucleation as a rare event

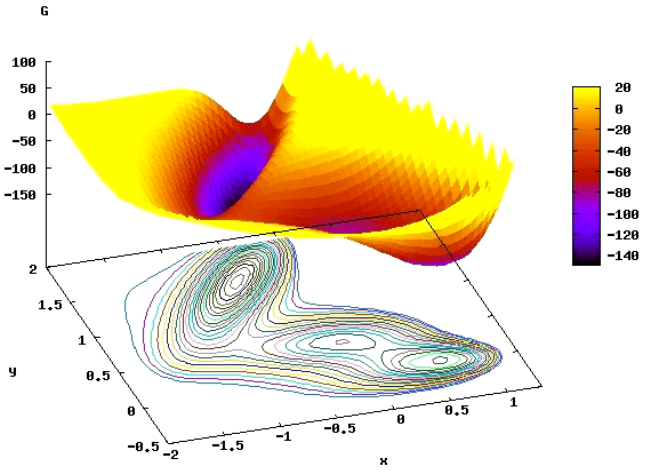


Energy benefit : $-\frac{4}{3}\pi r^3 \Delta\mu$

Energy penalty : $+4\pi r^2 \gamma$

- e.g. ice nucleation rates 10 – 10^6 nucleation events per cm^3 per second
- 1 event every 10^{25} nanoseconds in a simulation box $(100\ Å)^3$.

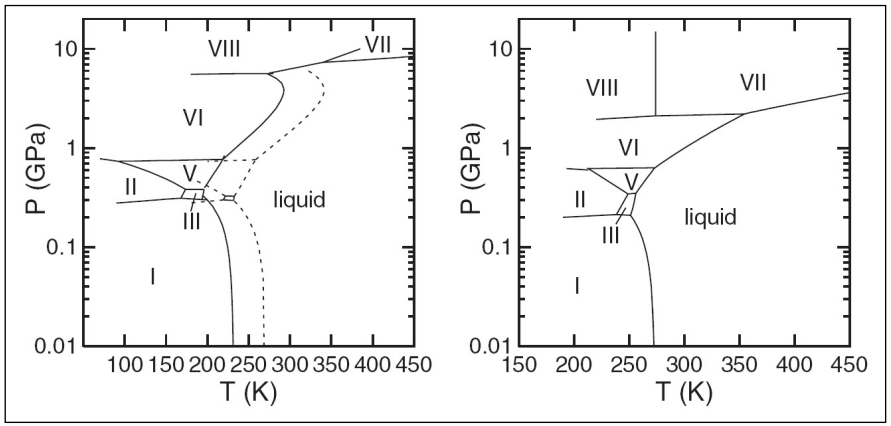
Crystallisation with metadynamics



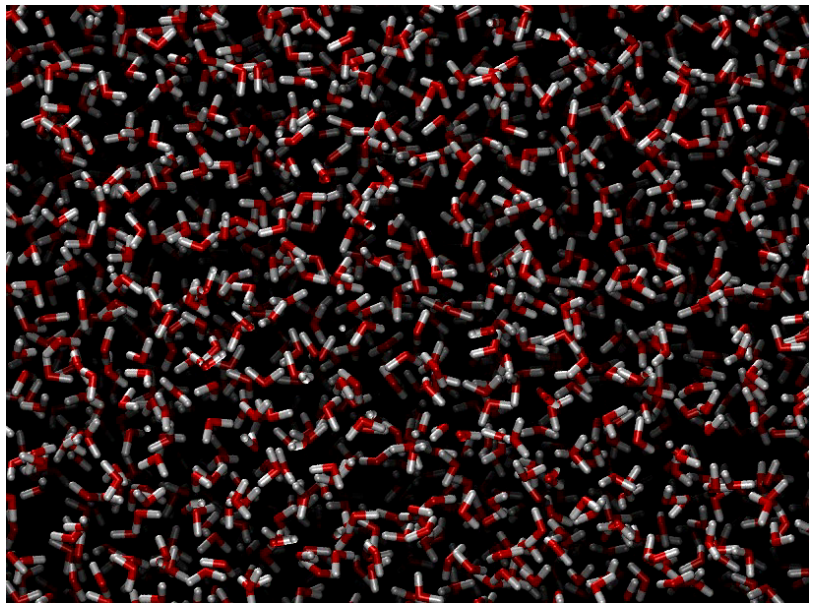
- Adapted collective variables from MC TIP4P ice nucleation studies of Trout.

[Radhakrishnan & Trout. *J.A.C.S.* **125**, 7743 – 7747 (2003)
Phys. Rev. Lett. **90** 158301 (2003)]

Steinhardt Q_6, Q_4 plus a tetrahedral order parameter and the potential energy.

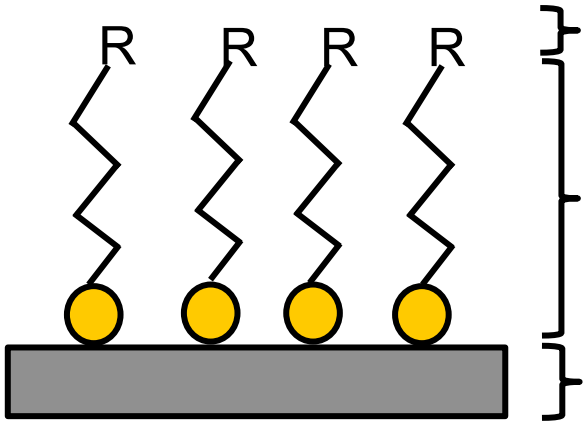


Sanz *et al. Phys. Rev. Lett.* **92**, 255701 (2004)



Orientation specificity

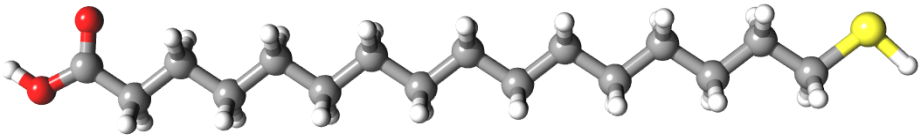
- Possible bio-mimetic control of crystal orientation.



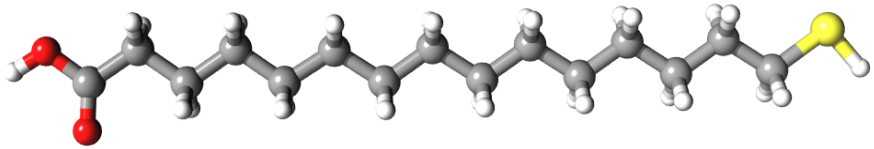
Functional group

Alkanethiol

Au / Ag



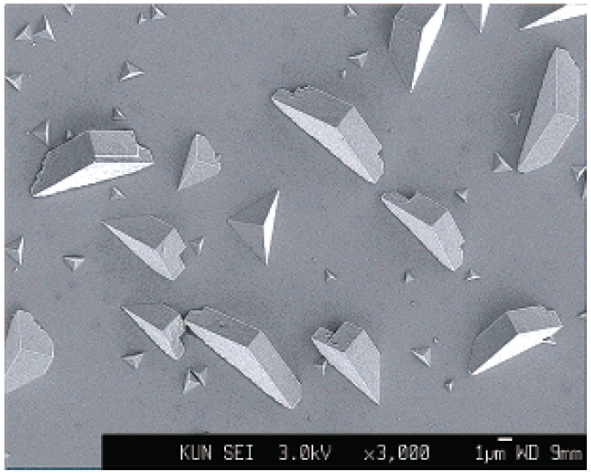
16-mecaptohexadecanoic acid (MHA)



15-mecaptopentaadecanoic acid (MPA)

Orientation specificity

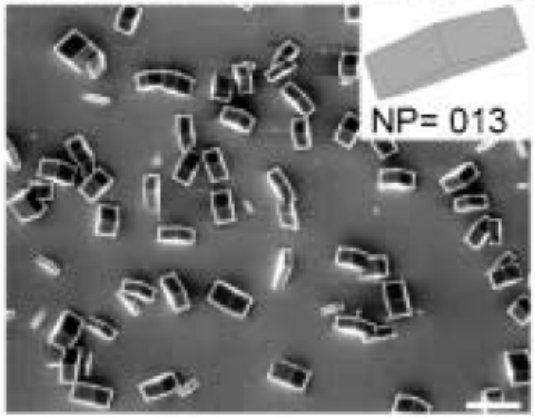
(012) nucleation plane on MHA



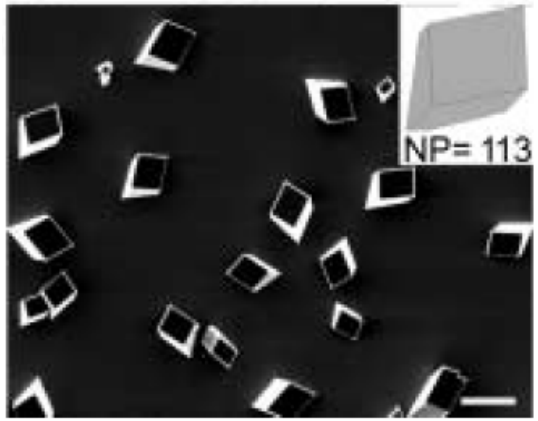
Travaille *et al J. Am. Chem. Soc.*, 2003, *125*, 11571-11577

Chain parity	Even (MHA)	Odd (MPA)
Nucleation plane (Au substrate)	(012) or (01x) x=2-5	(110) (113) (116)

even

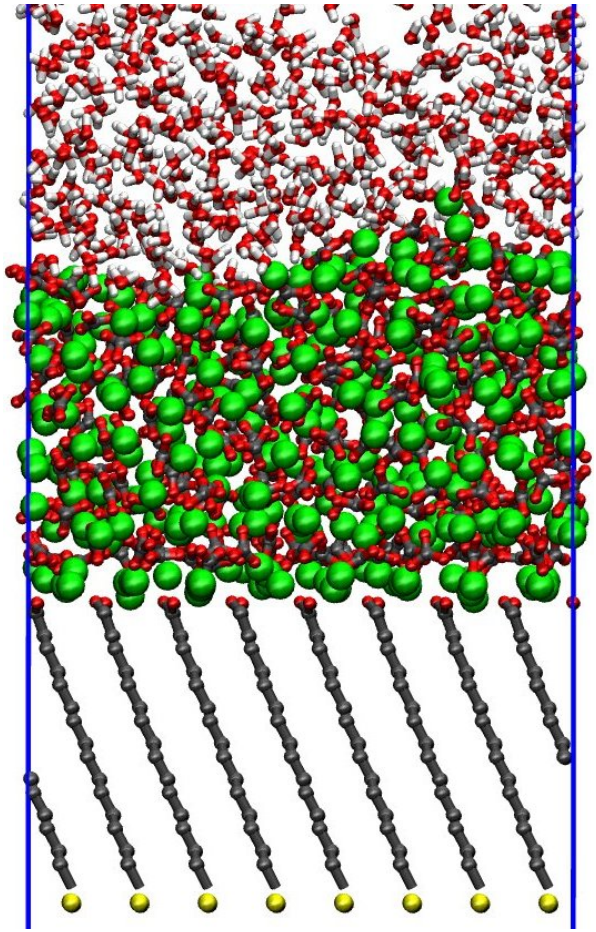


odd



Han & Aizenberg *Angew. Chem. Int. Ed.*, **2003**, *42*, 3668-3670

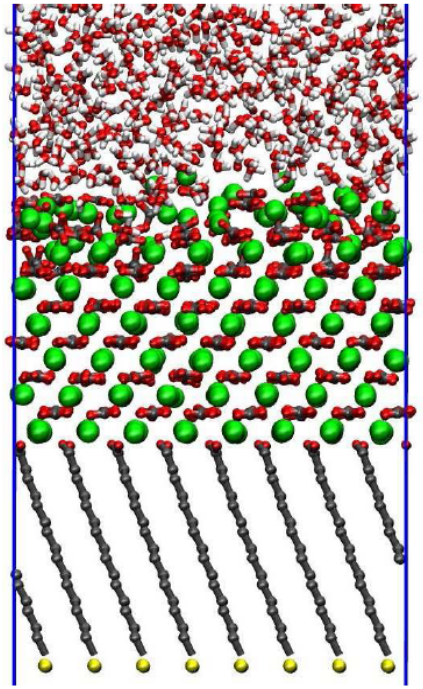
Simulating orientation specificity



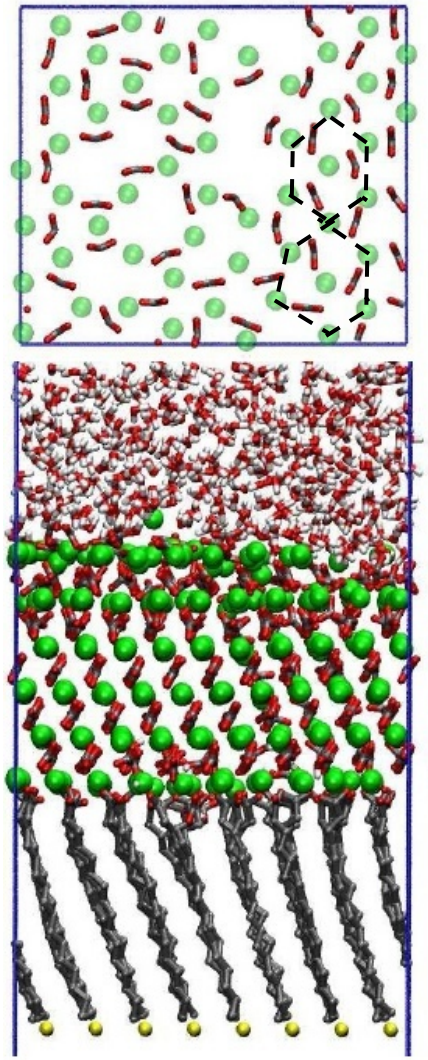
- Use metadynamics to (carefully) drive amorphous to crystalline transition.
- Use Gaussian height around 2% of smallest surface energy difference.
- SAMs modelled using CHARMM united atom force-field, TIP3P water.
- Mineral-organic terms in Freeman *et al J. Phys. Chem. C* 111,11943 (2007).
- 8.3 ns metadynamics simulations (or until crystallised) with 2 ns MD for analysis of crystal.
- 310 Kelvin, constant density.

Simulating orientation specificity

- Freezing the monolayer gives good epitaxial matching, but wrong result!
- Metadynamics allows us to simulate both the monolayer and the solvent at relevant temperatures.
- Reproduce (consistently) the experimental orientation when allowing flexibility.
- Simulations of polymorph-selecting monolayers are underway with improved potentials for $CaCO_3$.



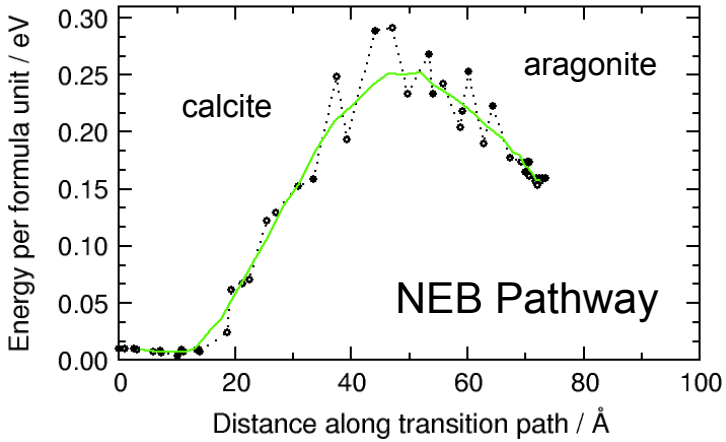
54 % bulk calcite
(001) nucleation plane

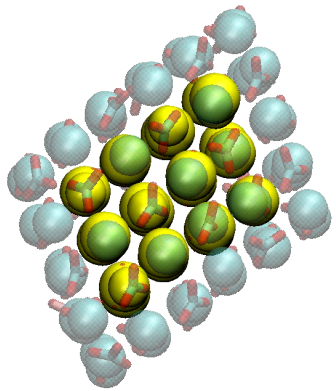


39 % bulk calcite
(012) nucleation plane

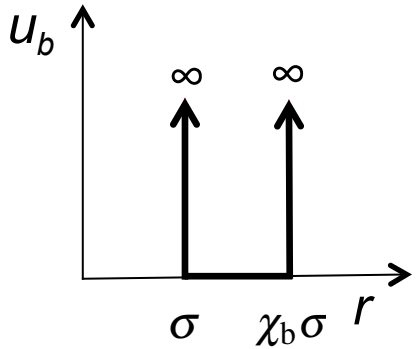
Methodology problems

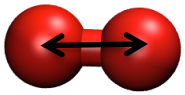
- Using metadynamics to;
  - Predict structures
  - Map gross features and changes in free energy landscapes
- Going beyond this requires better collective variables for crystallisation.
- Screen candidate CVs against path sampling data?
  - TPS/TIS/FFS + likelihood maximisation.
  - Issues with path sampling for systems with many glassy/amorphous minima?

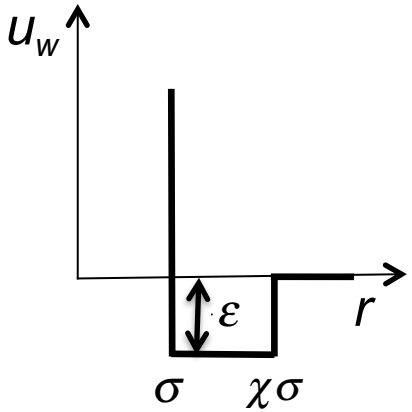


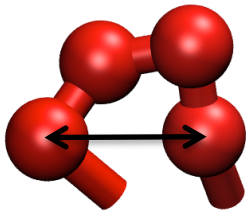


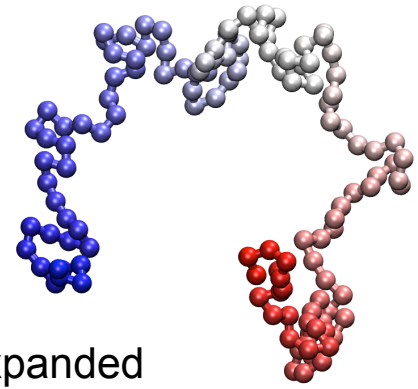
Attractive hard sphere chain



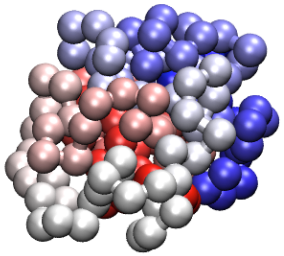




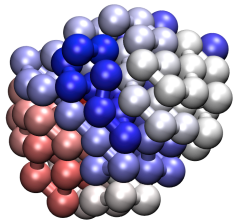




expanded



globule



crystal

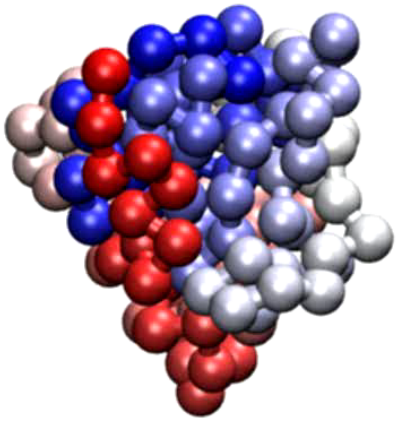
Temperature

Properties

- Thermodynamics of system extensively studied previously.

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

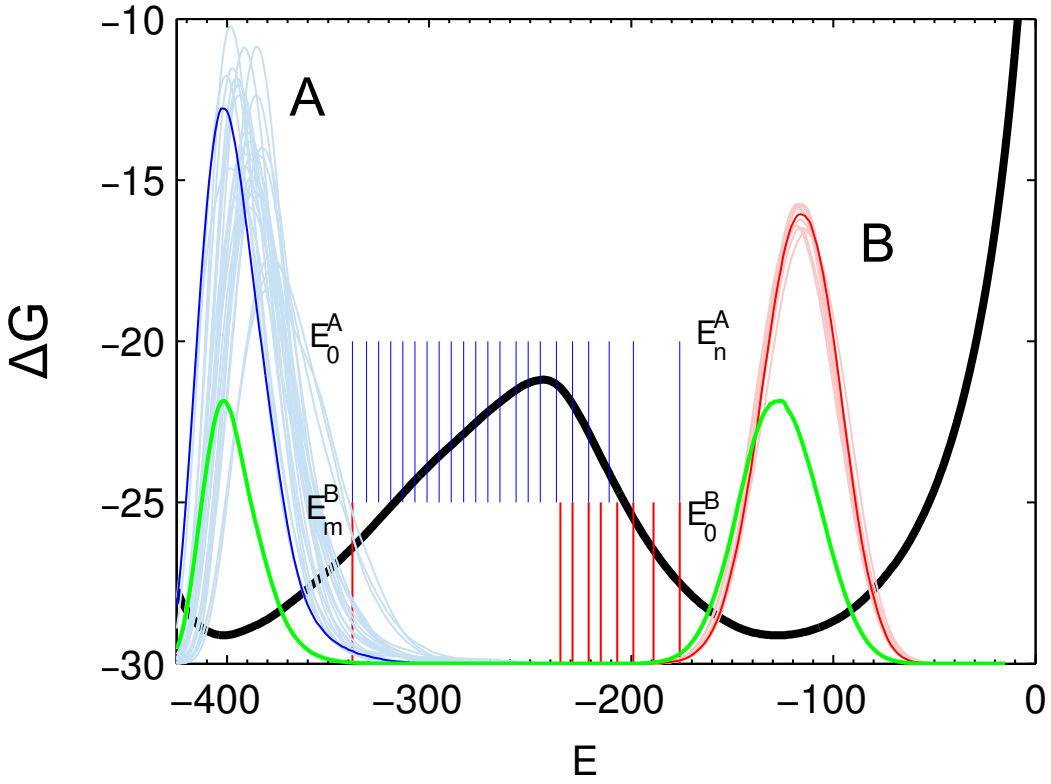
- Single stage “protein-like” collapse for $\chi \lesssim 1.06$
- We study globule-crystal transition for larger χ.
- Brute force sampling feasible for $\chi \geq 1.15$.
- Use forward flux sampling (FFS) for smaller χ.
- Simulations use collision dynamics (CD) with a stochastic component to represent coupling to a heat bath.



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

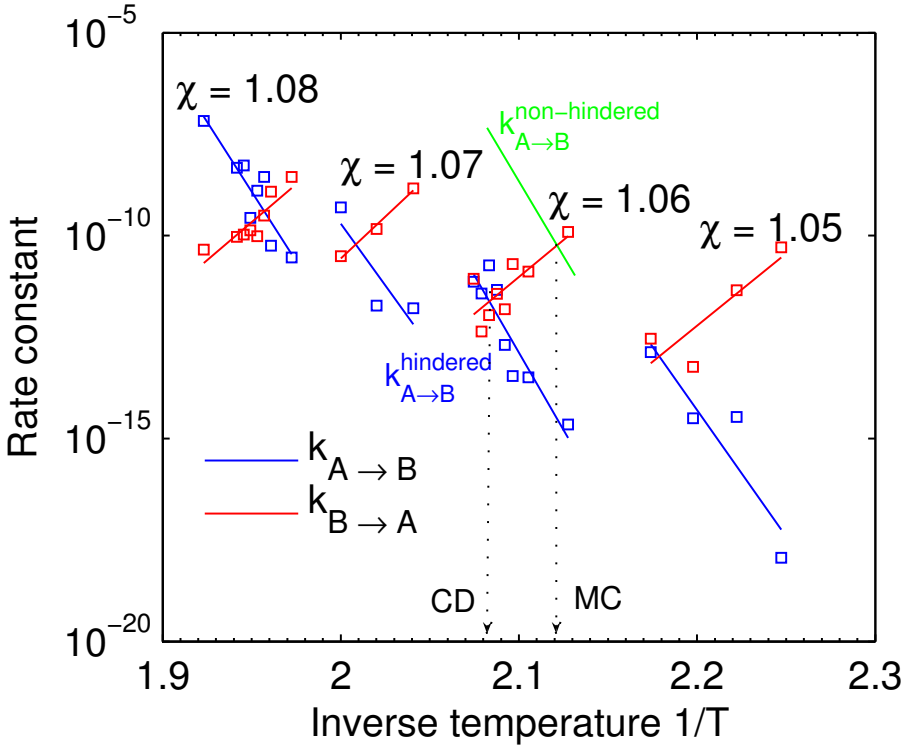
High T *P(E)*

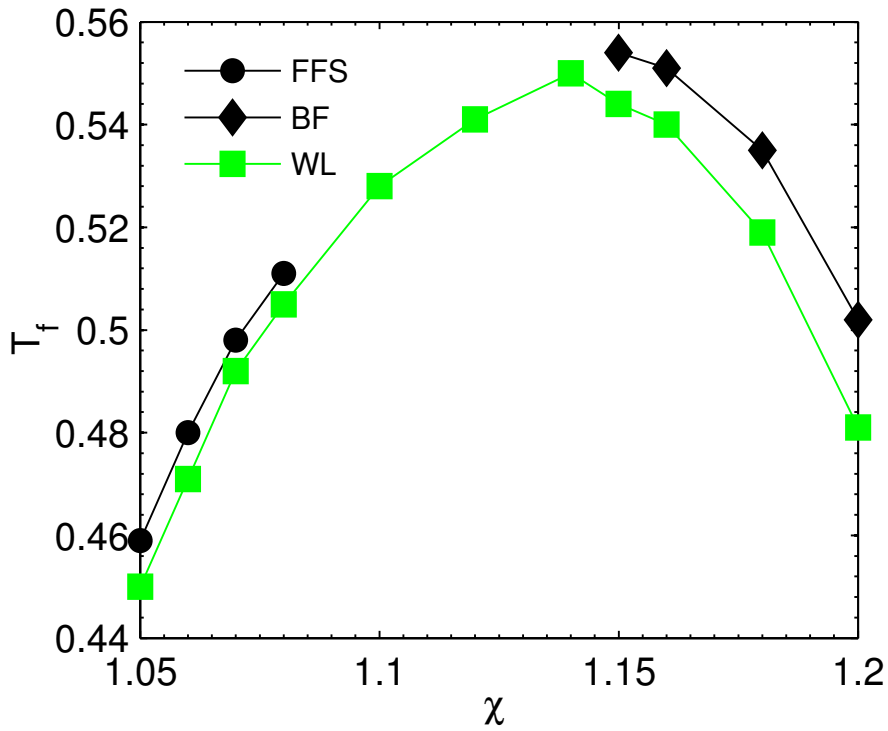
Low *T(E)*

8192 configurations at each FFS interface

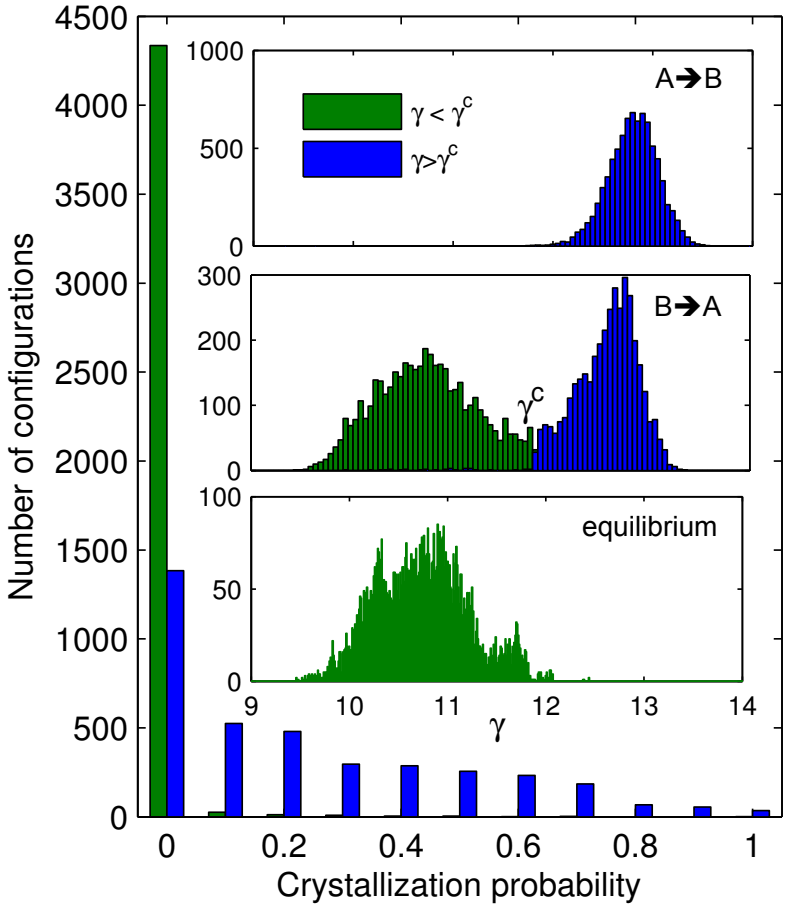
Transition temperature via kinetics

- 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

- Biomineralisation
  - Gained some insight via metadynamics using naïve collective variables.
  - Issues with going beyond this. Need better CVs and path sampling methods for *very* rugged landscapes.

- Kinetics of polymer crystallisation
  - Can a two-state treatment every capture rates correctly?
  - Insight into reaction coordinate from topology / mode analysis?

Crystallisation from the melt

- DQ & Rodger, P. M. A metadynamics-based approach to sampling crystallisation events. *Mol. Simul.*, **2009**, 35, 613-623.
- DQ & Rodger, P. M. Metadynamics simulations of ice nucleation and growth. *J. Chem. Phys.,* **2008***, 128*, 154518.

Crystallization on self-assembled monolayers

- DQ; Rodger, P. M.; Freeman, C. L.; Harding, J. H. & Duffy, D. M.
  Metadynamics simulations of calcite crystallization on self-assembled monolayers. *J. Chem. Phys.,* **2009***, 131*, 094703.

Kinetics of Homopolymer crystallisation

- Ruzicka, S.; DQ & Allen, M.P. Folding kinetics of a polymer. *Phys. Chem. Chem. Phys*., **2012**, DOI: 10.1039/C2CP00051B