Simulating orientational specificity in the growth of calcite on self-assembled monolayers

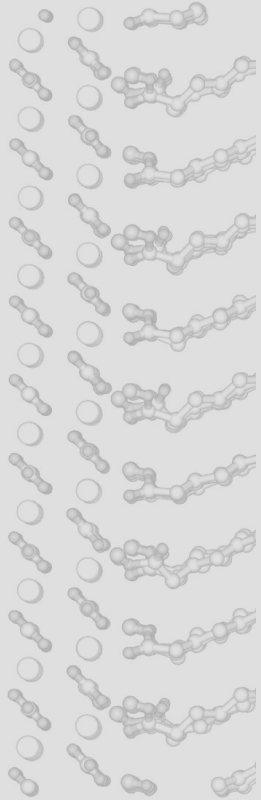**D. Quigley[1], C. L. Freeman[2],**

P. M. Rodger[3], J. H. Harding[2] and D. M. Duffy[4]

1. Dept. of Physics and Centre for Scientific Computing, University of Warwick.
2. Dept. of Engineering Materials, University of Sheffield.
3. Dept. of Chemistry and Centre for Scientific Computing, University of Warwick.
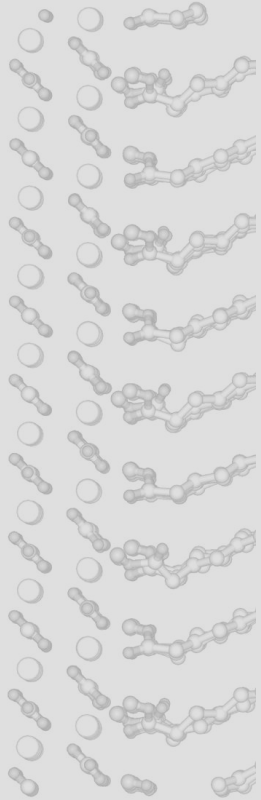4. Dept. Physics, University College London.

Outline

- Calcium carbonate and biomineralisation.

- Growth on self-assembled monolayers.

- Direct simulations and metadynamics.

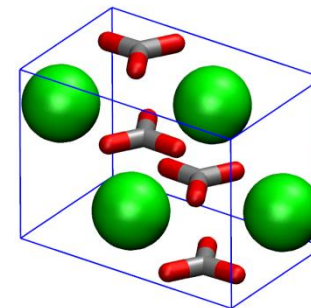- Testing and analysis.

- Results and challenges.

Outline

- **Calcium carbonate and biomineralisation.**

- Growth on self-assembled monolayers.

- Direct simulations and metadynamics.
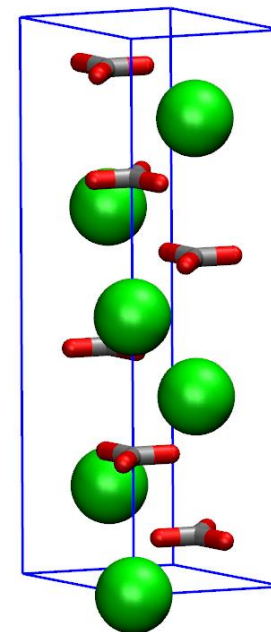
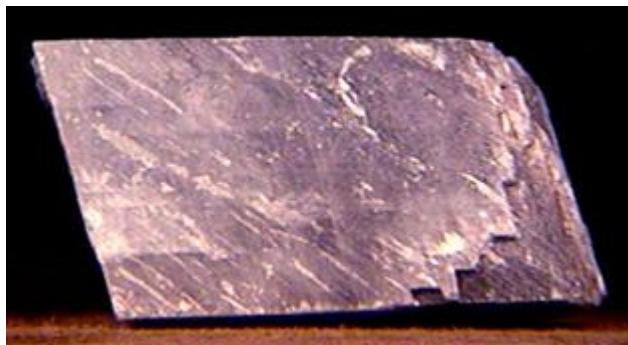- Testing and analysis.

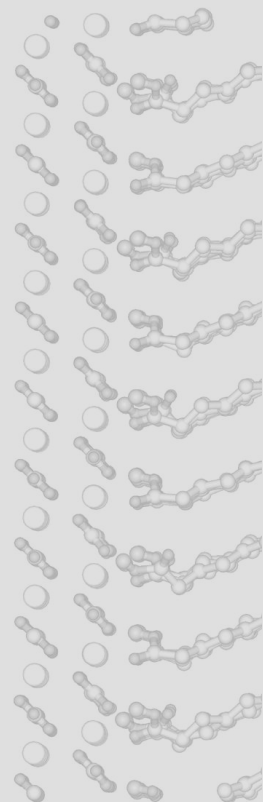- Results and challenges.

Calcium Carbonate

Aragonite

Calcite

http://www.cs.cmu.edu/~adg/adg-pcaimages.html

Calcium Carbonate

Ca^{2+}

CO$_3^{2-}$
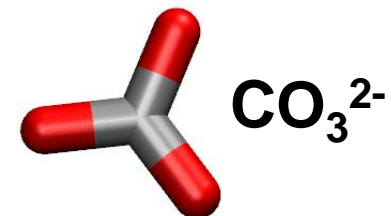
- Based on the model of Pavese *et al.*
  [Pavese *et al, Phys. Chem. Miner.* **19**, 90 (1992)]

$$q_{oxygen} = -1.045$$
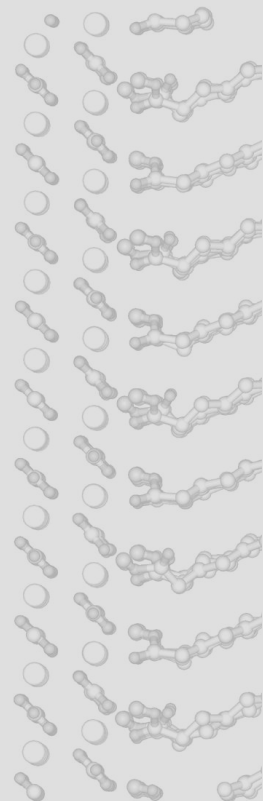$$q_{carbon} = +1.135$$

C-O bond energy modelled with a Morse potential.
O-C-O angles restrained with harmonic potentials.

Buckingham potentials between all O-O and Ca-O pairs.

$$\phi_{ij}(r) = A_{ij} \exp\left[-r/\rho_{ij}\right] - \frac{C_{ij}}{r^6}$$

- Cross terms between CaCO$_3$ and water / organics derived in Freeman *et al.*
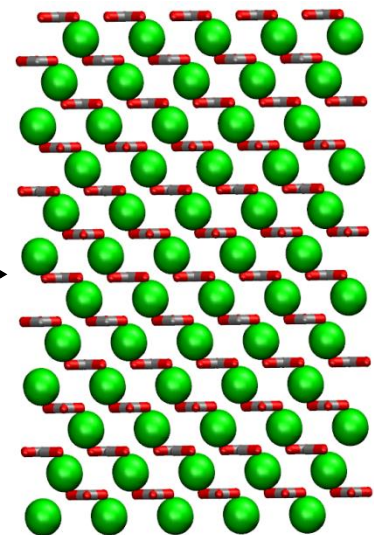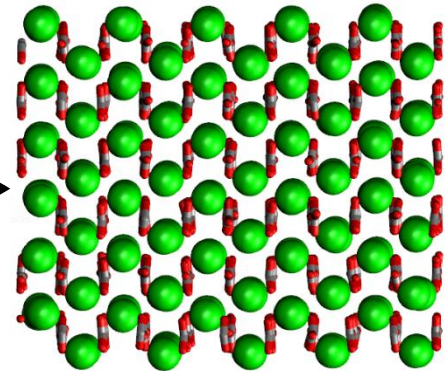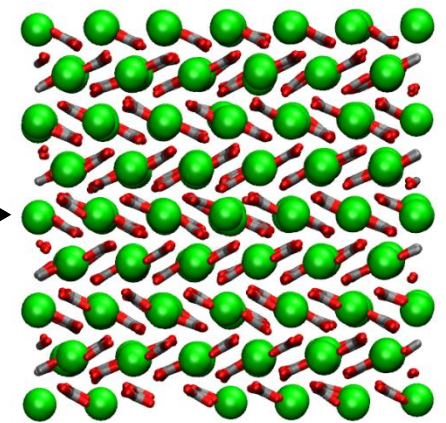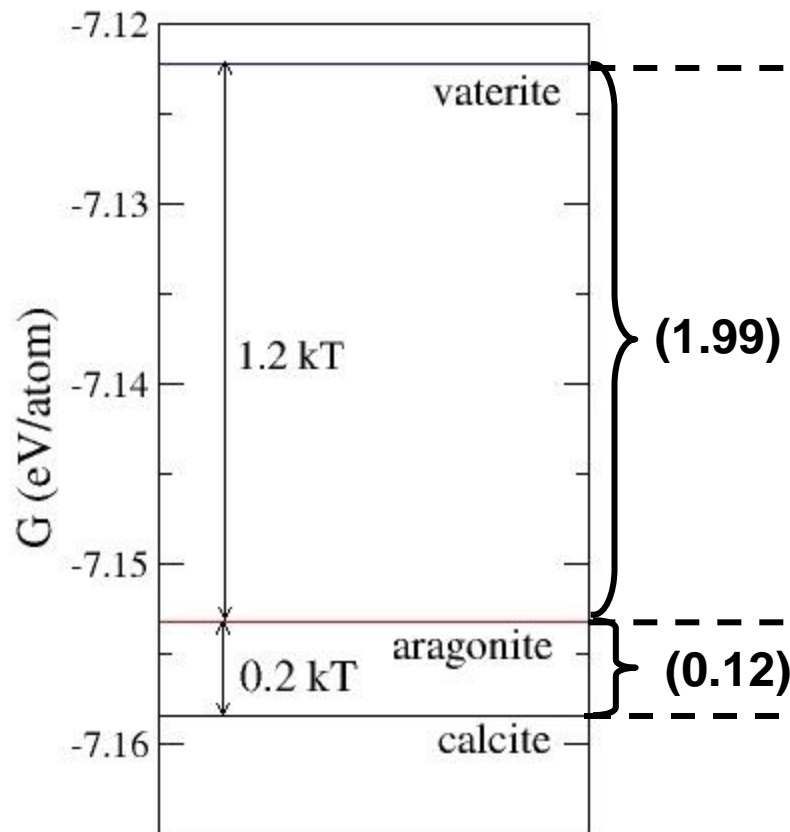 [Freeman *et al, J. Phys. Chem. C* **111**, 11943 (2007).]

Polymorphs

- Free energy calculations.

Morphology of calcite

surface (hexagonal indices)	$\gamma_{pure}/$ J m^{-2}	E_{attach} /kJ mol^{-1}	$\gamma_{hydrated}/$ J m^{-2}	$E_{hydration}/$ kJ mol^{-1}
$\{10\bar{1}4\}$	0.59	−75.4	0.16	−93.9
$\{0001\}$Ca	0.97	−334.3	0.68	−79.2
$\{0001\}$CO$_3$	0.99	−204.7	0.38	−93.2
$\{10\bar{1}0\}$	0.97	−759.6	0.75	−100.5
$\{10\bar{1}1\}$Ca	1.23	−307.2	0.63	−113.4
$\{10\bar{1}1\}$CO$_3$	1.14	−276.7	0.81	−100.9
$\{11\bar{2}0\}$	1.39	−291.3	0.43	−138.5

de Leeuw, & Parker, *J. Phys. Chem. B,* 1998*, 102*, 2914-2922
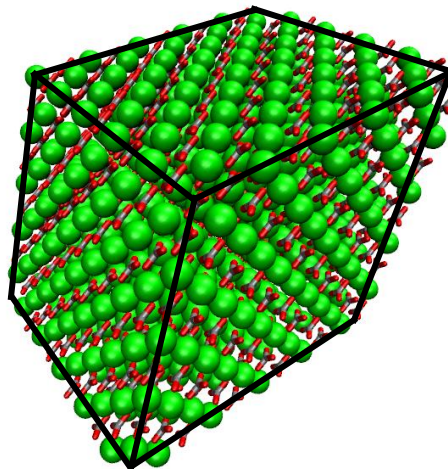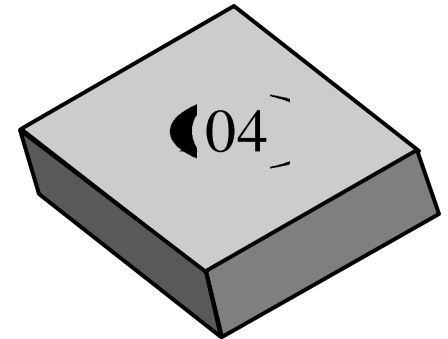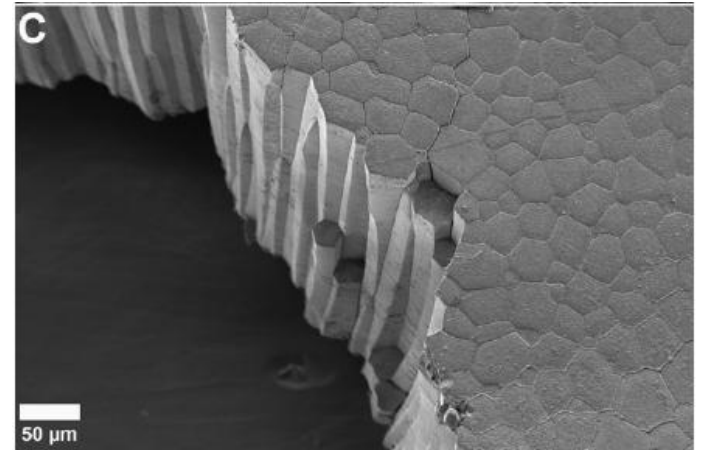

American Geological Institute
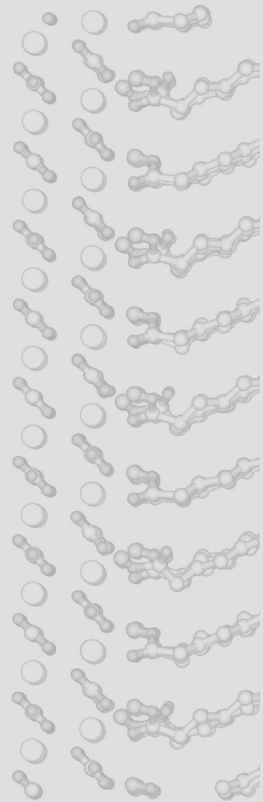
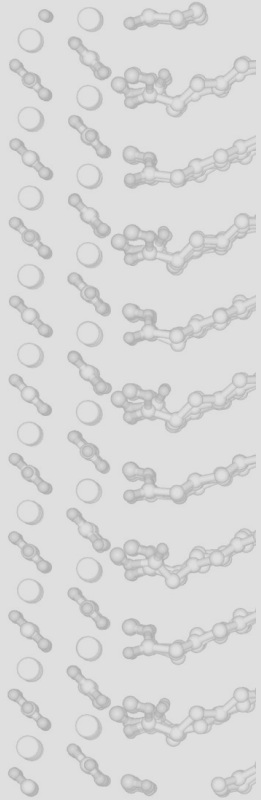# Biomineralisation
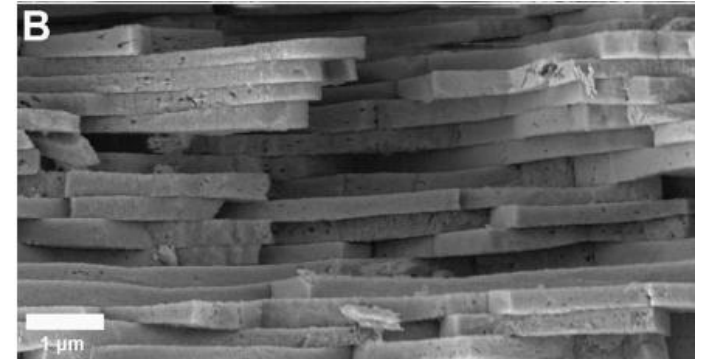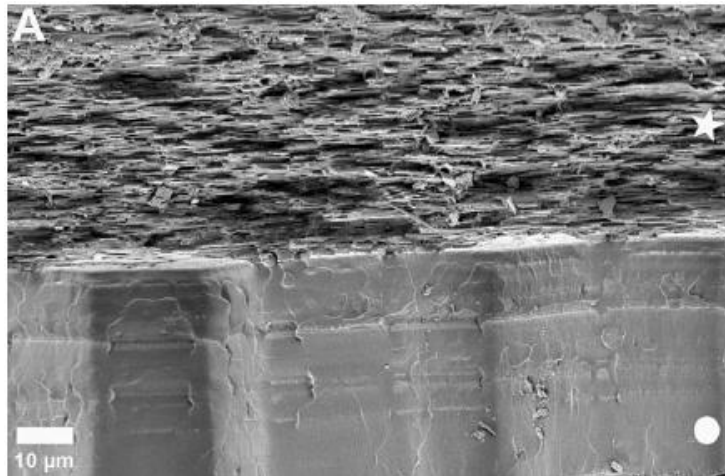
Sheets of aragonite tablets

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

Columns of calcite

Control of morphology and assembly?
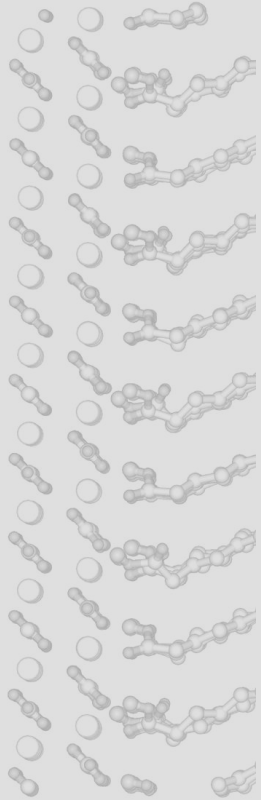
Control of polymorph selection?
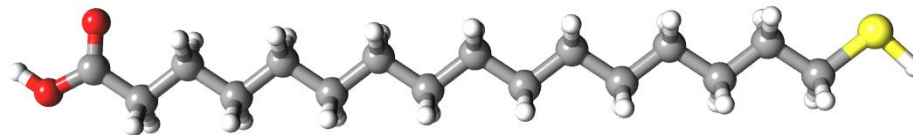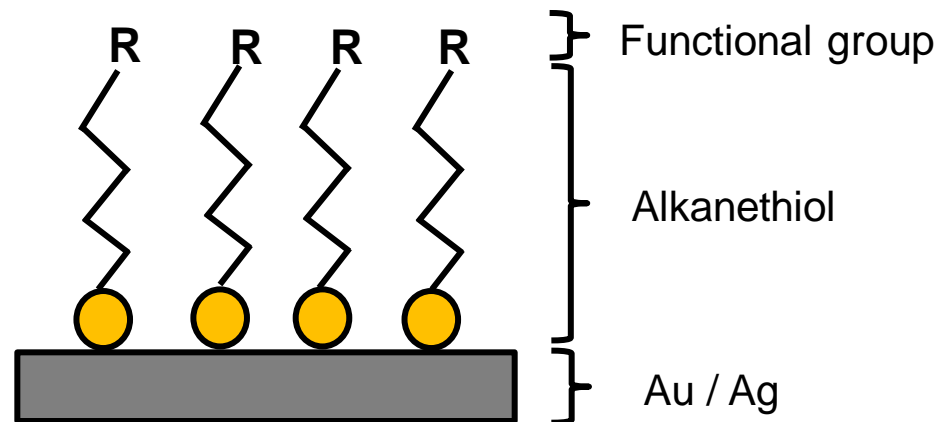
Control of orientation?

Outline

- Calcium carbonate and biomineralisation.

- **Growth on self-assembled monolayers.**

- Direct simulations and metadynamics.

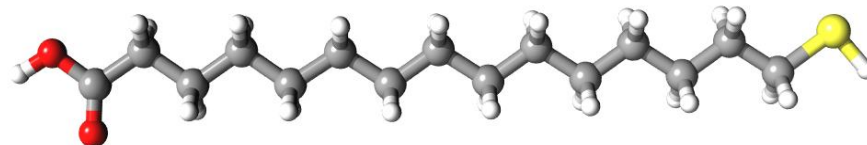- Testing and analysis.

- Results and challenges.

Self-assembled monolayers

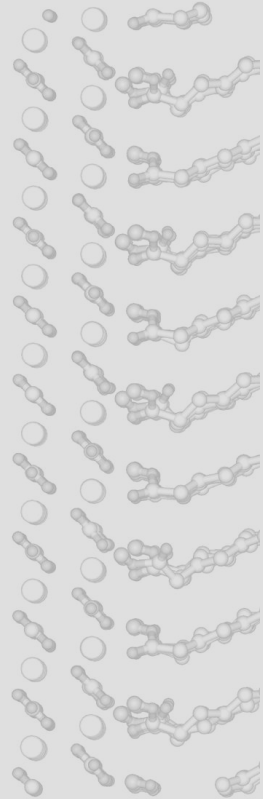- Possible bio-mimetic control of crystal orientation.
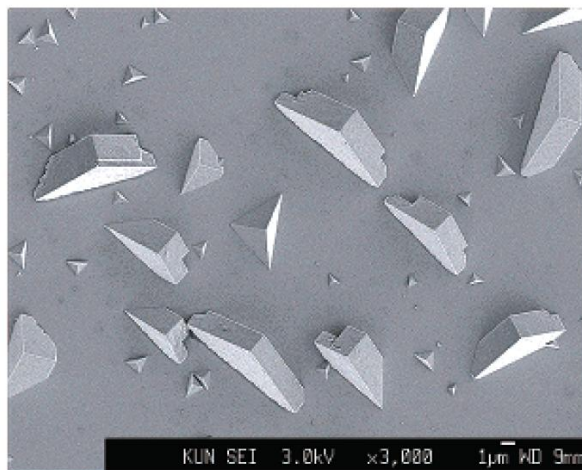

16-mecaptohexadecanoic acid (MHA)

even

15-mecaptopentaadecanoic acid (MPA)

odd

Calcite Growth

(012) nucleation plane on MHA

KUN SEI 3.0kV ×3,000 1μm WD 9mm

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

NP= 013

NP= 113
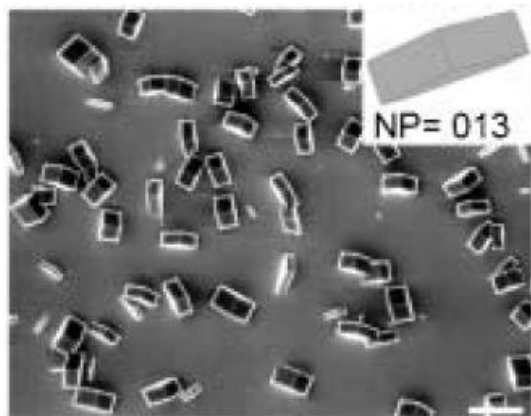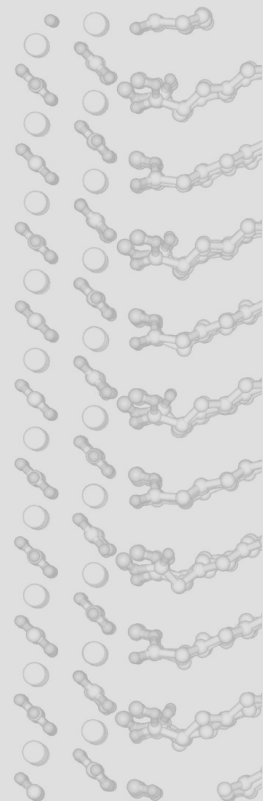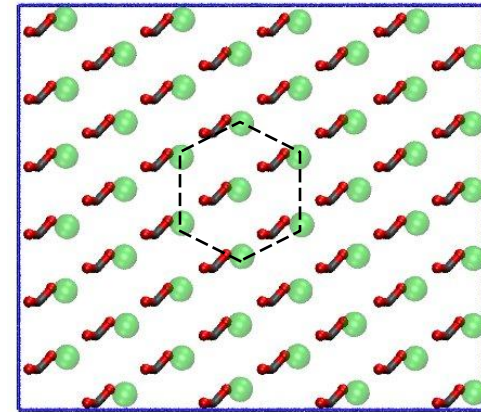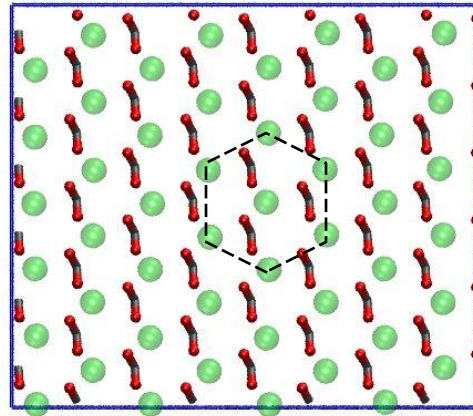
Han & Aizenberg *Angew. Chem. Int. Ed.,* **2003**, *42*, 3668-3670
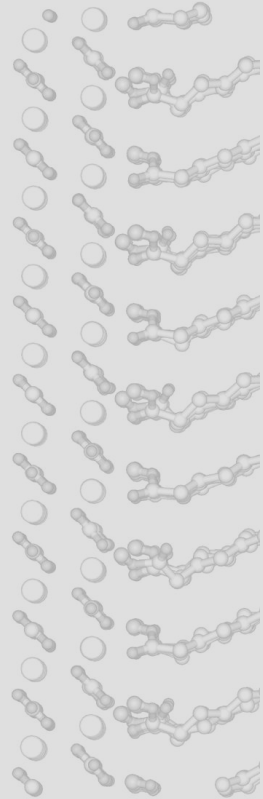
Epitaxy and surface energies

- Lowest energy MHA and MPA configurations.

- – Fully ionized carboxyl groups.
- – Good match to calcite (001) surface.

- Interfacial energy calculations on MHA show $\gamma_{calcite-sam}$ lower for (001) than (012).
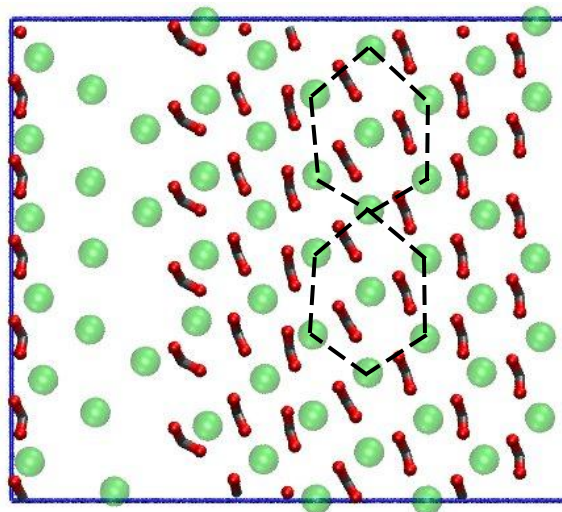
  [Duffy and Harding *Langmuir,* **2004***, 20*, 7637-7642]

Line defects

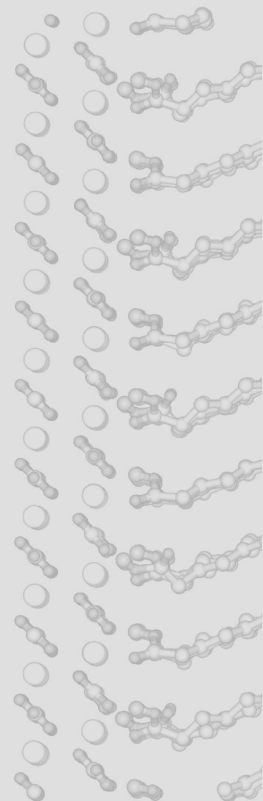- Can be induced by presence of bicarbonates.

e.g. MHA

Reasonable match to a slightly distorted (012) calcite surface.

Interfacial energy calculations now favour (012) over (001).

One possible mechanism for generating (012).

	(0001)			$(01\bar{1}2)$		
	γ_{cm} (J m^{-2})	m	$f(m)$	γ_{cm} (J m^{-2})	m	$f(m)$
even (MHA)	0.081	-0.62	0.90	0.074	-0.57	0.88
odd (MPA)	0.086	-0.66	0.92	0.095	-0.73	0.95

Duffy *et al J. Phys. Chem. B,* 2005, **109**, 5713-5718

Outline

- Calcium carbonate and biomineralisation.

- Growth on self-assembled monolayers.

- **Direct simulations and metadynamics.**

- Testing and analysis.

- Results and challenges.

Direct Simulations

- We aim to predict the crystal orientation without
  - (a) Prior knowledge from experiment.
  - (b) Manual construction of defects.
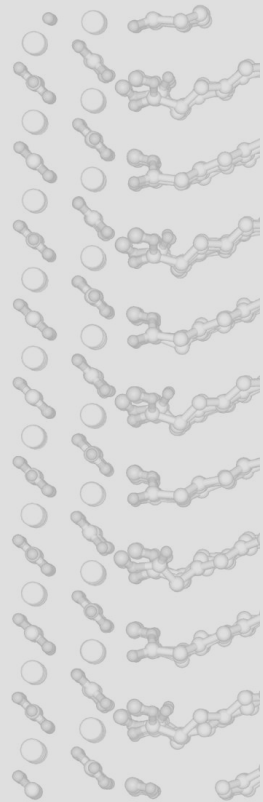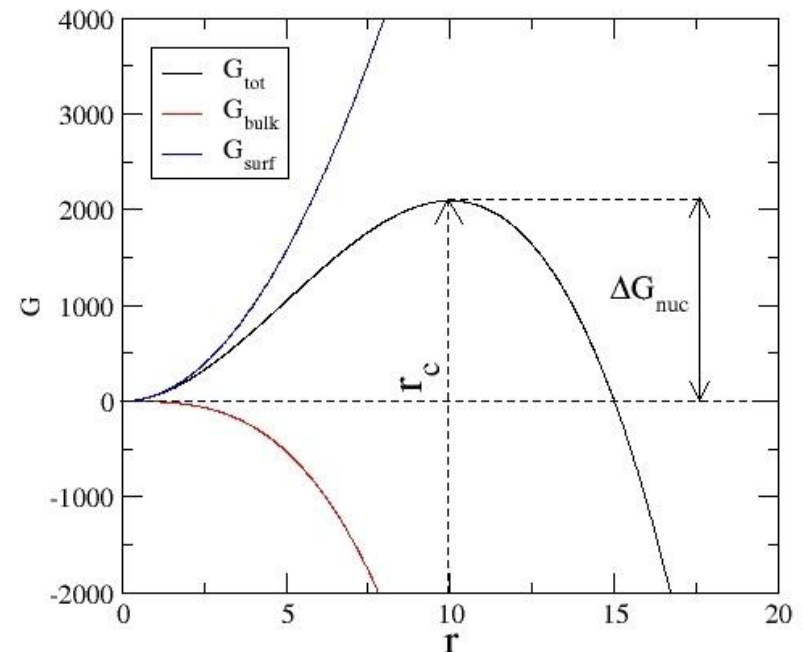 - (c) Imposing a unrealistic temperatures.

$$G_{\mathbf{bulk}} = \frac{4}{3}\pi\Delta\mu r^3$$

$$G_{\mathbf{surf}} = 4\pi\gamma r^2$$

$$\Delta\mu = \mu_{\mathbf{sol}} - \mu_{\mathbf{liq}}$$

Competition of bulk and surface free energy

Typically ΔG_{crit} ~ 10 -100 $k_B T$

Metadynamics

Augment the Hamiltonian with a history dependent potential V written as a function of some collective variables **s**,

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U\left(\mathbf{r}^N\right) + V\left[\mathbf{s}\left(\mathbf{r}^N\right), t\right].$$

V is constructed as,

$$V\left[\mathbf{s}\left(\mathbf{r}^N\right), t\right] = w \sum_{k=1}^{N_G} \exp\left[\frac{-\left|\mathbf{s}\left(k\tau_G\right) - \mathbf{s}\left(t\right)\right|^2}{2\delta h^2}\right]$$

where k runs over all $N_G = \mathrm{int}[t/\tau_G]$ previously deposited Gaussians. Provided the disposition rate w/τ_G is slow, V ultimately compensates for the underlying free energy landscape,

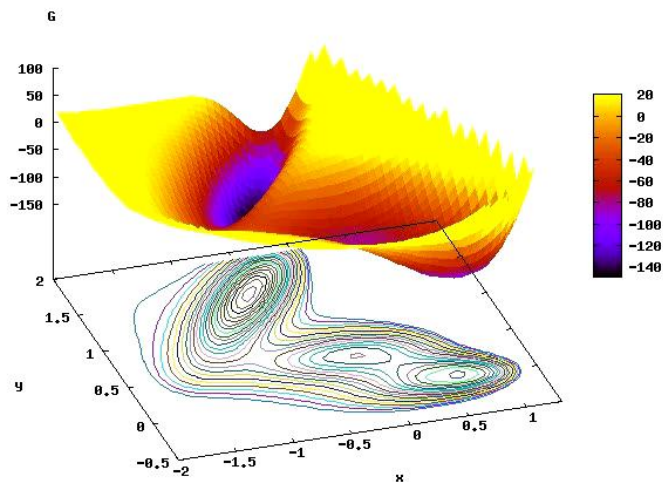$$F_G\left(\mathbf{s}\right) = -\lim_{t \to \infty} V\left[\mathbf{s}\left(\mathbf{r}^N\right), t\right].$$
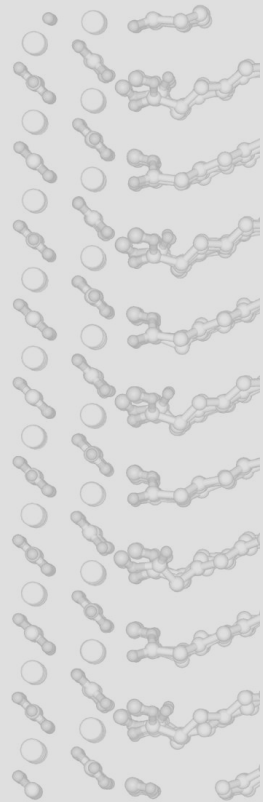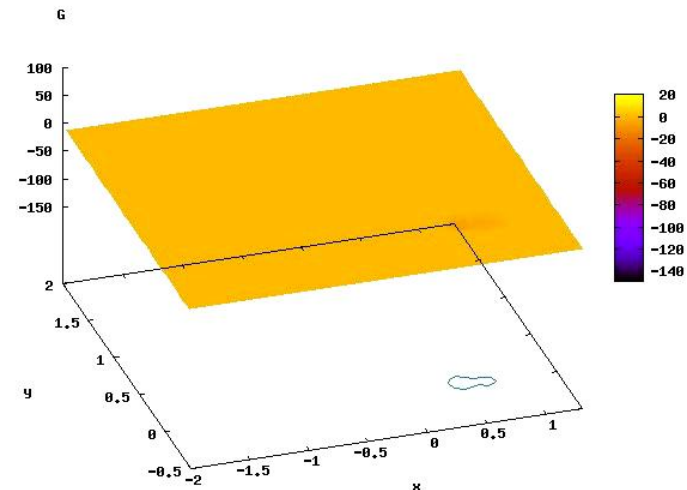
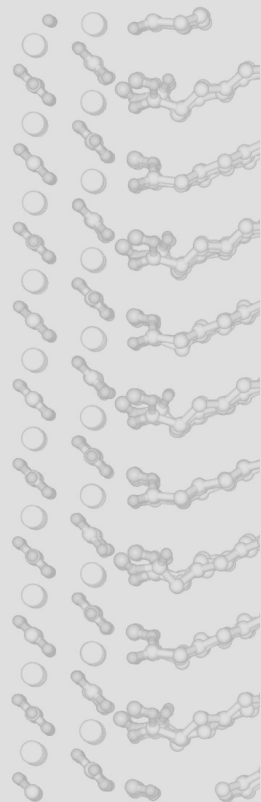# Metadynamics

[Laio & Parrinello *P.N.A.S.* **99** 12562 (2002)]

Small Gaussian bias potentials are added to current location in order parameter space at intervals T_{aug}.

Pushed over free energy barriers into unexplored regions.

Provided motion of order parameters is *adiabatically slow,* the free-energy is recovered as the negative of the total bias.
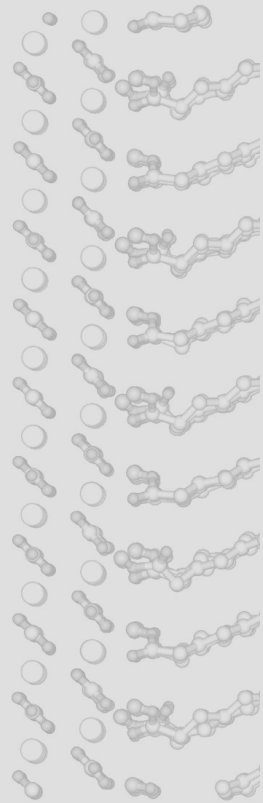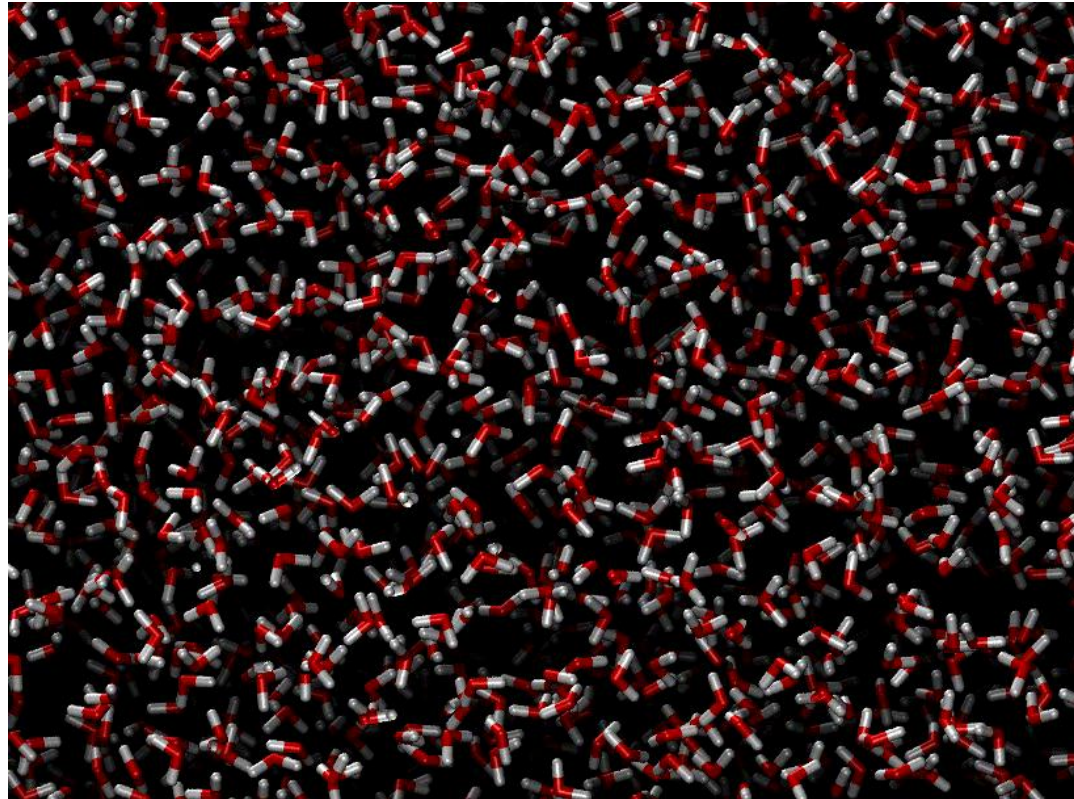
Crystallisation

- Apply to water, using Q_4, Q_6, ξ and potential energy as an order parameter.

Calcium Carbonate Scheme

Bias Q_4 or Q_6 separately for each of the five "bond types" listed below, plus the "local" energy of the calcite component (real-space part of all vdw/coulomb/bond/angle energies which include either Ca or CO_3).

$$f_c(r) = \begin{cases} 1 & \text{if } r \leq r_1; \\ \frac{1}{2}\left\{\cos\left[\frac{(r-r_1)}{r_2-r_1}\pi\right]+1\right\} & \text{if } r_1 < r \leq r_2; \\ 0 & \text{if } r > r_2. \end{cases}$$

$$Q_l^{\alpha\beta} = \left[\frac{4\pi}{2l+1}\sum_{m=-l}^{l}\left|\frac{1}{4N_{nn}}\sum_{b=1}^{N_b}f_c(r_b)Y_{lm}(\theta_b,\phi_b)\right|^2\right]^{1/2}$$

| pair type	calcite	aragonite	vaterite
Q_4(Ca-Ca)	0.2464 (0.0007)	0.0046 (0.0011)	0.5033 (0.0028)
Q_6(Ca-Ca)	0.4882 (0.0014)	0.3999 (0.0011)	0.4443 (0.0025)
Q_4(Ca-C)	0.7053 (0.0008)	0.2411 (0.0015)	0.4082 (0.0004)
Q_6(Ca-C)	0.4863 (0.0017)	0.4461 (0.0009)	0.1122 (0.0015)
Q_4(Ca-O)	0.5247 (0.0008)	0.4082 (0.0011)	0.0503 (0.0023)
Q_6(Ca-O)	0.2215 (0.0006)	0.1076 (0.0023)	0.2110 (0.0026)
Q_4(C-C)	0.2470 (0.0007)	0.5247 (0.0011)	0.1848 (0.0013)
Q_6(C-C)	0.4881 (0.0013)	0.4983 (0.0005)	0.4204 (0.0014)
Q_4(C-O)	0.8216 (0.0178)	0.5137 (0.0119)	0.1319 (0.0094)
Q_6(C-O)	0.7988 (0.0117)	0.6698 (0.0096)	0.2999 (0.0088)

bulk values for 300 units

Nanoparticles
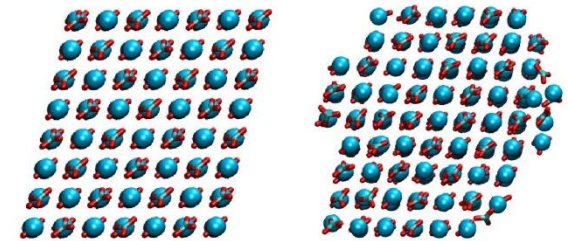

G/k_BT plotted as $Q_4(Ca-O)$ versus $Q_4(Ca-C)$
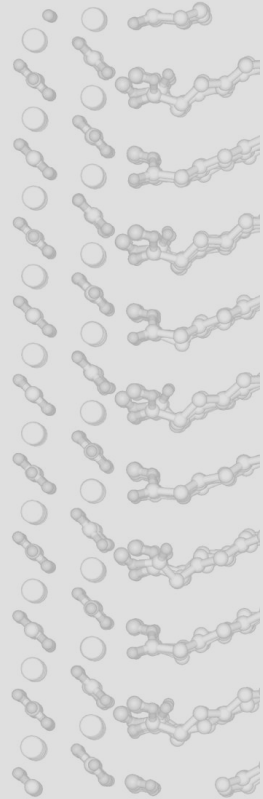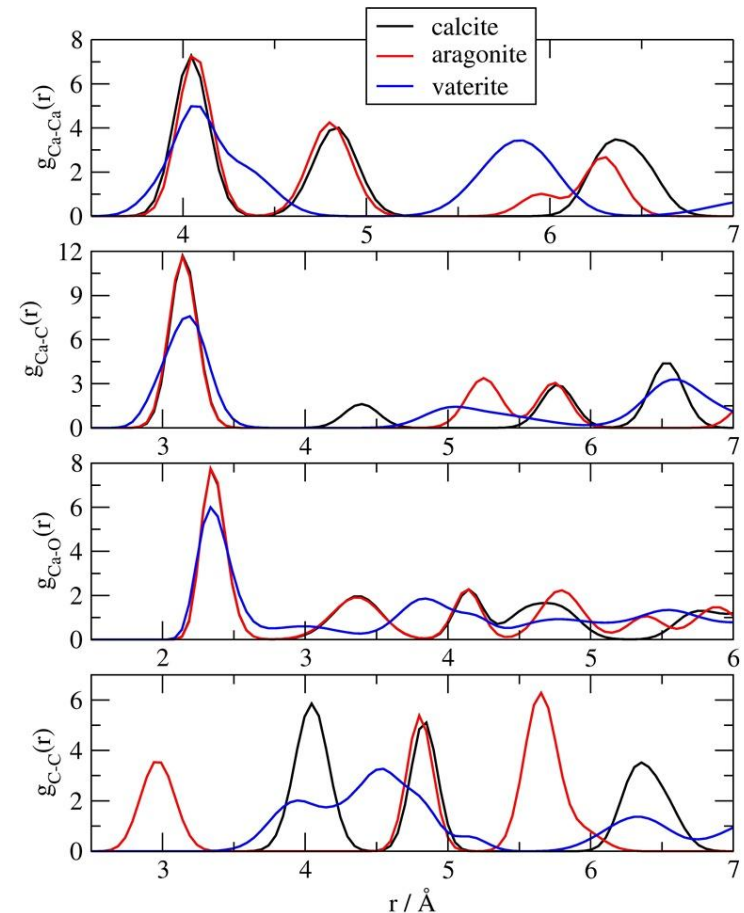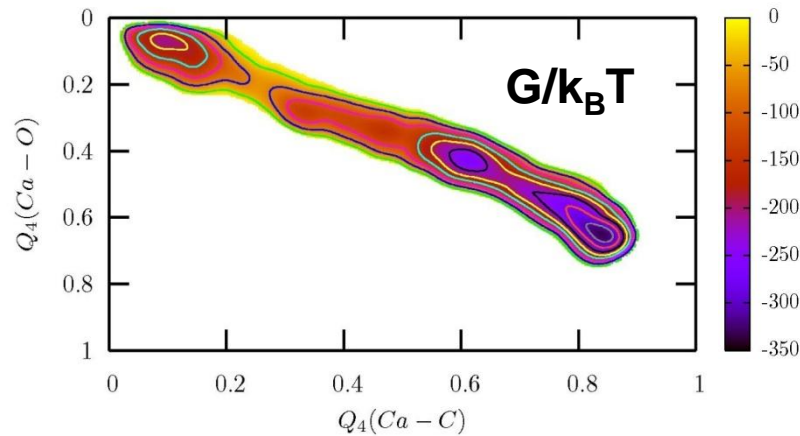
- 52,113 steps with w=3.78 k_BT (13 ns).
- 67,091 steps with w=1.0 k_BT (15.5 ns).
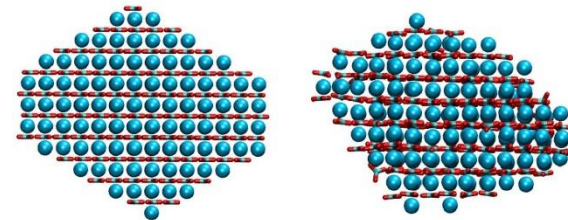
- Convergence of free energies is very slow.

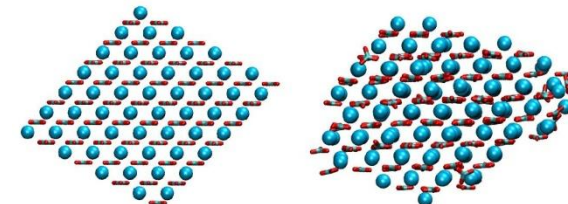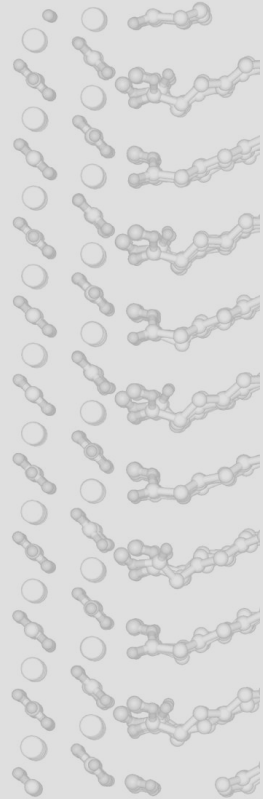- **BUT** generates sensible crystal morphologies very quickly.
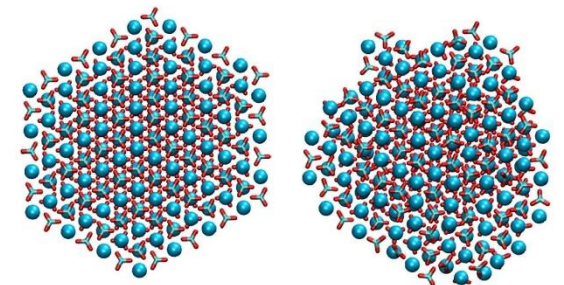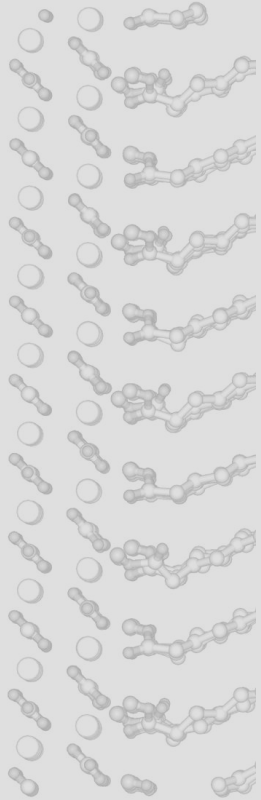

(00.1)

(02.0)

(10.4)

(11.0)

N=196   N=192
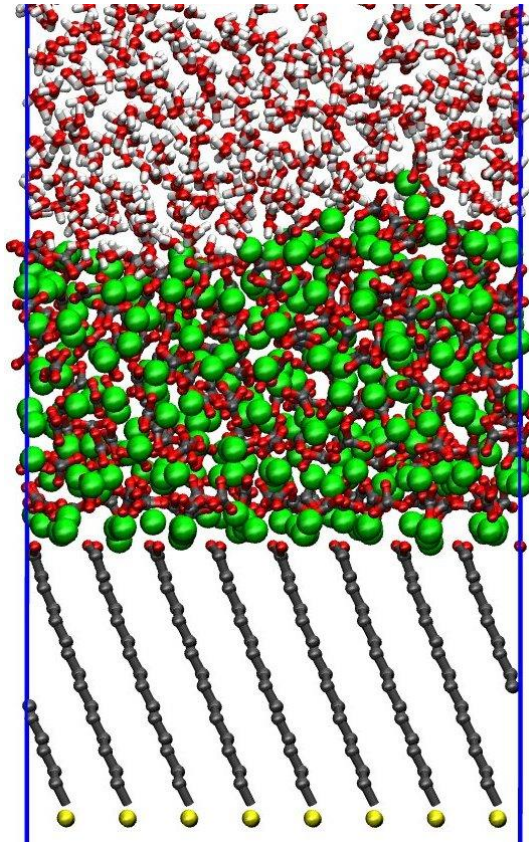
Outline

- Calcium carbonate and biomineralisation.

- Growth on self-assembled monolayers.

- Direct simulations and metadynamics.

- **Testing and analysis.**

- Results and challenges.

Crystallisation on SAMs

- 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.
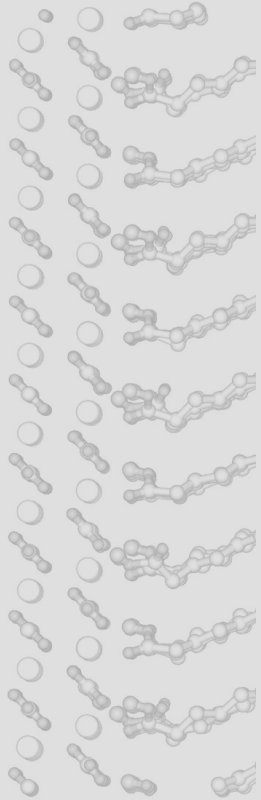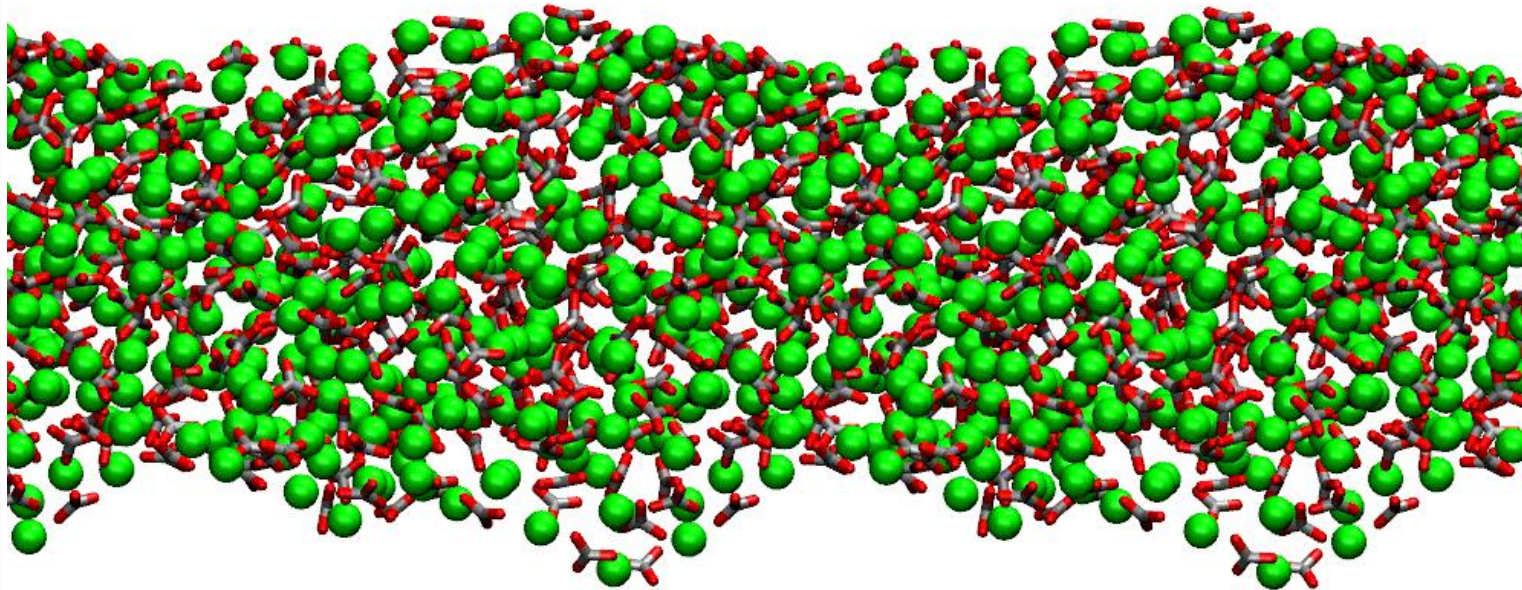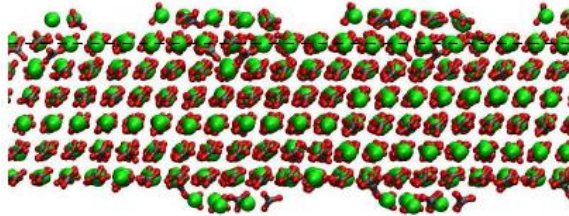
- 310 Kelvin, constant density.
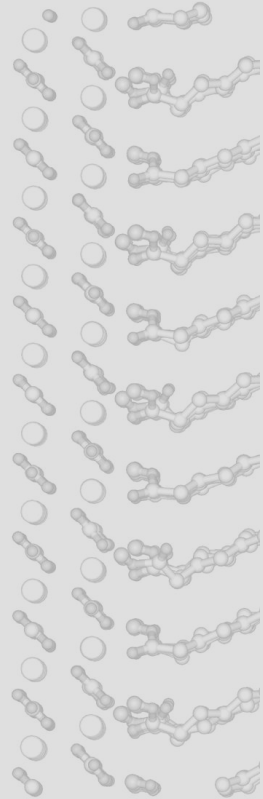
Testing – amorphous slabs

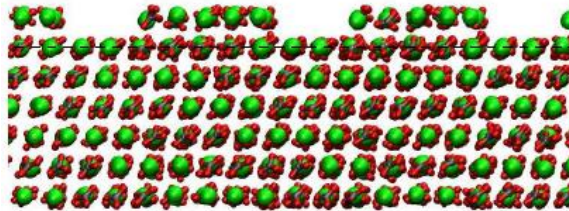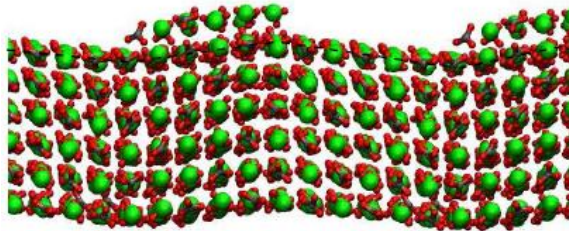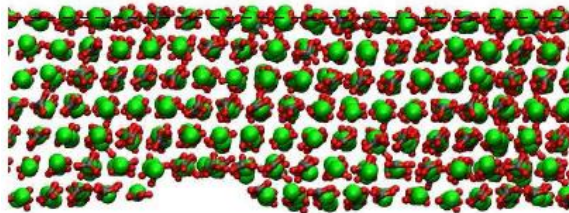- Crystallisation in vacuum should expose (104) surface.

Validation

$$\tau_G = 0.25\,ps$$
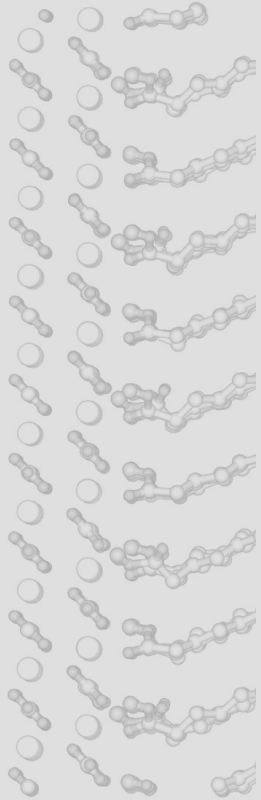
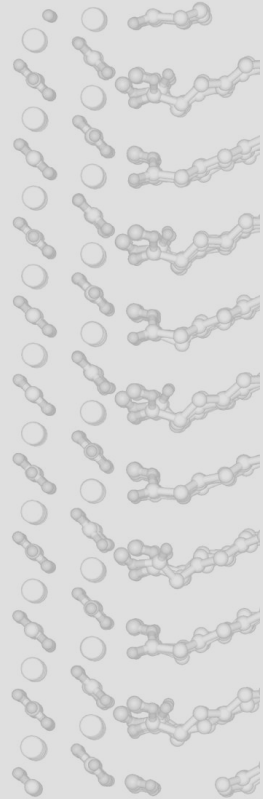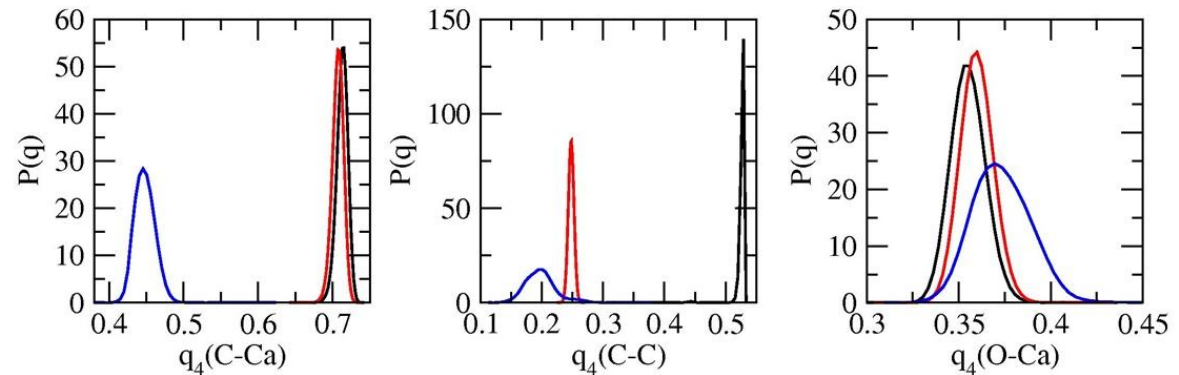$$\tau_G = 0.20\,ps$$

$$\tau_G = 0.15\,ps$$

$$\tau_G = 0.05\,ps$$

---------- **(104)**

Phase assignment

Based on computation of local per-ion order parameters and comparison to bulk reference values.
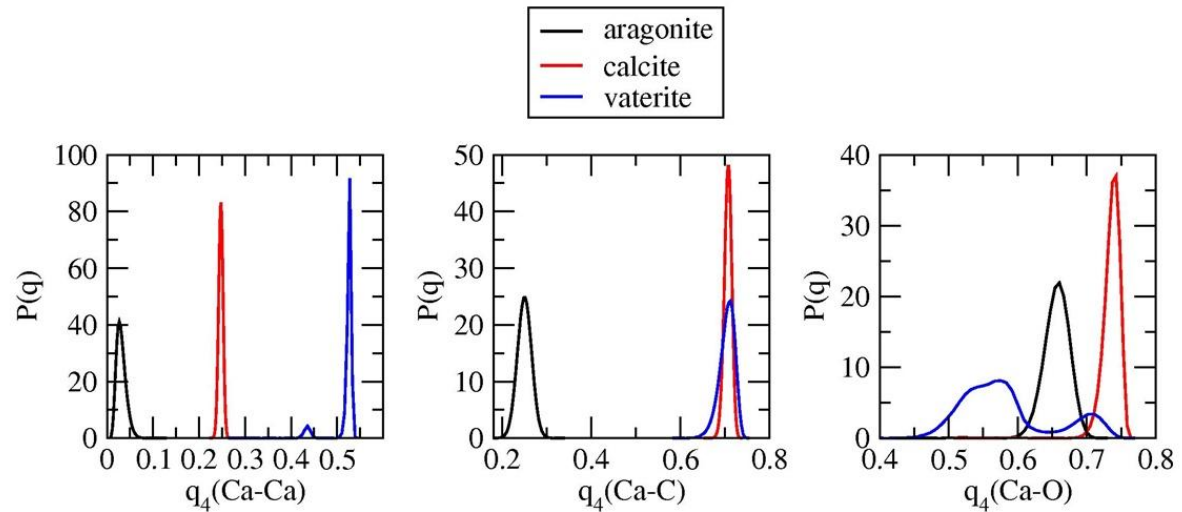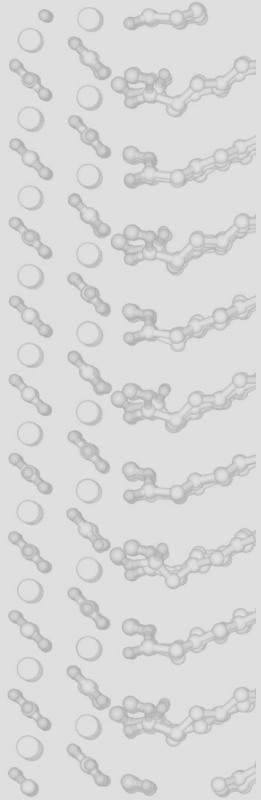
Surface identification

- **Epitaxial order parameter:** Compares Ca-Ca surface vectors at the SAM to known low energy surfaces.

- **Dominant carbonate angle:** Compared to that in bulk with crystal orientated perpendicular to known low energy surfaces.

N.B. Crystal not necessarily perpendicular to dominant exposed surface.
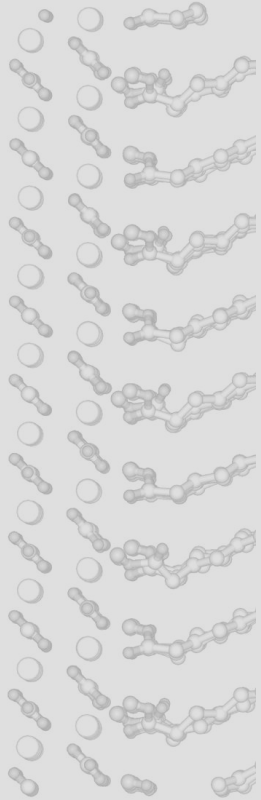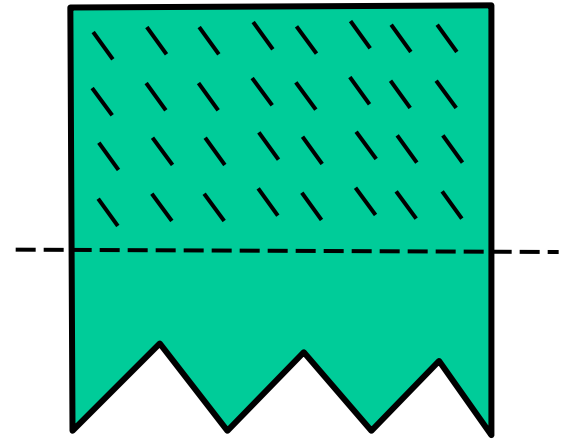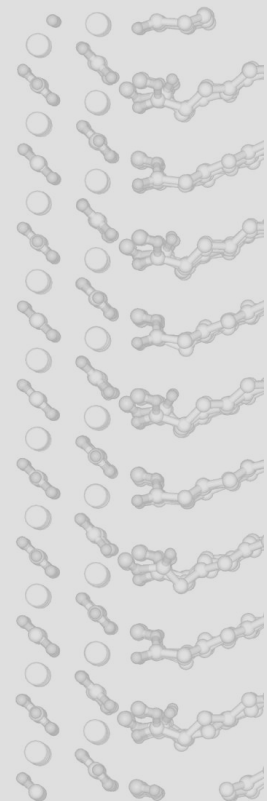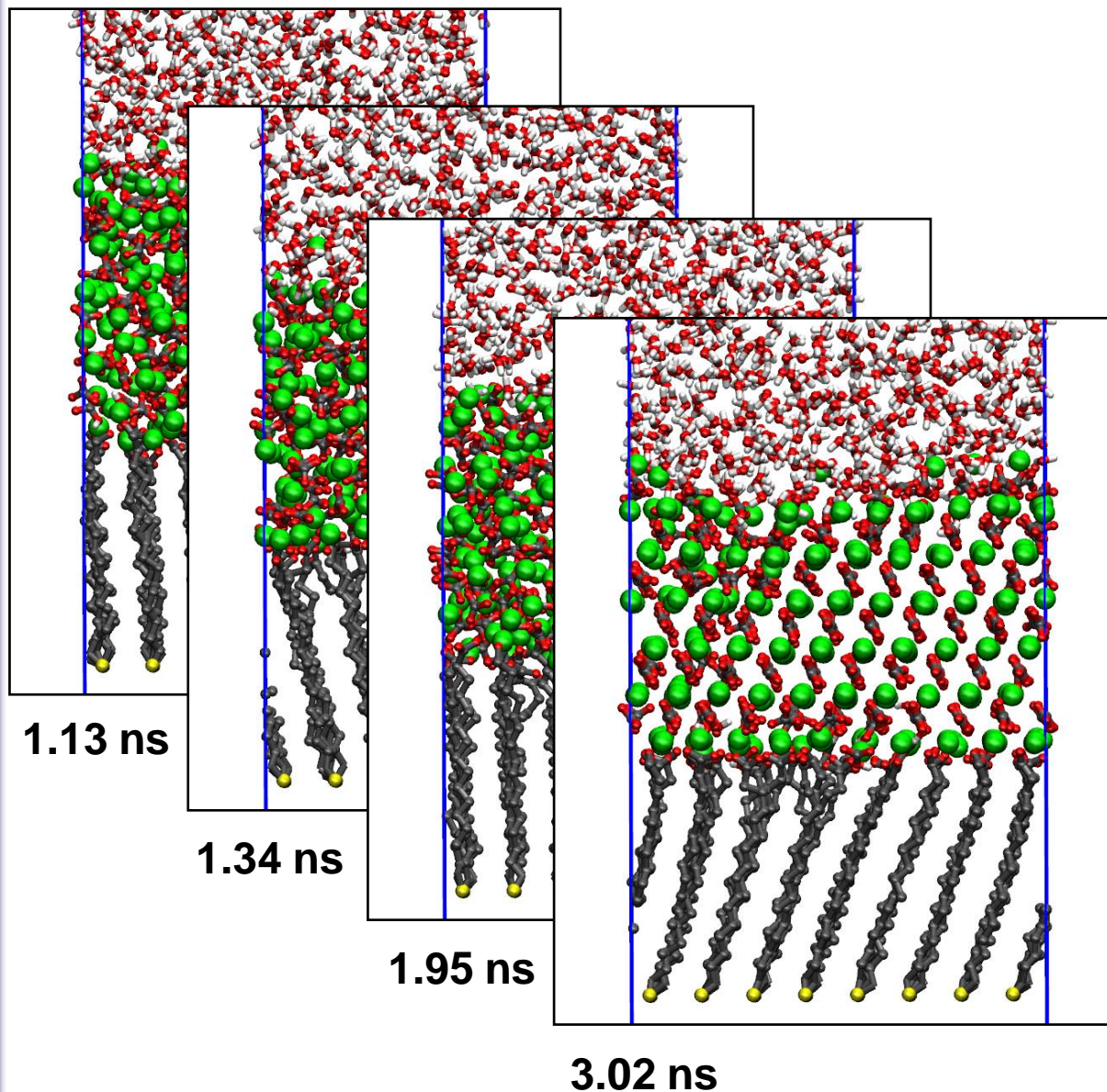
Outline

- Calcium carbonate and biomineralisation.

- Growth on self-assembled monolayers.

- Direct simulations and metadynamics.

- Testing and analysis.
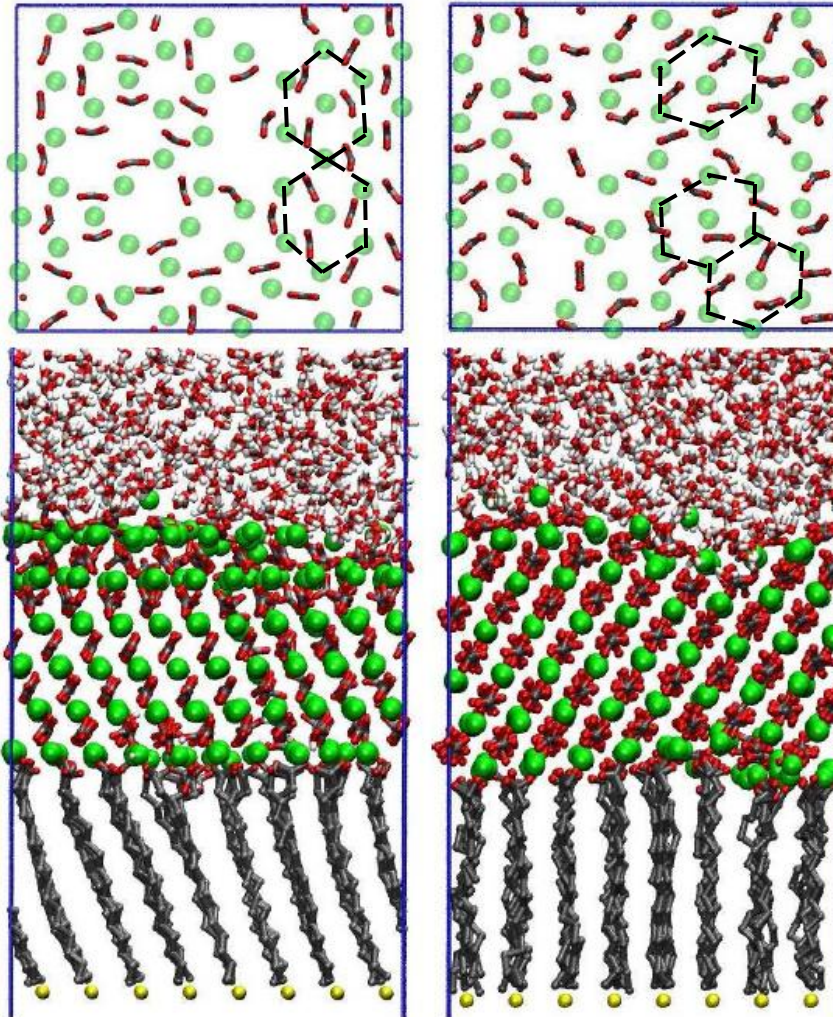
- **Results and challenges.**

Crystallisation on MHA

1.13 ns

1.34 ns

1.95 ns

3.02 ns

Crystallisation on MHA

**39 % bulk calcite
(012) nucleation plane**

**36 % bulk calcite
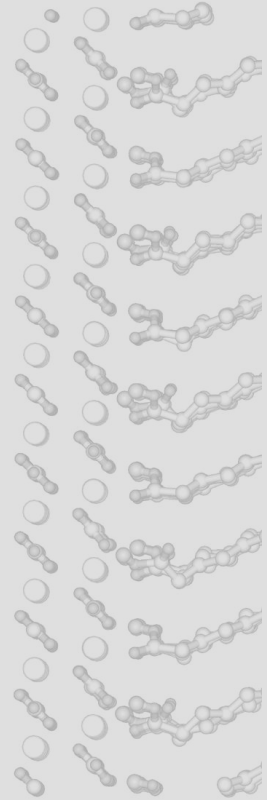(012) nucleation plane**

Lattice matching only over small area

Bicarbs+initial line defect on left.

No bicarbs on right.

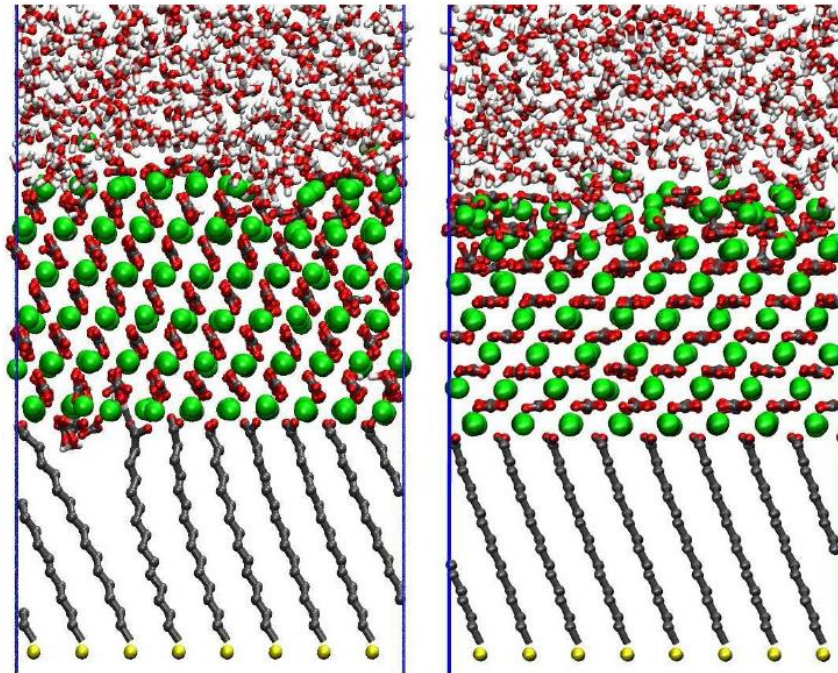**Flexibility leads to experimental result regardless of initial conditions.**

Frozen MHA

**44 % bulk calcite
(012) nucleation plane**

**54 % bulk calcite
(001) nucleation plane**

**Bicarbs+initial line
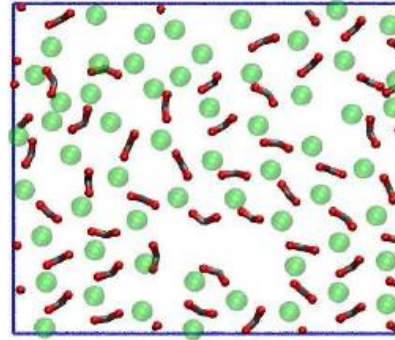defect on left.**

No bicarbs on right.

Freezing the monolayer leads to selection expected by purely epitaxial arguments.

Crystallisation on MPA

55 % bulk calcite (116) nucleation plane
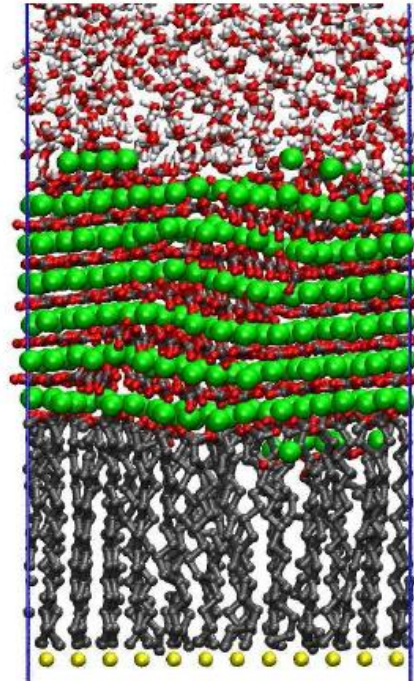
43 % bulk calcite Boundary problem?

Lattice matching in 116 case?

Bicarbs+initial line defect on left.

No bicarbs on right.
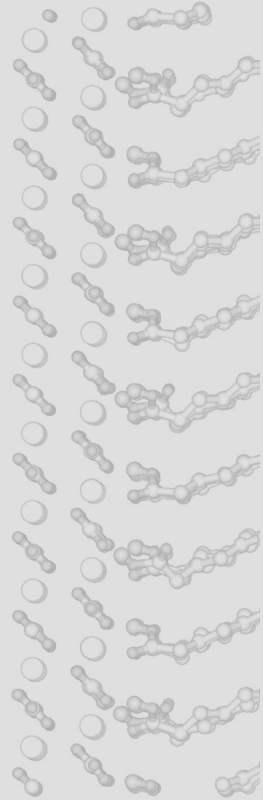
Successes
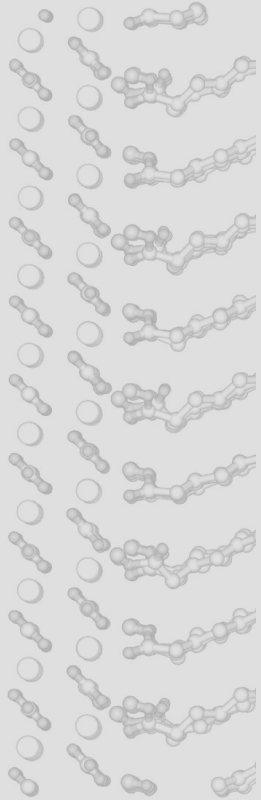
- Predict experimentally observed orientation on *fully ionised* MHA SAMs without imposing defects.

- Demonstrated that only *local* matching required at the interface to support (012) over (001).

- Suggests nucleation of combined SAM-calcite order rather than "nucleation of calcite" on the SAM.

- Also reproduced experimentally observed orientation on MPA and hence the odd-even effect.

Challenges

- Results on partially / non-ionised SAMs ambiguous.
    - Crystallises with (104) exposed.
    - Or crystallises very slowly.

- How to choose the distribution of ionised functional groups and its evolution?
    - Frozen with localised ionisation leads to (001) on MHA.
    - Flexible with uniform ionisation crystallises poorly.

- What is missing from (012) vs (001) surface energy calculations on MHA?

- Possible boundary and finite-size effects.

- Order parameter free methods?

Acknowledgements

Dr David Cooke

Dr Bill Smith

Dr Ilian Todorov

Dr Martyn Foster

Centre for Scientific Computing

EPSRC

Engineering and Physical Sciences
Research Council

HECToR

Modelling of the Biological Interface with Materials