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

D. Quigley¹, C. L. Freeman², P. M. Rodger³, J. H. Harding² and D. M. Duffy⁴

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.
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Calcium Carbonate

Aragonite

Calcite

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

- Based on the model of Pavese et al. [Pavese et al, Phys. Chem. Miner. 19, 90 (1992)]

\[
q_{\text{oxygen}} = -1.045 \\
q_{\text{carbon}} = +1.135
\]

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

<table>
<thead>
<tr>
<th>surface (hexagonal indices)</th>
<th>( \gamma_{\text{pure}} )</th>
<th>( E_{\text{attach}} )</th>
<th>( \gamma_{\text{hydrated}} )</th>
<th>( E_{\text{hydration}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>{1014}</td>
<td>0.59</td>
<td>-75.4</td>
<td>0.16</td>
<td>-93.9</td>
</tr>
<tr>
<td>{0001}Ca</td>
<td>0.97</td>
<td>-334.3</td>
<td>0.68</td>
<td>-79.2</td>
</tr>
<tr>
<td>{0001}CO(_3)</td>
<td>0.99</td>
<td>-204.7</td>
<td>0.38</td>
<td>-93.2</td>
</tr>
<tr>
<td>{1010}</td>
<td>0.97</td>
<td>-759.6</td>
<td>0.75</td>
<td>-100.5</td>
</tr>
<tr>
<td>{1011}Ca</td>
<td>1.23</td>
<td>-307.2</td>
<td>0.63</td>
<td>-113.4</td>
</tr>
<tr>
<td>{1011}CO(_3)</td>
<td>1.14</td>
<td>-276.7</td>
<td>0.81</td>
<td>-100.9</td>
</tr>
<tr>
<td>{1120}</td>
<td>1.39</td>
<td>-291.3</td>
<td>0.43</td>
<td>-138.5</td>
</tr>
</tbody>
</table>

Biomineralisation


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.

\[
\begin{align*}
\text{Functional group} & : R \quad R \quad R \quad R \\
\text{Alkanethiol} & : \text{Au / Ag} \\
\end{align*}
\]

- Even: 16-mecaptohexadecanoic acid (MHA)
- Odd: 15-mecaptopentaadecanoic acid (MPA)
Calcite Growth

(012) nucleation plane on MHA

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

<table>
<thead>
<tr>
<th>Chain parity</th>
<th>Even (MHA)</th>
<th>Odd (MPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation plane (Au substrate)</td>
<td>(012) or (01x) x=2-5</td>
<td>(110) (113) (116)</td>
</tr>
</tbody>
</table>

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 $\gamma_{\text{calcite-sam}}$ 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).

<table>
<thead>
<tr>
<th></th>
<th>(0001)</th>
<th>(01̅2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_{cm}$ (J m$^{-2}$)</td>
<td>$m$</td>
</tr>
<tr>
<td>even (MHA)</td>
<td>0.081</td>
<td>-0.62</td>
</tr>
<tr>
<td>odd (MPA)</td>
<td>0.086</td>
<td>-0.66</td>
</tr>
</tbody>
</table>

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Direct Simulations

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

\[ G_{\text{bulk}} = \frac{4}{3} \pi \Delta \mu r^3 \]

\[ G_{\text{surf}} = 4\pi \gamma r^2 \]

\[ \Delta \mu = \mu_{\text{sol}} - \mu_{\text{liq}} \]

Competition of bulk and surface free energy

Typically \( \Delta G_{\text{crit}} \sim 10 \text{ to } 100 \text{ } k_B T \)
Augment the Hamiltonian with a history dependent potential $V$ written as a function of some collective variables $s$, 

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

$V$ is constructed as,

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

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

$$F_G(s) = -\lim_{t \to \infty} V[s(r^N), t].$$
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 $Q_4$, $Q_6$, $\xi$ and potential energy as an order parameter.
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$_3$).

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

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

<table>
<thead>
<tr>
<th>pair type</th>
<th>calcite</th>
<th>aragonite</th>
<th>vaterite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_4$(Ca-Ca)</td>
<td>0.2464</td>
<td>0.0046</td>
<td>0.5033</td>
</tr>
<tr>
<td>$Q_6$(Ca-Ca)</td>
<td>0.4882</td>
<td>0.3999</td>
<td>0.4443</td>
</tr>
<tr>
<td>$Q_4$(Ca-C)</td>
<td>0.7053</td>
<td>0.2411</td>
<td>0.4082</td>
</tr>
<tr>
<td>$Q_6$(Ca-C)</td>
<td>0.4863</td>
<td>0.4461</td>
<td>0.1122</td>
</tr>
<tr>
<td>$Q_4$(Ca-O)</td>
<td>0.5247</td>
<td>0.4082</td>
<td>0.0503</td>
</tr>
<tr>
<td>$Q_6$(Ca-O)</td>
<td>0.2215</td>
<td>0.1076</td>
<td>0.2110</td>
</tr>
<tr>
<td>$Q_4$(C-C)</td>
<td>0.2470</td>
<td>0.5247</td>
<td>0.1848</td>
</tr>
<tr>
<td>$Q_6$(C-C)</td>
<td>0.4881</td>
<td>0.4983</td>
<td>0.4204</td>
</tr>
<tr>
<td>$Q_4$(C-O)</td>
<td>0.8216</td>
<td>0.5137</td>
<td>0.1319</td>
</tr>
<tr>
<td>$Q_6$(C-O)</td>
<td>0.7988</td>
<td>0.6698</td>
<td>0.2999</td>
</tr>
</tbody>
</table>

bulk values for 300 units
Nanoparticles

- 52,113 steps with $w=3.78 k_B T$ (13 ns).
- 67,091 steps with $w=1.0 k_B T$ (15.5 ns).

- Convergence of free energies is very slow.

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


- 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

\[ \tau_G = 0.25 \text{ps} \]

\[ \tau_G = 0.20 \text{ps} \]

\[ \tau_G = 0.15 \text{ps} \]

\[ \tau_G = 0.05 \text{ps} \]

--------- (104)
Phase assignment

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

\( \text{Ca}^{2+} \)

\( \text{CO}_3^{2-} \)
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.
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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

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

Bicarbs+initial line defect on left.

No bicarbs on right.

44 % bulk calcite (012) nucleation plane

54 % bulk calcite (001) nucleation plane
Crystallisation on MPA

Lattice matching in 116 case?

Bicarbs+initial line defect on left.

No bicarbs on right.

55% bulk calcite (116) nucleation plane

43% bulk calcite Boundary problem?
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