Multiscale modelling of clay-polymer nanocomposites

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Multiscale modelling: From Fundamental Understanding to Predictive Design of Layered Nanomaterials

- Aims of the project: To develop **quantitative** coarse-grained models of clay-polymer nanocomposites.
  - These models will be used to predict the thermodynamically favourable states of the composites.
  - These models will also be able to predict their elastic properties.

Clay + Polymer

This requires:

- Accurate potentials
- Realistic structures
- Task farming many different clays and polymer systems to create constitutive models of their properties.
Materials Science: Nanocomposites

- Mixture of properties of two different materials to give enhanced performance.
- Improved fire retardant properties.
- Similar performance to other composites at much lower filler volumes.
- Improved barrier properties to gases.
What is a Clay-Polymer Nanocomposite?

Montmorillonite clay

• Aluminosilicates such as montmorillonite clay sheets carry a negative charge.
• This is charge-balanced by cations such as Na\(^+\) and K\(^+\).
• The nano-scale clay sheets may be dispersed within a polymer in three ways:
  – As tactoids
  – With the polymer intercalated
  – Exfoliated
• Research shows a mixture of the latter two is typical.
Clay swelling

• The problem: Water based drilling fluid + reactive shale = swelling

• Source of the problem – smectite (i.e. montmorillonite clay) content

• Driving force for swelling / destabilisation is chiefly hydration of the interlayer Na$^+$ ions.

• Need to develop clay swelling inhibitors, which either replace the Na cations or bind to them - a high clay volume polymer-nanocomposite
Large-Scale Simulations of Clays

- Bending modulus computed from spectral analysis of sheet undulations

Clay-Polymer Nanocomposites: Elastic Properties

If we assume each mode of vibration has the same energy of $1/2 \ k_B T$ (the equipartition principle, with $k_B$ the Boltzmann constant), the amplitude of undulations becomes:

$$<h^2(k)> = \frac{k_B T}{A(k_c k^4 + \gamma k^2)}$$

where $A$ is the clay sheet area.

We see $k^{-4}$ behaviour at long wavelengths, the gradient is $k_c$.

Artifact due to imposed periodicity of model.

The collective motion exhibiting $k^{-4}$ behaviour is only apparent with wavelengths greater than 15 nm.
Clay polymer nanocomposites

- Large scale molecular dynamics simulations of an exfoliated sheet of montmorillonite immersed in amorphous poly(ethylene) glycol (PEG)

- We analyse the mechanical response of the system, and determine how the resistance of the polymer changes with distance from the clay sheet.

- This requires very large systems sizes, such that the polymer and clay sheets are of realistic size.
Clay polymer nanocomposites

• We find the polymer chains have a different conformation when adsorbed on the surface of the clay, due to the presence of the cations

Kink in the PEG chain, to allow polymer oxygen atoms to complex to the sodium ion
Clay polymer nanocomposites

- The different conformations of the innermost layer of polymer chains gives it more mechanical strength than polymer further away from the clay surface.

Inner-most layer of polymer
larger Young’s modulus

Stress-strain behaviour of the polymer in a clay polymer nanocomposite

The elastic response of the polymer will depend not only on its orientation, but also the proximity to the clay surface.

Any model of nanocomposites must reflect this.

(Soft Matter, 2009, 5, 2239. DOI: 10.1039/b822666k)
Clay-polymer Nanocomposites: multiscale modelling

- The question of whether periodic boundary conditions become limiting at large length scales remains to be addressed.
- **Answer: remove periodic boundary conditions!**
  - Simulating “life-sized” clay platelets (approx. 100nm across)
  - Will remove artificial constraints
  - Will allow us to examine unexplored behaviours, such as interactions at clay sheet edges and undulations.

- Clay sheets in a simulation box of water or polymer matrix
- We will require very large systems to ensure our models are realistic: between $10^6$ and $10^8$ atoms
Scale Separation Map

Time scale

Nanoscale level

Mesoscale level

Coarse Grained MD

Classical Molecular dynamics

Electron level

Quantum mechanics, DFT, ab initio MD

CPMD
Multiscale modelling: quantum level

- We want to calculate the interactions of the edge surfaces with water / polymer molecules.
- We calculate atomic charges for the edge atoms through matching to the electrostatic potential, taking into account the periodic boundary conditions (Chen et al. J. Phys. Chem. A, 2010, 114 (37), 10225–10233)
- Check using radial distribution functions at both quantum and classical level.
The length scale of a typical clay platelets is at the upper-limit of today’s computing resources with atomistic molecular dynamics. 

Answer: coarse-grained molecular dynamics, built using details from atomistic molecular dynamics. The two levels of simulation can be coupled together. We use a Boltzmann inversion of the radial distribution functions.
Coarse-Grained Molecular Dynamics

- Grouping atoms together and treating them as one object, which we then integrate over time using molecular dynamics

\[
M^N_R : r^n \mapsto R^N = M^N_R (r^n)
\]

\[
R_I = M_{RI} (r^n) = \sum_i c_{II} r_i
\]

Coarse-Graining is therefore a two stage operation:
1) defining a mapping operator that transforms an atomistic configuration onto a Coarse-Grained configuration
2) creating CG potentials that recreates required properties of the atomistic model (such as structural properties)

Atomistic Configuration Space

\[
p_r (r^n) \propto e^{-u(r^n)/k_B T}
\]

CG Configuration Space

\[
P_R (R^N) \propto e^{-U(R^N)/k_B T}
\]

Noid, Chu, ..., Voth, Andersen

Coarse-Grained Molecular Dynamics: Mapping Operator

If we want to task-farm CG simulations, we need a mechanism for automatically defining the mapping operator from an atomistic system and implementing the procedures required for creating the CG potentials.

From a molecular dynamics atomistic output (which may only contain atom positions) we calculate:

- the connectivity between atoms (may already be in the MD output)
- which molecules are present
- the backbone of these molecules (and side chains etc)
- define these molecules in terms of the Simplified Molecular-Input Line-Entry System (SMILES)
- Use the SMILES definition to compare with a CG fragment library and optimise to define the CG mapping operator.

SMILES: \((-\text{O})\text{C-C-O-C-C-O-C-C-O-C-\text{C(-O)}}\)  
Simple example, poly-(ethylene) glycol
Coarse-Grained Molecular Dynamics: defining an atomistic system

What if we don’t already have an atomistic system defined?

Ideally, we wish to create a realistic initial structure with only a mineral, polymer and their relative concentration as user inputs. We achieve this by:

1. Creating a mineral nanoparticle (with user defined shape and size), including correctly terminating any unsaturated bonds caused by forming the mineral surfaces.
2. Dispersing particles within a simulation cell box according to a user defined volume fraction.
3. Assigning the atoms to types within a selected forcefield; we may have to use quantum mechanics simulations to parameterise if the atoms are not described by the forcefield.
4. Grow the polymer around the dispersed nanoparticles to create a realistic, low energy initial structure for molecular dynamics simulations.
Coarse-Grained Molecular Dynamics: how do we ensure the accuracy of our CG potentials?

Our previous CG simulations used (somewhat arbitrary) Lennard-Jones parameters – the best we can hope for is qualitative results.

With atomistic systems defined and simulated, we can match features between the CG and atomistic levels to give more quantitative results.

**Structural matching with atomistic simulation:**

Find a pair potential for the coarse-grained system with the equal radial distribution function (RDF) $g(r)$

Target RDF $g_{\text{target}}(r)$ is taken from atomistic simulation

\[
V_{i+1}(r) = V_i(r) + k_B T \ln \left( \frac{g_i(r)}{g_{\text{target}}(r)} \right)
\]

Called the **Inverse Boltzmann Method (IBI)**

Note: neglects higher (> 2) body effects
Coarse-Grained Molecular Dynamics

- We have developed our own in-house code to perform IBI for LAMMPS simulation output.

Example of IBI for poly(ethylene)-glycol polymer (showing the first three iterations)

Extrapolation is required at low distance – however, these points are rarely visited in the simulation.

Problem with IBI: pressure is not conserved

Pressure is too large (it is not matched in the construction of the CG polymer potentials). We could apply an additional correction term – although this may remove the structural matching!

We are currently modifying the IBI procedure to include matching to both pressure and structural properties
Coarse-Grained Molecular Dynamics: clays

- CG potentials for clay minerals can not be generated in the same way – a single atomistic simulation can not sample all the arrangements of the clay sheets (interlayer spacing etc)
- Construct CG potentials by matching to potential of mean force calculations
Coarse-Grained Molecular Dynamics: accurate initial structures

- Once we have defined accurate CG potentials, we need to generate realistic polymer-nanocomposite initial structures.
- How do we achieve this? We do not have crystal structures – the polymers are often in a melted or amorphous state.

The relaxation time for large conformational changes in polymer melts can easily exceed the nanosecond MD time scale – we can not simply melt a polymer crystal, especially for long polymer chains.

Instead, we use a configuration bias monte carlo growth scheme to grow polymers, atom by atom, around clay nanoparticles.

This has been written and implemented for both atomistic and coarse-grained systems to create realistic initial structures.
Multiscale simulation

- As we have developed more accurate methods, both in the parameterization and initial conditions of the CG and atomistic systems, the coupling between levels has become more complicated.
- These will be integrated into the MAPPER scheme.
Multiscale simulation of clay nanocomposites: conclusions

• Deriving coarse-grained potentials that can be used for quantitative prediction is a non-trivial task.

• Creating realistic polymer-nanoparticle systems should be carefully considered; the polymer relaxation timescale means you are unlikely to see any major conformational changes during a simulation.

• We will be commencing production runs in the next few months, using our task farming to parameter sweep through a large-number of polymer/clay combinations, after we have completed our validation.

• We will then be integrating these steps into the MAPPER framework, following on from the simple coupling used last year.

• Next step: reverse mapping atomistic MD from coarse-grained structures.
Multiscale modelling: Pictures