Durham University

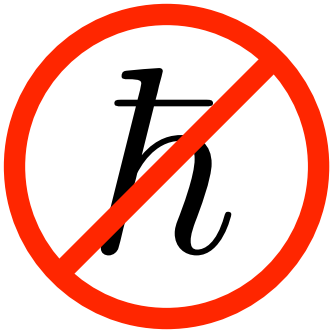
# Mathematical Aspects of Computational Chemistry

Mark Miller
Durham Chemistry
m.a.miller@durham.ac.uk

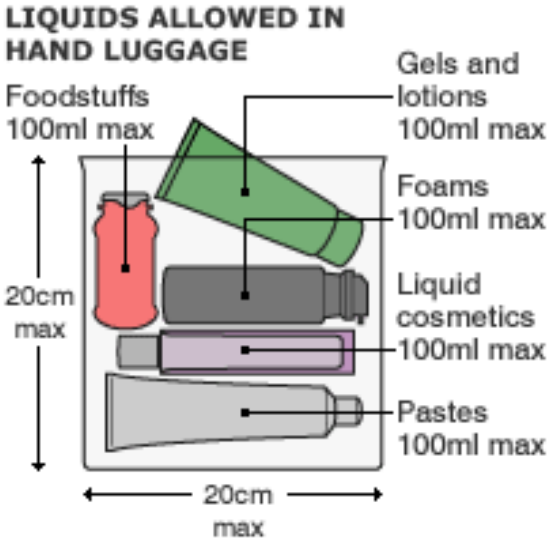
15 June 2017

# Research themes

- Computational chemistry (classical versus quantum)



- Soft matter



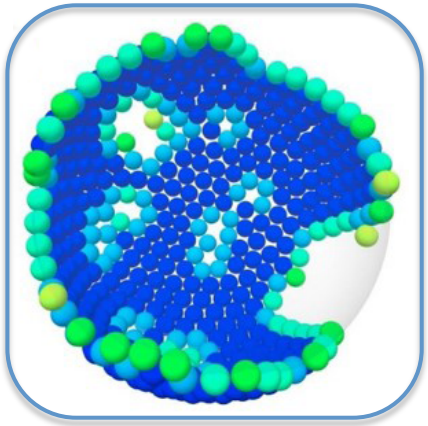

news.bbc.co.uk

- Coarse-grained modelling

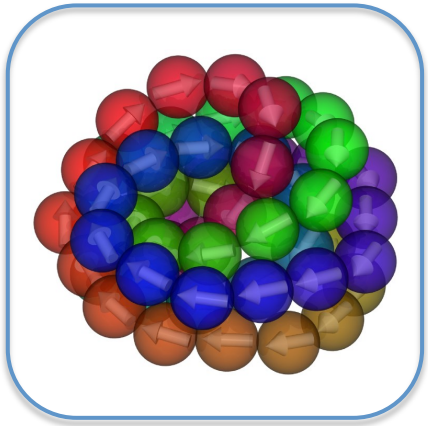
fotonin.com

2.bp.blogspot.com

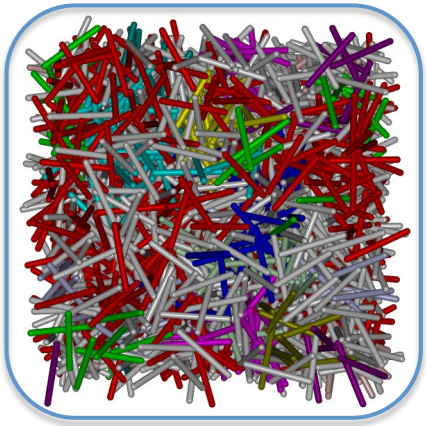
# Survey of projects



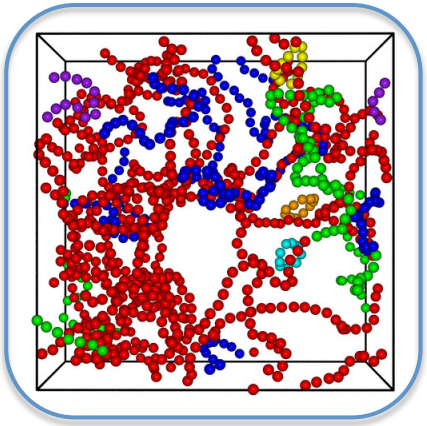
curved surfaces



knots

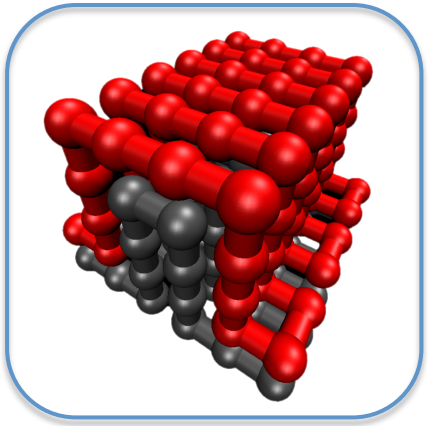


percolation



gels

self assembly

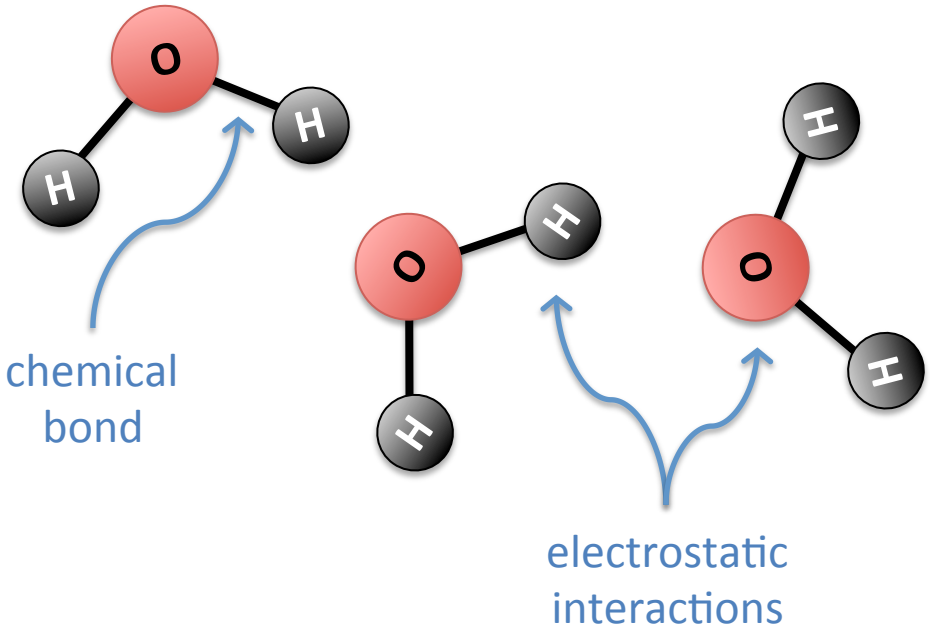


bio-inspired

# 1. Molecular Simulation

Energetic interactions + General laws of physics ⟶ Complex physical and chemical behaviour

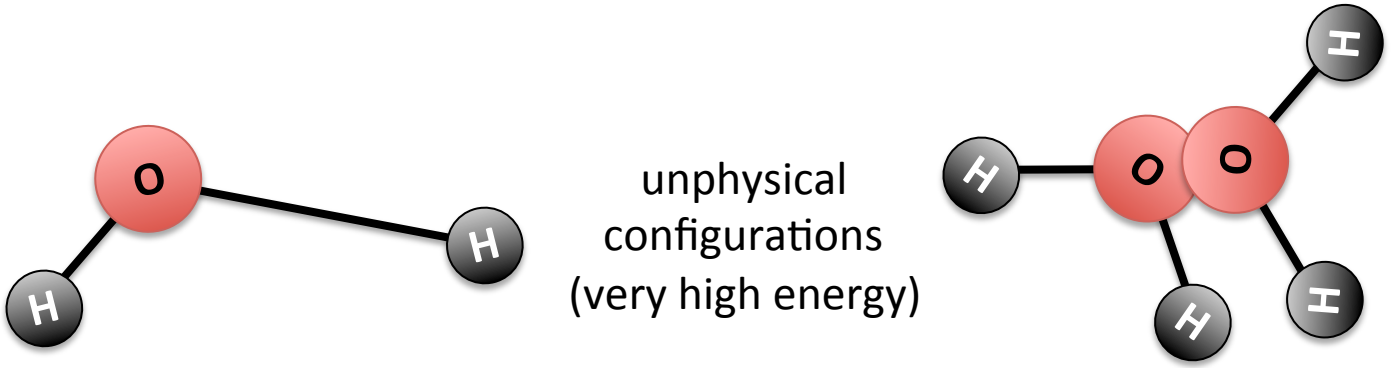
e.g. Newton's laws




- Freezing
- Boiling
- Viscosity
- Solvent properties
- + much more

# Molecular Simulations [cont.]

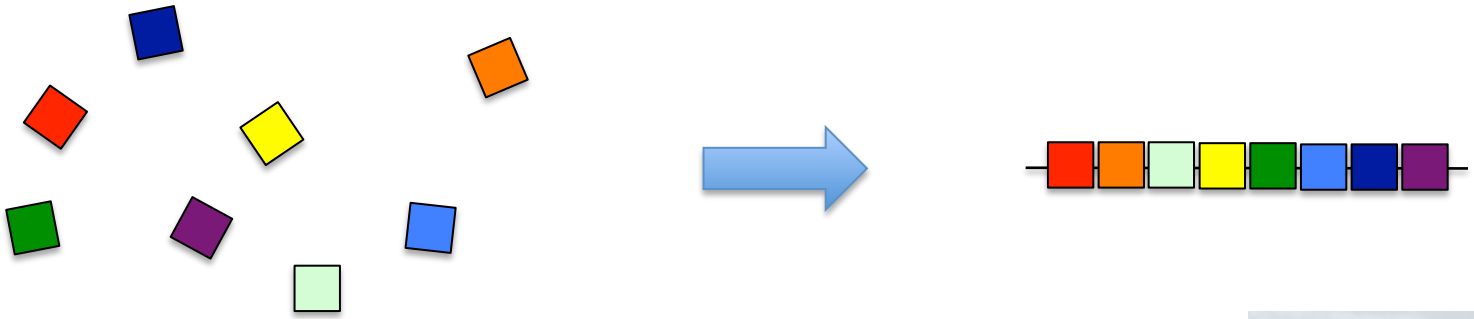
- Configuration $\mathbf{X}$ of $N$ atoms: $\mathbb{R}^{3N}$
- Potential energy: $3N$-dimensional scalar field $V(\mathbf{X})$
- Equilibrium statistical weight $\rho^{\mathrm{eqm}}(\mathbf{X}) \propto e^{-V(\mathbf{X})/kT}$




- Only a tiny fraction of configuration space is relevant
- Must navigate correctly: $\hat{A}\boldsymbol{\rho}^{\mathrm{eqm}} = \boldsymbol{\rho}^{\mathrm{eqm}}$
- and efficiently: $\lim_{n\to\infty} \hat{A}^n \boldsymbol{\rho} = \boldsymbol{\rho}^{\mathrm{eqm}}$

# 2. A Constrained Optimisation

- Addressable self-assembly
  - Spontaneous formation of a target structure
  - All components of target are unique

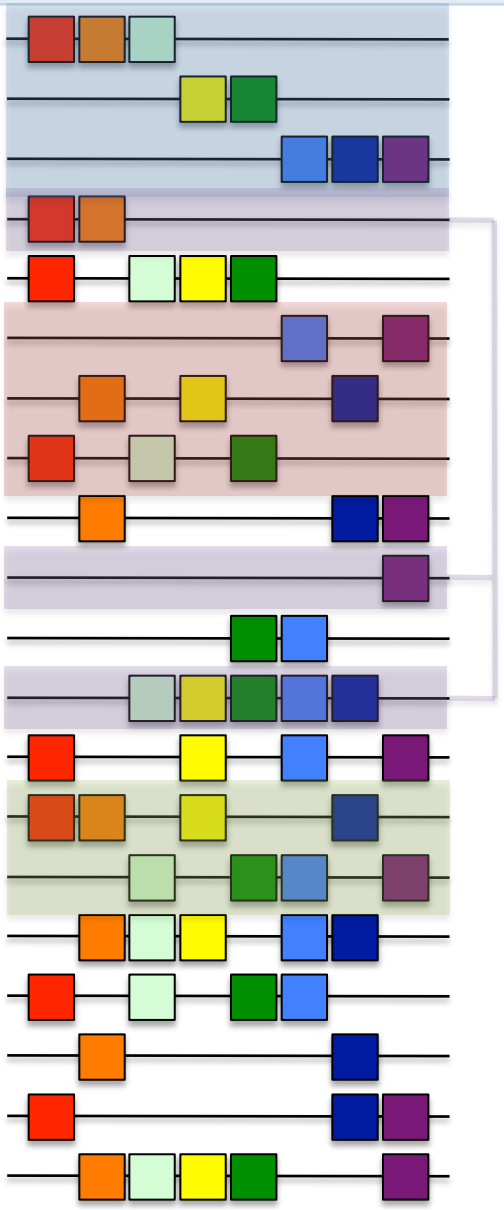


- Possible obstacles
  - Incorrect fragments (wrong partners bind)
  - Multiple correct fragments compete

Dr David Bourne

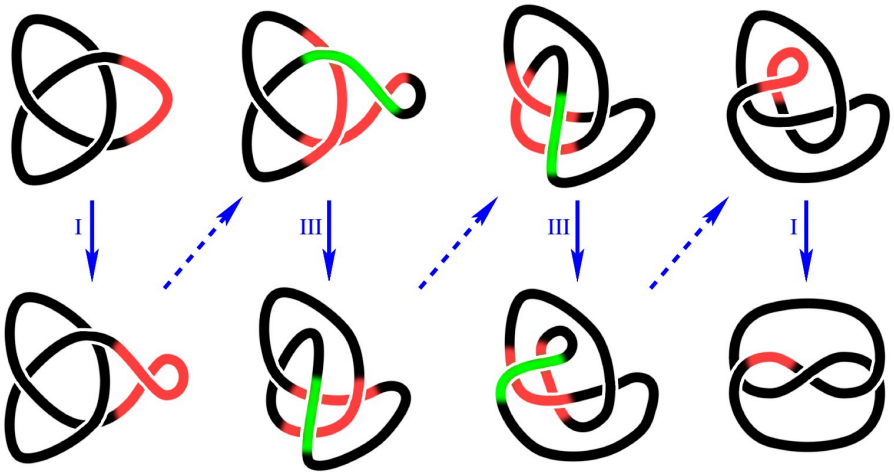
# A Constrained Optimisation [cont.]

- How frustrated are a given set of fragments?
- Combine into largest possible sets:
  - using each fragment no more than once
  - with no repeats of a given component in a set
- Constrained integer optimisation
- Quantify “completability”



# 3. Topological Invariants

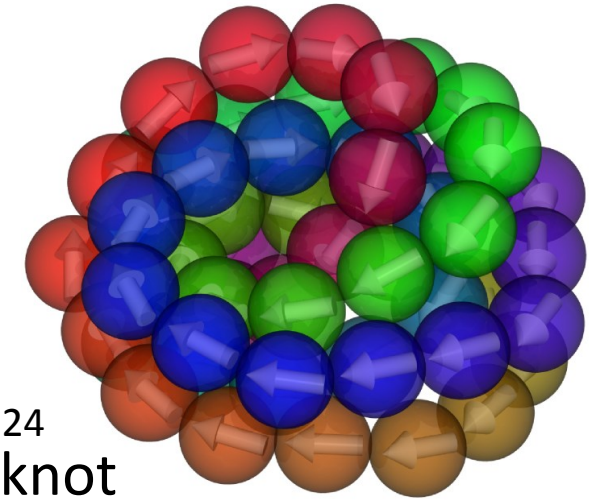
- Knots and links
  - Identification by topological invariants
  - Polynomial invariants: Jones, HOMFLY…




trefoil knot

$$V(t) = t + t^3 - t^4$$

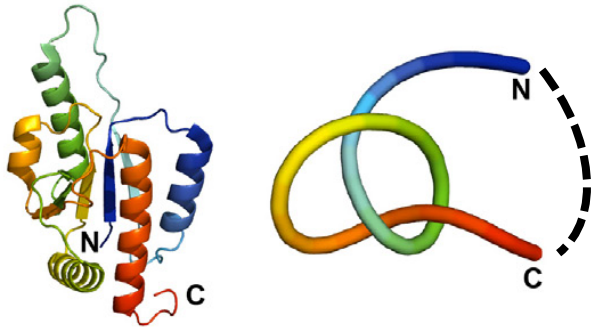
- Knotted clusters
  - Energy optimisation
  - Rearrangement pathways



$10_{124}$
torus knot

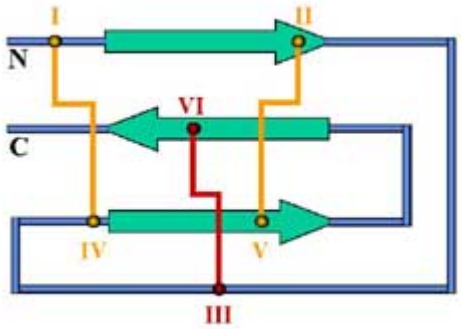
# Topological Invariants [cont.]

- Knotted proteins
  - Closure needed for open chain




Lim & Jackson
J Phys Cond Matt **27** 354101 (2015)

- Bonding networks
  - Topological invariants of (branched) graphs
  - Yamada polynomial




Dr Andrew Lobb