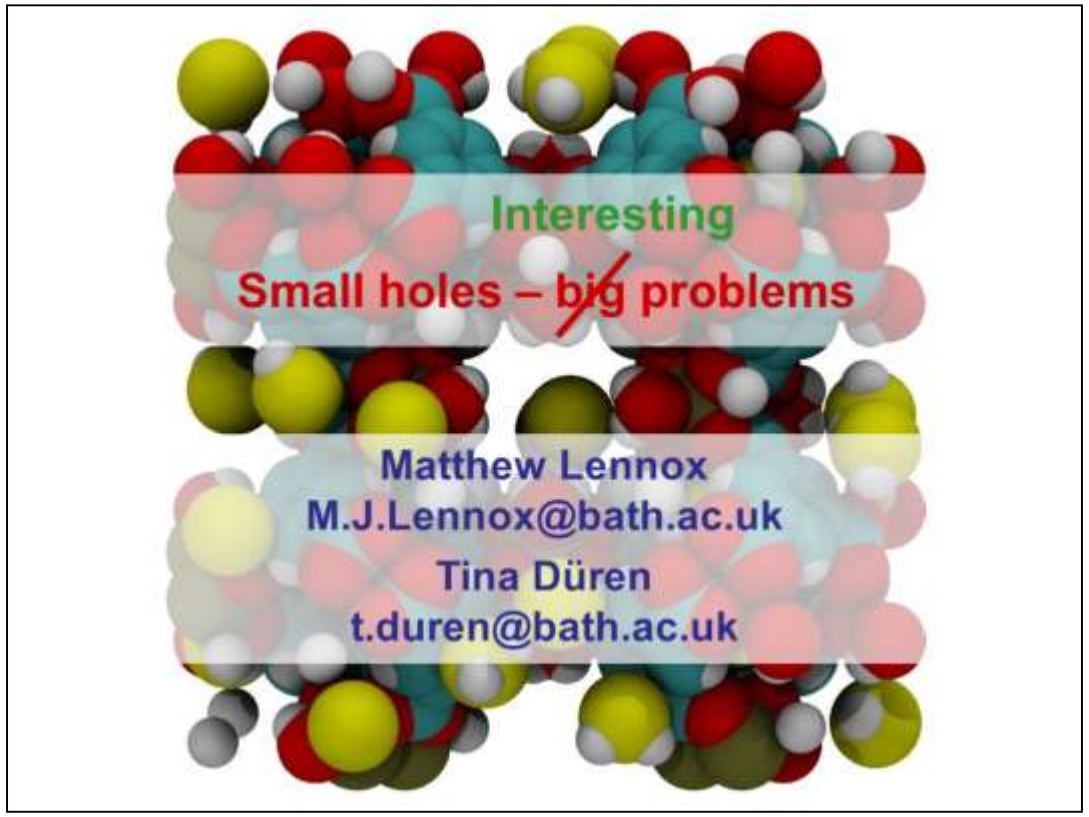

Interesting
Small holes – ~~big~~ problems
Matthew Lennox
M.J.Lennox@bath.ac.uk
Tina Düren
t.duren@bath.ac.uk

What is adsorption?

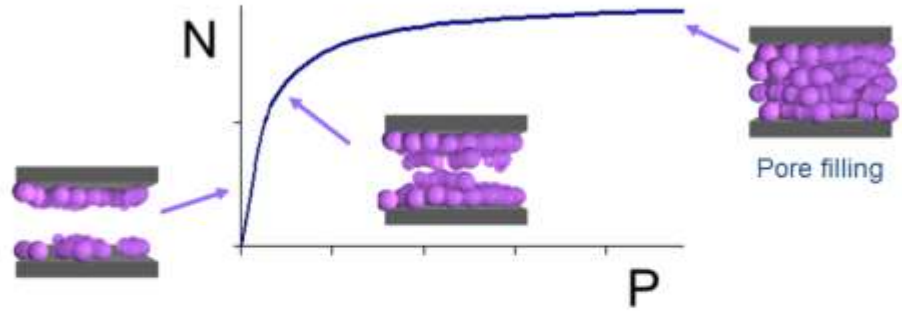
Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface.

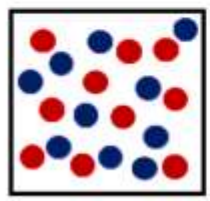
Adsorption
Surface process

Absorption
Bulk process

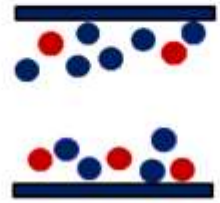
http://teaching.ust.hk/~ceng510/notes/CENG511/Lecture5.pdf

Adsorption isotherms & selectivities





y: mole fraction in bulk
$y_{red} = 0.5$



x: mole fraction in pore
$x_{red} = 2/3$

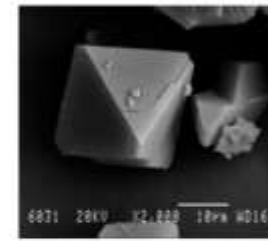
$$\text{Selectivity} = \frac{x_1/x_2}{y_1/y_2}$$

$S_{blue\ /\ red} = 2$

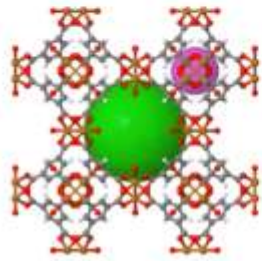
Length scales : from adsorption columns to individual molecules in the solid

m

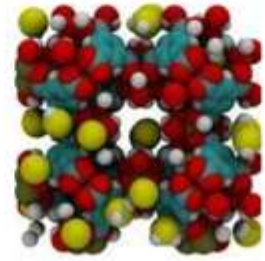
mm



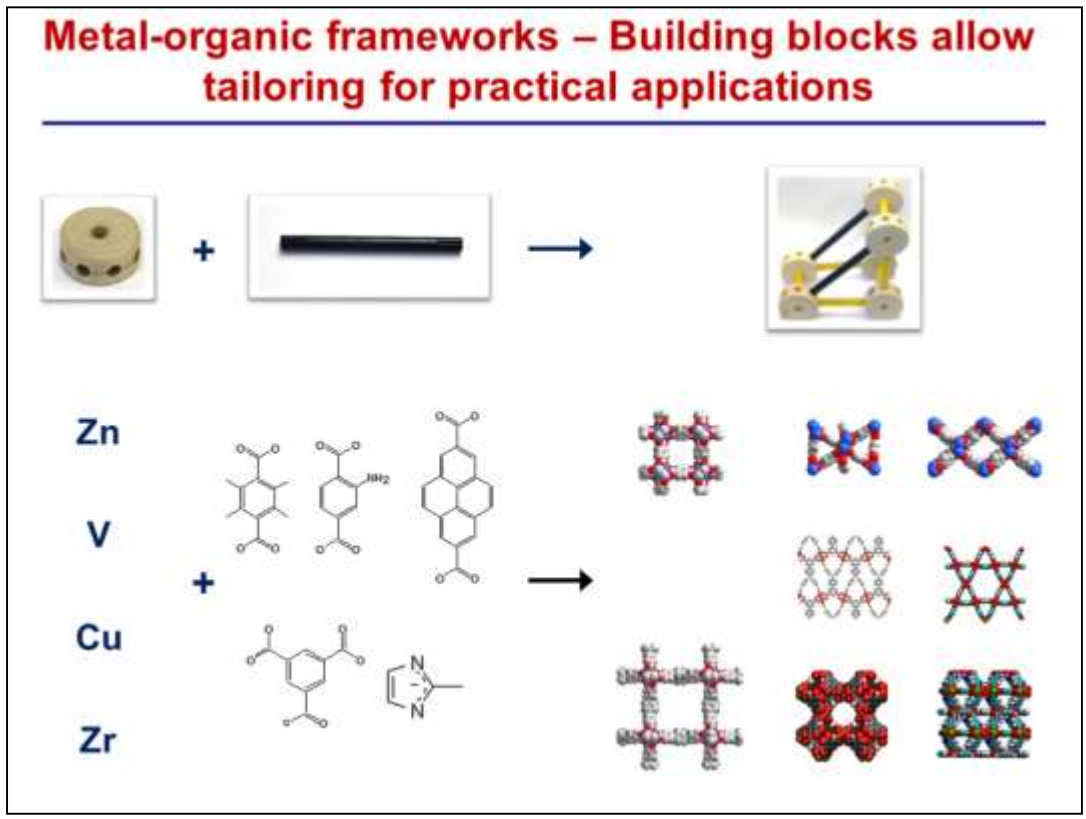
µm



nm = 10^{-9} m



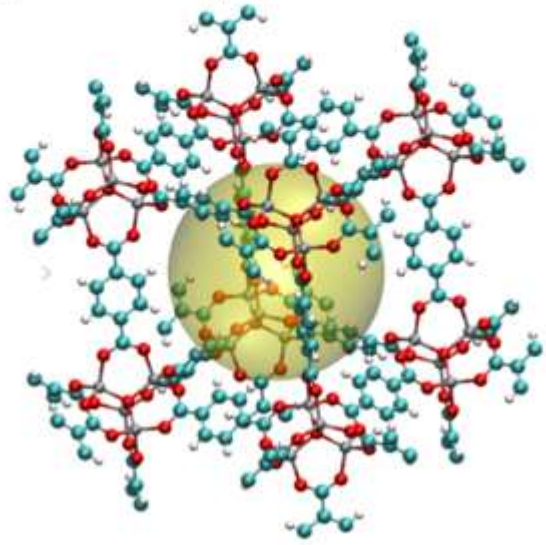
CO_2 & SO_2 in CuBTC

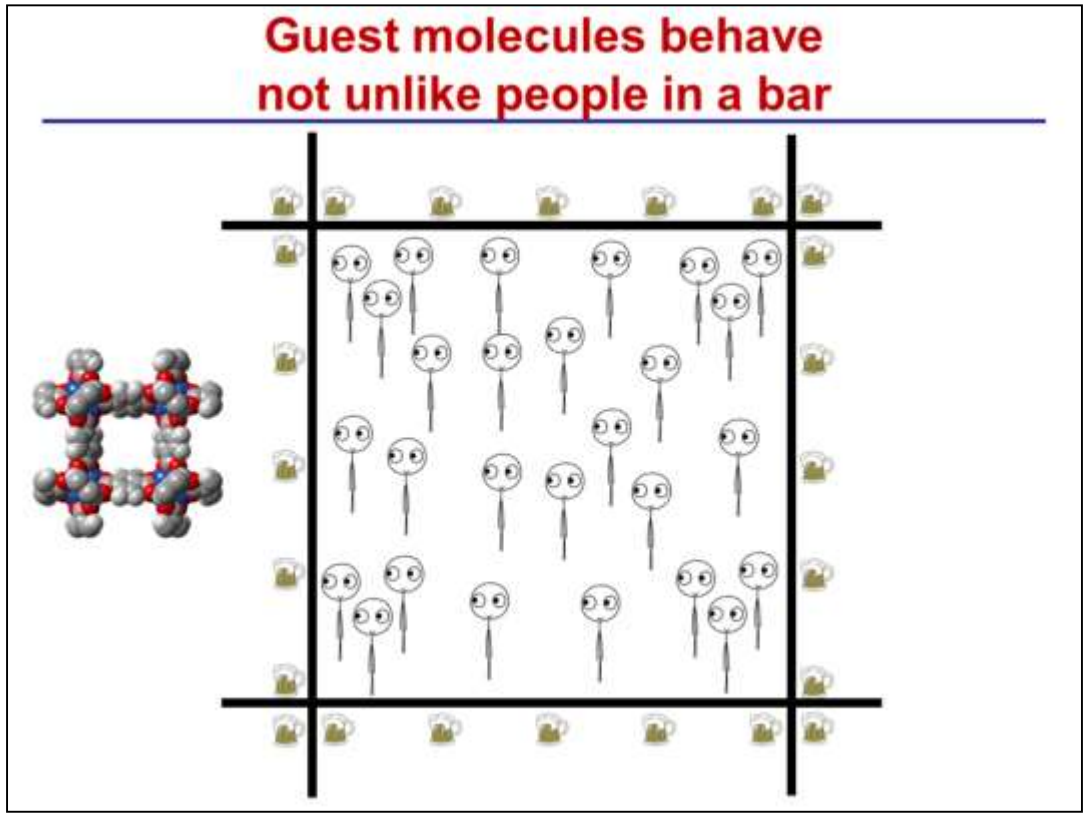


Lots of combinations – thousands of possible structures! How can we quickly identify promising MOFs for a particular application? How can we identify a good application for a new MOF?

What is it like inside IRMOF-1?

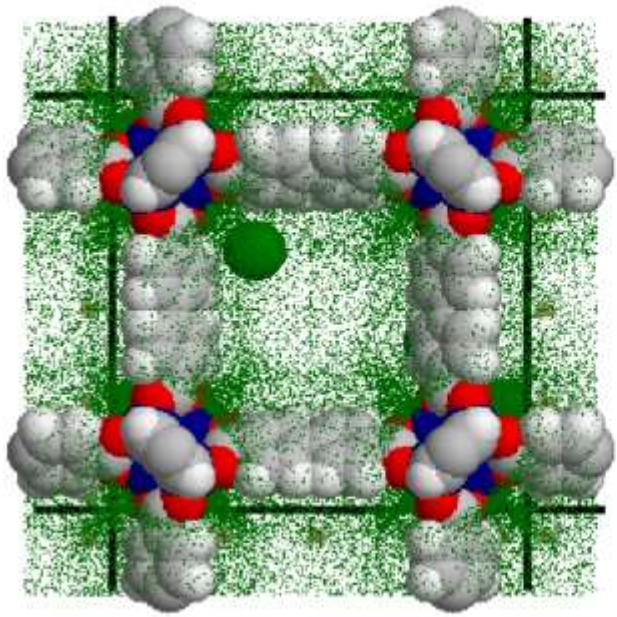
Video removed for ease of distribution – instead you get a pretty ball-and-stick diagram of IRMOF-1. The yellow sphere indicates empty space in the MOF (it is roughly 1 nm in diameter)

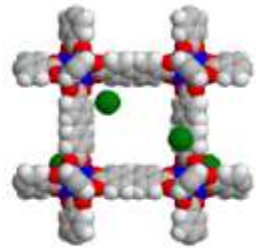


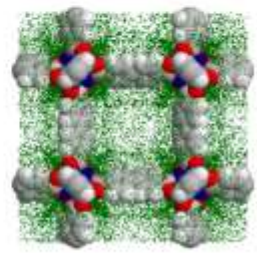


People tend to cluster near the beers – in a MOF, molecules will tend to hang out in locations where there are strong interactions with the framework (e.g. maximising the number of nearby framework atoms)

Low coverage, N ~ Q_{st}

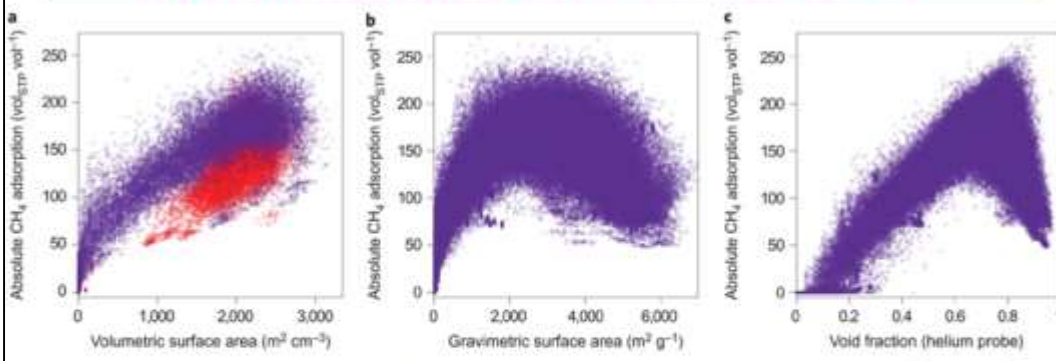






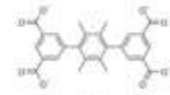
Lots of combinations – thousands of possible structures! How can we quickly identify promising MOFs for a particular application? How can we identify a good application for a new MOF?

Computational screening of 137,953 hypothetical MOFs for methane storage

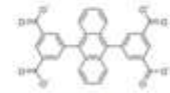


- Screening allows finding promising
  - Structures (NOTT-107 better than PCN-14)
  - Functional groups (methyl, ethyl, propyl)

NOTT-107



PCN-14

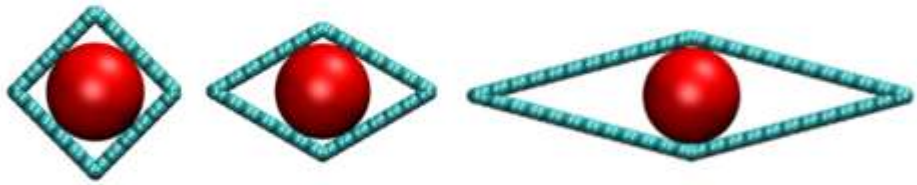


- But contain no information about how (if) structures can be synthesised.

Work from Northwestern University : C.E. Willmer et al Nature Chemistry 4, 83–89 (2012)

Geometry: size is not enough

- Pores often described by largest sphere diameter:

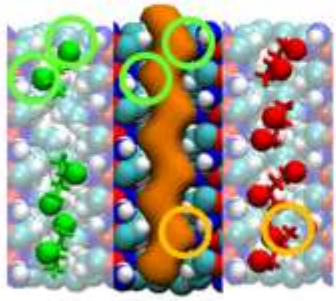


- Same 'size' but very different performance!

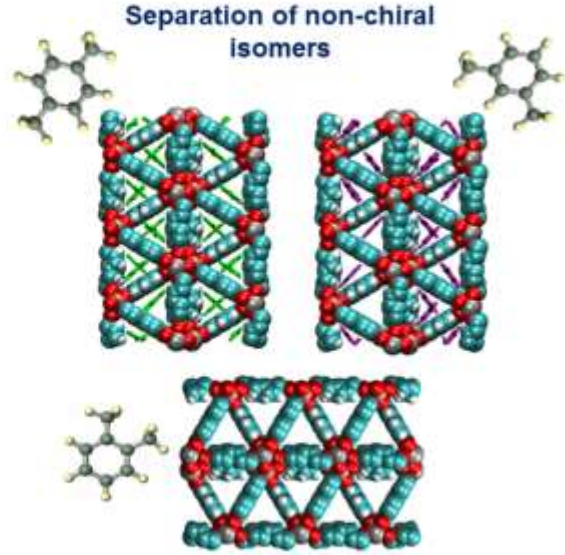
Can we quantify/characterise by shape – even for complex pore geometries?

Shape: important for (some) separations

Chromatographic separation of chiral molecules



Separation of non-chiral isomers

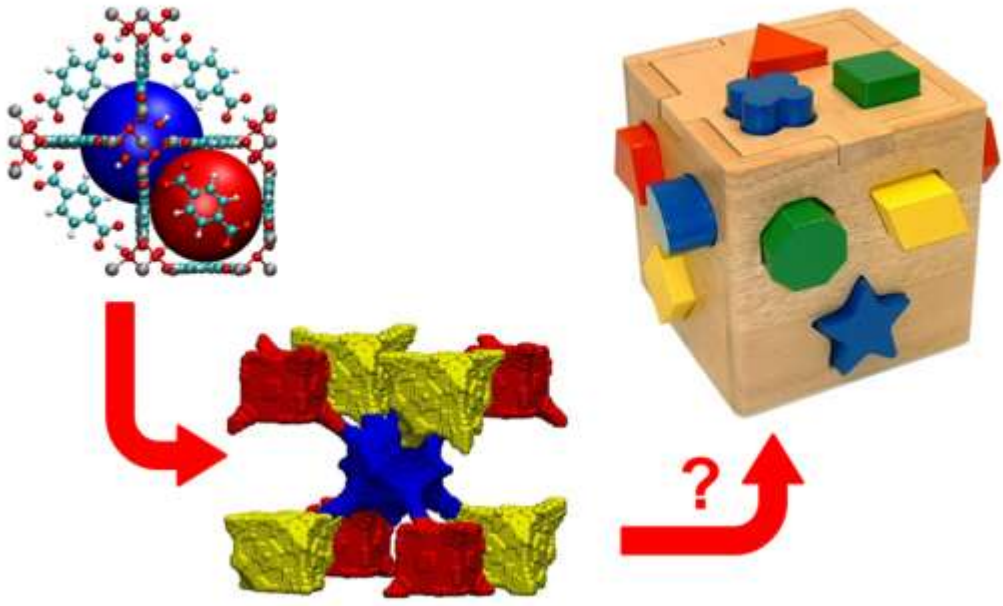


Is there a clever way of finding "similarity"?

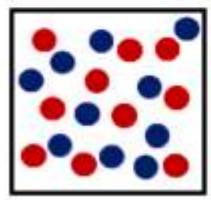
(1) Can we group MOFs by similarity? E.g MOF A has these particular characteristics, which mean it is pretty good for an application – is there another structure with similar properties?

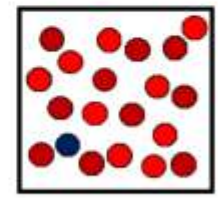
(2) Can we match pore geometries to the geometries of interesting molecules? For some separations, the packing of the molecules is what defines the selectivity or performance.

A new MOF – what can we do with it?



Sampling at very low concentrations

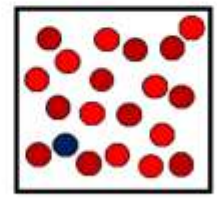




Adsorption is Often Multicomponent

- Currently: Ignore weakly interacting species (like nitrogen - e.g. CO_2 from air)
- Adsorption from solvents? Water, organics, etc. are *not* weakly interacting

Bio-products,
chromatographic separations,
liquid-phase separations

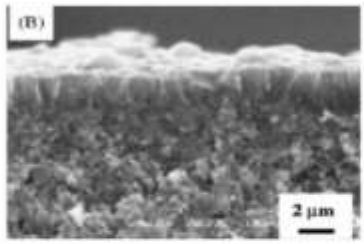


Is there a smart way of dealing with all that solvent?

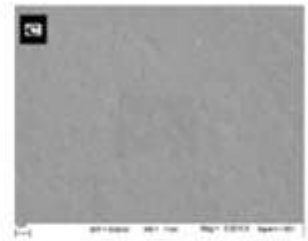
Multiscale modelling: connecting atomistic and continuum models

Mixed Matrix Membranes

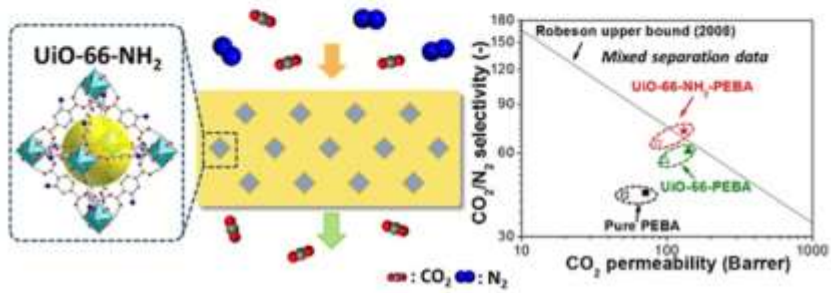
MOF membrane



Polymer membrane

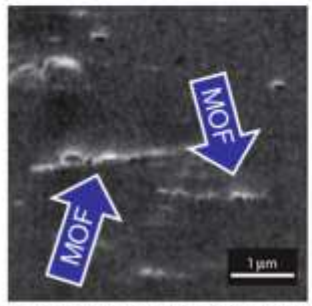


The best of both worlds: mixed matrix membranes

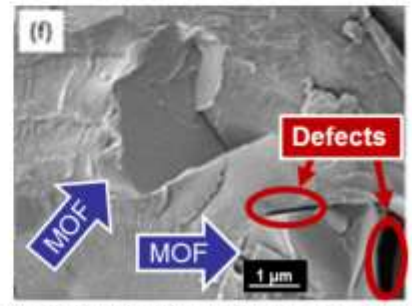


Mixed Matrix Membranes

- Detailed atomistic description for the MOF
- Bulk models for polymers
- But no good way of connecting the two
- Interfaces? Defects?



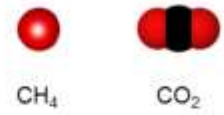
T. Rodenas et al, Nature Materials, 2014



R. Lin et al ACS Appl. Mater. Interfaces, 2014

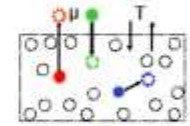
Molecular simulation

Input
e.g. model for fluids and solids
force fields to describe interactions



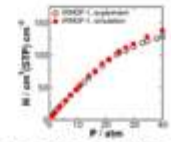

IRMOF-1

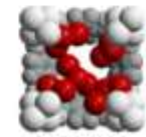
Simulation methods based on statistical mechanics
e.g. Monte Carlo
Molecular Dynamics



GCMC simulation

Output
e.g. adsorption isotherms
diffusion coefficients
detailed picture on molecular level


adsorption isotherm


snapshot