Empirical Potential Structure Refinement (EPSR): A method for structural modelling of liquids, glasses and complex nanoscale systems

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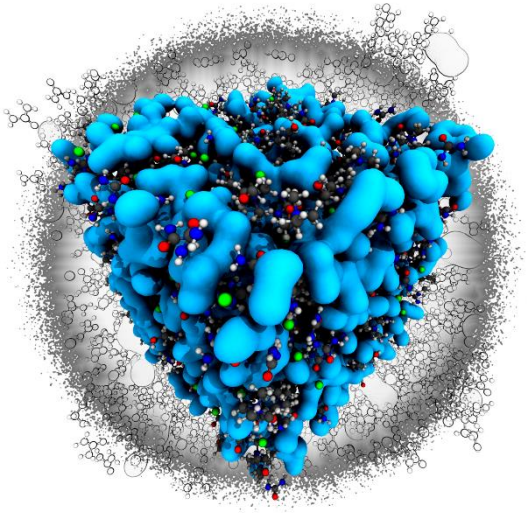

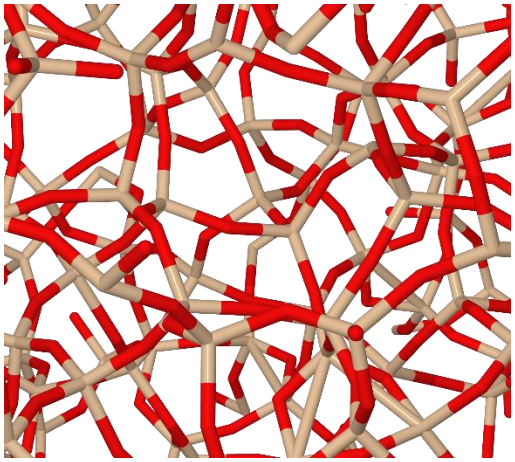

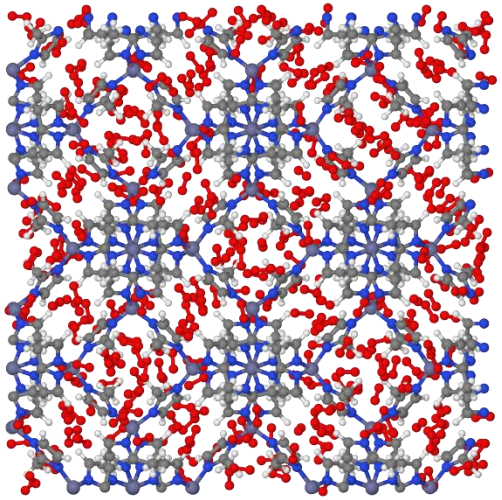

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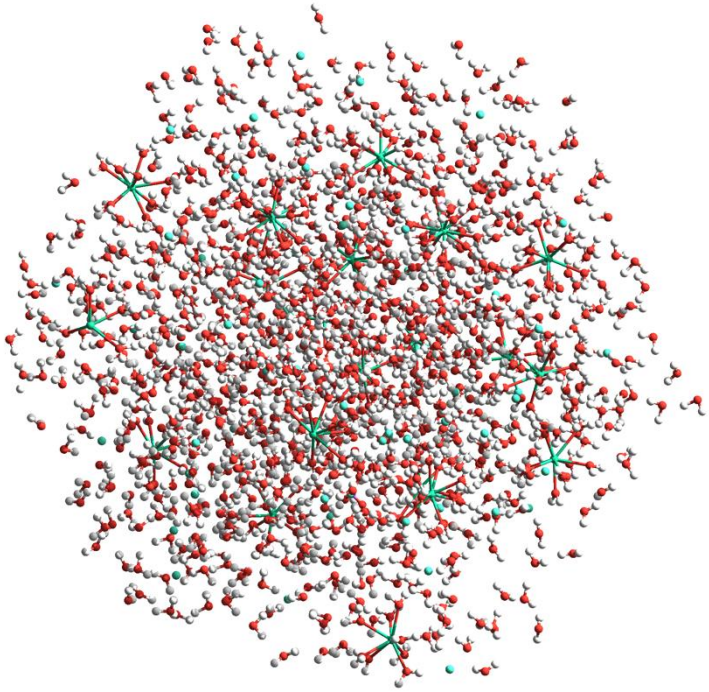
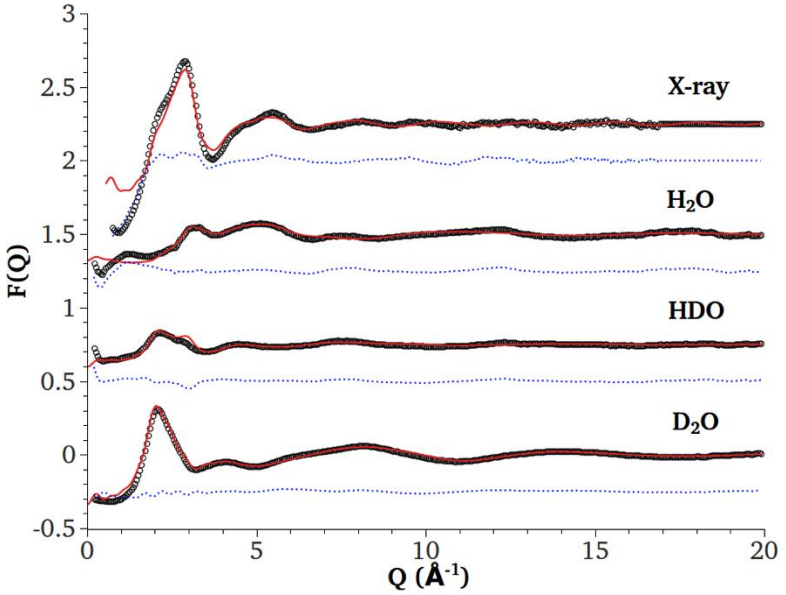
Empirical Potential Structure Refinement

A computational method developed by **Dr Alan Soper FRS**, for building atomic and molecular models of structurally disordered systems, that are consistent with neutron and x-ray scattering data, and known physical/chemical constraints.





[1] A. K. Soper, *Chem. Phys.* **202**, 295-306 (1996)
[2] A. K. Soper, *Physical Review B*, **72**, 104204 (2005)
[3] A. K. Soper *J. Phys. Condens. Matt.* **19**, 335206 (2007)

EPSR ≠ Computer simulation

Computer “simulations allow us to develop and test models, to evaluate approximate theories of liquids, and to obtain detailed information about the structure and dynamics of *model* liquids at the molecular level.” *Computer Simulation of Liquids*, M.P.Allen and D.J.Tildesley (Clarendon Press, Oxford 1987)

EPSR allows us to build atomistic models of *real* liquids (and glasses and complex nanoscale systems) that have been characterized by neutron or X-ray scattering methods, and to test the consequences of our underlying assumptions via refinement against experimental observables.

EPSR is built on a Monte Carlo simulation engine

Its ingredients are:

(1) A computer representation of a box of atoms and molecules – essentially a store of coordinates.

(2) A set of potential energy functions to model the interactions between the atoms and molecules in the box.

(3) A set of rules by which the atoms, molecules, functional groups within the model are moved e.g.

- (a) Atomic translations
- (b) Molecule translations
- (c) Molecule rotations
- (d) Molecule functional group rotations
- (e) Torsional operations on molecules etc.

(4) A set of tools to interrogate the development of the interatomic and intermolecular structures that the model will produce.

EPSR method

Classical

Molecular mechanics
(Empirical force fields)

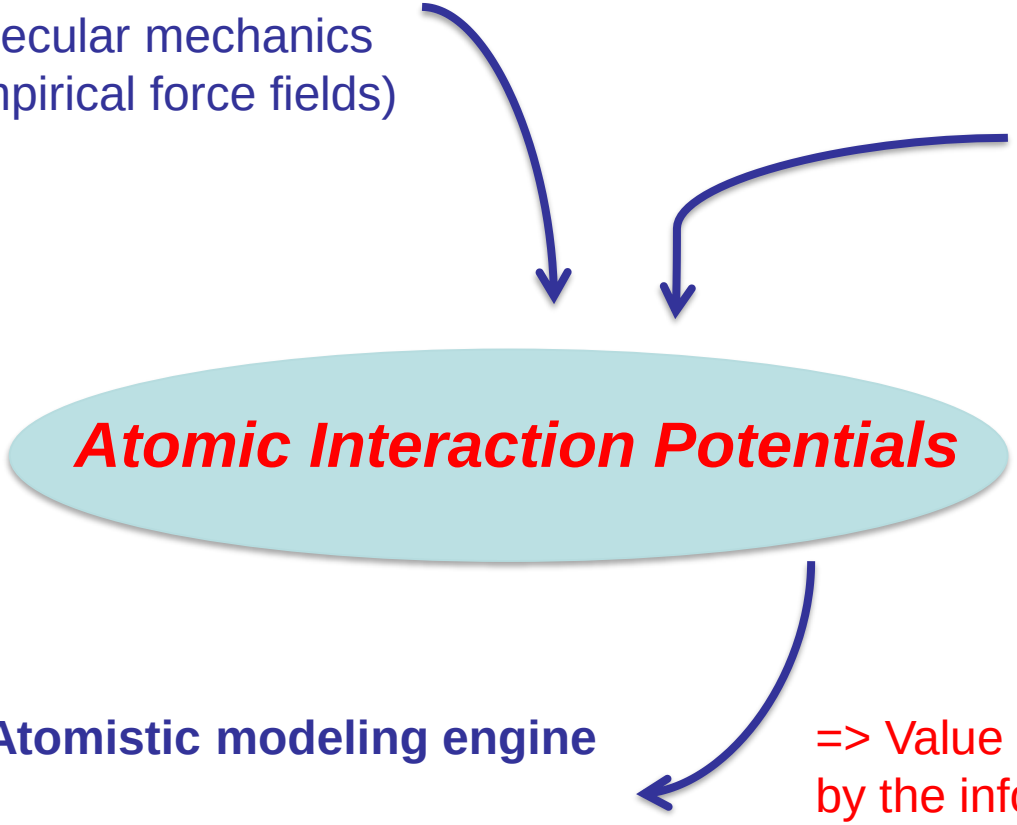
and

Experimental Data

Neutron Diffraction
(Nuclear correlations)

X-ray Diffraction
(Electron density correlations)

EXAFS Spectroscopy
(Chemically specific electron density)



Atomistic modeling engine

Metropolis Monte Carlo

=> Value of the resulting model is limited by the information content of the experimental data

The total potential runs and EPSR refinement

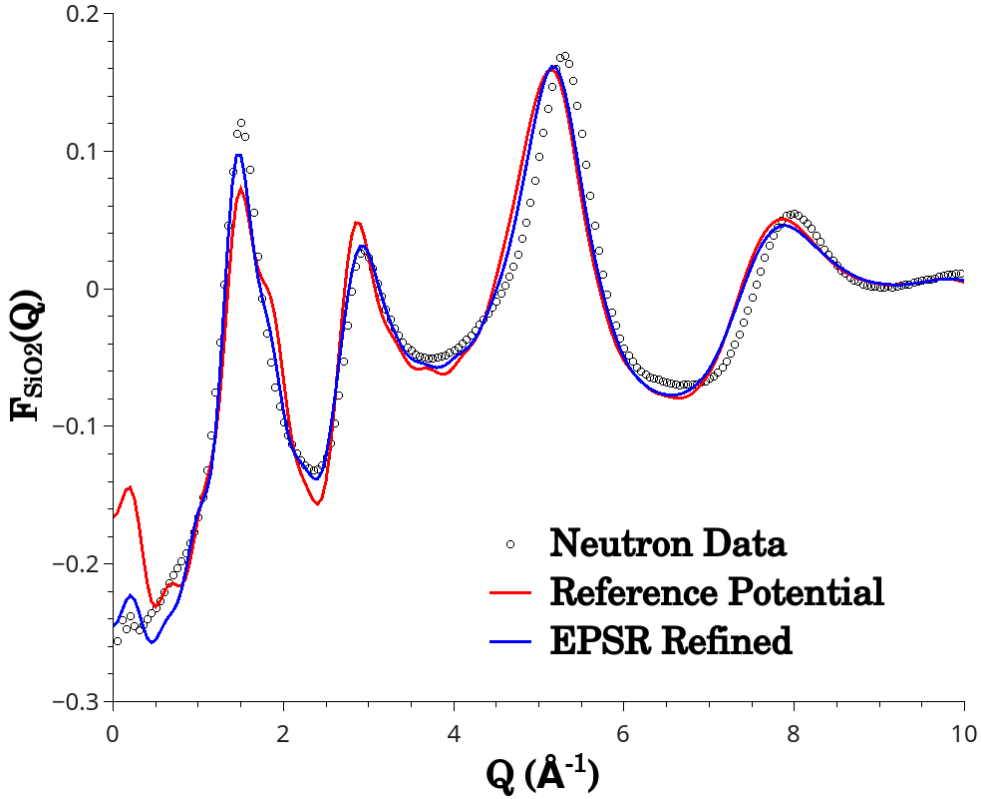
$$U_{\alpha\beta} = U^{ref}_{\alpha\beta}(r) + U^{EP}_{\alpha\beta}(r)$$

$$U^{ref} = \frac{1}{2}\sum_{i,j\neq i}\sum_{\alpha,\beta}\left(4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i\beta_j}}\right)^n - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i\beta_j}}\right)^6\right] + \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{\alpha_i\beta_j}}\right)$$

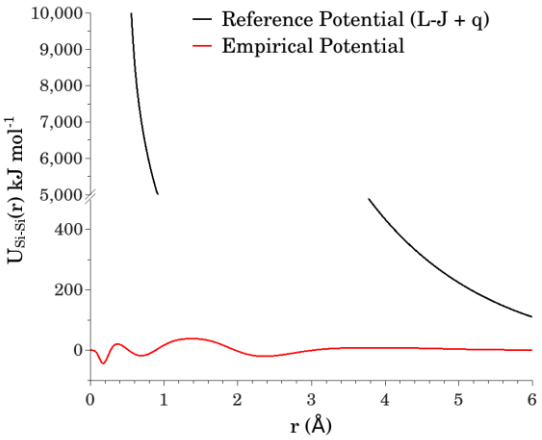
$$U^{tot} = \frac{1}{2}\sum_{i,j\neq i}\sum_{\alpha,\beta}\left(4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i\beta_j}}\right)^n - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i\beta_j}}\right)^6\right] + \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{\alpha_i\beta_j}} + U^{EP}_{\alpha\beta}(r)\right)$$

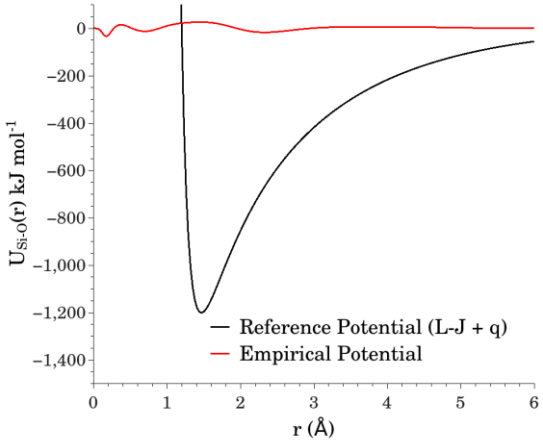
The result of performing an EPSR refinement

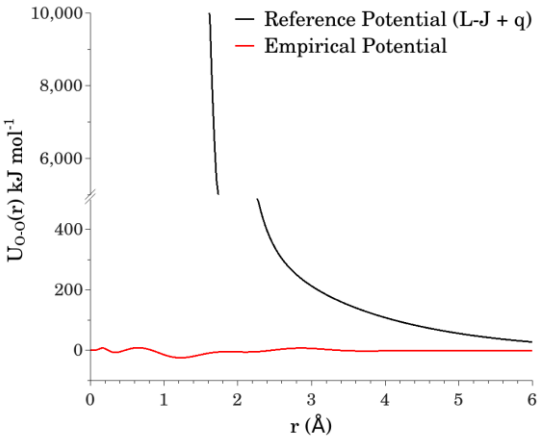
Refining a reference potential model against scattering data drives the calculated structure factor of the model towards improved agreement with the experimentally measured function.



The total potential runs and EPSR refinement







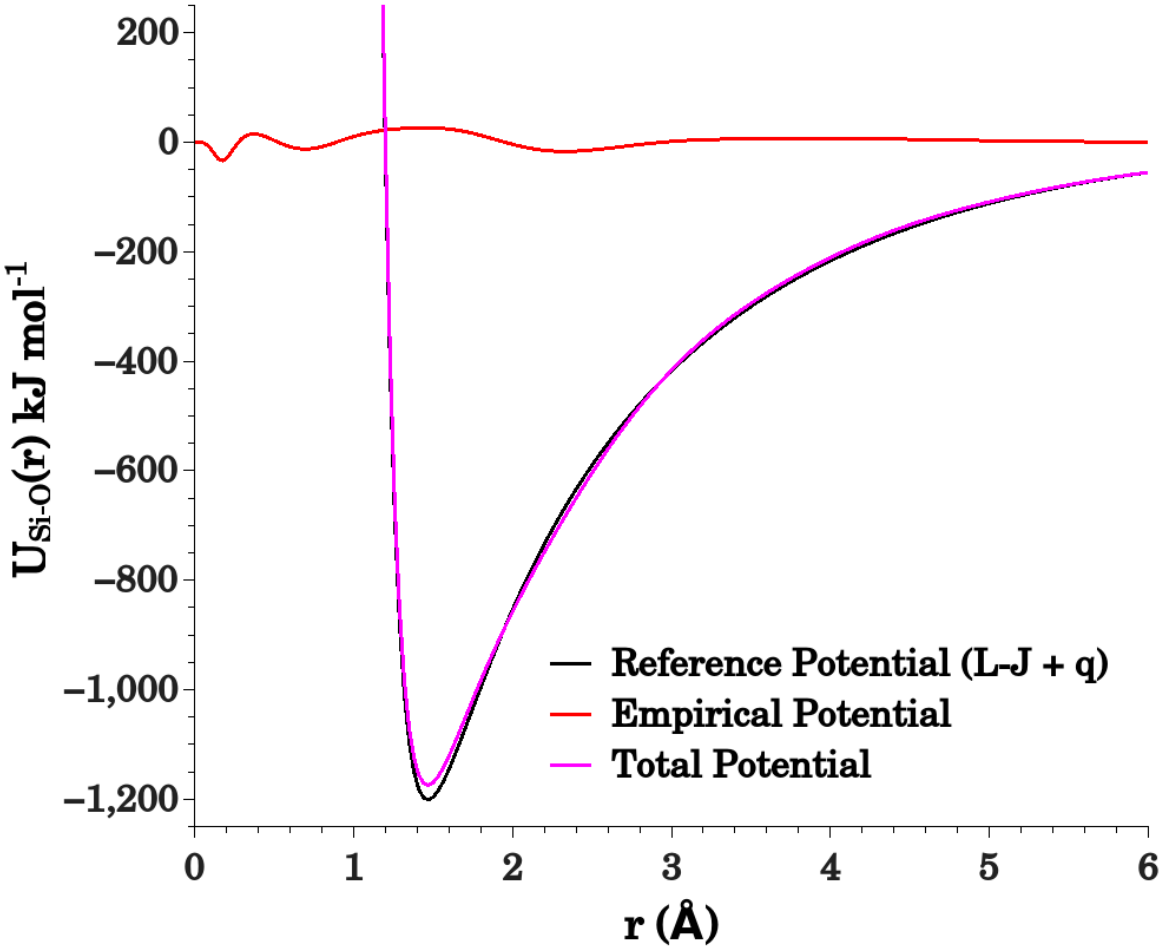
$$U_{\alpha\beta} = U^{ref}_{\alpha\beta}(r) + U^{EP}_{\alpha\beta}(r)$$

Element	σ (Å)	ε (kJmol^{-1})	q (e)
Si	1.03	0.1750	+2
O	3.60	0.1625	-1

$$U^{ref} = \frac{1}{2}\sum_{i,j\neq i}\sum_{\alpha,\beta}\left(4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i\beta_j}}\right)^n - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i\beta_j}}\right)^6\right] + \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{\alpha_i\beta_j}}\right)$$

$$U^{tot} = \frac{1}{2}\sum_{i,j\neq i}\sum_{\alpha,\beta}\left(4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i\beta_j}}\right)^n - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i\beta_j}}\right)^6\right] + \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{\alpha_i\beta_j}} + U^{EP}_{\alpha\beta}(r)\right)$$

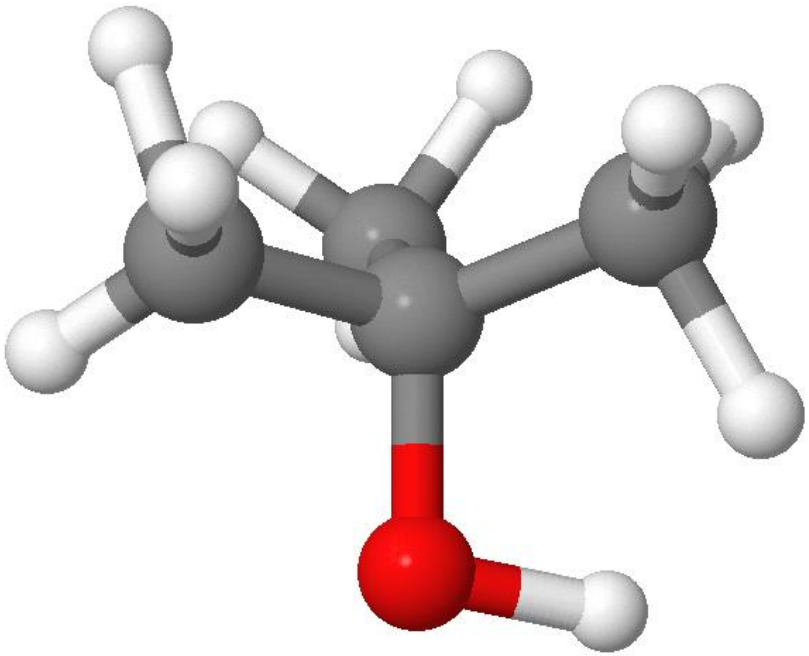
The total potential runs and EPSR refinement



$$U_{\alpha\beta} = U^{ref}_{\alpha\beta}(r) + U^{EP}_{\alpha\beta}(r)$$

EPSR is designed to function with both atoms and molecules

Molecules are defined using distance constraints

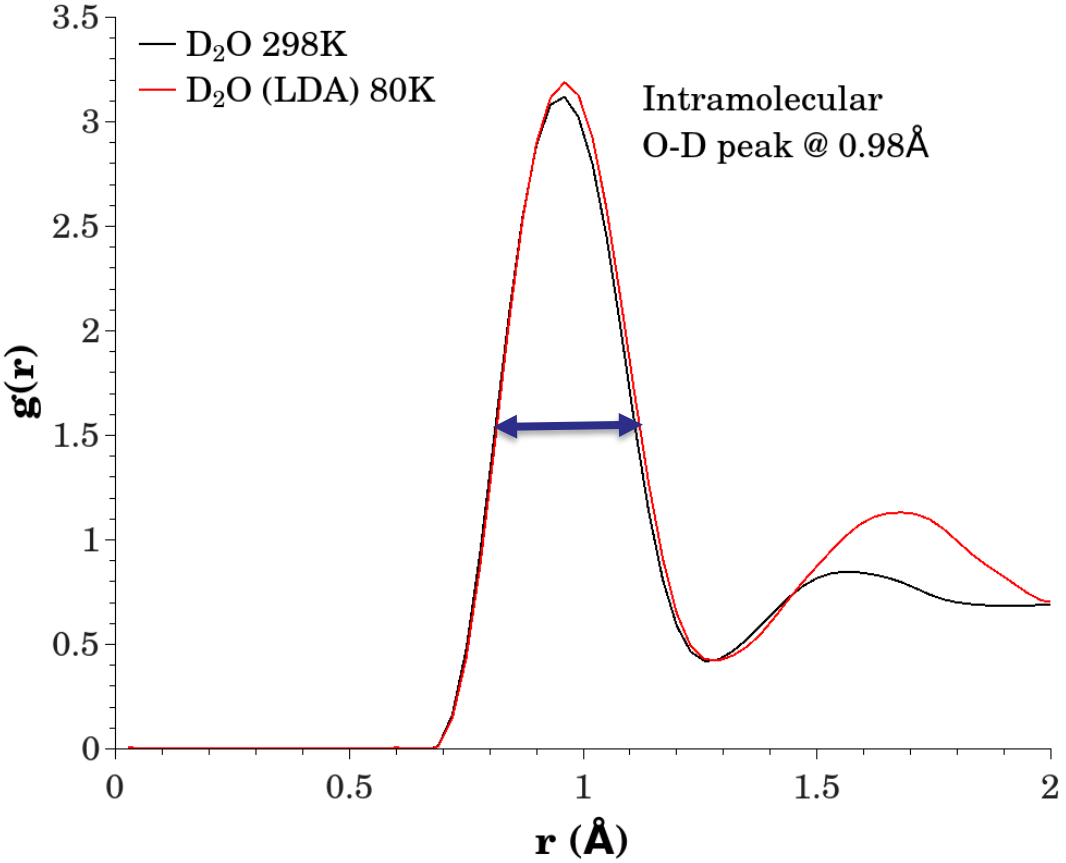


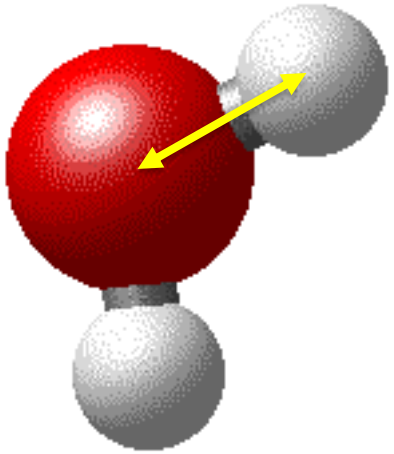
Within EPSR, molecules are defined by a criterion for the distances between first and second neighbour atoms. These two distances effectively constrain the angles.

For simplicity, the builder programs also allow you to specify the molecular structure in terms of first neighbour distances and angles.

Molecules are flexible to account for observed disorder

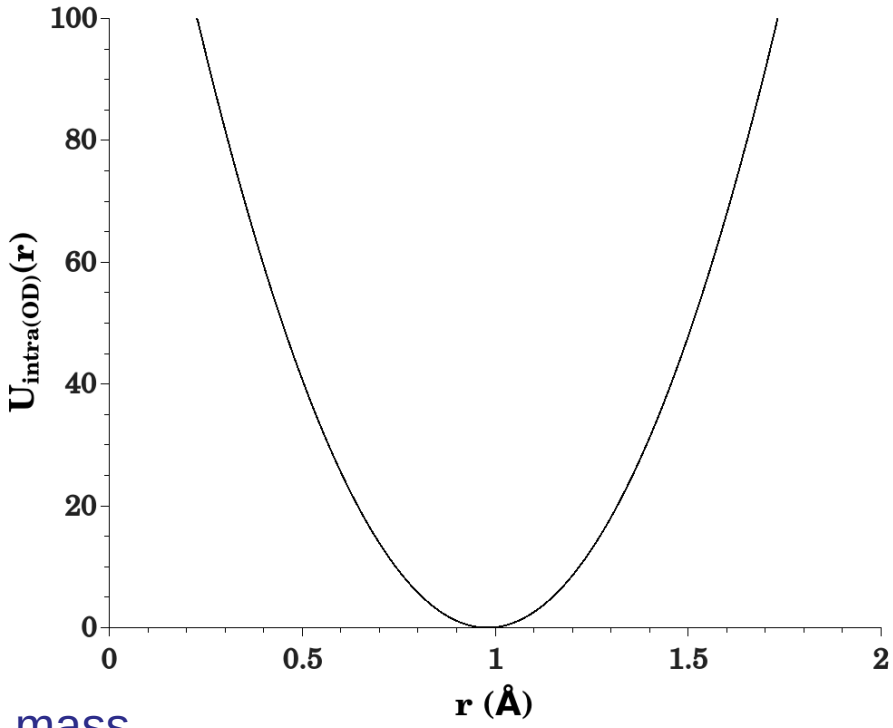
(and consequently every molecule in the model is slightly different)





Molecules are flexible to account for observed disorder

$$U_{intra} = C \sum_{i} \sum_{\alpha\beta \neq \alpha} \frac{(r_{\alpha_i \beta_i} - d_{\alpha\beta})^2}{2w_{\alpha\beta}^2}$$



C = 130 Å^{-1} amu^{-1}

$d_{\alpha\beta}$ = 0.98Å

w^2 = 0.98/((16 × 2)/(16+2))$^{1/2}$

Average distance

Reduced mass

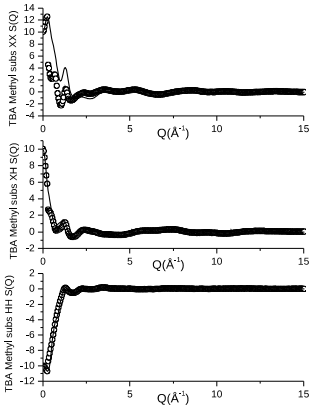
$$w_{\alpha\beta}^2 = \frac{d_{\alpha\beta}}{(\mu_{\alpha\beta})^{1/2}}$$

$$\mu_{\alpha\beta} = \frac{M_\alpha M_\beta}{(M_\alpha + M_\beta)}$$

Broadening function to avoid individual Debye-Waller factors for each distance

INPUT

Experimental data

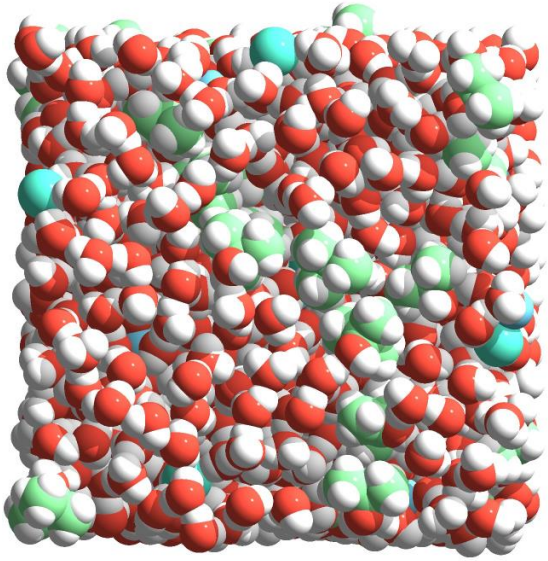


Constraints such as:

Density

Molecular geometry

EPSR



$$U^{N}_{\alpha\beta} = U^{O}_{\alpha\beta}(r) + U^{\Delta EP}_{\alpha\beta}(r)$$

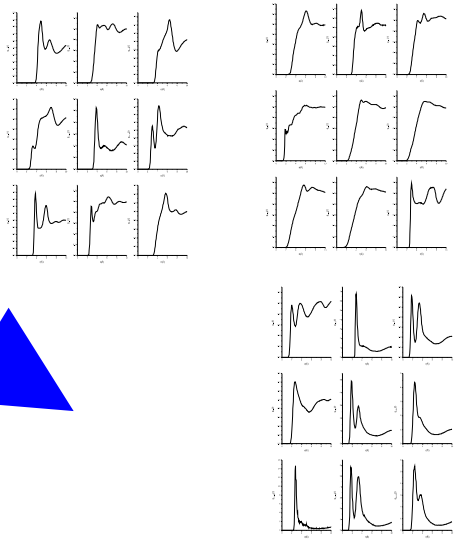
$$U^{O}_{\alpha\beta}(r) \approx U^{N}_{\alpha\beta}(r)$$

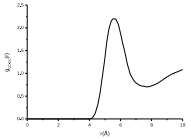
$$S^{Model}_{\alpha\beta}(Q) \approx S^{Data}_{\alpha\beta}(Q)$$

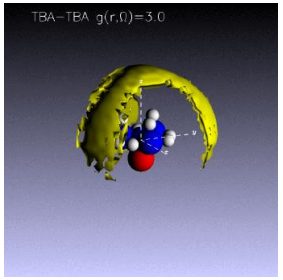
$$g^{Model}_{\alpha\beta}(r) \approx g^{Data}_{\alpha\beta}(r)$$

OUTPUT

A wealth of structural information







EPSR: a summary

Understanding the limits of what can safely concluded from disordered materials diffraction data

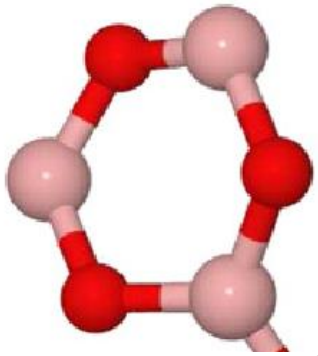
Does liquid or amorphous system diffraction data always
support the construction of a completely defined and unique structural model?

The informative case of vitreous B_2O_3

Does vitreous B_2O_3 contain a significant fraction of B_3O_3 ring structures?

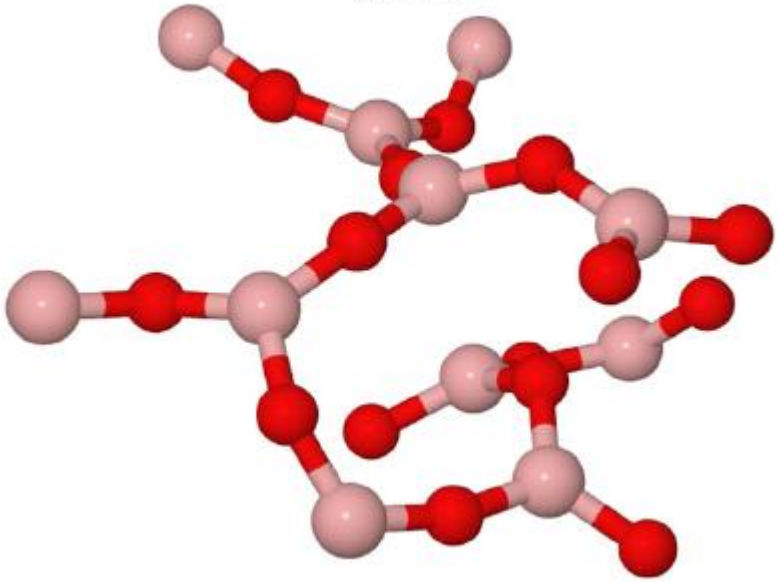
Raman scattering and NMR suggest ring fractions of ≈ 70%

Neutron and X-ray scattering models suggest < 20%

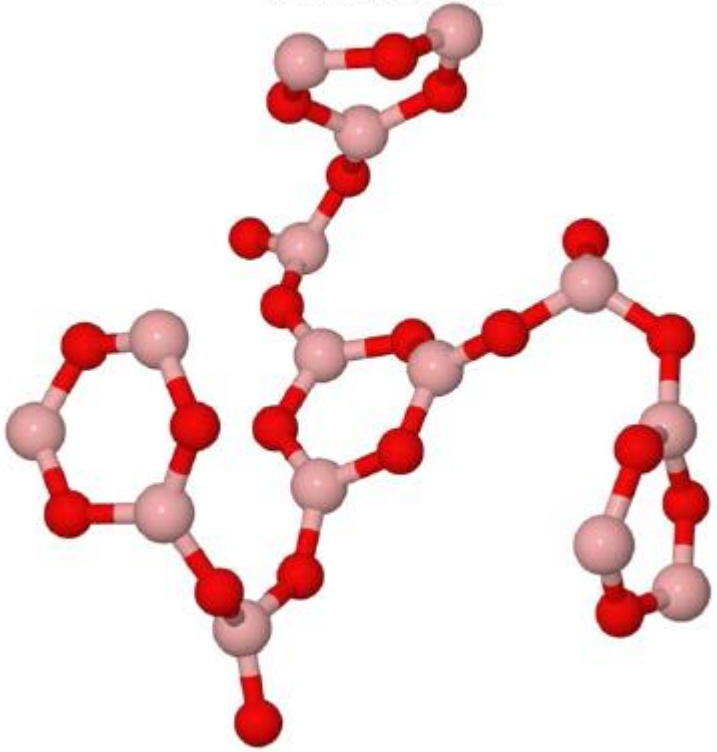


EPSR used as a hypothesis testing framework

(a) Model 1



(b) Revised Model 2

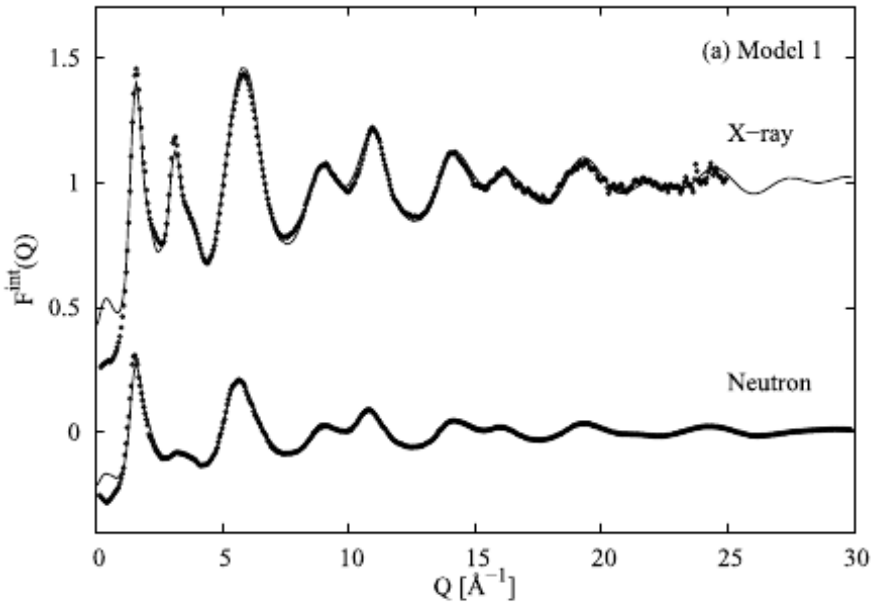


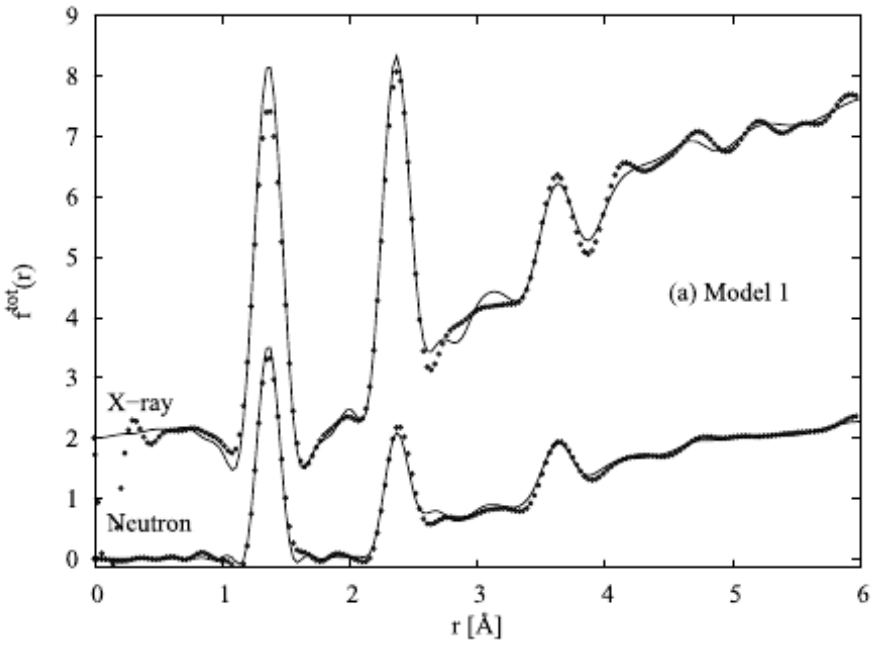
6% of boron in boroxyl rings

75% of boron in boroxyl rings

EPSR used as a hypothesis testing framework

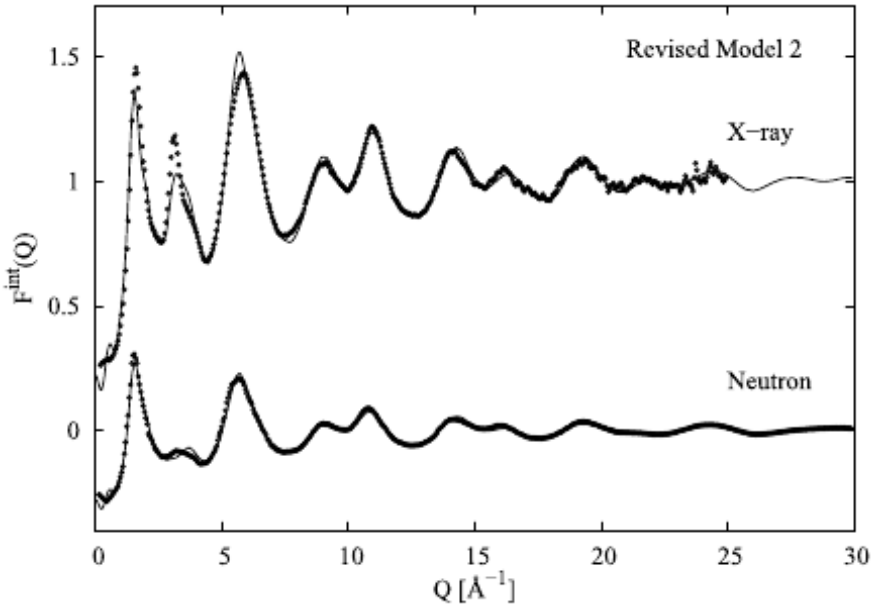
Model 1: 6% of boron in boroxyl rings

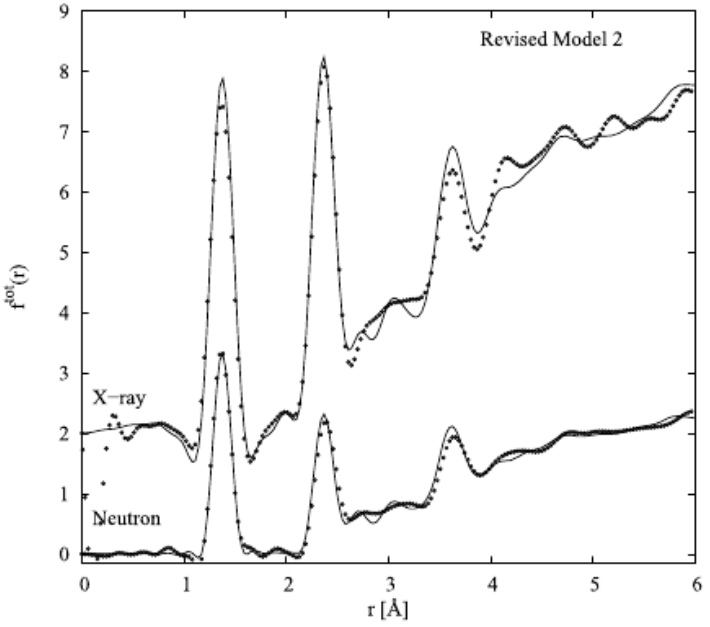




EPSR used as a hypothesis testing framework

Model 1: 75% of boron in boroxyl rings





EPSR used as a hypothesis testing framework

For the case of vitreous B_2O_3, the pair correlation sensitivity of diffraction techniques is insufficient to answer the question on ring structures. Such structural motifs not uniquely defined by atomic pair-correlations alone.

EPSR has been used to show that two structurally distinct models are equally capable of reproducing the experimental structure factors.

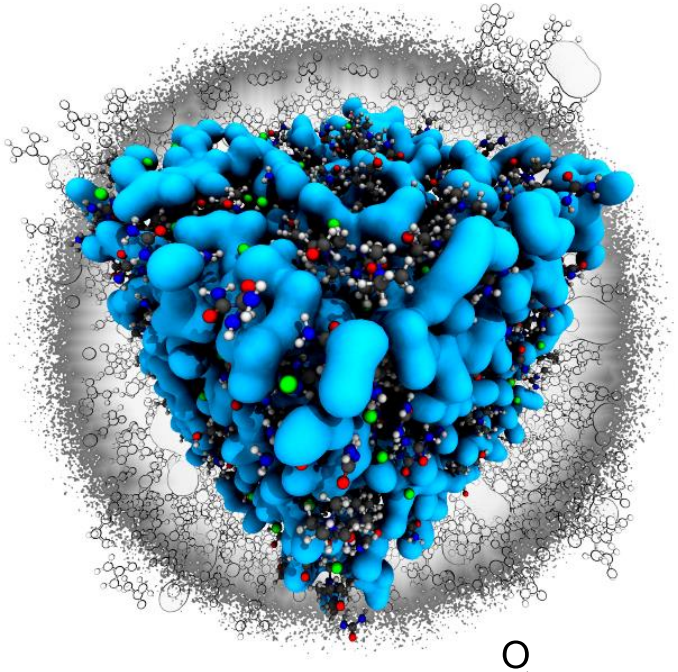
Information from independent experiments is necessary to resolve the issue.

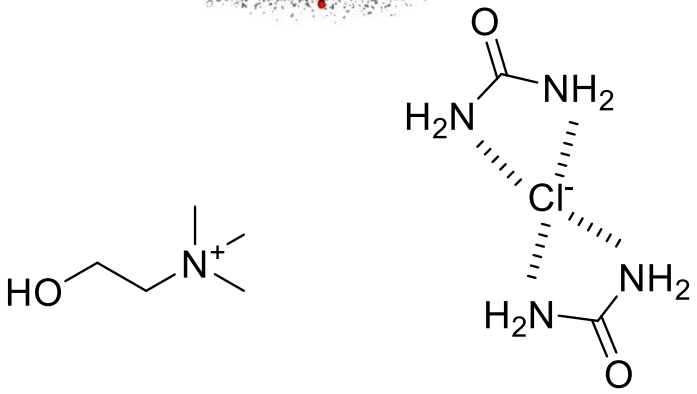
This uniqueness challenge is often most acute when attempting to model atomic materials. This is because every building block (atom) is spherical and displays no directional preferences.

Molecular materials are frequently easier systems to robustly model as the building blocks have distinct shapes and favoured connectivities that place constraints on how the many-body interactions between the atomic sites can be resolved for a given system density.

Recent applications of EPSR

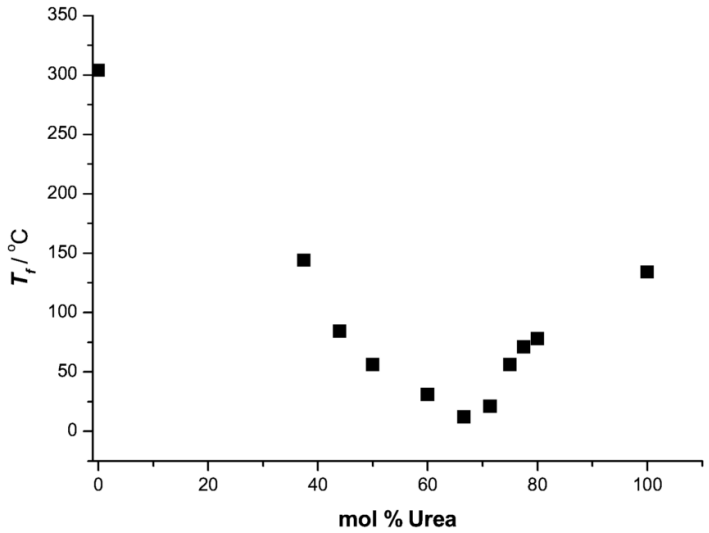
Example 1: The structure of Deep Eutectic Solvents





A salt $[A]^+[B]^-$ mixed with a molecular species [C]

Eg: choline chloride-urea (ChCl-Urea)



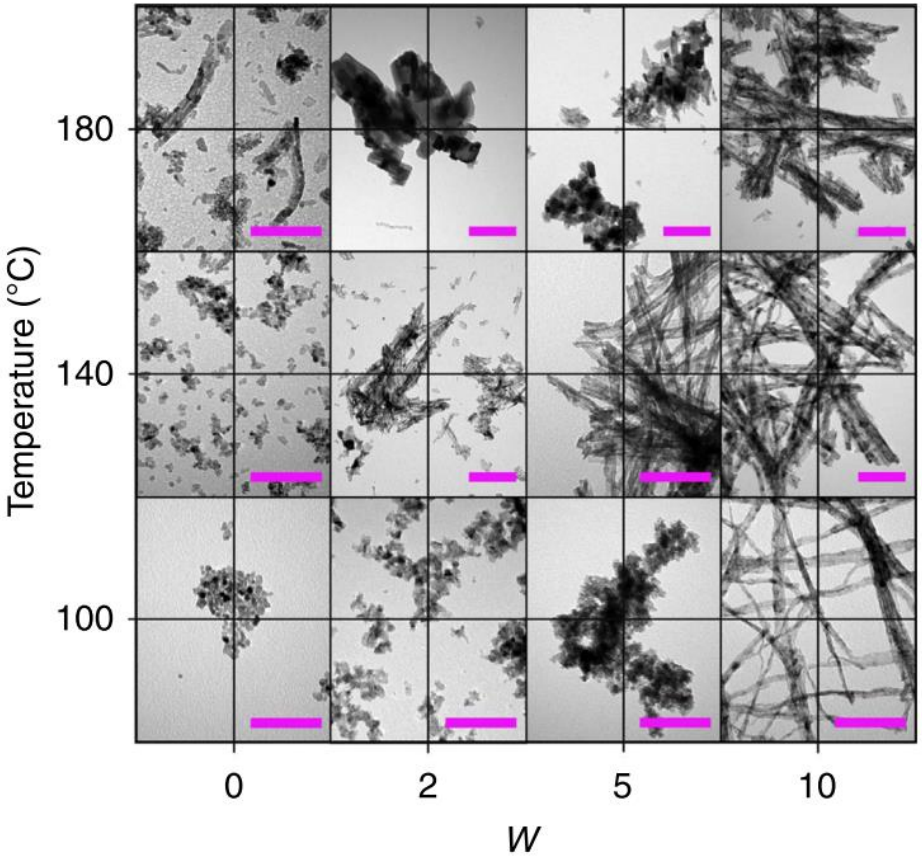
Melting point low at a certain (1:2) mixing ratio

O.S.Hammond, D.T.Bowron and K.J.Edler, *Green Chem.* (2016) **18** 2736

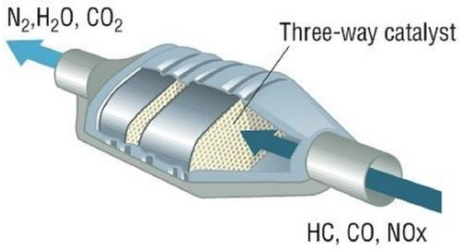
DES can be more environmentally friendly than common ionic liquids (ie. ChCl:U)

DES allow us to design the solvent to be more than a spectator

O.S.Hammond, K.J.Edler, D.T.Bowron and L.Torrente-Murciano, *Nature Comms* (2017) **8** 14150



DES for solvothermal synthesis of nanoparticulate CeO_2

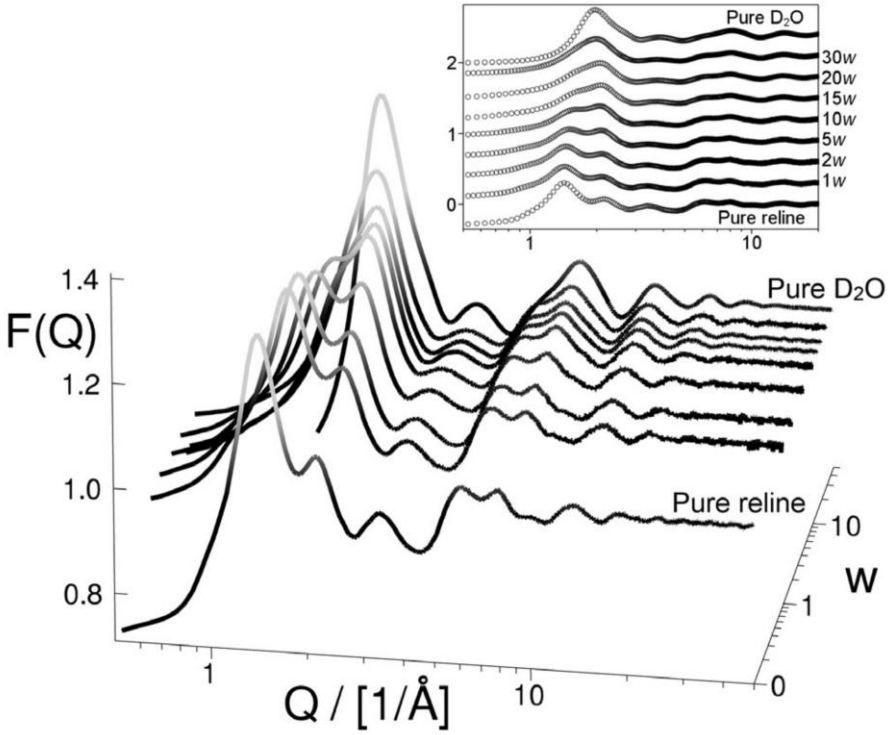


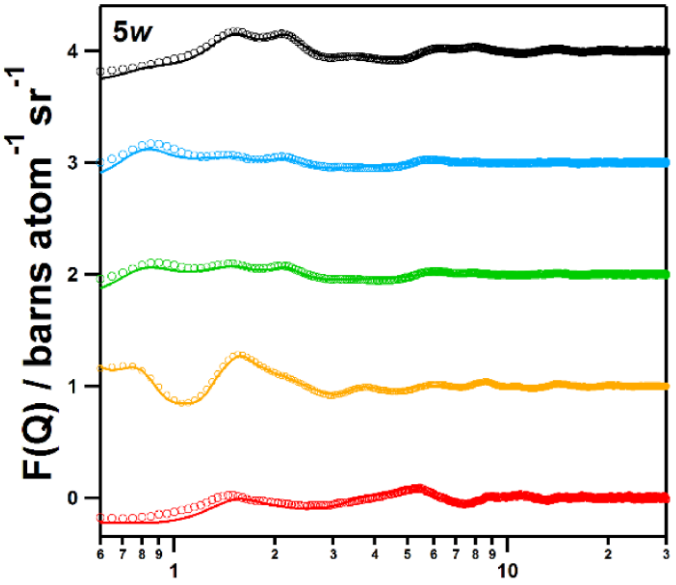
VIP Deep Eutectic Solvents | Very Important Paper

International Edition: DOI: 10.1002/anie.201702486
German Edition: DOI: 10.1002/ange.201702486

The Effect of Water upon Deep Eutectic Solvent Nanostructure: An Unusual Transition from Ionic Mixture to Aqueous Solution

*Oliver S. Hammond, Daniel T. Bowron, and Karen J. Edler** *Angew. Chem. Int. Ed.* **2017**, 56, 9782 –9785





GDCh Communications Angewandte International Edition Chemie

VIP Deep Eutectic Solvents Very Important Paper

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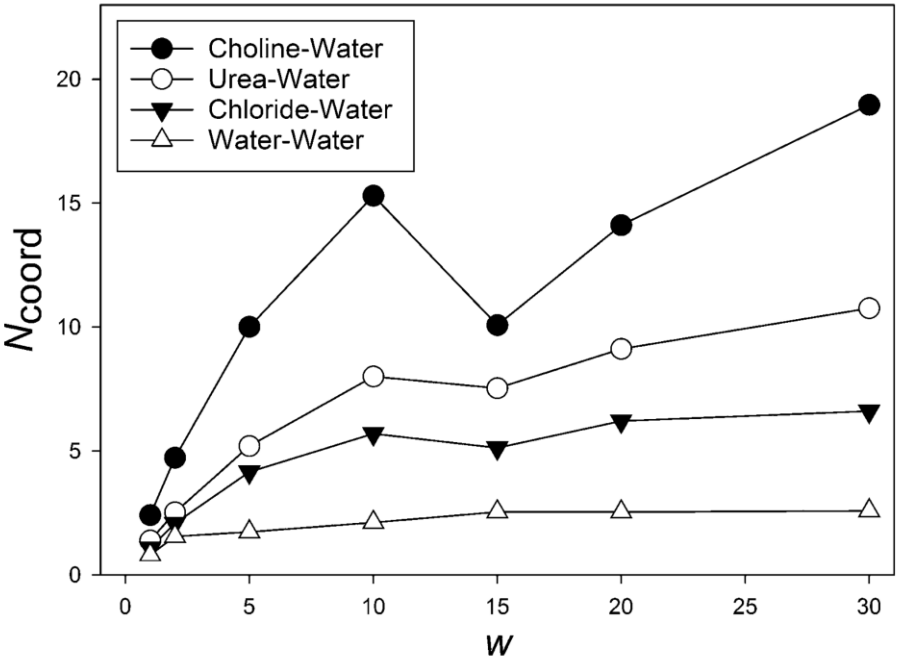
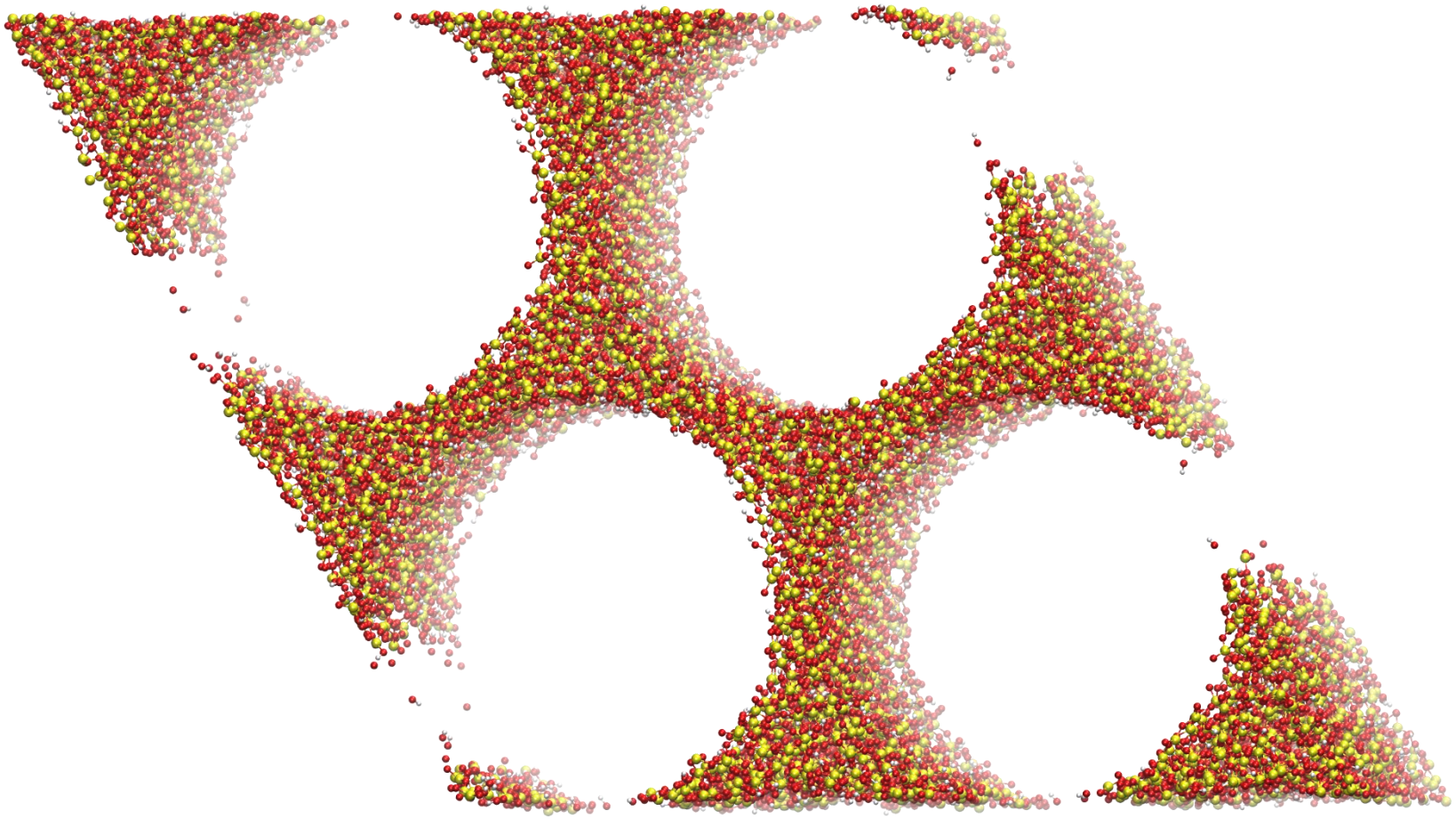


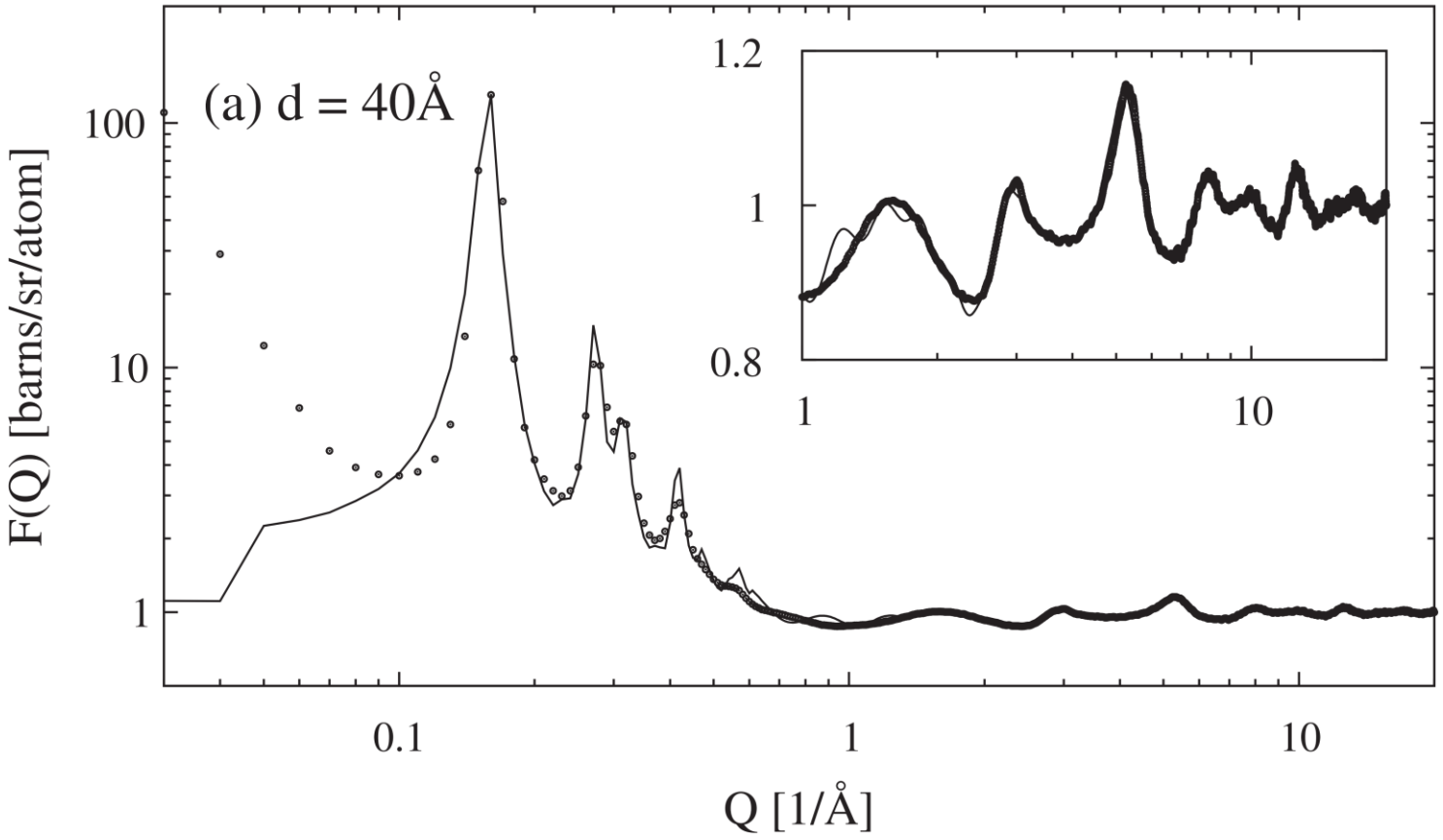
At low levels (≤1w), water contributes slightly to (rather than disrupting) the hydrogen-bonding network, and strengthens choline–urea bonding. This alters the structure enough that it is important for the water content of DES to be characterized. Between 2w and 10w, the DES–water mixture is in a regime where DES clusters still exist, but are separated by the diluent. DES intermolecular bonding persists as far as 10w because of the solvophobic sequestration of water into nanostructured domains around choline. At 15w, we observed a step change in solvation where many of the DES structural motifs cease to be prevalent as water clusters become unfavorable. At this point, the system is best described as an aqueous solution of DES components at the molecular level.

Example 2a: The structure of MCM-41



Density profile of nitrogen in cylindrical pores of MCM-41
A.K.Soper and D.T.Bowron
Chem. Phys. Lett. **683** 529-535 (2017)

EPSR refined model of MCM-41



Density profile of nitrogen in cylindrical pores of MCM-41
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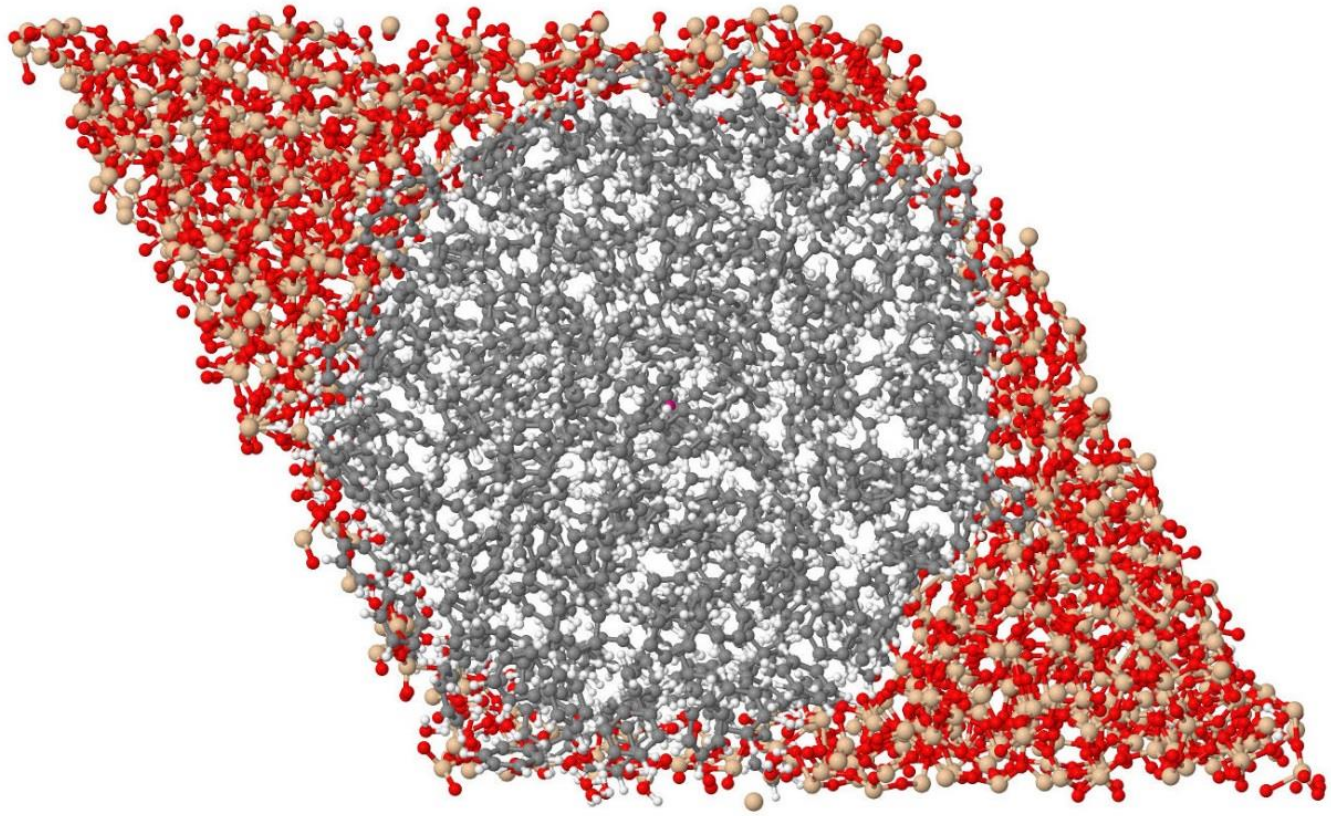
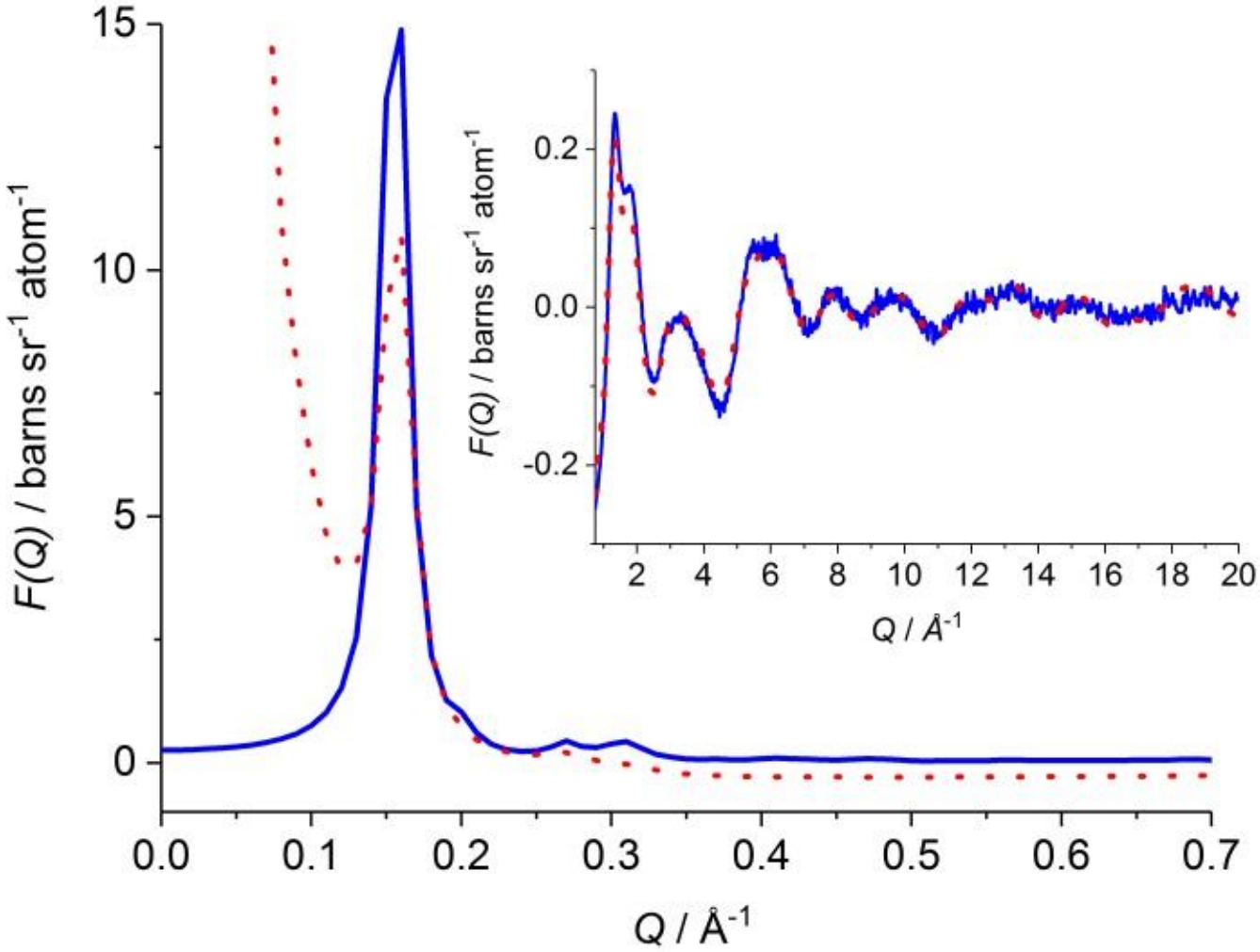
Chem. Phys. Lett. **683** 529-535 (2017)

Example 2b: MCM-41 vapour loaded with liquid benzene



Confinement Effects on the Benzene Orientational Structure
Marta Falkowska, Daniel T. Bowron, Haresh Manyar, Tristan G. A. Youngs and Christopher Hardacre
Angew Chemie Intl. Ed. Engl. **57** 4565-4570 (2018)

EPSR model of benzene confined in MCM-41



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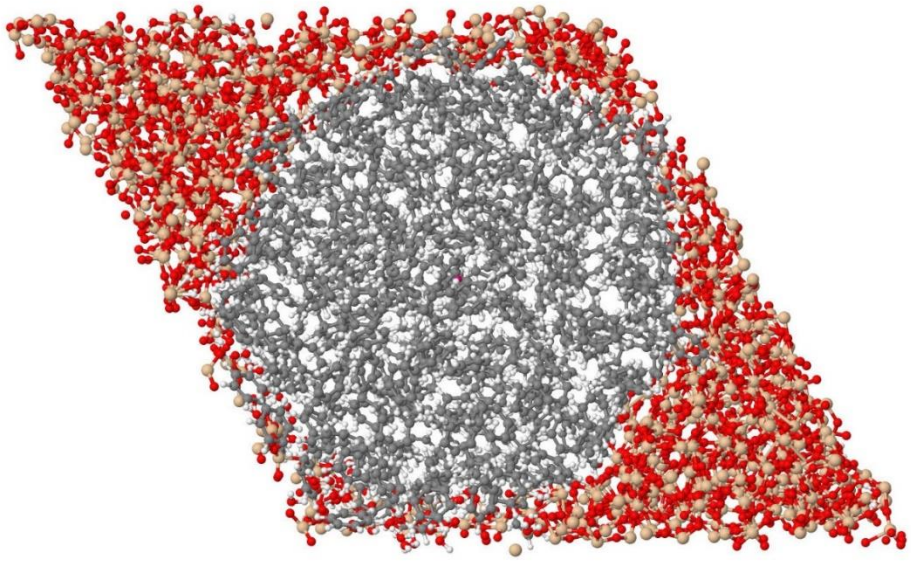
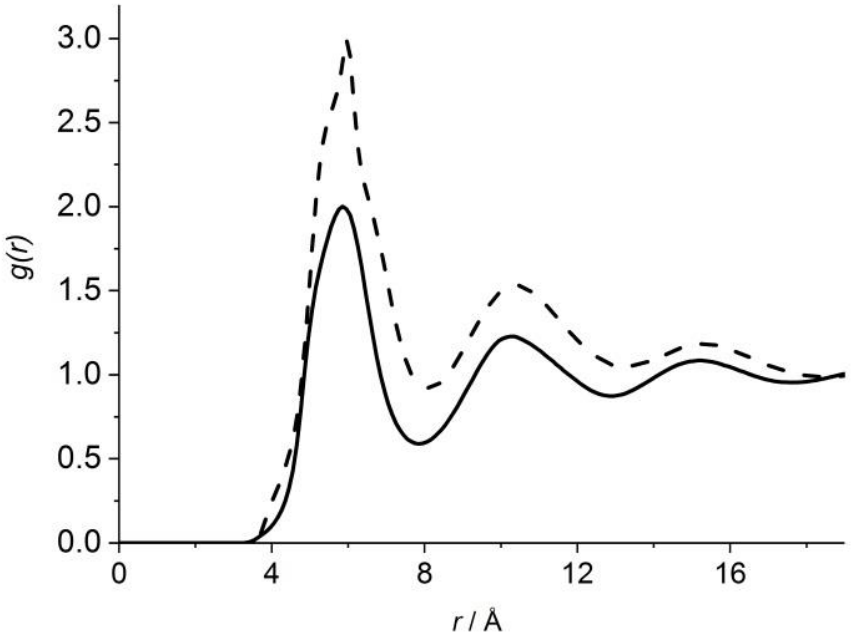
Radial distribution function of benzene within an MCM-41 pore





Radial distribution functions between molecular centers for benzene-d_6 confined in MCM-41 (dashed line). Solid line represents the radial distribution function for the bulk liquid.

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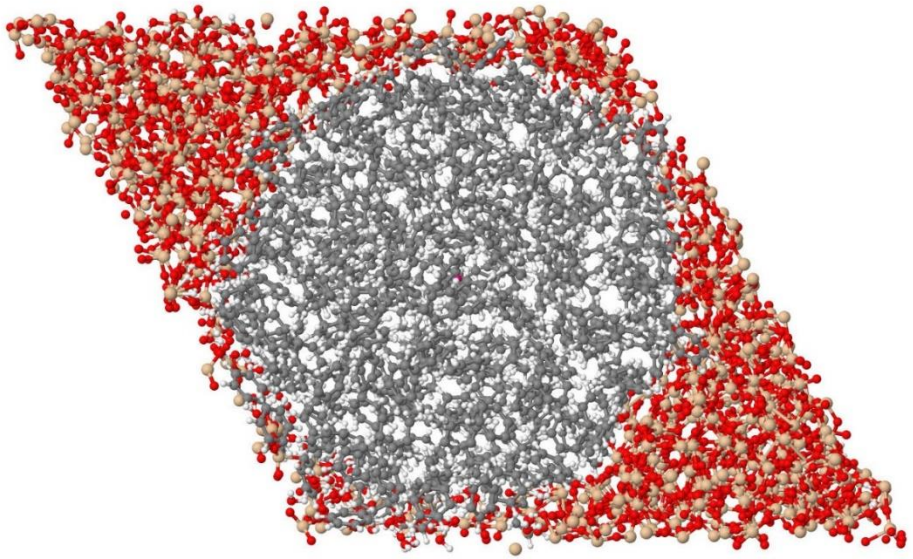
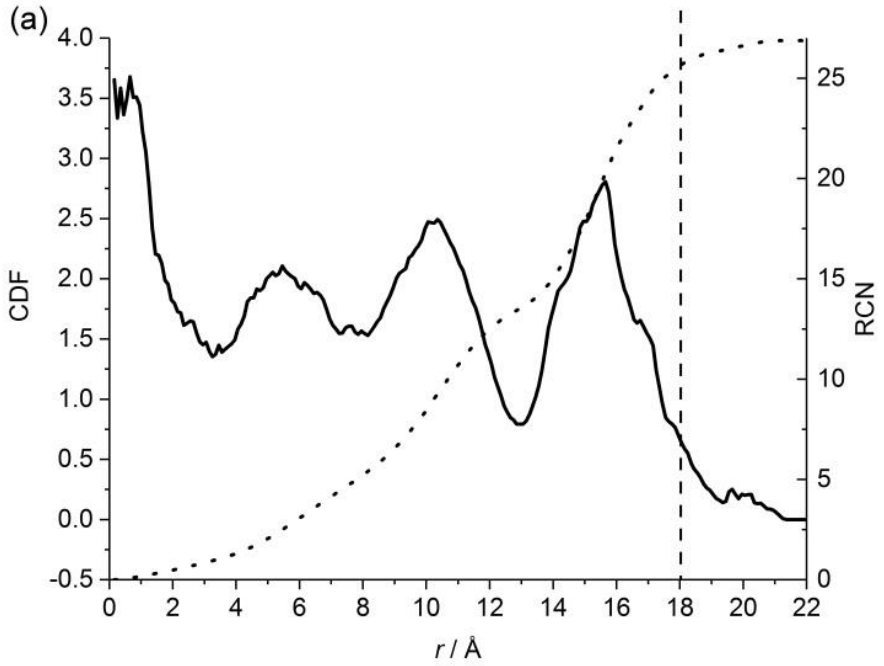
Cylindrical distribution of benzene within an MCM-41 pore





Cylindrical distribution of benzene centres as a function of pore radius and running coordination number in a 4Å slice along the length of the pore.

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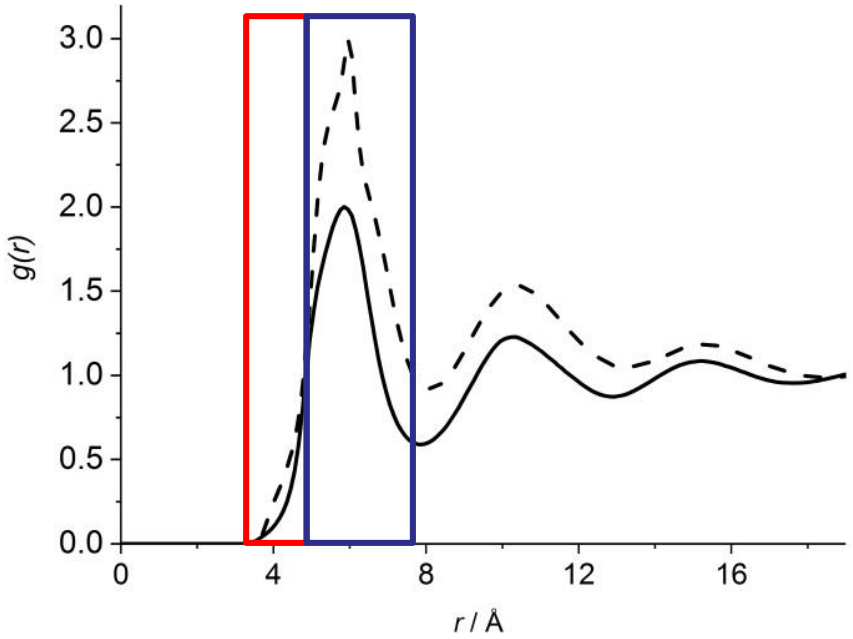
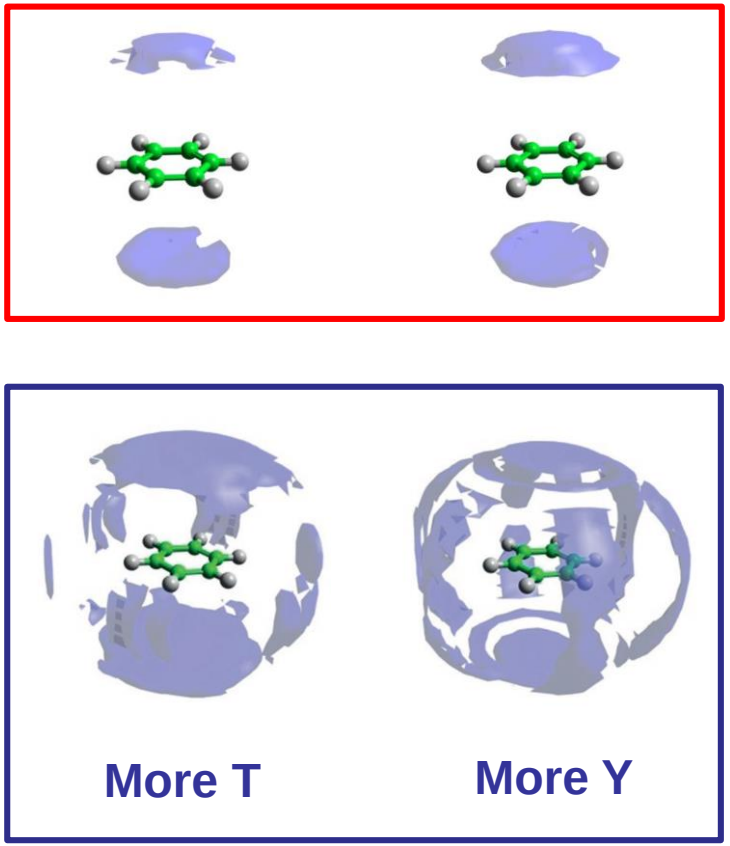
Benzene-benzene orientational correlations within an MCM-41 pore





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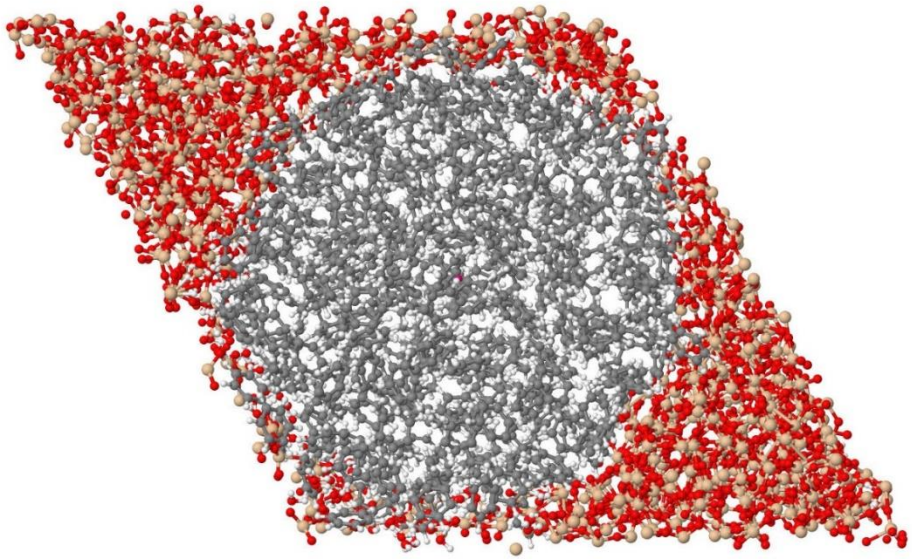
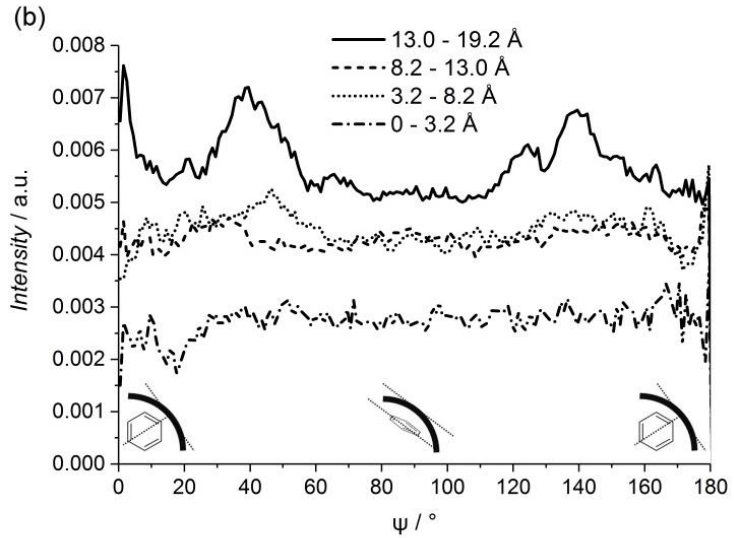
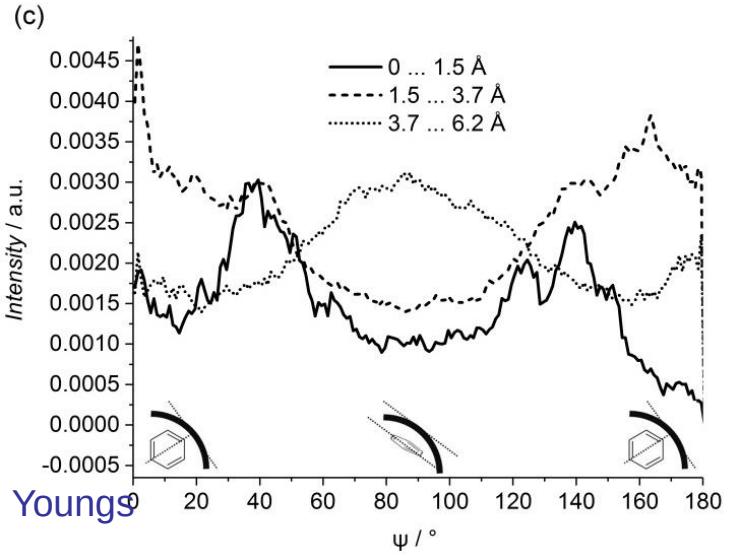
Orientational distribution of benzene within an MCM-41 pore







(b) Molecular orientations distribution calculated for each cylindrical concentric shell from centre of the pore.
(c) Molecular orientations distribution calculated for different regions within the concentric cylindrical shell that is located closest to the pore wall.

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Conclusions: Structure of benzene in MCM-41

(1) The distribution of molecules across the pore diameter displays well defined layering of the absorbed molecules.

(2) The confinement of the benzene molecules induces changes in the local ordering when compared with the bulk liquid structure:
- At short benzene-benzene distances (<4.85Å) the benzene molecules favour ***π*-**stacking
- At slightly longer distances (4.85Å – 7.90Å) the confined benzene-benzene correlations favour T-configurations (H towards ring centre) over Y-configures found in the bulk (H towards delocalized ***π*-** electrons).

(3) The interaction of benzene molecules with the inner silica-surface of the MCM-41 pore favours a canted configuration with the benzene molecules oriented at an angle of ~40° between the ring-plane and the wall surface.

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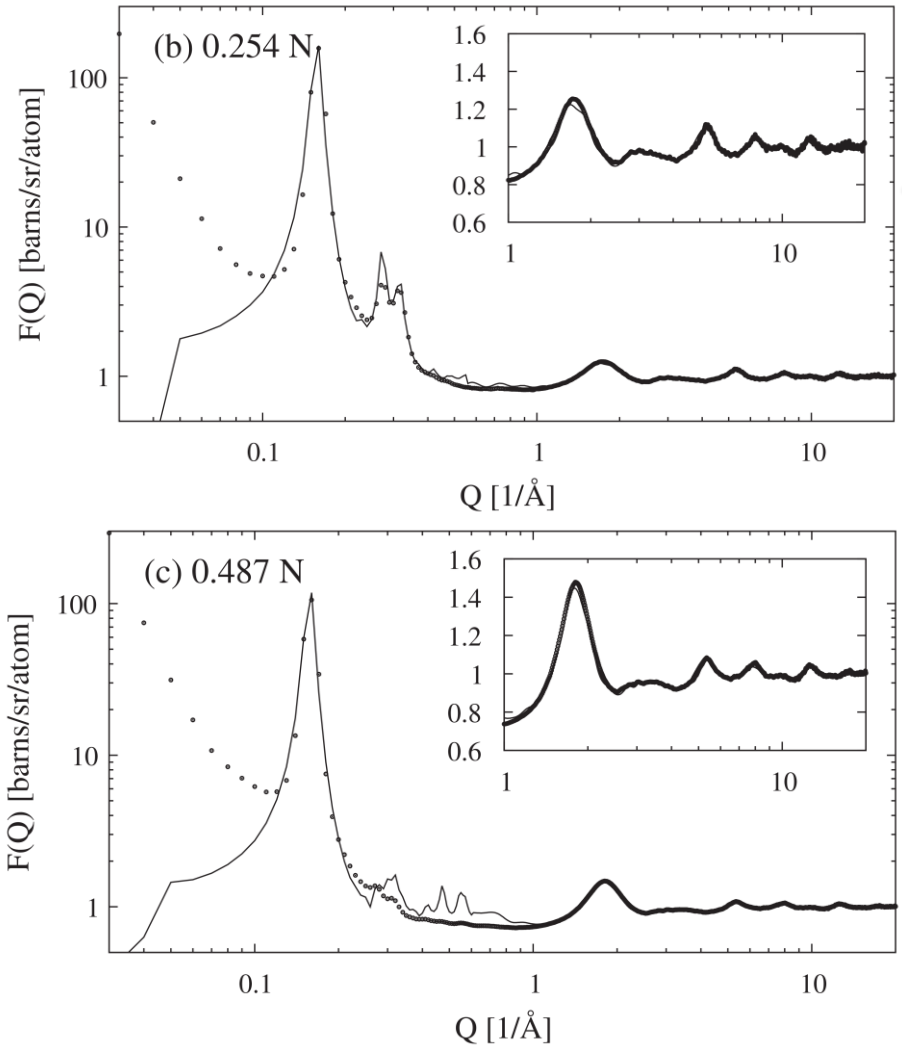
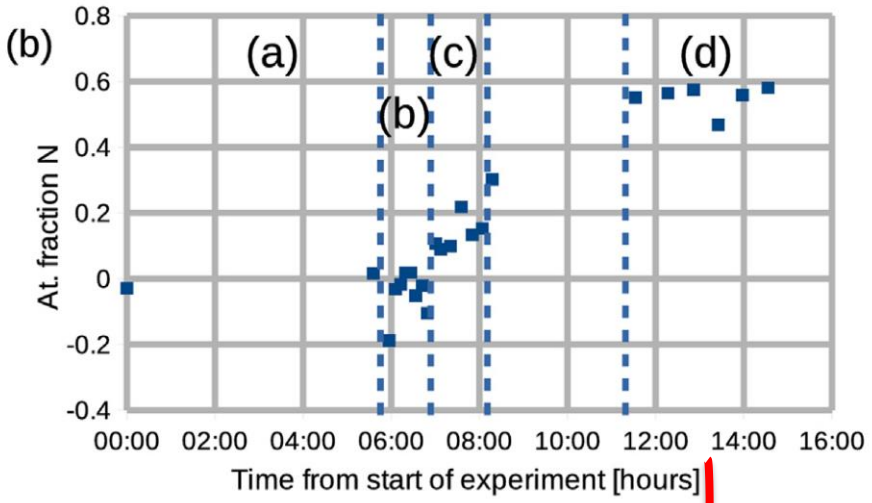
Example 2c: Loading fluids into nanoporous materials: N_2 into MCM-41



Absorbed N per mole of substrate
$Si_{0.28}O_{0.61}H_{0.11}$



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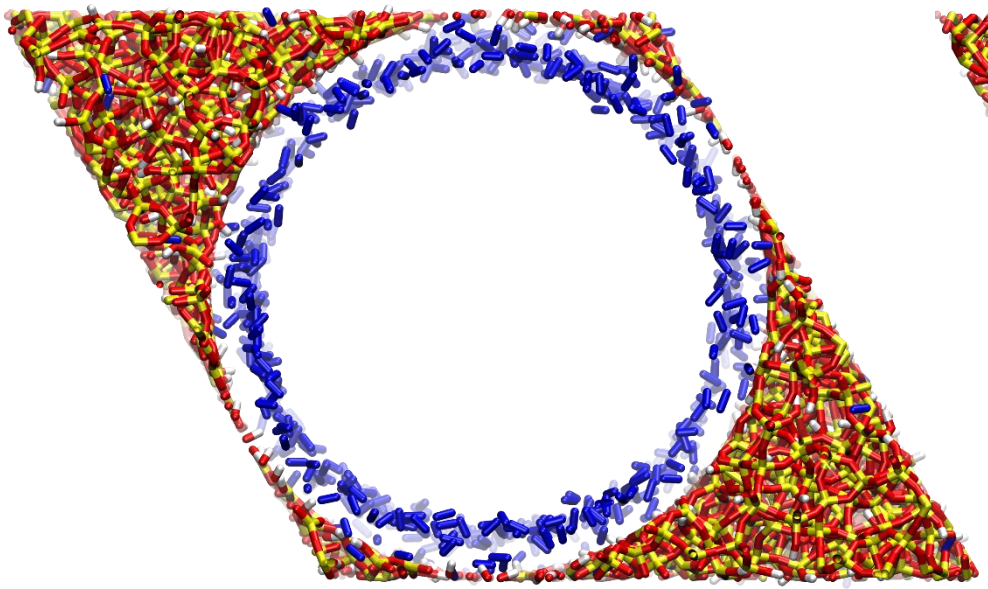
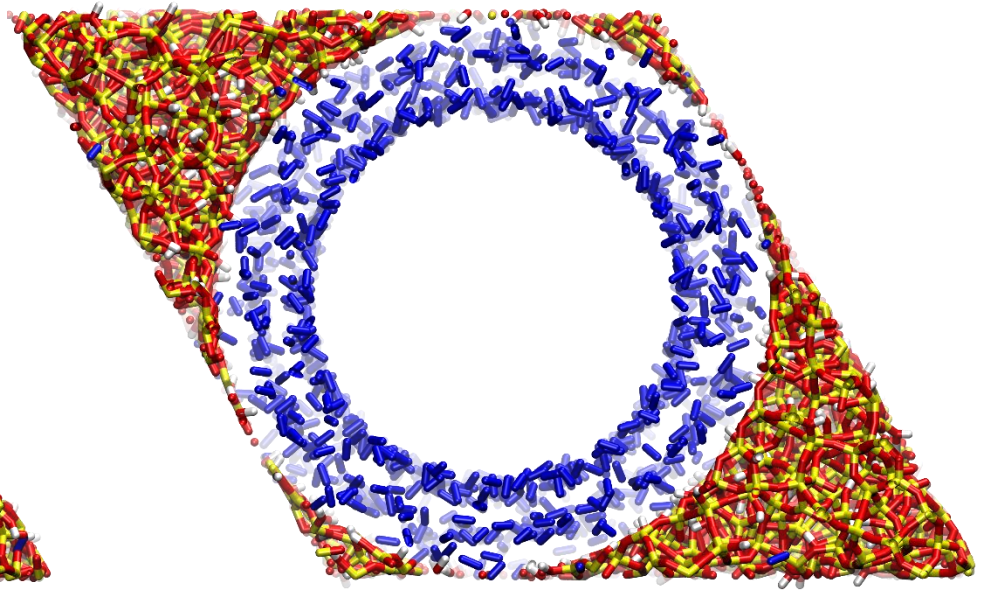
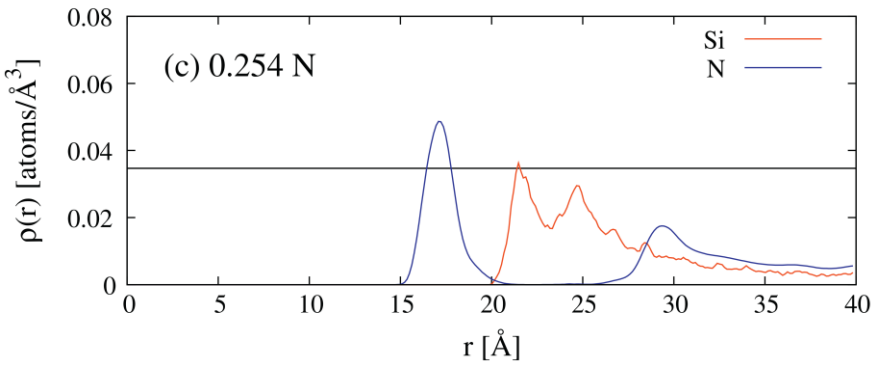
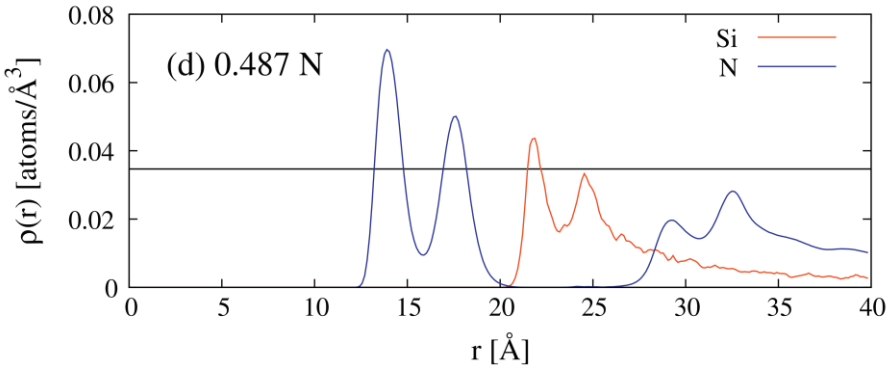
Example 2c: Loading fluids into nanoporous materials: N_2 into MCM-41









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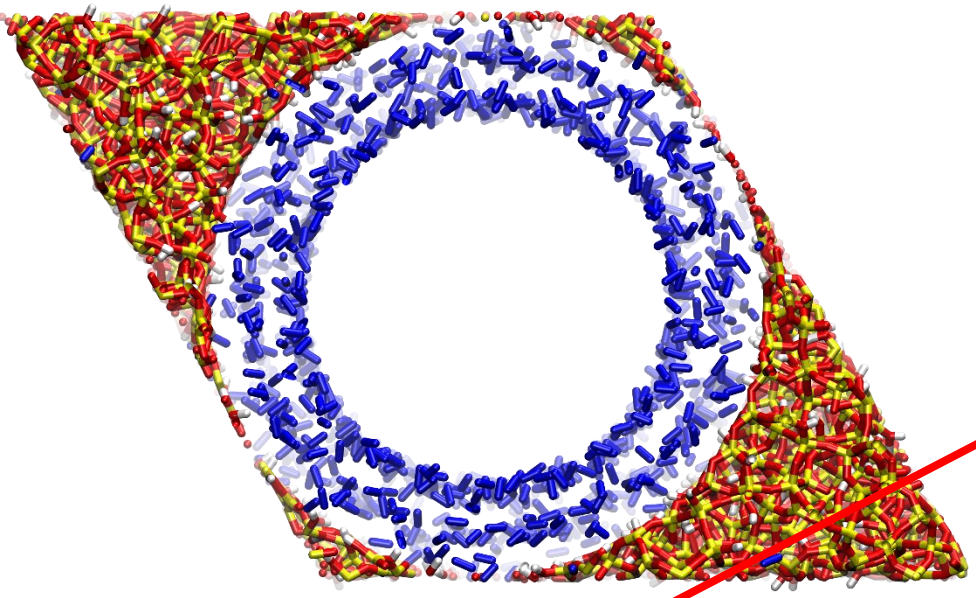
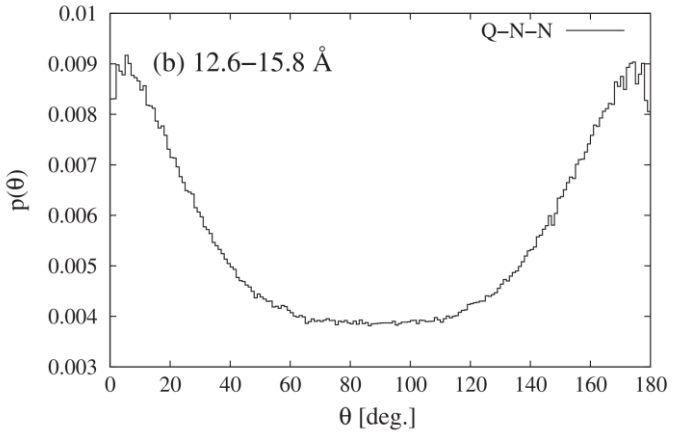
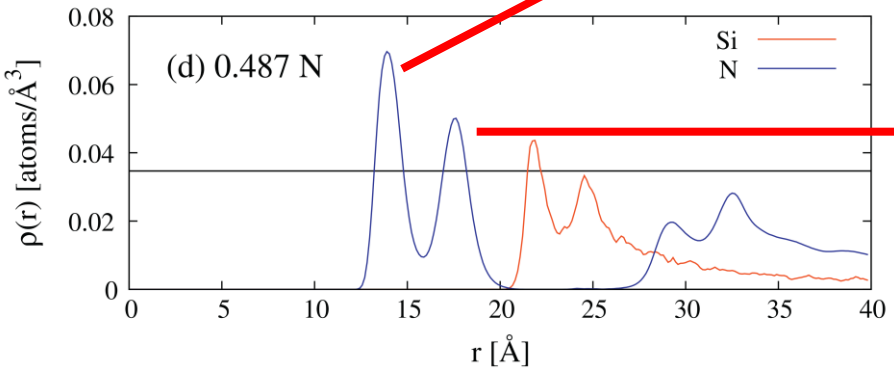
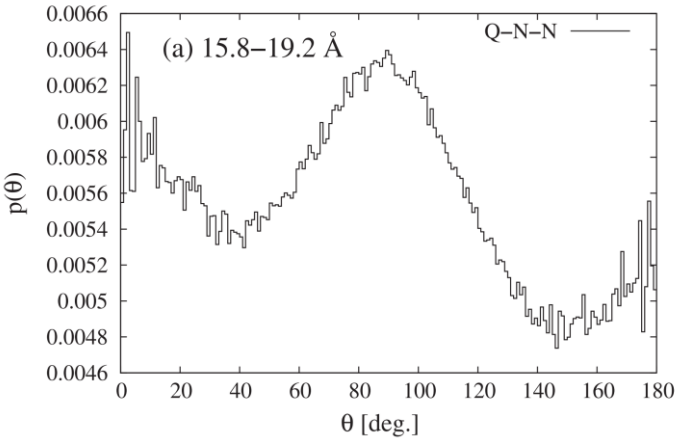
Orientation of N_2 molecules layered inside MCM-41









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Conclusions: Adsorption of N_2 in MCM-41

(1) Before the onset of capillary condensation of nitrogen into MCM-41 the gas is strongly adsorbed in distinct layers inside the pore space.

(2) Each layer of nitrogen has a strong orientational configuration
- The layer of N_2 molecules closest to the silica surface prefers to lie flat with the long-axis of the molecule parallel with the surface.
- The second layer of N_2 molecules favours a configuration where the long-axis of the molecule is oriented radially with respect to the pore axis.

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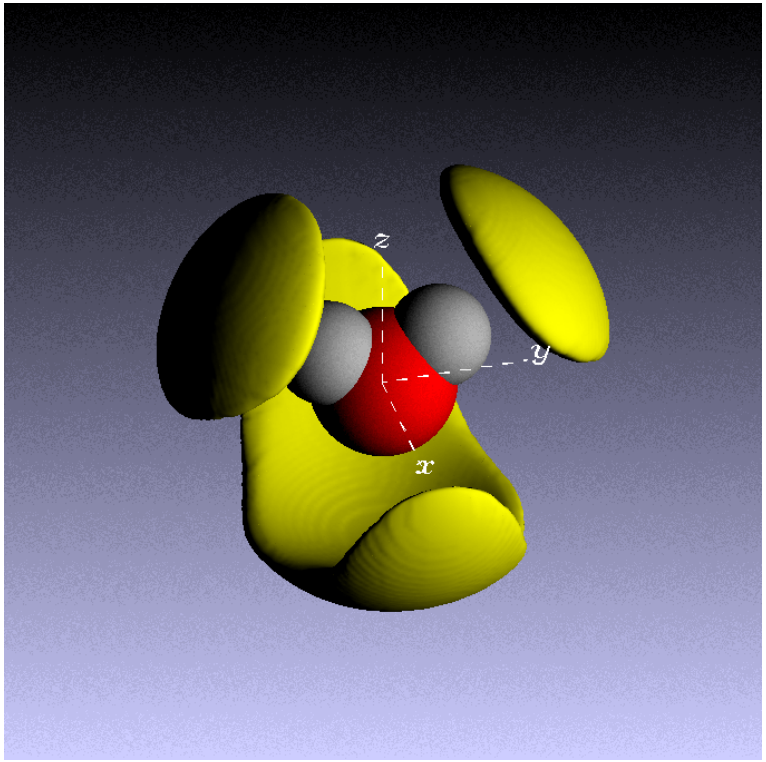
Empirical Potential Structure Refinement
Summary of Current Status
EPSR version 25

Atomic and molecular liquids	Yes
Atomic and molecular glasses	Yes
Neutron scattering data	Refine
X-ray scattering data	Refine
Large scale systems	100Å (120Å at a push) 150000 atoms 50000 molecules
Mesostructured systems	Yes
Ordered and partially ordered systems	Yes
Bragg scattering modeling	Yes
GUI front end	Yes

Empirical Potential Structure Refinement

Download your copy of EPSR from:

https://www.isis.stfc.ac.uk/Pages/Empirical-Potential-Structure-Refinement.aspx



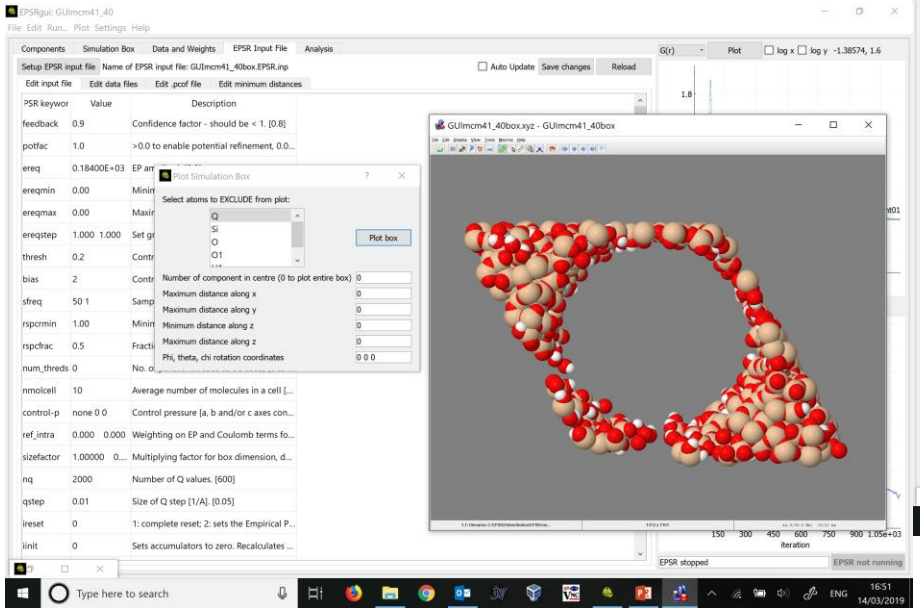
$$U^{N}_{\alpha\beta} = U^{O}_{\alpha\beta}(r) + U^{\Delta EP}_{\alpha\beta}(r)$$

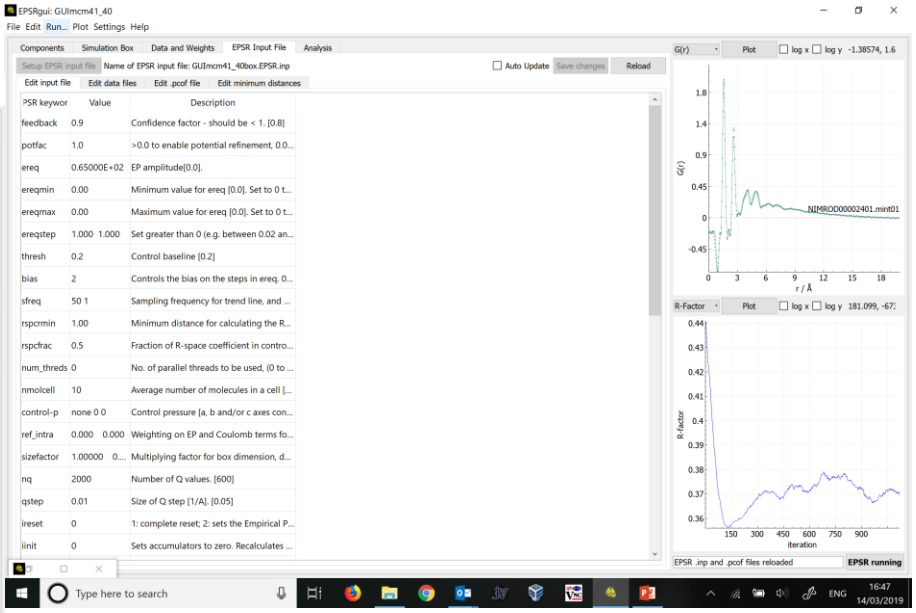
A.K.Soper *Chem Phys* **202** p.295 (1996)
A.K.Soper *Phys Rev B* ***72*** 104204 (2005)

EPSRgui: A more intuitive way to run EPSR

Download your copy of EPSRgui from:

https://www.isis.stfc.ac.uk/Pages/Empirical-Potential-Structure-Refinement.aspx





S.K.Callear, Rutherford Appleton Laboratory Technical Report
RAL-TR-2017-002

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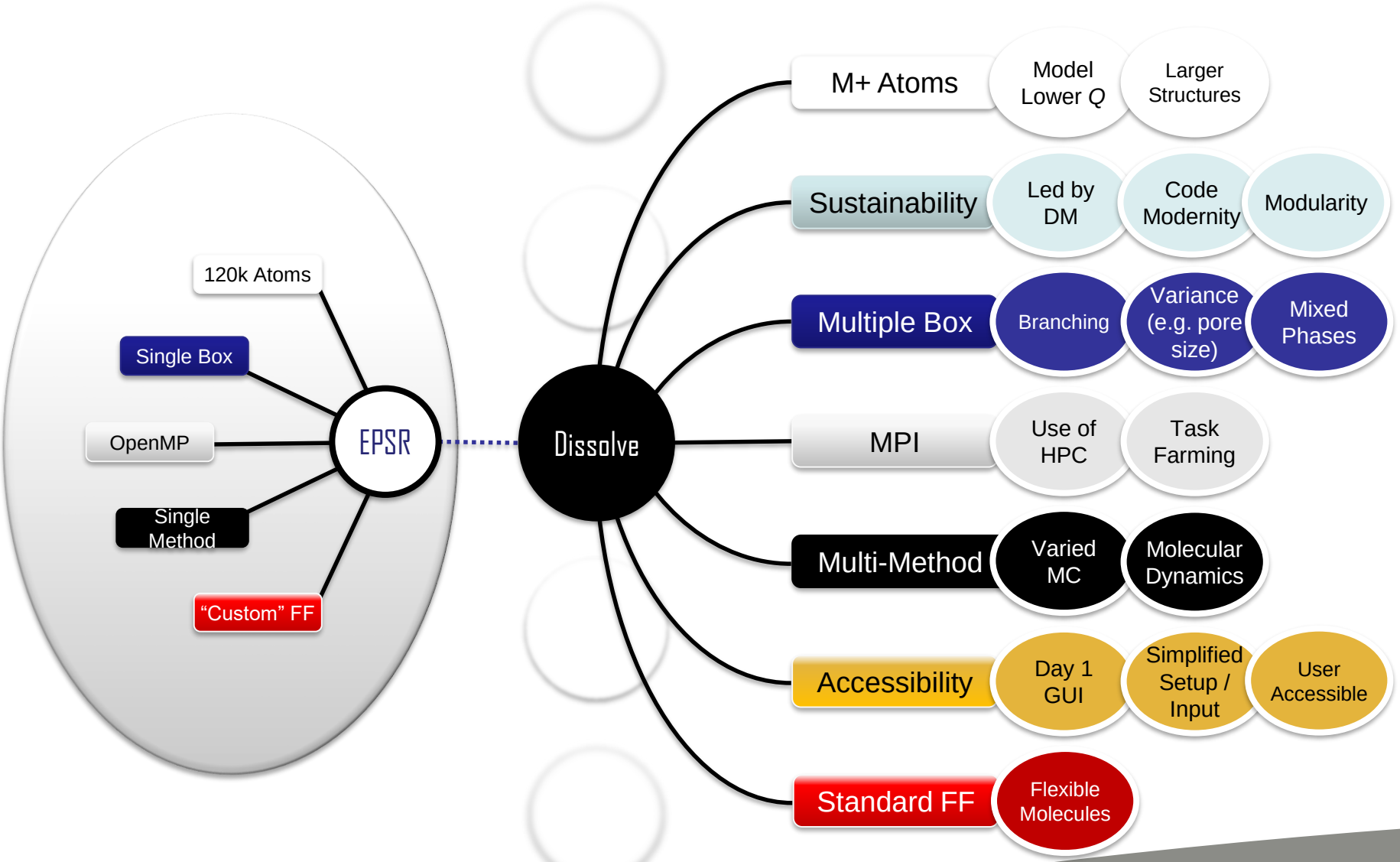
The future of EPSR - dissolve

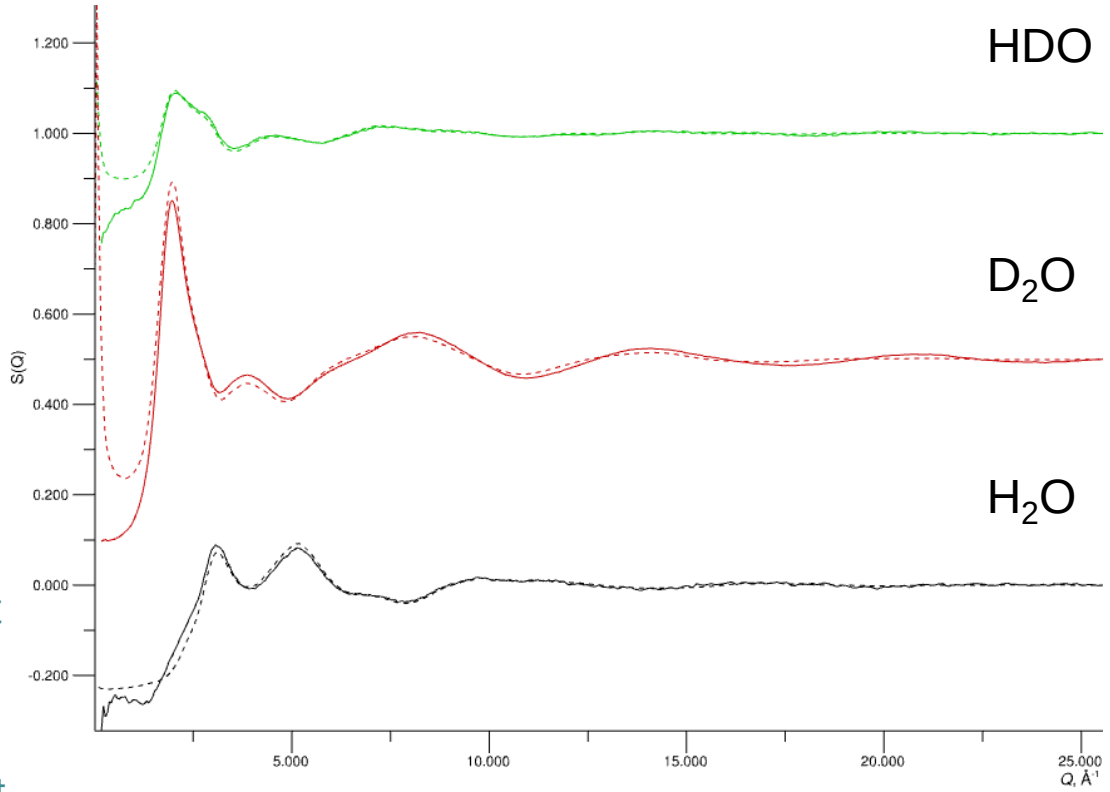


https://github.com/trisyoungs/dissolve

Dissolve – current status

- ✓ Monte Carlo
- ✓ Molecular dynamics
- ✓ Full user interface
- ✓ Potential refinement
- ✓ Million atom capable
  - 333,334 SPC/FW water
  - 15 Å cutoff
  - RDF r_{max} = 107.7 Å
  - 4 days / 8 cores on SCARF

  - Molecule MC : 2 m 40 s / it
  - Intra MC : 4 m 30 s / it
  - Partial g(r) : 29 m 30 s / it
  - Energy : 20 s / it



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