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ISIS Neutron and Muon Source

EPSR & Dissolve

Data-driven structural modelling of total scattering data

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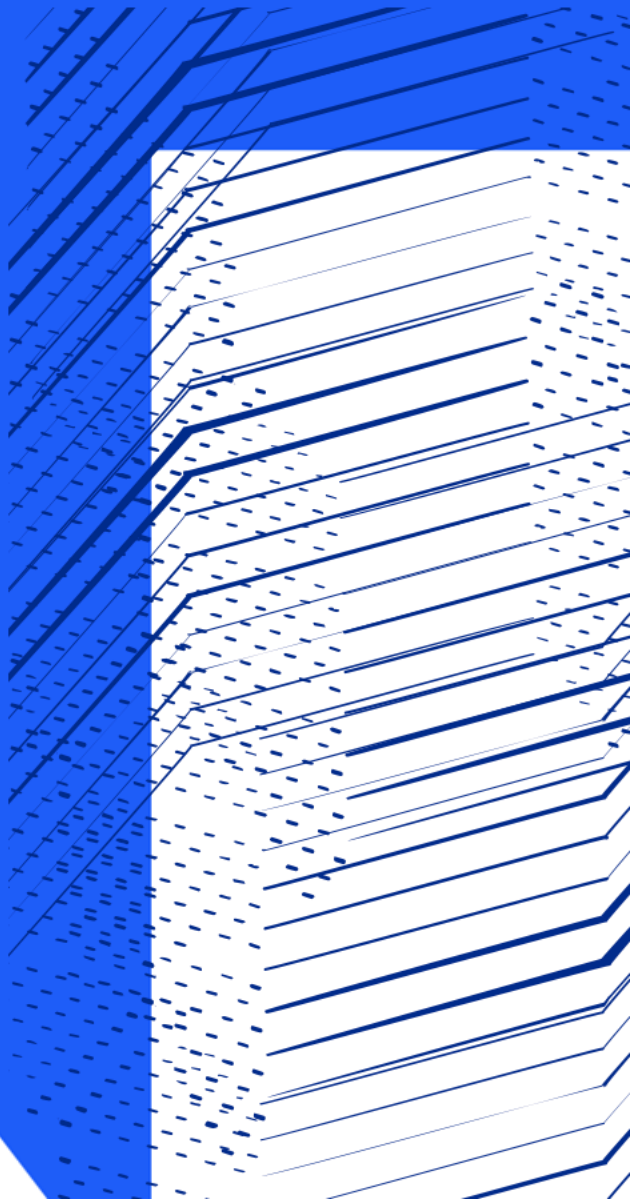

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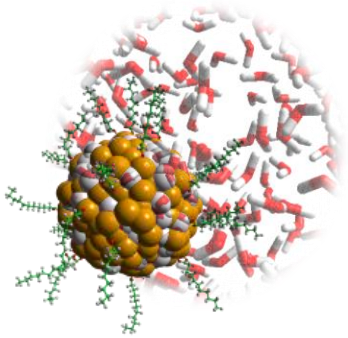
Disordered Materials and Total Scattering

Disordered Materials

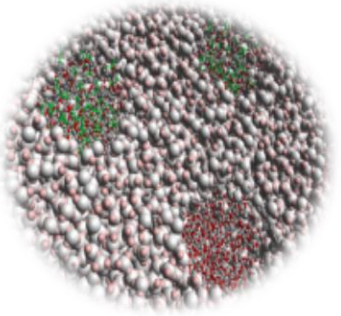
- Show predominantly local ordering (i.e. on the scale of atoms or molecules)
- Show primarily diffuse scattering (“soft” features in measured data)
- Are typically dynamic (e.g. liquids) – average structural picture is obtained
- May show long-range order (i.e. Bragg scattering)
- May contain large length-scale correlations (e.g. micelles, lamellae)

Liquids

Glasses

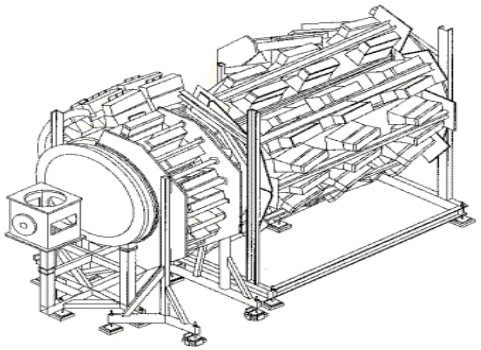


Solutions



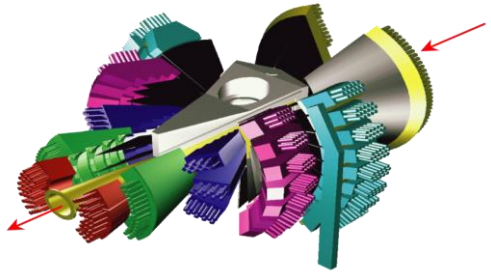
Condensed phases under confinement

Total Scattering Instruments @ ISIS



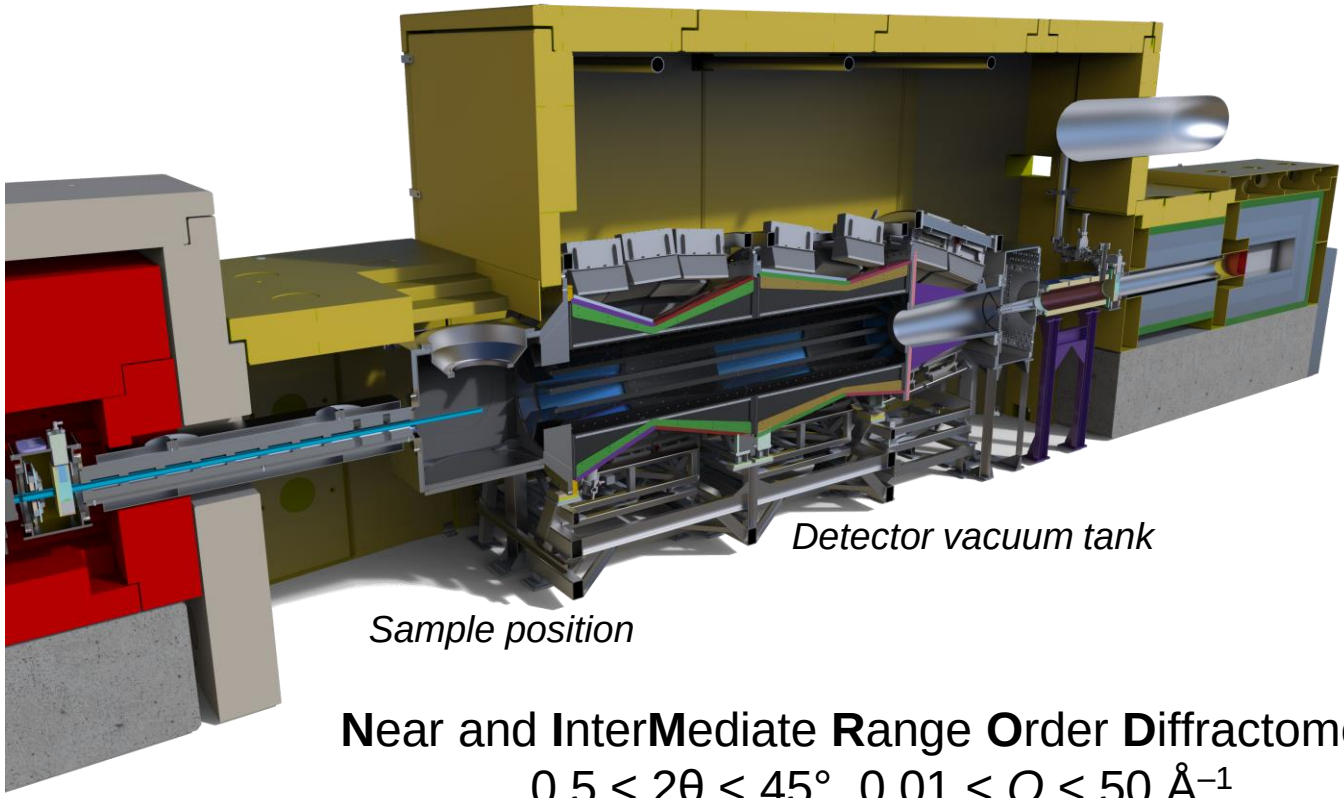
Small **A**ngle **N**eutron **D**iffractometer for **A**morphous and **L**iquid **S**amples

$3 < 2\theta < 38^\circ$, $0.1 < Q < 50$ Å^{-1}



General **M**aterials Diffractometer

$1.21 < 2\theta < 171.4^\circ$, $0.04 < Q < 50$ Å^{-1}



Near and **I**nter**M**ediate **R**ange **O**rder **D**iffractometer

$0.5 < 2\theta < 45^\circ$, $0.01 < Q < 50$ Å^{-1}

All three instruments exist to probe and understand material structure

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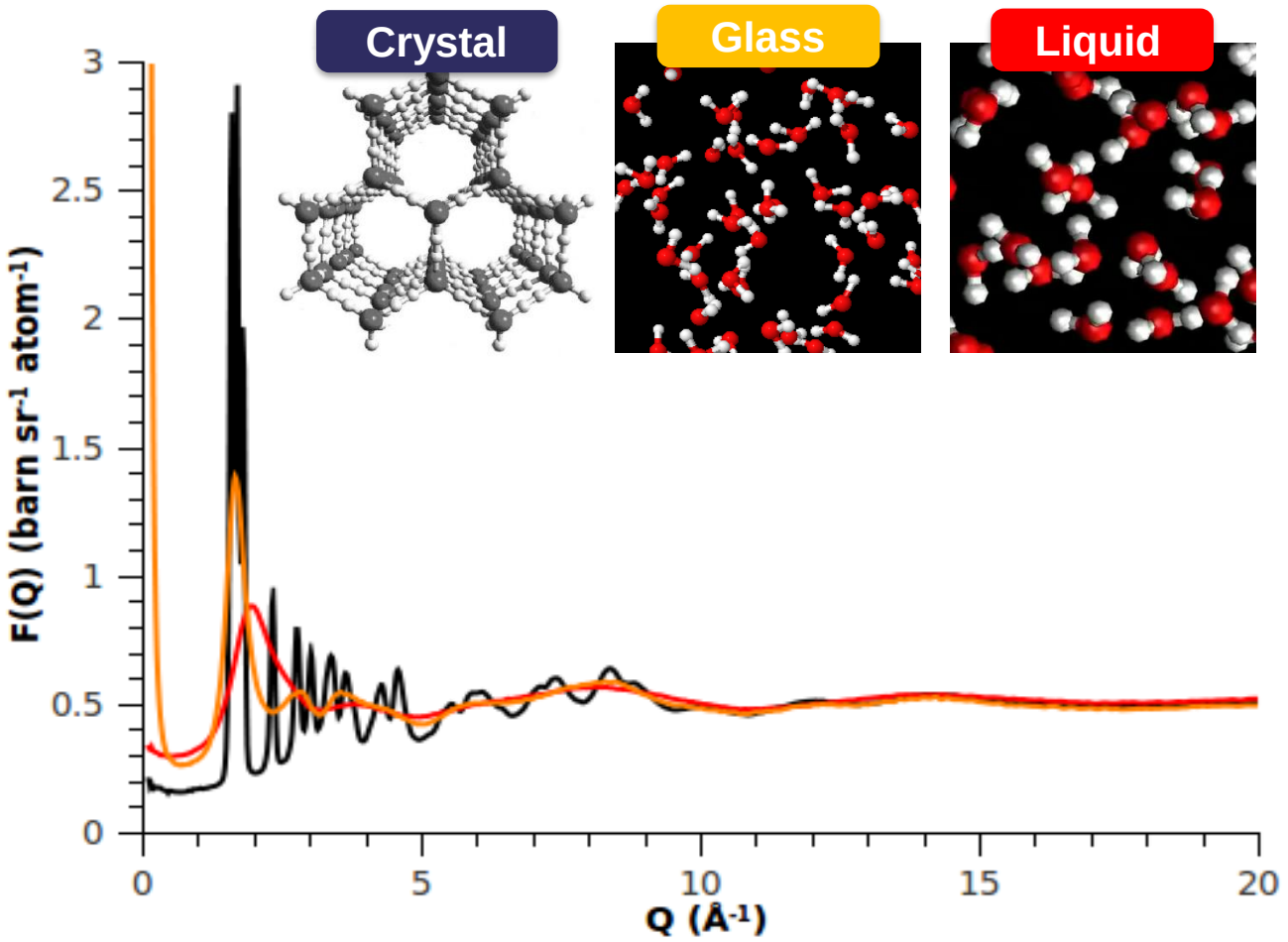
Total Structure Factor F(Q)



- Contains all correlation information between all “objects” in the system
- Also includes Bragg scattering
- Also includes any SANS

“A single dataset encompassing structural information on the target sample, no matter the phase, complexity, or composition of the system.”

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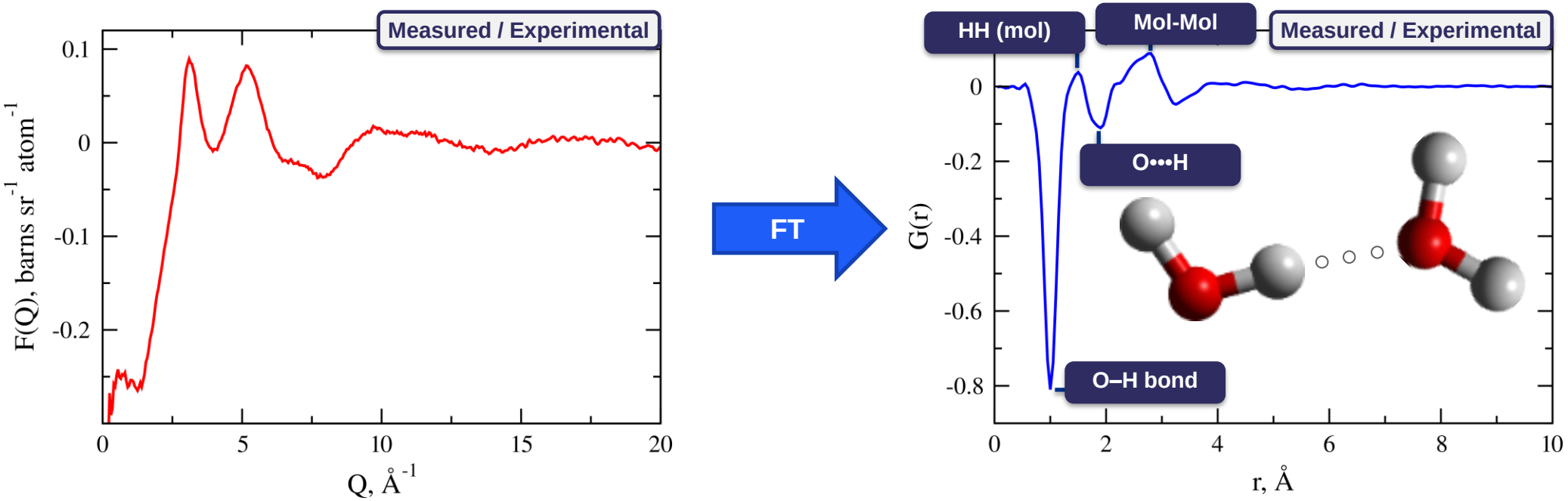
Interpreting F(Q)

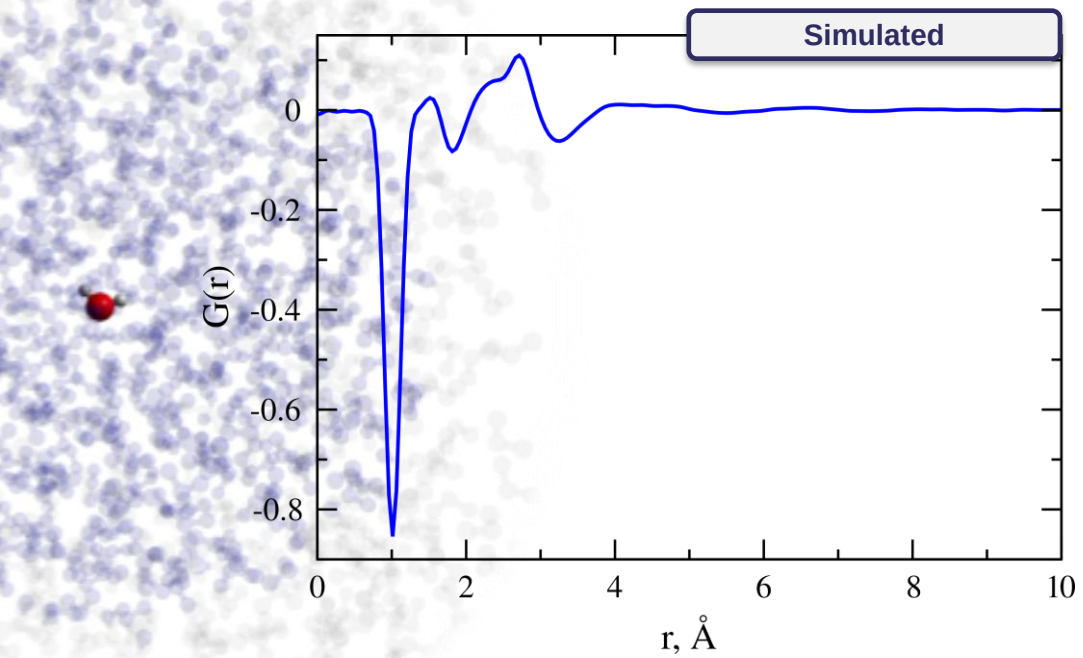
Can Fourier transform data from *Q*-space (instrument) to *r*-space (real)



Non-trivial to analyse by inspection. Angular correlations? 3D structure?

Simulating F(Q)

Atomistic simulation – molecular dynamics, Monte Carlo – using off-the-shelf forcefield.



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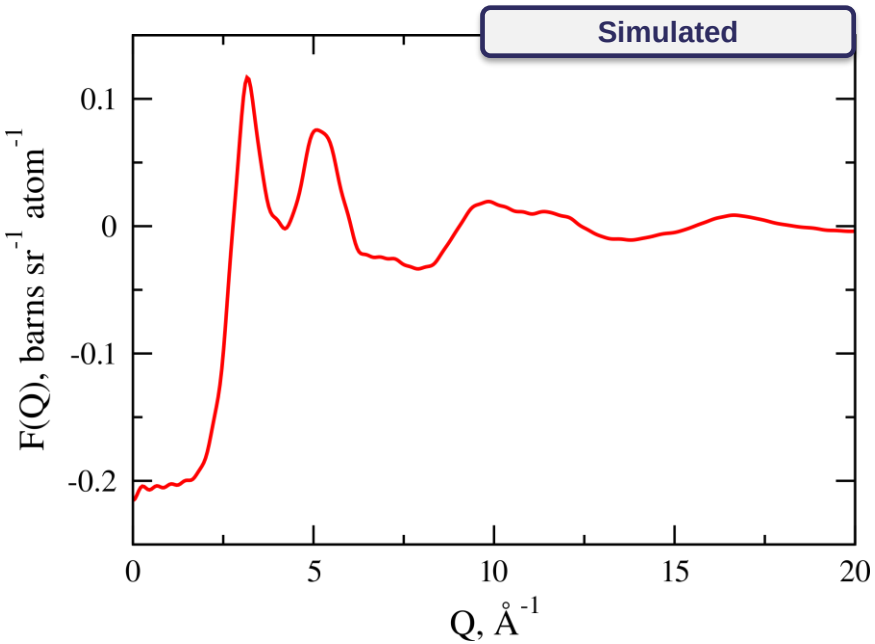
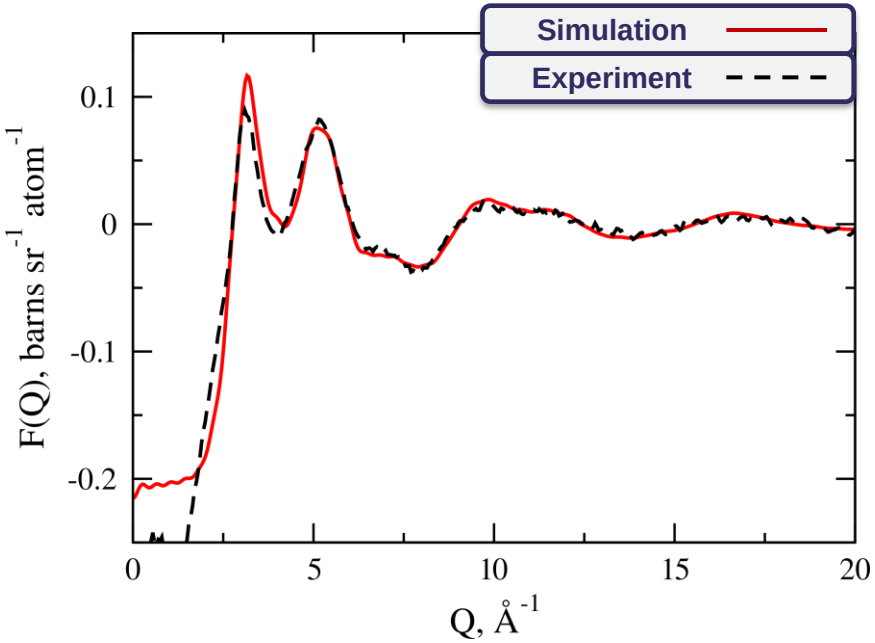


Can calculate any correlation I want from a simulation, but does it reflect reality?

Simulation vs Reality

Forcefields can give results close to experiment, but often show discrepancies.

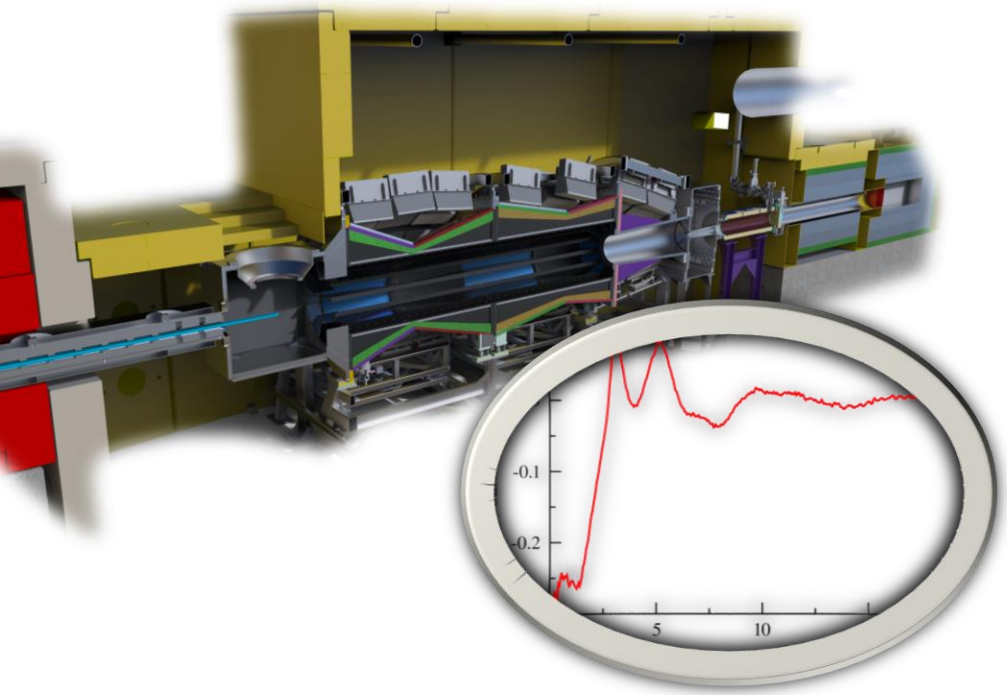
- Parameterised against phase data etc.
- Rarely against bulk structure data

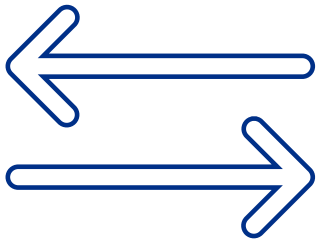


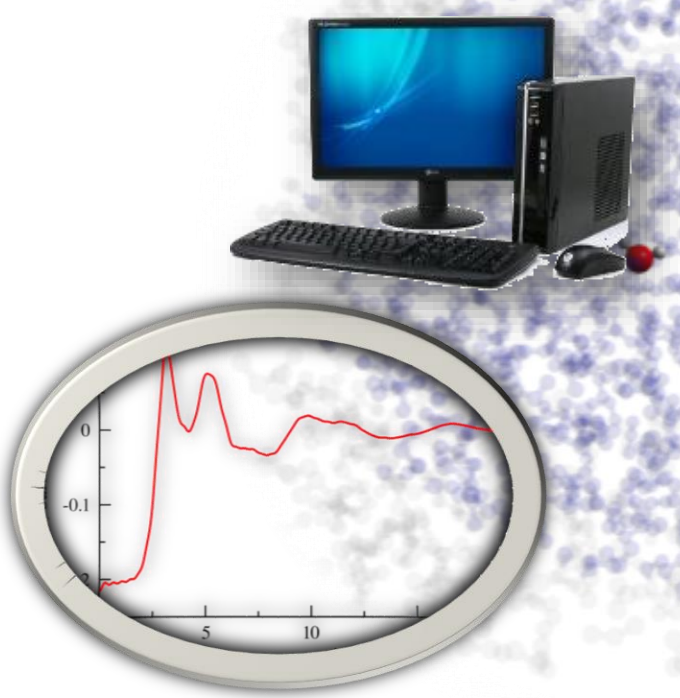
Solution?

- Modify the forcefield to improve it
- By hand? Tedious, impractical…
- Automatically, using the data? How?

Joining Simulation and Experiment







- How can I form a simulation consistent with the experimental data?
- How can I expand my experimental data to reduce underdetermination?

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Data-Driven Refinement

The Goal

- Make a simulation of a system of arbitrary complexity
- Compare available experimental F(Q) with simulated F(Q)

- **Adjust the underlying forcefield to improve agreement**

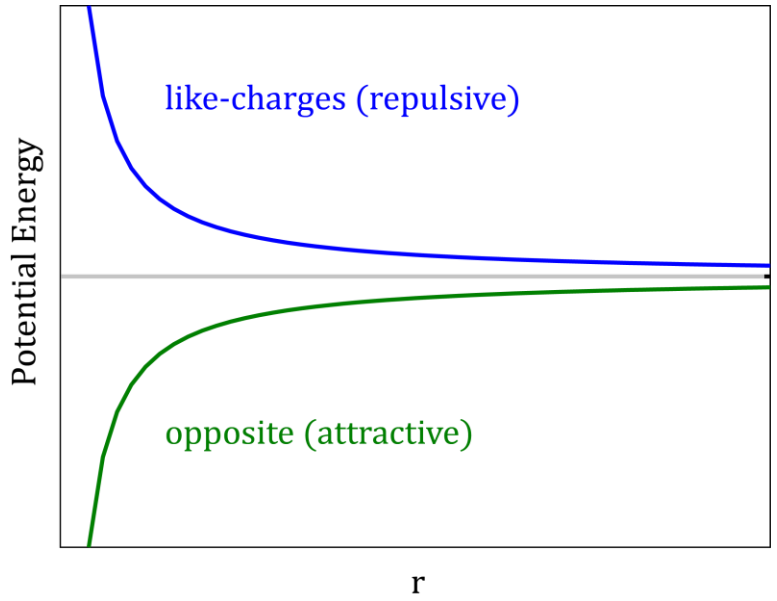
- Calculate structural properties of interest
- Write a paper
- Go home

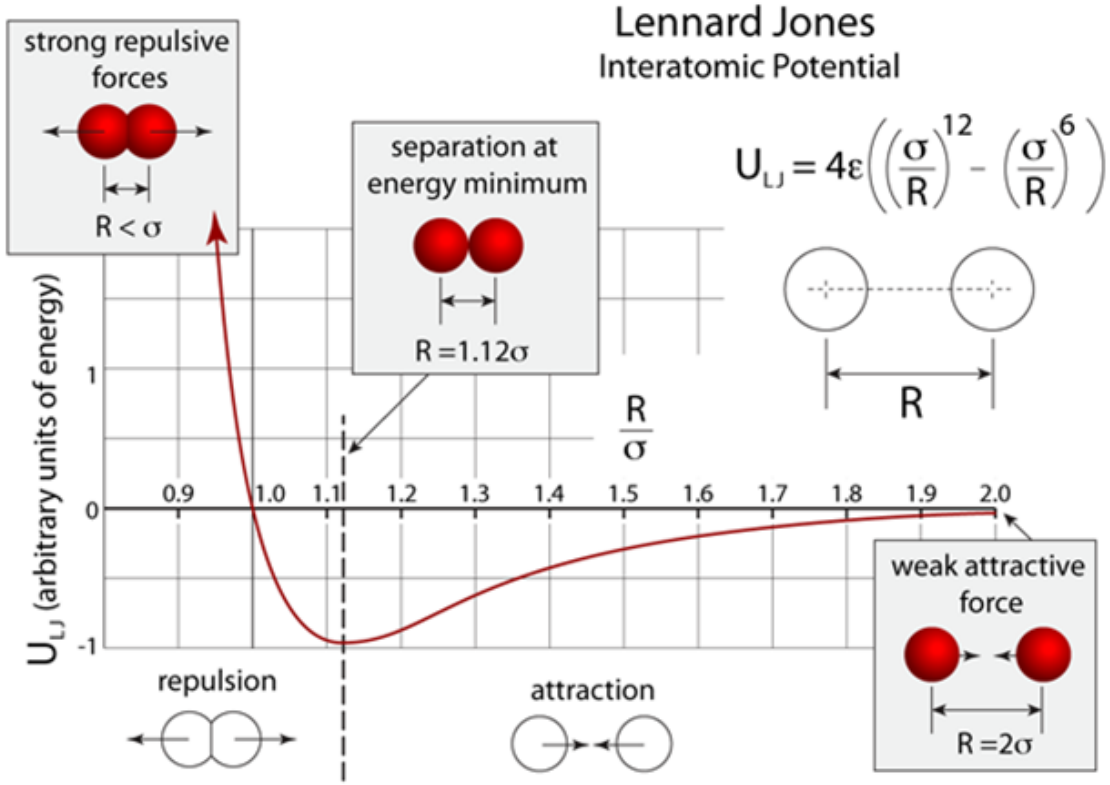
The Target: Pair Potentials

- Describes the interactions between atoms “through space”
- Parameters from:
  - Existing forcefields (LJ+q)
  - Calculated via QM / DFT (q)

Coulomb:

$$U = \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}^2}$$





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Constructing the F(Q)

$$F(Q) = \sum_{i,j} (2 - \delta_{ij}) c_i c_j b_i b_j S_{ij}(Q)$$

Total Structure Factor
(Experimental Observable)

$$c_i = \frac{n_i}{N} \qquad b_i = scattering\ length$$

$$S_{ij}(Q) = \rho \int_0^\infty 4\pi r^2 g_{ij}(r) \frac{\sin Qr}{Qr} \mathrm{d}r$$

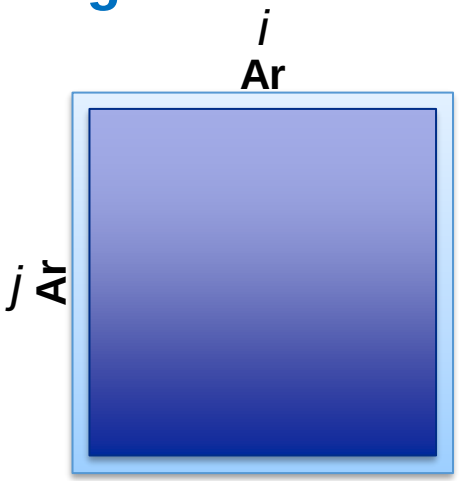
Partial Structure Factor

(Simulation Observable)

Atom Types

- A specific kind of atom *in the simulation*
  - Depends at least on the element. Can be split by chemical environment.
  - Does not depend on isotope...

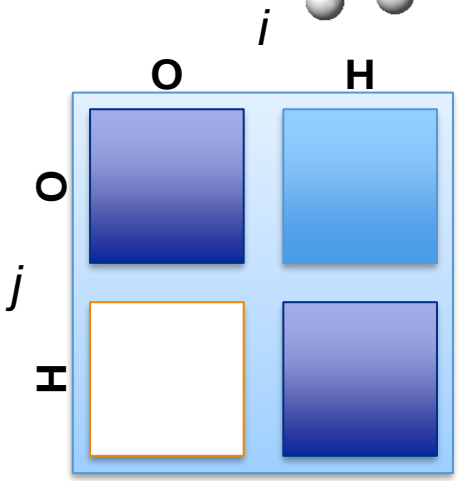
Argon



***N* = 1**

Also N_2, O_2…

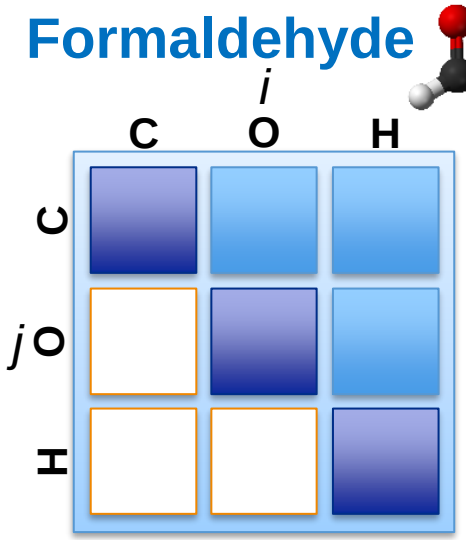
Water



***N* = 3**

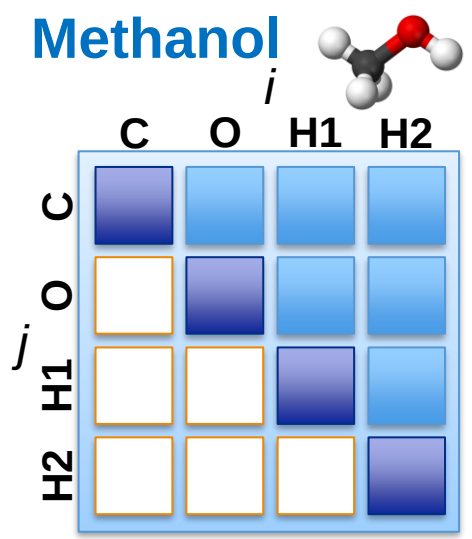
Also benzene, silica…

Formaldehyde



***N* = 6**

Methanol



***N* = 10**

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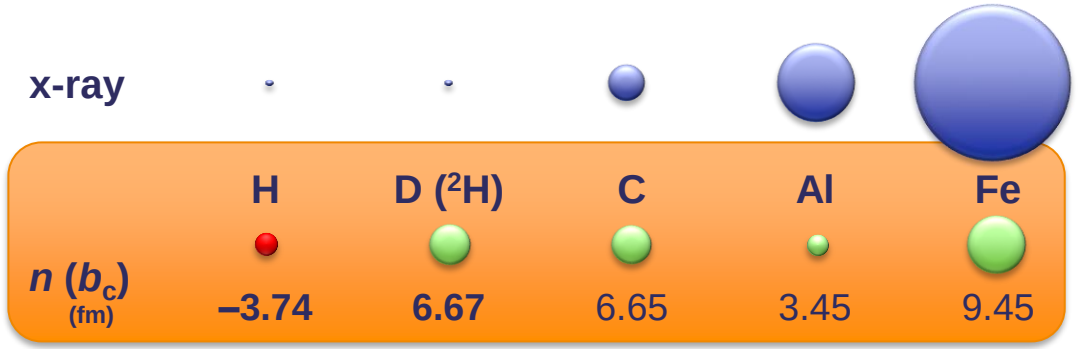
$$F(Q) = \sum_{i,j} (2 - \delta_{ij}) c_i c_j b_i b_j S_{ij}(Q)$$

Isotopic Substitution

$$F(Q) = \sum_{i,j} (2 - \delta_{ij}) c_i c_j \underbrace{\boldsymbol{b_i b_j}}_{\text{Scattering Lengths}} S_{ij}(Q)$$

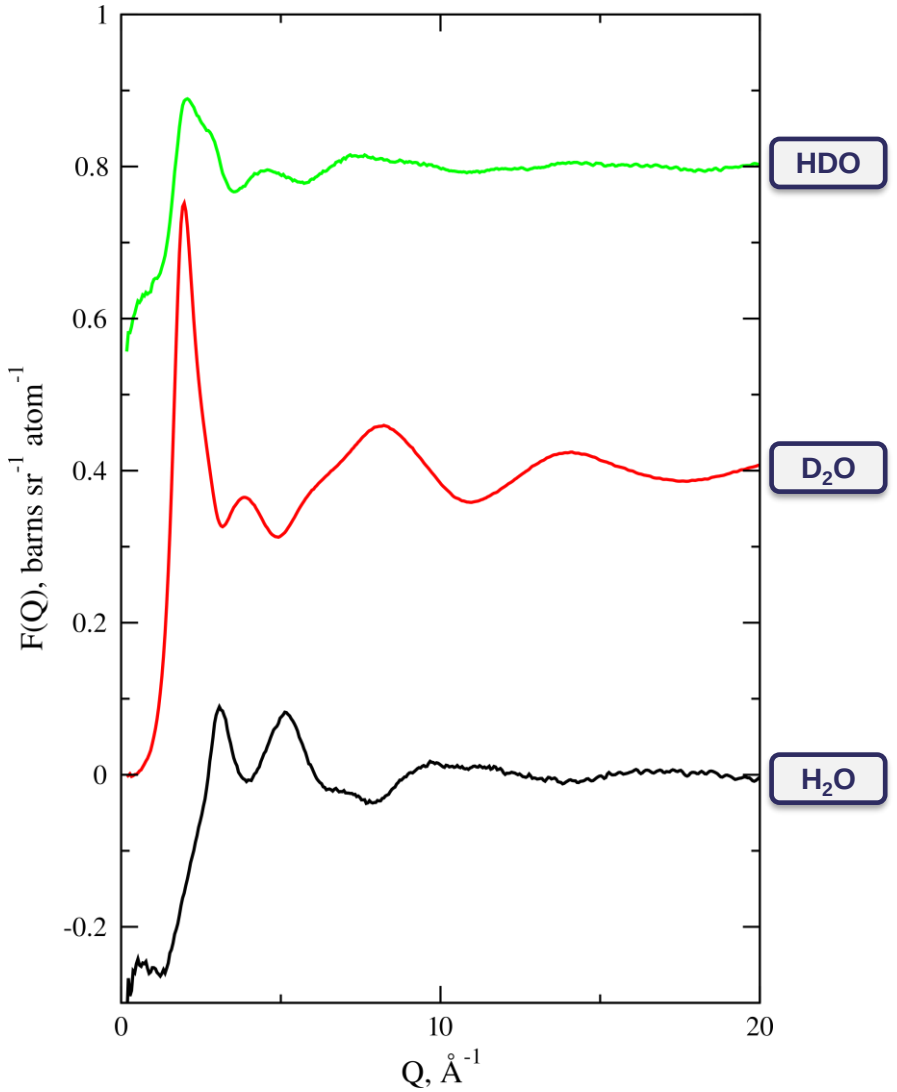


- Partial $S(Q)$ weighted by coherent scattering length, $\boldsymbol{b}$
- For neutrons, $\boldsymbol{b}$ is dependent on isotope
  - e.g. ^{2}H for H, ^{15}N for N, ^{6}Li for Li
- Key assumption: structure is independent of isotopes used
- Perform multiple measurements on the same system, with different isotopic substitutions

Isotopic Water

- Swapping H for ^2H (D) we can get three distinct datasets focussing on one atom type
  - H_2O
  - D_2O
  - 50:50 mix of H_2O and D_2O

Swapping isotopes always needs to involve enough atoms to produce a noticeable change in the F(Q)



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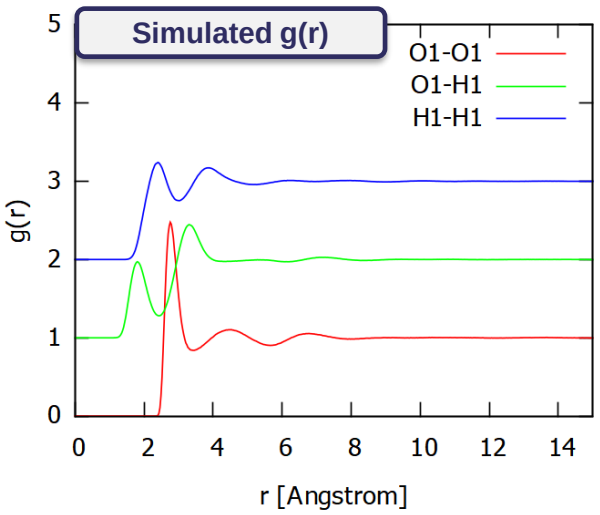
g(r) to S(Q) to F(Q) and back again?



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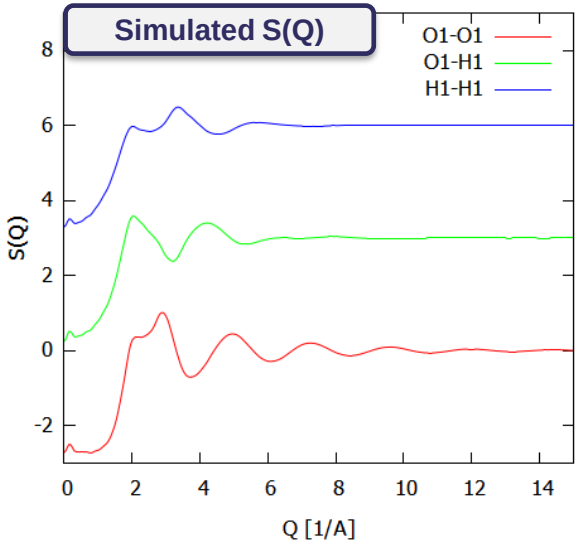

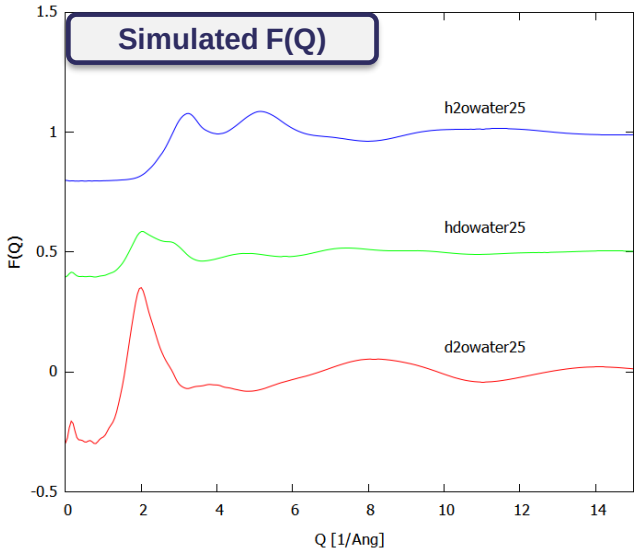

$$w_{ij} = c_i c_j \boldsymbol{b_i} \boldsymbol{b_j}$$

$$\begin{bmatrix} 0.0374 & -0.0964 & 0.0622 \\ 0.0374 & 0.1722 & 0.1980 \\ 0.0374 & 0.0378 & 0.0096 \end{bmatrix} \begin{bmatrix} S_{OO}(Q) \\ S_{OH}(Q) \\ S_{HH}(Q) \end{bmatrix} = \begin{bmatrix} F_{H_2O}(Q) \\ F_{D_2O}(Q) \\ F_{HDO}(Q) \end{bmatrix}$$

Invert

$$\begin{bmatrix} 4.8238 & -2.7037 & 24.6061 \\ -5.8227 & 1.6265 & 4.1962 \\ 4.1525 & 4.1525 & -8.3050 \end{bmatrix} \begin{bmatrix} F_{H_2O}(Q) \\ F_{D_2O}(Q) \\ F_{HDO}(Q) \end{bmatrix} = \begin{bmatrix} S_{OO}(Q) \\ S_{OH}(Q) \\ S_{HH}(Q) \end{bmatrix}$$

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The General Case

- For an “ideal” system such as H_2O where enough isotopic substitutions can be made, direct matrix inversion is possible
- What about cases where one or more partials only contribute weakly?
- What about cases where not enough isotopic substitutions can be made?

For example, silica:

$$\begin{bmatrix} F_{SiO_2}(Q) \end{bmatrix} = \begin{bmatrix} 0.0191 & 0.1070 & 0.1497 \end{bmatrix} \begin{bmatrix} S_{SiSi}(Q) \\ S_{SiO}(Q) \\ S_{OO}(Q) \end{bmatrix}$$

No inversion possible, so no route from $F(Q)$ to $S(Q)$ (and $g(r)$)

The Augmented Scattering Matrix

- We have a simulation which we assume gives us a good "guess" of the $F(Q)$ and hence a good guess for the partial $S(Q)$
- Define a feedback factor, $0 < f < 1$, and write new weighting factors

$$w_{ij} = f c_i c_j b_i b_j$$

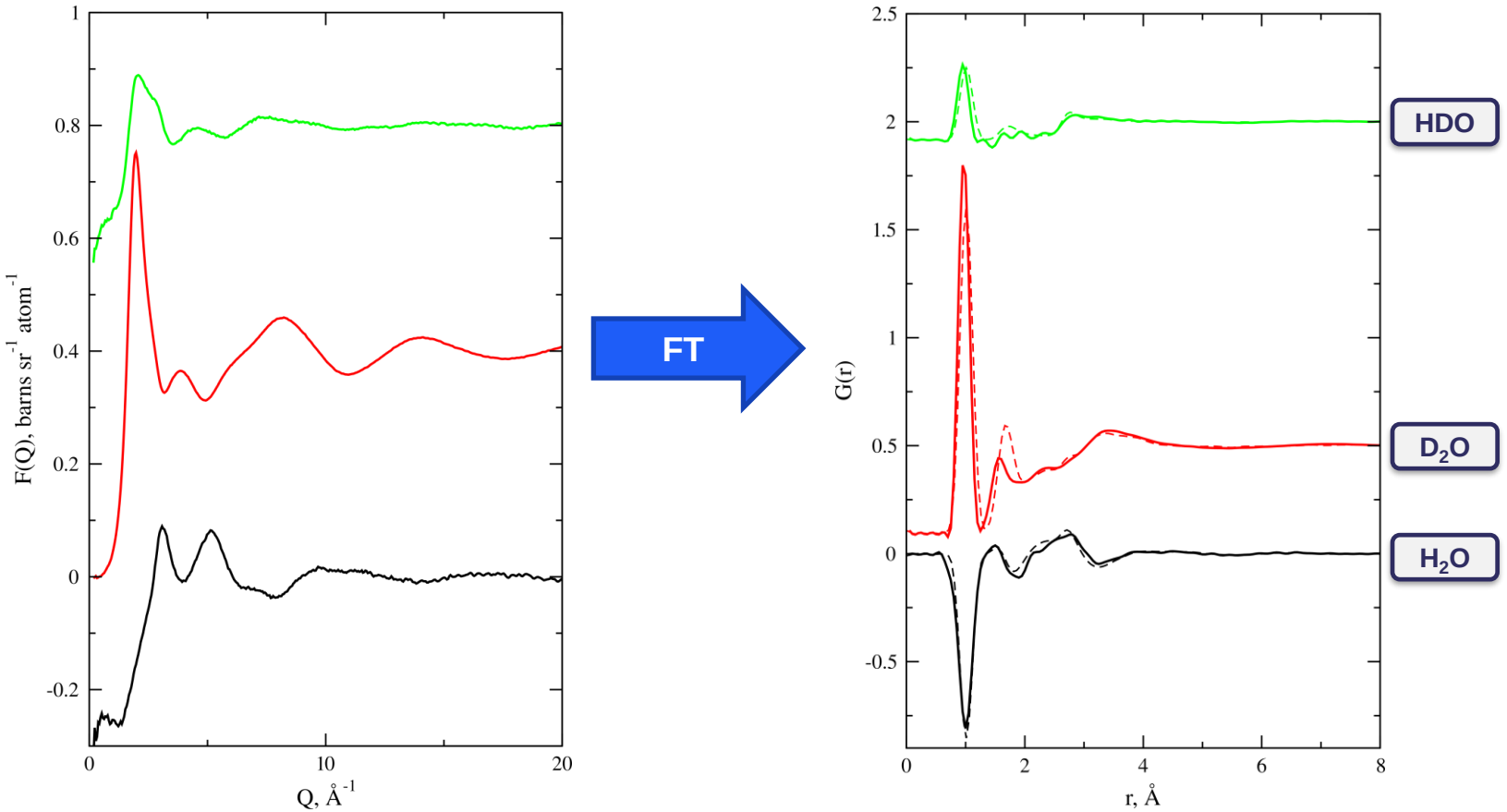
$$\begin{bmatrix} F_{SiO_2}(Q) \\ S^{sim}_{SiSi}(Q) \\ S^{sim}_{SiO}(Q) \\ S^{sim}_{OO}(Q) \end{bmatrix} = \begin{bmatrix} 0.0172 & 0.0963 & 0.1347 \\ 0.1 & 0.0 & 0.0 \\ 0.0 & 0.1 & 0.0 \\ 0.0 & 0.0 & 0.1 \end{bmatrix} \begin{bmatrix} S_{SiSi}(Q) \\ S_{SiO}(Q) \\ S_{OO}(Q) \end{bmatrix}$$

$$w_{ij} = (1 - f)$$

- Now we have an overdetermined matrix for which we can find a pseudoinverse

What About Bound Terms?

- Typically dealing with molecular species, so we have chemical bonds (and angles, torsions etc.)
- Assumed / forcefield-obtained values may not reflect reality…



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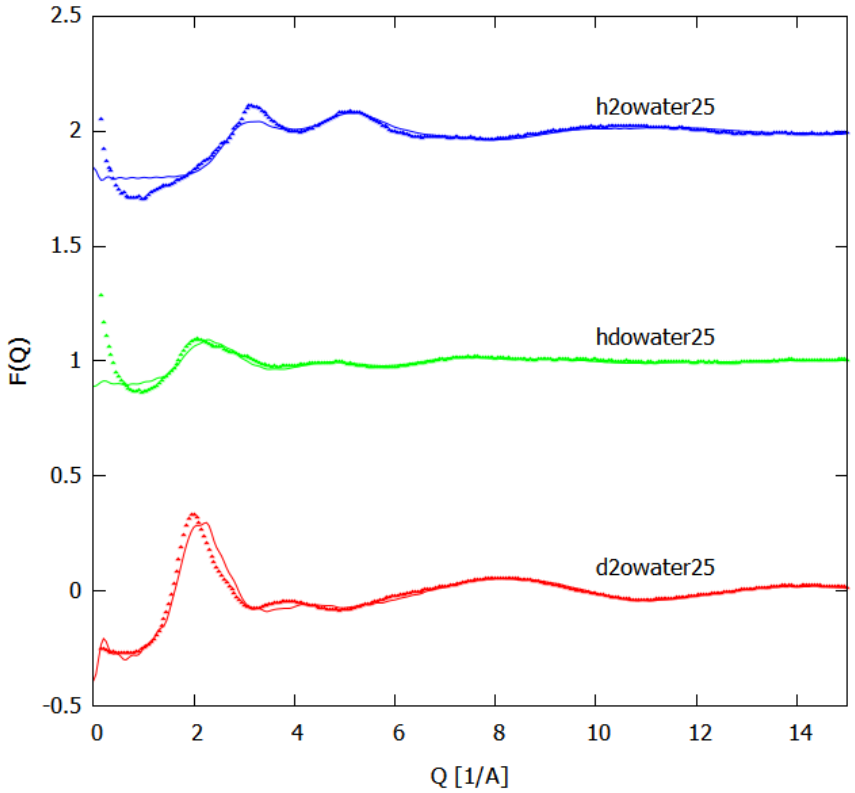
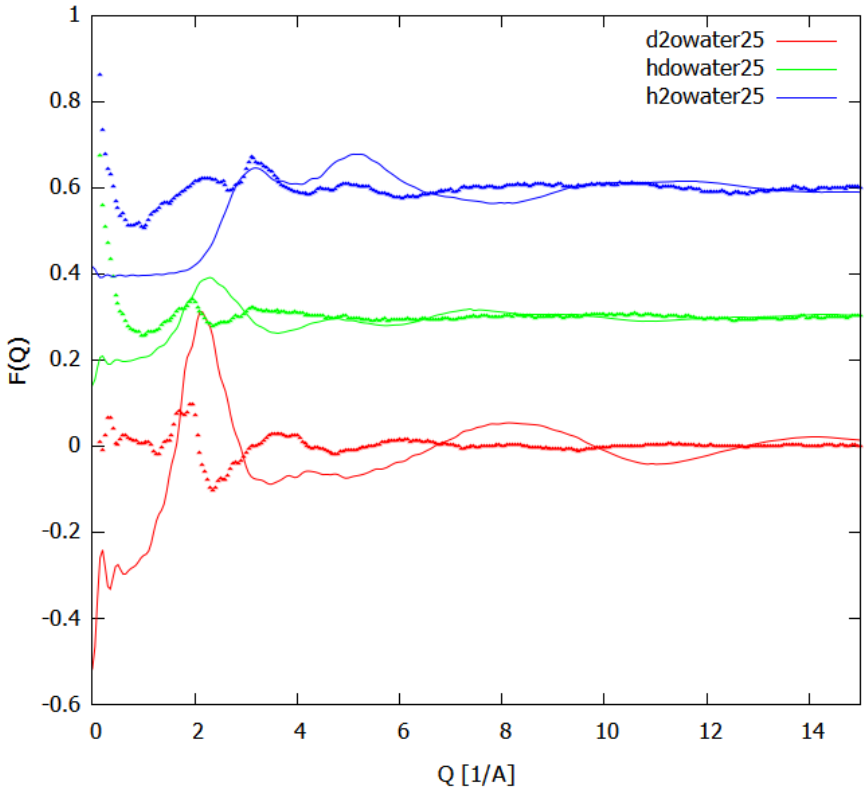
Empirical Potential Structure Refinement

The EPSR Method

1) Take differences between experimental and simulated $F(Q)$ to get $\Delta F(Q)$



F(Q) from simulation and experiment



ΔF(Q) between simulation and experiment

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The EPSR Method

1) Take differences between experimental and simulated $F(Q)$ to get $\Delta F(Q)$
2) Enter these $\Delta F(Q)$ into the inverse scattering matrix to generate $\Delta S(Q)$

$$\begin{bmatrix} \Delta S_{OO}(Q) \\ \Delta S_{OH}(Q) \\ \Delta S_{HH}(Q) \end{bmatrix} = \begin{bmatrix} 4.8238 & -2.7037 & 24.6061 \\ -5.8227 & 1.6265 & 4.1962 \\ 4.1525 & 4.1525 & -8.3050 \end{bmatrix} \begin{bmatrix} \Delta F_{H_2O}(Q) \\ \Delta F_{D_2O}(Q) \\ \Delta F_{HDO}(Q) \end{bmatrix}$$

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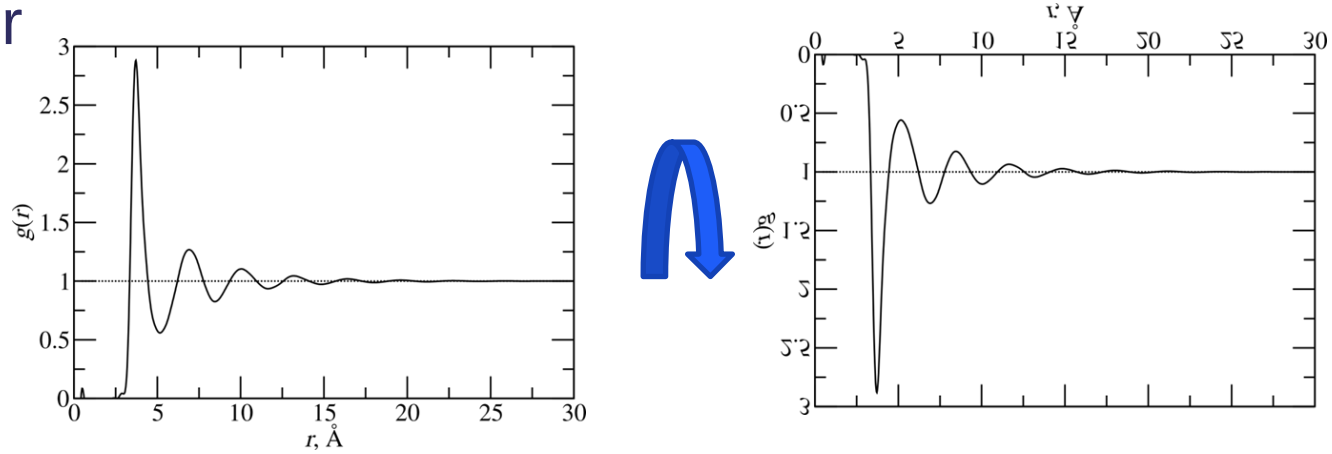
3) Transform the $\Delta S(Q)$ into $\Delta g(r)$ and use these to form an additional, empirical potential for each atom type pair



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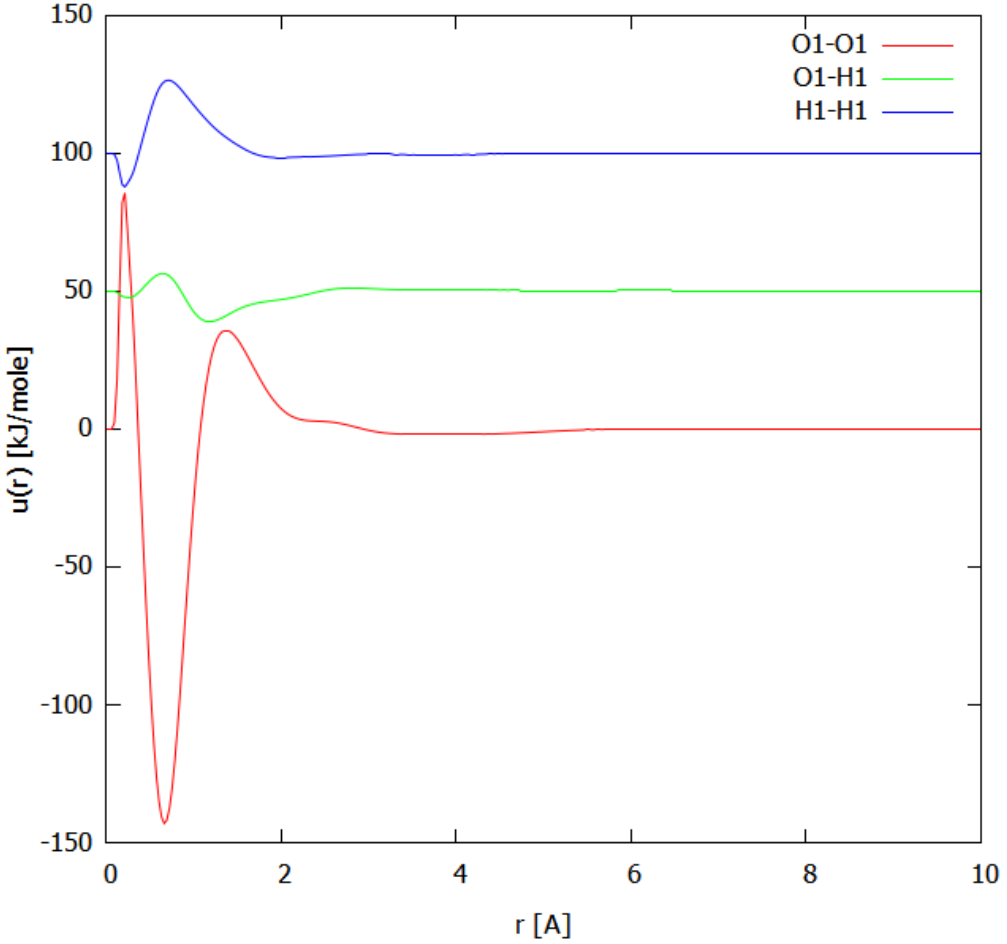
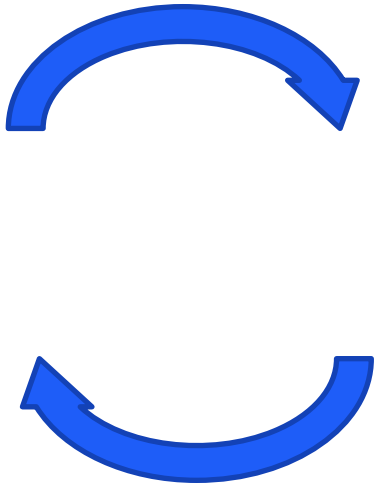
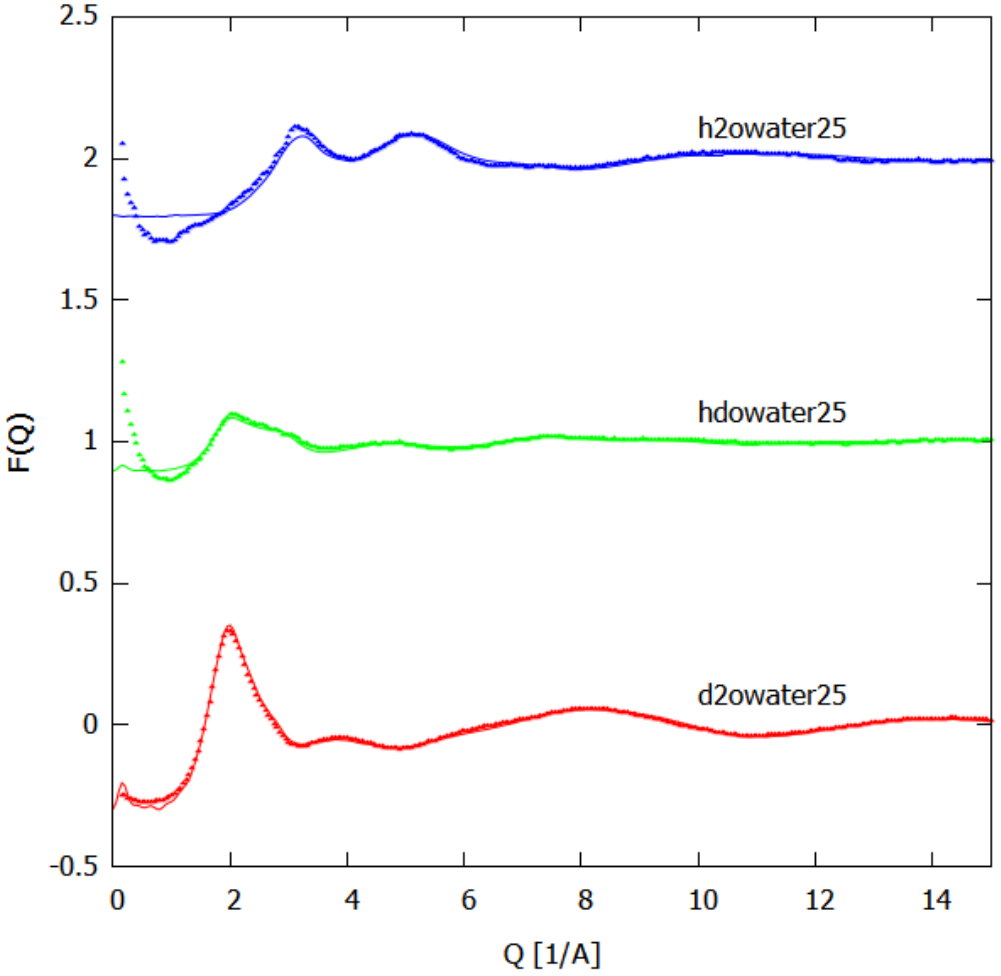
3) Transform the $\Delta S(Q)$ into $\Delta g(r)$ and use these to form an additional, empirical potential for each atom type pair
4) Repeatedly run the simulation and refine **additional potentials** until the experimental and simulated $F(Q)$ 'match'

Potential Refinement: EPSR results







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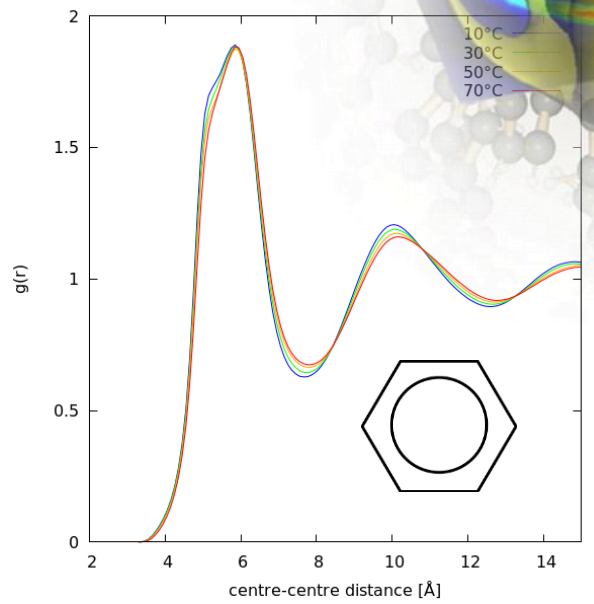
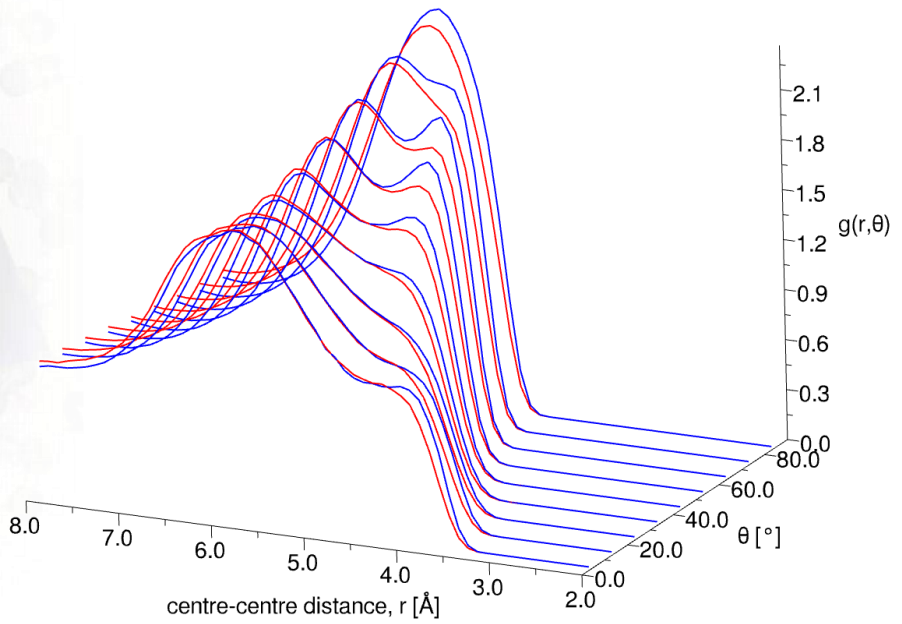
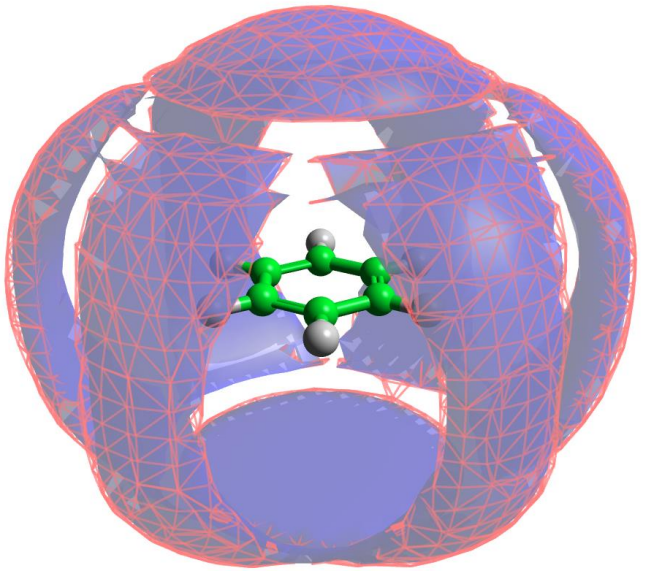
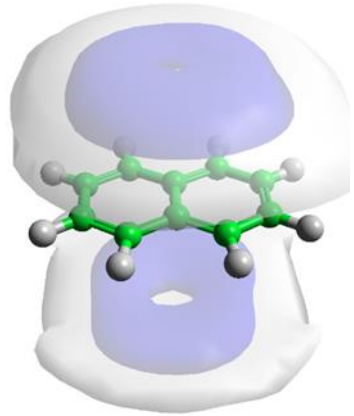
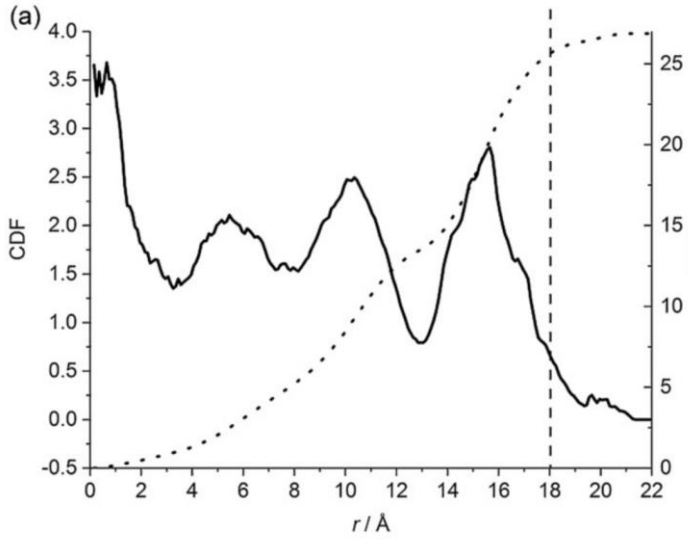
Analyse the Refined Simulation

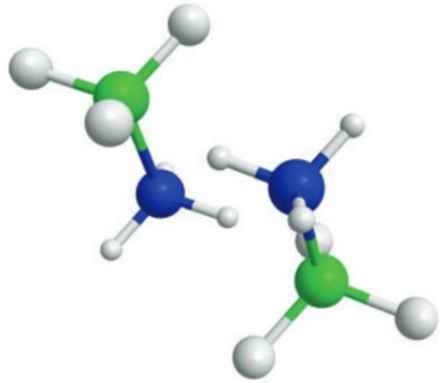


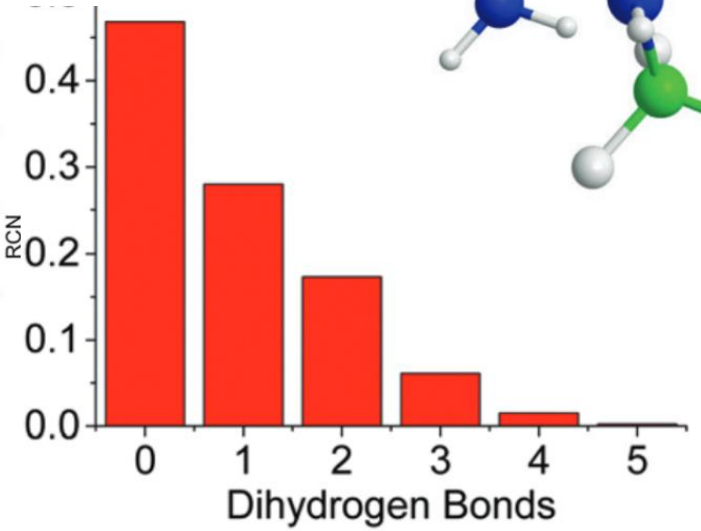












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The Tools & Their Limits

EPSR & Dissolve

Empirical Potential Structure Refinement (EPSR)

- Developed by Prof. A. K. Soper
- Fortran / OpenMP
- Monte Carlo, custom forcefield, 140k atoms

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

Dissolve

- Developed by Team Dissolve
- C++ / TBB / (OpenMPI)
- Monte Carlo / MD, standard forcefield, 3M+ atoms

https://www.projectdissolve.com

†With higher confidence than a simulation alone

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Data Quality

Both EPSR and Dissolve use (currently) the same procedure of matrix & potential inversion.

Theory can link measured scattering intensities to real-space simulation data – but is **idealised**

Data must be well processed:

- Sample environment and instrument backgrounds & containers removed
- Remove multiple scattering and beam attenuation effects
- Remove self-scattering – interference scattering only
- Remove inelastic scattering: important (and difficult) for light H.
- Have a normalised intensity on an absolute scale (barns sr^{-1} $atom^{-1}$)

It’s Just a Simulation!

Perfect reproduction of data is not possible

1. Unknown (or not completely removed) instrument effects
2. Limitations in forcefield functional forms / potentials
3. Finite simulation size
4. Real-world systems are not 100% pure or 100% isotopically substituted

Can arguably show improvement over pure simulation, even if underdetermined, and has been successfully applied to a huge variety of systems…

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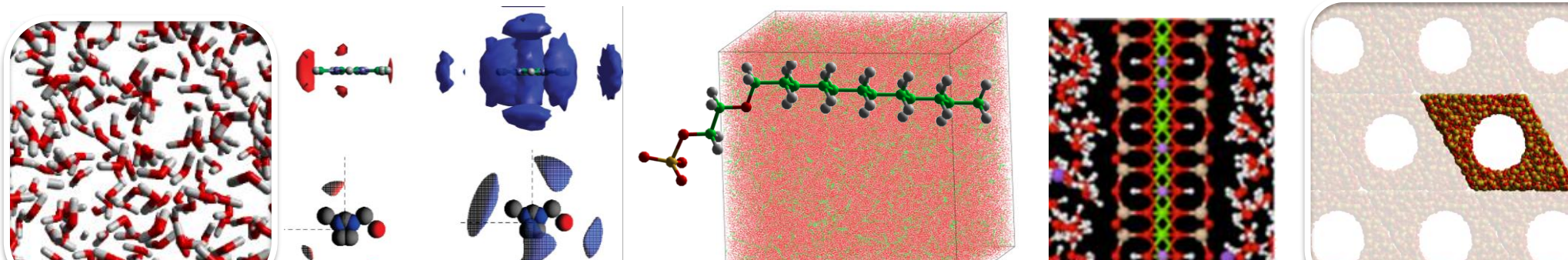


Confined Fluid Mixtures

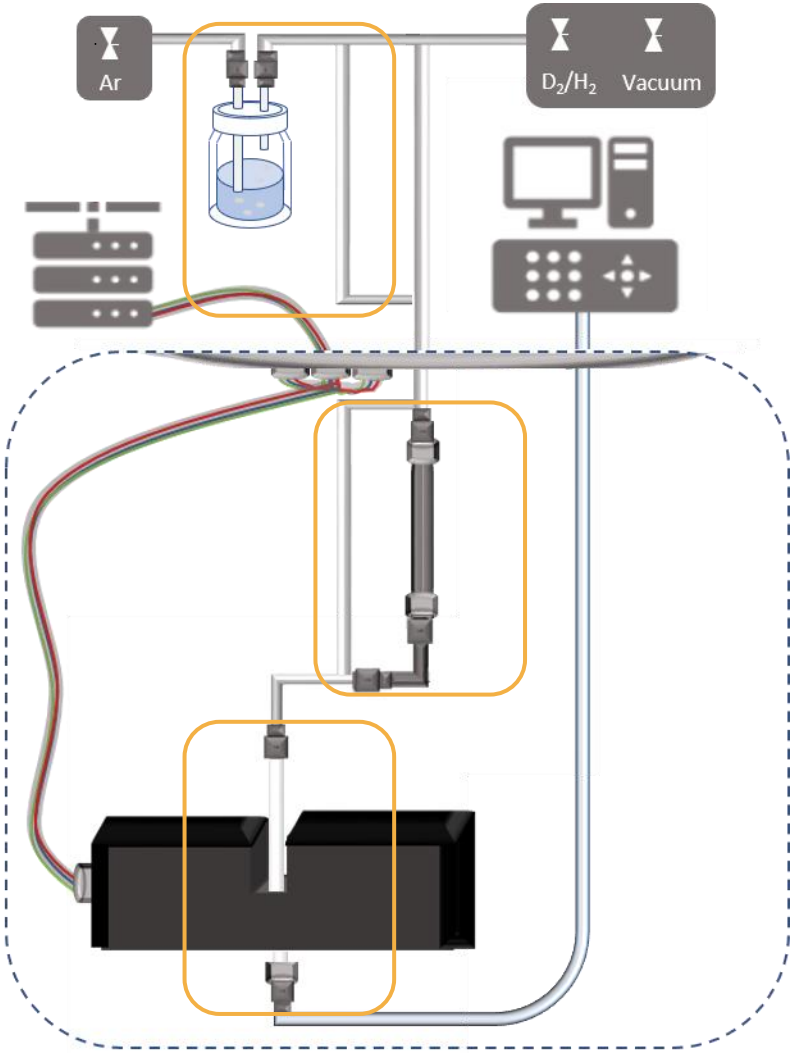
- Complete hydrogenation of benzene to cyclohexane using a 3wt% Pt catalyst supported on MCM-41

- Large contrast between reactant and product – adding six hydrogen atoms
- Mild conditions and no intermediates, good reaction to study prior to more complex more industrially relevant reactions.
- MCM-41 displays periodically arranged pores with minimal pore size disruption so could be modelled with less complexity than some less structurally ordered catalysts or catalyst supports.

Neutrons + NMR in Flow

- Use vanadium can (quartz would be good, but overlaps structurally with our substrate)
- Use Ar gas flow to (continually) deliver reactant / product mixture to neutron and NMR cells
- Flow H_2 or D_2 gas simultaneously
- Allows longer neutron data acquisition times
- NMR tells us the speciation

What is the liquid structure at various composition points within the catalyst support?



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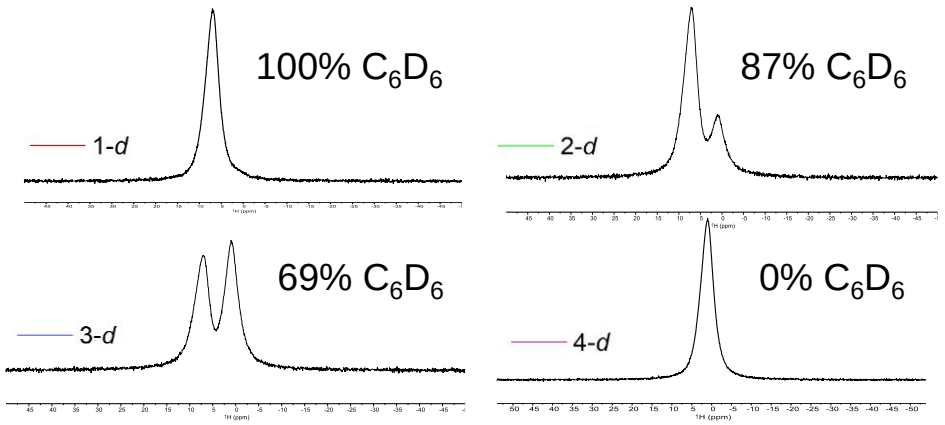
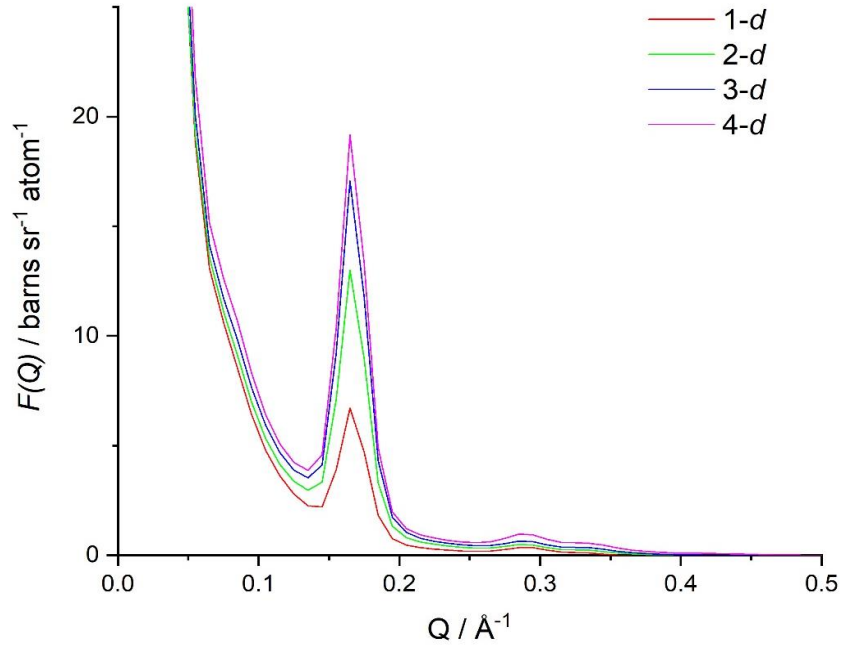
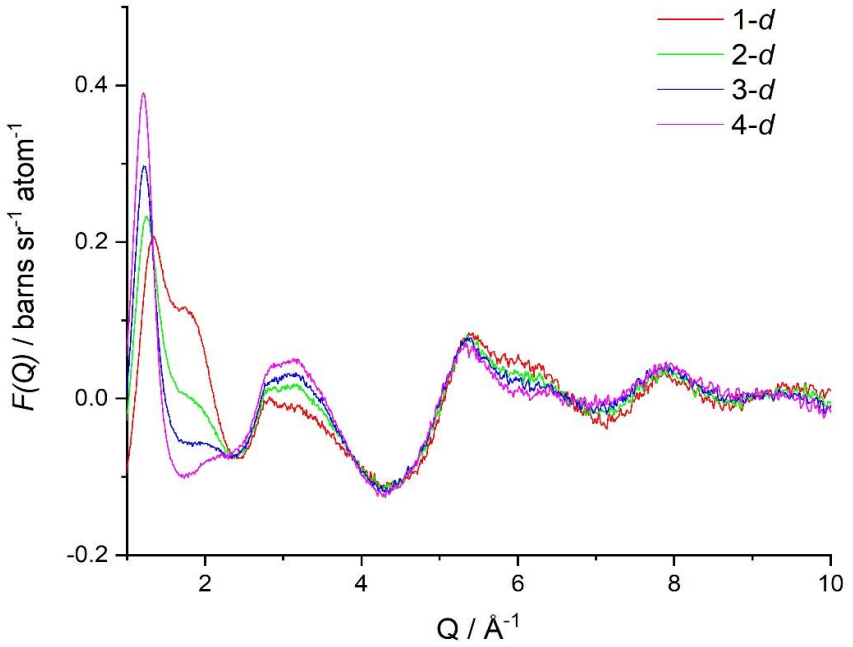
Experimental Data

- Data collected at four compositions
- <100> Bragg peak
  - Position reflects MCM-41 pore array spacing
  - Intensity dependent on mixture composition
  - Increases as C_6D_6 reacts to C_6D_{12}
- Higher *Q* regime indicates changes in liquid arrangement and intramolecular structure







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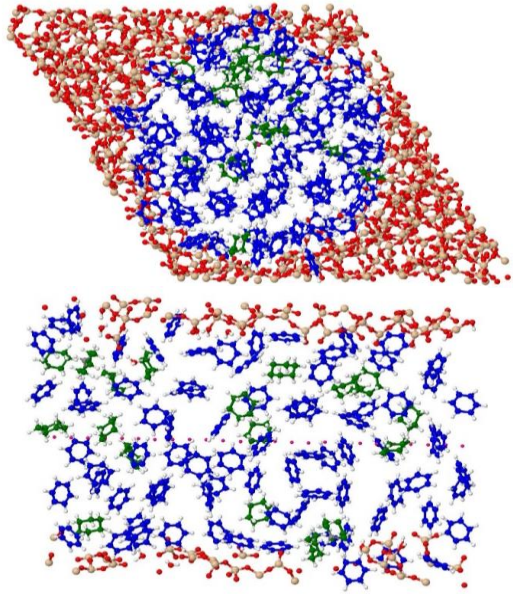
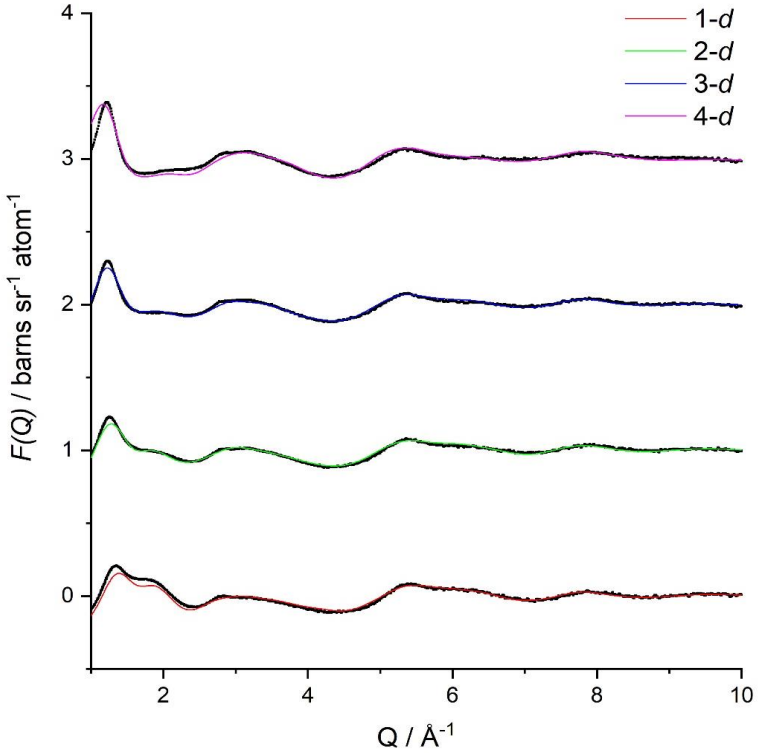
EPSR Simulation

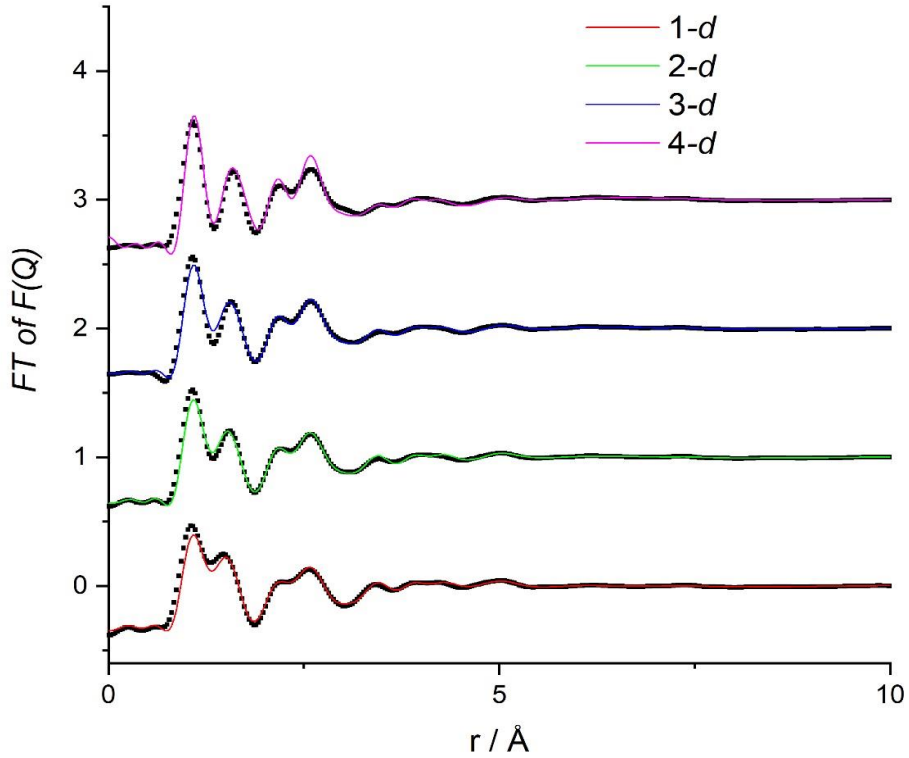
Two-stage process

1. Construct empty MCM-41 using <100> peak to inform unit cell size and pore radius

2. Add in NMR-determined ratio of benzene / cyclohexane at a sensible density and refine again







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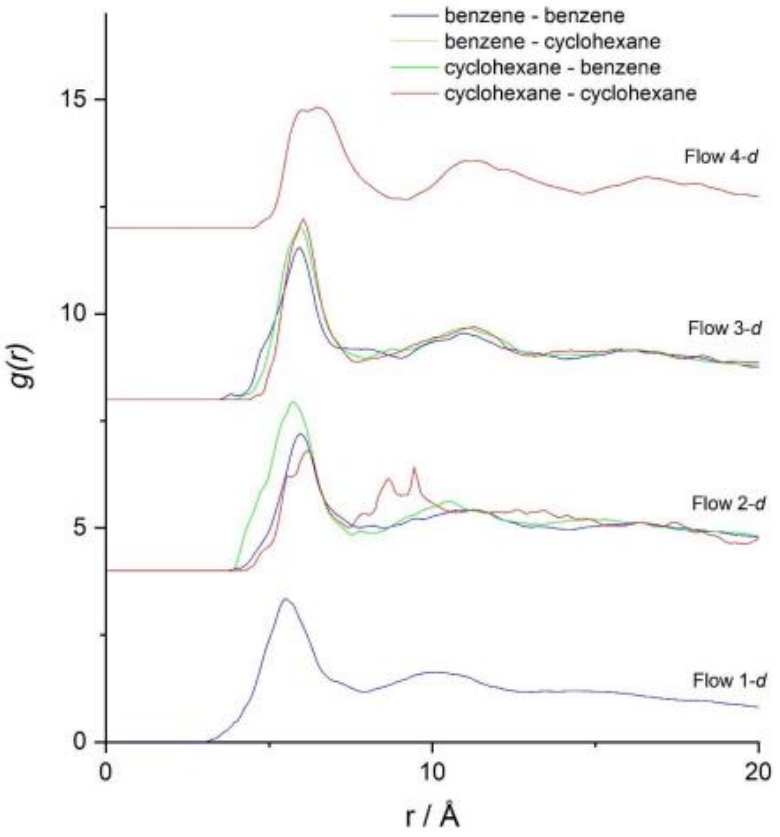
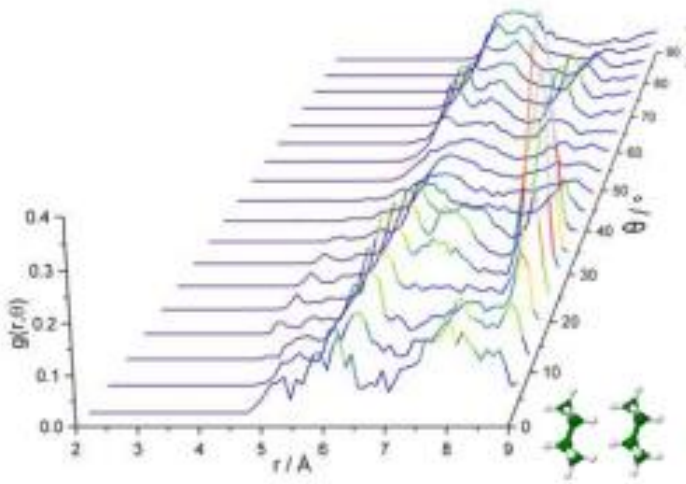
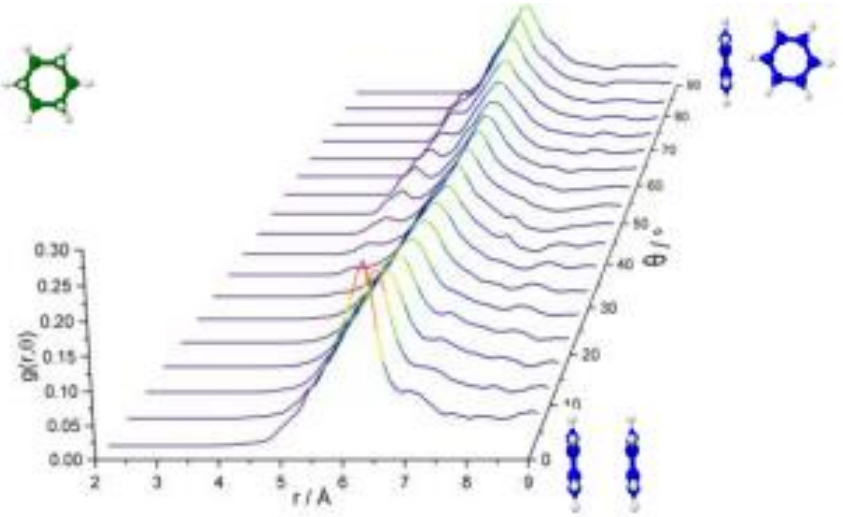
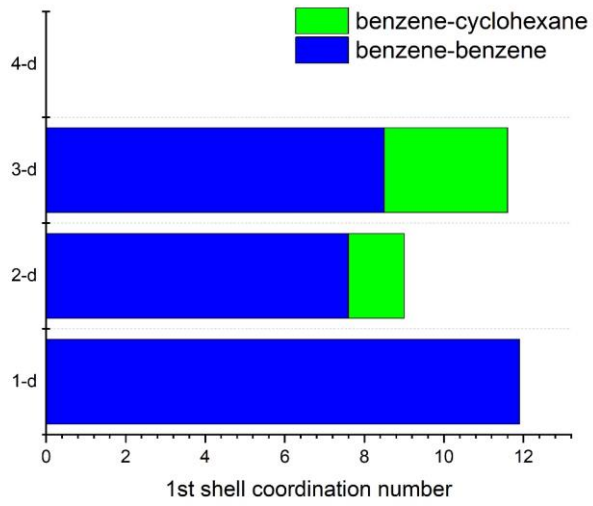
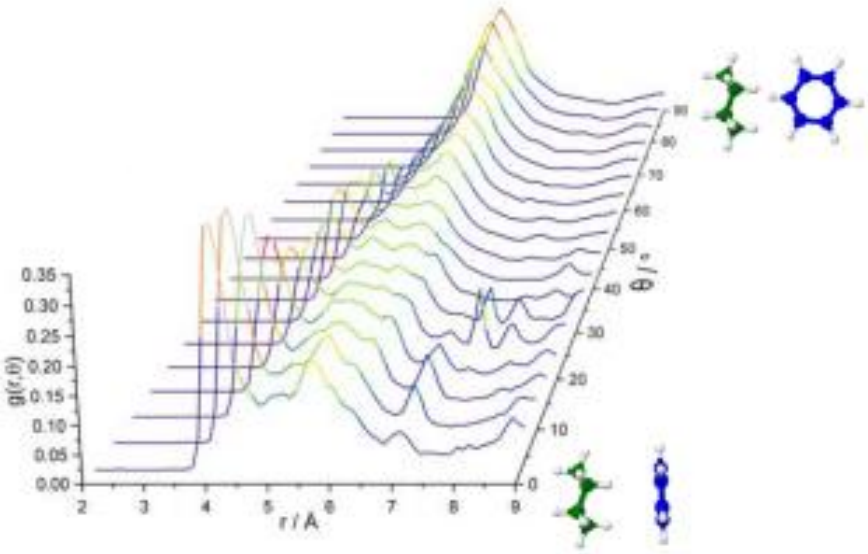
Basic Liquid Structure











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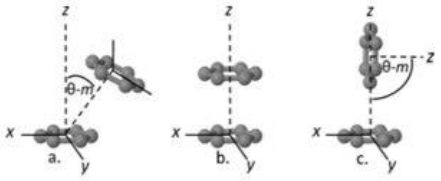
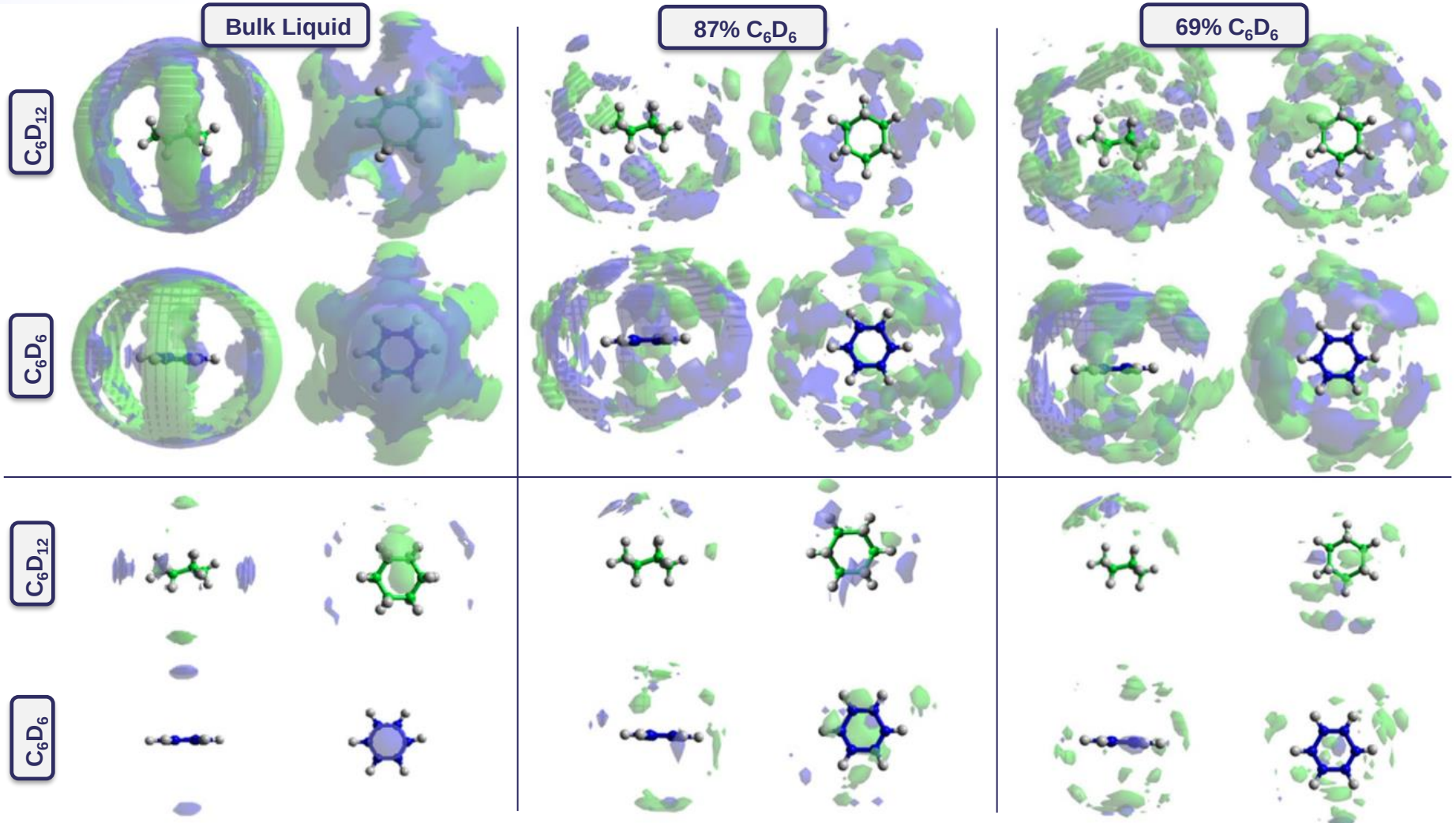
3D Structure

Parallel / r > 4.95 Å



Parallel / r < 4.95 Å



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Current / Emerging Challenges

- Accounting for heterogeneity of samples
  - Partial pore filling
  - Pore size distribution
- System size – coarse graining & refinement
- Soft link between data reduction and simulation
- Extending (improving?) the original EPSR methodology

Dissolve provides a modular framework on which all of this can be tested / built.

Acknowledgements

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Team Dissolve

A. Washington, D. Nixon, and all of our contributors

EPSR – Soper, *Mol. Phys.* **99**, 1503 (2001)
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ORIGINAL PAPER

Bulk and Confined Benzene-Cyclohexane Mixtures Studied by an Integrated Total Neutron Scattering and NMR Method

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