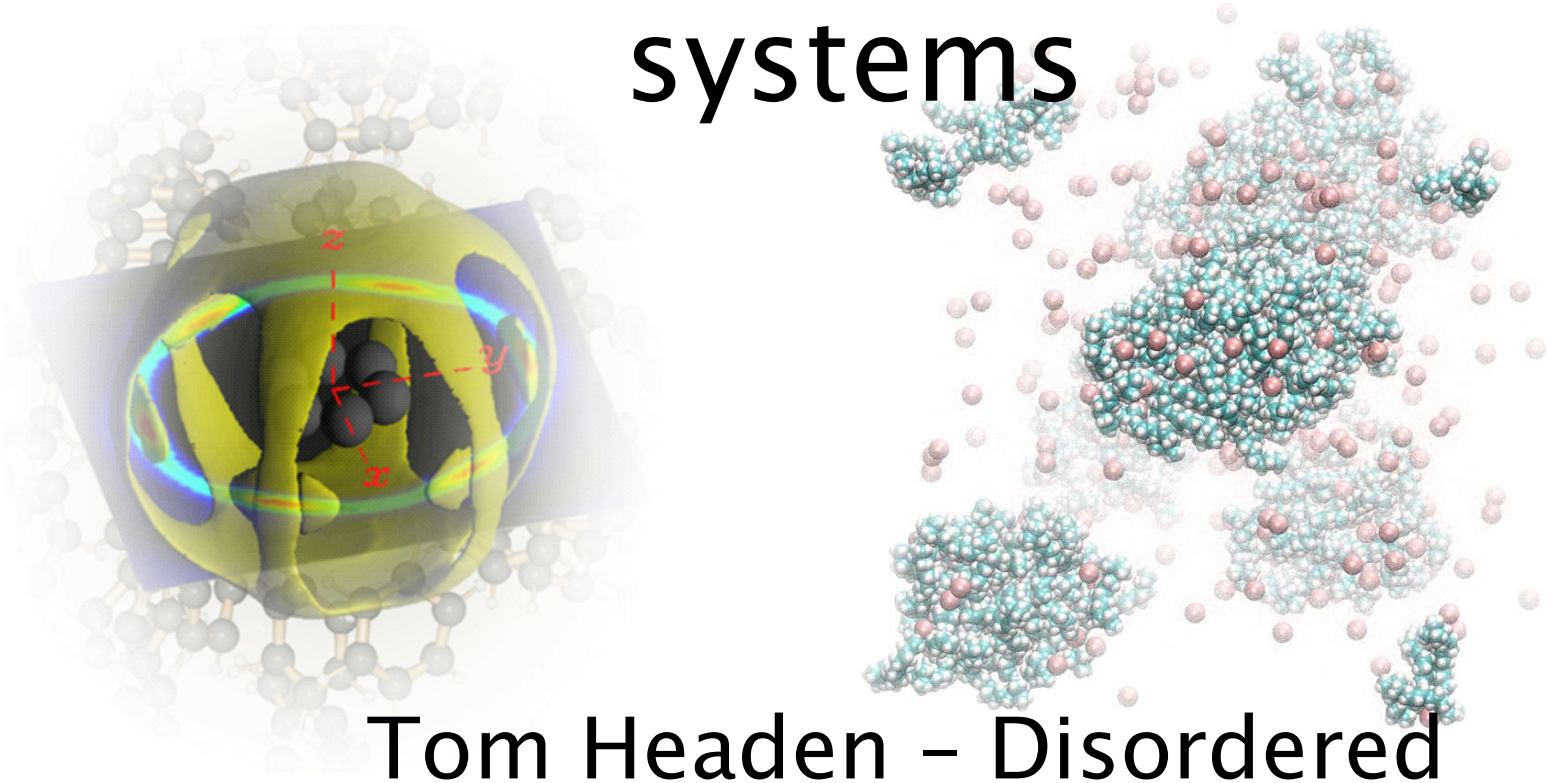
Atomistic structure refinement in disordered systems



Tom Headen – Disordered Materials Group - ISIS

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Neal Skipper (UCL)

Alan Soper (ISIS)

Karen Edler (Bath)

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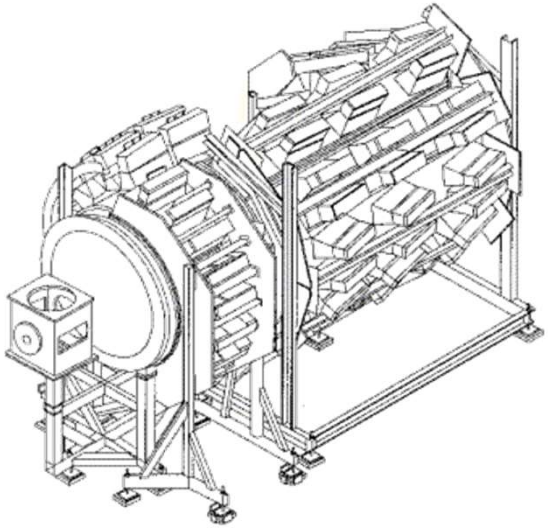
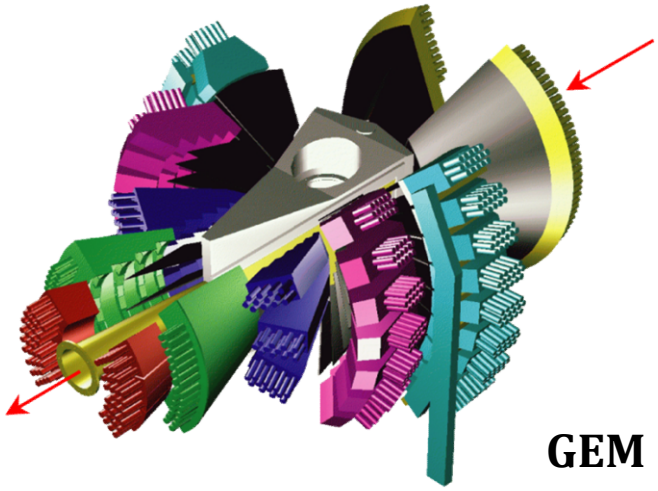
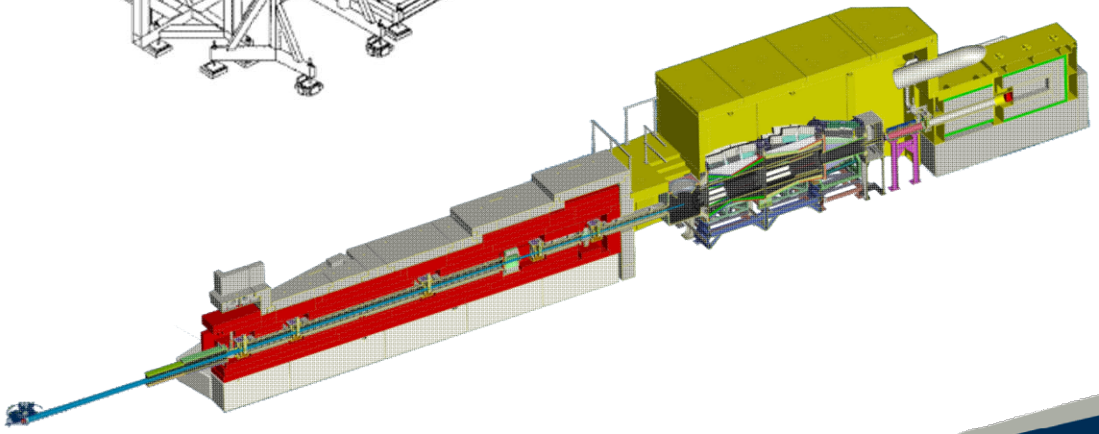
Disordered materials group

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





GEM
General **M**aterials
Diffractometer



NIMROD
Near and
Inter**M**ediate **R**ange
Order **D**iffractometer

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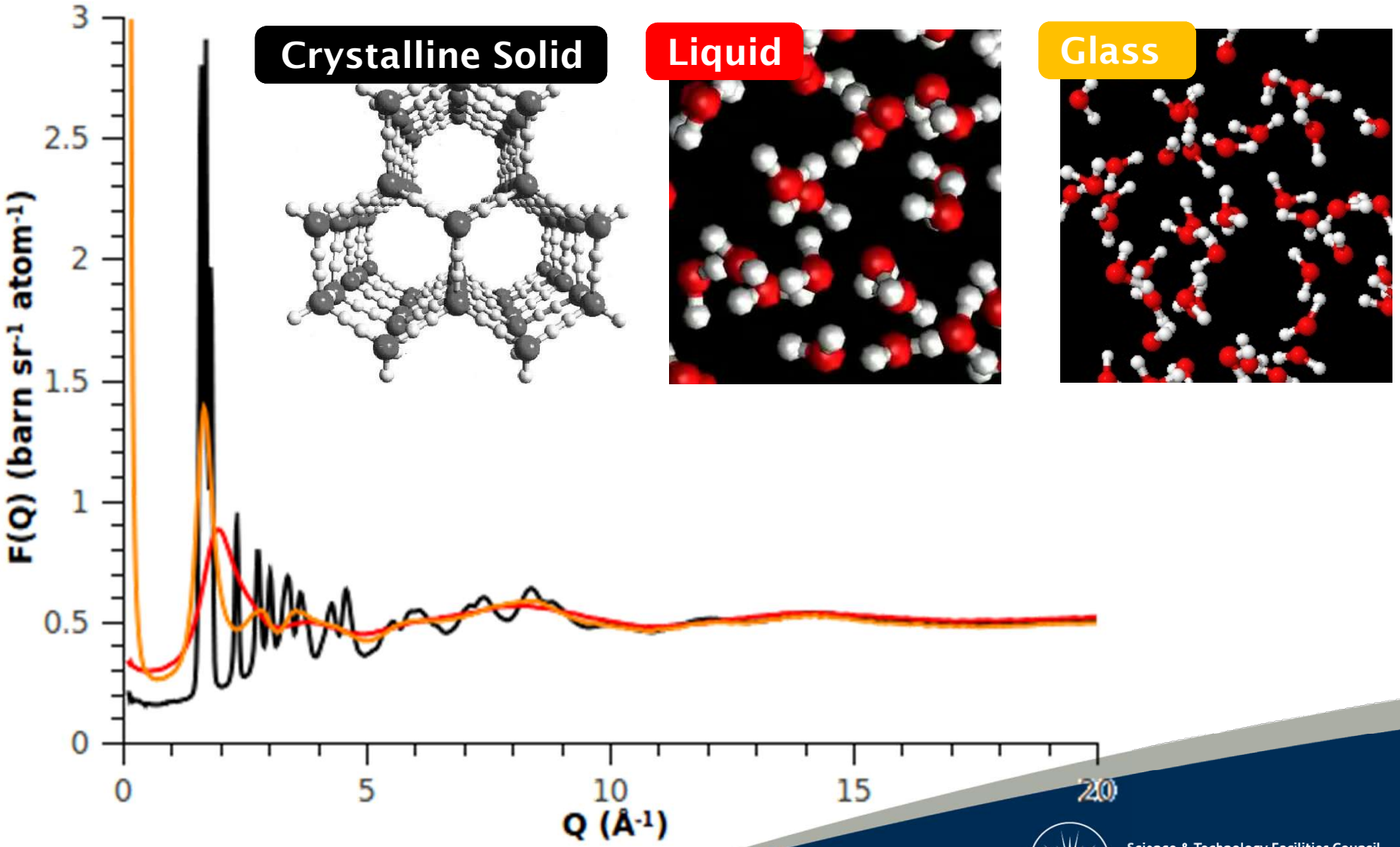
Typical data...



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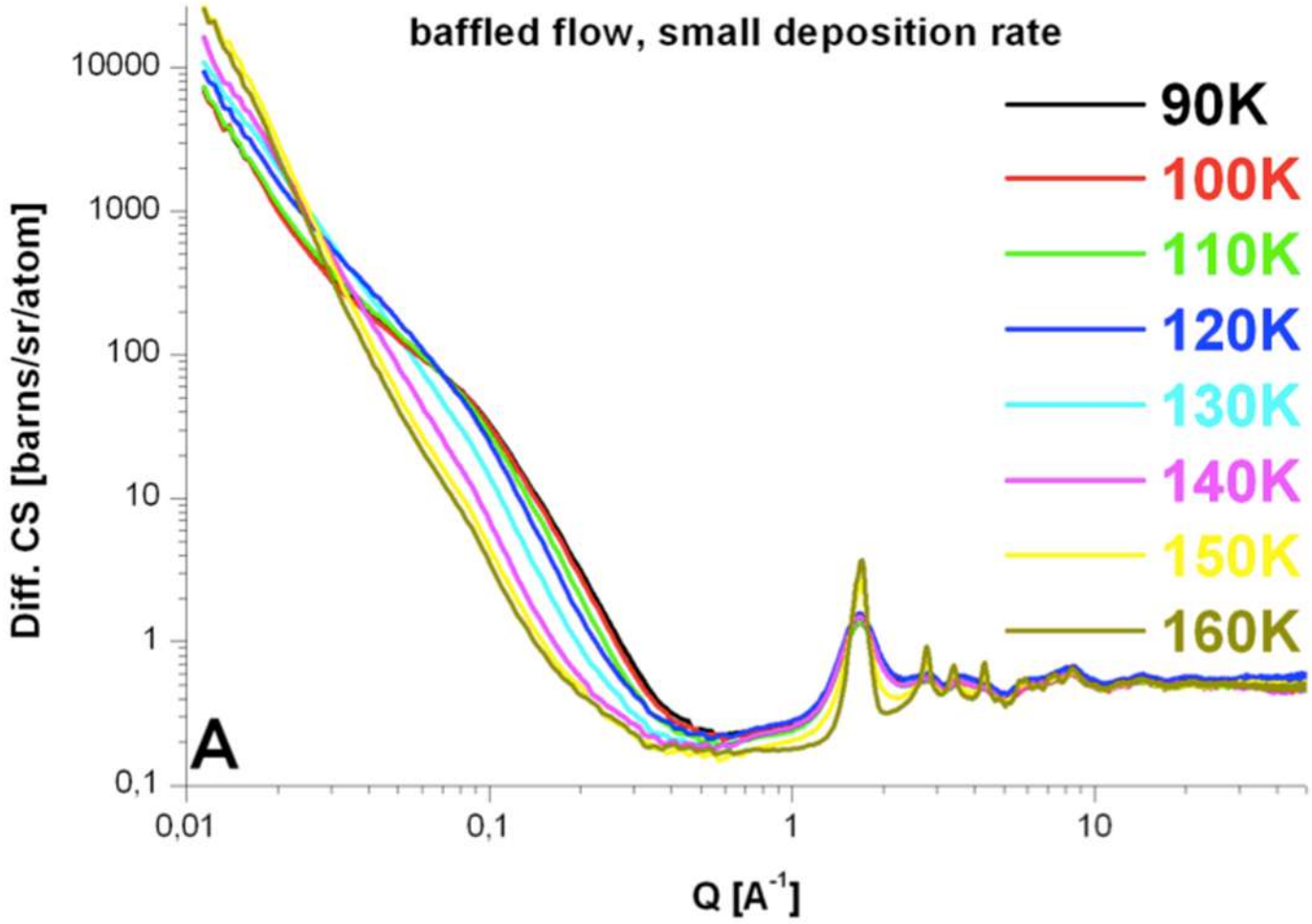
Over multiple length-scales...



Mitterdorfer et al. *Phys. Chem. Chem. Phys.* ***16***, 16013 (2014)

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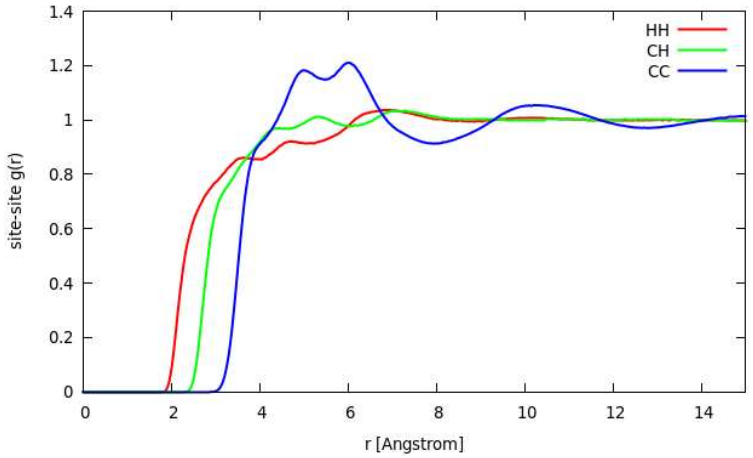
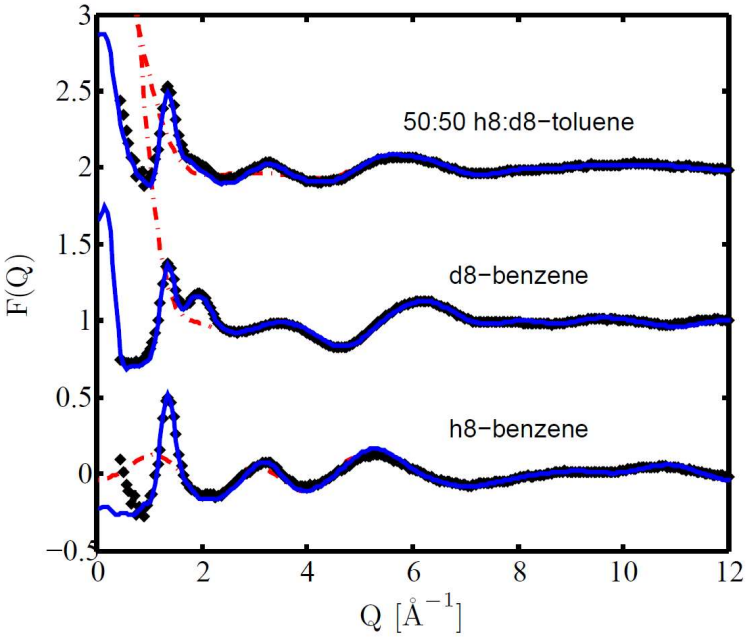
What is measured?

$$S_{ij}(Q) = 4\pi\rho \int r^2 \left(g_{ij}(r) - 1\right) \frac{\sin Qr}{Qr} dr$$

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





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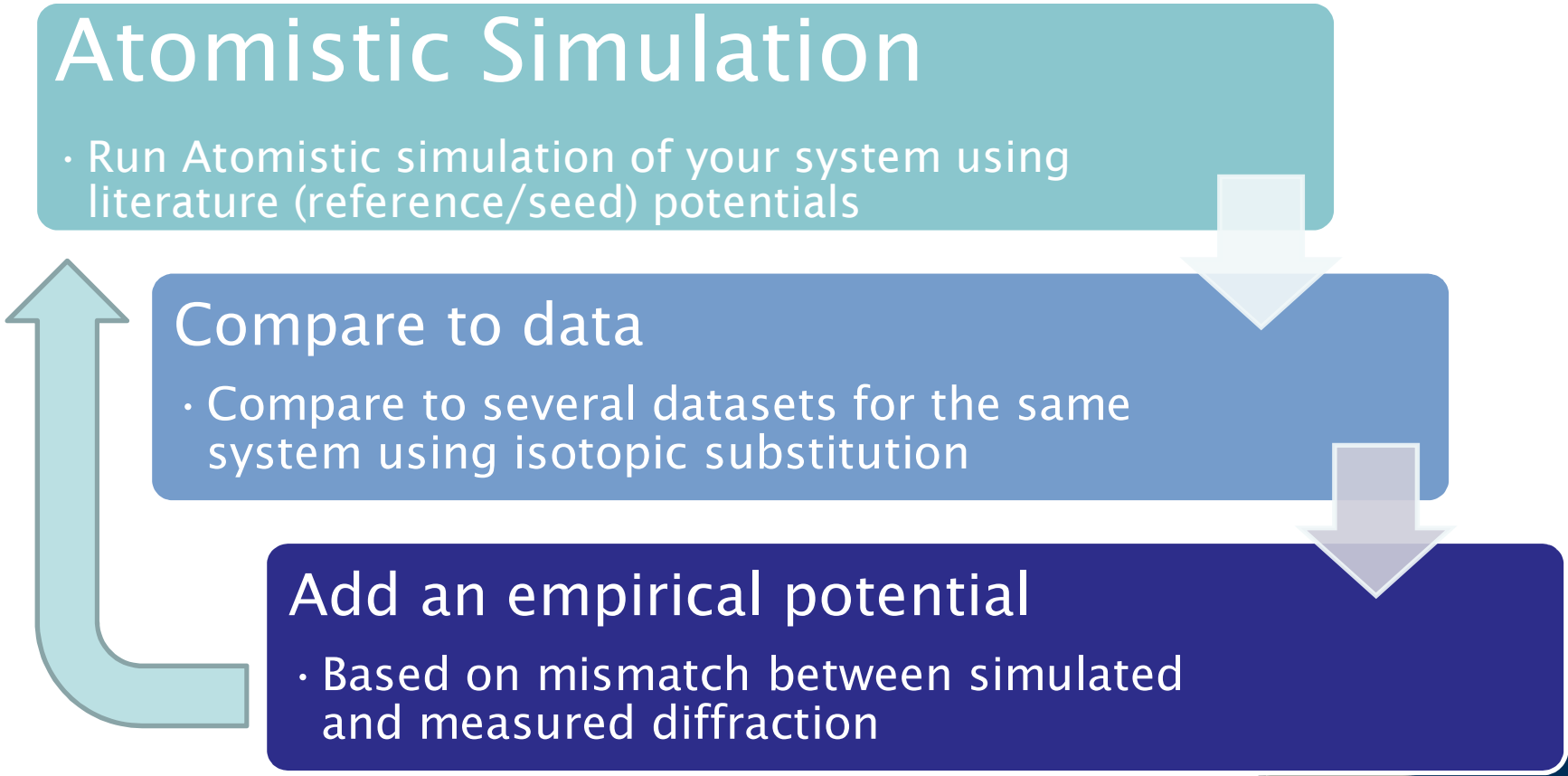
Structure refinement: Some options...

- Direct Fourier transform of the data to obtain partial radial distribution functions
- Reverse Monte Carlo
- Comparison to molecular simulation
- Refinement using molecular simulation

Empirical Potential Structure Refinement (EPSR)



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Example: Micelle formation

LANGMUIR

Article

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Decyltrimethylammonium Bromide Micelles in Acidic Solutions: Counterion Binding, Water Structuring, and Micelle Shape

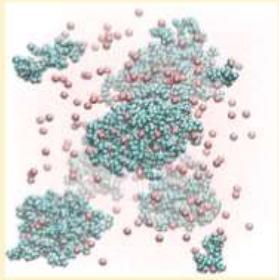
Daniel T. Bowron[†] and Karen J. Edler*[,‡]

[†]ISIS, Science and Technology Facilities Council Rutherford Appleton Laboratory, Harwell Oxford, Didcot OX11 0QX, U.K.

[‡]Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

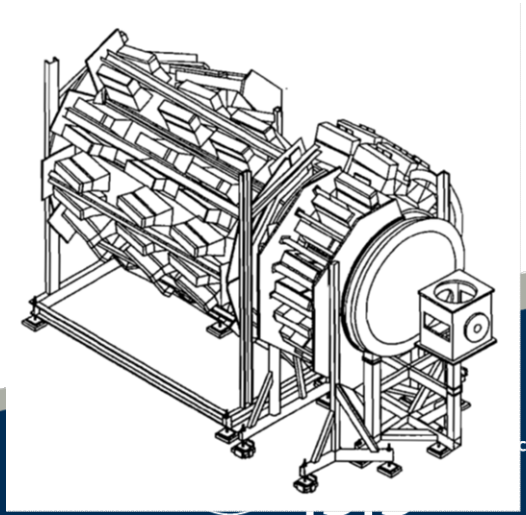
Supporting Information

ABSTRACT: Wide-angle neutron scattering experiments combined with empirical potential structural refinement modeling have been used to study the detailed structure of decyltrimethylammonium bromide micelles in the presence of acid solutions of HCl or HBr. These experiments demonstrate considerable variation in micelle structure and water structuring between micelles in the two acid solutions and in comparison with the same micelles in pure water. In the presence of the acids, the micelles are smaller; however, in the presence of HCl the micelles are more loosely structured and disordered while in the presence of HBr the micelles are more compact and closer to spherical. Bromide ions bind strongly to the micelle surface in the HBr solution, while in HCl solutions, ion binding to the micelle is similar to that found in pure water. The hydration numbers of the anions and extent of counterion binding follow the predictions of the Hofmeister series for these species.



Experiment on SANDALS using a series of isotopically labelled C10TAB samples with and without acid:

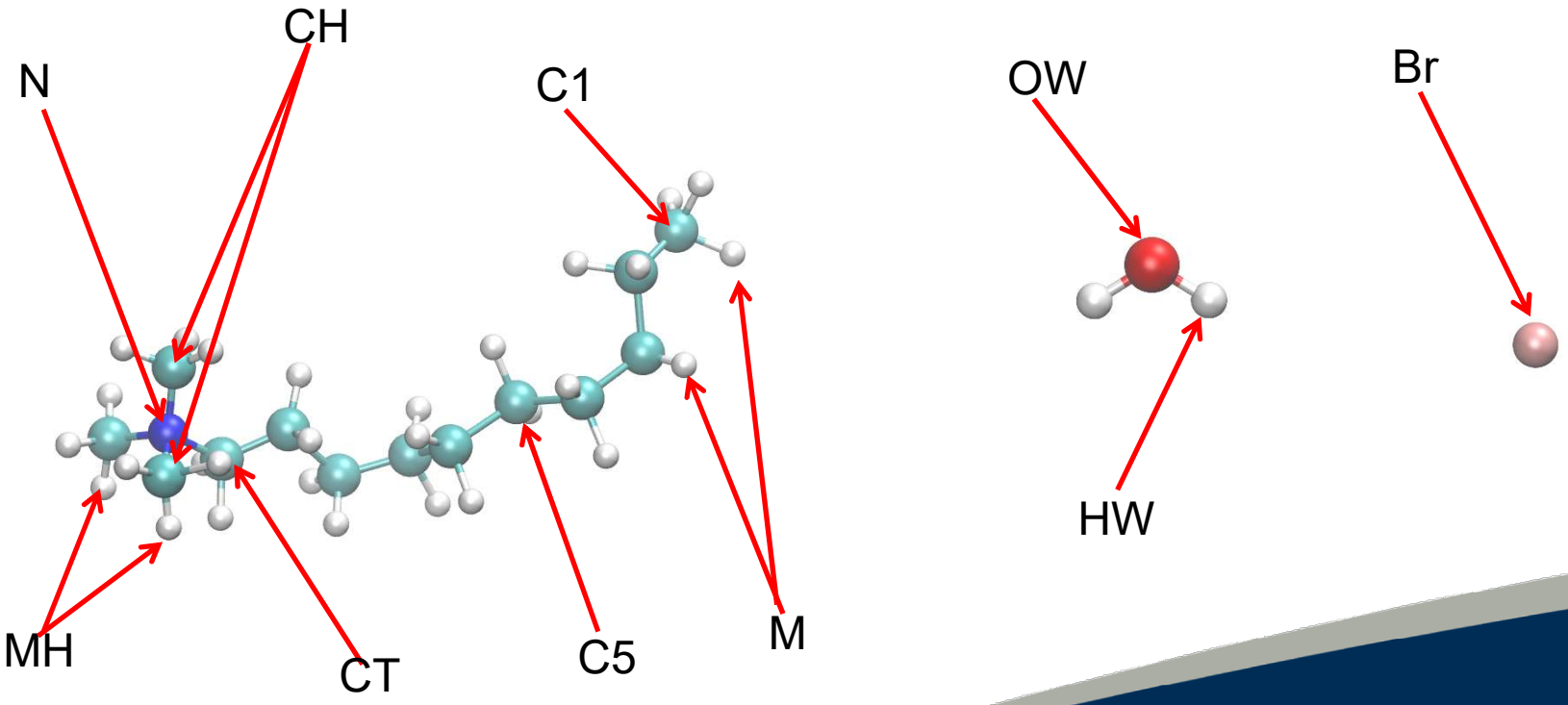
0.4M C10TAB
0.4M C10TAB + 0.2M HBr
0.4M C10TAB + 0.2M HCl



The EPSR models consists of

256	C_{10}TA cationic surfactants
256	Br^- anions
31232	Water molecules

Contained in a cubic simulation box of side dimensions 101.71Å
This gives a total of **105216** atoms at a density of 0.1 atomsÅ^{-3}



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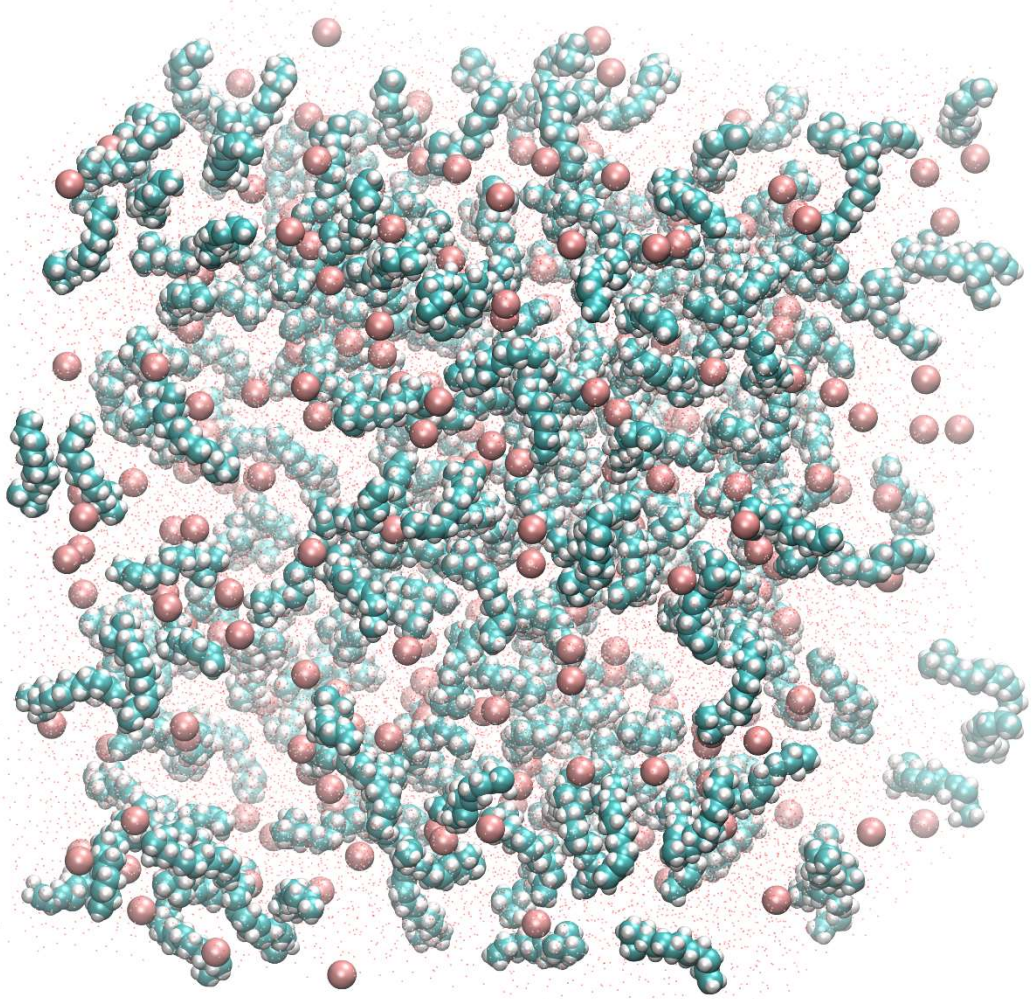
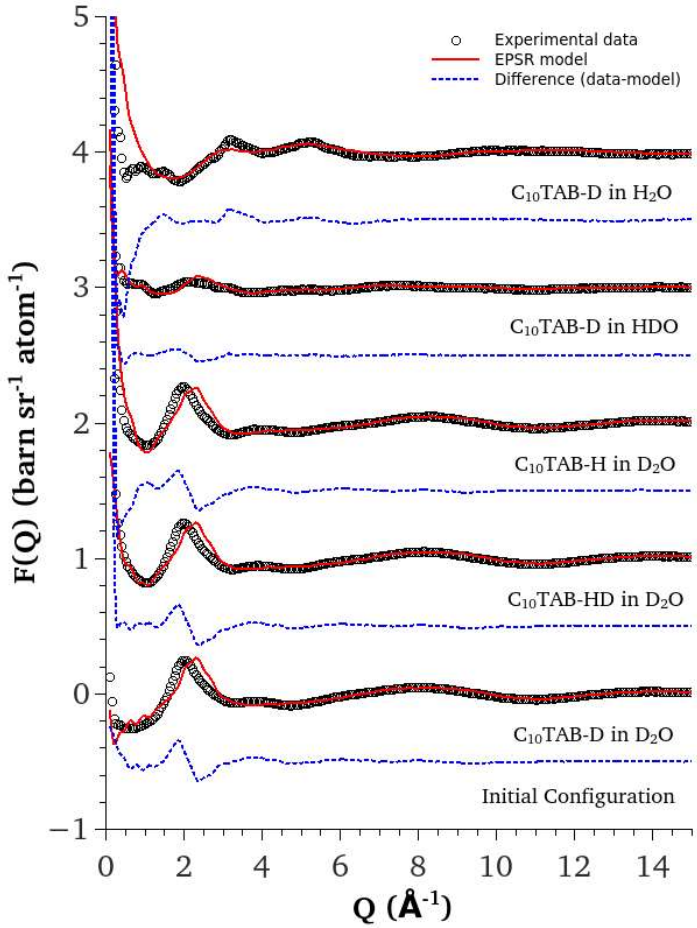


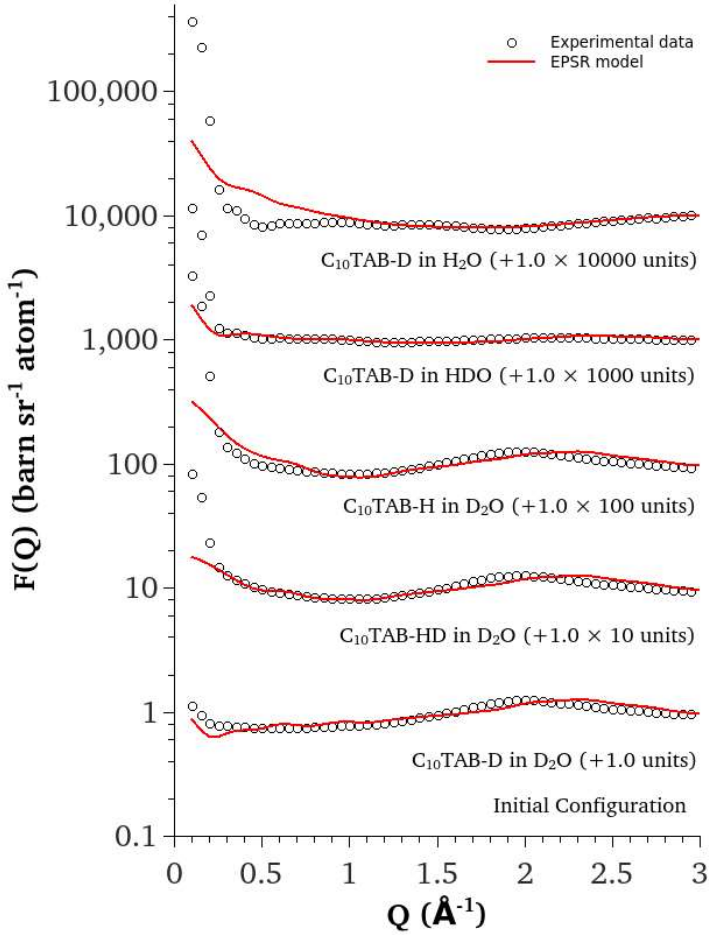
Initial configuration

The starting configuration was equilibrated under the reference potentials.

This leads to a box in which there are no micelles present – there is nothing in the reference potentials that will give rise to the spontaneous generation of aggregated structures

Comparison using reference potentials only





Although the reference model gives a reasonably close approximation of the experimental data, it significantly fails to capture the low-Q features indicative of micelles in solution.

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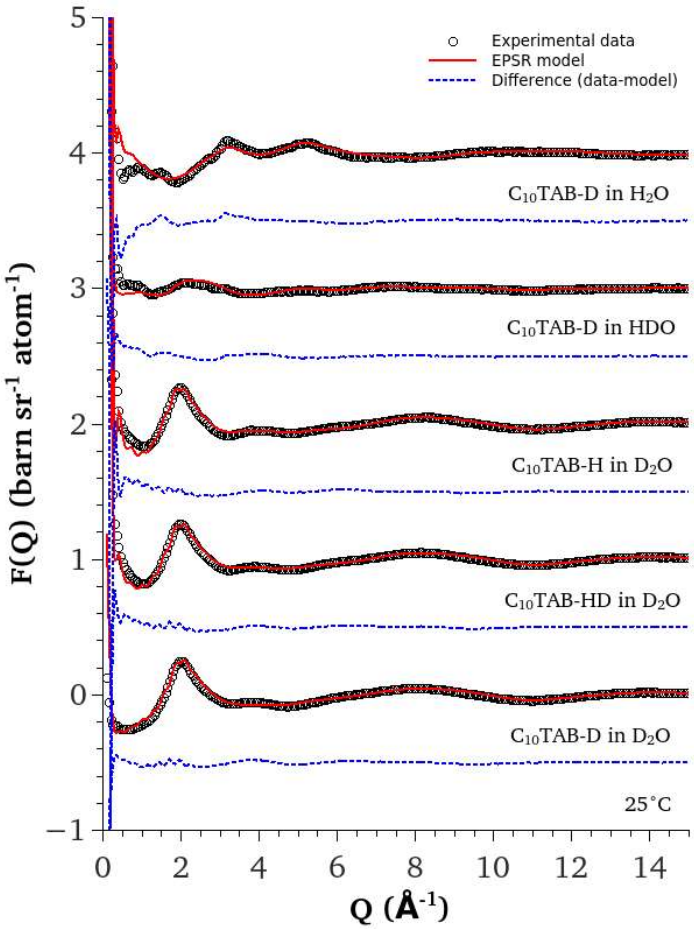
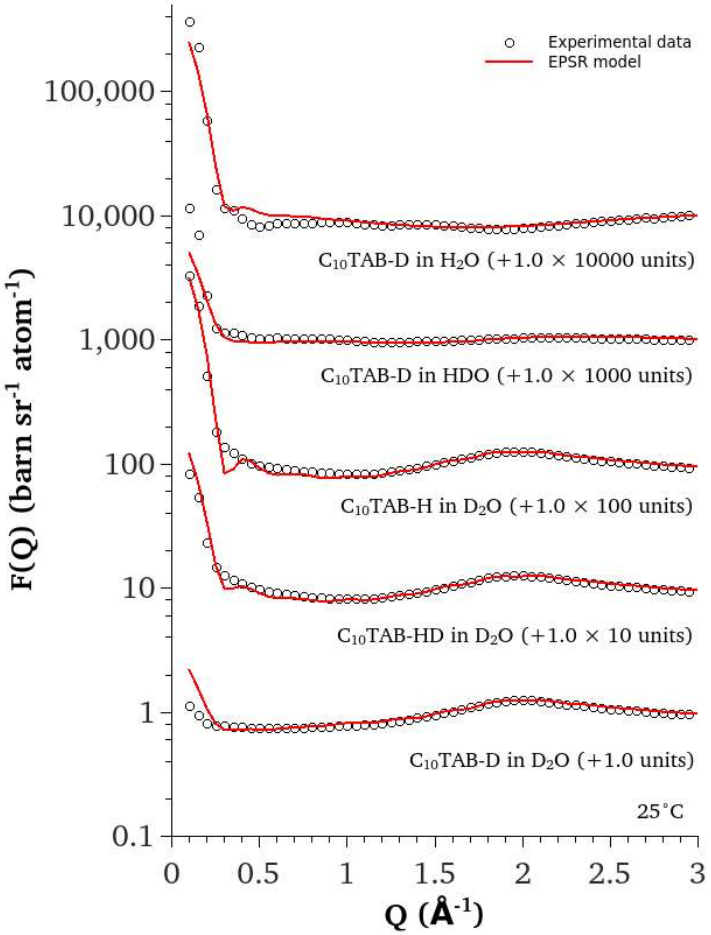
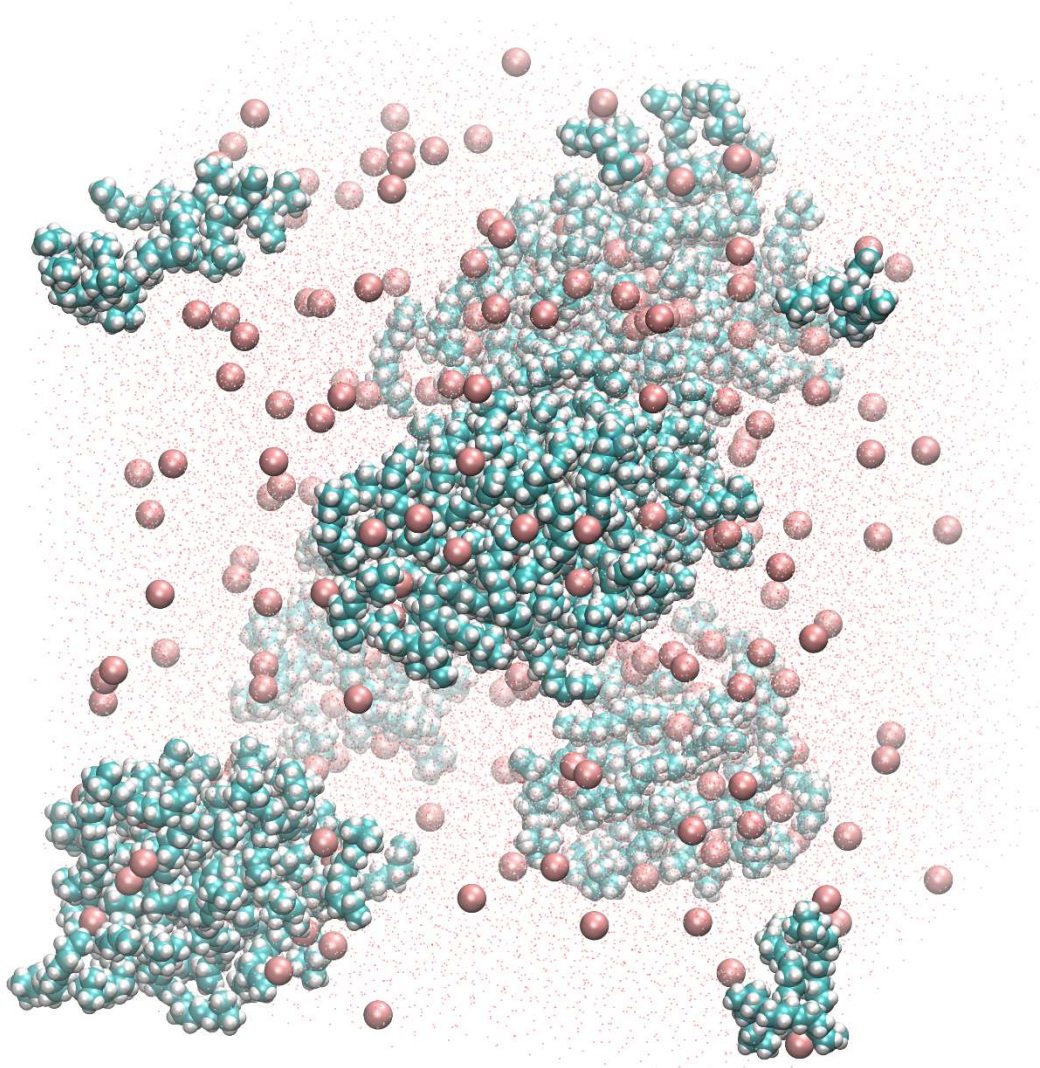
Comparison of interference differential scattering cross sections calculated from the EPSR models of the 25°C data.





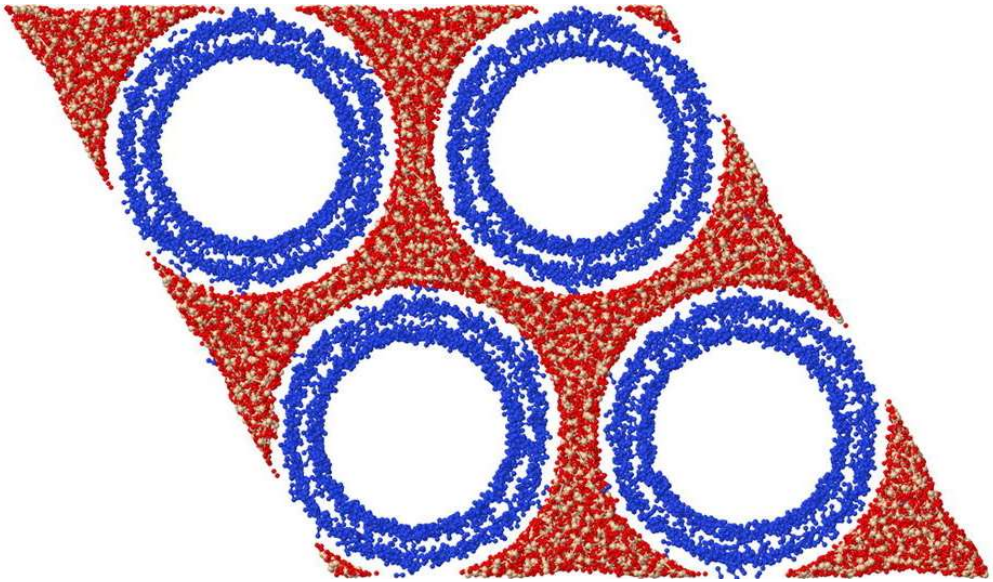
A notable achievement of the EPSR refined model is the improved agreement with the low-Q data that is indicative of the presence of aggregated micelle structures in the models.



EPSR on 25°C data

After refinement against the experimental data. Micellar aggregates are found to have formed in the model.

Example: Fluids in pores



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Chemical Physics Letters xxx (2017) xxx–xxx

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Research paper

Density profile of nitrogen in cylindrical pores of MCM-41

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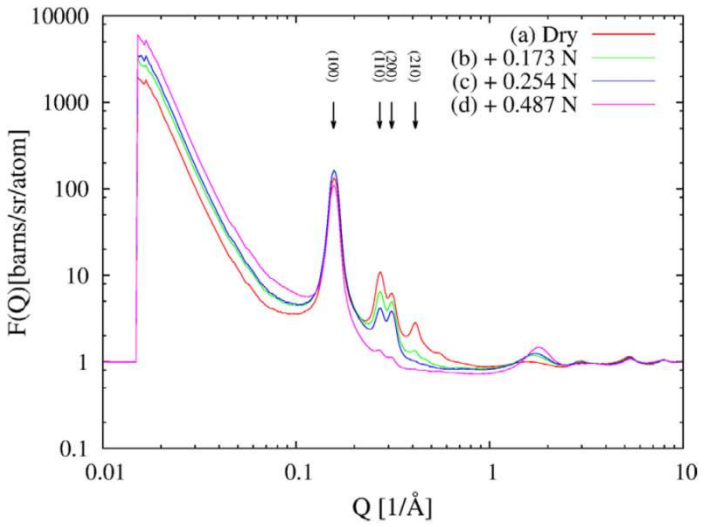
ABSTRACT

A straightforward approach using radiation scattering (X-ray or neutron) combined with atomistic modelling is used to accurately assess the pore dimensions in the porous silica, MCM-41. The method is used to calculate the density profile of nitrogen absorbed in this material at a variety of fractional pressures, p/p_0, where p_0 is the saturated vapour pressure, up to $p/p_0 = 0.36$ at $T = 87$ K in the present instance. At this pressure two distinct layers of liquid nitrogen occur on the silica surface, with a relatively sharp gas-



Nitrogen in mesoporous silica MCM-41
at T=87-123K and P=0.7-1bar

EPSR can simulate whole system

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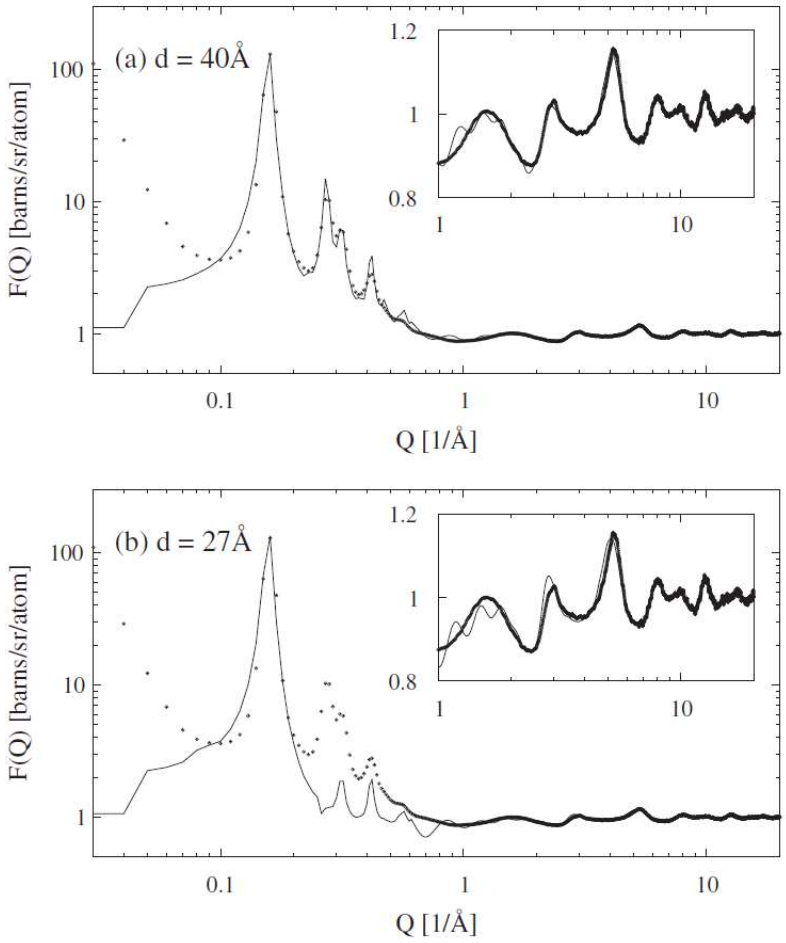
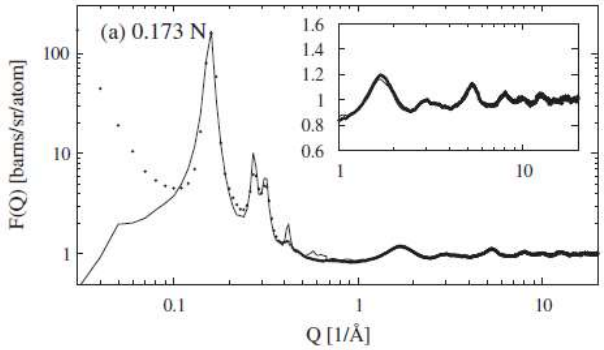
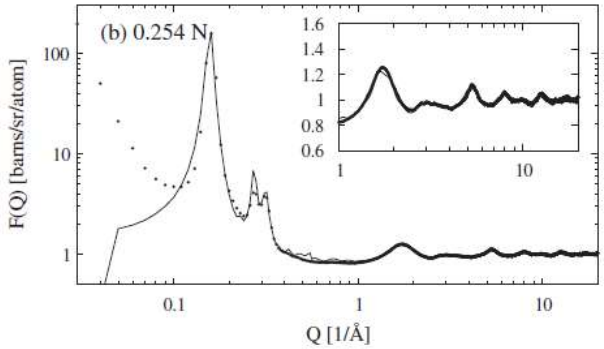
EPSR: Structure of MCM-41

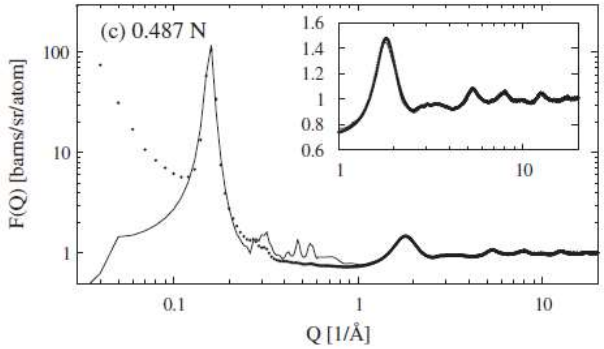


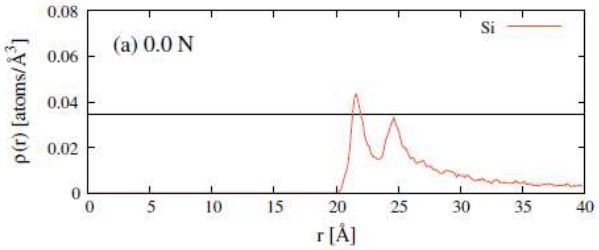
- Size of pore fitted on trial an error basis
- Dummy atom used to define centre of pore, and then repulsive potential used to define pore size
- Silica framework still fitted by EPSR method
- Diameter of 40Å gave best fit in Q and r-space. This is larger than predicted by BET

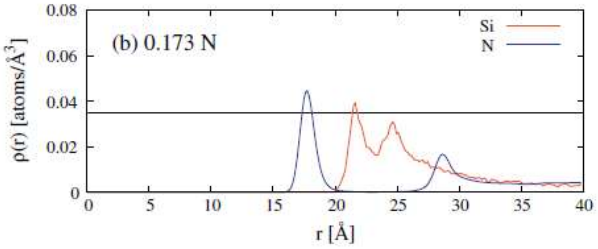
EPSR: Structure of N_2 in the pore

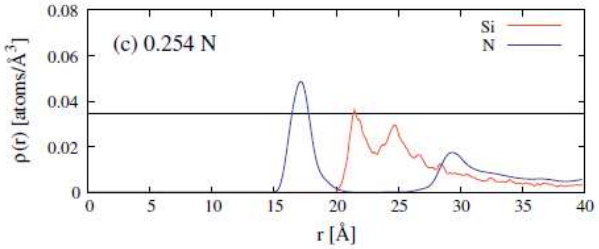


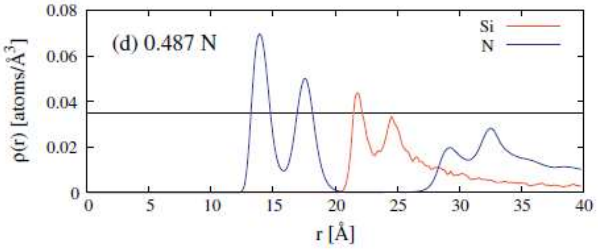












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Looking forward: CG-EPSR

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Coarse-grained empirical potential structure refinement: Application to a reverse aqueous micelle☆

A.K. Soper [a,*], K.J. Edler [b]

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Empirical potential structure refinement
EPSR
X-ray scattering
Neutron scattering

ABSTRACT

Conventional atomistic computer simulations, involving perhaps up to 10^9 atoms, can achieve length-scales on the order of a few 10s of nm. Yet many heterogeneous systems, such as colloids, nano-structured materials, or biological systems, can involve correlations over distances up 100s of nm, perhaps even 1 μm in some instances. For such systems it is necessary to invoke coarse-graining, where single atoms are replaced by agglomerations of atoms, usually represented as spheres, in order for the simulation to be performed within a practical computer memory and time scale. Small angle scattering and reflectivity measurements, both X-ray and neutron, are routinely used to investigate structure in these systems, and traditionally the data have been interpreted in terms of discrete objects, such as spheres, sheets, and cylinders, and combinations thereof. Here we combine the coarse-grained computer simulation approach with neutron small angle scattering to refine the structure of a heterogeneous system, in the present case a reverse aqueous micelle of sodium-dioctyl sulfosuccinate (AOT) and iso-octane. The method closely follows empirical potential structure refinement and involves deriving an empirical interaction potential from the scattering data. As in traditional coarse-grained methods, individual atoms are replaced by spherical density profiles, which, unlike real atoms, can inter-penetrate to a significant extent. The method works over an arbitrary range of length-scales, but is limited to around 2 orders of magnitude in distance above a specified dimension. The smallest value for this dimension is of order 1 nm, but the largest dimension is arbitrary. This article is part of a Special Issue entitled "Recent Advances in Bionanomaterials" Guest Editor: Dr. Marie-Louise Saboungi and Dr. Samuel D. Bader.

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1. Introduction

In the past decade or so empirical potential structure refinement (EPSR) has become a frequently used method for interpreting the atomistic structure of liquids and glasses based on X-ray and neutron total scattering data [1–8]. The EPSR method, which originally derived from by means of making use of the known ionic Coulomb forces in such systems to prevent unphysical local atom coordinations.

Currently EPSR has a technical limit of ~150,000 atoms [13], which is partly imposed by the constraints of the small computing architectures on which it is typically run. A significant constraint on making EPSR simulations arbitrarily large however is that as the system becomes larger,

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- Iso-octane, Na-AOT (sodium-dioctyl sulfosuccinate), water reverse micelle system in ratios 6:1:5 and 6:1:15
- Each bead treated as having a Gaussian distribution of scattering length density, and therefore has a form factor associated with it
- In current study the number of reverse micelles was a tuneable parameter using dummy atoms and "container" forces (cf MCM-41)

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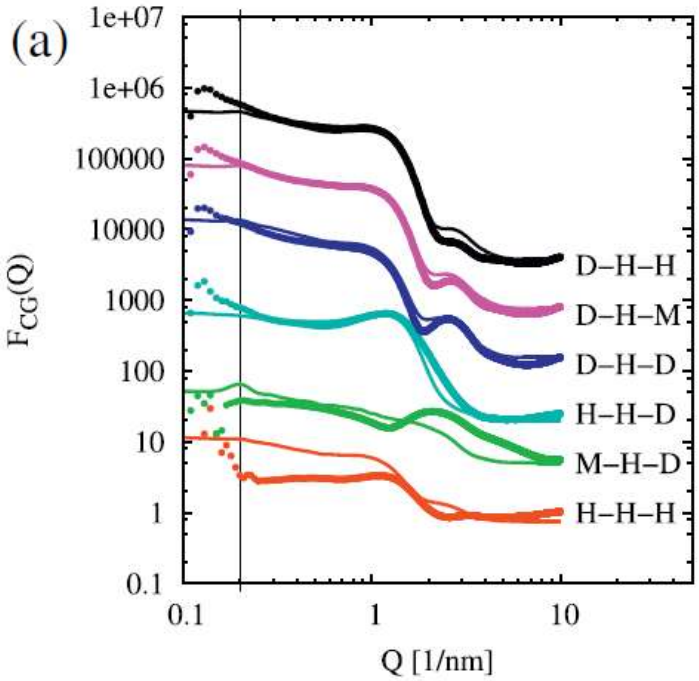
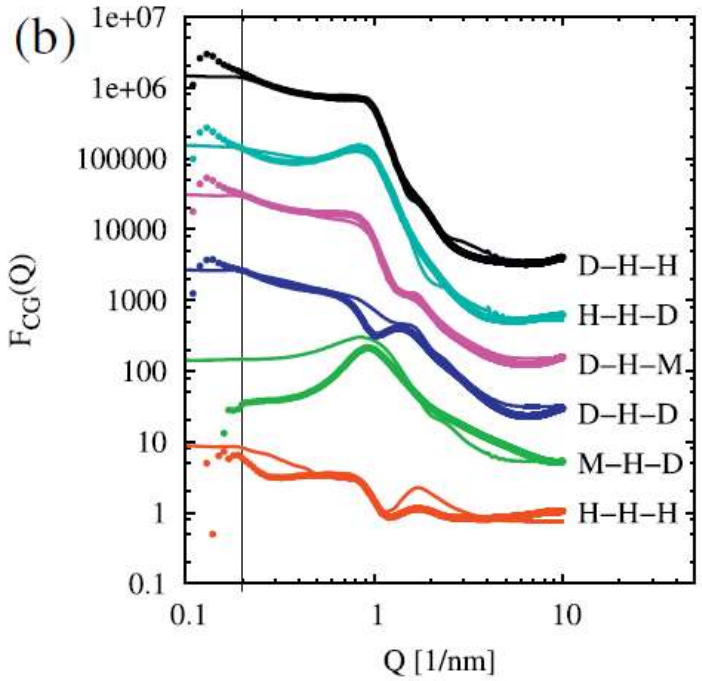
CG-EPSR: reverse micelles

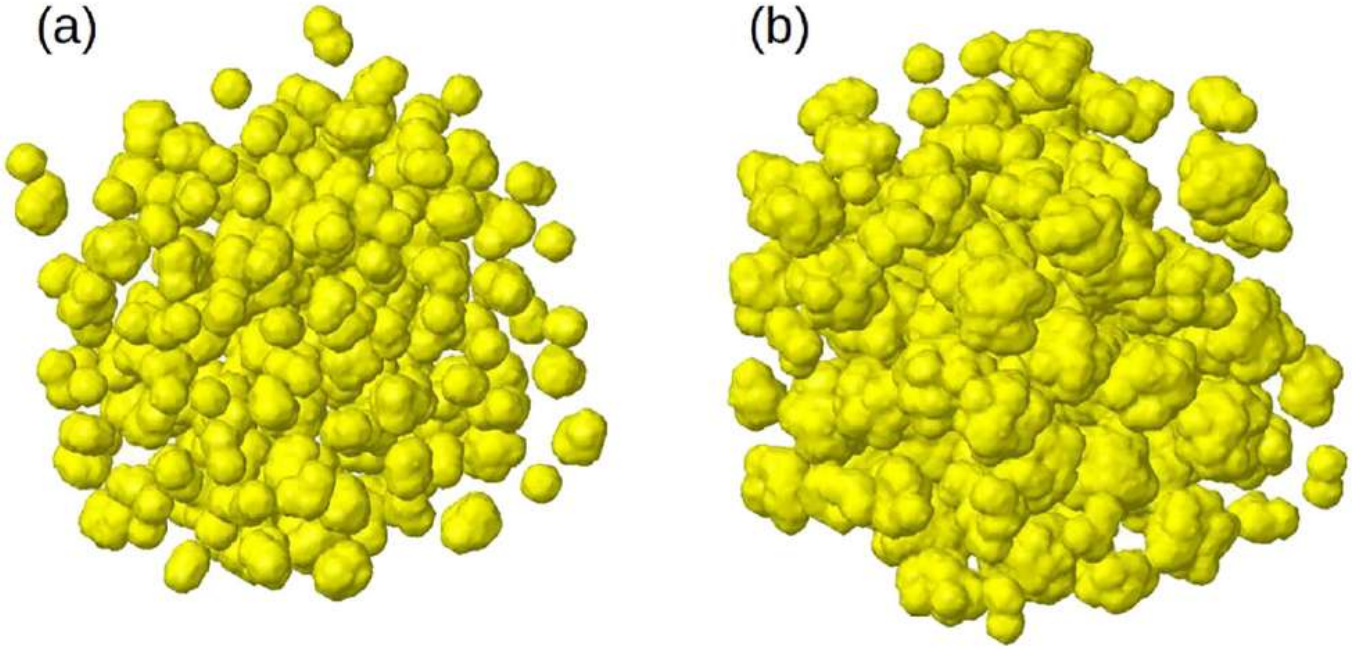


iso-octane:AOT:water = 6:1:5



iso-octane:AOT:water = 6:1:15

CG-EPSR: reverse micelles



iso-octane:AOT:water = 6:1:5

iso-octane:AOT:water = 6:1:15

In summary....

- Molecular simulation with EPSR has become a standard technique for structural analysis of liquid and amorphous systems on the atomic scale.

- NIMROD data presents a challenge: How to apply these techniques to very long length-scales?