Disordered materials II – Ionic Liquids

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Outline

- Introduction
- How to extract useful information from neutron scattering data
  - FT to distance information
  - Using NDIS (neutron diffraction/isotopic substitution) to identify partial structure factors
- Simulation using EPSR
  - Workflow to get useful data from *ionic liquids*

Introduction

- *"Studying structures of liquids is a slow and thankless task, so you need to start when you are young if you want to give yourself time to get somewhere!*

- *It is not difficult to collect diffraction data...The hard part is to know what to do with the data...and how to interpret the results."*

  - DWH Rankin, NW Mitzel and CA Morrison, Structural Methods in Molecular Inorganic Chemistry, 2013, Wiley.

Things that interest me...
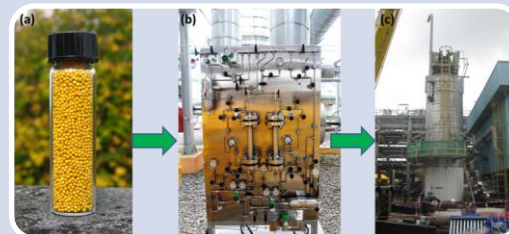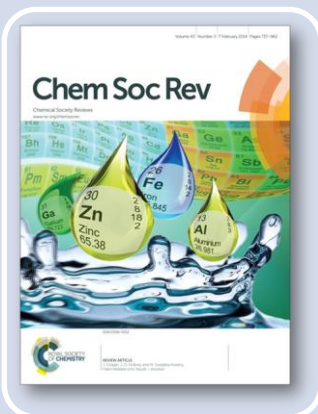
Catalysis

- Liquid Lewis acids
- Liquid-liquid **hetrogenisation of catalysts**

Construction

- **New functional materials** from cellulose
- Bioderived chemical intermediates

Energy

- Biomass to fuel
- Process enhancement (**separations and extractions**)

Using ionic liquids as 'soft' media to address chemical challenges

- Make use of integrated properties to enhance chemical processes

- Access organic chemistry, catalysis, and separations that can't be easily done in other media

- **Think** about processes and transformations **in a new light**
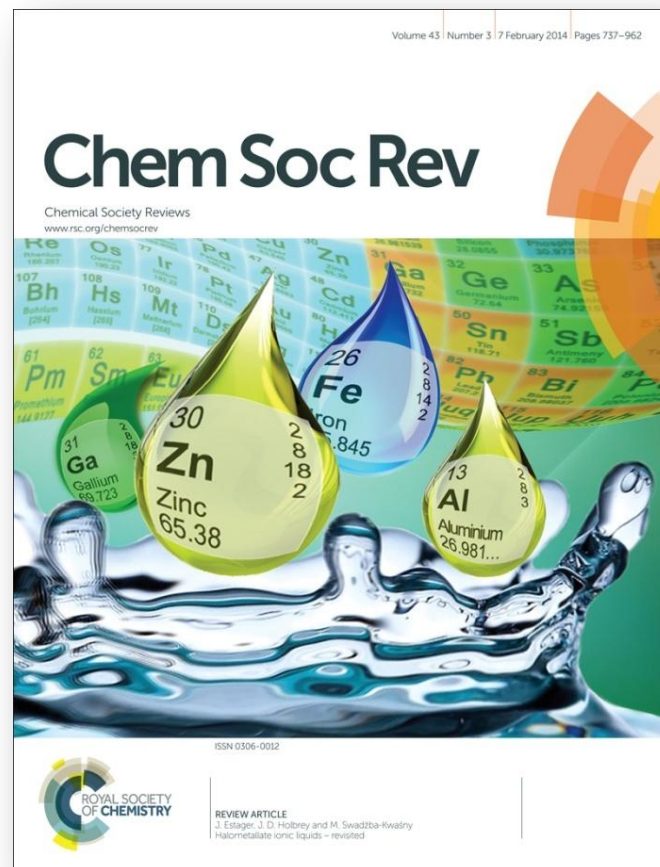
Halometallate ionic liquids - revisited,
J Estager, JD Holbrey and M Swadzba-Kwasny,
Chem Soc Rev, 2014, **43**, 847-886

What are room temperature ionic liquids?

- Salts that are liquids *or* the liquid state of salts

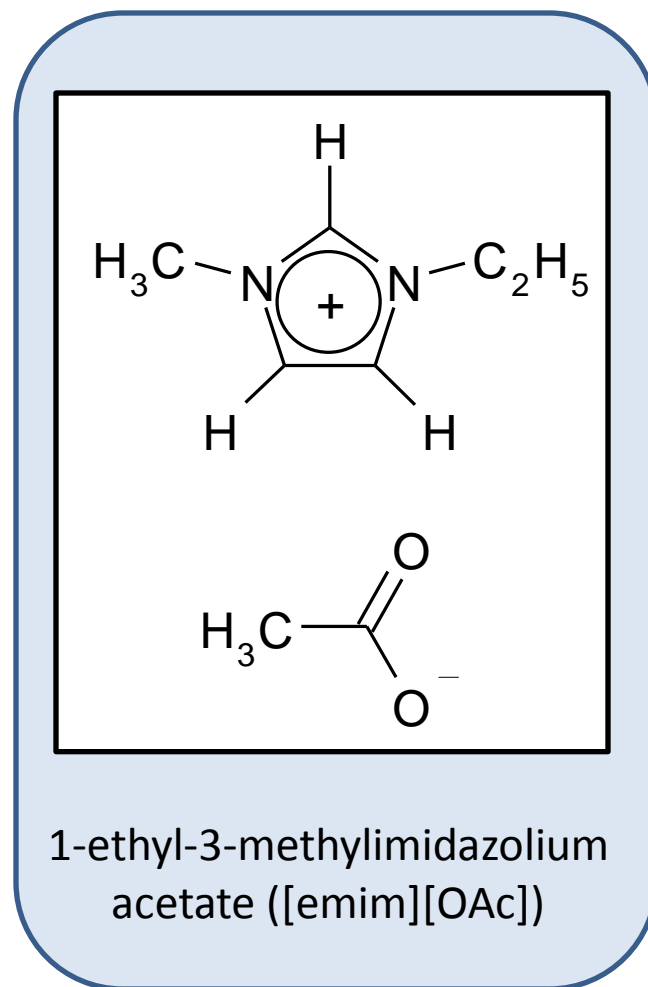 'Higher temperature' molten salts
  - **Cryolite**
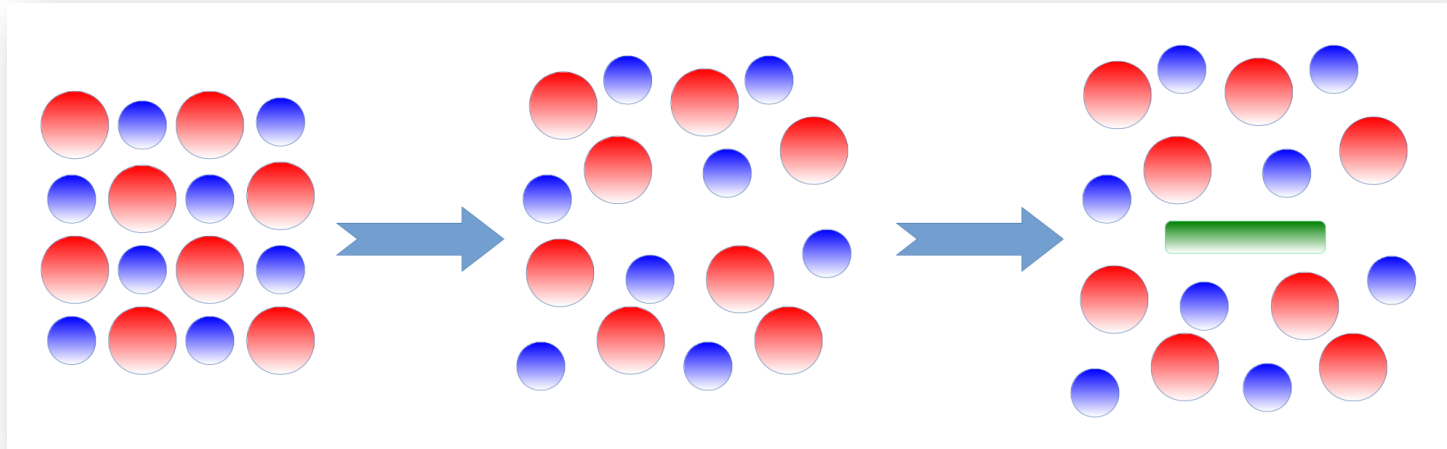   - Na_3AlF_6, molten electrolyte for Al production
  - **HITEC**
    - 40:7:53 $NaNO_2$:$NaNO_3$:KNO_3 (mp 142 °C) used as heat transfer fluids in parabolic solar heating systems

  Room temperature **ionic liquids**
  - usually incorporate **larger, more complex ions**
  - Often **decorated** organic cations

1-ethyl-3-methylimidazolium acetate ([emim][OAc])

Structure within ionic liquids…

- Questions…
  - Can we describe the structure of the ionic liquid?
  - What happens when a solute is dissolved?
  - Can we relate this information to changes in the chemical structure of the ions
  - Can we then use the information to design '*better systems*'?

Why study disordered materials?

- All the atoms in any condensed material (liquid or solid) have some correlation – *i.e.* they are not completely disordered

Why study disordered materials?

- Gain information about local molecular correlations
  - coordination environment
  - solvation shell
  - local lattice networks
  - hydrogen-bonding
- Basically, what makes a material behave the way it does.

Why neutron diffraction?

- Scattering length is not correlated to atomic number (*cf* X-rays)
  - **Light atoms** can contribute as much as heavy atoms to the scattering
  - Different **isotopes** can scatter considerably differently (most pronounced for hydrogen/deuterium)
- This means that you can collect multiple (different) data sets from 'equivalent' samples
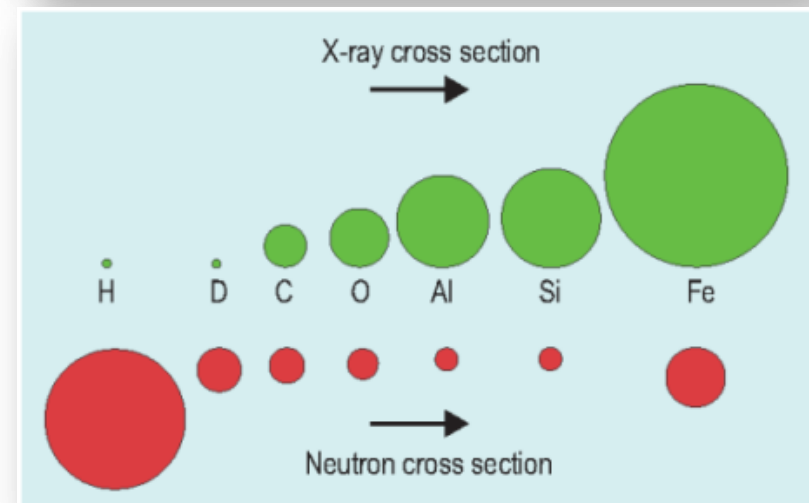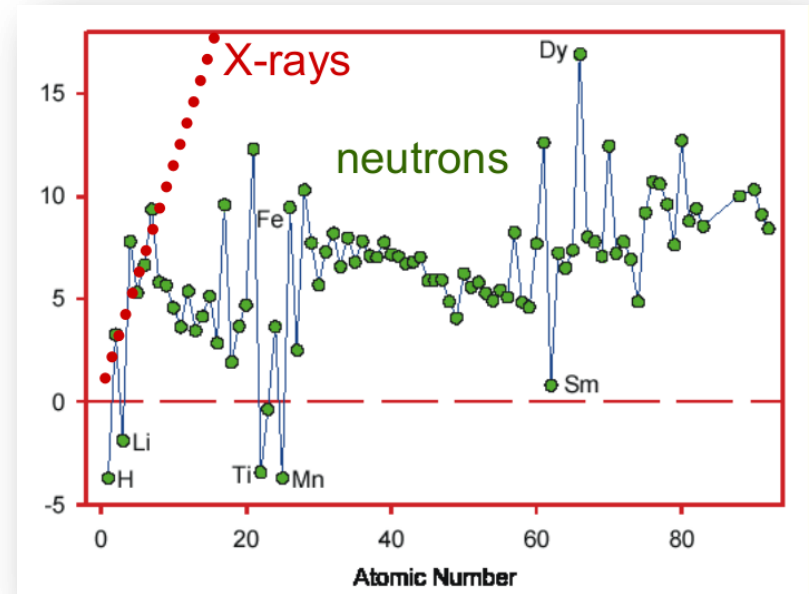
Neutrons *vs.* X-rays (theory)

Neutron

- Particle wave
- Mass, spin ½, magnetic dipole moment
- Interaction with atomic nucleus
- Scattering power independent of 2θ

X-ray

- Electromagnetic wave
- No mass, spin 1, no magnetic dipole moment
- Interaction with electrons
- Scattering power reduced with 2θ

Neutrons *vs.* X-rays (in practice)

Neutrons

- Lower absorption
  - Slow experiments (h)
- Sample size is larger
- Isotopic discrimination
- Light elements can be seen
- Low availability

X-rays

- Strong absorption
  - Rapid acquisition (s – min)
- Small samples needed
- No isotopic discrimination
- Heavy elements dominate
- Wide availability

Neutron diffraction with isotopic substitution (NDIS)

- **Different isotopes can scatter considerably differently**
  - Enables multiple (different) data sets from isostructural 'equivalent' samples

    - The worse example (for a chemist): **H_2O, HOD** and **D_2O**

  - Multiple experimental sets to check self consistency of a model
    - *cf* one data set from X-ray
  - Isotopic substitution enables partial structure factors (between pairs of atoms) to be extracted from multiple sets of total scattering data (later)

$g_{D2O}(r)$

$g_{HDO}(r)$
(50%H2O + 50%D2O)

$g_{H2O}(r)$

r(Å)
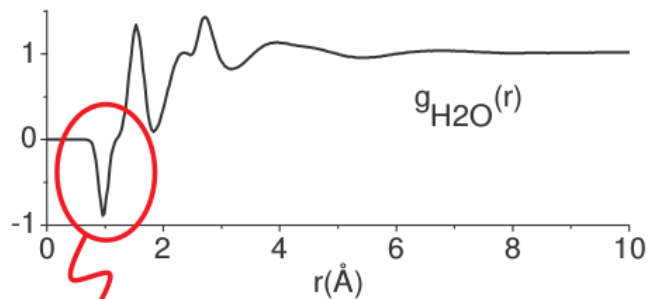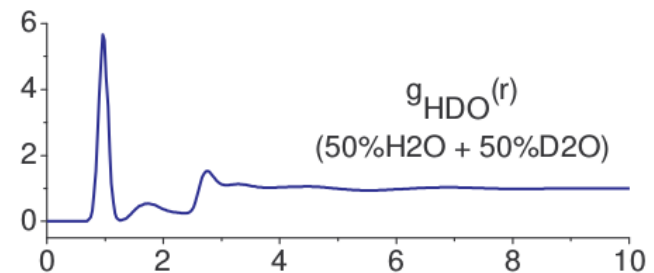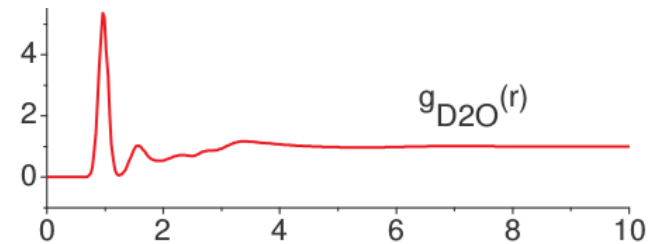
$b_H = -3.74$ fm

Table 1. Coherent scattering lengths (fm[a]) of important elements common to fluids found on and within the Earth (from Enderby et al. 1987).

| Element or Isotope	b	Element or Isotope	b	Element or Isotope	b
H	−3.74	^{40}Ca	4.9	^{65}Cu	11.1
D	6.67	^{44}Ca	1.8	Zn	5.686
^{6}Li	1.87	Fe	9.51	^{64}Zn	5.5
^{7}Li	−2.2	^{54}Fe	4.2	^{68}Zn	6.7
N	9.36	^{56}Fe	10.1	Ag	5.97
^{14}N	9.37	^{57}Fe	2.3	^{107}Ag	7.64
^{15}N	6.44	Ni	10.3	^{109}Ag	4.19
K	3.67	^{58}Ni	14.4	^{113}In	5.39
^{41}K	2.58	^{60}Ni	2.82	^{115}In	4.00
Cl	9.58	^{62}Ni	−8.7	Ba	5.07
^{35}Cl	11.7	^{64}Ni	−0.37	^{130}Ba	−3.6
^{37}Cl	3.1	Cu	7.718	^{137}Ba	6.82
Ca	4.9	^{63}Cu	6.7		

[a]1 fm = 10^{-15} m

# Extracting distance information from the scattering data

- Total scattering $S(Q)$ can be transformed into a radial distribution function $f(R)$ which includes all the distance correlations between different atomic sites in the system
  - function of Q (or 2θ) $\rightarrow$ function of r (or d)
  - Provides information on atom-atom separations distances

Generalised radial distribution function

First Coordination shell

Second Coordination shell
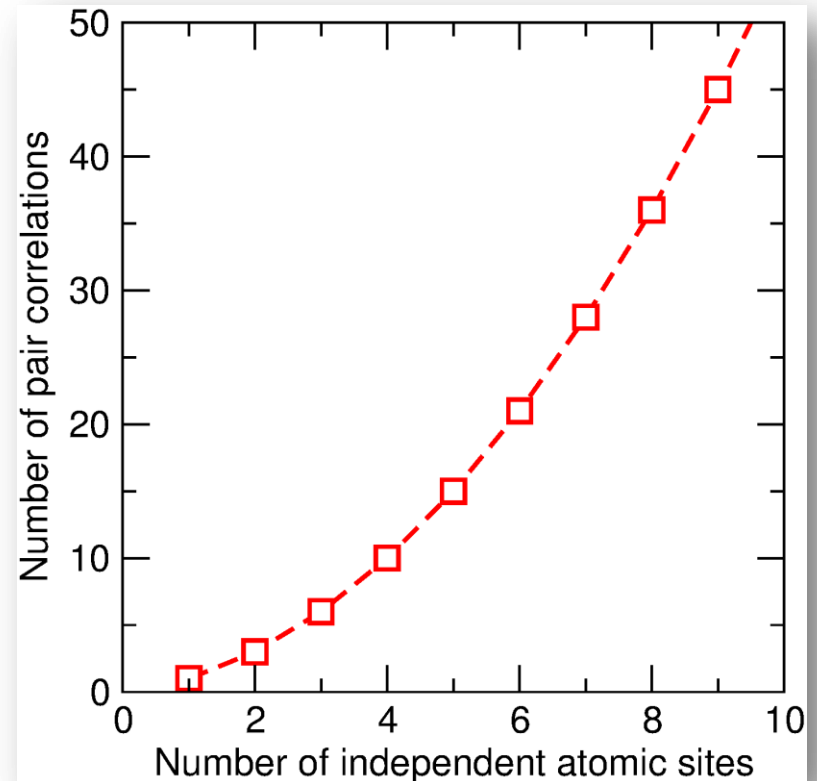
g(r)

1.0

0   σ   2σ   3σ
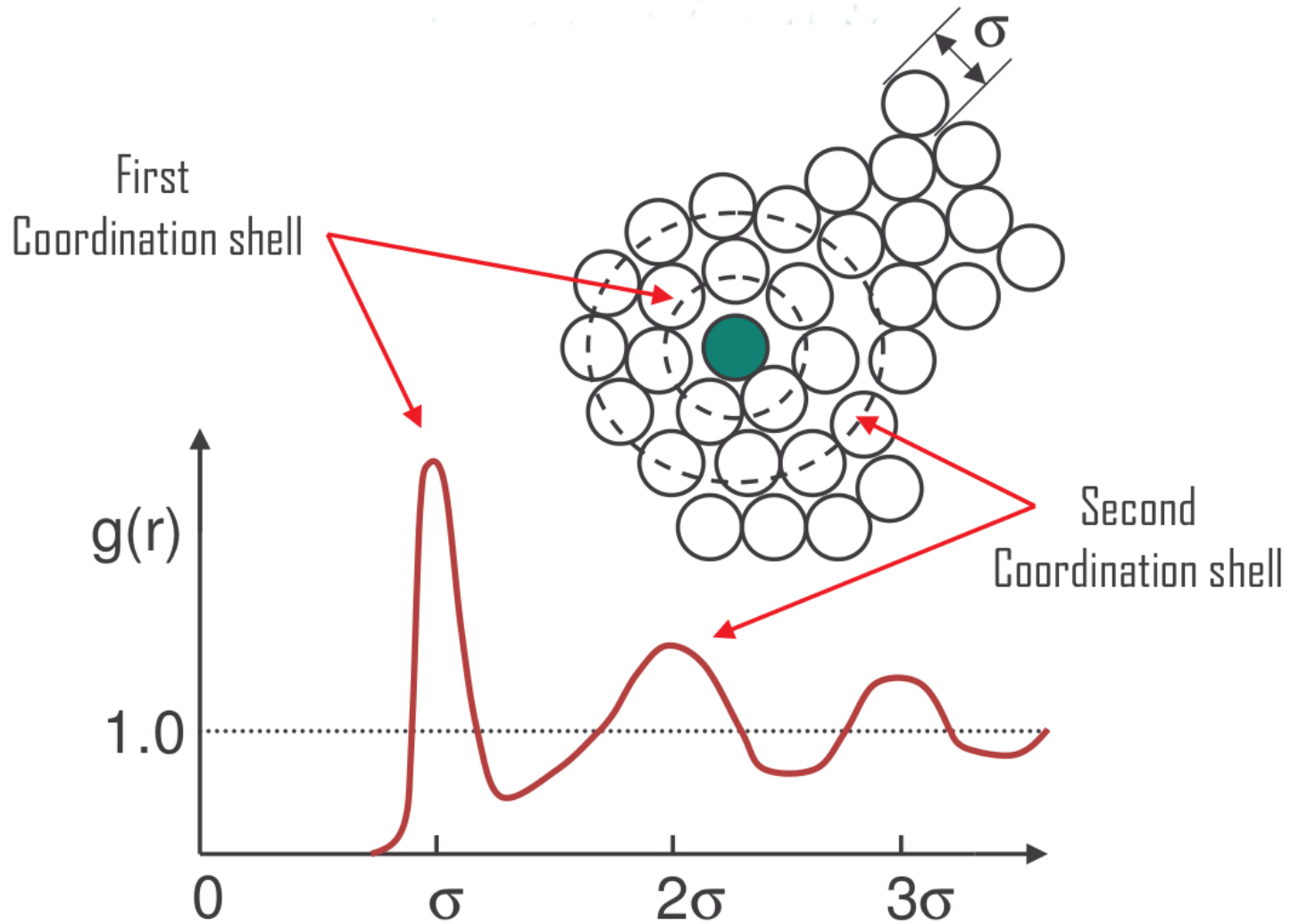
Example: neutron diffraction on NIMROD of mesoporous (MSU-H) silica
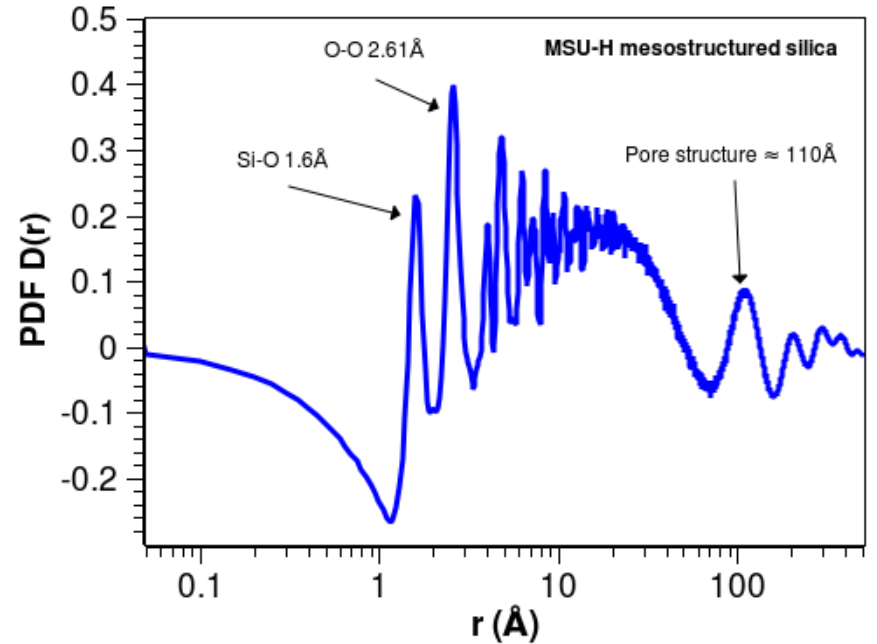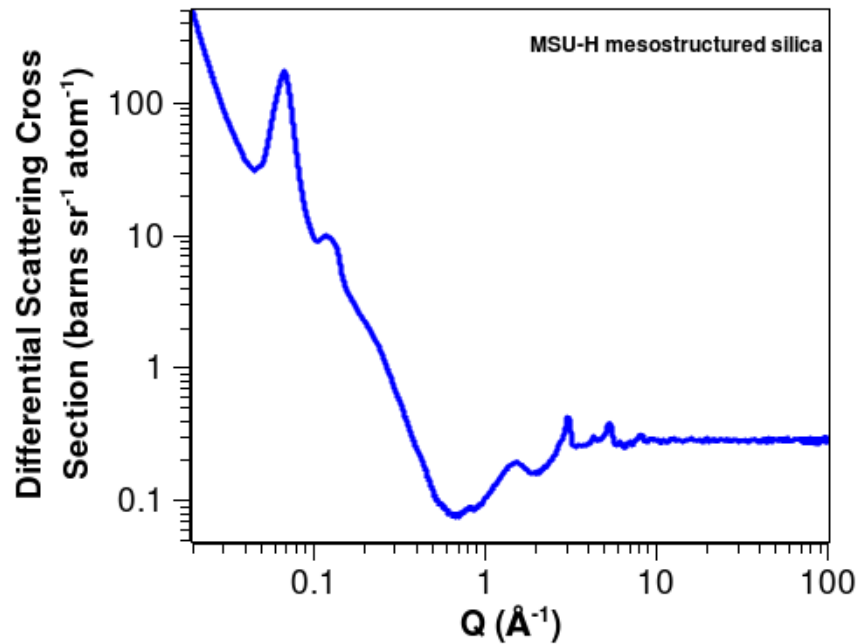
- Scattering data on *left*
- FT on *right*
  - Shows peaks corresponding to Si-O, and O-O separation distances (1.6 and 2.61 Å)

Increasing complexity in total RDF

- Number of site-site contributions to RDF
  - $N(N+1)/2$
    N is number of unique atomic sites in the system
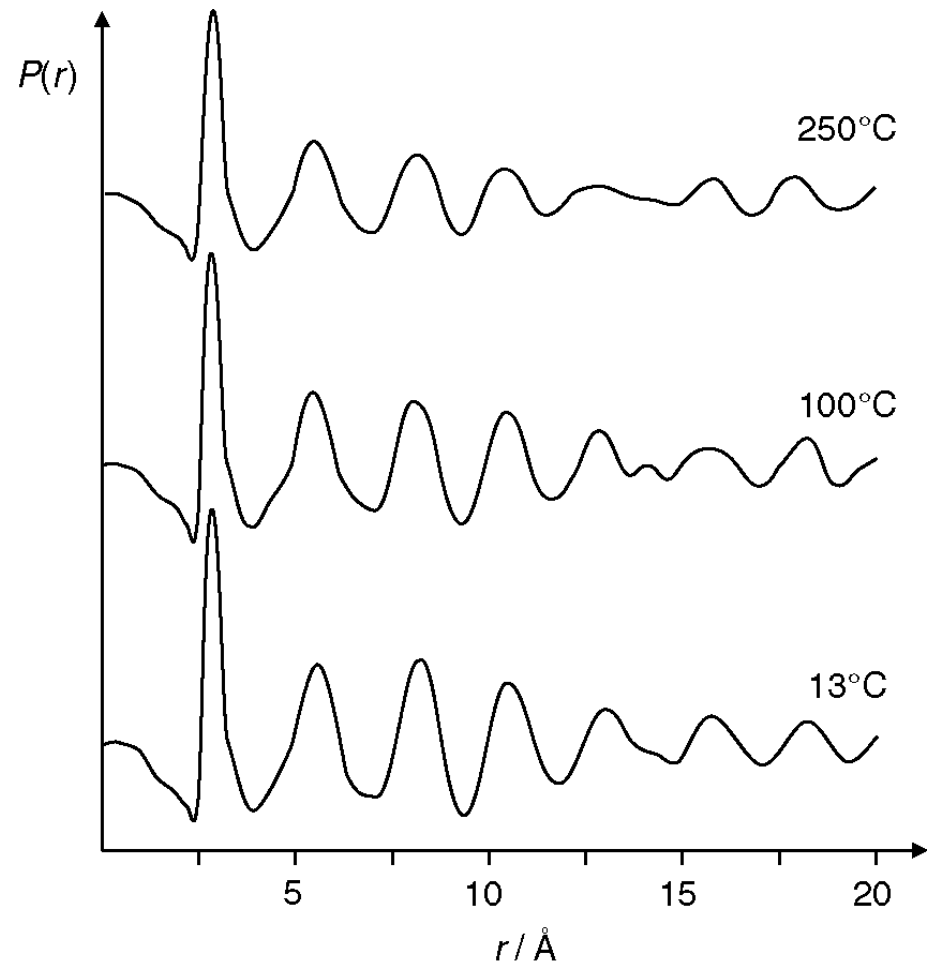
Increasing complexity in total RDF

- A simple monatomic liquid (Gallium, $N = 1$)

  Number of partial correlations
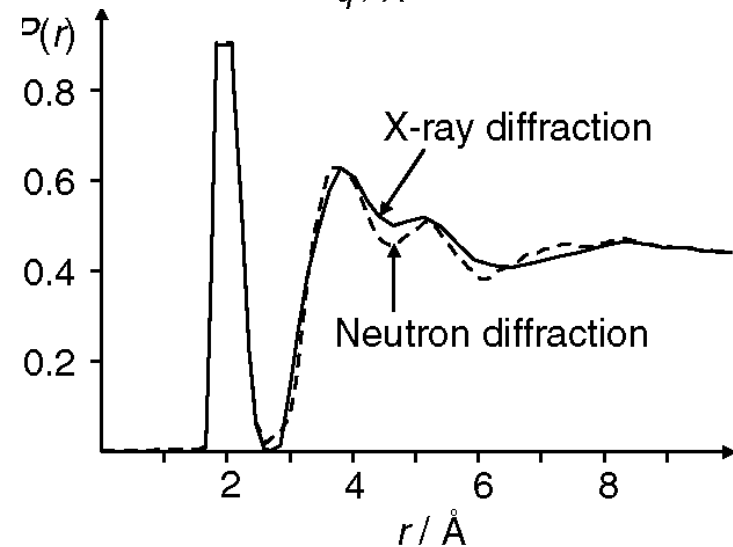
  $$= N(N+1)/2$$

  $$= 1$$

  correlation of Ga-Ga

$P(r)$

250°C

100°C

13°C
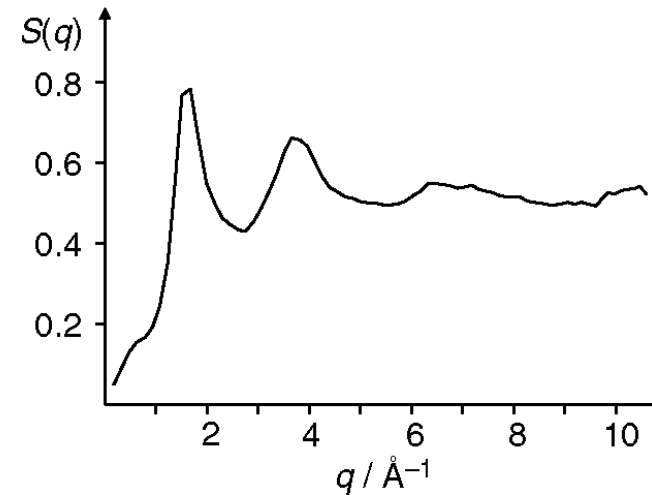
5   10   15   20

r / Å

Liquid Ga RDFs at different temperatures, *J Chem Phys*, 1977, **81**, 919

Increasing complexity in total RDF

- A simple diatomic liquid (chlorine, $N = 1$)
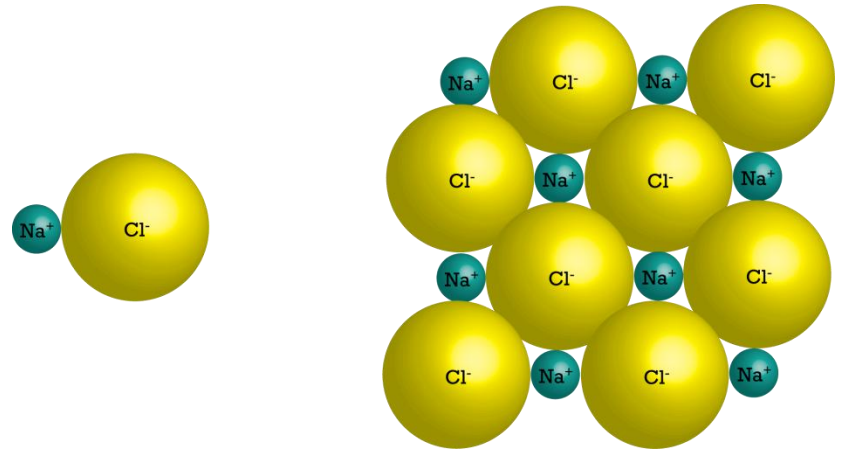
  Number of partial correlations

  $$= N(N+1)/2$$

  $$= 1$$

 But there should be *intra* and *inter*-molecular components because chlorine is Cl-Cl

Liquid Cl_2: $S(q)$ (top) from X-ray diffraction and RDF (bottom), *Mol Phys*, 1994, **82**, 1181

Increasing complexity in total RDF

- A simple salt (NaCl, $N = 2$)

  Number of partial correlations

  $$= N(N+1)/2$$
  $$= 3$$

  Na^+ - Na^+

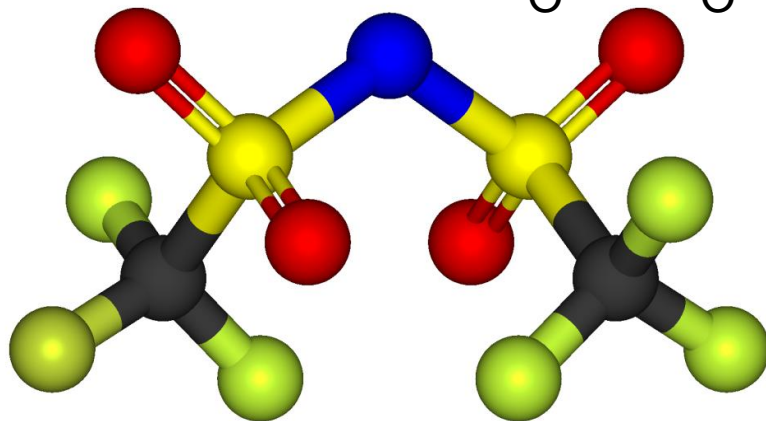 Na^+ - Cl^-

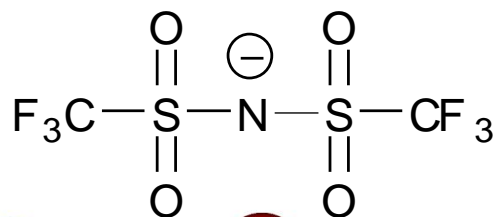 Cl^- - Cl^-

- A 'simple' alcohol (ethanol, CH_3CH_2OH, $N = 6$)

  Number of partial correlations

  $$= N(N+1)/2$$
  $$= 21$$

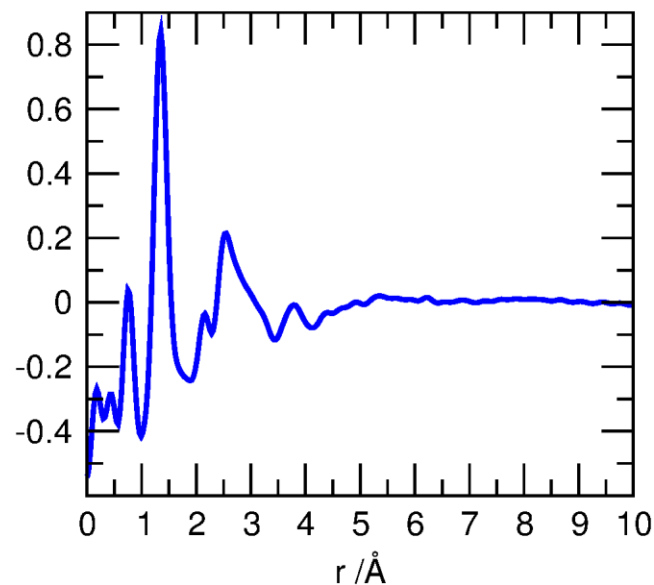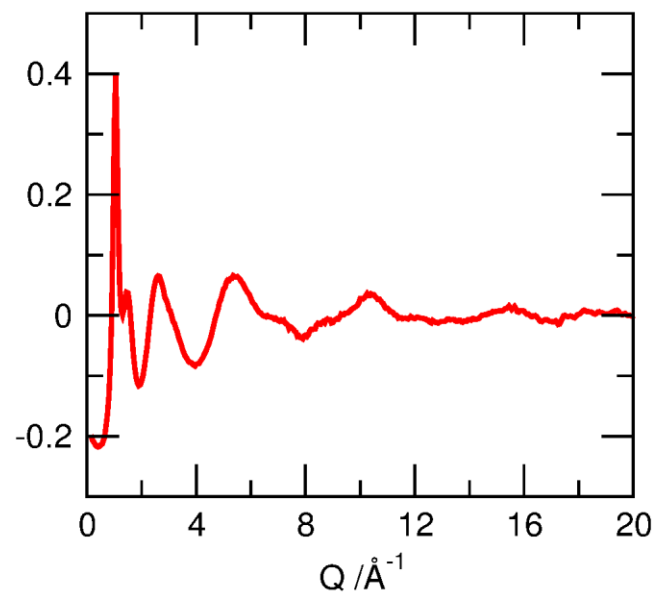 – Each site-site correlation contributes approximately 5% to the total data
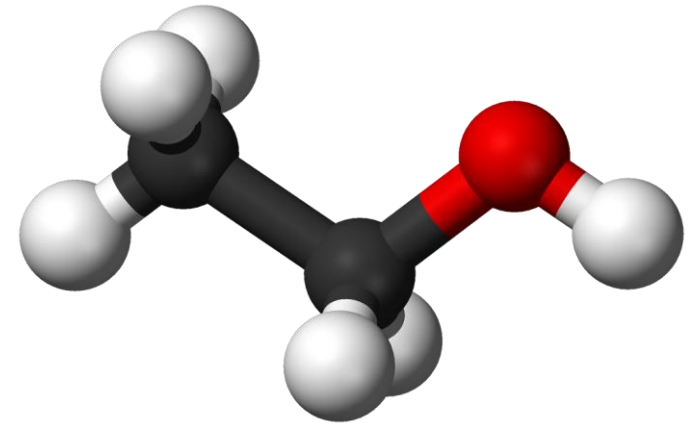
Real-life data…

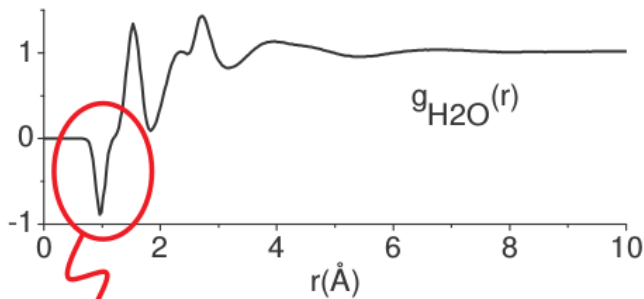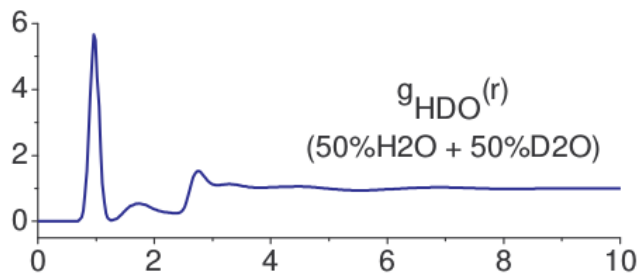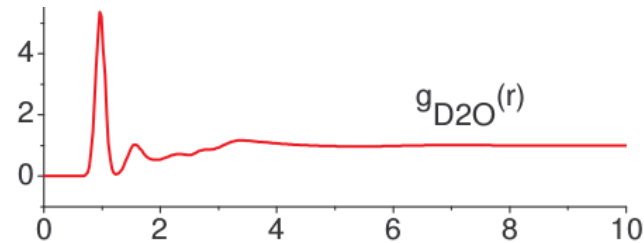- Molten $Cs[NTf_2]$ (200 °C)

  $N = 6$

Given the flexibility of the anion, it's unlikely that all the site-site contributions can be identified directly in the data – need to take advantage of isotopic differences
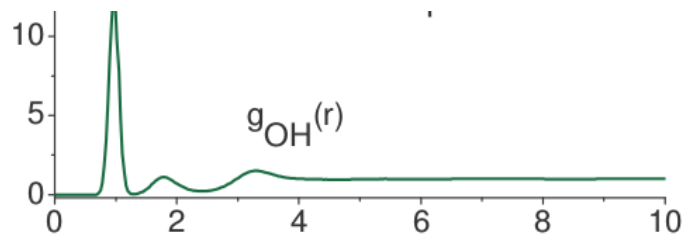
Neutron data from water (H/D)

$g_{D2O}(r)$

$g_{HDO}(r)$
(50%H2O + 50%D2O)

$g_{H2O}(r)$

r(Å)

$b_H = -3.74$ fm

- The three different *isotopomers* of water (H_2O, HDO, D_2O) have distinctly different scattering and rdf patterns
- From the differences between the data contributions from H/D-site correlations to the scattering can be identified
- *i.e.* to derive **partial structure factors**

Neutron data from water (H/D)

HDO,

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$g_{D2O}(r)$

$g_{OH}(r)$

$g_{HDO}(r)$
(50%H2O + 50%D2O)

$g_{OO}(r) \ (\sim g_{xray}(r))$

$g_{H2O}(r)$

$g_{HH}(r)$

r(Å)

r(Å)
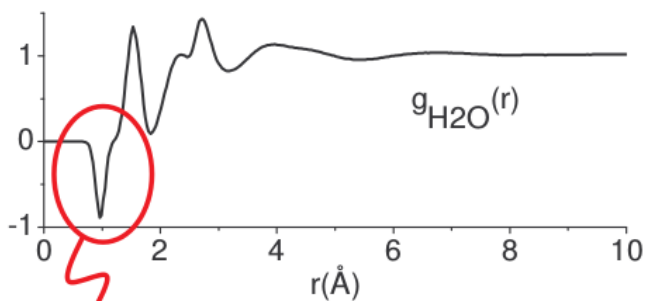
$b_H = -3.74$ fm

Structure of molten sodium chloride
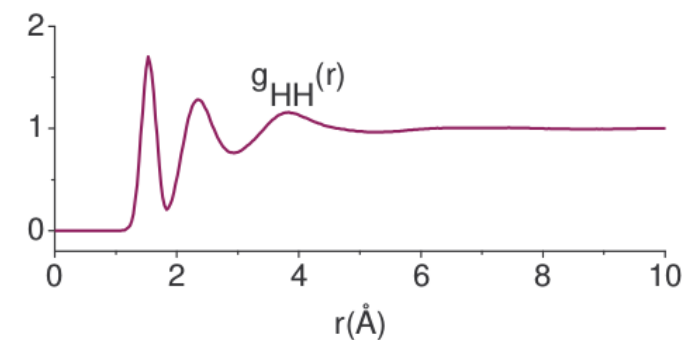
- Neutron diffraction data was collected on molten NaCl sample
- Isotopic substitution (Cl/^{35}Cl/^{37}Cl) was used
- The three partial structure factors were extracted from data
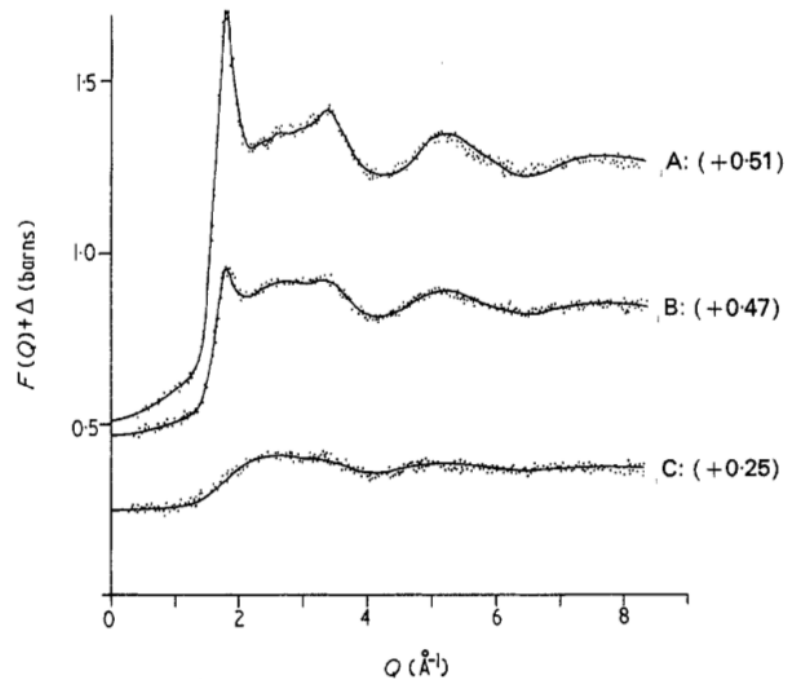
Figure 1. $F(Q)$ data for liquid Na^{35}Cl (curve A), NaCl (curve B) and Na^{37}Cl (curve C) at 875°C. The points are experimental and the curves are derived from the structure factors shown in figure 4. ($\Delta = c_a f_a^2 + c_b f_b^2$).

Edwards, Enderby, Howe and Page, *J. Phys. C,* 1975, **8,** 3483

Solvent Structure and Perturbations in Solutions of Chemical and Biological Importance

J. L. Finney
Department of Physics and Astronomy, University College Lond

A. K. Soper
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot,

- Partial distribution functions can be extracted from complementary data sets from isotopically substituted samples

- **First order difference**
  - Determine *S(Q)* for two samples which differ only by isotopic substitution at the point of interest (α)
  - Using three samples with different isotopic contrast, a difference function can be calculated, $Δ_α(Q)$, which includes terms relevant to the substituted site
  - This simplifies the distribution function…

This paper is required reading
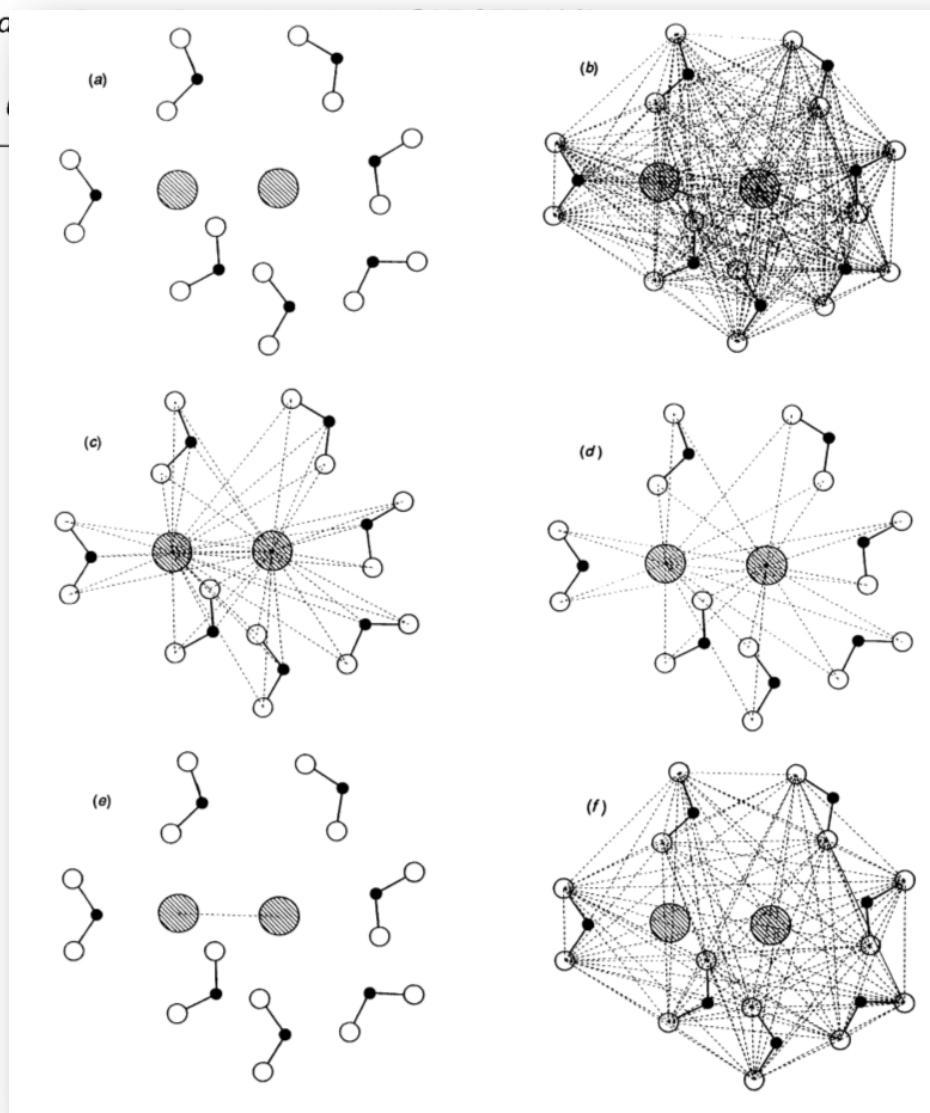
A/B isotopic substitutions to extract all correlations

	Data set	Solute	Solvent
Solute-solute (first order difference)	**1**	D	D
	2	D	HD
	3	D	H
Solvent-solvent first order difference)	1	D	D
	4	HD	D
	5	H	D
Solvent-solute (second order difference)	1	D	D
	6	HD	HD
	7	H	H

http://www.isis.stfc.ac.uk/instruments/sandals/technical/neutron-diffraction-with-isotopic-substitution8808.html

Neutron data from water (H/D)

HDO,

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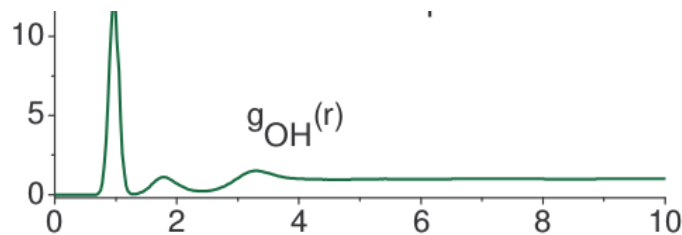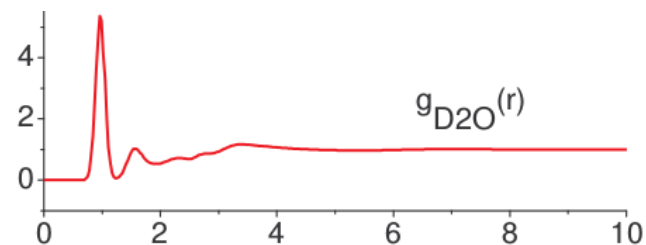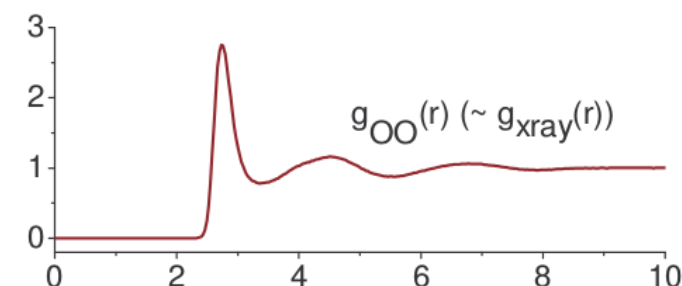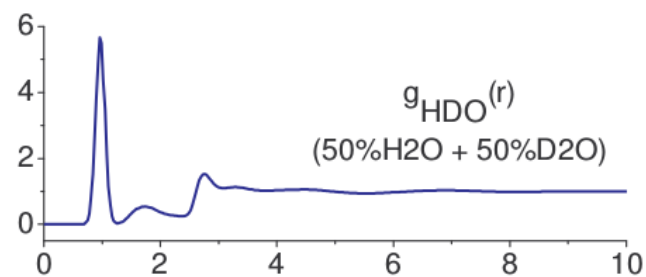
$b_H = -3.74$ fm
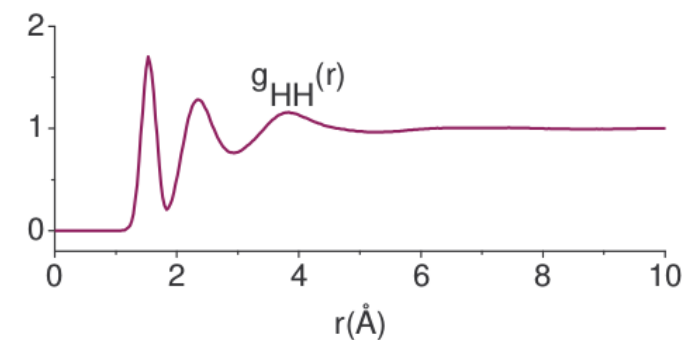
First order difference: hydrated guanidinium ions

Example

Hydration of guanidinium ions in water

– Mason *et al*, *PNAS*, 2003, **100**, 4557

– 1st order diff $^{Nat}N/^{15}N$-substituted guanidinium eliminates solvent-solvent correlations

• But…this is still pretty complex from a simple cation…

Where to now?

- NDIS isotopic substitution allows
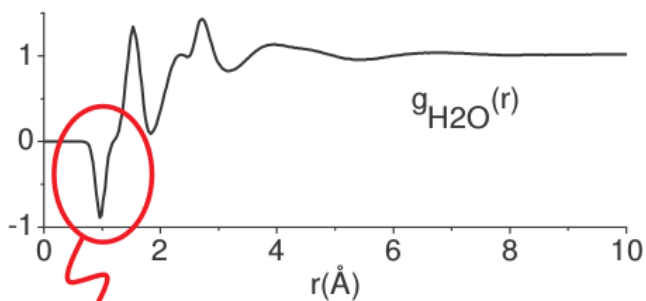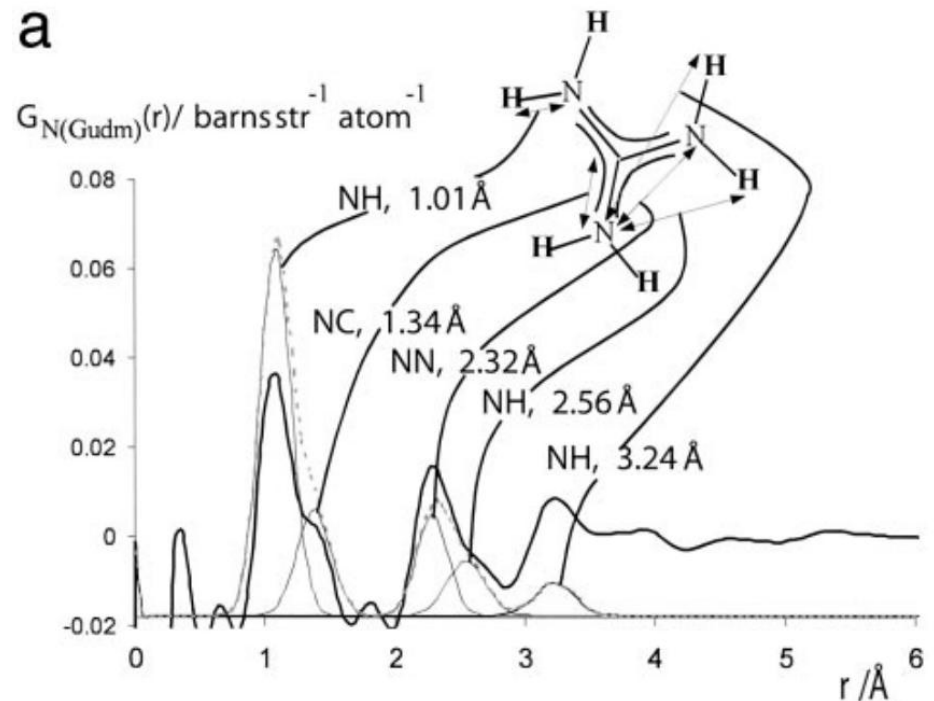 - specific site-site correlations to be highlighted (indicator) through 1st/2nd-order difference correlations
  - **But** explicit identification of **all** partial PDFs is not possible in many (most?) cases

- NDIS also provides multiple data-sets from the 'same' materials to test models against (multiple self-consistent data sets)
  - Computer modelling and simulation, testing against the experimental data, is the way to go
  - Alan Soper has indicated how to approach this using empirical potential structure refinement (EPSR)

- Describe the workflow needed get useful information **illustrated from ionic liquid systems** using epsr simulation to extract data

EPSR (Empirical Potential Structural Refinement)

- Monte Carlo simulation using Lennard-Jones potentials; the simulated data compared to experimental in Q space

- Difference between the structure factors for the real and simulated Q space data transformed to real space

- **<u>Uses experimentally collected data</u>** to guide refinement

- Selective isotopic substitution (usually deuterium-hydrogen) provides isotopic contrast for multiple data sets
  - Processed through background subtraction, normalisation, corrected for inelastic scattering from H…

- Site-site correlations, coordination numbers, radial and spherical distribution data (and much more) can be extracted by interrogating the epsr simulation

Workflow to determine (Ionic Liquid) Structure

- Have a worthwhile problem you want to address
  - **Beam-time proposal**
- Selective H/D isotopic substitution on cation (and anion)
  - **Think about the synthetic chemistry challenges**
- Collect experimental liquid structure data from neutron scattering experiments
  - **Measure**
- Analyse using EPSR (empirical structure refinement)
  - **Simulate**
- Use this model to compare with complementary experimental data (physical and theoretical/simulation)
  - **Compare**

Green processing using ionic liquids and CO_2

Many organic solvents evaporate into the atmosphere with detrimental effects on the environment and human health. But room-temperature ionic liquids, with low viscosity and no measurable vapour pressure[1], can be used as environmentally benign media for a range of industrially important chemical processes[2–6], despite uncertainties about thermal stability and sensitivity to oxygen and water. It is difficult to recover products, however, as extraction with water[7] works only for hydrophilic products, distillation is not suitable for poorly volatile or thermally labile products, and liquid–liquid extraction using organic solvents results in cross-contamination. We find that non-volatile organic compounds can be extracted from ionic liquids using supercritical carbon dioxide, which is widely used to extract large organic compounds with minimal pollution[8]. Carbon dioxide dissolves in the liquid to facilitate extraction, but the ionic

Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts[†]

Pierre Bonhôte,* Ana-Paula Dias, Nicholas Papageorgiou, Kuppuswamy Kalyanasundaram, and Michael Grätzel*

Institut de chimie physique, Ecole polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Received August 15, 1995[⊗]

New, hydrophobic ionic liquids with low melting points (< -30 °C to ambient temperature) have been synthesized and investigated, based on 1,3-dialkyl imidazolium cations and hydrophobic anions. Other imidazolium molten salts with hydrophilic anions and thus water-soluble are also described. The molten salts were characterized by NMR and elemental analysis. Their density, melting point, viscosity, conductivity, refractive index, electrochemical window, thermal stability, and miscibility with water and organic solvents were determined. The influence of ... as 35 ... cetate) ... stablish ...). The ... tions.

Room temperature ionic liquids as novel media for 'clean' liquid–liquid extraction

Jonathan G. Huddleston, Heather D. Willauer, Richard P. Swatloski, Ann E. Visser and Robin D. Rogers*[†]

Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA

The partitioning of simple, substituted-benzene derivatives between water and the room temperature ionic liquid, butylmethylimidazolium hexafluorophosphate, is based on the solutes' charged state or relative hydrophobicity; room temperature ionic liquids thus may be suitable candidates for replacement of volatile organic solvents in liquid–liquid extraction processes.

scientific correspondence

remains after extraction of the naphthalene and depressurization.

Lynnette A. Blanchard*, Dan Hancu†, Eric J. Beckman†, Joan F. Brennecke*

*Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA e-mail: jfb@nd.edu

†Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, USA

1. Seddon, K. R. *J. Chem. Tech. Biotechnol.* **68**, 351–356 (1997).
2. Chauvin, Y. & Olivier-Bourbigou, H. *Chemtech* **25**, 26–30 (1995).
3. Adams, C. J., Earle, M. J., Roberts, G. & Seddon, K. R. *Chem. Commun.* **19**, 2097–2098 (1998).
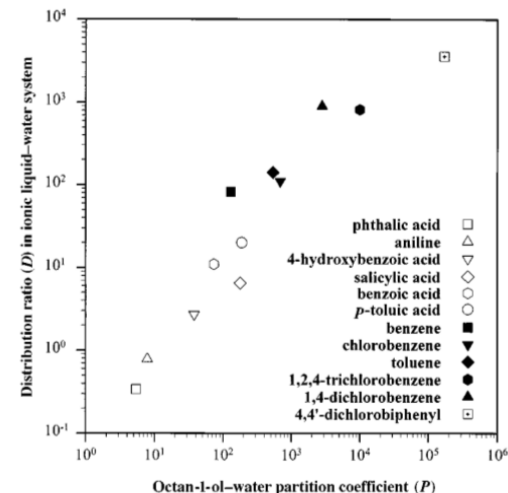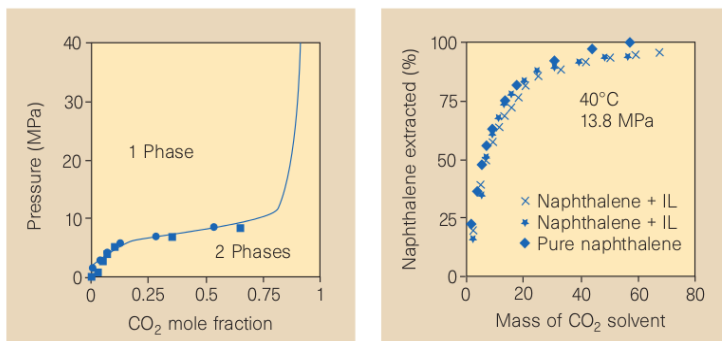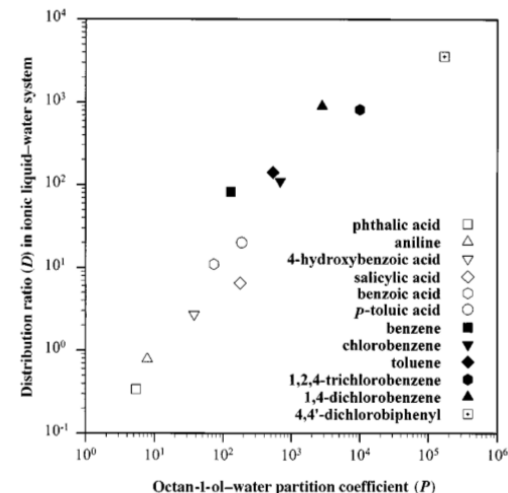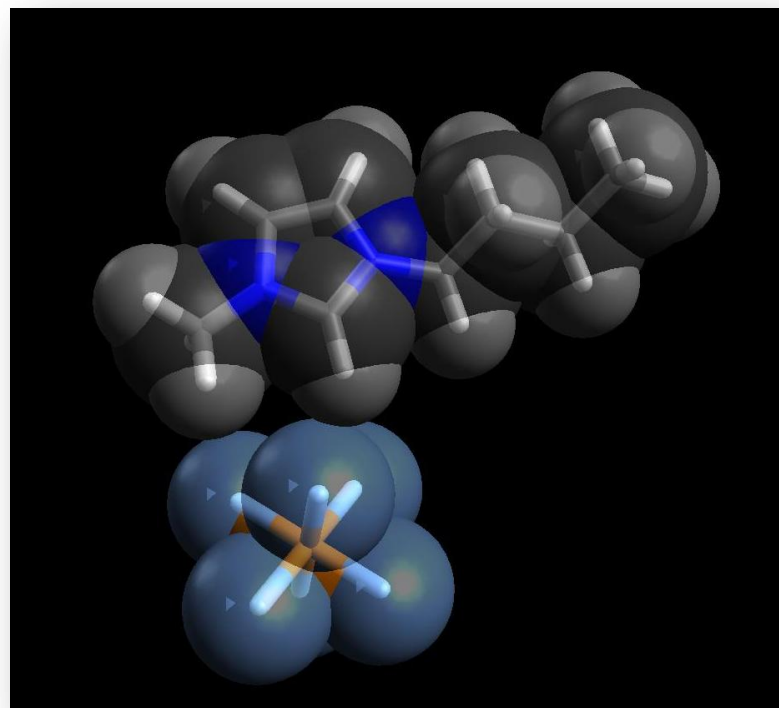

Fig. 1 Correlation of partitioning data between [BMIM][PF_6]–water and octan-1-ol–water biphasic systems

scCO₂ separations

Green processing using ionic liquids and CO₂

Many organic solvents evaporate into the atmosphere with detrimental effects on the environment and human health. But room-temperature ionic liquids, with low viscosity and no measurable vapour pressure[1], can be used as environmentally benign media for a range of industrially important chemical processes[2–6], despite uncertainties about thermal stability and sensitivity to oxygen and water. It is difficult to recover products, however, as extraction with water[7] works only for hydrophilic products, distillation is not suitable for poorly volatile or thermally labile products, and liquid–liquid extraction using organic solvents results in cross-contamination. We find that non-volatile organic compounds can be extracted from ionic liquids using supercritical carbon dioxide, which is widely used to extract large organic compounds with minimal pollution[8]. Carbon dioxide dissolves in the liquid to facilitate extraction, but the ionic

Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts[†]

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Dye sensitised solar cells

New, hydrophobic ionic liquids with low melting points (<−30 ℃ to ambient temperature) have been synthesized and investigated, based on 1,3-dialkyl imidazolium cations and hydrophobic anions. Other imidazolium molten salts with hydrophilic anions and thus water-soluble are also described. The molten salts were characterized by NMR and elemental analysis. Their density, melting point, viscosity, conductivity, refractive index, electrochemical window, thermal stability, and miscibility with water and organic solvents were determined. The influence of ... as 35 ...cetate) ...stablish ...). The ...tions.

Room temperature ionic liquids as novel media for 'clean' liquid–liquid extraction

Non-volatile liquid-liquid extraction

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The partitioning of simple, substituted-benzene derivatives between water and the room temperature ionic liquid, butylmethylimidazolium hexafluorophosphate, is based on the solutes' charged state or relative hydrophobicity; room temperature ionic liquids thus may be suitable candidates for replacement of volatile organic solvents in liquid–liquid extraction processes.

scientific correspondence

remains after extraction of the naphthalene and depressurization.

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1. Seddon, K. R. J. Chem. Tech. Biotechnol. **68**, 351–356 (1997).
2. Chauvin, Y. & Olivier-Bourbigou, H. Chemtech **25**, 26–30 (1995).
3. Adams, C. J., Earle, M. J., Roberts, G. & Seddon, K. R. Chem. ...

Fig. 1 Correlation of partitioning data between [BMIM][PF₆]–water and octan-1-ol–water biphasic systems
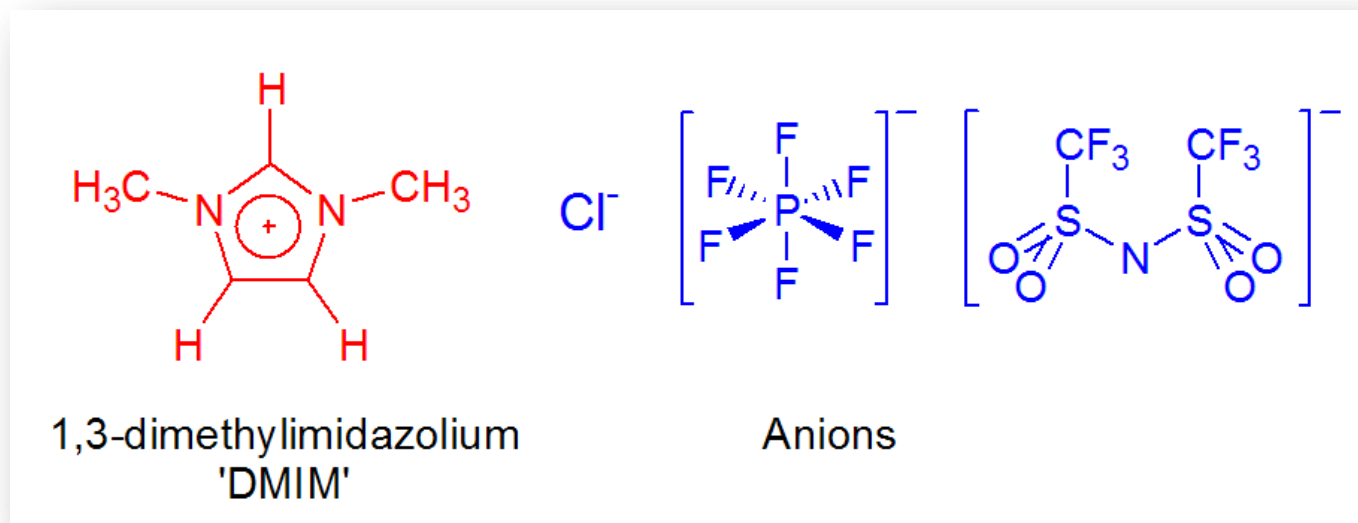
The first target for a 'room temperature' ionic liquid study

- 1-butyl-3-methylimidazolium hexafluorophosphate : [bmim][PF$_6$]

- Not possible!
  - Asymmetric cation, N = 21, 231 pair contributions to scattering
  - Impossible to solve from first principles

- The solution?
  - Collect data on a simpler model system
  - Anticipate that computing capabilities might improve in ten years time so the data can be analysed!
  - Use EPSR to refine a model, based on the fact that we 'know' about most of the connectivity and shape of the ions present (*intra*molecular structure)

Ionic liquid structure – model systems

- **1,3-dimethylimidazolium salts with Cl⁻, [PF$_6$]⁻, and [NTf$_2$]⁻ anions**

    – Observed an alternating Coulombic lattice structure in the liquid
   – Demonstrated effects of anion size/shape/polarisation on fine structure

1,3-dimethylimidazolium
'DMIM'

Anions

Ionic liquid structure – model systems

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Structure and solvation in ionic liquids
C Hardacre, JD Holbrey, M Nieuwenhuyzen, TGA Youngs, *Acc Chem Res*, 2007 **40** 1146.

Phenol solutions in ionic liquids

- 1:2 Phenol/*N*-methylpyridinium [NTf$_2$]
  - model system for phenol recovery from bio-oils
  - Experimental: data collected at 60 ˚C from liquids; 4 data sets from H/D substituted mixtures (SANDALS)

	Methyl	Ring	Phenol
[CD$_3$-Py-d$_5$][NTf$_2$] + phenol-d$_6$	D	D	D
[CD$_3$-Py-d$_5$][NTf$_2$] + phenol-h$_6$	D	D	H
[CH$_3$-Py-d$_5$][NTf$_2$] + phenol-d$_6$	H	D	D
[CD$_3$-Py-h$_5$][NTf$_2$] + phenol-d$_6$	D	H	D
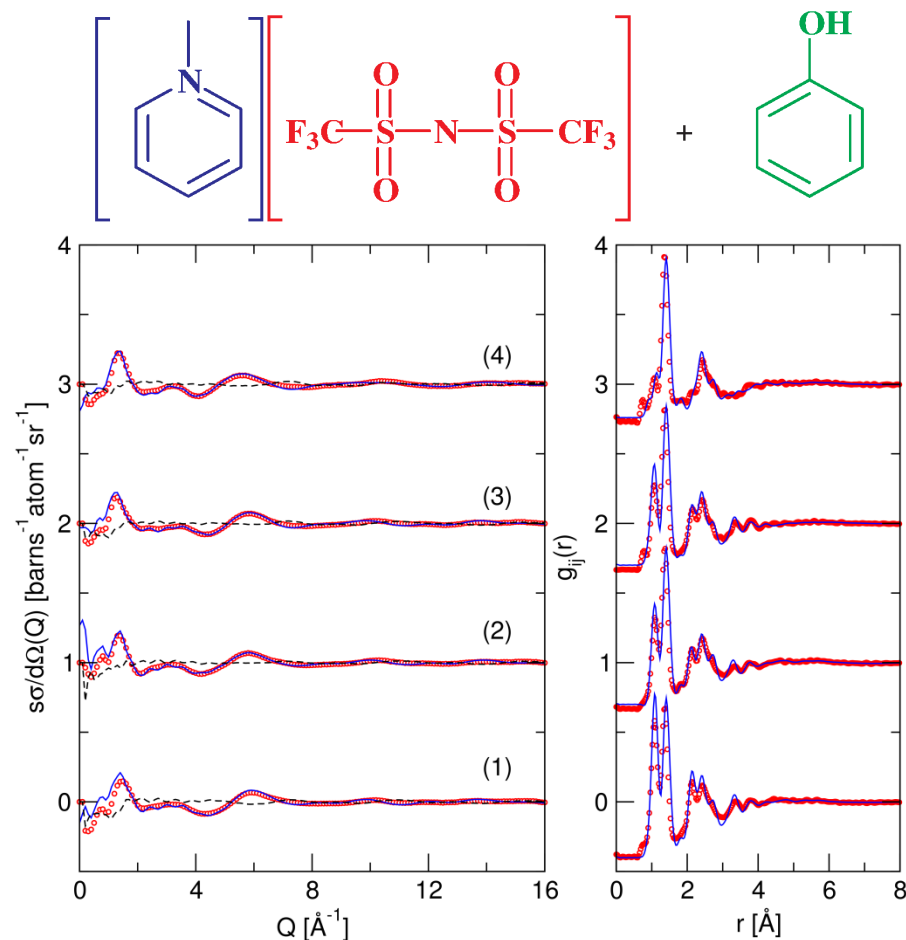
Experimental and modelled structure factors (*left*) and real space transforms (*right*) for isotopically substituted liquid 1:2 mixtures

JD Holbrey and AH Turner, *J. Solution Chem.*, 2015, **44**, 621-633.

# 1:2 phenol:IL RDFs extracted from epsr
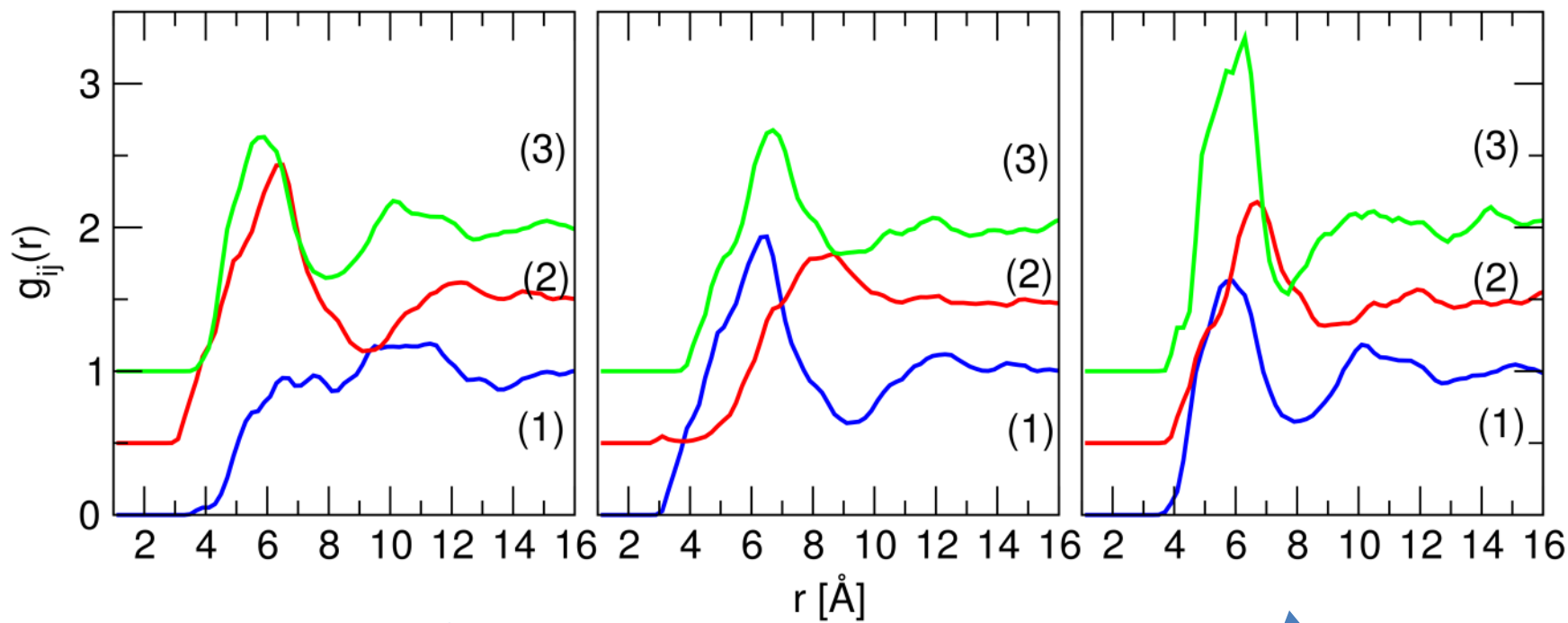
Centre of mass RDFs around the cation (left), anion (centre) and phenol (right) showing **cation** (1), **anion** (2) and **phenol** (3) correlations.

JD Holbrey and AH Turner, *J. Solution Chem.*, 2015, **44**, 621-633.

1:2 phenol:IL SDFs (cation centred)
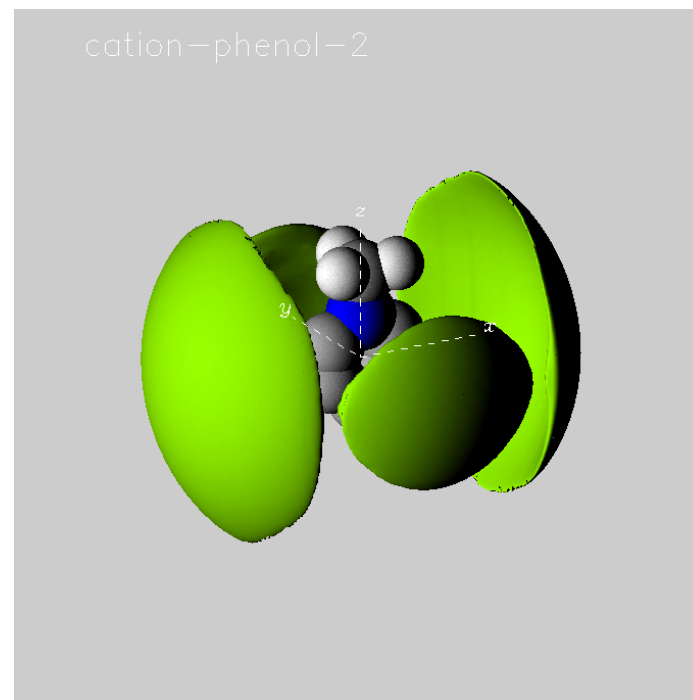
Spatial distribution functions (top 10%) of anions (left) and phenols (right) within 8 Å of the methylpyridinium cation centre-of-mass

JD Holbrey and AH Turner, *J. Solution Chem.*, 2015, **44**, 621-633.
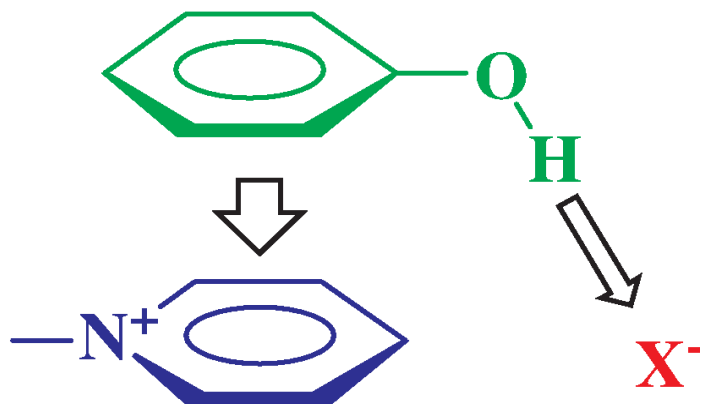
1:2 phenol:IL SDFs (phenol centred)
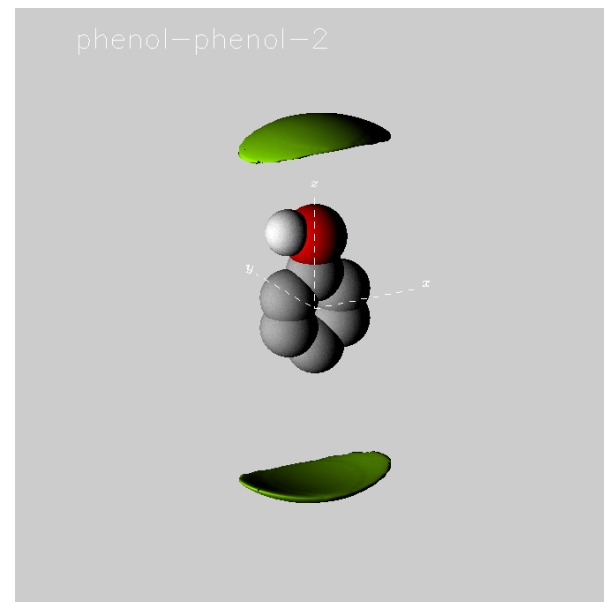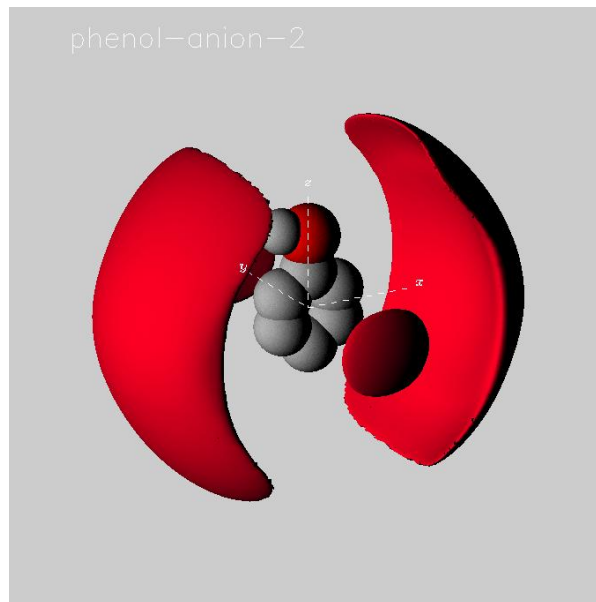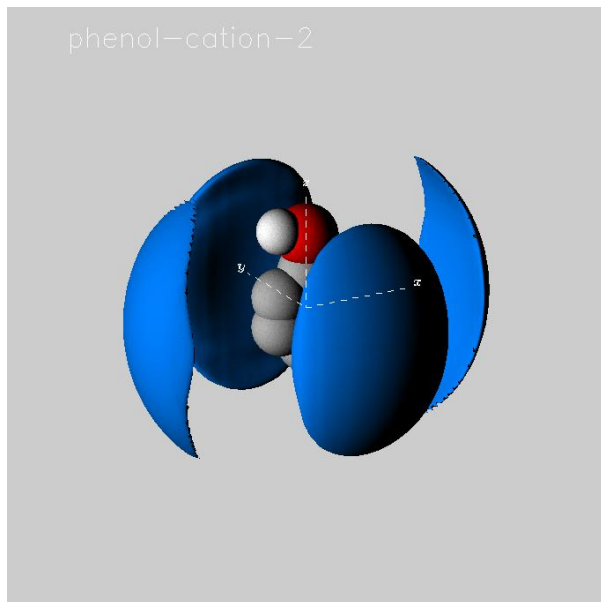
Spatial distribution functions(top 10%) of cations (left), anions (middle) and phenols (right) within 8 Å of the phenol centre-of-mass.

JD Holbrey and AH Turner, *J. Solution Chem.*, 2015, **44**, 621-633.

Phenol→anion interactions?
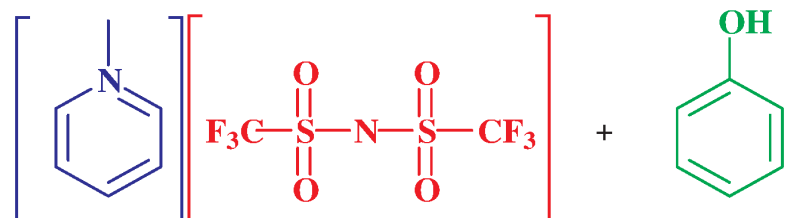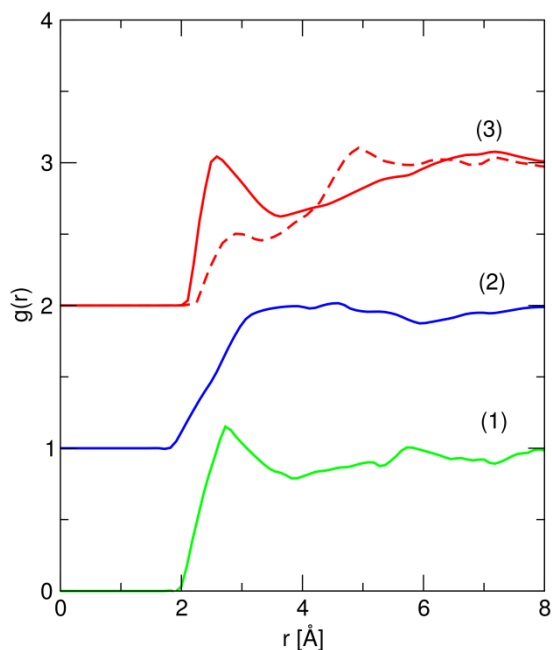
Partial RDFs for the phenol-OH group correlation to (1) phenol-OH, (2) cation-methyl, and (3) anion O (solid) and N (dashed).

- A hint of a H-bonding correlation of the phenol-OH to the anion

- Proposed that the phenol-OH⋯anion hydrogen bonding could be enhanced with more basic (coordinating) anions

JD Holbrey and AH Turner, *J. Solution Chem.*, 2015, **44**, 621-633.
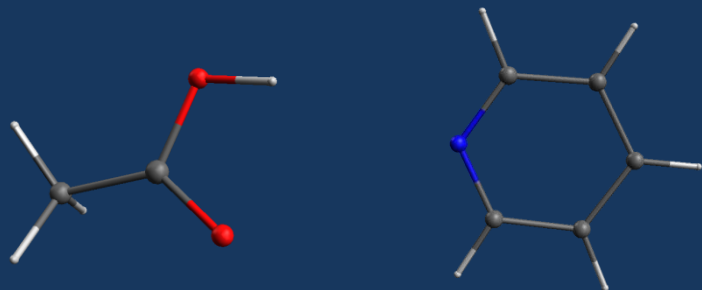
Pyridine + acetic acid

- **Non-ideal liquid** mixture
  - First studied in the 1930s
  - Maxima in many properties at χ_{HOAc} = 0.85
  - Many interpretations over the years of what is going on

- What happens when an acid and a base are combined and form a liquid?

  A-H + B $\leftrightarrow$ [B-H]$^+$ + A$^-$
  A-H + B $\leftrightarrow$ {A-H$\cdots$B}
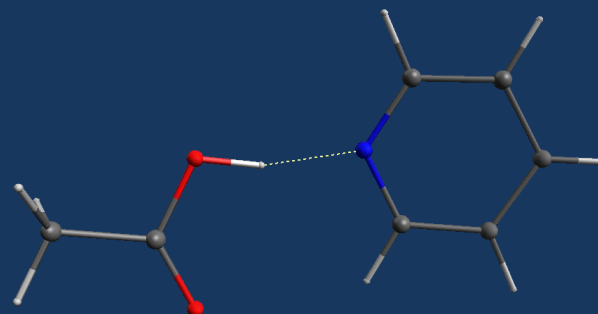 A-H + B $\leftrightarrow$ A-H + B
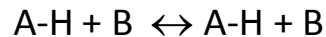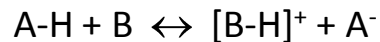
  Can NDIS help identify the species present and understand the liquid structure and properties?
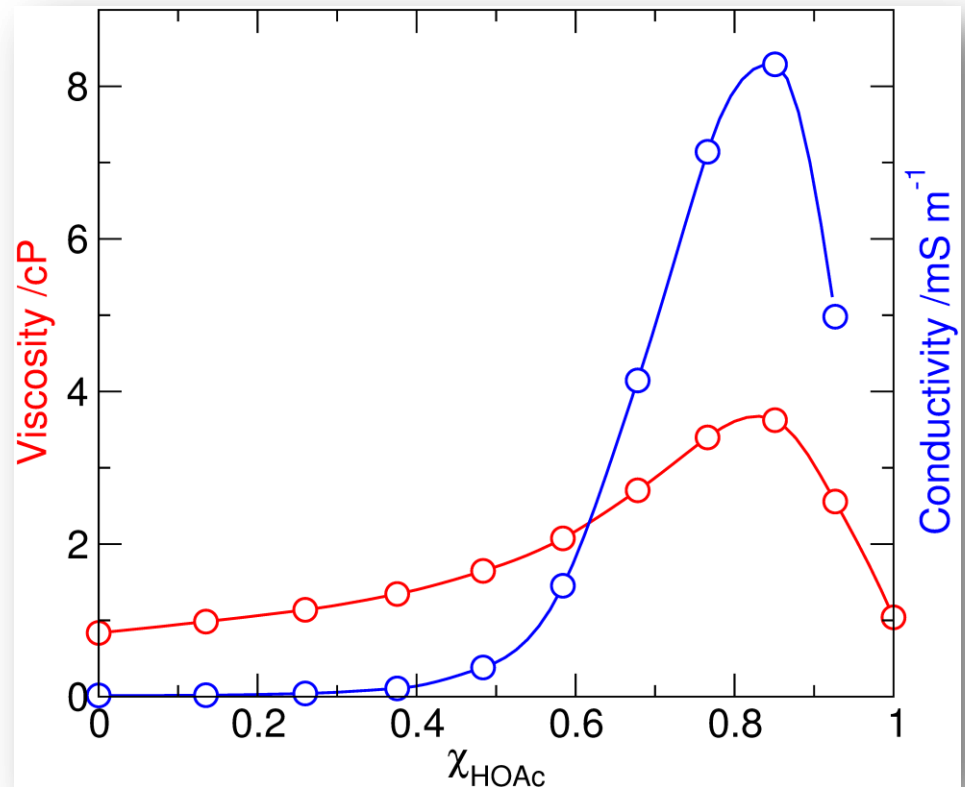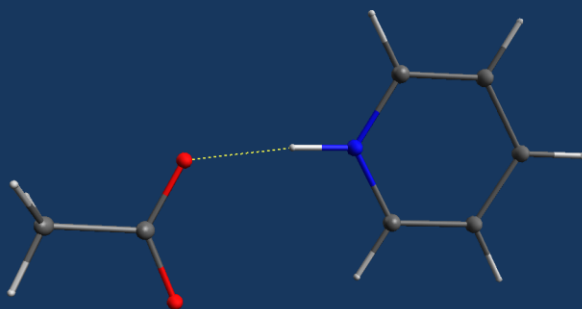
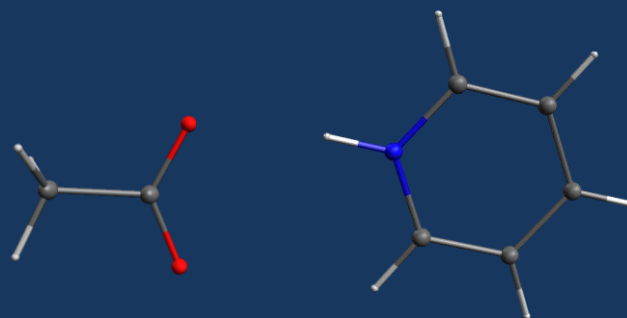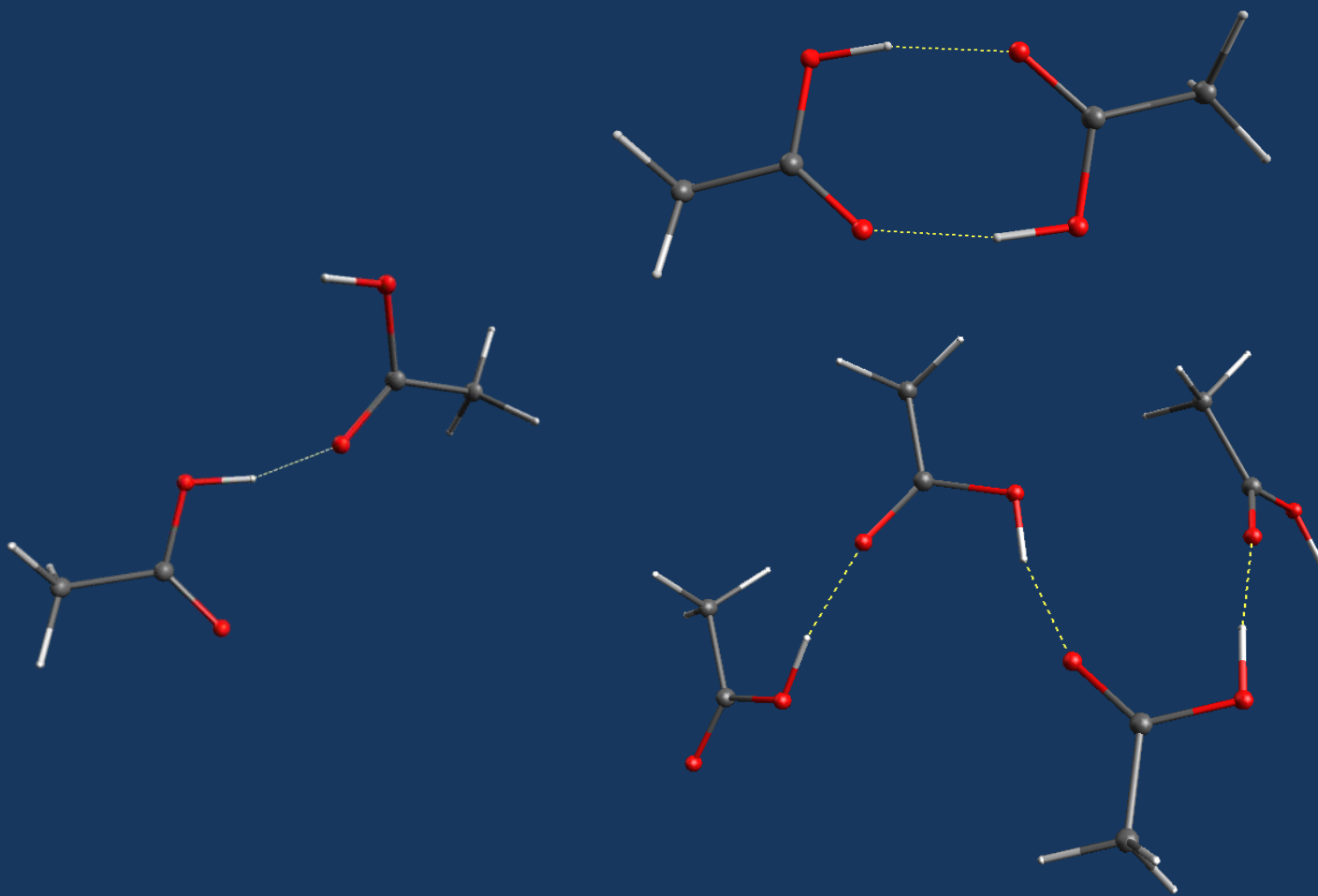# Acetic acid + pyridine?

acid + base

acid-base pair
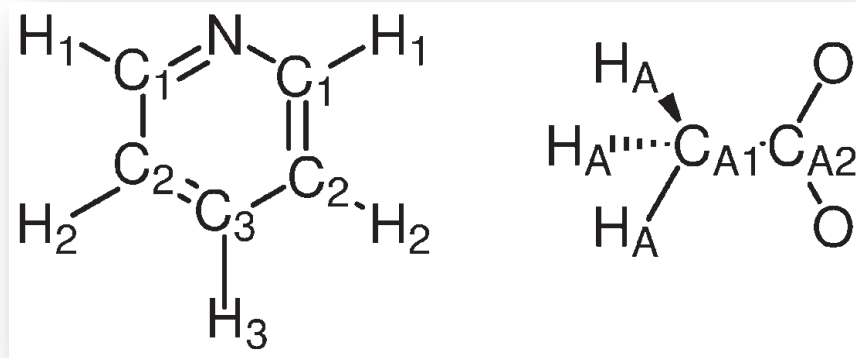
ion pair

discrete ions

NDIS (SANDALS): acetic acid

Approach

- Collect data for **suitable H/D-substituted samples** over a range of χ_{HOAc} compositions
 - pyridine-H/D, acetic acid-H/D, and CD_3-COOH/CH_3-COOD

- Set up **appropriate simulation models**
  - Assume full proton transfer?
  - Assume no proton transfer?
 - Estimate a degree of proton transfer?

- Approach used
  - Constrain only pyridine and acetate fragments
  - Include the acetic acid hydrogen as a non-bonded 'free' proton
  - Hydrogen will locate in EPSR simulation driven by best fit to the data

- EPSR refined with good fit to experimental data sets
  - Self consistent start point for refinements to χ_{HOAc} = 0.00, 0.20, 0.22, 0.50, 0.67, 0.83, 1.00
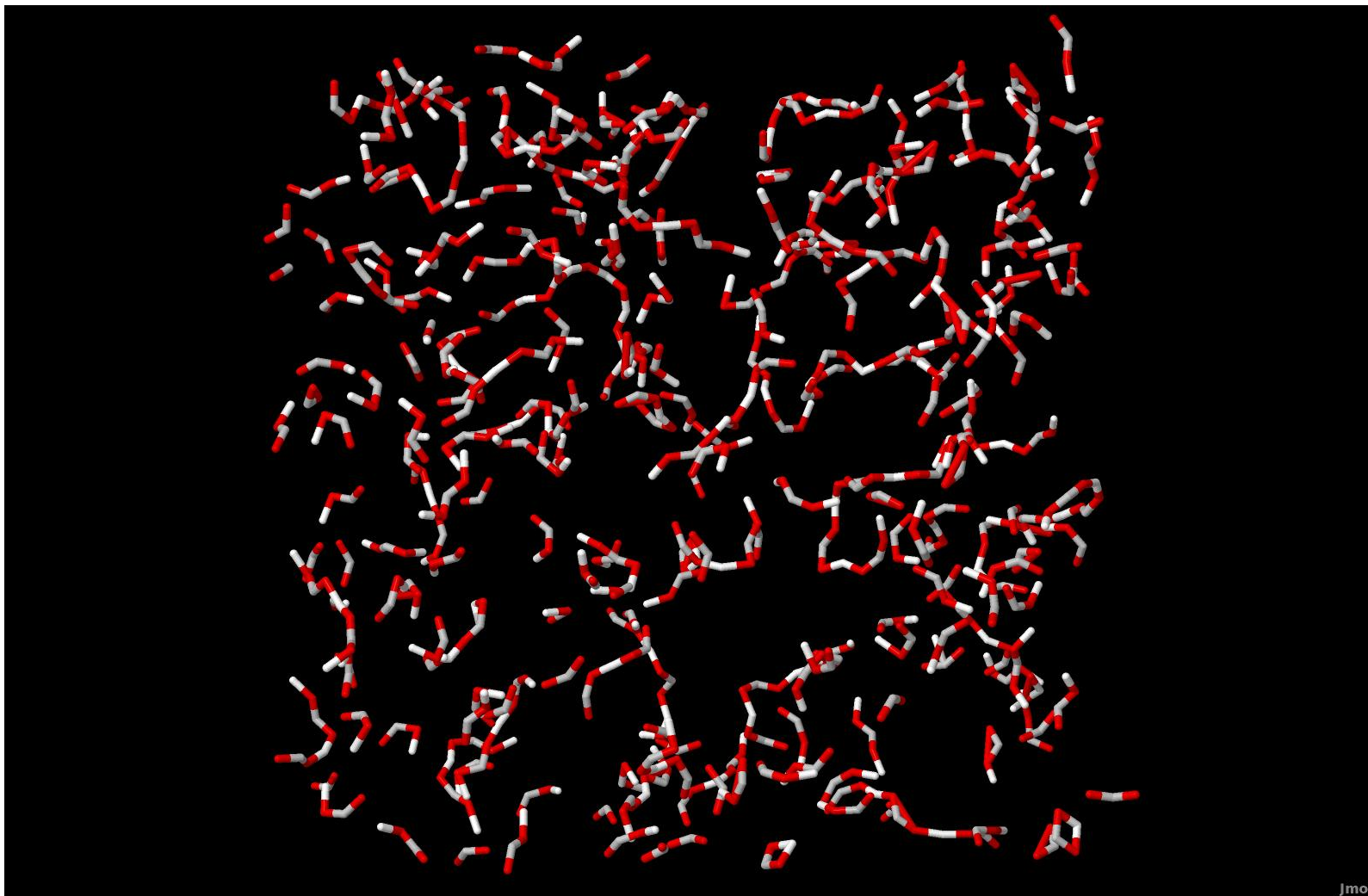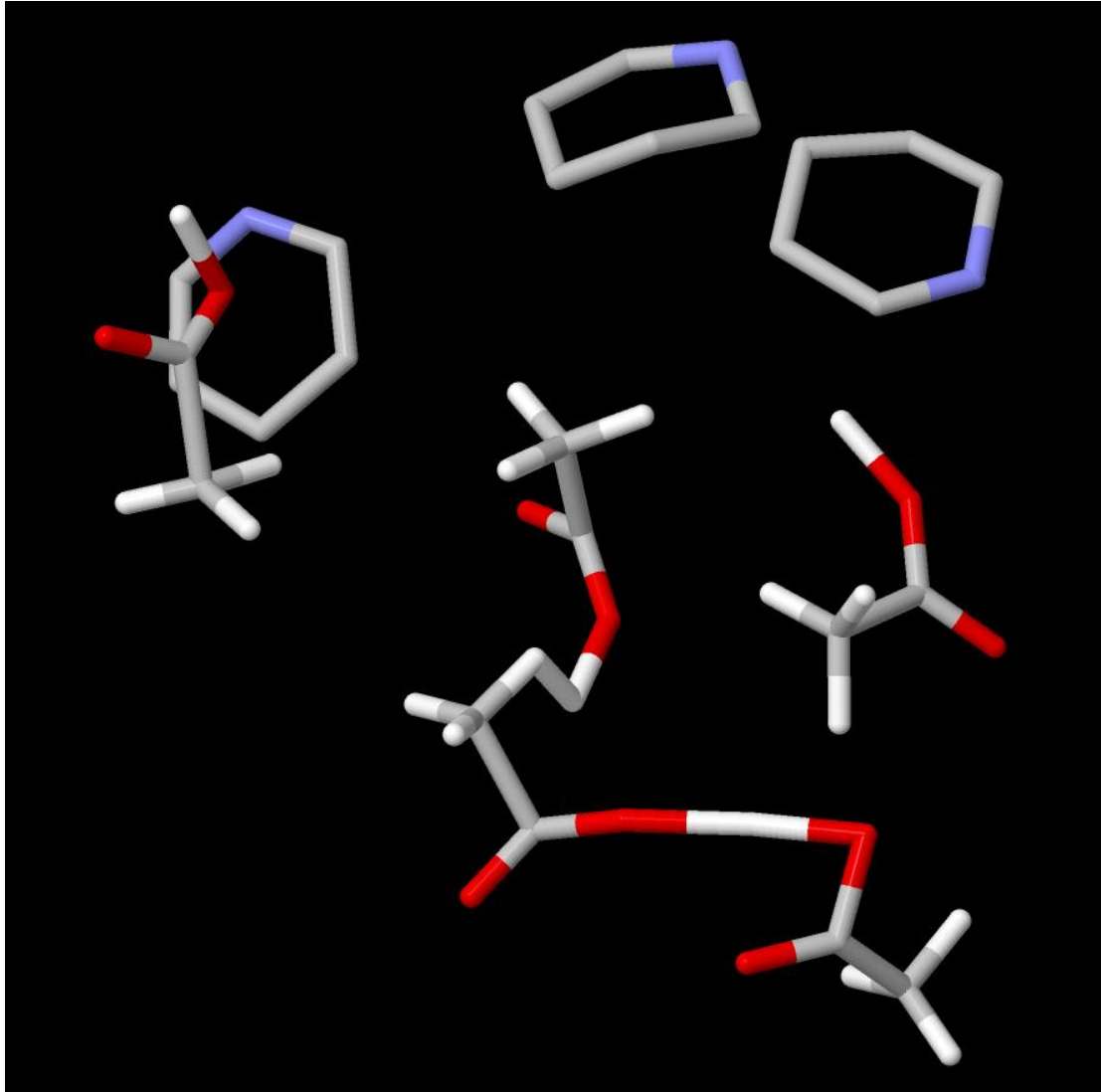
1:1 Pyridine:Acetic Acid
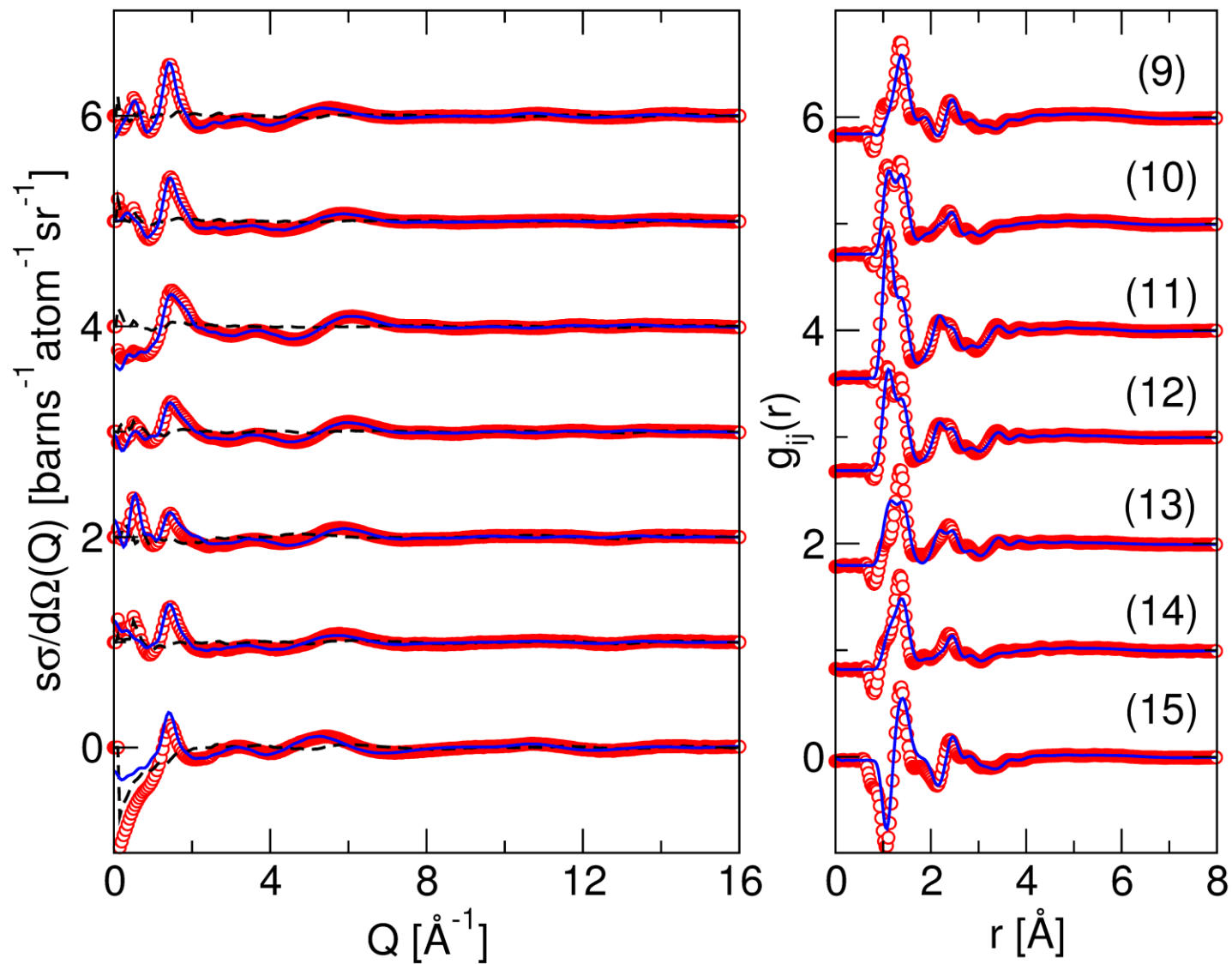
Simulation box for 1:1 acetic acid/pyridine
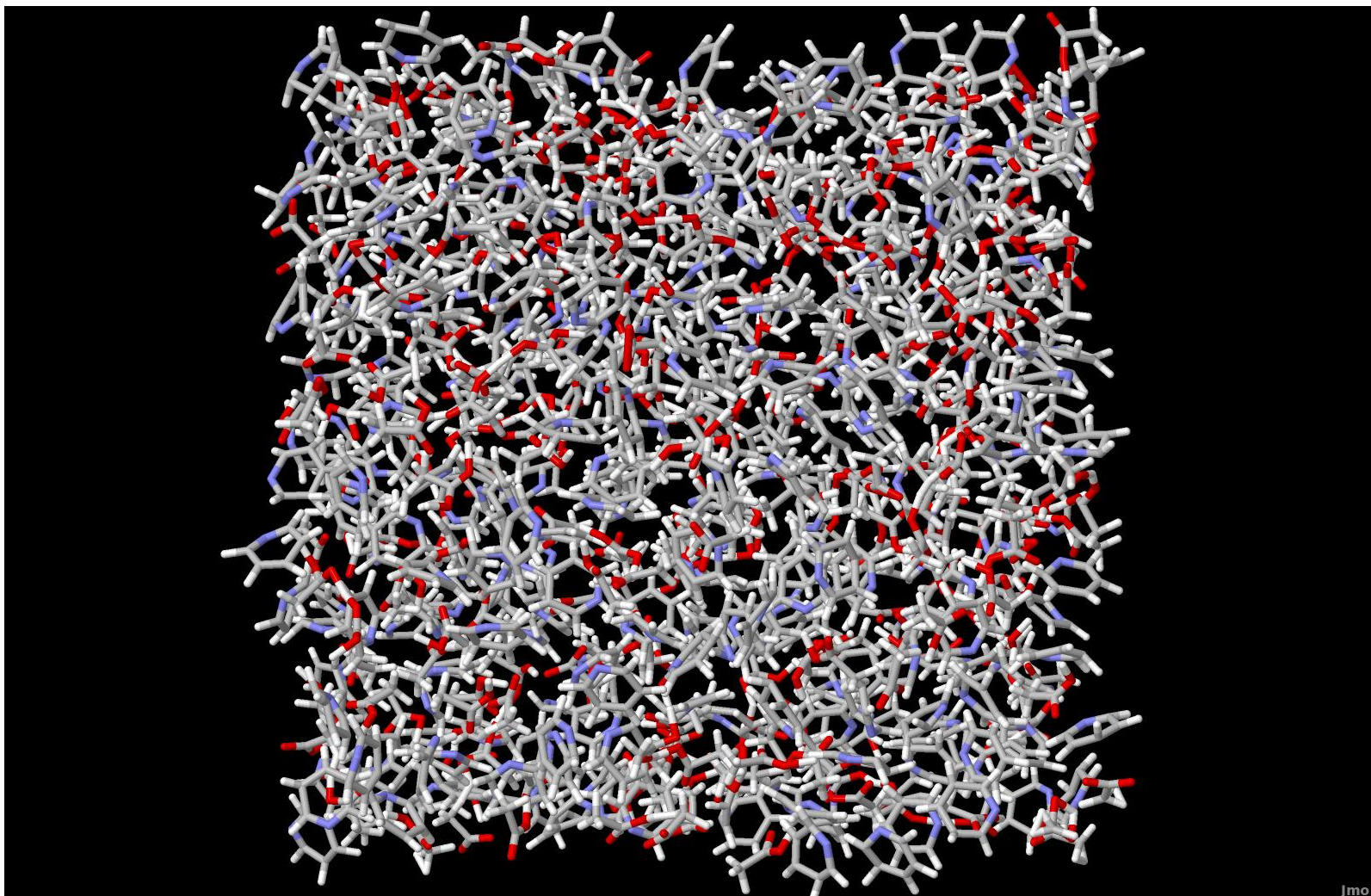
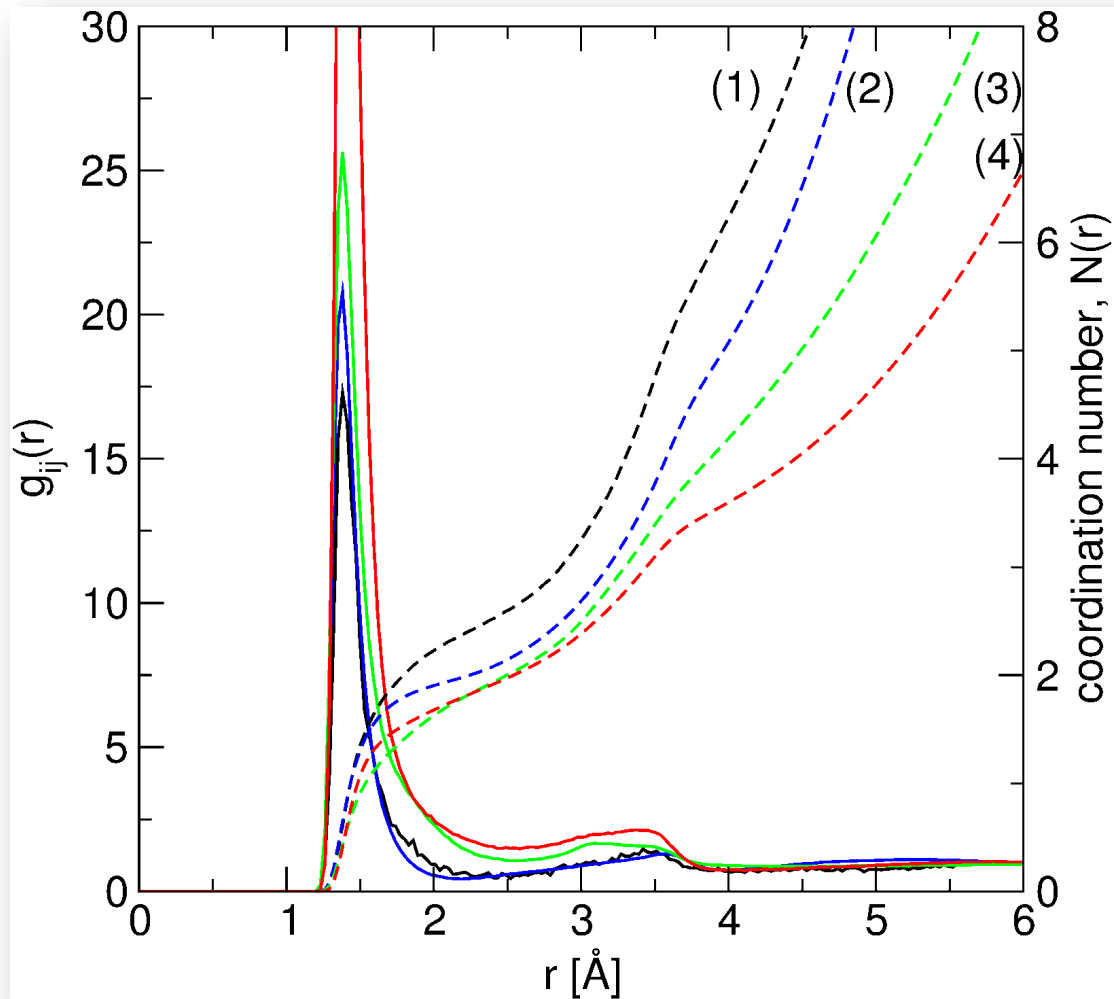# Simulation box for 1:1 acetic acid/pyridine

Zooming in – H-bonded acetic acid chains and discrete pyridine **molecules**

H⋯O(acetate) coordination
(χ = 0.33 − 1.00)
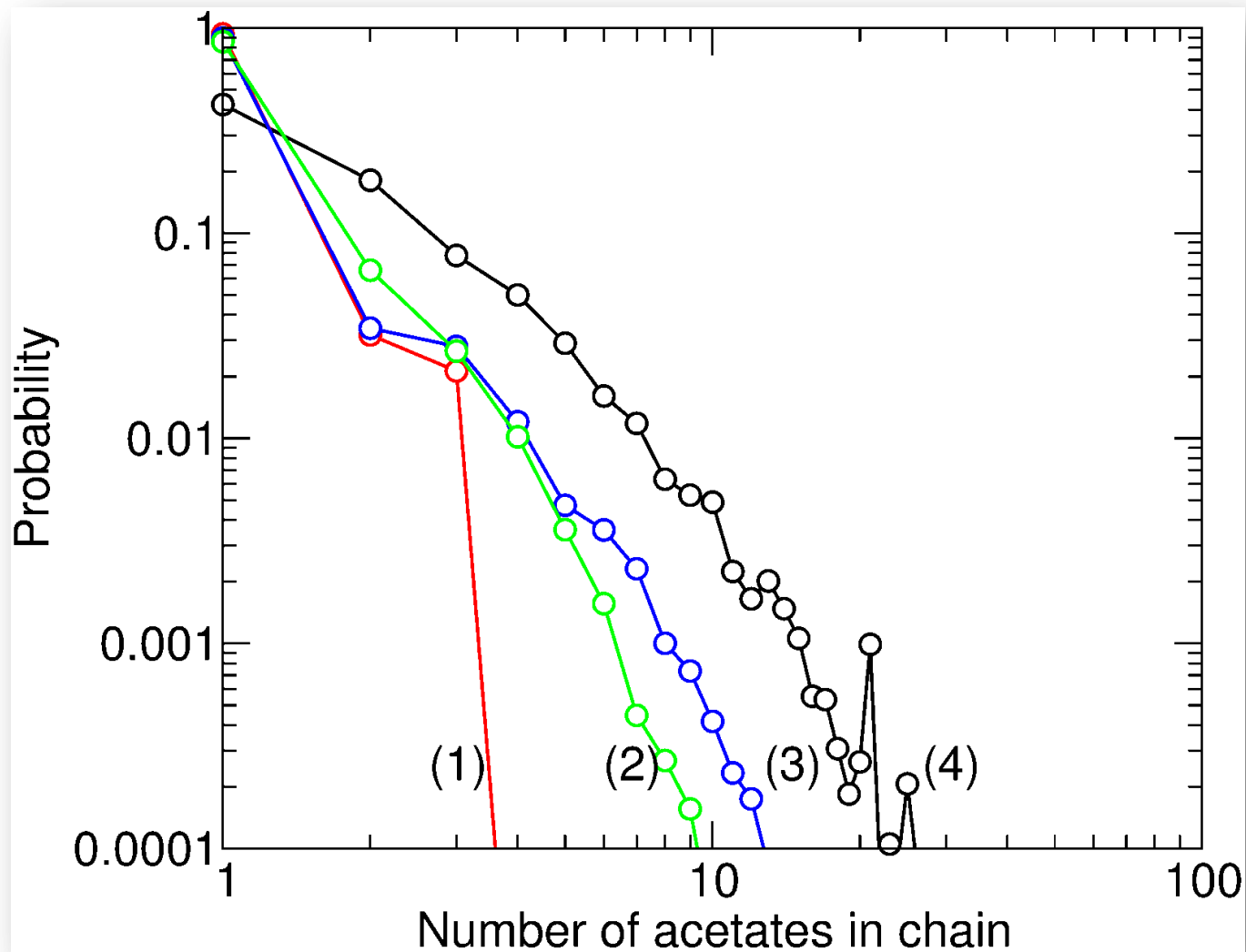
- Site-site data derived from epsr model

- 'free' acid hydrogen is located on the acetate oxygens
  - O-H = 1.4 Å
  - COO⋯H coordination number = 2

- No evidence for protonation of pyridine N
  - N-H coordination number = 0

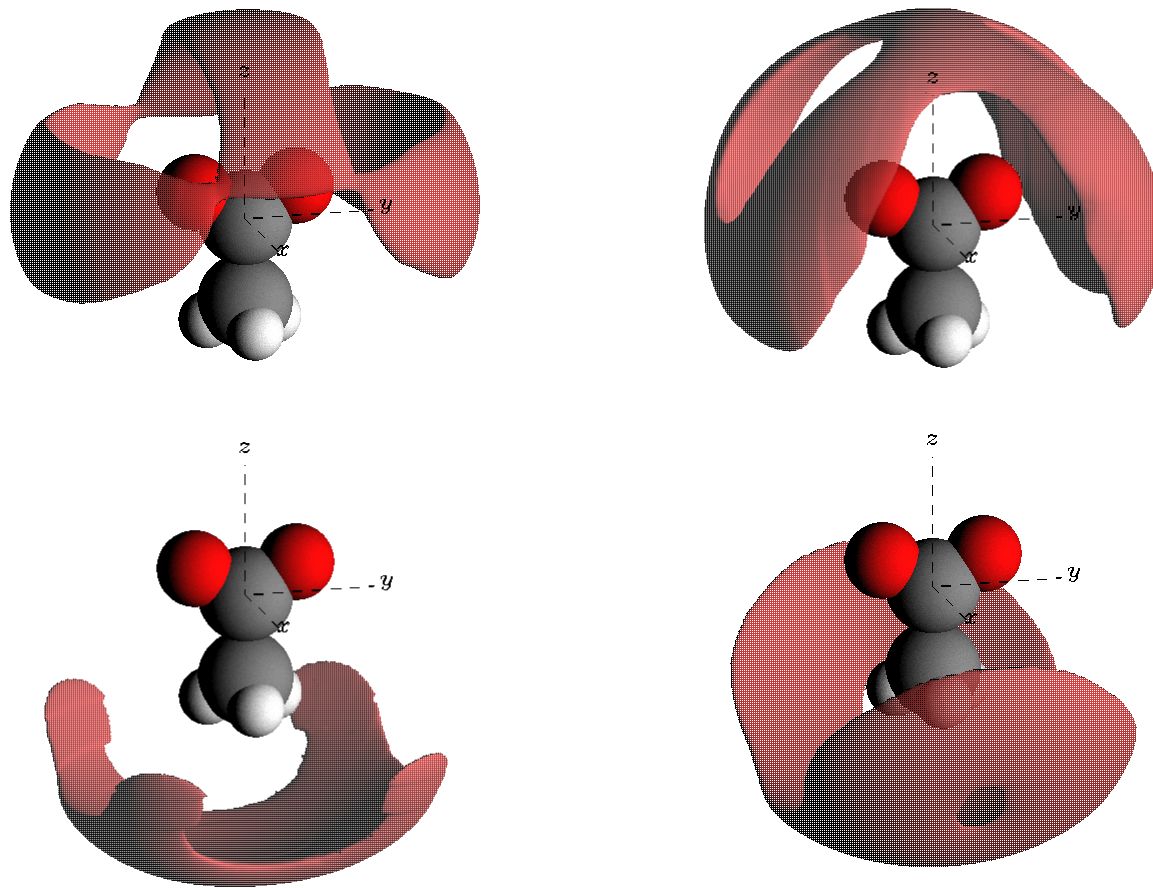# Acetic acid cluster size
(χ_{HOAc} = 0.33-1.00)

Acetic acid-acetic acid SDFs

SDFs (top 25%) of neat acetic acid (χ_{HOAc} = 1.00, left) and 1:1 acetic acid/pyridine (χ_{HOAc} = 0.50, right) between 2-5 (top) and 5-7 Å (bottom)

SDFs around pyridine ($\chi_{HOAc} = 0.50$)
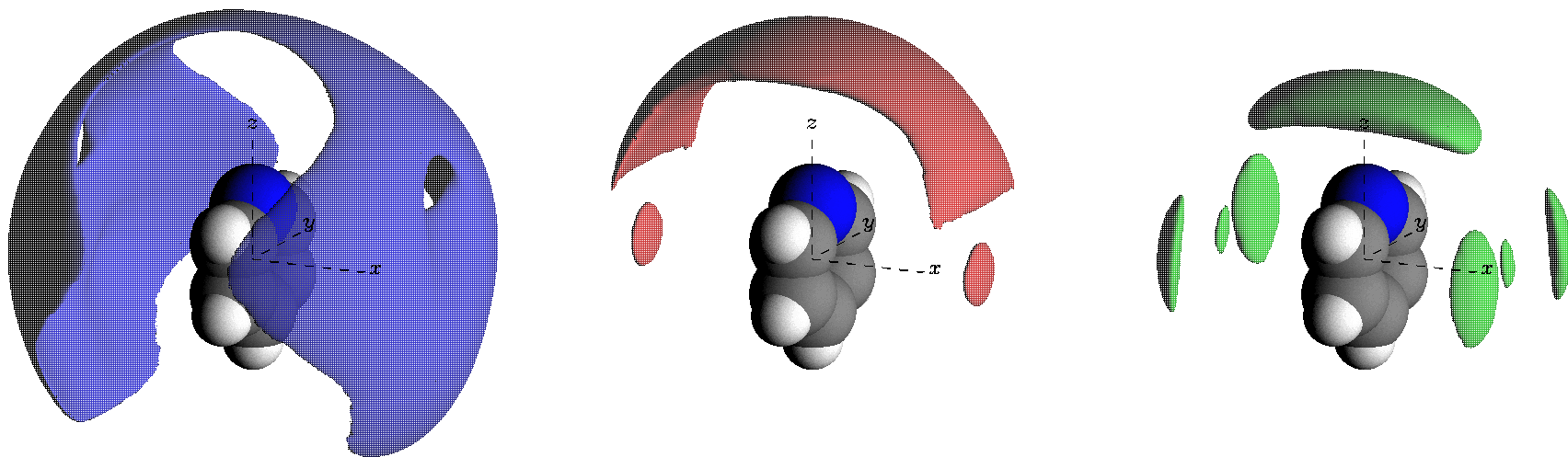
Broad, diffuse correlation of pyridine around pyridine (reduced structure relative to neat pyridine)

Broad acetic acid association with basic N site of pyridine (red), supported by acid proton correlation (green) with N site – was not obvious from site-site rdf map

Pyridine+acetic acid structure studies

- Acetate + pyridine + H^+ model
  - Produced neat acetic acid structure consistent with literature (oligomeric chains of acid)
  - Pyridine + chains of acetic acid in liquid mixtures
  - No evidence for proton transfer to pyridine (pyridinium ion formation)
- Questions
  - Is this method (reducing model to bases and free, mobile protons) transferrable (*i.e.* responsive to experimental data) or is it biased by the reference potential used?
  - What will happen in acid-base mixture with larger ΔpKa?

Summary

- Neutron experiments can effectively probe structure and dynamics of many important systems
  - Experiments can be expensive and challenging
  - Complementary to other methods
  - Especially valuable for 'seeing' hydrogen

- NDIS methods can reveal information about local correlation, structure and solvation environments in disordered materials
  - Data can be obtained through direct methods and difference spectra
  - Molecularly complex systems are 'impossible' to solve explicitly

- Computer simulation (epsr) can generate models and calculate distribution functions not directly accessible from the experiment
  - Some care needed with respect to over interpretation of modelled fits to data, rather than information abstracted directly from PDF

Summary II

- Structure and solvation in ionic liquids can be understood, applying NDIS methods
  - Chemical, energy and environmental applications: Catalysis, separations, CO_2-capture, photovoltaics, electrochemistry, batteries and supercapacitors, drug delivery
  - Examined briefly three ionic liquid systems: [dmim]X, [C_1py][NTf_2]+phenol, and pyridine+acetic acid

- Challenges still with the complexity of the systems under investigation
  - Chemistry (accesses appropiate isotopomers)
  - Systems
  - Analysis (computational expense)