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2054-5

Structure and Dynamics of Hydrogen-Bonded Systems

26 - 27 October 2009

Molecular solvents over heterogeneous surfaces and ionic liquids in the bulk

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Molecular solvents over heterogeneous surfaces and ionic liquids in the bulk

Experimental and theoretical study of hydrogen bonding systems

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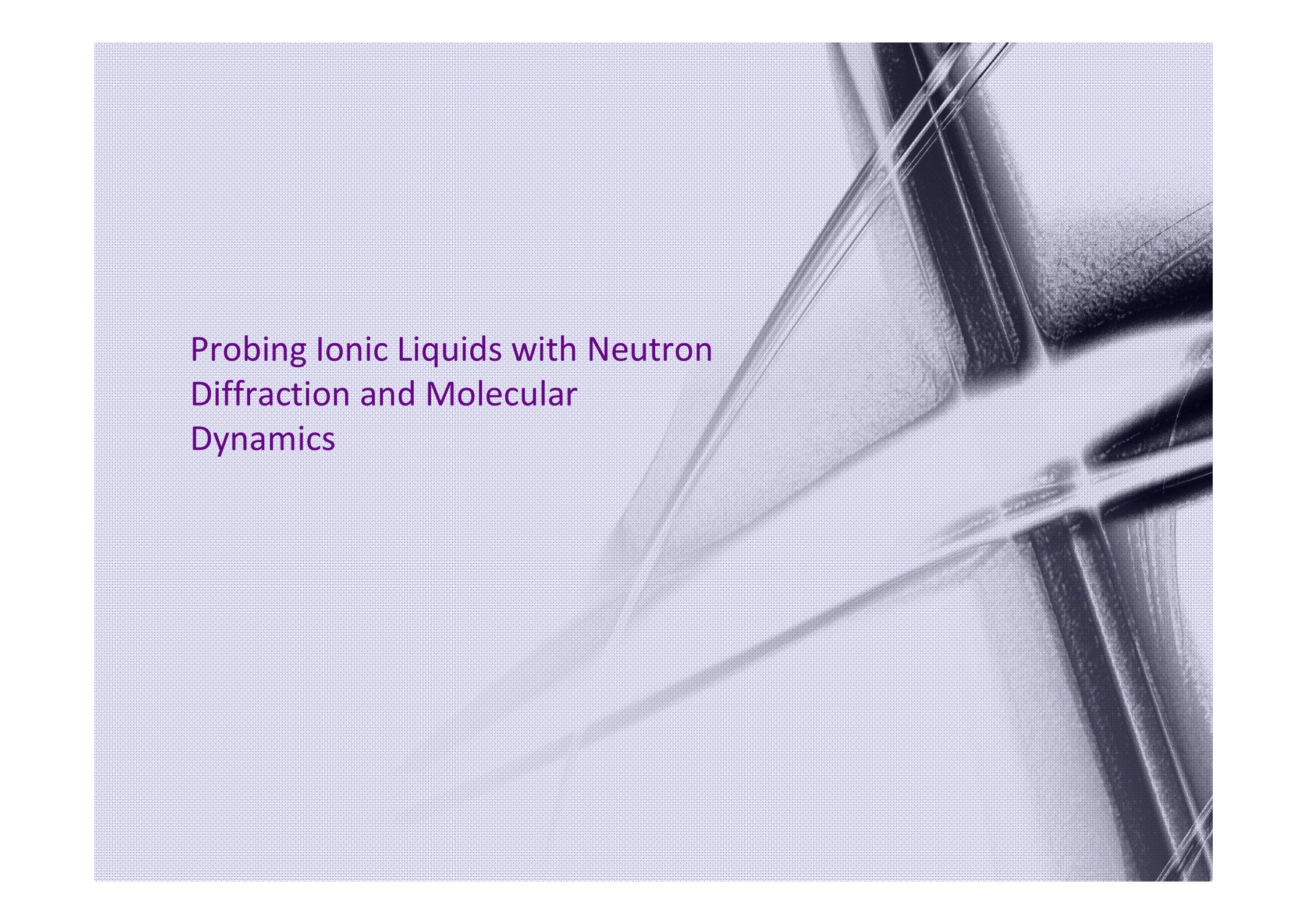
School of Maths and Physics

Queen's University Belfast

Probing Ionic Liquids with Neutron Diffraction and Molecular Dynamics



What is an Ionic Liquid?

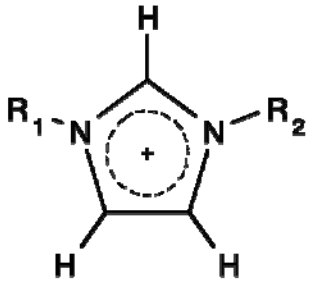
Ionic liquids typically comprise an organic cation and an inorganic anion

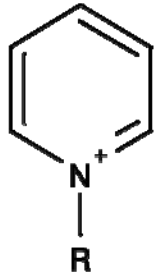
Also known as ‘room temperature molten salts’, but this doesn’t sound as trendy

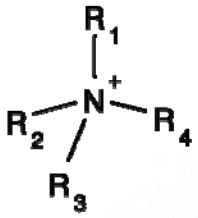
Very different properties from typical molecular solvents

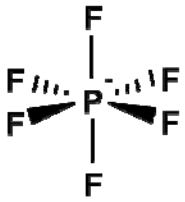
	Molecular Solvent	Ionic Liquid
Viscosity	Low	High
Conductivity	Low	High
Thermal Stability	Low	High
Volatility	High	Low
Flammability	High	Low
Toxicity	Low-High	Low-High?

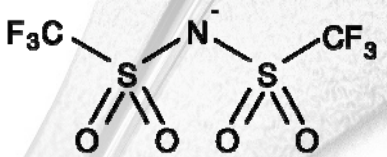
Examples of Ionic Liquids











- Lots of choice
  - Tunability?
- ‘Task-specific’ Ionic Liquids
  - Feasibility?
- Still expensive

Chemically, What Good are Ionic Liquids?

- Excellent reaction media
  - Can simultaneously dissolve both organic and inorganic material, making them useful in organic syntheses involving inorganic catalysts
  - Product extraction can sometimes be problematic

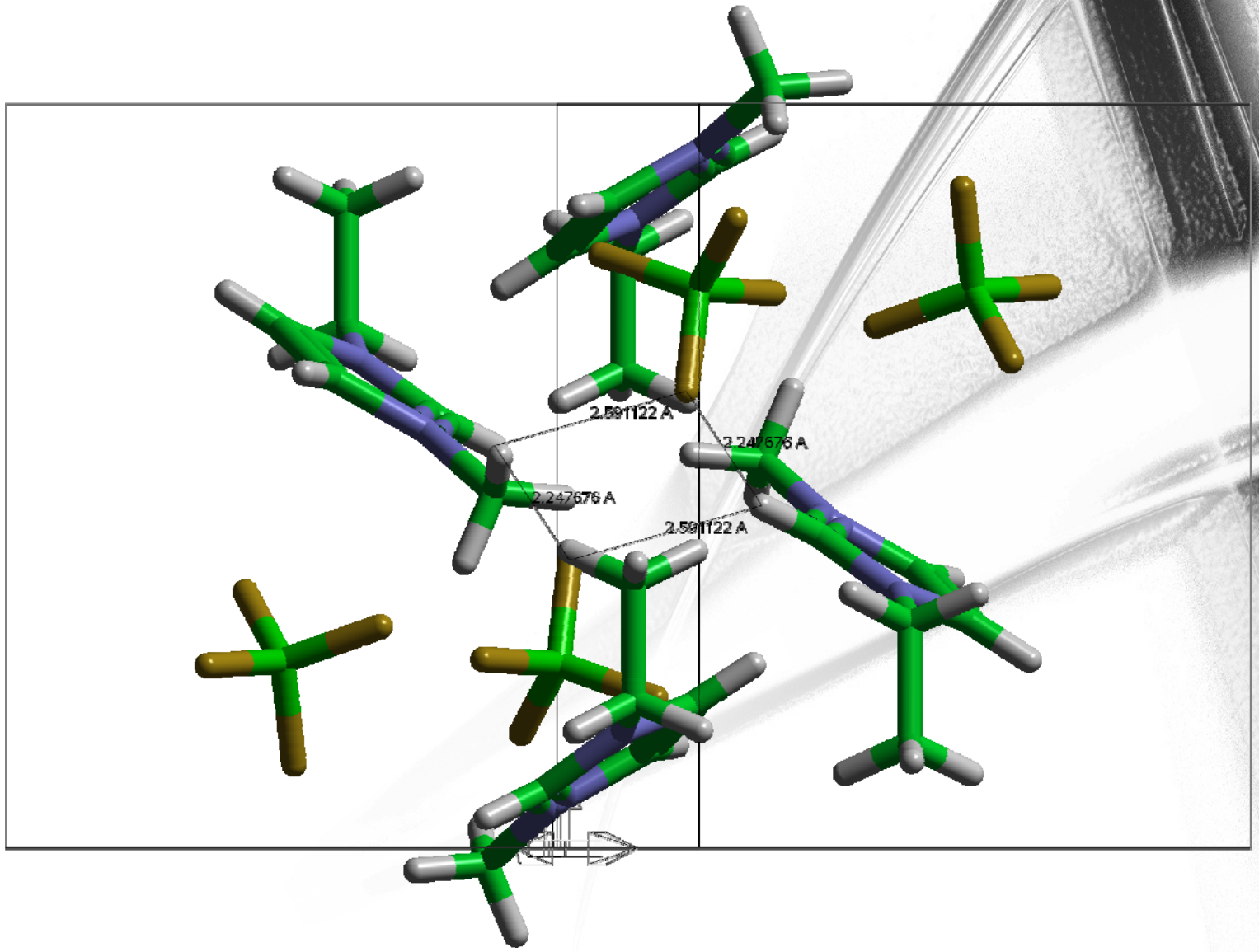
- Gas capture/storage media
  - Potential use as reactive CO_2 capture agents

- Stabilisation / safe storage of materials
  - Moisture-sensitive reagents, e.g. PCl_3 / $POCl_3$
  - Storage of 'nasty' gases such as PH_3, BF_3

- Liquid Pistons
  - H_2 delivery pumps

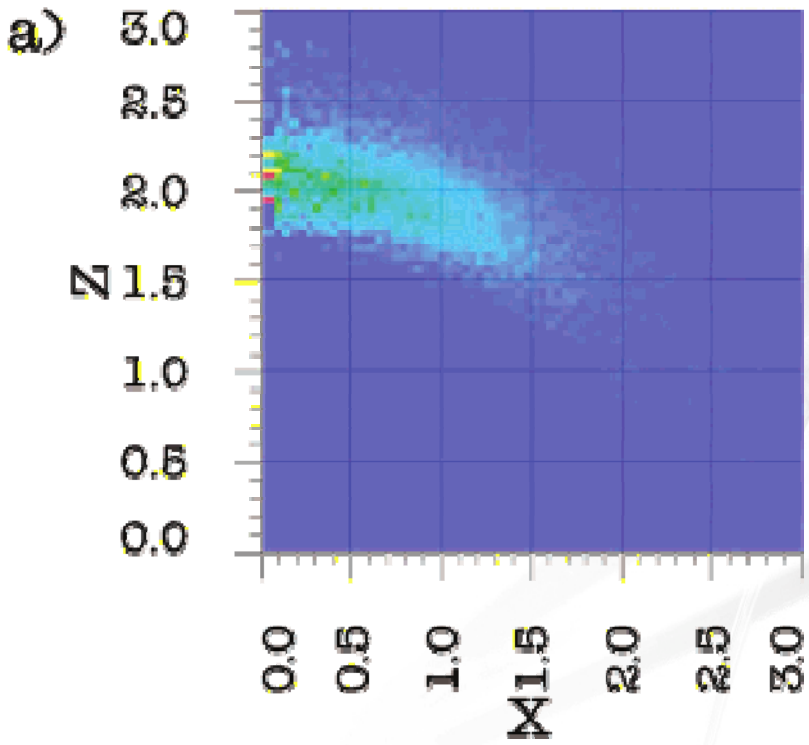
Are they Really Hydrogen Bonding Fluids?

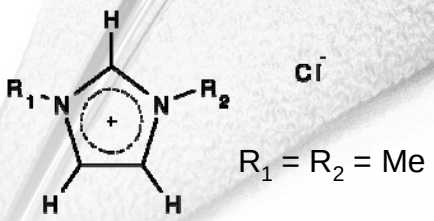
- Certainly hydrogen bonding in solid state



First QM Study of H-Bonding in an Ionic Liquid

- CPMD simulations of 8 (39 ps total) and 24 ion pairs (3.5 ps)
- Geometry of short Cl···H contacts suggests moderately strong H-bonds (2.2 Å, 151° for H2)
- C-H stretching frequency shows red-shift relative to gas-phase ion pair (cooperative effect in the liquid phase)

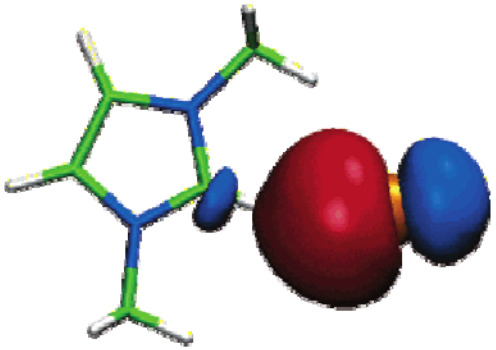




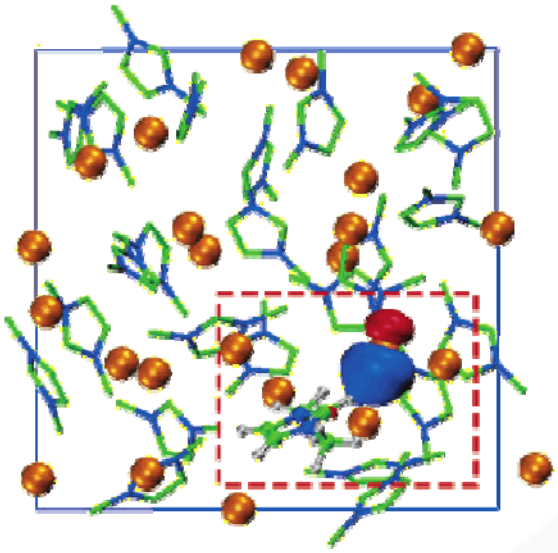
$R_1 = R_2 = Me$

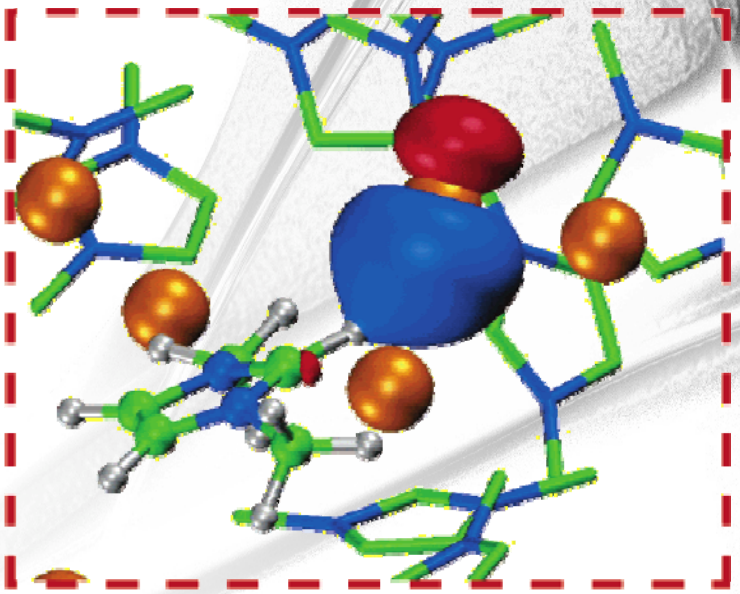
M. G. Del Pópolo, R. M. Lynden-Bell, and J. Kohanoff, *J. Phys. Chem. B*, **2005**, *109*, 5895-5902.

More Ab Initio Studies of H-Bonding



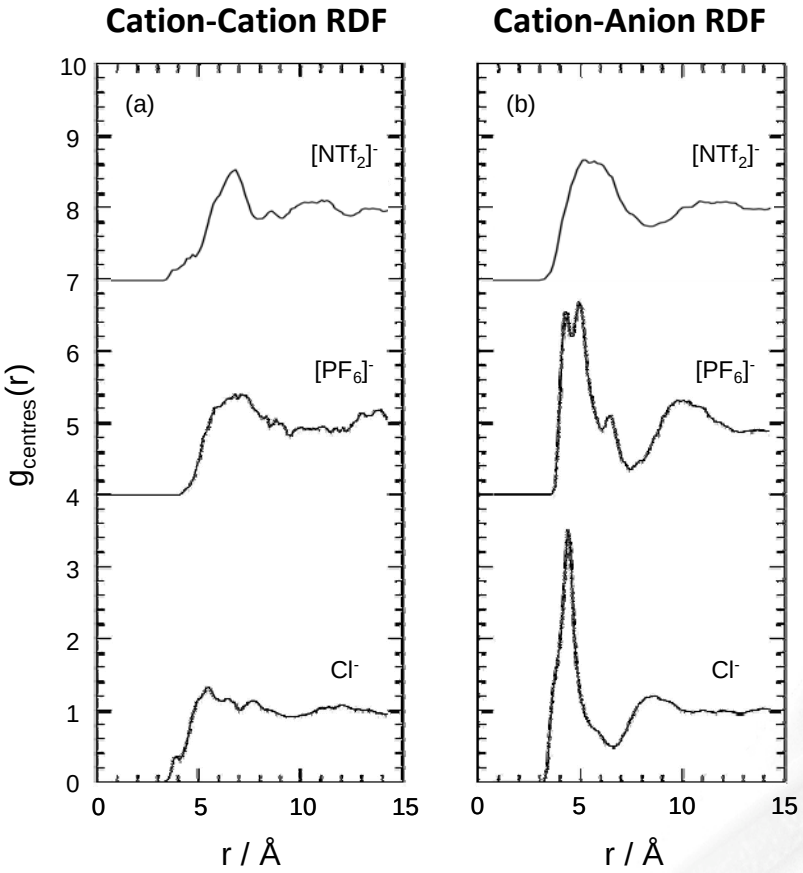
M. Bühl, A. Chaumont, R. Schurhammer, and G. Wipff, *J. Phys. Chem. B*, **2005**, *109*, 18591-18599.

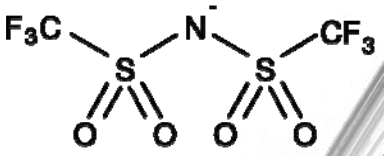




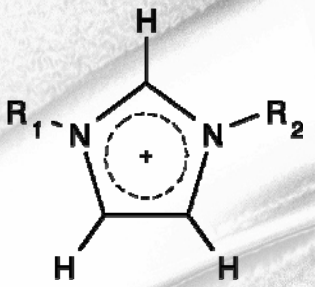
- CPMD simulations of 25 (5.3 ps) and 41 ion pairs (2.3 ps)
- Analysis with MPA, NPA, NBO and localised Wannier functions of Cl^- LPs
  - Find orbitals containing Cl^- LP and σ^*_{CH} MOs

Influence of Anion – The ‘dmim’ Studies





Cl^-



$R_1 = R_2 = Me$

- 1,3-dimethylimidazolium chloride, hexafluorophosphate, and bistrifylamide
- Decreasing ‘interactivity’ of anion, leading to less well-defined ion-ion structure in the liquid (and lower melting points)
- Basic inorganic molten salt ‘onion skin’ structure perturbed by directional interactions – e.g. hydrogen bonding

Mixing Experimental / Theoretical Study

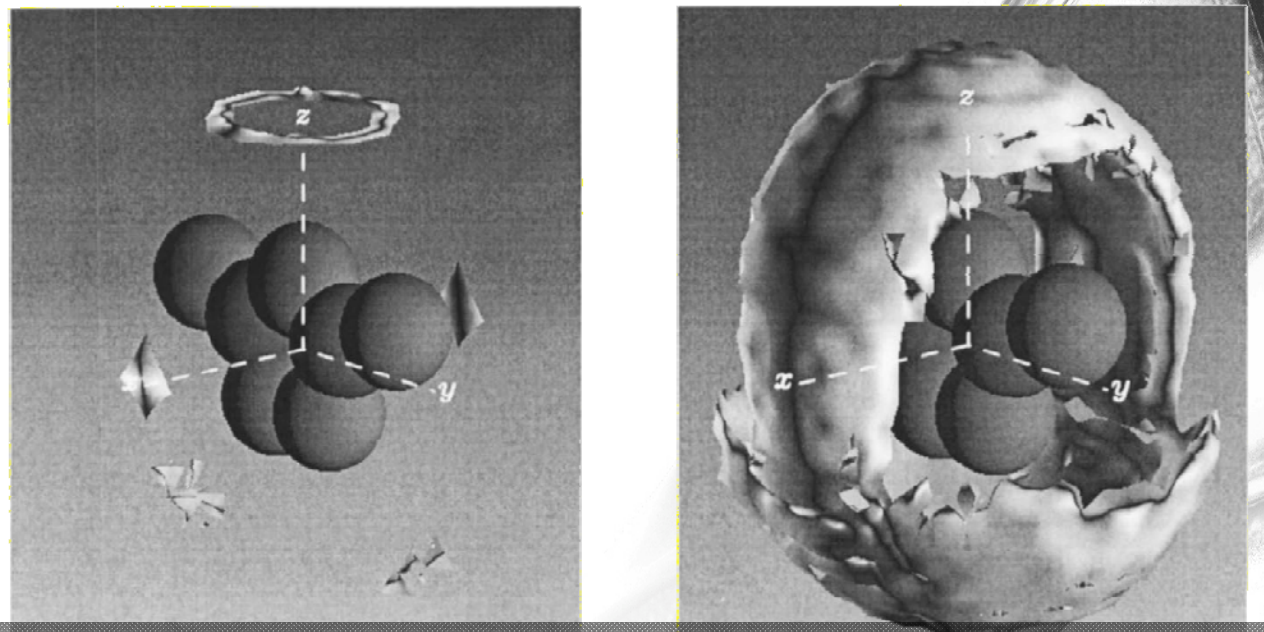
- Neutron Diffraction
  - Potential to give complete set of pair-pair correlation functions
  - Dependent on input set – isotopic substitution
  - Empirical Potential Structure Refinement (EPSR) procedure based on Monte Carlo simulation of target system using molecular mechanics-style forcefield
  - Refinement can be guided by adjustment of intermolecular potentials

- Molecular Dynamics
  - Gives complete set of pair-pair correlation functions regardless of system
  - Flexibility of forcefield choice
  - Results dependent on input forcefield

- Complementary Techniques
  - Best case – both methods agree, credibility of both results enhanced
  - Common case – differing results, clever analysis required
  - Worst case – both give different results; brains, bin or bludgeon?

First Study of the Liquid State

- 1,3-dimethylimidazolium chloride at 423 K using ND
  - C. Hardacre, J. D. Holbrey, S. E. J. McMath, D. T. Bowron, and A. K. Soper, *J. Phys. Chem. B*, **2003**, 118, 273-278.



Probability distributions of chloride anions around central cation at 8 (left) and 3.5 p (right) within 9.0 Å

- Many similarities with crystal structure, e.g. C-H···Cl hydrogen bonds
- Simulations at the time did not show Cl^- above/below imidazolium ring
  - C. G. Hanke, S. L. Price, and R. M. Lynden-Bell, *Mol. Phys.*, **2001**, 99, 801-809

Cacophony of Neutron Studies

- Pure Liquids
  - [dmim][PF_6]
  - [dmim][NTf_2]
  - [bmim][PF_6], [hmim][PF_6], [omim][PF_6]
  - [CNPy][NTf_2]
  - [emim][OAc]

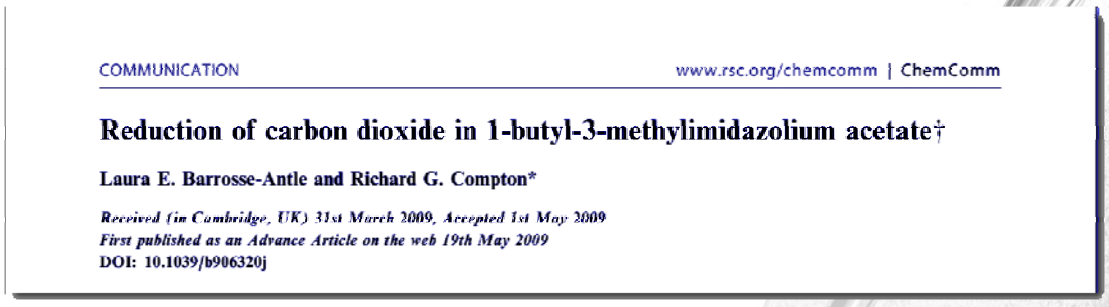
- Mixtures
  - [dmim][PF_6] / benzene
  - [dmim][NTf_2] / moisture-sensitive reagents
  - [dmim]Cl / glucose
  - [CNPy][NTf_2] / aromatics
  - [emim][OAc] / glucose

- Some successful, some not so successful
  - Decomposition, tendency of things not to dissolve when they should, amazing bad fortune etc.

A Good Example - Acetate-based Ionic Liquids

CO_2 Capture

- [BMIM][OAc] shown to have excellent CO_2 solubilising properties



COMMUNICATION www.rsc.org/chemcomm | ChemComm

Reduction of carbon dioxide in 1-butyl-3-methylimidazolium acetate†

Laura E. Barrosse-Antle and Richard G. Compton*

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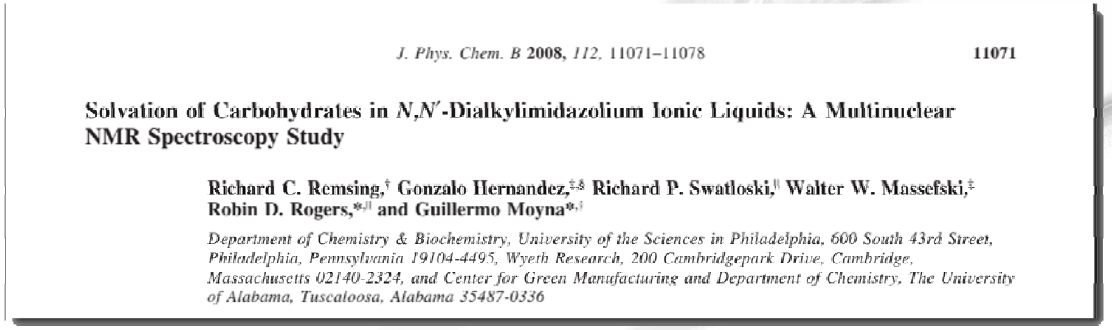
First published as an Advance Article on the web 19th May 2009
DOI: 10.1039/b906320j

Biomass

- Cellulose dissolution



J. Phys. Chem. B **2008**, *112*, 11071–11078 **11071**

Solvation of Carbohydrates in *N,N′*-Dialkylimidazolium Ionic Liquids: A Multinuclear NMR Spectroscopy Study

Richard C. Remsing,† Gonzalo Hernandez,‡,§ Richard P. Swatloski,|| Walter W. Massefski,‡ Robin D. Rogers,*,|| and Guillermo Moyna*,†

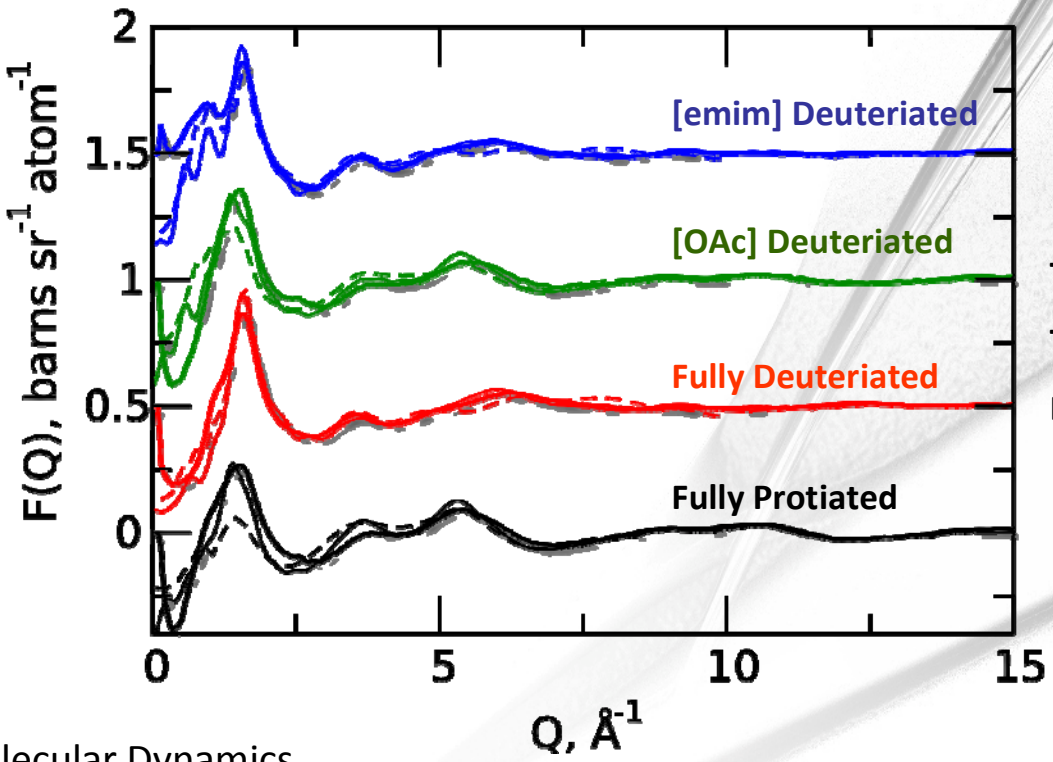
Department of Chemistry & Biochemistry, University of the Sciences in Philadelphia, 600 South 43rd Street, Philadelphia, Pennsylvania 19104-4495, Wyeth Research, 200 Cambridgepark Drive, Cambridge, Massachusetts 02140-2324, and Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336

Purely Scientific Reasons

- Structural implications for the liquid
- Where and how do the anions interact with the cations?

Total Scattering Functions

- Neutron Diffraction
  - Pure liquid measured at RAL on SANDALS 323 K
  - Isotopic substitution performed on cation and anion hydrogens



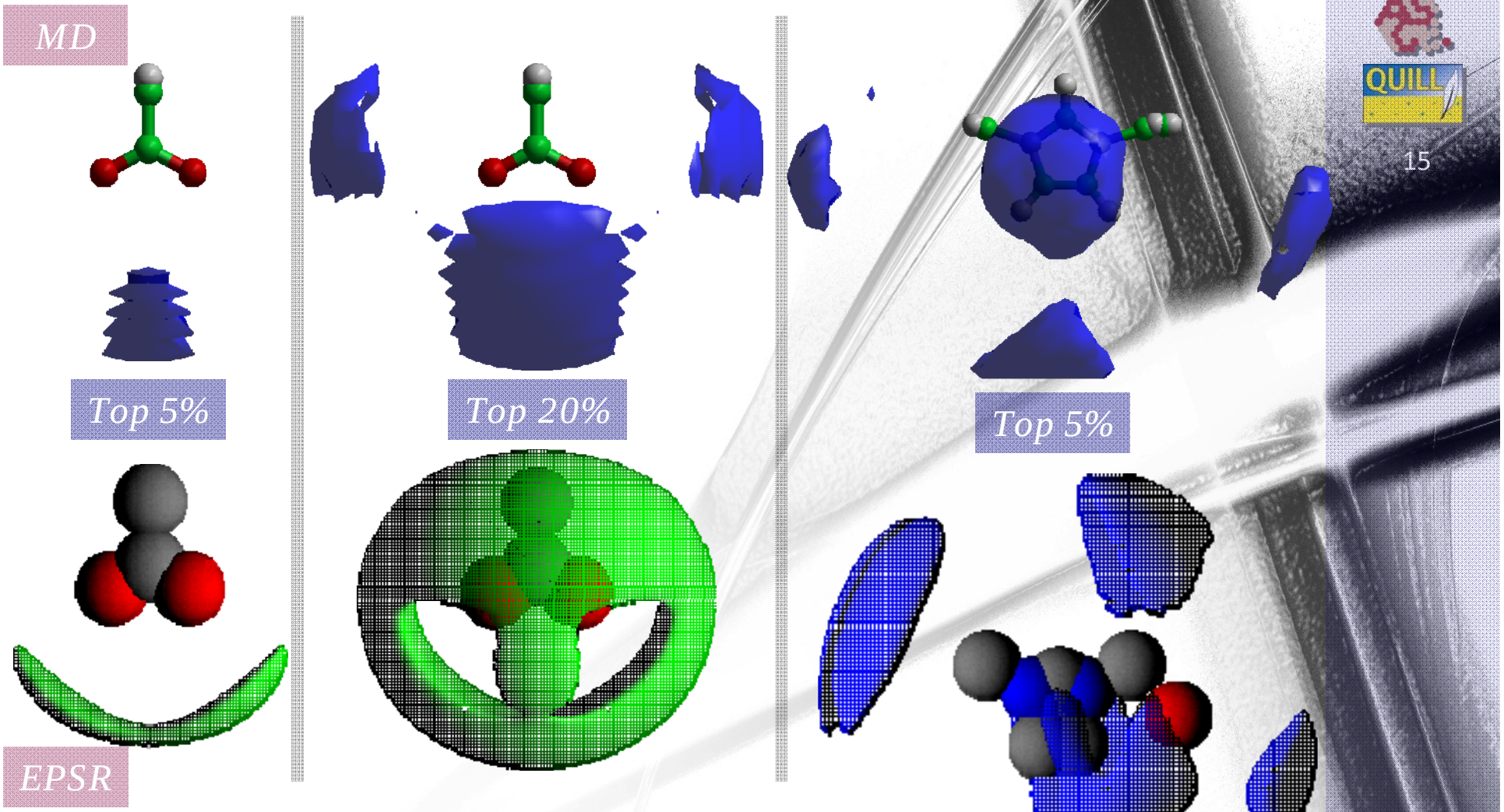
Thick solid lines : Exp

Thin solid lines : EPSR

Dashed lines : MD

- Molecular Dynamics
  - Simulations of the liquid state under the same conditions and at experimental density (1.086 g cm^{-3})
  - Common forcefield parameters used for [emim]$^{+}$ and OPLS-AA for [OAc]$^{-}$ and used without modification in the first instance

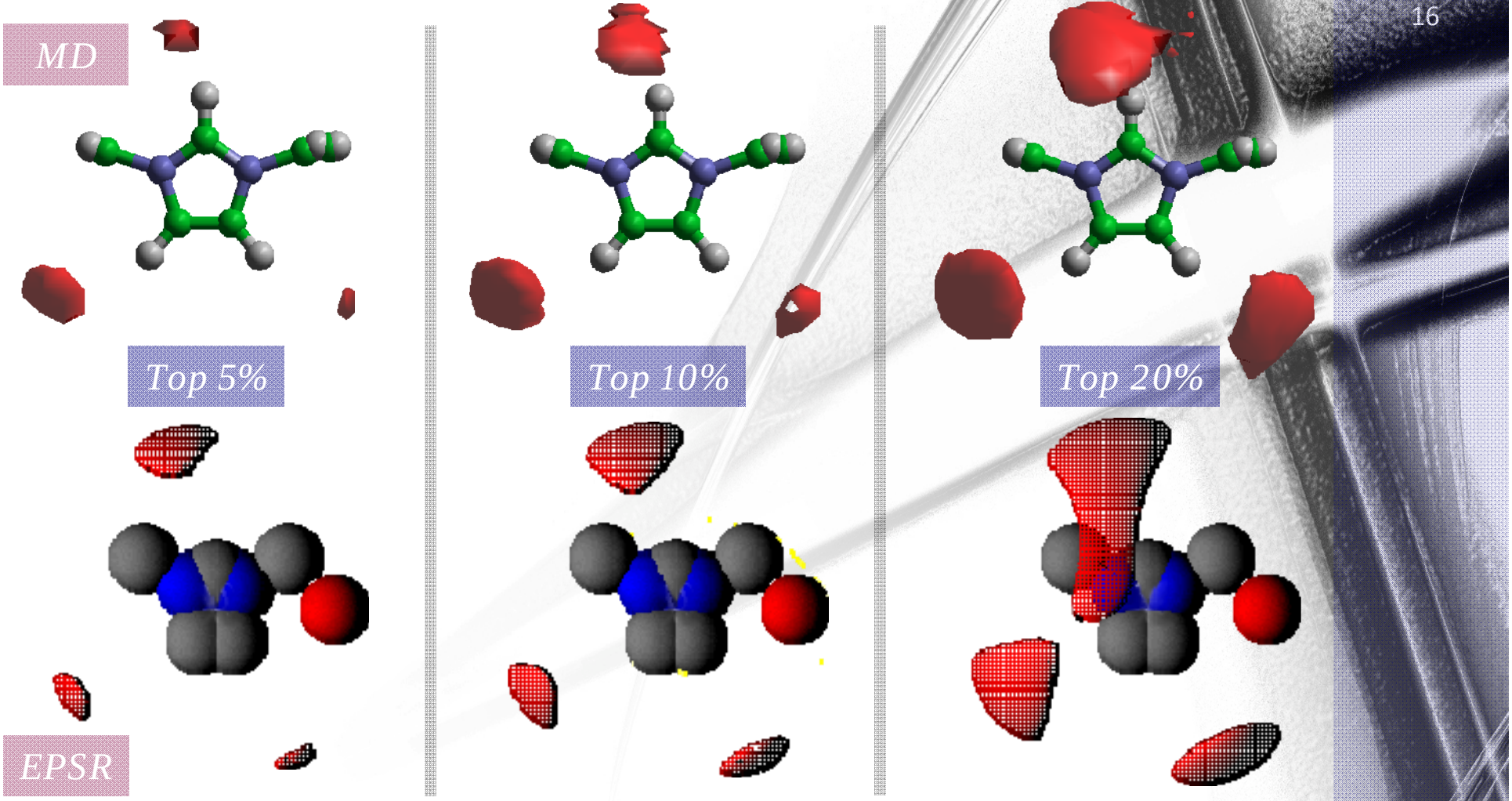
Localisation of Cations (within 10 Å)



- Cations localised around acetate O
- ‘Common’ distribution around imidazolium cation

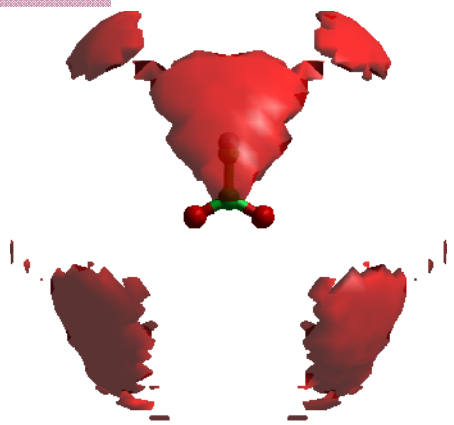
Localisation of Anions (within 7.2 Å)

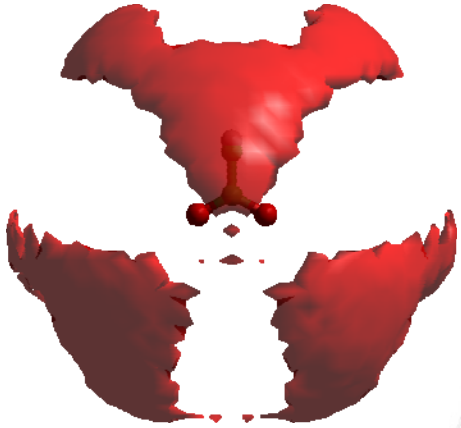
- ‘Traditional’ placement of anions – lobes associated to ring hydrogens, with H4 perturbed slightly by ethyl side chain
- Good correlation with EPSR-derived distributions



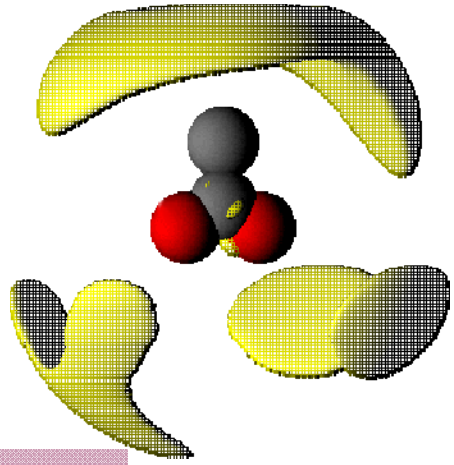
Anion-Anion Contacts?

MD

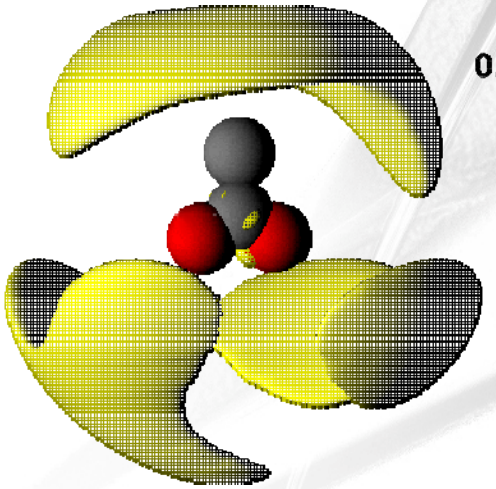




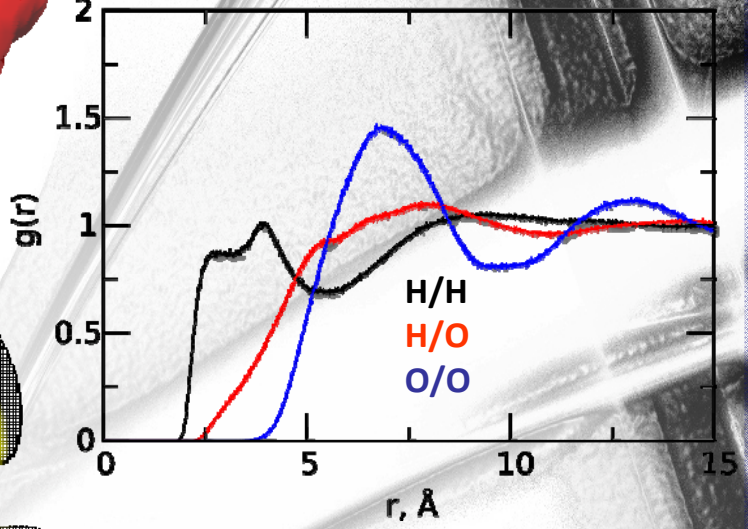
Top 5%



Top 10%

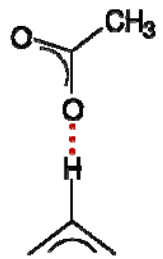
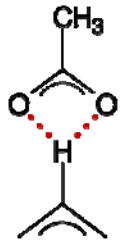
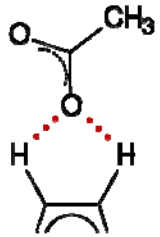
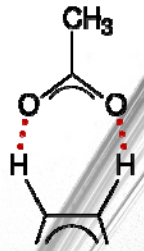


EPSR



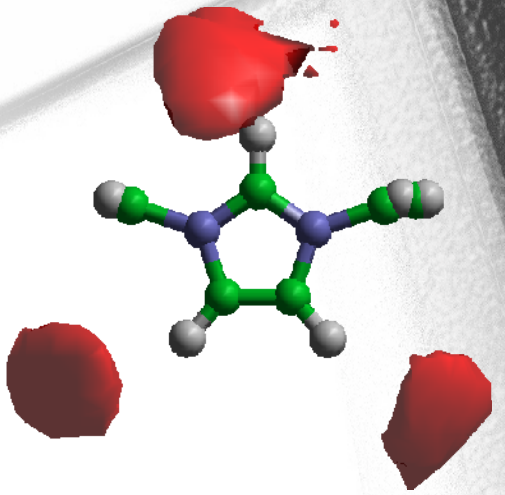
- Calculated within 10.4 Å.
- H-H contacts predominate at short distances
- Little evidence of ‘obvious’ O-H interactions

Acetate / Ring-H Interaction

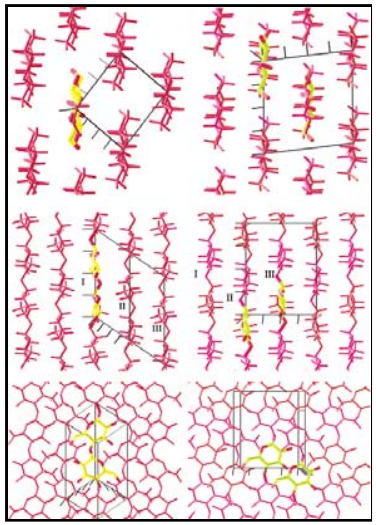





	$\%_{Single}$	$\%_{Bidentate}$	$\%_{Bifurcated}$	$\%_{Bridging}$	$\%_{Other}$
H2	47.1	51.8	0.1	0.2	0.8
H4	38.1	45.0	7.6	0.3	9.0
H5 (Et)	40.1	40.6	8.0	0.3	11.0

- All O···H contacts within 3.7 Å for a single cation
- Roughly equal proportion of single to bidentate interactions
- Bridging interaction over H4/H5 hydrogen is very uncommon



Another Example – [emim][OAc] / Glucose

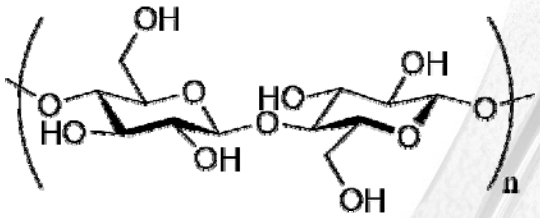


Langan *et al.*, *J. Am. Chem. Soc.*, **2003**, 125, 14300-14306.

Biomass (Re)processing - Cellulose

"With 700 billion tons in existence, and 40 billion more grown each year, cellulose is the planet's most abundant bio-renewable organic chemical…"

C. Böhme, BASF news release, 2006



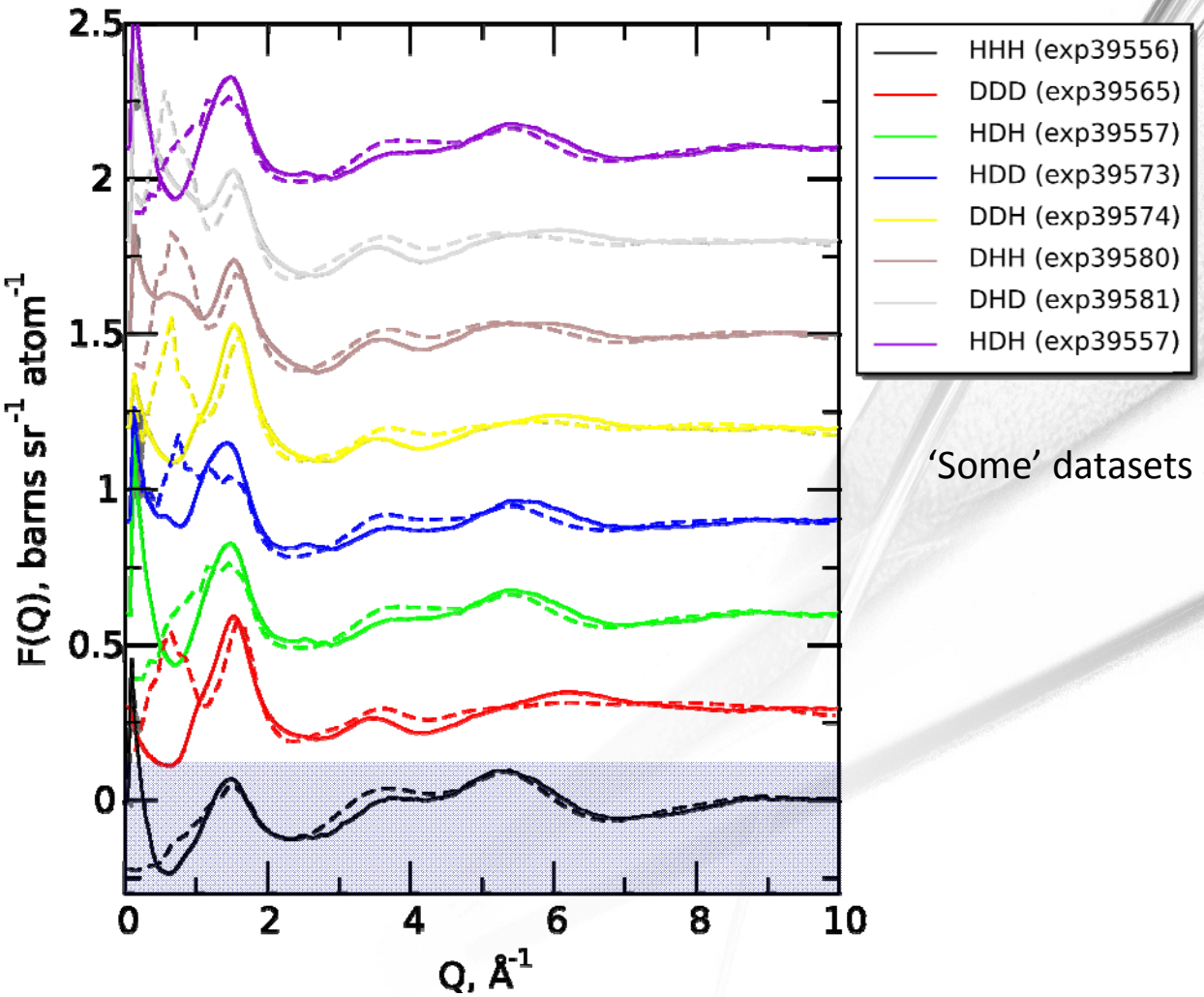
- Strong hydrogen bonding between polymer chains
- Insoluble in water and common organic solvents

Avtex Fibres

- Former rayon manufacturing plant in Front Royal, Virginia
- Closed in 1989
- 440 acre site contaminated with carbon disulfides, phenols, arsenic, cadmium, lead, sulfides, and PCBs
- $65m cleanup ongoing (projected total cost for cleanup, deconstruction, and redevelopment is $150m)

ND/MD Studies of 6:1 IL:Glucose Mixture

- Isotopic substitution on cation (alkyl-d8), anion (d3), and glucose (d12)
- MD simulations to match…



'Some' datasets agree…

ND/MD Studies of 6:1 IL:Glucose Mixture

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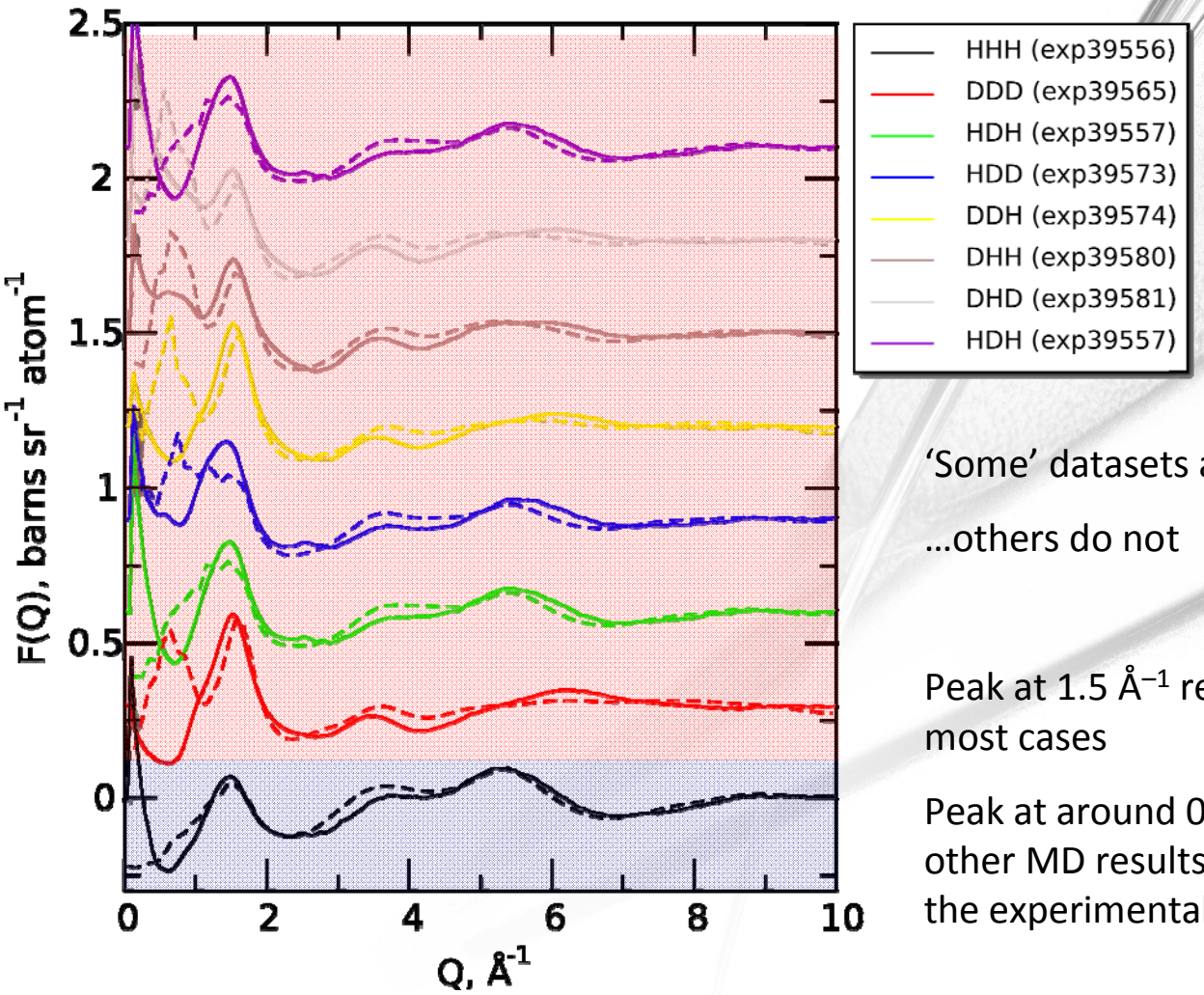


'Some' datasets agree…

…others do not

Peak at 1.5 Å^{-1} reproduced well in most cases

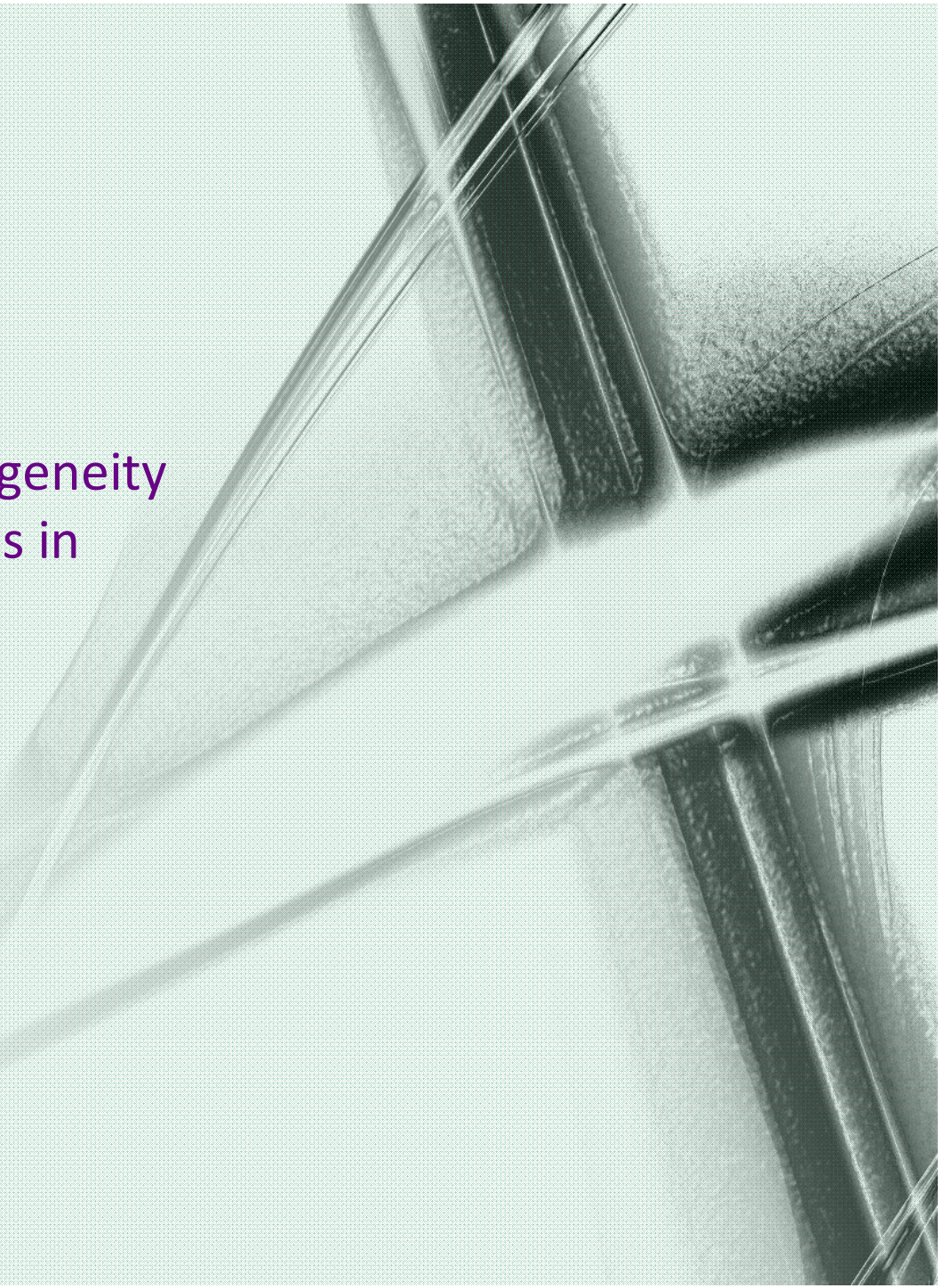
Peak at around 0.6 Å^{-1} seen for most other MD results, and which isn't in the experimental F(Q)

Summary

- Validation of one method by the other
  - For [dmim][Cl] differences are found between ND/EPSR and MD
    - Suggestions for forcefield improvements?
    - Validation of new models can be performed against ND data
  - For pure [emim][OAc] both methods give comparable results
  - Useful info on liquid structure from both experiment and theory

- Why the disagreement in the case of [emim][OAc]:glucose?
  1. Experiments are mostly rubbish?
  2. Simulations are mostly rubbish, and show something else?
     - Peak in simulated F(Q) corresponds to real length of around 10 Å
     - Clustering of glucose molecules?
     - Forcefield used in simulation to blame?

Effect of Nanoscale Heterogeneity on Hydrogen Bonding Fluids in Model Systems



Importance of Nanoscale Heterogeneity

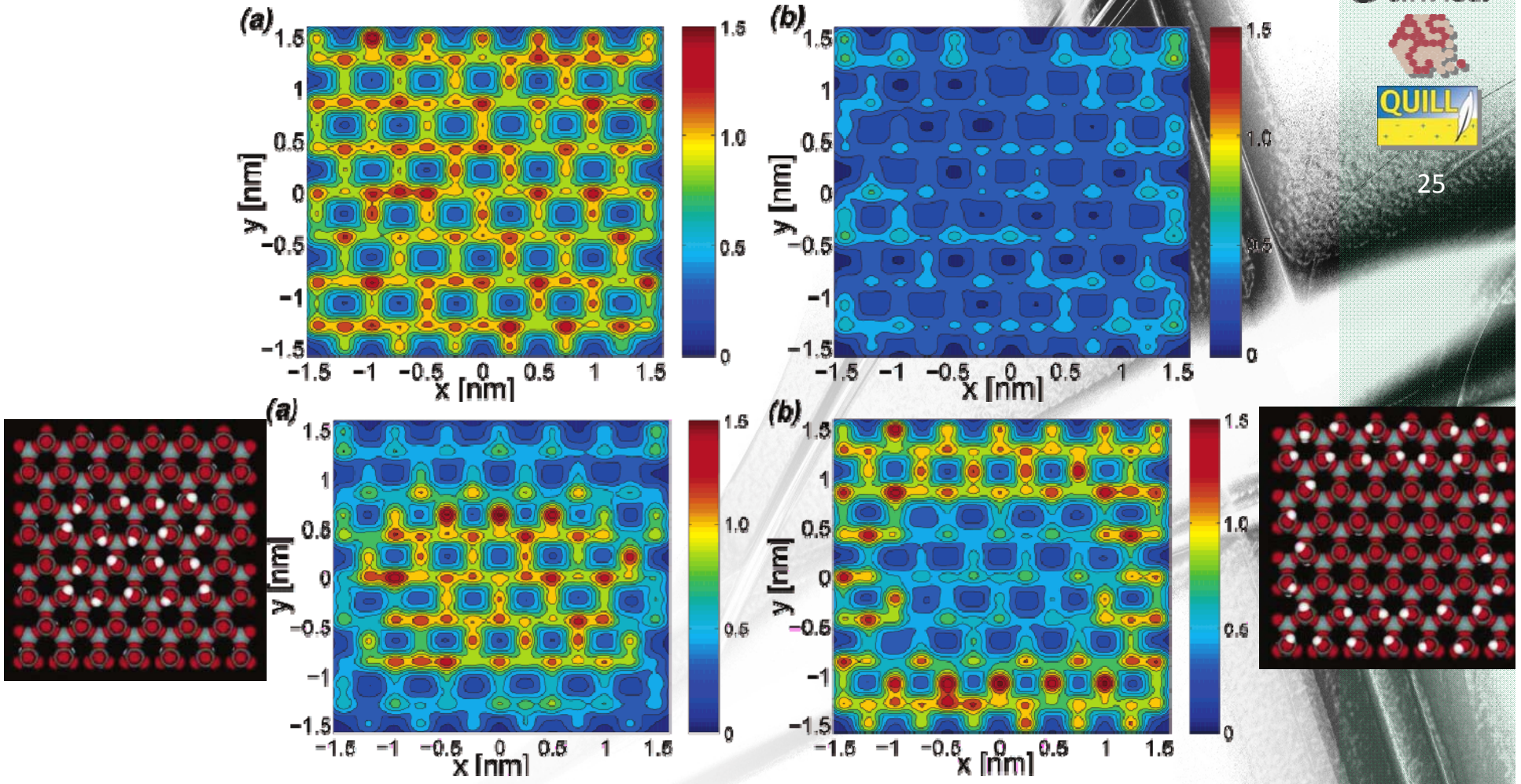
- Heterogeneous Catalysis
  - Small metal catalyst particles embedded on an oxide support
  - Diffusion of reactants to active site through liquid medium
  - Transport of products away from active site
  - Controlled by many factors, one of which is the liquid structure

- Superhydrophobic Materials
  - Nanostructure of surface (e.g. nanopillars) determines wetting

- Nanoscale Devices
  - Beyond microfluidics, and into the nanoscopic regime
  - At confinements in device channels approaching the sub-100nm scale, liquid behaviour can be completely different to that on the microscale
  - Surface structure can be used to promote flow, mixing etc.

- Crystal Growth
  - Initial seeding from suitable surface sites

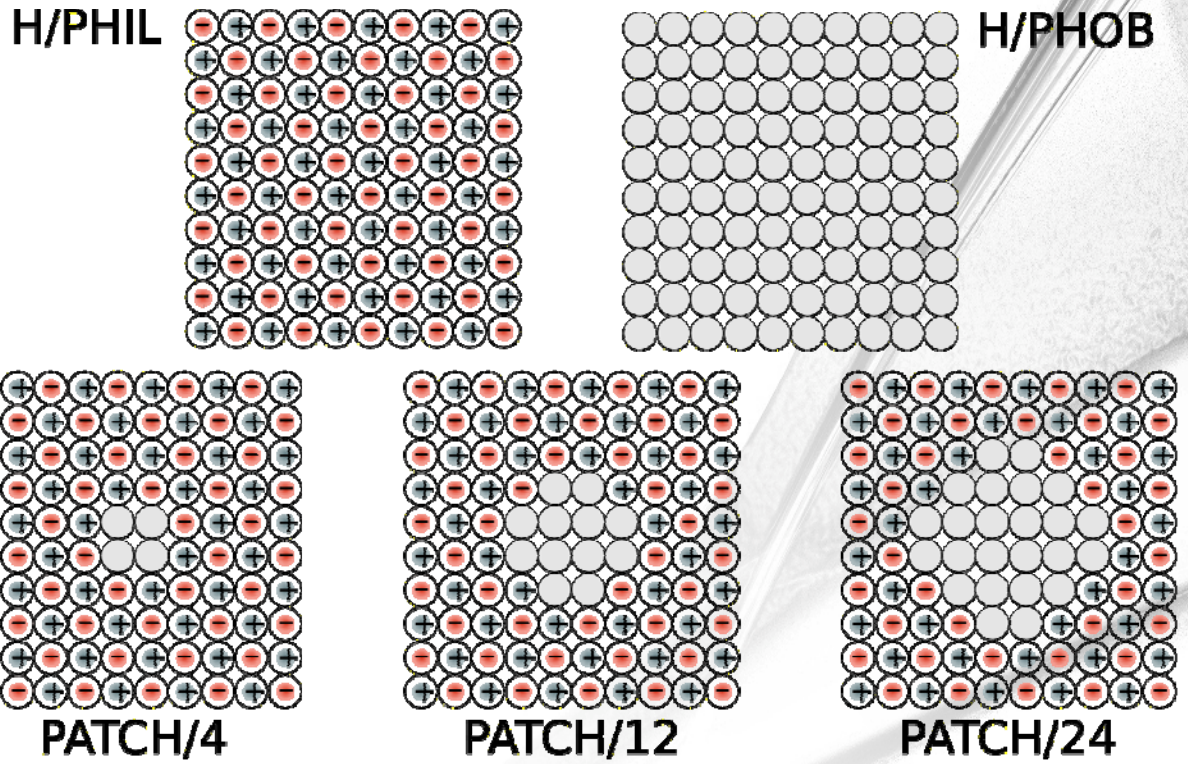
Surfaces with Patterned Hydrophob(phil)icity

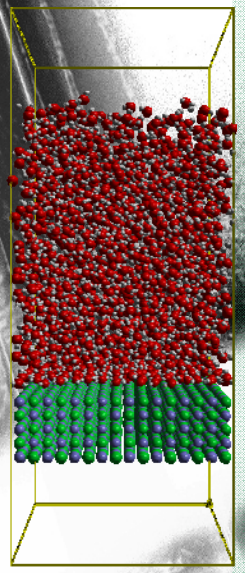


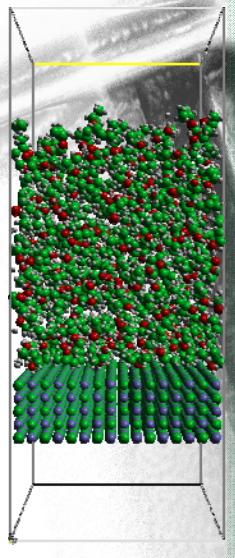
- Hydrophilic surround enhances water density over hydrophobic region
- Little structural influence seen in liquid beyond first adsorbed layer
- N. Giovambattista, P. G. Debenedetti, and P. J. Rossky, *J. Phys. Chem. C*, **2007**, 111, 1323-1332.

Simulation of Patchy Systems

- Simple surface – FCC ionic lattice (charges ±1 *e*)
- Introduce patches of uncharged atoms into topmost layer

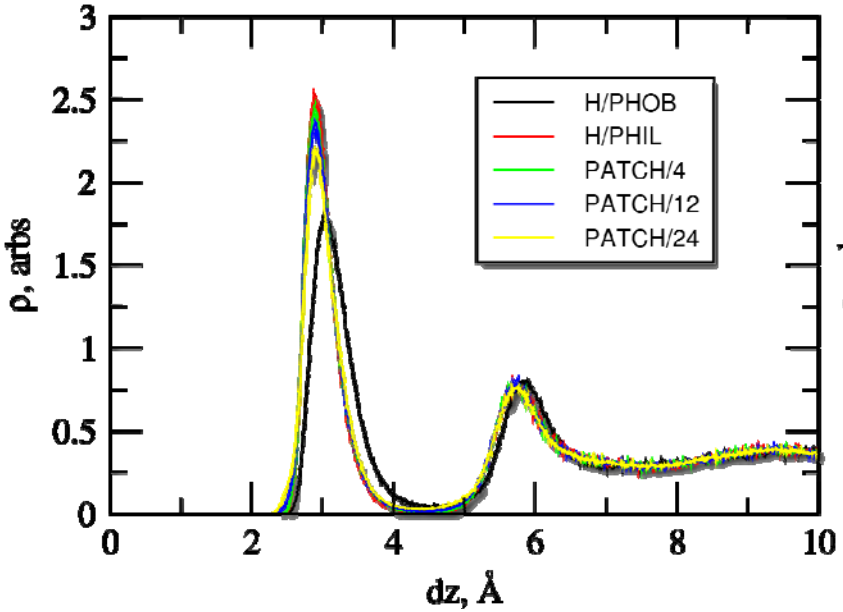


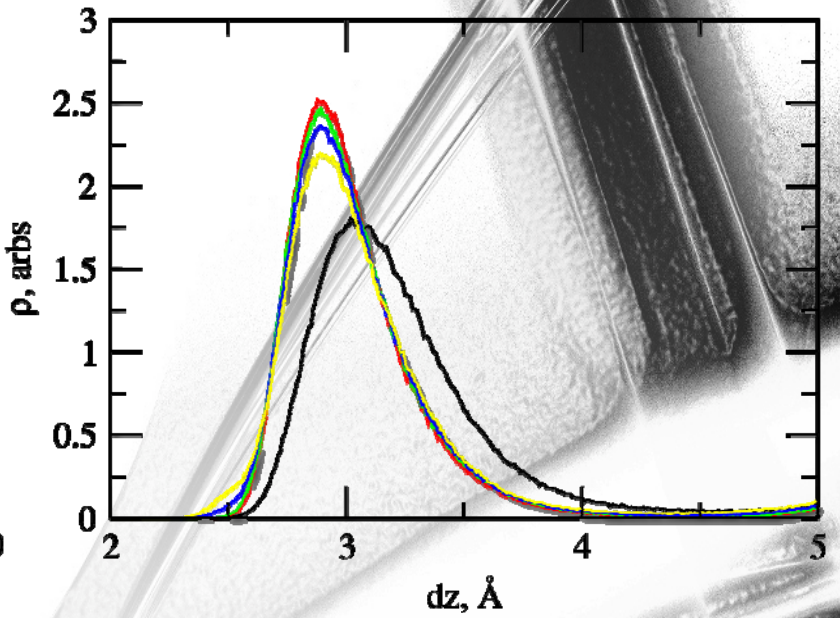




- Consider thin films of hydrogen bonding fluids – water and isopropanol
- Observe effects on the structure of the liquid promoted by the heterogeneity
- All surface atoms have same short-range (LJ) interaction with fluids
- 10 ns NVT simulations performed with DL_POLY (+Yeh-Berkowitz correction)

Water Z-Density Profiles

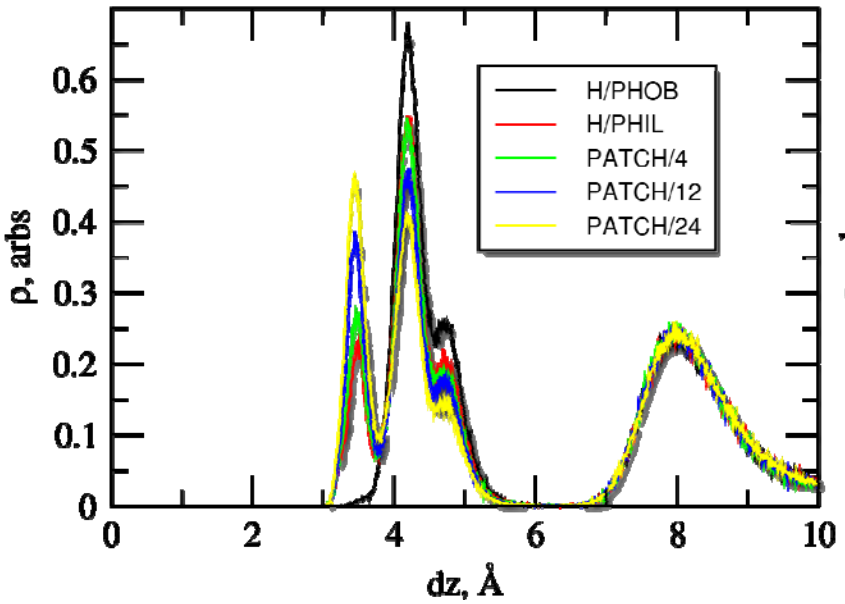


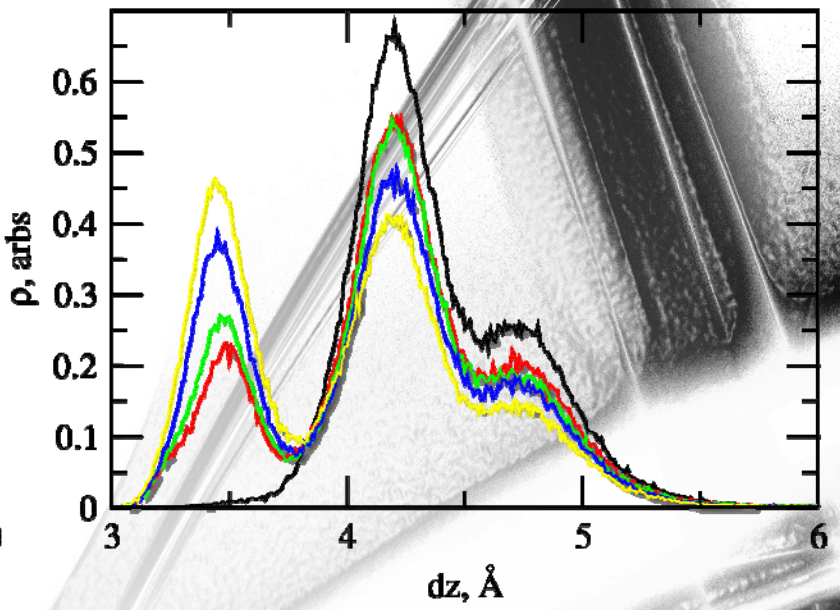


- Increasing patch size does decrease population of molecules in the first layer, but the effect is slight
- Increasing patch size appears to allow some water molecules to approach the surface more closely
  - Related to charged/uncharged boundary?

Surface	Layer 1	Layer 2	Layer 3
H/PHIL	127.7	105.9	111.7
PATCH/4	127.6	105.9	111.9
PATCH/12	127.1	106.4	112.0
PATCH/24	125.75	107.0	111.9
H/PHOB	120.8	105.1	112.4
z_{min}, Å	0	4.4	7.6
z_{max}, Å	4.4	7.6	10.9

Isopropanol Z-Density Profiles

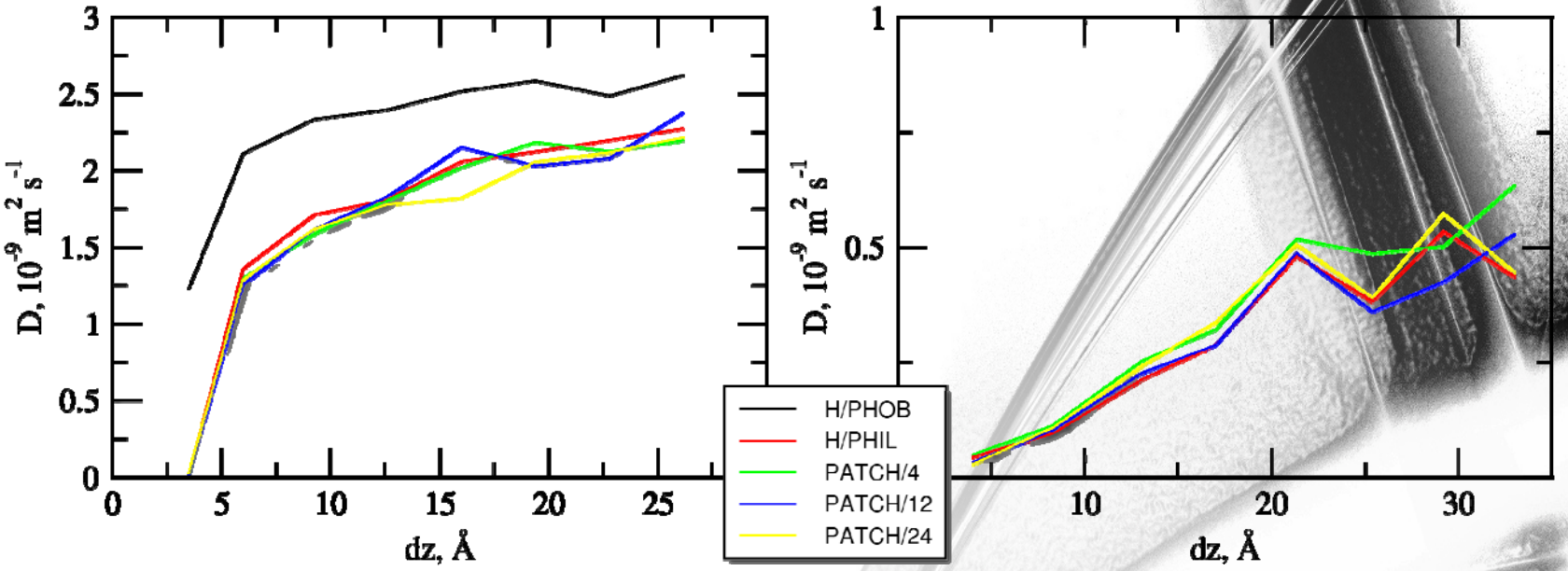




- Clear ‘triplet’ main peak for lattice surfaces corresponding to three different geometries of IPA (H/PHOB surface shows only two)
- Increasing patch size decreases 2° and 3° peaks in favour of 1°

Surface	Layer 1	Layer 2	Layer 3
H/PHIL	42.3	37.8	38.0
PATCH/4	42.0	37.8	38.2
PATCH/12	42.0	37.8	38.4
PATCH/24	41.9	38.1	38.0
H/PHOB	42.6	37.5	37.8
z_{min}, Å	0	6.2	10.4
z_{max}, Å	6.2	10.4	14.8

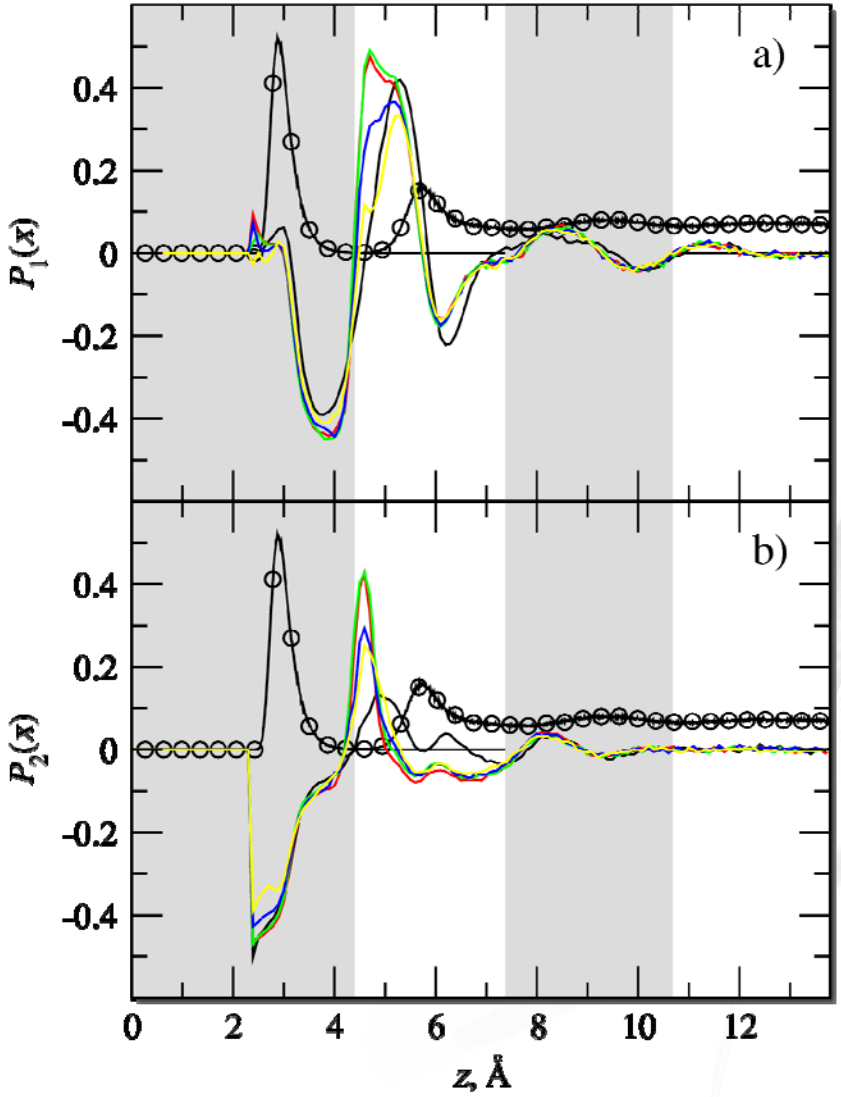
Liquid Dynamics



- Layer diffusion coefficients tend towards bulk liquid values (quickly in the case of the H/PHOB surface)
  - For water, D = 2.49 x 10^{-9} m^2 s^{-1} (SPC/E value)
  - For isopropanol, $D \approx 0.6\ 10^{-9}$ m^2 s^{-1} (PFG NMR value)
- No discernible effect arising from presence of patch
  - Too subtle?
  - Hidden by errors in MSD determinations?
- For isopropanol gradual increase in D with increasing z, c.f. water which increases quickly in the first instance

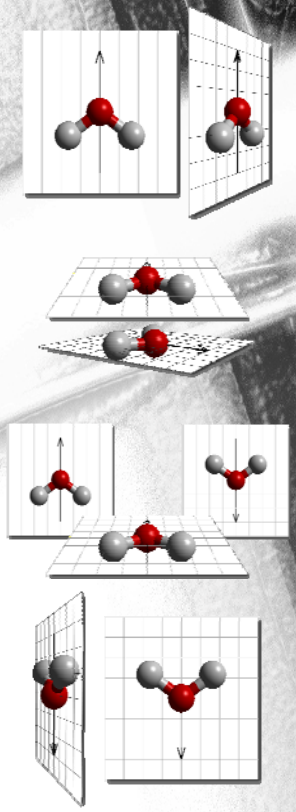
Molecular Orientation

- Use Legendre polynomials to quantify orientation

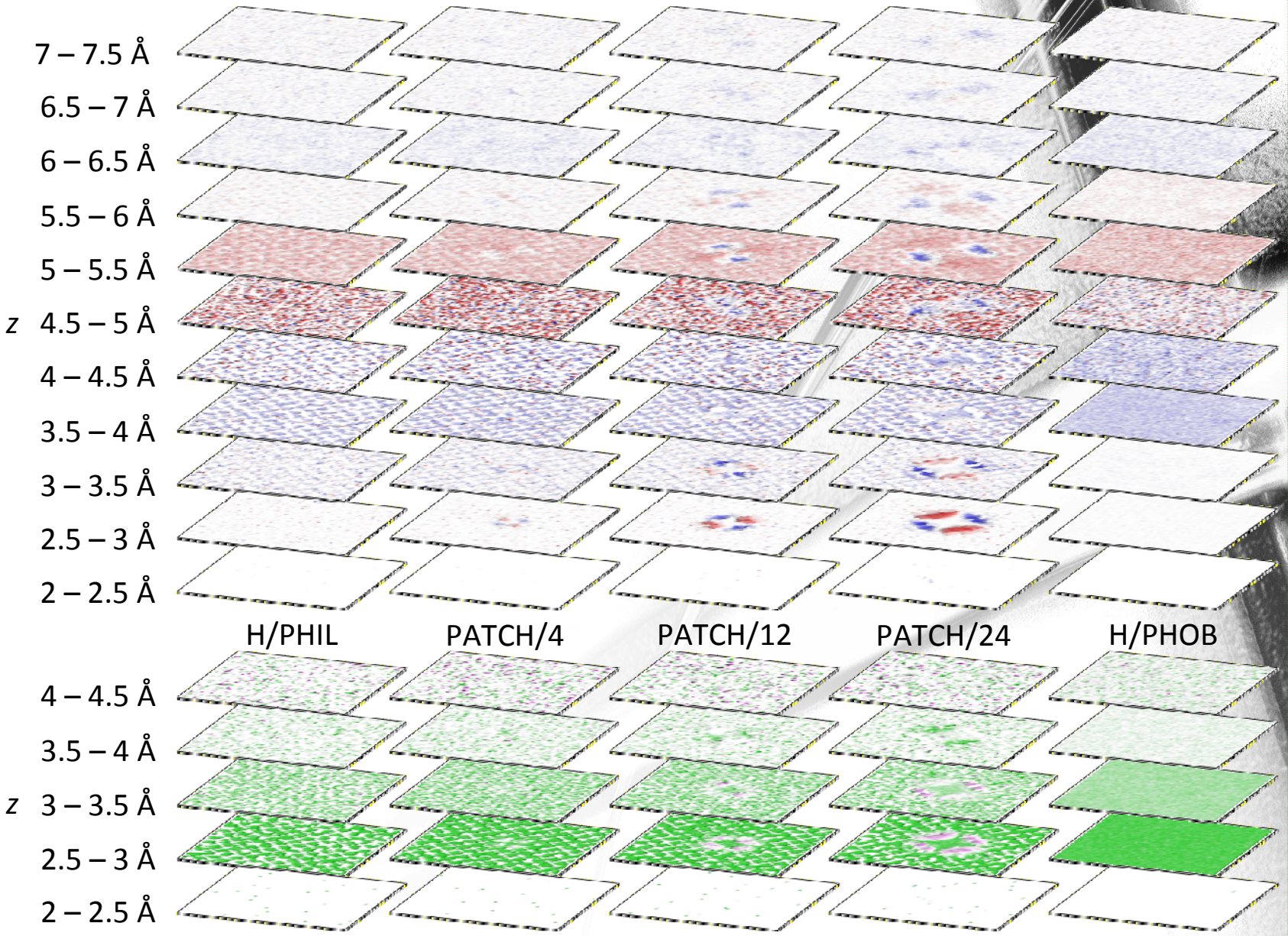


$$P_1(x) = x$$
$$P_2(x) = 0.5\left(3x^2 - 1\right)$$
$$x = \mathbf{u} \cdot \mathbf{v} = \cos\theta$$

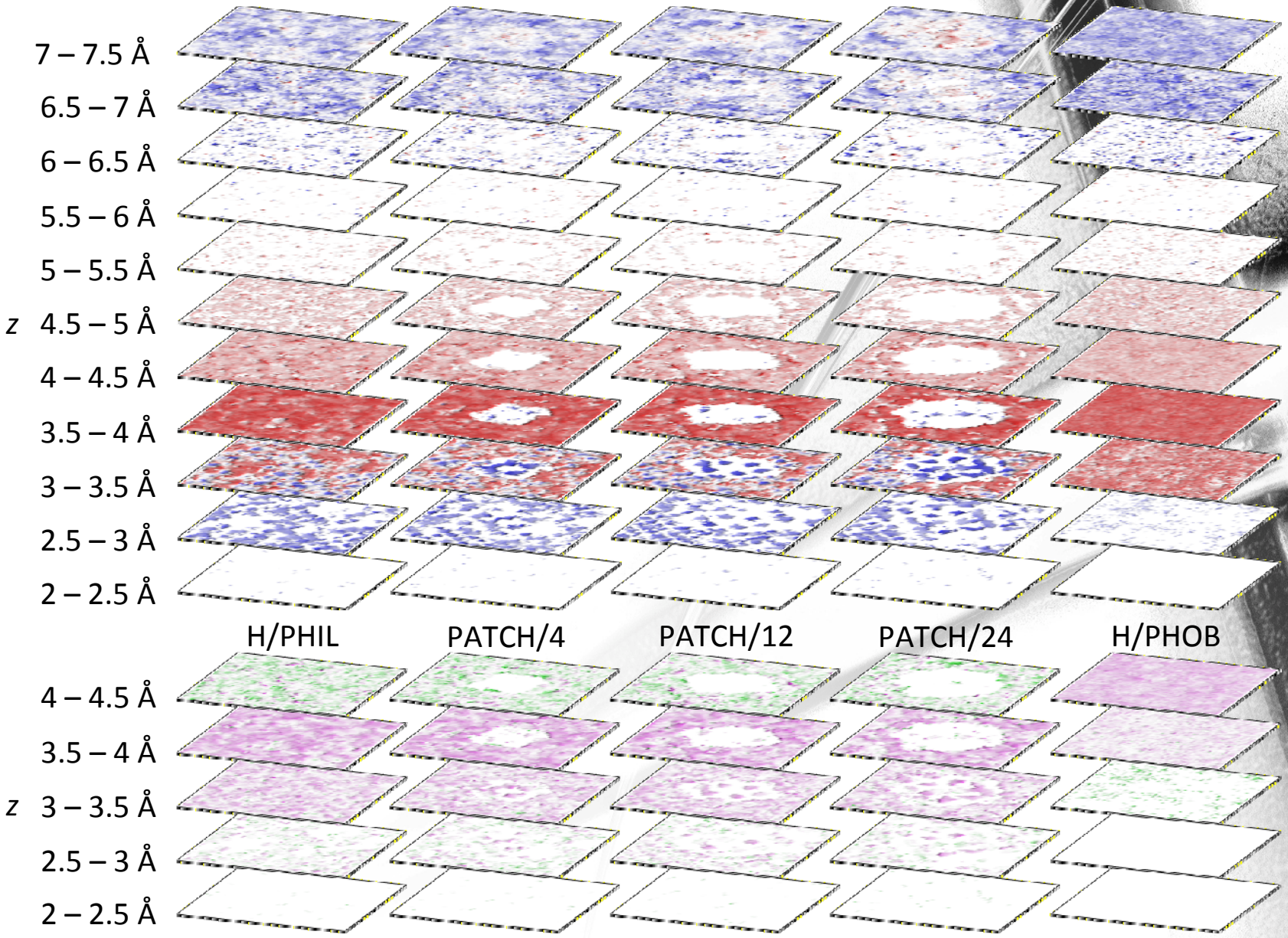
$P_1(x)$	$P_2(x)$
1	0.5
0	-0.5
0	0
-1	0.5



Patch Influence over Water



Patch Influence over Isopropanol



Summary

- For water
  - Negligible effect on adsorbed layer density
  - Orientational order imposed on the liquid molecules around patch edges
  - Order persists through first adsorbed layer, and weakly encroaches into the second liquid layer
  - Oxygen-down orientation promotes stronger ordering of other water molecules than does the hydrogen-down geometry

- For isopropanol
  - Negligible effect on adsorbed layer density
  - No edge effect – orientational order imposed by hydrophobic patch atoms
  - Ionic region surrounding patch promotes OH-down geometry
    - Might reasonably have expected methyl-down geometry over patch
    - Molecule orientation over hydrophobic patch is opposite to that seen over completely hydrophobic surface – c.f. Giovambattista et al.
  - Order persists visibly into second layer, with molecules in the opposite orientation to those at the surface
  - Apparent ‘voids’ created in presence of patches

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