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Title: Electronic Structure Calculations for the Interpretation of Neutron Scattering Results

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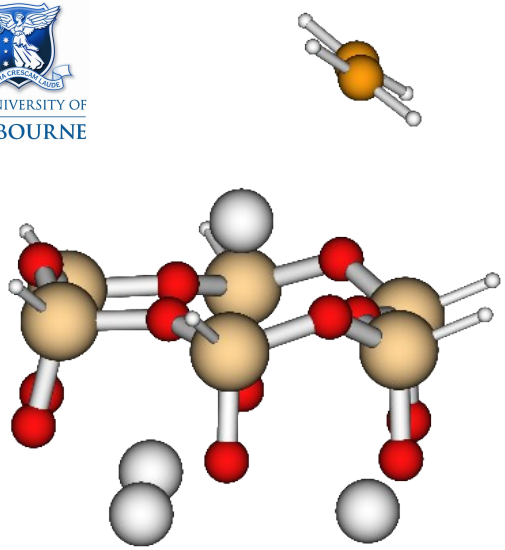
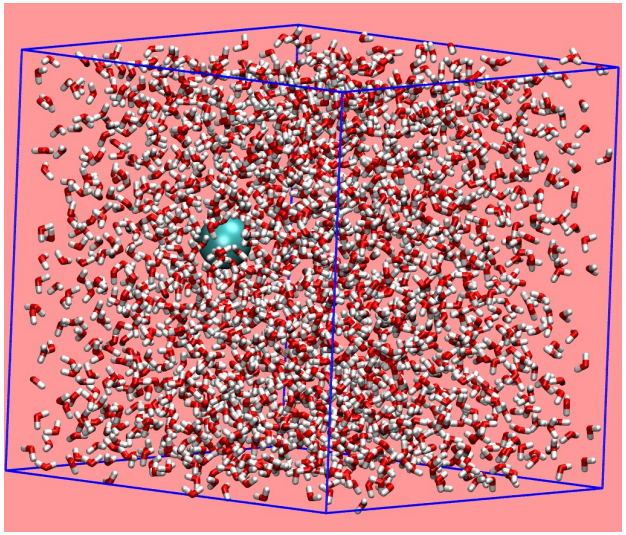
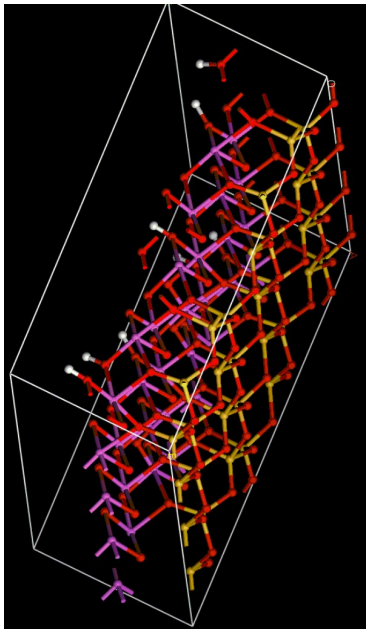
Electronic Structure Calculations for the Interpretation of Neutron Scattering Results







Neil Henson

Physics and Chemistry of Materials Group
Theoretical Division, Los Alamos National Laboratory

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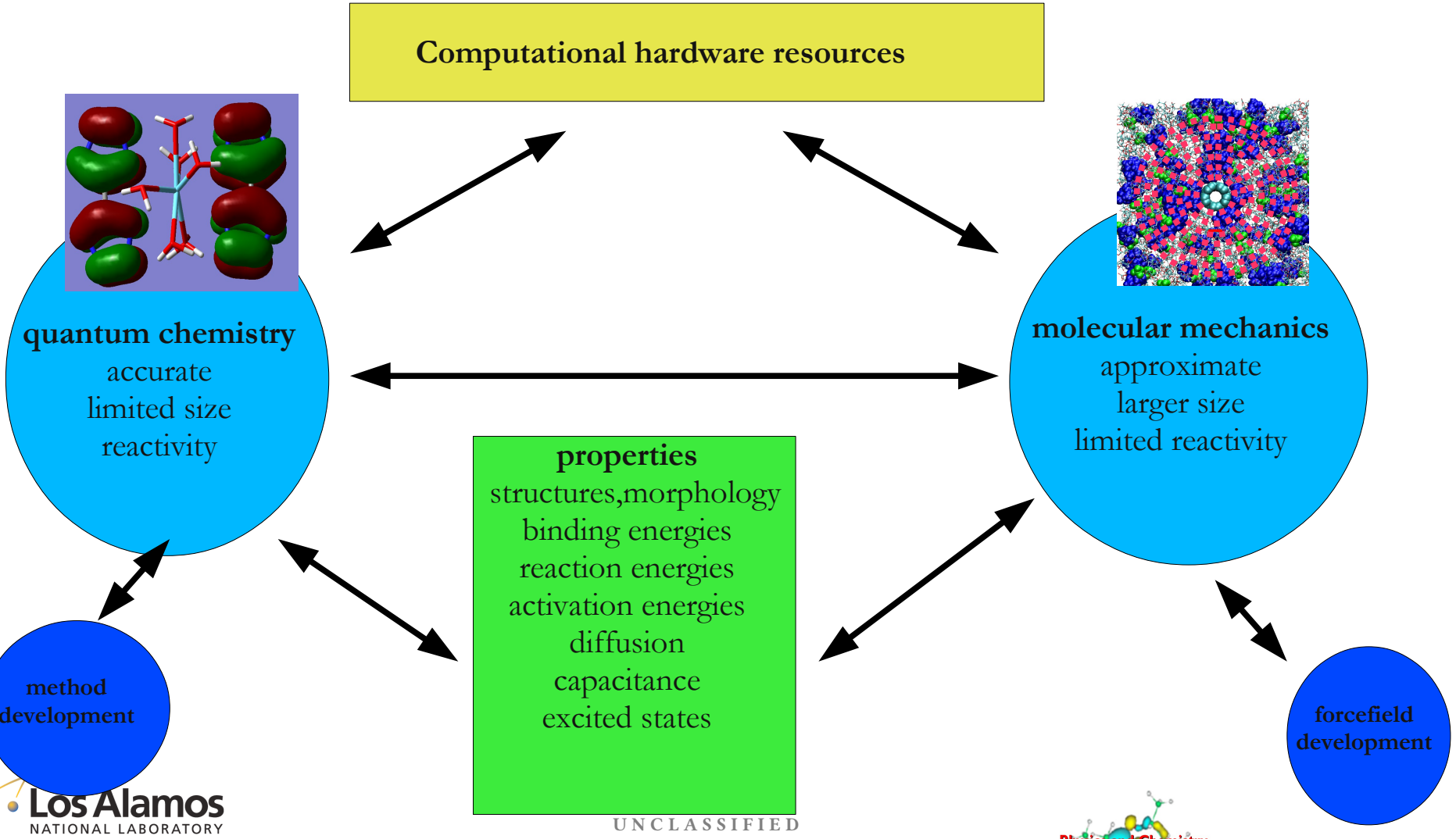
Layout of talk

- Electronic structure calculations: what can they do, what is available, why are they relevant to neutrons
- Case studies:
  - Using electronic structure directly
  - Using electronic structure to fit a potential energy surface
  - Using calculated energetics to determine structure, and as a calibration aid for coarse grained simulations

Tools for atomistic simulation

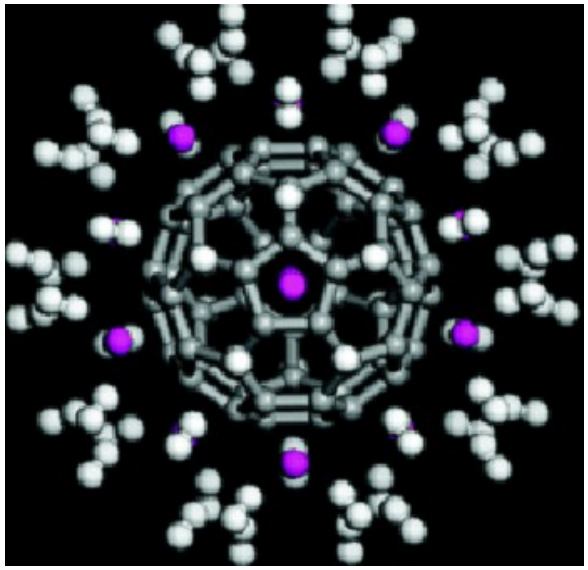


What can electronic structure provide....

.....for neutron scattering interpretation and assignment :

- an atomic level perspective on the results
- atomic positions, bond lengths $\longrightarrow$ structural information
- an idealised picture
- information on vibrations, normal modes

It's all about the model



Accuracy of various electronic structure methods

	bond lengths (Å)	bond angles (°)	Vibrational frequencies (cm^{-1})	Relative energies (kcal mol^{-1})
semi-empirical (PM3)	0.002-0.012			11.6 ΔH_f
Hartree Fock	±0.02	±2	±11	±25-40 dissociation
coupled cluster	±0.004	±0.03	±2%	±1.5 dissociation

- density functional theory almost always better than Hartree-Fock for only slight increase in calculation time
- hybrid functionals can sometimes reach the accuracy of coupled cluster, but always benchmark

Source: Sherrill web site

The right tool for the job

	accuracy	system size (atoms)
semi-empirical (PM3)	low	2000
Hartree Fock/density functional theory	medium	500
perturbation methods	high	50
coupled cluster	very high	20

Source: Sherrill web site

Three case studies

- Water solvation around lanthanide and actinide cations (diffraction, reflectivity)
  - electronic structure to produce an empirical forcefield for molecular dynamics
- Vibrational spectroscopy for molecules in porous solids (inelastic scattering)
  - electronic structure on cluster and periodic representations
- Structure of amorphous geopolymers (pair distribution function)
  - electronic structure energetics for coarse grain Monte Carlo

Case Study (1) : Inelastic neutron scattering (INS) of small molecules in zeolites

- Advantages
  - compared to infra-red and Raman spectroscopies, high sensitivity to vibrational modes involved hydrogen containing adsorbed molecules
  - framework vibrations give much weaker scattering
  - deuterium subsitution can allow focus on particular functional groups

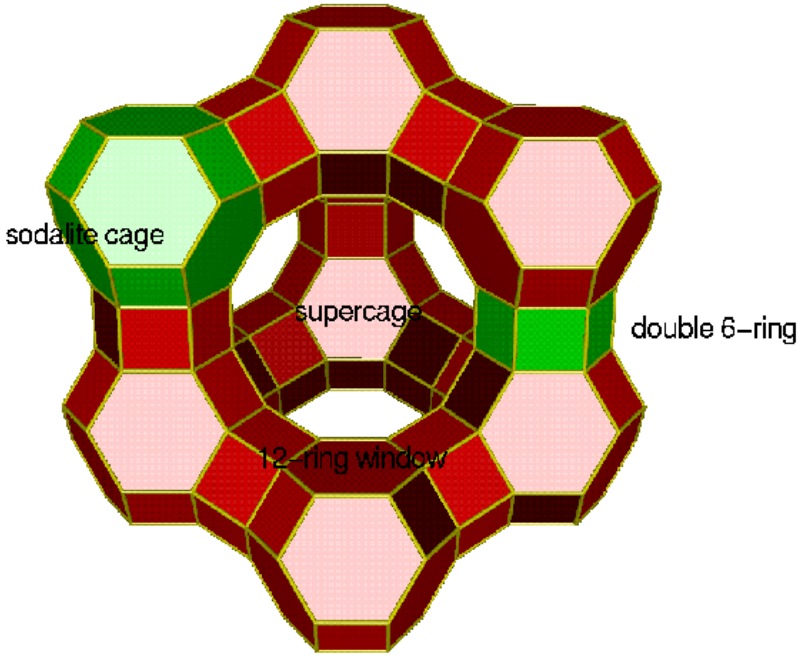
Neil Henson (LANL), Juergen Eckert (USF)

Aim of study

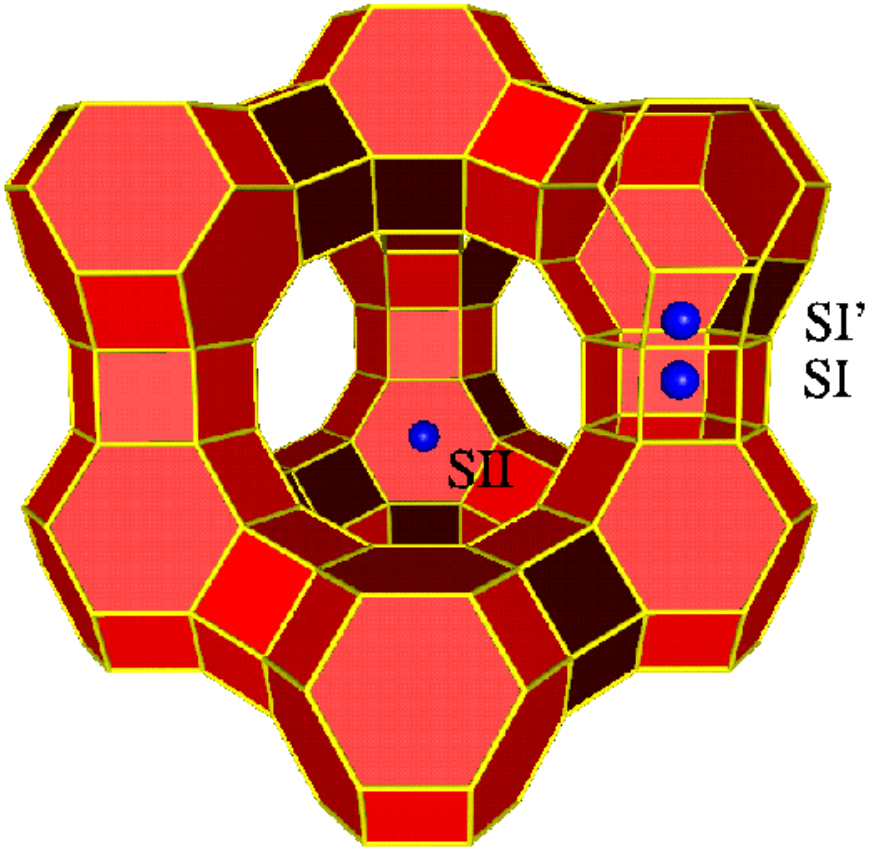
- study model zeolite system with two molecules with differing sorption properties
- measure and calculate INS spectra
- use calculated spectra to help fit and assign experimental data
- examine low frequency librational modes of molecules in zeolites

Choice of system

- sorption of ethane and ethane in Na-Y zeolite
- binding sites well determined for ot sorbates e.g. benzene
- two molecules should have differen binding characteristics
  - ethene : π-electrons strongly interacting with Na^+ cation, as for benzene
  - ethane : dispersive contributions dominate



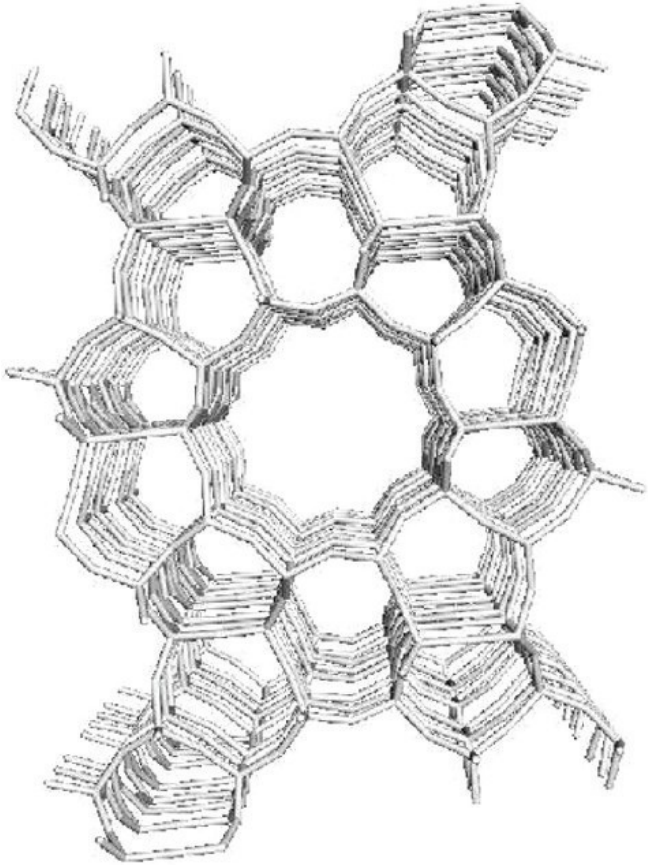
Theoretical details

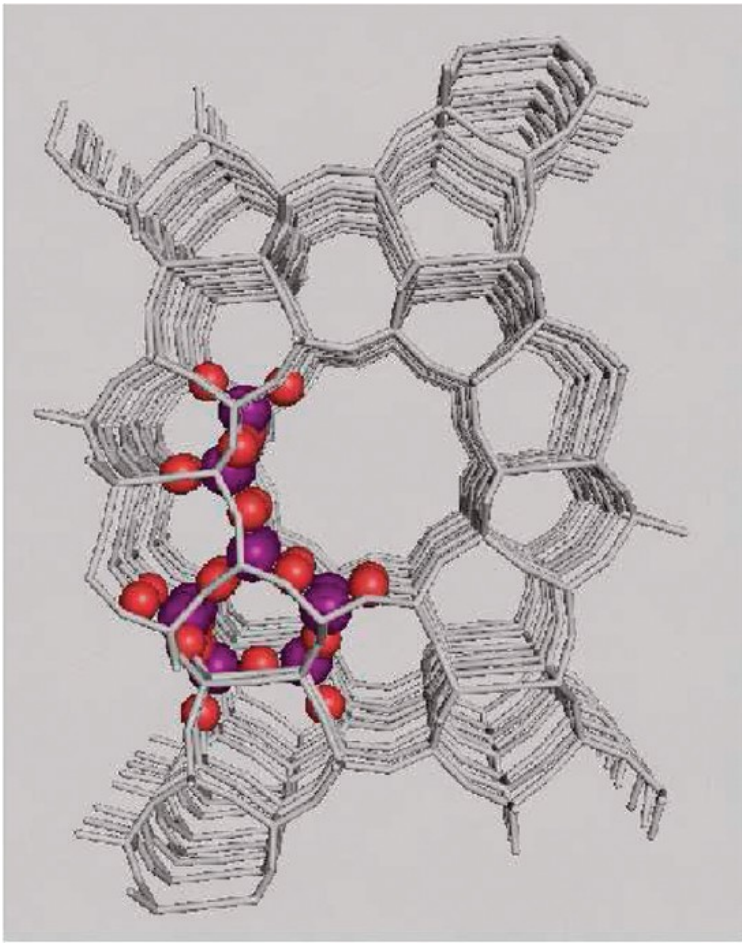


cation sites in faujasite (Na-Y) : (Si, Al, Na, O)

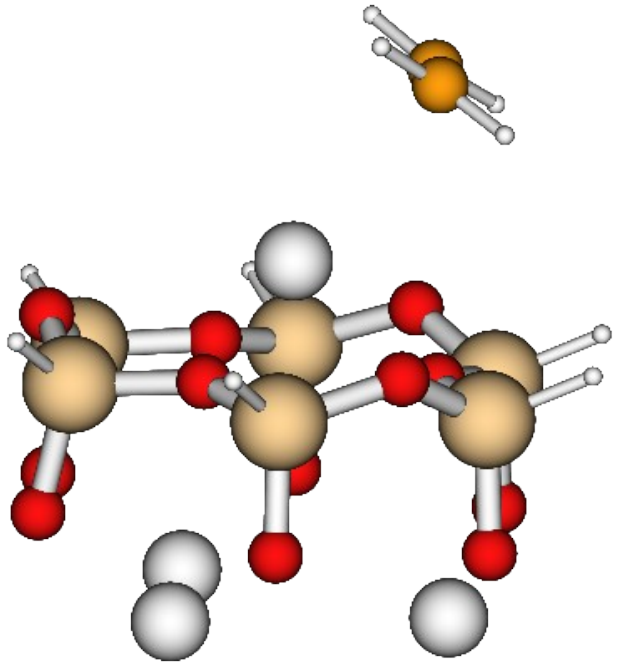
- Calculations performed on clusters at the Hartree Fock level with MP2 corrections (dispersion)
- 6-31G* basis set

Building a model : cluster from periodic structure



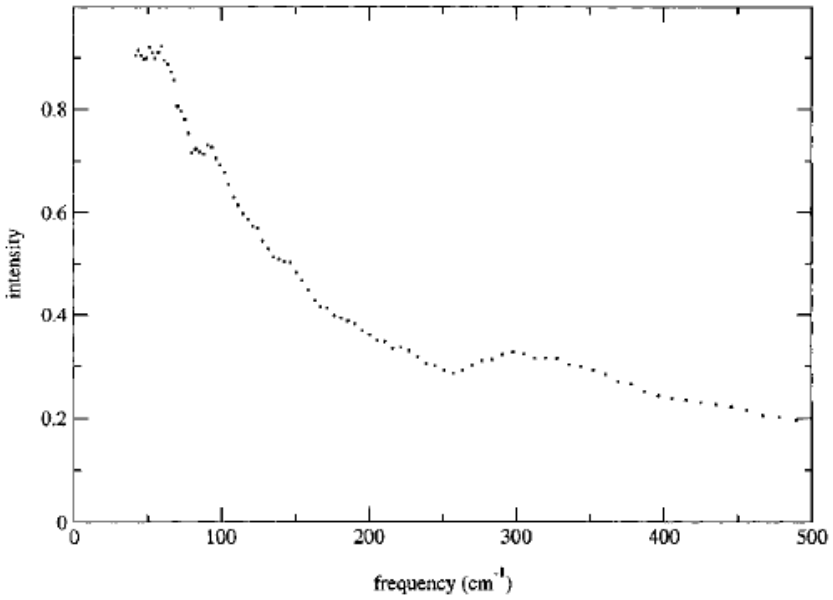


Cluster model for quantum mechanical calculations



- based on an all silica six-ring with hydride termination
- hydrogens and non SII sodium cations fixed.
- optimise and calculate vibrations

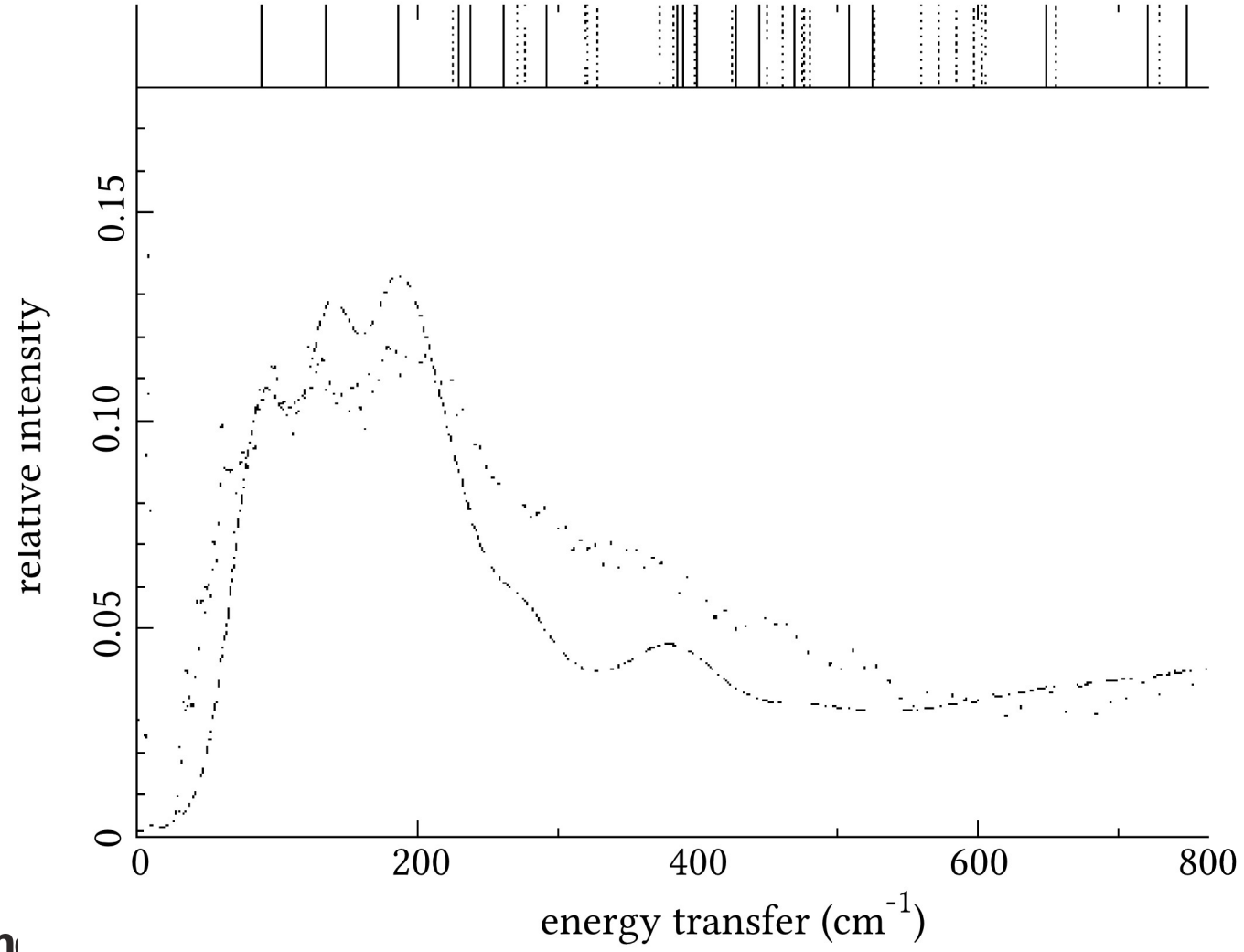
Results: ethane in Na-Y zeolite



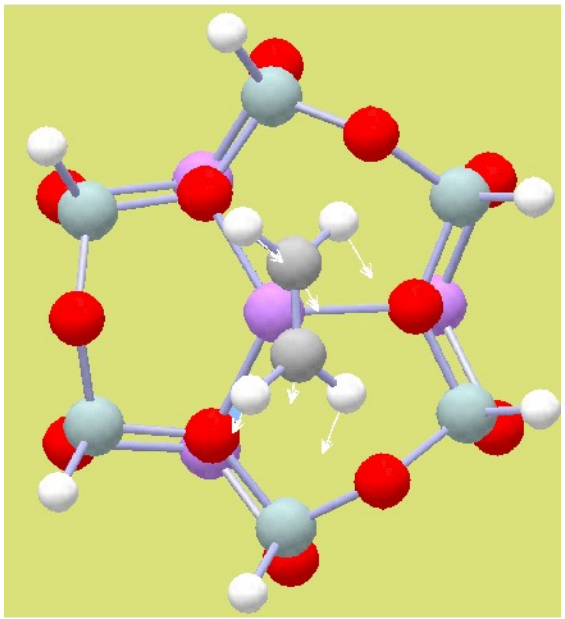
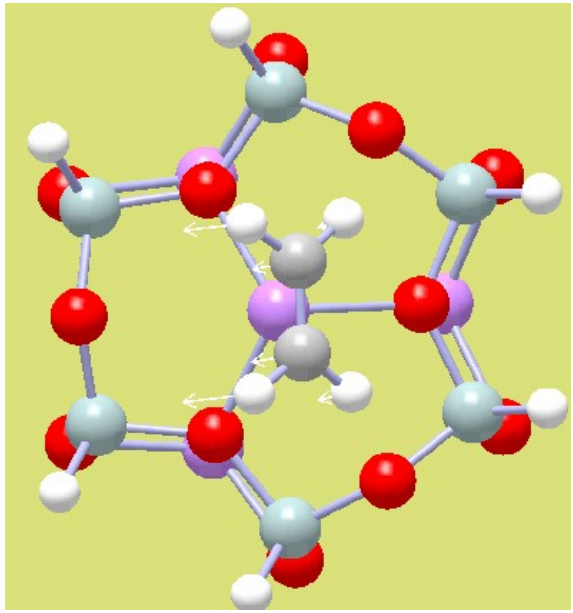
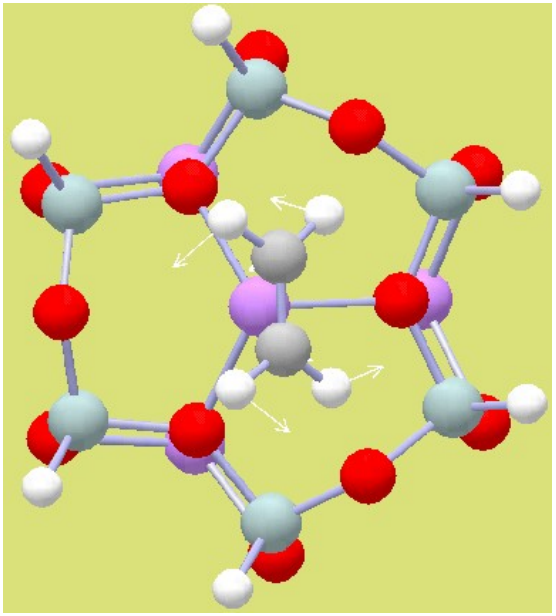
experimental INS spectrum

- broad lines in the low frequency region, unable to resolve peaks
- calculation predicts a large number of similar binding sites spanning a 5 kJmol-1 range
- no specific binding location

Experimental (···) and calculated (-·-) INS spectra for ethene in Na-Y



Vibrations

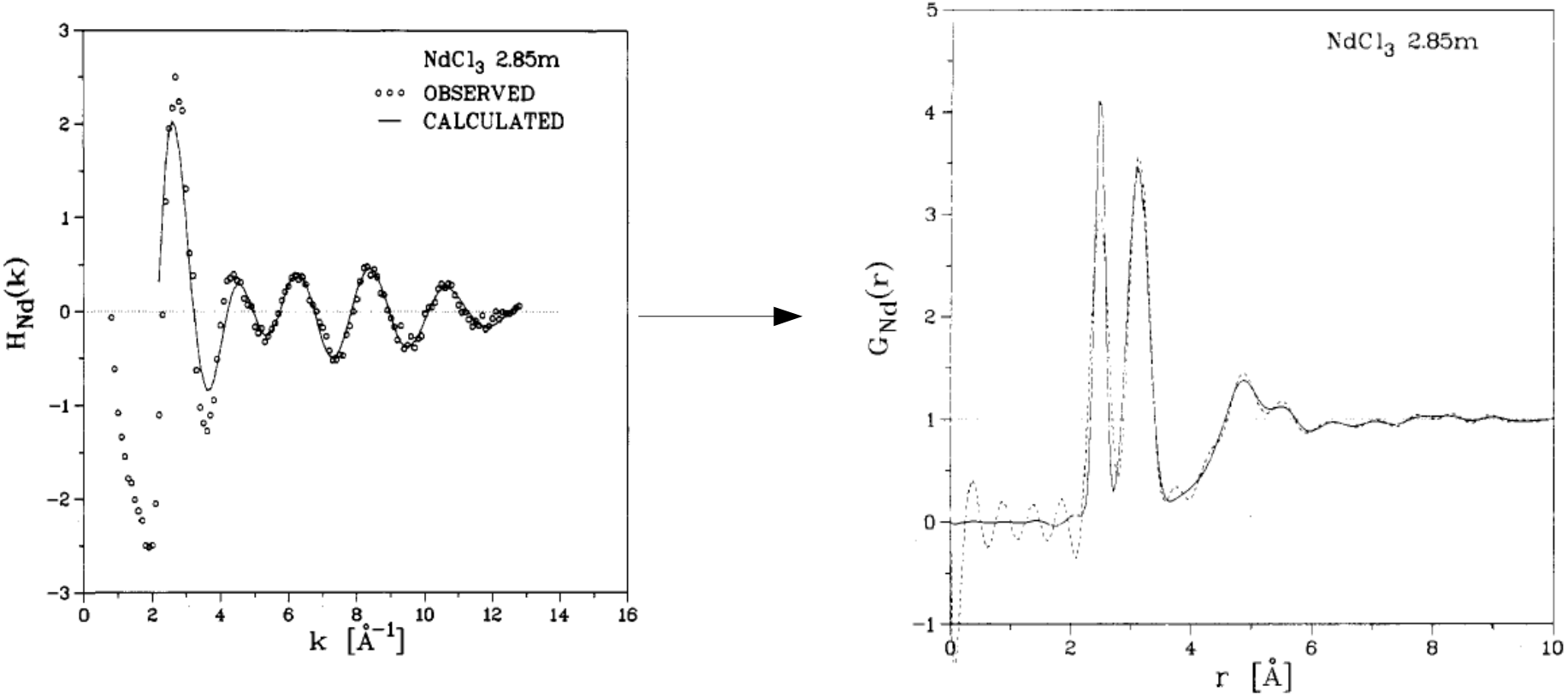
experiment	101 cm^{-1}	120 cm^{-1}	188 cm^{-1}
calculated	125 cm^{-1}	160 cm^{-1}	229 cm^{-1}

Case study (2) – Solvation of metal cations

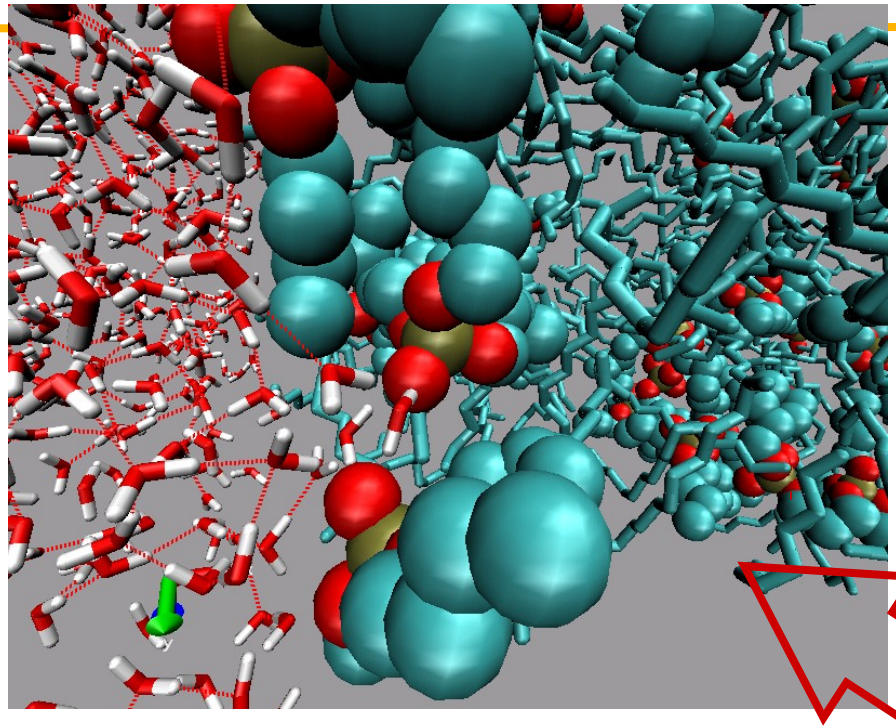
- Can we use electronic structure calculations to understand the interactions between lanthanides and actinide cations in solution to rationalise the separations process and scattering data?
- What is the effect of using a polarisable versus non-polarisable forcefield to study the molecular dynamics behaviour of cations in solution?
- How can we describe the perturbations of the hydrogen bonded network in water with cations present?

Prof. Aurora Clark, Washington State University

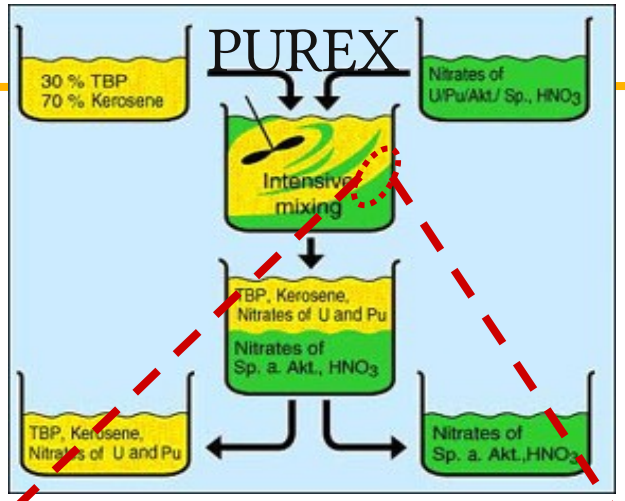
Typical Neutron Diffraction Data for Lanthanide Solvation



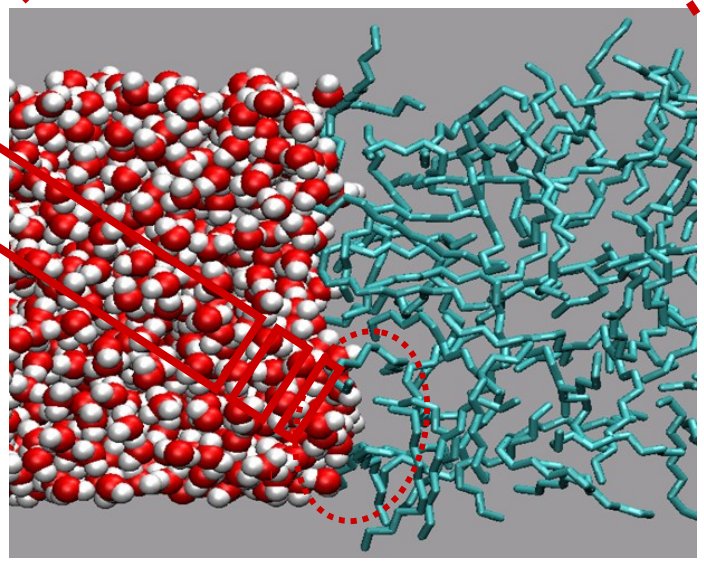
Separations at the molecular level via simulation



TBP at the water/n-dodecane interface



http://www.euronuclear.org/info/encyclopedia/images/purex.jpg



MD simulation of water/n-dodecane interface

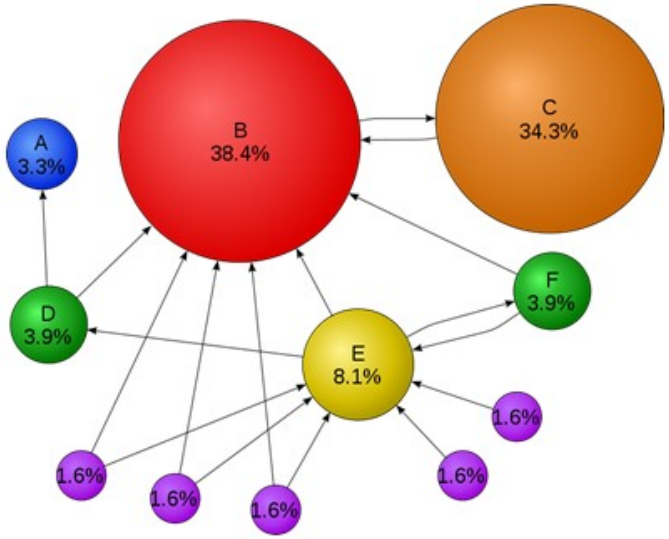
Important interactions occur on the molecular level at the liquid–liquid interface

Water network description – topological analysis from graph theory

- Largest modern impact – application to the WWW
  - PageRank algorithm (Google internet search engine)
  - Assigns numerical weight to each element of a hyperlinked set of documents

$$PR(p_i) = \frac{1-d}{N} + d \sum_{p_j \in M(p_i)} \frac{PR(p_j)}{L(p_j)}$$

- Web pages $p_i \ldots p_N$
- Outgoing links from page $L(p_j)$
- Set of pages that link to p_i is $M(p_j)$
- d is probability that surfer will follows a link on the page they are on
- $(1-d)/N$ is probability surfer will start a new session on page p_i



Brin, S.; Page, L., In *Proceedings of the 7th International Conference on the World Wide Web (WWW)*. Enslow, P. H.; Ellis, A., Eds. (Elsevier: Amsterdam, 1998), p 107.

Relating the PageRank (PR) to a water network

- Fundamentally PR is a measure of connectivity of a website
- Damping fator adjusts importance of adjacent/connected websites
- Does the PR of water indicate its organization?

- To adopt PR convention to a system of atoms:

  $p_1, p_2, \ldots, p_N$ becomes the list of atoms

  $PR(p_i)$ becomes the page rank of atom i

  $$PR(p_i) = \frac{1-d}{N} + d \sum_{p_j \in M(p_i)} \frac{PR(p_j)}{L(p_j)}$$

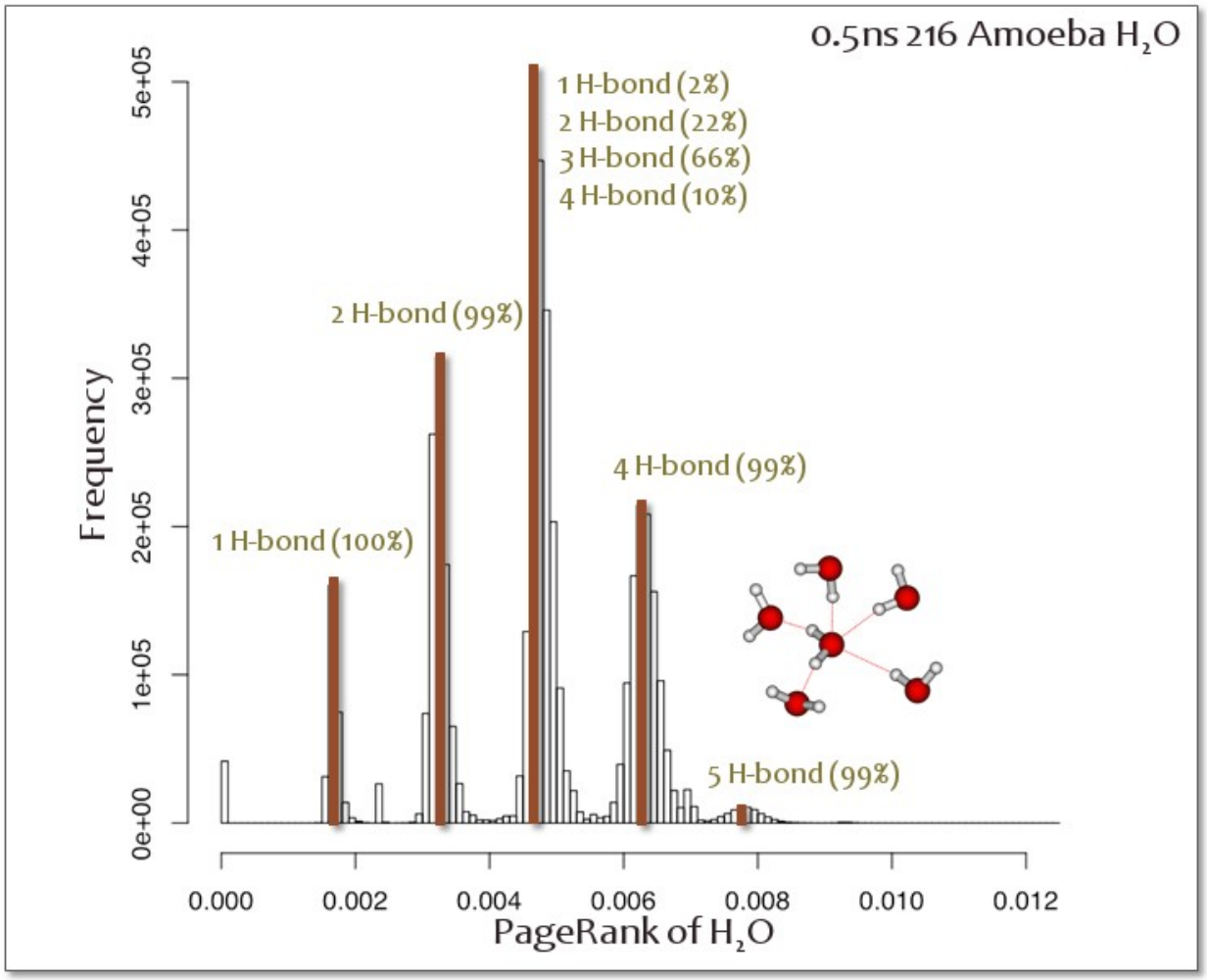
  $L(p_j)$ becomes the number of connections from atom j

  Connection is modulated by phenomena of interest (e.g., H-bond distance)

  d = probability that connection contributes to the graph (weighting factor

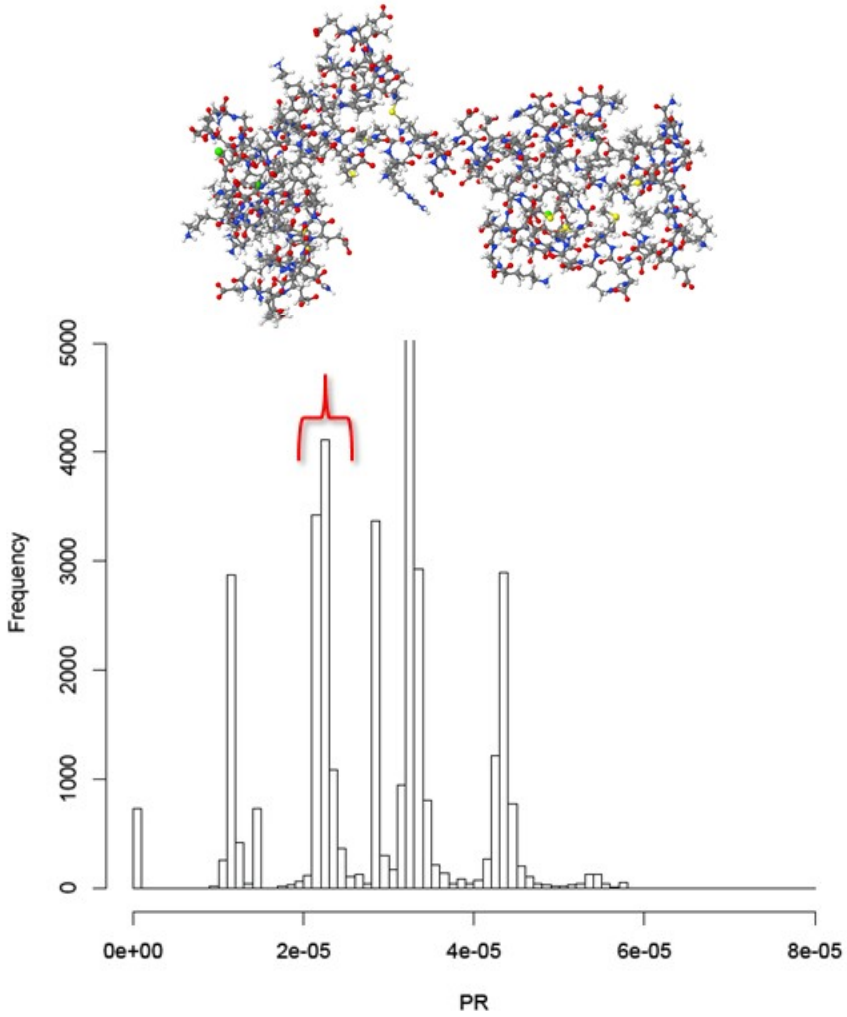
B. L. Mooney, L. R. Corrales, A. E. Clark J. Comp. Chem. **2012**, *33*, 853.

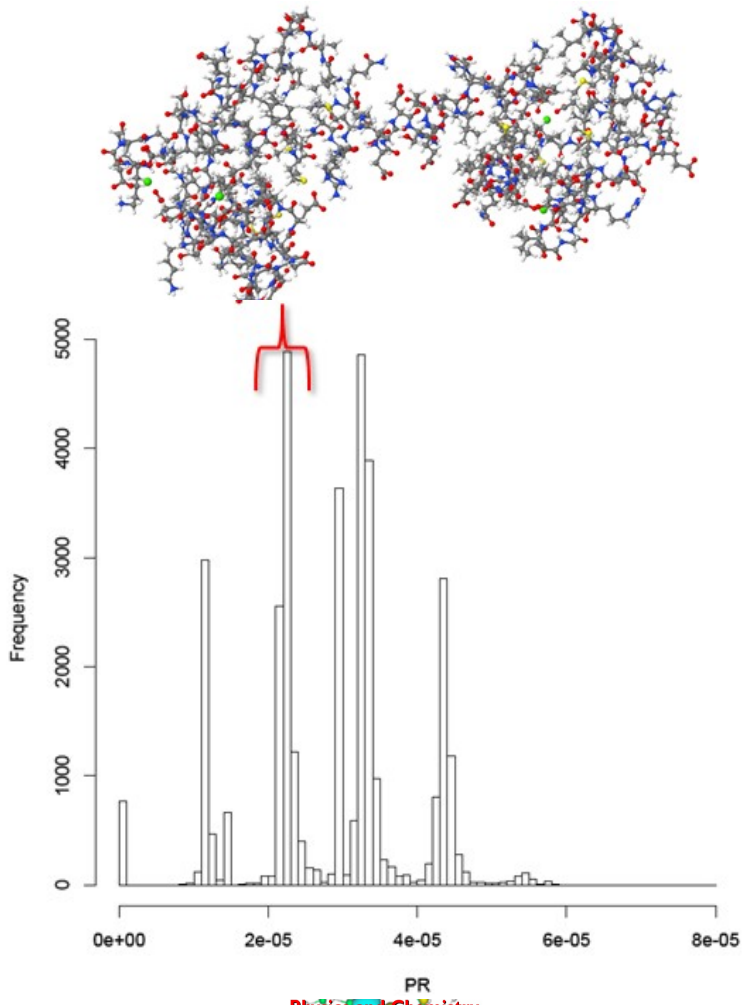
PageRank as a fingerprint for the water network



Sensitivity to conformations of a solute?

- calmodulin kinase in 35,208 H_2O



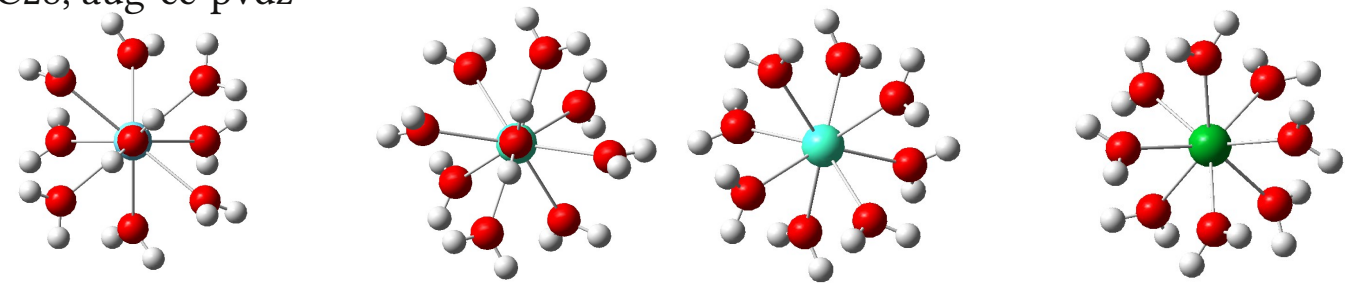


Implications and future uses

- How do solutes – metal ions, proteins, surfaces – disrupt the water H-bonded network?
  - Metal ions (dissolution, coordination with ligands)
  - Surfaces (variation in network structure close to, and far from surface) - reflectometry
- Can we usefully describe this with graph theory?
- Implications for entropy – informational vs. thermodynamic
- Freezing and melting

DFT Results for Ln-OH_2

RSC28, aug-cc-pvdz



$La(H_2O)_9^{3+}$ $Gd(H_2O)_9^{3+}$ $Gd(H_2O)_8^{3+}$ $Lu(H_2O)_8^{3+}$

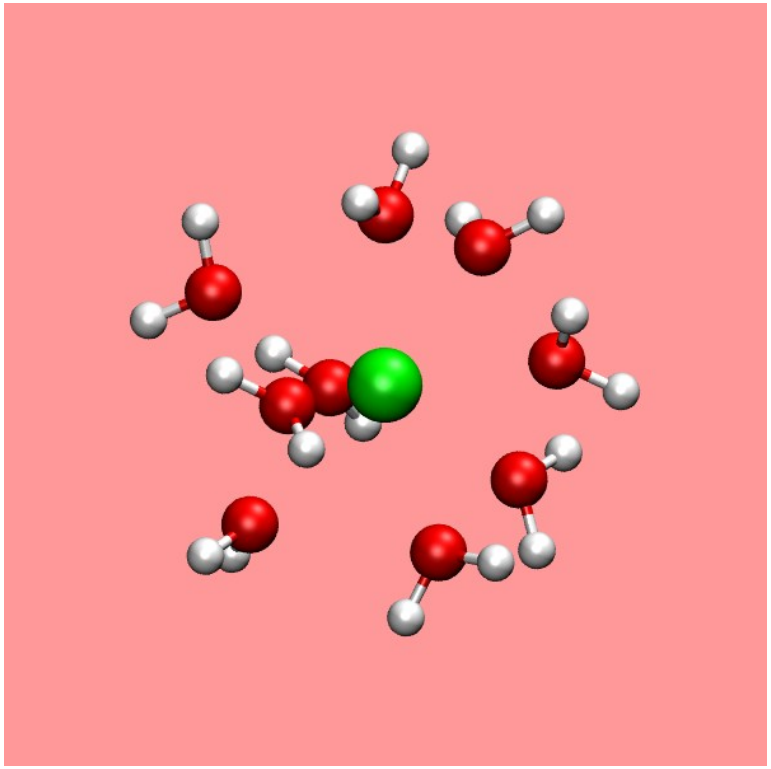
- B3LYP, SVWN5, TPSS, PBE functionals *R* agree within 0.07Å
- Addition of 2nd solvation shell improves geometric accuracy (<0.05 Å deviation)

	ΔG_{hyd} (kcal/mol)
$La(H_2O)_9^{3+}$	-765.9 (-763.1 expt)
$Gd(H_2O)_9^{3+}$	-825.5 (-817.6 expt)
$Gd(H_2O)_8^{3+}$	-823.9
$Lu(H_2O)_8^{3+}$	-857.6 (-862.6 expt)

Clark, A. E. *J. Comp. Theor. Chem.* 4, 708 (2008).; Dinescu, A.; Clark, A. E. *J. Phys. Chem. A.* 2008 12, 11198-11206 .; Kuta, J.; Clark, A. E. *In Prep.;* Rizkalla, E. N.; Choppin, G. R. *Handbook on the Physics and Chemistry of Rare Earths*, 15, (1991),

The starting point for a new forcefield

- a high quality quantum chemically determined potential energy surface including forces



$[La(H_2O)_9]^{3+}$

- calculations as a function of La-O separation
- produce a potential energy curve for fitting to forces only
- B3LYP or MP2?
- all the curve, or subset

Next step : fitting

- ForceFit : a new modular GUI-based fitting tool for lanthanide and actinides written in C++
  - reads potential energy surface data for multiple quantum chemistry codes: Gaussian, NWChem, CRYSTAL
  - interfaces to multiple molecular mechanics codes : DL_POLY, AMBER, LAMMPS, TINKER for iterative fitting procedure
  - reads energies, forces, eigenvectors from normal mode analysis
  - LGPL licence

ref: Clark et al, J. Comput. Chem, 2010, 31, 2307-2316
http://aclark.chem.wsu.edu/software

AMOEBA forcefield – polarisable water potential

- AMOEBA potential after Ray and Ponder (2003)
- we know water is a polarisable molecule (dipole moment 78 Debye)
- does this make a difference to the potential fitting MD results
- implemented in two codes : TINKER, AMBER (pmemd)

AMOEBA potential

- electrostatics
  - permanent atomic monopole, dipole and quadrupole on each atomic centre, $M=[q,\mu_1,\mu_2,\mu_3,Q_{11},Q_{12},.....Q_{33}]$
  - explicit polarisation via mutual induction of dipoles at atomic centres (needs atomic dipole polarisabities) damped at short range by smearing

$$\rho = \frac{3a}{4\pi}\exp(-au^3)$$

$$u = \frac{R_{ij}}{(\alpha_i\alpha_j)^{(1/6)}} \qquad \mu_{i,\alpha}^{ind} = \alpha_i E_{i,\alpha}$$

  - $E_{i,a}$ is sum of field components generated by permanent multipoles and induced dipoles

AMOEBA potential (2)

- valence terms

$$U_{bond} = K_b(b - b_0)^2[1 - 2.55(b - b_0) - 3.79(b - b_0)^2]$$

$$U_{angle} = K_\theta(\theta - \theta_0)^2[1 - 0.014(\theta - \theta_0) + 5.6\text{x}10^{-5}(\theta - \theta_0)^2 - 7.0\text{x}10^{-7}(\theta - \theta_0)^3 + 2.2\text{x}10^{-8}(\theta - \theta_0)^4]$$

$$U_{UB} = K_l(l - l_0)^2$$

b_0=0.9572Å, θ_0=108.5°, l_0=1.5326Å

AMOEBA potential (3)

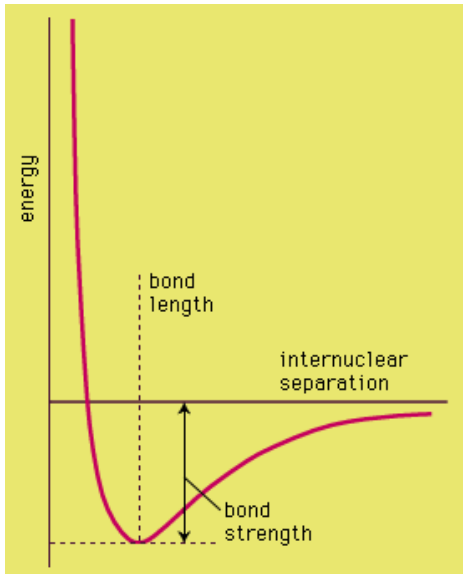
- van der Waals repulsion-dispersion term

$$U_{ij} = \epsilon_{ij}\left(\frac{1+\delta}{\rho_{ij}+\delta}\right)^{(n-m)}\left(\frac{1+\gamma}{\rho_{ij}^{m}+\gamma} - 2\right)$$

$$\rho_{ij} = \frac{R_{ij}}{R_{ij}^{0}}, n = 14, m = 7, \delta = 0.07, \gamma = 0.12$$

-	density ($g\ cm^{-3}$)	self-diffusion coeff ($10^5\ cm\ s^{-1}$)	static dielectric constant (D)	heat capacity, C_v ($cal\ mol^{-1}\ K^{-1}$)
AMOEBA	1.0004	2.02	82	28.4
expt	0.9970	2.3	78.3	17.8

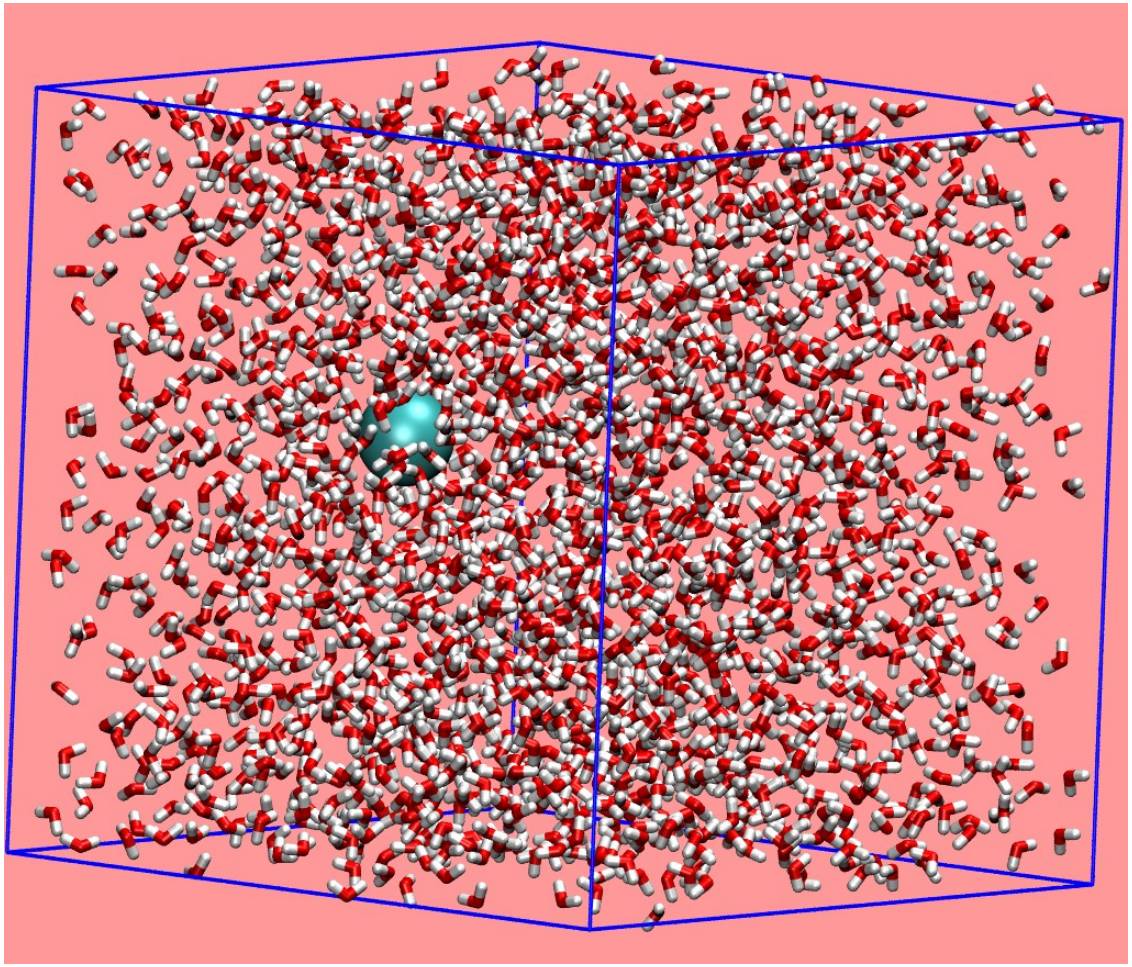
Several fitted AMOEBA parameters



DFT 1Å to either side of minimum every 0.20Å (11)	DFT 1Å to either side of minimum every 0.05Å (42)	DFT whole curve every 0.20Å (32)	DFT whole curve every 0.05Å (113)
MP2 1Å to either side of minimum every 0.20Å (11)	MP2 1Å to either side of minimum every 0.05Å (42)	MP2 whole curve every 0.20Å (32)	MP2 whole curve every 0.05Å (113)

() number of geometries in fit

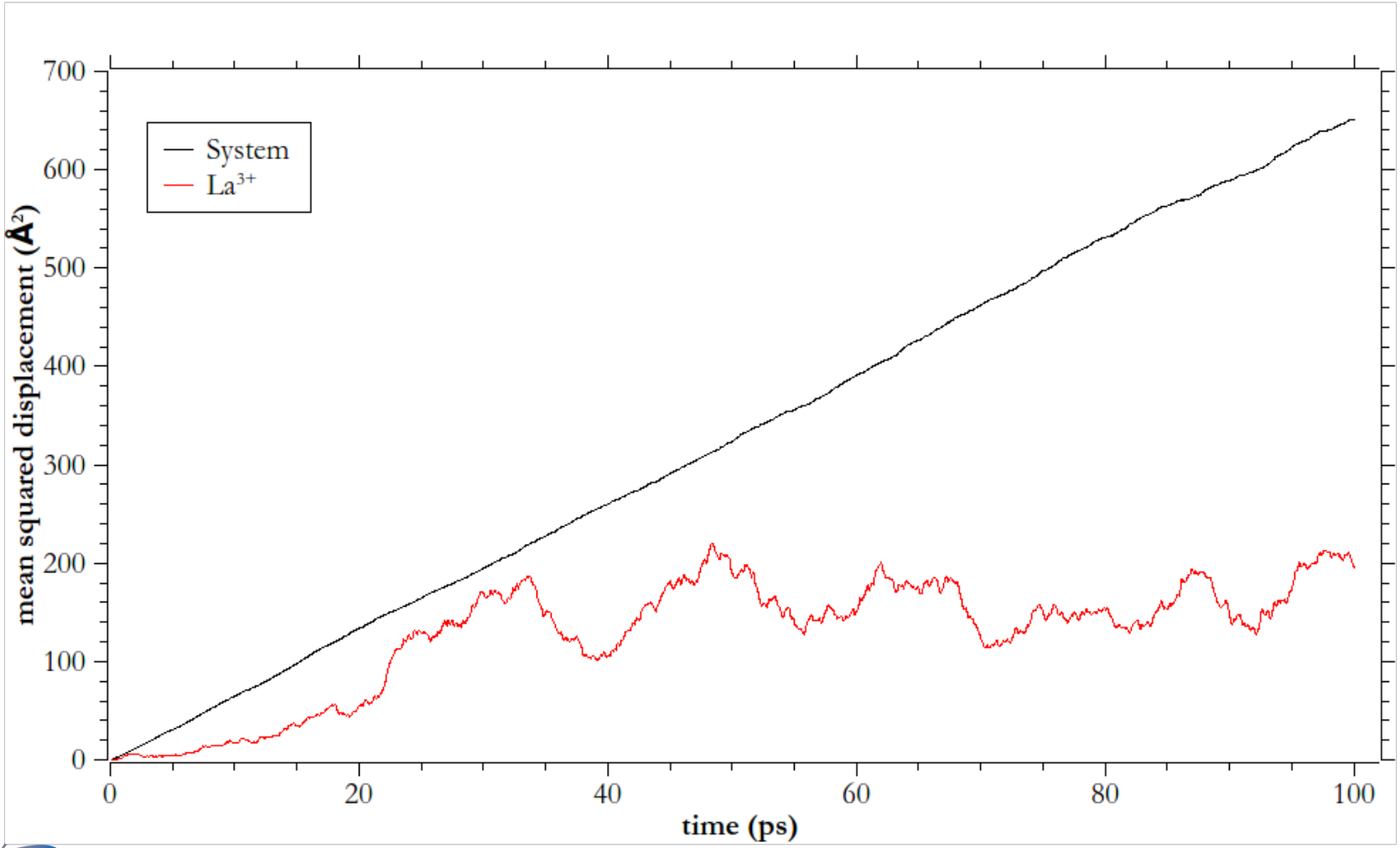
The model



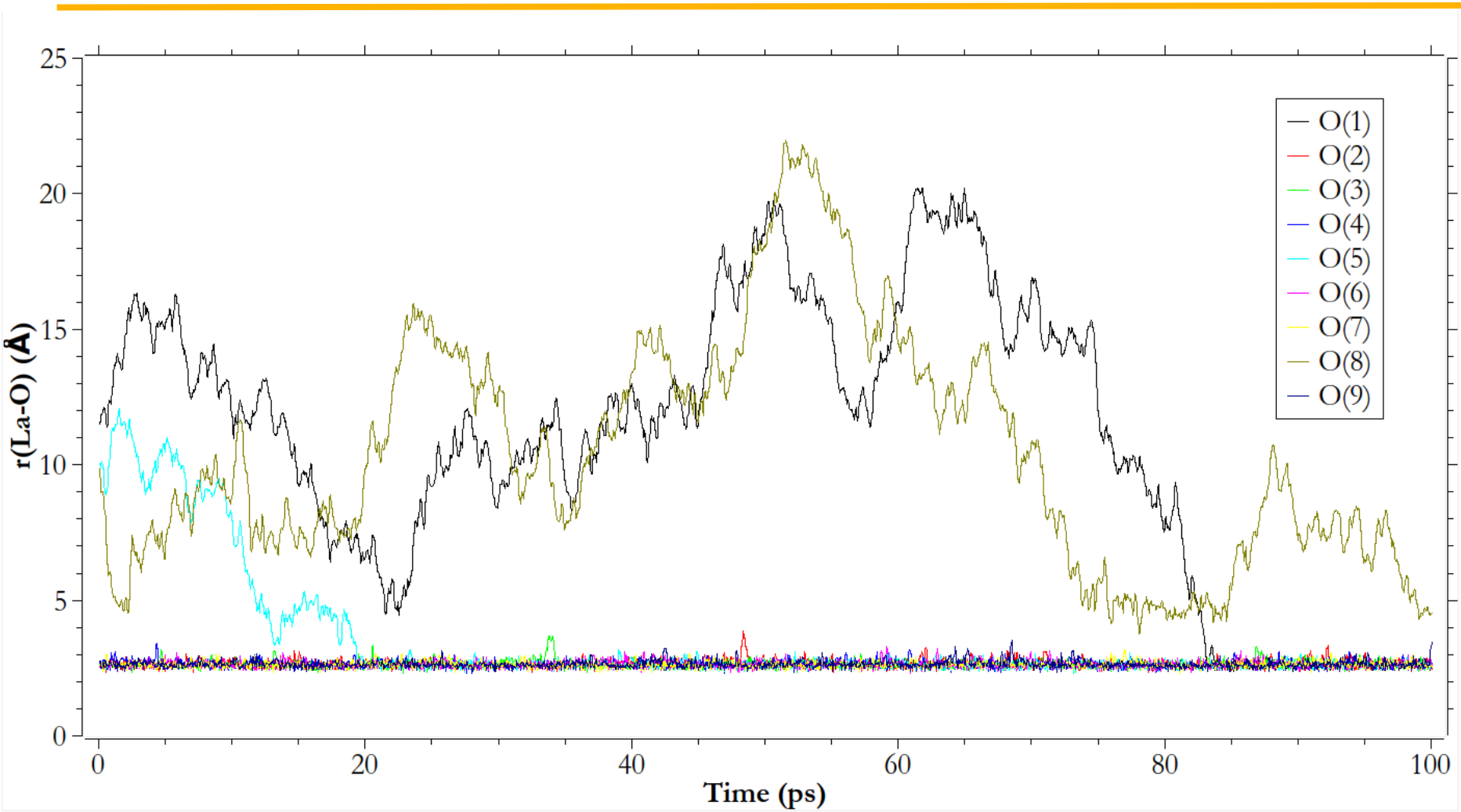
40Å x 40Å x 40Å
periodic cell
2040 water molecules, one
La^{3+} ion (cyan)

250ps NVT equilibration
250ps NPT simulation
1ns NVE simulation

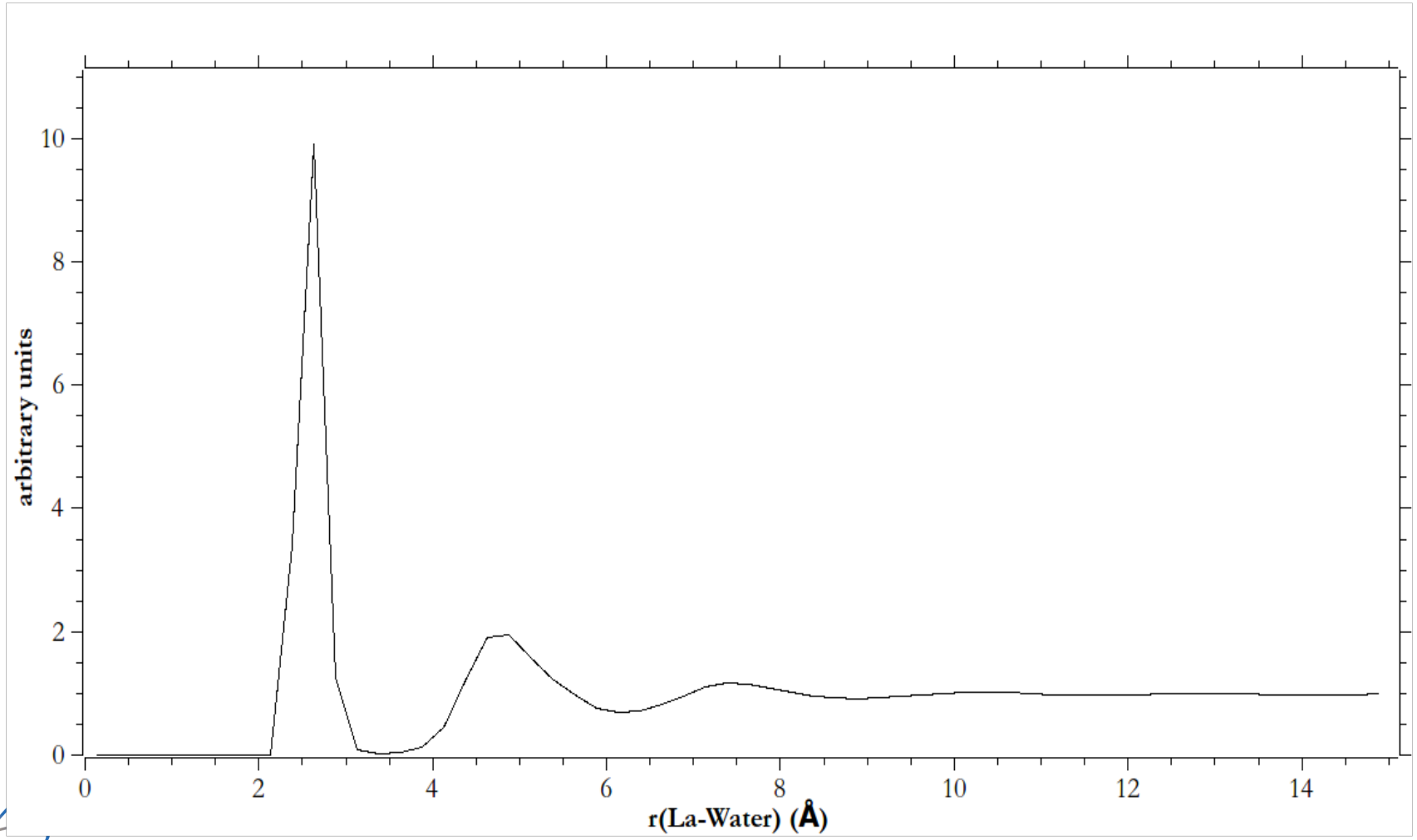
Diffusion


System
La3+
mean squared displacement (Å2)
time (ps)
0
100
200
300
400
500
600
700
0
20
40
60
80
100

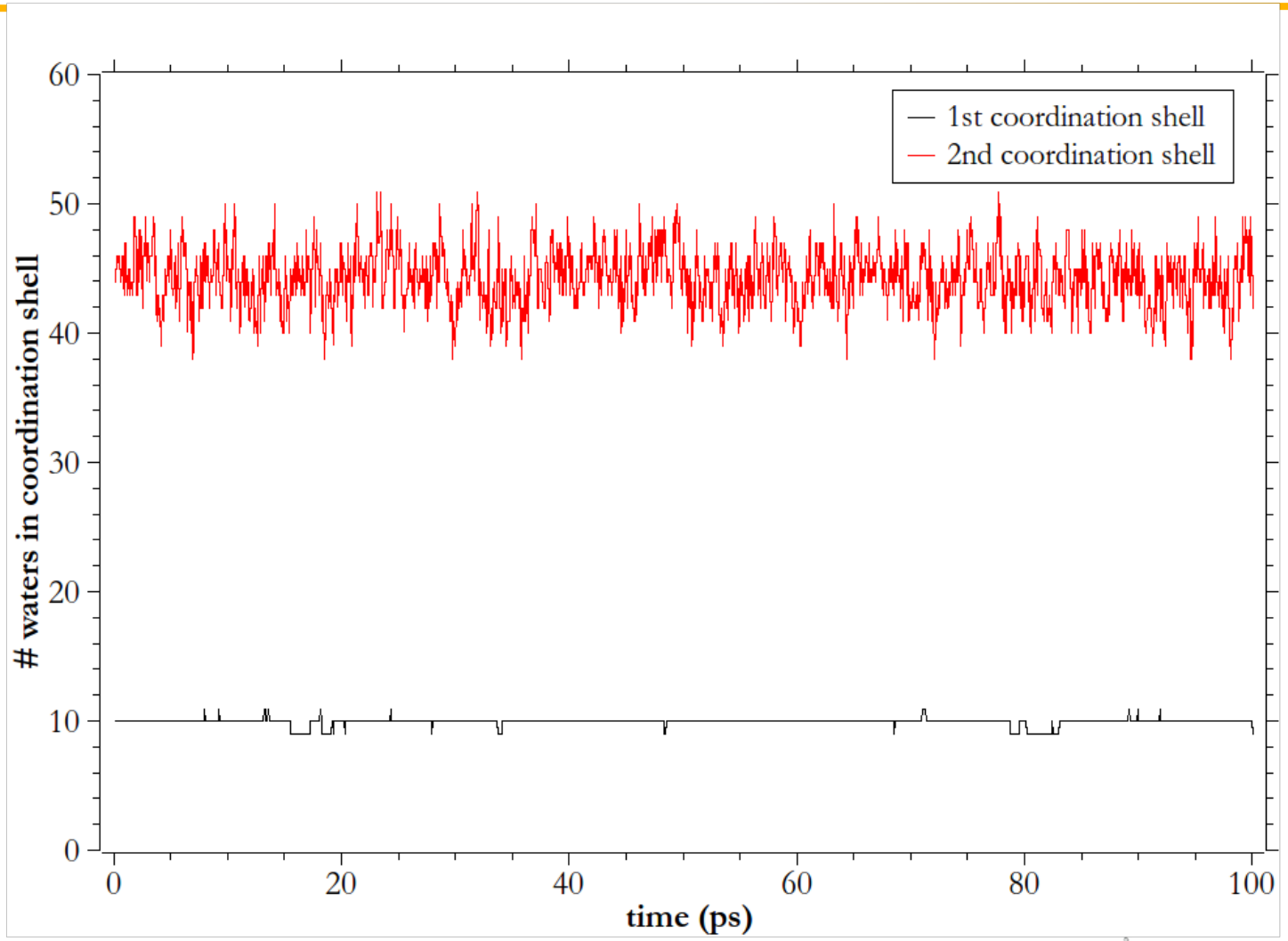
Do waters change coordination shells?



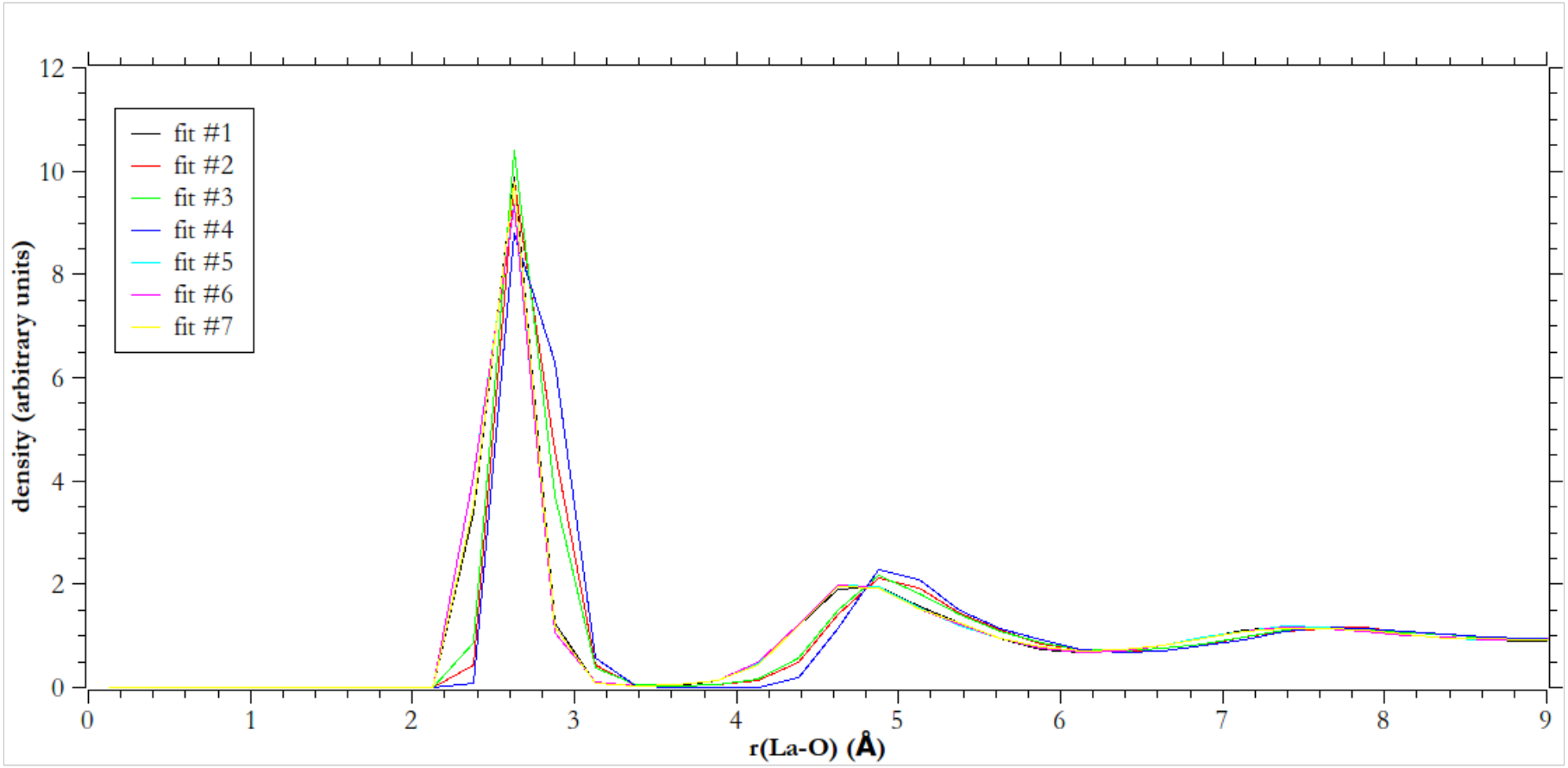
La-water radial distribution function



Coordination number



Changes in La-O radial distribution function with fit



Case Study (3) : Determination of the structure of amorphous metakaolin by neutron pair distribution analysis methods

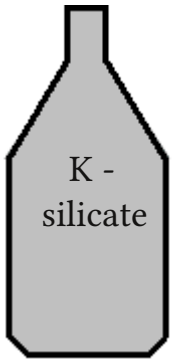
- to determine the atomic structure of metakaolin, an amorphous geopolymer precursor
- To understand the evolution of metakaolin-based geopolymeric gel at the atomic level

Dr. Claire White, Los Alamos National Laboratory

Making a geopolymer

- paste = aluminosilicate solid + alkaline solution

  { fly ash, slag, metakaolin, synthetic powder } → pH ~ 11-14

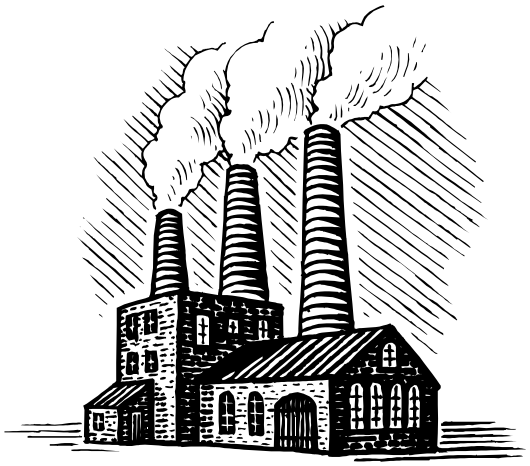


- paste mixed with sand and aggregate ⟶ concrete

The need for geopolymers

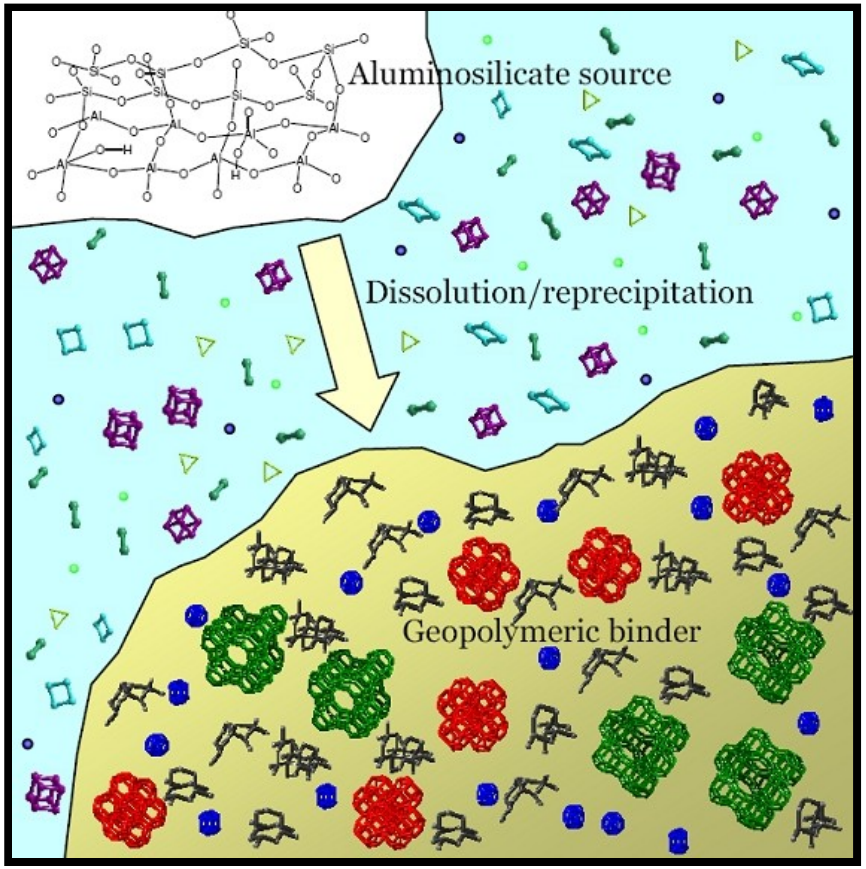
- Low-CO_2 alternative to Portland cement
  - Cement is: ~5-8% of global CO_2,
  - Geopolymers offer ~80-90% reduction
    - on a per cubic metre of concrete basis
    - not yet optimised!

→ Genuinely "green" concrete!



Geopolymer structure

Precursors - amorphous

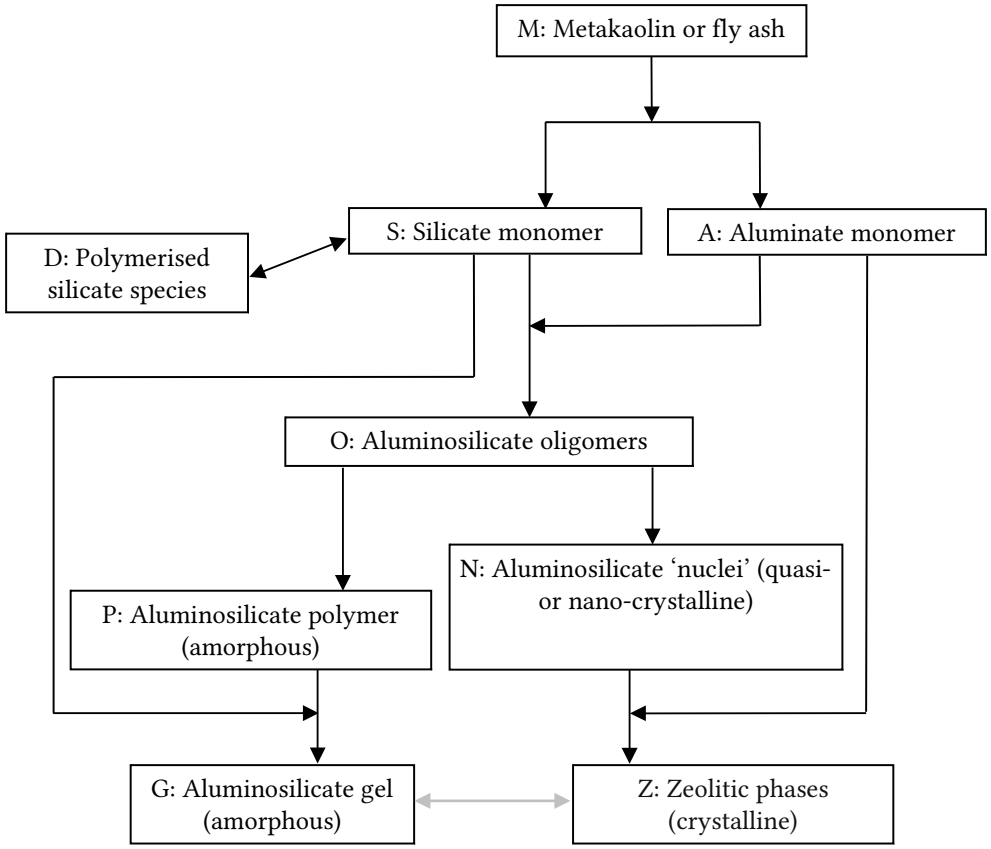


Binder - amorphous

Cover page of Chemistry of Materials, **17** *(12)* 2005

Courtesy of John Provis, GMPG graphics expert

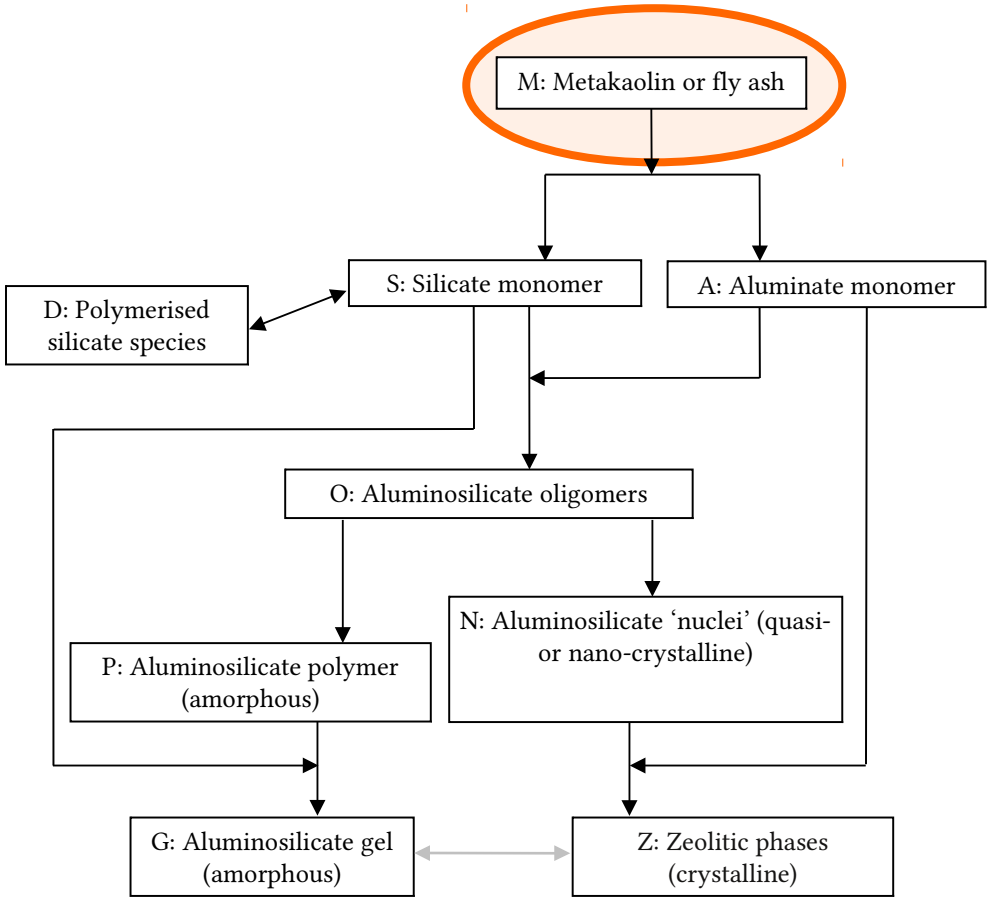
A complex process: in detail



J. Provis and Van Deventer, (2007) Chem Eng Sci, 62:2318

A complex process: in detail

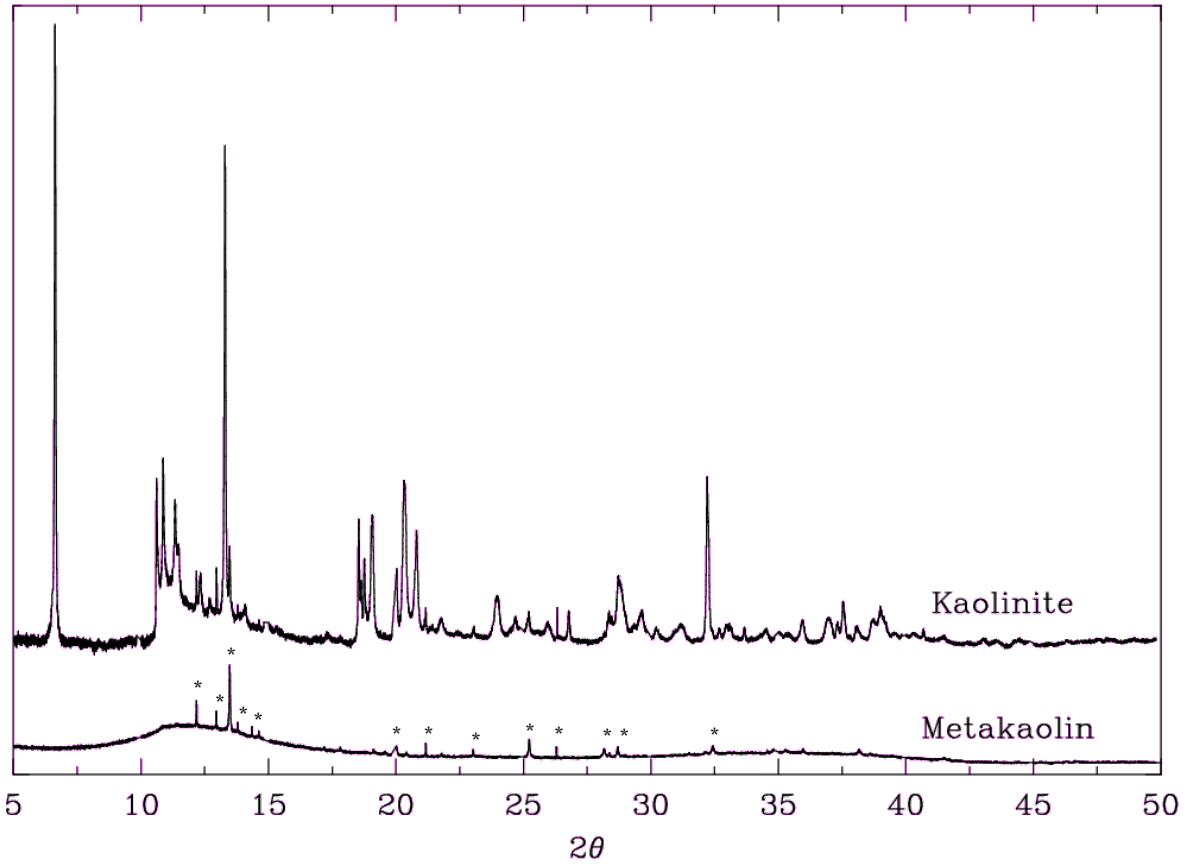
Metakaolin formation



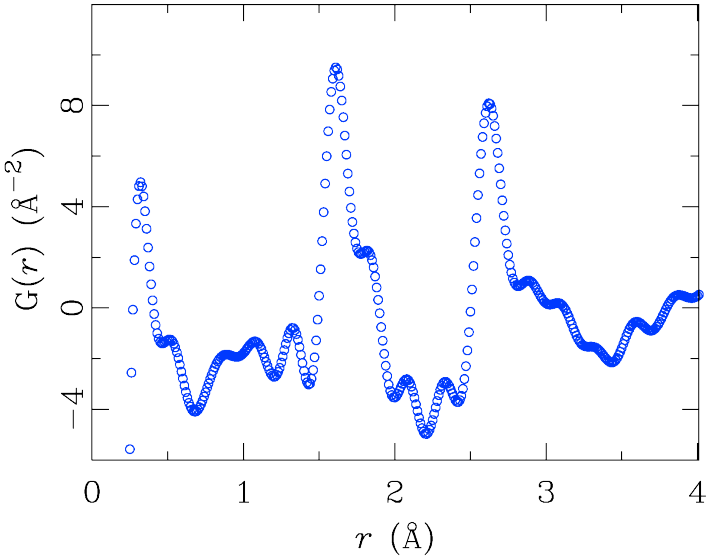
J. Provis and Van Deventer, (2007) Chem Eng Sci, 62:2318

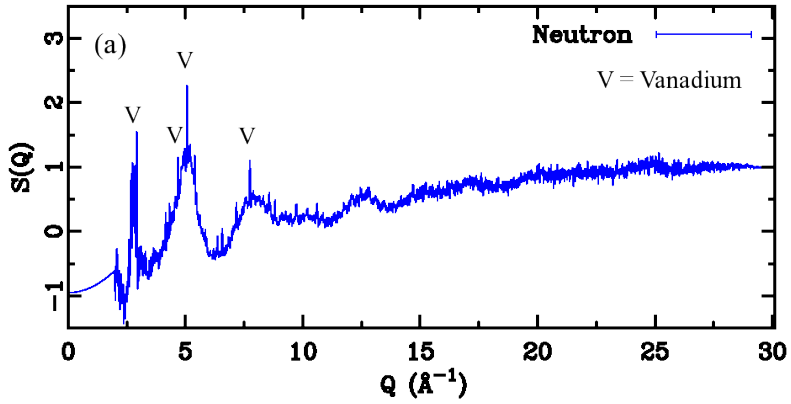
Formation of metakaolin

- Formed by the calcination of crystalline kaolinite, dehydroxylation
- product is amorphous

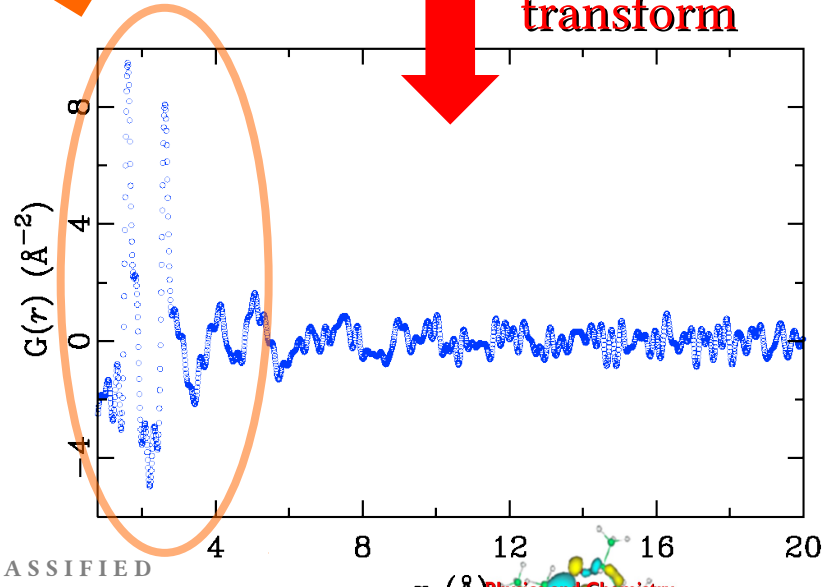


Metakaolin neutron pair distribution function data





Fourier transform



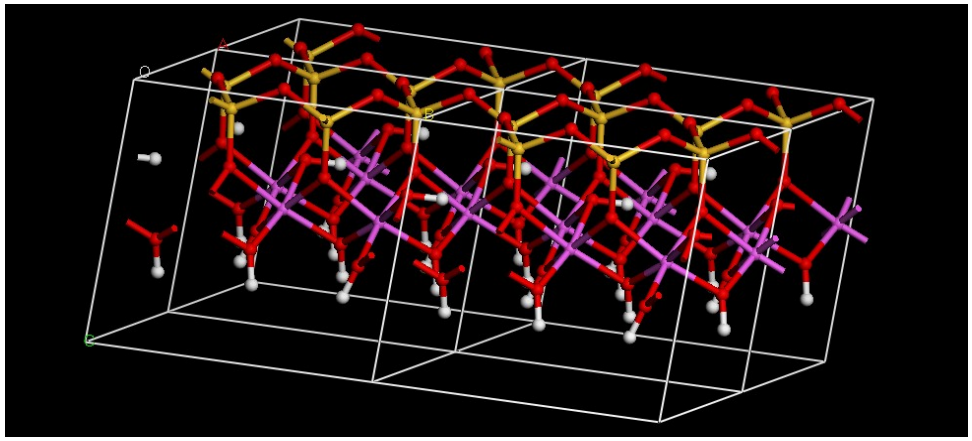
Method

- Metakaolin structure analysed using DFT
  - Parameters for DFT selected by validation using kaolinite
  - Energy minimization using DMol3 software
  - Dynamics calculations using VASP software
  - BLYP, “Double-Numerical with polarisation” basis set

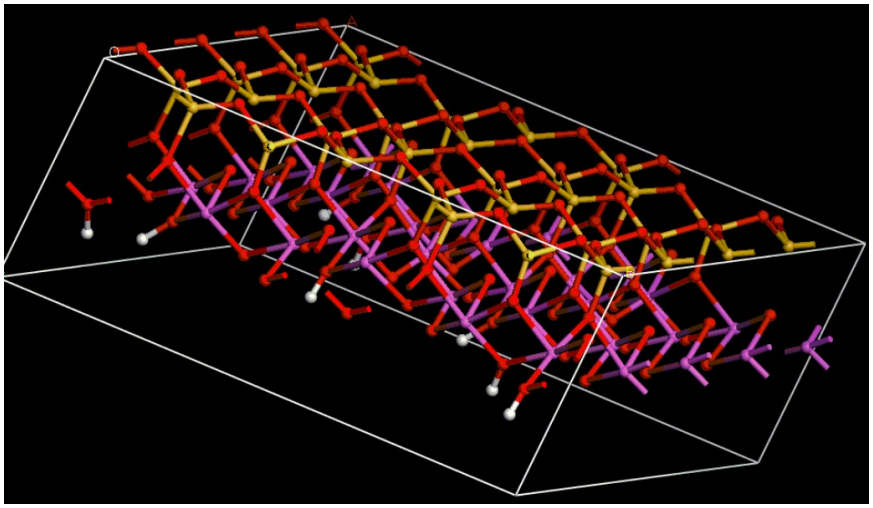
- Metakaolin structure obtained by energy minimization from supercell with correct stoichiometry
  - Supercell required – 282 atoms
  - Metastable structure – more than one configuration satisfies the lowest energy state

* C.E. White, J.L. Provis, D.P. Riley, G.J. Kearley, J.S.J. van Deventer, *J. Phys. Chem. B*, **2009**, *113*, 6756-6765

Initial Structural Model

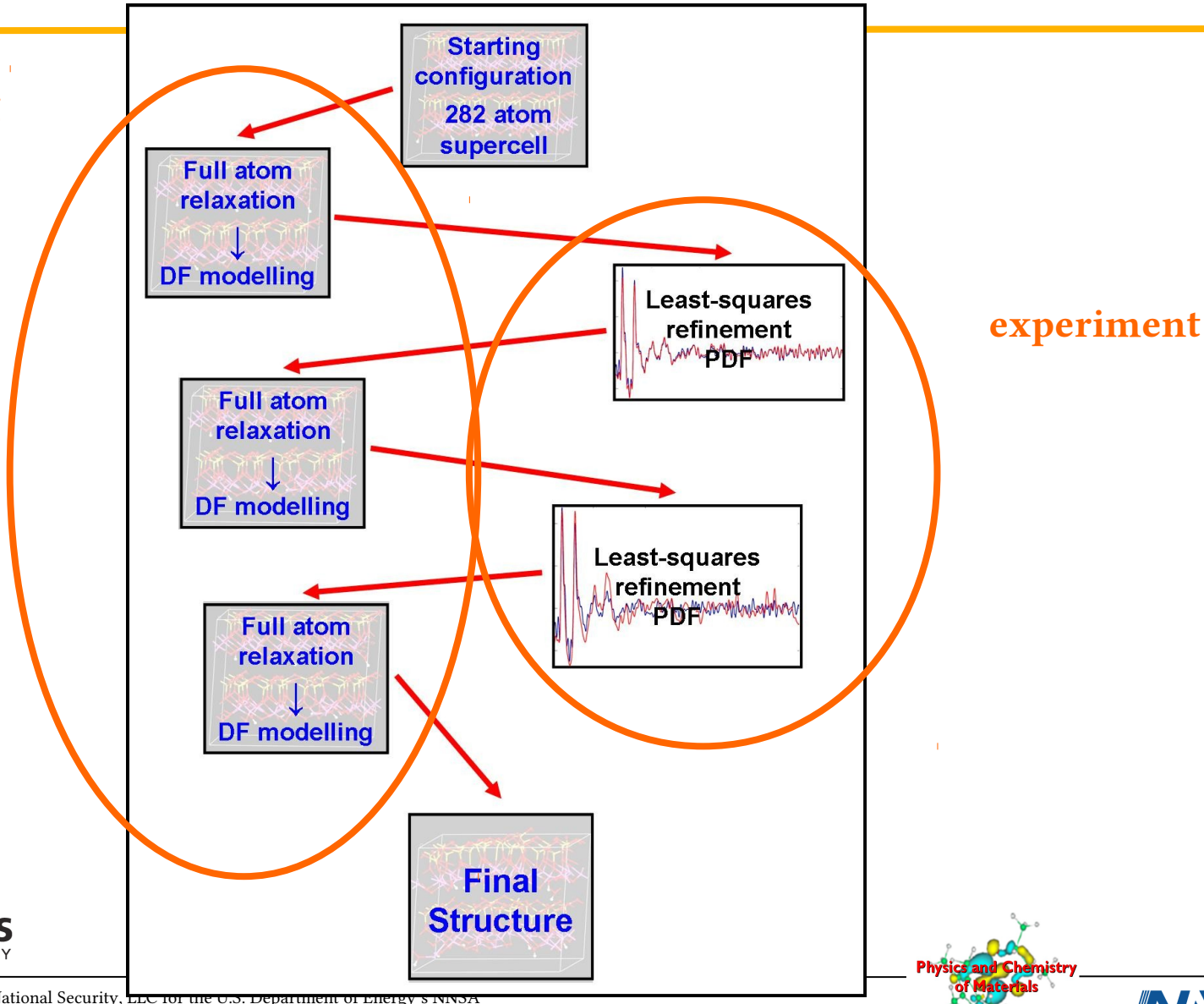


kaolinite

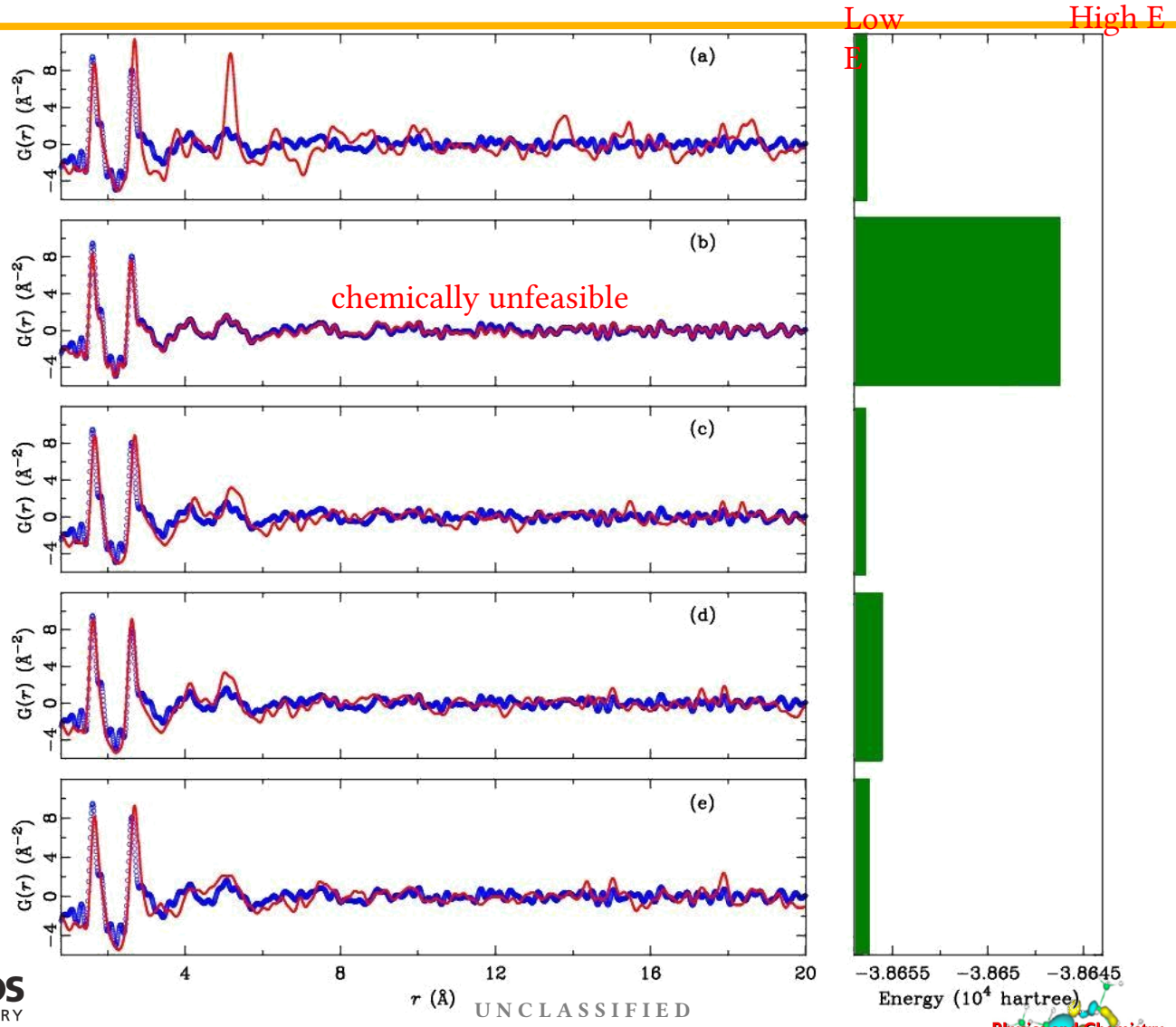


metakaolin

Methodology

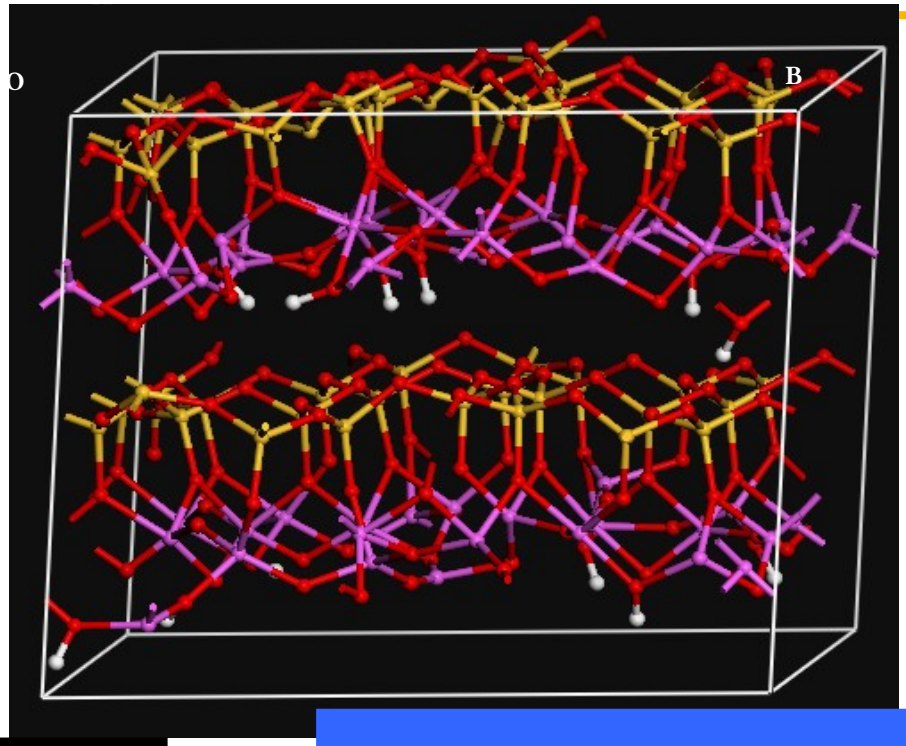


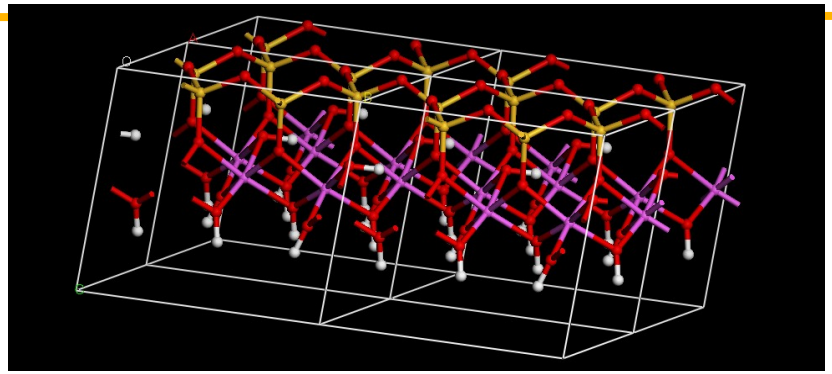
Illustrating the iterative process

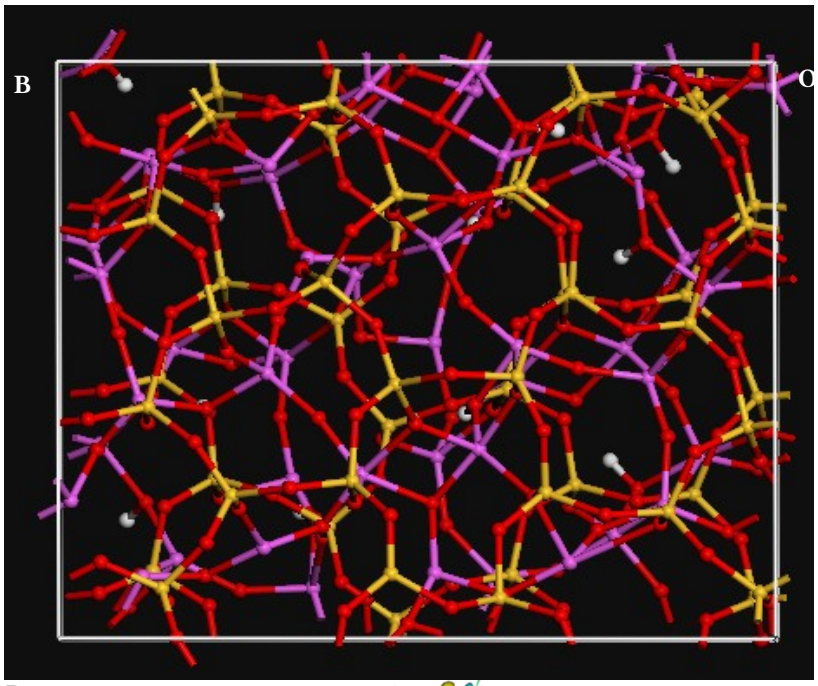


Final Structural Model

Kaolinite





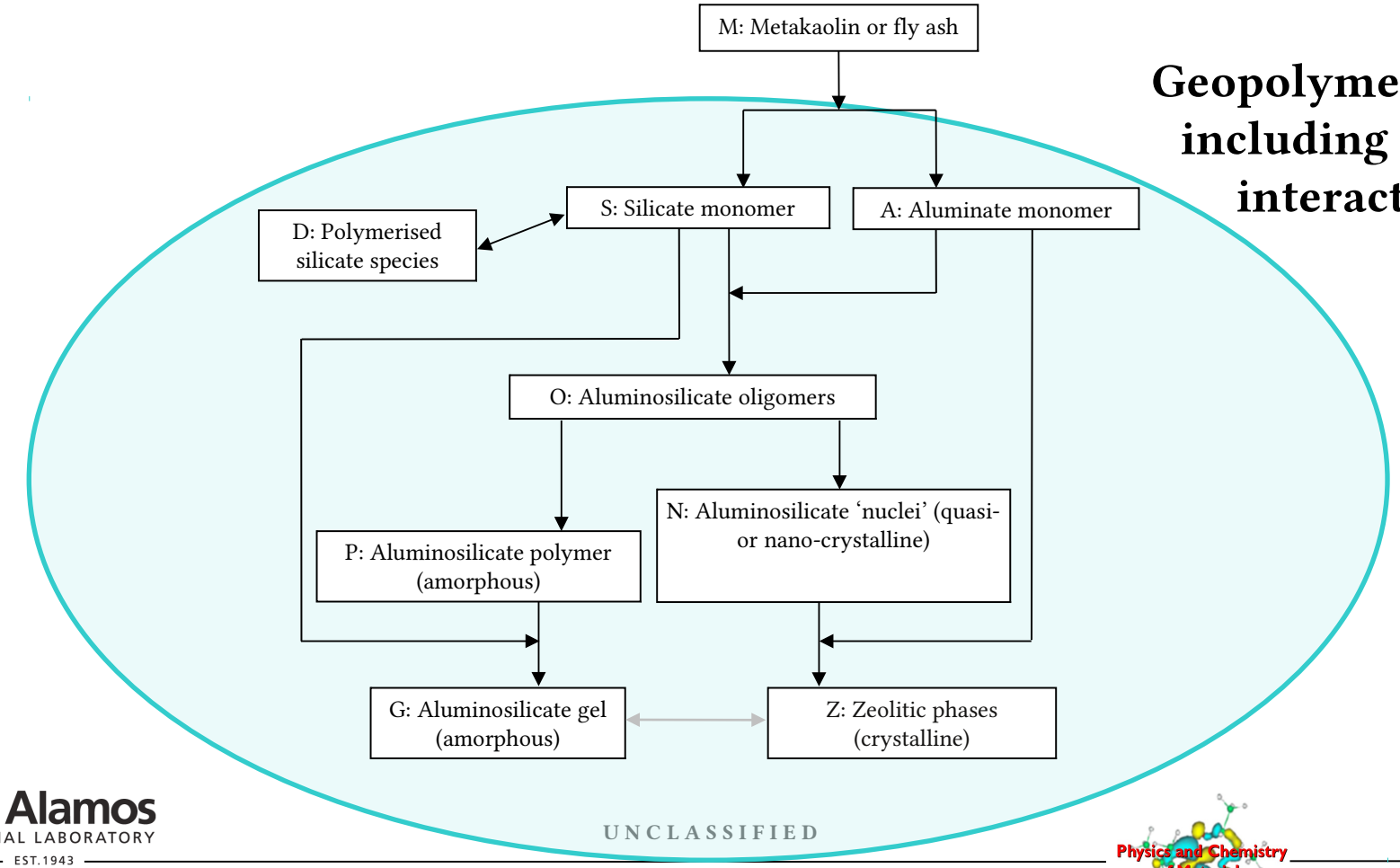


Silicon
Aluminum
Oxygen
Hydrogen

Metakaolin

C.E. White, J.L. Provis, T. Proffen, D.P. Riley, J.S.J. van Deventer, *Phys. Chem. Chem. Phys.*, **2010**

A complex process: in detai



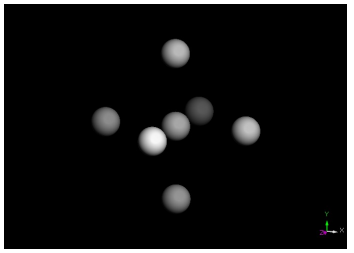
Geopolymerization, including species interactions

J. Provis and Van Deventer, (2007) Chem Eng Sci, 62:2318

Monte Carlo simulation: geopolymerization

Events being modeled

- Dissolution of metakaolin
- Polymerization of silica and alumina species

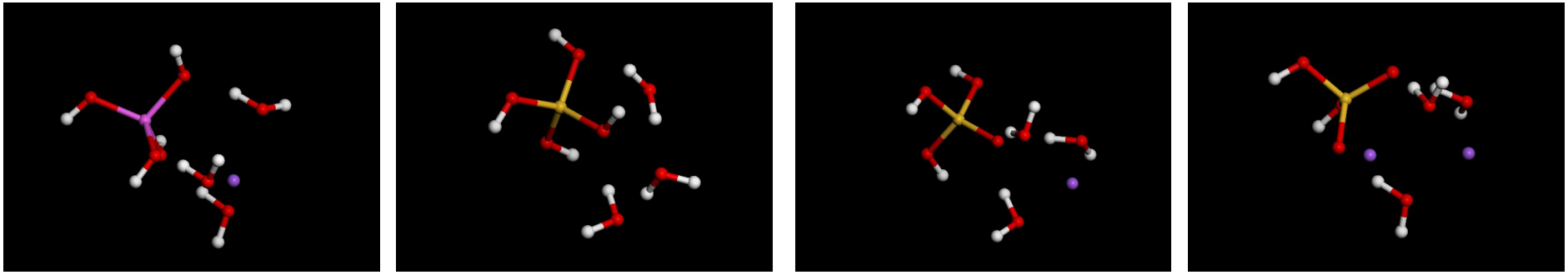


Method

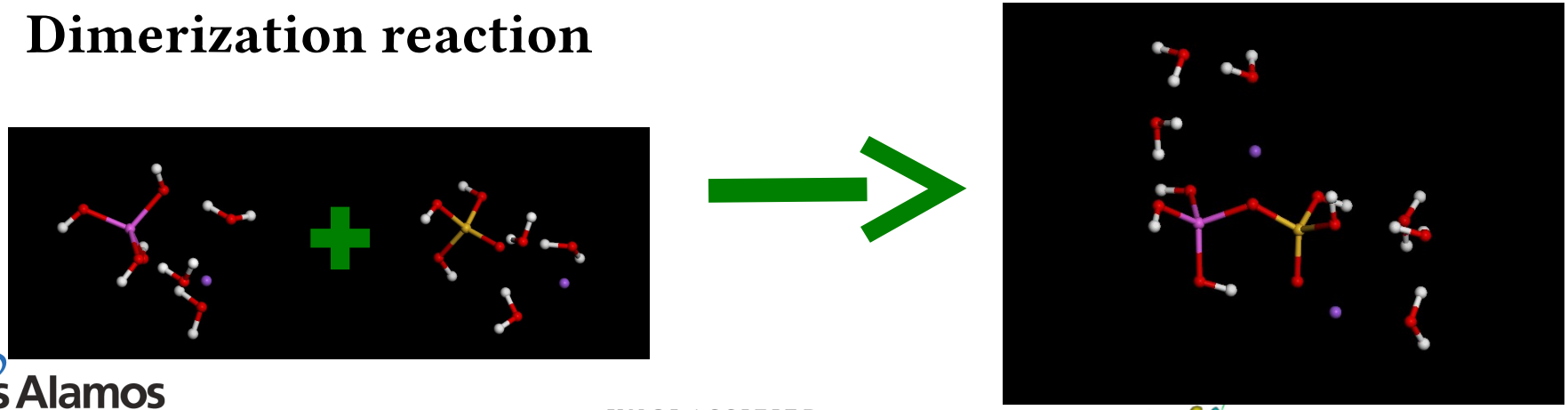
- Coarse-grained model
  - Cubic lattice, 10×10×10 100×100×100 1000×1000×1000
  - Lattice points can be occupied by monomeric species
  - Species can bond to neighboring sites, swap processes
- Metropolis algorithm
  - Effects of temperature, provides probability of unfavorable event occurring
- Each species and bonding of species have associated Gibbs Free Energy

Energies of species from density functional theory

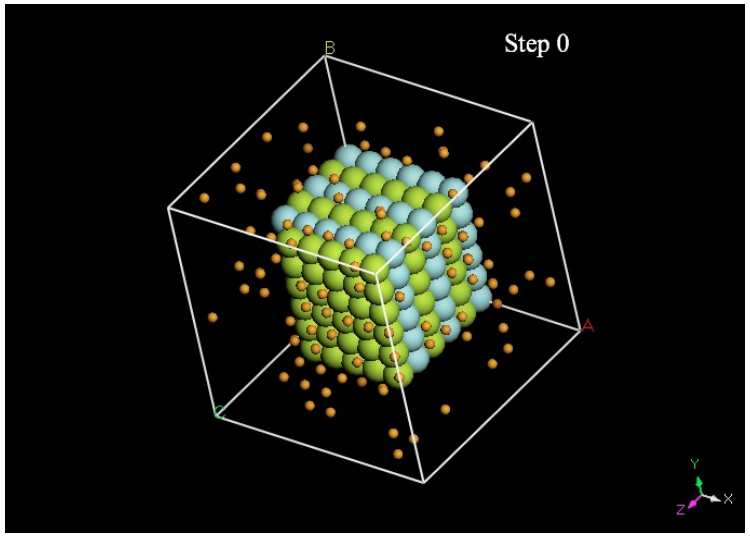
Monomeric species

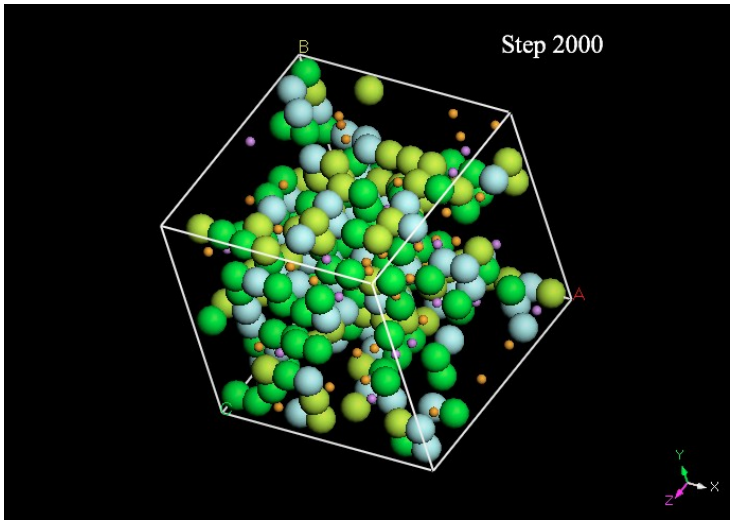


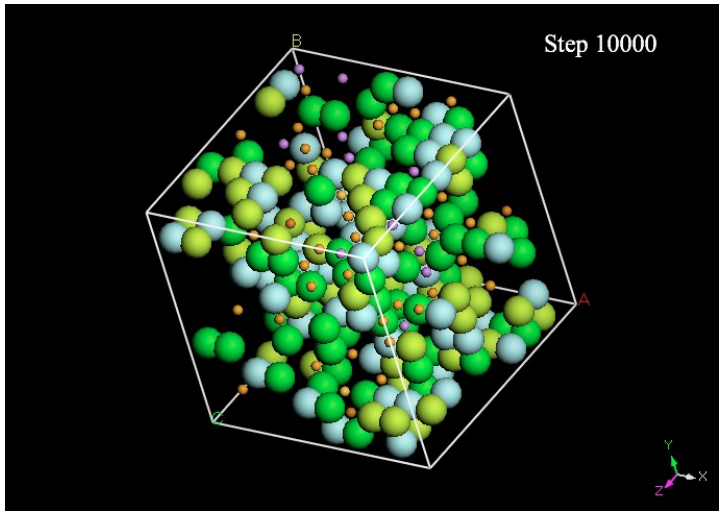
Dimerization reaction



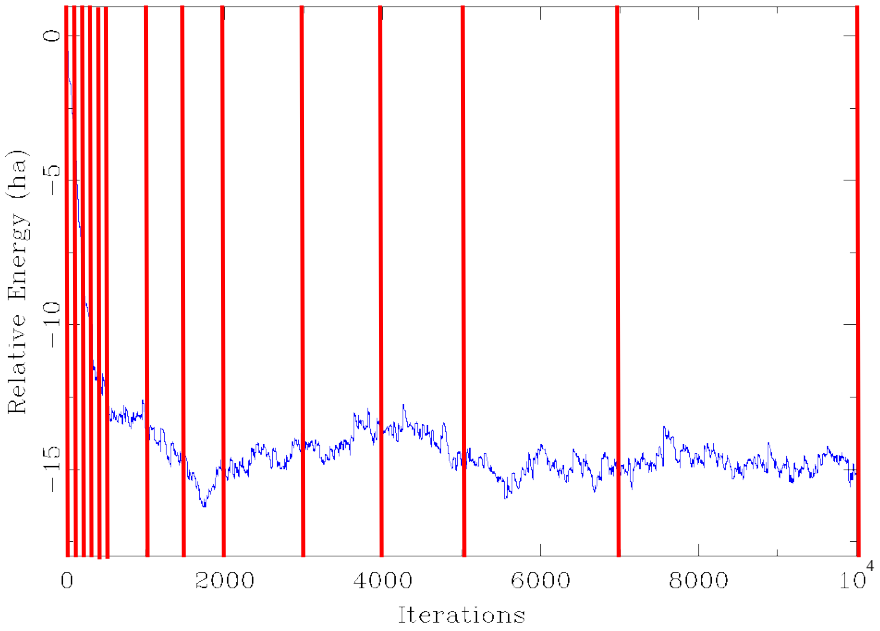
Evolution of structure



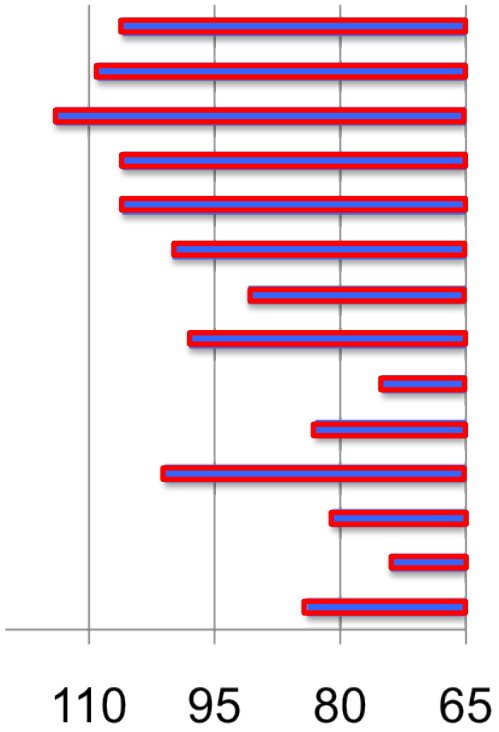




Evolution of structure



Number of unbonded monomers



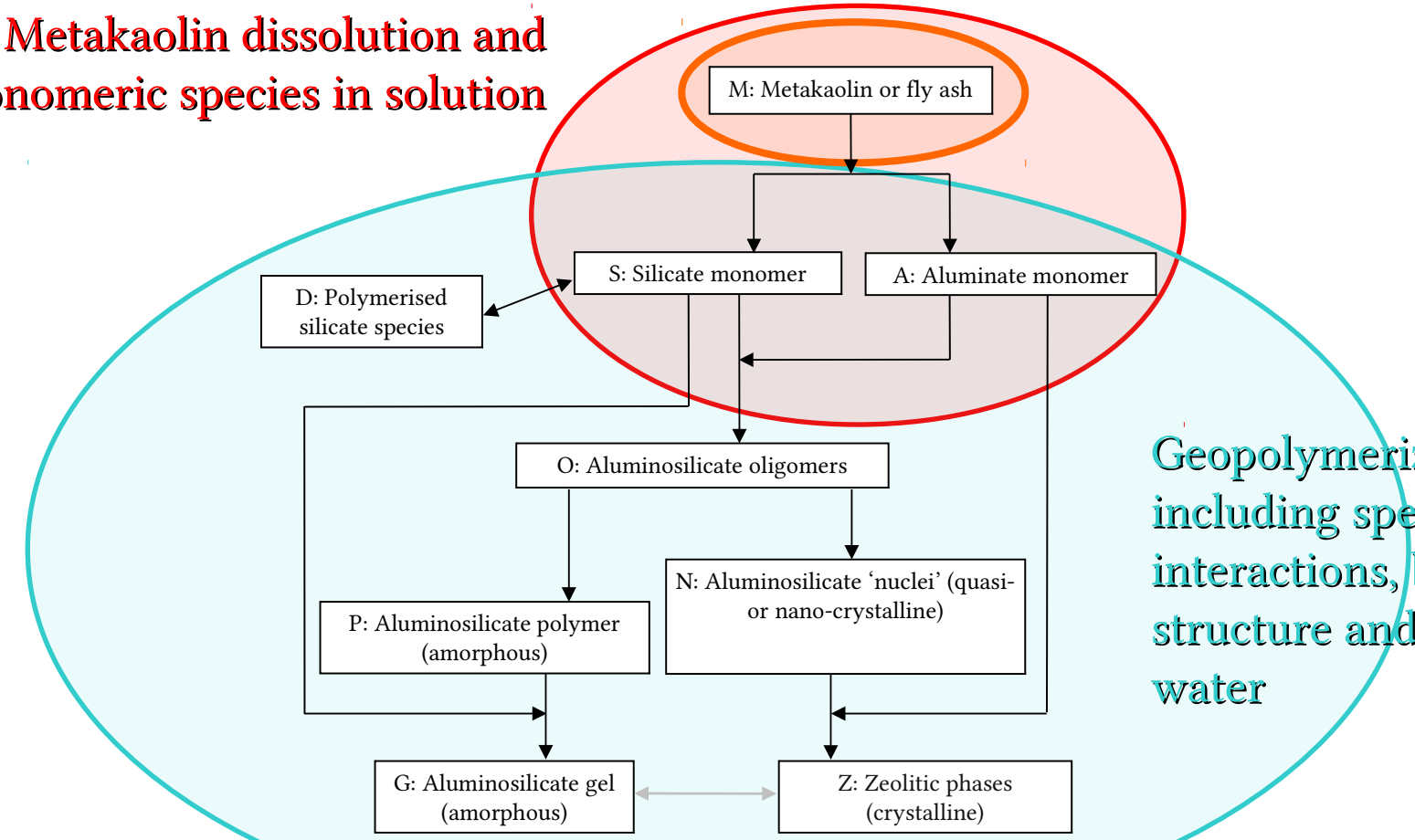
Monte Carlo simulation: discussion

- Metakaolin dissolution and polymerization of aluminosilicate gel can be modeled using coarse-grained Monte Carlo simulations
- Large clusters evolve, mostly Si-O-Si and Si-O-Al linkages
- Al-O-Al linkages present (small percentage)

A complex process: in detail

Metakaolin structure and formation

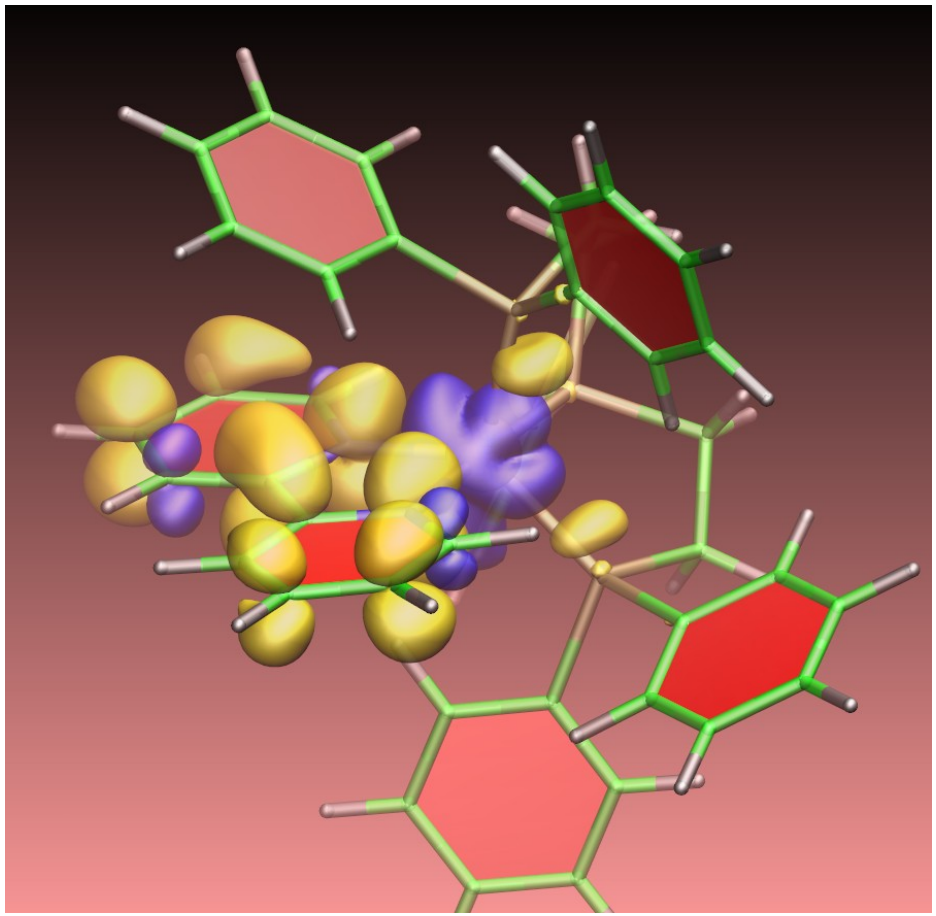
Metakaolin dissolution and monomeric species in solution



Geopolymerization, including species interactions, binder structure and role of water

J. Provis and van Deventer, (2007) Chem Eng Sci, 62:2318

Conclusions



- electronic structure calculations can be useful to interpret a wide variety of neutron scattering data
- but, use the correct tool for job, and be aware of accuracy and limitations of models
- we can use them to perform calculations on small models
- to develop forcefields for running larger scale calculations, such as molecular dynamics
- and to obtain relative energetics for input into longer length scale, coarse grained simulations

Thanks for listening!

Questions? Comments?