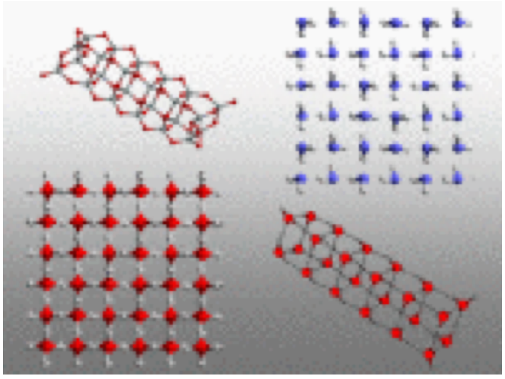
Modelling the structures and reactivity of silica and water: from molecule to macroscale



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September, 17th 2007

1 Workshop details

1.1 Details

Timing

Number of days : 3
Start : 2007-09-17
End : 2007-09-19

Location of the activity

CECAM
46 allée d'Italie
69007 Lyon
France

1.2 Description

The reactions between silica and water are central to a spectrum of diverse problems ranging from the subtle interactions of molecular/cluster species in hydrothermal silicate synthesis and biomineralisation to geochemical phenomena involving erosion and deposition at a macroscopic level. The scale and structure of the respective water and silica species involved in such processes, and further how these two factors are are influenced by external conditions, is critical to a full understanding of reactive silica-water systems. Computational modelling methods are now well established to deal with many aspects of water and silica as separate systems and such approaches are also increasingly contributing to our our detailed knowledge about interacting water-silica systems. The important question of the relevance of the scale and structure in interacting silica-water systems is, however, largely unexplored by computational means.

Considering scale, molecular silica is soluble in excess water yet nucleates to form silica materials from solution. Structurally, such nucleating silica species may be induced to form symmetric clusters and crystals, whilst bulk crystalline silica surfaces may in turn induce ordered arrays of absorbed water molecules. In these examples, water can facilitate the rearrangement and ordering of silica species and in turn, it can be ordered by the silica substrate. Furthermore, depending on the surface structure of bulk silica, it may act as a strong dissociating absorber of water or hardly interact at all. The tendency of both water and silica, when strongly interacting, to organise in mutually compatible ways is likely linked to a more fundamental propensity of both systems to display tetrahedral order in their respective multifarious bulk phases. Formally regarding bulk silica and water of as built up from corner-sharing tetrahedral units (SiO4 and OH4 respectively) at once helps to rationalise the links between the two systems in terms of their physical properties but also naturally gives rise to a common structural heritage via considering corner-sharing tetrahedral interactions. Both systems, for example, display analogous crystal structures; the clathrate hydrate water ices and the all-silica clathrates perhaps being the most well known. More remarkably is the possibility of crystals from frameworks consisting of water and silica species to form hybrid hydrate-silicate frameworks.

Requested Support

Simbioma

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4 Presentation list

Stress, Fracture, and Hydrolytic Effects in Nanoscale Silica Systems

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Abstract

Structures, energetics, and properties of realistic material and biological systems depend significantly on their environments. Water is an almost ubiquitous example of an environmental component.

Its presence in materials simulations complicates matters: the resulting systems do not present clean, well-abstracted problems.

An important category of environment-dependent situations is chemo-mechanical phenomena, i.e. material phenomena for which the inter-dependence among reactivity, bond breaking, stress, and solvents is crucial. To obtain predictive simulations, (i.e. more than sophisticated parameterization of experiment) requires methods capable of chemical realism and scale parity (comparable quality methods at all scales). Real predictive materials research also requires software that is reliable and useful for non-experts.

Hydrolytic weakening of silica long has been known in geology as a significant example of chemomechanical phenomena but the atomic-level mechanisms nevertheless remained obscure. The advent of silica nanostructures has provided a new stimulus to studying those. This talk will summarize the work of a large, multi-university collaboration on the problem. A brief survey of multi-scale methods (on-the-fly location of the quantum mechanical force region, transfer Hamiltonian and orbital-free DFT approaches to better quantum mechanics, consistent embedding potentials, the PUPIL software framework for systematic, automated inter-operation of existing codes) will be given. Then results from various teams within our collaboration on tensile and bending stress of silica nanotubes, straininduced behavior in water interactions with silica nanochains and nanotubes, and the relationship of these behaviors to simulation results of water at a silica surface will be presented. A key issue in the hydrolytic induction of fracture in these systems is the number of water molecules adjacent to the fracture site.

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PERIODIC B3LYP STUDY OF HYDROXYLATED CRYSTALLINE SILICA SURFACES AS SOURCE FOR FORCE FIELD DEVELOPMENT

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Coauthor(s) : A. Pedone, F. Musso and M. Corno

Abstract

PERIODIC B3LYP STUDY OF HYDROXYLATED CRYSTALLINE SILICA SURFACES AS SOURCE FOR FORCE FIELD DEVELOPMENT

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A B3LYP study of the properties of hydroxylated crystalline silica surfaces has been performed on periodic slab models derived from a-quartz, a-cristobalite and a-tridymite. All calculations have been performed with the CRYSTAL06 code[1], using B3LYP hybrid functional and Gaussian basis sets of double zeta plus polarization quality.
The study of each surface model includes: i) structure optimization; ii) the harmonic and anharmonic frequency of the hydroxyl groups; iii) the simulation of both IR and Raman spectra in the OH region; iv) the relative thermodynamic stability of the considered surfaces.
On selected models, the present results have been used to parameterize an entirely ab-initio new shell-ion model potential force field for silica-based materials which is able to incorporate the hydrogen bond features occurring between surface OH groups. The new force field has been tested by comparing molecular mechanics structures, vibrational frequencies and thermochemical data computed with the GULP code [2] with those computed at B3LYP, showing encouraging agreement.

Key References

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Simulation of the grafting of organosilanes at the surface of dry amorphous silica

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Abstract

Quantum mechanics/molecular mechanics (QM/MM) approaches are currently used to describe several properties of silica-based systems, which are local in nature and require a quantum description of only a small number of atoms around the site of interest, e.g., local chemical reactivity or spectroscopic properties of point defects. We present a QM/MM scheme for silica suitable to be implemented in the general QM/MM framework recently developed for large scale molecular dynamics simulations, within the Quickstep approach for the description of the quantum region. Our scheme has been validated by computing the structural and dynamical properties of an oxygen vacancy in quartz, a prototypical defect in silica [1]. We have applied this scheme aiming at getting insight onto the reactivity of the 2M ring with organosilanes usually used as coupling agents in the coating of the optical fibers, we have studied by ab-initio simulations the reaction of tetraethoxysilane (Si(OCH2CH5)4, TEOS) with a 2M ring or a surface silanol to assess the difference in reactivity of the two surface sites toward organosilanes. We have chosen TEOS as a prototypical organosilane, since it has the same functional groups (ethoxy) of most organosilanes used in the optical fibers technology. A model of the amorphous silica surface has been generated by quenching from the melt within classical molecular dynamics simulation [2]. Ab-initio metadynamics simulations have been performed to identify the reaction paths for TEOS adhesion [3]. It turns out that the activation energy for the grafting on the isolated silanol is sizably
larger than the barrier for adhesion of TEOS on the 2M ring.

Key References

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On the interaction between silica oligomers and template/water molecules.

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Abstract

We address the question how the interactions between silica precursor species and tetrapropylammonium ions evolve during the nucleation process. The simulations focus on three silica oligomers Si11 (as in the work by Kirschhock et al. [1]) that are proposed as intermediates for the formation of the channels inside the MFI structure. The method applied was the Molecular Dynamics technique and the interatomic potential used are those of the Universal ForceField as implemented in Cerius2 software. Formal charges have been assigned to the N atoms and to selected O atoms of the Si11 oligomers. The electrostatic interactions has been corrected with the dielectric constant of water.

We have found that water shell layers surrounding the silica species can be distinguished. There is only attractive interaction between positively charged template molecule and silica oligomers, when the latter carries a significant charge. Both these observations are in agreement with the results of work of Mora-Fonz et al. [2].

As far as interactions between silica oligomers and template molecules are concerned: we compare four possible cases: with one, two, three and four -Si-O-Si- bonds between two of Si11 oligomers (which are thus forming Si22 structure). The interaction strength (excluding interactions with H_2O) is increasing from -220 to -440 kcal/mol (calculated for all nine template molecules, with no correction of dielectric constant) along with the creation of second bond between two Si11 oligomers, then decreases to -360 kcal/mol when three bonds are created. However when the final structure of channel is fully formed, the interaction further decreases to -70 kcal/mol, which suggests the removal of TPAOH from the formed channel. This observation is supported by the increased number of water molecules in close contact with silica oligomers compared to the initial structure with no channel present. After that, the template molecule assumes the position equivalent to that in the MFI channel cross-section.

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To be or not to be corner sharing? That’s the question

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Abstract

Silica and water (ice) are just two examples of tetrahedral materials. Other exponents of this diverse class of materials include: oxides (GeO_2), sulphides (SiS_2, GeS_2), selenides ($SiSe_2$, $GeSe_2$), phosphates ($AlPO_4$, $BePO_4$, $GaPO_4$, $FePO_4$), arsenates ($AlAsO_4$, $GaAsO_4$) and anhydrous metal salts ($ZnCl_2$, BeF_2, $BeCl_2$, $BeBr_2$, BeI_2). All these materials have a rich landscape of structurally different polymorphs and a strong tendency to form locally disordered glasses in common but differ

in which particular polymorphs are obtained experimentally. Furthermore, some materials have a preference for corner sharing tetrahedra (e.g. SiO2) and others for edge sharing tetrahedra (e.g. GeSe2). In our talk we will show how a combination of experimental information and periodic Density Functional calculations can help us to understand these differences between otherwise so similar materials.

Morphing soft spheres to water and beyond: structural preferences of clusters

Bernd Hartke
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Abstract

We elucidate local structural preferences in small water clusters by examining a series of global minimum cluster structures (2-40 molecules). There is no simple build-up pattern. A few building blocks can be identified, but occur in seemingly unpredictable ways.

This is contrasted with the well-known series of global minimum cluster structures for the isotropic Lennard-Jones potential. Here, the laws for building successively larger clusters are rather well understood and are comparatively simple.

The connection between these extreme cases is made by "morphing" the Lennard-Jones potential quasi-continuously into a standard water potential (and also beyond this point), and keeping track of the structural changes. We hope that this ongoing work will lead to an improved understanding of the "confusing" structural sequences exhibited by small water clusters.

Computational studies of alpha-quartz: classical force field parameter development and ab initio molecular dynamics studies of the reconstruction of the surface.

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Abstract

Interactions of pulverized crystalline silica with biological systems, including the lungs, cause cell damage, inflammation, and apoptosis. To allow for the interactions between silica surfaces and biological molecules, most notably lipid bilayers, to be studied via empirical methods, CHARMM force field parameters were developed for quartz. The CHARMM protocol to optimize force field parameters, which includes reproduction of experimental geometries, ab initio vibrational spectra and interactions between model compounds and water was followed, thus ensuring compatibility with the existing parameters for proteins, nucleic acids and lipids. Properties analyzed include the variation of the density of water molecules in the plane perpendicular to the surface, disruption of the water H-bond network upon adsorption, and space-time correlations of water oxygen atoms in terms of Van Hove self-correlation functions.
Reconstruction of freshly fractured quartz surfaces was studied using ab initio molecular dynamics methods. Calculations were performed on the (011) surface of alpha-quartz. Pristine surface was obtained by homolytic cleavage of a-quartz, thus leaving exposed SiO• radicals. Spontaneous reconstruction was allowed for 1 ps, after which different clusters were formed. Details of the reconstruction and resulting surface moieties will be presented.

A B3LYP study of the interaction of water with differently hydroxylated silica surfaces

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Abstract

This study is an attempt to describe at a molecular level the interaction of water on silica surfaces, with particular emphasis on the role of the different species of surface hydroxyls. The aim is to model in a realistic way the behaviour of a real amorphous surface. An amorphous surface is characterized by a random arrangement of isolated, geminal and interacting hydroxyls, whose relative abundances were shown to depend on the thermal treatment of the surface.

An amorphous object is by far too big and complex to be treated at an ab initio level. The approach followed in this work was to design several ideal crystalline surfaces, each of which sports a periodic arrangement of a single species of hydroxyl. The crystalline surfaces are simple enough to be treated at ab initio level within a periodic approach. All the calculations reported here were done with the CRYSTAL06 code, which allows the treatment of both molecules and periodic systems with local Gaussian basis sets. The B3LYP hybrid Hamiltonian and a 6-31G(d,p) basis set were adopted.

The selected framework for surface design was the edingtonite (a polymorph of quartz), because surfaces with isolated, geminals and interacting hydroxyls can be easily defined. On the free fully optimized structures (internal coordinates and lattice parameters) the interaction with water was evaluated, both in terms of energy of interaction and IR frequencies.

After studying separately each surface, a comparison with experimental measurements on amorphous silica can be performed by convolving all the calculated data together. The calculated interaction energy, DE, spans from 30 kJ/mol per water molecule (isolated OH) to 60 kJ/mol (interacting OH), in reasonable agreement with microcalorimetric data. The increase of DE passing from isolated OH to self interacting OH indicates a relevant hydrogen bond cooperative effect.

A simulated IR spectra, built starting from the calculated frequencies and intensities, reproduces nicely the OH stretching region of the experimental spectra and its evolution at different water loadings and thermal pretreatment.

A model of fully dehydroxylated surface was also derived. It appears as a hexagonal arrangement of unstrained siloxane bridges. As expected, this surface has a hydrophobic behaviour, i.e. the interaction energy per water molecule is close to zero, and at high water loading a rearrangement takes place, leading to an ice like layer in very weak interaction with the silica surface.

Silicate-Water lnteractions in the Nucleation of Pure Silica Zeolites

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Abstract

In this work we calculate the relative strength of the water water, water silicate and silicate silicate interactions. An understanding of these interactions may help to assist in describing features of the clusters present during the hydrothermal nucleation of zeolites, and explain the low solubility of monosilicic acid (Si(OH)4).

The interactions analysed here are very difficult to study experimentally, with the exception of the water clusters in gas phase, where in particular the water dimer has been studied extensively. We used a DFT BLYP/DNP method including a dielectric (COSMO) to calculate these interactions. In the gas phase, DFT methods have been shown to model successfully the weak van der Waals interactions similar to those found in the H bonds for the clusters studied here.

We found that the strength of the interactions between silicate clusters will provide a strong driving force for their aggregation, which will play a major role in zeolite synthesis.

Global optimisation and energy landscapes of silica clusters

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Abstract

This presentation focuses on the problem of global optimisation of silica clusters in the size range of up to 30 SiO2 units. In our research we have used a combination of Density Functional Theory (DFT) calculations and classical force field calculations (based on a re-parameterised potential [1]) to locate low-energy cluster geometries and hopefully find the global minimum for cluster sizes up to 27 SiO2 units [2,3]. This has been achieved using the Basin Hopping global optimisation algorithm on the classical potential (being an approximate representation of the DFT energy surface) followed by post-optimisations using DFT.
Furthermore we have developed an alternative global optimisation strategy that specifically samples the set of fully-coordinated cluster geometries, i.e. those geometries where each silicon atom is chemically bonded to four oxygens and each oxygen atom forms a bridge between two silicons (as in the bulk). This algorithm uses Monte Carlo sampling on the set of graphs (the graph being the set of Si-O bonds) and a cascade of optimisations using 3 different cost-functions to produce a realisation of the graph as a 3D geometry. Results will be shown for clusters of a size of up to 30 SiO2 units. This approach can be easily generalised to clusters of other network-forming materials.

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Problems in developing water-water and water-silica potentials for the simulation of structural and dynamical properties

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Abstract

In recent years a sophisticated empirical model for simulating flexible water molecules was developed in our research group. The intramolecular part of the potential contains terms depending on the electric field acting on the molecule, in order to reproduce the deformations and the frequency shifts shown by the water molecules in an environment where an electric field is present.[1] This potential was fitted to the properties of liquid water but, as the dependence on the electric field entails a many body character of the intermolecular interactions, the reproduction of the experimental features of the water dimer was only approximate, and in particular its intermolecular energy was too small. Although this potential yielded good results when applied to hydrated zeolites, in particular to all-silica silicalite [2], bikitaite [3], Li-ABW [4] and natrolite [5,6], the comparison with experimental data resulted to be unsatisfactory in the case of zeolite A [7] and zeolite X, [8] in particular with low water content. This drawback is due mainly to the diffusion mechanism at low loadings, which was evidenced by the simulations. Water molecules are strongly bounded to exchangeable cations and at low loadings they can oscillate around the cations, which in turn vibrate about their equilibrium positions, so that, in order to diffuse, the water molecules must change the ions to which they are coordinated. This kind of jump is made possible and favoured by a temporary hydrogen bond with

another water molecule resulting in a concerted motion involving at least one cation and two water molecules. Therefore, in order to reproduce this mechanism the interactions between two water molecules and between water and cations must be carefully represented. These considerations most probably apply also in the case of open silica surfaces, containing charged groups, such as silanols, playing a role similar to that of cations presents on the internal surfaces of zeolites.

Our model of water – water potential includes terms representing electrostatic interactions, which were left unchanged, and a Lennard-Jones potential, besides other smaller terms. We found that it was possible to optimize only one parameter multiplying the Lennard-Jones term to improve both the water dimer bond energy and its geometry. To our surprise also the bulk water simulated using the modified potential, in spite of showing a too high sublimation heat, maintained excellent vibrational spectra, diffusion coefficient and radial distribution function. When applied to the study of diffusion in zeolite Na A at low loadings (40 and 120 molecules per unit cell), this modified water – water potential improved noticeably the reproduction of the diffusion coefficient derived from QENS technique, [7] yielding a good activation energy, but still absolute values slightly too low. The reason of this behaviour was in part evidenced when the simulation of hydrated zeolite X was performed. Indeed, in this case the experimental hydration energy is known [8] and the simulated value resulted too high by about 25%. It was evident that, even if the Na – water interactions were fitted accurately to ab initio calculations and experimental data for the system in vacuo, the many body effect of our potential worsened the agreement with the experiment when the system was embedded in the zeolite environment. A close inspection of the results obtained for natrolite [5,6] showed that, although reasonable, computed average Na - water distances were systematically smaller than the experimental ones, so that it appeared advisable to change the repulsive term of the potential, which has an exponential form, in order to obtain the best fit of the positions of the water molecules and of their vibrational spectra, besides the hydration energy. On the basis of these results, we optimized for the Na - water interactions the repulsive term of the Na – O potential and for the Na – framework interactions always the repulsive term of the Na – Of potential. The new potentials improved the reproduction of the properties of anhydrous and hydrated zeolite Na X [8]. As for the structure, which was already well approximated using the old potential, the improvement is nevertheless visible, especially for the Na – water distances. The vibrational frequencies are close to the experimental values within a few percent and the relative error of hydration energy diminishes from about 35% (for the old potentials) to about 15%. These findings could be useful for extending our empirical potentials to represent water - silica interactions.

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Transport processes at quartz-water interfaces: Insights from first-principles molecular dynamics simulations

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Abstract

Transport processes at quartz--water interfaces: Insights from first-principles molecular dynamics simulations

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Car-Parrinello ab-initio molecular dynamics (CP-MD) simulations [1] based on density functional theory have been performed at high temperature and pressure to investigate the transport processes at the α-quartz-water interface. The model system initially consists of a periodically repeated quartz slab with an O-terminated and a Si-terminated (1000) surface sandwiching a film of liquid water. In CP-MD simulations at 1000 K dissociation of H_2O molecules into H^+ and OH^- is observed at the Si-terminated surface eventually leading to complete hydroxylation of both surfaces. Due to the confinement between the two surfaces, water diffusion is reduced by one third in comparison with bulk water at almost similar conditions.

Diffusion properties of dissolved SiO_2, in the shape of

$Si(OH)_4$, in the water film have also been studied. No strong interactions between the hydroxylated quartz surfaces

and the $Si(OH)_4$ molecule have been observed. Thus the $Si(OH)_4$ diffusion coefficient is found to be comparable to that in pure aqueous solution [2], i.e. without the quartz surfaces.

The dissolution mechanism of a SiO_2 unit from the quartz surface into the water has been investigated using constrained CP-MD simulations [3]. A free energy profile along the reaction coordinate determined this way has been calculated revealing a step-wise dissociation process in which two Si-O bonds are successively broken.

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Characterisation of point defects at hydroxylated silica surfaces: optical and magnetic properties and charge trapping

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Abstract

Characterisation of point defects at hydroxylated silica surfaces: optical and magnetic properties and charge trapping

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In this contribution we focus on the detailed theoretical characterisation and comparative analysis of primary point defects at surfaces of several crystalline silica polymorphs. In particular, we consider the structure and spectroscopic properties of the paramagnetic nonbridging oxygen hole centre (NBOHC) and of the *E*' centre on hydroxylated edingtonite (100), β-cristobalite (111), and α-quartz (0001) surfaces. The isolated defects on the hydroxylated surfaces were modelled using an embedded cluster approach. The hybrid B3LYP density functional was used to calculate the ground state defect properties, while the excited states were calculated using the time dependent DFT approach. The calculations reproduce the essential properties of the centres: the optical transitions between well-localized defect electronic states and principal values of the g-tensors are in excellent agreement with the experimental data. The hyperfine coupling constants also agree well with the experimental findings. We find that the properties of both NBOHC and the *E*' centre depend on the spatial distribution and relative orientation of nearby hydroxyl groups. For example, these defects have similar structures on the edingtonite (100) and β-cristobalite (111) surfaces, but not on α-quartz (0001) surface. The results of our calculations demonstrate the importance of including solid state environment of the defects beyond small molecular models: this is required to reproduce characteristic optical absorption features which involve defect-induced states in the valence and conduction bands of the silica surfaces. We discuss the advantages and limitations of our approach in describing the properties of hydroxylated amorphous silica surface.

Reference:

L. Giordano, P. V. Sushko, G. Pacchioni, A. L. Shluger, *Phys. Rev. B* **75** 024109 (2007).

Ab initio molecular dynamics simulations of hydrous silica glasses and melts

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Abstract

We use ab initio molecular dynamics simulations to study a sample of liquid silica containing 3.84 wt.% H2O. We find that, for temperatures of 3000 K and 3500 K, water is almost exclusively dissolved as hydroxyl groups, the silica network is partially broken and static and dynamical properties of the silica network change considerably upon the addition of water. Water molecules or free O-H groups occur only at the highest temperature but are not stable and disintegrate rapidly. Structural properties of this system are compared to those of pure silica and sodium tetrasilicate melts at equivalent temperatures. These comparisons confirm the picture of a partially broken tetrahedral network in the hydrous liquid and suggest that the structure of the matrix is as much changed by the addition of water than it is by the addition of the same amount (in mole %) of sodium oxide. Finally, we study the diffusion mechanisms of the hydrogen atoms in the melt. It turns out that HOSi2 triclusters and SiO dangling bonds play a decisive role as intermediate states for the hydrogen diffusion.

The studied liquid samples are used in order to generate hydrous silica glasses employing different quench protocols. Using the Kohn-Sham density of states we find localized states in the band gap of the obtained glasses that can be associated to doubly occupied Si-O dangling bonds. We show that

the position of these states above the O 2p valence band depends on the local environment of the dangling bonds, in particular on the presence of other defects in their neighborhood, and on the hydrogen-bond length.

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1- First-principles molecular-dynamics simulations of a hydrous silica melt: Structural properties and hydrogen diffusion mechanism, Markus Poehlmann, Magali Benoit and Walter Kob, Phys. Rev. B 70, 184209 (2004).

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Structural analogies between ice, carbon, silica and zeolites

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Abstract

The structural analogies between dense ice phases, siliceous materials, water clathrates and zeolites are well established [1] - all are composed of tetrahedral units that share vertices and thus form infinite 4-connected nets. These tetrahedra can pack in a wide variety of ways to give a numerous different nets and a wide variety of solid phases - there are 15 known phases of ice, 7 dense silica phases and a staggering 170 known zeolite topologies. However, even this large number is only a tiny fraction of the set of mathematically possible infinite 4-connected nets, which can be obtained from titling theory [2].

Clearly, the variety of nets possible which a particular combination of chemical elements can crystallize into provides insight into the nature of the interatomic / intermolecular interactions in these substances as it is these which will control the position on the potential energy surface at which each possible net will find itself. Thus an understanding of what nets are possible and impossible for a given set of elements will provide insight into the nature of the potential, which can then be used to predict what, if any, other four connected nets may be possible for those elements. In other words the nature of the forces can be used to predict which of the vast number of possible four connected nets are possible to make out of a given set of chemical elements - the synthesisable territory of 4-connected net space.

There have been numerous attempts to understand the synthesisable territory for silica and pure silica zeolites. Early studies [3] simply compared the energies of known zeolitic phases and hypothetical phases with silicon atoms lying on the vertices of 4-connected nets derived from tiling theory. While, other work [4,5] has attempted to discover what are the low and high energy structural features in any given net and use this insight to search the vast database of hypothetical structures. However, there seem to be far fewer studies in the literature on the synthesisable region for ice and clathrate materials. This is attempted in this work and comparisons are made of SiO2 and waters potential energy landscapes. Furthermore, data mining is carried out that shows that the differences in the size of these territories can be explained using simple intuitive models for the differences in the intermolecular and intramolecular interactions of SiO2 and water. These models can hopefully be used to make predictions about the boundaries of what is synthesisable for other materials which form 4-connected structures.

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Ab Initio Si NMR Shifts of Small Species In The Pre-Nucleation Phase of Zeolite Synthesis

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Abstract

Work will also be presented in which theoretical NMR spectra for these species are compared with the experimental values[1]. Solvent effects on NMR shifts are well know and have been investigated to some extent on Nitrogen shielding constants[2-4]. The work which will be presented investigates the effects of the reaction field on Silicon NMR shifts and also the effects of variations in the solvation model on the values obtained. The work indicates that internal H-Bonding in the dimer and cyclic tetramer species is over emphasised. QMMD calculations of these species with explicit water molecules have provided alternative structures in which H-Bonding with water replaces the internal H-Bonding.

The shifts of the monomer, cyclic trimer, double-3-ring and double-4-ring were all calculated at full protonation and in a number of charge states with respect to the standard TMS reference species. The effects of deprotonation at different sites was considered on the cyclic trimer by deprotonating both trans and cis on adjacent hydroxyl groups and also by deprotonating a hydroxyl on the same Si centre rather than on an adjacent one. The results indicate a difference in the effect of deprotonation between Q^3 and Q^n sites where n = 0 - 2, it is also shown that the first deprotonation on a hydroxyl attached to a Si centre moves the shift down-frequency, while the second depronnonation moves the shift up-frequency, this helps to explain some experimental results for shift measurments of shift over a range of pH values [5] .

Results of work on the effect of conformational changes on NMR shielding will also be presented. It is hoped that good approximate values for the range of shielding constant possible for a given species can be used to investigate broadening of NMR peaks associated with anionic clusters in solution.

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Developing computational methodologies for modeling nucleation, crystal growth and interfaces

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Abstract

Developing computational methodologies for modeling nucleation, crystal

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The aim of this talk is to examine a number of methodological approaches that work towards the simulation of crystal growth from nucleation to the macroscopic crystal. Previous work has shown [1] that once the rates of fundamental growth steps are determined it is possible to simulate macroscopic crystallite properties, including morphology and surface features, under conditions of either thermodynamic or even kinetic control. However, the challenge remains to determine the rates of condensation and growth steps where covalent bonds are to be formed, as is the case for silica. In this talk, recent developments of the SIESTA methodology [2] for linear-scaling density functional theory will be presented that should make the determination of reactions in solution more practical.
A further problem is the determination of the details of initial nucleation of minerals from solution before the limit of an extended interface is reached. The issues of how to accelerate the sampling of nucleating cluster configurations and to understand induction times for nucleation will be discussed.

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Analysing the performance of water models to describe the phase diagram of water

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Development and Application of an Accurate Dissociative Water Potential for Bulk and Confined Water and for Water-Silica Interactions

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Structure and dynamics of the water/amorphous silica interface

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Abstract

The interface between amorphous silica and water is one of the most ubiquitous and technologically relevant surfaces. Starting with well-known interaction models for bulk amorphous silica (BKS) and bulk water (SPC/E), we have constructed a empirical force field for the water/amorphous silica interface based on *ab initio* fragment calculations. Protocols for hydroxylation of the freshly cleaved surfaces are developed. The surface properties (e.g. silanol density) can be controlled by varying the degree of annealing at various stages

of the process. The model allows for undissociated (-SiOH) and dissociated (-SiO^-) silanol groups. Macroscopic properties
The heat of immersion predicted by the model agrees well with experimental data. Progress calibrating this model by comparison with *ab initio* molecular dynamics simulations will be discussed.

Using this model, we explore the structure and dynamical properties of the interface that are relevant to fundamental electrochemical processes.

Molecular Dynamics simulations of transport at water-silicate interface

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The Role Of Water In Silica Oligomerization

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Abstract

The silicate oligerization reaction is key to sol-gel chemistry and zeolite synthesis. Numerous experimental and theoretical studies have been devoted to investigating the physical chemistry of silicate oligomer in the prenucleation stage of siliceous zeolite formation.
Most of the previous quantum chemical computational work used gas phase model or continuous solvent model for silica oligomeriazation. Here we apply Car-Parrinello Molecular Dynamics simulations with explicit inclusion of water molecule to investigate the reaction pathway for the anionic bond formation of siliceous oligemers. The rates of SiO-Si bond formation of linear or ring containing silicate oligomers become substantially enhanced, compared to gas phase results. Notwithstanding the more unfavourable thermodynamics that results from water molecule arrangement. Water molecules assist proton transfer and form stabilization hydrogen bond.
The interesting implication of this contribution is that in silicate oligomerization, the role of water reorganization can not be ignored.

Neutron diffraction and computer simulation study of water structure in a Vycor pore

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Abstract

In spite of a very broad interest in the properties of water at an interface, there is still a remarkable paucity of experimental information about how water structure is affected in confinement. A number of experiments on water confined in Vycor glass have been attempted [1, 2] but these generally have given limited detailed information on the arrangement water molecules near the surface. In an effort to improve the quality of the existing data a series of neutron diffraction experiments were undertaken on water absorbed in Vycor glass (approximately 40 A pore diameter) to establish how water structure might be altered in confinement compared to the bulk [3]. More recently we have undertaken a computer simulation structure refinement of these data [4] which has enabled us to give some fairly specific details about how water may be organised at a charged silica surface. The talk will describe some of the methododology and results from this study. The progress demonstrated

here has encouraged other researchers to investigate liquids in confinement using diffraction data as constraints.

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Exploring Silica using first-principles parameterized force field

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Abstract

We present a series of applications of Silica though atomistic simulations. By using an ab-initio parameterized polarizable interatomic potential for SiO2 [1] and molecular dynamics, we have been able to address and explain several of the issues and anomalies regarding Silica polymorphs and glass. This plethora of phenomena ranges from a unified picture of the compression mechanisms of Silica based on the pressure induced appearance of unquenchable fivefold defects [2]; a prediction though classical molecular dynamics of vibrational (infrared and Raman) spectra in highly anharmonic systems as high temperature/pressure crystalline phases [3]; the tuning of oxygen packing in silica by non-hydrostatic pressure [4] and applications on clathrasyls with the differences and similarities with the clathrates hydrates [5].

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The Structural, Electronic and Optical Properties of Silica Using the Standard Model: Pseudopotentials and Density Functional Theory

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Abstract

Silica provides a difficult challenge for any computational approach. The bonding in silica is both ionic and covalent, with lone pair contributions. This combination of bonding attributes is very difficult to model with interatomic forces. An accurate description of silica often requires the use of quantum forces, which can properly handle issues such as charge transfer and hybridization. The use of quantum forces necessitates a fully quantum mechanical and computationally intensive calculation. Moreover, silica can exist in a number of different crystal structures that have nearly identical energies, but different coordination. The energy differences in such structures are often at the limit of what can be calculated.
I will give an overview of how the electronic structure of silica can be approached using the “standard model” of condensed matter: pseudopotentials constructed within density functional

theory. In particular, I will start with descriptions of the energy bands of quartz and move on to more complex issues such as pressure induced amorphization of quartz, anomalous structural properties in silica such as the existence of a negative Poisson ratio, thermal properties of crystalline silica, and optical properties of quartz including the role of large excitonic effects.

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Emergence of tetrahedral networks in water: insights from simulation

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Abstract

Water shows an amazingly rich solid phase for such an apparently simple compound, reflecting the large variety of ways tetrahedral nodes can be connected into extended three-dimensional solids. There is still a great deal to be learnt about the way these networks emerge from the liquid phase, and in particular, how the outcome of the competition between different possible polymorphs — often with very small energetic differences — is determined. In this talk we present a series of molecular dynamics simulations designed to probe the spontaneous emergence of solid tetrahedral networks from liquid water. Two particular groups of results will be presented: (1) direct simulations, using conventional long timescale molecular dynamics, of the nucleation and growth of a clathrate hydrate at a methane / water interface; and (2) metadynamics simulations of ice formation from bulk water. The structure formation associated with nucleation of the crystal will be examined with the aid of a series of different order parameters and network descriptors.

Mr

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