

Computational molecular modeling of ions in aqueous solutions

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Nearly all geochemical processes in the Earth's crust involve the complexation of ions in aqueous fluids. Complexation by ligands such as Cl⁻ and HS⁻ is responsible for the extraction of metals from primary rocks and the formation of ore deposits. Complexation of metals by mineral surfaces limits the aqueous concentrations of biolimiting micronutrients and controls the mobility of toxic metals and radionuclides in soil and groundwater. For the past 50 years, geochemists have sought to develop thermodynamic models of the speciation of ions in complex aqueous solutions. Stability constants and mineral solubilities measured at low P and T can be extrapolated to high PT using models based on the Born theory of ion solvation. However, it is often ambiguous which complexes are necessary to account for measured mineral solubilities. There are a number of reasons why the Born model of aqueous solvation may be unreliable. We now have the ability to explore aqueous solutions at a molecular level using computational quantum chemistry (based on density functional theory) and atomistic simulations (based on classical interatomic potentials). Several examples will be given to illustrate the range of possibilities achievable with a small parallel computing cluster (< 20 nodes). Static calculations on large atomic clusters can be used to predict the structures and energetics of metal complexes on mineral surfaces. Insights from these calculations are used to develop surface complexation models to fit sorption isotherms. Examples include the sorption of As, Cu, U on FeOOH and kaolinite. Ab initio molecular dynamics simulations (100's of atoms, t < 10 ps) can be used to predict the speciation of metals such as Cu and Sn in hydrothermal fluids as a function of pressure and temperature. Classical molecular dynamics calculations allow very large simulations (1000's of atoms, t > 100 ps) that can predict phase separation and equations of state of NaCl-H₂O mixtures. For practical geochemical applications, we need to be able to predict the activities of aqueous species. Direct calculations of ion chemical potentials are possible but at much greater computational expense. It is anticipated, however, that such calculations will become increasingly practical and routine as computational technology develops.

Ab initio molecular dynamics of clay mineral surfaces and interfaces

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Sorption/desorption processes on surfaces or in interlayer spaces of clay minerals play an important role both in natural environments as well as in industrial production. Owing to the structural complexity of clay mineral surfaces it is often difficult to explain in detail the molecular mechanisms of these processes in spite of the application of various experimental techniques. In this situation, computer simulation methods provide a very powerful tool to model particular scenarios and to study surface complexes at molecular level for providing a detailed insight into the adsorption processes.

In this work we discuss ab initio molecular dynamics simulations of interactions between selected clay minerals (namely kaolinite and montmorillonite) and several polar molecules (water, acetic acid and phenoxyacetic-acid derivatives). These interactions are studied with either isolated molecules or entire molecular layers adsorbed on the surfaces or embedded in the interlayer space. Solvent effects are considered by including water molecules explicitly in the simulation. Structural, energetic and dynamic properties are evaluated. The most important phenomena in forming the surface complexes with the polar molecules are hydrogen bonds. The kaolinite surface formed from hydroxyl groups is chemically very active and hydroxyl groups are able to act as proton donors or acceptors. On the other hand, the kaolinite surface formed from basal oxygen atoms form only weak hydrogen bonds with polar molecules. In case of a water layer on this surface hydrogen bonds formed among water molecules prevail over hydrogen bonds formed with this surface. In contrast to kaolinite, the surface of the montmorillonite layer is formed only from basal oxygen atoms. Moreover, this layer also possesses an excess negative charge due to isomorphic substitutions within the layer. The models used here are more complex than in the previous cases since the sorption of polar or ionic species can proceed via a cation bridge mechanism. This situation was investigated and it was found that in the presence of water molecules the surface cation bridge complexes are less stable than the clay+cation complexes in the solution.

Electron transfer reactions in solution and at interfaces

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We present a molecular model for ferrous-ferric electron transfer in an aqueous solution and at interfaces that accounts for electronic polarizability and exhibits spontaneous cation hydrolysis, and allows estimation of *pH* dependence. In solution, the model predicts that the diabatic barrier to electron transfer increases with increasing *pH*, due to stabilization of the Fe³⁺ by fluctuations in the number of hydroxide ions in its first coordination sphere, in much the same way as the barrier would increase with increasing dielectric constant in the Marcus theory. As expected, increasing *pH* reduces the potential of mean force between the ferrous and ferric ions in the model system. The magnitudes of the predicted increase in diabatic transfer barrier and the predicted decrease in the potential of mean force nearly cancel each other at the canonical transfer distance of 0.55 nm. Even though hydrolysis is allowed in our calculations, the distribution of reorganization energies has only one maximum and is Gaussian to an excellent approximation, giving a harmonic free energy surface in the reorganization energy $F(\Delta E)$ with a single minimum. Evidently, fluctuations in hydrolysis state can be viewed on a continuum with other solvent contributions to the reorganization energy. There appears to be little justification for thinking of the transfer rate as arising from the contributions of different hydrolysis states.

We have used the same methods to examine electron transfer rates at interfaces. An important question is whether electron-hopping rates would be faster in the bulk or at the interface. On the one hand the enhanced conformational flexibility and coupling with proton hopping may facilitate surface-mediated electron hopping. On the other hand, the proximity of the high dielectric water layer will act to trap the electrons. Our calculations suggest that, at low *pH*, the dielectric contribution dominates and reorganization energies are higher near the interface than in the bulk.

First-principles simulation of solvation structure and deprotonation reactions in very nonideal solutions

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The structure of the water molecules neighboring an M3+ ion in an aqueous solution is strongly perturbed leading to a structured second and a weakly structured third solvation shell and increased acidity of the solution. For simple ions, e.g. Al³⁺, standard pseudopotential based first principle molecular dynamics methods can be applied. Simulation results agree well with the measured octahedral structure of the 1st solvation shell of Al³⁺. Less can be determined experimentally about the structure of the 2nd shell. However, the calculated average radius is in good agreement with the measured values. This shell contains roughly 12 water molecules, which are trigonally coordinated to the 1st shell waters. This is also consistent with experimental estimates. The emergence of tetrahedral bulk water coordination as a function of the distance from the ion center occurs in the third shell. While there is no transfer of waters from the first to the 2nd shell, there is picosecond time scale transfer between the 2nd shell and third shell. For high T the transfer of protons in the solvation shells leads to hydrolysis species. For transition metal ions pseudopotential methods are not reliable. For these systems we have implemented an augmented wave method which allows the use of a plane wave basis without the introduction of pseudopotentials. Results for the solvation structure of Fe³⁺ will be presented. As time allows, the local structure of counter ions in the solvation shells will also be discussed.

Isotopic effect on phase equilibria of pure fluids and mixtures: Molecular simulation, theory and experiment

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The temperature dependence of vapor – liquid and vapor – solid isotope fractionation factors was predicted by NVT-Molecular Dynamics and Gibbs Ensemble Monte Carlo simulations for atomic molecules (³⁶Ar/⁴⁰Ar, ²⁰Ne/²²Ne, ⁸⁰Kr/⁸⁴Kr) to assess the accuracy of h²-order Kirkwood-Wigner free energy expansion for specific Lennard – Jones parameterizations. In addition, the composition dependence of the corresponding fractionation factors for binary Ar–Kr mixtures was also predicted. Our simulation results compare very well with the existing experimental data. Fractionation factors were also predicted for other isotopic pairs, which have not been studied experimentally to date, including ²⁰Ne/²¹Ne, and ¹³²Xe/¹³⁶Xe. Some premises behind the microscopic interpretation of the fractionation factors are also tested. Relevant extensions of this study to polyatomic molecular systems of geochemical interest, including O₂, N₂, CO, and H₂O, are also discussed. The advantages of this approach over quantum mechanical calculations and the limitations of the methodology are addressed as well.

Acknowledgements

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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Ab initio molecular dynamics simulations of silicate liquids at high pressure

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Silicates liquids are primary agents of mass and heat transport, yet little is known of their properties over much of the vast range of pressures and temperatures that are relevant to planetary evolution. In the last few years, it has become possible to study for the first time silicate liquids with first principles quantum mechanical methods. We have applied density functional theory to the study of silicate liquids via ab initio molecular dynamics. The electronic structure, total energy, stress tensor, and forces acting on the atoms are computed self-consistently at each time step and atomic positions advanced according to Newton's equations of motion. The simulations are performed in the *NVT* ensemble with a Nose thermostat. Typical simulations consist of 80 atoms and are run for several picoseconds. We present initial results on MgSiO₃ liquid that span the entire pressure and temperature range of the deep earth. Preliminary results indicate that the fluid contains dominantly four-fold coordinated silicon and that the average coordination number increases gradually with increasing pressure. A surprise is that isotherms at 3000 K and 6000 K diverge on compression, behavior that is contrary to that of most crystals, and which implies a Grüneisen parameter that increases on compression. We will address issues including liquid-crystal density inversion, comparison with experiment, and analysis of the equation of state in terms of inherent structure.

Computer modeling of the equations of state of crystals and melts in the CaO-MgO-Al₂O₃-SiO₂ system

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Crystals and melts in the CaO-MgO-Al₂O₃-SiO₂ (CMAS) system are important components of the earth's crust and mantle. Both molecular dynamics (MD) and lattice dynamics (LD) methods are used to calculate the properties of crystals, while the MD technique is applied to simulate melts. The interionic potential is taken to be the sum of pairwise additive Coulomb, van der Waals, and repulsive interactions. In addition, in order to take account of many-body forces in crystals and melts, the breathing shell model (BSM; Matsui, 1998) is developed for simulation, in which the repulsive radii of O ions are allowed to deform isotropically under the effects of other ions in the system concerned. The net charges of the ions are constrained to be $q(\text{Ca}) = q(\text{Mg}) = 2/3q(\text{Al}) = 1/2q(\text{Si}) = -q(\text{O})$ to apply the potential to both crystals and melts with any composition in the CMAS system. Required energy parameters were derived empirically to reproduce the observed temperature-pressure-volume equations of state of a wide structural variety of crystals in the CMAS system, as well as the measured volumes of enstatite, wollastonite, diopside, and anorthite melts at high temperatures.

The LD and MD simulations with the BSM potential are quite successful in reproducing well these measured properties of both crystals and melts. In enstatite, wollastonite, diopside, and anorthite melts at 1900 K and 0 GPa, we found the simulated cation coordination numbers are four for Si, about four, five, and seven for Al, Mg, and Ca, respectively. The pressure dependences of cation coordination numbers in these melts are also investigated. The MD method is further applied to study the compositional dependences of the volumes of melts in the SiO₂-Al₂O₃, SiO₂-Ca₃Al₂O₆, and MgSiO₃-CaSiO₃ joins at high temperatures.

Molecular dynamics simulations of the structural and kinetic properties of amorphous intergranular films in alumina

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Thin, intergranular films (IGFs) of only one to a few nanometers thickness are prevalent in minerals and, while making up only a small volume percent of the material, often strongly influence material properties. However, the glassy nature and thickness of the IGF have made experimental observations of atomistic descriptions of these phases difficult to obtain until recently and computational techniques offer a complementary approach to understanding these atomistic details. The results of molecular dynamics computer simulations of the structural and kinetic properties of glassy calcium aluminosilicate (CAS) intergranular films (IGFs) in polycrystalline alumina will be presented. Calcia and silica can exist as impurities in alumina and segregate out to the crystal surface at high temperatures, affecting dissolution and grain growth. In experimental studies using liquid phase sintering, composition of the IGF was shown to significantly alter grain growth, although the mechanisms were not understood. The role of composition on the atomistic structure of the IGF and growth behavior of different crystallographic orientations will be presented. The simulations show ordering into the amorphous IGF caused by the presence of the crystal interface. Such structural changes also effect diffusion of species within the IGF. The simulations also show that grain growth along the surface normal of the basal plane is inhibited by preferential segregation of Ca ions at the IGF/crystal interface, although this behavior is affected by composition of the IGF. Dissimilar behavior occurs at the prism surface, where Al (and O) adsorption from the IGF onto the prism surface occurs in a manner consistent with grain growth along the surface normal. These simulation results are consistent with experimental studies regarding anisotropic grain growth in alumina as a function of composition and provide atomistic mechanisms regarding grain growth.

MgSiO₃ post-perovskite at D'' conditions

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The thermoelastic properties of the new polymorph of MgSiO₃ with the CaIrO₃ structure and more stable than the Pbnm-perovskite phase at conditions close to those expected in the D'' region has been investigated by first-principles computations and contrasted with those of the perovskite phase. Although we investigate only single and pure phases, the elasticity of aggregates containing predominantly these phases is expected to differ similarly, although in smaller magnitude. We therefore predict the major trends in seismic properties expected to occur in the presence of such phase change, such as velocity discontinuities, ratios of velocities and density anomalies, and anisotropy in aggregates with preferred orientation. Consequences of this model mineralogy for the D'' region will be discussed.

Acknowledgements

J. Tsuchiya and T. Tsuchiya thank JSPS for research fellowships. Research supported by NSF/EAR 0135533 (COMPRES), 0230319.

Development of transferable interatomic potentials for oxides and silicates using DFT calculations

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Atomistic modeling of physical properties of minerals and melts under extreme conditions of pressure and temperature requires a reliable and transferable representation of the interaction potential. Electronic structure calculations from first principles have proven the most accurate techniques, but their computational cost is still too high for systems that require a large number of atoms and long simulation times. It is, therefore, highly desirable to obtain interatomic potentials that include the essential interactions and that are transferable in a wide range of p/T and between different compositions.

Here we present an ionic interaction model that includes explicitly ionic polarization effects up to the quadrupolar level, and size and shape deformations of the ions that depend on the ionic environment of the individual ions. In the spirit of Born-Oppenheimer dynamics the energy due to these terms has to be minimized before the forces on the ions are calculated. The potential parameters are optimized by fitting forces and multipoles of individual ions and the stress tensor of different reference configurations to corresponding properties obtained by planewave-DFT calculations.

The resulting interaction potentials are shown to be transferable between different coordination environments and in a wide range of p/T. This is demonstrated for simple oxides, like MgO or Al₂O₃. Examples include phase stability of crystal polymorphs, thermoelastic properties, solid-melt interfaces, melt structure and transport properties. Finally, first results of new potentials for silica and silicates will be presented and discussed.

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O triclusters revisited: Classical MD and quantum cluster results for glasses of composition (Al₂O₃)₂(SiO₂)

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The ¹⁷O NMR spectrum of CaAl₂Si₂O₈ glass shows two types of O sites which are not present in the crystalline material. One of these, with ¹⁷O NMR parameters C_Q = 2.3 MHz and δ = +20 ppm, was assigned to a "tricluster" O, a local geometry in which the O is coordinated to three tetrahedrally coordinated atoms, either Al or Si. However, several different quantum chemical cluster calculations employing energy-optimized geometries for various tricluster species have given C_Q values considerably larger than that seen experimentally in the CaAl₂Si₂O₈ glass. We have recently shown that for edge-sharing geometries, in which the tricluster O atoms participate in "two-membered rings" of composition Al₂O₂, the calculated C_Q values are considerably lower, in the range identified in the glass. A recent classical MD simulation of the structure of glassy aluminum silicate AS₂, (Al₂O₃)₂(SiO₂) gave a predominance of O triclusters within 2-membered rings. We have now calculated ¹⁷O nuclear quadrupole coupling constants and NMR shielding values for clusters extracted from these simulations. The calculated C_Q values for these O triclusters are now in the range observed experimentally in the CaAl₂Si₂O₈ glass (around 2.3 - 2.6 MHz) when the tricluster O is surrounded by three Al, two of which are part of an Al₂O₂ ring.

Molecular orbital study on dissolution of allophane with dilute alkali solution

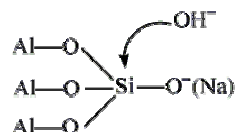
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Allophane is a hydrous aluminum silicate of hollow spherical morphology with some pores, and wall of the sphere is composed of gibbsite sheet with orthosilicate attached to inside of it. Allophane is known to be susceptible to alkaline condition than layer silicates, but detailed dissolution mechanism has not been known. Here we present molecular orbital calculation results for the interaction between allophane and dilute alkali solution, with focusing nucleophilic attack of hydroxyl ion on Si atom exposed at the pore region of allophane.

Model cluster of allophane simulated the pore region, in which each Si atom is attached to gibbsite sheet via three Si-O-Al bondings with one Si-OH exposed. Molecular orbital calculation was done with semiempirical MOPAC-PM3 and AM1 method in WinMOPAC program (ver. 3.9, Fujitsu).

We assumed that the hydroxyl ion first attacked Si atom at the pore, and formed five-coordinated Si as an intermediate product. The nucleophilic attack of hydroxyl ion was indicated to be promoted by adsorption of Na⁺ which added as NaOH, because calculated positive charge of Si atom was greater for Si-O-Na than for Si-O⁻. Si-O bond length was also greater for the Na⁺ exchanged model.



By forming five-coordinated Si, bond order of not only the original four Si-O bondings, but adjacent Al-O and O-Al inside bondings also decreased. This suggests that one Si atom dissolution may be followed by three Al atoms dissolution, and is in good agreement with our previous experimental results carried out at about pH 12.

Molecular orbital calculation was also done with some water molecules added around Na⁺ to simulate reactions in water, but the obtained result was similar to that in vacuo.

The overall reaction of allophane dissolution with dilute NaOH solution is proposed as: fast cation exchange reaction to produce Si-ONa, followed by nucleophilic attack of hydroxyl ion on Si atom of increased positive charge, then dissolution of Si and Al through bond weakening.

The effect of the sizes of alkali cations on structural variations in layered silicate materials

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Computational techniques were used to investigate the structures and stabilities of a series of solid solutions of the phyllosilicate material $\text{Li}_{2(1-x)}\text{M}_{2x}\text{Si}_2\text{O}_5$ ($M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and $x = 0, 0.25, 0.5, 0.75, 1$) as well as solid solutions of the mixed alkali phyllosilicate KLiSi_2O_5 with Na, K, Rb and Cs replacing the Li and K ions. To eliminate unnecessary duplication of calculations, a program based on symmetry arguments is employed to identify equivalent configurations. Even so, hundreds of calculations were still needed to sample the complete set of inequivalent configurations of a wide range of solid solutions.

Our simulations show that in the wide range of composition studied, solid solutions of the mixed KLiSi_2O_5 phyllosilicate with Na, Rb and Cs, retain the basic features of the KLiSi_2O_5 structure, e.g. a three-dimensional channel structure of six-membered rings made up of corner-sharing silica tetrahedral. However, the K ions rather than the Li ions are preferentially replaced by the guest ions, especially Rb and Cs. In the mono-cationic phyllosilicate $\text{Li}_2\text{Si}_2\text{O}_5$, the main features are a two-dimensional six-ring structure and symmetric chair-like conformation of the silicate groups. We found that this structure became significantly distorted when the bigger Rb and Cs cations replaced lithium ions. Although solid solutions of all guest ions in silicates are energetically feasible to some extent, only ion exchange of K ions for Na ions from aqueous solution is calculated to be an exothermic process.

Molecular dynamics simulation of the water/ α -quartz interface

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Interaction of water with oxide surfaces affects both the surface reactivity and functionality and the structure and dynamics of the near-surface aqueous phase. Quantitative understanding of these interactions is of great interest in many geochemical and technological systems. Silica is very important in this regard, because of its natural abundance and ubiquitous practical applications.

To better understand the molecular-level structural and dynamical properties of water/ α -quartz (0001) interfaces under different protonation states, we have performed MD computer simulations using the recently developed CLAYFF force field (Cygan et al., 2004). The effect of pH on the interfacial properties was emulated by varying the degree of surface protonation for the simulated models. For a fully protonated quartz surface (low pH), about 50% of surface OH groups are oriented parallel to the surface, form H-bonds to other surface OHs, and accept H-bonds from H_2O molecules. The other 50% of OHs are oriented perpendicular to the surface and donate H-bonds to the interfacial H_2O molecules.

On average, all surface water molecules donate or accept H-bonds to/from the surface OH groups with equal probability, and together they form a well interconnected H-bonding network similar to the ones observed for hydroxide interfaces (Kalinichev and Kirkpatrick, 2002; Wang et al., 2004). The structure and composition of the quartz surface imposes significant positional and orientational ordering on the H_2O molecules nearest to the surface. This is qualitatively consistent with the results of recent sum-frequency vibrational spectroscopic measurements for the same system, where some observed spectral features were interpreted as being "ice-like" (Ostroverkhov et al., 2004).

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New developments of fast computational methods for first principles geochemical and geophysical simulations

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Conventional methods of directly simulating the behavior of complex strongly interacting atomic systems (molecular dynamics, Monte Carlo) have provided important insight into the behavior of gases, fluids, and solids of geochemical and geophysical interest. The even wider application of these methods is limited by the difficulty of developing molecular level representations of potential interactions to capture complex chemistry commonly encountered in these systems (reactions, polarization, etc.). Static quantum chemistry methods have provided a means to calculate reactive mechanisms in cluster approximations to mineral systems. These methods are limited to small atomic sizes and generally cannot be applied to problems in which dynamics play a role. In this talk new developments in the implementations of methods to simultaneously simulate the electronic structure and molecular dynamics of nanoscale materials will be described (*ab-initio* molecular dynamics, AIMD). These methods, implemented into NWChem software, calculate of inter-atomic forces directly from the fast solution of DFT equations for very large systems and, therefore, avoid problems of force development limiting the application of MD. This talk will focus on the development and application in three areas:

(1) the implementation the PAW method an all-electron plane-wave method; *application* to the solvation structure of transition metal ions in solution;

(2) the development of a QM/MM method for simulations of large systems; *application*: simulation of enzyme reactions;

(3) the development of a plane wave implementation of exact exchange; *application*: the localization of charge in hematite.

The talk will focus on the fundamentals of these methods and the realities in terms of system size, computational requirements and simulation times that are required for their application.