Abstract of Selected Research Progress:

I. First-principles simulation of solvation structure and deprotonation reactions of ore forming metal ions in very nonideal solutions:

Advances in algorithms and computational performance achieved in this grant period have allowed the atomic level dynamical simulation of complex nanoscale materials using interparticle forces calculated directly from an accurate density functional solution to the electronic Schrödinger equation (ab-initio molecular dynamics, AIMD). Focus of this program was on the prediction and analysis of the properties of environmentally important ions in aqueous solutions. AIMD methods have provided chemical interpretations of these very complex systems with an unprecedented level of accuracy and detail. The structure of the solvation region neighboring a highly charged metal ion (e.g., 3+) in an aqueous solution is very different from that of bulk water. The many-body behaviors (polarization, charge transfer, etc.) of the ion-water and water-water interactions in this region are difficult to capture with conventional empirical potentials. However, a large numbers of waters (up to 128 waters) are required to fully describe chemical events in the extended hydrations shells and long simulation times are needed to reliably sample the system. Taken together this makes simulation at the 1st principles level a very large computational problem. Our AIMD simulation results using these methods agree with the measured octahedral structure of the 1st solvation shell of Al^{3+} at the 1st shell boundary and a calculated radius of 1.937Å (exp. 1.9Å). Our calculated average 2nd shell radius agrees remarkably well with the measured radius, 4.093 Å calculated vs. the measured value of 4.0-4.15 Å.

Less can be experimentally determined about the structure of the 2nd shell. Our simulations show that this shell contains roughly 12 water molecules, which are trigonally coordinated to the 1st shell waters. This structure cannot be measured directly. However, the number of 2nd shell water molecules predicted by the simulation is consistent with experimental estimates. Tetrahedral bulk water coordination reappears just after the 2nd shell. Simulations with 128 waters are close to the maximum size that can effectively be performed with present day methods. While the time scale of our simulation are not long enough to observe transfers of waters from the 1st to the 2nd shell, we do see transfers occurring on a picosecond time scale between the 2nd shell and 3rd shell via an associative mechanism. This is faster than, but consistent with, the results of measurements on the more tightly bound Cr^{3+} system. For high temperature simulations, proton transfers occur in the solvation shells leading to transient hydrolysis species. The reaction coordinate for proton transfer involves the coordinates of neighboring solvent waters as in the Grotis mechanism for proton transfer in bulk water. Directly removing a proton from the hexaqua Al^{3+} ion leads to a much more labile solvation shell and to a five coordinated Al^{3+} ion. This is consistent with very recent rate measurements of ligand exchange and the conjugate base labilization effect.

For the Al^{3+}-H_2O system results for high but subcritical temperatures are qualitatively similar to room temperature simulations.However, preliminary simulations for supercritical temperatures (750K) suggest that there may be a dramatic change in behavior in the hydration structure of ions for these temperatures. For transition metal ions the presence of d valence electrons plays a significant role in the behavior of the system. Our preliminary results for the Fe^{3+} ion suggest that this ion which is larger radius than the Al^{3+} ion has somewhat less rigid 1st and 2nd solvation shell.

II. Gibbs Ensemble Monte Carlo Simulation of Vapor/Liquid and Metastable Liquid/Liquid Phase Equilibria in the CO_2-CH_4-N_2 System

Many fluid inclusions have compositions in the system CO_2-CH_4-N_2. Estimates of the saturation pressures, compositions and volumetric properties of coexisting phases in the unaries, binaries and the ternary of this system have been obtained from simulations using the Gibbs Ensemble Monte Carlo method. The temperature and pressure range considered include liquid/vapor, gas/gas and metastable liquid/liquid regions. All the molecular interactions in the system were described with two-body Lennard-Jones potentials requiring only two temperature independent parameters for interactions between like molecules. The Berthhelot-Lorentz rules are used to define the Lennard-Jones interactions for unlike molecules with one additional temperature independent mixing parameter. The equilibrium compositions and molar volumes of the coexisting phases in all the mixtures are predicted with accuracy close to that of the data. These results, particularly for the phase densities and critical parameters, are considerably closer to the observed values than those that have been reported using equation of state methods(116). For very low temperatures liquid/metastable liquid/vapor coexistence was observed for the CO_2-N_2 and the CH_4-CO_2 systems, e.g. the L_1L_2V line. The possibility of gas-gas coexistence for the binary N_2-CO_2 at high temperatures and pressures was also investigated but not observed.