

1st principle dynamical simulation of hydrogen bond structure, dynamics and simple reactions in the hydration shells of highly charged metal ions

JOHN H. WEARE^{1*}, ERIC J. BYLASKA²,
STUART BOGATKO¹, EMILIE CAUET¹ AND JOHN FULTON²

¹Chemistry and Biochemistry, UCSD, San Diego, CA, 92093
(*correspondence: jweare@ucsd.edu)

²Pacific Northwest National Laboratory, Richland, WA, 99354

Highly charged (charge $\geq 2+$) metal ions are frequently encountered as important participants in geochemical processes involving aqueous solutions. Understanding the structure and dynamics of species in the structured hydration region surrounding these ions is critical to the interpretation of this chemistry. Because of the strong perturbation of the ion on the electronic structures of the neighbouring species conventional molecular dynamics based on assumed forms for the species interaction potentials have difficulty capturing important behaviours such as charge transfer, bond polarization, bond formation and breaking, etc, see figure of hydration shell charge transfer between a hydrating water to a transition metal ion (our simulation, left [1]).

Simulation using parameter free 1st principle based methods (forces calculated directly from the electronic Schrödinger equation, Seq) will be presented. These results focus on hydrogen bonding, electronic structure and the description of simple reactions such as ligand and proton transfer, and the formation of ion pair species and agree well with data (X-ray, EXAFS etc.). Present simulation methods are based on local DFT solution to the Seq is which is known to be inadequate for many problems. Our efforts to efficiently implement higher levels of solution to the Seq will be described.

[1] Bogatko, Bylaska & Weare (2010) *J. Phys. Chem. A* **114**, 2189–2200.

Predicting the chemical and physical properties of geothermal fluids: Model development and molecular level theoretical understanding

JOHN H. WEARE^{1*}, NANCY MOLLER¹, ZHENHAO DUAN²,
EMILIE CAUET¹ AND ERIC J. BYLASKA³

¹Chemistry and Biochemistry, UCSD, San Diego, CA, 92093
(*correspondence: jweare@ucsd.edu)

²Institute of Geology and Geophysics, Beijing, 100029, China

³Pacific Northwest National Laboratory, Richland WA, 99354

The development of free energy based equation of state (EOS) models of geothermal fluids with emphasis both on developing predictive tools and the improvement of the molecular level understanding of the structural and chemical properties of hydrothermal fluids will be discussed.

Our EOS models predict the solubility behavior of high and low density fluids in the system Na⁺-K⁺-H⁺-Ca²⁺-Al(H₂O)₆³⁺-Cl⁻-OH⁻-SO₄²⁻-CO₃²⁻-H₂O-H₄SiO₄-CO₂ (aq/g)-H₂S (aq/g)-CH₃ (aq/g) to high T and ionic strength. For temperatures below the critical point of water this system is most accurately modeled in terms of a model consisting of a low density phase in the system H₂O (g)-CO₂-CH₄ (g) in equilibrium with a high density liquid phase. The high density phase is described in terms of a specific interaction model accurate to high salt concentration with the inclusion of associated species where necessary. The new Al system model produces predictions with high accuracy for T to 300°C for a concentration range to 5m background salt. Our models of the low density phases and supercritical phases are based on a molecular level description via the application of thermodynamic perturbation theory and provide accurate predictions for reduced systems to much higher T and P.

A major problem with the efficient use of hydrothermal resources and the development of reliable models is the lack of understanding of the structure and processes in aqueous solutions under extreme conditions. Progress in the development of new molecular level simulation tools that are providing new insights into the structure and chemistry of hydrothermal fluids will be discussed. These methods are based on the direct solution of the electronic Schrödinger equation and, provide parameter free predictions. Results agree well with observation where available (X-ray structure and EXAFS spectra). We describe our progress in the extension of these methods to chemical processes occurring in the hydration shells of ions, and the structure and chemistry of ion associated and of oxo hydroxo polymeric species.