First-principles free energies by hybrid thermodynamic integration for phase equilibria and fission product solubility in molten salts

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ABSTRACT:

The overarching goal of this research project is quantitative microscopic modeling of phase diagrams and solubility of actinides and lanthanide-fission products in molten salts for molten salt reactors (MSRs). Application of molten salts as coolants and liquid fuels for next-generation reactors requires quantitative understanding of phase diagrams, equations of state and transport properties of binary and ternary molten salt mixtures, as well as solubility of fuel, fission products and reactor-wall corrosion products. *Ab initio* computational prediction of these properties is crucially necessary both to design future materials and to supplement challenging measurements involving short-lived radioactive species. However, liquid phase diagrams and solubility predictions remain beyond the reach of current first-principles computational techniques.

We will address this fundamental capability gap using a novel hybrid framework for thermodynamic integration to directly predict absolute free energies of solid and molten salts at any specified conditions of composition, temperature and pressure. This framework will combine a hierarchy of first-principles, molecular dynamics and continuum techniques to deliver first-principles-level accuracy at a fraction of the computational cost of conventional *ab initio* molecular dynamics approaches. Specifically, we aim to:

(1) Predict phase diagrams and equations of state of molten salt mixtures using first-principles calculations of absolute free energies. This will employ a new multi-step thermodynamic integration approach that applies first-principles refinement to a coarse estimate based on classical force fields. We will demonstrate this capability on NaCl, $MgCl_2$ and NaCl-$MgCl_2$ phase diagrams.

(2) Predict solubility of rare-earth fission products using first-principles calculations of solvation free energies, combining first-principles-refined grand-canonical Monte Carlo simulations for initial data generation and continuum solvation models for rapid subsequent predictions. We will focus on Ce, Gd and U chloride solubility in molten NaCl and $MgCl_2$ to establish this approach.

(3) Experimentally validate targeted predictions for NaCl-$MgCl_2$ phase boundaries and solubility of Ce, Gd, and U-chlorides. Specifically, we will perform calorimetric, *in-situ* x-ray diffraction (XRD) and spectroscopic measurements on compositions and conditions selected by Bayesian design of experiments.

Our results will provide the microscopic insights and quantitative parameters necessary for reliable thermophysical modeling of molten salts, and establish a reliable first-principles-based approach to target new salt compositions with reliable properties. We will develop and demonstrate this capability with chloride salts in this two-year project, with straightforward applicability to other molten salt systems including fluorides in future work. This work will thereby establish the foundation for computational design of molten salts for thermophysical and chemical properties desired in nuclear applications.