Computational Chemistry Project: Molten UCl_3 Structure Calculation

Matthew Louis

April 28, 2025

Introduction

Molten salt reactors (MSRs) have recently regained interest as viable candidates for the next wave of commercial advanced reactors. However, since the early development in the 50's there has been little research, and much is still unknown about the thermophysical and thermochemical properties of the actinide halide molten salts that are center to this reactor concept. Molten salts (especially actinide molten salts) are particularly hard to measure due to their often high melting points, and corrosivity, which has driven the use of computational methods for obtaining thermophysical properties. Though the use of machine learning models to generate semi-empirical potentials for molecular dynamics has dominated the field recently [6], ab initio molecular dynamics calculations (with density functional theory) still underly the data generation for these models.

Thermophysical Properties and Structure

Thermophysical properties (of most interest to engineers) can be broadly split into static and transport properties. Typical static properties are density and heat capacity, while typical transport properties are thermal conductivity, the diffusion coefficient, and viscosity. Static properties reflect equilibrium ensemble averages of the system, while transport properties are necessarily defined by time averages. While both *can* be computed from time dependent molecular dynamics simulations, only transport properties necessarily reflect time varying processes. Both types of properties are important for fluid mechanics and heat transfer, though transport properties, in practice, require much longer molecular dynamics simulations to properly converge [6].

For this project, transport properties were judged to be too difficult to calculate, so static properties were the focus. Perhaps the most important static property, from a theoretical standpoint, is the radial distribution function $g(r)$. This function is used to quantify the local structure in disordered systems like molten salts, and it is defined as

$$g(r) = \frac{1}{\rho N} \left\langle \sum_{i=1}^{N} \sum_{j \neq i} \delta \left(r - \| \boldsymbol{r}_i - \boldsymbol{r}_j \| \right) \right\rangle$$

where r is the scalar distance between two particles, ρ is the number density, N is the total number of particles, and $\langle \cdot \rangle$ denotes the ensemble average. In words, $g(r)$ describes how the density of particles deviates from that of an idea gas as a function of the distance from an arbitrary reference atom. Deviations from $g(r) = 1$ (essentially a random distribution) are characteristic of local ordering (e.g. coordination shells in molten salts). The radial distribution function is important for molten salts because it can be used to predict properties like viscosity, phase stability, ionic conductivity, and redox behavior [5]. As an example, formation of BeF_4 tetrahedral coordination networks in LiF-BeF_2 provide a nice theoretical explanation for an increase in the viscosity with increasing BeF_2 concentrations [5]. A schematic of this is shown in Fig. 1.