Development and Validation of Molecular Dynamics Simulation for FLiNaK

Department of Chemical Engineering

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Project Purpose

The purpose of this project is to develop molecular dynamics (MD) simulations to predict the thermophysical properties of the molten fluoride salt FLiNaK, and then to validate these simulations by comparing and fitting predicted values to values determined by other researchers. The density and heat capacity of FLiNaK will be derived from MD simulations for a wider range of temperatures than has previously been investigated. MD simulations will be performed using two programs: Large-scale Atomic/Molecular Massively Parallel Simulator will be used to perform classical MD simulations, and CPMD code will be used to perform *ab-initio* MD simulations. Using the *ab-initio* MD simulations and values reported by other researchers, the classical MD simulations will be fitted and validated. It is hypothesized that classical MD simulations can be used to predict the thermophysical properties of molten fluoride salts with accuracy within an order of magnitude after the simulations have been fitted to *ab-initio* simulations.

Project Context and Importance

In 2011, the Fukushima Daiichi Nuclear Power Plant experienced a major accident when an earthquake cut off external power and the following tsunami disabled on-site power[1]. This tragic accident highlighted a fundamental safety issue found in all existing commercial reactors: solid fuels melt at high temperatures. One potential solution to this problem is the "molten salt reactor" design, or MSR, which was highlighted as promising for future development by the Generation IV International Forum[2]. Molten salt reactors were first researched in the 1950's and 1960's, but progress stalled as funding was diverted to research on water-cooled reactors. However, facing

safety and waste disposal concerns in the wake of the Fukushima Daiichi nuclear disaster, attention has turned back to molten salt reactors[3]. In these reactors, high-temperature molten salts serve as the primary coolant as well as the fuel, so the reactor fuel cannot undergo "meltdown." Additional advantages of the molten salt reactor include efficient use of fuel and the potential to extract valuable fission products[4]. Among these fission products is Molybdenum-99, a critical medical isotope[5].

However, molten salt reactors run at higher temperatures than water-cooled reactors, and in order to design and develop MSRs, the thermophysical properties of potential molten salt coolants must be calculated with a high degree of accuracy. Furthermore, many thermophysical properties of salts have previously only been measured within a limited range of temperatures[6]. This honors thesis fits into a greater effort by researchers at Brigham Young University to study and measure the thermophysical properties of FLiNaK and other molten fluorides through a greater range of temperatures than has previously been recorded. Additionally, research on the development and validation of MD simulations for these molten salts will enable further development of MSR designs by allowing researchers to determine the thermophysical properties of molten salts with a greater degree of accuracy, and allowing researchers to predict thermophysical properties for molten salts that have not yet been measured experimentally.

component part of larger project.

Project Overview

The first stage of this project is to develop classical MD simulation models for FLiNaK using the program Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). LAMMPS is an open-source code for MD simulation developed by the Sandia National Laboratory, and because it is open-source, there are a variety of tutorials, pre-built models, and other resources available online. Additionally, other researchers at Brigham Young University have used LAMMPS and will be a

resource for developing the initial classical MD simulation models. Simulations will be run using the Fulton Supercomputing Lab. Initial MD simulations for FLiNaK will involve selecting simpler, pre-existing models for intermolecular forces, also known as force fields[7]. These initial MD simulations are not expected to reach the desired degree of accuracy, because simple MD force fields fail to fully account for the effects of polarizability, which is prevalent in molten salts. Multiple simulations will be performed to determine the density and heat capacity of FLiNaK by creating boxes of up to 1,000 atoms, with runs of several hundred picoseconds.

The second stage of this project is to develop an MD simulation model *ab-initio*, or in other words, from first principles of quantum chemistry, including atomic repulsion, dispersion, and polarization[8]. First, a theoretical model will be created, and then a simulation model will be created using CPMD code. CPMD code, named after the Car-Parrinello molecular dynamics method, is an open-source MD software package developed by IBM Corp. and Max Planck Institute. During the initial *ab-initio* MD simulations, fewer atoms (<100) will be simulated, and the simulation will be run for a shorter duration due to the computational load of *ab-initio* simulations.

The third stage will be to fit the classical MD simulations to the *ab-initio* simulations. Building *ab-initio* models allows a greater understanding of interatomic interactions, particularly the effects of polarizability[9]. However, *ab-initio* simulations are more computationally expensive than classical MD simulations, limiting the ability to model large numbers of atoms over a long time scale. The objective during this stage is instead to adjust the classical MD simulation model for the molten fluorides in order to fit the *ab-initio* simulations, through optimizing the parameters within the models used for simulation. Parallel "boxes" of atoms will be created with the classical MD model and the *ab-initio* model, and simulations will be run on each box to determine the density and heat capacity for FLiNaK for temperatures between 773 K and 1473 K. The parameters for the classical

MD force fields will be iteratively adjusted to match the output from the *ab-initio* model. It is anticipated that, by developing classical MD simulations for FLiNaK based upon *ab-initio* models, the thermophysical properties of FLiNaK will be determined with a greater degree of accuracy.

During the fourth and final stage, values from other researchers under will be used to validate both classical and *ab-initio* MD simulations for each molten salt. These values will be derived from existing literature, and if possible, measured values from other researchers at Brigham Young University will be used. Researchers under Dr. Matthew Memmott, also in the Department of Chemical Engineering, plan to measure the viscosity, heat capacity, thermal conductivity, and density for FLiNaK, FLiBe, and LiF in same range of temperatures investigated by the MD simulations. Consequently, the objective of this research is ultimately to compare the variables derived from the MD simulations to these experimental determined values, as opposed to values only extrapolated or predicted by other researchers. Additionally, the measurements will be used to suggest adjustments to the parameters used in the MD simulations in order to develop more accurate force fields and simulation models for these molten salts. If time permits, MD simulations for FLiBe and LiF will be performed, and the MD models will be adapted to predict viscosity and thermal conductivity.

Qualifications of Thesis Committee

The faculty advisor for this Honors Thesis will be Dr. Stella Nickerson. Dr. Nickerson received her PhD in chemical engineering from Arizona State University, where her work focused on understanding the physical properties of ionic liquid electrolytes through a combination of physical experiments and MD simulations. Compared to other simulationists, her work emphasizes the importance of physical measurements to validate and elaborate upon simulations. She currently collaborates with experts in nuclear engineering, studying the properties of molten salts in order to

enable the design of molten salt nuclear reactors. She is an expert on special challenges involved in the simulation of pure ionic systems. Jacob Ladd began working as a research assistant for Dr. Nickerson in September, 2017.

The faculty reader will be Dr. Matthew Memmott, also of the Department of Chemical Engineering. Jacob Ladd has been involved with research with Dr. Memmott since October 2014, including performing an ORCA project in Fall 2016. Dr. Matthew Memmott received his PhD in Nuclear Engineering from MIT. His work focused on improving the efficiency, safety and economics of advanced reactor designs, including molten salt reactors. He has extensive experience in researching and developing advanced reactors, including 5 years of experience in industry at Westinghouse Electric Company.

The Department Honors Coordinator for this project will be Dr. Dean Wheeler. In addition to being the Department Honors Coordinator for the Department of Chemical Engineering, Dr. Wheeler has experience in molecular dynamics simulation.

Project Timeline

Milestone	**Anticipated Completion**
Initial FLiNaK classical MD simulation	October 13, 2017
Determination of FLiNaK density and heat capacity	October 20, 2017
Ab-initio models for FLiNaK	October 27, 2017
Ab-initio CPMD simulations and calculations	November 17, 2017
Fitting of classical MD simulations to ab-initio simulations	December 1, 2017
Validation and fitting of simulations to experimental data	December 15, 2017
Final writing of thesis and scheduling of Thesis Defense	Early January 2018
Submission of research summary to 2018 ANS Student Conference	Late January 2018

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