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First-principles molecular dynamics modeling of the LiCl–KCl molten salt system

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ABSTRACT

Properties of molten salts are of interest for a wide-range of applications, including nuclear waste partitioning, heat transfer fluids, and synthesis methods. While there has been extensive work showing the value of molecular modeling with interatomic potentials to predict molten salt properties there have been very limited studies of molten salts from a fully first-principles approach. In order to establish optimal approaches and their strengths and limitations in first-principles molten salt modeling, this work provides extensive first-principles molecular dynamics simulations of the LiCl–KCl molten salt system that are validated against existing literature. The basic thermokinetic properties of volume, thermal expansion, bulk modulus, and diffusivity, are calculated for LiCl, KCl and the eutectic LiCl–KCl liquids at multiple temperatures. Convergence testing reveals 216-atom unit cells and simulation times of 6–12 ps are sufficient to provide results with acceptable uncertainties and agreement with experimental data. The results provide a framework of first principles molecular dynamics simulations in the LiCl–KCl molten salt system that can be extended in future research to predict less well-established properties, e.g., the behavior of solutes.

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1. Introduction

The aim of this paper is to explore the applicability of first-principles molecular dynamics (FPMD) simulations to the prediction of properties of LiCl–KCl molten salt system with various compositions (mole fraction of LiCl = 1, 0.58, and 0). In particular we seek to obtain converged liquids with stable structure factors from FPMD, calculate volumes, coefficients of thermal expansion, bulk moduli, species diffusion, and the Gibbs free energy of mixing as a function of temperature, and determine if error bars (precision) and accuracy are adequate with present simulation tools to guide experiments.

Measurements on molten salts can be limited by costly and demanding experiments and computational simulations provide a low cost alternative to experiments and can rapidly explore many different temperatures and salt compositions. However, FPMD methods have been applied only rarely to direct calculation of salt properties. Detailed calculations, with careful assessment of uncertainties and comparison to experiments, are needed to establish the optimal approaches and their limitations.

We focus the LiCl–KCl as it is a system of considerable interest for the nuclear community with both extensive quality data for validation and yet many open questions that can be investigated with the methods being considered here. Eutectic LiCl–KCl (58% LiCl, 42% KCl), is a common molten salt used in electrorefining of spent nuclear fuel to separate actinides and other fission products [1–4]. While the basic salt properties are known and can be used to validate our approaches, the thermokinetics of solutes within LiCl–KCl are not well characterized and can be a subject of future modeling [1,2,5–7].

The primary goal of the present work is to validate the practicality of direct FPMD approaches for molten salt studies, which are an increasingly viable alternative to the more commonly used interatomic potential molecular dynamics (IPMD) simulations.

In classical IPMD simulations, Newton's equations of motion are solved in a system where interactions between atoms are described by an interatomic potential, which typically contains the physics of ionic repulsion, attraction, dispersion and polarization. IPMD can be used to predict many properties of salts and their solutes [8–12] and is computationally many orders of magnitude faster than FPMD. However, each new salt and each solute and charge state requires fitting a different potential, which can be time consuming and is subject to the inevitable uncertainty of fitted potentials. Furthermore, such potentials do not typically treat the electronic structure explicitly, and therefore cannot easily be used to track electronic properties (e.g., magnetic moments) or redox reactions that might occur between species (although relative stabilities of equivalent impurities have been studied [13]).

FPMD simulations are similar to IPMD in that Newton's equations of motion are also solved, but the atomic interactions are

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calculated directly from first-principles in FPMD calculations. FPMD therefore requires no fitting to experimental or computed data and provides access to the full electronic structure of the material at every step. The main disadvantage is that FPMD calculations are very computationally intensive and therefore limited to much smaller systems and shorter simulation times than IPMD.

FPMD simulations have successfully modeled liquids such as $CaAl_2O_4$ [14], $CaMgSi_2O_6$ [15], $MgSiO_3$ [16], Ni alloys [17] and ionic liquids [18]. The NaCl and KCl molten salt systems were studied with density-functional-based tight-binding methods (DFT-TB) [19]. While DFT-TB methods are similar to FPMD, they are not fully self-consistent. Furthermore, volumes within the work of Hazebroucq et al. [19] were fixed to experimental values rather than predicted. FPMD simulations were conducted in the liquid Flibe (Li_2BeF_4) using the Car–Parrinello method [20], but the focus was primarily on diffusion, again at a fixed experimental volume. These limited studies to date show that these methods can be used effectively, but do not provide an extensive enough study of basic properties to establish optimal approach or assess limitations (e.g., in the ability to predict volumes).

Our study is the first full FPMD study on molten salt systems with fully relaxed volumes. Specifically, we will study the LiCl–KCl system and extend previous FPMD work on molten salt systems [20] to include calculations of equilibrium volume, convergence testing on key parameters as a function of unit cell size and simulation time, statistical errors on all values, and rigorous comparison to experiments, when possible. The LiCl–KCl molten salt system has been studied extensively with classical interatomic potential molecular dynamics [8–12] and this data was used for comparison.

2. Computational methods

A combination of first-principles molecular dynamics (FPMD) and interatomic potential molecular dynamics (IPMD) was used in this research. All liquids were equilibrated with IPMD and the final converged structure was used to start the FPMD calculation. FPMD calculations starting from the IPMD liquid reach equilibration within 0.3 ps. The technique of starting FPMD calculations from the liquid created with IPMD has been used successfully in the literature [17,21]. Note that it might seem to defeat at least part of the purpose of using FPMD if a potential needs to be developed for IPMD to initiate the FPMD calculations. However, while we do not demonstrate it here, it is reasonable to expect the FPMD is quite insensitive to the quality of the IPMD initiation, provided it gets qualitative structural features approximately correct. Thus we expect that no significant time will have to be spent on potential development for IPMD simulations provided they are used for no more than initiating a FPMD simulation.

For the pure LiCl and KCl, we started simulations with crystalline LiCl and KCl structure. In case of the LiCl–KCl eutectic mixture (58% LiCl, 42% KCl), initial configuration of atoms was created from Packmol [22], a code designed to randomly pack atoms into a given volume. While IPMD was typically initiated with a crystalline structure for LiCl and KCl, a randomly distributed initialization of the LiCl system from Packmol (see Computational methods section) also shows a converged liquid structure after the IPMD equilibration and showed same radial distribution functions as initialization from a crystal structure. All IMPD simulations were run with the LAMMPS [23] using the Born–Mayer–Huggins potentials for LiCl and KCl [9] with a radial cutoff of approximately half the lattice parameter for a given unit cell (6, 7, 9, 11, 15 Å for 64, 100, 216, 400, and 1000 atom unit-cells). Formal charges were used for Li (+1), Cl (−1), and K (+1). Simulations, unless otherwise noted, contained 216 atoms. The time step was 0.001 ps and thermal data was outputted every 100 steps.

A series of ensembles was used to equilibrate the liquid structures. The NVE ensemble with velocities generated from random numbers was run for 5000 steps to bring the system to the correct temperature. Next, a crude Berendsen barostat [24] for 50,000 steps brought the system to the target pressure. Then, simulations with the NPT ensemble (using the Nosé-Hoover thermostat and barostat) were run for 50,000 time steps for pure LiCl and KCl (500,000 for LiCl–KCl) to equilibrate system at desired pressure and temperature. The lattice was averaged over last quarter of the NPT time steps and used to start the NVT simulation. The NVT ensemble was run for 100,000 time steps for LiCl and KCl (600,000 for LiCl–KCl) for a final equilibration. The resulting structure file was resized for multiple volumes around the experimental volume. Each volume was run with the NVT ensemble for an additional 100,000 time steps. The resulting structure and velocities were used to initialize the VASP NVT simulations.

All FPMD simulations were run with the *Vienna Ab-Initio Simulation Package* VASP version 5.2.11 [21,25,26]. PAW-PBE potentials supplied with the VASP package were used for Li (s1p0 17Jan2003), Cl (s2p5 17Jan2003) and K (p6s1 K_sv 06Sep2000). All simulations were run with the canonical ensemble (NVT) using a Nosé thermostat [27] with a Nosé-mass with a period of 40 time steps. Note that the NPT ensemble is not available for VASP versions earlier than 5.3.2, which was recently released. Energy cutoff of 420 eV and a $1 \times 1 \times 1$ k-point mesh were used. Charges were calculated within the VASP code. A time step of 0.002 ps was used, which gave an energy drift of <1 meV/atom/ps, a value similar to that seen in other FPMD simulations [17]. Simulations were run for 3000 time steps (unless noted). Dispersion was added through the semi-empirical DFT-D2 method [28]. The DFT-D method has been shown to work well for ionic liquids [18]. Three compositions are considered within the 64-atom unit cell: LiCl (32 Li atoms, 32 Cl atoms), KCl (32 K atoms, 32 Cl atoms) and LiCl–KCl near the eutectic composition (19 Li atoms, 32 Cl atoms, 13 K atoms; 59.4% LiCl). Within the 216-atom unit cell, the eutectic composition is 63 Li atoms, 108 Cl atoms, and 45 K atoms (58.3% LiCl).

Periodic boundary conditions were used in both IPMD and FPMD and simulations represent an infinite bulk material. The pressure, temperature, volume and energy of the ensemble are the statistical averages over many time steps. The standard deviation in the mean was calculated from the autocovariance function [29]. To calculate the equilibrium volume with the NVT ensemble, calculations were run at multiple fixed volumes. The resulting pressures, volumes and their associated errors were fit with a Murnaghan equation of state [30] to determine the equilibrium volume and bulk modulus.

The pressure at a finite temperature includes both a kinetic energy and virial force term [31]:

$$PV = NK_BT + \langle W \rangle \tag{1}$$

VASP (versions prior to 5.3.2) does not automatically include the kinetic energy term in the pressure. The kinetic energy term, $\frac{NK_BT}{V}$, was added in post-processing to the pressure for each simulation. This term is usually on the order of 0.35–0.52 GPa in the temperature range 800–1096 K for the LiCl–KCl system.

Diffusion is related through the slope of the mean squared displacement (MSD) by the Einstein equation [31,32]:

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}(\mathrm{MSD}) \tag{2}$$

In practice, D was determined by fitting a linear function to MSD(t) for a subset of the times, as described below. The MSD is determined by a multiple time origin average [32]:

$$\mathrm{MSD(t)} = \langle \Delta r^2(t) \rangle = \frac{1}{N}\frac{1}{n_t}\sum_{j=0}^{n_t}\sum_{i=0}^{N}\left(r_i(t_{0j}+t) - r_i(t_{0j})\right)^2 \tag{3}$$