

Construction of an accurate two-body potential model for a molten salt based on first-principles calculations and a correction

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1. Introduction

Molten halide salts are promising materials for various engineering applications such as an energy storage system and Molten Salt Reactors (MSR), due to their favorable characteristics as energy storage and transfer fluids, including large heat capacity, high melting point, low vapor pressure, and high thermal/chemical stability. For example, FLiBe (mixture of LiF-BeF₂, 66-34 mol%) and FLiNaK (mixture of LiF-NaF-KF, 46.5-11.5-42 mol%) are candidate coolants for MSR.

Molecular dynamics (MD) simulation is utilized as an alternative or complement to experiments to acquire physicochemical properties of molten salts. Previously, for molten salts, empirical interatomic potential models in the form of Born-Huggins-Mayer (BHM) equation [1][2] have been widely used with Tosi-Fumi parameters [3], which were optimized to reproduce some experimental data. MD simulations using the BHM potentials show satisfactory reproductivity on thermodynamic properties but poor performance on elastic constants [4]. First-principles molecular dynamics (FPMD) based on density functional theory (DFT) is considered as a more accurate simulation method. For ionic materials such as molten salts, additional corrections for the van der Waals dispersion energy have been employed to improve the accuracy, such as DFT-D2 or D3 methods by Grimme [5] and Tkatchenko-Scheffler method [6]. However, due to high computational cost, the simulation length and system size in FPMD calculations are limited, which brings a large statistical error in calculated quantities. In addition, errors in DFT calculations of molten salts cannot be systematically reduced with the dispersion corrections. Thus, even with FPMD, an accurate calculation of physicochemical properties of molten salts is not an easy task.

Recently, machine-learning potentials have been developed for molten salts [7] with reference to FPMD results to reduce computational cost while achieving the accuracy of DFT. Although machine-learning potentials can successfully reproduce DFT/FPMD results, they cannot reproduce some experimental data such as density and compressibility accurately because FPMD based on DFT is not fully accurate for molten salts. Thus, to achieve an experimental accuracy, some correction should be developed and applied to FPMD-based potential models.

In this presentation, a correction method that we have recently developed will be introduced. As a test case, a

potential model was constructed and correction parameters were determined for KCl, demonstrating the performance of the correction method. We plan to extend this method to other alkali halide salts such as LiCl, LiF and KF, furthermore to binary or ternary salts such as FLiBe and FLiNaK in the future.

2. Methods

In this section, potential model construction and correction methods are described in 4 subsections.

2.1. Fitting reference for potential models

To make a potential model that can reproduce thermodynamic properties of an actual material, DFT data of energy, force and stress for various systems were collected and used for potential model fitting. Since we aim to simulate both liquid and solid states, data for both phases were included as follows: (1) 1000 configurations of liquid near melting temperature (1050 K); (2) each 1000 configurations of solid at 300 and 600 K with $\pm 5\%$ lattice deformation; (3) each 1000 configurations of high temperature liquid with fixed volumes (2000, 3000, 4000 K); (4) each 250 configurations of liquids and solids of $-10\% \sim +10\%$ deformation of the equilibrium cell constants; (5) total 250 configurations of solids with (111) and (100) direction displacement of an atom with various displacement amplitudes. All calculations were done with the following DFT and FPMD conditions.

2.2. DFT and FPMD calculations

The accuracy of a fitted potential is affected by the numerical precision of DFT/FPMD data. Thus, choosing appropriate calculation settings is critical.

DFT/FPMD calculations were performed with Vienna *Ab initio* Simulation Package (VASP) [8]. FPMD training data were generated using a canonical ensemble (NVT) with 1 fs timestep. To collect data at equilibrium, configurations in the last 1 ps of a 5 ps FPMD calculation were gathered. The systems composed of 128 and 64 atoms were used for liquid and solid KCl simulations, respectively. The plane-wave cutoff was set to be 600 eV. The band energy was sampled only on the gamma point for liquid and on a $2 \times 2 \times 2$ Monkhorst-Pack mesh for solid. The effect of core electrons was treated using the projector-augmented wave (PAW) method with *PAW_PBE K_cv*

17Jan2003 and PAW_PBE Cl 06Sep2000 datafiles contained in the VASP package.

For exchange-correlation functionals, which predominantly determine the accuracy of DFT calculation, several popular functionals of generalized gradient approximation (GGA) or meta-GGA were tested. The performance was evaluated in comparison with experimental cell constants [9] and PBEsol functional was used for all calculations in the present study.

2.3. Two-body potential model fitting

Using the prepared DFT/FPMD calculation results as reference data, a two-body potential model was constructed with a cutoff distance of 12.0 Å, which is approximately twice the lattice constant. A truncated cosine series were used to represent the potential energy as [10]

$$E_{pot} = \sum_{i,j}^{Ewald} \frac{q_i q_j}{r_{ij}} + \frac{1}{2} \sum_{i=1}^{N_A} \sum_{j=1}^{r_{ij} < r_{cut}} \left[\sum_{k=0}^{N-1} a_{i-j,k} \cos\left(\frac{k\pi r_{ij}}{r_{cut}}\right) \right] + E_{ref}$$

$$E_{ref} = n_{Cat} e_{Cat} + n_{An} e_{An}$$

Here, the first term represents the Coulomb interaction using Ewald summation. q_i and q_j are atomic charges. In this study, the Coulomb interaction was neglected, and thus the charges were set to be 0. The second term describes short-range interaction between two atoms. The last term is a reference energy of each atom, where n_{Cat} is the number of cations (K^+) in the system and e_{Cat} is the per-atom reference energy of a cation. The subscript 'An' is used for anions (Cl)

The parameters $a_{i-j,k}$ in the second term is fitted by solving linear simultaneous equations to minimize the loss function consisting of the sum of weighted mean square errors of the energy, force and stress with reference to first-principles calculations. The weighting factors were set to be 1.0, 10, and 0.1 for energy, force and stress, respectively.

2.4. Correction based on experimental results

To reduce discrepancy between fitted potential and experimental results, a pressure-based correction was applied to the potential model. In general, MD calculations should produce near zero pressure if the simulated density is the same with the experimental density. Thus, the main idea of this correction method is to adjust the pressure to zero by adding another two-body potential to the FPMD-based two-body potential constructed by the method described in Section 2.3. The densities at six conditions (static, 300/700 K solids, and 1100/1200/1300 K liquids) were selected as correction references. The correction potential was represented by 10 basis functions, each of which smoothly converges to 0 at long distances as

$$\sum_{i=1}^3 C_i (r_i - r)^3 + \sum_{i=1}^3 C_{i+3} (r_i - r)^4 + \sum_{i=1}^4 C_{i+6} \frac{1}{r^{4+2i}}$$

where r is the interatomic distance, r_i are three cutoff distances (4.0, 5.0, 6.0 Å), and C_i are coefficients. The pressure contribution of each basis function was calculated by MD simulation. The coefficients $C_1 \sim C_{10}$ were determined so that the target pressure (i.e., 1 bar) was achieved by solving the linear problem. Ridge regression was used to avoid overfitting. For regularization factor λ of Ridge regression, 1.0 was applied after several test calculations to avoid both overfitting and exceeding regularization. The shapes of the potential models with/without the correction as well as the correction potential itself for each atomic pair are presented in Figure 1. It is confirmed that the sizes of the correction potentials are not large in the distance ranges that can occur at equilibrium (> 3 Å for K-Cl, and > 4.4 Å for K-K and Cl-Cl, typically). By this, we can conserve atomic configurations created with original fitted potential MD while correcting the pressure to zero.

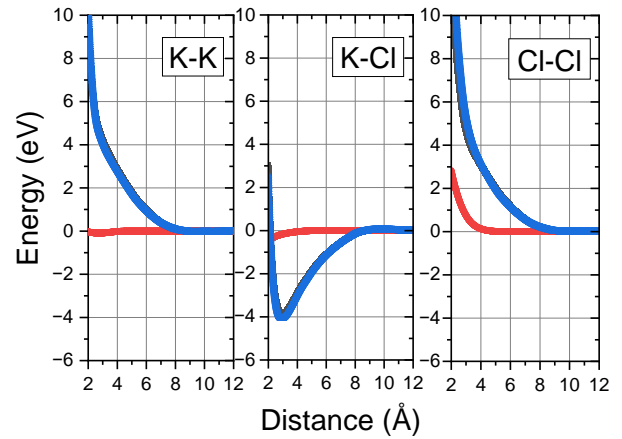


Figure 1. Two-body energy-distance relations of the fitted potentials (black), correction potentials (red), and fitted potentials with the correction (blue) for each atomic pair

3. Results and Discussion

3.1. Calculation results in solid

Figure 2 and 3 show the density and bulk modulus of solid KCl as a function of temperature, respectively. Quasi-harmonic approximation (QHA) results using DFT calculations were also included to check the performance of fitted potential without correction. Note that the QHA for some ionic crystals tends to contain large errors at high temperatures due to the vibration anharmonicity [11]. The potential model optimized with DFT/FPMD dataset without the correction shows good correspondence with DFT-QHA data at low temperatures, indicating that the potential model construction method described in Section 2.3 can

generate DFT-accuracy potential models. However, due to the error in the DFT calculation, the potential model without correction cannot reproduce experimental result even at low temperatures, showing poor performance compared with the conventional BMH potential model. With the pressure-based correction, the reproductivity of density and bulk modulus were significantly improved: the errors were reduced to 0.2% and 3%, respectively, from the experimental data. The calculation near zero temperature tends to have larger errors, which is due to the quantum effects that occur in experiments but cannot be considered with classical MD. Since such low temperatures are outside our interest, we do not apply corrections to account for the quantum effects in this study.

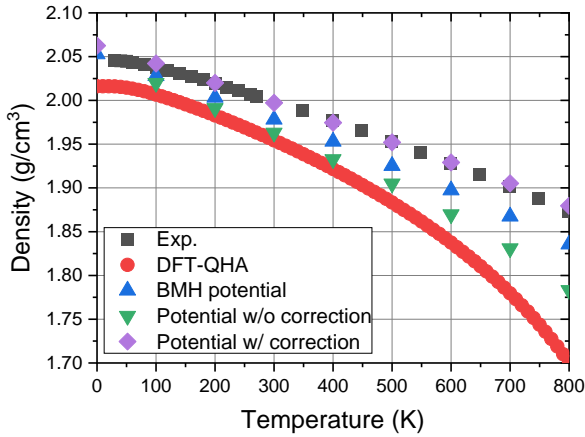


Figure 2. Comparison of density in solid KCl between experiment, DFT-QHA, conventional BMH potential, fitted potential with and without the correction. Experimental data were taken from Ref.12.

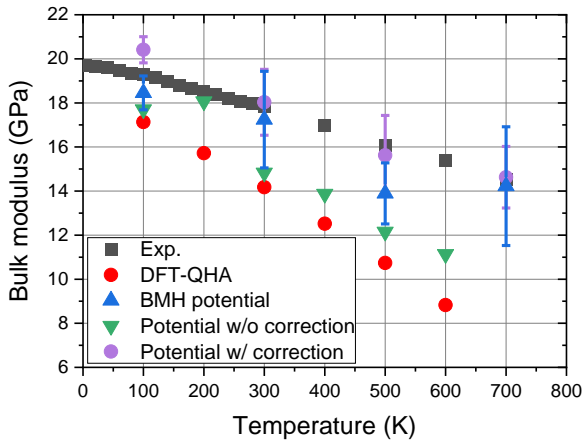


Figure 3. Comparison of bulk modulus in solid KCl between experiment, DFT-QHA, conventional BMH potential, fitted potential with and without the correction. Experimental data were taken from Ref.13.

3.2. Calculation results in liquid

Figure 4 and 5 show the density and bulk modulus of liquid KCl as a function of temperature, respectively.

Both BMH and fitted potential show large errors in the density calculation (~10%). The correction improved the agreement with the experimental data and reduced the error to approximately 1%. For bulk modulus, all potentials show reasonable accuracy, although the numerical precision was not sufficiently high. In the presentation, we will present a comparison using the results of calculations with improved numerical accuracy.

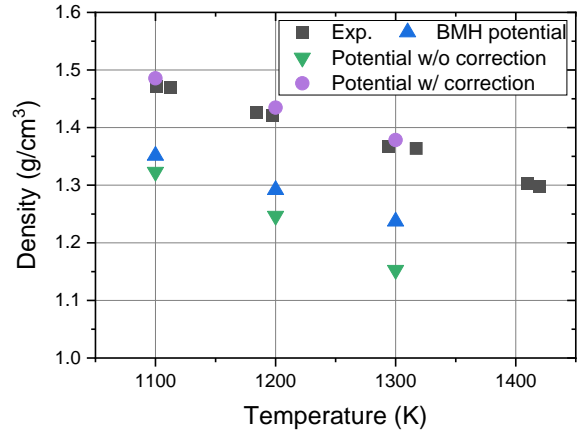


Figure 4. Comparison of density of liquid KCl between conventional BMH potential, fitted potential with and without the correction. Experimental data were taken from Ref. 14.

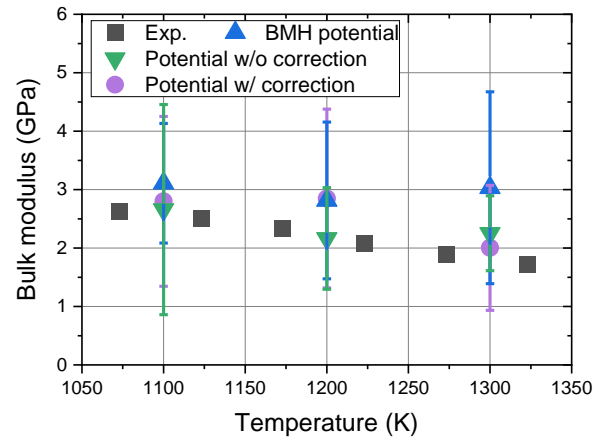


Figure 5. Comparison of bulk modulus of liquid KCl between conventional BMH potential, fitted potential with and without the correction. Experimental data were taken from Ref.15.

4. Conclusions

In this study, we first constructed DFT-accuracy two-body potential model based on FPMD calculation results. However, due to the systematic error in DFT, the FPMD-based potential cannot reproduce experimental data sufficiently. Thus, a correction method was developed to reduce the discrepancy between experiment and FPMD based on pressure information. The pressure-based correction enables

accurate reproduction of basic material properties such as density and bulk modulus, achieving better accuracy than the conventional BMH potential and the non-corrected potential. In future studies, we plan to further evaluate the reproductivity of other properties such as self-diffusivity and viscosity, and attempt to extended the correction method to more complex systems such as binary/ternary salts and systems containing impurities.

5. Acknowledgement

This research was supported by the Brain Korea 21 FOUR Program (No. 4199990314119).

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