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Development of potential models for alkali halides using first-principles calculation

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1. Introduction

Molten halide salts are considered as promising material for various purposes such as Molten Salt Reactor (MSR), electrorefining, and energy storage system, because they have preferable characteristics like high boiling point, noncombustible, wide liquid range, and high radioactive resistance.

In previous studies, the structures and physicochemical properties of molten halides have been widely investigated to understand their basic behaviors, for example, during the operation of MSR. However, due to the high melting point and volatile and corrosive characteristics, it is hard to accurately acquire these information from experiments. In addition, the inclusion of impurities such as moisture and oxygen greatly affects the chemistry of the salts. Hence, molecular dynamics (MD) calculation would be an alternative method to study molten halides, which can avoid the experimental difficulties. Predicting properties of mixed salts more accurately will help to operate the molten salt system more safely and efficiently.

Not only binary molten salt systems but also ternary systems such as LiCl/KCl and LiF/KF mixtures have been attracting attention because of their low melting point compared to binary salts. In previous studies using the classical MD calculation, potential parameters of 17 alkali halides developed by Tosi-Fumi [1] have been widely used. For simulating ternary or quaternary systems, the averaging rule by Larsen [2] is often applied to obtain potential model parameters. Thus potential parameters should be recalculated for each different composition.

Another possible computational approach is the first-principles molecular dynamics (FPMD) calculation, which can simulate interaction between ions more accurately without model parameters. However, due to the high calculation cost compared to the classical MD calculation, the simulated cell size is limited to a few hundred atoms, which makes evaluation of some properties (diffusion coefficient, etc.) difficult.

In this study, in order to take advantage of both classical MD and FPMD, we develop potential models of halide salts by fitting energies, forces and stresses of FPMD results. The performance of the developed potential models is evaluated in comparison with the Tosi-Fumi potential models [1] and experimental results. In this abstract, the result for LiF is presented as a typical case.

2. Method

2.1. Potential model functions

Born-Mayer-Huggins potential model, which is the form of Tosi-Fumi potentials [1], is expressed as follows:

$$U_{ij}(r) = \frac{q_i q_j}{r} + A_{ij} b \exp\left(\frac{\sigma_i + \sigma_j - r}{\rho}\right) - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} \quad \textbf{(1)}$$

The first term is the Coulomb interaction between ions, where q is the ionic charge and r is the interatomic distance. The second term is a short-range repulsive interaction because of overlapping of electron clouds. A_{ij} is the Pauling factor [1], σ is the crystal ionic radius, ρ is the hardness parameter, and b is a model parameter. The last two terms correspond to the dipole-dipole and dipole-quadrupole dispersion interactions, where C and D are the dispersion parameters. The model parameters such as b, C and D are adjusted so that reasonable material properties are obtained. In the Tosi-Fumi potential model, the Coulomb and repulsive interaction parameters were given by Tosi and Fumi [1], while the dispersion parameters were given by Mayer [3].

In the present study, two-body potential models are constructed using FPMD simulation results as the fitting target. The potential model function is described with Fourier cosine series as follows [4]:

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

$$E_{ref} = n_{Li} e_{Li} + n_F e_F \quad \textbf{(3)}$$

This potential model is designed to be applicable within the cutoff radius of the short-range two body interaction (r_{cut}), which is set to be around 10 Å. In the range of reasonable interatomic distances, namely from around 1 Å to r_{cut}, the model function should be smooth. To achieve the smoothness, a sufficiently large number of FPMD data need to be used as the fitting target.

In Eq. (2), the first term calculates the Coulomb interaction using Ewald summation. The second term is the short-range interaction term expressed with as set of cosine functions. The last term is the reference energy, which is the sum of the atomic energies (e_{Li} and e_F). N_a is the number of atoms in a unit cell, N is the number of cosine functions, and $a_{i-j,k}$ is the coefficient of k-th cosine function for i-j ion pair. N is set to be 60, which is sufficiently large, in the present study.

In the second term of Eq. (2), the first summation is taken over all N_a ions of i-element, and the second summation collects j-element ions within r_{cut}, and the last summation is up to all N cosine functions to calculate the potential energy between i and j ions. The division with 2 is required to correct the double counting. The last term is the reference energy, which is required to compare energies between the constructed potential model and FPMD because the absolute energy obtained in the density functional theory (DFT) calculation with pseudopotentials, which is used in the present FPMD, has no clear physical meaning. The reference energies e_{Li} and e_F are independent of configuration.

The coefficients $a_{i-j,k}$ and the reference energies e_{Li} and e_F are determined by solving linear equations to minimize the model error, which is the sum of the weighted mean square errors in the energy, force and stress in reference to the values obtained by the FPMD calculation.

$$
\begin{aligned}
& Error = P(a_{Li-Li,0},\cdots,a_{Li-F,0},\cdots a_{F-F,0},\cdots,e_{Li},e_F) \\
& = \frac{1}{N_c}\sum_{i=1}^{N_c}\{w_e(E^{i}_{fitted}-E^{i}_{FPMD})^2 \\
& + \frac{w_f}{3N_A}\sum_{j=1}^{3N_A}(F^{i,j}_{fitted}-F^{i,j}_{FPMD})^2 \\
& + \frac{w_s}{6}\sum_{j=1}^{6}(S^{i,j}_{fitted}-S^{i,j}_{FPMD})^2\}
\end{aligned} \quad \textbf{(4)}
$$

where E, F and S represent the energy, force and stress, respectively. N_c is the number of configurations in the FPMD data. i is the configuration index, and j is the component index, which is up to 1 in energy, 3 in force (3 dimensions), and 6 in stress (xx, yy, zz, xy, yz, zx). w_e, w_f and w_s are the weighting factors of energy, force and stress, respectively. In this study, the weighting factor is set to 1, 10 and 0.1 to make the weighted error contributions become comparable. The subscript 'pot' denotes a value determined with the potential model, and 'QM' denotes a value with FPMD calculation.

Then, $3N$+2 linear equations are constructed as follows:

$$
\frac{\partial P}{\partial a_{Li-Li,k}} = \frac{\partial P}{\partial a_{Li-F,k}} = \frac{\partial P}{\partial a_{F-F,k}} = \frac{\partial P}{\partial e_{Li}} = \frac{\partial P}{\partial e_F} = 0 \quad \textbf{(5)}
$$

where k ranges from 0 to $N-1$ (number of cosine functions). By solving the linear equations, $a_{i-j,k}$, e_{Li} and e_F that grant the minimum error in the form of Eq. (4) can be generated.

Because very short interatomic distances (for example, $r < 1$ Å) does not basically appear in the FPMD reference data, the constructed potential model may become unstable when interatomic distances become short, such as very high temperatures. Therefore, we additionally modify the generated potential model so that the potential model becomes repulsive at the short range.

2.2. FPMD calculations

For calculation of the fitting target data, FPMD simulations are performed with various configurations using Vienna ab-initio simulation package (VASP) based on DFT of PBE functional. For liquid states, FPMD calculation with NVT ensemble of Nose thermostat using a supercell containing 128 ions is performed at 1200 K. 10 ps simulation was conducted with a timestep of 1fs. We confirmed that the equilibration of energy, stress and force was achieved. The initial liquid structure is made by melting a crystal structure at 3000 K, then cooling to a desired temperature using classical MD with the Tosi-Fumi potential model. For solid states, FPMD calculations of NVT ensemble with 2×2×2 supercell containing 64 ions are performed at 300 K and 600 K for 2 ps each. In addition, the energy of single alkali ion is calculated for unique determination of the reference energies. To correct Pulay stress [5], 50 kbar and 100 kbar are added to diagonal components of stress tensors for the liquid and solid calculation results, respectively.

2.3. Classical MD calculations for performance test

After the generation of potential model, classical MD calculations are performed using LAMMPS code to evaluate the performance of the constructed potential model. A system composed of 128 ions is used. The system is first melted at 3000 K, and then cooled to 1750 K. Subsequently, the temperature is controlled to achieve a desired temperature. Finally, several material properties are calculated using NPT ensemble with Nose-Hoover thermostat and barostat.

The MD results obtained with the constructed potential model are compared with experimental data as well as the calculation results with the Tosi-Fumi potential model [1].

3. Results and Discussion

3.1. Fitted energy comparison

For the evaluation of the fitting quality, the energy calculated by FPMD and the constructed potential model are compared in Fig. 1. Fitting result show good correlation with the r-square value of 0.9982.

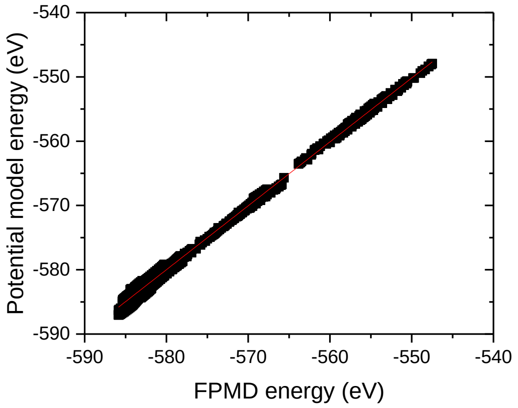

Fig. 1. Energy comparison between FPMD and the developed potential model.

3.2. Potential model shape

The potential energies of Tosi-Fumi model and the constructed model are compared in Fig. 2. In both cases, the potential energy of the same ion pair, i.e. Li-Li and F-F, is always repulsive, while that of different ion pair, i.e. Li-F, becomes attractive in some range. The energy difference between two models would be attributed to the fact that there is an explicit Coulomb interaction in the Tosi-Fumi model, while not in the constructed model.

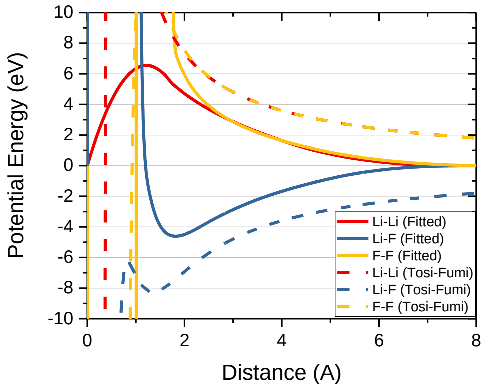

Fig. 2. Potential energies given by the constructed potential model (solid line) and Tosi-Fumi model (dotted).

3.3. Density

The density of molten LiF is calculated as a function of temperate and compared with experimental result [6] in Fig. 3. A good agreement is seen around 1250 K. However, at high temperatures, the constructed model underestimates the density. Because the FPMD calculation results used as the fitting target are gathered at 1200 K, 2000 K, 3000 K and 4000 K, the quality of the constructed model may not be sufficiently high in 1200~2000 K.

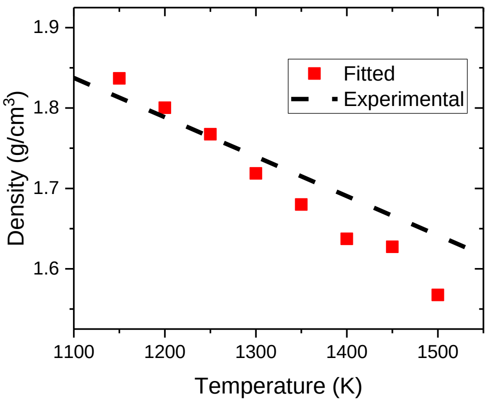

Fig. 3. Density of molten LiF calculated by the constructed potential model (red dots) in comparison with experimental data (dotted line) [6].

3.4. Radial distribution function

The radial distribution function (RDF), defined as *g(r)*, is widely used for describing atomic configuration of a liquid system. Therefore, RDF can be used to confirm whether the potential model describes liquid model good or not. RDF is expressed as follows:

$$g_{\alpha\beta}(r) = \frac{1}{4\pi\rho_\beta r^2}\frac{dN}{dr} \qquad \textbf{(6)}$$

where ρ_β is the number density of species β, and dN/dr is the mean number of β ions placed between sphere of radius r and r + dr from a reference α ion. In Fig. 4, RDFs of the constructed model at 1250 K are compared with RDF determined by Tsujida using FPMD at 1250 K [7]. RDF of this potential model shows a good agreement with that of FPMD.

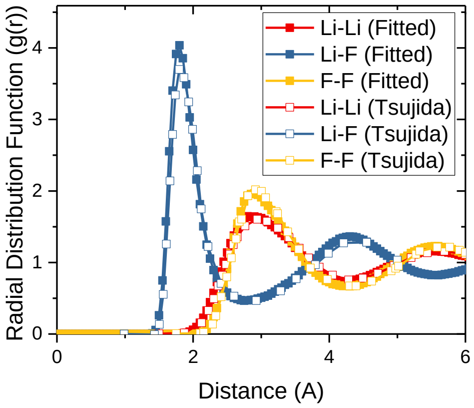

Fig. 4. Radial distribution function of the constructed model (solid square) and FPMD (empty square) [7] at 1250K.

3.5. Angular distribution function

The angular distribution function (ADF) can give information of angles between ions, which RDF cannot give. Here, ADF of Li-F-Li pair is calculated. ADF is calculated with the coordinates of three ions. First, for a centered ion F, nearest Li ions are listed up within a cutoff distance. Then, the distribution of Li-F-Li angles are calculated. The cutoff distance is usually determined from the first minimum point of Li-F RDF, which is the boundary between the first-neighboring ions and the second neighboring ions. In Fig. 4, the cutoff distance is obtained to be 2.75 Å.

Since there is little information available for ADF of LiF, ADF of LiF calculated by the constructed potential model is qualitatively compared with an ADF of LiCl calculated by Wang et al. using classical MD calculation with Tosi-Fumi potential model [8]. In Fig. 5, the overall shapes are comparable to each other. The difference in the peak angle between LiF and LiCl is considered to be caused by the difference in the ionic radius between F and Cl.

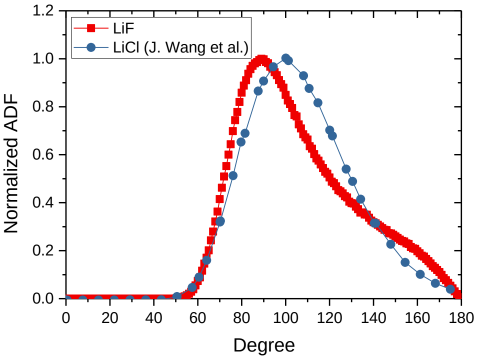

Fig. 5. Angular distribution function of molten LiF in comparison with molten LiCl calculated by Wang et al. [8].

3.6. Self-diffusion coefficient

The diffusion coefficient D can be calculated from the slope of the mean square displacement:

$$D = \frac{1}{2N}\frac{\left\langle (\mathbf{r}(t)-\mathbf{r}(0))^2 \right\rangle}{t} \qquad \textbf{(7)}$$

where N is the dimension, and $r(t)$ is the coordinates of atom at time t. The angle brackets indicate the ensemble average. In Table II, the diffusion coefficient calculated with the constructed potential model is compared with an experimental result and an MD result at 1123K of Sarou-Kanian et al. [9], which shows good agreement with the previous results.

Table II. Diffusion coefficient calculated by the constructed potential model in comparison with experimental and a previous MD result [9] at 1123K

Diffusion coefficient	Fitted	Experimental	MD
D_F (10^{-9} m^2/s)	6.9	7.2	6.74
D_Li (10^{-9} m^2/s)	8.566	8.9	8.83

4. Conclusion

In this study, potential models of molten alkali halides were constructed using FPMD results. Fourier cosine series were used to fit FPMD result into classical MD model. The constructed model gives energies reasonably comparable with the FPMD results. To evaluate how well this model describes molten halides, thermodynamic and structural properties were calculated and compared with previous simulation and experimental results. The comparison shows good coincidence in PDF, ADF and the diffusion coefficients. However, in the density, the constructed model does not give good results at high temperatures. We consider that the inclusion of high temperature data would improve the result.

In the presentation, results of other binary and ternary system will be shown and the performances of constructed potential models will be compared.

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