

# Calculation of oxygen diffusivity in liquid sodium using machine-learning potential model

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## 1. Introduction

Liquid sodium is a coolant for the sodium fast reactor (SFR), one of the Generation-IV advanced reactors. For the safe use of the SFR, solubility and diffusivity of impurities in liquid sodium must be carefully evaluated because these are fundamental properties closely related to engineering issues for liquid sodium, such as high chemical reactivity with air and/or water and transport of radionuclides. However, to the best of our knowledge, there are no experimental data on the diffusivity of impurities in liquid sodium. This could be attributed to difficulties in performing experiments with liquid sodium, including its high chemical reactivity with air and/or water and purity control.

Atomistic simulations are useful alternatives and complements to experiments in studying liquid sodium. In our previous studies, we conducted first-principles calculations based on density functional theory (DFT) to evaluate the solution enthalpy of impurities in liquid sodium [1,2]. Using first-principles molecular dynamics (FPMD) simulations and appropriate correction methods, it was demonstrated that the solution enthalpy can be obtained with reasonable accuracy compared to the experimental value [1,2].

However, the high computational cost of DFT limits the number and length of FPMD simulations for liquid sodium systems. Especially, FPMD simulations are not very efficient in the calculation of diffusivity because several simulations of sufficient length are required to obtain statistically significant results. Classical molecular dynamics (CMD) simulations can be performed for a sufficient length with much lower computational cost. Nevertheless, the accuracy of the calculation is highly dependent on the potential model used.

In this study, we employ a moment tensor potential (MTP) [3], one of the machine-learning potential models, to accurately and efficiently calculate the diffusivity of impurities in liquid sodium. By training the MTP from the FPMD simulation results for liquid Na systems, it is possible to achieve an accuracy comparable to that of DFT in the calculation of energy, force, and stress. As a test case, the diffusion coefficient of an oxygen impurity atom is calculated in the temperature range of 400 K to 1000 K. Specifically, MTP models for the O-including liquid Na system are constructed first, and CMD simulations are performed using the models. Next, the self-diffusion coefficient of liquid Na atoms evaluated from CMD is compared with experimental values. Finally, the diffusion coefficient of the O impurity atom evaluated from CMD is compared with the FPMD results.

## 2. Methods and Results

### 2.1 Construction of MTP model

Figure 1 outlines the training dataset to construct the MTP model for the O-including liquid Na system. FPMD simulations were performed on the model pure liquid Na system, consisting of 102 Na atoms, and the model O-including liquid Na system, consisting of 101 Na atoms and one O atom, at 600 K and 1000 K. By including the data for the two temperatures, it was expected that the constructed MTP model could be utilized at various temperatures. The cell constants of the model systems were basically set as the reference cell constant (RCC), which was determined to be 16.461 Å at 600 K and 17.106 Å at 1000 K so that the system pressure was close to the atmospheric pressure at each temperature [1]. To improve the stability of the MTP model, FPMD simulations were also performed when the cell constants were 99% and 101% of the RCC.

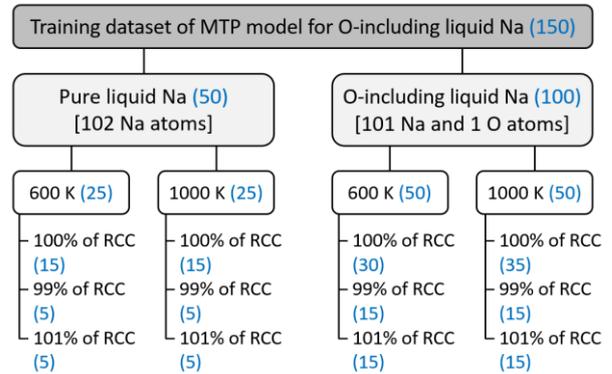


Fig. 1. Diagram of training dataset to construct MTP model for O-including liquid Na system. The number in parentheses indicates the number of configurations selected from each system and included in the training dataset.

Each FPMD simulation was performed for 1000 steps, and only a few configurations were selected and included in the training dataset; to select  $n$  configurations, the 1000 configuration data was divided into  $n$  blocks, and one configuration data was randomly selected from each block. The number of configurations ( $n$ ) selected for each system is shown in parentheses in Fig. 1. A total of 150 FPMD configurations were included in the training dataset to construct the MTP model for the O-including liquid Na system.

FPMD simulations were performed using the VASP code [4] with the Perdew–Burke–Ernzerhof functional [5]. The FPMD simulation settings are similar to those in our previous study [1]. The Skoltech Machine Learning Interatomic Potentials (MLIP) package [3] was used to construct MTP models. After several test calculations, the level of MTP, which determines the size of basis functions [3], was set to 16, and the minimum and maximum interatomic distances were set to 1.8 Å and 7.0 Å, respectively. With the prepared training set (Fig. 1), ten MTP models having different values of parameters were constructed from random initialization of the parameters [3].

## 2.2 Self-diffusion coefficient of liquid Na

Figure 2 shows the self-diffusion coefficient of liquid Na evaluated from CMD simulations in the temperature range of 400 K to 1000 K using the constructed MTP models, together with those determined experimentally in the previous studies [6,7]. The reason for comparing the self-diffusion coefficient of liquid Na with the experimental values is that there is no experimental data on the diffusion coefficient of O impurity in liquid Na. The overall temperature-dependent trend fairly agrees with that of the experimental data.

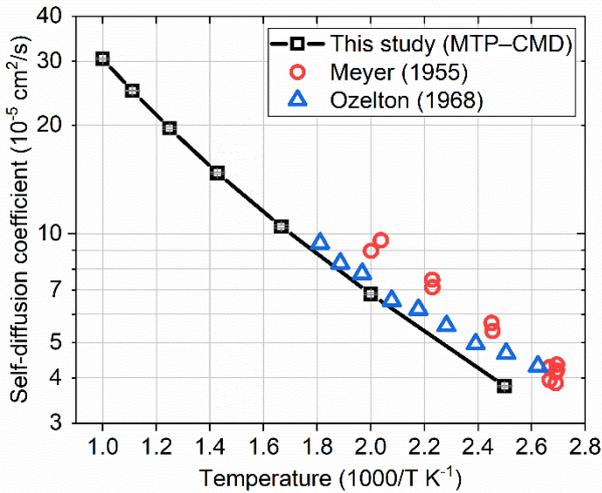


Fig. 2. Self-diffusion coefficients of liquid Na at several temperatures (i) evaluated from CMD simulations using MTP models constructed in this study (represented by squares connected with lines) and (ii) experimentally determined in previous studies (represented by circles and triangles) [6,7].

CMD simulations were performed using the LAMMPS code [8] built with the MLIP library [3]. The simulations were performed on the model O-including liquid Na system at 400 K, 500 K, 600 K, 700 K, 800 K, 900 K, and 1000 K with the time steps of 1.95 fs, 1.75 fs, 1.6 fs, 1.5 fs, 1.4 fs, 1.3 fs, and 1.2 fs, respectively. A canonical (NVT) ensemble was simulated by using a Nosé–Hoover thermostat [9]. At each temperature, the CMD simulation

was performed for 1 million steps after the equilibration of 0.1 million steps. The data of 1 million steps was divided into 50 blocks, and in each block, the mean square displacement (MSD) was calculated for every 1000 steps. These data were averaged over the 50 blocks to obtain an MSD–time relationship. Finally, the diffusion coefficient was calculated from the Einstein relation.

## 2.3 Diffusion coefficient of O impurity atom

Table I lists the diffusion coefficient of the O impurity atom in liquid Na evaluated from CMD simulations at 400 K, 500 K, 600 K, 700 K, 800 K, 900 K, and 1000 K using the constructed MTP models, together with those evaluated from direct FPMD simulations at 600 K and 1000 K. For the CMD results, the standard error of mean (SEM) for the deviation between the results obtained using the ten MTP models is shown together. For the direct FPMD simulations, the diffusion coefficient was evaluated from three 200-ps FPMD simulations at 600 K and 1000 K starting with different initial atomic configurations, and the SEM for the deviation between the three simulations is shown together. Considering the SEMs of the results, the diffusion coefficient obtained from the MTP–CMD simulations is in good agreement with that obtained from the direct FPMD simulations.

Table I: Diffusion coefficients of O impurity atom in liquid Na calculated from (i) CMD simulations using constructed MTP models and (ii) direct FPMD simulations.

Simulation Temperature (K)	MTP–CMD (10 <sup>-5</sup> cm <sup>2</sup> /s)	FPMD (10 <sup>-5</sup> cm <sup>2</sup> /s)
400	1.2 ± 0.1	-
500	2.1 ± 0.1	-
600	3.4 ± 0.2	3.6 ± 0.3
700	5.6 ± 0.2	-
800	8.4 ± 0.4	-
900	10.2 ± 0.5	-
1000	13.2 ± 0.7	13.9 ± 1.2

It is worth highlighting the significant reduction in the computational cost of the MTP–CMD method presented in this study compared to the direct FPMD simulation while the accuracy is almost maintained. Specifically, to obtain the results in Table I, the MTP–CMD method requires 12,000 steps of FPMD to construct the MTP model and 1 million steps of CMD at each temperature to calculate the diffusion coefficient. On the other hand, more than 350,000 steps of FPMD were performed for the direct FPMD. Considering that the computational cost of the CMD simulation using the MTP model is approximately 1/10000 of that of the FPMD simulation, the computational cost is reduced by more than 25 times when using the MTP–CMD method.

More details on the MTP–CMD method, simulation settings, calculated diffusion coefficients, and reduction in computational cost will be given in the presentation.

### 3. Conclusions

In summary, the diffusion coefficient of an O impurity atom in liquid Na was calculated in the temperature range of 400 K to 1000 K from the CMD simulations using the MTP models. The MTP models were constructed from the training dataset consisting of the FPMD simulation data on pure and O-including liquid Na at 600 K and 1000 K. The temperature-dependent trend of the self-diffusion coefficient of liquid Na evaluated from the MTP–CMD simulations reasonably agreed with that of the experimental data. The diffusion coefficient of the O impurity atom also showed a good agreement with that evaluated from the direct FPMD simulations.

By utilizing the machine-learning MTP model in the atomistic simulation for liquid sodium, the computational cost has been significantly reduced while the accuracy of DFT has been almost maintained. It is expected that the diffusivity of other various impurities in liquid sodium can also be systematically calculated in a relatively short time with DFT-level accuracy using the MTP, thereby establishing an accurate database of the diffusivity of impurities in liquid sodium.

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