

Development of a machine learning potential and evaluation of diffusion behavior in UO₂ using molecular dynamics simulations

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***Keywords :** uranium dioxide, ab-initio molecular dynamics, machine learning potential, molecular dynamics

1. Introduction

Due to nuclear accidents and recent changes in nuclear energy policies around the world, research on accident tolerant fuel (ATF) has become increasingly important. The main goal of ATF is to develop a fuel system that can delay the progress of an accident, even when the emergency cooling system fails. ATF research generally focuses on three areas: cladding materials, fuel, and other non-fuel components. Among the approaches related to fuel, improving UO₂ by introducing dopants has received considerable attention.

One of the main purposes of doping UO₂ is to strengthen the interaction between the fuel and fission products, thereby reducing their release during accident conditions. To evaluate this effect, it is first necessary to understand how fission products diffuse in UO₂. The diffusion behavior of gaseous fission products such as xenon and krypton has been widely studied because they are chemically inert and have low solubility in the fuel. In contrast, relatively few studies have investigated the diffusion of cesium. Its high volatility and hazardous nature make experimental investigations difficult. Although first-principles calculations can provide useful information on Cs behavior in UO₂, their computational cost limits the range of conditions that can be examined. Molecular dynamics simulations using a machine learning potential therefore provide an efficient approach for investigating Cs diffusion over a wider range of conditions.

In this study, we developed a machine learning potential to investigate the diffusion behavior of Cs in UO₂, with the aim of providing a computational framework for future ATF studies. The potential was trained using DFT+U data to obtain an accurate description of the UO₂-based system. It was further optimized to reproduce the thermal properties of UO₂ as well as the diffusion behavior of Cs. The calculated structural properties showed good agreement with ab initio results and previous studies. These results indicate that the developed potential can be used to investigate the high-temperature behavior of UO₂ and the diffusion of Cs. In addition, the potential may provide a useful computational tool for evaluating doped and sintered UO₂ fuel systems in future ATF applications.

2. Methods and Results

2.1 Ab-initio molecular dynamics simulations

The calculated data for the UO₂-Cs crystal system were obtained from ab initio molecular dynamics (AIMD) simulations to construct the training set for the moment tensor potential. All calculations were performed using the Vienna Ab initio Simulation Package (VASP) [1]. A total of 37 initial structural models were prepared by varying the positions of vacancies, substitutional defects, and interstitials to account for various system behaviors over a wide temperature range.

The initial structural models consisted of 2×2×2 supercells and were used for AIMD simulations with a Nosé-Hoover thermostat at temperatures of 500, 1500, 2500, and 3000 K. With a time step of 1 femtosecond (fs), each molecular dynamics (MD) simulation was carried out for 100 steps. Therefore, approximately 14,800 configurations were expected to be generated. However, some calculation steps did not converge, resulting in a final dataset of approximately 4,700 configurations.

One of the important aspects of simulating UO₂ is the accurate description of the strong correlation among the U 5f electrons. Conventional density functional theory calculations based on the local-density approximation (LDA) or generalized gradient approximation (GGA) often show limited accuracy for UO₂ because these approaches significantly underestimate strong electron correlation effects. Therefore, in this study, the DFT+U method was employed to improve the reliability of the calculated data [2]. The U and J parameters were set to 4.5 and 0.54 eV, respectively, as these values have been reported to provide good agreement with experimental data. In addition, the plane-wave cutoff energy was set to 500 eV, and the electronic energy convergence criterion was set to 4.0×10⁻⁵ eV.

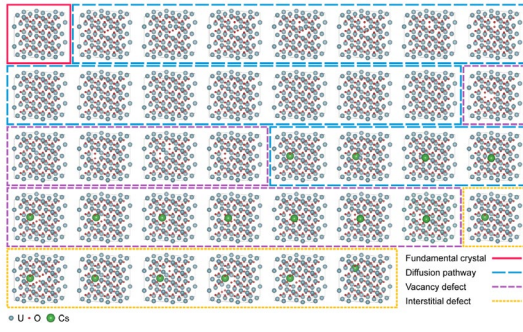


Fig. 1. Base structural model scheme for AIMD simulation

2.2 Developing moment tensor potential

The data obtained from the AIMD simulations were used to prepare the training and test sets for the construction of the moment tensor potential (MTP). The potential was developed using the Machine Learning Interatomic Potentials (MLIP) package, which has been widely used for constructing interatomic potentials for multicomponent systems [3].

During the construction of the MTP, the functional complexity parameter, referred to as the level, plays an important role in controlling both the accuracy and computational efficiency of the potential. Based on convergence tests of the mean absolute error (MAE) and root-mean-square error (RMSE) for energy, an untrained MTP with level 16 was selected as the initial model for constructing a more accurate UO_2 potential. The energy difference between the MTP predictions and DFT+U calculations was compared, as shown in Figure 2. In addition, configurations with interatomic distances ranging from 0.5 to 6 Å were selected to improve the accuracy while maintaining reasonable computational efficiency.

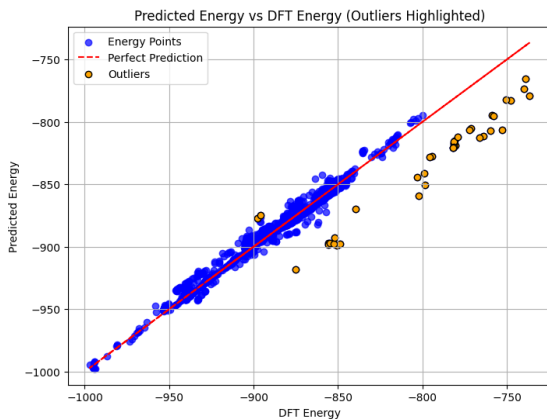


Fig. 2. Graph for comparison between predicted energy and DFT+U calculation energy.

To reduce bias caused by overrepresented data in the training and test sets, the data distributions were examined with respect to the energy per atom (EPA), volume, and maximum force ($\max|F|$). For each property, the data were divided into several ranges, and the data density within each range was evaluated. When

an excessive number of data points were concentrated in a specific region, a portion of those data was removed to obtain a more balanced dataset.

The sampling results and data densities according to each criterion are shown in Figure 3. The red dots indicate regions where similar data points were highly concentrated, and some of these points were selectively removed. The histograms in the lower panels compare the original dataset (gray bars) with the filtered dataset (colored bars), illustrating the changes in data distribution after removing overrepresented configurations.

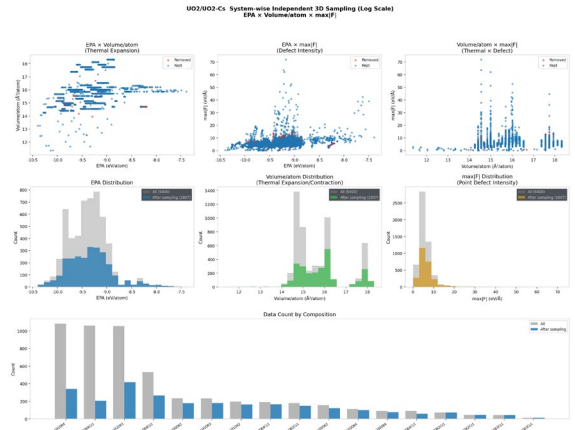


Fig. 3. Distribution of train and test data based on energy per atom (EPA), volume per atom, and maximum force.

2.3 Simulation result of structural properties of UO_2

To verify the high-temperature behavior of the UO_2 lattice, we first examined the temperature-dependent expansion of the lattice parameter using molecular dynamics (MD) simulations. The simulations were conducted using a $2 \times 2 \times 2$ UO_2 supercell under the NPT ensemble, in which the number of particles, pressure, and temperature were controlled. A time step of 1 fs was used, and each simulation was performed for a total of 1,000,000 steps.

Figure 4 compares the lattice parameters obtained from experiments, previously developed interatomic potentials, and the potential developed in this study. The results indicate that the temperature dependence of the lattice parameter and the corresponding thermal expansion behavior are in good agreement with those reported in previous studies [4–6]. Although some differences were observed between the experimental and calculated values, the overall trends were reproduced reasonably well. The calculated lattice parameters showed a slight tendency toward overestimation, which may be associated with the effective U parameter employed in the DFT+U calculations.

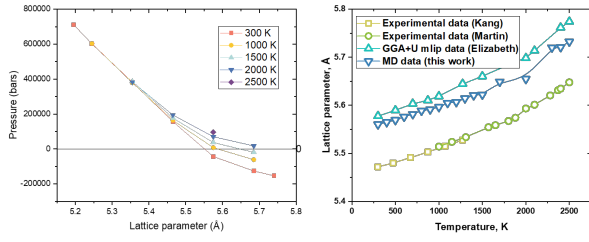


Fig. 4. Expansion behavior of lattice parameter depending on temperature.

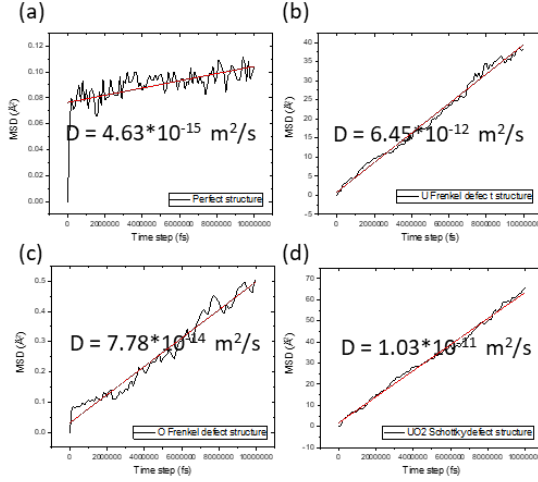


Fig. 5. Mean square displacement (MSD) of Cs in (a) perfect structure, (b) uranium Frenkel vacancy structure, (c) oxygen Frenkel vacancy structure, and (d) UO₂ Schottky vacancy structure.

The diffusion behavior of cesium and uranium was also investigated at 2000 K using MD simulations. The diffusion coefficient of each element was calculated from the mean square displacement (MSD) using the following equation:

$$D(t) = D_0 \exp\left(-\frac{E_a}{RT}\right) = \frac{\langle |S(t)|^2 \rangle}{6t}$$

where $\langle |S(t)|^2 \rangle$ is mean square displacement and t is time.

The diffusion of cesium was simulated using several structural models to first examine the effect of defect concentration on diffusion behavior. As shown in Figure 5, the diffusion coefficient of uranium increases in the presence of uranium vacancies, whereas oxygen vacancies cause only a slight increase in uranium diffusion. These results are consistent with uranium diffusion mechanisms reported in previous studies, in which uranium transport is mainly governed by self-diffusion processes [7]. Therefore, the developed MTP is considered sufficiently reliable for describing high-temperature diffusion behavior in UO₂.

Several limitations of the present model should also be noted. The MTP was trained using configurations sampled at discrete temperatures of 500, 1500, 2500, and 3000 K and a limited set of point-defect structures.

Therefore, its accuracy for defect configurations, compositions, or extended defects outside the training domain, such as grain boundaries, dislocations, and high-burnup microstructures, has not yet been established. In addition, the MD simulations were performed on the nanosecond timescale, which is much shorter than the timescales relevant to in-reactor Cs transport. Accordingly, the calculated diffusion behavior assumes that the trends observed in short-timescale MD simulations remain applicable to reactor-relevant conditions, and further validation using longer-timescale simulations or experimental release data is required.

3. Conclusions

We developed a machine learning potential to investigate the UO₂-Cs system and confirmed that the simulation results are in good agreement with DFT+U calculations and previous studies. These results indicate that the developed potential is suitable for simulating the thermal expansion behavior of UO₂ and the diffusion of cesium within the lattice at high temperatures. The potential may therefore be broadly applied to simulations aimed at evaluating the characteristics and practical feasibility of ATF fuel pellets. In addition, the Cs diffusion coefficients obtained from this framework can be used as physically based input parameters for engineering-scale fuel performance codes, such as FRAPCON-type models, to improve the prediction of Cs transport and fission-product release behavior under normal operating and accident conditions.

ACKNOWLEDGMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Science and ICT (MSIT) of the Republic of Korea (RS-2024-00420956, RS-2025-02353161), Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (RS-2025-02633904).

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