Machine learning molecular dynamics simulations toward exploration of high-temperature properties of nuclear fuel materials: case study of thorium dioxide

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Predicting materials properties of nuclear fuel compounds is a challenging task in materials science. Their thermodynamical behaviors around and above the operational temperature are essential for the design of nuclear reactors. However, they are not easy to measure, because the target temperature range is too high to perform various standard experiments safely and accurately. Moreover, theoretical methods such as first-principles calculations also suffer from the computational limitations in calculating thermodynamical properties due to their high calculation-costs and complicated electronic structures stemming from $f$-orbital occupations of valence electrons in actinide elements. Here, we demonstrate, for the first time, machine-learning molecular-dynamics to theoretically explore high-temperature thermodynamical properties of a nuclear fuel material, thorium dioxide. The target compound satisfies first-principles calculation accuracy because $f$-electron occupation coincidentally diminishes and the scheme meets sampling sufficiency because it works at the computational cost of classical molecular-dynamics levels. We prepare a set of training data using first-principles molecular dynamics with small number of atoms, which cannot directly evaluate thermodynamical properties but captures essential atomistic dynamics at the high temperature range. Then, we construct a machine-learning molecular-dynamics potential and carry out large-scale molecular-dynamics calculations. Consequently, we successfully access two kinds of thermodynamic phase transitions, namely the melting and the anomalous transition induced by large diffusions of oxygen atoms. Furthermore, we quantitatively reproduce various experimental data in the best agreement manner by selecting a density functional scheme known as SCAN. Our results suggest that the present scale-up simulation-scheme using machine-learning techniques opens up a new pathway on theoretical studies of not only nuclear fuel compounds, but also a variety of similar materials that contain both heavy and light elements, like thorium dioxide.

Thorium has attracted much attention as a potential nuclear fuel. Thorium is now estimated to be three to four times more abundant in nature than uranium the shortage of which might become a concern in the coming future. Moreover, its nuclear-fuel material form, thorium dioxide, is chemically more stable than the uranium-based counterpart. Owing to the above primary and other several advantages, thorium dioxide is considered to be a promising candidate fuel material in next-generation nuclear reactors.

The detailed information of nuclear fuel materials in a high temperature range around its melting point is a prerequisite for not only design of reactors but also nuclear safety. However, it is generally difficult to measure...
physical properties in such a high temperature range due to limitation of durability of experiment instruments and resultant concern about safety. It is also difficult to maintain the stoichiometry of some fuel compounds at such high temperatures (e.g. PuO$_2$). Therefore, the experimental data of thermal properties of thorium dioxide as well as other fuel materials has not been accumulated sufficiently in the temperature region. Thus, a theoretical approach accurately examining material properties in atomic-levels, i.e., molecular dynamics (MD) simulation has been intensively employed as an alternative important tool to complement insufficient experimental data.

Calculations of thermal properties through MD simulation require large-size and long-time runs in order to achieve statistical-mechanically reliable accuracy. Then, classical MD using empirical atomic force fields has been a primary scheme among various ones, because it allows statistically convergent properties to be obtained with reasonable computational costs. Indeed, several authors studied thermal properties of thorium compounds using classical MD. However, it should be noted that the obtained results strongly depend on the empirical parameters of the force field. This fact clearly indicates that careful development of atomic potentials is crucial for reliability of the calculated thermal properties. Then, their comparative studies among possible potential candidates are essential together with experimental results.

An alternative way to calculate thermal properties of materials is using first-principles calculations based on density functional theory (DFT). Its ab-initio style has made a great impact on atomic-level simulation studies because of their non-empirical modeling. However, first-principles calculations for thorium dioxide have been so far limited only in a few literatures. In the previous study, two of the authors have explicitly shown that first-principles molecular dynamics (FPMD) simulations provide reliable data of thermal properties of thorium dioxides in the high temperature range, but the system size and averaging time were severely restricted due to its huge computational costs.

In the last decade, machine learning has been used as a tool to construct atomic potentials. The machine learning techniques are utilized to train potential energy surfaces (PES) with first principles accuracy by interpolation among a large number of reference data obtained by first principles calculations. One of promising machine learning approaches is a method using artificial neural networks (ANN) proposed by Behler and Parrinello. We call the ANN Behler-Parrinello neural networks (BPNN) throughout this paper. In contrast to empirical atomic force fields, BPNN is not based on any physical modeling but have a large number of adjustable parameters. The rich flexibility in BPNN enables us to make PES of which accuracy is comparable to those calculated from first-principles.

Generally, machine learning molecular dynamics (MLMD) using BPNN is expected to access thermal properties with first-principles accuracy even in unavailable large system sizes and long average times for FPMD. Actually, using the advantage of MLMD, structural phase transitions have been successfully examined by MLMD. However, these cases demand not so large system size because the phase transition among different solid phases can be well captured with periodic boundary conditions. On the contrary, mixture of phases including liquids and/or gases require large systems to evaluate physical processes. In this paper, using MLMD with BPNN, we evaluate thermal properties of thorium dioxide, as an example of nuclear fuels, with first principles accuracy in a wide temperature range, whose upper limit is beyond the melting point.

Thorium dioxide has a fluorite structure with space group Fm$ar{3}$m, in which the 4a and 8c positions are occupied by thorium and oxygen ions, respectively. The lattice constant at room temperature is 5.592 Å, and the melting point is 3651 K. In addition, another kind of phase transition was reported below the melting point so far limited only in a few literatures. In the previous study, two of the authors have explicitly shown that first-principles molecular dynamics (FPMD) simulations provide reliable data of thermal properties of thorium dioxides in the high temperature range, but the system size and averaging time were severely restricted due to its huge computational costs.

Methods
Vienna ab initio Simulation Package (VASP) is used for obtaining reference data sets for BPNN. In all calculations, the projector-augmented wave method is employed, and 500 eV energy cutoff is chosen. In this study, we use three types of XC functionals: the local density approximation (LDA) in the parametrization of Ceperly and Alder, the generalized gradient approximation of Perdew–Burke–Ernzerhof for solids (GGA-PBEsol), and the strongly constrained and appropriately normed (SCAN) meta-GGA XC functional.

First, we perform FPMD NPT simulations with PBEsol functional from 300 to 5000 K with a 100 K temperature step. The combination of the Langevin thermostat and Parrinello–Rahman barostat is adopted to generate the NPT ensemble. The time step and simulation total time at each temperature are 2 fs and 16 ps, respectively. Potthoff et al. pointed out that the smallest cell size to capture the Bredig transition in MD simulations is 3 × 3 × 3 of the unit cell. Thus, we also choose 3 × 3 × 3 supercell of thorium dioxide (324 atoms) and only 1 point is used as a k-point mesh. We randomly pick up 9000 snapshots of the MD simulations as the reference data based on PBEsol. For creating the reference data based on LDA and SCAN functionals, we randomly select 3000 structures from the dataset based on PBEsol, and evaluate the energies and forces of the 3000 configurations by DFT calculations with LDA and SCAN. The 3000 structures recalculated by DFT with LDA and SCAN...
Table 1. RMSE of BPNN-LDA, BPNN-PBEsol and BPNN-SCAN for the training and test data.

|          | BPNN-LDA | BPNN-PBEsol | BPNN-SCAN |
|----------|----------|-------------|-----------|
| Energy (meV/atom) | 2.085 | 2.108 | 2.297 | 2.357 | 1.207 | 1.264 |
| Force (10⁻² eV/Å) | 5.705 | 6.551 | 7.906 | 8.239 | 5.812 | 5.769 |

are used as the reference data sets for BPNNs based on LDA and SCAN. Furthermore, the adaptive learning scheme\(^\text{39-41}\) is used to improve the quality of the reference datasets. In this scheme, we create two BPNNs with different initial weights and conduct MLMD simulations to generate various structures of ThO\(_2\). Next, we select structures with large force differences between the outputs of the two BPNNs from the generated structures. Finally, we re-evaluate the energies and forces for the selected structures by DFT and add these to the reference data. As a result, the total numbers of the reference data based on LDA and SCAN XC functionals are 7749 and 7007 structures, respectively.

We use the n2p2 code\(^\text{44}\) for training BPNN. In BPNN, a local environment of each atom with a cutoff radius \(R_c\) is encoded to descriptor vectors. We adopt the following type-2 and type-4 symmetry functions\(^\text{22}\) as the descriptors of the distances and the angles of atoms, respectively, i.e.,

\[
G_i^{(2)}(R) = \sum_j e^{-\eta(R_i-R_j)^2} f_c(R),
\]

\[
G_i^{(4)}(R) = 2^{1-\xi} \sum_{j\neq i} \sum_{k\neq i,j} (1 + \cos \theta_{ijk})^\xi e^{-\eta(R_i-R_j)^2 + R_i^2 + R_j^2} f_c(R_i) f_c(R_j) f_c(R_k),
\]

with the cutoff function

\[
f_c(R) = \begin{cases} 
0.5 \cos \left( \frac{R}{R_c} + 1 \right) & \text{for } R \leq R_c \\
0 & \text{for } R_c < R
\end{cases}
\]

where \(R_{ij}\) is the distance between the \(i\)-th and \(j\)-th atoms, \(\theta_{ijk}\) is the angle formed by line segments between the \(i\)-th and \(j\)-th atoms and the \(i\)-th and \(k\)-th ones. The cutoff radius \(R_c = 0.0\), and the other parameters were selected by CUR decomposition\(^\text{45}\). First, we creat symmetry functions with a total \(N_{\text{SF}} = 240\) dimension and construct \(N_{\text{SF}} \times N_{\text{SF}}\) feature matrix \(X\), where each column vector consist of the symmetry function of the corresponding sample. Then, we perform a CUR decomposition for the feature matrix \(X\) and select the symmetry functions that satisfies the following criteria: \(||X - \text{CUR}||_F / ||X||_F \leq 10^{-4}\), where \(||\cdot||_F\) denote the Frobenius norm. The detailed lists of the selected symmetry functions are shown in the Supplemental Materials. Using a dataset consisting of a selected descriptor vector and corresponding first-principles energy and forces, BPNNs are trained. We use two hidden layers with hyperbolic tangent activation functions with 30 nodes. The multistream Kalman filter method\(^\text{46}\) is adopted as an optimizer for BPNN. 90% of the reference data is assigned to training data and the remaining 10% as test data. We construct three machine learning potentials using data generated by DFT with the LDA, PBEsol and SCAN XC functionals, which are referred to as BPNN-LDA, BPNN-PBEsol and BPNN-SCAN, respectively.

In this paper, all MD simulations are carried out by LAMMPS\(^\text{47}\). NPT simulations are performed with Nosé–Hoover thermostat and barostat relaxation times being 0.1 ps and 0.5 ps, respectively.

### Results

#### Accuracy of machine learning potentials

Table 1 summarizes the root mean square errors (RMSE) of energy and force for the training and test data. The RMSEs of the present BPNNs for the reference data are below 2.4 meV/atom for the reference energies and \(8.3 \times 10^{-2}\) eV/Å for the forces, which are comparable with the typical RMSEs in previous studies\(^\text{20,61-63}\). In order to test the accuracy of BPNNs, we compare physical quantities obtained by DFTs, BPNNs, empirical atomic potentials, and experiments data. In this paper, we choose BD08 and the Cooper, Rushton and Grimes (CRG)\(^\text{49}\) empirical atomic potentials for comparison with DFTs and BPNNs. BD08 atomic potential is a relatively simple pairwise potential consisting of the Coulombic and the Buckingham potentials\(^\text{51}\). On the other hand, CRG atomic potential includes many-body EAM-type potential\(^\text{52}\) in addition to the pairwise potentials.

We compute the lattice constant, elastic properties, and phonon dispersion curves at zero temperature using DFTs, BPNNs, and empirical atomic potentials. The elastic constants are calculated by a numerical differential of the stress tensors with respect to finite strains. The phonon bands within the harmonic approximation are obtained using Phonopy\(^\text{38}\) with the finite difference method. In phonon calculations, to treat long range interaction of macroscopic electric field induced by polarization of atomic displacement near 1 point, we add non-analytical correction by dipole-dipole interaction to dynamical matrix\(^\text{59,60}\) (see also the Supplementary Materials). The computed results are shown in Table 2 and Fig. 1. The lattice constant and elastic data of BPNN are compared with those by DFT ones. The results computed by (BPNN-)PBEsol and (BPNN-)SCAN show similar lattice and elastic constants, which also agree with the experiment ones\(^\text{53-55}\), whereas (BPNN-) LDA slightly underestimates the lattice constant. Comparing the results obtained by DFTs, BPNNs and empirical...
atomic potentials, the lattice constant and elastic data calculated by BD08 and CRG potentials seem to be more accurate than the results obtained by DFTs and BPNNs. Note that this is not necessarily surprising given that the empirical potentials are fitted to these experimental properties. The phonon dispersion curves calculated by BPNNs are also in good agreement with the curves obtained by DFTs, as shown in Fig. 1a,b. Furthermore, DFTs and BPNNs reproduce the experimental data almost completely. Especially, we note that optical modes in the phonon dispersion curves calculated by the empirical atomic potentials show large deviation from the experimental data as shown in Fig. 1c though the results of DFTs and BPNNs are almost perfect in these modes. So far, we have validated the BPNN potentials using static calculations. However, the validations for dynamical calculations are also required, since inappropriate BPNN potentials sometimes cause unstable MLMD and result in structural collapse with a long simulation period, especially at high temperatures. On the other hand, MLMDs using the present BPNNs show good stability in long-period NVE simulations as shown in the supplementary.

Table 2. Lattice constant and elastic properties of ThO$_2$ obtained by DFTs, BPNNs, empirical potentials, and experiments (Exp.). The round brackets (·) in the BPNN columns represent the percentage errors of the BPNN results against the DFT results.

| Property                  | DFT LDA | DFT PBEsol | DFT SCAN | BPNN LDA | BPNN PBEsol | BPNN SCAN | Empirical potential | Exp. |
|---------------------------|---------|------------|----------|----------|-------------|-----------|---------------------|------|
| Lattice constant (Å)      | 5.529   | 5.576      | 5.598    | 5.531 (0.04) | 5.565 (0.20) | 5.610 (0.21) | 5.600               | 5.580 |
| Bulk modulus (GPa)        | 215.3   | 204.8      | 205.1    | 219.5 (1.95) | 199.0 (2.83) | 205.4 (0.15) | 193                 | 193.0 |
| Shear modulus (GPa)       | 98.0    | 96.6       | 100.0    | 90.0 (8.16)  | 91.1 (5.69)  | 87.7 (12.30) | 107.9               | 88.1  |

Figure 1. Phonon dispersion curves for ThO$_2$. (a–c) Phonon dispersion obtained by (BPNN-)LDA, (BPNN-)PBEsol, and (BPNN-)SCAN where black and red line are the results computed by DFT and BPNN, respectively. (d) Are the results obtained by BD08 (green line) and CRG potential (purple line). Circle dots in (a–d) represent the experimental data.57
Cp can be characterized as 

\[ \alpha(T) = \frac{\partial C_p}{\partial T} \]

ies give close values in the low-temperature range, but show different behavior in the high-temperature range.

MLMD enables us to easily evaluate these quantities by FPMD. Then, we perform numerical measurements at a large number of temperature points with a tiny temperature step elevation for averaging time to avoid the finite size effects. In addition, computations of the heat capacity and ACLTE require where

\[ C_p = \frac{1}{n} \frac{\partial H(T)}{\partial T}, \]

where \( n \) is the amount of substance in moles. Calculations of these properties require large system size and long averaging time to avoid the finite size effects. In addition, computations of the heat capacity and ACLTE require numerical measurements at a large number of temperature points with a tiny temperature step elevation for smooth numerical differentials. Therefore, it is difficult to evaluate these quantities by FPMD. Then, we perform MLMD \( NPT \) simulations using \( 6 \times 6 \times 6 \) supercell (2592 atoms) and totally 200 ps run per 10 K temperature step. The \( 6 \times 6 \times 6 \) supercell is large enough to neglect finite size effects and to evaluate the thermal properties of ThO\(_2\) as shown in the supplementary material. Moreover, in order to smooth the curves of heat capacity and ACLTE, we average their values over the interval of \( \pm 100 \) K twice as performed in reference\(^{64}\) (see also the Supplementary Material). For the comparison, we also calculate the thermal properties using classical MD with BD08 and CRG empirical potentials.

Figure 2 shows the temperature dependence of LTE, enthalpy, and specific heat capacity \( C_p \). Among the LTEs obtained by MLMDs and classical MDs as shown in Fig. 2a, the results computed by BPNN-SCAN show the best agreement with the Touloukian fitting of the experimental results, which is available up to 2000 K. The ACLTEs in the range from 300 to 1600K are listed in Table 3. The ACLTE computed by BPNN-SCAN also shows good agreement with the experimental data \( 9.5 \times 10^{-6} \text{ K}^{-1} \) from Momin (298–1600 K)\(^{62}\) and 9.67 \times 10^{-6} \text{ K}^{-1} by Rodriguez (293–2273 K)\(^{63}\).

In enthalpy calculation as shown in Fig. 2a, the results computed by BPNN-SCAN and CRG potential provide close values to the Bekker fitting of the experiment\(^{64}\) over the entire temperature range. All computed enthalpies give close values in the low-temperature range, but show different behavior in the high-temperature range where the specific heat anomaly emerges as shown in Fig. 2b. The onset temperature of the specific heat anomaly can be characterized as \( T_o \), which is defined as the temperature giving the minimum value of \( C_p/T^2 \). \( T_o \) are ordered as BPNN-LDA, BPNN-PBEsol < CRG, BPNN-SCAN < BD08 as listed in Table 3. The peak position of \( C_p \) obtained by BPNNs and CRG potential are in good agreement with the experimental results 2950 K\(^{27}\) and 3090 K\(^{29}\) reported as the Bredig transition temperature.

**Oxygen diffusion and defect concentration.** We evaluate the mean square displacements (MSD) defined as

\[ \text{MSD}(t) = \frac{1}{N_a} \sum_{i} N_a |r_i(t) - r_i(0)|^2, \]

Table 3. The lattice constant \( L(T) \) at 300 K, the averaged coefficient of linear thermal expansion (ACLTE), the onset temperature of heat capacity anomaly \( T_o \), and the \( \lambda \)-peak temperature \( T_c \) are summarized.

|          | BPNN-LDA | BPNN-PBEsol | BPNN-SCAN | BD08  | CRG   | Exp.  |
|----------|----------|-------------|-----------|-------|-------|-------|
| \( L(300) \) | 5.545    | 5.580       | 5.624     | 5.616 | 5.595 | 5.592\(^{25}\) |
| ACLTE (10^{-8} \text{ K}^{-1}) | 9.95     | 10.65       | 9.71      | 10.84 | 10.05 | 9.5\(^{41}\), 8.67\(^{30}\), 11.07\(^{26}\) |
| \( T_o \) (K) | 2360     | 2350        | 2460      | 2760  | 2450  |
| \( T_c \) (K) | 3040     | 2980        | 3200      | 3440  | 2930  | 2950\(^{27}\), 3090\(^{29}\) |
where $r_i(t)$ is the position of the $i$-th atom at time $t$ and $N_\alpha$ is the total number of $\alpha$ atoms ($\alpha$ is Th or O). The employed system size and total time-step are the same as the cases computing the thermal expansion and the molar specific heat capacity. We conduct NVE simulations with 1 fs time-step at various temperatures using the volumes previously calculated in NPT ensemble. Figure 3a shows the MSD computed by MLMD with BPNN-SCAN. In the previous study using FPMD19, accurate evaluations of MSD could not be performed due to its high computational costs. In contrast, MLMD easily overcomes such a limitation, and then sufficiently long simulations allow us to detect the diffusive regime even in the temperature region below $T_c = 3200$ K (see MSD of oxygen at 2300 K in Fig. 3a). It should also be mentioned that Th shows vibrational motions below and above the transition temperature. We evaluate the self-diffusion constant $D$ for the oxygen atoms from the slope of MSD in the range 25 to 100 ps. Figure 3b shows the temperature dependence of the self-diffusion constant for the oxygen atom. In all MLMD and classical MD simulations, one can find the bending of the Arrhenius plot above $T_c$. The deviation of the self-diffusion constant from Arrhenius law was experimentally reported in PbF$_2$66,67, which belongs to the fluorite-type structure like ThO$_2$. We calculate the activation energy of diffusion below $T_c$ using the Arrhenius relation, $D = D_0 \exp(-E_{AE}/kT)$. Table 4 shows the values of the activation energy obtained by MLMDs and empirical MDs. All BPNNs give similar activation energies, which are lower than those obtained by the empirical atomic potential.

The specific heat anomaly and dynamics of anions have been investigated related to the disorders in fluorite, and defect cluster models have been proposed so far.68,69 In this study, we focus on the vacancy concentration of oxygen in the regular site. In an ideal fluorite structure, one oxygen exits within a cube with vertices: (0, 0, 0), (0, 0, 1/2), (0, 1/2, 0), (1/2, 0, 0), (0, 1/2, 1/2), (1/2, 1/2, 0), (1/2, 0, 1/2), and (1/2, 1/2, 1/2). Thus, we count a number of cubes not including oxygen from MD trajectories and define the vacancy concentration as the ratio of the empty cubes. As with the self-diffusion constant for oxygen, the temperature dependence of the oxygen
vacancy concentrations obeys the Arrhenius law below $T_c$, and the Arrhenius plots bent downwards above $T_c$ as shown in Fig. 3c. These results indicate that the origin of the lambda transition and anion dynamics are closely related to the defect formation. The vacancy concentration of oxygen obtained by MLMDs and classical MDs are from 1 to 3% at $T_c$ and are within 10% above $T_c$. The low defect concentration of ThO$_2$ below $T_c$ is consistent with the experimental results of fluorite materials$^{70–72}$.

Melting temperature. The melting temperature of thorium dioxide can be determined by the so-called two-phase simulation approach. A $6 \times 6 \times 12$ supercell (5184 atoms) including both solid and liquid phases is prepared as an initial configuration as shown in Fig. 4a. MLMD NPT simulations are performed from 3000 to 4000 K, in which the simulation time is taken over 500 ps. Figure 4b shows averaged enthalpy calculated by BPNN-SCAN in the periods from 0 ps to 100 ps, 200 ps to 300 ps, and 400 ps to 500 ps, respectively. From Fig. 4b, we can confirm that the enthalpy jump at 3620 K and the melting point evaluated by MLMD with BPNN-SCAN lies between 3610–3620 K. The melting temperatures evaluated by MLMDs and classical MDs are also summarized in Table 5. BPNN-SCAN closely reproduce the experimental melting point (3651 K) while BPNN-LDA give somewhat lower melting point (3450–3460 K) and BPNN-PBEsol significantly underestimate it as 3250–3260 K. The choice of XC functional seems to be sensitive in evaluating accurate melting temperature. In calculation using empirical potentials, CRG potential provides accurate melting temperature, whereas BD08 potential over-estimates it as shown in Table 5.

| BPNN-LDA | BPNN-PBEsol | BPNN-SCAN | BD08 | CRG | Exp. |
|----------|-------------|-----------|------|-----|-----|
| $T_m$ (K)| 3450–3460   | 3250–3320 | 3610–3620 | 3810–3820 | 3640–3650 | 3651$^{71}$ |

Table 4. Activation energy of diffusion below $T_c$ and vacancy concentration at $T_c$.

| BPNN-LDA | BPNN-PBEsol | BPNN-SCAN | BD08 | CRG |
|----------|-------------|-----------|------|-----|
| Activation energy below $T_c$ (eV)| 4.851 | 4.446 | 4.400 | 7.049 | 6.696 |
| Vacancy concentration at $T_c$ (%)| 2.5 | 1.7 | 2.3 | 1.3 | 1.5 |

Table 5. The melting points evaluated by two phase simulations.

Conclusion
MLMD simulations using BPNN were extensively performed to evaluate the thermal properties of a fuel material, thorium dioxide. In this paper, we made three types of BPNNs based on DFT reference data with LDA, PBEsol, and SCAN XC-functionals. We confirmed that the constructed BPNNs have close accuracy with DFTs through the comparisons of lattice constant, elastic properties, and phonon dispersion, which also well agree with the experimental data. Moreover, large-size and long-run simulations being inaccessible for FPMD were successfully performed by using MLMD. Through the systematic studies for thermal properties of thorium
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Author contributions

K.K., M.O. and H.N. performed the simulations under the supervision of H.N. and M.M. K.K. and M.M. wrote the main manuscript. M.O., H.N. M.I. and M.W.D.C. improved the idea and revised the manuscript. All authors reviewed and approved the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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