

Evaluation of uranium dioxide thermal conductivity using molecular dynamics simulations

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1. Introduction

Uranium dioxide is the most common nuclear fuel materials among the present commercial reactors. So, it has been studied extensively for over half a century [1]. Uranium dioxide has high melting temperature ($T_m \sim 3120\text{K}$), radiation stability, and chemical compatibility [2] compare to properties of uranium metal. However, uranium dioxide has low thermal conductivity. Low heat releasing ability is the main cause of loss of mechanical integrity of fuel material such as, localized melting, swelling and oxygen diffusion. It shortens the fuel cycle and induce low reliability of reactor. Since above phenomena are based in microscopic phenomena, correct evaluation of thermal conductivity in microscopic scale is the first step of understanding the microscopic mechanisms of current issues. Also, it can be extended to larger space, time scale and even real reactor situation with fission product as multi-scale formalism.

Uranium dioxide is a fluorite structure with Fm3m space group. Since it is insulator, dominant heat carrier is phonon, rather than electrons. So, using equilibrium molecular dynamics (MD) simulation, we present the appropriate calculation parameters in MD simulation by calculating thermal conductivity and application of it to the thermal conductivity of polycrystal.

2.1 Force field model

In classical molecular dynamics simulation, effective force field (potential) model is introduced in order to describe the interatomic interaction. Effective potential model consists of two components: short-range interactions which describe approximately quantum mechanical effect of materials and a long-range electrostatic component which is traditional Coulomb force.

For short range model, we used Yamada potential [3]. The Yamada model is a Bushing-Ida type potential which is composed of the Buckingham potential and Morse potential. It is given by

$$\begin{aligned} \phi(r_{ij}) = & A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{c_{ij}}{r_{ij}^6} \\ & + D_{ij} \left[\exp\left(-2\beta_{ij}(r_{ij} - r_{ij}^*)\right) \right. \\ & \left. - 2 \exp\left(-\beta_{ij}(r_{ij} - r_{ij}^*)\right) \right] \quad (1) \end{aligned}$$

where r_{ij} is the interatomic distance between atom i and j . A_{ij} , ρ_{ij} , c_{ij} , D_{ij} , β_{ij} and r^* are the potential parameters between atom types which is presented in Table 1. Buckingham potential is the most common potential when describing ionic crystal and Morse potential, which provides 'covalent' component. However, this term is not strictly covalent in the sense that it does not have directionality. Due to the assumption of partial covalency, the charges of the ions are given by non-formal values. [4] (see Table 1).

Table 1. Potential parameters for Uranium dioxide

Yamada	U - U	O - O	U - O
$A_{ij}[\text{eV}]$	442.20	2346.15	1018.57
$\rho_{ij}[\text{\AA}]$	0.32	0.32	0.32
$c_{ij}[\text{eV \AA}^6]$	0	4.1462	0
$D_{ij}[\text{eV}]$	0	0	0.7810
$\beta_{ij}[1/\text{\AA}]$	0	0	1.25
$r_{ij}^*[\text{\AA}]$	0	0	2.369
$Q_U[e]$	+2.4		
$Q_O[e]$	-1.2		

Next, for long range potential, Coulomb potential is considered. Electrostatic terms are more difficult to approximate. Unlike quantum effects (few angstroms), electrostatic terms remain significant even at quite large distances (several tens of angstroms). Simply ignoring all terms beyond a specific distance results in large errors. The method of computing electrostatic interaction energy in large number of ionic crystal system with periodicity is called charge summation. Several methods have been developed such as Ewald [5] and Wolf summation [6]. In this work, we institute Wolf summation. Wolf summation calculate Coulomb term at a selected cutoff and compensate charge imbalance by surface charge on the truncated sphere. It offers both accuracy and highly improved computational performance [6].

Since elastic constant is directly related to force field, comparison of elastic constants from MD simulation and experiment is one way to verify both potential parameters and cutoff distance under given potential parameters. Table 2 presents the elastic properties of uranium dioxide from MD simulations with different cutoff and experiments. It gives reasonable values compared to the experimental results. Since MD simulation at 0K does not include kinetic motion of ions,

it is underestimated except C11. Accuracy of elastic constants will increase if elastic constants are calculated at 300K.

Table 2. Elastic constants for uranium dioxide: C1 is cutoff for short range potential and C2 is cut off for long range potential

	MD at 0K	Exp. [7-10] at 300K
	C1=8 Å, C2=10 Å	
C11[Gpa]	449.85	389–396
C12[Gpa]	71.647	119–121
C44[Gpa]	48.428	59.7–64.1
B[Gpa]	197.715	209–213

Our work is done by 10x10x10 cells, 12000 atoms, for pure crystal and 96000 atoms for poly crystal. Crystals are relaxed in NPT ensemble using Andersen barostat and Nose-Hoover thermostat and then heat flux is calculated on NVE ensemble which is standard MD calculation. Time step is 4 fs/step and total running steps are 80ps for relaxation and 200ps for calculating heat flux.

2.2 Green – Kubo formula

In equilibrium MD, thermal conductivity is calculated via fluctuation dissipation theorem. Heat flux in the system is defined as :

$$\mathbf{J} = \frac{1}{V} \frac{d}{dt} \sum_{\alpha} E_{\alpha} \mathbf{r}_{\alpha} = \frac{1}{V} \left[\sum_{\alpha} E_{\alpha} \mathbf{u}_{\alpha} + \frac{1}{2} \sum_{\alpha, \beta} (\mathbf{F}_{\alpha\beta} \cdot \mathbf{u}_{\alpha\beta}) \mathbf{r}_{\alpha\beta} \right] \quad (2)$$

With a definition of appropriate heat flux, the thermal conductivity can be obtained from the Green-Kubo formula.

$$\kappa_{ij} = \frac{V}{k_B T^2} \int_0^{\infty} \langle (J_i(0) - \langle J_i \rangle) (J_i(t) - \langle J_i \rangle) \rangle dt \quad (3)$$

Where J_i is the heat flux in i -direction, T is the temperature k_B is the Boltzmann constant, V is system volume and $\langle J \rangle$ is the average over the equilibrium ensemble. Generally, Green – Kubo formula can be written as

$$\xi = \lambda \int_0^{\infty} \langle \chi(0) \chi(t) \rangle dt = \lambda \int_0^{\infty} C(t) dt \quad (4)$$

which is equivalent to (3).

Here, ξ is the transport coefficient, χ is the fluctuation in flux, λ is $\frac{V}{k_B T^2}$ and $C(t)$ is auto correlation function. Clearly, the accuracy of the transport coefficient ξ depends directly on the accuracy of the calculated correlation and its integral [11]. Auto correlation function $C(t)$ is expressed as a time-average

$$C(t) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} \chi(s) \chi(s+t) ds = \lim_{\tau \rightarrow \infty} C_{\tau}(t) \quad (5)$$

Where $C_{\tau}(t)$ is an estimate of the correlation function $C(t)$ for a finite simulation time τ .

Also, integration cannot be applied up to infinite, integration for correlation function should be truncated. Thus, estimated thermal conductivity is given by

$$\xi_{\tau}(\tau_c) = \lambda \int_0^{\tau_c} C_{\tau}(t) dt \quad (6)$$

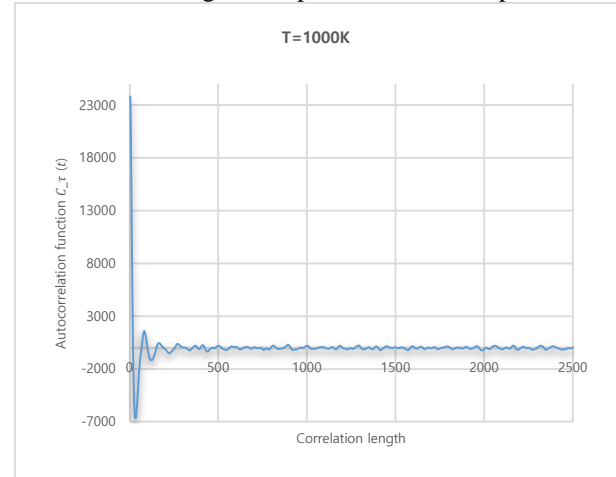
In MD calculation, integration is approximated to summation as :

$$\int_0^{\tau_c} C_{\tau}(t) dt \approx \sum_{n=0}^{N_c-1} C_{\tau}(n\Delta t) \Delta t \quad (7)$$

Here, N_c is the correlation length and Δt is the sample interval times timestep. Our work is optimizing these parameters to obtain thermal conductivity with high accuracy and efficiency in time.

Fig.1 shows autocorrelation function of uranium dioxide at 1000K. In this figure, correlation length is the number of samples which forms graph and sample interval is the steps of gap between each sampling. By this function being integrated, transport coefficient in converged to stable value.

Fig 1. Autocorrelation function at 1000K depending on correlation length. Sample interval is 5 steps.



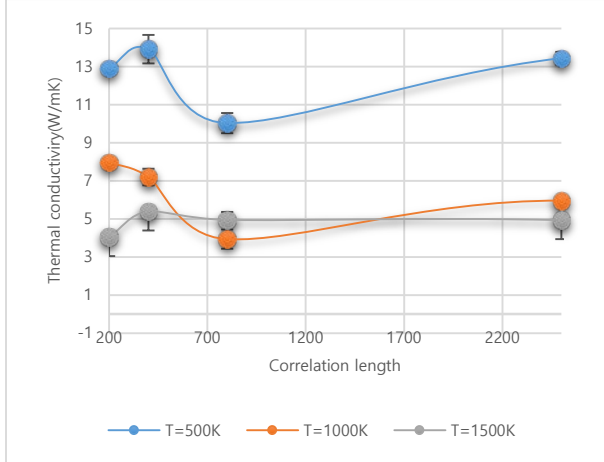
2.3 Correlation length

Correlation length is the number of correlation function sample. Theoretically, upper limit of correlation length is infinity. Thus, we can easily predict that larger correlation length is closer to correct answer. As shown in Fig 2, large correlation length gives converged thermal conductivity compared to small correlation length which shows undulating behavior.

It shows more improved result compared to the previous prediction of uranium dioxide thermal conductivity using molecular dynamics simulation with

Yamada potential. However, it still have some discrepancy when it measured it against experimental results. We estimated that modification of sample interval on ensemble integration and crystal structure arrangement can show reliable results. Next two sections are related with these factors.

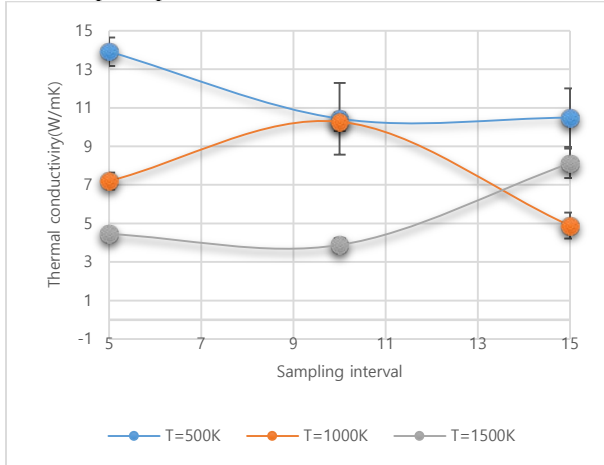
Fig. 2. Thermal conductivity of uranium dioxide depending on the correlation length at 500K, 1000K and 1500K.



2.4 Sample interval

Sample interval is slice of time step to integrate correlation function. Fig 3 is thermal conductivity at 500K, 1000K and 1500K with regard to sample interval change. We estimate that the shorter the sample interval, the more close result will be presented. In large sampling interval, thermal conductivity is not stable and also, it is mismatched with the theory, analytical slack relation [12]. Slack relation shows that thermal conductivity behavior in high temperature regime is inverse temperature ($1/T$) relation because the mean free path of phonon which is heat carrier of ion lattice decrease with $1/T$ relation and it is directly proportional to thermal conductivity. Thus, we can conclude that small sampling interval can be correct.

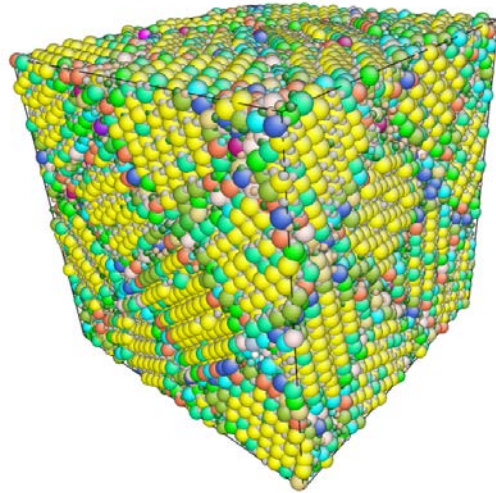
Fig. 3. Fraction of counts lost with voltage and charge sensitive preamplifiers as a function of the true count rate.



2.5 Polycrystal

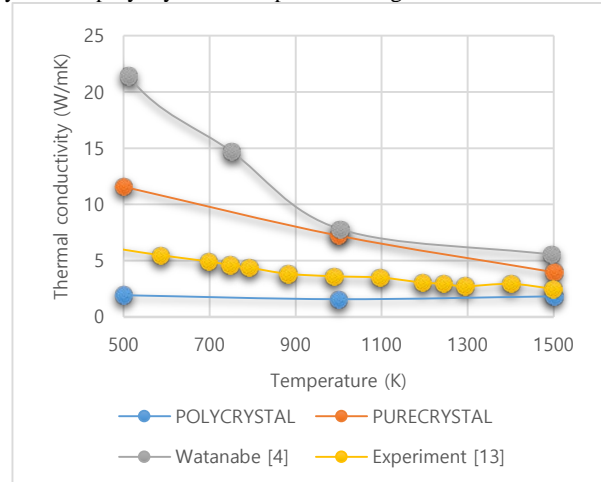
In real situation, previous pure crystal is unrealistic. Most real solid is polycrystal. In order to treat it, we made polycrystal using Voronoi construction from pure crystal sample. In this process, Voronoi construction make separations in lattice. The arrangement of these divided regions can be bcc (rhombic dodecadron), fcc (truncated octahedron) or random. After this, each regions are rotated randomly and crystal with rotated each region is polycrystal. Fig 4 shows polycrystal with rhombic dodecadron arrangement.

Fig. 4. Fraction of counts lost with voltage and charge sensitive preamplifiers as a function of the true count rate. Various colors of atom indicate the stress encodes of each atom. So it enables one to distinguish each grain. Large bead is uranium and small one is oxygen.



We obtain the thermal conductivity of uranium dioxide polycrystal with above strategies : large correlation length and short sample interval. Fig 5 is the thermal conductivity of pure crystal and polycrystal depending on temperature.

Fig. 5. Thermal conductivity of uranium dioxide pure crystal and poly crystal in temperature range of 500K ~ 1500K



Thermal conductivity of poly crystal is lower than that of pure crystal. Because in poly crystal long range acoustic phonon which is sensitive to temperature change is suppressed by the grain boundaries. As a result, it shows weaker temperature dependence.

3. Conclusions

In this work, we investigate thermal conductivity of uranium dioxide and optimize the parameters related to its process. In this process, called Green Kubo formula, there are two parameters i.e correlation length and sampling interval, which effect on ensemble integration in order to obtain thermal conductivity. Through several comparisons, long correlation length and short sampling interval give better results. Using this strategy, thermal conductivity of poly crystal is obtained and comparison with that of pure crystal is made. Thermal conductivity of poly crystal show lower value than that of pure crystal.

In further study, we broaden the study to transport coefficient of radiation damaged structures using molecular dynamics. Although molecular dynamics is tools for treating microscopic scale, most macroscopic issues related to nuclear materials such as voids in fuel materials and weakened mechanical properties by radiation are based on microscopic basis. Thus, research on microscopic scale would be expanded in this field and many hidden mechanism in atomic scales will be revealed via both atomic scale simulations and experiments.

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