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UO_2 bicrystal phonon grain-boundary resistance by molecular dynamics and predictive models

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ABSTRACT

Unlike phonon-boundary resistance at the interface of two dissimilar lattices, the phonon grain-boundary resistance $AR_{p,gb}$ is over an ultrathin atomic restructured region bounded by two identical lattices. Using nonequilibrium, classical molecular dynamic simulations on bicrystal UO_2 over 300–1200 K, we predict that $AR_{p,gb}$ (i.e., phonon, grain mean free path) is independent of temperature and the grain boundary type (e.g., tilt, twist). We compare these predictions with existing analytical models and identify those which include the proper grain-boundary phonon scattering mechanisms. Also, using the same embedded-atom interatomic potential models, we predict the phonon dispersion, density of states and bulk thermal conductivity of UO_2, and verify the predictions (comparing with available *ab initio* molecular dynamics and experimental results), under equilibrium and nonequilibrium simulations.

1. Introduction

Prediction of fuel thermal transport in commercial nuclear fuel materials, e.g., UO_2, is related to safety and economic efficiency of nuclear power plants. For several decades, modeling of thermal transport performance and other phenomena have been investigated actively in continuum or engineering scale based and mostly along with empiricism. A major drawback of this approach is that such phenomena in nuclear material are decoupled from existing empirical models [1]. For further advances, higher resolution modeling [2–5] has been proposed, including use of recent advances in computational capability and development. The multiscale modeling has ability to elucidate the underlying mechanisms [6] by decoupling internal state variables [7] from the atomic-scale modeling. In particular, the thermal transport modeling has received attention at atomic and mesoscale [8–14], due to strong microstructure dependence, these include the effects of gas bubbles [10,11,15], dislocation [9], hyper-stoichiometry [16–18], and radiation defects [8].

Here we study grain-boundary (GB) effect in UO_2, causing decrease in thermal conductivity by scattering phonons which are its dominant heat carrier. We use classical molecular dynamics (CMD) simulations with the newly proposed embedded-atom method (EAM) interatomic potentials, called the CRG potential [19]. We verify these potentials through predicted phonon dispersion, density of states, and bulk thermal conductivity by comparison with experimental and available non-equilibrium *ab initio* MD (AIMD) results. The thermal transport through GB, a bicrystal structure, is presented as the associated GB thermal resistance found using non-equilibrium MD. We compare this resistance with available results and predictive models. Calculated thermal resistance are good agreement with predictive models.

2. Methods

2.1. Interatomic potential models

In this work, we used the CMD simulations as the main tool for describing the UO_2 systems at the atomic scale. The CMD approach provides robust means for calculating the structure, energetics, surface, defects and thermal properties [20,21] with very efficient computational cost. Other fundamental approaches, such as the traditional band-structure calculations, are impractical for low symmetry systems, such as the GB [20]. In order to delineate the force field of the UO_2 system for the CMD simulations, we adopted the embedded-atom method (EAM) potential model [22] proposed by Cooper et al. [19]. This CRG (Cooper–Rushton–Grimes) potential includes the many-body perturbations to the traditional

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Buckingham–Morse pairwise interactions commonly used in ionic materials. It enables descriptions of the coordinate-dependent bonding and violation of the Cauchy relation by the many-body perturbations [23]. In the CRG potential, the total energy of atoms i surrounded by atom j is

$$\varphi_i = \frac{1}{2}\sum_j \phi_{\alpha\beta}(r_{ij}) - G_\alpha\left[\sum_j \sigma_\beta(r_{ij})\right]^{\frac{1}{2}}. \quad (1)$$

α and β stand for the species of atoms i and j, i.e., U or O. The first term is conventional pairwise interaction terms including short-range Buckingham [24] and Morse [25] potentials and the long-range electrostatic Coulomb contribution, i.e.,

$$\phi_{\alpha\beta}(r_{ij}) = A_{\alpha\beta}\exp\left(-\frac{r_{ij}}{\rho_{\alpha\beta}}\right) - \frac{C_{\alpha\beta}}{r_{ij}^6} + D_{\alpha\beta}\Big\{\exp\Big[-2\gamma_{\alpha\beta}(r_{ij}-r_o)\Big] - 2\exp\Big[-\gamma_{\alpha\beta}(r_{ij}-r_o)\Big]\Big\} + \frac{q_\alpha q_\beta}{4\pi_0 r_{ij}}. \quad (2)$$

The parameters for short-range pairwise terms and partial charges of ions are given in Table 1. The third Morse term relates to the degree of covalency of the bonds [19]. So, the parameters of Morse potential are only considered for the U–O interactions, except for the U–U and O–O pairs. For the Coulombic energy in the CMD simulations, the Wolf summation method [26] was employed with small enough damping parameter in the real-space summation and a long enough cutoff (11 Å).

The second term in Eq. (1) stands for a subtle many-body perturbation of the EAM. While the EAM term was originally expressed as an approximate function of the electron density functional in the density functional theory (DFT) for metals [28,30], with the mathematical analogy for the ionic system, it contemplates the many-body dependence from the surrounding ions. This term is composed of the embedding function or energy (G_α) and a set of pairwise functions (σ_β). The many-body term of the CRG model [29] is

$$\sigma_\beta(r_{ij}) = \left(\frac{n_\beta}{r_{ij}^8}\right)\frac{1}{2}\{1 + erf[20(r_{ij}-1.5)]\}. \quad (3)$$

The subtle many-body perturbation is inversely proportional to 8th power of the interatomic distance. The error function is added to prevent unrealistic interactions at very short range. The parameters for embedding energy and embedding function are listed in Table 2. As mentioned, the global cutoff distance is set to 11 Å in the CMD simulations.

2.2. Phonon thermal conductivity calculation

We use LAMMPS [27] MD package for thermal transport across the single crystal (bulk) or GB. Phonon thermal conductivity is obtained with equilibrium classical MD (ECMD) and non-equilibrium classical MD (NECMD) simulations.

For ECMD, the thermal conductivity is considered using the Green–Kubo (GK) autocorrelation decay based on the fluctuation dissipation theory [31,32], i.e.,

$$\boldsymbol{k}_p = \frac{V}{k_B T^2}\int_0^\infty \frac{\langle \boldsymbol{q}(t)\cdot\boldsymbol{q}(0)\rangle}{3}dt, \quad (4)$$

where T, V and k_B is system temperature and volume, and the Boltzmann constant. The $\langle \boldsymbol{q}(t)\cdots\boldsymbol{q}(0)\rangle$ is the ensemble averaged product of heat flux at time t and the initial state (after equilibrium is reached) or the heat current auto-correlation function (HCACF) in equilibrium state. The heat flux vector $\boldsymbol{q}$ is

$$\boldsymbol{q} = \frac{1}{V}\frac{d}{dt}\sum_i E_i\boldsymbol{r}_i = \frac{1}{V}\left[\sum_i E_i\boldsymbol{u}_i - \sum_i \boldsymbol{S}_i\boldsymbol{u}_i\right] = \frac{1}{V}\left[\sum_i E_i\boldsymbol{u}_i + \frac{1}{2}\sum_i(\boldsymbol{F}_{ij}\cdot\boldsymbol{u}_i)\boldsymbol{r}_{ij}\right], \quad (5)$$

where E_i, $\boldsymbol{r}_i$, $\boldsymbol{u}_i$, $\boldsymbol{S}_i$ are total energy, position vector, velocity vector and virial stress tensor of atom i, and $\boldsymbol{r}_{ij}$ and $\boldsymbol{F}_{ij}$ are position and force vector between atoms i and j. In general the ECMD has smaller size dependence compared to the NECMD [33,34]. System size of $5.4\times5.4\times5.4\,nm^3$ under periodic boundary conditions (PBC) is used and thermally equilibrated at 300, 500, 800, and 1200 K under NPT ensemble for 200 ps until steady state (equilibrium) is reached. The Nose–Hoover thermostat [35,36] and the Parrinello–Rahman barostat [37] are used. After that, the thermal conductivity is calculated using GK formula in the *NVE* ensemble, by integrating the HCACF every 50 ps.

In the NECMD method, the Fourier law of conduction, $\boldsymbol{q} = -k_p\nabla T$, is introduced to calculate the lattice thermal conductivity k_p, similar to the experimental procedures. For the simulation, thermal equilibration with the ECMD at 300, 500, 800, and 1200 K were initially achieved in the system under PBC. Then a heat flow rate of 1200 eV/ps was applied and extracted on both sides, over groups of atoms with thickness of about 2 Å. This process is carried out every time step for 100 ps. These atoms play a role of heat reservoir and sink to simulate the heat transfer in the system under nonequilibrium. It is achieved by controlling non-translational kinetic energy to atoms in the groups at thermostat region and the momentum of the atoms are conserved during the simulation. Through this process, temperature gradient is produced in the direction of heat flux. Both heat flux and temperature variations near thermostats were excluded to get accurate data, since the atoms near these regions show non-Newtonian dynamics [38]. Heat flux calculated from Eq. (5) is averaged temporally and spatially. Also, only linear portion of temperature distribution is temporally averaged except peripheral region. From the mean heat flux and the temperature gradient, the thermal conductivity is directly obtained using

$$k_p = -\frac{\langle\bar{q}\rangle}{\overline{(dT/dz)}}, \quad (6)$$

where $\langle\bar{q}\rangle$ is mean heat flux and $\overline{(dT/dz)}$ is average temperature gradient of the system. The NECMD results for ideal crystal (bulk) are size dependent, since the average phonon mean free path in the

Table 1
Parameters of the Buckingham and Morse potentials for the CRG model [19], and charges of the ions in the CMD simulations.

	U–U	U–O	O–O
$A_{\alpha\beta}$ (eV)	18,600	448.779	830.283
$\rho_{\alpha\beta}$ (Å)	0.2747	0.387758	0.352856
$C_{\alpha\beta}$ (eV Å^6)	0.0	0.0	3.884372
$D_{\alpha\beta}$ (eV)	–	0.66080	–
$\gamma_{\alpha\beta}$ (Å)	–	2.05815	–
r_o (Å^{-1})	–	2.38051	–
q_U (e)	+2.2208		
q_O (e)	−1.1104		

Table 2
Parameters of many-body interaction in CRG potentials [19].

	U	O
G_α (eV Å$^{1.5}$)	1.806	3450.995
n_β (Å^5)	0.690	106.856