SELECTING AN EMPIRICAL POTENTIAL FOR UO$_2$

by

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This thesis has been reviewed by the research advisor, thesis committee, and department chair and has been found satisfactory.
ABSTRACT

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Grain boundaries (GB’s) have a great influence on the physical properties of UO$_2$, commonly used in nuclear fuel. The computational materials group at Brigham Young University-Idaho is developing a model of GB energies to increase the accuracy of grain growth simulations in MOOSE. These GB energies are calculated with the Basak empirical potential. Through comparison with several other empirical potentials, the Basak potential was determined to be valid for developing a GB energy model.
ACKNOWLEDGEMENTS

A special thanks to my family for supporting me through this journey. I made it!

Also, thanks to Evan Hansen, without whom I would not have become involved in this project, as well as Stephen and Kit Dorrough, who helped fund this research.
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Chapter 1

Introduction

1.1 Grain Boundaries

A grain boundary (GB) is the two-dimensional region between two or more distinct crystal lattices in a material, known as grains. It is well established that the properties of crystalline-structured materials are affected by the presence of distinct GB’s. In the case of UO$_2$, commonly used for nuclear fuel, important physical properties affected by the presence of GB’s include thermal conductivity and fracture. These GB’s cause the energy of the overall crystal lattice to differ from the ideal minimum potential energy obtained from the formation of one homogenous crystal. In order to accurately model how a material will behave, it is necessary to be able to model these GB energies accurately as well. In theory, there are an infinite number of possible grain orientations.

There are two types of these fundamental GB’s: tilt boundaries and twist boundaries. Mixed boundaries, which are combinations of tilt and twist boundaries, also exist. A tilt boundary is one where the two interacting crystal lattices are tilted at an angle relative to each other, causing one lattice to extend into the other and creating a plane along this angle. These boundaries are categorized in our research by the rotation vector in this boundary plane of incidence that the axes of the lattices are tilted around. For twist boundaries, the two lattices are stacked one on top of the other like pages in a book, and
one is rotated relative to the other. The axis of rotation is perpendicular to the grain boundary. These boundaries are categorized by the angle through which the first lattice is rotated relative to the second and the axis about which it is rotated. An example of simple tilt and twist boundaries is shown in Figure 1.

Figure 1: Top: Sample tilt boundary. Bottom: Sample twist boundary.
1.2 Grain Boundary Energy Model Development

MOOSE (Multiphysics Object Oriented Simulation Environment), a program developed by Idaho National Labs, is commonly used to model the evolution of these grains to predict the behavior of nuclear fuel. Currently, MOOSE uses a single constant value for all GB energies in UO\textsubscript{2}. The computational materials group at Brigham Young University-Idaho, under the direction of Evan Hansen, is working to increase the accuracy of MOOSE simulations by developing a function to approximate GB energies. These GB energy calculations are carried out using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) using an empirical potential developed by Basak.

Work by Olmsted\textsuperscript{1} details 388 twist, tilt, and mixed GB's that are being used to develop the GB energy equation for MOOSE. Calculating and plotting these GB energies will allow the BYU-I Computational Materials group to fit an equation to these data. The first step in this process is to calculate the energies of these GB’s.

These calculations are done using LAMMPS and the creation of a gamma surface. A gamma surface is a means of finding the optimal configuration for a GB through minimization of potential energy. A gamma surface is created for each GB studied. It is made by calculating the GB energy with LAMMPS for a specific GB. Once that energy is calculated, the grains are moved relative to each other by a small amount, typically .1-.2 Å, and the GB energy is calculated for this new configuration of the GB. The process is repeated until a gamma surface of sufficient size to include all possible configurations is created. This is possible because GB’s show periodic behavior, so all possible configurations can be shown with a finite number of simulations. The number of
simulations required varies with each GB used, but typically requires roughly 10,000 simulations to develop a single gamma surface. A sample gamma surface is shown in Figure 2.

Figure 2: Sample gamma surface for uranium dioxide.

1.3 Potentials

LAMMPS calculates the energy of the GB by using a set of equations called an empirical potential. There are dozens of such potentials available, each commonly referred to by the name of its developer. As stated, the potential used by the BYU-I Computational Materials Group is the Basak potential, being developed by Basak². This potential has been shown previously to provide an accurate description⁹ of the physical behavior of UO₂, though its accuracy in our specific application of it has been questioned. My project’s goal is to determine whether using the Basak potential to develop a model of all possible GB energies in UO₂ crystals is a valid choice. The various potentials used in molecular dynamics (MD) simulations fall into several distinct categories, three of which I
will examine; namely, rigid ion potentials, core-shell potentials, and embedded atom method (EAM) potentials.

Code for these potentials calculate the potential energy between pairs of atoms through a combination of equations, given in Equations 1-5. Each potential studied in this work use either the Buckingham or the Born-Mayer-Huggins equation, given in Equations 1 and 2, respectively. These equations are more comprehensive versions of the classic Lennard-Jones potential, and account for attractive and repulsive behavior of atoms. Equation 3, the Coulomb-Wolf equation is also included in each potential studied in this work. This equation accounts for charge-based interactions between atoms. Equation 4, the Morse equation, is an additional corrective term that accounts for covalent behavior in UO$_2$, and is thus only present in some U-O interactions, and not at all in core-shell potentials. Equation 5 differs from the others in that it is a many-body term, while Equations 1-4 are all pairwise interactions. Equation 5 is only present in EAM potentials.

\[
E = A \exp \left( -\frac{r}{\rho} \right) - \frac{C}{r^6}
\]

*Equation 1: Buckingham equation.*

\[
E = A \exp \left( \frac{(\sigma - r)}{\rho} \right) - \frac{C}{r^6} + \frac{D}{r^8}
\]


\[
E = \frac{1}{2} \sum_{i \neq j} q_i q_j \text{erfc} \left( \frac{\alpha r_{ij}}{r_{ij}} \right) \frac{1}{r_{ij}} + \frac{1}{2} \sum_{i \neq j} q_i q_j \text{erf} \left( \frac{\alpha r_{ij}}{r_{ij}} \right) \frac{1}{r_{ij}}
\]

*Equation 3: Coulomb-Wolf equation.*

\[
E = D_0 \exp \left[ -2^{\alpha}(r-r_0) - 2 \exp \left( -\alpha(r-r_0) \right) \right]
\]

*Equation 4: Morse equation.*
Equation 5: Many-body correction term for EAM.

\[ G_a \sum \left( n\beta / r_{ij}^6 \right) \times 0.5 \left( 1 + \text{erf} \left( 20(r_{ij} - 1.5) \right) \right) \]

1.3.1 Rigid Ion Potentials

Rigid ion potentials are characterized by approximating each atom as a rigid charged ion. This approximation sacrifices some theoretical accuracy but is much easier to calculate computationally. As these simulations require a significant amount of time even on a supercomputer, this is not a trivial consideration. Some rigid ion potentials attempt to compensate for this simplification by assigning fractional charges to the uranium and oxygen ions in place of their full formal ionic charges. This helps to account for the distribution of electrons in the UO₂ crystal. Rigid ion potentials I examined for this project include the Arima1, Arima2, Basak, Lewis1, Yakub, and Yamada potentials. Figures 3-5 show graphs of the potential energy equations used by these potentials for U-U, O-O, and U-O interactions. These plots show a range in which the empirical potential is useful, and outside of which energy contributions are either insignificant or become large enough that the force atoms would experience being that close would drive them from the crystal lattice, crashing the simulation. Therefore, all potentials, not just rigid ion potentials, use cutoffs to avoid this behavior. A short range cutoff is employed to prevent atoms from coming too near each other and either crashing the simulation or exhibiting unrealistic behavior. This is typically on the order of 1-2 Å. A long range cutoff is also incorporated, beyond which pairwise contributions to the total potential energy are deemed insignificant.
This also decreases the runtime required for the simulation. Typical long range cutoffs are 10-11 Å.

**Figure 3:** Rigid ion potential energy plots, U-U interactions.

**Figure 4:** Rigid ion potential energy plots, O-O interactions.
Figure 5: Rigid ion potential energy plots, U-O interactions.
1.3.2 Core-shell Potentials

Core-shell potentials offer a more theoretically realistic approximation of atomic structure, though it is also an approximation. In a core-shell potential, each atom consists of two parts, a massive, positively charged nucleus and a massless, negatively charged sphere representing the electrons attached to it by two massless springs. This allows the electron sphere to move semi-independently of the nucleus. A drawback associated with core-shell potentials is that this harmonic two-piece model of atoms is much more computationally demanding than rigid ion potentials, and to create a gamma surface using one would require far more time as a result. Core-shell potentials examined for this project include the Grimes\textsuperscript{7} and Weis2\textsuperscript{8} potentials. Plots of the potential energy for each interaction in UO\textsubscript{2} are shown in Figures 6-8.
**Figure 6:** Core-shell potential energy plots, U-U interactions.

**Figure 7:** Core-shell potential energy plots, O-O interactions.

**Figure 8:** Core-shell potential energy plots, U-O interactions.
1.3.3 Embedded Atom Method (EAM)

The embedded atom method (EAM) is a new empirical potential developed by Cooper\textsuperscript{10-12}. This potential consists of the Yakub potential with the addition of a many body term. This differs from both rigid ion and core-shell potentials, which only feature pairwise interactions. This allows the Cooper potential to have greater theoretical accuracy than rigid ion potentials without sacrificing the associated greater computational speed. Given these considerations, the EAM could be an even better option than the Basak potential. However, this would also have to be tested, and a similar test for the Basak potential is the purpose of this work. Plots of the potential energy equations for the Cooper potential are shown in Figures 9 and 10 for U-U and O-O interactions. Due to the form the coefficients of the many-body term (see Equation 5) are presented in Cooper’s paper\textsuperscript{11}, a plot showing the U-O interaction could not be developed.
Figure 9: EAM potential energy plot, U-U interactions.

Figure 10: EAM potential energy plot, O-O interactions.
Chapter 2

Methods

2.1 Setup

All the calculations for this project are carried out computationally, running LAMMPS on the Marylou supercomputer at the Fulton Supercomputing Lab (FSL) at Brigham Young University and the Falcon supercomputer at the High Performance Computing (HPC) lab at Idaho National Labs (INL), using remote login procedures.

2.2 Selecting a Grain Boundary

The GB’s for this project were all boundaries that had been previously simulated using the Basak potential. 110 GB’s were used as a basis of comparison, each being generated by creating a gamma surface with the Basak potential and then finding the optimal configuration with that potential. It is probable that the optimal configuration generated through the Basak potential will not be the precise optimal configuration that would be generated using another potential to create the gamma surface, but the correlation plots should remain unaffected. A directory of these GB's was created on the FSL servers for each potential being tested, and batches were created for each axis of rotation, one each for the <100>, <110>, and <111> axes, with both tilt and twist boundaries included in each. These batches were submitted to calculate for each GB the associated GB energy with different potentials.
2.3 LAMMPS

The process of obtaining GB energies for a significant number of samples requires the use of a supercomputer in order to be completed in any reasonable amount of time. My simulations were run at the Fulton Supercomputing Lab (FSL) at Brigham Young University (BYU). The MD simulations were performed using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). LAMMPS requires two things to function; an input file and an interatomic potential. The input file is unique to each GB, while the interatomic potential is used for the entire set of GB’s. The input file contains information about the atoms that make up the simulation; their masses, charges, and positions. It defines the initial configuration of each GB to be simulated. The input files used in this work were previously obtained from a gamma surface search for work done using the Basak potential. Due to the time required to create a gamma surface, finding the optimum configurations using each potential examined in this work was impractical, and any differences between the optimum configuration found using Basak as opposed to any other potential were taken to be negligible. Doing so would have increased the computation time required by several orders of magnitude.

Where the input files hold the initial configuration of the UO$_2$ lattice, the interatomic potential is how LAMMPS simulates how the GB will evolve. The potential contains the equations used to calculate the pairwise potential energy at every iteration between every atom within a cutoff radius, commonly taken to be on the order of 11 Å. The potential file also contains constraints for the system, which can include artificially controlling the temperature, pressure, volume, and other parameters. These serve as checks to prevent one parameter, such as pressure, from increasing in a drastic and unrealistic manner and distorting
the results, or in some cases crashing the simulation. The final part of the potential file controls what type of simulation will be run and other information about runtime and the size of each time step. There are two types of simulation that were examined in this work; timestep runs and energy minimization.

Energy minimization is the first simulation we used. These simulations do not run for a set number of iterations; instead, they run until either the change in the total energy or the force experienced by each atom is smaller than a given threshold value. This ensures that when the atoms stop moving around, the simulation stops as well. A key aspect of this type of simulation is that there is an artificial limit imposed on how far any atom can move in a single iteration. This helps smooth out errors in atom placement, i.e., two atoms being placed so close together the resulting force is enough to launch them free of the simulation box and crash the simulation. Using input files optimized with the Basak potential for all the potentials studied here may cause some of these errors in atom placement, and running an energy minimization helps eliminate these errors.

After energy minimization is complete, each GB simulation is allowed to run for a set number of time steps. In these timestep runs, the temperature is increased slightly to 3K, before being lowered back down to 0K. This allows the atoms a small amount of excess energy to account for the possibility of local minima and allow the atoms to escape them and seek out a lower energy configuration.

Once the simulation is complete, a text file is created showing the characteristics of the UO$_2$ crystal throughout the simulation. The total potential energy of the system is among these quantities, and it is a straightforward calculation to obtain the GB energy from the system’s potential energy. The equation to do so is given in Equation 6.
In Equation 6, \( n \) is the number of atoms in the simulation, \( \text{ecoh} \) is the cohesive energy, \( e \) is the magnitude of the total potential energy given by LAMMPS, \( a \) is the area of the GB, and \( j \) is a conversion factor from the standard LAMMPS energy units of eV to J. The factor of 2 is required because our simulations use periodic boundary conditions, which means that in our simulation there is a GB where the grains meet, and another one at the top/bottom of the simulation cell. Once the GB energy is calculated, the process is repeated for each GB using each potential. The results are then plotted.

### 2.4 Potential Components

Once submitted, each GB energy was calculated in separate batches using several different potentials. These potentials calculate the pairwise potential energy between all atoms within a cutoff radius, taken in this experiment to be on the order of 11 Å. Each potential performed these calculations using three distinct sets of equations; one each for U-U, O-O, and U-O interactions. These sets of equations had the same form in a given potential, with the only difference being the parameters associated with the equation. Each potential used either the Buckingham or the Born/Mayer/Huggins equation, each a more detailed modification to the classic Lennard-Jones equation. The Buckingham equation formed the foundation of the Arima1, Grimes, Lewis1, Weis2, and Yakub potentials, while the Born/Mayer/Huggins equation is used in the Arima2, Basak, and Yamada potentials. The Coulomb/Wolf equation is included in each potential to account for electrostatic forces. Additionally, in the Basak, Yakub, and Yamada potentials, the Morse equation is added as an additional repulsive
corrective term, though it is only applied to the U-O interactions. Parameters for each potential are listed in Table 1. The Cooper potential parameters for $G_\alpha$ and $n_\beta$ are given in Table 2. Graphs of the potential energy equations can be found in Figures 3-10.

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<th>Arima1</th>
<th>Arima2</th>
<th>Basak</th>
<th>Grimes</th>
<th>Lewis1</th>
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Table 1: Potential parameters, rigid ion and core-shell.

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<tr>
<td>$n_\beta$ (Å$^5$)</td>
<td>3450.995</td>
<td>106.856</td>
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Table 2: Many body parameters, Cooper potential.
2.5 Min/Timestep Runs

Several different procedures exist for the simulation of the GB as it settles into a minimized energy state. Two were used in this experiment. Each calculates pairwise potential energy in iterative steps and applies an appropriate force to each atom determined by the gradient of the potential energy, but there are differences which make each useful. The first process used is an energy minimization run. This process doesn’t run for a set amount of steps; instead, it stops when one of its stopping criteria are met—either when the change in the overall energy is below a set parameter, or when the total force is below a parameter. When one of these criteria are met, the atoms in the simulation cell have stopped moving. The energy minimization also helps account for differences between optimal GB configurations with the Basak potential versus other potentials by featuring a cutoff for how far any atom can move in a single iteration. This prevents the simulations from crashing due to extreme forces caused by two atoms being placed too close to each other at the beginning of a simulation.

Once the energy minimization run is complete, a timestep run is also performed. The timestep run initially increases the temperature in the simulation by a small amount before lowering it to 0 K, to provide the atoms with sufficient energy to escape a local energy minimum in order to find a more energetically favorable configuration.

2.6 Supercomputer Jobs

These jobs were all run on the Marylou supercomputer at the Fulton Supercomputing Lab (FSL) at Brigham Young University (BYU), with the exception of the Cooper potential, which was run on Falcon at the High Performance Computing (HPC) at Idaho National Laboratories. Each job was submitted based on the axis the GB was rotated around, as stated earlier. FSL utilizes the language slurm for all its submissions, while HPC uses PBS.
2.7 Correlation Plots

In comparing the Basak potential to other potentials, it is necessary to construct a comparison that will either confirm or deny the validity of the Basak potential. By using other potentials as a basis for comparison, my intention is to plot results from each potential side-by-side with the Basak potential. However, simply plotting results from each potential on one graph will not necessarily show whether the two potentials are in agreement or not. This is because each potential uses different equations in calculating the GB energy, and so will produce different numbers for this GB energy. This difficulty will be avoided by creating correlation plots. Even though the numbers may be expected to differ, the shape of each graph can be expected to be the same if the two potentials agree with each other. Correlation plots provide a method to visualize all 6 different classes of GB at once to determine how well they share the same shape. For this reason, I will be plotting the results of two potentials against each other to show how well they correlate. Agreement between the two potentials, and therefore a confirmation of the validity of the Basak potential, will be seen as a correlation plot that follows a linear trend, while the presence of a nonlinear fit would be evidence against using the Basak potential. A linear trend in a correlation plot will show that the respective plots of GB energy versus angle for each potential would have similar shape, even if the actual values are different due to the different equations used in each potential. I will also create 1 degree of freedom (1D) plots showing the results for each potential.
Chapter 3

Results/Discussion

3.1 Cohesive Energies

In order to calculate the GB energies, it is necessary to first determine the cohesive energy for UO$_2$ with each potential. The cohesive energy is the energy associated with the formation of a single homogenous crystal lattice, instead of two distinct grains. The cohesive energies for each potential are given in Table 3. Cohesive energy is given in eV/atom, and represents the optimal configuration, or the lowest energy possible for a UO$_2$ crystal.

3.2 Lattice Parameters

Another calculated result affecting GB energies is the \( a_0 \) value, or the length of any side of the unit cells that make up UO$_2$ crystals. UO$_2$ crystals are arranged in a flourite configuration, and a unit cell is considered to be four uranium atoms and eight oxygen atoms, with uranium atoms forming the vertices of a cube. The \( a_0 \) value is the distance from a uranium atom to the next nearest uranium atom. The accepted value for \( a_0 \) in UO$_2$ crystals is 5.454 Å. Average \( a_0 \) values from my simulations are listed in Table 3.
<table>
<thead>
<tr>
<th>Potential</th>
<th>Arima1</th>
<th>Arima2</th>
<th>Basak</th>
<th>Lewis1</th>
<th>Yakub</th>
<th>Yamada</th>
<th>Cooper</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$ (Å)</td>
<td>6.514</td>
<td>5.640</td>
<td>5.516</td>
<td>6.749</td>
<td>5.386</td>
<td>5.475</td>
<td>5.516</td>
</tr>
</tbody>
</table>

Table 3. Cohesive energies and $A_0$ values for all potentials that produced data. Core shell potentials not shown due to lack of functionality on FSL. The Lewis1 potential $A_0$ value is averaged from 74 out of 110 results, due to the remainder of the simulations crashing.

### 3.3 Correlation Plots

Simulations on FSL produced results for four of the potentials examined. The two core shell potentials could not be run on FSL due to lack of the proper LAMMPS module. The Arima1 and Lewis1 potentials had errors in simulations that, as seen in Table 3, led to unit cells that were unrealistically large. Further, only 74 of the 110 GB's were successfully completed using the Lewis1 potential. The rest experienced errors which crashed the simulations. Specifically, atoms experienced enough force to launch them beyond the boundaries of the simulation box. In both the Arima1 and Lewis1 results, the GB energies were determined to be unrealistically high (roughly two orders of magnitude higher than results returned from the other four potentials) and so were disqualified as part of the comparison basis to test the validity of the Basak potential.

The remaining potentials were used to form a comparison basis, with the intent to verify or deny the validity of using the Basak potential to calculate UO$_2$ GB energies. Correlation plots were created to compare the results obtained by using the Basak potential with the results from the Arima2 and Yakub shown in Figures 11 and 12. As a way of checking the validity of the other potentials to test the validity of the Basak potential, a correlation plot comparing the Yakub and Arima2 potentials was also created (see Figure 13).
Figure 11: Basak-Arima2 correlation plot. Line of slope 1 added for reference.

Figure 12: Basak-Yakub correlation plot. Line of slope 1 added for reference.

Figure 13: Basak-Cooper correlation plot. Line of slope 1 added for reference.
These plots each show an overall linear trend, evidence that each pair of potentials correlate well with each other. In particular, the results obtained with the Arima2 and Yakub potentials can be seen to correlate well with Basak, supporting its validity. They also correlate well with each other, supporting the validity of using them as a means of testing the validity of other potentials. These correlation plots suggest that the overall shapes of the GB energy plots for any of these potentials would be similar. Results from the Cooper potential tended to have higher values than those from the Basak potential, with the notable exception in Figure 13 of a <110> twist GB with a low misorientation angle. This could suggest that the Cooper potential more quickly obtains a relaxed state and that insufficient time was allowed for the Basak potential to fully reach its lowest potential energy.

By contrast, the Basak-Yamada plot showed some disagreements, but this was because some GB’s, when simulated with the Yamada potential, produced negative GB energies, which cannot exist, as no GB can reach a lower energy than a perfect homogenous crystal. The Yamada potential is known to have issues of this sort, and since we were unable
to isolate the specific fault in the Yamada potential, the Basak-Yamada correlation plot is not included.

3.4 1 Degree of Freedom Plots

Although the correlation plots provide a means of examining the entire set of GB’s included in this work to ensure the plots have similar shapes, there is also insight that can be gained from the 1D plots of the energies of each class of GB. For this reason, these plots that show the data obtained from each potential are also included as Figures 15-20.

Figure 15: <100> Tilt GB energies.

Figure 16: <110> Tilt GB energies.
Figure 17: \(<111>\) Tilt GB energies.

Figure 18: \(<100>\) Twist GB energies.

Figure 19: \(<110>\) Twist GB energies.
Examination of these plots confirms that the plots of GB energies obtained with each potential do have the same general shape, with the exception of some data points obtained with the Yamada potential, which have already been discussed. Notably, the cusps seen in the results from the Basak potential are also observed in the results from the other potentials. These results confirm what was seen in the correlation plots, namely, that the Basak potential correlates well with the other potentials.
Chapter 4

Conclusion

This work set out to confirm the validity of the Basak potential for use in developing a model of GB energies. Simulations were carried out on FSL and HPC, using LAMMPS to calculate the GB energies for 110 different GB’s. These simulations were to be run with multiple different empirical potentials to show that the Basak potential does not use physics not present in other empirical potentials.

Of the empirical potentials initially studied, four produced results that could be compared with results obtained using the Basak potential. Core shell potentials were unsupported by the build of LAMMPS used, and the Arima1 and Lewis1 potentials yielded incomplete and unreliable results. Results obtained from the Arima2, Cooper, Yakub, and Yamada potentials were used to develop both 1D plots and correlation plots along with results using the Basak potential.

Both the correlation plots and the 1D plots show that the results obtained with the Basak potential agreed well with those obtained from the other potentials. Considering this, as well as the lack of results disagreeing with the Basak potential from any of the other potentials, we conclude that the Basak potential is a valid choice for developing a more comprehensive model of GB energies for use in grain growth simulations of UO$_2$. 
References


