

Molecular Dynamics Studies of Grain Boundary Mobilities in Metallic and Oxide Fuels

Jarin French

Dissertation submitted to the Faculty of
the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Materials Science and Engineering

Xianming (David) Bai, Chair
William T. Reynolds
Wenjun (Rebecca) Cai
Feng Lin

August 7, 2023

Blacksburg, VA 24060

Keywords: Grain boundary mobility anisotropy, solute drag, uranium alloys, uranium dioxide,
molecular dynamics simulation

Copyright © 2023 Jarin French.

Molecular Dynamics Studies of Grain Boundary Mobilities in Metallic and Oxide Fuels

Jarin French

Abstract

Energy needs are projected to continue to increase in the coming decades, and with the drive to use more clean energy to combat climate change, nuclear energy is poised to become an important player in the energy portfolio of the world. Due to the unique nature of nuclear energy, it is always vital to have safe and efficient generation of that energy. In current light water reactors, the most common fuel is uranium dioxide (UO_2), an oxide ceramic. There is also ongoing research examining uranium-based metallic fuels, such as uranium-molybdenum (U-Mo) fuels with low uranium (U) enrichment for research reactors as part of a broader effort to combat nuclear proliferation, and uranium-zirconium-based fuels for Generation IV fast reactors. Each nuclear fuel has weaknesses that need to be addressed for safer and more efficient use. Two major challenges of using UO_2 are the fission gas (e.g. xenon) release and the decreasing thermal conductivity with increasing burnup. In UMo alloys, the major weakness is the breakaway swelling that occurs at high fission densities. The challenges presented by both fuel types are heavily impacted by microstructure, and several studies have identified that the initial microstructure of the fuel in particular (e.g. initial grain size and grain aspect ratio) plays a large role in determining when and how quickly these processes occur. Thus, knowledge of how such initial microstructures evolve is paramount in having stable and predictable fission gas release and thermal conductivity decrease (in UO_2) and fuel swelling (in UMo alloys). Mobility is a critical grain boundary (GB) property that impacts microstructural evolution. Existing literature examines GB mobility for a few specific boundaries but does not (in general) identify the anisotropy relationships that this property has. This work first examined the anisotropy in GB mobility, specifically identifying the anisotropy trend for the low-index rotation axes for tilt GBs in BCC γ U, and fluorite UO_2 via molecular dynamics simulation. GB mobility is calculated using the shrinking cylindrical grain

method, which uses the capillary effect induced by the GB curvature to drive grain growth. The mobilities are calculated for different rotation axes, misorientation angles, and temperatures in these systems. The results indicated that the density of the atomic plane perpendicular to the (tilt) GB plane (which is also perpendicular to the rotation axis) significantly impacts which GB rotation axis has the fastest boundaries. Specifically, the atomic plane that has a higher density tends to have a faster mobility, because it is more efficient for atoms moving across the GB along such planes. For example, for body-centered cubic materials, the $\langle 110 \rangle$ tilt GBs are determined to have the fastest mobilities, while face-centered cubic (FCC) and FCC-like structures such as fluorite have $\langle 111 \rangle$ tilt GBs as the fastest.

Knowledge of GB mobility and its anisotropy in pure materials is helpful as a baseline, but real materials have solutes or impurities (both intentionally and unintentionally) which are known to affect GB mobility by processes such as solute drag and Zener pinning. Additionally, in reactors, nuclear fission can produce many fission products, each of which acts as an additional impurity that will interact with the GB in some way. Because the initial microstructure and its subsequent evolution are vital for addressing the challenges of using nuclear fuel as described above, knowledge of the impacts of these impurities on GB mobility is required. Therefore, this work examined the impact of solutes and impurities on GB mobility and its anisotropy. In particular, the solute effect was examined using the UMo alloy system, while the impurity effect was examined using Xe (a very common fission product) in the γ U, UMo, and UO₂ systems. It is found that both Mo and Xe can cause a solute drag effect on GB mobility in the γ U system, with the effect of Xe being stronger than Mo at the same solute/impurity concentration. Xe also causes a solute drag effect in UO₂, though the magnitude of the effect is interatomic-potential-dependent. The mobility anisotropy trend was found to disappear at high solute and impurity concentrations in the metallic U and UMo systems but was largely unaffected in the UO₂ system. These results not only increase our fundamental understanding of GB mobility, its anisotropy, and solute/impurity drag effects, but also can be used as inputs for mesoscale simulations to examine polycrystalline grain growth with anisotropic GB mobility and in turn examine how the fuel performance parameters change with these properties.

Molecular Dynamics Studies of Grain Boundary Mobilities in Metallic and Oxide Fuels

Jarin French

General Audience Abstract

Worldwide, energy needs continue to increase each year. Concerns related to climate change have led to an increased emphasis on renewable energies such as solar and wind, but the limitations of these resources prevent them from being the only energy sources. Nuclear energy is uniquely positioned to address several energy concerns: it is clean (no carbon emissions and air pollution), reliable (for example, 24/7 energy production, independent of weather), and energy-dense (one kilogram of fissile uranium provides roughly the same amount of energy as 3000 metric tons of coal). Currently, nuclear energy provides roughly 20% of the energy of the United States, but future predictions show a decrease in the total share of energy generation due to aging systems and a limited number of new reactors being built. The safety and efficacy of existing and future reactors are among the primary concerns for being able to allow nuclear energy to increase its energy share.

To determine the safety and efficacy of new reactor designs, a computer simulation tool called fuel performance modeling has been used over the last few decades. This tool requires several material properties as input, one of which is how the nuclear reactor fuel microstructure changes based on a variety of conditions. A significant process contributing to microstructural change is grain growth. Grains (crystallites that make up the whole material) meet at interfaces called grain boundaries (GBs), and these GBs have two properties that largely determine how grain growth occurs: energy and mobility. Significant effort is being put into understanding these properties and their anisotropy, or how they change based on the GB character which is the relative mismatch between the two grains.

This work contributes additional understanding of GB mobility anisotropy in two nuclear fuels: uranium dioxide (UO_2 , the primary fuel in current reactors) and a uranium-molybdenum (UMo) alloy (the primary fuel for newer research reactors). In particular, computer simulation is used to determine GB mobility for several unique GB systems. It is found that for pure nuclear fuels, GB mobility anisotropy is largely determined by which atomic plane has the highest density perpendicular to the GB. When the fuel is no longer pure (through the addition of alloying elements or other impurities) the anisotropy changes significantly in UMo fuels, such that at high concentrations of solute or impurities there is little to no anisotropy, while very little change is observed in the anisotropy in UO_2 .

Dedication

*To my immediate and extended family, who has supported me in every conceivable way
throughout this journey.*

Acknowledgments

First and foremost, I want to thank my advisor Dr. Xian-Ming Bai for advising me throughout this process. His constant focus on the big picture has helped expand my thinking, for which I am incredibly grateful.

I would additionally like to thank my committee members for their support. Their feedback and willingness to work with me has helped me develop into a competent researcher. The staff and professors at Virginia Tech also provided valuable support. A special thanks goes to Kim Grandstaff for the time and effort she put in to help me succeed as a graduate student.

In all scientific endeavors, colleagues are a vital part of the success of the work. To that end, I would like to thank the past and present fellow graduate students I had the opportunity to work with in our research group. Their insights and experiences have helped broaden my horizons.

This work was supported in part under an Integrated University Program Graduate Fellowship sponsored by the U.S. Department of Energy Office of Nuclear Energy. This work was supported in part by the U.S. Department of Energy Nuclear Energy University Program (#DE-NE0008279), Virginia Tech's ICTAS Junior Faculty Award, and the Materials Science and Engineering Department. Additionally, this work was made possible through the computational resources and technical support of Advanced Research Computing (ARC) at Virginia Tech, for which I am deeply grateful.

Finally, I would most like to acknowledge my wife's support throughout this whole process. Her unyielding support no matter how difficult the circumstances made this whole process bearable despite setbacks and difficulties.

Attribution

The work represented here is a culmination of several years of effort between myself and Dr. Bai. Throughout this work, I performed all simulations and wrote the initial manuscript drafts. Analysis was conducted jointly with Dr. Bai.

I, Jarin French, have the right as an Elsevier author to include the article French and Bai, “Molecular dynamics studies of grain boundary mobility and anisotropy in BCC γ Uranium,” *Journal of Nuclear Materials*, **565**, 153744 (2022) as part of my non-commercial dissertation according to Elsevier’s copyright policy. It is included as Chapter 3 of this Dissertation.

Table of Contents

Abstract	ii
General Audience Abstract	iv
Dedication	vi
Acknowledgments.....	vii
Attribution.....	viii
List of Figures	xii
List of Tables	xxi
Chapter 1. Introduction	1
1.1. Literature Review.....	1
1.1.1. Grain boundary mobility in UO ₂	2
1.1.2. Grain boundary mobility in U-based metallic fuels.....	4
1.2. Objectives	5
Chapter 2. Methodology	6
2.1. Grain growth fundamentals.....	6
2.2. Molecular Dynamics	7
2.3. Grain Boundary Structure Generation	7
2.4. Grain Boundary Mobility Calculation Procedure	8
Chapter 3. Grain Boundary Mobility in Pure γ U.....	12
3.1. Abstract.....	12
3.2. Introduction.....	12
3.3. Methods.....	16
3.4. Results.....	24
3.4.1. $\langle 100 \rangle$ mobility trends.....	24
3.4.2. $\langle 110 \rangle$ mobility trends.....	29

3.4.3. <111> mobility trends.....	31
3.4.4. Mobility trends between different rotation axes	33
3.4.5. Grain rotation behavior	35
3.5. Discussion	40
3.6. Conclusions.....	44
Chapter 4. Grain Boundary Mobility in the UO ₂ System	46
4.1. Abstract	46
4.2. Introduction.....	46
4.3. Methods.....	50
4.4. Results.....	56
4.4.1. Anisotropy Trends	56
4.4.2. Planar Density	61
4.5. Discussion	68
4.5.1. Shape of the Arrhenius Plot	68
4.5.2. General Discussion	71
4.6. Conclusions.....	80
Chapter 5. Grain Boundary Mobility in the UMo System.....	80
5.1. Abstract	81
5.2. Introduction.....	81
5.3. Methods.....	82
5.4. Results and Discussion	88
5.4.1. Grain Boundary Mobility versus Temperature	88
5.4.2. Grain Boundary Mobility versus Concentration.....	93
5.5. Conclusions.....	100
Chapter 6. Xe Effects on Grain Boundary Mobility in the γ U, UMo, and UO ₂ Systems.....	101

6.1. Abstract	101
6.2. Introduction.....	101
6.3. Methods.....	104
6.4. Results.....	109
6.4.1. Fission Gas Effects on γ U Grain Boundary Mobility	109
6.4.2. Fission Gas Effects on UMo Grain Boundary Mobility	112
6.4.3. Fission Gas Effects on UO ₂ Grain Boundary Mobility	115
6.5. Discussion	118
6.6. Conclusions.....	121
Chapter 7. Summary	123
List of Scientific Communications	124
Publications.....	124
Presentations	124
Bibliography	125
Appendix A. Activation Energies and Prefactors for the UMo System	146
Appendix B. Activation Energies and Prefactors for the UXe, UMoXe, and UO ₂ +Xe Systems	147
Appendix C. Slopes and Intercepts for Mobility versus Concentration in UXe, UMoXe, and UO ₂ +Xe	150

List of Figures

Fig. 2.1. Schematic of GB creation. (a) The quasi-2D structure of the system. The Z-axis is aligned along the desired crystal direction. (b) Top view.	8
Fig. 2.2. Example of the orientation parameter method. The first row colors the atoms by their assigned grain, while the bottom row shows the same atoms without any coloring. This particular structure is a $\langle 111 \rangle$ 30° boundary in BCC γ U at various stages of grain growth during a 1300 K anneal.	10
Fig. 2.3. Examples of the area versus time plots examined in this work. In general, increasing temperature leads to a higher rate of grain growth. This particular data set is from the $\langle 111 \rangle$ 30° BCC γ U system.	11
Fig. 3.1. Schematic of the as-created cylindrical GB structure that is projected on the X-Y plane. The rotation axis is along the Z direction (out of the page). Atoms within the radius r_{grain} are rotated by a desired misorientation angle θ . Red atoms belong to the inner cylindrical grain, while blue atoms belong to the outer matrix grain. The interface between them is the cylindrical GB.	17
Fig. 3.2. Example of inner grain shrinkage observed during simulation for a $\langle 110 \rangle$ 45° boundary using the EAM potential at 1200 K. (a) The initial structure. (b) After 600 ps. (c) After 1000 ps. In all figures, red atoms belong to the inner cylindrical grain while blue atoms belong to the outer matrix grain.	22
Fig. 3.3. Four representative examples for fitting the slope (dA/dt) from the inner grain area versus time plot. (a) The $\langle 100 \rangle$ 20° GB at 1200 K using the ADP potential. (b) The $\langle 100 \rangle$ 20° GB at 1050 K using the EAM potential. (c) The $\langle 111 \rangle$ 20° GB at 1100 K using the EAM potential. (d) The $\langle 111 \rangle$ 30° GB at 1250 K using the EAM potential. The solid line is the final fit in each figure. Grayed-out data points are not included in the fit.	22
Fig. 3.4. Representative examples of cylindrical grain rotation observed in this work. All three examples are obtained using the MEAM potential. (a) No rotation observed in the $\langle 100 \rangle$ 30° GB at 1400 K. (b) Clockwise (CW) rotation (indicated by the backward ‘S’ shape) observed in the $\langle 111 \rangle$ 45° GB at 1050 K. (c) Counterclockwise (CCW) rotation (indicated by the ‘S’ shape) observed in the $\langle 100 \rangle$ 45° GB at 1050 K. Although these examples are taken from the simulations using the MEAM potential, the other two potentials also demonstrated these behaviors.	23
Fig. 3.5. Calculated GB mobilities (displayed as Arrhenius plots) for the $\langle 100 \rangle$ rotation axis with three misorientation angles (20° , 30° , 45°) using the (a) EAM potential, (b) ADP potential, and (c)	

MEAM potential. Each data point is averaged over three to five independent simulations. Error bars represent standard error. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). . 25

Fig. 3.6. MSDs for the [001] rotation axis with three misorientation angles at 1100 K predicted by the EAM potential. (a) 20°. (b) 30°. (c) 45°. Note that in (c) the vertical (ordinate) axis has a different scale than in (a) and (b). 26

Fig. 3.7. Calculated GB mobilities (displayed as Arrhenius plots) for the <110> rotation axis with three misorientation angles (20°, 30°, 45°) using the (a) EAM potential, (b) ADP potential, and (c) MEAM potential. Each data point is averaged over three to five independent simulations. Error bars represent standard error. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). . 29

Fig. 3.8. Calculated GB mobilities (displayed as Arrhenius plots) for the <111> rotation axis with four misorientation angles (20°, 30°, 38.2°, 45°) using the (a) EAM potential, (b) ADP potential, and (c) MEAM potential. Each data point is averaged over three to five independent simulations. Error bars represent standard error. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). 32

Fig. 3.9. Arrhenius plot of GB mobilities displayed by different rotation axes with a fixed misorientation and a specific potential in each figure. Each row shows a misorientation while each column shows a potential. Each mobility is averaged over three to five independent simulations. Error bars show the standard error. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). 35

Fig. 3.10. Summary of the grain rotation behavior for simulations using the EAM potential, showing the percentage of simulations that underwent no rotation, counterclockwise (CCW) rotation, and clockwise (CW) rotation. (a) By GB type (bottom axis). The top axis indicates the number of simulations for each GB. (b) Overall statistics. Note that for the <100> 45° boundary only 15 simulations were analyzed here because the grain growth was very limited at temperatures below 1300 K and the grain rotation behavior could not be unambiguously determined. 36

Fig. 3.11. Summary of the grain rotation behavior for simulations using the ADP potential, showing the percentage of simulations that underwent no rotation, counterclockwise (CCW)

rotation, and clockwise (CW) rotation. (a) By GB type (bottom axis). The top axis indicates the number of simulations for each GB. (b) Overall statistics.....	37
Fig. 3.12. Summary of the grain rotation behavior for simulations using the MEAM potential, showing the percentage of simulations that underwent no rotation, counterclockwise (CCW) rotation, and clockwise (CW) rotation. (a) By GB type (bottom axis). The top axis indicates the number of simulations for each GB. (b) Overall statistics.....	
38	
Fig. 3.13. Summary of the grain rotation behavior for all simulations that underwent no rotation, clockwise (CW) rotation, and counterclockwise (CCW) rotation as a function of temperature and interatomic potential. The top axis indicates the number of simulations for each potential/temperature combination. No simulations were run using the ADP potential at 1350 and 1400 K, as they were above the melting temperature predicted by the potential.	
39	
Fig. 3.14. Comparison of GB mobilities (in an Arrhenius plot) between the calculated values in this work and extracted values from experiments at different temperatures. The hatched region represents the upper and lower bounds of calculated values and is bounded by the mobilities of the MEAM $\langle 110 \rangle$ 30° GB (upper bound) and the EAM $\langle 100 \rangle$ 45° GB (lower bound) as calculated based on their activation energies and mobility prefactors. Experimental values are as follows: Iltis <i>et al.</i> [18], Prabhakaran <i>et al.</i> [21], Mei <i>et al.</i> [10], Miao <i>et al.</i> [41], and Frazier <i>et al.</i> [16]. Note that the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right).....	
44	
Fig. 4.1. Representative area versus time comparison of two equilibration methods for the $\langle 111 \rangle$ 45° GB at 2900 K using the CRG potential: a simple (three-step) anneal, and a complex (five-step) anneal. Data points represent an average across three independent simulation runs.....	
52	
Fig. 4.2. Example of grain growth for the (a)-(c) $\langle 100 \rangle$ 45° , (d)-(f) $\langle 110 \rangle$ 45° , and (g)-(i) $\langle 111 \rangle$ 45° boundaries at 3000 K at various times during the simulation. Note that the $\langle 111 \rangle$ GB completely disappears after ~ 0.6 ns, while more than double the time is required for the $\langle 100 \rangle$, and the $\langle 110 \rangle$ requires more than 4 ns. Crystallographic directions are indicated for each subset.	
54	
Fig. 4.3. Example of area versus time plot used for determining the dA/dt to calculate the reduced mobility. This data is from one simulation for the $\langle 111 \rangle$ 45° boundary using the Basak potential at 2800 K. Greyed-out points were not included in the fit because the grain shrinkage had already stopped.	
56	

Fig. 4.4. Reduced GB mobility by rotation axis for a given fixed misorientation. (a) and (b) are for a 20° misorientation, and (c) and (d) are for a 45° misorientation. (a) and (c) were calculated using the Basak potential, and (b) and (d) use the CRG potential. Some data in (a) and (c) are recalculated from French [152] as indicated in the text. Error bars represent standard error of three independent simulations, but are generally too small to be seen. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). For (a)-(c), the mobility trend is $M_{111} > M_{100} > M_{110}$, while in (d) this is the trend at temperatures below 2500 K, and above 2500 K the trend is $M_{100} > M_{111} > M_{110}$. 57

Fig. 4.5. Representative reduced mobility as a function of misorientation at 2800 K (inset – 3300 K) using the Basak potential. The general trend is $M_{111} > M_{100} > M_{110}$ for the 20° and 45° misorientations. However, there is no consistent trend with the misorientation for each tilt axis. The lines are guides to the eye. 60

Fig. 4.6. Scaled MSD for the (a) $\langle 100 \rangle$ 45°, (b) $\langle 110 \rangle$ 45°, and (c) $\langle 111 \rangle$ 45° boundaries at 2800 K. Note that the Z MSD is higher than the X and Y MSD for both the $\langle 100 \rangle$ and $\langle 110 \rangle$ boundaries, but much lower for the $\langle 111 \rangle$ boundary. In each subplot, the MSD values are scaled by the maximum value between the X, Y, and Z directions, such that the ordinate (vertical) axis has a maximum value of one. 62

Fig. 4.7. Example of faceting behavior for the $\langle 110 \rangle$ 45° boundary at 2900 K after 5 ns using the Basak potential. $\langle 111 \rangle$ directions perpendicular to $[110]$ (out of the page) are indicated. 63

Fig. 4.8. Reduced mobility for the $\langle 111 \rangle$ rotation axis for (a) the Basak potential and (b) the CRG potential. Error bars denote standard error, but are generally too small to be seen. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). 65

Fig. 4.9. MSD for the Basak potential at the temperature extremes examined in this work for the (a) $\langle 111 \rangle$ 20°, (b) $\langle 111 \rangle$ 38.20°, and (c) $\langle 111 \rangle$ 45° boundaries. Solid lines indicate the lowest temperature (2000 K) and dashed lines indicate the highest temperature (3300 K). At low temperatures, the X and Y motion is higher than the Z motion. At high temperatures, there is a variety of behaviors: (a) Z lower than X and Y, (b) Z equal to the X and Y motion, and (c) Z greater than the X and Y motion. 66

Fig. 4.10. Average ratios of 2D planar (XY) to 1D (Z) diffusion as a function of temperature for the Basak potential. The lines are guides to the eye, and the dotted line indicates where the ratio is

1. Emphasized points (stars) are in the anti-thermal regions of $\langle 111 \rangle$ GBs. Error bars represent the standard error of the mean. The inset shows the converging behavior at high temperatures. 67

Fig. 4.11. GB mobility of the $\langle 100 \rangle$ 45° boundary using two different initial grain radii – 100 Å (green) and 75 Å (orange). Arrhenius fit parameters for the different regions are indicated on the plot in color, while Vogel-Fulcher fit parameters are indicated in black. The data with an initial radius of 100 Å is fitted by a single Arrhenius fit, while the 75 Å data has two (with a transition around 2200 K). Note that the mobility prefactors for the different regimes for the 75 Å data differ by six orders of magnitude, while the activation energy differs by a factor of ~ 3 . Additionally, the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right)..... 70

Fig. 4.12. Example of GB velocity as a function of inverse grain radius for the $\langle 100 \rangle$ 20° boundary at 2700 K using the Basak potential. Only at the end of the simulation does the linear relationship break down (circled point). 73

Fig. 4.13. (a) Atomic displacement vector plot, colored by magnitude, for the $\langle 100 \rangle$ 45° boundary at 2800 K using the Basak potential. (b) schematic of the motional ‘units’ in (a), where the centers (marked in green) tend to move either in or out of the plane, and the first nearest neighbors of these centers move alternately toward and away from the center. This circular region in (a) has a diameter of ~ 60 Å and is roughly centered on the embedded grain for ease of visualization..... 75

Fig. 4.14. Atomic displacement vector plot, colored by magnitude, for the $\langle 110 \rangle$ 45° boundary at 2800 K using the Basak potential. The general rotation trend is indicated. This circular region has a diameter of ~ 60 Å and is roughly centered on the embedded grain for ease of visualization. .. 76

Fig. 4.15. Atomic displacement vector plot, colored by magnitude, for the $\langle 111 \rangle$ 45° boundary at 2800 K using the Basak potential. The general rotation trend is indicated. This circular region has a diameter of ~ 60 Å and is roughly centered on the embedded grain for ease of visualization. Note that the larger displacements at the center of the embedded grain are due to the formation of a small void, which is assumed to form due to the grain creation (i.e., atom removal) procedure. 77

Fig. 4.16. Atomic displacement vector plot, colored by magnitude, for the $\langle 111 \rangle$ 20° boundary at 2800 K using the Basak potential. The general rotation trend is indicated. The inset shows the behavior around ‘rotation’ centers, showing an apparent diffusion around these central points. As the embedded grain shrinks, these centers overlap, leading to the general rotation behavior indicated. This circular region shows the whole embedded grain (~ 100 Å), while the inset shows

the atomic motion around the ‘rotation’ centers. Note that the larger displacements at the center of the embedded grain are due to the formation of a small void, which is assumed to form due to the grain creation (i.e., atom removal) procedure.....	78
Fig. 4.17. Atomic displacement vector plot, colored by magnitude, for the $\langle 111 \rangle \Sigma 7$ (38.20°) boundary at 2800 K using the Basak potential. This circular region has a diameter of ~ 60 Å and is roughly centered on the embedded grain for ease of visualization. Note that the larger displacements at the center of the embedded grain are due to the formation of a small void, which is assumed to form due to the grain creation (i.e., atom removal) procedure.....	79
Fig. 5.1. Schematic of GB creation. Atoms located within $r_{\text{grain}} = 100$ Å from the center of the simulation cell are rotated by the desired misorientation angle θ . The Z axis (out of the page) is aligned along one of the rotation axes specified in this work. Atoms are colored by grain (light/dark blue), while solute atoms are colored separately (orange).....	83
Fig. 5.2. Example of grain growth using the cylindrical grain growth method. This shows the top-down view of a $\langle 110 \rangle 45^\circ$ U1Mo system at 1050 K (a) as the initial structure after relaxation, (b) during grain growth, and (c) near the end of the simulation. Atoms are colored by grain (light/dark blue), with solute atoms colored separately (orange).	86
Fig. 5.3. Representative examples of area-versus-time plots with the relevant fitted slopes represented as dashed lines. Throughout this work, slopes are fitted to the entirety of the grain growth regime to get the average behavior. (a) $\langle 100 \rangle 20^\circ$ U3Mo at 1200 K. (b) $\langle 111 \rangle 30^\circ$ U10Mo at 1300 K. (c) $\langle 110 \rangle 45^\circ$ U21Mo at 1150 K.	86
Fig. 5.4. Representative example of Arrhenius plots for the UMo system. This shows the results of the 30° misorientation—trends for the 20° and 45° misorientation are similar. Each subplot has the mobility anisotropy trend and Mo concentration indicated. Error bars indicate the standard error; note that some data points do not have error bars because two of the three simulation runs did not result in sufficient grain growth. Also note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The data in (a) is taken from [49] for the pure γ U case for reference. Solute (Mo) concentrations are as follows: (a) 0at.% (pure U), (b) 1at.%, (c) 3at.%, (d) 5at.%, (e) 10at.%, (f) 14at.%, (g) 17at.%, (h) 21at.%.	89

Fig. 5.5. Activation energy as a function of Mo concentration for the boundaries examined in this work. Error bars indicate standard error. The lines are guides to the eye. Experimental values are taken from Frazier <i>et al.</i> [16].	90
Fig. 5.6. GB mobility anisotropy presented as a function of concentration for the 45° misorientation using the ADP potential. The mobility anisotropy trend is indicated in each subplot. Error bars indicate the standard error but are often too small to be seen on this scale. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The data in (a) is taken from [49] for comparison. Solute (Mo) concentrations are as follows: (a) 0at.% (pure U), (b) 1at.%, (c) 3at.%, (d) 5at.%, (e) 10at.%, (f) 14at.%, (g) 17at.%, (h) 21at.%.....	92
Fig. 5.7. GB mobility as a function of Mo concentration at 1050 K, 1200 K, and 1400 K. Error bars indicate the standard error but are usually too small to be seen on this scale. Columns indicate the rotation axis (left: $\langle 100 \rangle$, middle: $\langle 110 \rangle$, right: $\langle 111 \rangle$) and rows indicate misorientation (top: 20°, middle: 30°, bottom: 45°).....	96
Fig. 5.8. Average MSD (calculated via three independent simulations per system) in the XY plane of the $\langle 100 \rangle$ 20° GB for pure U, U1Mo, and U3Mo at 1400 K. The trends from 1150 K up to 1400 K are nearly the same, while 1050–1100 K (not shown) have Pure U with the lowest MSD.....	97
Fig. 5.9. Mobility as a function of Mo concentration for the (a) 20°, (b) 30°, and (c) 45° misorientations for all three rotation axes at 1400 K for the EAM potential. Error bars indicate standard error.	98
Fig. 5.10. Comparison of defect diffusion rates with the $\langle 110 \rangle$ 45° GB mobility as a function of Mo concentration for two different interatomic potentials: EAM (left) and ADP (right). Note that the scales of the left and right axes are not the same. Open points indicate that not enough grain growth occurred to reliably calculate GB mobility, but they are included as an estimate of the upper limit of mobility at the respective concentration. Diffusion rates were calculated at 1400 K for the EAM potential, and 1200 K for the ADP potential.	99
Fig. 6.1. Example of the GB structures created in this work. Xe atoms (large, orange) are distributed randomly throughout the system. The embedded cylindrical grain of radius r_{grain} (light blue) has atoms rotated by the desired misorientation angle, θ , relative to the matrix grain (dark blue). This is an input structure for the $\langle 100 \rangle$ 45° $\text{UO}_2 + 1.00\text{at.}\% \text{ Xe}$ system. O atoms are not shown for clarity, and U atoms are colored by their assigned grain.....	105

Fig. 6.2. Snapshots taken at the beginning (a, c) and end (b, d) of the simulations. (a) and (b) are for a U + 5at.% Mo + 0.75at.% Xe $\langle 111 \rangle$ 20° system at 1400 K, and (c) and (d) are for a UO₂ + 1.00at.%Xe $\langle 110 \rangle$ 45° system at 3000 K using the CRG potential. Xe atoms are colored red, and U atoms are colored black. In the UMoXe system, Mo atoms are colored green and in the UO₂+Xe system, O atoms are not shown for clarity..... 107

Fig. 6.3. Representative area versus time plots observed in this work, with linear fits to the growth regime shown as dashed lines. (a) UO₂+0.50at.% Xe $\langle 111 \rangle$ 38.20° at 3000 K—demonstrates rapid, linear growth. (b) U 0.25at.% Xe $\langle 100 \rangle$ 20° at 1050 K—shows a large stagnation step during grain growth. (c) UO₂+1.00at.% Xe $\langle 100 \rangle$ 20° at 2600 K—shows the growth starting with a smaller initial grain radius and also shows several small stagnation steps during grain growth. (d) U 5at.% Mo 0.75at.% Xe $\langle 111 \rangle$ 45° at 1400 K—demonstrates slow growth. 109

Fig. 6.4. Arrhenius plots of the reduced GB mobility for various concentrations of Xe for the 30° misorientation in the γ U system. Error bars indicate the standard error, though not all data points have error bars because of a lack of significant grain growth in two of the three simulations. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). Values in (a) are taken from Chapter 3 for comparison. Concentrations of Xe are as follows: (a) pure γ U (0at.%), (b) 0.25at.%, (c) 0.50at.%, (d) 0.75at.%, (e) 1.00at.%, (f) 1.25at.%, and (g) 1.50at.%. The anisotropy trend is indicated for each concentration. 110

Fig. 6.5. Reduced GB mobility as a function of Xe concentration for nine unique GBs. Error bars indicate standard error. Columns indicate the rotation axis (left: $\langle 100 \rangle$, middle: $\langle 110 \rangle$, right: $\langle 111 \rangle$) and rows indicate misorientation (top: 20°, middle: 30°, bottom: 45°). 112

Fig. 6.6. GB mobility as a function of temperature for the 45° misorientation. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The mobility anisotropy trend is indicated in each subplot. Error bars indicate standard error. Xe concentrations increase from 0at.% Xe in the far left subplots to 0.75at.% Xe in the far right subplots, while Mo concentrations increase from 0at.% Mo in the top row to 5at.%Mo in the bottom row. 113

Fig. 6.7. Mobility as a function of Xe concentration for various concentrations of Mo in UMo alloys at 1400 K. Error bars indicate standard error. The lines are guides to the eye. Columns

indicate the rotation axis (left: $\langle 100 \rangle$, middle: $\langle 110 \rangle$, right: $\langle 111 \rangle$) and rows indicate misorientation (top: 20° , middle: 30° , bottom: 45°).	114
Fig. 6.8. GB mobility as a function of temperature for the UO_2 system using the Geng (top row) and CRG (bottom row) potentials with a misorientation of 45° . Xe concentration increases from pure UO_2 (far left) to 1.00at.%Xe (far right). The data for pure UO_2 is taken from Chapter 4. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The lines are guides to the eye.	115
Fig. 6.9. GB mobility as a function of temperature for the UO_2 system using the Geng (top row) and CRG (bottom row) potentials with a misorientation of 20° . Xe concentration increases from pure UO_2 (far left) to 1.00at.% (far right). The data for pure UO_2 is taken from Chapter 4. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The lines are guides to the eye.	116
Fig. 6.10. GB mobility as a function of Xe concentration for the UO_2 systems examined at 3000 K. Columns indicate the misorientation angle (left: 20° , right: 45°), and rows indicate the interatomic potential (top: Geng, bottom: CRG).	118
Fig. 6.11. Mobility of the 75 Å initial radius plotted against the 100 Å initial radius. The dashed line indicates equal values for both initial radii.	119
Fig. 6.12. Fitted slopes plotted as a function of temperature. (a) UXe system, (b) UMoXe system, (c) UO_2 +Xe system for the Geng potential, (d) UO_2 +Xe system for the CRG potential. Error bars indicate standard error. The average slopes are the averages of all the slopes calculated at that specific temperature.	121

List of Tables

Table 3.1. Dimensions (in units of Å) of the initial single crystal used to generate GBs for the three rotation axes (in the Z direction) as well as for three interatomic potentials. The crystallographic orientations of the X and Y axes are also shown for completeness.....	17
Table 3.2. Some basic properties predicted by the three interatomic potentials used in this work, taken from the papers describing their creation. The experimental results are also shown for comparison.....	18
Table 3.3. Activation energies and GB mobility prefactors predicted by the EAM potential. Activation energies (Q) are given in eV and prefactors (M_0) in $\text{m}^2/\text{s} \times 10^{-9}$	26
Table 3.4. Activation energies and GB mobility prefactors predicted by the ADP potential. Activation energies (Q) are given in eV and prefactors (M_0) in $\text{m}^2/\text{s} \times 10^{-9}$	27
Table 3.5. Activation energies and GB mobility prefactors predicted by the MEAM potential. Activation energies (Q) are given in eV and prefactors (M_0) in $\text{m}^2/\text{s} \times 10^{-9}$	28
Table 4.1. System details for the GBs studied in this work. Size is given in Å for each direction.	52
Table 4.2. Activation energies (Q , in eV) and reduced mobility prefactors (M_0 , in m^2/s) for the GBs studied in this work fitted to typical Arrhenius behavior. Except where otherwise noted, the fitted values are across the whole range of calculated mobilities.	58
Table 4.3. Activation energies (in eV), and reduced mobility prefactors (in m^2/s) for the GBs studied in this work fitted to Vogel-Fulcher dynamics. Except where otherwise noted, the fitted values are across the whole range of calculated mobilities. An assumed characteristic temperature of $T_m/2.8$ was used throughout ($T_0 = 1264.29$ K for the Basak potential, and $T_0 = 1089.29$ K for the CRG potential).	70
Table 5.1. System information for the nine input structures. System dimensions are given in Å. For the $\langle 100 \rangle$ systems, the X direction is $[100]$ and the Y direction is $[010]$; the $\langle 110 \rangle$ systems have $[001]$ for the X direction and $[1\bar{1}0]$ for the Y direction; the $\langle 111 \rangle$ systems have $[1\bar{1}0]$ for the X direction and $[11\bar{2}]$ for the Y direction.	84
Table 5.2. Temperature- and concentration-dependent lattice parameter equation (Equation (3.1)) coefficients.	87
Table 6.1. Approximate system sizes for the rotation axes examined in this work. Dimensions are given as XYZ triples with units of Å. For the U(Mo)Xe systems, misorientations of 20° , 30° , and	

45° were examined, while for the UO ₂ +Xe systems, 20° and 45° were used for the low-index rotation axes (with an additional 38.20° misorientation for the <111> rotation axis), and 45° was used for the <112> boundary.	105
Table A.1. Activation energies (<i>Q</i> , in eV) and mobility prefactors (<i>M</i> ₀ , in m ² /s×10 ⁻⁶) for the UMo system. Error indicates standard error. Mo concentrations are given in atomic percent.	146
Table B.1. Activation energies (<i>Q</i> , in eV) and mobility prefactors (<i>M</i> ₀ , in m ² /s ×10 ⁻⁶) for the UXe system. Error indicates standard error. Italicized values indicate that not enough data was present to calculate the standard error in the fitting parameters. Xe concentrations are given in atomic percent.	147
Table B.2. Activation energies (<i>Q</i> , in eV) and mobility prefactors (<i>M</i> ₀ , in m ² /s ×10 ⁻⁶) for the UMoXe system. Error indicates standard error. Solute and impurity concentrations are given in atomic percent.	148
Table B.3. Activation energies (<i>Q</i> , in eV) and mobility prefactors (<i>M</i> ₀ , in m ² /s ×10 ⁻⁶) for the UO ₂ +Xe system. Error indicates standard error. Italicized values indicate that not enough data was present to calculate the standard error in the fitting parameters. Xe concentrations are given in atomic percent.	149
Table C.1. Slopes and intercepts for the log ₁₀ reduced mobility versus Xe concentration for the UXe system. Intercepts are given in log ₁₀ (m ² /s) and slopes are log ₁₀ (m ² /s)/at.%.	150
Table C.2. Slopes and intercepts for the log ₁₀ reduced mobility versus Xe concentration for the UMoXe system. Intercepts are given in log ₁₀ (m ² /s) and slopes are log ₁₀ (m ² /s)/at.%Xe.	153
Table C.3. Slopes and intercepts for the log ₁₀ reduced mobility versus Xe concentration for the UO ₂ +Xe system. Intercepts are given in log ₁₀ (m ² /s) and slopes are log ₁₀ (m ² /s)/at.%Xe.	159

Chapter 1. Introduction

The safety and efficacy of nuclear reactors have been the overarching focus of nuclear reactor research for over 80 years. Recent developments allow for new reactor designs to be developed, tested, and fine-tuned using computer simulation, saving a significant amount of time and money. One tool used in this process is fuel performance modeling, which predicts each reactor design's performance given the various properties of the materials and external factors (such as temperature) as inputs. Microstructural evolution is an important consideration in fuel performance modeling. Thus, for accurate models to exist, researchers need a thorough knowledge of how the material microstructure changes. Part of microstructural evolution is grain growth, which is largely determined by two grain boundary (GB) properties: energy and mobility. While the variation in both of these properties is known to impact grain growth kinetics [1–5], this work will focus specifically on GB mobility in nuclear fuels. Understanding this property is an important part of improving fuel performance because GB mobility is directly related to grain growth behavior, and consequently microstructural evolution.

Grain growth kinetics are an important property of the nuclear fuel material in a reactor, and understanding the kinetics will assist in the prediction of grain growth in the fuel and thus improve fuel performance modeling. All commercial nuclear reactors in the United States are light water reactors (LWRs), which use uranium dioxide (UO_2) as their primary fuel source. Research reactors are in the process of being switched from highly enriched uranium (HEU) to low-enriched uranium (LEU) fuels, with a promising candidate fuel being uranium-molybdenum (UMo) alloys. Average GB mobilities have been extracted from experimental studies of these materials across a range of temperatures, but very little information about how mobility changes with GB character. Therefore, identifying and understanding how GB mobility changes with GB character will allow more accurate models of fuel performance to be developed, ultimately contributing to the development of safer, more efficient nuclear reactors.

1.1. Literature Review

Microstructural evolution in nuclear fuels, such as grain growth, has long been at the forefront of nuclear materials research. This interest has led to many experimental and computational studies examining microstructural evolution in stoichiometric and non-stoichiometric UO_2 and various metallic uranium alloys under both non-irradiated and irradiated

conditions. The focuses of these studies cover a broad range of topics, including stoichiometric effects [6–9], grain size distribution effects [10], irradiation effects [11,12], porosity effects [13,14], second-phase particle effects [15–18], homogenization effects [19–21], and others [22–30]. While the existing literature on grain growth in UO_2 and U-based metal alloys is extensive, what follows is a selection of research relevant to the current dissertation. Specific background information will be given in the relevant chapters.

1.1.1. Grain boundary mobility in UO_2

One of the earliest experimental examinations of the average GB mobility in UO_2 was performed by Ainscough *et al.* in 1973, where grain growth was examined in stoichiometric UO_2 across a small range of temperatures. They found that a modified Arrhenius relationship that includes a maximum grain size generally does a good job of describing polycrystalline grain growth kinetics in UO_2 [31]. Later studies by Singh [32] and Bourgeois *et al.* [33] expanded the temperature range, confirming the good fit of the modified Arrhenius relationship but disagreeing on the specific mass transport mechanisms. Miao *et al.* [23] found that nano- and micro-grained grain growth in polycrystalline UO_2 is not directly comparable due to differing maximum grain sizes, where the former has a much faster effective GB mobility. In terms of how GB character impacts GB mobility, very few experimental sources are available. However, there are a number of studies about the GB character distribution in UO_2 , which could be directly related to GB energy and indirectly related to GB mobility. Nerikar *et al.* [28] used a combined experimental and atomic modeling approach to study the GB character distribution in polycrystalline UO_2 . In their samples, approximately 16% of the GBs were coincident-site lattice (CSL) boundaries, with the remainder being ‘general’ boundaries. CSL boundaries are known to have higher migration rates than general boundaries in the presence of impurities [34], suggesting that calculating average GB mobility across a polycrystalline sample is biased toward the slower-moving general boundaries. Rudman *et al.* [7] analyzed the GB character distribution for near-stoichiometric and hyperstoichiometric UO_2 . In both cases, $\{111\}$ GB planes with misorientations between 30° and 50° were not present in the samples, while a majority of GB planes were oriented along $\{113\}$ with misorientations between 30° and 40° . Though not directly related to GB mobility, Bourasseau *et al.* [29] recently found that GB formation energy decreases as its length fraction increases. This suggests a competing effect between longer, higher-energy GBs and shorter, low-energy GBs, especially if the former grows. Ainscough *et al.*, Singh, and Bourgeois *et al.* calculated average GB mobilities

from polycrystalline samples using an approach that necessitated assuming an isotropic GB mobility regardless of GB character. On the other hand, Nerikar *et al.*, Rudman *et al.*, and Bourasseau *et al.* identified the GB character distribution in polycrystalline UO_2 but did not examine how that character relates to GB mobilities. In general, a lack of experimental data exists for GB mobility as a function of GB character, especially in UO_2 .

There are some computational studies of grain growth in UO_2 , and most of them use mesoscale phase field simulations and assume an isotropic GB mobility [4,35]. Regarding the anisotropy effect, only two studies appear to have been done that examine GB mobility anisotropy to the best of the author's knowledge. Bai *et al.* [36] simulated five flat GBs using a thermal gradient driving force; however, only three boundaries experienced enough GB migration to calculate mobility values. Around the same time, Hallberg and Zhu [26] used a level-set method to examine how a simplified form of anisotropic GB energy and mobility affected GB texture in UO_2 . They concluded that the average grain growth kinetics are negligibly impacted by the specific form of GB property anisotropy they employed, but the grain size distribution and stability of grain textures are strongly impacted.

Several studies have examined the effect of impurities, dopants, or other defects on GB mobility in UO_2 . For example, several studies spanning from the late 1960s to the early 2000s studied the effect of stoichiometry on grain growth with the general finding that hyperstoichiometric UO_{2+x} experiences faster grain growth [7–9,22,24,25]. Researchers also studied the effect of porosity on grain growth behavior and found that pores hinder grain growth through a boundary-pinning (Zener pinning) mechanism [13,14]. Several studies [15,22,24,27,37] have examined the impact of various dopants on grain growth, finding that certain dopants (for example, Cr_2O_3 [22] or U_3O_8 [37]) lead to faster grain growth, while others (such as NiO [22]) inhibit grain growth. Pickering [27] specifically examined the effect of a variety of impurities on grain growth in UO_2 , finding that the concentration, segregation energy, and impurity diffusivity carry significant weight in determining the overall mobility of a GB in UO_2 . Fission gases such as Xe are important considerations for microstructural evolution in the fuel due to their prevalence in irradiated UO_2 and as such have been studied in some detail. However, past research has focused primarily on properties such as diffusivity [38,39] and segregation tendencies [40] rather than the

specific impacts of Xe on GB mobility. In all of these studies, the anisotropy of GB mobility (and the effects that such defects have on it) is ignored.

1.1.2. Grain boundary mobility in U-based metallic fuels

Experimental studies of GB mobility in metallic uranium and its alloys are limited. In fact, there is no literature currently available elucidating GB mobilities in the pure γ U system. All existing literature on grain growth in the metallic uranium system focuses on specific U-based alloys, with a subset of these focused on the UMo alloy. In particular, Mei *et al.* [10] combined two unpublished experimental studies of U-7wt%Mo (U-7Mo) powder anneals to estimate an activation energy of ~ 2.8 eV for grain growth. Frazier *et al.* [16] later examined polycrystalline grain growth in a U-10Mo alloy in the 700–900 °C range and determined an activation energy of ~ 1.8 eV, indicating that there is a large discrepancy between their work and Mei *et al.*'s, although the alloy compositions were different in the two studies. Additionally, Frazier *et al.* found that grain growth stagnated after a short annealing time due to the presence of stable second-phase particles. These studies represent the bulk of the available literature on experimentally determined grain growth in UMo alloys. A few other studies of UMo alloys with varied focuses (such as homogenization [21], microstructure characterization techniques [18], thermal conductivity analysis [41], phase transformation kinetics [42], or others [30]) present enough data to estimate grain growth constants without specifically focusing on grain growth properties. Computational studies of grain growth in uranium-based alloys are also limited: Frazier *et al.* used a Monte Carlo Potts model to examine post-recrystallization grain growth in a U-10Mo alloy [17] and the effect of homogenization on the hot-rolling and recrystallization processes [43]. These two studies represent all of the available literature on computational studies of grain growth in uranium-based alloys—both with and without impurities—to the best of the author's knowledge.

These studies in UO_2 and uranium-based alloys provide important background for understanding GB mobility in both the pure and impure cases of these materials but do not themselves indicate any sort of anisotropy trends, thus emphasizing the importance of this work. A couple of early experiments revealed that $\langle 111 \rangle$ tilt GBs in face-centered cubic (FCC) pure metals such as aluminum (Al) have higher mobility than other boundaries [34], but the specific anisotropy trends have not been elucidated. It is also unclear if such a trend can also be extended to oxide systems having an FCC-based fluorite structure such as UO_2 .

1.2. Objectives

This work will examine the form of GB mobility and its anisotropy for the FCC-based fluorite UO_2 and body-centered cubic (BCC) γ U and U-Mo systems using molecular dynamics (MD). What follows is a brief description of the objective of each chapter. Note that each Chapter is written to be self-contained, thus certain information will be repeated across the various Chapters.

In Chapter 2, the methods common to the remainder of this work are explained. As the general process is the same for each study, these methods are collected here for clarity. Specific methods unique to the particular chapter will be explained in the relevant chapter.

In Chapter 3, GB mobility in pure BCC γ U is examined via MD to determine its mobility and anisotropy trend in BCC materials for different rotation axes, misorientation angles, and temperatures.

In Chapter 4, GB mobility and its anisotropy trend are examined in UO_2 via MD to verify that $\langle 111 \rangle$ tilt GBs have higher mobility than other rotation axes for FCC-like fluorite crystal structures and explore the underlying reason behind that.

In Chapter 5, building off the results in Chapter 3, Mo is added as a solute in various concentrations to the pure U system to examine the effect of solute concentration on GB mobility and its anisotropy.

In Chapter 6, the effect of Xe fission gas on GB mobility and its anisotropy is examined in the γ U, UMo, and UO_2 systems, using MD simulation.

Chapter 2. Methodology

This chapter provides a summary of the background and major techniques utilized in this work.

2.1. Grain growth fundamentals

Grain growth is typically assumed to follow the form $v = M \times F$, where v is the migration velocity of the GB, M is the GB mobility, and F is the driving force acting on the GB. This is valid, provided that the driving force acting on the boundary is much less than the thermal energy, $F \ll k_B T / \Omega$, where Ω is the atomic volume. Mobility is assumed to have an Arrhenius relationship with temperature, $M = M_0 e^{-Q/k_B T}$, where M_0 is the preexponential factor and Q is the activation energy for boundary motion. In any given GB system, several different driving forces can act on a single boundary at a given time (see Ref. [34]), but a prevalent driving force in all polycrystalline microstructures is the curvature driving force, defined as $F_c = (\gamma + \gamma'')\kappa$ [44,45], where γ is the GB energy, γ'' is the second derivative of GB energy with respect to inclination, and κ is the curvature of the boundary ($\kappa = 1/r_1 + 1/r_2$ with r_1 and r_2 as the principal radii of the grain). In most cases, γ'' is not known. With the added complexity of GB energy dependence on all five degrees of freedom at the GB, the stiffness $(\gamma + \gamma'')$ is generally unknowable for a given GB. Because of this, the relationship between boundary velocity and mobility is often redefined as

$$v = M^* \kappa \quad (2.1.1)$$

where M^* is the reduced mobility of the boundary and is defined as $M^* = M(\gamma + \gamma'')$ (however, in the literature, the second derivative is usually neglected). Equation (2.1.1) provides the basic relationship upon which this work calculates all GB mobilities.

Experimentally determining GB mobility is usually done using the grain growth law, which is defined as

$$D^n - D_0^n = Kt, \quad (2.1.2)$$

where D_0 and D are the initial and final grain sizes respectively, t is the annealing time, K is the grain growth constant, and n defines the rate-controlling process (in pure materials $n = 2$ (ideal grain growth), but fitted values have ranged from 0.5 to 5). If $n = 2$, K can be related to GB mobility via the relationship $k = M\gamma$.

2.2. Molecular Dynamics

This research utilizes molecular dynamics (MD) as the primary tool for examining GB mobility. MD calculates the time evolution of an atomic system by solving Newton's second law of motion simultaneously for each atom within the system ($F_i = m_i a_i$, for $i = 1, 2, 3, \dots, N$ with N as the total number of atoms). The force is calculated by the gradient of the potential energy, and the potential energy of each atom is defined by the interatomic potential used. This work used the isothermal-isobaric ensemble (NPT—constant number of atoms, constant pressure, and constant temperature) for all simulations. A Nosé-Hoover barostat and thermostat maintained constant pressure and temperature respectively, where the pressure was fixed at 0 bars for all simulations, and the temperature was fixed on a per-simulation basis. The LAMMPS software [46] was used for all molecular dynamics simulations in this work. Periodic boundary conditions were employed for all simulations, and a timestep of 2 femtoseconds (fs) was used throughout. Snapshots of the atomic structure were saved every 20 picoseconds (ps) for later analysis.

2.3. Grain Boundary Structure Generation

For all simulations, the general process for creating a GB is as follows. First, a block of pure material is created with the Z axis of the block aligned along the desired rotation axis direction of the GB such as the [001], [110], or [111] crystallographic direction (see Fig. 2.1). Atoms within the cylinder of radius $r_{\text{grain}} = 100 \text{ \AA}$ centered in the XY plane are rotated by the desired misorientation angle, θ . After this rotation, some atoms are too close together. Starting an MD simulation with atoms arranged as such would lead to these atoms rapidly shooting away from each other, causing the local atomic arrangement to collapse. If the pair separation distance was less than some cutoff value (the specific values are indicated in the relevant chapters), one atom of the pair was removed. The resulting structure was annealed to allow for relaxation in the GB region, and the annealed structures were used as inputs for all subsequent simulations.

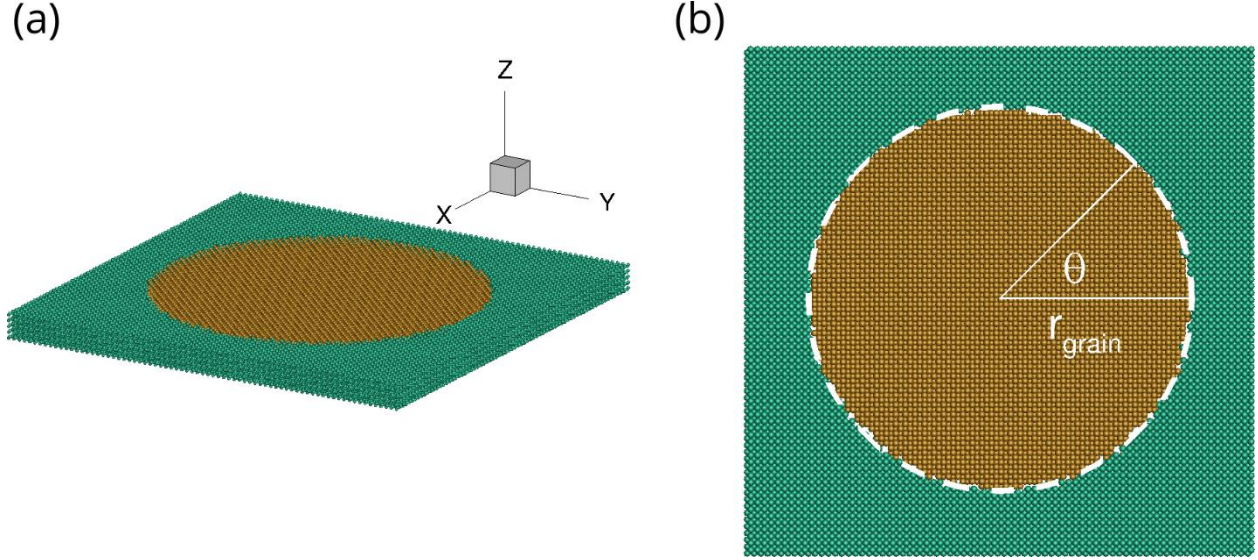


Fig. 2.1. Schematic of GB creation. (a) The quasi-2D structure of the system. The Z-axis is aligned along the desired crystal direction. (b) Top view.

2.4. Grain Boundary Mobility Calculation Procedure

To calculate GB mobility, a relationship between a trackable parameter and GB mobility is needed. Using the relationship established in Equation (2.1.1) and substituting $v = dr_{\text{grain}} / dt$ gives $r_{\text{grain}} dr_{\text{grain}} / dt = M^*$ (with $\kappa = 1/r_{\text{grain}}$, as the second principle radius is ∞). Integrating this equation gives the result

$$M^* = \frac{1}{2\pi} \frac{dA}{dt}, \quad (2.4.1)$$

where A is the cross-sectional area of the embedded cylindrical grain (see Fig. 2.1(b)).

The volume of the embedded grain can be expressed as a function of the number of atoms in the grain by $V_{\text{grain}} = N a_0^3 / n_{\text{cell}}$, where N is the number of atoms in the embedded grain, a_0 is the temperature-dependent lattice parameter of the material, and n_{cell} is the number of atoms in the unit cell of the material. As the volume of a cylinder is the cross-sectional area of the grain times the height of the cylinder (L_z), the cross-sectional area of the grain can be determined as

$$A = \frac{N a_0^2}{n_{\text{cell}} L_z}. \quad (2.4.2)$$

The number of atoms in the grain was determined using the orientation parameter method, whereby each atom is assigned a parameter based on its local surroundings. The specific orientation parameter used in this work is the one developed by Ulomek *et al.* [47], and simplified by Schratt and Mohles [48]. The orientation parameter for atom j is defined by [47,48]

$$\chi_j = \frac{1}{\mathcal{N}} \sum_{l=1}^3 [|\psi_l^I(\mathbf{r}_j)|^2 - |\psi_l^{II}(\mathbf{r}_j)|^2]. \quad (2.4.3)$$

In this expression, $\mathcal{N}$ is a factor that normalizes χ_j between $[-1, +1]$ at $T = 0$ K. At higher temperatures, this parameter can take on values outside this range, but this does not affect which grain the atoms are assigned to due to the use of a cutoff to determine grain assignment. The $\psi_l^\lambda(\mathbf{r}_j)$ term is a complex sum defined by $\psi_l^\lambda(\mathbf{r}_j) = \sum_{k \in \Gamma_j} w_{jk} \exp(i(\mathbf{r}_j - \mathbf{r}_k) \cdot \mathbf{q}_l^\lambda)$, which defines how well the local atomic arrangement for atom j (given a small neighbor list Γ_j) aligns with the matrix grain ($\lambda = I$) or the embedded grain ($\lambda = II$). The grains are independently defined by three reciprocal lattice vectors $\mathbf{q}_l^\lambda$ (where $l = 1, 2, 3$ is an index for the reciprocal lattice vectors). This sum is weighted by the distance between the atom and its neighbor with a function that smoothly goes from one (at atom j 's position, $\mathbf{r}_j$) to zero at a specified cutoff value via the relationship $w_{jk} = w(|\mathbf{r}_j - \mathbf{r}_k|)$. In this work, a value of $\chi_j > 0$ indicates the matrix grain, and $\chi_j \leq 0$ indicates the embedded grain. Further details regarding the derivation of this parameter are provided in Refs. [47,48]; this work simply utilizes this parameter to differentiate between the matrix grain and the embedded grain. Figure 2.2 provides an example of how this orientation parameter allows the embedded grain to be distinguished from the matrix grain, even at elevated temperatures. Once the number of atoms inside the embedded grain is known, the area (calculated via Equation (2.4.2)) is plotted as a function of time, and a line is fit to the grain growth regime. Several examples of this are shown in Fig. 2.3.

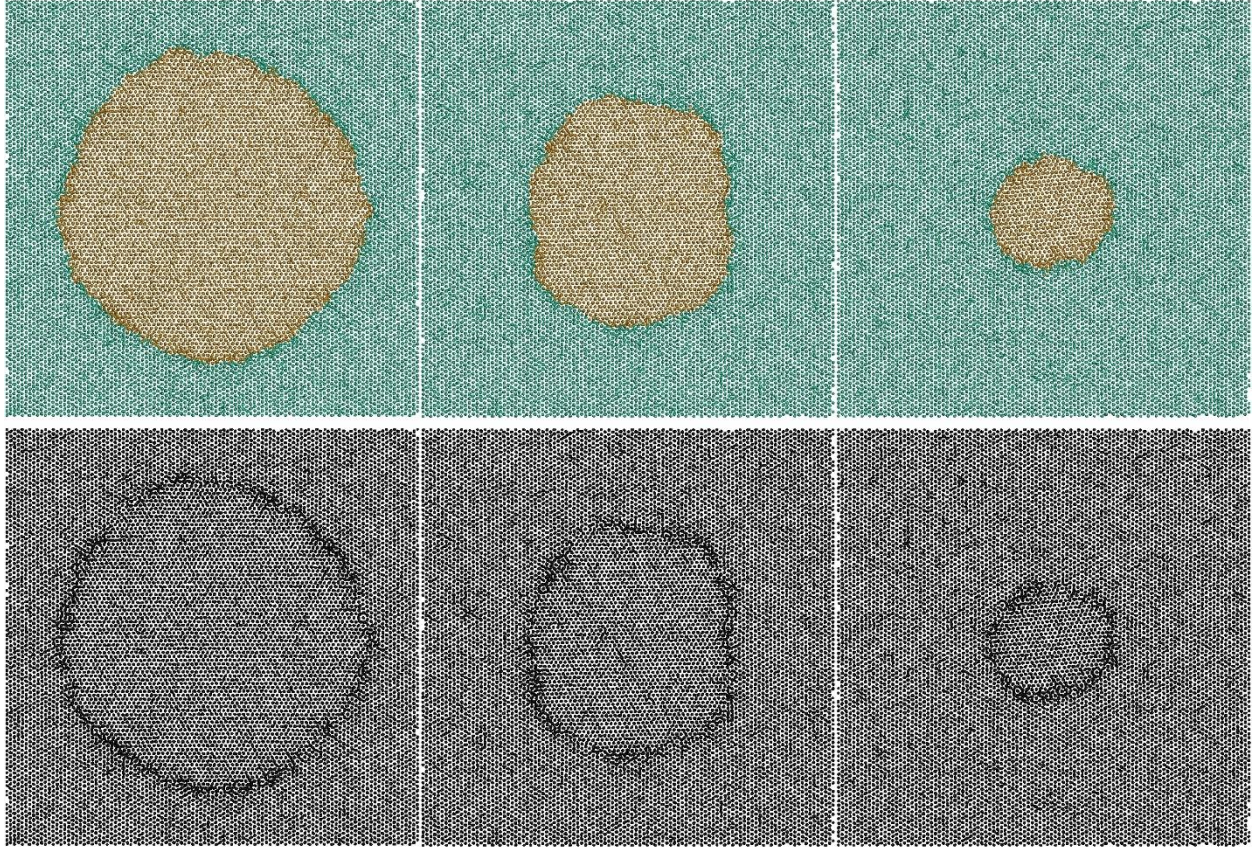


Fig. 2.2. Example of the orientation parameter method. The first row colors the atoms by their assigned grain, while the bottom row shows the same atoms without any coloring. This particular structure is a $\langle 111 \rangle$ 30° boundary in BCC γ U at various stages of grain growth during a 1300 K anneal.

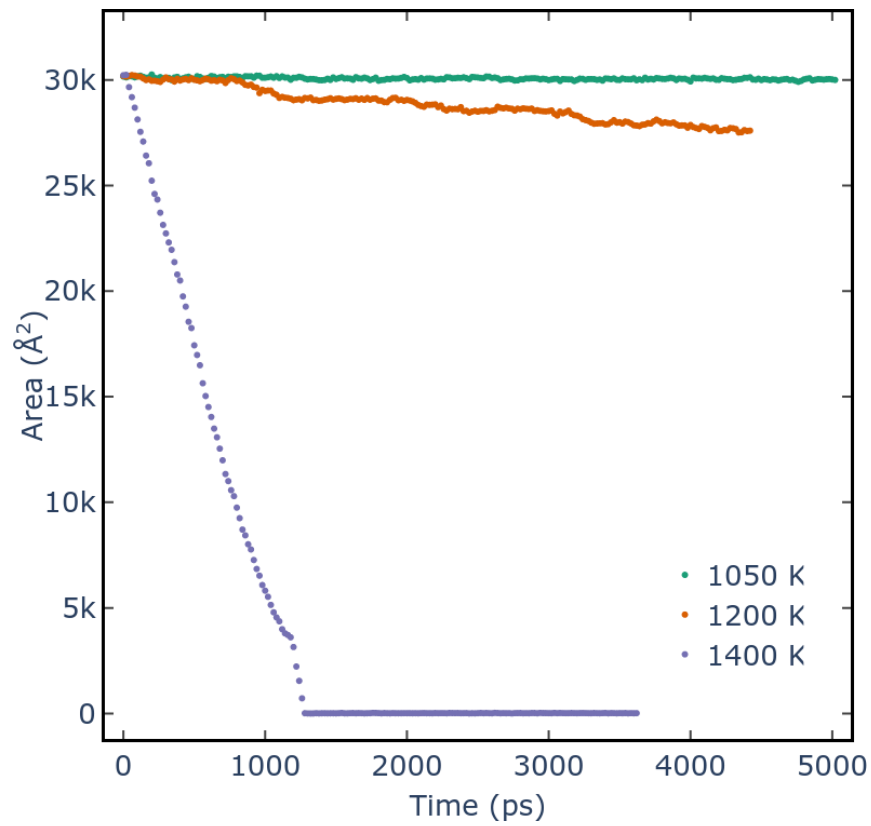


Fig. 2.3. Examples of the area versus time plots examined in this work. In general, increasing temperature leads to a higher rate of grain growth. This particular data set is from the $\langle 111 \rangle$ 30° BCC γ U system.

Chapter 3. Grain Boundary Mobility in Pure γ U

This chapter is reproduced from French and Bai [49]. I, Jarin French, have the right as an Elsevier author to include this article as part of my non-commercial dissertation according to Elsevier's copyright policy. Light edits have been made for clarity where appropriate.

3.1. Abstract

Grain morphologies such as grain size and aspect ratio in uranium-based metallic fuels are important microstructural features that can impact various fuel performance properties such as fission-gas-induced swelling, thermal transport, high burnup structure formation, and radiation resistance. Accurate prediction of the fuel grain morphologies requires knowledge of critical grain growth parameters such as grain boundary (GB) mobility and anisotropy. In this work, molecular dynamics (MD) simulations were performed to study GB mobility and its anisotropy in pure body-centered-cubic (BCC) γ uranium. Nine GBs with different combinations of misorientation angles (20° , 30° , 45°) and rotation axes ($\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$), as well as an additional $\langle 111 \rangle$ 38.2° GB were studied using three interatomic potentials. It is found that GB mobility anisotropy has complex trends, depending on both the rotation axis and misorientation. However, in general, the $\langle 110 \rangle$ rotation axis has the fastest GB mobility at the same misorientation. The results of this work can be used as not only a baseline for future studies of GB mobility in uranium-based alloys such as uranium-molybdenum (U-Mo) fuels but also as input for mesoscale modeling of grain growth in uranium-based alloys.

3.2. Introduction

The Global Threat Reduction Initiative (GTRI) Convert program has driven scientific understanding of nuclear fuels with high uranium (U) density and low enrichment through subprograms such as the US High-Performance Research Reactor (USHPRR) conversion program [50,51]. Pure U has a high density, making it a good candidate fuel form for this purpose. However, the stable phase of pure U is the α phase at temperatures below 668°C , which has an orthorhombic crystal structure and thus unsatisfactory radiation performance [52–54]. When temperatures are above the temperature range for stable α phase, the first stable crystal structure is a complex tetragonal β structure [55]. At temperatures above 776°C (1049 K), pure U has a body-centered-cubic (BCC) γ phase with good radiation tolerance [54]. Unfortunately, this temperature range is much higher than the typical operation temperatures of research and test reactors, which are usually

lower than 250 °C [54,56]. It has been found that alloying U with molybdenum (Mo) can stabilize the desired BCC γ phase in the research reactor temperature range [54], even though the stabilized γ phase is metastable according to the U-Mo phase diagram [57,58]. Therefore, the U-Mo-based metallic fuel system has been particularly focused on for its very high U density [59] and satisfactory fuel performance properties, such as high thermal conductivity [41,60], good fission gas stability [54,61], and excellent radiation resistance [12,54]. In terms of fuel design, both monolithic and dispersion U-Mo fuel forms have been extensively studied [57]. The typical fuel compositions are U-10wt.%Mo and U-7wt.%Mo, which are commonly referred to as U-10Mo and U-7Mo in literature [54].

However, one glaring weakness of U-Mo fuels is the accelerated fuel swelling observed at high fission density or burnup [62–64]. At low fission densities, U-Mo fuel swelling increases almost linearly with fission density, which is mainly induced by solid fission products [63–65]. At these lower fission densities, fission gases such as xenon (Xe) and krypton (Kr) can precipitate and form a stable face-centered-cubic (FCC) nano-bubble superlattice in the BCC U-Mo alloy so that the gas bubble swelling effect is suppressed [65,66]. At a threshold fission density, the fuel swelling deviates from the linear behavior and increases rapidly [62,63,65]. Such an accelerated fuel swelling behavior is closely related to the formation of large intergranular fission gas bubbles [65]. It has been found that the onset of accelerated fuel swelling coincides with the high burnup structure (HBS) formation [63,65]. The HBS formation is a grain subdivision process (i.e., a large grain splits into many small grains), which has been observed in both U-Mo-based metallic fuels [57,65,67] and uranium dioxide (UO₂)-based oxide fuels [68] at high burnups. The small grain size in the HBS can reduce the diffusion length of fission gas atoms from grain interior to grain boundaries (GBs). In addition, the high-density GBs in the HBS can provide fast diffusion paths for insoluble fission gas atoms to precipitate into large intergranular bubbles. Previous phase field modeling [10,69] and experimental studies [62,64,67] have identified that the initial grain morphology plays a vital role in affecting the onset of HBS formation and the accompanying accelerated fuel swelling. Typically, an increased average grain size and reduced grain aspect ratio delay the HBS formation and thus fuel swelling [12,69–72]. This is because GBs are favorable nucleation sites for HBS formation. If the initial average grain size is large, the number of HBS nucleation sites is low and therefore the HBS formation occurs at high fission densities. Thus, an ideal fuel microstructure for delaying the accelerated fuel swelling would consist of large and

equiaxed grains [16]. Since the swelling behavior of U-Mo fuels must be stable and predictable to meet safety requirements, the knowledge of how the fuel microstructure changes is important in determining the processing parameters used to create the fuel as well as the operating parameters for the desired fuel performance. This knowledge can also be applied to fuel performance modeling codes (e.g., MARMOT [73]) to predict the microstructural evolution during fuel fabrication as well as in the reactor's relevant conditions.

Since the initial fuel microstructure (more specifically, grain size and aspect ratio) is very important for the long-term U-Mo fuel performance in reactors, the initial fuel grain morphology needs to be controlled within specific parameters. During fuel fabrication, high-temperature treatment is usually used to control grain growth. Many experiments have shown that γ phase U-Mo alloys can have significant grain growth at high temperatures [16,18,19,21]. From the time (t) evolution of the average grain size (D), a grain growth constant (K) can be extracted based on the ideal grain growth model

$$D^2 - D_0^2 = Kt, \quad (3.2.1)$$

where D_0 is the initial grain size [16,74]. The grain growth constant is closely related to GB mobility [36]. The underlying assumption of such an analysis is that GB mobility is isotropic, i.e., does not depend on the GB character. Some researchers also used mesoscale phase-field modeling to predict the grain growth of U-Mo fuels under high-temperature treatment [10,17]. The GB-mobility-related kinetic parameters were empirically fitted from experimental data and thus are isotropic as well. Although such an approximation can lead to satisfactory prediction of grain growth at specific fuel fabrication conditions, the effect of anisotropy in GB properties is largely ignored. Grain growth is determined in part by two GB properties: GB energy and mobility, both of which are anisotropic [75,76]. Previously, researchers have used density functional theory (DFT) [10] or molecular dynamics (MD) [77] to calculate GB energies in U-Mo fuels. Although the results show that GB energy is anisotropic, it only varies less than 75% for the studied GBs [10,77]. For GB mobility in U or U-based alloys, to the best of the authors' knowledge, there are no experimental data or theoretical studies to directly demonstrate its anisotropic behavior. However, the average GB mobilities extracted from various U-Mo grain growth experiments are scattered, e.g., sometimes it can vary by a factor of 10 at the same temperature [10,18,21,41]. In addition, in other materials such as aluminum (Al), GB mobility can vary by a few orders of

magnitude, depending on the GB character [34,78]. Therefore, it is reasonably expected that GB mobilities in U-based metals are also anisotropic, although such information is still lacking to date. The effect of GB mobility anisotropy on grain growth morphology is controversial as some computational studies show that mobility anisotropy alone has little effect on the final grain texture [1–4], while others give contradictory conclusions [5]. However, some of these studies also show that the combination of both GB energy anisotropy and mobility anisotropy can have a significant impact on grain growth kinetics, local microstructures, and overall grain morphologies [3,79]. Therefore, if more sophisticated grain growth models are needed for more accurate fuel performance modeling, an in-depth understanding of GB mobility anisotropy is required.

GBs have five macroscopic degrees of freedom [34], creating a large parameter space to determine the anisotropic GB properties. Performing extensive experiments to map GB energies and mobilities in this five-parameter space is therefore impractical. Currently, most reported anisotropic GB properties are for GB energies [80,81]. Most of the limited reports of anisotropic GB mobilities focus on FCC metals such as Al and nickel (Ni) [34,82]. For Al, it has been found that both the rotation axis and misorientation angle can have significant effects on GB mobility. In general, the $\langle 111 \rangle$ rotation axis gives the fastest GB mobility compared to other low-index rotation axes (e.g., $\langle 100 \rangle$ and $\langle 110 \rangle$) [34,83,84]. In terms of misorientation angle, the $\langle 111 \rangle$ 38.2° GB has the fastest mobility [34,78,84]. For BCC metals, GB mobility and its anisotropy are rarely studied. To the best of the authors' knowledge, only a few GBs in a BCC Fe-20%Cr system [85], and a $\Sigma 11$ GB in BCC tungsten [86] were studied with MD simulations. Therefore, it is unclear whether the GB mobility trend observed for FCC metals can be extended to BCC metals.

In this work, MD simulations are conducted to study the GB mobilities in BCC γ U for different rotation axes and misorientations using three interatomic potentials. To the best of the authors' knowledge, this is the first study of GB mobilities of individual GBs as well as GB mobility anisotropy in BCC γ U or U-based alloys, as there are no previous experimental or modeling studies on this topic. The objectives of this work are twofold because this work has both nuclear engineering relevance and is of basic scientific interest. First, the mobilities of several GBs in BCC γ U will be calculated so that the results could be used as input for mesoscale fuel performance modeling of grain growth of U-based metallic fuels. This work focuses on pure γ U and the results can be used as references for later studies of GB mobility in U-based alloys. Second,

from a fundamental science viewpoint, this work can serve as an attempt to study the general trend of GB mobility anisotropy in BCC metals. In particular, this work seeks to know if the general trend of GB mobility anisotropy for FCC metals (i.e., GB mobility is fastest for the $\langle 111 \rangle$ rotation axis) also holds for BCC metals. If not, this work will determine which low-index rotation axis typically has the fastest mobility in BCC metals.

3.3. Methods

In this work, GB mobilities of BCC γ U were calculated using the widely used shrinking cylindrical grain method [87,88]. A representative simulation setup that is projected on the X-Y plane is shown in Fig. 3.1. To generate a cylindrical GB structure, first a U single-crystal slab was created with the Z-axis aligned along the desired rotation axis. Typically, the lengths in the X and Y directions are much longer than that in the Z direction so that the slab has a quasi-2D geometry. The dimensions of different single-crystal slabs are listed in Table 3.1. Next, the atoms that were within a radius $r_{\text{grain}} = 100 \text{ \AA}$ from the center of the slab (measured in the X-Y plane) were rotated along the Z axis by a desired misorientation angle θ (see Fig. 3.1). If the distance between two atoms is less than 70% of the first nearest neighbor distance ($\sim 2.1 \text{ \AA}$) after the rotation, one of them was removed to avoid atom overlap. After the overlapping atoms were removed, the simulation systems contained atoms in the range of 55,340 – 86,550. The structure was then equilibrated at the desired temperature for 20 picoseconds (ps) before beginning the remainder of the simulation. As shown in Fig. 3.1, the as-created simulation system consists of a cylindrical inner grain (red) and an outer matrix grain (blue). The interface between them is the cylindrical GB, which has a pure tilt character because its rotation axis (i.e., Z axis) is always parallel to the GB plane. It should be noted that no single inclination plane is specified in this method, meaning that the resulting GB mobility is an average over many inclinations for a specific misorientation. In this work, three rotation axes were used ($[001]$, $[110]$, $[111]$), and three misorientation angles (20° , 30° , 45°) were examined for each rotation axis. These combinations were used to investigate how GB mobility changes with both rotation axis and misorientation in γ U, or more broadly, in BCC metals. For the $\langle 111 \rangle$ rotation axis, an additional misorientation angle of 38.2° was also studied. This misorientation angle, associated with the $\Sigma 7$ boundary in FCC metals (e.g., Al), has been found to have the highest (or nearly the highest) migration rate or GB mobility [34,83,84].

While no such similar statement has been made about this GB in BCC metals to the best of the authors' knowledge, it is included here for comparison.

Table 3.1. Dimensions (in units of Å) of the initial single crystal used to generate GBs for the three rotation axes (in the Z direction) as well as for three interatomic potentials. The crystallographic orientations of the X and Y axes are also shown for completeness.

Rotation axis Potential	Z = [001] (X = [100], Y = [010])	Z = [110] (X = [001], Y = [1 $\bar{1}$ 0])	Z = [111] (X = [1 $\bar{1}$ 0], Y = [11 $\bar{2}$])
ADP [89]	264.0 × 264.0 × 17.60	264.0 × 248.9 × 24.9	248.8 × 250.0 × 30.5
MEAM [90]	259.7 × 259.7 × 17.30	259.7 × 259.6 × 19.6	259.6 × 263.0 × 18.0
EAM [91]	265.7 × 265.7 × 17.71	265.7 × 250.5 × 25.1	250.5 × 251.6 × 30.7

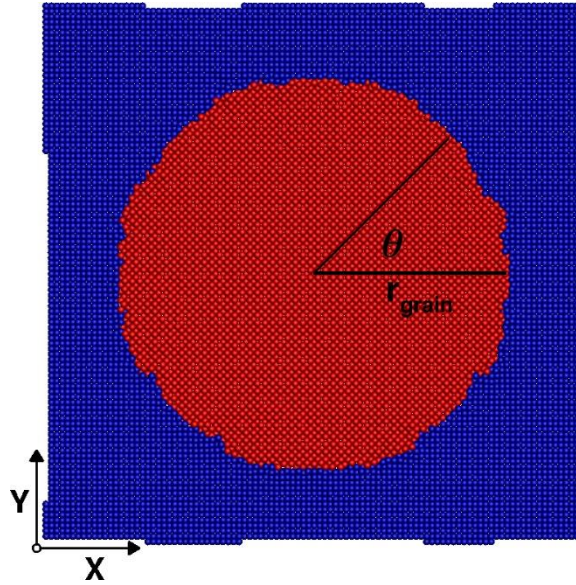


Fig. 3.1. Schematic of the as-created cylindrical GB structure that is projected on the X-Y plane. The rotation axis is along the Z direction (out of the page). Atoms within the radius r_{grain} are rotated by a desired misorientation angle θ . Red atoms belong to the inner cylindrical grain, while blue atoms belong to the outer matrix grain. The interface between them is the cylindrical GB.

At elevated temperatures, the inner grain will shrink due to its positive curvature (equivalently, the outer grain will grow) so that the GB moves inward. GB mobility can be extracted from GB migration velocity (more details will be provided later in this Section). In this work, the MD method is used to simulate the GB migration. All simulations were conducted using the LAMMPS software [92]. Three different interatomic potentials were used for comparison: an embedded atom method (EAM) potential for the U-Mo-Xe system [91], an angular dependent potential (ADP) for the U-Mo system [89], and a modified EAM potential (MEAM) for the pure U system [90]. Although the EAM and ADP potentials can model multi-component systems, only the pure U part was used as this work only studies GB mobilities in pure γ U. Table 3.2 lists some basic properties predicted by these potentials, such as the lattice parameter of BCC γ U, melting temperature, and the $\beta \rightarrow \gamma$ phase transition temperature (if applicable). Note that in reality, the U phase transition follows $\alpha \rightarrow \beta \rightarrow \gamma$ as the temperature increases [57,58]. However, in the EAM and MEAM potentials, the β phase is ignored. Therefore, in these cases, the $\alpha \rightarrow \gamma$ transition temperature is given. The experimentally determined values are also listed for comparison. Each of the potentials used in this work had a different focus during its development, which will be described in more detail in the Discussion Section. However, none of them have ever been used to evaluate GB mobility. Therefore, this work will elucidate if these potentials predict significantly different GB mobilities. For the EAM and MEAM potentials, a temperature range of 1050–1400 K was used in calculating the GB mobilities. Since the ADP potential estimates a lower melting point than the other two potentials, a narrower temperature range of 1050–1300 K was used. In all simulations, periodic boundary conditions were employed in all three Cartesian directions. All simulations were run using the isobaric-isothermal ensemble (NPT), where the pressure was maintained at zero bars. A time step of two femtoseconds (fs) was used for integration. Snapshots of the atomic structures were saved every 20 ps of simulated time for later analysis.

Table 3.2. Some basic properties predicted by the three interatomic potentials used in this work, taken from the papers describing their creation. The experimental results are also shown for comparison.

Potential	γ U lattice parameter (Å)	α or $\beta \rightarrow \gamma$ transition temperature (K)	Melting point (K)
EAM [91]	3.542 (at 900 K)	$< 900^*$	1530
ADP [89]	3.52 (at 1000 K)	$< 1000^\dagger$	1330
MEAM [90]	3.463 (unknown)	972.5 ‡	1505.4
Experimental	3.48 (at 1073 K) [93]	1033 § [93]	1407 [94]

*Note this potential can predict α and γ , but not the β phase. However, the $\alpha \rightarrow \gamma$ transition temperature was not given in the paper either. The authors of this paper indicated that their simulation of γ phase was done at 900 K, indicating an $\alpha \rightarrow \gamma$ transition temperature below this value.

† This potential can describe the α , β , γ and liquid (L) phases of pure U, though only the $\gamma \rightarrow L$ transition (melting) temperature was given. The lattice parameter of γ U was estimated at 1000 K, so the transition temperature should be lower than that.

‡ This potential describes the α and γ phases of pure U, ignoring the β phase. Thus, this is the estimated transition temperature for $\alpha \rightarrow \gamma$.

§ The $\alpha \rightarrow \beta$ transition occurs at approximately 913 K, and the $\beta \rightarrow \gamma$ transition occurs at approximately 1033 K.

GB mobility (M) is typically assumed to have the following relationship with GB migration velocity (v) under a driving force (F) [34]:

$$v = M \times F. \quad (3.3.1)$$

For the cylindrical GBs studied in this work (Fig. 3.1), the driving force is the ratio of GB energy (γ) to grain radius (R) [34]:

$$F = \gamma/R. \quad (3.3.2)$$

Therefore, the driving force increases with the decreasing grain radius or with the increasing grain curvature ($1/R$). The GB velocity is the shrinking rate of the cylindrical grain radius: $v = dR/dt$. In many previous studies [1,85,88], a reduced mobility was often used, which is defined as $M^* = M\gamma$. Using these equations, Eq. (3.3.1) can be rewritten to get a relationship between the reduced GB mobility and the shrinking rate of the cross-sectional area ($A = \pi R^2$) of the cylindrical grain:

$$M^* = \frac{1}{2\pi} \frac{dA}{dt}. \quad (3.3.3)$$

The instantaneous cross-sectional area (A) at a given time (t) can be determined by the number of atoms inside the cylindrical grain. To calculate this, for each snapshot, each atom was assigned to either the outer matrix grain or the inner cylindrical grain using the orientation parameter method described by Ulomek *et al.*, which uses diffraction theory to assign an orientation parameter (χ_j) to each atom (j) in a grain based on the arrangement of its neighbors in terms of both orientation and regularity [47]. Note that this orientation parameter is an average over each atom's local neighborhood and it depends on *a priori* knowledge of the grain orientations, and thus cannot be used to calculate the misorientation between grains. A cutoff distance of $1.2a_0$ (where a_0 is the lattice parameter from Table 3.2) around each atom was used to determine χ_j for each atom. Here, if $\chi_j < 0.0$, the atom was assigned to the inner grain. Otherwise, it was treated as an atom in the outer matrix grain. Other cutoff distances were also tested, but this one gave the most robust results. For example, the two grains shown in Fig. 3.1 are an outcome of using this cutoff distance for grain assignment. Figure 3.2 also demonstrates the robustness of this parameter to temperature fluctuations, when a $\langle 110 \rangle 45^\circ$ GB is shown at three different times as simulated at 1200 K using the EAM potential.

Once the instantaneous number of atoms (N) for the cylindrical (inner) grain was determined for each snapshot, its cross-sectional area was calculated by

$$A = \frac{Na_0^3}{2L_z}, \quad (3.3.4)$$

where L_z is the height of the cylindrical grain in the Z direction and the $a_0^3/2$ term represents the volume per atom in a BCC crystal. By plotting the cross-sectional area as a function of simulation time, the shrinking rate of the cylindrical grain area, or the slope of the plot (dA/dt), can be calculated, which will be used for Eq. (4). An in-house code was used to calculate the slope using a piecewise, linear-fitting routine [95]. Each area versus time plot was fit to a maximum of six linear functions; the initial regime was occasionally discounted to allow for further equilibration, and the final linear fit was often to a period of no growth (i.e., the cylindrical grain had completely disappeared). After discarding the linear fits that did not represent the average behavior, a single linear fit was performed over the domain specified by the remaining linear fits. Figure 3.3 shows several representative examples of the fitted slopes using this procedure. The grayed-out data

points were excluded from the overall fit. Figure 3.3(a) shows the area versus time plot for a $\langle 100 \rangle$ 20° GB at 1200 K using the ADP potential. In this case, the grain area decreased almost linearly with time so that the slope can be fitted straightforwardly. In most of the simulations, the results had similar behavior. Figure 3.3(b) shows the result of a $\langle 100 \rangle$ 20° GB at 1050 K using the EAM potential. The initial regime had a slightly different slope from the intermediate regime, and the final regime had rapid grain shrinkage until the grain disappeared. Overall, the area decreased nearly linearly with time. Therefore, to get an average rate of the three stages, fits were performed over the entire growth regime in such simulations. Figure 3.3(c) shows the result of a $\langle 111 \rangle$ 20° GB at 1100 K using the EAM potential. There was an initial regime of rapid grain shrinkage (for a few tens of picoseconds, shown as the grayed-out data points) followed by a longer regime of slower grain shrinkage. In this case, the initial regime was not included in the fits as it had a distinct behavior from the rest. Figure 3.3(d) shows the result of a $\langle 111 \rangle$ 30° GB at 1250 K using the EAM potential. The grain area does not have a linear decrease with time. This type of behavior was observed when the simulated GBs migrated slowly. Previously, such non-linear behavior was also observed in Cu when the cylindrical grain shrinkage method was used [88]. To avoid bias in selecting the fitting regimes, fits were performed over all data for these types of results. The results shown in Fig. 3.3 represent most of the behaviors of the shrinking grain, although sometimes a combination of them exists. Nevertheless, as much shrinking grain data as possible was included in the fits and only some distinctive data was discarded (e.g., the initial stage shown in Fig. 3.3(c)). In addition, for each simulation condition, three to five independent simulations were conducted to obtain statistically meaningful results, which reduces the unavoidable uncertainties in the fitting. After GB mobilities are obtained at different temperatures, an Arrhenius fit was conducted to obtain the mobility prefactor (M_0) and activation energy (Q),

$$M^* = M_0 \exp\left(-\frac{Q}{k_B T}\right). \quad (3.3.5)$$

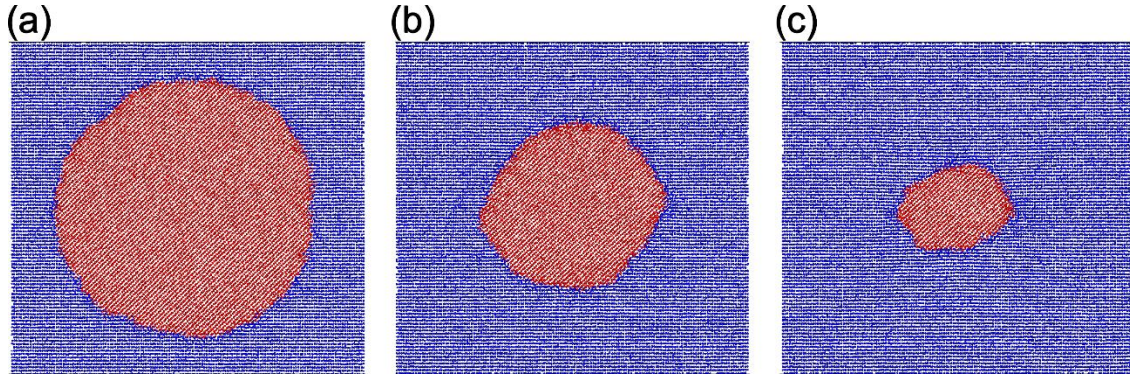


Fig. 3.2. Example of inner grain shrinkage observed during simulation for a $\langle 110 \rangle$ 45° boundary using the EAM potential at 1200 K. (a) The initial structure. (b) After 600 ps. (c) After 1000 ps. In all figures, red atoms belong to the inner cylindrical grain while blue atoms belong to the outer matrix grain.

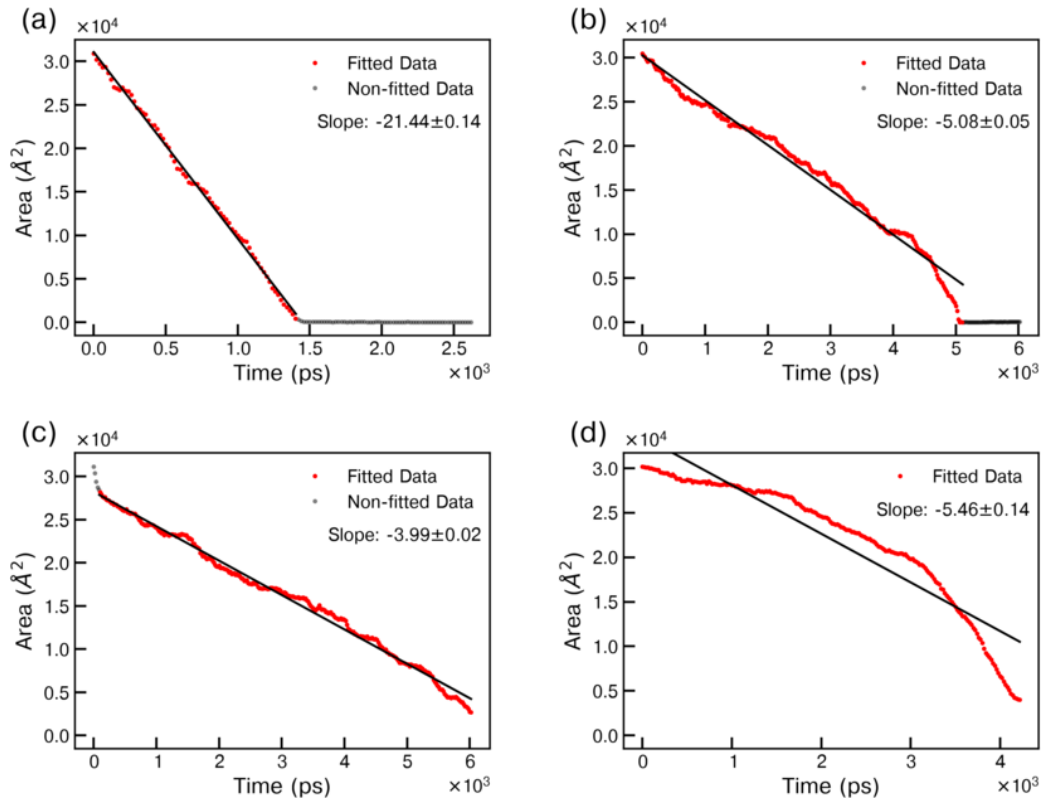


Fig. 3.3. Four representative examples for fitting the slope (dA/dt) from the inner grain area versus time plot. (a) The $\langle 100 \rangle$ 20° GB at 1200 K using the ADP potential. (b) The $\langle 100 \rangle$ 20° GB at 1050 K using the EAM potential. (c) The $\langle 111 \rangle$ 20° GB at 1100 K using the EAM potential. (d)

The $\langle 111 \rangle$ 30° GB at 1250 K using the EAM potential. The solid line is the final fit in each figure. Grayed-out data points are not included in the fit.

Previously, it was shown that the cylindrical grain can rotate during GB migration in FCC Cu [88]. The rotation can be either clockwise (CW) or counterclockwise (CCW). To investigate if such grain rotation behavior also occurs in BCC γ U, this work has examined the qualitative rotation behavior of the cylindrical grain. This analysis was done by specifying a strip of atoms down the center of the simulation cell consisting of all atoms in the middle 10% along the X direction. These atoms were used as “markers” and tracked throughout the simulation. If the strip orientation did not change after the grain shrinks completely (i.e., the strip remained straight as shown in Fig. 4(a)), the grain did not rotate. However, if the strip began twisting in on itself and making an ‘S’ shape, then rotation did occur. The orientation of the ‘S’ shape determines whether the rotation is CW (having a backward ‘S’ shape as shown in Fig. 4(b)) or CCW (having an ‘S’ shape as shown in Fig. 4(c)). The degree of rotation is unable to be precisely determined using this analysis, so only the qualitative rotation behavior (i.e., CW, CCW, or no rotation) is reported. This analysis was performed for each simulation, and the statistics of the grain rotation behavior will be presented in the Results Section.

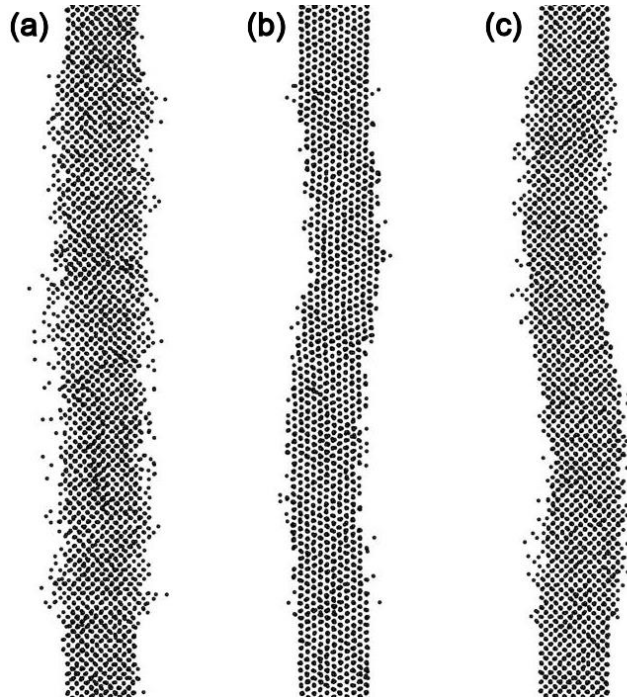


Fig. 3.4. Representative examples of cylindrical grain rotation observed in this work. All three examples are obtained using the MEAM potential. (a) No rotation observed in the $\langle 100 \rangle$ 30° GB at 1400 K. (b) Clockwise (CW) rotation (indicated by the backward ‘S’ shape) observed in the $\langle 111 \rangle$ 45° GB at 1050 K. (c) Counterclockwise (CCW) rotation (indicated by the ‘S’ shape) observed in the $\langle 100 \rangle$ 45° GB at 1050 K. Although these examples are taken from the simulations using the MEAM potential, the other two potentials also demonstrated these behaviors.

3.4. Results

GB mobility results are presented first by each rotation axis with different misorientation angles as predicted by different potentials. These results will elucidate if GB mobility in BCC γ U has a clear correlation with the misorientation angle. Next, these mobilities are compared at the same misorientation angle but with different rotation axes to identify if GB mobility in BCC γ U has a general trend with the rotation axis, like in the FCC metals (i.e., $\langle 111 \rangle$ rotation axis may have faster mobility than $\langle 100 \rangle$ and $\langle 110 \rangle$ in FCC metals [34]). Finally, the statistics of grain rotation behavior are presented to explore possible trends, if any.

3.4.1. $\langle 100 \rangle$ mobility trends

The GB mobilities for the $\langle 100 \rangle$ rotation axis at three misorientation angles predicted by the EAM potential are shown in Fig. 3.5(a), which is an Arrhenius plot. In the temperature range studied (1050–1400 K), overall, the mobility trend from slowest to fastest is $45^\circ < 20^\circ < 30^\circ$. Therefore, mobility does not increase or decrease monotonically with increasing misorientation angle. The mobilities of each of the 30° and 45° GBs can be well fitted by an Arrhenius relationship. However, it seems that the 20° boundary does not have a normal Arrhenius-type temperature dependence, having a step that looks like athermal behavior (i.e., mobility does not change with temperature) in the temperature range of 1200 K–1300 K. It is unclear if a different mechanism drives the grain growth behavior in this temperature range, as the mechanisms for anti-thermal (i.e., mobility decreases with the increasing temperature) or athermal GB motion are largely unknown [96]. On the other hand, this athermal behavior could be due to the insufficient statistics of GB mobility calculations. If the two temperature ranges above and below this athermal region are treated separately, the activation energy and prefactor for an Arrhenius fit in the temperature range of 1050–1200 K are 0.7 eV and 20.9×10^{-6} m²/s, and for the temperature range

of 1300–1400 K, they are 0.6 eV and $5.8 \times 10^{-6} \text{ m}^2/\text{s}$. If an Arrhenius behavior is assumed for the whole temperature range of 1050–1400 K, the values are 0.31 eV and $421.3 \times 10^{-9} \text{ m}^2/\text{s}$, which are shown in Table 3.3.

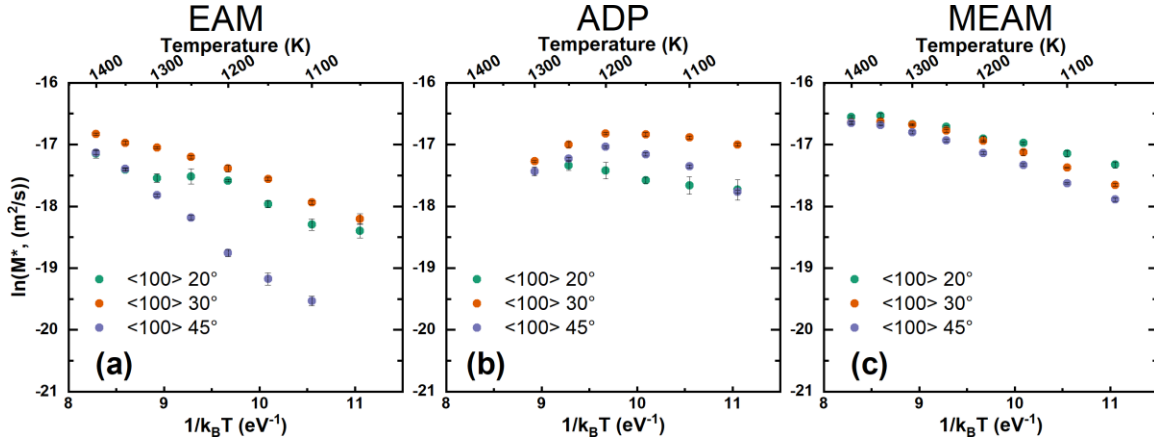


Fig. 3.5. Calculated GB mobilities (displayed as Arrhenius plots) for the $\langle 100 \rangle$ rotation axis with three misorientation angles (20°, 30°, 45°) using the (a) EAM potential, (b) ADP potential, and (c) MEAM potential. Each data point is averaged over three to five independent simulations. Error bars represent standard error. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right).

For a GB to migrate, atoms need to diffuse across the GB plane according to Burke and Turnbull's theory [97]. Therefore, atomic motion in the X and Y directions as shown in Fig. 3.1, which are both perpendicular to the GB plane, should contribute to GB motion directly. On the other hand, atomic motion in the direction parallel to the GB plane, which is the Z direction in Fig. 3.1, might not contribute to the GB motion significantly. To check this hypothesis, the mean square displacements (MSDs) of all atoms are tracked during GB motion. Figure 3.6 shows the MSD plots for the [001] rotation axis with 20°, 30°, and 45° misorientation angles at 1100 K predicted by the EAM potential. In all plots, the MSDs along the X and Y directions (i.e., across the GB plane) are approximately equal. This is consistent with the nearly circular shrinking behavior of the inner grain during GB motion (Fig. 3.2). The 20° boundary (Fig. 3.6(a)) overall appears to have relatively equal motion in all three Cartesian directions, although the X direction has a slightly larger MSD at the end of the simulation. For the 30° boundary (Fig. 3.6(b)), there was slightly

more atomic motion in the Z direction compared to the other two, which is parallel to the GB plane (also the rotation axis direction). The MSD of the 45° boundary (Fig. 3.6(c)) shows atomic motion primarily along the Z direction (i.e., parallel to the GB plane), the magnitude of which is significantly more than both the 20° and 30° boundaries. The MSDs in the X and Y directions seem to be congruent, but the zoom-in view shows that they are not identical (see the inset of Fig. 3.6(c)). From Fig. 3.5(a), the 45° boundary has the lowest mobility. Therefore, the MSD behavior is consistent with the above hypothesis that the atomic motion parallel to the GB plane might not contribute to GB motion significantly. In other words, if atomic motion is primarily parallel to the GB plane, GB mobility is likely to be slow. Regarding the aforementioned athermal behavior of the $\langle 100 \rangle$ 20° GB between 1200–1300 K (Fig. 5a), the MSDs were also examined. The MSDs in the X, Y, and Z directions (not shown) in this temperature range are all nearly equivalent (similar to Fig. 6a, which is not in the athermal regime). Therefore, the MSD behavior is unable to explain why the athermal region appears.

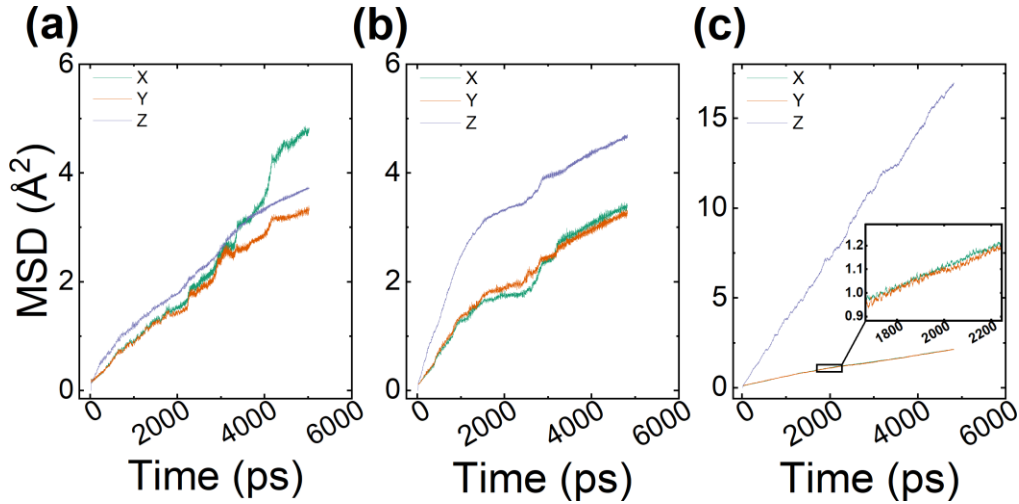


Fig. 3.6. MSDs for the [001] rotation axis with three misorientation angles at 1100 K predicted by the EAM potential. (a) 20°. (b) 30°. (c) 45°. Note that in (c) the vertical (ordinate) axis has a different scale than in (a) and (b).

Table 3.3. Activation energies and GB mobility prefactors predicted by the EAM potential. Activation energies (Q) are given in eV and prefactors (M_0) in $\text{m}^2/\text{s} \times 10^{-9}$.

Rotation axis Misorientation	<100>		<110>		<111>	
	Q	M_0	Q	M_0	Q	M_0
20°	0.31	421.3	0.29	848.3	0.88	93,300
30°	0.46	2400	0.48	3200	1.05	236,400
45°	1.12	426,500	0.42	2000	0.92	118,600
38.2°	—	—	—	—	0.93	107,300

For the ADP potential, the GB mobility trend of the <100> rotation axis is $20^\circ < 45^\circ < 30^\circ$ (Fig. 3.5(b)), although the differences are small. The 20° boundary structure completely melted at 1300 K, so no mobility data are available at this temperature. Significant GB pre-melting occurred for the 30° and 45° boundaries at this temperature as well, but the melt did not fully overtake the simulated domain. This is consistent with the original description of the ADP potential with a melting point of 1330 K [89]. The pre-melting behavior depends on the GB type, which is similar to GB pre-melting in other systems such as Ni [98]. Above 1200 K, there is a decrease in GB mobility with increasing temperature (or “anti-thermal” behavior), which is likely associated with GB pre-melting in these simulations. With the presence of the melt at the GB, the orientation parameter does not accurately identify the position of the GB plane, further contributing to the uncertainty of GB mobility calculations of this anti-thermal regime. Therefore, the Arrhenius fits were only conducted in the temperature range of 1050–1200 K, and the extracted GB mobility values are listed in Table 3.4. For the MSD plots (not shown), the three directions generally have similar values for each misorientation angle, with the Z direction sometimes having a slightly larger value (similar to Fig. 3.6(a) and (b)). From Fig. 3.5(b), it can be seen that the GB mobilities are similar for the three misorientations and are relatively fast in comparison with their counterparts in the EAM potential (Fig. 3.5(a)). Therefore, again, the MSD behavior is consistent with the mobility trend.

Table 3.4. Activation energies and GB mobility prefactors predicted by the ADP potential. Activation energies (Q) are given in eV and prefactors (M_0) in $\text{m}^2/\text{s} \times 10^{-9}$.

Rotation axis Misorientation	<100>		<110>		<111>	
	Q	M_0	Q	M_0	Q	M_0
20°	0.21	199.0	0.22	530.2	0.16	282.4
30°	0.12	156.5	0.14	187.4	0.37	1600
45°	0.51	5600	0.11	140.2	0.19	288.1
38.2°	—	—	—	—	0.33	956.5

The mobility trend predicted by the MEAM potential for the <100> rotation axis is $45^\circ < 30^\circ < 20^\circ$ (Fig. 3.5(c)), but the differences between misorientations are very small. As the temperature increases, the differences vanish and converge to nearly a single value at 1400 K. All three misorientations follow Arrhenius behavior well, and the extracted activation energies and GB mobility prefactors are listed in Table 3.5. In general, the MSD behavior (not shown) shows that the atomic motion is similar in the three directions, though the Z direction is higher only by a small margin (similar to Fig. 3.6(b)). However, this is not true for the 20° misorientation, where the MSD in the Z direction is slightly lower than the other two directions from 1050 K to 1300 K. Since the atomic motion across the GB (i.e., in the X and Y directions) contributes directly to the GB motion, the MSD behavior is consistent with the fact that the 20° boundary is the fastest one among the three misorientations.

Table 3.5. Activation energies and GB mobility prefactors predicted by the MEAM potential. Activation energies (Q) are given in eV and prefactors (M_0) in $\text{m}^2/\text{s} \times 10^{-9}$.

Rotation axis Misorientation	<100>		<110>		<111>	
	Q	M_0	Q	M_0	Q	M_0
20°	0.26	580.1	0.17	279.6	0.32	1000
30°	0.39	1700	0.24	616.0	0.22	438.5
45°	0.47	3100	0.21	421.3	0.26	557.4
38.2°	—	—	—	—	0.18	250.5

3.4.2. $\langle 110 \rangle$ mobility trends

The GB mobility trend of the $\langle 110 \rangle$ rotation axis predicted by the EAM potential is $30^\circ \approx 45^\circ < 20^\circ$ (Fig. 3.7a), which is different from that of the $\langle 100 \rangle$ axis (Fig. 3.5(a)). At the highest temperature (1400 K), mobility appears to converge to nearly a single value. There is a slight curvature in the Arrhenius plot for the 20° boundary, potentially [99] indicating the presence of multiple activated behaviors with a smooth transition between the preferred mechanisms with temperature [100]. However, a linear fit still fits the data well for this boundary as well as for the other two GBs. The extracted activation energies and prefactors for this rotation axis are listed in Table 3.3. Examining the MSD data (not shown) reveals that the 20° boundary has more atomic motion across the GB (in the X and Y directions) than that parallel to the GB (in the Z direction) at all temperatures except at 1400 K. For the 30° and 45° boundaries, the atomic motion is nearly equivalent in all three Cartesian directions. Therefore, the MSD behavior is consistent with the mobility trend (i.e., the 20° boundary is the fastest one). At 1400 K, the MSD for all misorientations as well as all directions were nearly equal. This behavior explains why the three boundaries have nearly the same mobility at this temperature.

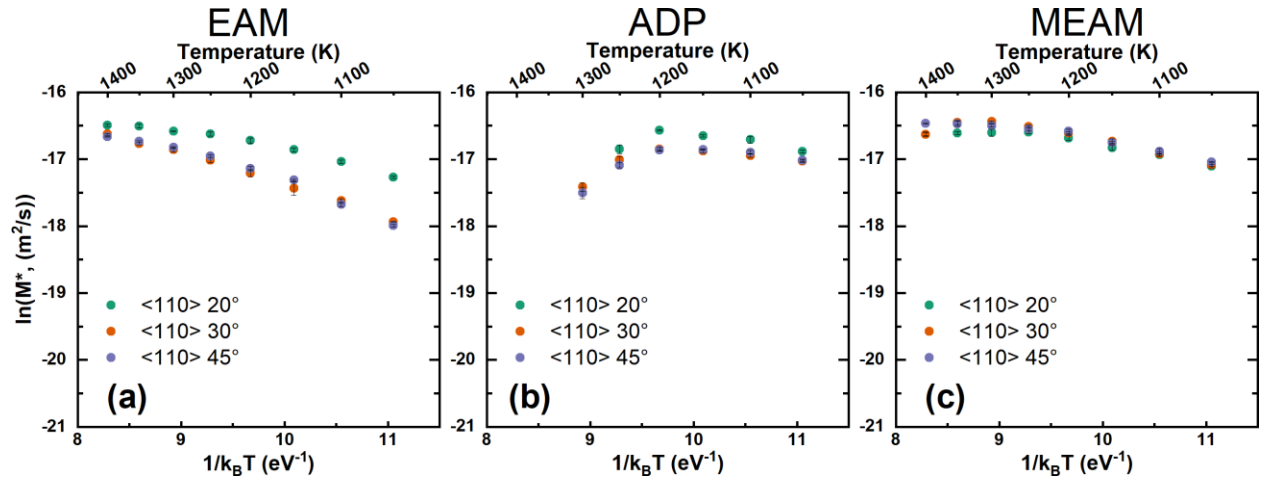


Fig. 3.7. Calculated GB mobilities (displayed as Arrhenius plots) for the $\langle 110 \rangle$ rotation axis with three misorientation angles (20° , 30° , 45°) using the (a) EAM potential, (b) ADP potential, and (c) MEAM potential. Each data point is averaged over three to five independent simulations. Error bars represent standard error. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right).

For the $\langle 110 \rangle$ rotation axis using the ADP potential, in terms of the misorientation dependence, the GB mobility order is the same as that using the EAM potential: $30^\circ \approx 45^\circ < 20^\circ$ (see Fig. 3.7(b)). As for the temperature dependence, the mobility behaviors are the same as the $\langle 100 \rangle$ rotation axis for this ADP potential, i.e., they exhibit an anti-thermal regime at temperatures above 1200 K, where mobility decreases as the temperature increases. Similar to the $\langle 100 \rangle$ rotation axis, the 20° misorientation experienced issues at 1300 K: although the structure did not completely melt, the melted interface expanded enough to prevent any meaningful calculation of GB mobility. Therefore, no mobility is reported for this 20° boundary at 1300 K in Fig. 3.7(b). The 30° and 45° boundaries also experienced significant GB pre-melting, but a mobility value was still able to be extracted. The anti-thermal regime between 1200–1300 K is once again attributed to the GB pre-melting, as for the $\langle 100 \rangle$ rotation axis (Fig. 3.5(b)). Excluding the anti-thermal regime in the Arrhenius fit, the extracted activation energies and GB mobility prefactors are shown in Table 3.4. The MSD data (not shown) corroborates the mobility trend. The 20° boundary has the highest magnitude of atomic motion in the two directions perpendicular to (i.e., across) the GB plane (X and Y directions) than the other two boundaries. This is consistent with the GB mobility trend that the 20° boundary has the highest mobility. For this boundary, initially, the MSD in the X and Y directions is higher than or similar to the Z direction in the temperature range of 1050–1200 K. However, when GB pre-melting occurs and GB mobility drops at 1250 K, the MSD in the Z direction is higher than in the other two directions. This behavior again proves that if the atomic motion is predominant in the direction parallel to the GB plane (Z direction), like in Fig. 3.6(c), the GB mobility is slow. For the 30° and 45° boundaries, the MSDs are roughly the same in all three directions from 1050 K to 1200 K. At 1250 K and 1300 K, the MSD in the Z direction is slightly higher (again it is consistent with the mobility drop), possibly due to the GB pre-melting.

The mobility trend of the misorientation dependence for the MEAM potential is not as clear-cut as the other two potentials for this $\langle 110 \rangle$ rotation axis (see Fig. 3.7(c), activation energies and prefactors in Table 3.5). Across the entire temperature range, the mobilities are almost equal for all three misorientations. Examining the MSD plots (not shown) reveals that the 20° boundary has faster atomic motion in the X and Y directions than in the Z direction in the temperature range of 1050–1300 K, while the 30° and 45° boundaries have nearly the same MSD in all three directions throughout the whole simulated temperature range. Comparing the three misorientations, the MSDs in the X and Y directions (across the boundary) of the 20°

misorientation are higher than its counterparts until about 1300 K. Interestingly, the 20° boundary does not have a higher GB mobility, which is different from other systems as discussed earlier. In general, it appears that mobility is strongly correlated with atomic motion perpendicular to the GB plane. However, additional factors may still play a role (at least for this potential or the individual boundaries) to either slow down the 20° boundary or speed up the other two boundaries.

3.4.3. <111> mobility trends

The EAM potential has a general mobility trend of $30^\circ < 45^\circ < 38.2^\circ < 20^\circ$ (see Fig. 3.8(a)) for the <111> rotation axis, although at lower temperatures (≤ 1150 K) the 38.2° boundary has slightly higher mobility than the 20° boundary. For the 30° boundary, the GB did not move significantly at temperatures below 1250 K, so no mobility data was reported below this temperature. Each misorientation has some nonlinearity or curvature in the Arrhenius plot. This could be indicative of a Vogel-Fulcher type of temperature dependence for GB mobility because the atom diffusion and structural relaxation at GBs could be similar to glass-forming liquids, as suggested by Zhang et al [101]. The nonlinearity could also be an outcome of separate regimes where different mechanisms dominate. For example, some literature shows that there can be different mechanistic regimes (e.g., a diffusional, or slow-moving regime, where the boundary motion is due to occasional and thermally activated atomic jumps, and a ballistic, or fast-moving regime, where the boundary motion is due to the rapid displacement of atoms [102,103]) having very different activation energies and prefactors, though the transitions between different regimes are sharp, rather than the gradual change observed here. The determining factors for which regime a boundary falls into are the driving force and temperature, with the diffusional regime associated with low driving forces and temperatures, and the ballistic regime associated with high driving forces and temperatures. Strontium titanate (SrTiO_3) has also been found to have an odd temperature dependence of GB mobility with an anti-thermal regime (i.e., mobility decreases as temperature increases) [104], thought to be associated with the coexistence of two different types of GBs of different space charge segregations. Therefore, many factors could cause the non-Arrhenius behavior of GB mobility so the root cause of the nonlinear behavior in this system is not clear. Here, an Arrhenius fit is still used across the entire temperature range to extract the activation energies and mobility prefactors (see Table 3.3), because the curvature is not very large. At most temperatures, the MSDs of these boundaries (not shown) reveal that the preferred atomic direction is the Z ([111]) direction, parallel to the GB plane. This is indicative that these GBs may

have relatively low mobilities, which is consistent with Fig. 3.8(a). The 20° boundary at 1200 K and the 30° boundary at 1300 K show that the atomic motion in the X and Y directions (across the GB) becomes equal to the motion in the Z direction, staying nearly equal at higher temperatures. The MSD trends share some characteristics that the mobility trend exhibits, but there are some discrepancies as well, as described previously. This indicates that atomic diffusion behavior alone may not be sufficient to predict GB mobility trends for this potential.

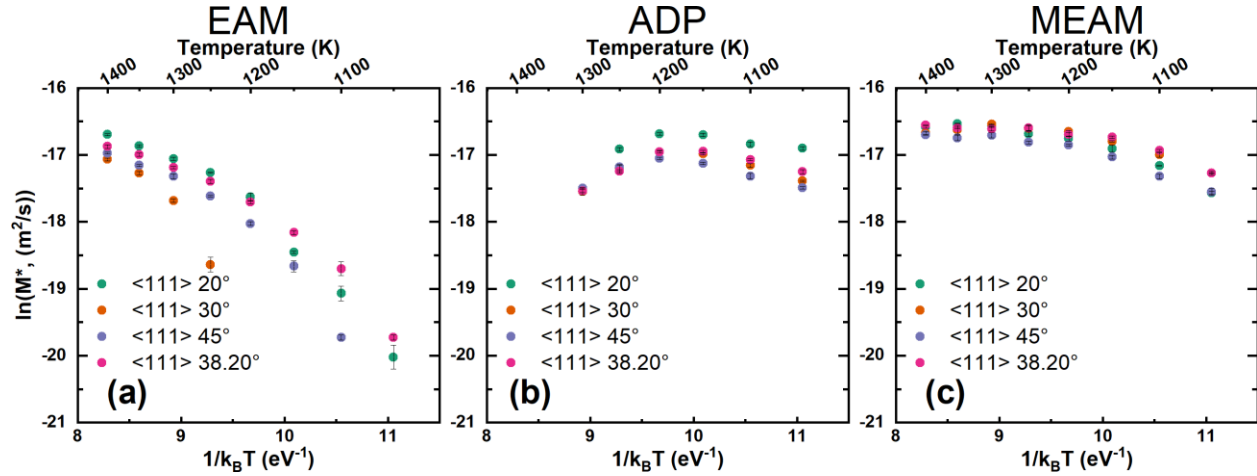


Fig. 3.8. Calculated GB mobilities (displayed as Arrhenius plots) for the $\langle 111 \rangle$ rotation axis with four misorientation angles (20°, 30°, 38.2°, 45°) using the (a) EAM potential, (b) ADP potential, and (c) MEAM potential. Each data point is averaged over three to five independent simulations. Error bars represent standard error. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right).

For the $\langle 111 \rangle$ rotation axis using the ADP potential, the trend is $45^\circ < 30^\circ < 38.2^\circ < 20^\circ$ (Fig. 3.8(b)). The differences between the 30°, 38.2°, and 45° boundaries are quite small, while the 20° boundary has a clear margin over other boundaries. The overall temperature dependence is similar to the $\langle 100 \rangle$ and $\langle 110 \rangle$ rotation axes using the same ADP potential (Fig. 3.5(b) and Fig. 3.7(b)), i.e., there is an anti-thermal regime above 1200 K where mobility decreases with increasing temperature. Once again, for the 20° boundary at 1300 K, the GB structure melted completely. There was a significant amount of GB pre-melting for the other three boundaries as well, but the structure did not completely melt. To extract the activation energies and prefactors

(listed in Table 3.4), only the mobility data below 1200 K are included in the Arrhenius fit. For the MSD behaviors of these GBs (not shown), typically the atomic motion in the Z direction (parallel to the GB) dominates (partially due to the pre-melting behavior at high temperatures), except for the 20° and 30° at very low temperatures.

The GB mobility of the MEAM potential using the $\langle 111 \rangle$ rotation axis does not appear to have significant differences between the four misorientation angles (see Fig. 3.8(c)), which is similar to the $\langle 110 \rangle$ rotation axis using the same potential (Fig. 3.7(c)). At high temperatures (above 1250 K), GB mobility seems to have an athermal region, where mobility does not change much with increasing temperature. Table 3.5 lists the activation energies and mobility prefactors based on an Arrhenius fit across all temperatures. Even though the differences in mobility between these boundaries are small, the 45° boundary is consistently the slowest of the four, while the 38.2° boundary tends to be the fastest. For the MSD behavior (not shown), typically the atomic motion in all three directions is similar at low temperatures while the Z direction ([111]) becomes dominant at high temperatures. The 20° boundary with this potential has a different MSD behavior: it has slower atomic motion in the Z direction at temperatures below 1250 K then the trend is reversed. However, the MSD behaviors of these boundaries cannot be correlated to their GB mobilities.

Overall, for each rotation axis, the GB mobility shows some anisotropy with the misorientation angle. However, the anisotropy trend strongly depends on each potential. In most cases, the 20° misorientation has the fastest or similar mobility compared to the other misorientations. The $\langle 111 \rangle$ 38.2° GB, which is the fastest one in FCC metals, is not always the fastest among the four boundaries studied, although it is close to the fastest one if it is not. The MSD behavior sometimes is consistent with the GB mobility trend. For example, if the MSD (atomic motion) in the Z direction (parallel to the GB plane) is much higher than the other two directions (perpendicular to the GB plane), GB mobility is typically low as atomic motion in that direction may not contribute to GB motion directly.

3.4.4. Mobility trends between different rotation axes

By fixing the misorientation angle it is possible to examine the anisotropy within the rotation axis degrees of freedom. Here the mobility data reported in Figs. 5, 7, and 8 are rearranged to study the anisotropy related to the rotation axis, as shown in Fig. 9. Each figure of Fig. 3.9 shows

the GB mobility anisotropy for the same misorientation angle but with a different rotation axis for a specific potential. Some literature identifies that in general the $\langle 111 \rangle$ rotation axis has higher mobilities than $\langle 100 \rangle$ and $\langle 110 \rangle$ axes in FCC metals (e.g., Al), and the highest mobility is around the $\langle 111 \rangle$ 40° GB [34,83]. However, no statements on mobility anisotropy in BCC metals have been made to the best of the authors' knowledge. Fig. 3.9 shows that, in BCC U, the $\langle 110 \rangle$ rotation axis tends to be the fastest out of the three rotation axes examined. The EAM potential is the most consistent in this regard (Fig. 3.9(a, d, g)). For the ADP and MEAM potentials, the $\langle 110 \rangle$ rotation axis is or at least close to the fastest. For the $\langle 100 \rangle$ axis, it has a greater tendency to be the slowest rotation axis in many cases (Fig. 3.9(b, f – i)), although sometimes it can be close to the fastest axis (Fig. 3.9(c – e)). The $\langle 111 \rangle$ rotation axis fluctuates significantly, but it never becomes the fastest one. The MEAM potential has the most consistent anisotropy trend out of the three potentials in terms of the rotation axis dependence, which is $M_{110} > M_{111} > M_{100}$. However, this potential also gives the least amount of variability among the rotation axes.

An analysis of the mobilities of nearly 400 GBs in FCC Ni found that most GB mobilities will converge to a single value near the melting temperature, regardless of the temperature-dependence trend in the mobility of these GBs (e.g., thermally activated, athermal, anti-thermal) [105]. In this work, this convergence at high temperatures was observed in the ADP and MEAM potentials across all boundaries with a fair degree of reliability (Figs. 9(b, c, e, f, h, i)). For the EAM potential, however, the mobilities did not converge to a single value at high temperatures (Figs. 9(a, d, g)). One possible explanation for this behavior is that the highest temperature studied for the EAM potential is not close enough to its melting or pre-melting temperature. This is consistent with the fact that the EAM potential has the highest melting temperature among the three potentials (Table 3.2). This is also consistent with the non-existence of an athermal or anti-thermal regime at high temperatures for the EAM potential (unlike the other two potentials).

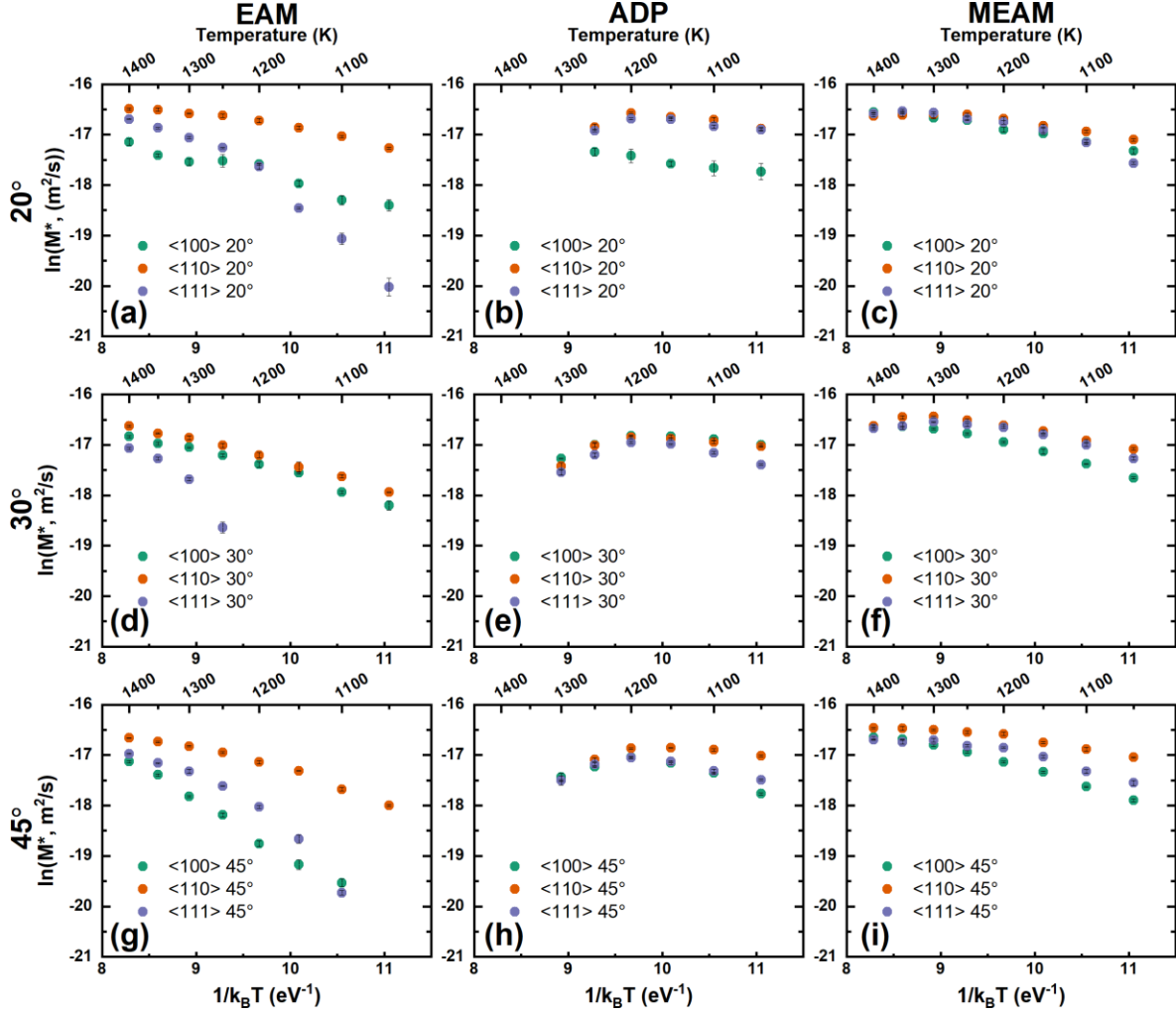


Fig. 3.9. Arrhenius plot of GB mobilities displayed by different rotation axes with a fixed misorientation and a specific potential in each figure. Each row shows a misorientation while each column shows a potential. Each mobility is averaged over three to five independent simulations. Error bars show the standard error. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right).

3.4.5. Grain rotation behavior

During the simulations, the inner grain (see Fig. 3.1) was sometimes observed to rotate while it was shrinking. The rotation behavior was either CW, CCW, or stationary, as shown in Fig. 4. In other systems, grain rotation has been observed both experimentally and computationally (see

Ref. [88] and references therein). Grains will rotate to drive the free energy of the system down by (typically) creating a new GB with a lower GB energy. Grain rotation is not universally observed though, meaning that additional factors also govern the grain rotation. For a more in-depth discussion of grain rotation and possible reasons for not rotating, see Ref. [88]. This work examined the qualitative rotation behavior for each simulation. Figures 3.10–3.12 show the percentages of all simulations that rotated either CW, CCW, or had no observable rotation for the three potentials respectively. The EAM potential (Fig. 3.10) across all simulations tended to have no rotation (74.85%). A majority of the remainder of the simulations had CCW (18.4%), while the CW rotation is only 6.75%. For individual GBs (i.e., a rotation axis and misorientation pair), the predominant rotation behavior was to not rotate, though the $\langle 110 \rangle 20^\circ$ has a predominant CCW rotation. For those GBs with mixed rotation behavior (e.g., $\langle 100 \rangle 45^\circ$), the rotation direction is stochastic and does not depend on the temperature. Through cross-comparisons between different rotation axes and misorientations, no clear trend can be identified. For the ADP potential (Fig. 3.11), again the majority of GBs (60%) had no rotation, although the percentage is lower than that for the EAM potential. The percentages of CCW (26.27%) and CW (13.73%) are higher than their counterparts of the EAM potential. All GBs have a mixed rotation behavior; all except the $\langle 110 \rangle 45^\circ$ GB have all three rotation behaviors. Again, no clear trend can be identified in terms of rotation axis or misorientation dependence. For the MEAM potential (Fig. 3.12), the majority of GBs had no rotation (55.15%), followed by CCW (34.93%) and CW (9.93%) rotation. Most individual GBs also had a mixed rotation behavior, although many of them only had two rotation behaviors.

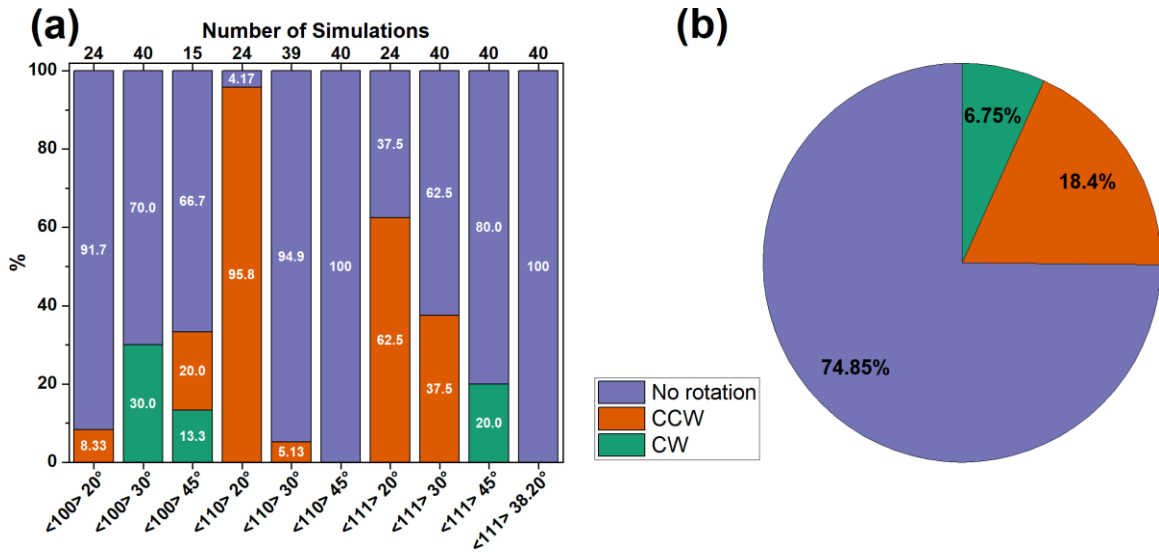


Fig. 3.10. Summary of the grain rotation behavior for simulations using the EAM potential, showing the percentage of simulations that underwent no rotation, counterclockwise (CCW) rotation, and clockwise (CW) rotation. (a) By GB type (bottom axis). The top axis indicates the number of simulations for each GB. (b) Overall statistics. Note that for the $\langle 100 \rangle 45^\circ$ boundary only 15 simulations were analyzed here because the grain growth was very limited at temperatures below 1300 K and the grain rotation behavior could not be unambiguously determined.

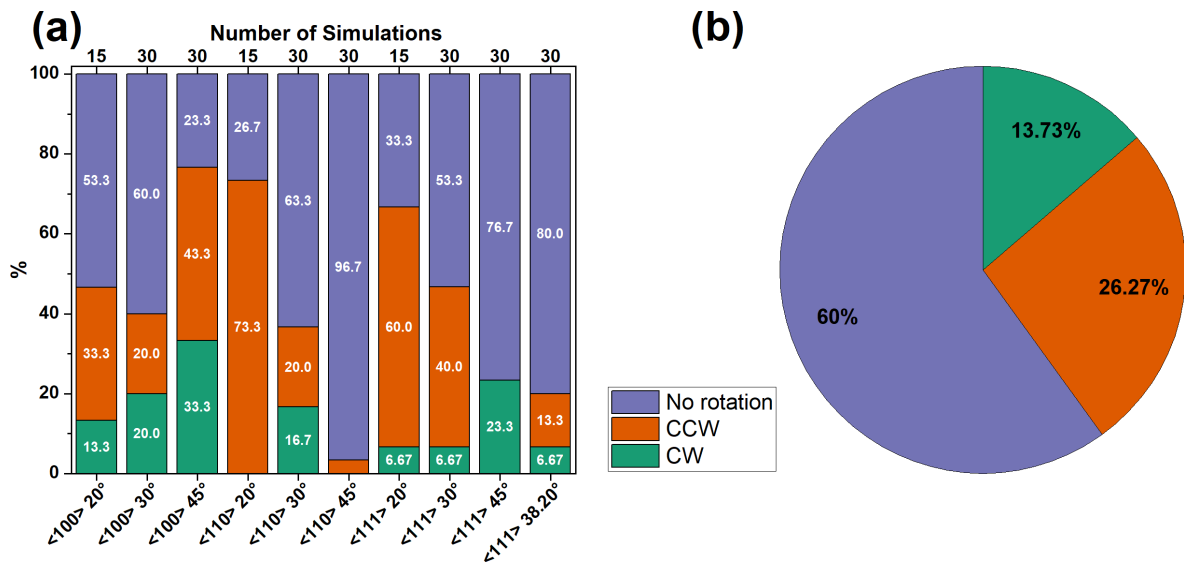


Fig. 3.11. Summary of the grain rotation behavior for simulations using the ADP potential, showing the percentage of simulations that underwent no rotation, counterclockwise (CCW) rotation, and clockwise (CW) rotation. (a) By GB type (bottom axis). The top axis indicates the number of simulations for each GB. (b) Overall statistics.

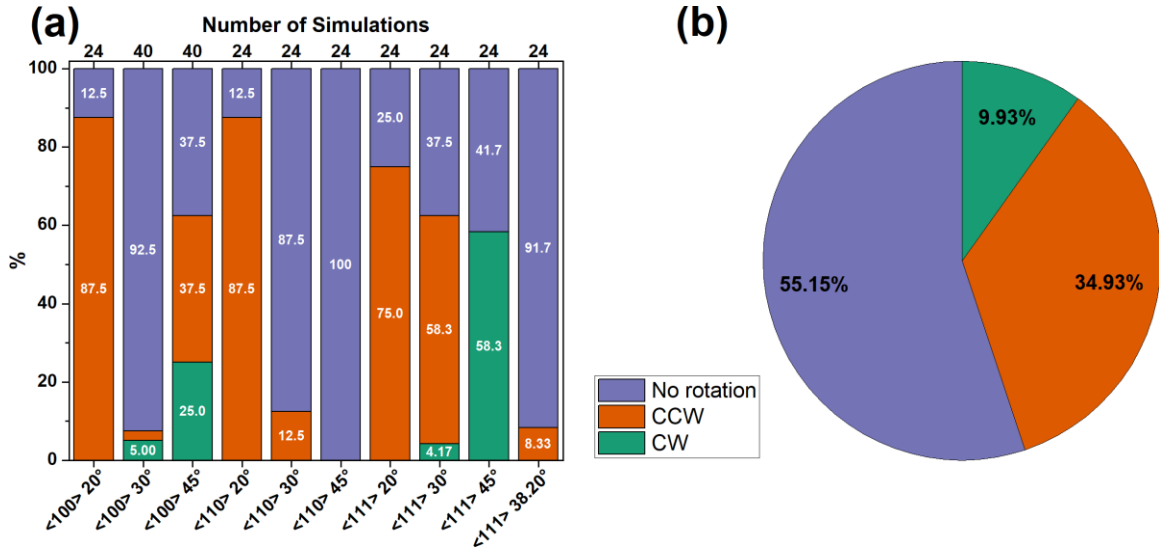


Fig. 3.12. Summary of the grain rotation behavior for simulations using the MEAM potential, showing the percentage of simulations that underwent no rotation, counterclockwise (CCW) rotation, and clockwise (CW) rotation. (a) By GB type (bottom axis). The top axis indicates the number of simulations for each GB. (b) Overall statistics.

At high temperatures (near the melting point of the material), grain rotation is not expected to happen due to the disappearance of the coupling factor between normal and tangential boundary velocity, which occurs when the GB premelts [88]. Trautt and Mishin found in their simulations on FCC Cu that grain rotation ceased when the temperature rose above 80% of the melting temperature [88]. In this work, only the ADP potential underwent GB pre-melting, and in most cases, there was no grain rotation observed. However, some rotation was still observed at these elevated temperatures (see Fig. 3.13). Even in the presence of the GB melt, nearly 50% of the simulations at 1300 K and over 20% at 1250 K for the ADP potential demonstrated some grain rotation. If the trend of grain rotation ceasing is consistent between FCC Cu and BCC U, the expected temperatures (80% of the melting temperature) at which grain rotation ceases would be ~ 1225 K for the EAM potential, ~ 1060 K for the ADP potential, and ~ 1200 K for the MEAM potential. As shown in Fig. 3.13, this clearly is not the case, as grain rotation is observed across the whole simulated temperature range. Therefore, grain rotation has been observed at high temperatures in this work, which is different from the no-rotation behavior observed in Cu by Trautt and Mishin [88] at high temperatures. The cause of grain rotation at these elevated

temperatures where (presumably) the coupling factor between the normal and tangential velocities is zero remains unknown.

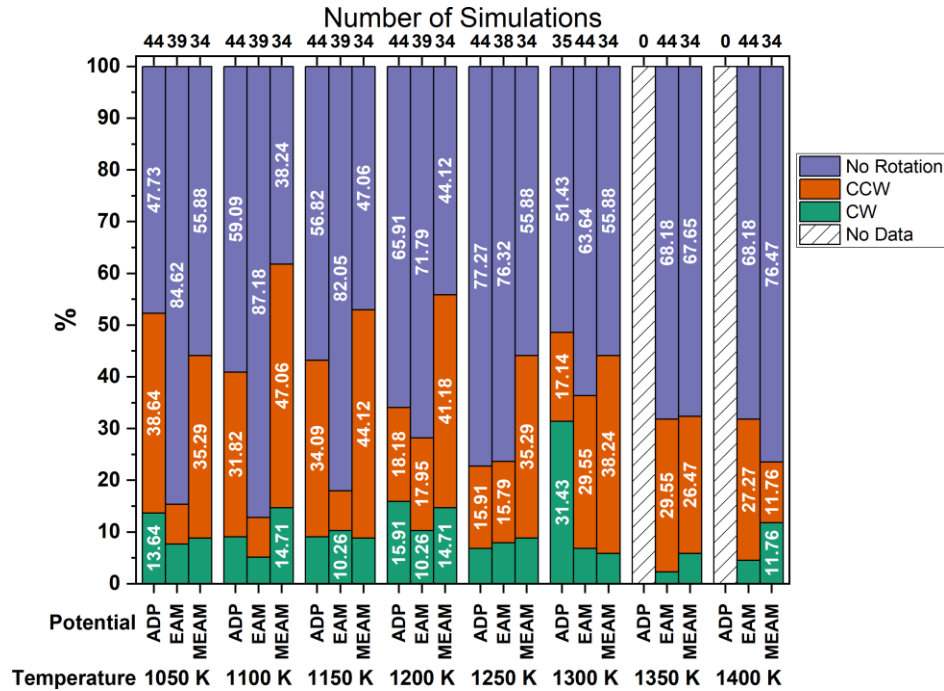


Fig. 3.13. Summary of the grain rotation behavior for all simulations that underwent no rotation, clockwise (CW) rotation, and counterclockwise (CCW) rotation as a function of temperature and interatomic potential. The top axis indicates the number of simulations for each potential/temperature combination. No simulations were run using the ADP potential at 1350 and 1400 K, as they were above the melting temperature predicted by the potential.

Overall, among the three potentials, the EAM potential led to the most no-rotation behavior, the ADP potential gave the most clockwise rotation, while the MEAM potential resulted in the most counterclockwise rotation. For each GB system, the grain rotational behavior is rarely consistent. In only three cases was the rotation behavior the same for every simulation for one system: $\langle 110 \rangle$ 45° and $\langle 111 \rangle$ 38.2° by the EAM potential, and $\langle 110 \rangle$ 45° by the MEAM potential. They all had no rotation. All other systems had mixed rotation behaviors, indicating that other factors such as temperature and stochastic effects can affect the direction of rotation.

Previous MD simulations have shown that in an FCC Cu some $\langle 100 \rangle$ GBs tend to rotate to a specific misorientation around 37° [88]. This angle is the transition angle between the $\langle 100 \rangle$

and $\langle 110 \rangle$ branches of the coupling factor between the normal and tangential GB velocities. If the same rotation tendency can be applied to the BCC structure as in this study, the expected rotation behavior would be counterclockwise for the $\langle 100 \rangle$ 20° and 30° boundaries and clockwise for the $\langle 100 \rangle$ 45° boundary. In this work, only the $\langle 100 \rangle$ 20° by the MEAM potential (Fig. 3.12) is consistent with this expectation, though this could be just a coincidence. Therefore, the grain rotation behavior in BCC γ U is very different from that observed in FCC Cu.

3.5. Discussion

In this work, different interatomic potentials resulted in different GB mobilities (values, anisotropy, temperature dependence), even if for the same GB type. This is not unique to this work, as a recent study examining GB mobility behavior in FCC Ni using four different interatomic potentials found that the potential plays a strong role in the calculated GB mobilities [106]. The EAM potential used in this work was developed to model defect evolution in the U-Mo system, including the presence of Xe gaseous fission products [91]. Even though this potential was aimed at modeling U-Mo alloys, it captures the physical properties of pure U fairly well for the γ phase. However, it predicts a much higher vacancy formation energy compared to experiments [91,107]. Although it has been found that an interstitial mechanism dominates the self-diffusion in bulk γ U [107–109], vacancy formation and migration at a GB region could still play an important role in mass transport during boundary migration. The ADP potential was developed with a special focus on two metastable phases that both pure U and U-Mo systems go through when quenched [89]. This potential overestimates the vacancy formation energy in bulk γ U [107], like in the EAM potential. The focus of the MEAM potential is the atomic directional bonding, with the fitting procedure focused on vacancy mobility and the energy hierarchies of different phases as calculated using first principles. Additionally, there is a stronger focus on accurately describing the α U $\rightarrow$ γ U phase transformation at high temperatures (note that the β phase is ignored in this potential due to its narrow temperature range in which it exists) [90]. To the best of the authors' knowledge, GB properties were not directly considered during the development of these potentials. Therefore, it is reasonable that these potentials have large discrepancies in predicting GB properties, including the mobility studied here.

Since GB motion is related to the atom transfer across the boundary plane, point defect diffusion could have a potential correlation with GB mobility. At the GB region, it is likely that

both interstitials and vacancies contribute to the GB motion. Previously, the defect self-diffusion coefficients in pure bulk U (which consider both interstitial and vacancy contributions) predicted by the same potentials as used in this work (except for the MEAM potential) have been reported [89,107]. In general, the EAM potential predicts a slower self-diffusion coefficient than the ADP potential at the same temperature. For example, at 1000 K, the EAM potential predicts [107] 10^{-13} m²/s while the ADP potential predicts [89] 10^{-12} m²/s for the bulk self-diffusion coefficient. If the GB mobility trend follows the bulk self-diffusion trend, the EAM potential should result in a slower GB mobility than the ADP potential. The GB mobility results from this work indicate that in general, this is true especially at low temperatures, although the two potentials predict similar mobilities at high temperatures. On the other hand, for the self-diffusion at GBs, previous studies show that GB self-diffusion does not have a strong correlation with GB mobility, and they can be considered as two distinct processes [36,110]. Therefore, it seems that GB mobility might not have a simple relationship with the point defect self-diffusion in the bulk or GB region. More systematic studies are certainly needed for clarifying this topic in the future.

Like in many previous studies of using curved GBs to calculate mobility [88], the cylindrical GBs created in this work may contain a high concentration of defects, primarily vacancies due to the removal of overlapping atoms at the GB. To achieve the equilibrium defect concentration at a GB, some novel methods such as the evolutionary algorithm [111] and GB annealing with an open surface [112,113] can be used, especially for flat GBs. It has been shown in these studies that the equilibrium GB structures can be very different from the as-created ones. Unfortunately, such an approach was not employed for the curved GBs studied in this work. The high defect concentration at a GB may lead to artificially high GB mobilities. For example, Korneva et al. [114] compared the MD-calculated mobilities using different GB geometries (flat, spherical, and polycrystalline) and found that the spherical or curved GBs lead to a much smaller activation energy than other GB geometries. Therefore, future studies should pay more attention to the effects of oversaturated defect concentration on the mobility of curved GBs.

In FCC Al, the experimental results show that GBs with the $\langle 111 \rangle$ rotation axis typically have faster mobilities than $\langle 100 \rangle$ and $\langle 110 \rangle$ rotation axes at most misorientations, although sometimes the $\langle 100 \rangle$ rotation axis can have comparable mobilities with $\langle 111 \rangle$ rotation axis [34]. If Al is representative of FCC metals in terms of mobility anisotropy, it can be argued that $\langle 111 \rangle$

GBs are the fastest in FCC metals. However, from Fig. 3.9, $\langle 111 \rangle$ GBs in BCC U are never the fastest, sometimes the slowest. Therefore, it seems that the mobility anisotropy related to the rotation axis for FCC metals cannot be applied to BCC metals, at least for the γ U studied here. In this work, the $\langle 110 \rangle$ boundaries have the fastest mobilities in almost all cases (Fig. 3.9). To the best of the authors' knowledge, currently there is no reasonable explanation about why a particular rotation axis can have faster GB mobilities than other rotation axes in both FCC and BCC materials. This could be explained from the viewpoint of atomic planar density. In the cylindrical grain system (Fig. 3.1), the X-Y plane is perpendicular to the rotation axis (the Z direction). This plane is also perpendicular to the GB plane. To have GB motion, atoms need to diffuse across the GB plane according to Burke and Turnbull's theory [97]. In the Results section, the MSD analysis shows that if the atomic motion in the X-Y plane is high, then the boundary typically moves fast, although there are also some exceptions. If the X-Y plane has a high atomic planar density, then the mass transport within that plane should be more efficient than other lower-density planes due to its short in-plane interatomic distance. The highest density plane is $\{111\}$ in FCC materials and $\{110\}$ in BCC materials, which are consistent with the observations that the fastest GBs are $\langle 111 \rangle$ boundaries in FCC Al and $\langle 110 \rangle$ boundaries in BCC U. In BCC materials, the atomic planar density from high to low is: $\rho_{110} > \rho_{100} > \rho_{111}$. If GB mobility anisotropy is fully determined by the planar density, the mobility order in BCC materials should be $M_{110} > M_{100} > M_{111}$. In Fig. 3.9, only the EAM potential predicts this trend, and only for the 30° misorientation. In other cases, $\langle 111 \rangle$ boundaries have faster or similar mobilities compared to $\langle 100 \rangle$ boundaries. Therefore, the planar density argument seems to only work for predicting the fastest boundaries in BCC γ U. This is reasonable because GB migration mechanisms are complex (e.g., atomic shuffles [85,86,99]) and different mechanisms may be activated under different conditions. For FCC materials, the atomic planar density order is $\rho_{111} > \rho_{100} > \rho_{110}$. The experimental results of FCC Al [34] seem to be consistent with this order, although exceptions do exist.

Experimentally, the average GB mobilities (K) can be extracted from grain growth experiments using the ideal grain growth equation (Eq. (3.2.1)). Here the authors use either the directly reported mobility values in literature or an estimate of the mobilities based on the reported grain sizes at different annealing times according to Eq. (1). It should be noted that U-based alloys (e.g., U-7Mo, U-10Mo) [10,16,18,21,41] rather than pure U were studied in experiments. Figure 3.14 shows the comparison between the MD-calculated mobilities in this work and the

experimentally extracted values at different temperatures. Note that the comparison of GB mobilities between MD and experiments is in the same temperature range. Clearly, the MD values are about 5 – 6 orders of magnitude higher than the experimental values. Interestingly, the slope of the lower bound of the MD-calculated mobilities is similar to the slope of the experimental data, though this is likely coincidental. The large discrepancies in GB mobility between MD simulations and experiments have been observed in other systems as well, such as UO_2 [36], among others [115,116]. There could be a number of reasons for the large discrepancies. First, the material in MD simulations is pure U without any impurities or solutes (so the calculated mobilities are intrinsic for γ U), while the materials in experiments are U-Mo based alloys that could contain many impurities in addition to Mo solute (so the extracted mobilities are extrinsic). Although solutes and impurities can have complex effects on GB motion, in general, they can cause solute drag effects and reduce the effective GB mobilities [34]. Second, GB migration is driven by curvature in this work. It has been argued that such a driven method may result in artificially high GB mobilities compared to the zero-driving-force method such as the random walk method [102,103,114,117]. However, this argument is also controversial. For example, a comparison of three methods (thermal gradient driven, curvature driven, and random walk) in a UO_2 system reveals that different simulation methods give similar GB mobilities [36]. In addition, a comparison between the stress-driven and random-walk methods also shows that they predict similar GB mobilities in Ni [118]. Third, as discussed earlier, the cylindrical GBs created in this work may contain oversaturated defects. Such defects may promote the GB migration and lead to artificially high GB mobilities than in experiments.

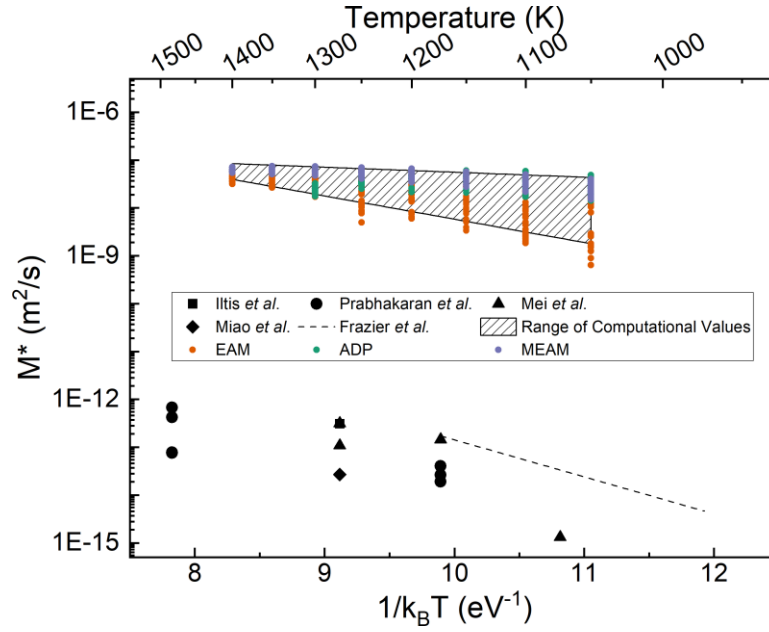


Fig. 3.14. Comparison of GB mobilities (in an Arrhenius plot) between the calculated values in this work and extracted values from experiments at different temperatures. The hatched region represents the upper and lower bounds of calculated values and is bounded by the mobilities of the MEAM $\langle 110 \rangle 30^\circ$ GB (upper bound) and the EAM $\langle 100 \rangle 45^\circ$ GB (lower bound) as calculated based on their activation energies and mobility prefactors. Experimental values are as follows: Iltis *et al.* [18], Prabhakaran *et al.* [21], Mei *et al.* [10], Miao *et al.* [41], and Frazier *et al.* [16]. Note that the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right).

3.6. Conclusions

In this work, MD was used to perform many curvature-driven grain growth simulations for ten unique cylindrical GBs using three interatomic potentials (EAM, ADP, MEAM) for the pure BCC γ U system across a wide range of temperatures. To the best of the authors' knowledge, this is the first computational study to directly calculate the mobilities of individual GBs in this system. The obtained GB mobilities and the associated anisotropy could be used in mesoscale modeling to study grain growth in U-based metallic fuels.

In terms of GB mobility anisotropy, both misorientation and rotation axis dependencies have been investigated. Although anisotropy does exist, the trend depends strongly on the

interatomic potential. Nevertheless, the mobilities of the $\langle 110 \rangle$ boundaries are consistently found to be the fastest for the same misorientation using three potentials. The origin of this anisotropy trend is interpreted based on the viewpoint of atomic planar density. In BCC metals, the $\{110\}$ plane has the highest planar density. This plane is perpendicular to the GB plane and the rotation axis for the circular GBs studied in this work. The high atomic density (and therefore the short in-plane nearest-neighbor distance) may facilitate the mass transport across the GB plane and thus the GB migration. This planar density argument can also be applied to explain why in experiments the $\langle 111 \rangle$ boundaries in FCC Al are the fastest. However, this argument cannot be applied to the $\langle 100 \rangle$ and $\langle 111 \rangle$ boundaries in this work's BCC U results, suggesting that additional aspects need to be considered to predict the rotation-axis-dependent GB mobility trends.

This work also finds that the interatomic potential plays a strong role in GB mobility – in terms of both magnitude and anisotropy. This suggests that the results from MD simulations should be carefully interpreted, as some phenomena or trends could be specific for a potential. For temperature dependence, sometimes GB mobility does not follow perfect Arrhenius behavior. Nonlinear behaviors (e.g., anti-thermal and athermal) have been observed, similar to many other studies. This observation suggests that GB migration is a complex process and that multiple migration mechanisms may operate simultaneously. The Arrhenius assumption for the temperature dependence of GB mobility may not be sufficient to describe the GB migration behavior at all temperatures.

During the cylindrical GB migration in this work, the inner grain can either have no rotation or rotate in the clockwise/counterclockwise directions. The statistics show that in most cases the inner grain has no rotation. For the cases with rotation, the rotation direction seems stochastic because no correlation can be established with the rotation axis, misorientation angle, or interatomic potential. Finally, MD-calculated GB mobilities in pure U were compared with the experimentally extracted average mobilities in U-Mo-based alloys, the latter of which assumes ideal grain growth behavior. Similar to other systems such as UO_2 , the calculated mobilities are about 5 – 6 orders of magnitude higher than the experimental values. The possible underlying causes for the large discrepancies are discussed in the context of solute drag effects and the large driving forces used in simulations.

Chapter 4. Grain Boundary Mobility in the UO₂ System

This chapter is intended to be included in a journal article and is in the process of being submitted.

4.1. Abstract

Current light water reactors utilize uranium dioxide (UO₂) as their primary fuel source, thus making understanding the behavior of UO₂ of particular interest. Efforts are ongoing to understand the complex relationships between material properties, environmental conditions, and fuel performance so that accurate predictions of fuel performance can be made. Microstructural evolution has been identified as a target behavior for its relationship with thermal conductivity, fission gas release, and other important fuel performance-related material properties. Grain growth (part of microstructural evolution) is impacted by both grain boundary (GB) energy and mobility, which are known to be anisotropic. The form of mobility anisotropy in the UO₂ system is unknown. This work uses molecular dynamics to examine the mobility of eight unique GBs and finds a mobility trend of $M_{111} > M_{100} > M_{112} > M_{110}$. These results are discussed in terms of the planar density argument.

4.2. Introduction

Nuclear energy has a strong potential to address worldwide issues, most notably climate change, and a growing energy need [119]. Nuclear energy benefits from a high energy density, and low carbon dioxide output compared to fossil fuels [120]. However, most of the existing nuclear reactors are reaching the end of their operational lifetimes, and relatively few new reactors are being built in the U.S. [121]. Among the reasons for delaying the construction of new reactors are the desire to reduce the potential for nuclear proliferation [51], and to have increased efficacy and safety during reactor operation [122]. Efforts toward the former have focused on developing low-enriched uranium-based alloys [51], while efforts toward the latter have focused on understanding all aspects of reactor materials' behaviors at a fundamental level [123]. Uranium dioxide (UO₂) in particular has been extensively examined over the last several decades due to its use as the primary fuel source for light water reactors. However, missing from these studies is a deep understanding of grain boundary (GB) mobility and its anisotropy, which can affect its grain growth behavior during reactor operation and thus other fuel performance properties. Therefore, this work analyzes GB mobility in UO₂ to further the atomistic-level understanding of this

material, which could ultimately contribute toward increasing the safety and efficacy of nuclear power.

Studies have explored the material behaviors of UO_2 with an overarching goal of maximizing fuel performance. Predicting (via simulation) and improving fuel performance have long been a focus of the nuclear community to improve safety and efficiency in nuclear power generation. There are two main challenges in achieving these goals: the difficulty in understanding the intrinsic material properties and behaviors of the fuel and understanding how various environmental conditions couple with them. Fuel performance is made up of a complex set of relationships that are at various stages of understanding [123–126]. Among the relationships that have been established, some of the key material properties that directly impact fuel performance are thermal conductivity, fission gas retention and release, and fuel swelling [127]. Several studies have identified that the fuel microstructure (e.g., grain size) and its evolution have significant impacts on these properties [22,128–132], emphasizing the importance of understanding and predicting how such evolution occurs.

During its time in a reactor, UO_2 undergoes significant microstructural changes, including high burnup structure (HBS) formation, pore and bubble formation and evolution, and grain growth. HBS formation occurs in the rim region of the fuel at high fission densities and is characterized by small grain sizes and large pores [68]. When the HBS forms, there is a positive change in the rate at which the thermal conductivity decreases with increasing burnup, effectively leading to a higher thermal conductivity relative to if this structure did not form [133]. Pores and bubbles have been shown to have non-negligible impacts on fuel performance properties. In particular, grain growth is expected to be rate-limited by pore pinning at the GB [33,134], and thermal conductivity is heavily dependent on the volume fraction of pores and bubbles [135]. Grain growth occurs due to the high temperatures that are reached in the center of the fuel pellet [136], and the resulting increased grain size has been demonstrated to have fuel performance-related impacts, including reducing fission gas release [128]. Much of the experimental effort toward understanding microstructural evolution in UO_2 has focused on the properties of the HBS, with relatively little effort given to understanding grain growth behaviors. However, for fuel performance codes (such as BISON [137]) to give high-fidelity predictions, accuracy in the rates and behaviors of grain growth is essential.

Grain growth is defined by the relationship $v = M \times F$, where v is the velocity of the boundary, M is the mobility of the boundary, and F is the driving force. The curvature driving force, prevalent in all polycrystalline materials, is defined (in simplified form [44,45]) as $F_c = \gamma\kappa$, where γ is the GB energy and κ is the curvature of the grain. From these relationships, it is evident that grain growth is dependent on at least two GB properties: energy and mobility [34]. GBs are defined by five macroscopic degrees of freedom, with three describing the relative rotation between the two grains (the misorientation), and the remaining two defining the inclination of the GB plane [138]. This means the parameter space for GBs is very large, making it infeasible to thoroughly examine how GB energy and mobility vary in this space with current methods. Because of the expansive space of GB character (and because of the difficulty in determining the character of individual GBs experimentally), most studies assume that GB energy and mobility are isotropic. However, it is known that these properties are anisotropic [75,76,139], therefore making an understanding of the anisotropy in these properties an important step in predicting microstructural evolution, and therefore fuel performance.

Of the two GB properties, GB energy has been much more extensively studied. Several materials [34], recently including UO_2 [29,140–142], have had their GB energy trends examined, with specific trends identified in face-centered cubic (FCC) metals [143], body-centered cubic (BCC) metals [144], and fluorite-structured ceramics [141]. This makes it relatively straightforward to estimate GB energy and its anisotropy for an arbitrary GB in one of these types of materials. On the other hand, there is significantly less known about the anisotropy trend of GB mobility. Most studies of GB mobility only examine FCC metals [82,88,100,102,103,110,115,116,145], with comparatively limited focus on other crystal structures [49,85] or materials [36]. While improved general knowledge has been gained from these studies, relatively little attention has been given to examining the anisotropy in detail. Instead, the focus has been on understanding the mobility trends for specific variables: (coincident site lattice – CSL) boundaries [36,99,100,102,103,110], temperature ranges [36,85,116], and/or (generally bicrystal) geometries [85,88,116,145–147]. In terms of anisotropy, these studies (and others) have revealed that, in FCC metals, $\langle 111 \rangle$ tilt boundaries tend to migrate faster than other boundaries [34,83]. Currently, the largest single database of GB mobilities consists of the 388 unique CSL boundaries in Ni studied in Ref. [82], which, though impressive in its scope, is still

too small to examine general trends in the GB parameter space. Since a detailed analysis of this database concludes that there is no simple model for mobility [105], more studies are needed to understand all aspects of this property. More recent studies of various flat GBs cover a subset of this database, for example by looking at specific boundaries in more detail [105], or examining specific boundaries over different (extended) temperature ranges [99]. An additional purpose in studying these well-researched systems is to understand the mechanisms by which GBs move. Various mechanisms have been identified, including rotational shuffles [85,99,145], coordinated shuffles (martensitic or ‘military’ transformations) [99,110,138], uncoordinated shuffles [99], short-range shuffles initiated by long-range diffusion [100], etc. [138]. No studies to date have identified a clear reason for why a boundary moves or does not move a certain way, nor has a clear model for predicting motion mechanisms been presented. As shown in the previous Chapter, the present author has collaborated with his colleague [49] to argue via simulation studies of BCC γ uranium that the fastest (tilt) GB orientation axis can be determined via planar density arguments, where the plane normal to the GB plane (and also the tilt axis) with the highest density can experience more rapid growth due to the smaller distance for atomic jumps across the GB, and the implied lower activation energy required to make such jumps. For example, the $\langle 111 \rangle$ rotation axis in FCC materials [83], and the $\langle 110 \rangle$ rotation axis in BCC materials [49] both tend to have the highest mobilities, and the corresponding (111) and (110) planes are the highest-density planes in the respective crystal structures.

GB mobility anisotropy in UO_2 , a fluorite oxide, is much less well understood. Experimental studies of grain growth in UO_2 are highly limited in their ability to determine individual GB mobilities, instead examining the average mobility [23,29,31,32], using an assumption of isotropic mobility. Research investigating the average grain growth kinetics in UO_2 has identified that a modified Arrhenius relationship with a defined maximum grain size accurately describes experimental observations and additionally incorporates the finding that pore mobility is the rate-limiting factor in grain growth [31–33]. Studies of grain growth during fuel pellet preparation have found that certain processes increase grain size, and that bimodal grain size distributions (present during the initial stages of sintering) become monomodal with most of the growth occurring among clusters of smaller grains [22,148]. In 2017, two groups examined grain growth in nano-grained, near-stoichiometric UO_2 and found that the grain growth of the nano-grains is generally not comparable to the conventionally-sized micro-grained UO_2 , the former

having much faster initial grain growth [6,23]. Yu *et al.* [11] assessed irradiation-induced grain growth in nanocrystalline UO_2 over a wide temperature range (50–1075 K). They found clear examples of cryogenic grain growth that follows the thermal spike mechanism in the range of 50–475 K, with thermally driven grain growth becoming increasingly important at higher temperatures. While the number of studies examining the effect of GB character on GB mobility is limited, some experimental studies have characterized the distribution of GB character, which could be indirectly related to GB mobility. For example, Rudman *et al.* [7] examined the GB misorientations in stoichiometric and hyperstoichiometric UO_2 after annealing and found no $\{111\}$ planes with misorientations in the 30° to 50° range. Instead, they found that misorientations in the 30° to 40° range had boundary planes oriented along $\{113\}$ directions for both samples and $\{112\}$ or $\{011\}$ planes for the stoichiometric or hyperstoichiometric samples respectively. Only over the last decade have simulation studies for individual GB mobilities in UO_2 been performed, though most studies still examine the general mobility behavior in polycrystals. Bai *et al.* [36] determined the GB mobility of five GBs using a thermal gradient driving force via molecular dynamics (MD), though only three of the boundaries experienced enough grain growth to calculate a mobility value. Hallberg and Zhu [26] examined GB texture in UO_2 via a level-set method with a simplified form of anisotropic GB energy and mobility, finding that grain growth kinetics are negligibly impacted by anisotropic (as compared to isotropic) GB properties, while the grain size distribution and stability of grain textures are strongly impacted. Neither of these studies examined the GB mobility anisotropy trend. Thus, this work will examine the GB mobility anisotropy trend in UO_2 via MD simulations of several tilt GBs to (1) determine the mobility anisotropy trend in UO_2 , if any, (2) clarify if the planar density argument holds for the fluorite crystal structure, and (3) provide anisotropic mobility data that could be used in mesoscale simulation of pure UO_2 by the research community.

4.3. Methods

The shrinking cylindrical grain method [149] was used to calculate GB mobility in this work. This method has previously been successfully used in several grain growth studies to determine reduced GB mobilities in the UO_2 [36], Cu [88], and γ U [49] systems. Systems are created in the same way as in [49], with specific attention to maintaining a charge-neutral system: atoms within a radius $r_{\text{grain}} = 100 \text{ \AA}$ from the center of a block of the pure crystal are rotated about

the Z axis by the desired misorientation angle, where the Z axis is aligned along the desired crystal direction to use as a rotation axis. After rotation, if a pair of U atoms were closer than 2.5 Å, one of the U and two of its nearest neighbor O atoms were removed. Removing the atoms in this way ensured that the system remained charge-neutral. Several interatomic cutoffs were tested for ‘too-close’ U-U interactions, ranging from 0.1–0.99 of the first nearest neighbor (1NN) interatomic distance. For cutoffs ranging from 0.2–0.7 of the 1NN distance, the resulting changes were quite small—note that this includes the 2.5 Å cutoff (~ 0.65 of the 1NN distance). Because of the small changes in this range, the 2.5 Å cutoff was deemed acceptable to use generally. The single-crystal blocks of UO_2 were created using the GBStudio software [150], and the grain rotation and subsequent atom removal were performed using an in-house code. The axes of rotation used in this work are the [001], [110], [111], and $[11\bar{2}]$ directions (hereafter referred to as the $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ rotation axes). The misorientations used are 20° for the first three axes, 45° for all rotation axes, and 38.20° for the $\langle 111 \rangle$ rotation axis. Note that the $\langle 111 \rangle 38.20^\circ$ GB is associated with the fastest grain growth or nearly the fastest grain growth in FCC metals [34,78,84]. To check if this is also true for UO_2 , it is included here for comparison. Individual system details are given in Table 4.1. The number of atoms in each system ranged from $\sim 150,000$ up to $\sim 250,000$. Each system was equilibrated via a three-step process: a conjugate-gradient minimization, a thermal anneal at 1500 K for 20 ps in the canonical (NVT) ensemble, and another conjugate-gradient minimization. Equilibration via this method ensured that the structure was close to its equilibrium state at 0 K before beginning any given NPT simulation at a finite temperature. A separate, more complex minimization strategy with five steps, aimed at reducing the number of atoms removed, was tested to determine if and how the equilibration method impacted the mobility results. This second, more complex method used a smaller cutoff value and started the minimization procedure with a cosine potential defining the atomic interactions to nudge atoms that were too close to each other. Short simulations using the microcanonical (NVE) ensemble were then performed using interatomic potential parameters defined for the UO_2 system to further equilibrate the structure, with a per timestep displacement limit of 0.1 Å. An NVT anneal at 1200 K for 5 ps was followed by a 30 ps quench (using an NVE + Langevin thermostat). The resulting structure was minimized twice using a conjugate-gradient minimization – the first allowed the box size to relax, and the second did not. Representative results comparing these two strategies are shown for a $\langle 111 \rangle 45^\circ$ GB at 2900 K in Fig. 4.1, and show almost identical shrinkage

rates of the embedded cylindrical grain regardless of the equilibration method. Overall, the methods of equilibration examined in this work do not seem to significantly impact mobility trends, and therefore the simpler method was used throughout.

Table 4.1. System details for the GBs studied in this work. Size is given in Å for each direction.

Rotation Axis	<100>	<110>	<111>	<112>
Orientation	X = [100]	X = [001]	X = [$1\bar{1}0$]	X = [111]
	Y = [010]	Y = [$1\bar{1}0$]	Y = [$11\bar{2}$]	Y = [$1\bar{1}0$]
	Z = [001]	Z = [110]	Z = [111]	Z = [$11\bar{2}$]
Size (Å ³)	272.7×272.7×27.3	299.9×300.8×38.6	269.9×267.1×28.3	236.1×231.4×40.1

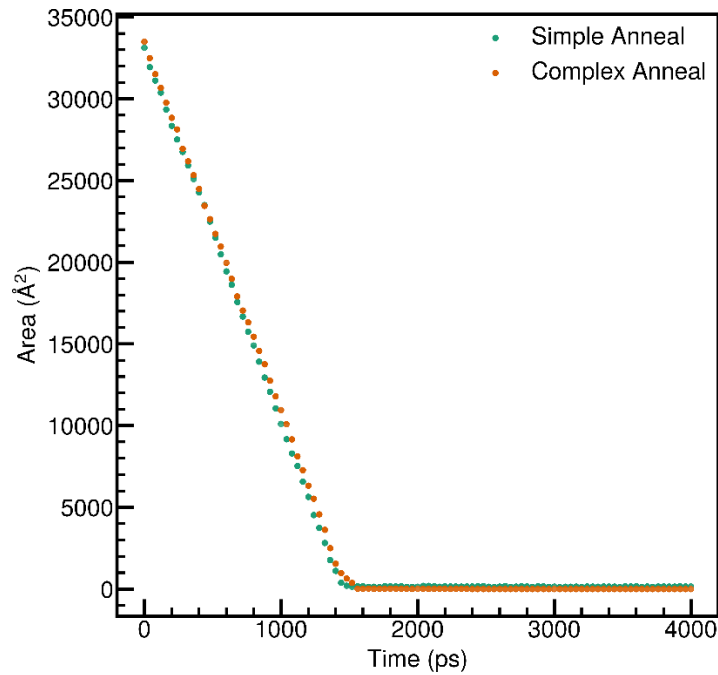


Fig. 4.1. Representative area versus time comparison of two equilibration methods for the <111> 45° GB at 2900 K using the CRG potential: a simple (three-step) anneal, and a complex (five-step) anneal. Data points represent an average across three independent simulation runs.

MD simulations were performed using the LAMMPS software [92] using the well-known Basak potential [151], which predicts a 0 K lattice parameter of 5.454 Å. The predicted melting temperature of this potential is ~3540 K, thus the range of temperatures used in this work is 2000 to 3300 K in increments of 100 K. A subset of the data was calculated in Ref. [152] (specifically, the 20° and 45° data for the low-index rotation axes), and is re-evaluated in this work. Similar calculations were performed using an embedded-atom method (EAM) potential [153] (hereafter referred to as the Cooper-Rushton-Grimes or CRG potential), which predicts the same 0 K lattice parameter for validation of the results. This potential predicts a lower melting temperature between 3000 and 3100 K (closer to the experimental value), thus the temperature range is from 2000 to 3050 K (the assumed melting temperature used in this work is 3100 K). The CRG potential is based in part on the Basak potential but includes an EAM term that can correctly demonstrate the Cauchy violation ($C_{12} \neq C_{44}$) observed experimentally [154] due to the many-body effects. All GB mobility simulations were performed in the isobaric-isothermal ensemble (NPT) with a Nosé-Hoover thermostat and barostat for 20 ps at the desired temperature to allow for volume equilibration (pressure set to 0 bars), and then for up to 8 ns to simulate the GB motion. Snapshots were saved every 40 ps for later analysis (Fig. 4.2 shows several snapshots for a few GBs). K-space summation was computed via the particle-particle particle-mesh (pppm) method [155] as implemented within LAMMPS, with the cutoff between real space and K-space at 11 Å. At each temperature, three independent simulations were performed to get the average mobility behavior. During the grain growth portion of the simulation, the mean-square displacement (MSD) for each type of ion as well as all atoms collectively was saved every 10 ps for later analysis.

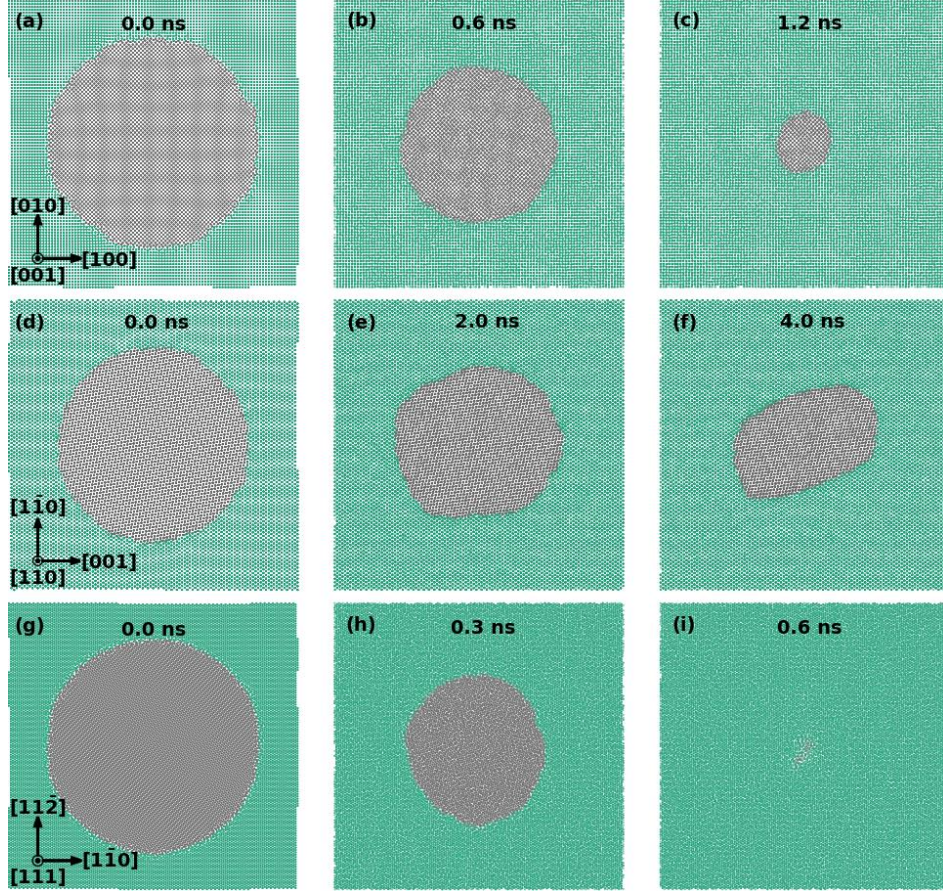


Fig. 4.2. Example of grain growth for the (a)-(c) $\langle 100 \rangle$ 45° , (d)-(f) $\langle 110 \rangle$ 45° , and (g)-(i) $\langle 111 \rangle$ 45° boundaries at 3000 K at various times during the simulation. Note that the $\langle 111 \rangle$ GB completely disappears after ~ 0.6 ns, while more than double the time is required for the $\langle 100 \rangle$, and the $\langle 110 \rangle$ requires more than 4 ns. Crystallographic directions are indicated for each subset.

GB mobility was calculated following the method given in Chapter 3 as well as in Ref. [49]. A brief description is given here. The mobility calculation is based on the relationship $v = M \times F$, with M as the mobility, and F as the curvature driving force of γ_{GB} / r_{grain} . This method relates the rate at which the cross-sectional area of the embedded grain shrinks to the (reduced) mobility via $M^* = \frac{1}{2\pi} \frac{dA}{dt}$, where reduced mobility is the product of mobility and GB energy ($M^* \equiv M\gamma$), and is assumed to follow the Arrhenius relation ($M^* = M_0^* \exp\left[-\frac{Q}{k_B T}\right]$). The number of atoms in the embedded grain was tracked via the orientation parameter first defined by Ulomek

et al. [47] and simplified in Schratt and Mohles [48], where an atom j is assigned a value χ_j given by $\chi_j = \frac{1}{\mathcal{N}} \sum_{l=1}^3 [|\psi_l^I(\mathbf{r}_j)|^2 - |\psi_l^{II}(\mathbf{r}_j)|^2]$. Here, $\mathcal{N}$ is a normalization factor that keeps the orientation parameter between 1 and -1 at 0 K. The $\psi_l^\lambda(\mathbf{r}_j)$ term is a complex weighted sum defined by $\psi_l^\lambda(\mathbf{r}_j) = \sum_{k \in \Gamma_j} w_{jk} \exp(i(\mathbf{r}_j - \mathbf{r}_k) \cdot \mathbf{q}_l^\lambda)$ and defines how well the environment of atom j (defined by a small neighbor list Γ_j) matches the perfect orientation of grain λ (I or II), which is defined by the independent reciprocal lattice vectors $\mathbf{q}_l^\lambda$, with $l = 1, 2, 3$ used as the index for each vector. The weighting term $w_{jk} = w(|\mathbf{r}_j - \mathbf{r}_k|)$ smoothly transitions from 1 at $\mathbf{r}_j$ to 0 at a specified cutoff value. Atoms can be assigned to one of the grains or a GB region, depending on the cutoff for grain assignment (for example, if the cutoff is specified as ± 0.75 , atoms with $|\chi_j| < 0.75$ would be assigned to a GB region). In this work, the cutoff for grain assignment is 0.0 (meaning a GB region was not defined), where values less than zero indicate the embedded cylindrical grain, and values greater than zero indicate the matrix grain. Once the number of atoms in the embedded grain was known, the area was calculated and plotted as a function of time, and the slope was extracted using a piecewise, linear-fitting routine [95], an example of which is shown in Fig. 4.3. Previous work [152] calculated GB mobility in UO_2 using the Basak potential and the orientation parameter defined by Zhang *et al.* [116]. The data from [152] is recalculated using the orientation parameter defined by Ulomek *et al.* [47] and presented here—note that the recalculated values are consistent with the original work. The lattice parameter as a function of temperature was calculated for both the Basak and CRG potentials via ten independent simulations for each temperature, ranging from 50 K up to 3500 K in increments of 50 K. All of these lattice parameter simulations used a 5x5x5 block of UO_2 , periodic boundary conditions, and the NPT ensemble. The block was initially equilibrated at the desired temperature for 10 ps, then the lattice parameter in the X, Y, and Z directions was independently averaged over the next 100 ps. The X, Y, and Z values of the lattice parameter were then averaged together to increase the statistical accuracy of the lattice parameter function. The lattice parameters as a function of temperature (given in Kelvin) were fit to a third-degree polynomial with the resulting equations given below:

$$\begin{aligned}
& -1.09 \times 10^{-12} T^3 + 1.26 \times 10^{-8} T^2 + 4.59 \times 10^{-5} T + 5.4454 \text{ (Basak)} \\
& 2.848 \times 10^{-12} T^3 + 1.16 \times 10^{-9} T^2 + 5.26 \times 10^{-5} T + 5.4532 \text{ (CRG)}
\end{aligned}
\tag{4.3.1}$$

Equation (4.3.1) is used to calculate the temperature-dependent cross-sectional area of the embedded grain. While the temperature-dependent lattice parameter is not expected to significantly alter the calculated mobility, it is included here for completeness.

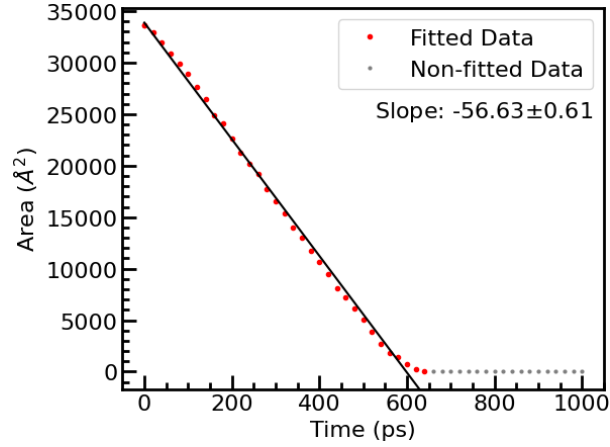


Fig. 4.3. Example of area versus time plot used for determining the dA/dt to calculate the reduced mobility. This data is from one simulation for the $\langle 111 \rangle$ 45° boundary using the Basak potential at 2800 K. Greyed-out points were not included in the fit because the grain shrinkage had already stopped.

4.4. Results

4.4.1. Anisotropy Trends

Figure 4.4 shows the reduced GB mobility for both the Basak and CRG potentials on an Arrhenius plot, with each subplot having a fixed misorientation of 20° or 45° (the $\langle 111 \rangle$ 38.20° data is examined separately). These plots clearly show that the $\langle 111 \rangle$ rotation axis is generally the fastest, and the $\langle 110 \rangle$ rotation axis is the slowest among the examined rotation axes, for a fixed misorientation. Therefore, the general mobility anisotropy trend is $M_{111} > M_{100} > M_{112} > M_{110}$. For the CRG potential at high temperatures, the trend deviates for the 45° misorientation due to an abrupt change in the mobility for the $\langle 111 \rangle$ rotation axis at $T = 2300$ K.

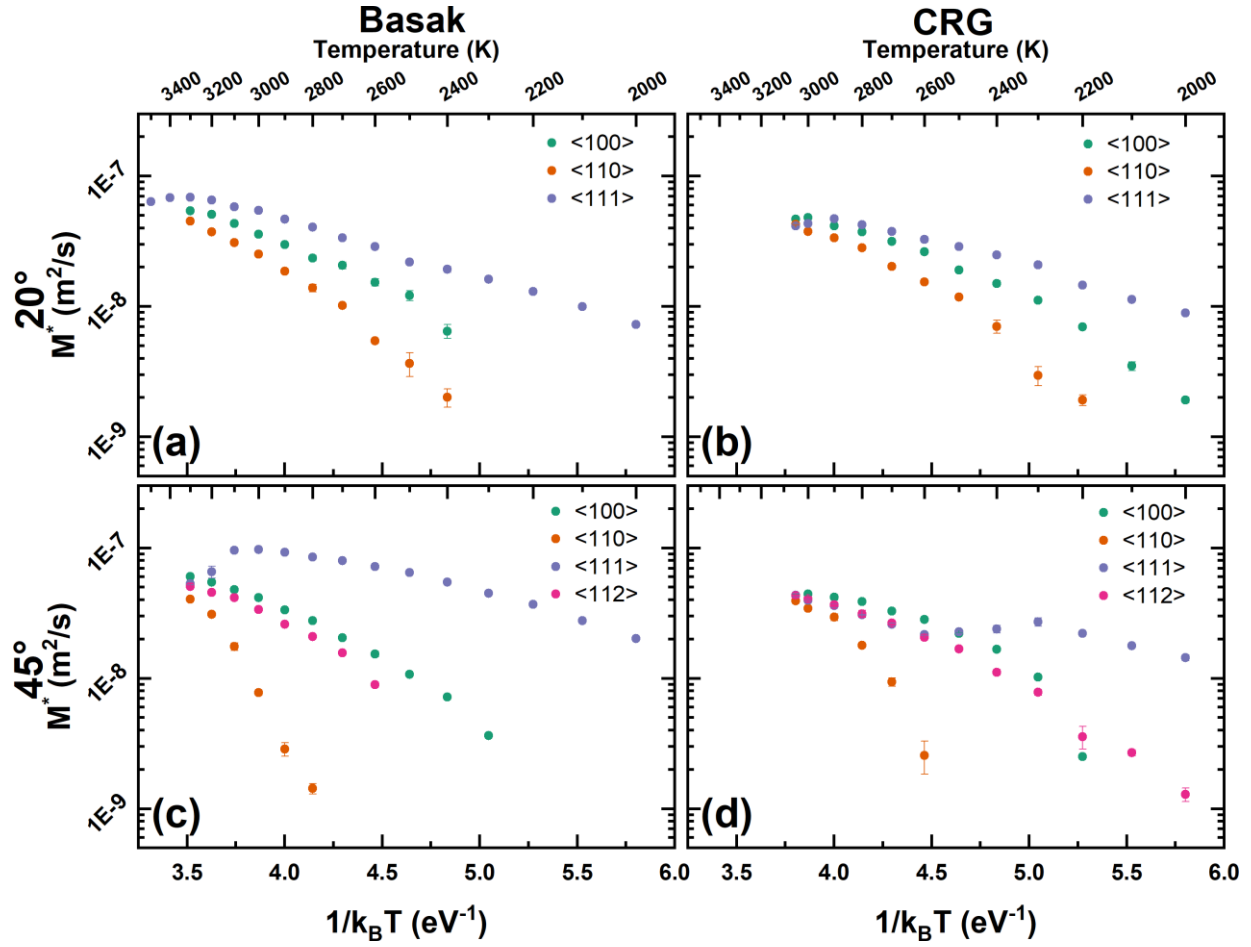


Fig. 4.4. Reduced GB mobility by rotation axis for a given fixed misorientation. (a) and (b) are for a 20° misorientation, and (c) and (d) are for a 45° misorientation. (a) and (c) were calculated using the Basak potential, and (b) and (d) use the CRG potential. Some data in (a) and (c) are recalculated from French [152] as indicated in the text. Error bars represent standard error of three independent simulations, but are generally too small to be seen. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). For (a)-(c), the mobility trend is $M_{111} > M_{100} > M_{110}$, while in (d) this is the trend at temperatures below 2500 K, and above 2500 K the trend is $M_{100} > M_{111} > M_{110}$.

Activation energies and prefactors for the various GBs are given in Table 4.2. These values are generally fitted across the whole domain for the Basak potential, except for the $\langle 111 \rangle$ 45° and 38.20° boundaries (due to their anti-thermal regions). The CRG potential can have single fits for

most of the boundaries, but some boundaries are fit better by multiple regimes due to their curvature (such as the $\langle 100 \rangle 45^\circ$ boundary), or their anti-thermal regimes (such as the $\langle 111 \rangle$ boundaries). Mobility values are roughly similar between the two potentials, though the Basak potential has slightly higher values at the same homologous temperature. For both potentials, the boundary with the highest activation energy is the $\langle 110 \rangle 45^\circ$ boundary and the lowest activation energy is the $\langle 111 \rangle 38.20^\circ$ boundary. The boundary with the highest-quality Arrhenius fit for both potentials is the $\langle 111 \rangle 20^\circ$ boundary, with R^2 values of 0.9958 and 0.9981 for the Basak and CRG potentials respectively, though Arrhenius fits generally approximate the data very well ($R^2 \geq 0.95$).

Table 4.2. Activation energies (Q , in eV) and reduced mobility prefactors (M_0 , in m^2/s) for the GBs studied in this work fitted to typical Arrhenius behavior. Except where otherwise noted, the fitted values are across the whole range of calculated mobilities.

Potential	Basak			CRG		
GB	M_0 (m^2/s)	Q (eV)	R^2	M_0 (m^2/s)	Q (eV)	R^2
$\langle 100 \rangle 20^\circ$	8.8×10^{-6}	1.42	0.9887	6.3×10^{-6}	1.25	0.9277
$\langle 100 \rangle 45^\circ$	21.5×10^{-6}	1.63	0.9736	17.9×10^{-6}	1.45	0.7899
$\langle 110 \rangle 20^\circ$	71.8×10^{-6}	2.06	0.9654	8.2×10^{-6}	1.38	0.9089
$\langle 110 \rangle 45^\circ$	3.9×10^0	5.18	0.9756	574.0×10^{-6}	2.51	0.9601
$\langle 111 \rangle 20^{*\circ}$	2.5×10^{-6}	1.01	0.9958	2.1×10^{-6}	0.95	0.9981
$\langle 111 \rangle 38.20^{*\dagger}$	1.6×10^{-6}	0.75	0.9881	483.1×10^{-9}	0.48	0.8735
$\langle 111 \rangle 45^{*\ddagger}$	2.1×10^{-6}	0.78	0.9856	2.2×10^{-6}	1.03	0.9965
$\langle 112 \rangle 45^\circ$	7.4×10^{-6}	1.42	0.9679	7.2×10^{-6}	1.33	0.9574

*For the CRG potential, the fitted range for the $\langle 111 \rangle 20^\circ$ boundary is 2000–2900 K, due to the anti-thermal regime from 2900–3050 K.

[†]For both potentials, the fitted range for the $\langle 111 \rangle 38.20^\circ$ boundary is truncated due to the presence of an anti-thermal regime. The CRG potential is fitted to the range 2000–2800 K, and the Basak potential is fitted to the range 2000–3100 K. Anti-thermal regimes are 2800–2900 K and 3100–3300 K respectively.

[‡]For the CRG potential, the anti-thermal regime is from 2300–2600 K. The values shown here are for the higher temperature domain (2600–3050 K). Fitting to the 2000–2300 K range gives a mobility prefactor of $2.0 \times 10^{-6} \text{ m}^2/\text{s}$, an activation energy of 0.85 eV, and an R^2 value of 0.9973.

For the Basak potential, the fitted range for this boundary is 2000–3000 K due to the anti-thermal regime from 3000–3300 K.

While a clear general trend can be extracted for the anisotropy trend between rotation axes with a fixed misorientation, the trend between misorientations for a fixed rotation axis is inconsistent, although this observation is only based on a limited number of misorientations. Figure 4.5 shows mobility as a function of misorientation for the Basak potential at 2800 K. Across all temperatures, the general trends are that the $\langle 100 \rangle$ rotation axis mobility is weakly dependent on misorientation (the 20° and 45° boundaries are nearly equal to each other, as represented by the nearly flat line), while the $\langle 110 \rangle$ rotation axis mobility is strongly dependent on the misorientation (the 20° boundary is faster than the 45° boundary, as represented by the large negative slope). The $\langle 111 \rangle$ rotation axis mobility is also dependent on the misorientation, but each potential has a different trend. The Basak potential shows the 45° boundary as the fastest, then the 38.20° boundary, then the 20° boundary at nearly all temperatures (the 45° boundary becomes slightly slower than the 38.20° boundary at 3300 K, see inset to Fig. 4.5). On the other hand, the CRG potential (not shown) shows the 38.20° boundary as the fastest, and the 20° and 45° boundaries swap, with the 20° boundary slowest at lower temperatures (below 2400 K), and the 45° boundary slower at higher temperatures (above 2400 K).

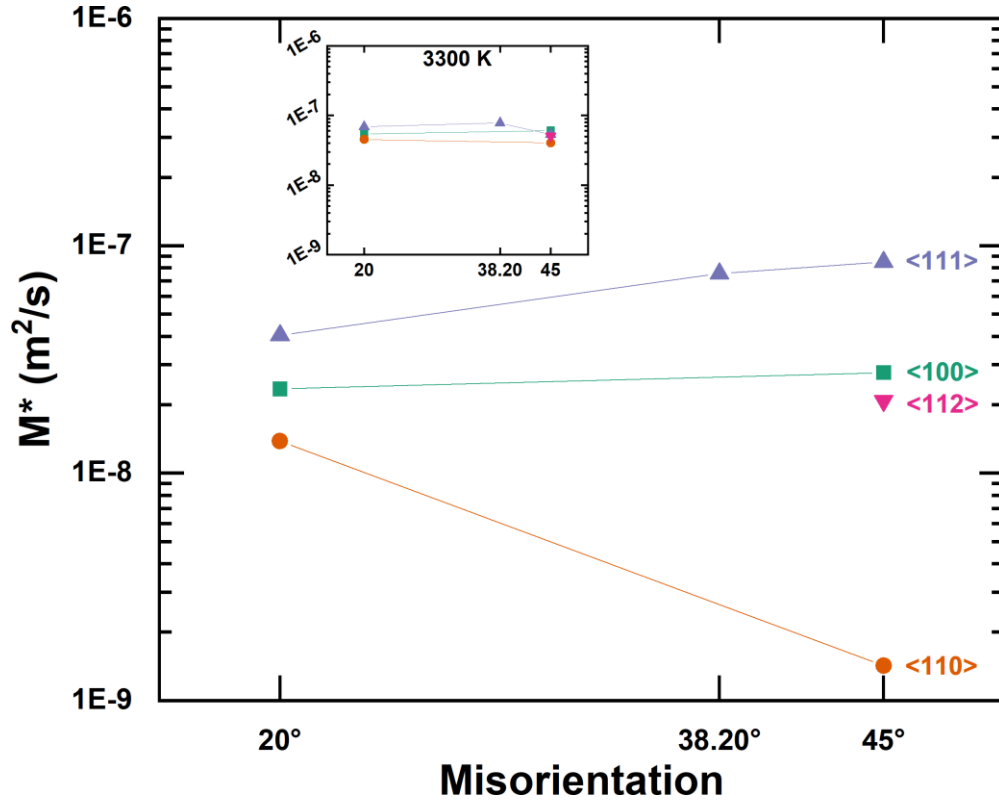


Fig. 4.5. Representative reduced mobility as a function of misorientation at 2800 K (inset – 3300 K) using the Basak potential. The general trend is $M_{111} > M_{100} > M_{110}$ for the 20° and 45° misorientations. However, there is no consistent trend with the misorientation for each tilt axis. The lines are guides to the eye.

Generally speaking, GB mobility tends toward a single value at high temperatures for both potentials. For example, at 3050 K for the CRG potential, mobility seems independent of GB character, as the values are all nearly equivalent (see Fig. 4.4(b) and (d)). Similar convergence behavior is observed for the Basak potential at 3300 K (see inset to Fig. 4.5), but not to the same degree, as the mobility trend of $M_{111} > M_{100} > M_{110}$ can be clearly identified for the 20° boundary, and a different trend of $M_{100} > M_{111} > M_{110}$ for the 45° boundary (discussed in more detail below). The better convergence in the CRG potential is likely due to its lower melting temperature, and thus the higher homologous temperature of the simulations performed; simulations using the CRG potential ran up to ~98% of the melting temperature, while simulations for the Basak potential ran up to ~93% of the melting temperature. This converging behavior is consistent with previous studies of GB mobility [105,152]. At these near-melting-point temperatures, the GB structure becomes disordered and loses its original identity (e.g., due to pre-

melting). As a result, all GBs have a similarly disordered structure so that all GBs have a near-singular value of GB mobility.

4.4.2. Planar Density

In Chapter 3 and also Ref. [49], the present author and his collaborator proposed that the density of the plane normal to the GB plane (and also the tilt axis) can be used to determine general mobility anisotropy trends for BCC and FCC metals. This idea can be expanded upon when looked at in the context of the results of this work. To start, the fluorite crystal structure consists of an FCC sublattice of cations (U), with the anions (O) located at the tetrahedral sites, forming a simple cubic sublattice. Cations are the slower-moving (rate-limiting) species, thus the expectation is that the GB mobility anisotropy trend in fluorite will exhibit similar characteristics to the FCC mobility trend of $\langle 111 \rangle$ tilt GBs migrating the fastest, which is observed in Fig. 4.4. Extending the planar density approach to the $\langle 112 \rangle$ rotation axis is more difficult, however, as the surface could contain additional sub-surface layers so there is some uncertainty in determining the planar density of the higher-index planes. If the planar density cannot be calculated easily, an alternative approach is to use the surface energy trend in metals to estimate the order of planar density. In metals, surface energy is directly related to the number of broken bonds at a surface. Lower surface energy means higher planar density (fewer broken bonds) at the surface and vice versa. Surface energy calculations have been done for several FCC metals, thus making it a trivial exercise to compare different surface energies. In FCC metals, the surface energy trend is $\gamma_{111}^S < \gamma_{100}^S < \gamma_{112}^S < \gamma_{110}^S$ [156]. Thus, the surface planar density for an FCC structure should be $\rho_{111} > \rho_{100} > \rho_{112} > \rho_{110}$, which is exactly the same GB mobility trend for UO_2 as shown in Fig. 4.4, $M_{111} > M_{100} > M_{112} > M_{110}$. It should be noted that although this planar density order is derived from FCC metals, this geometric information also applies to the U-cation sublattice because it has the same FCC structure. However, one cannot use the surface energy trend in UO_2 to determine the planar density order because UO_2 has ionic bonds and its surface energy is not a simple linear function of the number of broken bonds as in metals. In addition, a UO_2 surface could be a non-stoichiometric (polarized) surface, which further complicates the surface energy trend. For example, the UO_2 surface energy calculations show a trend of $\gamma_{111}^S < \gamma_{110}^S < \gamma_{100}^S$ [29,157–159], which is not inversely related to the planar density order in the FCC structure.

Examining the mean-square displacement (MSD) is an effective method of determining the preferred direction of atomic motion for a given tilt axis. Figure 4.6 shows the scaled MSD of the Basak potential for some representative GBs. Generally, the $\langle 111 \rangle$ boundaries display more X and Y motion (i.e., across the GBs) than the Z motion, while the $\langle 100 \rangle$ and $\langle 110 \rangle$ boundaries show more Z motion (along the tilt axis or parallel to the GBs). The MSD results indicate that the atoms across the GBs for the $\langle 111 \rangle$ boundaries are more efficient, thus leading to faster mobilities than other tilt axes. Therefore, the MSD results are consistent with the planar density argument. By examining the MSD of specific boundaries across the simulated temperature domain, this work can explain some of the unique GB mobility behaviors in the context of planar density.

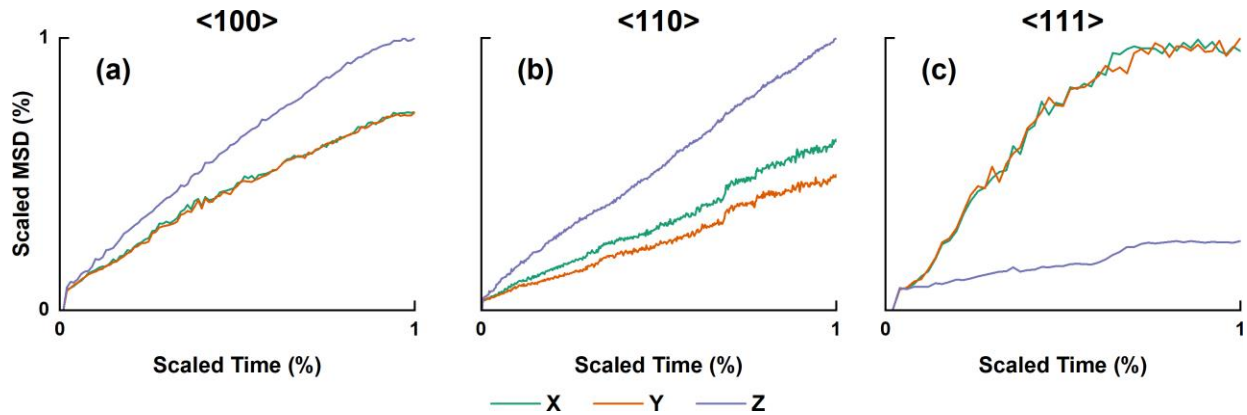


Fig. 4.6. Scaled MSD for the (a) $\langle 100 \rangle$ 45°, (b) $\langle 110 \rangle$ 45°, and (c) $\langle 111 \rangle$ 45° boundaries at 2800 K. Note that the Z MSD is higher than the X and Y MSD for both the $\langle 100 \rangle$ and $\langle 110 \rangle$ boundaries, but much lower for the $\langle 111 \rangle$ boundary. In each subplot, the MSD values are scaled by the maximum value between the X, Y, and Z directions, such that the ordinate (vertical) axis has a maximum value of one.

4.4.2.1. Faceting in $\langle 110 \rangle$ boundaries

This work has shown that the $\langle 110 \rangle$ boundaries are consistently the slowest among the examined rotation axes (see Fig. 4.4 and Fig. 4.5). One reason for this behavior is the presence of significant faceting that the other rotation axes did not experience, an example of which is shown in Fig. 4.7. When a GB facets, local curvature driving forces along the length of the facet are eliminated, effectively stopping curvature-driven grain growth along that interface. Among the rotation axes used in this work, only the $\langle 110 \rangle$ axis has multiple, nondegenerate $\{111\}$ -type planes

that are parallel to the GB. Specifically, the $[110]$ direction (aligned along the Z axis in Fig. 4.7) is perpendicular to the $[1\bar{1}\bar{1}]$, and $[1\bar{1}1]$, directions (and their antiparallels). As shown in Fig. 4.7, the longer facets tend to form along these $\{111\}$ planes, which is likely related to the low surface energy of the $\{111\}$ planes. Additionally, once these $\{111\}$ facets form, the atomic transfer is more efficient within that plane rather than perpendicular to it, contributing to the slower GB motion. For the other rotation axes studied in this work, only the $\langle 112 \rangle$ has one set of anti-parallel $\langle 111 \rangle$ directions, which is not enough to form a bounded region as in the $\langle 110 \rangle$ rotation axis. A recent Monte Carlo study of preferred void and bubble shapes in UO_2 found that $\{111\}$ and $\{100\}$ planes dominate the void and bubble shapes [160]. While this work only examines cylindrically shaped GBs, there appears to be a connection between the types of facets a GB will form and the preferred shapes of voids and bubbles in UO_2 . Examining the MSD of the $\langle 110 \rangle$ boundaries (see Fig. 4.6(b)) across all temperatures reveals significantly higher Z motion compared to the X and Y motion, resulting in overall slower GB mobility.

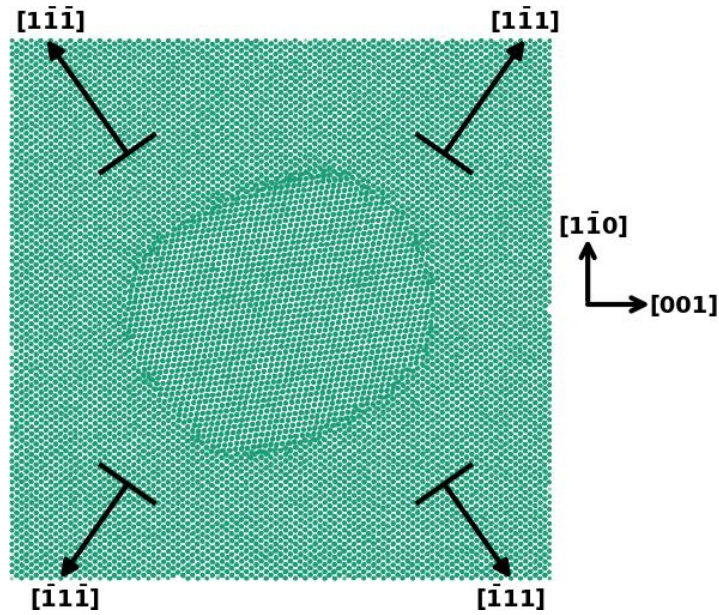


Fig. 4.7. Example of faceting behavior for the $\langle 110 \rangle$ 45° boundary at 2900 K after 5 ns using the Basak potential. $\langle 111 \rangle$ directions perpendicular to $[110]$ (out of the page) are indicated.

4.4.2.2. Anti-thermal grain growth behavior in $\langle 111 \rangle$ axis

Unique to the $\langle 111 \rangle$ rotation axis is the presence of anti-thermal regimes for nearly every GB (see Fig. 4.8). In the Basak potential, the 45° boundary experiences an anti-thermal regime from ~ 3000 K up to 3300 K, and the 38.20° boundary from ~ 3100 K to 3300 K (see Fig. 4.8(a)). The 20° boundary does not appear to have an anti-thermal regime in the simulated temperature range. However, additional simulations at temperatures of 3400 and 3500 K were performed for the $\langle 111 \rangle$ 20° boundary (see Fig. 4.8(a)), which did reveal the presence of an anti-thermal regime, indicating that anti-thermal behavior is consistent across all of the misorientations examined. The CRG potential shows an anti-thermal regime for all three misorientations examined, but across very different temperature ranges (Fig. 4.8(b)). The 45° boundary has an anti-thermal regime from 2300 K to 2600 K, the 38.20° boundary from 2800 K to 2900 K, and the 20° boundary from 2900 K to 3050 K. In terms of the homologous temperatures, the Basak potential experienced anti-thermal regimes from 0.96–0.99 for the 20° boundary, 0.85–0.93 for the 45° boundary, and 0.88–0.93 for the 38.20° boundary. The CRG potential's anti-thermal regimes were from 0.94–0.98, 0.74–0.84, and 0.87–0.94 for the 20° , 45° , and 38.20° boundaries respectively. Thus, the 20° and 38.20° boundaries share similar anti-thermal regimes. The MSD of the U atoms for each simulation was examined across the entire range of simulated temperatures to determine why this occurs (see Fig. 4.9 for a comparison between the temperature extremes for the Basak potential). In all cases, at low temperatures, the motion in the Z direction is low (near zero), while at high temperatures the Z motion is near the X and Y motion. Analysis of the MSD at the intermediate temperatures (not shown) reveals that in all cases of anti-thermal behavior, the anti-thermal region begins where the Z motion starts increasing relative to the X and Y motion. Specifically, in the cases of the $\langle 111 \rangle$ 45° and $\langle 111 \rangle$ 38.20° boundary using the CRG potential, the anti-thermal behavior continues until the Z motion becomes the dominant behavior, at which point typical Arrhenius kinetics resumes. In the other boundaries, typical Arrhenius behavior was not recovered. The temperature range over which this “activation” occurs appears to be primarily dependent on the misorientation, as the homologous temperatures are similar for the 20° and 38.20° boundaries between the two potentials—the 45° boundary being the exception in this work. Further inspection of the MSD for the other rotation axes (not shown) reveals that, at the lowest temperatures where grain growth is observed, the Z motion is either fully activated (as in Fig. 4.6(a) and (b), where the motion in the Z direction dominates) or nearly fully activated (defined as the Z motion being

approximately equal to the X and Y motion) and thus follows Arrhenius kinetics with increasing temperature. In the context of planar density, it is easy to move within high-density planes (e.g., {111} planes, or in the plane of the page in Fig. 4.2(g)-(i)), and much harder to move within different planes. If the $\langle 111 \rangle$ plane is normal to the GB plane as in the $\langle 111 \rangle$ tilt GBs, the preferred motion will be within that plane, though higher temperatures activate motion in less-dense planes. For the $\langle 111 \rangle$ rotation axis, it appears that once motion in a lower-density plane is activated (i.e., parallel to the tilt axis) the GB moves less efficiently (i.e., anti-thermal grain growth) until a new ‘equilibrium’ is reached, at which point normal Arrhenius kinetics is recovered, while the $\langle 100 \rangle$ and $\langle 110 \rangle$ do not have to change how they move at different temperatures.

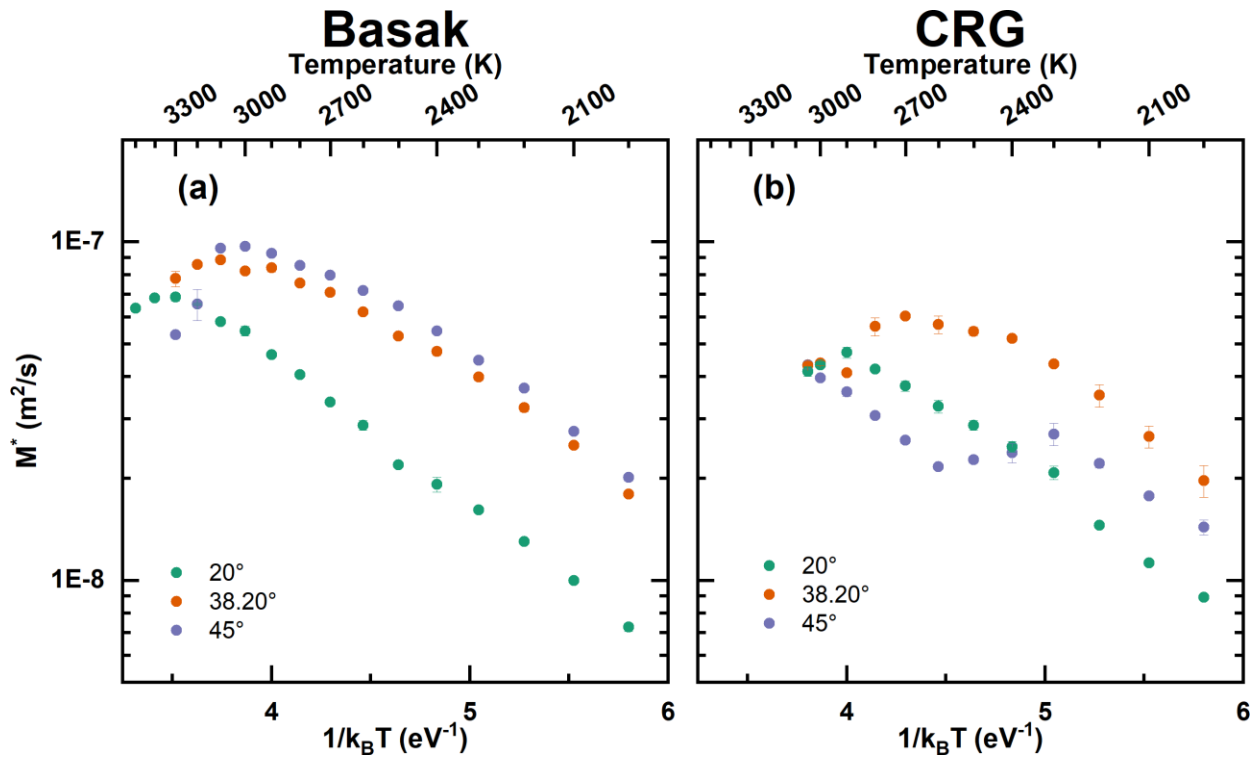


Fig. 4.8. Reduced mobility for the $\langle 111 \rangle$ rotation axis for (a) the Basak potential and (b) the CRG potential. Error bars denote standard error, but are generally too small to be seen. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right).

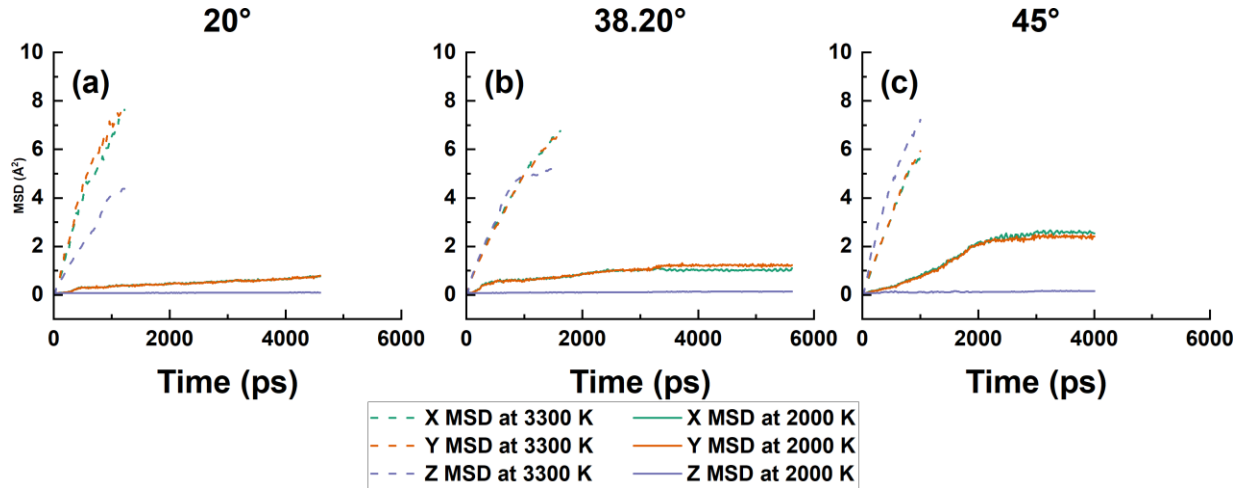


Fig. 4.9. MSD for the Basak potential at the temperature extremes examined in this work for the (a) $\langle 111 \rangle$ 20° , (b) $\langle 111 \rangle$ 38.20° , and (c) $\langle 111 \rangle$ 45° boundaries. Solid lines indicate the lowest temperature (2000 K) and dashed lines indicate the highest temperature (3300 K). At low temperatures, the X and Y motion is higher than the Z motion. At high temperatures, there is a variety of behaviors: (a) Z lower than X and Y, (b) Z equal to the X and Y motion, and (c) Z greater than the X and Y motion.

By examining the ratio of the 2D (XY, across the GB) to the 1D (Z, along the tilt axis) diffusion coefficients, further clarification on the effect planar density has on grain growth can be revealed. These ratios are plotted against temperature in Fig. 4.10 for the Basak potential (note that the CRG potential shows similar behavior). At low temperatures the $\langle 111 \rangle$ GBs have high ratios, indicating that most of the motion is in the XY plane, directly contributing to the GB motion. As temperature increases, the $\langle 111 \rangle$ GB diffusion ratios decrease, becoming nearly indistinguishable from the other boundary trends beyond 3100 K. This is likely because the GB structures become more disordered due to pre-melting at high temperatures. As a result of this structural transition, the $\langle 111 \rangle$ GBs no longer have preferred X-Y motion across the boundary planes, contributing to the drop of GB mobilities (i.e., anti-thermal behavior). Conversely, the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 112 \rangle$ boundaries all have a ratio near unity, indicating no preferred direction for atomic motion.

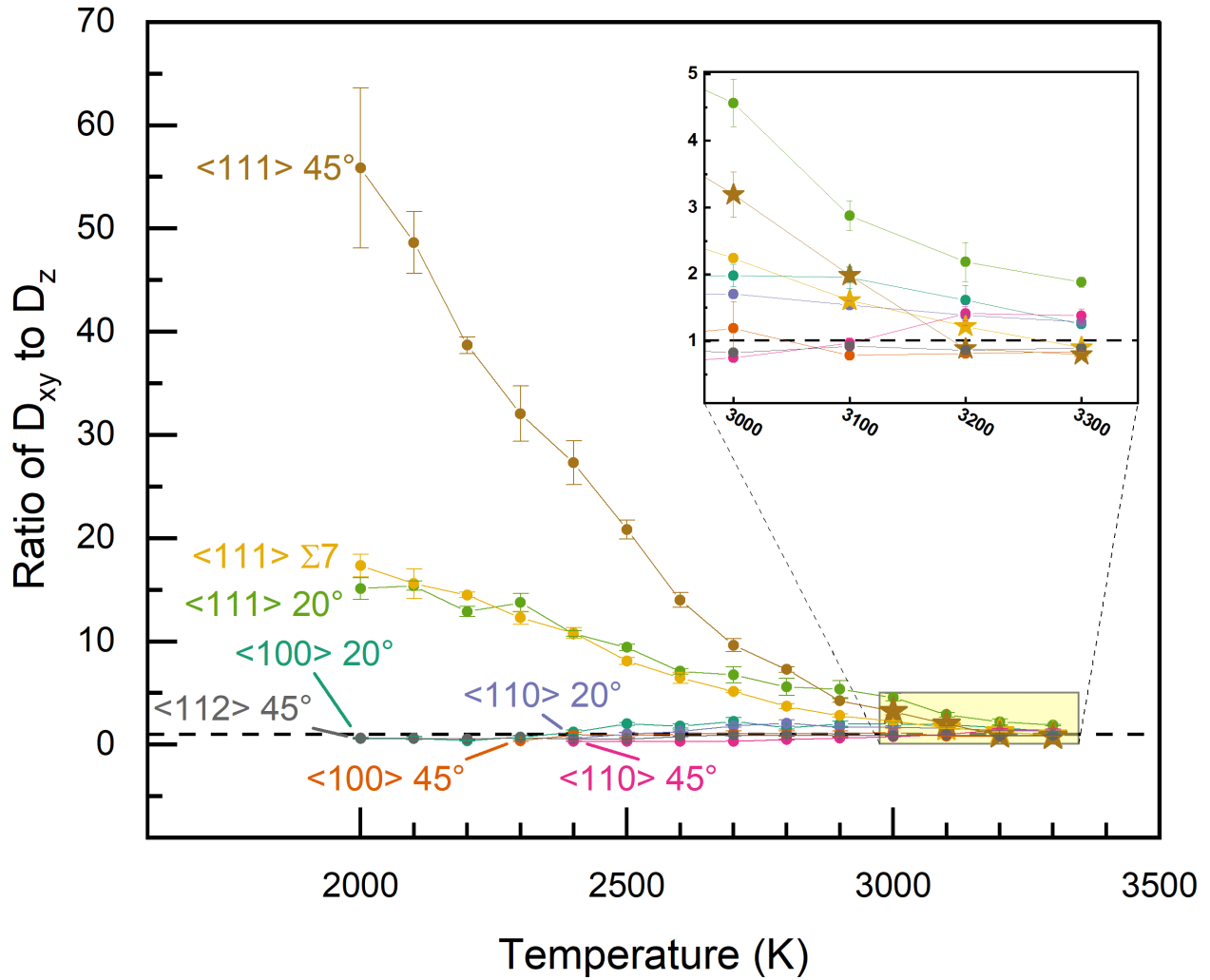


Fig. 4.10. Average ratios of 2D planar (XY) to 1D (Z) diffusion as a function of temperature for the Basak potential. The lines are guides to the eye, and the dotted line indicates where the ratio is 1. Emphasized points (stars) are in the anti-thermal regions of $\langle 111 \rangle$ GBs. Error bars represent the standard error of the mean. The inset shows the converging behavior at high temperatures.

In addition to the above explanation where the GB transitions to a disordered structure at high temperature, other possible reasons for the presence of the anti-thermal regimes include O sublattice melting (or a superionic phase transition), space charge effects (similar to SrTiO_3 [161–163]), or grain rotation, as studies have shown that it can be coupled to GB migration [88,147,164–166]. The O sublattice is experimentally observed to melt at around 80% of the melting temperature [167] and can be estimated based on how the MSD of the O atoms changes with

temperature. If a superionic phase transition is responsible for the anti-thermal regime, it would be expected that any significant changes in the MSD of the O atoms would correlate with changes in the mobility of the respective boundary. Examination of the O MSD (not shown) does not correlate with the anti-thermal regimes in mobility. Rather, for the CRG potential, the O MSD tends to rapidly increase around 2900 K, while in the Basak potential, this transition occurs around 3000 K. Since the anti-thermal regimes only occur in the $\langle 111 \rangle$ rotation axis, and the increased O MSD applies across all the GBs examined, a superionic phase transition does not seem to be the primary contributor to the anti-thermal regime. Space charge effects can impact the structure of a GB, as they do in SrTiO_3 , where they lead to specific GB complexions that have different mobility values due to differing defect concentrations [161,162]. Such effects could be observed in UO_2 , but no mention of anti-thermal behavior has been reported from experiments to the best of the author's knowledge. Further experimental examination of $\langle 111 \rangle$ tilt GBs is needed to examine if there is anti-thermal behavior for these boundaries. Grain rotation was tracked qualitatively using the central strip method outlined in [49,88], where a central strip of atoms was tracked throughout the simulations. For the $\langle 111 \rangle$ 38.20° boundary there was generally no rotation for both the Basak (100% of simulations) and CRG potentials (94.4%, 5.6% rotated counterclockwise). For the $\langle 111 \rangle$ 20° boundary, in all cases where grain rotation occurred, it was counterclockwise (increasing the misorientation) for both the CRG and Basak potentials, where 100% of the simulations rotated counterclockwise for the latter. The $\langle 111 \rangle$ 45° rotated counterclockwise (increasing the misorientation angle) about 75% of the time, with the other $\sim 25\%$ having no rotation for both potentials. If the rotation behavior correlates with the anti-thermal regime, then this implies that the $\langle 111 \rangle$ 45° boundary in the CRG potential rotates through a GB structure with a mobility minimum before increasing again. Visual analysis does not appear to indicate any significant changes in grain rotation from temperature to temperature, though future quantitative analysis could clarify this further.

4.5. Discussion

4.5.1. Shape of the Arrhenius Plot

While typical Arrhenius behavior is a decent approximation for the results shown in this work, nearly every GB system has at least a slight curvature to the Arrhenius plot, possibly indicating that Arrhenius kinetics do not fully (or incorrectly) describe GB mobility behavior.

Homer *et al.* [105] claimed that such curvature on an Arrhenius plot indicates that different mechanisms may become more important at different temperatures, or over different temperature ranges. O'Brien and Foiles [99] examined one such example of curvature in the Arrhenius plot and did not find anything to support the idea of separate motion mechanisms, instead finding that grain growth occurred via a complex, multi-step process which lends itself to the idea that a single Arrhenius activation energy (for that boundary) is insufficient to accurately describe the growth kinetics. An alternative explanation is that the GB acts as a glass-forming fluid, and thus should be fit using Vogel-Fulcher dynamics [101]. Performing a fit to the Vogel-Fulcher (VF) equation ($M_0^{VF} \exp[-Q^{VF}/(k_B(T - T_0))]$) results in the values given in Table 4.3 (assuming a T_0 of $T_m/2.8$, with T_m the melting temperature [101]). Of particular note, for both potentials, the VF activation energies are ~ 3 times smaller than their corresponding Arrhenius activation energies, while the VF prefactors are about an order of magnitude smaller. The characteristic temperature (T_0) generally fits the data well except for the $\langle 100 \rangle$ 45° boundary using the CRG potential.

Some of the mobility plots have sharper transitions rather than gradual curves, which could be explained by a sudden change in the migration mechanism. Sharp transitions have been observed in previous studies [88,102,103,105,110]. To examine this in more detail, additional simulations were performed using a smaller initial grain radius ($r_{\text{grain}} = 75 \text{ \AA}$) with a smaller temperature step at lower temperatures (2000–2400 K in increments of 50 K, 2400–3300 in increments of 100 K) for the $\langle 100 \rangle$ 45° boundary. The smaller initial radius increases the driving force on the boundary, which should lead to more grain growth compared to the larger initial radius at lower temperatures. The results of these simulations are shown in Fig. 4.11. The mobilities calculated from the two systems of different sizes agree reasonably well, especially at high temperatures. The transition appears to be relatively smooth at the resolution of this data. Alternatively, if a transition temperature of 2200 K is assumed, the Arrhenius activation energies are 4.31 eV and 1.44 eV for the low- and high-temperature regimes respectively (with mobility prefactors of $3.06 \times 10^1 \text{ m}^2/\text{s}$ and $1.10 \times 10^{-5} \text{ m}^2/\text{s}$ respectively). Such a transition at these temperatures could be correlated with a superionic phase transition, but the O MSD (not shown) does not reveal any changes at these lower temperatures.

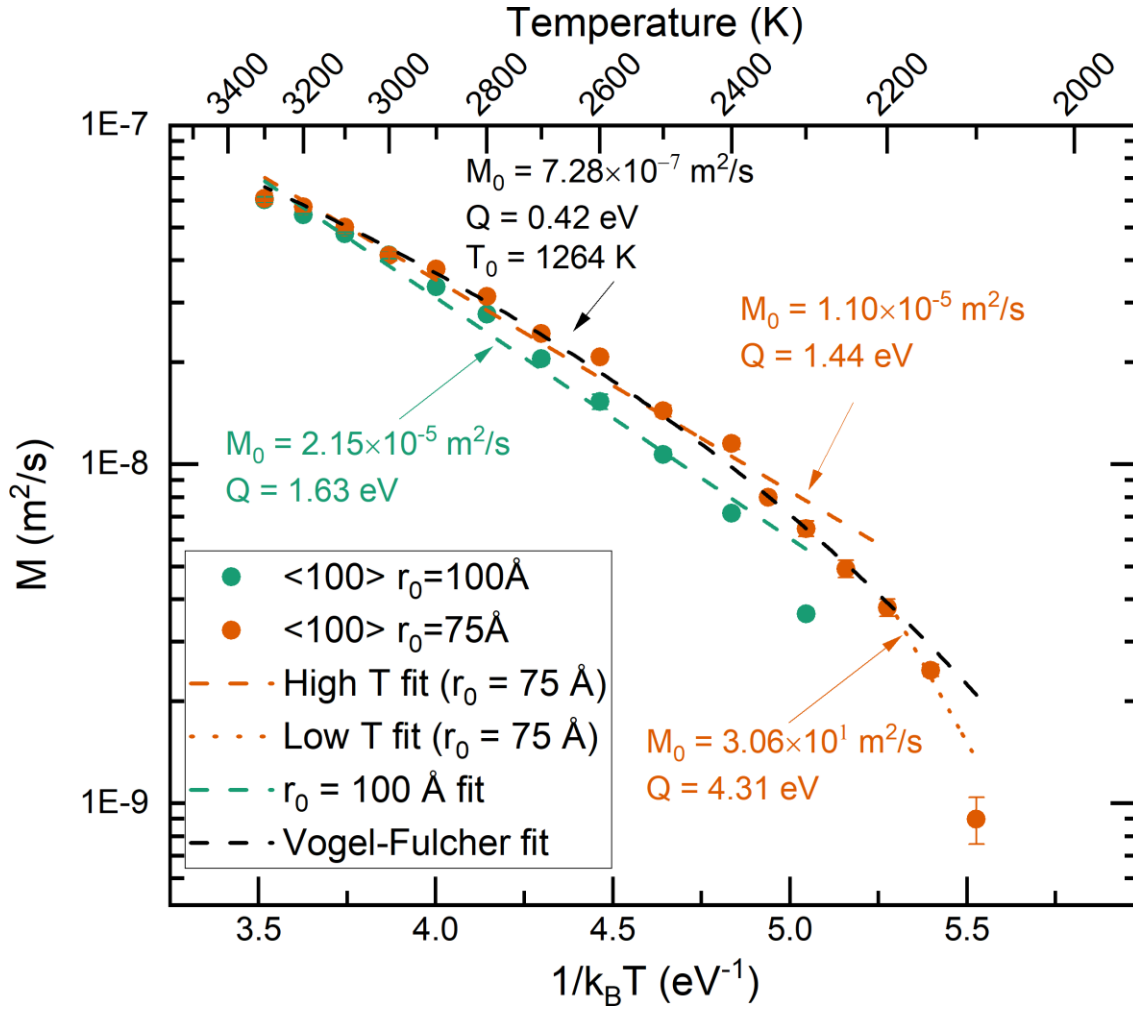


Fig. 4.11. GB mobility of the $\langle 100 \rangle$ 45° boundary using two different initial grain radii – 100 Å (green) and 75 Å (orange). Arrhenius fit parameters for the different regions are indicated on the plot in color, while Vogel-Fulcher fit parameters are indicated in black. The data with an initial radius of 100 Å is fitted by a single Arrhenius fit, while the 75 Å data has two (with a transition around 2200 K). Note that the mobility prefactors for the different regimes for the 75 Å data differ by six orders of magnitude, while the activation energy differs by a factor of ~ 3 . Additionally, the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right).

Table 4.3. Activation energies (in eV), and reduced mobility prefactors (in m^2/s) for the GBs studied in this work fitted to Vogel-Fulcher dynamics. Except where otherwise noted, the fitted values are across the whole range of calculated mobilities. An assumed characteristic temperature of $T_m/2.8$ was used throughout ($T_0 = 1264.29$ K for the Basak potential, and $T_0 = 1089.29$ K for the CRG potential).

Potential	Basak			CRG		
GB	M_0^{VF} (m^2/s)	Q^{VF} (eV)	R^2	M_0^{VF} (m^2/s)	Q^{VF} (eV)	R^2
<100> 20°	0.8×10^{-6}	0.46	0.9936	0.7×10^{-6}	0.43	0.9876
<100> 45°*	1.0×10^{-6}	0.49	0.9934	2.0×10^{-6}	0.56	0.1458
<110> 20°	2.3×10^{-6}	0.68	0.9905	1.1×10^{-6}	0.55	0.9895
<110> 45°	1325.7×10^{-6}	1.81	0.9615	21.9×10^{-6}	1.06	0.9552
<111> 20°†	0.3×10^{-6}	0.25	0.9772	0.3×10^{-6}	0.27	0.9932
<111> 38.20°‡	0.3×10^{-6}	0.17	0.9917	0.4×10^{-6}	0.16	0.9405
<111> 45°§	0.3×10^{-6}	0.18	0.9958	0.2×10^{-6}	0.38	0.9968
<112> 45°	0.9×10^{-6}	0.50	0.9768	0.7×10^{-6}	0.47	0.9926

*The CRG potential is not well fitted by a characteristic temperature (T_0) of $T_m/2.8$. If T_0 is allowed to vary during the fit, the values that lead to the best fit are $M_0^{VF} = 0.07 \times 10^{-6} \text{ m}^2/\text{s}$, $Q^{VF} = 0.05 \text{ eV}$, and $T_0 = 2029 \text{ K}$ ($\sim T_m/1.5$), with an R^2 of 0.9868.

†The CRG potential has a fitted range of 2000 – 2900 K for this boundary due to the anti-thermal regime from 2900-3050 K.

‡For the CRG potential, the fitted range for this boundary is 2000 – 2700 K due to the anti-thermal regime from 2700 – 3050 K.

§The CRG potential only has a Vogel-Fulcher fit from 2600 – 3050 K. Fitting to the 2000-2300 K range gives a prefactor of $0.2 \times 10^{-6} \text{ m}^2/\text{s}$, an activation energy of 0.20 eV, and an R^2 value of 0.9867. For the Basak potential, the fitted range for this boundary is 2000 – 3000 K due to the anti-thermal regime from 3000 – 3300 K.

4.5.2. General Discussion

One of the major criticisms of driven methods (including the curvature-driven method used in this work) of grain growth in MD is that the driving force is much higher than what would typically be observed experimentally. Related to this is the idea that at such high driving forces, the assumptions relating GB velocity to mobility break down. One such assumption is that the driving force acting on the GB should have a linear relationship with the driving force over time ($v \propto F$).

Recently, an experimental analysis of the boundary velocity of several GBs compared to their curvature showed a lack of any correlation [168], though this is likely related to the effects of having multiple GBs (e.g., triple junctions), rather than the simple bicrystals studied in this work. As the driving force in this work is the curvature driving force, the GB velocity should be linearly correlated with the inverse of the grain radius (assuming that changes in GB energy γ are negligible over the inclinations) $v \propto r^{-1}$. To check this, the instantaneous GB velocity was calculated for each snapshot based on the previous and next snapshots, and the grain radius was estimated based on the number of atoms in the embedded grain for each snapshot. Plotting the velocity as a function of the inverse grain radius reveals that the velocity is fairly linear with the inverse radius (and therefore the driving force) for a majority of the simulation (a representative example of this for the Basak potential is shown in Fig. 4.12). Note that toward the end of a simulation (generally the last few data points for a simulation) the linear relationship no longer holds. This could be due to the uncertainty of getting reliable GB velocity and grain radius when the inner grain is very small. Different GB systems maintained the linear relationship for different ranges: for the $\langle 111 \rangle$ rotation axis (not shown), the linear relationship ends at a grain radius of ~ 25 Å for the Basak potential, and ~ 15 Å for the CRG potential (except for the 45° boundary, not shown, which maintained the linear relationship for the duration of grain growth). For the $\langle 100 \rangle$ and $\langle 110 \rangle$ rotation axes the linear relationship is valid for the duration of grain growth with the exception of the last few points as in Fig. 4.12. As the majority of grain growth (from 100 Å to ~ 25 Å in the worst case for the $\langle 111 \rangle$ rotation axis) does have a linear relationship between velocity and inverse radius, and the grain area versus time plots are also linear (see Fig. 4.3), it seems justifiable to assume that the curvature-driven method does not affect the results of this work.

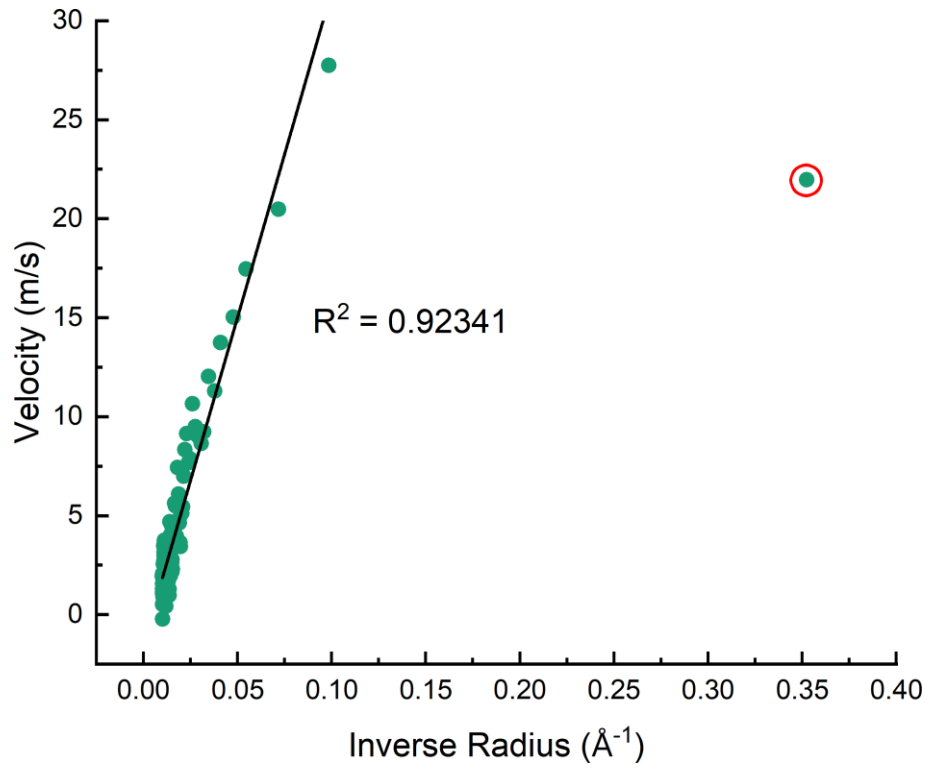


Fig. 4.12. Example of GB velocity as a function of inverse grain radius for the $\langle 100 \rangle$ 20° boundary at 2700 K using the Basak potential. Only at the end of the simulation does the linear relationship break down (circled point).

GBs are known to migrate using a wide variety of mechanisms, yet little is understood about the mechanisms themselves (see for example Ref. [99]). Examination of the atomic displacement (relative to the input structure) throughout the simulation shows the general behaviors of the atoms at the GB. Figures 4.13–4.17 show representative displacements observed across all simulations. Figure 4.13(a) shows a complex shuffle experienced by the $\langle 100 \rangle$ 45° boundary using the Basak potential where there are specific atoms located regularly through the grain that move primarily within the boundary plane (i.e., into or out of the page), and the atoms surrounding these ‘centers’ move alternately toward and away from the center (schematically shown in Fig. 4.13(b)). Such ‘centers’ have been observed in other grain growth simulations, but without the specific behavior observed here [85,99], rather, the atoms around the centers rotate clockwise or counterclockwise. For the $\langle 110 \rangle$ 45° boundary, both the Basak and CRG potentials have most of the motion confined to the embedded grain edges, with some clockwise grain rotation

in the interior (Fig. 4.14). Viewing the vector plot edge-on (not-shown) reveals that the displacement tends to primarily be along the cylinder axis. Because motion in this direction does not directly contribute to the overall boundary motion, this provides another verification of Burke and Turnbull's theory of atomic hops across an interface drive boundary motion [97]. The $\langle 111 \rangle$ 45° boundary (Fig. 4.15) appears to undergo a collective rotational shuffle, where all atoms rotate in roughly the same direction as the embedded grain shrinks. Figure 4.16 shows the $\langle 111 \rangle$ 20° using the Basak potential. Along the edges of the embedded grain (especially during the initial stages of grain growth) the displacement seems to display rotation about a fixed center, similar to [85]. However, a closer look at the atomic displacement along the edge (see inset to Fig. 4.16) reveals that instead of rotating about the fixed centers, the atoms appear to flow around them. As the grain shrinks, the rotational units appear to overlap until the grain rotates as a whole. The general motion of atoms in the embedded grain (counterclockwise motion) is representative of atomic displacements for the $\langle 100 \rangle$ and $\langle 110 \rangle$ 20° boundaries for the Basak potential, and the 20° and 45° boundaries for $\langle 100 \rangle$ and $\langle 111 \rangle$ rotation axes using the CRG potential. Interestingly, the $\langle 110 \rangle$ 20° boundary using the CRG potential (not shown) shows similar 'flow centers' to the $\langle 111 \rangle$ 20° boundary, but with no significant overlapping of these centers. In Fig. 4.17, the displacements for the $\langle 111 \rangle$ 38.20° boundary using the Basak potential are shown. No rotation centers or preferred general grain rotation is present—instead, the atoms appear to collectively shuffle from the embedded grain orientation to the matrix grain orientation (evidenced by the displacements being primarily oriented away from the embedded grain center, or roughly perpendicular to the GB). Such collective displacements might be energetically easier to perform, supporting the idea that misorientations near 38.2° migrate faster. Note that the centers of the grains can show significant motion due to the formation of a small void that is assumed to form due to the grain creation (i.e., atom removal) process.

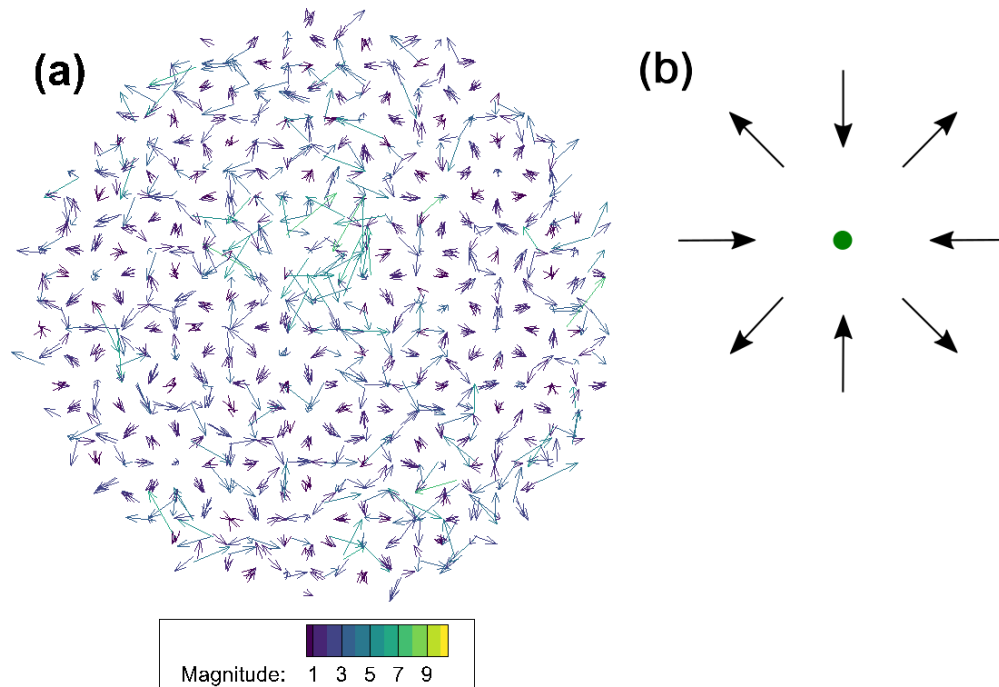


Fig. 4.13. (a) Atomic displacement vector plot, colored by magnitude, for the $\langle 100 \rangle$ 45° boundary at 2800 K using the Basak potential. (b) schematic of the motional ‘units’ in (a), where the centers (marked in green) tend to move either in or out of the plane, and the first nearest neighbors of these centers move alternately toward and away from the center. This circular region in (a) has a diameter of ~ 60 Å and is roughly centered on the embedded grain for ease of visualization.

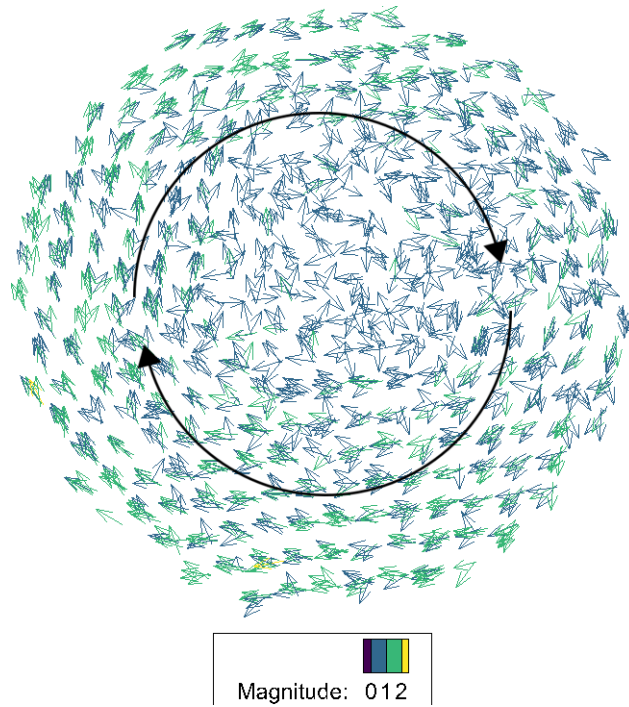


Fig. 4.14. Atomic displacement vector plot, colored by magnitude, for the $\langle 110 \rangle$ 45° boundary at 2800 K using the Basak potential. The general rotation trend is indicated. This circular region has a diameter of ~ 60 Å and is roughly centered on the embedded grain for ease of visualization.

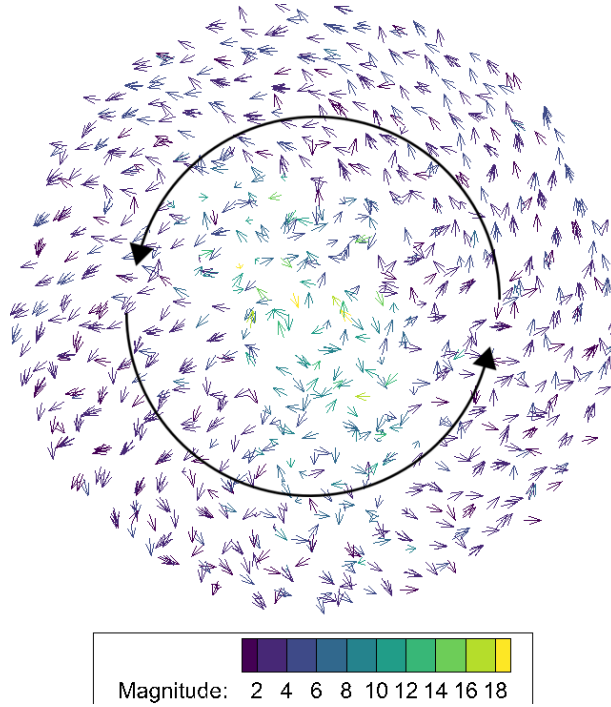


Fig. 4.15. Atomic displacement vector plot, colored by magnitude, for the $\langle 111 \rangle$ 45° boundary at 2800 K using the Basak potential. The general rotation trend is indicated. This circular region has a diameter of ~ 60 Å and is roughly centered on the embedded grain for ease of visualization. Note that the larger displacements at the center of the embedded grain are due to the formation of a small void, which is assumed to form due to the grain creation (i.e., atom removal) procedure.

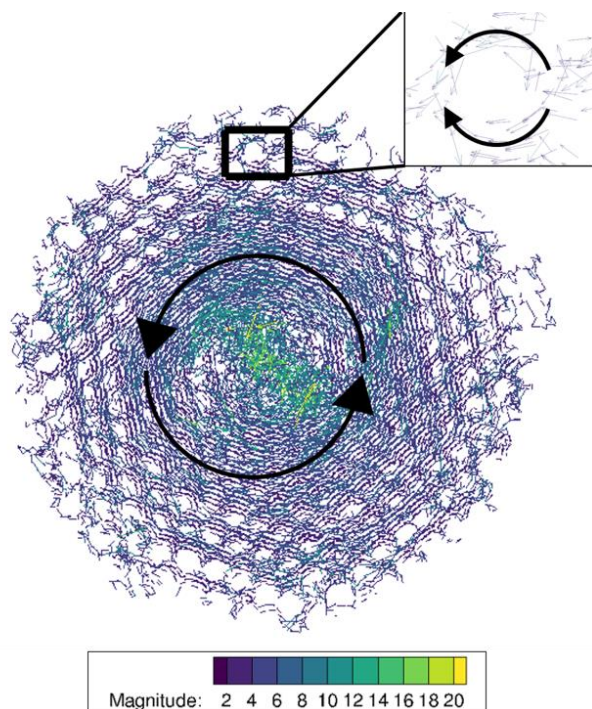


Fig. 4.16. Atomic displacement vector plot, colored by magnitude, for the $\langle 111 \rangle$ 20° boundary at 2800 K using the Basak potential. The general rotation trend is indicated. The inset shows the behavior around 'rotation' centers, showing an apparent diffusion around these central points. As the embedded grain shrinks, these centers overlap, leading to the general rotation behavior indicated. This circular region shows the whole embedded grain (~ 100 Å), while the inset shows the atomic motion around the 'rotation' centers. Note that the larger displacements at the center of the embedded grain are due to the formation of a small void, which is assumed to form due to the grain creation (i.e., atom removal) procedure.

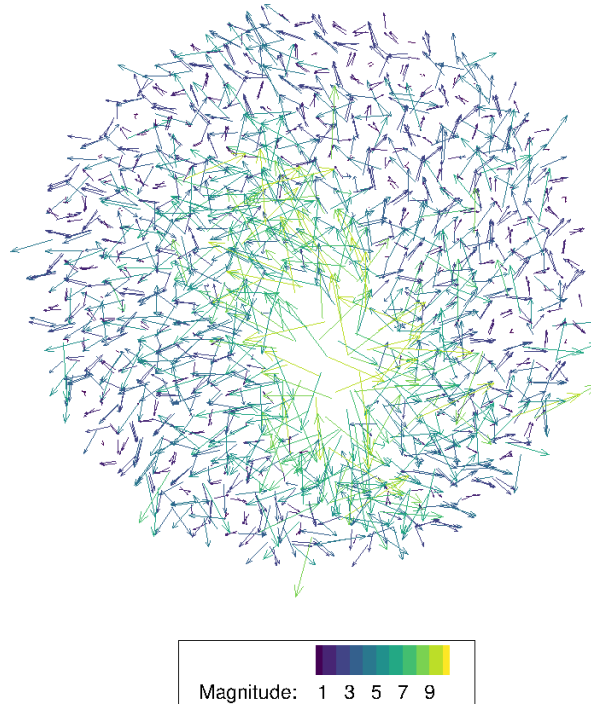


Fig. 4.17. Atomic displacement vector plot, colored by magnitude, for the $\langle 111 \rangle \Sigma 7$ (38.20°) boundary at 2800 K using the Basak potential. This circular region has a diameter of ~ 60 Å and is roughly centered on the embedded grain for ease of visualization. Note that the larger displacements at the center of the embedded grain are due to the formation of a small void, which is assumed to form due to the grain creation (i.e., atom removal) procedure.

Experimentally it has been shown that the $\Sigma 7$ boundary ($\langle 111 \rangle 38.20^\circ$ in this work) migrates the fastest, or is near (e.g., $\langle 111 \rangle 40^\circ$) the fastest in FCC metals [34,78,84]. In this work, while it has been shown that the $\langle 111 \rangle$ rotation axis migrates the fastest (see Fig. 4.4), only for the CRG potential is the $\Sigma 7$ boundary the fastest for a majority of the temperatures examined (Fig. 4.8). For the Basak potential, this boundary is slightly slower than the 45° boundary. This suggests that mobility anisotropy trends may also depend on the interatomic potential. Nevertheless, both potentials predict that the $\Sigma 7$ boundary has a very high mobility among the misorientations examined here, consistent with the experimental observations.

As is typically pointed out in comparisons between MD-simulated GB mobilities and experimentally extracted mobilities, the mobilities calculated in this work are several orders of magnitude higher (see Ref. [31]). Comparison with other computational works (e.g., Ref. [36])

reveals similar discrepancies. Further research is needed to fully explain the discrepancies between computationally and experimentally extracted GB mobilities. Recent studies on GB mobilities in polycrystalline iron [169] have identified that factors other than the GB character (e.g., triple junction drag [170]) appear to play a more significant role in the overall mobility of the respective boundary, though a similar analysis of nickel reveals exactly the opposite result, namely that there is a strong correlation between boundary velocity (and therefore GB mobility) and GB character [168]. This work seeks to provide GB mobility data for individual boundary motion without the triple junction effect as in polycrystal grain growth experiments. Further research is needed to examine how GB networks change individual GB behaviors.

4.6. Conclusions

In this work, GB mobilities in UO_2 were calculated using the shrinking cylindrical grain method using two interatomic potentials (Basak and CRG) with rotation axes of $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ and up to three misorientations per axis. The general trend is that the $\langle 111 \rangle$ rotation axis has the fastest mobility values, and the $\langle 110 \rangle$ has the lowest ($M_{111} > M_{100} > M_{112} > M_{110}$), consistent with the planar density argument given in Chapter 3 and also Ref. [49]. Both an Arrhenius and a VF fit have been performed on the mobility data, with the VF giving a better quality fit in nearly all cases due to the distinct curvature present in nearly all the results. The $\langle 111 \rangle$ rotation axis is observed to have distinct anti-thermal behavior across a variety of temperatures depending on the misorientation. The reason for this anti-thermal behavior is likely due to the more disordered GB structure at high temperatures, which changes the preferred atomic motion across the GB plane. Another finding of this work is a further confirmation that the interatomic potential plays a significant role in GB mobility, emphasizing the need to use an interatomic potential designed for studying GB properties. The Basak potential maintains the same mobility trend across nearly the entire temperature domain, while the CRG potential has at least two trends depending on the temperature. Furthermore, the anti-thermal behaviors are present across different temperatures, depending on the potential.

Chapter 5. Grain Boundary Mobility in the UMo System

This chapter is intended for journal publication, the submission process of which is ongoing.

5.1. Abstract

Ongoing research into alternatives to highly enriched uranium fuels has highlighted uranium-molybdenum (UMo) as an ideal candidate for its body-centered cubic crystal structure, high thermal conductivity, and stable fission gas bubble behaviors. Microstructural properties such as grain boundary mobility now need to be studied in more depth to facilitate accurate models of this material to use in fuel performance modeling. This work examines the grain boundary mobility anisotropy trends in the UMo system and compares them to previously calculated metallic γ U results described in Chapter 3. At concentrations below 5at.% Mo, the anisotropy relationship of pure γ U is maintained, but at higher concentrations, there are significant changes due to the effects of solute drag. Furthermore, the relationship between interstitial diffusion and GB mobility as a function of Mo solute concentration suggests that interstitial diffusion has a greater contribution to GB motion than vacancy diffusion.

5.2. Introduction

To reduce nuclear proliferation, current U.S. high-performance research reactors (USHPRR) are in the process of shifting from highly enriched uranium (HEU) fuel to low-enriched uranium (LEU) fuel [50,51,171]. One of the proposed fuel alternatives is a uranium-molybdenum (UMo) alloy with Mo concentrations ranging from 7–10wt% (corresponding to 15.7–21.6at.%). This alloy is favorable because of the metastability of the desired BCC γ U phase at reactor operating temperatures [54], phase reversion process (where the γ U phase is stabilized via fission) [172], high thermal conductivity [41,60,173], and stability against breakaway swelling [54,57,172]. Studies of this material have covered a wide range of topics; however, limited work has been done to understand how the Mo content influences its grain growth kinetics, particularly concerning grain boundary (GB) mobility and its anisotropy. As discussed in Chapter 3, the initial grain size and its evolution can significantly affect the fuel performance properties of a UMo fuel such as fission-gas-induced swelling. In the context of microstructural evolution, it is observed that Mo in UMo fuels tends to segregate away from a GB [174]. Beeler *et al.* [77] posit that the reason for this desegregation tendency is the lower interfacial energies of pure U relative to pure

Mo. Other than this, no information is available on the explicit relationship between the Mo concentration and GB mobility, to the best of the author's knowledge. Thus, this work will examine how various concentrations of Mo impact GB mobility and its anisotropy in the γ U system.

As described in Chapter 3 and also in Ref. [49], the present author and his collaborator have examined GB mobility anisotropy in the pure γ U system using molecular dynamics (MD) simulations and found that $\langle 110 \rangle$ tilt GBs tend to migrate the fastest based on a planar density argument. In summary, for a given GB, the density of the plane perpendicular to the GB plane and also the tilt axis is a significant contributor to the anisotropy trend, with the highest density plane—for example, (110) for the BCC crystal structure, and (111) for the FCC (and its derivative fluorite) crystal structure—associated with the fastest moving GBs. This argument has been demonstrated in Chapter 3 for BCC γ U and Chapter 4 for FCC-based fluorite UO_2 . This provides a clear baseline for understanding GB mobility trends in the γ U system, but the effects of solutes on mobility trends, particularly for Mo, remain unknown. Solutes (or impurities) in a GB system have long been known to have a significant effect on GB mobility [175] through processes such as solute drag and Zener pinning. Solute drag has been studied extensively over the last several decades, including the original works of Cahn and Lücke and Stüwe [176,177]. Recently, solute drag has been found to be both misorientation- and rotation-axis-dependent [178], though the specific relationship between GB character and solute drag has not been elucidated. This work thus seeks to utilize MD simulations to examine the solute drag effect using UMo as a model system to determine the following: (1) if the anisotropy relationships established in Chapter 3 and Ref. [49] still hold in the presence of solutes and (2) if there is a distinct relationship between the solute concentration and the magnitude of the impact on GB mobility.

5.3. Methods

Similar to Chapters 3 and 4 as well as in literature [49,88], this chapter utilizes the curvature-driven grain growth technique to study the GB mobility trend for the UMo system. As a simple overview, the initial GB structure is generated by creating a block of pure BCC γ U with the Z-axis of the block oriented along the desired rotation axis and then rotating all atoms within a distance r_{grain} from the center of the simulation block by the desired misorientation angle, θ (see Fig. 5.1). This research uses the [001], [110], and [111] directions in the crystal (hereafter referred to as the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ rotation axes) and misorientations of 20°, 30°, and 45° to be

consistent with previous analyses of pure γ U in Chapter 3 and also Ref. [49]. After the embedded cylindrical grain is rotated, any pairs of overlapping atoms (where atoms closer than ~ 2.1 Å are considered overlapping) have one of the paired atoms removed. This pure U structure is then annealed at 1100 K for 20 ps to relax the structure, and the resulting system is used as the input for all subsequent simulations. Solute (Mo) atoms are substituted for solvent (U) atoms on a per-simulation basis to get a better statistical representation of the solute effect on GB mobility. The solute concentration ranged from 1–21at.% Mo (0.4–9.6wt% Mo). For convenience, here the U-10at%Mo is denoted as U10Mo, although in literature such a notation typically refers as weight percent. Table 5.1 contains the number of atoms and dimensions of the input structures used in this work.

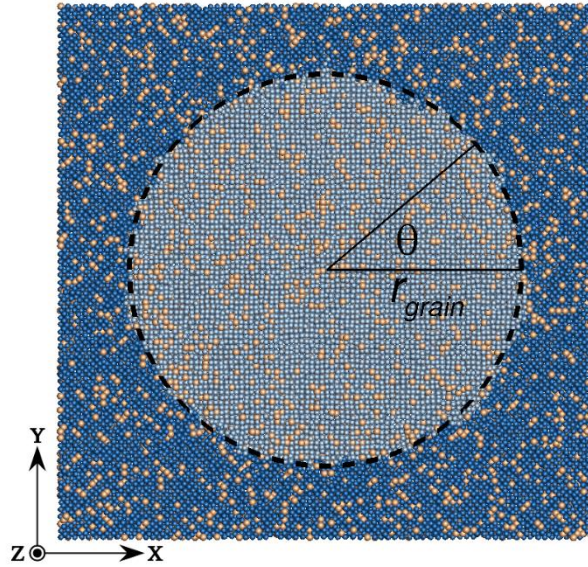


Fig. 5.1. Schematic of GB creation. Atoms located within $r_{\text{grain}} = 100$ Å from the center of the simulation cell are rotated by the desired misorientation angle θ . The Z axis (out of the page) is aligned along one of the rotation axes specified in this work. Atoms are colored by grain (light/dark blue), while solute atoms are colored separately (orange).

Table 5.1. System information for the nine input structures. System dimensions are given in Å. For the <100> systems, the X direction is [100] and the Y direction is [010]; the <110> systems have [001] for the X direction and $[1\bar{1}0]$ for the Y direction; the <111> systems have $[1\bar{1}0]$ for the X direction and $[11\bar{2}]$ for the Y direction.

GB system	System domain (Å)	Number of atoms
<100> 20°	$265 \times 265 \times 17.7$	55960
<100> 30°	$265 \times 265 \times 17.7$	55900
<100> 45°	$265 \times 265 \times 17.7$	55990
<110> 20°	$265 \times 265 \times 20$	63448
<110> 30°	$266 \times 250 \times 25$	74590
<110> 45°	$266 \times 250 \times 25$	74615
<111> 20°	$264 \times 268 \times 18.4$	58764
<111> 30°	$265 \times 268 \times 18.4$	58896
<111> 45°	$264 \times 268 \times 18.4$	58731

All simulations were performed using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software [46]. The interatomic potential used is an embedded atom potential (EAM) that describes the UMoXe ternary system [91] (and the relevant unary and binary systems), though only the U and Mo portions of the potential are utilized here. This potential was designed to examine irradiation-induced defect formation and the subsequent evolution of those defects. The predicted mechanical properties align well with experimental values, thus making this potential a good fit for examining the GB migration behavior.

Simulations ran for 8 ns or until the embedded grain disappeared. During the simulations, snapshots were saved periodically every 20 ps (see Fig. 5.2) and the mean-squared displacement (MSD) of U and Mo atoms individually and collectively was tracked for later analysis. Similar to the previous two Chapters, GB mobility was calculated based on the typically assumed form $v = M \times F$, where v is the boundary velocity, M is the mobility, and F is the driving force. The driving force in the cylindrical GB system is the curvature driving force, represented here as $F = \gamma \kappa$, where κ is the instantaneous GB curvature ($1/r$) and γ is the GB energy. An alternative

formulation of the mobility relationship that factors out the effects of GB energy is $v = M^* \kappa$, where $M^* \equiv M\gamma$ is the reduced GB mobility [146]. By rearranging the equation and solving for M^* , a relationship between the shrinkage rate of the cross-sectional area of the grain (A) and M^* is found: $M^* = \frac{1}{2\pi} \frac{dA}{dt}$. Thus, calculating GB mobility requires extracting the slope of the area-versus-time plot for the embedded grain. The cross-sectional area of the embedded grain was determined via the number of atoms in the embedded grain. Atoms were assigned to either the matrix grain or the embedded grain using the method developed by Ulomek *et al.* [47], which assigns an atom to a grain based on the orientation of the atoms within a cutoff distance from a central atom and is based on classical diffraction theory. This method has been successfully used previously [49] and clearly differentiates between the matrix grain and the embedded grain (see Figs. 5.1 and 5.2 for examples). Each snapshot was analyzed to determine the number of atoms in the embedded grain and, subsequently, the cross-sectional area of the grain, which area was then plotted as a function of time. Figure 5.3 shows several representative examples of the area-versus-time plot, demonstrating the various behaviors observed herein. Due to the solute drag effect, the area-versus-time plot was often found to have a non-linear behavior. The slope was therefore determined based on the following criteria:

- If the embedded grain completely disappeared during the simulation, the slope was fitted to all points up until the grain disappeared (see Fig. 5.3 line (a)).
- If the embedded grain did not completely disappear, the slope was fitted to all data points over the simulated time (see Fig. 5.3 lines (b) and (c)).

This approach loses some of the detail of the grain growth in favor of calculating the average behavior. In general, this approach gives a good approximation of GB mobility without significant compromise on specific behaviors.

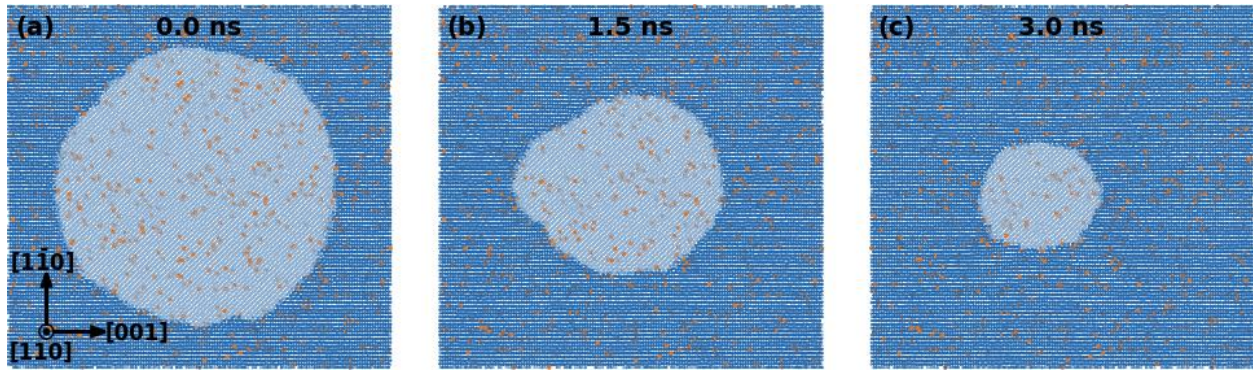


Fig. 5.2. Example of grain growth using the cylindrical grain growth method. This shows the top-down view of a $\langle 110 \rangle$ 45° U1Mo system at 1050 K (a) as the initial structure after relaxation, (b) during grain growth, and (c) near the end of the simulation. Atoms are colored by grain (light/dark blue), with solute atoms colored separately (orange).

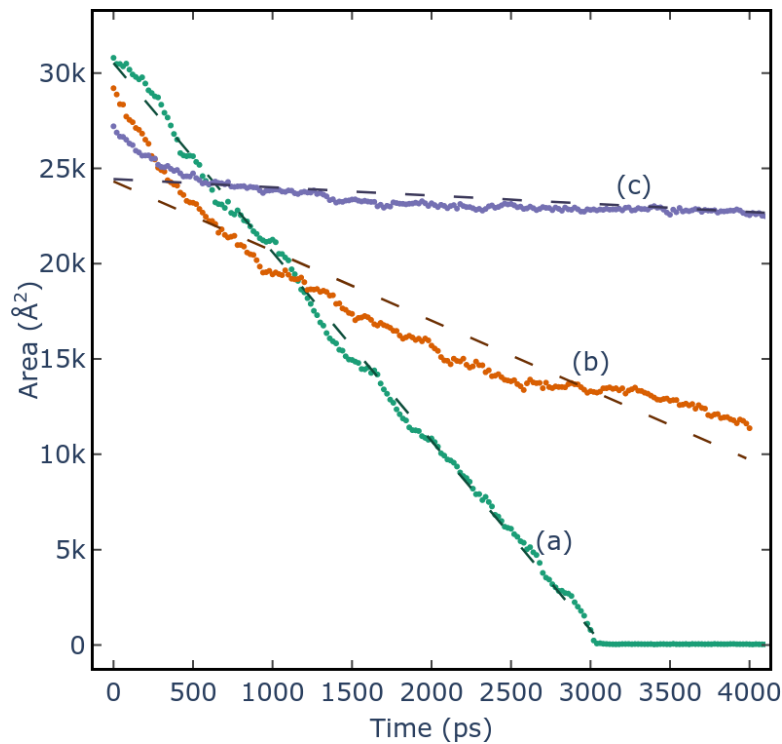


Fig. 5.3. Representative examples of area-versus-time plots with the relevant fitted slopes represented as dashed lines. Throughout this work, slopes are fitted to the entirety of the grain growth regime to get the average behavior. (a) $\langle 100 \rangle$ 20° U3Mo at 1200 K. (b) $\langle 111 \rangle$ 30° U10Mo at 1300 K. (c) $\langle 110 \rangle$ 45° U21Mo at 1150 K.

Calculation of the cross-sectional area of the grain was performed using the relationship $A = V * N / L_z$, where $V = a^3 / 2$ (a is the temperature- and concentration-dependent lattice parameter), N is the number of atoms in the embedded grain, and L_z is the height of the simulation cell (scaled in the same manner as a). Several independent simulations of a 10x10x10 cell determined this dependence using temperatures varying from 300–1600 K and concentrations varying from 0–99at.% Mo. The parameters used to define the temperature- and Mo concentration-dependent lattice constant (a) are provided in Table 5.2 and are fitted to the cubic polynomial:

$$a = a_1c^3 + a_2c^2 + a_3c + a_4T^3 + a_5T^2 + a_6T + a_7cT + a_8cT^2 + a_9c^2T + a_0 \quad (3.1)$$

Here, c is the Mo concentration in atomic percent and T is the temperature in Kelvin. Once the area was determined as a function of time, the slope, dA/dt , was extracted to calculate GB mobility. Three independent simulations ran for each condition. A GB mobility value was determined only if the reduction in grain area was at least 25% of the initial area (corresponding to the GB migrating ~ 13 Å). The presented mobility values are arithmetic averages of the calculated mobilities for each simulation run. Standard errors are calculated and displayed in the following plots, but in many cases, the error bars are too small to be seen.

Table 5.2. Temperature- and concentration-dependent lattice parameter equation (Equation (3.1)) coefficients.

Parameter	Value	Parameter	Value
a_1	-0.19487	a_6	-1.932e-5
a_2	0.52414	a_7	9.597e-5
a_3	-0.72744	a_8	-83145e-9
a_4	-1.053e-12	a_9	-6.670e-5
a_5	1.408e-8	a_0	3.547

5.4. Results and Discussion

5.4.1. Grain Boundary Mobility versus Temperature

Plotting GB mobility as a function of temperature on an Arrhenius plot (see Fig. 5.4 for the 30° trends—the other misorientations have similar trends) reveals Arrhenius kinetics appears to accurately capture the behavior of GB mobility in the UMo system across the range of Mo concentrations examined. Therefore, the fitted activation energies and mobility prefactors are tabulated in Appendix A, with the activation energies plotted as a function of Mo concentration in Fig. 5.5. Three types of behavior are shown in Fig. 5.5: (1) a near-monotonic increase in activation energy with Mo concentration ($\langle 100 \rangle$ and $\langle 110 \rangle$ 20° boundaries), (2) an increase in activation energy up to a maximum, then maintaining that value ($\langle 100 \rangle$ and $\langle 110 \rangle$ rotation axes with 30° and 45° misorientations), and (3) an increase in activation up to a maximum followed by a decrease ($\langle 111 \rangle$ 20°, 30°, and 45° boundaries). Experimental evidence [175,179,180] and solute drag theory generally [176,177,181,182] account for (2) and (3), where the maximum value is associated with the solute saturating the GB, although the average bulk concentrations examined in these works are several orders of magnitude smaller than what is presented here. However, the local solute concentration at GBs in these works can be a few orders of magnitude higher than the average bulk concentration due to the GB segregation effect. Behavior (1) has been observed experimentally [34] in lead (doped with both silver and gold) and aluminum (doped with silver), and in simulation using a Cu-Ag alloy [183]. However, this behavior seems to be the exception rather than the rule and could be related to the idea that the specific boundary has not yet reached its saturation point.

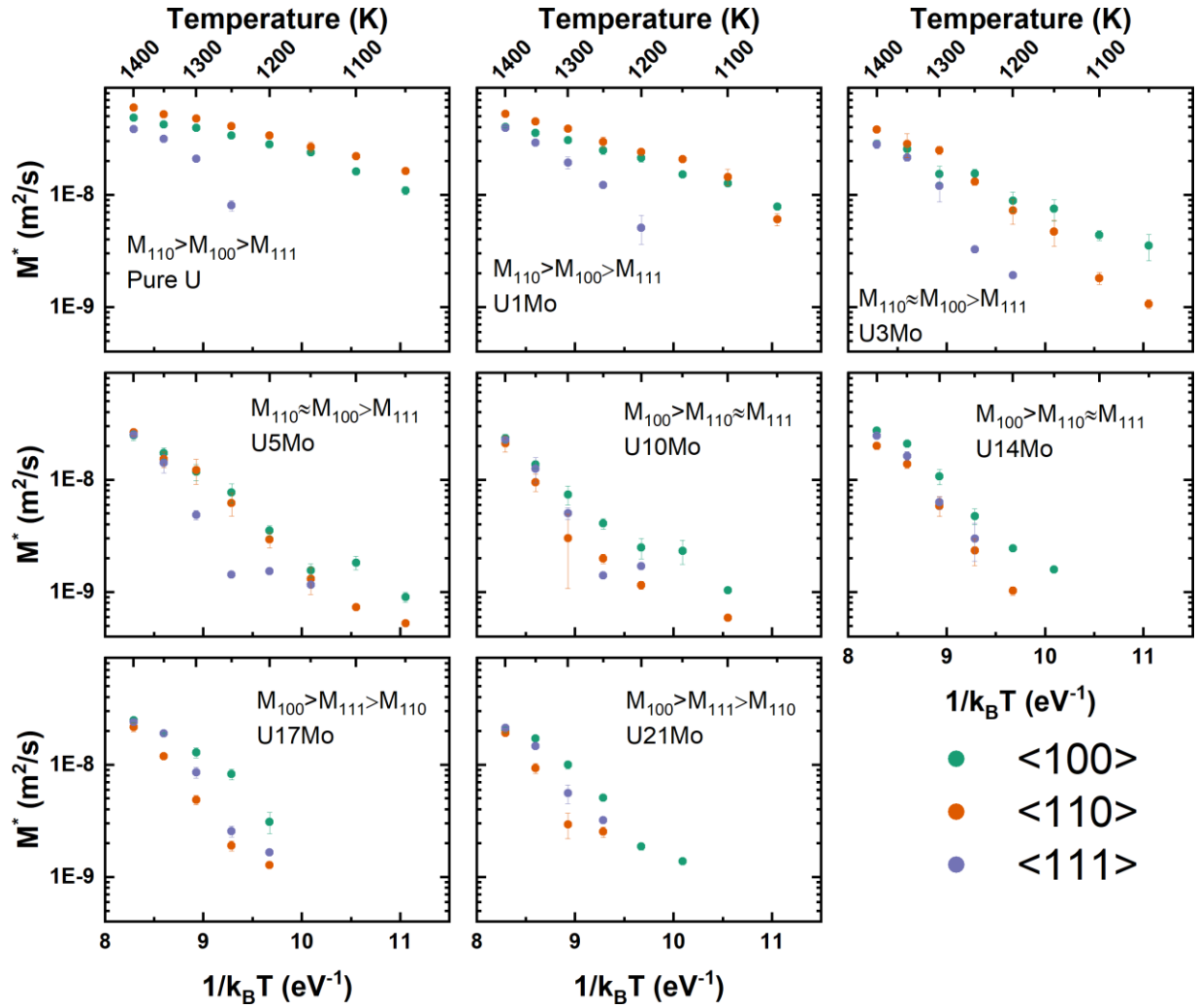


Fig. 5.4. Representative example of Arrhenius plots for the UMo system. This shows the results of the 30° misorientation—trends for the 20° and 45° misorientation are similar. Each subplot has the mobility anisotropy trend and Mo concentration indicated. Error bars indicate the standard error; note that some data points do not have error bars because two of the three simulation runs did not result in sufficient grain growth. Also note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The data in (a) is taken from [49] for the pure γ U case for reference. Solute (Mo) concentrations are as follows: (a) 0at.% (pure U), (b) 1at.%, (c) 3at.%, (d) 5at.%, (e) 10at.%, (f) 14at.%, (g) 17at.%, (h) 21at.%.

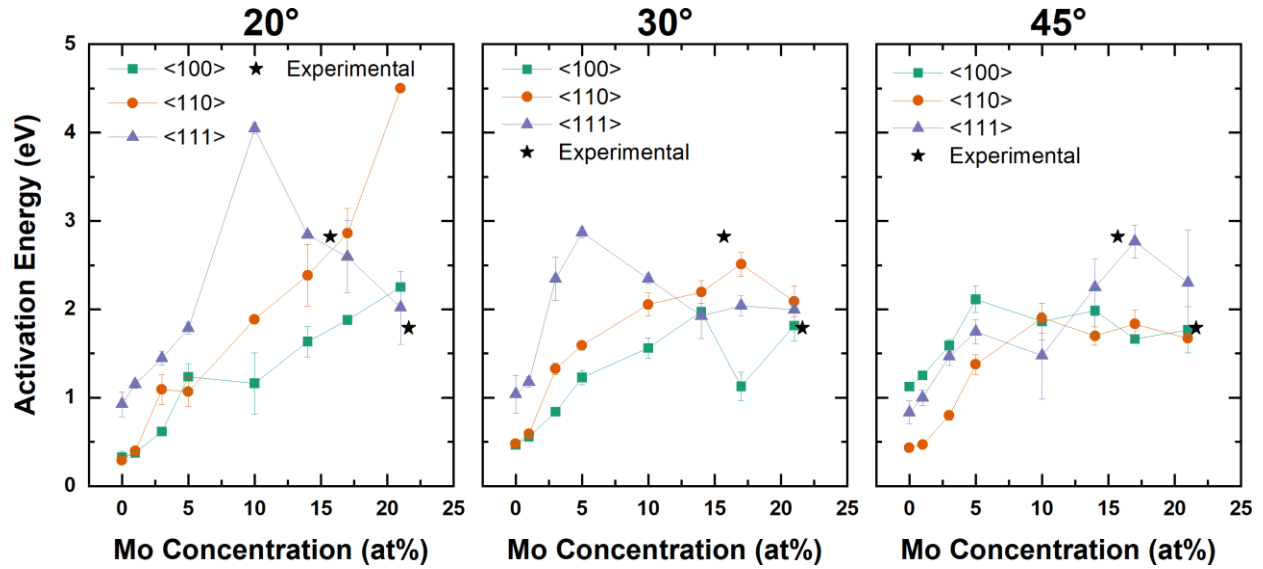


Fig. 5.5. Activation energy as a function of Mo concentration for the boundaries examined in this work. Error bars indicate standard error. The lines are guides to the eye. Experimental values are taken from Frazier *et al.* [16].

Figure 5.5 includes (the only) two experimental determinations of GB mobility activation energy from Refs. [10,16]. Frazier *et al.* [16] noted the large discrepancy between the measured activation energies, indicating that the reason for the discrepancy was unknown. While the experiments extracted the activation energies for grain growth from a polycrystalline system (compared to the bicrystal systems examined in this work), the values appear to match the calculated activation energies for both Mo concentrations across each misorientation. This suggests that the noted discrepancy could be due to the difference in Mo concentrations, although there could be many other factors for causing this observation. Additionally, this gives some support to the idea that the large discrepancy in activation energies between experimental and computational works in pure materials could be due to the solute or impurity drag effect, as the activation energy of pure U is much lower than in UMo alloys as shown in Fig. 5.5. It should be noted that the samples used in experiments could contain additional impurities in addition to the solute Mo.

Further examination of mobility as a function of temperature reveals that the mobility anisotropy trend identified for pure BCC U in Chapter 3 and also Ref. [49] does not hold for Mo

concentrations higher than 5at.%. In [49], the authors identified a mobility trend of $\langle 110 \rangle$ tilt boundaries in BCC U as the fastest based on the planar density argument. Figure 5.4 shows that this trend is maintained only with Mo concentrations less than or equal to 5at.%. At solute concentrations higher than 5at.%, mobility anisotropy seems to vanish because the mobilities for different tilt axes are similar. Although it appears that the $\langle 100 \rangle$ rotation axis has slightly faster mobilities than the other two axes, the differences could be induced by the stochastic effect as well as the uncertainty in extracting GB mobility.

To determine if the change in the anisotropy trend is specific to the interatomic potential, several additional simulations examined the GB mobility of the 45° boundary for the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ rotation axes using an angular-dependent potential (ADP) for the UMo system [89]. Temperatures of 1050, 1200, and 1300 K were used. For pure U, the ADP potential predicts a melting temperature of ~ 1330 K, hence the lower maximum temperature for the mobility simulations. Note that the addition of Mo solutes to the γ U system increases the melting temperature, which is the primary reason for the disappearance of the anti-thermal behavior which was previously observed in [49] for the ADP potential. Figure 5.6 shows the results of these simulations. While there are some minor changes in the anisotropy trend with increasing Mo concentration using this potential, the trend does not change as significantly as in the EAM potential used above; in all cases, the $\langle 111 \rangle$ rotation axis was the slowest. However, it should be pointed out that the mobility anisotropy predicted by the ADP potential is much smaller, even in pure U. Therefore, the solute effect on anisotropy, if it exists, is small as well. This could be one reason why the ADP potential seems to have different behavior from the EAM potential. Another possible reason for the difference in these two potentials is that the ADP potential was developed with a different focus than the EAM potential. The ADP potential was developed specifically with a focus on properly representing the intermediate phases between the BCC γ phase and the orthorhombic α phase [89], while the EAM potential concentrated on examining defect evolution in UMo, especially in the presence of fission gases [91]. Additionally, it has been demonstrated that the EAM potential incorrectly describes self-diffusion behavior by significantly overestimating the diffusivity [107]. (Note that the ADP potential described in [107] is different from the ADP potential used here.) While these reasons may impact the overall mobility anisotropy relationship, the solute drag effect is likely the most important reason for the change in anisotropy.

Solute drag (F_{drag}) can be represented in the grain growth relationship as $v = M_0(F - F_{drag})$ [182,184]. The postulated reason for the change in the anisotropy trend is that the F_{drag} term becomes more important than the driving force term (F) at a certain critical concentration. In this case, the solute-drag effect dominates mobility and overpowers the GB character effect (i.e., mobility anisotropy). In the case of the EAM potential, the critical concentration appears to be around 10at.% Mo. The results from the ADP potential also appear to change around 10at.% Mo, though the changes are far less dramatic.

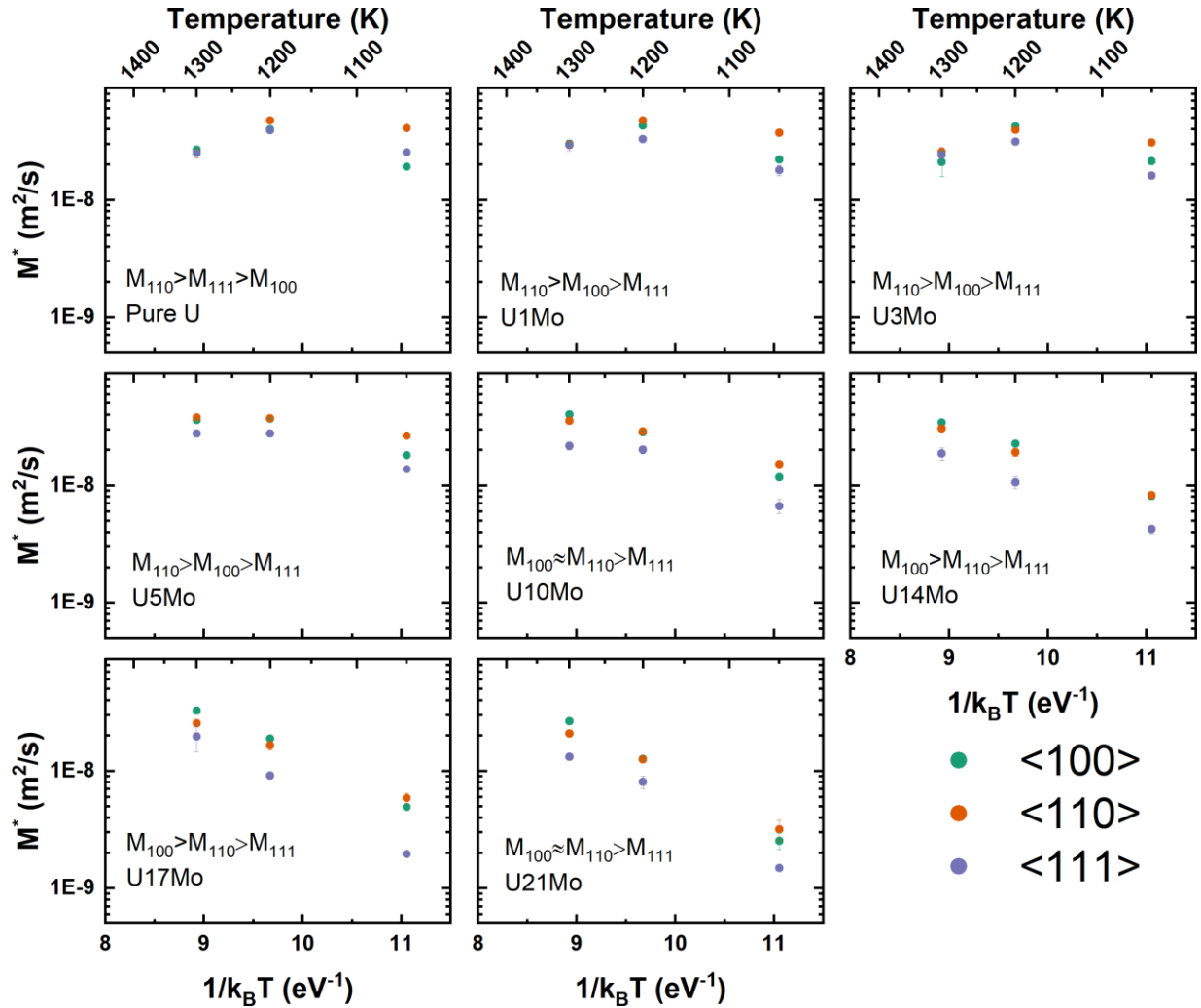


Fig. 5.6. GB mobility anisotropy presented as a function of concentration for the 45° misorientation using the ADP potential. The mobility anisotropy trend is indicated in each subplot. Error bars indicate the standard error but are often too small to be seen on this scale. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The data in (a) is taken from [49] for comparison. Solute (Mo) concentrations are as follows: (a) 0at.%, (b) 1at.%, (c) 3at.%, (d) 5at.%, (e) 10at.%, (f) 14at.%, (g) 17at.%, (h) 21at.%.

As demonstrated in this section, grain growth in the presence of solutes results in a change (usually a decrease) in GB mobility. Solute drag is usually described as solutes lagging behind the GB due to the boundary moving faster than the solute can diffuse. One argument for why this

decrease occurs is that solutes cluster together, which in turn drags the GB near the cluster. This has been observed in a simulation of a Cu-Ag alloy [183]. In the UMo system, experimental evidence shows that Mo both desegregates from the boundary and forms Mo-rich bands [174]. It has been shown that the desegregation behavior occurs due to the lower GB energies in pure γ U compared to pure Mo [77]. However, this work does not show any apparent clustering behavior. One possible reason for this is that the timescales required for Mo atoms to cluster together are much larger than is easily accessible in these MD simulations. Of particular note, the desegregation tendency of Mo was determined by Beeler *et al.* using the hybrid Monte Carlo/Molecular Dynamics (MC/MD) simulation method, with comparatively much smaller systems (3000–6500 atoms) [77]. Examination of the radial distribution frequency (RDF) of the U-Mo and Mo-Mo bonds before and after the GB sweeps through a region (not shown) reveals no significant changes, suggesting that (at least in this potential, for these Mo solute concentrations) there is no clustering tendency. This is consistent with the experimental heat of mixing curve in UMo [185], which is negative below $\sim 17\text{at.}\%$, indicating a preference for unlike bonds (no clustering), but is at odds with the heat of mixing curve calculated for this potential. The heat of mixing curve for the EAM potential (not shown) is entirely positive across all Mo solute concentrations, and this indicates a preference for like bonds (or clustering behavior). In comparison, the heat of mixing curve for the Cu-Ag system is also entirely positive [186], which supports the formation of clusters and was observed in simulation [183]. Despite the similarity between the heat of mixing curves for the UMo and Cu-Ag systems, no similar clustering tendencies were observed, indicating that other factors (such as, for example, the diffusivity of the solute in the GB region) play a larger role in overall clustering behavior.

5.4.2. Grain Boundary Mobility versus Concentration

Figure 5.7 shows GB mobility plotted as a function of Mo concentration to examine how Mo concentration impacts GB mobility. Up to a concentration of 5at.% Mo, GB mobility decreases nearly linearly with increasing Mo concentration. The $\langle 100 \rangle$ 20° boundary has an interesting exception, where 1at.% Mo is faster than pure U. Examining the MSD in the XY-direction of the pure U, U1Mo, and U3Mo cases (see Fig. 5.8 for representative examples at 1400 K) reveals that the U1Mo system has consistently lower MSD compared to the pure U and U3Mo systems, which suggests a lower mobility. In fact, the trend suggested by Fig. 5.8 ($\text{MSD}_{\text{U1Mo}} < \text{MSD}_{\text{PureU}} < \text{MSD}_{\text{U3Mo}}$) is exactly the opposite of what is shown in Fig. 5.7

($M_{\text{U1Mo}} > M_{\text{PureU}} > M_{\text{U3Mo}}$). This MSD trend is consistent from 1150 K up to 1400 K, while at 1050–1100 K, the MSD trend is $\text{MSD}_{\text{PureU}} < \text{MSD}_{\text{U1Mo}} \approx \text{MSD}_{\text{U3Mo}}$. Calculation of the GB diffusion coefficients in the XY direction for pure U, U1Mo, and U3Mo reveals that the activation energies seem inversely related to the mobility-versus-concentration trend: $Q_{\text{U1Mo}}^{\text{GB}} < Q_{\text{PureU}}^{\text{GB}} < Q_{\text{U3Mo}}^{\text{GB}}$, where $Q_{\text{U1Mo}}^{\text{GB}} = 0.76$ eV, $Q_{\text{PureU}}^{\text{GB}} = 0.77$ eV, and $Q_{\text{U3Mo}}^{\text{GB}} = 0.93$ eV. This lower activation energy suggests that motion in the XY direction is easier for the U1Mo system compared to pure U and U3Mo, which matches the observed trend in Fig. 5.8, although the activation energy in U1Mo is only slightly lower than pure U. There is some experimental evidence of accelerated GB motion in the presence of a small amount of solute in an Al-Ga system [187] and in the CeO_2 [188] and Y_2O_3 [189] oxides. Molodov *et al.* [187] found that Al doped with a small amount (10 ppm) of Ga resulted in accelerated GB motion by approximately an order of magnitude in $\langle 111 \rangle$ tilt boundaries with misorientations of 38.2° and 40.5° . However, it is unclear if the accelerated GB mobility is applicable beyond these GBs. They argued that the reason for this change is due to a change in GB structure—specifically the formation of a second, liquid-like phase at the GB. Later analysis of this phenomenon bears out this reasoning for the Al-Ga system [184]. In the oxide systems [188,189], the accelerated behavior was a general pattern of a polycrystalline microstructure (characteristic of all GBs, not just a select few) and was explained as one of two reasons. In Y_2O_3 , acceptor dopants accelerate GB mobility because they increase oxygen vacancies (related to the binding energies of dopants to defects), which in turn accelerates cation interstitial diffusion [189], while in CeO_2 , severely undersized dopants result in large lattice distortions which likely increases defect diffusion [188]. In this work, the increased defect concentration due to the charge compensation effect in oxides cannot happen here as the U1Mo is an alloy. The formation of a second phase at the GB is unlikely for at least two reasons. First, solute Mo atoms tend to segregate away from the GB [77,174], theoretically leading to the GB being mostly pure U, though this would occur over much longer timescales than is possible to examine in this work. Second, at the temperatures examined here for the U1Mo system, the BCC γ -(U, Mo) phase is the only stable phase [58,190]. Building off of the first point, the formation of the U_2Mo intermetallic (the only other stable phase in this temperature range, but requiring a much larger Mo concentration) at the GB is unlikely again because of the Mo desegregation behavior. Additionally, forming the intermetallic would require significant enrichment not possible in the U1Mo simulated structure.

Even if a second phase forms, it does not mean mobility will increase. Solute-defect binding energies in the UMo alloy system are unknown, making it unclear what impacts (if any) would be present. Large lattice distortions are possible because of the large lattice size difference between γ U (3.542 Å) and Mo (3.1474 Å). However, examination of the snapshots does not reveal significant distortion, nor does the radial distribution frequency (not shown) reveal any significant changes from the expected BCC structure. Furthermore, examination of the hydrostatic stress per atom does not reveal any large localized compressive or tensile stresses. In summary, the reason for the accelerated $\langle 100 \rangle$ 20° boundary in the U1Mo alloy system is unclear, though there is some support for structure-related impacts.

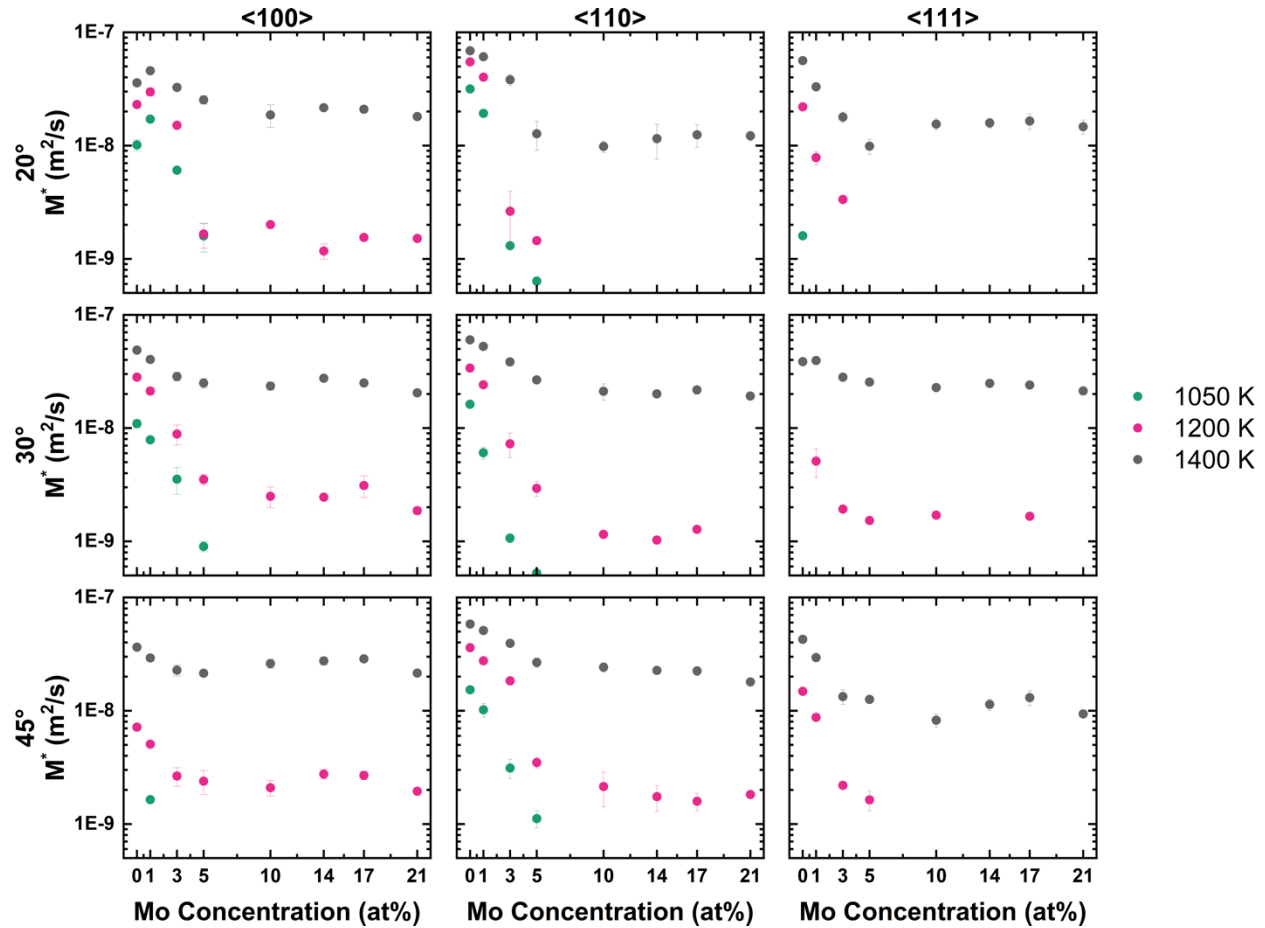


Fig. 5.7. GB mobility as a function of Mo concentration at 1050 K, 1200 K, and 1400 K. Error bars indicate the standard error but are usually too small to be seen on this scale. Columns indicate the rotation axis (left: $\langle 100 \rangle$, middle: $\langle 110 \rangle$, right: $\langle 111 \rangle$) and rows indicate misorientation (top: 20°, middle: 30°, bottom: 45°).

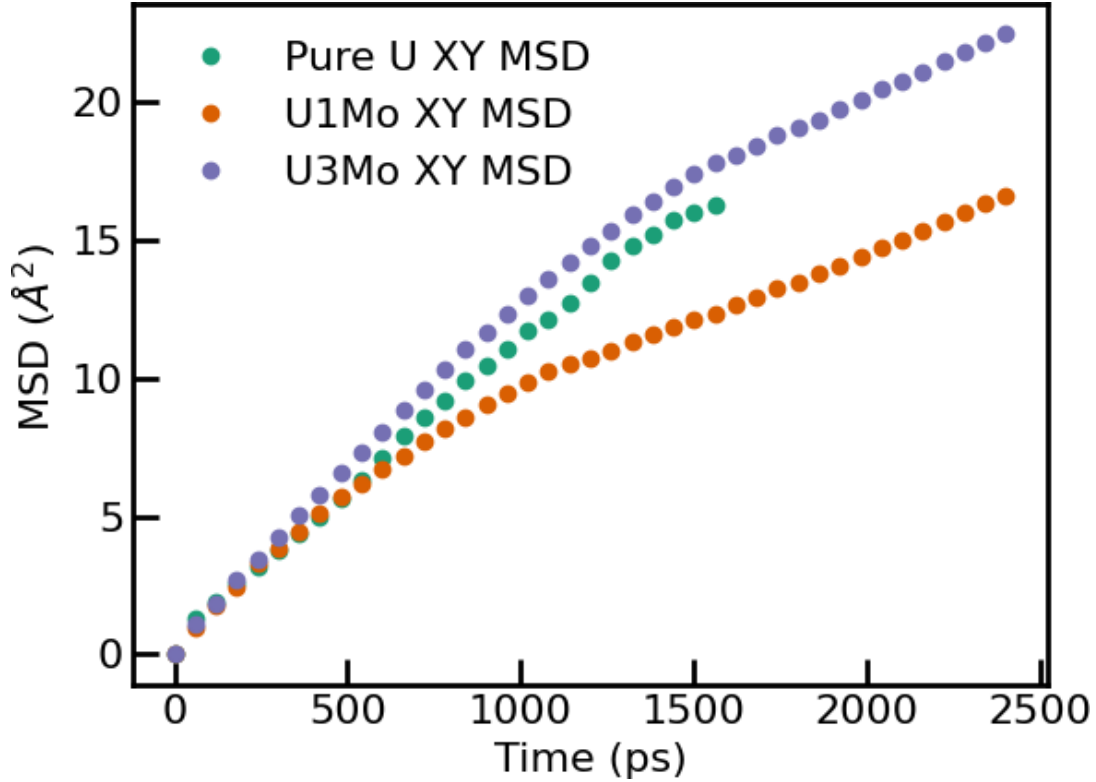


Fig. 5.8. Average MSD (calculated via three independent simulations per system) in the XY plane of the $\langle 100 \rangle$ 20° GB for pure U, U1Mo, and U3Mo at 1400 K. The trends from 1150 K up to 1400 K are nearly the same, while 1050–1100 K (not shown) have Pure U with the lowest MSD.

Figure 5.7 shows that irrespective of rotation axis or misorientation, there is an apparent saturation effect, where increasing Mo concentration above 5–10at.% no longer decreases GB mobility. Ref. [49] argues that $\langle 110 \rangle$ tilt GBs in BCC materials are expected to migrate the fastest based on a planar density argument, where the density of the plane normal to the GB largely determines the mobility anisotropy trend. Figure 5.7 shows that this argument does not hold in the presence of solutes—at the highest solute concentrations, the $\langle 110 \rangle$ rotation axis is generally the slowest. This can be seen clearly by replotting the mobility of the three rotation axes on the same plot, as in Fig. 5.9 for the three misorientations examined in this work at 1400 K. At low Mo concentrations, the $\langle 110 \rangle$ rotation axis has the highest mobility for all three misorientations. At 10at.% Mo for the 20° and 30° boundaries, it has the lowest. The $\langle 111 \rangle$ rotation axis is consistently the slowest for the 45° misorientation.

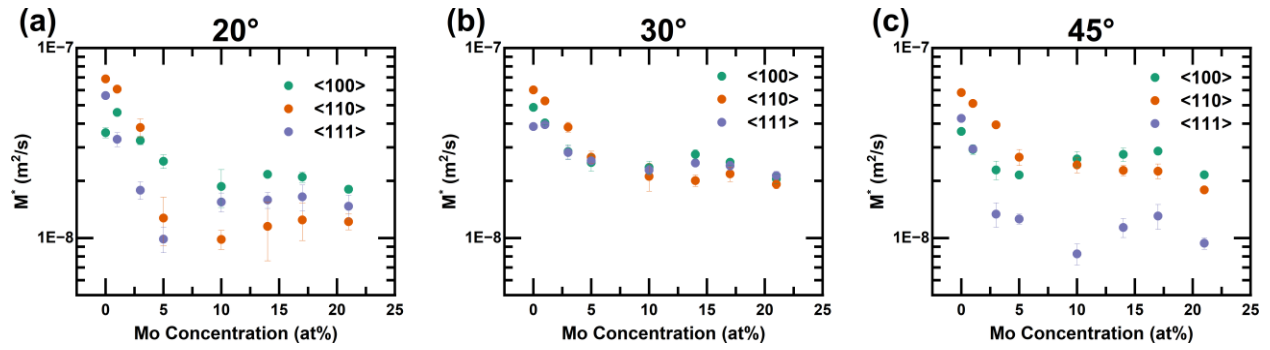


Fig. 5.9. Mobility as a function of Mo concentration for the (a) 20°, (b) 30°, and (c) 45° misorientations for all three rotation axes at 1400 K for the EAM potential. Error bars indicate standard error.

To examine this saturation effect in further detail, both vacancy and interstitial diffusion were examined in the EAM and ADP potentials (at 1400 K and 1200 K respectively) for Mo concentrations ranging from pure U to pure Mo, using a 10x10x10 block of material. As GB motion is related to defect diffusion, via either interstitial or vacancy or both, the overall behaviors between defect diffusion and GB mobility could show similarities. In all cases, a single vacancy ($N = 1999$ atoms) or a single octahedral interstitial ($N = 2001$ atoms) was introduced to the system, and the atomic square displacement (ASD) was tracked for 20 ns. The three-dimensional defect diffusion was then calculated by fitting the slope of the ASD versus time plot and dividing the result by six. Figure 5.10 shows the resulting interstitial and vacancy diffusion as a function of Mo concentration. Several interesting conclusions can be drawn from these results. First, the saturation effect noted in mobility using the EAM potential also appears in both defect diffusion plots, with the saturation effect holding from approximately 7–21at.% Mo. When the Mo concentration increases past 21at.%, the EAM defect diffusion rates both decrease at roughly the same rate until the interstitial diffusion reaches a minimum at ~60at.%. At this point, the interstitial diffusivity increases, while vacancy diffusion continues to decrease with increasing Mo concentration, up to pure Mo. Conversely, in the ADP potential, no saturation effect is visible. Instead, both vacancy and interstitial diffusion decrease at roughly the same rate until ~75at.% Mo, where the interstitial diffusion then increases, while vacancy diffusion decreases at a faster rate.

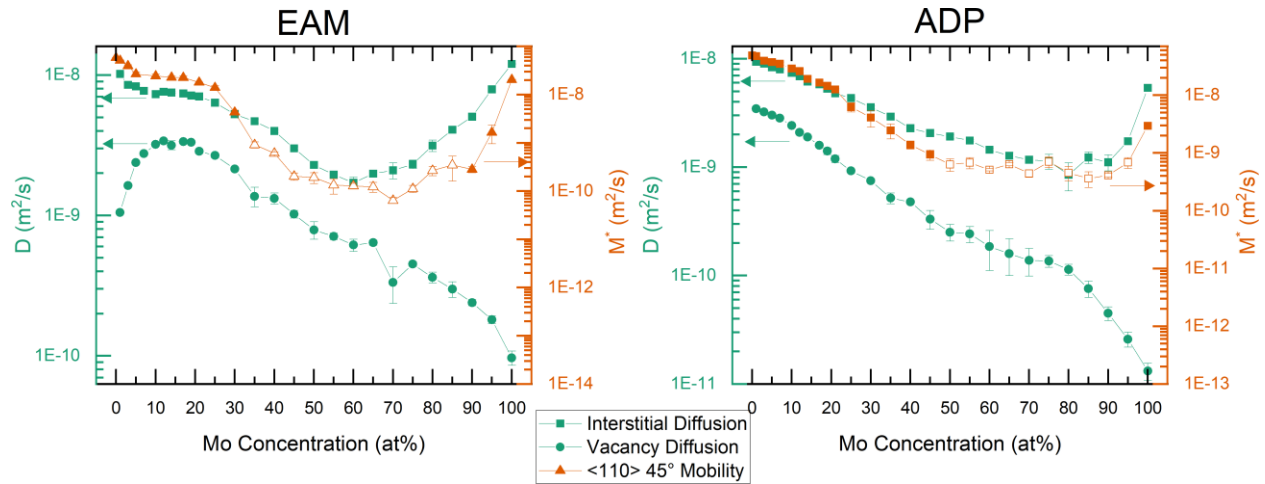


Fig. 5.10. Comparison of defect diffusion rates with the $\langle 110 \rangle$ 45° GB mobility as a function of Mo concentration for two different interatomic potentials: EAM (left) and ADP (right). Note that the scales of the left and right axes are not the same. Open points indicate that not enough grain growth occurred to reliably calculate GB mobility, but they are included as an estimate of the upper limit of mobility at the respective concentration. Diffusion rates were calculated at 1400 K for the EAM potential, and 1200 K for the ADP potential.

Because both defect diffusion behavior and mobility have the same saturation effect from ~10–21at.% Mo, several additional grain growth simulations were performed for the $\langle 110 \rangle$ 45° boundary with Mo concentrations from 25–100at.% to determine if the overall shape of the plots is similar. The temperatures for these simulations were 1400 K for the EAM potential and 1200 K for the ADP potential for consistency with the defect diffusion results. These results are also plotted in Fig. 5.10. Note that many of the intermediate Mo concentration simulations did not result in at least a 25% reduction in the cross-sectional area due to their slow mobility but did still experience some growth. These points are indicated by the open symbols in Fig. 5.10 and should be thought of as an approximate upper limit for the mobility of that boundary. Though the scales are different, the mobility and interstitial diffusion trends share very similar shapes for both the EAM and ADP potentials. These results indicate that in the UMo alloy system, GB mobility is more likely related to interstitial diffusion. In other words, interstitial diffusion across the GB might contribute to the GB motion more than the vacancy diffusion.

5.5. Conclusions

In this work, MD simulations examined the GB mobility of nine unique, low-index GBs with varying amounts of Mo solute. In terms of the anisotropy trend, Mo concentrations below ~5at.% follow the expected trend from the planar density argument ($M_{110} \approx M_{100} > M_{111}$ for the 20° and 30° misorientations, $M_{110} > M_{100} \approx M_{111}$ for the 45° misorientation). At higher concentrations, the mobility anisotropy trend is interatomic-potential-dependent: in the EAM potential, the trend becomes $M_{100} > M_{111} > M_{110}$, while the ADP potential shows very little change from the pure γ U system across the range of Mo concentrations examined. The change in the mobility anisotropy trend for the EAM potential is attributed to solute drag becoming the dominant factor in determining GB mobility. Additionally, this work shows that—in UMo systems—GB mobility is likely more related to interstitial diffusion than vacancy diffusion.

Chapter 6. Xe Effects on Grain Boundary Mobility in the γ U, UMo, and UO₂ Systems

This chapter is intended for journal publication, the submission process of which is ongoing.

6.1. Abstract

During reactor operation, nuclear fuels experience a buildup of fission gases. This buildup changes the microstructure and its evolution. While significant research has gone into understanding the fission gas bubble evolution within nuclear fuel, limited research has been done regarding how fission gases change grain growth behavior, specifically concerning grain boundary mobility and its anisotropy. This work uses molecular dynamics simulations to examine the trends of grain boundary mobility and its anisotropy in uranium dioxide (UO₂), γ Uranium (U), and uranium-molybdenum (UMo) alloys in the presence of xenon (Xe). In general, increasing the Xe concentration leads to a decrease in mobility. At elevated Xe concentrations, the UXe and UMoXe systems lose their anisotropic mobility trend, while the UO₂+Xe system does not. This suggests a complex relationship between grain boundaries and impurities, impurity drag, and GB mobility anisotropy that depends on both temperature and impurity concentration which necessitates further study.

6.2. Introduction

During normal nuclear reactor operation, fission products can build up in the fuel. One of the most prevalent fission gases is xenon (Xe) [191], which is insoluble in the fuel matrix. As the quantity of this and other fission gases increases, the fuel microstructure changes to accommodate, leading to microstructural features such as the fission gas bubble superlattice in uranium-molybdenum (UMo) fuels [192]. Related to this buildup of gas is the formation of the high burnup structure (HBS), where large bubbles form in the subdivided grain—a characteristic microstructure shared by both oxide and metallic fuels [67,193]. Several concerns arise due to the buildup of fission gases, among which is fuel swelling behavior [54,194]. Research over the last several decades in both ceramic and metallic fuels has shown that grain size is an important parameter related to fuel swelling. Specifically, an increased grain size both reduces overall swelling [12,70,71] and limits the amount of fission gas released [128,195]. What has not been studied

extensively, and what this research seeks to determine, is the specific impacts that fission gas has on grain growth kinetics.

Grain growth kinetics, by themselves, have been studied extensively across a wide variety of systems [196]. Burke and Turnbull [97] formalized the description of several grain growth behaviors and identified that the rate of grain boundary (GB) migration (v) is directly proportional to the driving force (F) acting on it, with the migration rate scaled by a GB-character-dependent parameter (M , or GB mobility) as $v = M \times F$. Several driving forces exist [34], but this work focuses on curvature-driven boundaries. The curvature (or capillary) driving force is defined as $F_c = (\gamma + \gamma'')\kappa$, where γ is the GB energy, γ'' is its second derivative with respect to inclination, and κ is the curvature of the grain. The sum of GB energy and its second derivative with respect to inclination is called the GB stiffness [87]. Little is known about the stiffness, and it is thus often ignored despite evidence of its importance [45,87,116]. Instead, most efforts toward studying grain growth have circumvented the issue of determining the stiffness by calculating the reduced mobility, defined as $M^* = M(\gamma + \gamma'')$. This changes the grain growth relationship to

$$v = M^* \kappa \quad (6.2.1)$$

and limits the effects of the GB character to one parameter (M^*).

Despite this simplification, relatively little is known about the anisotropy trend in GB mobility (or the reduced GB mobility). Studies of GB mobility in face-centered cubic (FCC) aluminum revealed that $\langle 111 \rangle$ tilt GBs tend to migrate the fastest [34,197], from which came the generalization that $\langle 111 \rangle$ tilt GBs are the fastest for FCC metals [83]. Until Chapter 3, little about GB mobility anisotropy in BCC metals was known. From that study, it was postulated that the density of the plane normal to the GB plane and the tilt axis is a significant factor in determining the overall mobility trend. The fluorite crystal structure follows this hypothesis, with fast $\langle 111 \rangle$ tilt GBs, as shown in Chapter 4. Experimental studies of GB mobility rely on fitting it to the grain growth power law, $D^n - D_0^n = kt$, where n and k are fitting parameters, and k relates to mobility by $k = M\gamma$ [36]. The original derivation of the power law has $n = 2$ [97], which is for ideal grain growth, but later works changed this to a fitting parameter to account for the presence of different microstructural features, such as pores and inclusions. An alternative formulation of this relationship puts the exponent on the time instead of the grain size [196]. Inherent in the grain

growth power law is the idea that grain growth and therefore its affecting parameters are isotropic; all GBs migrate in the same manner, regardless of their individual characters. Thus, any experimental studies of grain growth that use this power-law relationship report the average grain growth rate, not the specific GB mobilities for the individual GBs. Such an average is useful for determining macro-scale properties but neglects the finer details of how such properties vary locally and any impacts such local variations may have. Additionally, fitting to this relationship does nothing to examine the specific impacts of solute or impurity drag on mobility anisotropy.

The effects of solutes or impurities on grain growth have been studied in some depth, but those studies have focused on things such as solute drag, Zener pinning, or their effects on the overall grain growth kinetics. A systematic study of mobility anisotropy with impurities is very limited to the best of the author's knowledge. It is well known that impurities generally slow down GB migration according to the solute drag model of Cahn and Lücke and Stüwe [176,177]. (Later models of solute drag have been developed, but the underlying physics remains consistent such as in [198].) The specific impact of solute drag on mobility is generally unknown. In Chapter 5 the author examined how mobility anisotropy changes with solute concentration in the UMo alloy. The mobility trend as a function of solute concentration for all rotation axes followed the same general trend as interstitial diffusion as a function of concentration up to 21at.% Mo. The $\langle 110 \rangle$ 45° boundary was examined across a larger range of concentrations and was found to follow the interstitial diffusion trend fairly well. Additionally, at high solute concentrations, the mobility anisotropy trend (which, at low concentrations is $M_{110} > M_{100}, M_{111}$) disappears ($M_{110} \approx M_{100} \approx M_{111}$), which was hypothesized to occur due to the increasing importance of solute drag over GB character.

This work expands the study of impurity effects on GB mobility anisotropy by examining how fission gases (using Xe as a representative element) impact grain growth anisotropy in metallic UMo alloys and ceramic UO₂. Molecular dynamics simulations are run to examine the following: (1) how Xe impacts GB mobility and its anisotropy in the UXe, UMoXe, and UO₂+Xe systems, and (2) if the change in GB mobility can be predicted based on Xe concentration. These results can be utilized in fuel performance modeling codes [137,199] to incorporate the effect of Xe on GB mobility, which could result in more accurate grain growth kinetics that is important for predicting fuel swelling and fission gas release rate.

6.3. Methods

Similar to the previous chapters, the shrinking cylindrical grain growth method was used for ease of comparison to previous studies of γ U (Chapter 3), pure UO_2 (Chapter 4), and UMo (Chapter 5). In this method, a block of the pure material (γ U or UO_2) was created with the Z axis of the block oriented along one of the [001], [110], or [111] directions, hereafter referred to as the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ rotation axes respectively. With the block properly oriented, a cylindrical grain of radius r_{grain} was created by rotating all atoms within the distance r_{grain} from the center of the simulation block in the X-Y directions by a desired misorientation angle, θ (see Fig. 6.1). Misorientation angles of 20° and 45° were used for all systems. The UXe and UMoXe systems had an additional 30° misorientation for comparison with pure U (Chapter 3) and UMo (Chapter 5). The UO_2 +Xe system also examined a $\langle 111 \rangle$ 38.20° GB and a $\langle 112 \rangle$ 45° boundary to examine how the presence of Xe impacts the nominally fastest GB ($\langle 111 \rangle$ 38.20° [34,83]) and a higher-index rotation axis ($\langle 112 \rangle$ 45°). System dimensions are noted in Table 6.1—note that the number of atoms in the metallic U systems ranged from 55,000–75,000, and $\sim 150,000$ –255,000 in the UO_2 systems. After the rotation operation, some pairs of atoms were closer than a system-dependent cutoff distance, so one atom of each pair was removed. In the UO_2 system, charge neutrality was maintained by removing two neighboring O atoms for each U atom removed. Each GB system was then equilibrated for 20ps to relax the structure (metallic U systems at 1100 K and UO_2 systems at 1500 K) to generate the input structures for the subsequent production runs. After this equilibration, Xe atoms were randomly substituted for U atoms on a per-simulation basis, with charge neutrality maintained in UO_2 as above. Concentrations ranged from 0.25–1.50at.% for the UXe system, 0.25–0.75at.% for the UMoXe system (with Mo concentrations ranging from 1–5at.%), and 0.25–1.00at.% for the UO_2 +Xe system.

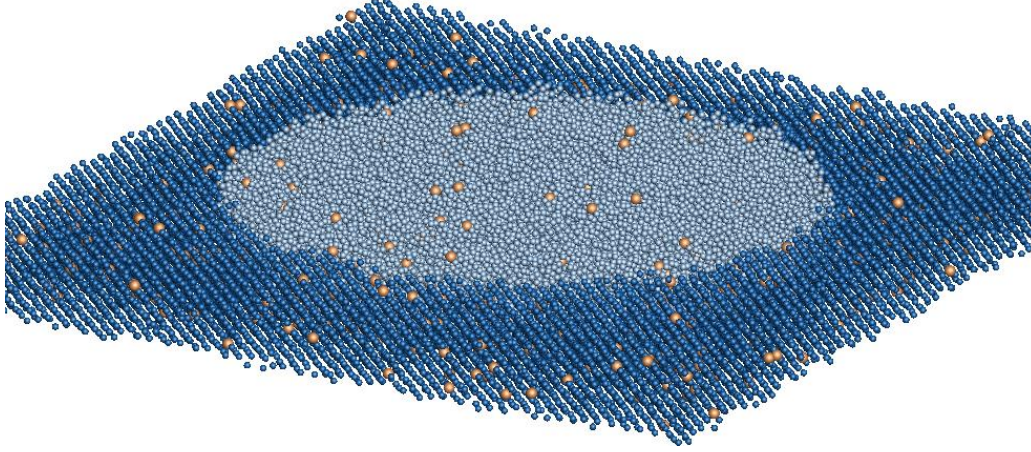


Fig. 6.1. Example of the GB structures created in this work. Xe atoms (large, orange) are distributed randomly throughout the system. The embedded cylindrical grain of radius r_{grain} (light blue) has atoms rotated by the desired misorientation angle, θ , relative to the matrix grain (dark blue). This is an input structure for the $\langle 100 \rangle$ 45° $\text{UO}_2 + 1.00\text{at.}\% \text{Xe}$ system. O atoms are not shown for clarity, and U atoms are colored by their assigned grain.

Table 6.1. Approximate system sizes for the rotation axes examined in this work. Dimensions are given as XYZ triples with units of Å. For the U(Mo)Xe systems, misorientations of 20° , 30° , and 45° were examined, while for the $\text{UO}_2 + \text{Xe}$ systems, 20° and 45° were used for the low-index rotation axes (with an additional 38.20° misorientation for the $\langle 111 \rangle$ rotation axis), and 45° was used for the $\langle 112 \rangle$ boundary.

System Orientation	U(Mo)Xe System	$\text{UO}_2 + \text{Xe}$
$X=[100], Y=[010], Z=[001]$	$264 \times 264 \times 18$	$273 \times 273 \times 27$
$X=[001], Y=[1\bar{1}0], Z=[110]$	$265 \times 250 \times 25$	$300 \times 300 \times 39$
$X=[1\bar{1}0], Y=[11\bar{2}], Z=[111]$	$264 \times 268 \times 18$	$270 \times 268 \times 28$
$X=[111], Y=[1\bar{1}0], Z=[11\bar{2}]$	--	$236 \times 231 \times 40$

Molecular dynamics simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [46]. For the metallic U systems, an embedded atom method (EAM) potential for the U-Mo-Xe ternary system was used that was developed specifically to examine irradiation-induced defects and their evolution, including the effects of fission gas [91]. The $\text{UO}_2 + \text{Xe}$ system was examined with two potentials: the Basak [151] potential with Geng *et*

al.'s description of the Xe interactions [200] (hereafter referred to as the Geng potential) and the Cooper-Rushton-Grimes (CRG) EAM potential describing several actinide oxides and their interactions with Xe and krypton [153,201]. Simulations were run using the isobaric-isothermal (NPT) ensemble, with pressure maintained at 0 bars. Temperatures in the metallic U systems ranged from 1050–1400 K in 50 K steps, while the UO₂ systems used temperatures of 2200, 2600, and 3000 K. (Simulations for UO₂ ran for much longer due to the larger number of atoms in the systems, hence the sparser data.) For each condition, three independent simulations were performed to get the nominal average grain growth behavior. Each simulation ran for a maximum of 8 ns or until the embedded grain disappeared due to grain shrinkage. Snapshots were saved periodically throughout the duration of the simulations for later analysis (see Fig. 6.2).

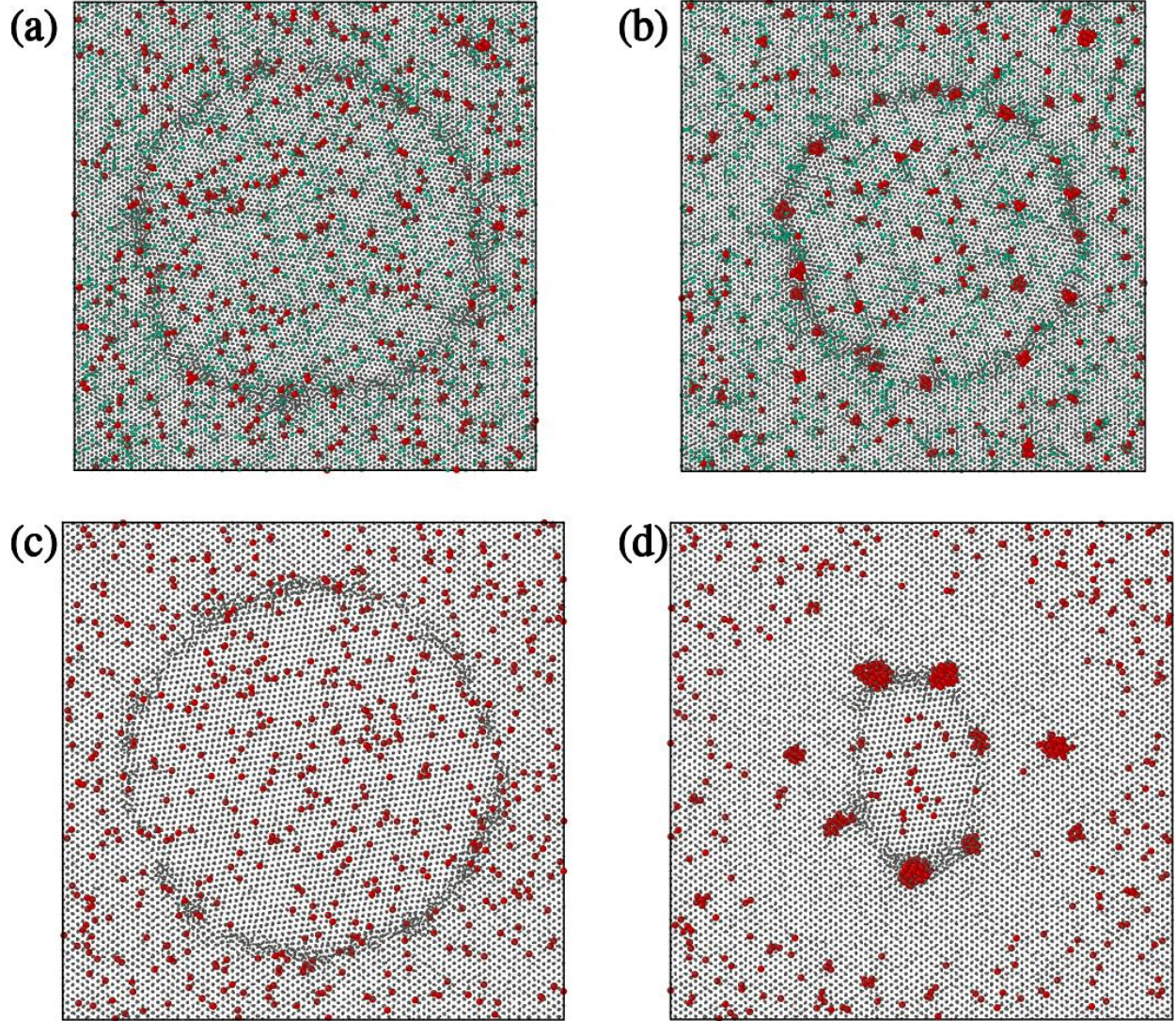


Fig. 6.2. Snapshots taken at the beginning (a, c) and end (b, d) of the simulations. (a) and (b) are for a U + 5at.% Mo + 0.75at.% Xe $\langle 111 \rangle$ 20° system at 1400 K, and (c) and (d) are for a UO_2 + 1.00at.%Xe $\langle 110 \rangle$ 45° system at 3000 K using the CRG potential. Xe atoms are colored red, and U atoms are colored black. In the UMoXe system, Mo atoms are colored green and in the UO_2 +Xe system, O atoms are not shown for clarity.

GB mobility was determined using Eq. (6.2.1). As the velocity of the GB is the rate at which the radius of the embedded grain shrinks, the relationship between the cross-sectional area (A) of the grain and the reduced mobility is determined via integration to be $\frac{dA}{dt} = 2\pi M^*$. The

area was determined as a function of the number of atoms (N) in the embedded cylindrical grain as $A = N\Omega / L_z$, where L_z is the height of the simulation cell and Ω is the atomic volume. (For the body-centered cubic (BCC) metallic U systems, $\Omega = a_0^3 / 2$, while for fluorite-structured UO_2 systems, $\Omega = a_0^3 / 4$ —note that only the cations were used to determine the atomic volume.) The number of atoms in the embedded grain was determined using a method adapted from Ulomek *et al.* [47,48], where each atom is assigned an orientation parameter based on its local environment using ideas from classical diffraction theory. After the number of atoms in the embedded grain was determined, the cross-sectional area of the embedded grain was calculated and then plotted as a function of time (see examples in Fig. 6.3). The presence of Xe in these systems occasionally manifests as stop-and-go motion of the grain shrinkage rather than a single linear decrease over time (Fig. 6.3(b) and (c)). While a piecewise, linear fit would identify the specific mobilities for a particular GB condition (such as Xe position and relative GB concentration), a simple linear fit to the entirety of the growth regime is utilized to get the generic grain growth behavior across longer timescales. This is assumed to better relate to experiments, as they are determined over longer time scales and generally represents the grain growth behavior well. With the imposed time constraint (no more than 8 ns of simulation time), some simulations did not experience enough grain growth to determine dA/dt (defined as the embedded grain shrinking less than 25% of the initial cross-sectional area). In several cases, particularly at lower temperatures, this resulted in only one valid data point for determining “average” grain growth behavior. In such cases, no error bar is displayed. For cases where at least two simulations for a given condition experienced enough grain growth, the standard error is displayed. To expand the range of data for the $\text{UO}_2 + \text{Xe}$ systems, a smaller initial grain radius of 75 Å was used to increase the driving force. The validity of this approach is examined in the Discussion section.

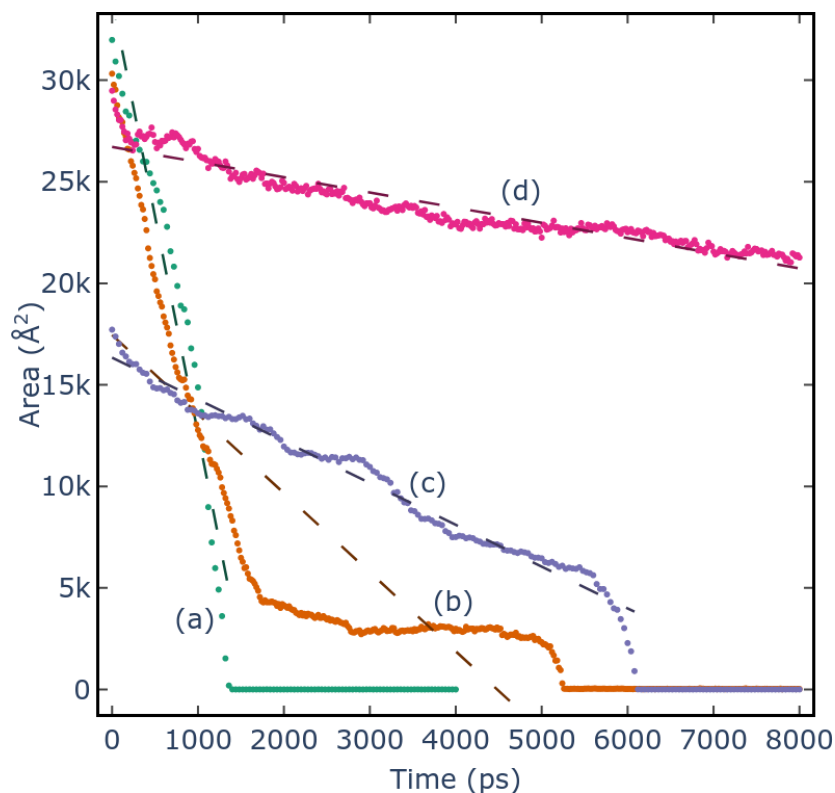


Fig. 6.3. Representative area versus time plots observed in this work, with linear fits to the growth regime shown as dashed lines. (a) $\text{UO}_2+0.50\text{at.}\% \text{Xe}$ $\langle 111 \rangle$ 38.20° at 3000 K—demonstrates rapid, linear growth. (b) $\text{U } 0.25\text{at.}\% \text{Xe}$ $\langle 100 \rangle$ 20° at 1050 K—shows a large stagnation step during grain growth. (c) $\text{UO}_2+1.00\text{at.}\% \text{Xe}$ $\langle 100 \rangle$ 20° at 2600 K—shows the growth starting with a smaller initial grain radius and also shows several small stagnation steps during grain growth. (d) $\text{U } 5\text{at.}\% \text{Mo } 0.75\text{at.}\% \text{Xe}$ $\langle 111 \rangle$ 45° at 1400 K—demonstrates slow growth.

6.4. Results

In this section, each system is examined independently, with discussions limited to observations from the Arrhenius plots and the plots of mobility as a function of Xe concentration. Comparisons between the systems are examined in the Discussion section. Unless otherwise indicated, for each figure the x and y scales of each subfigure are the same. Results are first presented for the γ U-Xe system, then the UMoXe system, and finally the UO_2+Xe system.

6.4.1. Fission Gas Effects on γ U Grain Boundary Mobility

Figure 6.4 shows the Arrhenius plot of GB mobility for the UXe system with a 30° misorientation for all rotation axes. (Note that the general behaviors observed across the different misorientations, not shown, are generally the same.) Similar to the results for the UMo system examined in Chapter 5, increasing levels of impurities lead to a decrease in the reduced mobility. However, different from the results for the UMo system is that the anisotropy trend remains fairly consistent; only at the higher Xe concentrations (1.25at.% and 1.50at.%—see Fig. 6.4 (f) and (g)) does mobility roughly converge for the different rotation axes. For all other Xe concentrations, the anisotropy trend of $M_{110} > M_{100} \geq M_{111}$ remains. As the Xe concentration increases, the error bar length also increases due to the GB occasionally becoming pinned by the Xe atoms and clusters (see Fig. 6.2(b) and Fig. 6.3(b)). Arrhenius parameters are determined via fitting (see Appendix B), though the validity of using such an approach at the higher Xe concentrations is unclear. Thus, these values are presented for comparison purposes only.

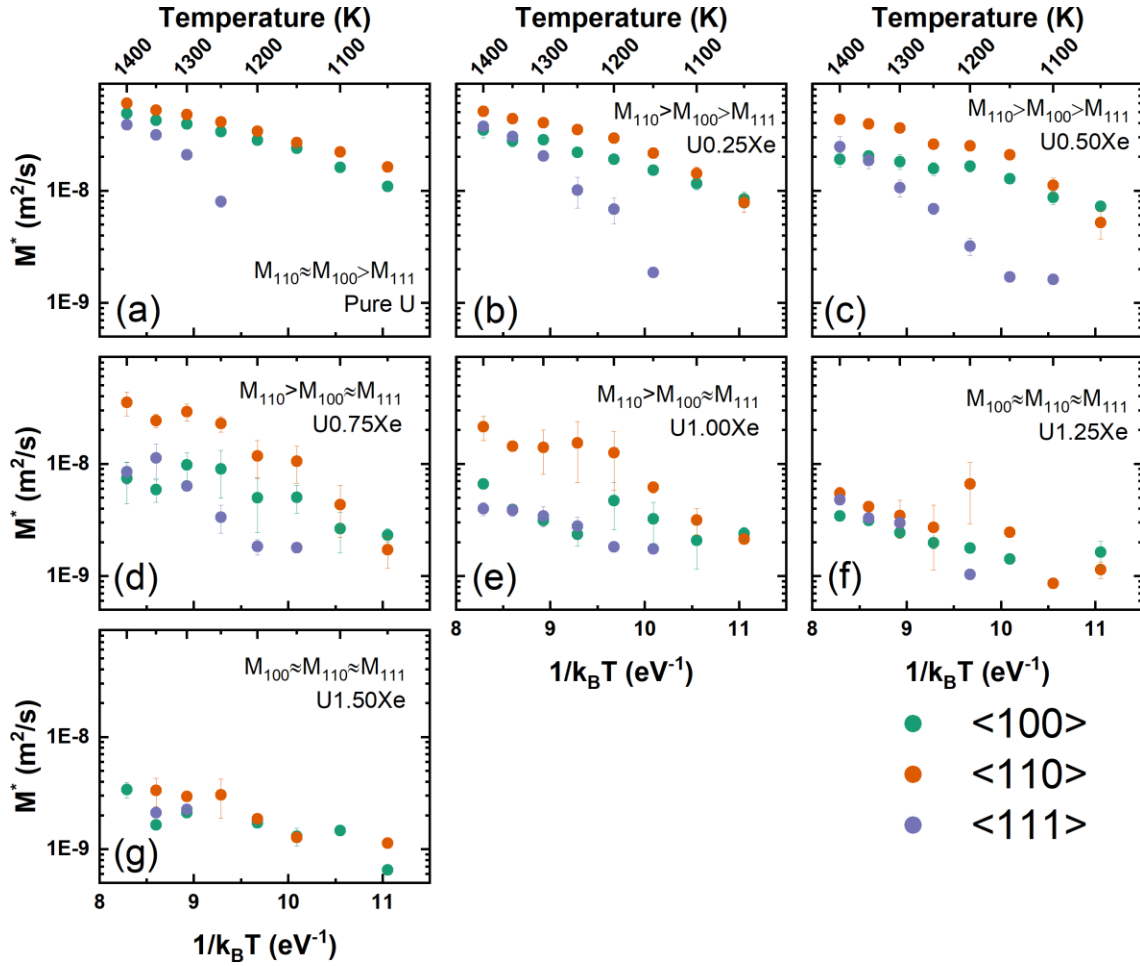


Fig. 6.4. Arrhenius plots of the reduced GB mobility for various concentrations of Xe for the 30° misorientation in the γ U system. Error bars indicate the standard error, though not all data points have error bars because of a lack of significant grain growth in two of the three simulations. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). Values in (a) are taken from Chapter 3 for comparison. Concentrations of Xe are as follows: (a) pure γ U (0at.%), (b) 0.25at.%, (c) 0.50at.%, (d) 0.75at.%, (e) 1.00at.%, (f) 1.25at.%, and (g) 1.50at.%. The anisotropy trend is indicated for each concentration.

Plotting the reduced mobility as a function of Xe concentration (as shown in Fig. 6.5) shows a fairly consistent trend of decreasing mobility with increasing Xe concentration, as expected. Similar to the UMo system, however, is the fact that the $\langle 100 \rangle$ 20° boundary shows a

slight acceleration for the U0.25Xe system as compared to the pure γ U case. In Chapter 5, no clear reason for why this occurs was found, but because the same behavior appears for a different impurity element, GB structure likely plays a significant role in how solutes or impurities affect GB motion. Unique to the UXe system is the lack of an (apparent) effect on GB mobility for the $\langle 111 \rangle$ rotation axis at low temperatures (see Fig. 6.5(c) and (i)), though this could be due to the uncertainties associated with insufficient shrinkage of the grain. For both the 20° and 45° boundaries at 1050 K (the 30° boundary did not experience enough growth to reliably calculate a GB mobility at this temperature), concentrations between 0at.% and 1at.% Xe show a relatively minor impact on mobility, especially compared to the other rotation axes. As the (111) plane is the least dense in the BCC crystal structure for the three low-index planes, and the lower temperatures mean less frequent attempts for atom hops across the boundary interface (thus leading to slower GB mobility), the assumed reason for the minor impact on the $\langle 111 \rangle$ 20° and 45° boundaries at lower temperatures is that such conditions make the GB motion relatively immune to impurity drag effects, possibly because the GB migration rate and Xe diffusion rate is comparable. Additionally, the Xe concentrations in question for this behavior are quite low at less than or equal to 1at.%. Similar behaviors for the UMo system are unclear, as no mobility values were reported for Mo concentrations in this narrow range except for 1at.% Mo. The results in Chapter 5 indicated that not enough grain growth occurred to calculate GB mobility values at 1050 K for the $\langle 111 \rangle$ rotation axis. Based on the results of the higher temperature simulations in that work, the expectation is that the lower temperatures follow the same trend: decreasing mobility with increasing Mo concentration up to ~ 10 at.%, then saturating at that value. The mechanism for the saturation effect in the UMo system was identified as relating to the interstitial diffusion at the specified Mo concentration, while in the UXe system examined here, the mechanism is expected to be different due to the different mixing behaviors.

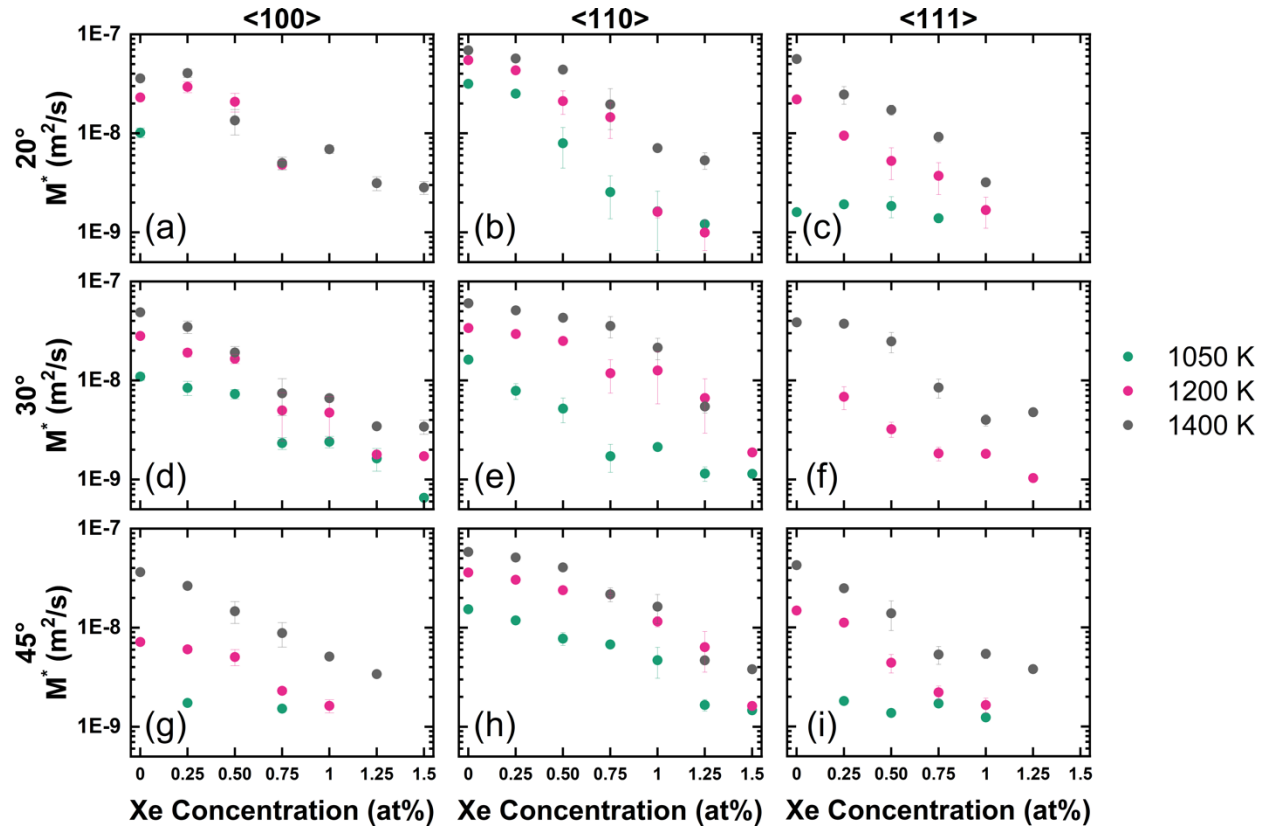


Fig. 6.5. Reduced GB mobility as a function of Xe concentration for nine unique GBs. Error bars indicate standard error. Columns indicate the rotation axis (left: $\langle 100 \rangle$, middle: $\langle 110 \rangle$, right: $\langle 111 \rangle$) and rows indicate misorientation (top: 20° , middle: 30° , bottom: 45°).

6.4.2. Fission Gas Effects on UMo Grain Boundary Mobility

Figure 6.6 shows the results of the combined UMoXe system as a function of temperature for the range of Mo and Xe concentrations examined. In general, it appears that with increasing Xe concentration, there is a relatively minor impact (if any) on the anisotropy trend. This is compared to the effect of Mo, where the anisotropy trend disappears at high Mo concentrations (see Chapter 5). Figure 6.6 shows the anisotropy trend disappearing only in the highest Mo and Xe concentrations, suggesting that, at least at the concentrations examined here, Mo has a stronger impact on the mobility anisotropy trend when combined with Xe in the γ U system, although Mo concentration is also much higher than Xe. Arrhenius parameters are presented in Appendix B, as the general behaviors of these plots are linear decreases. Notably, at Xe concentrations above 0.50 at.% and Mo concentrations above 1 at.%, some anti-thermal behavior appears, possibly

because the Mo solute and Xe impurity cause GB disordering (e.g., pre-melting) at high temperatures. Despite their presence, Arrhenius fits are to the entire temperature domain, as the fluctuations are attributed primarily to the effect of GB pinning and release. With a maximum of three simulations per data point, the quantitative results likely need further refining, but the qualitative behavior is expected to be correct. Therefore, these results can be used as a reference for further investigations.

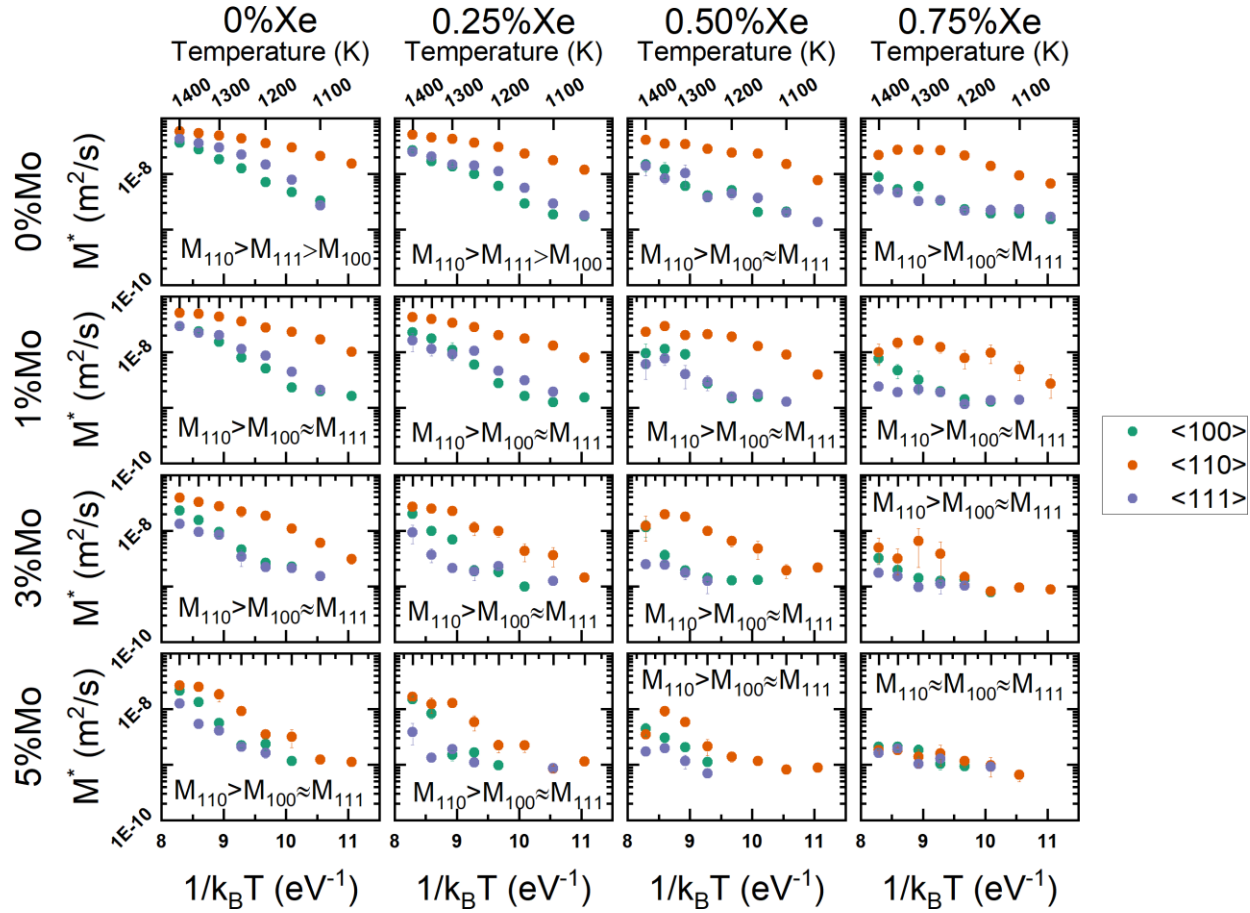


Fig. 6.6. GB mobility as a function of temperature for the 45° misorientation. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The mobility anisotropy trend is indicated in each subplot. Error bars indicate standard error. Xe concentrations increase from 0at.% Xe in the far left subplots to 0.75at.% Xe in the far right subplots, while Mo concentrations increase from 0at.% Mo in the top row to 5at.% Mo in the bottom row.

A plot of the same results as a function of Xe concentration is shown in Fig. 6.7. The general trend across all systems examined here is that increasing Xe concentration leads to a decrease in the overall GB mobility. (The exception of $\langle 100 \rangle$ 20° for the U0.25Xe system is noted above.) There appears to be a generally linear relationship between Xe concentration and mobility, suggesting a simple relationship between the change in mobility and the Xe concentrations for a given UMo alloy and GB character. Additionally, the combined effects of Mo and Xe appear to linearly affect mobility, though several exceptions are noted (e.g. $\langle 100 \rangle$ 30° U5Mo0.25Xe is faster than U3Mo0.25Xe). It is unclear if these exceptions are the rule or due to the uncertainty of extracting GB mobility during the complex grain shrinkage behavior (e.g., Fig. 6.3).

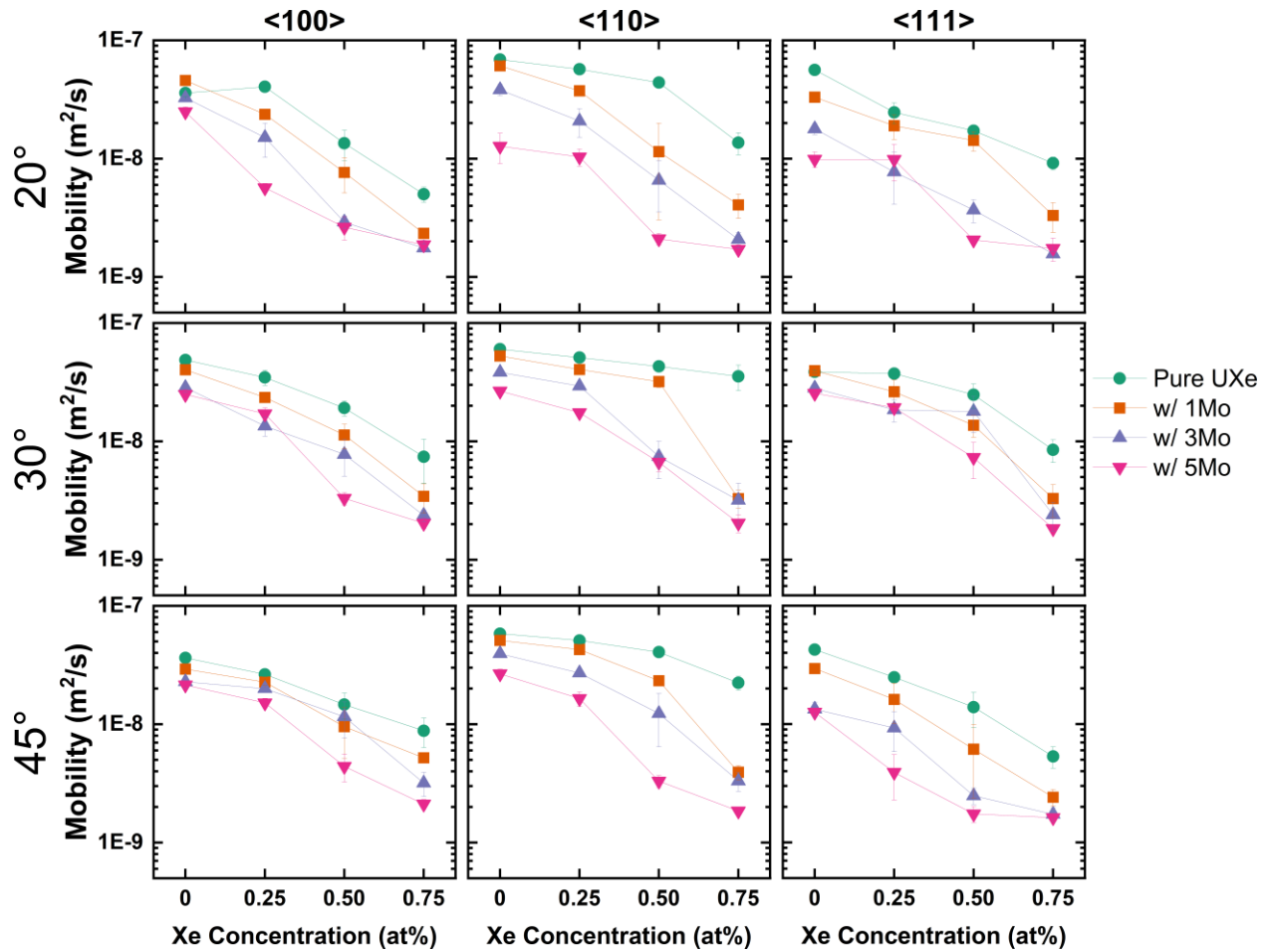


Fig. 6.7. Mobility as a function of Xe concentration for various concentrations of Mo in UMo alloys at 1400 K. Error bars indicate standard error. The lines are guides to the eye. Columns indicate the rotation axis (left: $\langle 100 \rangle$, middle: $\langle 110 \rangle$, right: $\langle 111 \rangle$) and rows indicate misorientation (top: 20° , middle: 30° , bottom: 45°).

6.4.3. Fission Gas Effects on UO₂ Grain Boundary Mobility

Figure 6.8 shows the Arrhenius plot of the mobilities for the Geng and CRG potentials for all rotation axes with a 45° misorientation. As Xe concentration increases, mobility decreases, consistent with the expectations of solute drag. For the Geng potential, the 45° misorientation does not appear to have any changes in the anisotropy trend with the addition of Xe; across all Xe concentrations, the mobility anisotropy trend remains $M_{111} > M_{100} > M_{112} > M_{110}$. For the CRG potential, the mobility anisotropy trend for pure UO₂ is less clear than the Basak potential (see Chapter 4). In particular, at 3000 K the different rotation axes converge toward a singular value, consistent with the results in Chapter 4, though the convergence at 1.00at.% Xe is less significant. At 2200 K, the anisotropy trend is fairly consistent with $M_{111} > M_{100} \approx M_{112} > M_{110}$. At 2600 K, the $\langle 110 \rangle$ rotation axis is always the slowest by a wide margin, but the other three rotation axes have very similar values.

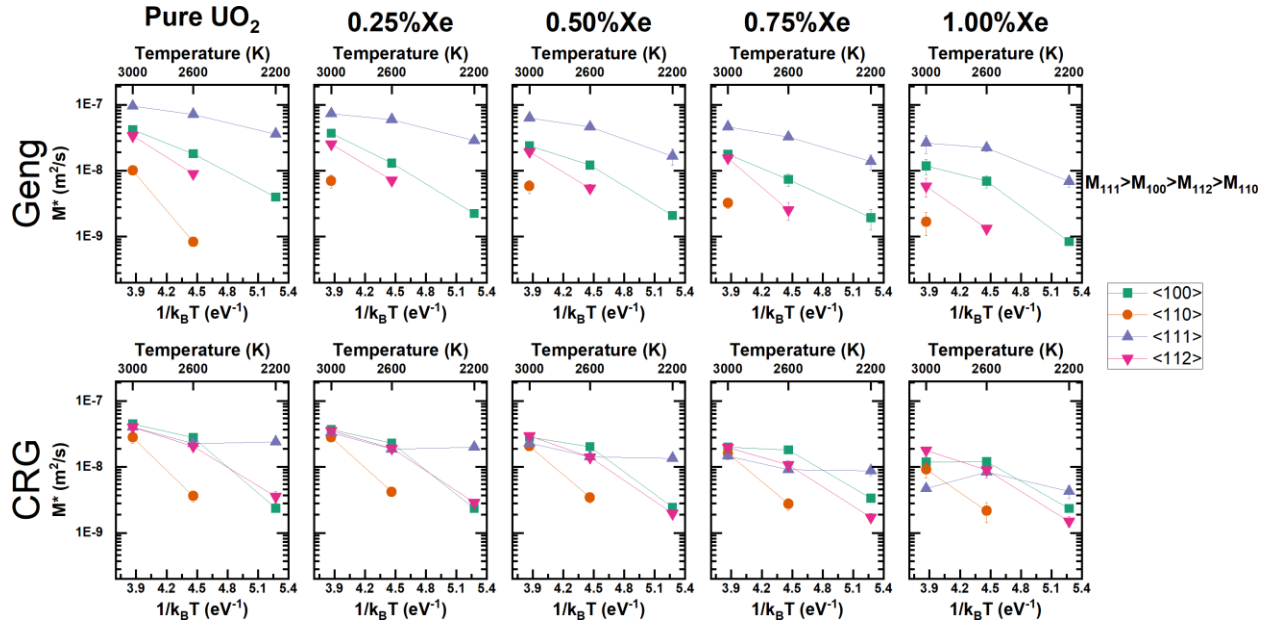


Fig. 6.8. GB mobility as a function of temperature for the UO₂ system using the Geng (top row) and CRG (bottom row) potentials with a misorientation of 45°. Xe concentration increases from pure UO₂ (far left) to 1.00at.%Xe (far right). The data for pure UO₂ is taken from Chapter 4. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The lines are guides to the eye.

For the 20° misorientation (Fig. 6.9), the Geng potential shows a consistent anisotropy trend of $M_{111} \geq M_{100} > M_{110}$ up to 0.50at.% Xe. At 0.75at.% the anisotropy trend changes to $M_{100} > M_{111} > M_{110}$, except for at 2200 K, where M_{100} and M_{111} swap places. The $\text{UO}_2 + 1.00\text{at.}\%$ Xe system has the $\langle 111 \rangle$ rotation axis as the slowest at 3000 K, then swaps with the $\langle 110 \rangle$ rotation axis at 2600 K. The CRG potential converges toward a singular value at 3000 K, similar to the 45° boundary. Up through 0.75at.% Xe, the mobility trend is $M_{111} \geq M_{100} > M_{110}$, while at 1.00at.% Xe the trend changes to have the $\langle 111 \rangle$ rotation axis as the slowest.

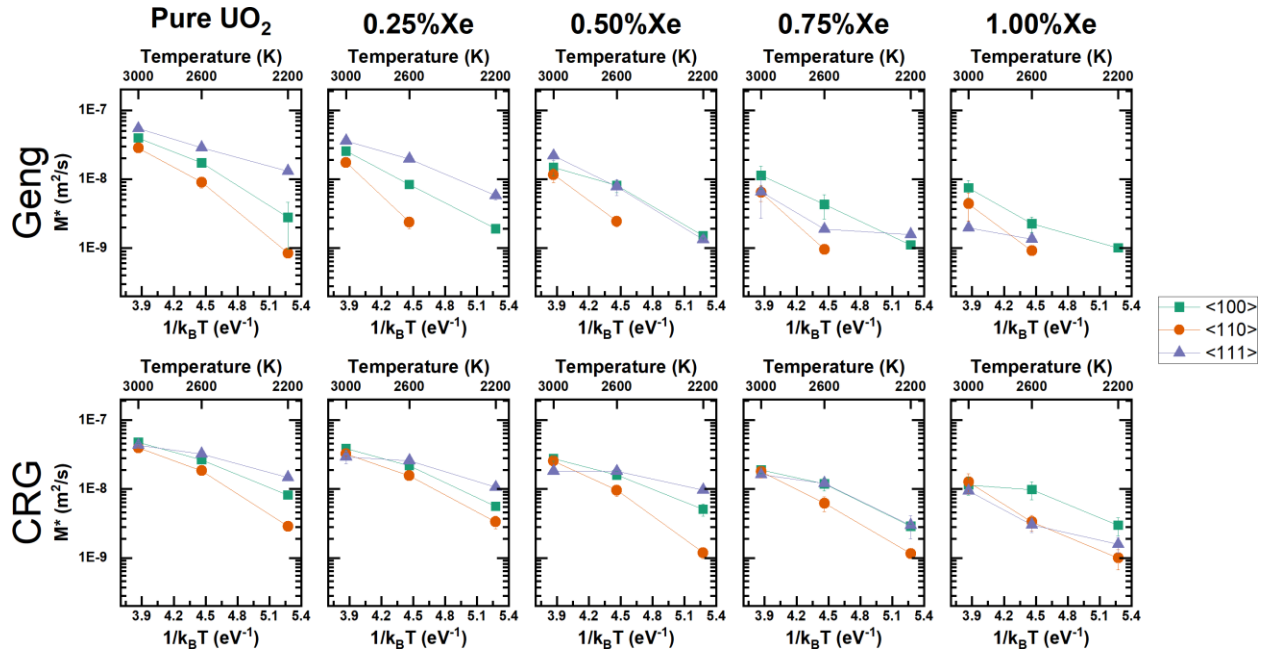


Fig. 6.9. GB mobility as a function of temperature for the UO_2 system using the Geng (top row) and CRG (bottom row) potentials with a misorientation of 20°. Xe concentration increases from pure UO_2 (far left) to 1.00at.% (far right). The data for pure UO_2 is taken from Chapter 4. Note that in each figure the bottom axis is $1/(k_B T)$, while the top axis shows the absolute temperature on a reversed scale (temperature decreases from left to right). The lines are guides to the eye.

In Chapter 5, and as shown with the UXe and UMoXe systems above, it was argued that the anisotropy trend for higher solute concentrations disappears due to the (assumed) increased importance of solute drag over the effects of GB character. If this is the case in the $\text{UO}_2 + \text{Xe}$ system

as well, the expected behavior of the Arrhenius plot at high Xe concentrations would show little to no differences between the rotation axes. As is shown in Figs. 6.8–6.9, such convergence is only achieved by the CRG potential at high temperatures. This is due to the higher relative temperature in the CRG potential (~97% of the melting temperature) at which the GB structure may become significantly disordered due to pre-melting. According to the MSD plots (not shown), atomic diffusion is nearly isotropic, making mobility almost independent of the GB character. This contrasts with the idea that solute drag becomes increasingly important over anisotropy due to the GB character. Higher Xe concentrations would possibly be needed to observe the same effect as in the γ U system with the elevated concentrations of Mo and Xe, suggesting a critical concentration at which mobility anisotropy disappears (or, where solute drag is the determining factor for GB mobility).

Plotting mobility as a function of concentration for the UO_2+Xe system at 3000 K (in Fig. 6.10) shows similar behavior to the UXe and UMoXe systems: increasing Xe concentration leads to a linear decrease in the logarithm of mobility. At 3000 K, both potentials show a significant contrast in the degree of anisotropy between the two misorientations. The 20° boundary shows very little anisotropy between rotation axes, with the CRG potential showing nearly duplicated values across the range of Xe concentrations. Additionally, increasing the Xe concentration seems to affect each rotation axis in the same way; the only exception to this is the Geng potential at 0.75–1.00at.% and 1.00at.% for the CRG potential. The 45° boundary shows no change in the anisotropy trend for the Geng potential, while there is some shuffling of all but the $\langle 110 \rangle$ rotation axis in the CRG potential.

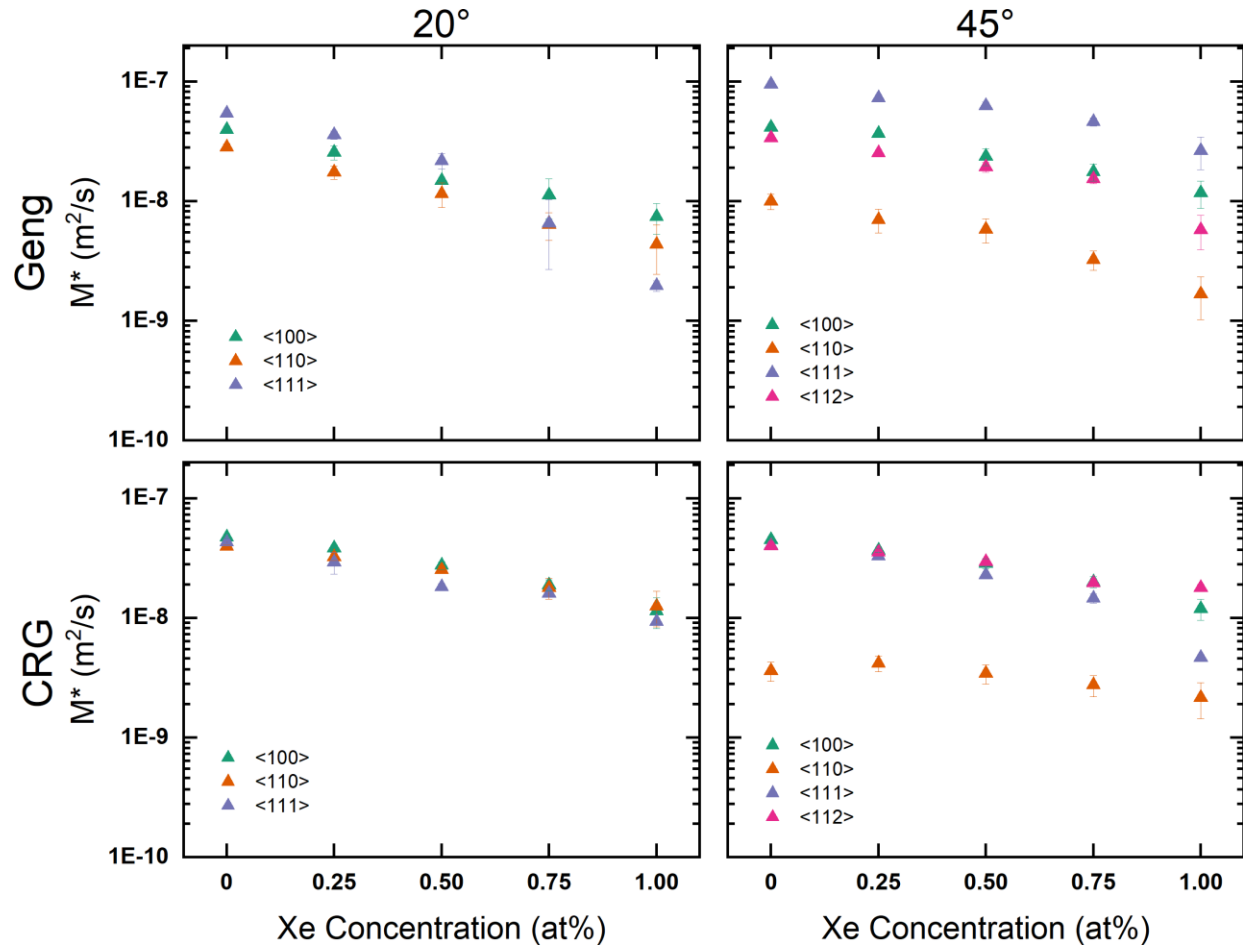


Fig. 6.10. GB mobility as a function of Xe concentration for the UO_2 systems examined at 3000 K. Columns indicate the misorientation angle (left: 20° , right: 45°), and rows indicate the interatomic potential (top: Geng, bottom: CRG).

6.5. Discussion

For the UO_2+Xe system, in an attempt to expand the temperature range over which mobilities could be calculated, a smaller initial grain radius of $75 \text{ \AA}$ was used. In Fig. 6.11, the mobility of the $r_0 = 100 \text{ \AA}$ and $r_0 = 75 \text{ \AA}$ GBs are plotted against each other, where each data point represents one unique GB. As mobility decreases, the smaller initial grain radius appears to migrate slightly faster than the larger initial radius, but the overall agreement is good, indicating that the smaller initial grain radius gives similar values of GB mobility. This suggests that smaller initial radii could be used, with a correction factor, to examine very slow GB migration.

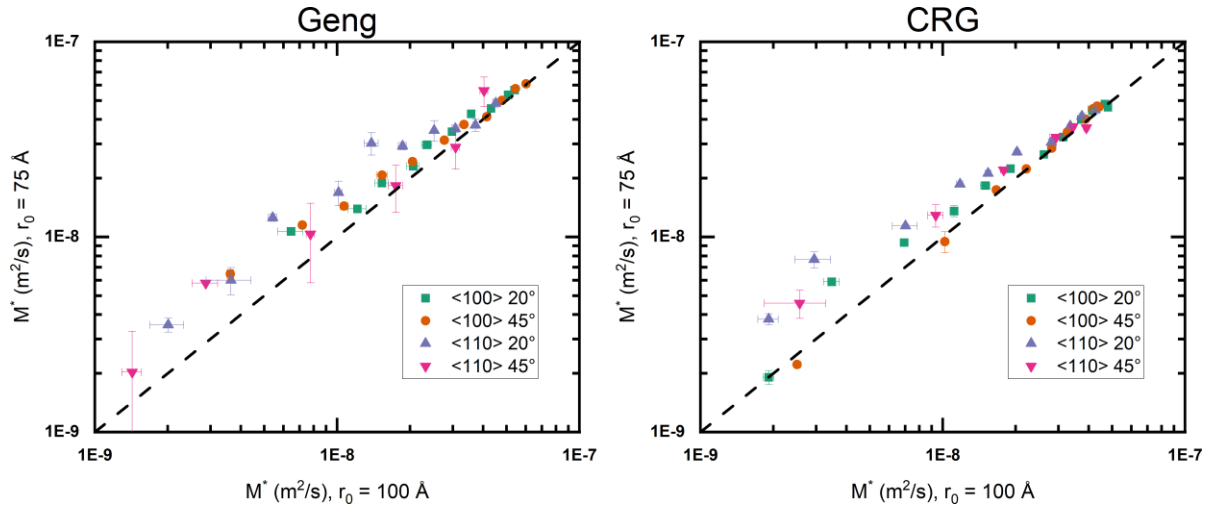


Fig. 6.11. Mobility of the 75 Å initial radius plotted against the 100 Å initial radius. The dashed line indicates equal values for both initial radii.

During reactor operation, fission gases tend to build up at GBs. This is primarily because of GB's preferred segregation sites and ultimately leads to fission gas release when the interconnected GB fission gas bubbles reach a free surface. In the simulations examined here, no free surfaces are available, limiting the behavior of the fission gases to only their impurity-dragging effects. As observed in Fig. 6.2 for both the UMoXe and UO₂+Xe systems, the Xe atoms are swept by the GB, then diffuse along the GBs due to their fast mobility at GBs, and form larger Xe clusters within the GB region. During this process, the GB motion is typically stopped. In UO₂ at a certain critical Xe cluster size, the GB appears to break free, leaving the Xe cluster behind the GB region and allowing grain growth to continue. Therefore, the Xe effect transitions from the impurity drag by individual Xe atoms to Zener pinning by large Xe clusters. This is corroborated by the area versus time plots (see Fig. 6.3(b)), where impurity drag (the stronger pinning effect) occurs when the Xe concentration in the GB region is high, and Xe atoms have not yet clustered together, leading to the stagnant growth regime, followed by the rapid growth once the boundary breaks away once the Xe atoms have clustered together (transitioning into the weaker Zener pinning effect). Therefore, individual Xe atoms have a stronger drag or pinning effect than their clusters if the total number of Xe atoms is the same. Similar behavior is observed for the UXe systems. This impurity dragging and releasing behavior has been observed in Goss-oriented steels [202,203] during the recrystallization process.

In the UMo alloy system, Mo is known to desegregate from the boundary due to the lower GB energy of pure γ U GBs [77], suggesting a segregation energy with the opposite sign of Xe (where Xe atoms tend to segregate toward the GB). Co-segregation effects have not been studied in any significant depth, except for a few studies [204,205]. In [204], the authors identified that for the case of a strongly segregating impurity, and a weakly desegregating solute, the expectation for mobility as a function of impurity concentration is a rapidly decreasing mobility as impurity concentration increases. The results presented in Fig. 6.7 are generally consistent with this idea, though how to define ‘rapid’ for the specific systems considered here is unclear. It is important to note that these ideas were developed under an assumption of steady-state, an assumption that is not valid in the cylindrical GB systems examined here. Additionally, as explained in [205], impurity interactions (e.g., how Xe and Mo interact) are not considered in the derivation of this relationship.

Examination of Figs. 6.5, 6.7, and 6.10 show that the general behavior for increasing Xe concentration for the given system is an approximately linear decrease in the logarithm of the mobility. This suggests a simple relationship between Xe concentration and GB mobility. Therefore, each mobility versus Xe concentration plot was fitted to a line, with the slopes, y-intercepts, and R^2 value included in Appendix C. In Fig. 6.12 the slopes of the reduced mobility versus Xe concentration plots are plotted as a function of temperature for the UXe, UMoXe, and UO_2 +Xe systems. For the metallic U systems, the lower temperatures (<1200 K) are much more spread out, especially in the UMoXe system. At 1200 K and above, the slopes are generally more concentrated, with the averages being consistently around the same value for increasing temperatures. This contrasts with the results of the UO_2 +Xe system, where the average slopes are relatively unchanged from temperature to temperature. The consistency of average slopes suggests a general relationship between Xe concentration and the change in mobility of a GB, independent of the GB character.

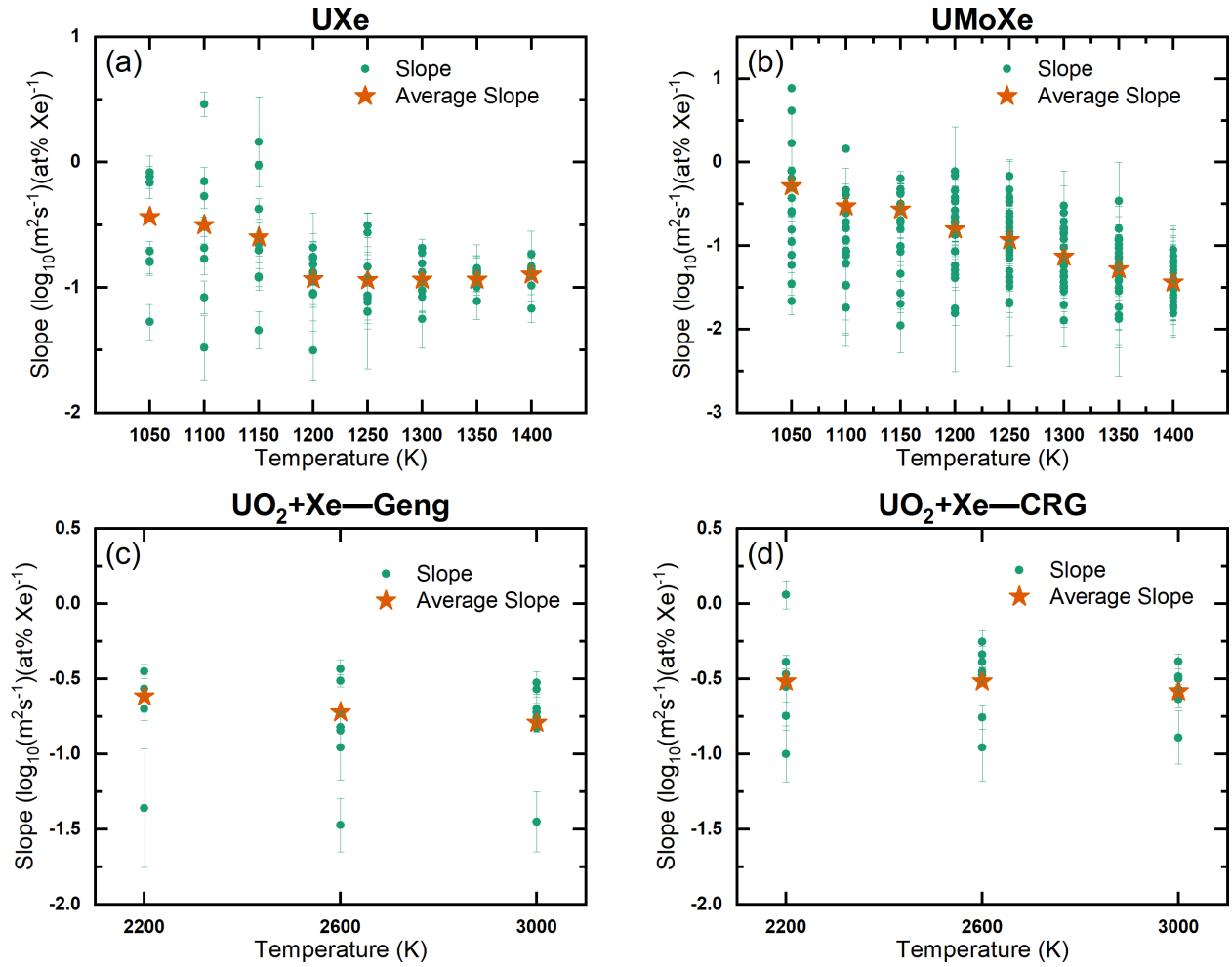


Fig. 6.12. Fitted slopes plotted as a function of temperature. (a) UXe system, (b) UMoXe system, (c) UO₂+Xe system for the Geng potential, (d) UO₂+Xe system for the CRG potential. Error bars indicate standard error. The average slopes are the averages of all the slopes calculated at that specific temperature.

6.6. Conclusions

This work examined the effects of Xe on GB mobility anisotropy in three systems—UXe, UMoXe, and UO₂+Xe—using molecular dynamics. Specifically, the following questions were examined: (1) How does Xe impact GB mobility and its anisotropy trends in these systems? (2) Can the change in GB mobility be predicted based on Xe concentration? For question (1), for all three systems, the mobility anisotropy trend is dependent on the GB misorientation and Xe concentration. In general, low concentrations of Xe have little to no effect on the anisotropy trend,

but high concentrations lead to the anisotropy trend disappearing. This is explained by assuming that impurity drag becomes more important than the effects of GB character on mobility. However, this behavior was not observed in the UO_2+Xe system—this is explained by the Xe concentrations not reaching the critical concentration needed for this to occur in this system. The answer to question (2) for the three systems is ‘yes’: as the Xe concentration increase, the general behavior is a linear decrease in the logarithm of the mobility, which suggests a simple relationship between Xe concentration and GB mobility. Additionally, it is noted that Xe will prefer to be located within the GB region. Furthermore, because of the high mobility of Xe at GBs, they will rapidly diffuse to form a cluster. This cluster will continue to grow as additional Xe atoms join in until the GB breaks free, at which point the cluster will be left behind in the encroaching grain. This process also indicates that the effect from Xe transitions from a stronger impurity drag by many isolated Xe atoms to a weaker Zener pinning by their clustering status. The results from this study could be used as inputs for further investigation via, for example, phase-field simulation of polycrystalline grain growth in the presence of Xe gas in these systems.

Chapter 7. Summary

This work utilized molecular dynamics simulations to analyze GB mobility and its anisotropy trends in the BCC γ U and UMo alloy and UO_2 systems. This work is part of a broader effort to understand how the detailed atomistic process influences the microstructural evolution in nuclear materials, which could facilitate more accurate fuel performance modeling. In Chapter 3, the GB mobility anisotropy trend was established for BCC γ U to be $M_{110} > M_{100}, M_{111}$. This relationship is explained based on a planar density argument, where the density of the plane normal to the GB plane and also the rotation axis plays a significant role in determining the overall anisotropy trend. This chapter also identified that the interatomic potential plays a significant role in the overall GB mobility anisotropy behavior. Chapter 4 verifies the validity of the planar density argument using UO_2 with the fluorite crystal structure (an FCC-based structure) using the same low-index rotation axes ($\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$) and a higher-index rotation axis of $\langle 112 \rangle$. The planar density argument was found to work very well for the UO_2 system. Verification of the importance of choosing the correct potential was emphasized in this work as well—the overall trends between the Basak and CRG potentials were similar, but each one exhibited different unique behaviors that the other did not.

The effects of solutes on the GB mobility anisotropy trend were examined in Chapter 5 for the UMo system. At low solute concentrations, the anisotropy trend remained the same, but at higher concentrations, the anisotropy trend disappears. The proposed reason for this is that solute drag becomes more important than the effects of GB character. In Chapter 6, the effects of Xe impurities on GB mobility and its anisotropy were examined in the γ U, UMo, and UO_2 systems. In general, a linear relationship between the Xe concentration and mobility fits well within the Xe concentration range studied here. The mobility anisotropy trend remained largely unchanged for each system, except at the highest Xe concentrations for the metallic U systems, where the anisotropy trend disappears, similar to the results discussed in Chapter 5.

These results could be used as part of a broader effort to understand microstructural evolution via multiscale modeling, where these atomistic results can be used as inputs for mesoscale simulations of anisotropic, polycrystalline grain growth.

List of Scientific Communications

Publications

J. French and X.M. Bai, “Molecular Dynamics Studies of Grain Boundary Mobility and Anisotropy in BCC γ Uranium,” Journal of Nuclear Materials **565**, 153744 (2022).

J. French and X.M. Bai, “Grain Boundary Mobility Anisotropy in UO_2 ,” *manuscript in preparation*.

J. French and X.M. Bai “Solute Effects on Grain Boundary Mobility in UMo Alloys,” *manuscript in preparation*.

J. French and X.M. Bai “Fission Gas Effects on Grain Boundary Mobility in γ U, UMo and UO_2 ”, *manuscript in preparation*

Presentations

J. French, X.M. Bai, “Atomistic Modeling of Anisotropic Grain Boundary Energies and Mobilities in UO_2 ”, 2018 Materials Research Society (MRS) Spring Meeting, Phoenix, AZ, 04/2018.

J. French and X.M. Bai, “Atomistic Modeling of Anisotropic Grain Boundary Energies and Mobilities in UO_2 ”, MSE Department Seminar, January 2019.

J. French and X.M. Bai, “Molecular Dynamics Simulations of Grain Boundary Mobility in Metallic γ U”, MSE Department Seminar, March 2022.

Bibliography

- [1] M. Upmanyu, G.N. Hassold, A. Kazaryan, E.A. Holm, Y. Wang, B. Patton, D.J. Srolovitz, Boundary Mobility and Energy Anisotropy Effects on Microstructural Evolution During Grain Growth, *Interface Science*. 10 (2002) 201–216.
<https://doi.org/10.1023/A:1015832431826>.
- [2] A. Kazaryan, Y. Wang, S.A. Dregia, B.R. Patton, Grain growth in systems with anisotropic boundary mobility: Analytical model and computer simulation, *Phys. Rev. B*. 63 (2001) 184102. <https://doi.org/10.1103/PhysRevB.63.184102>.
- [3] A. Kazaryan, Y. Wang, S.A. Dregia, B.R. Patton, Grain growth in anisotropic systems: comparison of effects of energy and mobility, *Acta Materialia*. 50 (2002) 2491–2502.
[https://doi.org/10.1016/S1359-6454\(02\)00078-2](https://doi.org/10.1016/S1359-6454(02)00078-2).
- [4] M.R. Tonks, P.-C.A. Simon, J. Hirschhorn, Mechanistic grain growth model for fresh and irradiated UO₂ nuclear fuel, *Journal of Nuclear Materials*. 543 (2021) 152576.
<https://doi.org/10.1016/j.jnucmat.2020.152576>.
- [5] V.Yu. Novikov, Crystallographic texture and grain growth, *Materials Letters*. 254 (2019) 230–232. <https://doi.org/10.1016/j.matlet.2019.07.017>.
- [6] T. Yao, K. Mo, D. Yun, S. Nanda, A.M. Yacout, J. Lian, Grain growth and pore coarsening in dense nano-crystalline UO_{2+x} fuel pellets, *Journal of the American Ceramic Society*. 100 (2017) 2651–2658. <https://doi.org/10.1111/jace.14780>.
- [7] K. Rudman, P. Dickerson, D. Byler, R. McDonald, H.C. Lim, P. Peralta, C. Stanek, K. McClellan, Three-dimensional characterization of sintered uo_{2+x}: Effects of oxygen content on microstructure and its evolution, *NUCLEAR TECHNOLOGY*. 182 (2013) 145–154. <https://doi.org/10.13182/NT13-A16426>.
- [8] C. Sari, Grain growth kinetics in uranium-plutonium mixed oxides, *Journal of Nuclear Materials*. 137 (1986) 100–106. [https://doi.org/10.1016/0022-3115\(86\)90038-3](https://doi.org/10.1016/0022-3115(86)90038-3).
- [9] H. Stehle, H. Assmann, F. Wunderlich, Uranium dioxide properties for LWR fuel rods, *Nuclear Engineering and Design*. 33 (1975) 230–260. [https://doi.org/10.1016/0029-5493\(75\)90024-2](https://doi.org/10.1016/0029-5493(75)90024-2).
- [10] Z.-G. Mei, L. Liang, Y.S. Kim, T. Wiencek, E. O'Hare, A.M. Yacout, G. Hofman, M. Anitescu, Grain growth in U–7Mo alloy: A combined first-principles and phase field

- study, *Journal of Nuclear Materials*. 473 (2016) 300–308.
<https://doi.org/10.1016/j.jnucmat.2016.01.027>.
- [11] Z. Yu, X. Xu, W.-Y. Chen, Y. Sharma, X. Wang, A. Chen, C.J. Ulmer, A.T. Motta, In-situ irradiation-induced studies of grain growth kinetics of nanocrystalline UO₂, *Acta Materialia*. 231 (2022) 117856. <https://doi.org/10.1016/j.actamat.2022.117856>.
- [12] M.K. Meyer, G.L. Hofman, S.L. Hayes, C.R. Clark, T.C. Wiencek, J.L. Snelgrove, R.V. Strain, K.-H. Kim, Low-temperature irradiation behavior of uranium–molybdenum alloy dispersion fuel, *Journal of Nuclear Materials*. 304 (2002) 221–236.
[https://doi.org/10.1016/S0022-3115\(02\)00850-4](https://doi.org/10.1016/S0022-3115(02)00850-4).
- [13] K. Ahmed, J. Pakarinen, T. Allen, A. El-Azab, Phase field simulation of grain growth in porous uranium dioxide, *Journal of Nuclear Materials*. 446 (2014) 90–99.
<https://doi.org/10.1016/j.jnucmat.2013.11.036>.
- [14] V. Tikare, E.A. Holm, Simulation of Grain Growth and Pore Migration in a Thermal Gradient, *Journal of the American Ceramic Society*. 81 (1998) 480–484.
<https://doi.org/10.1111/j.1151-2916.1998.tb02365.x>.
- [15] V. Peres, L. Bourgeois, P. Dehaut, Grain growth and Ostwald ripening in chromia-doped uranium dioxide, *J. Phys. IV France*. 03 (1993) C7-1477-C7-1480.
<https://doi.org/10.1051/jp4:19937231>.
- [16] W.E. Frazier, S. Hu, N. Overman, C. Lavender, V.V. Joshi, Short communication on Kinetics of grain growth and particle pinning in U-10 wt.% Mo, *Journal of Nuclear Materials*. 498 (2018) 254–258. <https://doi.org/10.1016/j.jnucmat.2017.10.041>.
- [17] W.E. Frazier, S. Hu, N. Overman, C. Lavender, V.V. Joshi, Simulations of post-recrystallization grain growth in monolithic U–10Mo fuel processing, *Journal of Nuclear Materials*. 526 (2019) 151763. <https://doi.org/10.1016/j.jnucmat.2019.151763>.
- [18] X. Iltis, I. Zacharie-Aubrun, H.J. Ryu, J.M. Park, A. Leenaers, A.M. Yacout, D.D. Keiser, F. Vanni, B. Stepnik, T. Blay, N. Tarisien, C. Tanguy, H. Palancher, Microstructure of as atomized and annealed U-Mo₇ particles: A SEM/EBSD study of grain growth, *Journal of Nuclear Materials*. 495 (2017) 249–266. <https://doi.org/10.1016/j.jnucmat.2017.07.056>.
- [19] A.J. Clarke, K.D. Clarke, R.J. McCabe, C.T. Necker, P.A. Papin, R.D. Field, A.M. Kelly, T.J. Tucker, R.T. Forsyth, P.O. Dickerson, J.C. Foley, H. Swenson, R.M. Aikin, D.E. Dombrowski, Microstructural evolution of a uranium-10 wt.% molybdenum alloy for

- nuclear reactor fuels, *Journal of Nuclear Materials*. 465 (2015) 784–792.
<https://doi.org/10.1016/j.jnucmat.2015.07.004>.
- [20] C.P. Coughlen, P.A. Evans, A.B. Townsend, HOMOGENIZATION EVALUATION OF A CAST URANIUM--MOLYBDENUM ALLOY., 1969.
<https://doi.org/10.2172/4768453>.
- [21] R. Prabhakaran, L. Gardner, V. Joshi, D. Burkes, C. Lavender, Effect of homogenization and hot rolling on the mechanical properties, microstructure and corrosion behavior of U–10Mo monolithic fuel, *Journal of Nuclear Materials*. 527 (2019) 151804.
<https://doi.org/10/gjn4nx>.
- [22] Y. Zhong, R. Gao, B. Li, Z. Yang, Q. Huang, Z. Wang, L. Duan, X. Liu, M. Chu, P. Zhang, B. Bai, Y. Wang, L. Cheng, B. Yan, T. Liu, R. Li, Preparation and Characterization of Large Grain UO₂ for Accident Tolerant Fuel, *Frontiers in Materials*. 8 (2021) 49. <https://doi.org/10/gnmdbt>.
- [23] Y. Miao, T. Yao, J. Lian, J.-S. Park, J. Almer, S. Bhattacharya, A.M. Yacout, K. Mo, In situ synchrotron investigation of grain growth behavior of nano-grained UO₂, *Scripta Materialia*. 131 (2017) 29–32. <https://doi.org/10.1016/j.scriptamat.2016.12.025>.
- [24] I. Amato, R.L. Colombo, A.P. Balzari, Grain growth in pure and titania-doped uranium dioxide, *Journal of Nuclear Materials*. 18 (1966) 252–260. [https://doi.org/10.1016/0022-3115\(66\)90166-8](https://doi.org/10.1016/0022-3115(66)90166-8).
- [25] H. Chevreil, P. Dehaut, B. Francois, J.F. Baumard, Influence of surface phenomena during sintering of overstoichiometric uranium dioxide UO₂ + x, *Journal of Nuclear Materials*. 189 (1992) 175–182. [https://doi.org/10.1016/0022-3115\(92\)90530-X](https://doi.org/10.1016/0022-3115(92)90530-X).
- [26] H. Hallberg, Y. Zhu, Stability of grain boundary texture during isothermal grain growth in UO₂ considering anisotropic grain boundary properties, *Journal of Nuclear Materials*. 465 (2015) 664–673. <https://doi.org/10.1016/j.jnucmat.2015.06.052>.
- [27] S. Pickering, The effect of impurities on grain growth in uranium dioxide, Ph.D., University of Surrey (United Kingdom), 1976.
<https://www.proquest.com/docview/2021101101/abstract/B16F4928C2074EF1PQ/1>
 (accessed March 29, 2023).
- [28] P.V. Nerikar, K. Rudman, T.G. Desai, D. Byler, C. Unal, K.J. McClellan, S.R. Phillpot, S.B. Sinnott, P. Peralta, B.P. Uberuaga, C.R. Stanek, Grain Boundaries in Uranium

- Dioxide: Scanning Electron Microscopy Experiments and Atomistic Simulations, *Journal of the American Ceramic Society*. 94 (2011) 1893–1900. <https://doi.org/10.1111/j.1551-2916.2010.04295.x>.
- [29] E. Bourasseau, A. Mouret, P. Fantou, X. Iltis, R.C. Belin, Experimental and simulation study of grain boundaries in UO₂, *Journal of Nuclear Materials*. 517 (2019) 286–295. <https://doi.org/10.1016/j.jnucmat.2019.02.033>.
- [30] J.-F. Jue, T.L. Trowbridge, C.R. Breckenridge, G.A. Moore, M.K. Meyer, D.D. Keiser, Effects of heat treatment on U–Mo fuel foils with a zirconium diffusion barrier, *Journal of Nuclear Materials*. 460 (2015) 153–159. <https://doi.org/10.1016/j.jnucmat.2015.02.017>.
- [31] J.B. Ainscough, B.W. Oldfield, J.O. Ware, Isothermal grain growth kinetics in sintered UO₂ pellets, *Journal of Nuclear Materials*. 49 (1973) 117–128. [https://doi.org/10.1016/0022-3115\(73\)90001-9](https://doi.org/10.1016/0022-3115(73)90001-9).
- [32] R.N. Singh, Isothermal grain-growth kinetics in sintered UO₂ pellets, *Journal of Nuclear Materials*. 64 (1977) 174–178. <https://doi.org/10/c3vsz4>.
- [33] L. Bourgeois, P. Dehaudt, C. Lemaignan, J.P. Fredric, Pore migration in UO₂ and grain growth kinetics, *Journal of Nuclear Materials*. 295 (2001) 73–82. [https://doi.org/10.1016/S0022-3115\(01\)00502-5](https://doi.org/10.1016/S0022-3115(01)00502-5).
- [34] G. Gottstein, L.S. Shvindlerman, *Grain Boundary Migration in Metals: Thermodynamics, Kinetics, Applications*, 2nd ed., CRC Press, Florida, 2010.
- [35] M.R. Tonks, Y. Zhang, X. Bai, P.C. Millett, Demonstrating the Temperature Gradient Impact on Grain Growth in UO₂ Using the Phase Field Method, *Materials Research Letters*. 2 (2014) 23–28. <https://doi.org/10/gnmdb3>.
- [36] X.-M. Bai, Y. Zhang, M.R. Tonks, Testing thermal gradient driving force for grain boundary migration using molecular dynamics simulations, *Acta Materialia*. 85 (2015) 95–106. <https://doi.org/10.1016/j.actamat.2014.11.019>.
- [37] Y.-W. Rhee, D.-J. Kim, K.-S. Kim, Effect of U₃O₈-seed on the grain growth of uranium dioxide, *Journal of the Korean Crystal Growth and Crystal Technology*. 17 (2007) 75–81.
- [38] K. Govers, S.E. Lemehov, M. Verwerft, Molecular Dynamics Study of Grain Boundary Diffusion of Fission Gas in Uranium Dioxide, *DDF*. 323–325 (2012) 215–220. <https://doi.org/10.4028/www.scientific.net/DDF.323-325.215>.

- [39] Y. Xia, Z. Wang, L. Wang, Y. Chen, Z. Liu, Q. Wang, L. Wu, H. Deng, Molecular Dynamics Simulations of Xe Behaviors at the Grain Boundary in UO₂, *Metals*. 12 (2022) 763. <https://doi.org/10.3390/met12050763>.
- [40] P.V. Nerikar, D.C. Parfitt, L.A. Casillas Trujillo, D.A. Andersson, C. Unal, S.B. Sinnott, R.W. Grimes, B.P. Uberuaga, C.R. Stanek, Segregation of xenon to dislocations and grain boundaries in uranium dioxide, *Phys. Rev. B*. 84 (2011) 174105. <https://doi.org/10/fvp76n>.
- [41] Y. Miao, M.C. Rajagopal, K. Valavala, K. Mo, Z.-G. Mei, S. Bhattacharya, L. Jamison, S. Sinha, A.M. Yacout, An exploration of measuring lower-length-scale structures in nuclear materials: Thermal conductivity of U-Mo fuel particle, *Journal of Nuclear Materials*. 527 (2019) 151797. <https://doi.org/10.1016/j.jnucmat.2019.151797>.
- [42] S. Jana, N. Overman, T. Varga, C. Lavender, V.V. Joshi, Phase transformation kinetics in rolled U-10 wt. % Mo foil: Effect of post-rolling heat treatment and prior γ -UMo grain size, *Journal of Nuclear Materials*. 496 (2017) 215–226. <https://doi.org/10.1016/j.jnucmat.2017.09.030>.
- [43] W. Frazier, C. Wang, Z. Xu, N. Overman, S. Hu, V.V. Joshi, Recrystallization and Grain Growth Simulations for Multiple-Pass Rolling and Annealing of U-10Mo, *Metall and Mat Trans A*. 51 (2020) 533–544. <https://doi.org/10.1007/s11661-019-05582-6>.
- [44] C. Herring, Surface Tension as a Motivation for Sintering, in: J.M. Ball, D. Kinderlehrer, P. Podio-Guidugli, M. Slemrod (Eds.), *Fundamental Contributions to the Continuum Theory of Evolving Phase Interfaces in Solids: A Collection of Reprints of 14 Seminal Papers*, Springer Berlin Heidelberg, Berlin, Heidelberg, 1999: pp. 33–69. https://doi.org/10.1007/978-3-642-59938-5_2.
- [45] S.M. Foiles, J.J. Hoyt, Computation of grain boundary stiffness and mobility from boundary fluctuations, *Acta Materialia*. 54 (2006) 3351–3357. <https://doi.org/10.1016/j.actamat.2006.03.037>.
- [46] A.P. Thompson, H.M. Aktulga, R. Berger, D.S. Bolintineanu, W.M. Brown, P.S. Crozier, P.J. in 't Veld, A. Kohlmeyer, S.G. Moore, T.D. Nguyen, R. Shan, M.J. Stevens, J. Tranchida, C. Trott, S.J. Plimpton, LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales, *Computer Physics Communications*. 271 (2022) 108171. <https://doi.org/10/gmwrnb>.

- [47] F. Ulomek, C.J. O'Brien, S.M. Foiles, V. Mohles, Energy conserving orientational force for determining grain boundary mobility, *Modelling and Simulation in Materials Science and Engineering*. 23 (2015) 025007. <https://doi.org/10.1088/0965-0393/23/2/025007>.
- [48] A.A. Schratt, V. Mohles, Efficient calculation of the ECO driving force for atomistic simulations of grain boundary motion, *Computational Materials Science*. 182 (2020) 109774. <https://doi.org/10/gg4jfd>.
- [49] J. French, X.-M. Bai, Molecular dynamics studies of grain boundary mobility and anisotropy in BCC γ -uranium, *Journal of Nuclear Materials*. 565 (2022) 153744. <https://doi.org/10.1016/j.jnucmat.2022.153744>.
- [50] D.J. Senior, D.E. Burkes, Fuel Fabrication Capability Research and Development Plan, Pacific Northwest National Laboratory, United States, 2014. <https://doi.org/10.2172/1149235>.
- [51] E.H. Wilson, D. Jaluvka, A.S. Hebden, J.A. Stillman, L.M. Jamison, U.S. High Performance Research Reactor Preliminary Design Milestone for Conversion to Low Enriched Uranium Fuel, in: *Research Org.: Argonne National Lab. (ANL), Argonne, IL (United States)*, 2019. <https://www.osti.gov/biblio/1515073>.
- [52] S.F. Pugh, Swelling in alpha uranium due to irradiation, *Journal of Nuclear Materials*. 4 (1961) 177–199. <https://doi.org/10/ftvdjz>.
- [53] F.G. Di Lemma, X. Liu, T.V. Holschuh, C.P. Folsom, D.J. Murray, F. Teng, C.B. Jensen, Investigation of the microstructure evolution of alpha uranium after in pile transient, *Journal of Nuclear Materials*. 542 (2020) 152467. <https://doi.org/10/gmbdzj>.
- [54] M.K. Meyer, J. Gan, J.F. Jue, D.D. Keiser, E. Perez, A. Robinson, D.M. Wachs, N. Woolstenhulme, G.L. Hofman, Y.S. Kim, Irradiation Performance of U-Mo Monolithic Fuel, *Nuclear Engineering and Technology*. 46 (2014) 169–182. <https://doi.org/10.5516/NET.07.2014.706>.
- [55] J. Donohue, H. Einspahr, The Structure of β -Uranium, *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*. 27 (1971) 1740–1743. <https://doi.org/10/fv57zz>.
- [56] Nuclear Research Reactors - World Nuclear Association, (n.d.). <https://world-nuclear.org/information-library/non-power-nuclear-applications/radioisotopes-research/research-reactors.aspx> (accessed July 25, 2021).

- [57] T. Ajantiwalay, C. Smith, D.D. Keiser, A. Aitkaliyeva, A critical review of the microstructure of U–Mo fuels, *Journal of Nuclear Materials*. 540 (2020) 152386. <https://doi.org/10.1016/j.jnucmat.2020.152386>.
- [58] V.P. Sinha, P.V. Hegde, G.J. Prasad, G.K. Dey, H.S. Kamath, Phase transformation of metastable cubic γ -phase in U–Mo alloys, *Journal of Alloys and Compounds*. 506 (2010) 253–262. <https://doi.org/10.1016/j.jallcom.2010.06.187>.
- [59] J. Rest, Y.S. Kim, G.L. Hofman, M.K. Meyer, S.L. Hayes, U-Mo fuels handbook. Version 1.0, United States, 2006. <https://doi.org/10.2172/1335129>.
- [60] R.M. Hengstler, L. Beck, H. Breitzkreutz, C. Jarousse, R. Jungwirth, W. Petry, W. Schmid, J. Schneider, N. Wieselha, Physical properties of monolithic U8wt.%–Mo, *Journal of Nuclear Materials*. 402 (2010) 74–80. <https://doi.org/10.1016/j.jnucmat.2010.04.024>.
- [61] S. Van den Berghe, W. Van Renterghem, A. Leenaers, Transmission electron microscopy investigation of irradiated U–7wt%Mo dispersion fuel, *Journal of Nuclear Materials*. 375 (2008) 340–346. <https://doi.org/10.1016/j.jnucmat.2007.12.006>.
- [62] Y.S. Kim, G.L. Hofman, J.S. Cheon, Recrystallization and fission-gas-bubble swelling of U–Mo fuel, *Journal of Nuclear Materials*. 436 (2013) 14–22. <https://doi.org/10.1016/j.jnucmat.2013.01.291>.
- [63] S. Van den Berghe, Y. Parthoens, G. Cornelis, A. Leenaers, E. Koonen, V. Kuzminov, C. Detavernier, Swelling of U(Mo) dispersion fuel under irradiation – Non-destructive analyses of the SELENIUM plates, *Journal of Nuclear Materials*. 442 (2013) 60–68. <https://doi.org/10.1016/j.jnucmat.2013.08.020>.
- [64] J. Rest, A model for the effect of the progression of irradiation-induced recrystallization from initiation to completion on swelling of UO₂ and U–10Mo nuclear fuels, *Journal of Nuclear Materials*. 346 (2005) 226–232. <https://doi.org/10.1016/j.jnucmat.2005.06.012>.
- [65] A.B. Robinson, W.J. Williams, W.A. Hanson, B.H. Rabin, N.J. Lybeck, M.K. Meyer, Swelling of U-Mo Monolithic Fuel: Developing a Predictive Swelling Correlation under Research Reactor Conditions, *Journal of Nuclear Materials*. 544 (2021) 152703. <https://doi.org/10/gmcgxxg>.
- [66] J. Gan, B.D. Miller, D.D. Keiser, A.B. Robinson, J.W. Madden, P.G. Medvedev, D.M. Wachs, Microstructural characterization of irradiated U–7Mo/Al–5Si dispersion fuel to

- high fission density, *Journal of Nuclear Materials*. 454 (2014) 434–445.
<https://doi.org/10/f6n6sx>.
- [67] A. Leenaers, W. Van Renterghem, S. Van den Berghe, High burn-up structure of U(Mo) dispersion fuel, *Journal of Nuclear Materials*. 476 (2016) 218–230.
<https://doi.org/10.1016/j.jnucmat.2016.04.035>.
- [68] J. Noirot, L. Desgranges, J. Lamontagne, Detailed characterisations of high burn-up structures in oxide fuels, *Journal of Nuclear Materials*. 372 (2008) 318–339.
<https://doi.org/10/fk876n>.
- [69] L. Liang, Z.-G. Mei, Y.S. Kim, B. Ye, G. Hofman, M. Anitescu, A.M. Yacout, Mesoscale model for fission-induced recrystallization in U-7Mo alloy, *Computational Materials Science*. 124 (2016) 228–237. <https://doi.org/10.1016/j.commatsci.2016.07.033>.
- [70] L. Liang, Z.-G. Mei, A.M. Yacout, Fission-induced recrystallization effect on intergranular bubble-driven swelling in U-Mo fuel, *Computational Materials Science*. 138 (2017) 16–26. <https://doi.org/10.1016/j.commatsci.2017.06.013>.
- [71] S. Hu, D. Burkes, C.A. Lavender, V. Joshi, Effect of grain morphology on gas bubble swelling in UMo fuels – A 3D microstructure dependent Booth model, *Journal of Nuclear Materials*. 480 (2016) 323–331. <https://doi.org/10.1016/j.jnucmat.2016.08.038>.
- [72] S. Hu, V. Joshi, C.A. Lavender, A Rate-Theory–Phase-Field Model of Irradiation-Induced Recrystallization in UMo Nuclear Fuels, *JOM*. 69 (2017) 2554–2562.
<https://doi.org/10.1007/s11837-017-2611-4>.
- [73] M.R. Tonks, D. Gaston, P.C. Millett, D. Andrs, P. Talbot, An object-oriented finite element framework for multiphysics phase field simulations, *Computational Materials Science*. 51 (2012) 20–29. <https://doi.org/10/d94vs3>.
- [74] C.V. Thompson, Grain Growth in Thin Films, *Annu. Rev. Mater. Sci.* 20 (1990) 245.
<https://doi.org/10/djtsz5>.
- [75] K. Chen, J. Han, X. Pan, D.J. Srolovitz, The grain boundary mobility tensor, *Proc Natl Acad Sci USA*. 117 (2020) 4533–4538. <https://doi.org/10.1073/pnas.1920504117>.
- [76] W.T. Read, W. Shockley, Dislocation Models of Crystal Grain Boundaries, *Phys. Rev.* 78 (1950) 275–289. <https://doi.org/10.1103/PhysRev.78.275>.

- [77] B. Beeler, Y. Zhang, Y. Gao, An atomistic study of grain boundaries and surfaces in γ U-Mo, *Journal of Nuclear Materials*. 507 (2018) 248–257.
<https://doi.org/10.1016/j.jnucmat.2018.05.007>.
- [78] D.A. Molodov, U. Czubayko, G. Gottstein, L.S. Shvindlerman, On the effect of purity and orientation on grain boundary motion, *Acta Materialia*. 46 (1998) 553–564.
<https://doi.org/10/cqr445>.
- [79] N. Ma, A. Kazaryan, S.A. Dregia, Y. Wang, Computer simulation of texture evolution during grain growth: effect of boundary properties and initial microstructure, *Acta Materialia*. 52 (2004) 3869–3879. <https://doi.org/10.1016/j.actamat.2004.05.001>.
- [80] G.S. Rohrer, E.A. Holm, A.D. Rollett, S.M. Foiles, J. Li, D.L. Olmsted, Comparing calculated and measured grain boundary energies in nickel, *Acta Materialia*. 58 (2010) 5063–5069. <https://doi.org/10.1016/j.actamat.2010.05.042>.
- [81] D.L. Olmsted, S.M. Foiles, E.A. Holm, Survey of computed grain boundary properties in face-centered cubic metals: I. Grain boundary energy, *Acta Materialia*. 57 (2009) 3694–3703. <https://doi.org/10.1016/j.actamat.2009.04.007>.
- [82] D.L. Olmsted, E.A. Holm, S.M. Foiles, Survey of computed grain boundary properties in face-centered cubic metals—II: Grain boundary mobility, *Acta Materialia*. 57 (2009) 3704–3713. <https://doi.org/10.1016/j.actamat.2009.04.015>.
- [83] A.D. Rollett, G. Gottstein, L.S. Shvindlerman, D.A. Molodov, Grain boundary mobility – a brief review, *MEKU*. 95 (2004) 226–229. <https://doi.org/10.3139/146.017938>.
- [84] M.L. Taheri, D.A. Molodov, G. Gottstein, A.D. Rollett, Grain boundary mobility under a stored-energy driving force: a comparison to curvature-driven boundary migration, *Zeitschrift Fur Metallkunde*. 96 (2005) 1166.
- [85] I. Toda-Caraballo, P.D. Bristowe, C. Capdevila, A molecular dynamics study of grain boundary free energies, migration mechanisms and mobilities in a bcc Fe–20Cr alloy, *Acta Materialia*. 60 (2012) 1116–1128. <https://doi.org/10.1016/j.actamat.2011.11.021>.
- [86] L. Zhou, N. Zhou, G. Song, Collective motion of atoms in grain boundary migration of a bcc metal, *Philosophical Magazine*. 86 (2006) 5885–5895. <https://doi.org/10/fgnxxp>.
- [87] H. Zhang, D. Du, D.J. Srolovitz, M.I. Mendelev, Determination of grain boundary stiffness from molecular dynamics simulation, *Appl. Phys. Lett.* 88 (2006) 121927.
<https://doi.org/10/c2n3p4>.

- [88] Z.T. Trautt, Y. Mishin, Grain boundary migration and grain rotation studied by molecular dynamics, *Acta Materialia*. 60 (2012) 2407–2424.
<https://doi.org/10.1016/j.actamat.2012.01.008>.
- [89] S.V. Starikov, L.N. Kolotova, A.Yu. Kuksin, D.E. Smirnova, V.I. Tseplyaev, Atomistic simulation of cubic and tetragonal phases of U-Mo alloy: Structure and thermodynamic properties, *Journal of Nuclear Materials*. 499 (2018) 451–463.
<https://doi.org/10.1016/j.jnucmat.2017.11.047>.
- [90] J.R. Fernández, M.I. Pascuet, On the accurate description of uranium metallic phases: a MEAM interatomic potential approach, *Modelling and Simulation in Materials Science and Engineering*. 22 (2014) 055019. <https://doi.org/10.1088/0965-0393/22/5/055019>.
- [91] D.E. Smirnova, A.Y. Kuksin, S.V. Starikov, V.V. Stegailov, Z. Insepov, J. Rest, A.M. Yacout, A ternary EAM interatomic potential for U–Mo alloys with xenon, *Modelling and Simulation in Materials Science and Engineering*. 21 (2013) 035011.
<https://doi.org/10.1088/0965-0393/21/3/035011>.
- [92] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, *Journal of Computational Physics*. 117 (1995) 1–19. <https://doi.org/10.1006/jcph.1995.1039>.
- [93] A.S. Wilson, R.E. Rundle, The structures of uranium metal, *Acta Crystallographica*. 2 (1949) 126–127. <https://doi.org/10/c4xgn3>.
- [94] I. Grenthe, J. Drożdżynski, T. Fujino, E.C. Buck, T.E. Albrecht-Schmitt, S.F. Wolf, Uranium, in: L.R. Morss, N.M. Edelstein, J. Fuger (Eds.), *The Chemistry of the Actinide and Transactinide Elements*, Springer Netherlands, Dordrecht, 2006: pp. 253–698.
https://doi.org/10.1007/1-4020-3598-5_5.
- [95] C.F. Jekel, G. Venter, *pwlf: A Python Library for Fitting 1D Continuous Piecewise Linear Functions*, (2019). https://github.com/cjekel/piecewise_linear_fit_py.
- [96] P.R. Cantwell, E.A. Holm, M.P. Harmer, M.J. Hoffmann, Anti-thermal behavior of materials, *Scripta Materialia*. 103 (2015) 1–5.
<https://doi.org/10.1016/j.scriptamat.2015.02.011>.
- [97] J.E. Burke, D. Turnbull, Recrystallization and grain growth, *Progress in Metal Physics*. 3 (1952) 220–292. <https://doi.org/10/dnvp49>.

- [98] S.J. Fensin, D. Olmsted, D. Buta, M. Asta, A. Karma, J.J. Hoyt, Structural disjoining potential for grain-boundary premelting and grain coalescence from molecular-dynamics simulations, *Phys. Rev. E*. 81 (2010) 031601. <https://doi.org/10/dp2pmd>.
- [99] C.J. O'Brien, S.M. Foiles, Exploration of the mechanisms of temperature-dependent grain boundary mobility: search for the common origin of ultrafast grain boundary motion, *Journal of Materials Science*. 51 (2016) 6607–6623. <https://doi.org/10.1007/s10853-016-9944-1>.
- [100] F. Ulomek, V. Mohles, Separating grain boundary migration mechanisms in molecular dynamics simulations, *Acta Materialia*. 103 (2016) 424–432. <https://doi.org/10.1016/j.actamat.2015.10.021>.
- [101] H. Zhang, D.J. Srolovitz, J.F. Douglas, J.A. Warren, Grain boundaries exhibit the dynamics of glass-forming liquids, *Proceedings of the National Academy of Sciences*. 106 (2009) 7735–7740. <https://doi.org/10.1073/pnas.0900227106>.
- [102] C. Deng, C.A. Schuh, Atomistic Simulation of Slow Grain Boundary Motion, *Phys. Rev. Lett*. 106 (2011) 045503. <https://doi.org/10.1103/PhysRevLett.106.045503>.
- [103] C. Deng, C.A. Schuh, Diffusive-to-ballistic transition in grain boundary motion studied by atomistic simulations, *Phys. Rev. B*. 84 (2011) 214102. <https://doi.org/10.1103/PhysRevB.84.214102>.
- [104] W. Rheinheimer, E. Schoof, M. Selzer, B. Nestler, M.J. Hoffmann, Non-Arrhenius grain growth in strontium titanate: Quantification of bimodal grain growth, *Acta Materialia*. 174 (2019) 105–115. <https://doi.org/10.1016/j.actamat.2019.05.040>.
- [105] E.R. Homer, E.A. Holm, S.M. Foiles, D.L. Olmsted, Trends in Grain Boundary Mobility: Survey of Motion Mechanisms, *JOM*. 66 (2014) 114–120. <https://doi.org/10.1007/s11837-013-0801-2>.
- [106] I. Chesser, E. Holm, Understanding the anomalous thermal behavior of $\Sigma 3$ grain boundaries in a variety of FCC metals, *Scripta Materialia*. 157 (2018) 19–23. <https://doi.org/10.1016/j.scriptamat.2018.07.011>.
- [107] D.E. Smirnova, A.Yu. Kuksin, S.V. Starikov, V.V. Stegailov, Atomistic modeling of the self-diffusion in γ -U and γ -U-Mo, *Phys. Metals Metallogr*. 116 (2015) 445–455. <https://doi.org/10.1134/S0031918X1503014X>.

- [108] D.E. Smirnova, A.Yu. Kuksin, S.V. Starikov, Investigation of point defects diffusion in bcc uranium and U–Mo alloys, *Journal of Nuclear Materials*. 458 (2015) 304–311.
<https://doi.org/10.1016/j.jnucmat.2014.12.080>.
- [109] G. Park, B. Beeler, M.A. Okuniewski, An atomistic study of defect energetics and diffusion with respect to composition and temperature in γ U and γ U–Mo alloys, *Journal of Nuclear Materials*. 552 (2021) 152970. <https://doi.org/10/gkc83p>.
- [110] B. Schönfelder, G. Gottstein, L.S. Shvindlerman, Comparative study of grain-boundary migration and grain-boundary self-diffusion of [001] twist-grain boundaries in copper by atomistic simulations, *Acta Materialia*. 53 (2005) 1597–1609.
<https://doi.org/10.1016/j.actamat.2004.12.010>.
- [111] T. Frolov, W. Setyawan, R. J. Kurtz, J. Marian, A. R. Oganov, R. E. Rudd, Q. Zhu, Grain boundary phases in bcc metals, *Nanoscale*. 10 (2018) 8253–8268.
<https://doi.org/10/gn9842>.
- [112] S. Starikov, M. Mrovec, R. Drautz, Study of grain boundary self-diffusion in iron with different atomistic models, *Acta Materialia*. 188 (2020) 560–569.
<https://doi.org/10/gn9843>.
- [113] T. Frolov, Y. Mishin, Molecular dynamics modeling of self-diffusion along a triple junction, *Phys. Rev. B*. 79 (2009) 174110. <https://doi.org/10/cgfv5k>.
- [114] M.A. Korneva, S.V. Starikov, A.P. Zhilyaev, I.S. Akhatov, P.A. Zhilyaev, Atomistic Modeling of Grain Boundary Migration in Nickel, *Adv. Eng. Mater.* 22 (2020) 2000115.
<https://doi.org/10/gn9844>.
- [115] K.G.F. Janssens, D. Olmsted, E.A. Holm, S.M. Foiles, S.J. Plimpton, P.M. Derlet, Computing the mobility of grain boundaries, *Nature Materials*. 5 (2006) 124–127.
<https://doi.org/10.1038/nmat1559>.
- [116] H. Zhang, M. Upmanyu, D.J. Srolovitz, Curvature driven grain boundary migration in aluminum: molecular dynamics simulations, *Acta Materialia*. 53 (2005) 79–86.
<https://doi.org/10.1016/j.actamat.2004.09.004>.
- [117] Z.T. Trautt, M. Upmanyu, A. Karma, Interface Mobility from Interface Random Walk, *Science*. 314 (2006) 632. <https://doi.org/10.1126/science.1131988>.
- [118] M.I. Mendelev, C. Deng, C.A. Schuh, D.J. Srolovitz, Comparison of molecular dynamics simulation methods for the study of grain boundary migration, *Modelling and Simulation*

- in Materials Science and Engineering. 21 (2013) 045017. <https://doi.org/10.1088/0965-0393/21/4/045017>.
- [119] INTERNATIONAL ATOMIC ENERGY AGENCY, The potential role of nuclear energy in national climate change mitigation strategies, INTERNATIONAL ATOMIC ENERGY AGENCY, Vienna, 2021. <https://www.iaea.org/publications/15001/the-potential-role-of-nuclear-energy-in-national-climate-change-mitigation-strategies>.
- [120] I. Hore-Lacy, Nuclear Energy in the 21st Century : World Nuclear University Press, Elsevier Science & Technology, Burlington, UNITED STATES, 2006. <http://ebookcentral.proquest.com/lib/vt/detail.action?docID=297054>.
- [121] IEA, Nuclear Power in a Clean Energy System, 2019.
- [122] L. Zhan, Y. Bo, T. Lin, Z. Fan, Development and outlook of advanced nuclear energy technology, Energy Strategy Reviews. 34 (2021) 100630. <https://doi.org/10.1016/j.esr.2021.100630>.
- [123] M.R. Tonks, D. Andersson, S.R. Phillpot, Y. Zhang, R. Williamson, C.R. Stanek, B.P. Uberuaga, S.L. Hayes, Mechanistic materials modeling for nuclear fuel performance, Annals of Nuclear Energy. 105 (2017) 11–24. <https://doi.org/10.1016/j.anucene.2017.03.005>.
- [124] J.Y.R. Rashid, S.K. Yagnik, R.O. Montgomery, Light water reactor fuel performance modeling and multi-dimensional simulation, JOM. 63 (2011) 81–88. <https://doi.org/10.1007/s11837-011-0144-9>.
- [125] C.E. Beyer, C.R. Hann, D.D. Lanning, F.E. Panisko, L.J. Parchen, GAPCON-THERMAL-2: A computer program for calculating the thermal behavior of an oxide fuel rod, 1975. <https://doi.org/10.2172/4113463>.
- [126] K. Lassmann, C.T. Walker, J. van de Laar, F. Lindström, Modelling the high burnup UO₂ structure in LWR fuel, Journal of Nuclear Materials. 226 (1995) 1–8. [https://doi.org/10.1016/0022-3115\(95\)00116-6](https://doi.org/10.1016/0022-3115(95)00116-6).
- [127] K. Geelhood, Fuel Performance Considerations and Data Needs for Burnup above 62 GWd/MTU, Pacific Northwest National Laboratory, Richland, Washington, 2019.
- [128] G. Pastore, L.P. Swiler, J.D. Hales, S.R. Novascone, D.M. Perez, B.W. Spencer, L. Luzzi, P. Van Uffelen, R.L. Williamson, Uncertainty and sensitivity analysis of fission gas

- behavior in engineering-scale fuel modeling, *Journal of Nuclear Materials*. 456 (2015) 398–408. <https://doi.org/10.1016/j.jnucmat.2014.09.077>.
- [129] J.A. Turnbull, The effect of grain size on the swelling and gas release properties of UO_2 during irradiation, *Journal of Nuclear Materials*. 50 (1974) 62–68. [https://doi.org/10.1016/0022-3115\(74\)90061-0](https://doi.org/10.1016/0022-3115(74)90061-0).
- [130] K. Shrestha, T. Yao, J. Lian, D. Antonio, M. Sessim, M.R. Tonks, K. Gofryk, The grain-size effect on thermal conductivity of uranium dioxide, *Journal of Applied Physics*. 126 (2019) 125116. <https://doi.org/10.1063/1.5116372>.
- [131] M.R. Tonks, Y. Zhang, X. Bai, NEAMS FPL M2 Milestone Report: Development of a UO_2 Grain Size Model using Multiscale Modeling and Simulation, Idaho National Lab.(INL), Idaho Falls, ID (United States), 2014.
- [132] K. Ahmed, C.A. Yablinsky, A. Schulte, T. Allen, A. El-Azab, Phase field modeling of the effect of porosity on grain growth kinetics in polycrystalline ceramics, *Modelling Simul. Mater. Sci. Eng.* 21 (2013) 065005. <https://doi.org/10.1088/0965-0393/21/6/065005>.
- [133] C.T. Walker, D. Staicu, M. Sheindlin, D. Papaioannou, W. Goll, F. Sontheimer, On the thermal conductivity of UO_2 nuclear fuel at a high burn-up of around 100MWd/kgHM, *Journal of Nuclear Materials*. 350 (2006) 19–39. <https://doi.org/10.1016/j.jnucmat.2006.03.001>.
- [134] Y. Guo, Z. Liu, Q. Huang, C.-T. Lin, S. Du, Abnormal grain growth of UO_2 with pores in the final stage of sintering: A phase field study, *Computational Materials Science*. 145 (2018) 24–34. <https://doi.org/10.1016/j.commatsci.2017.12.057>.
- [135] C.-W. Lee, A. Chernatynskiy, P. Shukla, R.E. Stoller, S.B. Sinnott, S.R. Phillpot, Effect of pores and He bubbles on the thermal transport properties of UO_2 by molecular dynamics simulation, *Journal of Nuclear Materials*. 456 (2015) 253–259. <https://doi.org/10.1016/j.jnucmat.2014.09.052>.
- [136] T. Abe, K. Asakura, 2.15 - Uranium Oxide and MOX Production, in: R.J.M. Konings (Ed.), *Comprehensive Nuclear Materials*, Elsevier, Oxford, 2012: pp. 393–422. <https://doi.org/10.1016/B978-0-08-056033-5.00036-7>.
- [137] R.L. Williamson, J.D. Hales, S.R. Novascone, M.R. Tonks, D.R. Gaston, C.J. Permann, D. Andrs, R.C. Martineau, Multidimensional multiphysics simulation of nuclear fuel behavior, *Journal of Nuclear Materials*. 423 (2012) 149–163. <https://doi.org/10.1016/j.jnucmat.2012.03.001>.

- [138] A.P. Sutton, R.W. Balluffi, Interfaces in crystalline materials, Clarendon Press, Oxford, 1995.
- [139] D. Wolf, A Read-Shockley Model for High-Angle Grain Boundaries, *Scripta Metallurgica*. 23 (1989) 1713–1718. [https://doi.org/10.1016/0036-9748\(89\)90348-7](https://doi.org/10.1016/0036-9748(89)90348-7).
- [140] H. Hallberg, V.V. Bulatov, Modeling of grain growth under fully anisotropic grain boundary energy, *Modelling Simul. Mater. Sci. Eng.* 27 (2019) 045002. <https://doi.org/10.1088/1361-651X/ab0c6c>.
- [141] Y. Zhang, E.D. Hansen, T. Harbison, S. Masengale, J. French, L. Aagesen, A molecular dynamics survey of grain boundary energy in uranium dioxide and cerium dioxide, *Journal of the American Ceramic Society*. 105 (2022) 4471–4486. <https://doi.org/10.1111/jace.18340>.
- [142] A. Ksibi, E. Bourasseau, X. Iltis, D. Drouan, M. Gaudet, A. Germain, A. Pena, G. Lapertot, J.-P. Brison, R.C. Belin, Experimental and numerical assessment of grain boundary energies in polycrystalline uranium dioxide, *Journal of the European Ceramic Society*. 40 (2020) 4191–4201. <https://doi.org/10.1016/j.jeurceramsoc.2020.04.041>.
- [143] V.V. Bulatov, B.W. Reed, M. Kumar, Grain boundary energy function for fcc metals, *Acta Materialia*. 65 (2014) 161–175. <https://doi.org/10.1016/j.actamat.2013.10.057>.
- [144] S. Ratanaphan, D.L. Olmsted, V.V. Bulatov, E.A. Holm, A.D. Rollett, G.S. Rohrer, Grain boundary energies in body-centered cubic metals, *Acta Materialia*. 88 (2015) 346–354. <https://doi.org/10.1016/j.actamat.2015.01.069>.
- [145] R.-J. Jhan, P.D. Bristowe, A molecular dynamics study of grain boundary migration without the participation of secondary grain boundary dislocations, *Scripta Metallurgica et Materialia*. 24 (1990) 1313–1318. [https://doi.org/10.1016/0956-716X\(90\)90348-K](https://doi.org/10.1016/0956-716X(90)90348-K).
- [146] M. Upmanyu, R.W. Smith, D.J. Srolovitz, Atomistic Simulation of Curvature Driven Grain Boundary Migration, *Interface Science*. 6 (1998) 41–58. <https://doi.org/10.1023/A:1008608418845>.
- [147] M. Upmanyu, D.J. Srolovitz, A.E. Lobkovsky, J.A. Warren, W.C. Carter, Simultaneous grain boundary migration and grain rotation, *Acta Materialia*. 54 (2006) 1707–1719. <https://doi.org/10.1016/j.actamat.2005.11.036>.

- [148] K.W. Song, W.K. Choo, Changes in the duplex grain structure of UO₂ with a bimodal grain size distribution and irregular grains, *Journal of Nuclear Materials*. 203 (1993) 122–127. [https://doi.org/10.1016/0022-3115\(93\)90048-4](https://doi.org/10.1016/0022-3115(93)90048-4).
- [149] S.G. Srinivasan, J.W. Cahn, Challenging Some Free-Energy Reduction Criteria for Grain Growth, *Science and Technology of Interfaces*. (2002) 1–14.
- [150] H. Ogawa, GBstudio: A Builder Software on Periodic Models of CSL Boundaries for Molecular Simulation, *Mater. Trans.* 47 (2006) 2706–2710.
<https://doi.org/10.2320/matertrans.47.2706>.
- [151] C.B. Basak, A.K. Sengupta, H.S. Kamath, Classical molecular dynamics simulation of UO₂ to predict thermophysical properties, *Journal of Alloys and Compounds*. 360 (2003) 210–216. <https://doi.org/10/c92632>.
- [152] J. French, Molecular Dynamics Studies of Anisotropy in Grain Boundary Energy and Mobility in UO₂, Masters of Science, Virginia Polytechnic Institute and State University, 2019.
https://vtechworks.lib.vt.edu/bitstream/handle/10919/89643/French_J_C_T_2019.pdf?sequence=5&isAllowed=y (accessed November 27, 2021).
- [153] M.W.D. Cooper, M.J.D. Rushton, R.W. Grimes, A many-body potential approach to modelling the thermomechanical properties of actinide oxides, *J. Phys.: Condens. Matter*. 26 (2014) 105401. <https://doi.org/10.1088/0953-8984/26/10/105401>.
- [154] K. Govers, S. Lemehov, M. Hou, M. Verwerft, Comparison of interatomic potentials for UO₂ Part I: Static calculations, *Journal of Nuclear Materials*. 366 (2007) 161–177.
<https://doi.org/10.1016/j.jnucmat.2006.12.070>.
- [155] S. Plimpton, R. Pollock, M. Stevens, Particle-Mesh Ewald and rRESPA for Parallel Molecular Dynamics Simulations., in: Citeseer, 1997.
- [156] S.G. Wang, E.K. Tian, C.W. Lung, Surface energy of arbitrary crystal plane of bcc and fcc metals, *Journal of Physics and Chemistry of Solids*. 61 (2000) 1295–1300.
[https://doi.org/10.1016/S0022-3697\(99\)00415-1](https://doi.org/10.1016/S0022-3697(99)00415-1).
- [157] F.N. Skomurski, R.C. Ewing, A.L. Rohl, J.D. Gale, U. Becker, Quantum mechanical vs. empirical potential modeling of uranium dioxide (UO₂) surfaces: (111), (110), and (100), *American Mineralogist*. 91 (2006) 1761–1772. <https://doi.org/10.2138/am.2006.2180>.

- [158] P.W. Tasker, The surface properties of uranium dioxide, *Surface Science*. 87 (1979) 315–324. [https://doi.org/10.1016/0039-6028\(79\)90531-4](https://doi.org/10.1016/0039-6028(79)90531-4).
- [159] R. Chatzimichail, S. Bebelis, P. Nikolopoulos, Temperature Dependence of the Surface Energy of the Low Index Planes of UO₂ and ThO₂, *J. of Materi Eng and Perform*. 25 (2016) 1691–1696. <https://doi.org/10.1007/s11665-016-2030-7>.
- [160] C.O.T. Galvin, M.J.D. Rushton, M.W.D. Cooper, D.A. Andersson, P.A. Burr, R.W. Grimes, The predicted shapes of voids and Xe bubbles in UO₂, *Journal of Nuclear Materials*. 543 (2021) 152622. <https://doi.org/10.1016/j.jnucmat.2020.152622>.
- [161] M.N. Kelly, W. Rheinheimer, M.J. Hoffmann, G.S. Rohrer, Anti-thermal grain growth in SrTiO₃: Coupled reduction of the grain boundary energy and grain growth rate constant, *Acta Materialia*. 149 (2018) 11–18. <https://doi.org/10.1016/j.actamat.2018.02.030>.
- [162] W. Rheinheimer, M.J. Hoffmann, Non-Arrhenius behavior of grain growth in strontium titanate: New evidence for a structural transition of grain boundaries, *Scripta Materialia*. 101 (2015) 68–71. <https://doi.org/10.1016/j.scriptamat.2015.01.021>.
- [163] W. Rheinheimer, M.J. Hoffmann, Grain growth in perovskites: What is the impact of boundary transitions?, *Current Opinion in Solid State and Materials Science*. 20 (2016) 286–298. <https://doi.org/10.1016/j.cossms.2016.04.004>.
- [164] A. Vuppuluri, Theory and simulation of microstructure evolution due to simultaneous grain boundary migration and grain rotation with misorientation dependent energy and mobility, *Materials Science and Engineering: A*. 713 (2018) 118–124. <https://doi.org/10.1016/j.msea.2017.12.031>.
- [165] A. Vuppuluri, S. Vedantam, Simulation of grain growth under simultaneous grain boundary migration and grain rotation using multi-order parameter phase-field model, *Journal of Materials Science*. 54 (2019) 506–514. <https://doi.org/10.1007/s10853-018-2857-4>.
- [166] N. Bernstein, The influence of geometry on grain boundary motion and rotation, *Acta Materialia*. 56 (2008) 1106–1113. <https://doi.org/10.1016/j.actamat.2007.11.002>.
- [167] L.V. Matveev, M.S. Veshchunov, High-temperature transition of uranium dioxide to the super-ion state, *J. Exp. Theor. Phys*. 84 (1997) 322–329. <https://doi.org/10.1134/1.558120>.

- [168] A. Bhattacharya, Y.-F. Shen, C.M. Hefferan, S.F. Li, J. Lind, R.M. Suter, C.E. Krill, G.S. Rohrer, Grain boundary velocity and curvature are not correlated in Ni polycrystals, *Science*. 374 (2021) 189–193. <https://doi.org/10.1126/science.abj3210>.
- [169] J. Zhang, W. Ludwig, Y. Zhang, H.H.B. Sørensen, D.J. Rowenhorst, A. Yamanaka, P.W. Voorhees, H.F. Poulsen, Grain boundary mobilities in polycrystals, *Acta Materialia*. 191 (2020) 211–220. <https://doi.org/10.1016/j.actamat.2020.03.044>.
- [170] G. Gottstein, D.A. Molodov, L.S. Shvindlerman, Grain Boundary Migration in Metals: Recent Developments, *Interface Science*. 6 (1998) 7–22. <https://doi.org/10.1023/A:1008641617937>.
- [171] J.L. Snelgrove, G.L. Hofman, C.L. Trybus, T.C. Wiencek, Development of Very-High-Density Fuels by the RERTR Program, (1997) 10.
- [172] M.K. Meyer, D.D. Keiser, J.-F. Jue, E. Shaber, Research reactor fuels, in: *Advances in Nuclear Fuel Chemistry*, Elsevier, 2020: pp. 273–312. <https://doi.org/10.1016/B978-0-08-102571-0.00008-2>.
- [173] L. Liang, Y.S. Kim, Z.-G. Mei, L.K. Aagesen, A.M. Yacout, Fission gas bubbles and recrystallization-induced degradation of the effective thermal conductivity in U-7Mo fuels, *Journal of Nuclear Materials*. 511 (2018) 438–445. <https://doi.org/10.1016/j.jnucmat.2018.09.054>.
- [174] W. Williams, F. Rice, A. Robinson, M. Meyer, B. Rabin, Afip-6 mkii post-irradiation examination summary report, in: *Technical Report INL/LTD-15-34142*, Idaho National Laboratory, 2015.
- [175] G. Gottstein, L.S. Shvindlerman, On the orientation dependence of grain boundary migration, *Scripta Metallurgica et Materialia*. 27 (1992) 1515–1520. [https://doi.org/10.1016/0956-716X\(92\)90137-4](https://doi.org/10.1016/0956-716X(92)90137-4).
- [176] J.W. Cahn, The impurity-drag effect in grain boundary motion, *Acta Metallurgica*. 10 (1962) 789–798. [https://doi.org/10.1016/0001-6160\(62\)90092-5](https://doi.org/10.1016/0001-6160(62)90092-5).
- [177] K. Lücke, H.P. Stüwe, On the theory of impurity controlled grain boundary motion, *Acta Metallurgica*. 19 (1971) 1087–1099. [https://doi.org/10.1016/0001-6160\(71\)90041-1](https://doi.org/10.1016/0001-6160(71)90041-1).
- [178] C. Yang, I. Baker, Effect of solute on microstructural evolution during directional recrystallization, *Journal of Alloys and Compounds*. 815 (2020) 152358. <https://doi.org/10.1016/j.jallcom.2019.152358>.

- [179] P. Gordon, R.A. Vandermeer, Mechanism of boundary migration in recrystallization, Transactions of the Metallurgical Society of AIME. 224 (1962) 917-.
- [180] Y. Huang, F.J. Humphreys, The effect of solutes on grain boundary mobility during recrystallization and grain growth in some single-phase aluminium alloys, Materials Chemistry and Physics. 132 (2012) 166–174.
<https://doi.org/10.1016/j.matchemphys.2011.11.018>.
- [181] K. Lücke, K. Detert, A quantitative theory of grain-boundary motion and recrystallization in metals in the presence of impurities, Acta Metallurgica. 5 (1957) 628–637.
[https://doi.org/10.1016/0001-6160\(57\)90109-8](https://doi.org/10.1016/0001-6160(57)90109-8).
- [182] E. Hersent, K. Marthinsen, E. Nes, The Effect of Solute Atoms on Grain Boundary Migration: A Solute Pinning Approach, Metallurgical and Materials Transactions A. 44 (2013) 3364–3375. <https://doi.org/10.1007/s11661-013-1690-2>.
- [183] R.K. Koju, Y. Mishin, The Role of Grain Boundary Diffusion in the Solute Drag Effect, Nanomaterials. 11 (2021) 2348. <https://doi.org/10/gmwsdm>.
- [184] D. Weygand, Y. Breichet, E. Rabkin, B. Straumal, W. Gust, Solute drag and wetting of a grain boundary, Philosophical Magazine Letters. 76 (1997) 133–138.
<https://doi.org/10.1080/095008397179075>.
- [185] Yu.V. Vamberskiy, A.L. Udovskiy, O.S. Ivanov, Experimental determination and calculation of excess thermodynamic functions of molybdenum solid solutions in gamma-uranium, Journal of Nuclear Materials. 46 (1973) 192–206. [https://doi.org/10.1016/0022-3115\(73\)90135-9](https://doi.org/10.1016/0022-3115(73)90135-9).
- [186] P.L. Williams, Y. Mishin, J.C. Hamilton, An embedded-atom potential for the Cu–Ag system, Modelling Simul. Mater. Sci. Eng. 14 (2006) 817–833.
<https://doi.org/10.1088/0965-0393/14/5/002>.
- [187] D.A. Molodov, U. Czubayko, G. Gottstein, L.S. Shvindlerman, B. Straumal, W. Gust, Acceleration of grain boundary motion in Al by small additions of Ga, Philosophical Magazine Letters. 72 (1995) 361–368. <https://doi.org/10.1080/09500839508242475>.
- [188] P.-L. Chen, I.-W. Chen, Grain Growth in CeO₂: Dopant Effects, Defect Mechanism, and Solute Drag, Journal of the American Ceramic Society. 79 (1996) 1793–1800.
<https://doi.org/10.1111/j.1151-2916.1996.tb07997.x>.

- [189] P.-L. Chen, I.-W. Chen, Grain Boundary Mobility in Y₂O₃: Defect Mechanism and Dopant Effects, *Journal of the American Ceramic Society*. 79 (1996) 1801–1809.
<https://doi.org/10.1111/j.1151-2916.1996.tb07998.x>.
- [190] Y. Park, N. Eriksson, R. Newell, D.D. Keiser, Y.H. Sohn, Phase decomposition of γ -U (bcc) in U-10 wt% Mo fuel alloy during hot isostatic pressing of monolithic fuel plate, *Journal of Nuclear Materials*. 480 (2016) 271–280.
<https://doi.org/10.1016/j.jnucmat.2016.08.022>.
- [191] T.R. England, B.F. Rider, Evaluation and compilation of fission product yields 1993, Los Alamos National Lab, 1994. <https://t2.lanl.gov/nis/publications/endf349.pdf> (accessed June 8, 2023).
- [192] B.D. Miller, J. Gan, D.D. Keiser, A.B. Robinson, J.F. Jue, J.W. Madden, P.G. Medvedev, Transmission electron microscopy characterization of the fission gas bubble superlattice in irradiated U-7wt%Mo dispersion fuels, *Journal of Nuclear Materials*. 458 (2015) 115–121. <https://doi.org/10/f6zsdb>.
- [193] V.V. Rondinella, T. Wiss, The high burn-up structure in nuclear fuel, *Materials Today*. 13 (2010) 24–32. [https://doi.org/10.1016/S1369-7021\(10\)70221-2](https://doi.org/10.1016/S1369-7021(10)70221-2).
- [194] J.A. Turnbull, M.O. Tucker, Swelling in UO₂ under conditions of gas release, *Philosophical Magazine*. (2006). <https://doi.org/10/bg9crk>.
- [195] A. Cheniour, G. Pastore, J.M. Harp, C.M. Petrie, N.A. Capps, Application of BISON to UO₂ MiniFuel fission gas release analysis, *Journal of Nuclear Materials*. 565 (2022) 153686. <https://doi.org/10.1016/j.jnucmat.2022.153686>.
- [196] F. Najafkhani, S. Kheiri, B. Pourbahari, H. Mirzadeh, Recent advances in the kinetics of normal/abnormal grain growth: a review, *Archiv.Civ.Mech.Eng.* 21 (2021) 29.
<https://doi.org/10.1007/s43452-021-00185-8>.
- [197] G. Gottstein, D.A. Molodov, L.S. Shvindlerman, D.J. Srolovitz, M. Winning, Grain boundary migration: misorientation dependence, *Current Opinion in Solid State and Materials Science*. 5 (2001) 9–14. [https://doi.org/10.1016/S1359-0286\(00\)00030-9](https://doi.org/10.1016/S1359-0286(00)00030-9).
- [198] M. Alkayyali, F. Abdeljawad, Grain Boundary Solute Drag Model in Regular Solution Alloys, *Phys. Rev. Lett.* 127 (2021) 175503. <https://doi.org/10/gngpwj>.

- [199] B. Ye, A. Oaks, S. Hu, B. Beeler, J. Rest, Z.-G. Mei, A. Yacout, Integrated Simulation of U-10Mo Monolithic Fuel Swelling Behavior, *Journal of Nuclear Materials*. (2023) 154542. <https://doi.org/10.1016/j.jnucmat.2023.154542>.
- [200] H.Y. Geng, Y. Chen, Y. Kaneta, M. Kinoshita, Molecular dynamics study on planar clustering of xenon in UO₂, *Journal of Alloys and Compounds*. 457 (2008) 465–471. <https://doi.org/10.1016/j.jallcom.2008.04.056>.
- [201] M.W.D. Cooper, N. Kuganathan, P.A. Burr, M.J.D. Rushton, R.W. Grimes, C.R. Stanek, D.A. Andersson, Development of Xe and Kr empirical potentials for CeO₂, ThO₂, UO₂ and PuO₂, combining DFT with high temperature MD, *J. Phys.: Condens. Matter*. 28 (2016) 405401. <https://doi.org/10.1088/0953-8984/28/40/405401>.
- [202] Y. Hayakawa, Mechanism of secondary recrystallization of Goss grains in grain-oriented electrical steel, *Science and Technology of Advanced Materials*. 18 (2017) 480–497. <https://doi.org/10.1080/14686996.2017.1341277>.
- [203] V.Y. Gol'dshteyn, O.P. Bobkova, S.G. Nitskaya, Influence of grain boundary migration on the parameters of an inhibitor phase in alloy Fe-3% Si., *Phys. Metals Metallog.* 54 (1982) 85–90.
- [204] M.I. Mendeleev, D.J. Srolovitz, Co-Segregation Effects on Boundary Migration, *Interface Science*. 10 (2002) 191–199. <https://doi.org/10.1023/A:1015880314987>.
- [205] E. Hersent, K. Marthinsen, E. Nes, A Solute Pinning Approach to Solute Drag in Multi-Component Solid Solution Alloys, *Modeling and Numerical Simulation of Material Science*. 4 (2014) 8–13. <https://doi.org/10.1016/j.mnms.2014.03.001>.

Appendix A. Activation Energies and Prefactors for the UMo System

Table A.1. Activation energies (Q , in eV) and mobility prefactors (M_0 , in $\text{m}^2/\text{s} \times 10^{-6}$) for the UMo system. Error indicates standard error. Mo concentrations are given in atomic percent.

GB	Pure U		U1Mo		U3Mo		U5Mo		
	Q	M ₀	Q	M ₀	Q	M ₀	Q	M ₀	
<100>	20°	0.33±0.07	0.4±0.3	0.37±0.02	1.1±0.2	0.62±0.02	6±1	1.2±0.2	600±800
	30°	0.46±0.03	2.4±0.8	0.56±0.02	4±1	0.84±0.05	30±10	1.23±0.08	600±500
	45°	1.12±0.04	400±200	1.25±0.03	1100±400	1.59±0.07	13000±8000	2.1±0.2	1±1×10 ⁶
<110>	20°	0.29±0.02	0.8±0.2	0.40±0.03	1.8±0.5	1.1±0.2	400±600	1.1±0.2	100±100
	30°	0.48±0.01	3.2±0.2	0.59±0.04	7±3	1.33±0.07	3000±2000	1.59±0.05	0.14±0.06×10 ⁶
	45°	0.43±0.04	2.2±0.7	0.47±0.03	2.6±0.7	0.80±0.05	30±20	1.4±0.1	3000±3000
<111>	20°	0.9±0.1	100±200	1.15±0.05	500±200	1.45±0.08	3000±2000	1.79±0.07	30000±20000
	30°	1.0±0.2	200±400	1.18±0.06	700±400	2.4±0.2	10±20×10 ⁶	2.87±0.06	600±300×10 ⁶
	45°	0.8±0.1	50±50	1.00±0.09	100±100	1.5±0.1	3000±3000	1.8±0.1	0.02±0.03×10 ⁶
GB	U10Mo		U14Mo		U17Mo		U21Mo		
	Q	M ₀	Q	M ₀	Q	M ₀	Q	M ₀	
<100>	20°	1.2±0.3	100±300	1.6±0.2	0.02±0.02×10 ⁶	1.88±0.04	0.12±0.04×10 ⁶	2.25±0.01	2.3±.2×10 ⁶
	30°	1.6±0.1	9000±9000	1.97±0.04	0.5±0.2×10 ⁶	1.1±0.2	300±400	1.8±0.2	0.1±0.2×10 ⁶
	45°	1.9±0.2	0.2±0.3×10 ⁶	2.0±0.3	1×10^6±1×10 ⁶	1.66±0.04	0.03±0.01×10 ⁶	1.8±0.3	0.1±0.1×10 ⁶
<110>	20°	1.89±0.03	0.06±0.02×10 ⁶	2.4±0.4	3±10×10 ⁶	2.9±0.3	300±700×10 ⁶	4.50±0.04	190±60
	30°	2.1±0.1	0.5±0.6×10 ⁶	2.2±0.1	2±2×10 ⁶	2.5±0.1	30±30×10 ⁶	2.1±0.2	0.6±0.9×10 ⁶
	45°	1.9±0.2	0.2±0.2×10 ⁶	1.7±0.1	0.03±0.03×10 ⁶	1.8±0.2	0.1±0.1×10 ⁶	1.67±0.04	18000±5000
<111>	20°	4.05±0.06	6±3	2.84±0.02	280±50×10 ⁶	2.6±0.4	40±100×10 ⁶	2.0±0.4	0.2±0.7×10 ⁶
	30°	2.34±0.06	6±3×10 ⁶	1.9±0.3	0.2±0.4×10 ⁶	2.0±0.1	0.6±0.7×10 ⁶	2.0±0.1	0.3±0.4×10 ⁶
	45°	1.5±0.5	2000±7000	2.3±0.3	1±4×10 ⁶	2.8±0.2	100±200×10 ⁶	2.3±0.6	2±9×10 ⁶

Appendix B. Activation Energies and Prefactors for the UXe, UMoXe, and UO₂+Xe Systems

Table B.1. Activation energies (Q , in eV) and mobility prefactors (M_0 , in $\text{m}^2/\text{s} \times 10^{-6}$) for the UXe system. Error indicates standard error. Italicized values indicate that not enough data was present to calculate the standard error in the fitting parameters. Xe concentrations are given in atomic percent.

GB	Pure U		U0.25Xe		U0.50Xe		U0.75Xe	
	Q	M_0	Q	M_0	Q	M_0	Q	M_0
<100>	20°	0.33±0.07	0.5±0.3	0.26±0.04	0.3±0.1	0.1±0.2	0.04±0.08	0.0±0.2
	30°	0.46±0.03	2.4±0.8	0.49±0.03	2.1±0.6	0.37±0.05	0.5±0.2	0.47±0.08
	45°	1.12±0.04	400±200	0.98±0.08	90±60	0.72±0.08	4±4	0.48±0.08
<110>	20°	0.29±0.02	0.8±0.2	0.29±0.04	0.6±0.2	0.45±0.02	1.9±0.4	0.6±0.2
	30°	0.48±0.01	3.2±0.2	0.43±0.06	2±1	0.42±0.04	1.4±0.6	0.9±0.2
	45°	0.43±0.04	2.2±0.7	0.54±0.04	5±2	0.35±0.07	0.8±0.5	0.6±0.1
<111>	20°	0.93±0.14	100±200	1.01±0.03	130±50	0.7±0.1	4±5	0.8±0.2
	30°	1.0±0.2	200±400	1.1±0.1	300±300	1.48±0.08	6000±5000	1.1±0.2
	45°	0.8±0.1	50±50	0.9±0.1	40±30	0.6±0.2	1±2	0.43±0.08
GB	U1.00Xe		U1.25Xe		U1.50Xe			
	Q	M_0	Q	M_0	Q	M_0		
<100>	20°	1.5±0.5	2000±6000	1.5±0.1	600±600	1.1±0.3	30±60	
	30°	0.39±0.06	0.16±0.09	0.25±0.06	0.02±0.01	0.52±0.05	0.2±0.1	
	45°	0.55±0.02	0.47±0.08	0.47±0.02	0.16±0.03	--	--	
<110>	20°	0.4±0.2	0.1±0.3	1.21±0.02	120±20	--	--	
	30°	0.77±0.04	11±5	0.35±0.01	0.09±0.01	0.37±0.02	0.07±0.02	
	45°	0.25±0.08	0.11±0.08	0.43±0.06	0.2±0.1	-1.41±0.04	2±8×10 ⁻⁹	
<111>	20°	0.45±0.04	0.14±0.06	0.4±0.3	0.1±0.1	--	--	
	30°	0.34±0.06	0.07±0.04	0.32±0.01	0.053±0.006	-0.20	3.9×10 ⁻³	
	45°	0.51±0.07	0.3±0.2	0.25	0.02995	--	--	

Table B.2. Activation energies (Q , in eV) and mobility prefactors (M_0 , in $\text{m}^2/\text{s} \times 10^{-6}$) for the UMoXe system. Error indicates standard error. Solute and impurity concentrations are given in atomic percent.

GB	Pure U			U1Mo0.25Xe			U1Mo0.50Xe			U1Mo0.75Xe			U3Mo0.25Xe		
	Q	M_0		Q	M_0		Q	M_0		Q	M_0		Q	M_0	
<100>	20°	0.33±0.07	0.5±0.3	-0.1±0.2	0.01±0.03	0.4±0.2	0.3±0.5	0.2±0.1	0.01±0.01	0.54±0.09	1±1				
	30°	0.46±0.03	2.4±0.8	0.5±0.1	2±2	0.59±0.09	2±2	0.3±0.1	0.04±0.04	0.91±0.08	30±20				
	45°	1.12±0.04	400±200	1.50±0.05	6000±3000	1.5±0.4	0.003±0.01×10 ⁶	1.25±0.06	200±100	1.7±0.2	0.03±0.05×10 ⁶				
<110>	20°	0.29±0.02	0.8±0.2	0.32±0.07	0.6±0.4	0.5±0.1	2±2	0.4±0.3	0.1±0.2	2.5±0.3	40±100×10 ⁶				
	30°	0.48±0.01	3.2±0.2	0.6±0.1	8±9	0.76±0.06	20±10	1.1±0.1	400±500	1.27±0.08	1100±800				
	45°	0.43±0.04	2.2±0.7	0.54±0.02	4±0.8	0.43±0.07	1±0.7	0.6±0.2	2±3	1.0±0.1	100±100				
<111>	20°	0.9±0.1	100±200	1.3±0.2	2000±4000	0.6±0.3	1±3	0.40±0.08	0.06±0.05	0.8±0.2	4±7				
	30°	1.0±0.2	200±400	2.0±0.1	0.7±0.7×10 ⁶	1.7±0.3	0.03±0.07×10 ⁶	0.4±0.1	0.1±0.1	2.4±0.3	10±20×10 ⁶				
	45°	0.8±0.1	50±50	1.0±0.1	100±100	0.7±0.1	3±3	0.30±0.04	0.03±0.01	0.3±0.2	0.03±0.06				
GB	U3Mo0.50Xe			U3Mo0.75Xe			U5Mo0.25Xe			U5Mo0.50Xe			U5Mo0.75Xe		
	Q	M_0		Q	M_0		Q	M_0		Q	M_0		Q	M_0	
<100>	20°	0.39±0.09	0.08±0.06	0.59±0.08	0.3±0.2	0.7±0.1	2±2	0.48±0.07	0.1±0.07	0.5±0.6	0.1±0.4				
	30°	0.1±0.2	0.003±0.007	0.80±0.07	2±1	0.8±0.2	10±10	0.30±0.06	0.03±0.02	0.6±0.2	0.3±0.5				
	45°	1.7±0.3	0.01±0.02×10 ⁶	0.70±0.08	0.8±0.6	2.0±0.3	0.2±0.6×10 ⁶	1.5±0.1	1000±2000	0.6±0.2	0.3±0.5				
<110>	20°	1.6±0.1	7000±8000	0.6±0.1	0.3±0.3	1.4±0.2	1000±1000	0.8±0.2	2±3	1.32±0.01	93±6				
	30°	1.0±0.6	200±900	1.1±0.3	100±300	1.6±0.2	0.01±0.02×10 ⁶	1.2±0.2	100±200	0.6±0.1	0.3±0.3				
	45°	0.92±0.08	50±40	0.6±0.3	0.3±0.9	1.1±0.1	300±400	0.9±0.2	10±20	0.39±0.05	0.05±0.02				
<111>	20°	1.2±0.3	100±200	0.41±0.03	0.05±0.01	3.54±0.09	50±40×10 ⁹	0.98±0.06	7±4	1.81±0.08	6000±4000				
	30°	2.2±0.4	1±5×10 ⁶	1.3±0.2	100±100	2.7±0.2	100±200×10 ⁶	1.9±0.3	0.03±0.06×10 ⁶	0.53±0.07	0.15±0.08				
	45°	0.5±0.3	0.2±0.5	0.9±0.2	3±5	0.4±0.6	0.04±0.2	1.0±0.3	10±20	0.71±0.00	0.6±0.02				

Table B.3. Activation energies (Q , in eV) and mobility prefactors (M_0 , in $\text{m}^2/\text{s} \times 10^{-6}$) for the UO_2+Xe system. Error indicates standard error. Italicized values indicate that not enough data was present to calculate the standard error in the fitting parameters. Xe concentrations are given in atomic percent.

Geng		Pure UO_2		$\text{UO}_2+0.25\text{Xe}$		$\text{UO}_2+0.50\text{Xe}$		$\text{UO}_2+0.75\text{Xe}$		$\text{UO}_2+1.00\text{Xe}$	
GB		Q	M_0	Q	M_0	Q	M_0	Q	M_0	Q	M_0
<100>	20°	1.9±0.2	70±80	1.84±0.02	32±2	1.7±0.3	10±10	1.65±0.01	6.8±0.4	1.4±0.3	1±2
	45°	1.7±0.1	30±20	2.0±0.1	90±50	1.8±0.3	20±30	1.58±0.05	8±2	1.9±0.5	20±50
<100>	20°	2.5±0.3	600±700	3.35	7.51×10 ³	2.62	286.8	3.19	1.45×10 ³	2.64	120.58
	45°	4.18	106.6×10 ³	--	--	--	--	--	--	--	--
<111>	20°	1.01±0.03	2.7±0.3	1.3±0.1	6±4	2.0±0.1	50±30	1.0±0.5	0.2±0.5	0.64	0.0234
	45°	0.7±0.1	1.5±0.7	0.7±0.2	1.1±0.8	1.0±0.2	3±3	0.9±0.1	1.4±0.8	1.0±0.3	1±2
<112>	38.20°	0.7±0.1	1.1±0.5	0.8±0.1	1.5±0.7	0.7±0.2	1±1	1±0.2	1±1	1.58±0.05	10±2
	45°	2.23	186.78	2.13	97.57	2.15	77.63	3.04	2.0×10 ³	2.48	85.13
CRG		Pure UO_2		$\text{UO}_2+0.25\text{Xe}$		$\text{UO}_2+0.50\text{Xe}$		$\text{UO}_2+0.75\text{Xe}$		$\text{UO}_2+1.00\text{Xe}$	
GB		Q	M_0	Q	M_0	Q	M_0	Q	M_0	Q	M_0
<100>	20°	1.3±0.1	7±4	1.4±0.2	9±8	1.2±0.1	3±2	1.4±0.3	4±5	1.0±0.3	1±1
	45°	2.2±0.6	300±700	2.0±0.6	100±300	1.8±0.6	40±100	1.3±0.5	4±10	1.2±0.6	2±4
<100>	20°	1.9±0.3	70±90	1.6±0.2	20±20	2.2±0.3	100±200	1.96±0.08	40±10	1.8±0.2	10±10
	45°	3.44	17100	3.19	6380	3.00	2270	2.97	1550	2.44	113.84
<111>	20°	0.8±0.1	0.9±0.6	0.7±0.3	0.6±0.7	0.5±0.2	0.1±0.1	1.2±0.4	2±3	1.2±0.3	1±1
	45°	0.3±0.3	0.1±0.2	0.3±0.3	0.1±0.1	0.4±0.2	0.08±0.08	0.4±0.2	0.05±0.05	0.1±0.5	0.01±0.02
<112>	38.20°	0.3±0.3	0.1±0.2	0.3±0.5	0.2±0.3	0.2±0.5	0.1±0.2	0.2±0.7	0.04±0.1	0.2±0.8	0.03±0.1
	45°	1.8±0.3	40±50	1.8±0.4	50±80	2.0±0.3	100±100	1.8±0.4	20±30	1.8±0.3	20±30

Appendix C. Slopes and Intercepts for Mobility versus Concentration in UXe, UMoXe, and UO₂+Xe

Table C.1. Slopes and intercepts for the log₁₀ reduced mobility versus Xe concentration for the UXe system. Intercepts are given in log₁₀(m²/s) and slopes are log₁₀(m²/s)/at. %.

Axis	Misorientation(°)	Temperature (K)	Intercept	Slope
100	20	1050	--	--
100	20	1100	-7.93±0.03	0.5±0.1
100	20	1150	-7.8±0.1	0.2±0.4
100	20	1200	-7.5±0.2	-0.9±0.5
100	20	1250	-7.4±0.2	-1.2±0.5
100	20	1300	-7.5±0.2	-1.0±0.2
100	20	1350	-7.4±0.1	-1.0±0.1
100	20	1400	-7.4±0.1	-0.8±0.1
100	30	1050	-7.89±0.08	-0.80±0.09
100	30	1100	-7.8±0.1	-0.8±0.1
100	30	1150	-7.57±0.06	-0.92±0.07
100	30	1200	-7.50±0.08	-0.89±0.09
100	30	1250	-7.39±0.10	-1.1±0.1
100	30	1300	-7.35±0.08	-0.96±0.09
100	30	1350	-7.34±0.07	-0.98±0.08
100	30	1400	-7.33±0.07	-0.85±0.08
100	45	1050	-8.73	-0.11
100	45	1100	-8.55±0.06	-0.27±0.10
100	45	1150	-8.41±0.06	-0.37±0.08
100	45	1200	-8.08±0.07	-0.7±0.1
100	45	1250	-7.99±0.09	-0.50±0.10
100	45	1300	-7.75±0.05	-0.68±0.07
100	45	1350	-7.6±0.1	-0.9±0.1
100	45	1400	-7.41±0.02	-0.86±0.03
110	20	1050	-7.5±0.1	-1.3±0.1
110	20	1100	-7.3±0.2	-1.5±0.3
110	20	1150	-7.1±0.1	-1.3±0.1
110	20	1200	-7.0±0.2	-1.5±0.2
110	20	1250	-7.1±0.1	-1.1±0.2
110	20	1300	-7.1±0.2	-1.3±0.2
110	20	1350	-7.1±0.1	-1.1±0.1
110	20	1400	-7.03±0.09	-1.0±0.1
110	30	1050	-7.9±0.1	-0.8±0.1
110	30	1100	-7.56±0.10	-1.1±0.1
110	30	1150	-7.40±0.10	-0.9±0.1
110	30	1200	-7.3±0.1	-0.8±0.1

Slopes and intercepts for the $\log_{10}$ reduced mobility versus Xe concentration for the UXe system.

Intercepts are given in $\log_{10}(\text{m}^2/\text{s})$ and slopes are $\log_{10}(\text{m}^2/\text{s})/\text{at.}\%$, continued.

Axis	Misorientation($^{\circ}$)	Temperature (K)	Intercept	Slope
110	30	1250	-7.2 $\pm$ 0.1	-0.8 $\pm$ 0.2
110	30	1300	-7.1 $\pm$ 0.1	-0.9 $\pm$ 0.2
110	30	1350	-7.1 $\pm$ 0.1	-0.9 $\pm$ 0.1
110	30	1400	-7.1 $\pm$ 0.1	-0.7 $\pm$ 0.2
110	45	1050	-7.75 $\pm$ 0.07	-0.71 $\pm$ 0.08
110	45	1100	-7.56 $\pm$ 0.08	-0.69 $\pm$ 0.09
110	45	1150	-7.41 $\pm$ 0.09	-0.7 $\pm$ 0.1
110	45	1200	-7.3 $\pm$ 0.1	-0.8 $\pm$ 0.2
110	45	1250	-7.2 $\pm$ 0.1	-0.9 $\pm$ 0.1
110	45	1300	-7.1 $\pm$ 0.1	-1.0 $\pm$ 0.2
110	45	1350	-7.1 $\pm$ 0.1	-0.9 $\pm$ 0.1
110	45	1400	-7.09 $\pm$ 0.10	-0.9 $\pm$ 0.1
111	20	1050	-8.75 $\pm$ 0.06	-0.1 $\pm$ 0.1
111	20	1100	-8.36 $\pm$ 0.06	-0.52 $\pm$ 0.08
111	20	1150	-8.1 $\pm$ 0.1	-0.6 $\pm$ 0.1
111	20	1200	-7.70 $\pm$ 0.05	-1.06 $\pm$ 0.08
111	20	1250	-7.57 $\pm$ 0.06	-1.19 $\pm$ 0.09
111	20	1300	-7.46 $\pm$ 0.10	-1.1 $\pm$ 0.1
111	20	1350	-7.5 $\pm$ 0.1	-0.8 $\pm$ 0.2
111	20	1400	-7.25 $\pm$ 0.07	-1.2 $\pm$ 0.1
111	30	1050	--	--
111	30	1100	--	--
111	30	1150	-8.74 $\pm$ 0.02	-0.02 $\pm$ 0.03
111	30	1200	-8.1 $\pm$ 0.1	-0.8 $\pm$ 0.1
111	30	1250	-7.98 $\pm$ 0.09	-0.6 $\pm$ 0.2
111	30	1300	-7.63 $\pm$ 0.06	-0.72 $\pm$ 0.06
111	30	1350	-7.38 $\pm$ 0.08	-0.88 $\pm$ 0.08
111	30	1400	-7.3 $\pm$ 0.1	-0.9 $\pm$ 0.2
111	45	1050	-8.72 $\pm$ 0.09	-0.2 $\pm$ 0.1
111	45	1100	-8.55 $\pm$ 0.05	-0.2 $\pm$ 0.1
111	45	1150	-8.10 $\pm$ 0.03	-0.66 $\pm$ 0.05
111	45	1200	-7.79 $\pm$ 0.07	-1.0 $\pm$ 0.1
111	45	1250	-7.7 $\pm$ 0.1	-1.1 $\pm$ 0.2
111	45	1300	-7.6 $\pm$ 0.1	-0.8 $\pm$ 0.1
111	45	1350	-7.49 $\pm$ 0.09	-1.0 $\pm$ 0.1
111	45	1400	-7.42 $\pm$ 0.08	-0.9 $\pm$ 0.1

Table C.2. Slopes and intercepts for the $\log_{10}$ reduced mobility versus Xe concentration for the UMoXe system. Intercepts are given in $\log_{10}(\text{m}^2/\text{s})$ and slopes are $\log_{10}(\text{m}^2/\text{s})/\text{at.}\% \text{Xe}$.

Axis	Misorientation ($^{\circ}$)	Mo (at.%)	T (K)	Intercept	Slope
100	20	1	1050	-7.75 $\pm$ 0.07	-1.5 $\pm$ 0.1
100	20	1	1100	-7.7 $\pm$ 0.2	-1.5 $\pm$ 0.4
100	20	1	1150	-7.57 $\pm$ 0.07	-1.6 $\pm$ 0.1
100	20	1	1200	-7.4 $\pm$ 0.4	-1.8 $\pm$ 0.8
100	20	1	1250	-7.4 $\pm$ 0.4	-1.7 $\pm$ 0.8
100	20	1	1300	-7.3 $\pm$ 0.1	-1.9 $\pm$ 0.3
100	20	1	1350	-7.3 $\pm$ 0.2	-1.9 $\pm$ 0.3
100	20	1	1400	-7.27 $\pm$ 0.07	-1.7 $\pm$ 0.2
100	20	3	1050	-8.2 $\pm$ 0.1	-1.2 $\pm$ 0.4
100	20	3	1100	-8.2 $\pm$ 0.2	-1.5 $\pm$ 0.7
100	20	3	1150	-7.90 $\pm$ 0.05	-1.7 $\pm$ 0.1
100	20	3	1200	-7.77 $\pm$ 0.07	-1.8 $\pm$ 0.1
100	20	3	1250	-7.7 $\pm$ 0.2	-1.7 $\pm$ 0.4
100	20	3	1300	-7.66 $\pm$ 0.06	-1.5 $\pm$ 0.1
100	20	3	1350	-7.5 $\pm$ 0.1	-1.7 $\pm$ 0.3
100	20	3	1400	-7.5 $\pm$ 0.1	-1.8 $\pm$ 0.3
100	20	5	1050	-8.80	-0.43
100	20	5	1100	-8.8 $\pm$ 0.1	-0.5 $\pm$ 0.5
100	20	5	1150	-8.84 $\pm$ 0.06	-0.4 $\pm$ 0.2
100	20	5	1200	-8.7 $\pm$ 0.1	-0.7 $\pm$ 0.4
100	20	5	1250	-8.3 $\pm$ 0.1	-1.4 $\pm$ 0.3
100	20	5	1300	-8.1 $\pm$ 0.1	-1.2 $\pm$ 0.3
100	20	5	1350	-7.84 $\pm$ 0.02	-1.51 $\pm$ 0.04
100	20	5	1400	-7.7 $\pm$ 0.1	-1.5 $\pm$ 0.3
100	30	1	1050	-8.05 $\pm$ 0.06	-1.1 $\pm$ 0.1
100	30	1	1100	-7.84 $\pm$ 0.08	-1.1 $\pm$ 0.2
100	30	1	1150	-7.81 $\pm$ 0.08	-1.0 $\pm$ 0.2
100	30	1	1200	-7.6 $\pm$ 0.1	-1.1 $\pm$ 0.2
100	30	1	1250	-7.5 $\pm$ 0.1	-1.0 $\pm$ 0.3
100	30	1	1300	-7.4 $\pm$ 0.2	-1.4 $\pm$ 0.5
100	30	1	1350	-7.3 $\pm$ 0.2	-1.5 $\pm$ 0.5
100	30	1	1400	-7.33 $\pm$ 0.09	-1.4 $\pm$ 0.2
100	30	3	1050	-8.46 $\pm$ 0.02	-0.60 $\pm$ 0.05
100	30	3	1100	-8.39 $\pm$ 0.06	-0.9 $\pm$ 0.1
100	30	3	1150	-8.2 $\pm$ 0.2	-1.0 $\pm$ 0.3
100	30	3	1200	-7.99 $\pm$ 0.09	-1.3 $\pm$ 0.2
100	30	3	1250	-7.85 $\pm$ 0.05	-1.4 $\pm$ 0.1
100	30	3	1300	-7.7 $\pm$ 0.1	-1.2 $\pm$ 0.3

Slopes and intercepts for the $\log_{10}$ reduced mobility versus Xe concentration for the UMoXe system. Intercepts are given in $\log_{10}(\text{m}^2/\text{s})$ and slopes are $\log_{10}(\text{m}^2/\text{s})/\text{at.}\% \text{Xe}$, continued.

Axis	Misorientation (°)	Mo (at.%)	T (K)	Intercept	Slope
100	30	3	1350	-7.53±0.06	-1.4±0.1
100	30	3	1400	-7.52±0.07	-1.4±0.2
100	30	5	1050	-9.0±0.1	0.2±0.4
100	30	5	1100	-8.71±0.06	-0.6±0.2
100	30	5	1150	-8.83±0.04	-0.20±0.09
100	30	5	1200	-8.47±0.04	-0.78±0.08
100	30	5	1250	-8.2±0.1	-0.9±0.2
100	30	5	1300	-7.9±0.1	-1.4±0.2
100	30	5	1350	-7.74±0.04	-1.20±0.09
100	30	5	1400	-7.5±0.1	-1.6±0.3
100	45	1	1050	-8.79	-0.10
100	45	1	1100	-8.70	-0.79
100	45	1	1150	-8.66±0.04	-0.32±0.08
100	45	1	1200	-8.34±0.08	-0.8±0.2
100	45	1	1250	-8.07±0.06	-0.9±0.1
100	45	1	1300	-7.8±0.1	-0.9±0.2
100	45	1	1350	-7.57±0.08	-0.9±0.2
100	45	1	1400	-7.48±0.07	-1.1±0.1
100	45	3	1050	--	--
100	45	3	1100	--	--
100	45	3	1150	-8.7±0.1	-0.5±0.2
100	45	3	1200	-8.61±0.06	-0.4±0.1
100	45	3	1250	-8.43±0.10	-0.7±0.2
100	45	3	1300	-8.0±0.1	-1.2±0.2
100	45	3	1350	-7.77±0.06	-1.2±0.1
100	45	3	1400	-7.5±0.1	-1.1±0.3
100	45	5	1050	--	--
100	45	5	1100	--	--
100	45	5	1150	--	--
100	45	5	1200	-8.7±0.2	-0.5±0.4
100	45	5	1250	-8.67±0.04	-0.47±0.08
100	45	5	1300	-8.4±0.2	-0.5±0.4
100	45	5	1350	-7.86±0.07	-1.1±0.1
100	45	5	1400	-7.60±0.09	-1.4±0.2
110	20	1	1050	-7.67±0.08	-1.7±0.2
110	20	1	1100	-7.4±0.1	-1.7±0.3
110	20	1	1150	-7.4±0.2	-2.0±0.3
110	20	1	1200	-7.32±0.09	-1.3±0.2

Slopes and intercepts for the $\log_{10}$ reduced mobility versus Xe concentration for the UMoXe system. Intercepts are given in $\log_{10}(\text{m}^2/\text{s})$ and slopes are $\log_{10}(\text{m}^2/\text{s})/\text{at.}\% \text{Xe}$, continued.

Axis	Misorientation (°)	Mo (at.%)	T (K)	Intercept	Slope
110	20	1	1250	-7.3±0.2	-1.1±0.3
110	20	1	1300	-7.2±0.1	-1.2±0.2
110	20	1	1350	-7.1±0.3	-1.9±0.7
110	20	1	1400	-7.14±0.09	-1.6±0.2
110	20	3	1050	--	--
110	20	3	1100	-8.6±0.3	-1.2±0.9
110	20	3	1150	-8.41±0.08	-1.1±0.2
110	20	3	1200	-8.7±0.1	-0.6±0.3
110	20	3	1250	-7.8±0.2	-1.5±0.4
110	20	3	1300	-7.6±0.1	-1.7±0.3
110	20	3	1350	-7.4±0.2	-1.8±0.4
110	20	3	1400	-7.35±0.08	-1.7±0.2
110	20	5	1050	-9.20	0.62
110	20	5	1100	-9.03	-1.12
110	20	5	1150	-8.89±0.07	-0.5±0.2
110	20	5	1200	-8.84	-0.11
110	20	5	1250	-8.69	-0.47
110	20	5	1300	-8.3±0.2	-1.0±0.4
110	20	5	1350	-7.97±0.05	-1.3±0.1
110	20	5	1400	-7.8±0.2	-1.3±0.3
110	30	1	1050	-8.1±0.1	-1.0±0.3
110	30	1	1100	-7.83±0.07	-0.9±0.1
110	30	1	1150	-7.67±0.02	-0.69±0.03
110	30	1	1200	-7.61±0.07	-0.8±0.1
110	30	1	1250	-7.51±0.02	-0.43±0.05
110	30	1	1300	-7.3±0.1	-0.8±0.3
110	30	1	1350	-7.3±0.1	-0.8±0.3
110	30	1	1400	-7.1±0.3	-1.5±0.6
110	30	3	1050	-8.90±0.08	-0.3±0.2
110	30	3	1100	-8.75±0.01	-0.39±0.05
110	30	3	1150	-8.4±0.1	-0.8±0.3
110	30	3	1200	-8.0±0.2	-0.8±0.5
110	30	3	1250	-7.94±0.08	-0.8±0.2
110	30	3	1300	-7.62±0.04	-0.71±0.08
110	30	3	1350	-7.4±0.2	-1.2±0.4
110	30	3	1400	-7.3±0.1	-1.5±0.3
110	30	5	1050	-9.28	0.89
110	30	5	1100	-9.14	0.16

Slopes and intercepts for the $\log_{10}$ reduced mobility versus Xe concentration for the UMoXe system. Intercepts are given in $\log_{10}(\text{m}^2/\text{s})$ and slopes are $\log_{10}(\text{m}^2/\text{s})/\text{at.}\% \text{Xe}$, continued.

Axis	Misorientation (°)	Mo (at.%)	T (K)	Intercept	Slope
110	30	5	1150	-8.92±0.05	-0.4±0.1
110	30	5	1200	-8.6±0.1	-0.7±0.2
110	30	5	1250	-8.3±0.2	-1.0±0.4
110	30	5	1300	-8.1±0.2	-1.2±0.4
110	30	5	1350	-7.819±0.003	-0.989±0.006
110	30	5	1400	-7.49±0.10	-1.5±0.2
110	45	1	1050	-7.96±0.05	-0.8±0.1
110	45	1	1100	-7.73±0.04	-0.72±0.09
110	45	1	1150	-7.635±0.005	-0.50±0.01
110	45	1	1200	-7.52±0.10	-0.7±0.2
110	45	1	1250	-7.42±0.04	-0.61±0.08
110	45	1	1300	-7.35±0.03	-0.60±0.06
110	45	1	1350	-7.2±0.1	-0.9±0.3
110	45	1	1400	-7.1±0.2	-1.4±0.4
110	45	3	1050	-8.5±0.1	-0.6±0.3
110	45	3	1100	-8.20±0.03	-1.06±0.05
110	45	3	1150	-7.9±0.2	-1.3±0.4
110	45	3	1200	-7.7±0.1	-1.4±0.3
110	45	3	1250	-7.66±0.09	-0.9±0.2
110	45	3	1300	-7.5±0.1	-0.8±0.2
110	45	3	1350	-7.3±0.2	-1.3±0.5
110	45	3	1400	-7.3±0.1	-1.4±0.3
110	45	5	1050	-8.93±0.05	-0.2±0.1
110	45	5	1100	-8.94±0.04	-0.34±0.08
110	45	5	1150	-8.50±0.05	-0.7±0.1
110	45	5	1200	-8.48±0.04	-0.65±0.08
110	45	5	1250	-8.03±0.08	-1.1±0.2
110	45	5	1300	-7.6±0.1	-1.5±0.3
110	45	5	1350	-7.5±0.2	-1.4±0.3
110	45	5	1400	-7.5±0.1	-1.7±0.3
111	20	1	1050	--	--
111	20	1	1100	--	--
111	20	1	1150	--	--
111	20	1	1200	-8.14±0.08	-1.1±0.2
111	20	1	1250	-7.9±0.2	-1.3±0.5
111	20	1	1300	-7.7±0.1	-1.5±0.2
111	20	1	1350	-7.57±0.02	-1.24±0.03
111	20	1	1400	-7.4±0.1	-1.2±0.3

Slopes and intercepts for the $\log_{10}$ reduced mobility versus Xe concentration for the UMoXe system. Intercepts are given in $\log_{10}(\text{m}^2/\text{s})$ and slopes are $\log_{10}(\text{m}^2/\text{s})/\text{at.}\% \text{Xe}$, continued.

Axis	Misorientation (°)	Mo (at.%)	T (K)	Intercept	Slope
111	20	3	1050	--	--
111	20	3	1100	--	--
111	20	3	1150	--	--
111	20	3	1200	-8.48±0.07	-0.9±0.2
111	20	3	1250	-8.44±0.08	-0.8±0.2
111	20	3	1300	-8.3±0.1	-0.9±0.2
111	20	3	1350	-7.92±0.10	-1.3±0.2
111	20	3	1400	-7.75±0.01	-1.40±0.03
111	20	5	1050	--	--
111	20	5	1100	--	--
111	20	5	1150	-8.82	-0.58
111	20	5	1200	-8.87	-0.16
111	20	5	1250	-8.7±0.1	-0.9±0.3
111	20	5	1300	-8.6±0.2	-0.6±0.3
111	20	5	1350	-8.21±0.03	-1.09±0.07
111	20	5	1400	-7.9±0.2	-1.2±0.4
111	30	1	1050	--	--
111	30	1	1100	--	--
111	30	1	1150	--	--
111	30	1	1200	-8.34±0.05	-0.9±0.1
111	30	1	1250	-7.94±0.05	-0.9±0.1
111	30	1	1300	-7.6±0.1	-1.2±0.3
111	30	1	1350	-7.5±0.1	-1.2±0.3
111	30	1	1400	-7.3±0.1	-1.4±0.3
111	30	3	1050	--	--
111	30	3	1100	--	--
111	30	3	1150	--	--
111	30	3	1200	-8.8±0.1	-0.4±0.2
111	30	3	1250	-8.5±0.1	-0.7±0.2
111	30	3	1300	-7.94±0.09	-1.4±0.2
111	30	3	1350	-7.68±0.10	-1.3±0.2
111	30	3	1400	-7.4±0.2	-1.3±0.5
111	30	5	1050	--	--
111	30	5	1100	--	--
111	30	5	1150	--	--
111	30	5	1200	-8.9±0.2	-0.3±0.8
111	30	5	1250	-8.92±0.08	-0.2±0.2
111	30	5	1300	-8.3±0.1	-0.8±0.3

Slopes and intercepts for the $\log_{10}$ reduced mobility versus Xe concentration for the UMoXe system. Intercepts are given in $\log_{10}(\text{m}^2/\text{s})$ and slopes are $\log_{10}(\text{m}^2/\text{s})/\text{at.}\% \text{Xe}$, continued.

Axis	Misorientation (°)	Mo (at.%)	T (K)	Intercept	Slope
111	30	5	1350	-7.83±0.10	-1.4±0.2
111	30	5	1400	-7.5±0.1	-1.5±0.3
111	45	1	1050	--	--
111	45	1	1100	--	--
111	45	1	1150	--	--
111	45	1	1200	-8.07±0.08	-1.2±0.2
111	45	1	1250	-7.9±0.1	-1.2±0.3
111	45	1	1300	-7.71±0.02	-1.31±0.05
111	45	1	1350	-7.6±0.1	-1.4±0.3
111	45	1	1400	-7.49±0.05	-1.5±0.1
111	45	3	1050	--	--
111	45	3	1100	--	--
111	45	3	1150	--	--
111	45	3	1200	-8.60±0.09	-0.5±0.2
111	45	3	1250	-8.52±0.06	-0.7±0.1
111	45	3	1300	-8.2±0.1	-1.2±0.3
111	45	3	1350	-8.09±0.07	-1.0±0.2
111	45	3	1400	-7.8±0.1	-1.3±0.2
111	45	5	1050	--	--
111	45	5	1100	--	--
111	45	5	1150	--	--
111	45	5	1200	--	--
111	45	5	1250	-8.8±0.2	-0.3±0.4
111	45	5	1300	-8.46±0.08	-0.8±0.2
111	45	5	1350	-8.5±0.2	-0.5±0.5
111	45	5	1400	-8.0±0.1	-1.2±0.3

Table C.3. Slopes and intercepts for the $\log_{10}$ reduced mobility versus Xe concentration for the UO_2+Xe system. Intercepts are given in $\log_{10}(\text{m}^2/\text{s})$ and slopes are $\log_{10}(\text{m}^2/\text{s})/\text{at.}\%\text{Xe}$.

Axis	Misorientation ($^\circ$)	Potential	Temperature (K)	Intercept	Slope
100	20	Basak	2200	-8.59 $\pm$ 0.03	-0.45 $\pm$ 0.05
100	20	Basak	2600	-7.78 $\pm$ 0.07	-0.8 $\pm$ 0.1
100	20	Basak	3000	-7.42 $\pm$ 0.02	-0.72 $\pm$ 0.04
110	20	Basak	2200	--	--
110	20	Basak	2600	-8.2 $\pm$ 0.1	-1.0 $\pm$ 0.2
110	20	Basak	3000	-7.55 $\pm$ 0.02	-0.82 $\pm$ 0.03
111	20	Basak	2200	-7.9 $\pm$ 0.2	-1.4 $\pm$ 0.4
111	20	Basak	2600	-7.5 $\pm$ 0.1	-1.5 $\pm$ 0.2
111	20	Basak	3000	-7.1 $\pm$ 0.1	-1.4 $\pm$ 0.2
100	45	Basak	2200	-8.42 $\pm$ 0.08	-0.6 $\pm$ 0.1
100	45	Basak	2600	-7.75 $\pm$ 0.04	-0.43 $\pm$ 0.06
100	45	Basak	3000	-7.34 $\pm$ 0.03	-0.57 $\pm$ 0.05
110	45	Basak	2600	--	--
110	45	Basak	3000	-7.95 $\pm$ 0.06	-0.75 $\pm$ 0.09
111	45	Basak	2200	-7.41 $\pm$ 0.05	-0.70 $\pm$ 0.08
111	45	Basak	2600	-7.12 $\pm$ 0.03	-0.51 $\pm$ 0.04
111	45	Basak	3000	-6.99 $\pm$ 0.05	-0.52 $\pm$ 0.07
112	45	Basak	2600	-7.97 $\pm$ 0.07	-0.8 $\pm$ 0.1
112	45	Basak	3000	-7.42 $\pm$ 0.09	-0.7 $\pm$ 0.1
100	20	CRG	2200	-8.11 $\pm$ 0.05	-0.47 $\pm$ 0.08
100	20	CRG	2600	-7.57 $\pm$ 0.01	-0.45 $\pm$ 0.02
100	20	CRG	3000	-7.28 $\pm$ 0.03	-0.62 $\pm$ 0.05
110	20	CRG	2200	-8.5 $\pm$ 0.1	-0.6 $\pm$ 0.2
110	20	CRG	2600	-7.67 $\pm$ 0.05	-0.75 $\pm$ 0.08
110	20	CRG	3000	-7.38 $\pm$ 0.02	-0.50 $\pm$ 0.04
111	20	CRG	2200	-7.7 $\pm$ 0.1	-1.0 $\pm$ 0.2
111	20	CRG	2600	-7.4 $\pm$ 0.1	-1.0 $\pm$ 0.2
111	20	CRG	3000	-7.38 $\pm$ 0.03	-0.63 $\pm$ 0.06
100	45	CRG	2200	-8.63 $\pm$ 0.06	0.06 $\pm$ 0.09
100	45	CRG	2600	-7.54 $\pm$ 0.03	-0.34 $\pm$ 0.05
100	45	CRG	3000	-7.31 $\pm$ 0.04	-0.57 $\pm$ 0.06
110	45	CRG	3000	-7.48 $\pm$ 0.06	-0.48 $\pm$ 0.09
110	45	CRG	2600	-8.37 $\pm$ 0.05	-0.25 $\pm$ 0.08
111	45	CRG	2200	-7.55 $\pm$ 0.06	-0.8 $\pm$ 0.1
111	45	CRG	2600	-7.63 $\pm$ 0.03	-0.47 $\pm$ 0.05
111	45	CRG	3000	-7.3 $\pm$ 0.1	-0.9 $\pm$ 0.2
112	45	CRG	2200	-8.46 $\pm$ 0.03	-0.39 $\pm$ 0.04
112	45	CRG	2600	-7.66 $\pm$ 0.02	-0.39 $\pm$ 0.04
112	45	CRG	3000	-7.37 $\pm$ 0.03	-0.38 $\pm$ 0.05

