MULTISCALE COMPUTATIONAL MODELING OF DEFECTS IN URANIUM DIOXIDE

By

ANUJ GOYAL

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2015
To my family with love and gratitude
ACKNOWLEDGMENTS

First and foremost I would like to give my deepest gratitude to my advisor Prof. Simon R. Phillpot, who has provided me inspiration and invaluable guidance throughout my Ph.D study. His enthusiasm towards science, cheerfulness and great sense of humor has made my Ph.D, a wonderful journey and I feel extremely fortunate to have him as my advisor. He has both motivated me and given me the opportunity to explore other avenues as a researcher while working with him.

I also owe a great debt to Dr. Blas P. Uberuaga, with whom I had the fortune to work as a visiting researcher at Los Alamos National Laboratory (LANL). He is one of the most passionate and dedicated people I have ever met, and throughout my time at LANL and thereafter, he has been a constant source of energy, ideas and enthusiasm. I would like to sincerely thank Dr. David A. Andersson, who was my co-mentor at LANL and Dr. Subramanian Gopinath. This thesis has immensely benefitted from many thought-provoking discussions I had with them on computational methods and defects in nuclear materials.

I would like to thank my committee, Prof. Susan B. Sinnott, Prof. Youping Chen, Prof. Juan C. Nino and Prof. Yong Yang, for their support and advice. The introduction to nuclear materials course I took from Prof. Yong Yang gave me good background for my research on nuclear materials. I am grateful to Prof. Sinnott and Prof. Richard G. Hennig for listening to my research developments during the weekly meetings and always giving me critical assessment, especially from the perspective of chemistry and electronic structure methods. I also want to thank Prof. Hennig for providing me
additional computational resources. I want to thank Dr. Aleksandr Chernatynskiy for his always helping attitude and useful discussions on uncertainty quantification.

I would like to take this opportunity to thank Drs. Chris Stanek, Amit Misra, Samrat Choudhary, Pratik Dholabhai, Jeffery A. Aguiar, Ghanshyam Pilania, Satyesh Yadav and everyone else in MST-8, MST-6 and T-1 divisions at LANL, who made my time at LANL productive and pleasurable.

I would like to thank Jean Gindreau, Metodi Illeav, Dr. Prashant Jain, Michelle Donahne and Dr. Alan Hurd, for their love, friendship and making my stay in Los Alamos very comfortable. Dr. Siddhartha Pathak and Dr. Shraddha Vachhani for introducing me to skiing and hiking in the beautiful outdoors of New Mexico and Colorado.

I would like to thank all the current and previous members of the SinPot and FLAMES group, for their warm friendship and the great environment they helped create for me here at UF. I owe my thanks to the International Center at UF, MSE academic and payroll services. I also like to thank all my teammates in the UF Cricket team, Gainesville cycling club, and group R-151, for all the wonderful experiences, and memories.

Finally, I want to thank my parents, my sister and my brother for their unconditional love and constant support. I am grateful to my family for encouraging and directing my interests in science since I was very young. I am greatly indebted to them, and I dedicate my work to them.
<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>4</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>9</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>11</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>17</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>18</td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>20</td>
</tr>
<tr>
<td>1.1 Background</td>
<td>20</td>
</tr>
<tr>
<td>1.2 Multiscale Computational Modeling</td>
<td>23</td>
</tr>
<tr>
<td>1.3 Objectives</td>
<td>25</td>
</tr>
<tr>
<td>1.4 Outline</td>
<td>26</td>
</tr>
<tr>
<td>2 SIMULATION METHODOLOGY</td>
<td>27</td>
</tr>
<tr>
<td>2.1 Theoretical Background</td>
<td>27</td>
</tr>
<tr>
<td>2.2 Density Functional Theory</td>
<td>30</td>
</tr>
<tr>
<td>2.2.1 Hohenberg and Kohn Theorems</td>
<td>30</td>
</tr>
<tr>
<td>2.2.2 Kohn-Sham Equations</td>
<td>31</td>
</tr>
<tr>
<td>2.2.3 Exchange – Correlation Functionals</td>
<td>33</td>
</tr>
<tr>
<td>2.2.4 Pseudopotential Approximation</td>
<td>34</td>
</tr>
<tr>
<td>2.2.5 Strong Correlation</td>
<td>35</td>
</tr>
<tr>
<td>2.2.6 Plane Waves as Basis Functions</td>
<td>36</td>
</tr>
<tr>
<td>2.2.7 K-Point Sampling</td>
<td>38</td>
</tr>
<tr>
<td>2.2.8 Strengths and Weaknesses of DFT Calculations</td>
<td>39</td>
</tr>
<tr>
<td>2.3 Molecular Dynamics</td>
<td>40</td>
</tr>
<tr>
<td>2.4 Kinetic Monte Carlo Method</td>
<td>41</td>
</tr>
<tr>
<td>2.4.1 Introduction</td>
<td>41</td>
</tr>
<tr>
<td>2.4.2 Method Details</td>
<td>42</td>
</tr>
<tr>
<td>2.4.3 Strengths and Weaknesses</td>
<td>43</td>
</tr>
<tr>
<td>3 DEFECT STRUCTURES</td>
<td>45</td>
</tr>
<tr>
<td>3.1 Intrinsic Point Defects in the Fluorite Structure</td>
<td>45</td>
</tr>
<tr>
<td>3.1.1 Defect Dipole Tensor</td>
<td>46</td>
</tr>
<tr>
<td>3.1.2 Defect Symmetry and Dipole Tensor</td>
<td>49</td>
</tr>
<tr>
<td>3.2 Dislocations in the Fluorite Structure</td>
<td>53</td>
</tr>
<tr>
<td>3.2.1 Edge Dislocations</td>
<td>54</td>
</tr>
</tbody>
</table>
3.2.2 Screw Dislocation

4 SEGREGATION OF FISSION PRODUCTS TO DISLOCATIONS IN URANIUM DIOXIDE

4.1 Background
4.1.1 Experimental
4.1.2 Computational
4.2 Methodology
4.3 Results
4.3.1 Segregation of Fission Products to Dislocations
4.3.2 Comparison with Continuum Elasticity
4.3.3 Effect of Ionic Radius and Charge on Segregation
4.4 Conclusions

5 DISLOCATION LOOPS IN URANIUM DIOXIDE

5.1 Background
5.1.1 Experimental
5.1.2 Computational Modeling
5.2 Theory: Dislocation Loop
5.3 Results and Discussion
5.3.1 Prismatic Dislocation Loops
5.3.2 Dislocation Loop Energy

6 IMPACT OF HOMOGENEOUS STRAIN ON POINT DEFECT DIFFUSION IN URANIUM DIOXIDE

6.1 Background
6.2 Methodology
6.2.1 Density Functional Theory Calculations
6.2.2 Kinetic Monte Carlo Simulations
6.2.3 Dipole Tensor
6.3 Results
6.3.1 Migration Paths and Energy Barriers
6.3.2 Dipole Tensor Calculations
6.3.2.1 Single uranium vacancy
6.3.2.2 Uranium di-vacancy
6.3.3 Homogeneous Strains
6.3.3.1 Single uranium vacancy
6.3.3.2 Uranium di-vacancy
6.4 Discussion and Conclusions

7 UNCERTAINTY QUANTIFICATION AND SENSITIVITY ANALYSIS IN A MULTISCALE MODEL

7.1 Background
7.2 Methodology
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>Components of the dipole tensor G values (in eV) for point defects. The major X, Y and Z axes of the simulation cell are oriented along [100], [011] and [001] crystallographic directions, respectively.</td>
</tr>
<tr>
<td>3-2</td>
<td>Types of dislocations in fluorite structure</td>
</tr>
<tr>
<td>6-1</td>
<td>Migration parameters for a single uranium vacancy and a uranium divacancy. The first column gives the migration barrier ($E_{mig}$) in eV and second column the rate prefactor ($\nu_{m}$) in sec$^{-1}$, taken from reference [21].</td>
</tr>
<tr>
<td>6-2</td>
<td>Calculated $\Delta G_{ijmig}$ (in eV) for charged and neutral uranium vacancy</td>
</tr>
<tr>
<td>6-3</td>
<td>$\Delta G_{ij}$ (in eV) for the full charged and neutral uranium divacancy</td>
</tr>
<tr>
<td>6-4</td>
<td>Summary of the relative diffusivities $D/D_0$, where $D_0$ is the diffusivity at 0% strain, for different strain states for the four defects considered here, at a strain of 2% and temperature $T = 1800$ K.</td>
</tr>
<tr>
<td>7-1</td>
<td>Details of DFT method and parameter employed in calculations with the system studied.</td>
</tr>
<tr>
<td>7-2</td>
<td>The computed principal components or eigenvectors using the PCA.</td>
</tr>
<tr>
<td>7-3</td>
<td>List of all possible combinations of varying two components of the dipole tensor at a time.</td>
</tr>
<tr>
<td>8-1</td>
<td>Calculated lattice parameters $a_0$ in Å, elastic constants and Bulk modulus (B) in GPa and dielectric constant $\varepsilon$ from DFT calculations in UO$_2$ (LSDA+U), Si (GGA) and GaAs (LDA).</td>
</tr>
<tr>
<td>8-2</td>
<td>Defect relaxation volumes of both neutral and charged defects calculated from DFT.</td>
</tr>
<tr>
<td>8-3</td>
<td>Calculated energy correction to defect formation energy (in eV) due to image interaction between charged defects, using the definition from Eq. 9 and corresponding correction to pressure (in GPa) (1 eV/Å$^3 = 160.2$ GPa) and volume (in Å$^3$) in DFT calculations. Charge state $q=1$ is considered for all systems.</td>
</tr>
<tr>
<td>8-4</td>
<td>Calculated background energy correction (in eV) to the total energy, using the definition from Eq.16 and corresponding correction to pressure (in GPa) and volume (in Å$^3$) for various charge defects in different considered systems.</td>
</tr>
</tbody>
</table>
Defect formation volume $\Delta \Omega_f$ for charged defects calculated from DFT compared with their relaxation volume $\Delta \Omega$ from DFT as well as empirical potential. (OS) stands for a calculation in which all of the corresponding defects were placed in one supercell in the DFT calculation. .......................... 166

Computed lattice parameter and bulk modulus using Birch-Murnaghan equation of state fit to the energy-volume data, as shown in Fig. C-1. ............... 178
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Structure evolution of the nuclear fuel.</td>
<td>22</td>
</tr>
<tr>
<td>1-2</td>
<td>Schematic of different time and length scale methods and properties encountered in this work.</td>
<td>25</td>
</tr>
<tr>
<td>2-1</td>
<td>Flowchart describing the computational approach used to calculate the total energy of the system, using the Density functional theory.</td>
<td>32</td>
</tr>
<tr>
<td>2-2</td>
<td>Schematic illustration of all-electron (dashed lines) and pseudo electron (solid lines) potentials and their corresponding wavefunctions.</td>
<td>35</td>
</tr>
<tr>
<td>2-3</td>
<td>Calculated energy per atom from DFT as function of cut-off energy for UO$_2$.</td>
<td>37</td>
</tr>
<tr>
<td>2-4</td>
<td>Calculated energy per atom for UO$_2$ from DFT as function of $k$-points mesh.</td>
<td>39</td>
</tr>
<tr>
<td>2-5</td>
<td>Flowchart to illustrate the Object kMC algorithm.</td>
<td>43</td>
</tr>
<tr>
<td>3-1</td>
<td>UO$_2$ unit cell. Uranium (small, blue) ions are arranged in FCC lattice; oxygen (large, red) ions occupy tetrahedral sites forming a simple cubic lattice.</td>
<td>49</td>
</tr>
<tr>
<td>3-2</td>
<td>Schematic showing symmetry rotation operations represented by the space group $F\overline{4}m\overline{3}m$.</td>
<td>50</td>
</tr>
<tr>
<td>3-3</td>
<td>Possible defect sites that can occur in a simple face centered cubic lattice.</td>
<td>51</td>
</tr>
<tr>
<td>3-4</td>
<td>Schematic of the UO$_2$ unit cell with Burgers vector $\frac{1}{2}[110]$ (in red) and slip plane (001) and dislocation line along [1-10] (dashed). On the right atomic arrangement on (1-10) planes A and B is shown.</td>
<td>55</td>
</tr>
<tr>
<td>3-5</td>
<td>Schematic of $&lt;110&gt;${001} edge dislocation core, showing the termination of ion type and local charge at the edge dislocation core.</td>
<td>56</td>
</tr>
<tr>
<td>3-6</td>
<td>Atomic structure of the $&lt;110&gt;${001} edge dislocation core. Colored by coordination number with light blue (5), red (6), dark blue (8) and green (10).</td>
<td>57</td>
</tr>
<tr>
<td>3-7</td>
<td>Schematic of the UO$_2$ unit cell with Burgers vector $\frac{1}{2}[110]$ (in red) and slip plane (110) and dislocation line along [001] (dashed). On the right atomic arrangement on (001) planes A B and C type is shown.</td>
<td>58</td>
</tr>
<tr>
<td>3-8</td>
<td>Schematic of $&lt;110&gt;${110} edge dislocation core, showing the termination of ion type and local charge at the edge dislocation core.</td>
<td>58</td>
</tr>
<tr>
<td>3-9</td>
<td>Atomic structure of the $&lt;110&gt;${110} edge dislocation core. Colored by coordination number with light blue (5), red (6), dark blue (8) and green (10).</td>
<td>59</td>
</tr>
</tbody>
</table>
3-10 Showing the steps to create edge dislocation structure in a simulation supercell. ................................................................. 61

3-11 Atomic structure of <110>{110} edge dislocation, showing only the uranium atoms, color coded by their potential energy. ................................................................. 61

3-12 Schematic showing introduction of 4 screw dislocation cores in a single crystal in order to apply periodic boundary conditions along all the three axes....................................................... 62

3-13 Atomic structure of <110>{110} screw dislocation, showing only the uranium atoms, color coded by their potential energy. ................................................................. 63

4-1 TEM image of UO$_2$ under high dosage after annealing to 1500 °C. ............... 66

4-2 TEM image of UO$_2$ at the burnup of 92 MWd/kgU (gigawatt-days/ton of heavy metal). .......................................................................................................................... 66

4-3 Atomic structure of $\frac{1}{2}a_o<110>{110}$ edge dislocation projected along [001] direction, showing only U atoms, color-coded based on their potential energy. . 70

4-4 Segregation profile of Ru$^{4+}$ across a pair of $\frac{1}{2}a_o<110>{110}$ edge dislocation within a simulation cell. ................................................................. 70

4-5 Ru$^{4+}$ Segregation profile with distance from the dislocation core along [1-10] direction for $a_o/2<110>{110}$ edge dislocation and for $a_o/2<110>{001}$ edge dislocation along [001] direction. ................................................................. 71

4-6 Cs$^{1+}$ Segregation profile with distance from the dislocation core along [1-10] direction for $a_o/2<110>{110}$ edge dislocation and for $a_o/2<110>{001}$ edge dislocation along [001] direction. ................................................................. 72

4-7 Xe Segregation profile with distance from the dislocation core along [1-10] direction for $a_o/2<110>{110}$ edge dislocation. ................................................................. 73

4-8 Ru$^{4+}$ Segregation profile with distance from the dislocation core along [1-10] and [001] direction for $a_o/2<110>{110}$ screw dislocation ................................................................. 74

4-9 A periodic simulation cell (solid rectangle) with vectors X, Y and Z (out of plane), containing a dislocation dipole with Burgers vector $\pm b$ and are separated by $d$ along Y and by $h$ along X. ................................................................. 75

4-10 Average stress, $\sigma = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, within the simulation cell having a pair of dislocations, calculated using the continuum elastic solution. ................................................................. 76

4-11 Stress field and difference in stresses as distance from the $a_o/2<110>{110}$ edge dislocation core along [1-10]; (Δ) corresponds to atomistic calculation and (•) to the continuum elastic solution. ................................................................. 77
Segregation Energy $E_S$ (red star) and relative energy $E_R$ (blue triangle) and difference ($E_S-E_R$) with distance from core for the $a_0/2<110>{110}$ edge dislocation along [1-10]................................. 79

Segregation Energy $E_S$ (red star) and relative energy $E_R$ (blue triangle) and difference ($E_S-E_R$) with distance from core for the $a_0/2<110>{001}$ edge dislocation along [001]................................................................. 80

$a_0/2<110>{110}$ edge dislocation in UO$_2$. Color map of uranium atoms, based on their relative energy. Preferred segregation sites (C and T) are marked............. 81

Segregation energy variation with ionic radii of the fission products, (Δ) represent compressive site and (*) represent tensile site................................................. 82

Variation in segregation energy of artificial ruthenium ion with ionic charge at the compressive site (Δ)................................................................. 83

The set of dislocation loops and networks observed in a UO$_2$ specimen irradiated to dose of 1.6 x10$^{20}$ fissions/cm$^3$ and 2.2 x 10$^{19}$ fission/cm$^3$, respectively......................................................... 86

Schematic of dislocation loops, (A) Slip loop, (B) Prismatic loop with $b$ representing the Burgers vector and $n$ the normal to the loop plane. ...................... 89

Schematic showing formation of vacancy prismatic dislocation loop (top) with Burgers vector $b$ and loop diameter $d$ and an interstitial prismatic dislocation loop (bottom). ................................................................. 90

Glide cylinder or prism for prismatic dislocation loop........................................... 91

Schematic of a 4 sided $<110>{110}$ dislocation loop, formed by edge dislocations........................................................................................................... 92

Atomic structure of $<110>$ prismatic dislocation loop. Atoms in grey represent uranium and ones in red are oxygen............................................. 93

Core structure of the $<110>$ interstitial dislocation loop along [1-10] direction, showing formation of $\frac{1}{2} a<110>{001}$ edge dislocation. C and T – represent the compressive and tensile regions........................................... 93

Interatomic spacing along X [110] through the tensile and compressive region across the $\frac{1}{2} a<110>{001}$ edge dislocation core for various location along the dislocation line along Y [1-10]................................................. 94

Core structure of the $<110>$ interstitial dislocation loop along [001] direction, showing formation of $\frac{1}{2} a<110>{110}$ edge dislocation................................. 95
5-10 Interatomic spacing along X [110] through the tensile, and compressive region across the $\frac{1}{2}a_{[110]}$ edge dislocation core for various location along the dislocation line along Z [001]. ................................................................. 96

5-11 Formation energy of $<110>\{110\}$ type interstitial dislocation loops of different shape and sizes. Square, triangle, and circle represent 4, 6 and 8 sided dislocation loops, respectively. ................................................................. 97

5-12 Binding energy of $<110>\{110\}$ type interstitial dislocation loops of different shape and sizes.................................................................................................................. 98

6-1 Uranium (small/blue) ions and oxygen (large/red) ions in the fluorite structure UO$_2$ unit cell.................................................................................................................. 107

6-2 Snapshots of uranium vacancy migrating to its nearest neighbor position along the $<110>$ direction, as predicted from DFT calculations. The migrating uranium ion is shown in yellow, the dashed black line represents the straight path along the [110] direction. ............................................................................................... 108

6-3 Schematic of the energy vs. the migration path for the uranium vacancy, showing an intermediate shallow minimum, corresponding to the migrating ion..... .................................................................................................................. 109

6-4 Two-fold rotation symmetry along the $<110>$ directions in the fluorite structure and schematic of all four reconstructed paths along one [110] direction. .................................................................................................................. 109

6-5 The six distinct di-vacancy configurations within first nearest neighbors in a UO$_2$ unit cell and four possible sites a single di-vacancy can hop to in order to maintain a di-vacancy pair. .................................................................................................................. 112

6-6 Schematic showing that the migration of a uranium di-vacancy (dashed line) is related to the migration of one of its constituent vacancies........................................................................... 113

6-7 Schematic showing the change in migration barrier (transition from A to B) for one of the paths oriented along [110] for an applied tensile strain of 1% along [100] for $VU \times$. .................................................................................................................. 116

6-8 Schematic showing the applied tensile strain along the [100] direction and change in the migration barrier $\Delta E_{mig}$ for $VU \times$ under applied uniaxial tensile strain along [100] for migration paths oriented along [110] (open diamonds) and [011] directions (solid diamonds). .................................................................................................................. 117

6-9 Relative diffusivity of the fully charged uranium vacancy under tensile and compressive strains at 1800 K.................................................................................................................. 117

6-10 Relative diffusivity of the fully charged uranium vacancy as a function of temperature under uniaxial tensile strain.............................................................................................................. 118
6-11 Schematic showing the applied shear strain in the (001) plane and change in migration barrier under applied shear strain for paths oriented in plane (open diamonds) and normal (solid diamonds) to the shear plane. .......................... 119

6-12 Relative diffusivity of a charged uranium vacancy under shear strain as a function of temperature........................................................................................................... 120

6-13 Comparison of diffusivities of neutral and charged uranium vacancies under uniaxial strain along [100] and shear strain along [110] at 1400 K. .......................... 120

6-14 Relative diffusivity of the neutral and charged uranium di-vacancy under tensile strain as function of temperature................................................................. 122

7-1 Phases on modeling and simulation and role of verification and validation..... 126

7-2 Schematic showing that the dipole tensor approach is the link between the DFT and KMC simulation. .................................................................................................................. 129

7-3 Schematic of a displacement along x for a single trajectory. ......................... 131

7-4 Distribution of MSD obtained from each trajectory for different lag times. The Gaussian curves in the bottom right panel are the same as the dotted lines in the other three panels........................................................................................................... 132

7-5 Computed diffusivity as function of the lag time and the number of independent trajectories. ......................................................................................................................... 133

7-6 Mean square displacement MSD along the major axis $i = [x, y, z]$ as function of lagtime......................................................................................................................... 134

7-7 Distribution of MSD obtained from each trajectory for X, Y and Z at lag time (A) $\tau \cong 6.2\ sec$ and (B) $\tau \cong 640\ sec$ .......................................................................................................................... 134

7-8 Uncertainty in diffusion coefficient as function of maximum length of lag time used to compute the diffusivity ...................................................................................................... 135

7-10 Relative change in diffusivity as given by Eq. (7-15) as function of % changes in the respective value of dipole tensor components................................................. 140

7-11 The sensitivity of each variable on the computed diffusivity based on the first principal component. ............................................................................................................. 143

7-12 Relative change in diffusivity as given by Eq. (7-15), as function of fifteen combinations (variables) of changing two dipole tensor components at a time..................................................................................................................................................................................... 144

7-13 The influence of each of the fifteen variables on the computed diffusivity based on the first principal component. .................................................................................. 145
8-1 Relaxation volume of a single uranium vacancy in UO$_2$ as a function of supercell size for neutral (blue) and fully charged (red) states. Closed symbols represent relaxation volumes obtained by using higher energy cut-off and much denser K-point meshes compared to data represented by open symbols. ................................................................. 156

8-2 Defect formation energy of a charged uranium vacancy as function of volume or hydrostatic strain. ...................................................................................................................... 162

A-1 Schematic of four equivalent paths along one particular [110] direction and steps on how to obtain the dipole tensors for four paths along a specific [110] direction. .................................................................................................................. 175

B-1 Charge alignment correction of vacancy of Gallium (charge -3) in a 3x3x3 cubic GaAs supercell. The electrostatic potentials are averaged along X, Y-axes. The defect is located at Z = 10.46 Å. .................................................................................. 177

B-2 Charge alignment correction of Silicon interstitial (charge 1+) in a 2x2x2 cubic Si supercell. The electrostatic potentials are averaged along X, Y-axes. The defect is located at Z = 4.96 Å. .................................................................................. 177

C-1 Energy of the perfect UO$_2$ obtained as function of volume, obtained volume for the minimum energy is 1944.36 Å$^3$ and energy of the supercell with a single uranium vacancy (charge -4) as function of volume, the volume obtained at the energy minima is 1984.75 Å$^3$. ................................................................. 178

D-1 Cubic axes, and orientation of $\frac{1}{2} a<110>{001}$ edge dislocation, and $\frac{1}{2} a<110>{110}$ edge dislocation. .................................................................................................................. 179
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI-NEB</td>
<td>Climbing Image Nudge Elastic Band Method</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>EAM</td>
<td>Embedded Atom Method</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>KMC</td>
<td>Kinetic Monte Carlo</td>
</tr>
<tr>
<td>LAMMPS</td>
<td>Large-Scale Atomic/Molecular Massively Parallel Simulator</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>SFE</td>
<td>Stacking Fault Energy</td>
</tr>
<tr>
<td>TST</td>
<td>Transition State Theory</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna Ab Initio Simulation Package</td>
</tr>
</tbody>
</table>
MULTISCALE COMPUTATIONAL MODELING OF DEFECTS IN URANIUM DIOXIDE

By

Anuj Goyal

August 2015

Chair: Simon R. Phillpot
Major: Materials Science and Engineering

Manufacturing, extreme operation conditions, and storage introduce large variety of defects into uranium dioxide (UO₂) nuclear fuel, which have diverse effects on fuel properties. In this study, a multiscale computational approach to model defect behavior in UO₂ is presented, by passing information in stages from electronic structure and atomistic calculations to a stochastic kinetic method.

Understanding the interaction of fission products with dislocations is critical to interpret their interaction with fuel microstructure. Atomistic simulations are employed to predict the segregation of ruthenium and cesium, both fission products, to edge and screw dislocations. Dislocation loops of different shapes and sizes are simulated to investigate their atomic structure. To understand the segregation behavior, comparisons are made between atomistic simulations and continuum-elastic based results. Segregation behavior is found to be directly related to the elastic strain field around the dislocation core and is affected by the orientation of dislocation and electrostatic interactions at the atomic defect site.
A detailed mechanism of, and the effect of homogeneous strains on, the migration of uranium vacancies in UO$_2$ is presented. Migration pathways and barriers are identified using density functional theory and the effect of strain fields are accounted for using a dipole tensor approach. This information is then passed to the kinetic Monte Carlo simulations, to compute the diffusivities in the presence of external strain fields. We report complex migration pathways for uranium vacancy and show under homogeneous strain, only the dipole tensor of the saddle with respect to the minimum is required to correctly predict the change in energy barrier between the strained and the unstrained case.

Homogeneous strains as small as 2% have considerable effect on diffusivity of both single and di-vacancies, with the effect of strain more pronounced for single vacancies than di-vacancies. Further, strain lead to anisotropies in the mobility of vacancy and degree of anisotropy is sensitive to nature of applied strain field. Our results suggest that the influence of strain on vacancy diffusivity is greater when single vacancies dominate the defect structure, such as sintering, while the effect will be much less substantial under irradiation conditions where di-vacancies dominate.

An early uncertainty quantification study is presented. The source as well as the nature of errors in the input parameters is investigated, and the sensitivity of each of these input parameters on the final computed diffusion rates is analyzed.
CHAPTER 1
INTRODUCTION

1.1 Background

Uranium dioxide (UO$_2$) is the ubiquitous nuclear fuel used to power light water nuclear reactors (LWRs)\textsuperscript{1}. During its operation, the UO$_2$ fuel pellet experiences extreme conditions of radiation, temperature, and mechanical stresses. UO$_2$ can undergo fission processes which produces various fission products\textsuperscript{2,3}. The chemical and physical state of fission products influences the properties of the fuel.\textsuperscript{1,4} Not only does the concentration of fission products increase with increasing burn-up, but also the formation of extended defects such as dislocations, dislocation loops, voids and defect clusters is initiated\textsuperscript{5–7}. Some of these defects may be present in the structure even before irradiation, typically as a result of the fabrication and sintering processes.

The evolution of defects in nuclear fuel is closely coupled to their performance. For example, the formation and retention of fission gas bubbles induces fuel swelling, which in turn leads to mechanical interaction with the clad, thereby increasing the probability of cladding failure\textsuperscript{1,8,9}. Most fission gases and metallic fission precipitates of such as Mo, Tc, Ru and Cd have low solubility in the fuel matrix\textsuperscript{8–10}; moreover, there is a significant driving force for segregation of these fission products to dislocation and grain boundary sinks. Dislocation structures such as mixed dislocations and dislocation loops form with increasing burn-up of UO$_2$ and significantly contribute to the microstructural changes in the fuel matrix over time\textsuperscript{1,11,12}. Therefore, subsequent release of these insoluble fission products is closely related to their interaction with the fuel microstructure.
As a ceramic, UO$_2$ has low thermal conductivity and high brittleness at low temperatures$^{13-15}$. However, at high temperatures and under irradiation UO$_2$ can be subject to time-dependent creep$^{1,13,14,16}$. Depending on the proposed mechanisms for the high temperature thermal creep$^{17-19}$, the rate-determining step is thought to be governed by either diffusion of point defects$^{1,17}$, or by the glide and climb of dislocations$^{18-20}$. More generally, the strain-induced anisotropy of point defect diffusion should be taken into account in calculating the defect fluxes to sinks such as dislocations and cavities because accurate evaluation of the sink absorption efficiency for point defects is critical in determining creep rates$^{21}$. Hence, understanding diffusion rates as a function of sink type and point defects such as vacancies and interstitials, is important in calculating creep rates and dislocation substructures$^{22,23}$.

Therefore, understanding the properties of UO$_2$ subjected to the formation of defects under extreme conditions is a complex problem and poses a key challenge for researchers and engineers seeking to predict the reliability and safety of nuclear reactors. A critical part of the challenge is wide variability of fuel properties, through variations in microstructure and stoichiometry, both as a result of fabrication and fission. The nuclear fuel pellet temperature in normal operation ranges from about 800 °C on the periphery to well over 2000 °C at the center line less than 1 cm away. The temperature and thermal gradients are so high that they induce significant fuel restructuring$^1$. Figure 1-1, shows restructuring and microstructure evolution of the fuel pellet, involving formation of large columnar grains adjacent to a central void, which appear under particular conditions but not in most systems, and the region with equiaxed grains moving outward from the column-region.
Similarly, microstructure is sensitive to fuel burn-up, with the characteristic microstructure close to the pellet surface due to enhanced fission rate and local burn-up usually referred to as the “rim zone structure”\textsuperscript{1,12,24,25}. The formation of this structure starts at local burn-up of about 60-70 MWd/KgU (Mega-Watt Days per Kilogram of Uranium); as burn-up increases, the changes increase. The most obvious effects are characterized by reduction in grain size, increased porosity, fission gas release and accumulation of the fission products\textsuperscript{12,25}. Additional complexity in the defect behavior can be attributed to the wide range of physical length scales, ranging from inter-atomic
spacing (sub nanometer) to meters, and times scales ranging from nanoseconds to years. Macroscopic behavior such as fuel swelling, creep and fission gas release, depend on events occurring at the atomic scale, including the formation of fission gas bubbles and voids at dislocations and grain boundaries, and interaction of point defects to sinks.

In addition to the vast amount of experimental work, significant efforts have been made in recent years to understand various aspects of UO$_2$ using computational studies. Some of the earliest works include fission gas diffusion, defect behavior and fission product stability in UO$_2^{10,26}$. More recent studies include thermal transport, radiation damage, defect energetics and development of empirical potentials to model UO$_2^{27–31}$. There has also been work to understand fission gas behavior at the atomic scale and to develop engineering scale fuel performance codes$^{32,33}$. However, there has been little work on modeling dislocations in nuclear fuels$^{34–36}$, especially to quantify their effect on fission product evolution. Further, there is a lack of understanding of the diffusivities of defects in the presence of strain fields governed by microstructure details, such as dislocations, and how they relate to the mechanical behavior of fuel such as high temperature thermal creep.

1.2 Multiscale Computational Modeling

Multiscale materials modeling combines methods from diverse scientific disciplines to bridge the wide range of time and length scales that are inherent to a number of essential phenomena and processes in materials science and engineering. A proper linkage of small-scale electronic structure theory and large-scale statistical methods is necessary to describe the physics and chemistry that govern material processes under realistic temperature and pressure conditions. There is growing
interest in using multiscale modeling for materials discovery, simulation-guided product
design\textsuperscript{37} and complex phenomena such as nuclear fuel behavior\textsuperscript{38}. However, there are
various challenges in this multiscale approach. First, it is necessary to develop a
consistent theoretical framework that can couple particle-based and continuum-based
models with seamless transitions between the two. The second challenge is to design
appropriate experiments that can validate modeling predictions, as experiments
observations are often influenced by initial and boundary conditions imposed during
experimentation. Finally analysis of errors and uncertainties in simulations linked across
length and timescale is less advanced, and has not been systematically recognized for
materials simulations. In this dissertation, I have used three different length and
timescale approaches, integrated into a framework of hand-shaking sequences with the
aim of incorporating electronic or atomistic results, including parameters and
mechanisms into a stochastic modeling method.
Figure 1-2   Schematic of different time and length scale methods and properties encountered in this work.

These approaches include 1) ab-Initio based density functional theory to calculate the physical and electronic structure of bulk materials and point defects, 2) atomistic simulations, which model materials at the level of atoms, and 3) a mesoscale kinetic Monte Carlo (kMC) approach, which is a stochastic method based on rate theory applied at atomic scale.

1.3 Objectives

The objectives of this thesis are:

1. To understand the interaction and anisotropic diffusion of point defects in the presence of external as well as internal strain fields of the material. This is important for
accurate computation of higher length scale measured quantities such as dislocation climb velocities.

2. To understand the interaction of fission products with dislocations and develop structural insight of the complex dislocation structures in UO₂. This is critical in predicting the fuel swelling behavior and release of volatile fission products.

3. To take the first steps towards quantifying uncertainty and errors in the computed values, as well as performing a sensitivity analysis of input parameters on model outputs. Estimation of the accuracy of a model is vital and needs to be rigorously quantified before any model predictions can be adopted as reliable and complementary to the experimental methods.

1.4 Outline

This dissertation is organized as follows. It begins by giving details of methods in Chapter 2, and defect structures at various length scales in Chapter 3. Interaction of fission products with dislocations lines and loops using molecular statics simulations is presented in Chapters 4 and 5. Chapter 6 and 7 discuss point defect structures and migration paths from DFT calculations and an approach to implement these point defect details into kMC simulations. Chapter 8, is devoted to developing systematic methods to analyze the sensitivity of model predictions on input parameters and to quantify uncertainty and error propagation in the modeling approach used. The conclusions and future perspectives of this work are given in Chapter 9.
Computational simulations are extensively used to study defect properties of materials, as they can provide valuable information and understanding with atomic resolution that sometimes is difficult to obtain from experiments. In this present study, electronic structure calculations at the level of density functional theory (DFT), atomistic simulations at level of molecular statics, and mesoscale simulations at the level of kinetic Monte Carlo (kMC) method are employed. This chapter briefly describes relevant aspects of these methods.

2.1 Theoretical Background

Density functional theory (DFT) is a quantum mechanical based theory used to investigate the electronic structure of many-body systems. The quantum state of a system consisting of electron and nuclei is described using the Schrödinger Equation.

The time independent, nonrelativistic Schrödinger Equation is given as

$$\hat{H}\psi = E\psi$$ (2-1)

where $\hat{H}$ is the Hamiltonian operator, $\psi$ is the eigenstate wave function and $E$ is the eigenvalue. For a system consisting of atoms (with electrons and nuclei), $\hat{H}$ is expressed as

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_i^2 - \frac{\hbar^2}{2M_I} \sum_j^M \nabla_j^2 + \sum_{i,j} \frac{Z_i e^2}{|r_i - R_j|} + \frac{1}{2} \sum_{i\neq j} \frac{e^2}{|r_i - r_j|} + \sum_{i\neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|}$$ (2-2)

where, the subscripts $i, j$ denote the N electrons in the system and $I, J$ denote the M nuclei in the system, $m_e$ is the mass of electron, $M_i$ is the mass of nuclei. $Z_i$ is the atomic number or the nuclear charge of the nuclei. The spatial coordinates of the electrons and nuclei are $\vec{r}_i$ and $\vec{R}_j$, respectively. The Hamiltonian in Eq. 2-2 consists of
five terms, the first two term represent the kinetic energy, $\hat{T}$, of the electrons and nuclei respectively. The third term gives the attractive electrostatic interaction between electrons and nuclei, $\hat{V}_{Ne}$. The fourth and fifth terms are the repulsive potentials acting between one electron and another, $\hat{V}_{ee}$, and between two nuclei, $\hat{V}_{NN}$. Analytical solutions to Hamiltonian are only available for very few simple cases, such as the one-dimensional potential well or the hydrogen atom\(^{39,42}\). For complex many electron systems, only approximate solutions are possible.

Typically, the first key approximation applied in analyzing quantum mechanics to a system of atoms is the **Born-Oppenheimer approximation**\(^{43}\), based on the observation that electrons respond much more rapidly to changes in their surrounding than nuclei because electrons weigh much less than the nuclei. The result of this is that the kinetic energy terms in Eq. 2-2 can be separated and $\hat{V}_{NN}$ becomes constant. Since the nuclear coordinates no longer contribute to the full wave function, the Hamiltonian reduces to the so-called electronic Hamiltonian, $\hat{H}_{elec}$, written as

$$\hat{H}_{elec} = \left[ -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i \neq j} \frac{Z_i e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \right] = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee}$$  \hspace{1cm} (2-3)

and

$$\hat{H}_{elec}\psi_{elec} = E_{elec}\psi_{elec}$$  \hspace{1cm} (2-4)

The total energy of the system is then, given as

$$E_{tot} = E_{elec} + E_{nuc}$$  \hspace{1cm} (2-5)

where $E_{nuc} = \sum_{i \neq j} \frac{Z_i Z_j e^2}{|r_i - r_j|}$

The motion of the ions can usually be described satisfactorily by classical Newtonian mechanics. The time independent nonrelativistic Schrödinger equation (Eq. 2-1) can be
solved precisely for system containing only a single electron. However, when we
encounter a system with more than one electron we are faced with overwhelmingly
difficult problem of electron interactions, referred as exchange and correlation\textsuperscript{39,40}. First, electrons repel one another by virtue of their charge; hence the motion of one electron is correlated with the motion of the other electrons in the system. Thus, there is a complex relationship between the behavior of the electrons in many electron system. Second, because they are fermions (particles which have spin $\pm\frac{1}{2}$), the electrons are governed by the Pauli exclusion principle\textsuperscript{42}, which states that no two electrons can be in the same quantum state. In other words, the wavefunction of the two electron system has to be antisymmetric under exchange. This change in sign of wavefunction when two electrons are interchanged is called the exchange symmetry, and the change in energy of the electron system due to this is call the exchange energy\textsuperscript{39}. However, there is no exact solution to this problem, and approximations have to be introduced. All the above equations are expressed in term of wavefunctions. By itself, the wavefunction is not an observable quantity, but the square of the wavefunction can be interpreted as the probability of finding an electron within a given volume element at a particular position in space and is expresses as electron density $n(r)$, given as

$$n(r) = \sum_i \psi_i^*(r)\psi_i(r)$$

(2-6)

where $\psi_i^*$ is the complex conjugate of the wavefunction $\psi_i$. This link between the wavefunction and electron density makes the electron density a fundamental variable of the system.
2.2 Density Functional Theory

2.2.1 Hohenberg and Kohn Theorems

The foundation of density functional theory (DFT) is that it depends on the electron density, \( n(r) \), with only three spatial coordinates. Although there were some early attempts to use the electron density instead of the wavefunction to solve the Schrödinger equation\(^\text{39}\), it was the theorems of Hohenberg and Kohn\(^\text{44}\) which proved that a variational treatment of the electron density could yield the ground state energy of the system.

The first Hohenberg-Kohn theorem states, “For any system of electrons in an external potential \( V_{\text{ext}}(r) \), the total energy of the system is determined uniquely, except for a constant, by the ground state electron density \( n_0(r) \)”\(^\text{44}\). The second important aspect of Hohenberg and Kohn’s work was to show that the variation principle could be applied to find the ground state energy, \( E_0 \). The second Hohenberg-Kohn theorem states, “A universal functional for the energy \( E[n] \) of the density \( n(r) \) can be defined for all electron systems. The exact ground state energy \( E_0[n] \) is the global minimum for a given \( V_{\text{ext}}(r) \), and the density which minimizes this functional is the exact ground state density \( n_0(r) \)”\(^\text{44}\). Thus, it is now possible to write the ground state energy, \( E_0 \), as a function of the ground state electron density, \( n_0(r) \), as

\[
E_0[n_0] = T[n_0] + E_{ee}[n_0] + E_{Ne}[n_0]
\quad (2-7)
\]

where, the components and their subscripts have same meaning as in Eq. 2-3 and are themselves the functionals of electron density. Although the Hohenberg-Kohn theorems are very powerful, neither defined the functional of electron density or indicated a
systematic way of finding the functional. Much of what follows describes the search for suitable functionals, which started with landmark work of Kohn and Sham\textsuperscript{45}.

2.2.2 Kohn-Sham Equations

Kohn and Sham built on the theorems of Hohenberg and Kohn by showing how to determine an approximation to the ground state energy, which is a functional of the ground state density. The Kohn-Sham equations\textsuperscript{45} assume that the exact ground state density can be represented by the ground state electron density of a non-interacting auxiliary (or model) system. The one-electron Hamiltonian of this fictitious non-interacting system of electrons depends on the kinetic energy of electrons and an effective local potential $V_{\text{eff}}(r)$, given as

\[
\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(r) \right] \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad \text{(2-8)}
\]

where $V_{\text{eff}}(r) = V_{\text{ext}}(r) + V_{\text{Hartree}}(r) + V_{\text{xc}}(r)$ \quad \text{(2-9)}

and the electron density is given by

\[
n(r) = \sum_i \varphi_i^*(r) \varphi_i(r) \quad \text{(2-10)}
\]

where $\varepsilon_i$ are the energies (or Kohn-Sham eigenvalues) of the Kohn-Sham orbitals, $\varphi_i(r)$; $V_{\text{ext}}(r)$ is the external potential from the stationary nuclei and any external potential; $V_{\text{H}}(r)$ is the Hartree potential; and $V_{\text{xc}}(r)$ is the exchange correlation potential. The Hartree potential describes the Coulomb repulsion between an electron and the total electron charge density by all the electrons in the system and is defined as

\[
V_{\text{H}}(r) = e^2 \int \frac{n(r')}{|r-r'|} d^3r' \quad \text{(2-11)}
\]

The link between this model system and a real system of interest is made by choosing $V_{\text{ext}}(r)$ such that the resulting electron density, $n(r)$, is the same as the ground state density in the true system of interacting electrons.
The solution of the Kohn-Sham equation is an eigenvalue problem. For a given system of electrons and nuclei, the only system dependent parameters are the number of electrons present, N, and the nuclear potential (often referred as external potential). It is then necessary to determine the eigenfunctions (that is the wavefunctions) and the corresponding eigenvalues of the electronic Hamiltonian, \( \hat{H} \). To find the ground state wavefunction, a variation principle is employed, which always yields a calculated energy that is greater than the groundstate energy.

\( V_{\text{ext}}(r) \) depends on the electron density, and therefore on the orbitals; thus the Kohn-Sham equations must be solved iteratively. Hence DFT is typically implemented as a self-consistent (SC) method, as shown in Fig. 2-1.

Figure 2-1 Flowchart describing the computational approach used to calculate the total energy of the system, using the Density functional theory. (Adapted from M. C. Payne et al.\textsuperscript{46}, 1992)
Note that everything except the functional form of the exchange correlation is known exactly in the Kohn-Sham equations. Thus realistic approximations to the exchange and correlation are required\textsuperscript{39,40}, which we discuss in the next section.

2.2.3 Exchange–Correlation Functionals

The exchange-correlation potential is given by the functional derivative of the exchange-correlation energy $E_{xc}(r)$ and is defined as

$$V_{xc}(r) = \frac{\delta E_{xc}(r)}{\delta n(r)}$$  \hspace{1cm} (2-12)

One way of approximating the exchange-correlation energy, introduced by Kohn-Sham, is the local-density approximation (LDA)\textsuperscript{39}. In this scheme the value of $E_{xc}$ per atom is taken to be the same as that of an electron in homogeneous electron gas that has the same density at $r$. The use of the term ‘local’ means that the exchange-correlation energy $E_{xc}(r)$ in this approximation depends only on the electron density itself; contributions to $E_{xc}$ from inhomogeneities in the real electron density (that is, ‘non-local’ contributions) are not considered\textsuperscript{39}. Despite this approximation, LDA works remarkably well for many systems, even in inhomogeneous systems. The local spin density approximation (LSDA) scheme is an extension to LDA, which allows for different interactions for like-unlike spins and non-degenerate spin states\textsuperscript{40}. Two of the principle failings of the LDA method are that the binding energies are overestimated, leading to cell parameters being underestimated by several percent (3% is a widely quoted average)\textsuperscript{40}; and insulating systems which exhibit strong correlation effects (e.g. NiO and UO$_2$) are predicted to be metallic.

Moving beyond the LDA means incorporating non-local correlation effects. This is partially achieved by introducing a dependence on the gradient in the electron density,
and this is known as the generalized gradient approximation (GGA)\textsuperscript{47}. Broadly speaking, GGA corrects many of the deficiencies of LDA. Specifically, it tends to undo the overbinding effect, though in some cases this leads to severe underbinding\textsuperscript{47}. It does not however solve the problem of the band gap in strongly correlated systems.

Further improvements have come about by pairing correlation functionals with exact exchange energy functionals. These hybrid functionals use the exact exchange corresponding to that for a Slater determinant, and the some of the available functionals at this time are B3LYP, PBE0, EECE, and HSE\textsuperscript{48–51}. In addition to hybrid functionals, other approximations that have been developed to address the shortcoming of the LDA and GGA method. These include the self-interaction correction (SIC)\textsuperscript{52}, approximations based on the addition of a Hubbard term to the Hamiltonian, namely the DFT + U approach\textsuperscript{53,54}, and the dynamical mean field theory (DFT + DMFT)\textsuperscript{55}.

### 2.2.4 Pseudopotential Approximation

The key idea of the Pseudopotential approach is that the core electrons and the strong ionic potential are replaced with an empirical pseudopotential that acts on a set of pseudowavefunctions\textsuperscript{46}. The idea of a pseudopotential is to replace the strong Coulomb potential between the nucleus and the tightly bounded core electron with an effective ionic potential that acts on the valence electrons and has the same scattering properties as the all electron potential beyond the given cut-off radius, \( r_c \) (Fig. 2-2)\textsuperscript{46}. The pseudopotential approximation is based on the fact that most of the properties of the system are only determined by the valence electrons. The advent of norm-conserving pseudopotentials (NCPBs)\textsuperscript{56} and ultrasoft pseudopotential (USPPs)\textsuperscript{57} has led to accurate electronic structure calculations that are the basis of much computational research.
**Projector Augmented Wave (PAW) Method:** The PAW method\textsuperscript{58} for electronic structure calculations combines the pseudopotential approach with the linear augmented plane wave (LAPW) method. It can be shown that NCPPs and USPPs are approximations to the PAW method\textsuperscript{59}. In general, the PAW method is expected to be as accurate as all electron methods while being as efficient as pseudopotentials approach\textsuperscript{59}.

![Figure 2-2](image)

Figure 2-2  Schematic illustration of all-electron (dashed lines) and pseudo electron (solid lines) potentials and their corresponding wavefunctions. (Adapted from M.C. Payne et al.\textsuperscript{46}, 1992)

### 2.2.5 Strong Correlation

As mentioned in Sec. 2.2.3, exchange-correlation approximations neglect strong correlations; as a result, they fail to capture the correct band structure of Mott insulators with d or f orbitals\textsuperscript{53,60}. To overcome this problem, a number of approaches have been
developed of which the DFT+U approach is widely used. DFT+U attempts to improve the band structure of a Mott insulator by adding an onsite repulsion term to the DFT Hamiltonian, which results in a localization of d or f electrons. Many methods of DFT+U have been published in literature. Among them, Dudarev’s method is most widely used due to its easy implementation and relatively low computational cost. In Dudarev’s method, the total energy of the system is expressed as

$$E_{\text{DFT+U}} = E_{\text{DFT}} + \frac{U-J}{2} \sum_{\sigma} n_{m,\sigma} - n_{m,\sigma}^2$$  \hspace{1cm} (2-13)$$

where $n_{m,\sigma}$ is the occupation number of the $m$-th d or f state. The $U$ and $J$ are empirical parameters. In Dudarev’s method, only the difference between $U$ and $J$ ($U-J$) is meaningful.

### 2.2.6 Plane Waves as Basis Functions

Solid-state DFT calculations involve investigating properties of periodic arrangement of atom in space. Bloch’s theorem states that the wavefunction in periodic system can be expressed as the product of a periodic terms and a wave-like term, as

$$\varphi_i(\mathbf{r}) = u_i(\mathbf{r}) \exp[i(\mathbf{k} \cdot \mathbf{r})]$$  \hspace{1cm} (2-14)$$

where $u_i(\mathbf{r})$ is periodic in space with the same periodicity as the system. Functions of the form $\exp[i(\mathbf{k} \cdot \mathbf{r})]$ are plane waves, where the space of vectors $\mathbf{r}$ is in real space, and the space of $\mathbf{k}$ vectors is in reciprocal space. The periodic term, $u_i(\mathbf{r})$, can also be expanded as a linear sum of plane waves with wave vectors that are reciprocal lattice vectors, $\mathbf{G}$ of the real lattice vectors, $\mathbf{r}$ of the solid, as

$$u_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{G}} \exp[i(\mathbf{G} \cdot \mathbf{r})]$$  \hspace{1cm} (2-15)$$
Therefore, the wavefunction can be expressed as a plane-wave sum, as

$$\psi_i(\vec{r}) = \sum_{\vec{G}} c_i e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$  \hspace{1cm} (2-16)

The Bloch theorem reduces the problem of calculating infinite wavefunctions over an infinite volume of space to a problem of calculating the wavefunction of a finite number of particles at selected k-points in the reciprocal space. The other component of the Bloch theorem is the wave like part. To expand the wavefunction in terms of a wave-like part, one would need an infinite basis set in the plane wave method but this is not possible. Instead, the expansion is truncated at some finite cut off value, $E_{\text{cut}}$, of the plane-wave kinetic energy. Having a finite basis set can introduce error in the computed total energy. However, since plane-waves with larger kinetic energy contribute much less to the total energy, the error can be minimized by increasing $E_{\text{cut}}$ until the total energy converges. From DFT calculations (see Fig. 2-3), we observe that in perfect UO$_2$ for a cut-off value (ENCUT) greater than 450 eV, the errors in the energy per atom are less than 0.05 eV.

![Figure 2-3](image)

**Figure 2-3** Calculated energy per atom from DFT as function of cut-off energy for UO$_2$. 

37
2.2.7 K-Point Sampling

In the plane-wave approximation the total energy is evaluated from the contribution of each occupied electronic state at selected \( \vec{k} \)-point wave vectors in the solid. Bloch's theorem and the inherent symmetry of the crystal can be exploited so that electronic states need be evaluated only at a set of small number of \( \vec{k} \)-points determine total a good approximation to the energy of the solid. Specifically, this involves sampling the electronic states at \( \vec{k} \)-points only within the primitive cell in reciprocal space, that is within the first Brillouin zone (BZ). The reason that this can be done is that the electronic wavefunctions at \( \vec{k} \)-points that are very close together will almost be identical\(^{39,40}\). The particular method used here to calculate electronic states at set of special \( \vec{k} \)-points is that of Monkhorst and Pack\(^{63}\). The error incurred in the total energy due to this approximation can be made small by choosing a sufficiently dense set of \( \vec{k} \)-points. From our DFT calculations on perfect cubic UO\(_2\), we show in Fig. 2-4 that the error in the total energy diminishes with increasing number of \( \vec{k} \)-point or sampling density, with total energy ultimately converges.
2.2.8 Strengths and Weaknesses of DFT Calculations

In general, DFT is regarded to be very accurate in predicting various properties, especially total energies, as it does not depend on any fitted parameters. By this argument, all properties that can be related to the total energies can also be determined accurately\(^\text{40}\). However, when considering defects there are additional sources of error that should be taken into account. One such source is associated with the size of the supercell used under periodic boundary conditions (PBCs) in DFT. Simulations of a defect under PBCs actually results in computing a periodic array of defect images rather than as an isolated defect. This introduces extra elastic interactions between the defect and its images, which need to be corrected for in calculation of the DFE\(^\text{64,65}\).

Additionally, the simulation of charge defects leads to a spurious electrostatic interaction between defect and its periodic images\(^\text{66–69}\). Ideally, using a very large supercell can reduce these errors, but that can enormously increase the computational burden.

Another component of error in DFT calculations is purely numerical and is associated
with the plane wave cut-off, the K-point mesh size, and the force and energy convergence criteria. However, well converged calculations are regarded as being very precise, with an error of about 0.1 eV or so\textsuperscript{40}. All the DFT calculations in this study are performed using the Vienna Ab Initio Simulation Package (VASP)\textsuperscript{70,71}.

2.3 Molecular Dynamics

Molecular dynamics (MD)\textsuperscript{72} simulation is a computational technique that describes many-body systems based on the positions and momenta of particles in the system. The atomic movement is determined by solving Newton’s equation of motion from the calculated total energy, which is given as

\[ \ddot{r}_i = m_i \frac{d^2 r_i}{dt^2} = -\frac{\partial E(r_{ij})}{\partial r_i} \]  

(2-17)

where \( \ddot{r}_i \) is the force vector, \( m_i \) is the mass and \( r_i \) is the position vector if atom \( i \), \( t \) is the time and \( E \) is the total energy. The equation of motion is integrated with finite difference methods\textsuperscript{72}. There are many algorithms for solving the equation of motion including the Verlet, leap frog, and gear predictor-corrector algorithm\textsuperscript{72}. A Velocity-Verlet integrator is used in the preferred MD code LAMMPS\textsuperscript{73}. Here I use a molecular statics approach, in which the energy is minimized through use of empirical potentials for interatomic interactions. This approach is referred as ‘static’ because it do not explicitly take into account the lattice vibrations. The energy minimization is performed via the conjugate gradient approach as implemented in the MD code LAMMPS\textsuperscript{73}. The advantage of atomistic approaches, including molecular dynamics and molecular statics, is that larger supercell sizes can be treated at a small fraction of the computational cost of DFT calculations. This is very important for simulations, particularly those involving extended defects like dislocations and stacking faults.
**Interatomic Interactions:** The force on each atom in molecular static simulations is calculated from the gradient of the potential energy \( U \), given by Eq. 2-17. The functional form of the potential is determined by the nature of bonding (ionic, covalent, metallic etc.) in various materials. For our studies of UO\(_2\), an ionically bonded system, we have employed the widely-used Buckingham potential for the short-range interactions along with the long-range Coulomb interactions.

\[
U(r_{ij}) = U_{\text{Buck}}(r_{ij}) + E_{\text{Coul}} = \left[ A_{ij} \exp \left( \frac{-r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6} \right] + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i=1}^{N} \frac{q_i q_j}{r_{ij}} \tag{2-18}
\]

where \( A_{ij}, \rho_{ij}, C_{ij} \) are the empirical parameters and \( r_{ij} \) is the separation between the two ions \( i \) and \( j \). The potential parameters are defined for each ion pair in the system. For e.g. for UO\(_2\) the potential parameters are defined for \( O^{2-} - O^{2-} \), \( U^{4+} - O^{2-} \), and \( U^{4+} - U^{4+} \) pairs, respectively. The first and second terms in Eq. (2-18) correspond to repulsive and attractive interactions, respectively. The \( r^{-1} \) dependence of the Coulomb interaction makes the sum conditionally convergent. Hence, the summation of the Coulomb term over the system with \( N \) atoms is often carried out using either the Ewald sum\(^{72}\) or charge-neutralized direct sum\(^{74}\).

**2.4 Kinetic Monte Carlo Method**

**2.4.1 Introduction**

In the 1960’s researchers began to develop a Monte Carlo algorithm for systems evolving dynamically from state to state; this is known as kinetic Monte Carlo (kMC) method\(^{41}\). The primary tool in atomic simulation to simulate the dynamic evolution of systems of atoms is MD. A serious limitation of MD is that accurate solution to classical equation of motion via accurate integration requires time steps short enough (~ 10\(^{-15}\) sec) to resolve atomic vibrations. Consequently, the total simulation time is typically
limited to less than one microsecond, while the process that we wish to study, such as diffusion of defects, often take place on much longer time scales. This is referred to as the “time-scale problem”. kMC attempts to overcome this limitation by exploiting the fact that the long-time dynamics of system typically consists of diffusive jumps from state to state. Rather than following the trajectory through every vibration period, the state to state transitions are treated directly.

kMC is a widely used technique to simulate the long time evolution of systems of practical interest. A number of enhancement over the last decade have resulted in improving methods such as absorbing Markov chains\textsuperscript{75}, adaptive kMC\textsuperscript{76} and object kMC\textsuperscript{77}. In the kMC method, a system is advanced from one minimum energy configuration to the next, provided all transition pathways and the diffusion rates for each of these pathways are specified. It has been used to study variety of phenomena such as bulk and surface diffusion\textsuperscript{78}, cascade annealing\textsuperscript{79} and thin film growth\textsuperscript{80}. In these applications, one is particularly interested in knowing how a system of atoms evolves in the presence of strain. For example, in thin film growth, lattice mismatches lead to strains and eventually different thin film morphologies\textsuperscript{81}.

2.4.2 Method Details

The initial (or minimum) configuration of a point defect (object), transitions associated with each minimum, and displacement vector $d\vec{r}$ associated with each transition form the basic of kMC catalog. The full kMC catalog includes all possible degeneracies of the minimum and saddle points due to crystal symmetry, and accounts for symmetry transformations of the various displacement vectors $d\vec{r}$. Given this rate catalog, the entire kMC procedure is outlined using a flowchart, as shown in Fig. 2-5.
2.4.3 Strengths and Weaknesses

The power of this method is that quantities such as point defects absorption rates, which depend on sinks like dislocation, grain boundaries, can be directly calculated. This method allows more accurate computation of parameters, such as sink strength and sink efficiency that are used in traditional radiation damage models\textsuperscript{82}. Accurate computations of point defect absorption rates are critical for predicting mesoscale phenomenon, such as dislocation climb and loop growth, which determine microstructural evolution of the material under irradiation.

The kMC approach has certain assumptions too. The main assumption of this approach, as implemented here, is that the fundamental structure (displacement vectors, dipole tensor) of kMC catalog is unchanged by introduction of strain. This is
result of assuming that the underlying topology of the potential energy surface does not change under relatively low strains. Under this assumption, strain serves only to change the relative height of the stationary points on the energy surface. This is valid assumption under small external strains, where the effects are within the linear elastic regime\textsuperscript{83,84}. Another important assumption of this approach is that the defect is in a bulk-like environment. Thus, this technique should not be applied to defects at or near free surface or interfaces.
Defects can be classified based on the spatial dimensions as, point defects (zero-dimensional), dislocations (one-dimensional), stacking faults, grain-boundaries and surfaces (two-dimensional), and defect clusters, voids and cracks (three-dimensional). In this chapter, we present a brief discussion on zero, one and two-dimensional defects, based on material type studied, which are central to this dissertation.

3.1 Intrinsic Point Defects in the Fluorite Structure

Intrinsic point defects involve a single atom, either missing from crystalline a lattice site or present in an open space in a crystal. An atom missing from its crystalline site is called a vacancy and an additionally present atom is called an interstitial. These defects may be regarded as elementary point defects, in contrast to composite defects or defect complexes, which can be created by combining two or more elementary defects. Fluorite structured UO$_2$ is composed of two atomic species and in such systems, the type of point defects is determined by the symmetry of the sublattices, and the requirement of preservation of stoichiometry and electrical charge balance$^{85,86}$. In order to maintain the electrical neutrality and stoichiometry in an ionic crystal, vacancies may not form on one sublattice alone, but it is possible to form vacancies on both sublattices. The most common type of defects in stoichiometric UO$_2$ involves Schottky and Frenkel defects. The Schottky defect comprises a uranium vacancy and two oxygen vacancies. Using Kröger-Vink notation$^{87}$, a Schottky defect in UO$_2$ is expressed as

$$\emptyset \ (null) \Leftrightarrow V^{'''}_{U} + 2V^{'}_{O} \quad (3-1)$$
A Frenkel defect consists of a vacancy and an interstitial of same species. A typical Frenkel defect on the anion (O) lattice in UO$_2$ can be expressed as

$$O_o^− \leftrightarrow O_i^{''} + V_o^−$$  \hspace{1cm} (3-2)

Point defects are of interest because their presence controls the mobility of the atoms in the solid. In addition, the primary effect of high-energy radiation in a solid is to create point defects (i.e. vacancy-interstitial pairs) by dislodging atoms from normal lattice sites. The presence of point defects in the lattice can affect the symmetry of the perfect lattice and can produce local elastic distortions around the defect site. The next section introduces the concept of defect dipole tensor, which characterizes a point defect, its interaction with an external stress field, and some aspects of the symmetry associated with defect dipole tensor.

3.1.1 Defect Dipole Tensor

Point defects can introduce lattice distortions on both short and long ranges. The short range distortions consist of relatively large displacements of ions in the immediate neighborhood of the defect, whereas long range distortions can be understood from linear elasticity theory$^{64,88,89}$. A point defect or the lattice distortion associated with it interacts with external strains, which induces a change in the defect’s formation energy. This change in energy due to external strain can be described, to first order, by the elastic dipole tensor$^{64,85,88,90,91}$. The change in energy is given by

$$\Delta E = - tr(G \cdot \varepsilon) = -G_{ij} \varepsilon_{ij}$$  \hspace{1cm} (3-3)

where $\Delta E$ is the change in the energy of formation of the defect between the strained and unstrained environments. $G_{ij}$ is a component second-rank elastic dipole tensor and $\varepsilon_{ij}$ is a component of the external strain tensor. $G$ and $\varepsilon$ are symmetric tensors and the
right hand side of Eq. 3-3 assumes the Einstein summation convention. Note that, from the definition of $G$, it is a property of the defect, has units of energy (eV) and, in the linear elastic regime, is independent of the externally applied strain. Techniques to compute the elastic dipole tensor $G$ were first developed in the mid-1950s, and can be broadly grouped into three methods: the Kanzaki-Hardy force method$^{91,92}$, Gillan’s strain derivative method$^{64,88}$, and the stress/strain-based method$^{93,94}$. In the present work, we have used the stress/strain-based method, since it is computationally less expensive than the others, requiring only the examination of a single defect configuration. Gillan’s strain derivative method involves calculation of the energy of formation of the defect at different strain states and computing the derivative of the energy with respect to the strain. The Kanzaki-Hardy force method on the other hand, as discussed in literature$^{64,88}$, can be difficult to apply, especially for more complex defect structures. Gillan’s method and the stress/strain method have been shown to be more accurate than the Kanzaki-Hardy force method.$^{64,93}$ For the purpose of verification the dipole tensor via Gillan and stress/strain method for the simpler case of a vacancy in zirconium are compared and the calculated dipole tensor using both approach is found to be very close to the reported values.$^{82}$

The calculation of the dipole tensor $G$ from the stress/strain-based method is quite straightforward and can easily be applied to the common supercell approach used in atomistic and electronic-structure calculations for impurities and point defects. Point defect calculations based on DFT can be carried out in two ways. One way of introducing the defect is to keep the supercell size and shape fixed with respect to the bulk (defect free) structure ($\varepsilon_{ij} = 0$) and allow only relaxation of atomic coordinates. I
refer to this as the constant volume or strain-controlled approach. In this approach a
simulation box containing a defect will develop a finite stress $\sigma_{ij}$, which gives the
measure of the dipole tensor $G$ for the point defect. An alternative to the above method
is to perform atomic simulations where the supercell size and shape, as well as the
atomic coordinates, are allowed to relax to zero stress ($\sigma_{ij} = 0$). This is the constant
pressure or stress-controlled approach, where the simulation box containing the defect
will develop a strain $\varepsilon_{ij}$, which then gives a different measure of the dipole tensor $G$.
Note that the above defined stress $\sigma_{ij}$ and strain $\varepsilon_{ij}$ of the defect are measured with
reference to the equilibrium bulk (defect free) structure. The general expression to
calculate the dipole tensor $G$ from the stress/strain-based method has been derived in
the literature$^{93,94}$ and is given by

$$G_{ij} = V \left( C_{ijkl} \varepsilon_{kl} + \sigma_{ij} \right)$$

(3-4)

where $V$ is the volume of the simulation cell containing the point defect, $C_{ijkl}$ is the
elastic constant tensor, and $\sigma_{ij}$ and $\varepsilon_{kl}$ are the stress and strain of the defect structure
as mentioned in the discussion above. Calculations of the dipole tensor via both the
stress and strain controlled approaches, as discussed next, show very good agreement.
Further, after evaluating the energy vs. volume curves (which are related to the elastic
constants) for both the perfect and defect structures, we find both curvatures to be very
close. It is thus reasonable to assume that the elastic constants $C_{ijkl}$ do not change
much from the bulk value for the studied concentrations of defects and small-applied
strains. For the strain-controlled limit ($\varepsilon = 0$), Eq. 3-4 reduces to

$$G_{ij} = V_0 \sigma_{ij}$$

(3-5)
where \( V_0 \) is the volume of simulation cell containing the point defect, which is the same as the volume of the perfect-crystal structure. \( \sigma_{ij} \) is the stress of the defect simulation cell calculated from atomistic calculations. In the stress-controlled limit \((\sigma = 0)\), Eq. 3-4 reduces to

\[
G_{ij} = V C_{ijkl} \varepsilon_{kl}
\]

(3-6)

where \( \varepsilon_{kl} \) is the strain of the relaxed defect simulation cell (with volume \( V \)) with respect to the bulk simulation cell. The computed dipole tensors for point defects in UO\(_2\) and Au are summarized in Table 3-2.

### 3.1.2 Defect Symmetry and Dipole Tensor

It is only appropriate to discuss symmetry of the defect lattice after establishing and understanding the symmetry of the perfect fluorite UO\(_2\) lattice. In the fluorite crystal structure, cations occupy face centered cubic (FCC) sites while anions occupy the eight tetrahedral sites, as shown in Fig. 3-1. The four cations and eight anions have coordination numbers of eight and four respectively. The space group of fluorite structure is \( Fm\overline{3}m \) (number 225) and the point group symmetry is \( m\overline{3}m \) or \( 4 \overline{3}m \) \( 95,96 \).

![Figure 3-1](#) UO\(_2\) unit cell. Uranium (small, blue) ions are arranged in FCC lattice; oxygen (large, red) ions occupy tetrahedral sites forming a simple cubic lattice.
The first letter in the space group, the centering type, represents the translation symmetry in three dimensions, therefore F represent FCC symmetry operations. The three entries following F are representative the symmetry in the primary, secondary, and tertiary directions\textsuperscript{96}. For the cubic lattice, the primary directions are <100> type; secondary are <111> type and tertiary are <110> type. For $F \frac{4}{m} \frac{3}{m} \frac{2}{m}$ symmetry, 4/m represents 4-fold rotation symmetry around the primary <100> direction and two perpendicular mirror planes normal to rotation direction. $\frac{3}{m}$ represents rotation–inversion symmetry about the <111> direction, and lastly, $\frac{2}{m}$ represents 2-fold rotation about the <110> direction and two perpendicular mirror planes normal to it. Figure 3-2 shows the symmetry operations represented by space group $F \frac{4}{m} \frac{3}{m} \frac{2}{m}$. Figures 3-2 (A) shows the 4-fold rotation symmetry along the primary [100] direction, 3-2(B) 3-fold inversion symmetry along the secondary [111] direction and 3-2(C) 2-fold rotation symmetry along tertiary [110] direction.

![Figure 3-2](image.png)

In this discussion of defect symmetry, we consider the case of a crystal, which contain just one point defect. The presence of a defect destroys the translation symmetry of the crystal, and we refer the point-group symmetry of this defective crystal as the “defect
symmetry”. The defect symmetry may be lower than or equal to that of the perfect crystal; if the defective crystal has a lower symmetry than perfect crystal, then there must exist more than one distinguishable configuration or orientation of the defect\(^{85,90}\).

The defect symmetry of various crystal structures is discussed in Chapter 8 of the book “Anelastic Relaxation in Crystalline Solids” by A. S. Nowick and S. Berry\(^{85}\). Here a short summary of the subject adapted from this book is presented focusing only on fluorite crystal structure, and summarizing the symmetry associated with elementary defects, including the vacancy and interstitial in a fluorite lattice. The symmetry of some of the simple defect sites (shown in Fig. 3-3) can be defined in terms of point groups symbols usually designated in Hermann-Mauguin notations (international notations)\(^{97}\).

![Figure 3-3 Possible defect sites that can occur in a simple face centered cubic lattice.](image)

Site A, at a cube corner, has full cubic symmetry similar to that discussed for perfect UO\(_2\) lattice, and is given by point group, (m\(3\)m). Site B, at the center, has tetragonal symmetry (4/mmm) with the tetragonal axis along the Z-axis, i.e., perpendicular to the
plane of Fig. 3-3. And Site C, on an edge center, also has (4/mmm) symmetry, but now the tetragonal axis is parallel to the Y-axis.

The dipole tensors are symmetric tensors because they are derived from stresses or strains introduced by defect, which are symmetric to reflect the balance of forces in the crystal lattice. Therefore, it is only necessary to determine six components of the tensor. For elementary point defects such as vacancies, it is easy to see that the defect symmetry has the point symmetry of the perfect crystal at the lattice site at which the defect is created\(^{85}\). Thus, a typical defect site usually represents the symmetry of the lattice site, unless the symmetry is broken to lower the energy of the system. For example asymmetric defects can form in various ways, such as under a Jahn-Teller distortion of lattice, formation of off-center ions, and split interstitials in metals\(^ {86}\). The dipole tensor \(\mathbf{G}\) values for a vacancy in FCC Au and point defects in fluorite-structured UO\(_2\) are reported in Table 3-1. The values reported for Au are from DFT calculations and for UO\(_2\) using molecular static calculations employing an empirical potential\(^ {98}\).

The metal vacancy and uranium vacancy in UO\(_2\) has full cubic symmetry of the lattice similar to site A in Fig. 3-3, hence components \(G_{11} = G_{22} = G_{33}\) are equal and the off-diagonal elements are exactly zero. The positive and negative signs of the dipole tensor elements represent the compressive and tensile nature of the stresses, respectively, along the major directions around the defect site. For a di-vacancy (pair 1-2 in Fig. 3-3) along the two nearest neighbor uranium atoms along <110> has a mid-point site similar to site B in Fig. 3-3. However, the axis passing through the midpoint site and perpendicular to the (001) plane only has two-fold rotation symmetry and hence two-fold defect symmetry type \(D_{2h}\) (mmm). The three symmetric axes are along [110],
[1-10] and [001] with mirror planes perpendicular to each of the symmetric axes. The dipole tensor has three different components with \( (G_{11} = G_{33}) \neq G_{22} \neq G_{13} \), based on the choice of directions.

Table 3-1 Components of the dipole tensor \( G \) values (in eV) for point defects. The major axes of the simulation cell are oriented along [100], [011] and [001] crystallographic directions, respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>Defect</th>
<th>Dipole Tensor (eV)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (FCC)</td>
<td>Vacancy ( V_U'''' )</td>
<td>( G_{11} )</td>
<td>-7.82</td>
</tr>
<tr>
<td>UO(_2) (Fluorite)</td>
<td>( V_U'''' ) - ( V_O'''' )</td>
<td>( G_{12} )</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>( V_O'''' )</td>
<td>( G_{13} )</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>( Q'_i'''' )</td>
<td>( G_{22} )</td>
<td>36.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( G_{33} )</td>
<td>36.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( G_{12} )</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( G_{13} )</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( G_{23} )</td>
<td>0.0</td>
</tr>
</tbody>
</table>

3.2 Dislocations in the Fluorite Structure

Dislocations are structural line defects that may form in the material during their growth, through subsequent plastic deformation and under the effect of irradiation. Dislocations are characterized by a line direction and Burgers vector. The Burgers vector is defined when an integral circuit along the lattice site around the dislocation line, results in a non-zero vector (as shown in Fig. 3-6). The Burgers vector for the most prevalent dislocation in the fluorite structure is \( b = \frac{1}{2}a(110) \), where \( a \) is the lattice parameter in a cubic unit cell. Dislocations can slip in planes containing both the dislocation line and the Burgers vector. This plane is known as the slip or glide plane; a dislocation that is able to move in this way is called glissile\(^{99}\). Experimental studies on single crystal UO\(_2\)^{100,101} have demonstrated that family of \( \{001\} \) and \( \{110\} \) slip planes are most active in UO\(_2\). Another particular type of dislocation has been observed in UO\(_2\) under irradiation\(^{102}\); it has Burgers vector along \( (110) \). However, no such dislocation has been described for the generic fluorite structure.
There are two primary (or basic) types of dislocations: edge dislocation and screw dislocations. For these basic dislocations, the dislocation line is straight. However, in general cases, mixed dislocations, combining aspects of both types, can form, for which the dislocation line is not straight. The major types of primary dislocations in fluorite structured UO$_2$ are summarized in Table 3-2, labeled by their line direction, Burgers vector and slip plane. Primary dislocations can be denoted by their slip system, which include Burgers vector direction and followed by slip plane.

Table 3-2 Types of dislocations in fluorite structure

<table>
<thead>
<tr>
<th>Type</th>
<th>Burgers vector</th>
<th>Dislocation line</th>
<th>Slip plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edge &lt;110&gt;{001}</td>
<td>$\frac{1}{2} [110]$</td>
<td>[1-10]</td>
<td>(001)</td>
</tr>
<tr>
<td>Edge &lt;110&gt;{110}</td>
<td>$\frac{1}{2} [110]$</td>
<td>[001]</td>
<td>(1-10)</td>
</tr>
<tr>
<td>Screw &lt;110&gt;{110}</td>
<td>$\frac{1}{2} [110]$</td>
<td>[110]</td>
<td>(110)</td>
</tr>
</tbody>
</table>

3.2.1 Edge Dislocations

An edge dislocation is formed by the addition or removal of a half-plane of atoms or lattice sites in the crystal (as shown in Fig. 3-5). The dislocation line is the line where the half-plane of atoms terminate and Burgers vector is perpendicular to this extra half-plane of atoms as well as the dislocation line direction. The major difference in the structure of edge dislocation in a metallic and an ionic system like UO$_2$ is the presence of charged ions, whose electrostatic interactions dominate the structure in ionic crystals.

$\frac{a}{2}<110>{001}$ Edge Dislocation in UO$_2$: The $\frac{a}{2}<110>{001}$ dislocation consists of extra an half of (110) types planes terminating on (001) plane with dislocation line along [1-10], and has a Burgers vector of $\frac{1}{2}a(110)$, as shown in Fig. 3-4. The uranium and oxygen ions are shown in blue and red, respectively.
A closer crystallographic examination of $\frac{a}{2}[110]/\{001\}$ edge dislocation (see Fig. 3-5) suggests that the dislocation core (end of extra half-planes) consists of two extra plane of (110) types (marked as A and B). There are couple of configurations possible for core structure of the $\frac{a}{2}[110]/\{001\}$ edge dislocation (see Fig. 3-5), based on the termination of the (110) planes. The electric charge of the core can change depending on the species of the ions in the last row of the inserted plane. Core with plane terminating with O-U-O triplet (Fig. 3-5A) will be neutral, whereas a plane ending in uranium (Fig. 3-5B) or oxygen rows (Fig. 3-5C) will induce positive or negative charge, respectively.
Figure 3-5  Schematic of <110>{001} edge dislocation core, showing the termination of ion type and local charge at the edge dislocation core.

In a perfect fluorite lattice, oxygen ions are bonded to two uranium ions in the same (110) plane and to one uranium ion on adjacent (110) planes. Similarly each uranium ion is bonded with four oxygen ions in the same (110) plane and two oxygen ions on adjacent (110) planes. However, extra half-planes in configuration B and C, lead to missing bonds for these terminating atoms and hence give rise to uncompensated charge at the dislocation core\textsuperscript{103,104}. The core terminating with uranium ions has a unit positive charge per Burgers vector length of $a_0/2[110]$. This inherent charge is due to the missing bonds for uranium ions marked as 1 and 2 in Fig. 3-5B. Similarly the core terminating with oxygen ions has a unit negative charge, due to missing bonds for oxygen ions marked as 3, 4 and 5 in Fig. 3-5C. Figure 3-6 shows the atomic structure of the $\frac{a}{2}<110>{001}$ edge dislocation core obtained for a neutral configuration from
molecular dynamics simulations, by annealing the defect structures at temperature about 1200 K, followed by cooling and subsequent energy minimization.

Figure 3-6  Atomic structure of the \( \frac{a}{2} \langle 110 \rangle \{110\} \) edge dislocation core. Colored by coordination number with light blue (5), red (6), dark blue (8) and green (10)

\[ \frac{a}{2} \langle 110 \rangle \{110\} \text{ Edge Dislocation in UO}_2: \text{The } \frac{a}{2} \langle 110 \rangle \{110\} \text{ edge dislocation consists of an extra half of (110) types planes terminating on (110) planes with a dislocation line along [001] and Burgers vector of } \frac{1}{2} a(110), \text{ as shown in Fig. 3-7. The atomic arrangement at an } \frac{a}{2} \langle 110 \rangle \{110\} \text{ edge dislocation core consist of two extra planes of (110) atoms with alternating uranium and oxygen ions, as shown in Fig. 3-8. This configuration does not have any inherent charge along the dislocation line, as both missing bonds for uranium and oxygen ions are in stoichiometric units}^{103,104}. \]
Figure 3-7 Schematic of the UO$_2$ unit cell with Burgers vector $\frac{1}{2}[110]$ (in red) and slip plane (110) and dislocation line along [001] (dashed). On the right atomic arrangement on (001) planes A B and C type is shown.

Figure 3-8 Schematic of $<110>$[110] edge dislocation core, showing the termination of ion type and local charge at the edge dislocation core.
Dislocation Structure in Computational Simulation: The simple approach to introducing an edge dislocation in a simulation supercell is to create a planar misfit between two crystals, such that subsequent atomic relaxation during energy minimization leads to formation of a dislocation core. For example, let us start by creating a rectangular slab (using a tetragonal unit, Fig. 3-10 A) of fluorite crystal with dimensions, $L_{x1} = 6[1\text{-}10]$, $L_{y1} = 24[110]$ and $L_{z1} = 35[001]$, and label it crystal 1. Next, build a crystal 2 with dimensions, $L_{x2} = 6[1\text{-}10]$, $L_{y2} = 25[110]$ and $L_{z2} = 35[001]$, that has one unit cell more in $Y$ [110] direction than the crystal 1. Then elongate crystal 1 and compress crystal 2 along $Y$ [110] direction to same final length 24.5 [110]. Joining
the two crystals along X-Y plane produce a bi-crystal (Fig. 3-10C) with a misfit interface on the X-Y (001) plane.

Since periodic boundary conditions (PBCs) are employed along the X,Y and Z axis, a dislocation dipole is introduced, rather than a single dislocation. As illustrated in Fig. 3-10C, a periodic repeating unit of crystal 1 (in red) appears along Z [001] over crystal 2 (in blue), creating an additional misfit (001) plane at the top, resulting in formation of dislocation dipole, with Burgers vector along [110] direction. There are other methods to introduce single edge dislocation in a simulation cell\textsuperscript{105}, but they usually involve free surface along one of the major axes. The atomistic configuration obtained at the end of the energy minimization using a MD code is shown in Fig. 3-11, where the misfit between two crystals has condensed into a dislocation dipole. The line direction of the dislocation is parallel to the X [1-10] axis.
Figure 3-10  Showing the steps to create edge dislocation structure in a simulation supercell.

Figure 3-11  Atomic structure of $<110>${$\{110\}$ edge dislocation, showing only the uranium atoms, color coded by their potential energy.
3.2.2 Screw Dislocation

A screw dislocation is formed by shearing a half-plane of atoms in one crystal with respect to the other, along the Burgers vector direction (see Fig. 3-12 (A)). The Burgers vector lies in the plane of sheared half-plane of atoms and is parallel to the dislocation line direction. In UO$_2$, the screw dislocation is denoted by $<110>{110}$ slip system, with Burgers vector $\frac{1}{2}(110)$, on the $\{110\}$ slip plane and the dislocation line along $<110>$. The screw dislocation is not charged.\textsuperscript{103,104} To construct a screw dislocation in a 3D periodic simulation cell, a quadrupole of screw dislocations is introduced as shown in Fig. 3-12 and the final energy minimized atomic structure is shown in Fig. 3-13.

Figure 3-12  Schematic showing introduction of 4 screw dislocation cores in a single crystal in order to apply periodic boundary conditions along all the three axes.
Figure 3-13  Atomic structure of $<110>\{110\}$ screw dislocation, showing only the uranium atoms, color coded by their potential energy.
CHAPTER 4
SEGREGATION OF FISSION PRODUCTS TO DISLOCATIONS IN URANIUM DIOXIDE

4.1 Background

4.1.1 Experimental

Extensive work has been performed in the past to classify fission products in irradiated UO₂ on the basis of their chemical state. Fission products can be conveniently classified into four groups: volatile fission products (He, Kr, Xe, Br and I); metallic precipitates (including Mo, Tc, Ru, Rh, Cd and Sb); oxide precipitates: (including Rb, Cs, Ba, Mo and Te); and fission products dissolved as oxides in the fuel matrix (including Sr, Zr, Nb and La). The knowledge of the chemical state and evolution of fission products within the fuel is necessary as it influences important physical properties such as thermal conductivity, creep, melting point and swelling. Gaseous fission products like Xe and Kr are insoluble in the fuel matrix and are known to form bubbles within the fuel, which contribute to swelling of the fuel pellet. Fission gases and other mobile fission products like Cs can be released from the fuel under certain conditions. Recently, there has been increased interest in the behavior of ruthenium within the fuel. This is due to the release of ruthenium at a similar rate as other volatile fission products in the Chernobyl accident. Ruthenium can typically be found in the form of metallic inclusions within the fuel, normally an alloy of metallic fission products: Ru, Mo, Pd, Rh, Tc, and Te. In addition, Ru under oxidizing conditions can form the highly volatile oxide RuO₄, which if released into the atmosphere, can be very hazardous as it is both chemically toxic and radioactive.
To understand the release of fission products from the nuclear fuel it is important to understand their evolution, precipitation and interaction with other defect within the fuel pellet. With increasing burnup, defects such as voids, grain boundaries and dislocation act as preferred sinks for fission gases and fission product precipitates\textsuperscript{11,106,109,112}. Figure 4-1 shows the TEM image of UO\textsubscript{2} showing clumps of bubbles in the matrix, large bubbles on dislocation lines, and coarsening of fission product precipitates. Experimental studies on light water reactor (LWR) UO\textsubscript{2} fuel suggest that the interactions between dislocations and fission product precipitates contribute to the microstructural changes in fuel matrix resulting from burn-up and elevated temperature. In a transmission electron microscopy (TEM) study of high burn-up UO\textsubscript{2} disk fuel, Sonoda et al.\textsuperscript{12} reported anchoring of dislocations by fission gas bubbles and precipitates of solid fission products (see Fig. 4-2). It was observed that the dislocations are anchored by precipitates and begin to pile up, resulting in a significant amount of strain within the grains. This in turn leads to the formation of various low angle sub-grain boundaries that are heavily decorated with fission product precipitates and gas bubbles\textsuperscript{12}. 
Figure 4-1  TEM image of UO$_2$ under high dosage after annealing to 1500 °C (obtained with permission from A.D. Whapham$^{11}$, 1966).

Figure 4-2  TEM image of UO$_2$ at the burnup of 92 MWd/kgU (gigawatt-days/ton of heavy metal) (obtained with permission from T. Sonoda et al.$^{12}$, 2002).
4.1.2 Computational

There are relatively few computational studies\cite{34-36,113-115} of dislocation behavior in nuclear fuel; these studies are primarily motivated to develop a better structural understanding of these defects and their interaction with point defects and fission products. Nerikar et al.\cite{116} examined the segregation of Xe fission gas to dislocations (edge and screw) and grain boundaries ($\Sigma 5$ tilt, twist and random) in UO$_2$. They predicted that under stoichiometric and hyper-stoichiometric conditions it is energetically more favorable for Xe to occupy a uranium vacancy site than an interstitial site. They further found lower segregation energies in regions under tensile strain than under compressive strain for an $a_0/2<110>$\{110\} edge dislocation. They reported a significant dependence of segregation energy on the type of dislocation: $\sim 2.7$ eV and $\sim 5.5$ eV for $<110>$\{110\} edge and screw dislocations, respectively. However, there was no clear dependence of the segregation energy on the strain or the electrostatic interactions; they thus concluded that segregation depends on the detailed atomic structure of the defect site at these dislocation structures. In a very recent study on $\frac{1}{2}a_0<110>$\{001\} edge dislocations in similar fluorite structured doped-CeO$_2$\cite{117}, it was reported that segregation of the dopants to edge dislocation is highly sensitive to the size of the dopant ions ($\text{Gd}^{3+}$, $\text{Y}^{3+}$, $\text{Sc}^{3+}$) and the strain field of the dislocation and presence of dislocation slows downs oxygen ion diffusion in doped CeO$_2$.

There is little information on how these fission products precipitate and distribute themselves around dislocations, which can possibly affect their diffusion and ultimate release from the fuel matrix. Therefore as a first step to such an understanding, here we examine the interaction of a single Ru$^4$ and Cs$^{1+}$ to edge and screw dislocations in UO$_2$ using molecular statics. Calculations on Xe segregation to edge and screw dislocations
are done to compare the results with published literature. The rest of this chapter is organized as follows. In Section 4.2, we describe briefly the empirical potentials used in these simulations. In Section 4.3, we present the results on the segregation energy to the $a_0/2<110>{001}$, $a_0/2<110>{110}$ edge dislocations, and to the $a_0/2<110>{001}$ screw dislocation, and a detailed analysis of the segregation phenomenon. Our conclusions are in Section 4.4

4.2 Methodology

The long-range Columbic forces are determined using the charge-neutralized direct summation method\textsuperscript{74}. A Buckingham potential is used to describe the short-ranged interatomic interactions as described in Eq. (2-18). The parameters for the interatomic interactions are taken from Grimes et al.\textsuperscript{98}. This particular parameterization was chosen among the more than twenty in the literature\textsuperscript{29,30,118} because it also has parameters for the fission products studied in this work. Specifically, the parameters for the interactions of Ru$^{4+}$ ions and other fission products with uranium and oxygen ions are taken from the work of Busker et al.\textsuperscript{119}. From previous experimental findings it is known that Ru forms metallic precipitates in stoichiometric UO$_2$; energetic calculations made by Grimes et al.\textsuperscript{98} using this potential were consistent with this. For our segregation calculations, U$^{4+}$ is substituted with fission product. The approach used here is similar to that used by Stanek et al.\textsuperscript{120,121} to determine the segregation energy as function of distance from a surface and a grain boundary.

4.3 Results

In the present simulations, we are interested in understanding the segregation of the fission products to edge dislocations in single crystal UO$_2$. Results are presented for both edge dislocation geometries and for the $a_0/2<110>{001}$ screw dislocation. To
calculate the segregation energy, a uranium ion (U⁴⁺) is substituted with a fission product, for e.g Ru⁴⁺ (Ru⁺³); the system is then relaxed until the forces and stresses are small. A second cell without a dislocation provides a reference for energy calculations. The total energy change on substituting a U⁴⁺ atom by fission product is then calculated at constant volume and with a fixed number of atom. Our segregation calculations are all performed at 0 K and under no external stress.

4.3.1 Segregation of Fission Products to Dislocations

Segregation can be understood as the interaction of an isolated zero dimensional defect with an extended defect such as a dislocation. The segregation energy (Eₛ) is defined as the total energy difference between placing the fission product close to the dislocation relative to placing it far apart from the dislocation, i.e., in the perfect lattice. Therefore the energy of placing a fission product in the pure (defect-free) UO₂ lattice is taken as the reference state with zero segregation energy. Figure 4-3, shows the simulated structure of a₀/2<110>{110} dislocation on a (001) plane cutting through the dislocation line along [001] direction, with the spacing between the dislocation dipoles approximately 17.5 nm. The highlighted region in red represents the core of the dislocation with range of about 3 – 4 nm. The segregation profile shown in Fig. 4-2 for Ru⁴⁺, is obtained by substituting uranium ion with ruthenium in a typical (001) plane, as shown in Fig. 4-4.
Figure 4-3  Atomic structure of $\frac{1}{2}a_0<110>{110}$ edge dislocation projected along [001] direction, showing only U atoms, color-coded based on their potential energy.

Figure 4-4  Segregation profile of $\text{Ru}^{4+}$ across a pair of $\frac{1}{2}a_0<110>{110}$ edge dislocation within a simulation cell.

$\text{Ru}^{4+}$ has segregation energy of $\sim -4$ eV to the $a_0/2<110>{110}$ edge dislocation and $\sim -3$ eV to the $a_0/2<110>{001}$ edge dislocation. Such negative energies indicate that is energetically favorable for Ru to segregate to the dislocations. For both the edge dislocation types, the segregation energy approaches a saturation value as the defect site moves away from the dislocation core. This typically occurs over distance of
approximately 5 - 6 unit cells (30 - 40Å) away from the dislocation core (see Fig. 4-5).
The bulk values do not saturate to the same value in the tensile and compressive regions within the simulation cell. This is due to the presence of a finite stress field (both compressive and tensile) in these regions. Ideally, the stress field would decrease to zero far away from a single dislocation core, but here we observe a non-zero value due to the presence of dislocation dipoles in the simulation cell (Fig. 4-5) as well as the image dislocations produced by the PBCs.

Figure 4-5  Ru⁴⁺ Segregation profile with distance from the dislocation core along [1-10] direction for a₀/2<110>{110} edge dislocation and for a₀/2<110>{001} edge dislocation along [001] direction.

It is instructive to examine the vacancies at the core of the dislocation. A Ru⁴⁺ atom is placed at the vacancy at the core of the dislocation and segregation energy is calculated with reference to placing a Ru⁴⁺ atom at an interstitial site far away (6 – 7 nm) from the dislocation core. For the a₀/2<110>{110} edge dislocation, the segregation energy is approximately –11.0 eV, whereas for the a₀/2<110>{001} edge dislocation it varies between –5.0 and –10.2 eV. We further look at segregation of placing a Ru⁴⁺ at
interstitial sites across the core of dislocation and deduce that the segregation energy follows the same trend as seen for substitutional sites, supporting our analysis of segregation for both dislocation types, which are validated with continuum elastic theory in Section 4.3.3. However, a comparison of the energetics for substitutional sites with that of vacancy at the dislocation core or at interstitial sites is not possible with empirical potentials, because the reference states needed for an appropriate treatment of the chemical potential are not correctly modeled.

Figure 4-6 shows the corresponding segregation trend for Cs\textsuperscript{1+} substituted at the U\textsuperscript{4+} site. Cesium as an impurity not only has a different charge than the host uranium atom but its ionic size (Cs\textsuperscript{1+} = 1.72 Å) is much larger than uranium ion (1.0 Å) at the same octahedral site. On comparing Cs\textsuperscript{1+} segregation results with Ru\textsuperscript{4+} on same system we find that cesium is likely to segregate in tensile regions around the edge dislocation core as against ruthenium’s preference for the compressive region. However, the relative values of segregation energy are quite similar for both impurities.

![Figure 4-6](image)

Figure 4-6  Cs\textsuperscript{1+} Segregation profile with distance from the dislocation core along [1-10] direction for a\textsubscript{0}/2<110>{110} edge dislocation and for a\textsubscript{0}/2<110>{001} edge dislocation along [001] direction.
For the edge dislocation the segregation energy for Xe atom falls to its lowest value close to the core and in the tensile region of the dislocation strain field (see Fig. 4-7). This is reasonably intuitive as the $Xe_U$ defect has a large, positive defect volume\textsuperscript{32,122} (i.e. crystal expands upon incorporation of these defects) and does not form chemical bonds. The segregation energies are approximately $-4.2$ eV and $-3.1$ eV, for $a_0/2<110>\{110\}$ and $a_0/2<110>\{001\}$ edge dislocations, respectively. Our values are in good agreement with another computational study\textsuperscript{116}, with reported segregation energy of roughly $-2.7$ eV for a Xe atom to the $a_0/2<110>\{001\}$ edge dislocation.

![Figure 4-7](image)

Figure 4-7 Xe Segregation profile with distance from the dislocation core along [1-10] direction for $a_0/2<110>\{110\}$ edge dislocation.

For Ru$^{4+}$ the segregation energy is $\sim -2.0$ eV at the core of the screw dislocation. The energies saturate to the bulk value at a distance of $20 - 30$ Å from the dislocation core. The strain field around the screw dislocation is symmetric and is compressive in nature. Therefore, smaller Ru$^{4+}$ ions are driven energetically to the core of the screw dislocation.
Figure 4-8  Ru$^{4+}$ Segregation profile with distance from the dislocation core along [1-10] and [001] direction for a$\pi$/2<110>{110} screw dislocation.

4.3.2 Comparison with Continuum Elasticity

To quantitatively understand the non-vanishing stress/strain fields on the segregation energy, we evaluate the stress fields associated with a two dimensional dislocation array. Our atomic model convolutes two effects: the interaction between the two dislocations forming the dipole, and the interaction between the dipole and its images under the periodic boundary conditions. We minimize this effect by separating the cores, by relatively large distance: d = 17.4 nm, and h = 9.5 nm (see Fig. 4-9).
Figure 4-9  A periodic simulation cell (solid rectangle) with vectors X, Y and Z (out of plane), containing a dislocation dipole with Burgers vector $\pm \mathbf{b}$ and are separated by $d$ along Y and by $h$ along X.

The continuum elastic solution to the stress field around a single edge dislocation is well known\textsuperscript{99,123}. Also, the stress fields for an infinite one-dimensional edge dislocation walls have also been calculated\textsuperscript{124,125}. However, there does not appear to be a functional form for the stress fields for a two-dimensional array of edge dislocations. Therefore, we calculate the stress field for the two-dimensional array, using the existing solution to the stresses for the one-dimensional array as given below:

$$
\sigma_{xx}(X, Y) = -\sigma_0 [2 \sinh(2\pi Y) \{ \cosh(2\pi Y) - \cos(2\pi X) \} - 2\pi Y \{ \cosh(2\pi Y) \cos(2\pi X) - 1 \}]
$$

(4-1)

$$
\sigma_{yy}(X, Y) = -\sigma_0 2\pi Y [\cosh(2\pi Y) \cos(2\pi X) - 1]
$$

(4-2)

$$
\sigma_{xy}(X, Y) = \sigma_0 \sin(2\pi X) [\cosh(2\pi Y) - \cos(2\pi X) - 2\pi Y \sinh(2\pi Y)]
$$

(4-3)

$$
\sigma_{zz}(X, Y) = \nu (\sigma_{xx} + \sigma_{yy})
$$

(4-4)

$$
\sigma_0 = \frac{\mu b}{2h(1-\nu)[\cosh(2\pi Y) - \cos(2\pi X)]^2}
$$

(4-5)
where, $\mu$ is the shear modulus; $\nu$ is the Poisson’s ratio; $b$ is the Burgers vector length and $h$ is spacing between dislocations in the linear array, see Fig. 4-9. The physical inputs, shear modulus ($\mu = 162.22$ GPa) and Poisson’s ratio ($\nu = 0.219$) for UO$_2$ are derived using the Grimes potential$^{96}$ and the Burgers vector length $b = 0.707 \ a_0$ and the spacing $h = 17.26 \ a_0$, where $a_0 = 5.46 \ \text{Å}$ are taken from the simulation setup. Figure 4-10 shows the variation in stresses within a simulation cell, due to 2D periodic array of edge dislocation.

Figure 4-10  Average stress, $\sigma = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, within the simulation cell having a pair of dislocations, calculated using the continuum elastic solution.

For most of the discussion in the rest of this section, we use the results on Ru$^{4+}$, primarily for the comparison with continuum elastic results. However, we show later in Sec. 4.3.4 that trends in segregation energy can similarly be understood for other fission products based on elastic and electrostatic effects.
The stresses calculated from the atomic simulations using well-known virial formula\textsuperscript{126}, are averaged over a volume of $0.5a_0^3$, and compared with the continuum elastic solution evaluated from Fig. 4-11. The positive and negative stress values correspond to the regions of compressive and tensile stress respectively. The continuum stress field rises sharply and diverges at the dislocation core, but saturates to an almost constant value in the region away from the core. These changes in the stress field are expected, as the dislocation core is a region of high structural disorder, with large non-elastic internal stresses compared to the bulk-like region, which is likely to behave elastically.

Figure 4-11  Stress field and difference in stresses as distance from the $a_0/2<110>{110}$ edge dislocation core along [1-10]; (Δ) corresponds to atomistic calculation and (★) to the continuum elastic solution.
It is evident from Fig. 4-11 that the continuum elastic field can reproduce the stress field for an atomistic model very closely, with a particularly good match in the regions away from the dislocation core. The segregation energy falls to its lowest value close to the core and in the compressive region of the dislocation stress field. This is physically reasonable as Ru\(^{4+}\) ion has a smaller ionic radii (~0.6 Å) than U\(^{4+}\) ionic radii (~1.0 Å). Hence, Ru\(^{4+}\) relieves the compressive stress in the compressively strained region. Also in the tensile region we observe an increase in segregation energy as the smaller defect volume further increases the tensile strain and thus the total energy of system. The stress profile illustrated in Fig. 4-11 represents the elastic distortion of lattice around the dislocation core with which the solute impurities interacts. The undersized substitutional atoms are likely to migrate toward the compressed region above the slip plane. This stress-induced migration therefore may lead to the segregation of solutes along dislocation lines and to the formation of solute enriched dislocation regions.

To further elucidate the trends in segregation based on the stress field of a dislocation, we compare the segregation energies obtained from our atomistic calculations with energy trends obtained from a simple model of strained bulk UO\(_2\). The purpose of this comparison is to understand the contribution of the elastic distortion created by the dislocation to the segregation energy. A defect-free UO\(_2\) single crystal is strained according to the continuum elastic stress field of associated with various locations around dislocation dipole, derived in Sec 4.3.3. The simulation box for calculations on strained bulk is constrained to be fixed in shape and size by applying finite external strain along the \(x\), \(y\) and \(z\)-axes. The change in the Ru formation energy
under strain, $E_R$, can then be defined as the difference in the total energy of the strained bulk UO$_2$ system with Ru$_x$ defect with the unstrained bulk UO$_2$ system with Ru$_x$ defect.

![Graph showing Segregation Energy $E_S$ (red star) and Relative Energy $E_R$ (blue triangle) and difference ($E_S - E_R$) with distance from core for the $\alpha/2<110>$ edge dislocation along [1-10].]

Figure 4-12 compares the relative energy, $E_R$, with the segregation energy, $E_S$, calculated in Sec. 4.3.1 for $\alpha/2<110>$ edge dislocation. From Fig. 4-12, we see that the trend for $E_R$ follows that for $E_S$, especially at the distances away from the core (region within elastic continuum). The disagreement on approaching the dislocation core is small and is presumably due to the well-known breakdown of elastic continuum theory in this region; moreover, at the core itself the local arrangement of atoms around an atomic site can greatly affect the preferred segregation site for Ru$^{4+}$ atom and therefore, there are few sites spatially very close to the core, which have high segregation energies. The trend in the relative segregation energies is similar for the


$a_0/2<110>{001}$ edge dislocation is similar. However, the difference in segregation and relative energies in the elastic regions (away from the core) is smaller ($\sim 0.2$ eV) for $<110>{110}$ system, than of about $\sim 0.4$ eV for $<110>{001}$ system, as shown in Figs. 4-12 and 4-13.

![Segregation Energy](image)

Figure 4-13 Segregation Energy $E_S$ (red star) and relative energy $E_R$ (blue triangle) and difference ($E_S - E_R$) with distance from core for the $a_0/2<110>{001}$ edge dislocation along [001].

4.3.3 Effect of Ionic Radius and Charge on Segregation

The effect of impurity segregation to dislocations and GB in ionic crystals has been studied previously$^{127-129}$. The focus of the previous studies was to understand the possible mechanism for solution hardening and GB strengthening in the ionic compounds. It was found that both the size and charge of the impurity ion are necessary to explain the segregation behavior to dislocations$^{127,129}$. Therefore, in this
section an attempt is made understand the segregation of fission products to \( \frac{a_0}{2} < 110 \{110\} \) edge dislocation in UO\(_2\) based on their charge and ionic radii.

Fission products studied are Ru\(^{4+}\), Zr\(^{4+}\), Ce\(^{4+}\), Y\(^{3+}\), La\(^{3+}\), Rb\(^{1+}\), Cs\(^{1+}\) in order of increasing ionic radii and decreasing charge. The segregation energy is calculated in the manner as defined in Sec. 4.3.1. Uranium is substituted with fission products (Ru\(_U^x\), Zr\(_U^x\), Ce\(_U^x\), Y\(_U^x\), La\(_U^x\), Rb\(_U^{'''x}\), Cs\(_U^{'''x}\)) in the regions of both the compressive and tensile stress across the dislocation. Based on the segregation energy profile, the most preferred site in the compressive and tensile regions is selected, and the segregation energies of the fission products are compared at these two sites. Sites marked C and T in Fig. 4-14 are the most preferred sites for all fission product studied. However, the preference for C-site vs T-site depends on the type of fission product, which is highlighted in Fig. 4-15 and explained below.

Figure 4-14  \( \frac{a_0}{2} < 110 \{110\} \) edge dislocation in UO\(_2\). Color map of uranium atoms, based on their relative energy. Preferred segregation sites (C and T) are marked.
As expected, ions with smaller ionic radii than uranium prefer to segregate in the compressive region, while those with larger ionic radii prefer to segregate to tensile regions. Further, unsurprisingly, the larger the difference in the radius of impurity ion with respect to uranium, the larger the driving force for segregation. Both Ru⁴⁺ (0.62 Å) and Cs¹⁺ (1.74 Å) show a high tendency to segregate at the compressive and tensile sites, respectively, whereas Ce⁴⁺ (0.92 Å) and Y³⁺ (1.02 Å) with marginally different ionic radii from U⁴⁺ (1.0 Å) have a very weak driving force for segregation. These results further validate the importance of the pure elastic distortion arising from ionic radius mismatch on segregation.

It is also important to understand the effect of charge on segregation. To do this, we fix the potential parameters $A$, $\rho$, $C$ for the Ru–O²⁻, Ru–U⁴⁺ interactions to that for Ru⁴⁺–O²⁻, Ru⁴⁺–U⁴⁺, as defined in Buckingham type formulation and vary only the
charge on the Ru cation from 0 to 4+. The segregation energy of the artificial Ru ion is then calculated at the compressive site as a function of charge as shown in Fig. 4-16.

![Graph showing variation in segregation energy of artificial ruthenium ion with ionic charge at the compressive site (Δ).](image)

**Figure 4-16** Variation in segregation energy of artificial ruthenium ion with ionic charge at the compressive site (Δ).

Decreasing the charge on ruthenium at the compressive site, while keeping the ionic radii constant, reduces its tendency to segregate. This reflects the importance of ionic bonds and charge compensation at the core of the structure. Possibly, the excess negative charge on the aliovalent substituted site is unstable in the presence of neighboring oxygen ions and hence decreases its segregation energy.

### 4.4 Conclusions

The objective of this work was to understand the segregation behavior of fission products in UO₂, so as to make better predictions about its microstructural evolution and release from the fuel matrix. Ru⁴⁺ shows a strong tendency to segregate at the edge dislocation core in UO₂, with stronger preference to the \( a_0/2<110>\{110\} \) edge dislocation than to the \( a_0/2<110>\{001\} \) edge dislocation. Analysis shows that the trends in segregation energy for all the investigated fission products can be understood in terms
of bulk behavior and continuum elasticity. The small Ru$^{4+}$ tends to segregate in the compressive region of the strain field for both the edge dislocations types in UO$_2$. Our results support the conclusions of a recent study$^{116}$ that found segregation of Xe to the tensile regions around the dislocations in UO$_2$. This study also illuminates the value that a simple elastic model might have in predicting the segregation behavior in other ionic systems, such as CeO$_2$, (U,Pu)O$_2$ and MgO which display the same slip systems. In conclusion, this work provides the insight into segregation behavior to edge dislocations, which will be helpful in predicting the fission product retention and release in nuclear fuels.
CHAPTER 5  
DISLOCATION LOOPS IN URANIUM DIOXIDE

5.1 Background

5.1.1 Experimental

There is considerable experimental evidence\textsuperscript{7,12,102,106,131–133} that dislocation loops form during radiation damage of nuclear fuel UO\textsubscript{2}. Most of these investigations were motivated by studying the evolution of defects and cause of microstructure changes in the fuel pellet under irradiation.

Radiation damage induced by fission fragments was studied experimentally by Whapham and Sheldon\textsuperscript{7}. They observed the presence of small interstitial type dislocation loops 2.5 nm in diameter, lying on \{110\} planes with Burgers vector $\frac{a}{2} \langle 110 \rangle$. At low dose, a large number of roughly circular and isolated dislocation loops are formed from interstitials atoms, which at higher radiation dosage ($> 10^{19}$ fissions/cm\textsuperscript{3}), coalesce with neighboring loops to form both larger loops and eventually constitute a tangled dislocation network, as shown in Fig. 5-1. Some of these findings were later confirmed by Souillard\textsuperscript{102} in samples irradiated at a slightly higher dosage. The average dislocation loop had nearly twice the size in diameter of those found by Whapham\textsuperscript{7}. However, $\frac{a}{2} \langle 111 \rangle$ loops lying on \{111\} planes are also reported in addition to $\frac{a}{2} \langle 110 \rangle$ loops. The \{111\} type loops corresponds to interstitial array of uranium and oxygen atoms in stoichiometric units. In the UO\textsubscript{2} fluorite lattice, the O atom diffuses at a much higher rate than the U atoms, leading to formation of dislocation loops with more oxygen interstitials.
Figure 5-1 The set of dislocation loops and networks observed in a UO$_2$ specimen irradiated to dose of $1.6 \times 10^{20}$ fissions/cm$^3$ and $2.2 \times 10^{19}$ fission/cm$^3$, respectively. (Obtained with permission from A. Whapham et al.$^7$, 1965).

The dislocation activity in the fuel increases with increasing burn-up$^{131,132}$. It was suggested that increasing the number of dislocations loops and more complex dislocation network play crucial role in microstructure changes at the periphery of the fuel with increasing burn-up. At high temperatures, however, the dislocation density can decrease due to annealing of point defects; this can affect the orientation of dislocation loops$^7$. The formation of vacancy aggregates has also been observed under radiation damage$^{11,102}$; these vacancy aggregates are counterparts to interstitial dislocation loops and can act as sinks to interstitial atoms and insoluble fission product atoms. As a result, the dislocation and void size distribution and its evolution is dictated to a great extent by the radiation dosage and the concentration of insoluble fission products$^{112}$. In a more recent ion (Xe$^{3+}$, Cs$^{2+}$) irradiation study on single crystal UO$_2$ thin film$^{107}$, a characterization of the defect structure by transmission electron microscopy (TEM) reveals formation of dislocation loops at the fluence of $5 \times 10^{13}$ ions/cm$^2$, their growth and development of dislocation networks for higher fluence of $10^{15}$ ions/cm$^2$; this is
consistent with earlier studies\textsuperscript{7,131}. In a study of high burn up PWR UO\textsubscript{2} fuel samples\textsuperscript{133}, loop radii of 19-38 nm and loop density of 1.9 – 7.6 x10\textsuperscript{21} loops/m\textsuperscript{3} were obtained.

CeO\textsubscript{2} has been studied as a surrogate for UO\textsubscript{2} as they both have the fluorite structure and similar lattice parameters. Yasunaga et al.\textsuperscript{134,135} observed dislocation loops in CeO\textsubscript{2} under electron irradiation. At low energies of 200 – 1250 keV, interstitial type non-stoichiometric dislocation loops of \textless111\rangle\{111\} type were formed by aggregation of oxygen ions. By contrast, under electron irradiation with energy range from 1500 to 3000 keV, stoichiometric interstitial type dislocation loops of \frac{1}{2}\langle110\rangle\{110\} type were found. Due to the difference in mass and diffusivities of Ce and O ions, the structures of defect clusters formed under electron irradiation are expected to depend on the incident electron energy. In an ion (Kr) implantation study\textsuperscript{136} on single crystal CeO\textsubscript{2}, interstitial type dislocation loops lying on the \{111\} planes with suggested Burgers vector along \textless111\rangle direction were observed. The average diameter of the loops grew from the range 4.4 to 6.4 nm, when the ion dose increased from 3x10\textsuperscript{14} ions/cm\textsuperscript{2} to 1x10\textsuperscript{15} ions/cm\textsuperscript{2} at 600 °C, and diameter from 10 to 25.6 nm at 800 °C. In an electron and ion (He\textsuperscript{+}, O\textsuperscript{+}) irradiation study of stabilized cubic zirconia (YSZ)\textsuperscript{137}, charged dislocation loops formed primarily by displacement of oxygen ions in the ZrO\textsubscript{2}-Y\textsubscript{2}O\textsubscript{3} system. It was suggested that growing loops under irradiation become unstable beyond a critical size, due to accumulation of charge and elastic stresses near dislocation loops\textsuperscript{137}.

TEM is a very powerful experimental technique to characterize the microstructure in many materials\textsuperscript{138}. An interstitial dislocation loop is an additional plane of atoms in a perfect crystal, it causes the electron beam to diffract differently than through the perfect
crystal. This difference in diffraction results in contrast in images. The contrast of a
dislocation depends on both the diffraction conditions and the imaging mode. If the
Bragg condition is fulfilled or not during diffraction depends on the magnitude of the
scalar product between the reciprocal lattice vector \( g \) and the Burgers vector \( b \), \( g \cdot b \). If
\( g \cdot b \) is zero or very small, then the contrast is weak, meaning the dislocation is invisible.
In a bright field imaging, the diffracted beam is blocked, which causes the defect image
to be dark. In Fig. 5-1, the dark regions represent dislocations. In dark field imaging by
contrast, the diffracted beam is used to form image and transmitted beam is blocked.
This shows defects as bright contrast in the image.

5.1.2 Computational Modeling

Molecular dynamics (MD) simulations using empirical potentials have been
employed to study radiation damage and formation of interstitial type dislocation
loops\textsuperscript{139,140}. In an MD study\textsuperscript{139} characterizing defect clusters resulting from 10keV
displacement cascades in UO\(_2\), nanometer size cavities and dislocation loops appeared
as a result of the irradiation process. Simulations predict the formation of interstitial type
dislocation loop on \{111\} planes approximately 5 nm in diameter, consistent with earlier
experiments\textsuperscript{102,141}. In simulation of CeO\(_2\), Aidhy et al.\textsuperscript{140} reported 1/3 \textit{<111>} \{111\} type
interstitial dislocation loop consisting of Ce interstitial ions stoichiometrically surrounded
by O interstitials on \{111\} planes. These dislocation loops were shown to be charge
neutral, containing twice the number of O interstitials as Ce interstitials.

In summary, it widely accepted that dislocation loops of interstitial atomic clusters
form on \{110\} or \{111\} type planes in the fluorite structure. However, a detailed
structural understanding of these dislocation loop is still lacking. In this chapter, I
investigate the \{110\} and \{111\} type interstitial dislocation loops for various shapes and sizes, and determine the energetics of dislocation loop formation in a single crystal UO$_2$.

### 5.2 Theory: Dislocation Loop

As discussed above, dislocation in irradiated and single crystal UO$_2$ can form three-dimensional loop structure and tangled networks of dislocations. A dislocation loop, typically means a closed dislocation line inside a crystal\textsuperscript{99,142}. So, in a similar manner to dislocations, dislocation loops are usually formed on specific crystallographic planes. According to the relative orientation of the Burgers vector, loops can be divided into two groups (Fig 5-2):

1. Slip loop, the Burgers vector of which lies in the loop plane,
2. Prismatic loop, the Burgers vector of which does not lie on the loop plane.

![Dislocation Loops](image)

**Figure 5-2** Schematic of dislocation loops, (A) Slip loop, (B) Prismatic loop with $b$ representing the Burgers vector and $n$ the normal to the loop plane.

Slip loops are usually formed in slip planes under external shear stress e.g. by the Frank-Read source mechanism\textsuperscript{99} or by stress concentration on inhomogeneities. These loops can further extend by gliding and can reach dimensions up to few microns\textsuperscript{142}. 


The formation of prismatic dislocation loops was first proposed by Nabarro in 1947\textsuperscript{143}. He found that vacancies precipitate on special crystallographic planes, forming a disc and that a dislocation loop can then be formed by the collapse of vacancy disc (Fig 5-3). Besides vacancies, prismatic dislocation loops can also be formed by precipitation of interstitial atoms in irradiated crystals\textsuperscript{7,102,144} (see Fig. 5-3).

![Diagram of vacancy prismatic dislocation loop](image1)

Figure 5-3  Schematic showing formation of vacancy prismatic dislocation loop (top) with Burgers vector $b$ and loop diameter $d$ and an interstitial prismatic dislocation loop (bottom).

Prismatic dislocation loops can also form during plastic deformation of a crystal. A common example is the observed prismatic dislocation loop in nanoindentation studies in FCC metals\textsuperscript{145}. A prismatic loop can glide along its slip cylinder (Fig. 5-4) but can only extend or contract in plane by diffusion of point defects\textsuperscript{146}. 


5.3 Results and Discussion

5.3.1 Prismatic Dislocation Loops

$<1\text{10}>\{1\text{10}\}$ Type: The $\frac{1}{2}<1\text{10}>\{1\text{10}\}$ type prismatic dislocation loop is constructed in a simulation cell by introducing two extra $\{1\text{10}\}$ type planes, consisting of both uranium and oxygen ions, between the existing $\{1\text{10}\}$ planes. The prismatic dislocation loop is bounded by the $\frac{1}{2}<1\text{10}>\{1\text{10}\}$ and $\frac{1}{2}<1\text{10}>\{0\text{01}\}$ type edge dislocations (Fig 5-5), whose Burgers vector $\frac{a}{2}\langle 1\text{10}\rangle$ is normal to (110) plane. A subsequent energy minimization of the starting structure gives the final relaxed geometry of the dislocation loop, as shown in Fig. 5-6.
Figure 5-5  Schematic of a 4 sided \( <110> \{110\} \) dislocation loop, formed by edge dislocations.

The geometry of this dislocation loop is rectangular. The inserted extra planes contain twice as many oxygen ions to the uranium ions and hence, this loop structure is overall charge neutral. The atomic structure around the dislocation loop is analyzed along the Y [1-10] and Z [001] dislocation lines. The dislocation along Y [1-10] is a \( \frac{1}{2} \) \( a<110> \{001\} \) edge dislocation type as shown in Fig. 5-7. The details of atomic arrangement around the dislocation core characterized by the interatomic positions in the compressive and tensile region around the edge dislocation core; we label them as C and T in Fig. 5-7.
Figure 5-6  Atomic structure of {110}<110> prismatic dislocation loop. Atoms in grey represent uranium and ones in red are oxygen.

Figure 5-7  Core structure of the {110}<110> interstitial dislocation loop along [1-10] direction, showing formation of $\frac{1}{2} a<110>$<001> edge dislocation. C and T – represent the compressive and tensile regions.
Figure 5-8  Interatomic spacing along X [110] through the (A) tensile and (B) compressive region across the $\frac{1}{2} a_{<110> \{001\}}$ edge dislocation core for various location along the dislocation line along Y [1-10].

The spacing between (110) planes in the perfect fluorite structure is $b = \frac{1}{2} a_{<110>} = 3.86$ Å. The difference between the X – coordinates ($X_{i+1} - X_i$) represents the interatomic distance between the two adjacent atoms along X [110] axis. The parameter
\( (X_{i+1} - X_i - b) \) is the measure of the change in interatomic spacing in the dislocation loop structure and the perfect fluorite structure. In Fig. 5-8, this change in interatomic spacing along the Burgers vector direction X [110] is plotted for atomic rows both above and below the (001) slip plane. The plot show the peak at the center of the edge dislocation core and confirms the tensile and compressive nature of strain below and above the slip plane (001). The peak at the tensile region of the dislocation core is larger in magnitude and has a narrow spread as compared to the peak compressive region of dislocation core, indicating high and concentrated tensile strains.

![Dislocation Loop Diagram](https://via.placeholder.com/150)

Figure 5-9  Core structure of the \{110\}<110> interstitial dislocation loop along [001] direction, showing formation of \( \frac{1}{2} a <110>(110) \) edge dislocation.

The core structure of the dislocation loop along the Z [001] direction is comprised of the \( \frac{1}{2} a <110>(110) \) edge dislocation (Fig. 5-9). The core structure along the Z [001] is more...
compact and relatively higher strain compared to the core structure along Y [1-10], as can be inferred from the plots in Fig. 5-10.

Figure 5-10  Interatomic spacing along X [110] through the (A) tensile, and (B) compressive region across the $\frac{1}{2} a<110>{110}$ edge dislocation core for various location along the dislocation line along Z [001].
Both the atomic structure and the interatomic spacing along the dislocation lines confirm the edge character throughout the four-sided dislocation loop. The edges of the dislocation loop represent the formation of the kink structure, with dislocation lines lying on two perpendicular slip planes, i.e. (001) and (1-10), with the common Burgers vector $\frac{1}{2} a<110>$.

5.3.2 Dislocation Loop Energy

The formation energy of the dislocation loop or the interstitial cluster is calculated as the difference between the potential energy of the relaxed defect structure and the potential energy of single crystal UO$_2$, containing same number of atoms$^{147}$. There also exists an analytical solution for the dislocation loop energy or more accurately the self-energy of dislocation loop, based on its shape and size$^{99}$.

![Graph showing formation energy vs. number of Schottky units](image)

Figure 5-11 Formation energy of $<110>{110}$ type interstitial dislocation loops of different shape and sizes. Square, triangle, and circle represent 4, 6 and 8 sided dislocation loops, respectively.

Another useful way of characterizing defect clusters is via their binding energy. The binding energy, $E_b$, is calculated as$^{147}$
\[ E_b = \frac{(N \times E_{\text{Schottky}}) - E_f}{N} \]  

(5-1)

where \( E_{\text{Schottky}} \) is the formation energy of the Schottky defect and is calculate to be 8.89 eV, \( E_f \) is the interstitial cluster or interstitial dislocation loop formation energy and \( N \) is total number of Schottky units in the interstitial dislocation loop.

Figure 5-12  Binding energy of \(<110>\{110\> type interstitial dislocation loops of different shape and sizes.

The binding and formation energy increases with increasing size of the interstitial dislocation loop (Fig 5-7 and 5-8), and is investigated for different shapes (4-sided, 6-sided and 8-sided) of the interstitial dislocation loops. Both the formation energy and binding energy seems to depend strongly on the size of the interstitial loop than their shape, as all 4-sided, 6-sided and 8-sided loop have very similar energies. However, the structures of 6-sided and 8-sided loops are much more complicated than the 4-sided dislocation loop. They involve more number of dislocation intersections and also not all core dislocation structure can be broken into perfect \( \frac{1}{2} a<110>\{001\> and \( \frac{1}{2} a<110>\{110\> edge dislocations.
In this chapter, I present a detailed mechanism of, and the effect of homogeneous strains on, the migration of uranium vacancies in UO$_2$. Vacancy migration pathways and barriers are identified using density functional theory (DFT) and the effect of uniform strain fields are accounted for using the dipole tensor approach. Diffusivities under strains of up to 2\% are computed using kinetic Monte Carlo (KMC) simulations for both neutral and charged states of uranium single and di-vacancies. I calculate the effect of strains on migration barriers in the temperature range 800 – 1800 K for both vacancy types.

6.1 Background

At high temperatures and under irradiation UO$_2$ can be subject to time-dependent creep. The transition temperature from irradiation-induced creep$^{148-150}$ to thermal creep$^{17,18,151,152}$ is approximately 1100 °C$^{13,148}$. Compared to the creep of metals, the creep behavior of UO$_2$ is much more complex, depending strongly on the O/M ratio$^{17,153}$ and microstructural features$^{152,153}$ such as grain size and porosity, as well as temperature$^{13,17,152}$ and stress state$^{18,20,151}$. Dozens of mechanisms have been proposed for high temperature thermal creep. These mechanisms can be broadly classified into lattice controlled diffusion$^{1,17,152}$, grain boundary diffusion$^{20,154-156}$, and dislocation glide/climb controlled diffusion$^{18,20,151,152}$. In the case of UO$_2$, lattice diffusion controlled creep, known as Nabarro-Herring creep, involves vacancy transport within grains, with the rate controlled by the diffusion of uranium vacancies. Dislocation controlled creep falls in two regimes: Harper-Dorn creep at low stresses and a power-law regime at high stresses. The power-law regime involves both glide and climb of...
dislocations. The dislocation climb rate is determined by the diffusion of vacancies to the core of the dislocation. There is no consensus in the literature as to the dominant mechanism of thermal creep in UO$_2$. This can be attributed, at least in part, to the wide variability of the microstructure, stoichiometry, temperature, and presence of fission products, all of which affect the creep mechanism. To begin to re-address this complex problem in UO$_2$, we attempt to understand the diffusion of uranium vacancies as a function of temperature, stress state of the fuel and their interaction with dislocations.

In an earlier study, Dorado et al.$^{157}$ performed a detailed investigation of uranium self-diffusion using DFT theory and compared their computed diffusion rates with the available experimental literature.$^{9,158–160}$ They used the point defect model for UO$_2$, originally introduced by Matzke$^9$ and Lidiard$^{159}$ and first introduced in context of DFT calculations by Crocombette et al.$^{161}$, to establish uranium vacancy and interstitial formation energies and possible migration mechanisms for both vacancy and interstitial. Their calculated migration barriers for the uranium vacancy from DFT calculations are 4.8 and 3.6 eV for LDA+U and GGA+U, respectively. The experimental value reported by Matzke$^9$ is ~ 2.4 eV, about 1 eV lower but of the same order of magnitude. They argued that the experimentally reported migration barrier for uranium self-diffusion might correspond to diffusion of defect clusters rather than single uranium vacancies$^{157}$. Later, Andersson et al.$^{32}$ reported migration barrier for uranium di-vacancy of ~2.84 eV, using the same defect model as Dorado’s and echoed with some of Dorado’s arguments with respected to experimentally reported migration barriers.

This study employs the already established models by Andersson and Dorado for diffusion of uranium single and di-vacancies, and builds on them to investigate migration
of a uranium vacancy under the effect of external strain. DFT calculations are employed to accurately calculate the migration barriers of the single vacancy and di-vacancies of uranium as a function of their charge state. This permits us to address uranium vacancy diffusion not only in UO$_2$ but also in UO$_{2+x}$, where, in addition to the charged vacancy dominant in UO$_2$, neutral and di-vacancies are also important. Our focus is on cation vacancy diffusion as this will be the rate limiting species controlling phenomena. We use the kinetic Monte Carlo (kMC) method$^{162,163}$ to calculate the uranium diffusivity at relevant fuel temperatures.

The rest of the chapter is organized as follows. In Sec. 6.2 we discuss the DFT and KMC methodologies, as well as the method to calculate the dipole tensor, which is used to address the effects of simple and complex strain fields on diffusivity. We then report the migration barriers and dipole tensor values calculated using DFT for uranium vacancies (Sec. 6.3.1 and Sec. 6.3.2) as well as diffusivities for both single and di-vacancies as a function of homogeneous strain fields and temperature (Sec. 6.3.3). Our discussion and conclusions are presented in Sec. 6.4.

6.2 Methodology

6.2.1 Density Functional Theory Calculations

The DFT calculations are performed with the Vienna Ab Initio Simulation Package (VASP)$^{70,164}$ using the projector-augmented-wave (PAW) method$^{58,59}$. The electron exchange and correlation potential is described by the local density approximation (LDA) with the LDA+U functional used for the correlated U 5f electrons$^{53}$. In accord with the earlier studies, the U and J values are set to U = 4.5 eV and J = 0.51 eV; i.e., U – J = 3.99 eV. Defect properties are calculated using a 2×2×3 supercell (with
144 atoms for stoichiometric UO$_2$). A 2×2×1 k-point mesh is used for all calculations. This relatively large supercell is used in order to better treat the more extended divacancy clusters, and keep the interactions among periodic images as small as possible. Similarly the size of the k-point mesh is adjusted for the smaller Z dimension in reciprocal space. The supercells are allowed to fully relax, both in volume and atomic coordinates. The migration barriers are calculated using the climbing-image nudge elastic band (CI-NEB) method$^{165}$. For each barrier we apply three, four or five nudged elastic band images, depending on the complexity of the migration path. The data reported here represent the lowest energy solution which, for both stoichiometric and defect containing UO$_2$, corresponds to the phase with a small Jahn-Teller distortion of the oxygen sublattice$^{32,122}$.

6.2.2 Kinetic Monte Carlo Simulations

The Kinetic Monte Carlo (KMC) method$^{162,163}$ is used to simulate the long time evolution of uranium vacancies in UO$_2$. While molecular dynamics (MD) simulation has been used to simulate uranium vacancy dynamics in UO$_2$$^{166,167}$, it is limited by the accessible timescale, which is typically in the range of nanoseconds. However, processes such as uranium diffusion occur on much longer time scales, even at elevated temperatures. The initial (or minimum) configuration of a point defect such as a uranium vacancy in UO$_2$, is created by removing a single atom from a perfect crystal and performing an energy minimization via DFT calculations. The different type of atomic migrations that the vacancy can undergo depends on the neighboring atomic sites and the symmetry of the crystal. For a uranium vacancy in fluorite structured UO$_2$, there are twelve nearest neighboring uranium sites, and the displacement vector $d\vec{r}$, for
each of these transitions is along \( <110> \) type direction with magnitude equal to \(|d\vec{r}| = \frac{1}{2} a_0 [110]\), where \( a_0 \) is the lattice parameter of the cubic fluorite unit cell.

The list of minima, transitions associated with each minimum, and displacement vector \( d\vec{r} \) associated with each transition form the basic of kMC catalog. The full kMC catalog includes all possible degeneracies of the minimum and saddle point due to crystal symmetry, and accounts for symmetry transformations of the various displacement vectors \( d\vec{r} \) and dipole tensor. This full rate catalog (as discussed in Appendix A) is then used in an object kMC simulation\(^82\), where multiple objects (for e.g. a uranium vacancy is one object), each with their own rate catalog, are present in the simulation. The strain-induced changes to the migration barrier are computed using the dipole tensor approach\(^64,85,88\), as described in Chapter 2 and 3. The diffusion rate of uranium vacancies are calculated by an Arrhenius relation:

\[
k = \nu_m \exp\left(\frac{-E_{mig}}{k_BT}\right)
\]

(6-1)

Where, \( E_{mig} \) is the migration barrier to carry the vacancy from an initial equilibrium (or minimum) state to a saddle state, \( T \) is the absolute temperature, \( k_B \) is Boltzmann’s constant and \( \nu_m \) is the migration prefactor, a measure of the entropy of migration for the process.\(^{168}\) Here, \( E_{mig} \) is calculated using DFT and \( \nu_m \) from empirical potential calculations\(^{32}\); the values for \( E_{mig} \) and \( \nu_m \) for the vacancy species studied in this work are listed in the Table 6-1.
Table 6-1 Migration parameters for a single uranium vacancy and a uranium di-vacancy. The first column gives the migration barrier ($E_{mig}$) in eV and second column the rate prefactor ($\nu_m$) in sec$^{-1}$, taken from reference [21].

<table>
<thead>
<tr>
<th>Defect</th>
<th>$E_{mig}$</th>
<th>$\nu_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_U^X$</td>
<td>4.95</td>
<td>$2.38 \times 10^{12}$</td>
</tr>
<tr>
<td>$V_U^{'''}$</td>
<td>4.72</td>
<td>$2.38 \times 10^{12}$</td>
</tr>
<tr>
<td>$V_{U_2}$</td>
<td>3.27</td>
<td>$1.82 \times 10^{14}$</td>
</tr>
<tr>
<td>($V_U^{'''} - V_U^X$)</td>
<td>2.84</td>
<td>$1.82 \times 10^{14}$</td>
</tr>
</tbody>
</table>

The diffusivity is computed from the KMC simulations using the relation between the mean square displacement (MSD) as a function of time,

$$\langle R^2 \rangle = 6D t$$

$$\langle R^2_i \rangle = 2D_i t$$

(6-2)

where, $\langle R^2 \rangle$ represents the MSD averaged over 400 independent trajectories and D the overall diffusivity. Also the main diffusion equation can modifies to calculated diffusivity $D_i$ along the major directions $i \in [x, y, z]$ using MSD $\langle R^2_i \rangle$ along these respective directions.

6.2.3 Dipole Tensor

We discussed in detail the formalism of defect dipole tensor in Chapter 3. Here, we limit the discussion to specific results that apply to defect migration under homogeneous strain field. Given the dipole tensor of the defect in a given configuration, the change in defect energy $\Delta E$ due to strain can be calculated using Eq. (3-3) and it can be used to recompute the migration barrier, $E_{mig}$, which is defined as

$$E_{mig} = E_{saddle} - E_{minimum}$$

(6-3)
where $E_{\text{saddle}}$ and $E_{\text{minimum}}$ are the energy of the migrating ion at the saddle point and the minimum site, respectively. Under external strain, $E_{\text{mig}}$ will be modified due to changes in both $E_{\text{saddle}}$ and $E_{\text{minimum}}$ as

$$E_{\text{mig}}^{\text{strained}} = [E_{\text{saddle}} + \Delta E_{\text{saddle}}] - [E_{\text{min}} + \Delta E_{\text{min}}] = E_{\text{mig}} + \Delta E_{\text{mig}}^{\text{strained}} \quad (6-4)$$

Where $\Delta E_{\text{mig}} = \Delta E_{\text{saddle}} - \Delta E_{\text{min}}$ is the change in migration barrier due to strain. Thus, generally, the dipole tensor $\mathbf{G}$ must be calculated for both the saddle point structure and the minimum energy structure to estimate the change in the migration energy.

Expanding Eq. 6-4 using the definition of the dipole tensor from Eq. 3-3, we can write

$$E_{\text{mig}}^{\text{strained}} = [E_{\text{saddle}} - E_{\text{min}}] - \left[ G_{ij}^{\text{saddle}} \epsilon_{ij} - G_{ij}^{\text{min}} \epsilon_{ij} \right] \quad (6-5)$$

Generally, the strain $\epsilon_{ij}$ may not always be same at the saddle and minimum site; for example in the case of a dislocation, the strain field varies with the distance from the dislocation core. However, under homogeneous external strains such as uniaxial tensile, or shear, where the strain does not vary spatially, the strain $\epsilon_{ij}$ will be same at both the saddle and the minimum, and therefore, Eq. 6-5 can be further simplified as

$$E_{\text{mig}}^{\text{strained}} = [E_{\text{saddle}} - E_{\text{min}}] - \left[ (G_{ij}^{\text{saddle}} - G_{ij}^{\text{min}}) \epsilon_{ij} \right]$$

$$= [E_{\text{saddle}} - E_{\text{min}}] - (\Delta G_{ij}^{\text{mig}}) \epsilon_{ij} \quad (6-6)$$

and hence, using Eq. 6-4 we can define $\Delta E_{\text{mig}}^{\text{strained}}$, the change in migration barrier under homogeneous strains, as

$$\Delta E_{\text{mig}}^{\text{strained}} = -tr(\Delta \mathbf{G}_{\text{mig}} \cdot \epsilon) \quad (6-7)$$

The elastic response of both the minimum and saddle to external strain is then completely embedded in $\Delta G_{ij}^{\text{mig}} = G_{ij}^{\text{saddle}} - G_{ij}^{\text{min}}$. This is an important relation, as it shows that the change in migration barrier $\Delta E_{\text{mig}}$ depends on the dipole tensor of the
saddle state with respect to the minimum state, i.e. to the difference $\Delta G_{ij}$ under homogeneous strains, and not on the individual dipole tensors of the saddle and minimum. This is in line with the recent study by Hinterberg et al.\textsuperscript{169} who employed an activation volume tensor $\Delta V_{mig}$ approach to study the effect of different homogeneous strain states (uniaxial, biaxial and isotropic) on oxygen vacancy diffusion. In their approach, the modified migration barrier $\Delta H_{mig}$ changes in an external strain field by 
$$-tr(\sigma \cdot \Delta V_{mig})$$
where $\sigma$ is the externally applied stress tensor and $\Delta V_{mig}$ is the activation volume tensor of the defect. The elements of the tensor $\Delta V_{mig,kl}$ are calculated for the saddle state with respect to the initial state.

6.3 Results

Migration barriers and prefactors computed using DFT and empirical potentials, respectively, are used to parameterize the KMC model that uses rates modified by imposed external strains as calculated via the dipole tensor formalism. The detailed pathway for both the uranium vacancy and di-vacancy migration is first described, and followed by the results on the computed diffusivity of both single vacancies and uranium di-vacancies using the KMC model under homogeneous external strains. Uniaxial and shear strains up to $\pm$ 2$\%$ have been considered. The diffusivities are found to be highly sensitive to the applied strain and, as expected, on the vacancy type (single or di-vacancy). The responses of the single and di-vacancy diffusion to strain are very different and are discussed in detail below.

6.3.1 Migration Paths and Energy Barriers

The migration energies for uranium self-diffusion in non-stoichiometric and stoichiometric UO$_2$ have been studied experimentally$^{9,159,170,171}$. However, a detailed
exploration of the defect energies, energy barriers and uranium migration paths has only been made possible recently by DFT calculations.\textsuperscript{28,32,122,157,161,172} This work is in continuation of the previous work of Andersson et al.\textsuperscript{32} in which various charged single uranium vacancies and their clusters have been studied in detail for UO$_{2-x}$, UO$_2$, and UO$_{2+x}$, both for intrinsic and irradiation conditions. For stoichiometric UO$_2$, the fully charged uranium vacancy (\(V'_{U}''''\)) is the thermodynamically stable defect\textsuperscript{28,122,173} and hence controls uranium diffusion. For UO$_{2+x}$, and under irradiation conditions, clusters of two uranium vacancies can be present and can contribute significantly to transport as they have a much lower migration barrier than the single uranium vacancies.

![Figure 6-1](image)

*Uranium (small/blue) ions and oxygen (large/red) ions in the fluorite structure UO$_2$ unit cell.*

The diffusion mechanism of a uranium ion involves migration from its equilibrium lattice site (minimum) to its nearest uranium vacancy site along \(<110>\) type directions, as shown schematically in Fig. 6-1. This involves significant displacement of oxygen ions close to the migration path of the uranium ion\textsuperscript{157}. The migration of the uranium vacancy actually follows a curved path between the vacancy and its nearest neighbor rather than the direct path along the \(<110>\) direction, i.e., the uranium vacancy passes close to an empty octahedral position in the unit cell, as shown in Fig. 6-2. A similar
curved path for oxygen diffusion in perovskite-type oxides\textsuperscript{174} as well as in $\delta$-Bi$_2$O$_3$, whose structure is related to the fluorite structure, has been seen experimentally\textsuperscript{175} and has been discussed in atomic simulations\textsuperscript{176} of oxygen diffusion in $\delta$-Bi$_2$O$_3$.

![Figure 6-2](image_url)

**Figure 6-2** Snapshots of uranium vacancy migrating to its nearest neighbor position along the $<110>$ direction, as predicted from DFT calculations. The migrating uranium ion is shown in yellow, the dashed black line represents the straight path along the [110] direction.

At the saddle point, the two nearest oxygen ions are significantly displaced to make way for the migrating uranium ion; moreover, the saddle point is not located halfway between the initial and final positions. Instead, Andersson et al.\textsuperscript{32,122} observed a two-saddle pathway for a migrating uranium vacancy forming a split vacancy structure (see Fig. 6-2C) between the two saddles, corresponding to a shallow minimum at the mid-way point along the path. A schematic of the energy landscape is shown in Fig. 6-3.

Further, the migration path of the uranium ion from one lattice site to another is tilted by a small angle of about 1.2° from the (001) plane [dotted line in Fig. 6-4B]. Hence, as shown in Figure 6-4C, due to the curved migration path and the 2-fold symmetry along the $<110>$ directions, migration of the uranium ion can occur via a total of four symmetric paths for any given $<110>$ direction.
6.3.2 Dipole Tensor Calculations

6.3.2.1 Single uranium vacancy

An ideal cation vacancy in the fluorite structure has cubic symmetry, as it can be visualized as residing at a center of the cube formed by the first eight neighboring oxygen ions. As discussed by Leslie\textsuperscript{89} and Freedman\textsuperscript{94}, the dipole tensor for a defect in an ideal cubic symmetry has only diagonal elements. However, UO\textsubscript{2} may actually deviate from ideal symmetry due to Jahn-Teller distortions of the oxygen sub-lattice at
low temperature, thereby lowering the symmetry as well as the energy of the
system.\textsuperscript{122,177,178} This Jahn-Teller distortion is directly linked to the orientation of the
magnetic moment of the uranium ions.\textsuperscript{177,179,180} In our calculations, 1k antiferromagnetic
(AFM) ordering is employed, as UO\textsubscript{2} is AFM below Neel temperature (T = 30.8 K) and it
has been argued to be a good approximation for defect energies.\textsuperscript{122,181} Most practical
application of UO\textsubscript{2} refer to the high temperature paramagnetic state; but since it is
difficult to model in DFT, the AFM state is used as an approximation of the true
magnetic structure. However, all possible orientations of both minimum and saddle point
structures are incorporated for diffusivity computation using kMC simulations, as at finite
temperature local fluctuations make it more appropriate to consider all possible
reconstructions. Although still imperfect, the DFT calculations, do provide higher
materials fidelity than atomistic simulations using empirical potential, which do not
capture the electronic and magnetic details of UO\textsubscript{2}.

Consistent with this, DFT+U calculations of UO\textsubscript{2} show deviations from cubic
symmetry for the uranium vacancy and, therefore, we observe small off-diagonal
elements for the dipole tensor along with relatively large diagonal components. In this
study, we have looked at only the two extreme charge states for vacancies and di-
vacancies: neutral and fully charged. The calculated dipole tensor (in eV) of a neutral
uranium vacancy ($V^\times_U$) and the saddle point along the curved path along the <110>
direction are

\[
\mathbf{g}^{\text{min}}_{V^\times_U} = \begin{bmatrix}
-10.83 & -0.14 & 3.06 \\
-0.14 & -17.10 & -1.46 \\
3.06 & -1.46 & -9.35
\end{bmatrix} \text{ eV}
\]

\[
\mathbf{g}^{\text{saddle}}_{V^\times_U} = \begin{bmatrix}
13.29 & -2.18 & -1.80 \\
-2.18 & -1.50 & 11.76 \\
-1.80 & 11.76 & 1.72
\end{bmatrix} \text{ eV}
\]
The negative diagonal components of the dipole tensor for the minimum state express the tendency of the crystal to contract due to the presence of the uranium vacancy \((V_{U}^{\ominus})\). A major part of this contraction comes from the \(U^{5+}\) ions present in the neutral supercell that form spontaneously to compensate for the missing electrons due to the missing uranium ion. The largest element of the dipole tensor of the minimum coincides with the direction of the plane containing the highest concentration of \(U^{5+}\) ions. To account for diffusion of the uranium vacancy in the KMC simulations, one has to consider all possible paths of a single uranium vacancy to its twelve nearest neighbor sites, each lying along a different but equivalent <110> direction. Since the path to a single neighboring uranium ion has four-fold degeneracy (Fig. 6-4C), and a uranium vacancy has twelve nearest neighbor uranium atoms, it has a total of forty-eight unique paths by which it can hop from one uranium site to another. Further, because each path actually is comprised of two saddles and an intermediate minimum, there are 96 saddles that represent the hop of one uranium vacancy to a nearest neighbor site in \(\text{UO}_2\).

As discussed in Sec. 6.2.3, the change in the migration barrier due to homogeneous strain depends only on the relative dipole tensor \(\Delta G_{ij}^{\text{mig}}\) of the saddle with respect to the minimum. In Table 6-2, we report \(\Delta G_{ij}^{\text{mig}}\) for the charged and neutral uranium vacancy. The reported relative dipole tensors are for one particular direction (i.e. [110]); dipole tensors for the remaining 47 paths are calculated by applying tensor operations that account for the crystal and path symmetry, as discussed in the appendix (A).
Table 6-2 Calculated $\Delta G^{mig}_{ij}$ (in eV) for charged and neutral uranium vacancy

<table>
<thead>
<tr>
<th>Dipole tensor</th>
<th>$\Delta G_{11}$</th>
<th>$\Delta G_{22}$</th>
<th>$\Delta G_{33}$</th>
<th>$\Delta G_{12}$</th>
<th>$\Delta G_{13}$</th>
<th>$\Delta G_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G^{mig}<em>{V</em>{U}'}$</td>
<td>24.67</td>
<td>11.13</td>
<td>12.04</td>
<td>-0.16</td>
<td>-0.16</td>
<td>7.53</td>
</tr>
<tr>
<td>$\Delta G^{mig}<em>{V</em>{U}''}$</td>
<td>24.12</td>
<td>15.61</td>
<td>11.07</td>
<td>-2.03</td>
<td>-4.86</td>
<td>13.22</td>
</tr>
</tbody>
</table>

6.3.2.2 Uranium di-vacancy

A single uranium vacancy can form a di-vacancy ($V_{U}^{-} - V_{U}^{-}$) with another uranium vacancy present at any of its twelve nearest uranium sites along <110> type directions. However, only six of these are distinct orientations. For example a uranium vacancy at (0,0,0) can form a di-vacancy configuration with neighboring uranium sites at ($\frac{1}{2}, \frac{1}{2}, 0$), ($\frac{1}{2}, -\frac{1}{2}, 0$), ($0, \frac{1}{2}, \frac{1}{2}$), ($0, -\frac{1}{2}, \frac{1}{2}$), ($\frac{1}{2}, 0, \frac{1}{2}$), ($\frac{1}{2}, 0, -\frac{1}{2}$), as shown in Fig. 6-5A. The dipole tensor for a uranium di-vacancy oriented along [110] is given as

$$G^{\text{min}}_{(V_{U}^{-} - V_{U}^{-})} = \begin{bmatrix}
-24.25 & 5.47 & -1.50 \\
5.47 & -24.82 & -2.09 \\
-1.50 & -2.09 & -24.79 \\
\end{bmatrix} \text{ eV}$$

Figure 6-5 The six distinct di-vacancy configurations within first nearest neighbors in a UO$_2$ unit cell and four possible sites a single di-vacancy can hop to in order to maintain a di-vacancy pair.
Migration of the uranium di-vacancy can be understood in terms of migration of one of its constituent vacancies, with one vacancy fixed at its lattice site and the other vacancy hopping to the nearest uranium site (Fig. 6-6A). In order to preserve the low energy \((V_{U}^{\times} - V_{U}^{\times})\) pairing (binding energy of \(-0.01\) eV\(^{32}\) and \(-0.30\) for \((V_{U}^{''''} - V_{U}^{''''})\) pair), a migrating vacancy is comprised of the di-vacancy complex. The di-vacancy complex is constrained to move to one of the four nearest uranium di-vacancy sites (Fig. 6-5B) because the site to which it migrates should be a nearest neighbor to both the migrating vacancy and to the non-migrating vacancy. Either vacancy in the di-vacancy cluster can hop to one of its four nearest neighboring sites via two distinct paths; therefore, for a di-vacancy there are 16 possible paths (2 vacancies \(\times\) 2 paths per vacancy \(\times\) 4 neighboring states) to hop from one state to another instead of the 48 paths for a single vacancy, as illustrated in Appendix A. However, the overall KMC catalog for the di-vacancy is much more complex, as there are six distinct di-vacancy states; thus, there is a total of ninety-six paths with two saddles per path. The migration path is similar to that of a single vacancy as discussed in Sec. 6.3.1, which is a curved path along the \(<110>\) direction consisting of two saddles (shown in Fig. 6-6B and 6-6C).
As mentioned, a di-vacancy has sixteen possible migration paths and, to account for
dipole tensors for all the saddles, we apply tensor operations depending on the
symmetry of the system. The dipole tensor for a saddle specific to migration path along
[011] is given as

\[
G_{(V_0^1-V_0^2)}^{saddle} = \begin{bmatrix}
-11.19 & 4.51 & -5.33 \\
4.51 & -9.49 & 2.82 \\
-5.33 & 2.82 & -28.54
\end{bmatrix} \text{ eV}
\]

The calculated $\Delta G$ values for the charged and neutral di-vacancy are reported in Table
6-3.

<table>
<thead>
<tr>
<th>Dipole tensor</th>
<th>$\Delta G_{11}$</th>
<th>$\Delta G_{22}$</th>
<th>$\Delta G_{33}$</th>
<th>$\Delta G_{12}$</th>
<th>$\Delta G_{13}$</th>
<th>$\Delta G_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_{mig}^{(V_0^{iii'}-V_0^{iii''})}$</td>
<td>10.86</td>
<td>9.73</td>
<td>-4.80</td>
<td>-0.76</td>
<td>-4.67</td>
<td>4.04</td>
</tr>
<tr>
<td>$\Delta G_{mig}^{(V_0^i-V_0^i)}$</td>
<td>13.05</td>
<td>15.33</td>
<td>-3.75</td>
<td>-0.96</td>
<td>-3.83</td>
<td>4.91</td>
</tr>
</tbody>
</table>

6.3.3 Homogeneous Strains

The strain state of the fuel pellet in operation can be very complex, as it depends
on such factors as the temperature distribution, presence of fission products, changes in
microstructure, and pellet-clad interaction. Nevertheless, simple strain states such as
uniaxial tension, compression and shear can provide useful insight into the much more
complex strain problem. Here we report the effect of homogenous strain states (uniaxial
and shear) on the diffusion rate of uranium single and di-vacancies. KMC simulations
based on the dipole tensor approach are used to calculate diffusion rates, as they
explicitly incorporate the effect of strain on all paths (48 paths for single vacancy and 96
paths for six distinct di-vacancy states) as well as their saddles.
6.3.3.1 Single uranium vacancy

Both neutral and charged point defects in uranium dioxide have been studied.\textsuperscript{28,32,122,172} Charged defects are thermodynamically more favorable in stoichiometric UO\textsubscript{2}; however neutral defects may be favored under non-stoichiometric conditions, more specifically in UO\textsubscript{2-x} for which the Fermi level is close to the valence band edge\textsuperscript{122,161}. The change in migration barrier $\Delta E_{mig}$ from Eq. 6-7 using the dipole tensor $\Delta G_{ij}^{mig}$ is listed for single vacancies in Table 6-2, followed by diffusion coefficients as a function of temperature as well as strain state. $E_{mig}$ and $\nu_m$ values for the unstrained case are listed in Table 6-1.

Figure 6-7 shows the change in migration barrier $\Delta E_{mig}$ for a neutral uranium vacancy, for a specific path in the [110] direction under a uniaxial tensile strain of 1% along the [100] direction. A uniaxial tensile strain decreases the energy barriers compared to the unstrained case (as $\Delta E_{mig} < 0$ for both saddles along a given path, Figure 6-7 solid red curve) and hence, a [100] tensile strain will increase the diffusion rate along [110]. The energies of the two saddles change by different amounts at 1% tensile strain, with the energy of one saddle decreasing by 0.16 eV and that of the other by 0.11 eV. In the kMC simulations, the change in barrier height for both the saddles due to strain are calculated, but only the higher of the two barrier is used in the KMC simulations to calculate the diffusion rate from site A and B. This is justified because the minimum at state C is very shallow, with depths of only $\sim$0.3 eV and $\sim$0.8 eV for the single and di-vacancy, respectively, especially compared to the unstrained barrier of 4.72 eV. Therefore, the true trajectory would not thermalize in this shallow metastable state and it is appropriate to not explicitly consider it in the kMC rate catalog. Hence our
KMC model selects the highest of the barriers after explicitly calculating the change in barrier height for the both of the saddles under strain. For a uniaxial strain along [100], the change in barrier energy along each of the four [110] paths is effectively the same (-0.11 eV), though which of the two saddles changes more in energy depends on the details of the path.

Figure 6-7  Schematic showing the change in migration barrier (transition from A to B) for one of the paths oriented along [110] for an applied tensile strain of 1% along [100] for $V_U$.

Further, the change in migration barrier $\Delta E_{mig}$ is determined as a function of the orientation of the path relative to the strain. Figure 6-8A illustrates the relative orientation of two different paths to a tensile strain in the [100] direction. Figure 6-8B shows that directions that are normal to the applied strain, i.e. of <011> type respond differently than the <110> and <101> families of directions that have some component of applied strain parallel to them. This asymmetry in the diffusion is expected because the tensile strain along [100] will affect paths in the (100) plane and normal to the (100)
plane differently. In the first case, there is a component of strain along the pathway, in the second case there is not.

**Figure 6-8** Schematic showing the applied tensile strain along the [100] direction and change in the migration barrier $\Delta E_{\text{mig}}$ for ($V_{U}^{+}$) under applied uniaxial tensile strain along [100] for migration paths oriented along [110] (open diamonds) and [011] directions (solid diamonds).

**Figure 6-9** Relative diffusivity of the fully charged uranium vacancy under (A) tensile and (B) compressive strains at 1800 K.

In Fig. 6-9, the relative diffusivities of charged uranium vacancies are calculated at 1800 K, which is a reasonable temperature for intrinsic diffusion within the fuel; these are plotted as a function of temperature in Fig. 6-10. A uniaxial strain along X [100],
enhances the diffusivities in all the three cubic directions $X \, [100]$, $Y \, [010]$ and $Z \, [001]$ with $D_X \neq D_Y \sim D_Z$. This is expected because a uniaxial strain will change the cubic symmetry of the unstrained fluorite structure to tetragonal symmetry. We also note that $\Delta E_{\text{mig}} > 0$ for compressive strains and $\Delta E_{\text{mig}} < 0$ for tensile strains (see Fig. 6-8B) for both of the charge states of the single vacancy. The magnitude of the increase in diffusivity under tension is greater than the reduction in diffusivity observed when the same amount of compressive strain is applied. Such effects have also been observed in simulations of strained fluorite-structured CeO$_2$.\textsuperscript{182} The relative diffusivity is found to be less sensitive to the charge state of the single vacancy when subjected to the same uniaxial strain state (Fig. 6-13A).

Figure 6-10  Relative diffusivity of the fully charged uranium vacancy as a function of temperature under uniaxial tensile strain.
Figure 6-11 Schematic showing the applied shear strain in the (001) plane and change in migration barrier under applied shear strain for paths oriented in plane (open diamonds) and normal (solid diamonds) to the shear plane.

Next, the effect of shear strain on diffusivity is analyzed. A fuel pellet can develop torsional and shear strains along with hydrostatic components during initial synthesis processes such as hot pressing\(^{183}\). Moreover, under operating conditions within the reactor the stress states on the fuel pellet can be quite complex. Therefore it is relevant to characterize the effect of shear strain on diffusivity, in particular to understand diffusion as it relates to the sintering process. The computed \(\Delta E_{mig}\) shows that the shear strain decreases the migration barrier by a greater amount for paths oriented in the plane of the shear as compared to paths oriented normal to the shear plane. Figure 6-12 shows that the overall diffusivity increases with increasing shear strain, with the relative increase being more prominent at lower temperatures. The diffusion coefficients of neutral and charged vacancies under the same shear strain states are significantly different. Under a shear strain along \(<110>\), the diffusivity of the neutral vacancy increases by a factor of two more than that of the charged vacancy (Fig. 6-13B). This is a significant difference, even at temperatures as high as 1800 K.
Figure 6-12 Relative diffusivity of a charged uranium vacancy under shear strain as a function of temperature.

Figure 6-13 Comparison of diffusivities of neutral and charged uranium vacancies under uniaxial strain along [100] and shear strain along [110] at 1400 K.

6.3.3.2 Uranium di-vacancy

In UO$_{2+x}$ (i.e. in an oxidizing environment) and under irradiation conditions, the uranium di-vacancy can be an important defect due to its higher overall concentration, as suggested by Andersson et al.$^{32}$ DFT calculations predict that the di-vacancies have low migration barriers compared to that of the single uranium vacancy (see Table 6-1).
and can thus increase the overall uranium diffusivity, even if they are only present in small concentrations. The difference in response to uniaxial and shear strain between the single vacancy and the di-vacancy is due to the difference in the dipole tensor $\Delta \mathbf{G}_{ij}^\text{mig}$ for the two defects. The magnitude of the diagonal and some of the off-diagonal elements of the dipole tensor for the di-vacancy are smaller than for the single vacancy (Table 6-3). However, it is not just the magnitude but also the sign of the elements of the dipole tensor that determine the overall change in diffusivity. One clear difference between the two defects is in the response to shear strain. For a single vacancy, shear strain significantly increases the in-plane relative diffusivity but only increases the out-of-plane relative diffusivity by a small amount (Fig. 6-11). However, the di-vacancy has both lower out-of-plane and in-plane relative diffusivities because of its positive and negative off diagonal elements, which can couple with specific orientations of shear strains.

The calculated diffusivity for the neutral and charged uranium di-vacancy as a function of strain and temperature are presented in Fig. 6-14 (A-D). As expected, the effect of strain is substantial at relatively low temperatures, less than 1200 K, at which U diffusion is slow. A neutral di-vacancy is found to interact more strongly with the external uniaxial strain, as the increase in its diffusivity is about three times more than that for a charged di-vacancy (Fig. 6-14 C). For a uniaxial strain along <100>, we find that the diffusion rates for a neutral di-vacancy (Fig. 6-14B) follow the trend $D_{(100)} < D_{(010)} < D_{(001)}$. For shear strain, we see a small decrease in overall diffusivity for strain up to 1% and then an increase for higher shear strains (Fig. 6-14D) for both neutral and charged di-vacancy.
6.4 Discussion and Conclusions

The diffusivities of a single uranium vacancy and a di-vacancy were studied as a function of external homogeneous strains, temperature and charge state of the defect. We reported curved migration paths and non-cubic symmetry for the uranium vacancy. This is different from the straight migration paths and cubic symmetry of an ideal cation vacancy in the fluorite structure. A dipole tensor approach was used to calculate the change in migration energy barriers due to external strains. We have shown (Eq. 6-7) that under homogeneous strain fields, only the dipole tensor of the saddle with respect...
to the minimum i.e. $\Delta G_{ij}^{mig} = G_{ij}^{saddle} - G_{ij}^{min}$ is required to correctly calculate the change in energy barrier $\Delta E_{mig}$ between the strained and the unstrained case.

Table 6-4 Summary of the relative diffusivities $D/D_0$, where $D_0$ is the diffusivity at 0\% strain, for different strain states for the four defects considered here, at a strain of 2\% and temperature $T = 1800$ K.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Tensile $\epsilon_{&lt;100&gt;}$</th>
<th>Compressive $\epsilon_{&lt;100&gt;}$</th>
<th>Shear $\epsilon_{&lt;110&gt;}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_u^\times$</td>
<td>10.12</td>
<td>0.11</td>
<td>1.64</td>
</tr>
<tr>
<td>$V_u^{''''}$</td>
<td>10.7</td>
<td>0.16</td>
<td>0.99</td>
</tr>
<tr>
<td>$(V_u^\times - V_u^\times)$</td>
<td>2.97</td>
<td>0.24</td>
<td>1.03</td>
</tr>
<tr>
<td>$(V_u^{''''} - V_u^{''''})$</td>
<td>1.87</td>
<td>0.42</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Table 6-4 compares the effect of strain for different types of applied strain on the four different defect structures considered in this manuscript. As is evident from the table, the changes in relative diffusivity are less sensitive to the charge of the defect than the size of the defect. Further, single vacancies are more sensitive to applied strain than di-vacancies. This has important implications for the evolution of the fuel, particularly thermal creep and sintering. During sintering, a thermal process, the majority of the vacancies will be single vacancies. The diffusivity of these defects is particularly sensitive to the strain state and thus the sintering kinetics will be sensitive to the detailed microstructure of the material. In contrast, irradiation induced creep will be controlled, to a greater extent, by the kinetics of di-vacancies which does not vary as significantly with strain. Thus, to first order, creep rates in the irradiated fuel will be less sensitive to the overall strain state of the fuel. These conclusions imply that it is more critical to understand the strain state for predicting sintering under thermal conditions than it is for predicting creep in irradiated fuel.
More generally, the strain-induced anisotropy of point defect diffusion should be taken into account in calculating the defect fluxes to sinks such as dislocations and cavities, as accurate evaluation of the sink absorption efficiency for point defects is critical in determining creep rates\textsuperscript{21}. Sinks create an elastic strain field in their vicinity, which lead to anisotropic diffusion of point defects and therefore a biased flux of point defects to those sinks. Hence, understanding diffusion rates as a function of major crystal directions as well defect type is important in calculating creep rates, swelling behavior and dislocation substructures\textsuperscript{22,23}. The results in Fig. 6-9 and Fig. 6-14B show diffusivities of single and di-uranium vacancies as function of major crystal directions $<100>$, $<010>$ and $<001>$ under a homogeneous uniaxial strain along $<100>$ and report that the diffusion along $<010>$ and $<001>$ is more favored compared to diffusion along $<100>$. That is, the strains couple with defect diffusion in complex ways, with strains along one direction significantly influencing diffusion in perpendicular directions. These anisotropies mean that, in the complex strain fields associated with dislocations, the flux of defects to the dislocations will be convoluted, in contrast to the assumptions made by simple cylinder models of defect fluxes to dislocations\textsuperscript{184}. For example, while the strain fields of edge dislocations indicate that defects and fission products will be attracted to the core\textsuperscript{116,185}, the coupling with the dipole tensors suggests that greater enhancements in diffusion might occur along the edge dislocation line rather than toward the core (perpendicular to the line direction). These insights have important implications in understanding fuel creep and point to the need of comprehensive models that account for these anisotropies.
CHAPTER 7
UNCERTAINTY QUANTIFICATION AND SENSITIVITY ANALYSIS IN A MULTISCALE MODEL

This chapter presents a systemic analysis and methodology to account for propagation of uncertainties from atomic scale to mesoscale in a model that re-computes the diffusion coefficient of point defects, modified in the presence of strain field. The effect of sensitivity of each component of the defect dipole tensor is explored on the overall diffusion rates by varying its components individually and collectively within physically defined limits. This study is applied to uranium vacancy in fluorite-structured, UO$_2$.

7.1 Background

A proper understanding and modeling of material properties require a precise knowledge of defect formation and their evolution. First principles calculations based on DFT have become a valuable tool to compute defect formation and migration energies, which can then be used to build quantitative models to predict macroscopic material properties such as diffusion processes$^{186,187}$, phase transformations$^{188}$, irradiation induced creep$^{80}$. The presence of strain can alter atomic scale events and the overall evolution of the system. Therefore with these particular applications in mind, our model makes use of an elasticity theory based dipole tensor approach to connect the atomic level details such as defect migration paths and barriers determined from DFT calculation$^{187}$ (Sec. 6.3.1 and 6.3.2) with kMC simulations$^{82}$, of diffusion behavior, including the effects of strain field (Sec. 6.3.3). One of the main goals of \textit{ab initio} informed multiscale approaches is to make accurate predictions of materials behavior without having to perform detailed experiments. However, the accuracy of these models
needs to be rigorously quantified before they can be adopted as reliable tools, complementary to experimental methods.

Figure 7-1  Phases on modeling and simulation and role of verification and validation (Adapted from the book by W. L. Oberkampf and C. J. Roy\textsuperscript{189}, 2010).

Uncertainty quantification (UQ) plays a fundamental role in validation of simulation methodologies and aims at developing rigorous methods to characterize the impact of variability and lack-of-knowledge on the final predictions of materials simulations\textsuperscript{190,191}. A key milestone in the area was the publication of set of concepts, terminologies, and methodology for Verification and Validation (V&V) by the Society of Computer Simulation (SCS) in 1979. Figure 7-1 identifies two types of model: a conceptual model and a computerized model. The conceptual model (or the theory) comprises the information, modeling assumptions and mathematical equations that will be used to describe the process of interest. The computerized model, or the computer code, implements a conceptual model using computer programming\textsuperscript{189,190}. Figure 7-1 emphasizes that verification deals with relationship between the conceptual model and
the computerized model and that validation deals with the relationship between the computerized model and reality.

The objective of this chapter is to carefully establish the nature and sources of uncertainties in various input parameters to our model across different length scales and perform sensitivity analysis of the input parameter on final computed diffusivities. Verification and Validation are large topics in themselves and are thus not the focus of this study.\textsuperscript{189}

This chapter is structured as follows: in Sec. 7.2, details of the DFT and kMC methods specific to this work and the uncertainties associated with input parameters for each of these methods are described. In Sec. 7.3 results on sensitivity analysis of possible combination of dipole tensor elements on the computed diffusivity are presented. Discussions and preliminary conclusions are presented in Sec. 7.4.

7.2 Methodology

7.2.1 Density Functional Theory

DFT calculations are performed using the projector-augmented-wave (PAW) method\textsuperscript{58,59}. The electron exchange and correlation potential is described by the local density approximation\textsuperscript{53} (LDA). Details of the method used for the specific system studied in this work are summarized in the Table 7-1.

<table>
<thead>
<tr>
<th>System</th>
<th>DFT method</th>
<th>DFT parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Super-cell size</td>
</tr>
<tr>
<td>Au</td>
<td>PAW, LDA</td>
<td>2 x 2 x 2</td>
</tr>
<tr>
<td>UO\textsubscript{2}</td>
<td>PAW, LSDA+U</td>
<td>2 x 2 x 2</td>
</tr>
</tbody>
</table>
For UO$_2$ calculations, spin polarized LSDA+U functional for the exchange correlation is used to account for the correlation due to localized U 5f electrons$^{60}$. The convergence criterion for the total energy is $10^{-6}$ eV and the Hellman-Feynman force components acting on atoms are relaxed to at least $10^{-3}$ eV Å$^{-1}$. In addition to computing the energy of the defect site in a perfect lattice, DFT calculations are also used to investigate the migration barriers of point defects from one equilibrium site to another using the climbing-image nudge elastic band (CI-NEB) method$^{165}$. The volume of the simulation cell with point defects is calculated as function of system size, energy cut-off and density of the k-point mesh and the accuracy in computation of volume is within ±0.8 Å$^3$.

It is important to establish uncertainty associated with DFT calculations, besides discussed convergence criterion in the computed energies, forces and volumes via these calculations. Types of uncertainties in DFT calculations can be either aleatory or epistemic in nature$^{189}$. For example, there is epistemic uncertainty (also called the reducible uncertainty) in the computed total energies due to the input variables such as energy cut-off and k-points in DFT calculations. Therefore, this uncertainty can be reduced to very small (as shown in convergence results in Fig 2-3 and 2-4) by using sufficient high energy cut-off and larger k-point meshes. More importantly approximations such as LDA and GGA would yield different results and there is an epistemic uncertainty there also.

In this work, the effect of homogeneous external strain on diffusion of point defect is approximated using the dipole tensor approach, as discussed in detail in Chapters 3 and 6. The dipole tensor approach assumes that the change in energy is linear with strain. Higher order terms may be included in Eq. (3-3) depending on the type of the
defect, and particularly in high strain situations\textsuperscript{82,192}. Subramanian et al.\textsuperscript{82} validated the dipole tensor approach for an elementary point defect, such as a Zr vacancy, by comparing the energy barriers predicted from the dipole tensor approach with the energy barriers explicitly calculated under external strain from NEB method using Molecular Dynamics (MD) simulations. They reported that the explicitly calculated values and values determined using the dipole tensor approach are in good agreement for small strains of up to about 2-3\%. Similar qualitative agreement between atomistic simulations and dipole tensor approach for point defects has also been reported for other materials systems\textsuperscript{93,193}.

Figure 7-2  Schematic showing that the dipole tensor approach is the link between the DFT and KMC simulation.

7.2.2 Kinetic Monte Carlo Simulations

The diffusion rates or diffusivity (D) are computed from the kMC simulations using the time evolution of the mean squared displacement (MSD),

Overall diffusivity  \[ \langle \Delta r^2 \rangle = 6Dt \]  \hspace{1cm} (7-1)

Diffusivity along the major cubic directions  \[ \langle \Delta r_i^2 \rangle = 2D_i t \]  \hspace{1cm} (7-2)

where \( i \in [x, y, z] \) and \( \langle R^2 \rangle \) is the MSD.

The MSD is calculated using a standard formula\textsuperscript{194,195}
\[ MSD(\tau) = \langle \Delta r_i(\tau)^2 \rangle = \langle [r_i(t + \tau) - r_i(t)]^2 \rangle \] (7-3)

where \( r_i(t) \) is the position of the particle at time \( t \) along \( i \), and \( \tau \) is the lag time between the two positions taken by the particle used to calculate the displacement \( \Delta r_i(\tau) = r_i(t + \tau) - r_i(t) \). The average \( \langle \ldots \rangle \) designates a time-average over \( t \) and/or an ensemble-average over several trajectories. It is a time average because the displacements originate from various time along each trajectory. The MSD can be calculated from a single trajectory (given that it has been run for sufficiently long time) by only performing a time average. To calculate the MSD from a trajectory, this trajectory is divided into distinct hops (or kMC steps). A trajectory (shown as schematic in Fig. 7-3) which last for \( n \) kMC steps from time \( t_0 \) to \( t_n \), the lag time for one hop corresponds to \((t_1 - t_0)\) or \((t_2 - t_1)\) or \((t_3 - t_2)\) ..., two hops to \((t_2 - t_0)\) or \((t_3 - t_1)\) or \((t_4 - t_2)\) ..., three hops to \((t_3 - t_0)\) or \((t_4 - t_1)\) ...... and lastly, for total \( n \) hops the lag time is \((t_n - t_0)\). Similarly the displacements \( \Delta r_i(\tau) \) for each lag time are calculated for a given trajectory. There are \( n \) displacements within a trajectory for single hop, \( n - 1 \) displacements for two hops, and ultimately single displacement for \( n \) hops. \( MSD(\tau) \) is then calculated for a trajectory by averaging over displacements for a given lag time. We repeat this calculation for all the trajectories.
For a given lag time, a list (or sample) of displacements $\Delta r_i(\tau)$ coming from several trajectories can be made. The distribution (or the histogram) of the square of the displacements $\Delta r_i(\tau)^2$ (relative to their mean and $i = x$) for three different lag time, using 1000 independent trajectories with each trajectory ran over 10,000 kMC steps, is shown in Fig. 7-4. The distribution can be nicely fitted with a Gaussian distribution. The variance of this distribution is precisely the mean square displacement. It is an ensemble average because these displacements come from different trajectories. From Fig. 7-4 (D) we can observe the increase in variance with increase in lag time and diffusivity is calculated from the slope of the $MSD(\tau)$ as function of lag time plot.
Uncertainty in Computation of Diffusivity from KMC: As mentioned before, the longer the trajectory (larger $n$), and more number of independent trajectories, the more displacements can be extracted and hence, the more accurate estimation of the MSD can be made. This tells us that there is an epistemic uncertainty$^{190}$ also called as reducible uncertainty associated with the calculated MSD and diffusivities using Eq. 7-1 from kMC simulations. This uncertainty is due to the lack of data collected from our model simulations and it is possible to reduce it by collecting more data. The computed diffusivities are plotted as function of number of independent trajectory and the time for each trajectory in Fig. 7-5. The most accurate value of diffusivity ($D = 3.903 \times 10^{20}$ m$^2$/sec) corresponds to the one that is computed over the
trajectory that ran for the longest time ($\tau = 5.27 \text{ hr}$) and averaged for 1500 number of independent trajectories. This gives a reasonably good estimate of the uncertainty (or the error) in diffusivity computed over smaller lag times and less number of independent trajectories. From the computed values (in Fig. 7-5), the uncertainty is in the range $-0.12 \times 10^{20} \text{ m}^2/\text{sec}$ to $0.15 \times 10^{20} \text{ m}^2/\text{sec}$, which is within ±2.5 % of the most accurate value.

![Figure 7-5](image)

**Figure 7-5**  Computed diffusivity as function of the lag time and the number of independent trajectories.

Another important point to note is that, the larger the lag time, the fewer displacements can be extracted within a trajectory and therefore, the measured $\Delta r_i(\tau)^2$ for larger lag time will be less accurate. This can be seen in Fig. 7-6, as the lag time increases the uncertainty in diffusivity increase as MSD(x) and MSD(y) MSD(z) deviate. Fig. 7-7, shows the $\Delta r_i(\tau)^2$ for all $i = [x, y, z]$ for a smaller and very larger lag time, respectively.
One way to avoid this uncertainty is to use only small lag time in calculation $\Delta r_i(\tau)^2$ with sufficiently large number of displacements. The answer to how small the lag time can be is estimated by doing the uncertainty estimation or the error analysis on the final computed diffusivities. For example, as shown in Fig. 7-8, for a trajectory with total of 10,000 kMC steps (with total time $t = 5065$ sec or 1.41 hour), the diffusivity is plotted...
corresponding to different lag times. It is clear from Fig. 7-8 that uncertainty in diffusivity decreases by considering smaller lag times, for which there are a large number of trajectories. For the calculations on sensitivity analysis, discussed in the next section, diffusivities are computed over 1000 independent trajectories, with 8000 kMC steps (lag time = 1.23 hrs) and the estimated error is less than 1.5 %.

Therefore based on our results on computation of MSD (Eq. (7-3) and diffusion rates (Eq. 7-1) from kMC simulations, we deduce that there is an error of about ± 4% associated with their values due to the epistemic uncertainty. This uncertainty can be reduced to about ± 2 – 2.5% of the expected value by increasing the run time for each trajectory and by taking the average over more than 1000 number of independent trajectories. By choosing relative smaller lag times within a given trajectories to compute the MSD further reduces this uncertainty to less than 1.5 % of the expected value.

Figure 7-8  Uncertainty in diffusion coefficient as function of maximum length of lag time used to compute the diffusivity
Results and Discussion on Sensitivity Analysis

Sensitivity analysis is a method to inspect the responsiveness of the final measured output value due to changes in the input parameters. Here, I apply this analysis to understand the sensitivity in computed diffusion coefficient by systematically varying the value of one of the input parameter, the defect dipole tensor.

7.3.1 Mathematical Description

Before applying sensitivity analysis in practice, I briefly rewrite some of the important relations already discussed earlier, and derive some new relations which are core to this model. This is helpful in understanding sensitivity analysis.

The change in energy due to strain under the dipole tensor definition is given by Eq. (3-3), which in often found in several different notations as

\[ \Delta E = - tr(G \cdot \epsilon) = - G_{ij} \epsilon_{ij} = G : \epsilon \] (7-4)

where, change in the energy \( \Delta E \) is given as a trace of the dot product of tensors \( G \) and \( \epsilon \) and is also defined as the “double dot product” or “double-inner product” of two tensors.

It is a scalar quantity and both \( G \) and \( \epsilon \) are symmetric tensors.

\[
G = \begin{bmatrix}
G_{11} & G_{12} & G_{13} \\
G_{12} & G_{22} & G_{23} \\
G_{13} & G_{23} & G_{33}
\end{bmatrix}, \quad \text{and} \quad \epsilon = \begin{bmatrix}
\epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\
\epsilon_{12} & \epsilon_{22} & \epsilon_{23} \\
\epsilon_{13} & \epsilon_{23} & \epsilon_{33}
\end{bmatrix}
\] (7-5)

and double dot product is given as

\[
\Delta E = G_{11} \epsilon_{11} + G_{12} \epsilon_{12} + G_{13} \epsilon_{13} + G_{22} \epsilon_{22} + G_{23} \epsilon_{23} + G_{33} \epsilon_{33} = \sum_{i=1}^{3} \sum_{j=1}^{3} G_{ij} \epsilon_{ij} = \sum_{i=1}^{3} \sum_{j=1}^{3} G_{ij} \epsilon_{ij} \] (7-6)

The expression in the extreme right of Eq. 7-6 is true, since, strain is a symmetric tensor, \( \epsilon_{ji} = \epsilon_{ij} \). The energy barrier for migration is given as difference in the energy of the minimum and saddle point. Under a homogeneous strain field, the strain field at the
saddle and the minimum will be same and hence the expression for change in the energy barrier, $\Delta E_{mig}^{\text{strained}}$ reduces to

$$\Delta E_{mig}^{\text{strained}} = - \left[ (G_{ij}^{\text{saddle}} - G_{ij}^{\text{min}}) \varepsilon_{ij} \right] = - \left[ \Delta G_{ij}^{mig} \varepsilon_{ij} \right] = - \text{tr}(\Delta G^{mig} \cdot \varepsilon) \quad (7-7)$$

which is same as Eq. (6-7) derived in Chapter 6. Let us keep this equation in mind for a moment and look at the effect of this energy change, $\Delta E_{mig}^{\text{strained}}$, on the diffusivity rates, which, are given by an Arrhenius relation:

$$D = v_m \exp \left( \frac{-E_{mig}}{k_BT} \right) \quad (7-8)$$

Under an external strain, the energy barrier for migration changes and so will the diffusivity, and is given as

$$D_{\text{strained}} = v_m \exp \left( \frac{-E_{mig} + \Delta E_{mig}^{\text{strained}}}{k_BT} \right)$$

$$D_{\text{strained}} = D \exp \left( \frac{-\Delta E_{mig}^{\text{strained}}}{k_BT} \right) \quad (7-9)$$

Under no external strain, $\varepsilon_{ij} = 0$, $\Delta E_{mig}^{\text{strained}} = 0$ and $\Delta D_{rel} = 0$, as $D_{\text{strained}} = D$.

Let us denote the uncertainty in the numerical computation of defect dipole tensor $G_{ij}$, as $\Delta(G)$. $\Delta(G)$ has its source in the numerical uncertainty, $u_{ij}$, in any of the individual component of the dipole tensor, which for a symmetric tensor $G_{ij}$, reduces to only six distinct components.

$$G \pm \Delta(G) = \begin{bmatrix} G_{11} \pm u_{11} & G_{12} \pm u_{12} & G_{13} \pm u_{13} \\ G_{12} \pm u_{12} & G_{22} \pm u_{22} & G_{23} \pm u_{23} \\ G_{13} \pm u_{13} & G_{23} \pm u_{23} & G_{33} \pm u_{33} \end{bmatrix} \quad (7-10)$$

Further, to understand the sensitivity in $D_{\text{strained}}$ to variations in $G_{ij}$, let us first discuss the changes in $\Delta E_{mig}^{\text{strained}}$, due to $\Delta(G)$. Under a homogeneous strain field using Eqs. (7-6) and (7-7), the expression for $\Delta E_{mig}^{\text{strained}}$ is given as
\[ \Delta E_{\text{strained}}^{\text{mig}} = \sum_{i,j=1}^{3} \Delta G_{ij}^{\text{mig}} \varepsilon_{ij} \]  

(7-11)

Applying the uncertainty in \( \Delta G_{ij}^{\text{mig}} \) to \( \Delta E_{\text{strained}}^{\text{mig}} \), leads to

\[ \Delta E_{\text{strained}}^{\text{mig}} \pm \Delta(\Delta E_{\text{strained}}^{\text{mig}}) = \sum_{i,j=1}^{3} (\pm (\Delta G_{ij}^{\text{mig}}) \varepsilon_{ij}) \]  

(7-12)

which as expected from its definition, gives changes in \( \Delta E_{\text{strained}}^{\text{mig}} \), as a linear function of uncertainty (or variations) in \( \Delta G_{ij}^{\text{mig}} \), as

\[ \pm \Delta(\Delta E_{\text{strained}}^{\text{mig}}) = \sum_{i,j=1}^{3} (\pm (\Delta G_{ij}^{\text{mig}}) \varepsilon_{ij}) \]  

(7-13)

However, the diffusivity, \( D_{\text{strained}} \), has an exponential dependence on \( \Delta E_{\text{strained}}^{\text{mig}} \), as given by Eq. (7-9). Therefore the change in \( D_{\text{strained}} \) due to uncertainty in individual component of the dipole tensor can be written as

\[ D_{\text{strained}} \pm \Delta(D_{\text{strained}}) = D \exp \left( \frac{-\Delta E_{\text{strained}}^{\text{mig}}}{k_B T} \right) \]  

(7-14)

This can be simplified as

\[ \frac{\pm \Delta(D_{\text{strained}})}{D_{\text{strained}}} = \exp \left( \frac{\pm \Delta \sum_{i,j=1}^{3} (\Delta G_{ij}^{\text{mig}}) \varepsilon_{ij})}{k_B T} \right) - 1 \]  

(7-15)

Some observations that can be made on \( \Delta(D_{\text{strained}}) \) from Eq. (7-15) are:

1. \( \Delta(D_{\text{strained}}) = 0 \), if either, each of \( \Delta(G_{ij}^{\text{mig}}) = 0 \) explicitly, or the sum,

\[ \sum_{i,j=1}^{3} (\pm \Delta \Delta G_{ij}^{\text{mig}}) \varepsilon_{ij}) = 0 \]

2. \( \Delta(D_{\text{strained}}) \) has a strain sensitive exponential dependence on the changes associated with individual \( \Delta(G_{ij}^{\text{mig}}) \).
3. The Value of $\Delta(D_{\text{strained}})$ obtained by varying multiple components of $\Delta G_{ij}^{\text{mig}}$ is not the same as taking a linear sum of $\Delta(D_{\text{strained}})$ values obtained by varying individual component of $\Delta G_{ij}^{\text{mig}}$ one at a time.

Another important point that should be mentioned is that $\Delta G_{ij}^{\text{mig}}$ corresponds to a particular migration path. Defect can have many possible orientations of the migration path due to the symmetry of the crystal structure, with $\Delta G_{ij}^{\text{mig}}$, related by tensor transformations under crystal symmetry. Hence, it is important to analyze all these possibilities by incorporating dipole tensors for all possible paths in the kMC rate catalog. The following sections are devoted to quantifying the sensitivity of varying each component of $\Delta G_{ij}^{\text{mig}}$ one at a time, and in all possible combinations of two at a time, on the overall change in diffusivity computed using kMC simulations.

7.3.2 Single Component Analysis

The change in diffusivity of the uranium vacancy is analyzed as a consequence of variation in the numerical value of six components of the dipole tensor, varied one at a time. The dipole and strain tensor used in this calculations are

$$
\Delta G_{ij} = \begin{bmatrix}
24.67 & -0.16 & -0.16 \\
-0.16 & 11.13 & 7.53 \\
-0.16 & 7.53 & 12.04 
\end{bmatrix}; \quad \varepsilon_{ij} = \begin{bmatrix}
0.01 & 0.01 & 0.01 \\
0.01 & 0.01 & 0.01 \\
0.01 & 0.01 & 0.01 
\end{bmatrix}
$$

(7-16)

Each component is varied discretely within ± 1, 2, 5, 7, and 10% of their original value. In Fig. 7-10, relative change in diffusivity (Eq. 7-15) is plotted for each of the 6 varied components for the dipole tensor. As inferred from the plots in Fig. 7-10, the relative change is directly sensitive to the sign and magnitude of the respective components of the dipole tensor, Eq. (7-16).
Figure 7-10  Relative change in diffusivity as given by Eq. (7-15) as function of % changes in the respective value of dipole tensor components.

An important point to infer from these plots is the magnitude of variation in diffusivity compared to the uncertainty in dipole tensor components. Changes in $G_{11}$ within 5 – 10% of its value leads to a relatively large variation in diffusivity, roughly of the order of 15 – 20 %, compared to the changes of same magnitude in $G_{12}$ and $G_{13}$, which result in only about 5% variation in diffusivity. The variations in diffusivity are not symmetric about 0% change due to the exponential dependence as given in Eq. (7-15). Positive changes in the dipole tensor components result in larger variation in magnitude
of diffusivity than the negative changes. This reflects that the uncertainty in diffusion rates for defects that introduce large tensile strains in the lattice will be relatively more than those that introduce compressive strains. Another tool of establishing the sensitivity of the input parameters on the final measured output value is a well-known statistical procedure, called Principal component analysis (PCA). It is a way of identifying patterns in data, and expressing the data in such a way as to highlight their similarities and differences. Once these patterns are established, the dimensionality of data can be reduced without much loss of information, as I explain in more detail using this example.

In this problem I look at the data set consisting of total of 60 data points due to variations in 6 input variable, or 6 dimensional space, with each dimension corresponding to each component of the dipole tensor. PCA helps in transforming the present data set, which depend on 6 correlated input variables into a data set of linearly uncorrelated variables called principal components. PCA finds the correlation between the variables using the covariance between these variable, and yields a set of eigenvectors (principal components) of the covariance matrix. Covariance is a statistical term, and it provides a measure of strength of the correlation between two or more set of random variables. The covariance of two random variables X and Y, each with sample size N, is defined by expectation value as

$$\text{cov}(X, Y) = \sum_{i=1}^{N} \frac{(x_i - \bar{x})(y_i - \bar{y})}{N}$$

(7-17)

In this problem, we have 6 variables, which are varied over sample size of 10 different values (N=10). For uncorrelated variables $\text{cov}(X, Y) = 0$, however, if the variables are correlated, then their covariance is non-zero. The magnitude of the covariance tells how
strongly variable are related and sign of covariance tells the nature of this relationship. Positive covariance means that if one variable increases and other variable also increases, and negative covariance means that if one variable increases and other variable decreases. The obtained eigenvectors (or principal components) from the covariance matrix using PCA are given in Table 7-2.

Table 7-2 The computed principal components or eigenvectors using the PCA.

<table>
<thead>
<tr>
<th>Eigenvalue</th>
<th>Variable</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>146.8</td>
<td>G_{11}</td>
<td>0.85</td>
<td>-0.03</td>
<td>0.29</td>
<td>-0.24</td>
<td>0.17</td>
<td>0.33</td>
</tr>
<tr>
<td>14.9</td>
<td>G_{12}</td>
<td>-0.01</td>
<td>0.95</td>
<td>-0.02</td>
<td>-0.04</td>
<td>-0.22</td>
<td>0.19</td>
</tr>
<tr>
<td>8.6</td>
<td>G_{13}</td>
<td>-0.13</td>
<td>-0.19</td>
<td>-0.49</td>
<td>0.05</td>
<td>-0.06</td>
<td>0.82</td>
</tr>
<tr>
<td>4.3</td>
<td>G_{22}</td>
<td>0.35</td>
<td>-0.16</td>
<td>-0.16</td>
<td>0.22</td>
<td>-0.86</td>
<td>-0.15</td>
</tr>
<tr>
<td>0.2</td>
<td>G_{23}</td>
<td>0.19</td>
<td>0.11</td>
<td>0.02</td>
<td>0.93</td>
<td>0.28</td>
<td>0.03</td>
</tr>
<tr>
<td>1.4</td>
<td>G_{33}</td>
<td>0.34</td>
<td>0.12</td>
<td>-0.79</td>
<td>-0.13</td>
<td>0.29</td>
<td>-0.36</td>
</tr>
</tbody>
</table>

The first principal component is found to be the most significant, as it has the maximum eigenvalue, which means that the variations in the present data set can be largely understood in terms of the first principal component. The first principal component correlated most strongly to variable G_{11}. It also suggests that if G_{11} increases then G_{22}, G_{23} and G_{33} also increase, whereas G_{12} and G_{13} decrease. This makes complete sense, as the earlier analysis in Fig 7-10, showed similar correlation between input variables and the computed diffusivities. The influence of each of the input variable (G_{11}, G_{12}, G_{13}, G_{22}, G_{23} and G_{33}) based on the first principal component is summarized in the Fig. 7-11. This is an important outcome, as it indicates that any combinations of dipole tensor component (input parameter) involving G_{11} will have a much stronger influence on the final measured outcome, than other combinations of dipole tensor components not involving G_{11}. This sensitivity in outcome is further
analyzed by varying two components of the dipole tensor paired together in all possible combinations in the section below.

Figure 7-11 The sensitivity of each variable on the computed diffusivity based on the first principal component.

7.3.2 Two-Component Analysis

This section presents the similar PCA on the data set obtained by changing two dipole tensor components at a time. There are total of 15 variables based on the possible combinations of changing 2 dipole tensors components at a time out of total 6 components, as summarized in Table 7-3. This leads to a data set of total 1500 data points on a 15-dimensional variable space. The relative change in diffusivity as function of each of the 15 variables is summarized in Fig. 7-12. Each variable is varied with ± 10% of their respective values, and as can be seen from the Fig. 7-12, this leads to variation of about 20-30 % in the computed diffusivities for some of the variables. These changes in diffusivities are larger than variation due to changes in single components, as discussed in previous section. Using PCA, the relative influence based on the first principal component is summarized in Fig. 7-13. The change in diffusivity is more
sensitive to 5 variables correspond to combinations $G_{11}$-$G_{12}$, $G_{11}$-$G_{13}$, $G_{11}$-$G_{22}$, $G_{11}$-$G_{23}$, $G_{11}$-$G_{33}$ than any other combinations.

Table 7-3 List of all possible combinations of varying two components of the dipole tensor at a time.

<table>
<thead>
<tr>
<th>Combinations</th>
<th>Combinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$G_{11}$ - $G_{12}$</td>
</tr>
<tr>
<td>1</td>
<td>$G_{11}$ - $G_{13}$</td>
</tr>
<tr>
<td>2</td>
<td>$G_{11}$ - $G_{22}$</td>
</tr>
<tr>
<td>3</td>
<td>$G_{11}$ - $G_{33}$</td>
</tr>
<tr>
<td>4</td>
<td>$G_{12}$ - $G_{13}$</td>
</tr>
<tr>
<td>5</td>
<td>$G_{12}$ - $G_{22}$</td>
</tr>
<tr>
<td>6</td>
<td>$G_{12}$ - $G_{23}$</td>
</tr>
<tr>
<td>7</td>
<td>$G_{12}$ - $G_{23}$</td>
</tr>
<tr>
<td>8</td>
<td>$G_{12}$ - $G_{33}$</td>
</tr>
<tr>
<td>9</td>
<td>$G_{13}$ - $G_{22}$</td>
</tr>
<tr>
<td>10</td>
<td>$G_{13}$ - $G_{23}$</td>
</tr>
<tr>
<td>11</td>
<td>$G_{13}$ - $G_{33}$</td>
</tr>
<tr>
<td>12</td>
<td>$G_{22}$ - $G_{23}$</td>
</tr>
<tr>
<td>13</td>
<td>$G_{22}$ - $G_{33}$</td>
</tr>
<tr>
<td>14</td>
<td>$G_{23}$ - $G_{33}$</td>
</tr>
</tbody>
</table>

Figure 7-12 Relative change in diffusivity as given by Eq. (7-15), as function of fifteen combinations (variables) of changing two dipole tensor components at a time.

Therefore as speculated in the previous sections components involving $G_{11}$ have larger affect on the computed diffusivity than any other combination. However, interestingly the sensitivity due to varying two component of the dipole tensor at the
same time does not appear to be the linear sum of the varying the individual component at a time. For example, $G_{12}$ and $G_{13}$ have negative influence on diffusivity when varied individually as shown in PCA Fig. 7-11. However when varied together $G_{12} - G_{13}$ have positive influence (Fig. 7-13), though very small. This suggests possibility of coupling between the dipole tensor components that cannot be understood just as linear sum.

![Bar chart showing influence of combinations of variables on computed diffusivity](image)

Figure 7-13  The influence of each of the fifteen variables on the computed diffusivity based on the first principal component.

### 7.4 Summary and Conclusions

In this study, we established that the uncertainty in computation of MSD is directly propagated to the uncertainty in diffusivity calculates using kMC simulations. The uncertainty in the diffusivity is estimated to be about ±1.5 % of the most accurate expected value, obtained for an ensemble of 1500 independent trajectories that ran for much longer simulated time. The dependence of diffusivity on individual components of the dipole tensor is analyzed. While this analysis is somewhat preliminary, it does show that diffusivity is more sensitive to the case when two components are varied as
compared to the single component. We learned that sensitivity due to varying two component of the dipole tensor at the same time is not the linear sum of the varying the individual component at a time and suggest possible coupling between dipole tensor components. Further, it will be interesting to further investigate the nature and magnitude of this coupling when more than two or may be all the dipole tensor components are varied together. We showed that statistical tools such as PCA could be helpful tool in establishing sensitivities of the final output on the input parameters.
CHAPTER 8
RELAXATION VOLUME OF CHARGED DEFECTS FROM DENSITY FUNCTIONAL STUDY

The defect relaxation volumes obtained from density-functional theory (DFT) calculations of charged defects such as vacancies, interstitials in UO$_2$ show very large and seemingly anomalous magnitudes compared to their neutral counterparts. In this chapter I investigate the possible reasons for this and revisit the methods that address the issues of large defect relaxation volume of charged defects from DFT calculations. Any dependence of the proposed energy corrections to charge defect formation energy on relaxation volumes is probed. The aggregate formation volume for the net neutral defect complexes comprised of individual charge defects is shown to have reasonable magnitudes.

8.1 Background

The introduction of point defects or impurities in a crystal causes a lattice distortion around the defect site, which leads to a finite volume change with respect to the defect free lattice. This volume change can affect various material properties, in particular those that are sensitive to strain, such as diffusion, dislocation motion, interaction of point defects with other point defects, grain boundaries, and interfaces. The volume change is also an important measure of some experimentally observed phenomena. For example, in UO$_2$, the formation of defect clusters under irradiation can cause swelling and can lead to a phase change which is accompanied by significant volume changes$^1$. In pure or doped 2D materials, both external and defect induced mechanical strains can significantly affect relevant electronic properties and thus affect the strategies to tune their potential application in energy devices$^{196}$. The charge state of a defect is also important, as neutral defects may not be energetically stable under
certain thermodynamic conditions. For example, previous theoretical calculations\textsuperscript{28,122,173} of stoichiometric UO\(_2\) have shown that defects clusters such as Frenkel pairs, Schottky defects and fission product complexes are likely to consist of charged individual components as the formation of such structures is consistent with experimental observations\textsuperscript{8,9}. Also the chemistry of the operating fuel can be complicated due to presence of impurity (fission products) as a consequence of irradiation, which can affect the charge state of defects in the fuel matrix\textsuperscript{1}. Therefore an understanding of the lattice distortion associated with the formation of charged defects is crucial in predicting material properties sensitive to strain.

Experimental measurements of the volume change associated with point defects is limited to charge neutral defect complexes\textsuperscript{197,198}; as a result we have little understanding of the volume change or elastic distortion associated with individual charged defects. First principles based computational methods over the past decade have emerged as a powerful tool to study charged point defects\textsuperscript{199,200}. However, such calculations of charged defects, by necessity using periodic boundary conditions and relatively small supercell sizes (a maximum of a few hundred atoms) pose a variety of challenges and have led to several proposed computational approaches that correct the defect formation energies and for dilute concentrations\textsuperscript{200}. The calculation of the relaxation volume of charged defects via first principles based methods have received significant attention recently\textsuperscript{201,202} due to the observed large magnitude of relaxation volumes of these charged defects compared to their neutral counterparts. Further, if we use the elastic dipole tensor approach for charged defects to assess their interaction with external strains, we obtain seemingly very large (perhaps, even unphysical)
magnitudes for segregation energies to sinks, such as dislocations, as well as large changes in their migration barriers under external strains.

The chapter is arranged as follows. Sec. 8.2 presents the density functional theory (DFT) methodology used in calculating defect properties in UO$_2$ as well as in Si and GaAs. Si and GaAs are chosen to compare and validate our results with literature values. Section 8.3.1 discusses the definition to calculate defect formation and relaxation volume. Large magnitude of relaxation volumes, encourage us to examine various schemes to correct the total energy of charged supercells simulated via DFT calculation and relation to relaxation volume in Sec. 8.3.2. In Sec. 8.3.3, I discuss the thermodynamic approach for calculating the defect formation volume via defect reaction models.

### 8.2 Methodology

The DFT calculations are performed using the projector-augmented-wave (PAW) method$^{58,59}$. The exchange-correlation energy is described by the local density approximation (LDA) with the LDA+U approach, used to describe the correlated uranium 5f electrons in UO$_2$.$^{53}$ In accordance with earlier studies, the U and J values are set to U=4.5 eV and J=0.51 eV; i.e., U-J=3.99 eV$^{60}$. The Perdew-Burke-Ernzerhof GGA (PBE-GGA) functional$^{47}$ for silicon and LDA for GaAs are used. The cut-off energy employed for UO$_2$ is 500 eV, 520 eV for Si, and 275 eV for GaAs. Defect properties in UO$_2$ are calculated using $2 \times 2 \times 2$ and $2 \times 2 \times 3$ supercells with $2 \times 2 \times 2$ and $2 \times 2 \times 1$ k-point meshes, respectively. Defect calculations are performed at both constant volume and fully relaxed (both in volume and atomic coordinates) conditions. Defects in silicon are simulated in a $2 \times 2 \times 2$ and $3 \times 3 \times 3$ size supercell with k-point meshes of
and $3 \times 3 \times 3$, respectively, while those in GaAs are simulated in a $3 \times 3 \times 3$ supercell with a k-point mesh of $2 \times 2 \times 2$. The dielectric tensors are important for the correction schemes for the defect formation energies of charged systems and are calculated using density functional perturbation theory\textsuperscript{203,204} as implemented in VASP. The computed bulk structural properties of interest in UO$_2$, Si, and GaAs are summarized in Table 8.1. Energy vs. volume static calculations on defects are performed starting from the converged wave functions for the minimized defect structure. This is done to avoid the that the self-consistency loop in DFT getting stuck in a metastable configurations of the localized uranium f-electrons\textsuperscript{205}, and is shown in detail in the Appendix C.

Table 8-1 Calculated lattice parameters $a_0$ in (Å), elastic constants and Bulk modulus (B) in GPa and dielectric constant $\varepsilon$ from DFT calculations in UO$_2$ (LSDA+U), Si (GGA) and GaAs (LDA).

<table>
<thead>
<tr>
<th>System</th>
<th>$a_0$</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>B</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$</td>
<td>5.451</td>
<td>377.8</td>
<td>133.2</td>
<td>78.2</td>
<td>220.5</td>
<td>5.86</td>
</tr>
<tr>
<td>DFT\textsuperscript{206}</td>
<td>5.448</td>
<td>380.9</td>
<td>140.4</td>
<td>63.2</td>
<td>220.6</td>
<td>5.53</td>
</tr>
<tr>
<td>Expt.\textsuperscript{207}</td>
<td>5.473</td>
<td>389.3</td>
<td>118.7</td>
<td>59.7</td>
<td>209.0</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>5.468</td>
<td>153.1</td>
<td>56.8</td>
<td>74.6</td>
<td>88.9</td>
<td>10.62</td>
</tr>
<tr>
<td>DFT\textsuperscript{208,209}</td>
<td>5.47</td>
<td>154.6</td>
<td>58.1</td>
<td>74.4</td>
<td>90.2</td>
<td>12.98</td>
</tr>
<tr>
<td>Expt.\textsuperscript{208}</td>
<td>5.431</td>
<td>167.7</td>
<td>65.0</td>
<td>80.4</td>
<td>99.2</td>
<td>11.17</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.628</td>
<td>117.4</td>
<td>54.1</td>
<td>56.0</td>
<td>75.2</td>
<td>16.06</td>
</tr>
<tr>
<td>DFT\textsuperscript{210}</td>
<td>5.627</td>
<td>124.2</td>
<td>51.4</td>
<td>63.4</td>
<td>75.6</td>
<td>15.7</td>
</tr>
<tr>
<td>Expt.\textsuperscript{211}</td>
<td>5.654</td>
<td>121.7</td>
<td>54.6</td>
<td>61.6</td>
<td>76.9</td>
<td>13.1</td>
</tr>
</tbody>
</table>

### 8.3 Results and Discussion

#### 8.3.1 Defect Formation and Relaxation Volume

The defect formation volume is the volume change in the system upon formation of a defect. It can be understood as a macroscopic volume change in the system caused by the elastic distortion due to the introduction of the defect. It is an important
intrinsic property of the defect and direct comparison between theory and experiments for Frenkel and Schottky defect has been made in the past\textsuperscript{197,198}. As mentioned above, the defect formation volume is related to the elastic properties of the defect, which provide a description of how the defect interacts with strain fields within a material\textsuperscript{93,187}. Thus, an accurate determination of the defect formation volume and the associated elastic response of the defect are critical for predicting properties of materials. Because it is not possible to experimentally determine the defect formation volume of individual charged defects, it is useful to calculate formation volumes from electronic structure calculations which, given the present status of first-principles calculations of point defects in solids, can be expected to be very reliable. The very first theoretical expression for the vacancy formation volume was derived for metals\textsuperscript{212} (a crystal of neutral atoms). Gillan et al.\textsuperscript{197,213} later expanded on that initial treatment in the investigation of Schottky and Frenkel defects in alkali halides and alkaline earth fluorides. They dubbed this approach the volume derivative method, based on the thermodynamic relation between the defect formation volume $\Delta \Omega^f$ and the Gibbs free energy of formation of a defect $\Delta G$ at constant pressure and temperature, given as

$$\Delta \Omega^f = \left( \frac{\partial \Delta G}{\partial P} \right)_T + \Omega^0$$

(8-1)

where $\Omega^0$ correspond to the volume of defect specie or atom. In literature, the term relaxation volume is often used instead of the formation volume, and it is given as\textsuperscript{197}

$$\Delta \Omega^f - \Omega^0 = \Delta \Omega = \left( \frac{\partial \Delta G}{\partial P} \right)_T$$

(8-2)

The relaxation volume $\Delta \Omega$ can be understood as the change in volume due to relaxation of the crystal lattice around the defect. It is the volume change in the system upon introducing the defect without regard for where the excess atoms come from or go to.
contrast, the formation volume accounts for the volume of the atomic specie constituting the defect. Thus, the relaxation volume and the formation volume differ by a constant that accounts for the atomic volume associated with the origin or placement of the defect. For example, for a typical Frenkel defect, the formation volume is the same as the relaxation volume, but for Schottky defect $\Omega^0$ is the volume of the formula unit of the lattice and hence, the formation and relaxation volumes are not the same. However, the challenging part in defect calculations is the determination of the relaxation volume, as the formation volume can be easily calculated by properly defining $\Omega^0$.

Depending upon the thermodynamic condition, the change in free energy can be defined in terms of the Gibbs free energy $\Delta G(P,T)$ (Eq. 8-3) at constant pressure and temperature, or under constant volume and temperature condition change as Helmholtz free energy $\Delta F(\Omega,T)$ (Eq.8-4) which can be expanded in terms of the internal energy (E) and the entropy (S) of the system as

$$\Delta G(P,T) = \Delta E(P,T) + P\Delta \Omega - T\Delta S(P,T) \quad (8-3)$$

$$\Delta F(\Omega,T) = \Delta E(\Omega,T) - T\Delta S(\Omega,T) \quad (8-4)$$

Experimentally, defects are created at constant pressure and finite temperature conditions, whereas DFT calculations traditionally use a constant volume and zero temperature approach. Therefore care should be taken when comparing the results of simulations with those of the experiments. The change in Gibbs free energy $\Delta G$ between two configurations (defect and perfect bulk) having different volumes can equally be obtained as the difference of Helmholtz free energy $\Delta F$ of defect and bulk lattices at constant volume$^{197}$.

$$\Delta G(P,T) = \Delta F(\Omega,T) \quad (8-5)$$
This simply means that the same work is required to form a defect at constant volume and at constant pressure because the work done by crystal in expansion or contraction at constant pressure is equal and opposite to that done by pressure at constant volume. Therefore, the relaxation volume in Eq. 8-2 can be rewritten as

\[ \Delta \Omega = \left( \frac{\partial \Delta F}{\partial P} \right)_T = \left( \frac{\partial \Delta F}{\partial \Omega} \right)_T \left( \frac{\partial \Omega}{\partial P} \right)_T \approx -\kappa_T \Omega_{\text{bulk}} \left( \frac{\partial \Delta F}{\partial \Omega} \right)_T \] (8-6)

where \( \kappa_T \) is the isothermal compressibility and \( \Omega_{\text{bulk}} \) is the volume of the original bulk system in which the defect is created. Note that an entropy contribution, which is hidden inside \( \Delta G \) and \( \Delta F \), respectively in Eqs. 8-2 and 8-6, vanishes for zero temperature calculations. Hence, the formation volume as a function of the change in internal energy as

\[ \Delta \Omega = -\kappa_T \Omega_{\text{bulk}} \left( \frac{\partial \Delta E(\Omega, T)}{\partial \Omega} \right)_T \] (8-7)

Where \( \kappa_T \) is the isothermal compressibility. However, at high temperatures, the entropy contribution can be added along with changes in the internal energy \( \Delta E \) and a more accurately determination of both formation energies as well as formation volumes can be done. As mentioned before, defect simulations are traditionally carried out at constant volume approach and hence defect supercell have an additional pressure \( \Delta P \) compared to perfect bulk supercell, which is simple given as

\[ \Delta P = - \frac{\partial \Delta E(\Omega, T)}{\partial \Omega} \] (8-8)

Further, the relaxation volume can either be directly calculated as the difference in equilibrium volume of the defect supercell with respect to bulk supercell for simulations done at constant pressure, or from a simple calculation involving the pressure:

\[ \Delta \Omega = \Omega(\text{defect}) - \Omega(\text{bulk}) \approx \kappa_T \Omega_{\text{bulk}} \Delta P \] (8-9)
In real systems, defects may be charged or neutral depending on the stoichiometry of the system. Moreover, they usually occur as an ensemble of one or more types of point defects, rather than a single defect. Therefore it might be more accurate to define defect properties by considering them in a stoichiometry conserving defect reaction model rather than considering them individually. This is discussed in more detail in Sec. 8.3.3, but here I briefly touch upon the question of how to define the volume change for a defect reaction than that of an individual defect. Also, an attempt is made to be consistent with the Kröger-Vink notation for defects in this study with some of already present literature on defects in UO\textsubscript{2}\textsuperscript{32,122,157,161}. For example, consider a general Schottky defect reaction in UO\textsubscript{2} written in two different ways
\[
\begin{align*}
U^\times + 2O^\times & \rightleftharpoons V^\text{''''}_U + 2V^\text{--}_O + U^\times_{\text{surface}} + 2O^\times_{\text{surface}} \\
\phi(\text{null}) & \rightleftharpoons V^\text{''''}_U + 2V^\text{--}_O
\end{align*}
\] (8-10)
While the first follows explicitly conserves charge, atom site and atom species, the second is more compact and displays the essentials aspects more clearly. The analogous formation volume for Schottky defect can then be defined as
\[
\Delta\Omega^f_{\text{Schottky}} = \Delta\Omega_{V^\text{''''}_U} + \Omega^0_U + 2\Delta\Omega_{V^\text{--}_O} + 2\Omega^0_O - \Omega^0_U - 2\Omega^0_O = \Delta\Omega_{V^\text{''''}_U} + 2\Delta\Omega_{V^\text{--}_O} \quad (8-11)
\]
Therefore the formation volume of a defect reaction is equal to sum of the relaxation volumes \(\Delta\Omega_X\) of the individual defects (\(X = V^\text{''''}_U, V^\text{--}_O\)). This is an important relation and further adds to the importance of the need to accurately determine the defect relaxation volume. Therefore we concentrate here on relaxation volumes. Also, this is consistent with the Schottky formation energy defined on similar lines, where the sum of the formation energy of individual charge defects is shown to be much better agreement with Schottky formation energy for infinitely separated defects in a single
supercell. The calculated defect relaxation volumes (using Eq. 8-9) for various charged and neutral individual defects from the DFT calculations are summarized in Table 8-2. For defects in UO₂, one can see that the relaxation volumes are larger for U defects compared to O defects, with the U-vacancy causing the volume to shrink and O-vacancy leading to a marginal increase in volume. The opposite sign of the volume change due to U and the O-vacancy is interesting and can be understood by analyzing in detail the changes in atomic distances between the defect site and its neighboring atoms. For the U-vacancy, the first eight nearest neighbor O atoms move outward from the vacancy site but the twelve second neighbor U atom move closer to the vacancy due to removal of Coulomb interaction among cations, resulting in negative volume change. For an O-vacancy, the first four nearest neighbor U atoms move outward but the displacement of six second neighbor O atoms is complex and depend on 5f electrons at the U site. For an O-interstitial at octahedral site, the atomic displacements are affected more strongly by the Coulomb interactions than by the atomic sizes. Further, as evident from Table 8-2, calculations involving charged defects result in very large relaxation volumes, as compared to their neutral counterparts. The relaxation volumes for charged defects are also opposite in sign to the relaxation volume for the same defect in a neutral charge state. We calculated the relaxation volume of both neutral and charged uranium vacancy as a function of system size and found that the as-calculated relaxation volumes are essentially independent of system size, as shown in Fig. 8-1. This rules out system-size effects as the origin of this behavior, but motivates our next section where we investigate in more detail the origin of relatively large relaxation volume associated with the charged defects.
Table 8-2 Defect relaxation volumes of both neutral and charged defects calculated from DFT.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Relaxation volume ΔΩ (Å³)</th>
<th>Defect</th>
<th>Relaxation volume ΔΩ (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_U^X$</td>
<td>-9.07</td>
<td>$V_{Si}^X$</td>
<td>-15.36</td>
</tr>
<tr>
<td>$V_{U'''}$</td>
<td>40.11</td>
<td>$V_{Si}''$</td>
<td>20.57</td>
</tr>
<tr>
<td>$(V_U^X - V_U^X)$</td>
<td>-17.97</td>
<td>$V_{Ga}^X$</td>
<td>-26.29</td>
</tr>
<tr>
<td>$(V_{U'''} - V_{U''''})$</td>
<td>87.21</td>
<td>$V_{Ga}'''$</td>
<td>112.17</td>
</tr>
<tr>
<td>$V_o^X$</td>
<td>0.56</td>
<td>$V_{As}^X$</td>
<td>-24.36</td>
</tr>
<tr>
<td>$V_o''$</td>
<td>-18.5</td>
<td>$V_{As}''$</td>
<td>8.1</td>
</tr>
<tr>
<td>$O_i^X$</td>
<td>-3.38</td>
<td>$O_i''$</td>
<td>20.37</td>
</tr>
</tbody>
</table>

Figure 8-1  Relaxation volume of a single uranium vacancy in UO₂ as a function of supercell size for neutral (blue) and fully charged (red) states. Closed symbols represent relaxation volumes obtained by using higher energy cut-off and much denser K-point meshes compared to data represented by open symbols.
8.3.2 Correction schemes to relaxation volume for charge defects

There have been relatively few theoretical investigations of the relaxation volumes of charged defects\textsuperscript{201,202,215}, as compared to the large literature on the formation energies of charged defects. Erhart et al\textsuperscript{215}, reported relaxation volumes (using Eq.8-9) of vacancies and interstitials in ZnO and more recently Bruneval and co-workers\textsuperscript{201,202} analyzed the relaxation volume of charged defects in silicon. Both groups simulated defects using DFT and report relaxation volume as a strong function of charge state of the defect. The defect relaxation volume in DFT calculations follows directly from the defect formation energy (DFE) (Eq.8-1); recently, Bruneval and co-workers\textsuperscript{201,202} proposed that energy corrections to defect formation energies of charged defects have a significant volume dependence. Therefore in this section we investigate the volume dependence of a number of corrections to total energy of charged defects in UO\textsubscript{2}, Si and GaAs. The objective is to establish a reliable method to determine the relaxation volume, free of artifacts of the simulation methodology.

Defect Formation Energy: The widely accepted definition to calculate the defect formation energy ($E^f$) from DFT calculations for a neutral defect ($X^0$) is given as\textsuperscript{68,200}

$$\Delta E = E^f(X^0) = E_{\text{tot}}(X^0) - E_{\text{tot}}(\text{bulk}) - \sum_i n_i \mu_i$$

(8-12)

where $E_{\text{tot}}(X^0)$ is the total energy of the DFT supercell with a neutral defect, $E_{\text{tot}}(\text{bulk})$ is the total energy of the defect-free bulk supercell, and $n_i$ and $\mu_i$ are the number and chemical potential of each element accounting for the defect. Note that the above definition hold for constant volume and temperature calculations $E^f = \Delta E(\Omega,T)$; if we need to define a thermodynamically relevant Gibbs free energy definition for constant
pressure and temperature simulations, then an extra term $\rho \Delta \Omega$ should be added to Eq.8-12.

For a charged defect, the situation is more complicated. In DFT calculations, a homogeneous background charge density (opposite in sign to the charge of the defect) is introduced to ensure global charge neutrality so that the total energy of the charged system does not diverge. Further, the average electrostatic potential over the entire volume of the supercell is set to zero$^{69,210,216}$ in order to evaluate the electrostatic Coulomb energy. In addition to these DFT conventions, the total energy of a charged defect in a supercell also needs to be corrected for several reasons. First, the chemical potential of the electrons must be accounted for, just as was done in Eq.8-12 for atomic species. Second, the interaction between a charged defect (in a homogeneous background charge density) and its periodically repeated charged images needs to be corrected as it add a spurious electrostatic energy. Third, the potential far away from the defect no longer matches that of the perfect bulk system and therefore a correction in potential is needed to account for change in the reference energy of electrons in the charged supercell compared to the electrons in the neutral pristine bulk (the so-called potential alignment correction). And lastly, as recently reported by Bruneval et al.$^{216}$, the total energy calculations of the charged DFT supercells involving the PAW method need a background correction term (explained later in more detail below). These corrections brings additional terms in the DFE of charged defects, which is given by

$$E^f(X^q) = \left[ E_{tot}(X^q) + q(\epsilon_v + \epsilon_F) + E_{corr}^q + q \Delta V + E_{corr^{bkgd}} \right] - E_{tot}(\text{bulk}) - \sum_i n_i \mu_i \quad (8-13)$$

where $q$ is the charged state of the defect, $\epsilon_v$ is the valence band maximum (VBM) calculated in the defect free bulk supercell$^{210}$ and $\epsilon_F$ is the Fermi level with respect to
the valence band maximum. The \( q(\epsilon_v + \epsilon_F) \) term yields the chemical potential of electrons. The \( E_{corr}^q \) term accounts for the charged image interaction correction in supercell calculations, \( \Delta V \) is referred to as the potential alignment correction, and \( E_{corr}^{bkgd} \) is the correction needed in the total energy of charged systems calculated using PAW method\(^{216} \). We discuss all these corrections and their volume dependence in more details in subsections below.

Based on recent literature\(^{68,69,200,210,216,217} \) on corrections to the total energy of charged defects, we carefully investigate any relation of these energy corrections to the observed large relaxation volumes computed via DFT calculations. It is important to understand that any change in the total energy that depends on the volume of the simulation cell affects the computed forces and hence the stress tensor (Eq.8-8) and relaxation volumes (Eq.8-9) in DFT simulations. Therefore both volume and stresses need to be corrected in a manner consistent to those applied to the total energy.

**Charge Image Correction:** The charge image correction is needed because in periodic supercell calculations a charged defect and the homogeneous background charge density will have long-range electrostatic interactions with the periodic charged images. If the dimensions of the unit cell were infinite, this electrostatic interaction would be zero. However, in periodic DFT calculations the dimensions are relatively small; therefore the total energy of the charged systems need to be corrected to account for this interaction. This correction corresponds to the Madelung energy of the model charge\(^{89} \) (a point or Gaussian charge distribution in a simplified model) and is designed to transform the electrostatic energy of a periodic lattice of model charges in a
neutralizing background into the electrostatic energy of single model charge. The form of this correction term$^{66,69,210}$ is given as

$$E_{corr}^q = E_{isolated} - E_{periodic} = \frac{1}{2} \int V_{corr}(r) \rho_{model}(r) dr \approx \frac{\alpha q^2}{2\varepsilon} \Omega^{-1/3}$$

(8-14)

where $\alpha$ and $\varepsilon$ are the Madelung and dielectric constant of the lattice and $q$ is the charge on the defect. This corresponding correction to pressure (Eq. 8-8) scales as $\Omega^{-4/3}$, where $\Omega$ is the volume of the cubic unit cell.

The calculated energy correction, pressure and volume corrections for charge defects in three different systems types are summarized in Table 8-3. For UO$_2$ $E_{corr}^q = 0.26$ eV for a unit charge and the corresponding correction to the volume using Eq. 8-9, is 0.06 Å$^3$ for a 2x2x2 (with volume 1291.1 Å$^3$) UO$_2$ supercell with 96 atoms, which is a negligible correction compared to the relaxation volumes of any of the charge defects (see Table 8-2) in UO$_2$. Even for charge defects in GaAs and Si, we find very small correction to relaxation volume. This is in agreement with a previous study on charge defects in Si by Bruneval and Crocombette$^{201}$. Hence, we can conclude that the correction to the relaxation volume as well as stresses due to the charged images energy correction is effectively negligible. It is also important to note that the correction to the relaxation volume decreases as the size of the simulation supercell and is independent of the sign of the charge on the defect, depending only on the magnitude of the charge.
Table 8-3 Calculated energy correction to defect formation energy (in eV) due to image interaction between charged defects, using the definition from Eq. 9 and corresponding correction to pressure (in GPa) (1 eV/A³ = 160.2 GPa) and volume (in A³) in DFT calculations. Charge state q =1 is considered for all systems.

<table>
<thead>
<tr>
<th>System</th>
<th>E_{corr}^q</th>
<th>P_{corr}^q</th>
<th>ΔΩ_{corr}^q</th>
<th>Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.176</td>
<td>-7.1x10⁻³</td>
<td>0.105</td>
<td>1308.16</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.072</td>
<td>-7.9x10⁻⁴</td>
<td>0.051</td>
<td>4813.43</td>
</tr>
<tr>
<td>UO₂</td>
<td>0.267</td>
<td>-7.3x10⁻³</td>
<td>0.066</td>
<td>1291.1</td>
</tr>
</tbody>
</table>

**Alignment Correction:** The alignment correction is needed because the total potential of a defect system (even for the neutral defect) will be different from the total potential of the bulk system (the typical reference in defect formation energy calculations). Since the total energy of the charged system depends on the Fermi level (which is often referenced to the bulk valence band maximum (VBM) and hence depends on the average electrostatic potential in the bulk), it is necessary to align the electrostatic potential of the defect supercell to that of the bulk.

Various schemes proposed by Makov and Payne (MP), Freysoldt, Neugebauer and Van de Walle (FNV), Lany and Zunger (LZ), Taylor and Bruneval are available for alignment correction for charged defects. Recent reviews have carefully examined the performance of these proposed schemes and found the FNV scheme to be most appropriate as it offers the most robust DFE for defects with a localized charge distribution in a variety of systems studied. The potential alignment term \(ΔV\), in the FNV scheme is obtained by comparing the electrostatic potential from the model charge density \(V_{model}^{\text{model}}\) to the difference in DFT electrostatic potential between the charge defect \(V_{q\text{DFT}}\) and perfect bulk \(V_{b\text{DFT}}\):

\[
ΔV = ΔV_{q/b} = (V_{q\text{DFT}} - V_{b\text{DFT}})|_{\text{far}} - V_{\text{model}}|_{\text{far}}
\]

(8-15)
The alignment correction via the FNV scheme is reported to be independent of the adopted charge model if the defect charge is well localized within the simulation cell. In our calculations we have adopted a Gaussian charge distribution, as originally proposed, and we have provide all of the steps to compute alignment correction in Appendix B. After applying both image charge correction and alignment correction, the defect formation energy for the uranium vacancy is plotted as function of volume, as shown in Fig. 8-2. The volume corresponding to minimum for the uncorrected energies is 1971.1 Å$^3$, whereas the volume for minimum after applying the image charge and alignment correction to the DFE is 1972.3 Å$^3$. This change 1.2 Å$^3$ is very small compared to original volume of 1984.7 Å$^3$ of the charged uranium vacancy. This suggests that both image charge correction and alignment correction term have very little effect on the volume under hydrostatic strain.

![Figure 8-2](image.png)

Figure 8-2  Defect formation energy of a charged uranium vacancy as function of volume or hydrostatic strain.
**Background Correction:** As recently demonstrated by Bruneval et al.\textsuperscript{216}, the current formalism of the PAW total energy and Hamiltonian in DFT code, VASP, does not incorporate the compensating background charge contribution to the total energy in a consistent manner. An extra term must be added to the total energy of charged system for results to reproduce the reference all electron calculations. This extra term (or correction) is added to the Coulomb term in the total energy. The correction to the total energy due to background charge is given as

$$E_{\text{corr}}^{\text{bkgrd}} = \frac{q}{\Omega} \sum_\alpha \beta^\alpha$$ (8-16)

where the $\beta^\alpha$ measures the difference between the physical potential due to the nucleus and the core electrons with the PAW method, summed over all the atomic positions, $\alpha$. This correction to the total energy is zero for charge-neutral cells and only modifies the total energy of charged supercell due to the compensating background charge. The correction to the diagonal component of the computed stress tensors in DFT calculations due to background energy correction is given as.

$$P_{\text{corr}}^{\text{bkgrd}} = -\frac{dE_{\text{corr}}^{\text{bkgrd}}}{d\Omega} = \frac{q}{\Omega^2} \sum_\alpha \beta^\alpha$$ (8-17)

The computed energy correction (Eq. 8-16) and correction to pressure (Eq. 8-17) and volume (Eq. 8-9) of the charge defects are summarized in Table 8-4. The corrections to energy, pressure and volume are much larger than those arising from the image charge and alignment corrections. Figure 8-4 shows the total energy of $V''''$ as function of volume, when the background correction is included, which shows a change in volume of about 16.43 A\textsuperscript{3}. It is important to note that the background correction to energy, pressure and volume scale linearly with the magnitude and sign of charge and
is independent of the nature (atomic structure) of the defect. Hence, this is likely to
cancel in defect reactions that are overall charge neutral.

Table 8-4 Calculated background energy correction (in eV) to the total energy, using the
definition from Eq.16 and corresponding correction to pressure (in GPa) and
volume (in A$^3$) for various charge defects in different considered systems.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$E_{corr}^{Bkgrd}$</th>
<th>$P_{corr}^{Bkgrd}$</th>
<th>$\Delta \Omega_{corr}^{Bkgrd}$</th>
<th>$\Delta \Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_i'''$</td>
<td>22.67</td>
<td>-1.83</td>
<td>16.9</td>
<td>40.11</td>
</tr>
<tr>
<td>$V_{Sl}''$</td>
<td>-0.83</td>
<td>0.11</td>
<td>-2.01</td>
<td>-18.5</td>
</tr>
<tr>
<td>$V_{Ga}'''$</td>
<td>12.30</td>
<td>-0.41</td>
<td>27.19</td>
<td>112.17</td>
</tr>
</tbody>
</table>

8.3.3 Defects Reactions

This section presents a thermodynamic basis for calculating defect properties,
such as volumes and formation energies, involving charged defects from the point
defect reaction model$^{87,218}$. The reaction for oxygen Frenkel pair is given as

$$O_i^{\times} + V_i^{\times} \rightleftharpoons O_i'' + V_i.$$  \hspace{1cm} (8-18)

Under non-stoichiometric conditions, for example in UO$_{2+x}$, oxygen interstitials and
uranium vacancies can be the dominant defects$^{122,157}$. In the defect reaction model, the
defect constituents are assumed to be non-interacting and charge compensation is
controlled by electrons and holes created in the intrinsic ionization process.

Experiments on U$_4$O$_9$ have shown that oxide contain a mixture of U$^{4+}$ and U$^{5+}$ ions
under hyper-stoichiometric conditions$^{219}$ and the electronic disorder is assumed to be
controlled by the disproportionation of two U$^{4+}$ (5f$^2$) ions to one U$^{5+}$ (5f$^1$) and one U$^{3+}$
(5f$^3$) ion$^{157}$, which may be written as

$$2U_i^{\times} \rightleftharpoons e^' + h.$$

Where $U_i^{\times}$ designates a uranium atom on a normal uranium lattice site (U$^{4+}$) and $h^*$ and
e$'$ designates holes (U$^{5+}$) and electrons (U$^{3+}$), respectively. As discussed previously, the
calculation to relaxation volume should then directly follow from its relation to defect formation energy (given by Eq. 8-8 and 8-9). For example, Dorado et al.\textsuperscript{157} derived the formation energy of the uranium vacancy using a defect reaction model as follows:

\[
E^f(V_{U''''}) = 2E_{O_i} + E_S - 2E_{eh} - 2E_{FP_O} + E_{PO_2}
\]  

(8-20)

where \(E_X\) is the defect formation energy for the oxygen interstitial \((X = O_i)\), Schottky defect \((X = S)\), electron-hole pair \((X = eh)\) and Frenkel pair of oxygen \((X = FP_O)\). \(E_{PO_2}\) is the energy of the oxygen buffering reaction. The volume of the defect reaction for uranium vacancy can then be defined from Eq. 8-20 as

\[
\Delta \Omega^f(V_{U''''}) = 2\Delta \Omega_{O_i} + \Delta \Omega_S - 2\Delta \Omega_{eh} - 2\Delta \Omega_{FP_O}
\]  

(8-21)

where \(\Delta \Omega_X\) represents the relaxation volume for each of the species defined in Eq. 8-20 for defect formation energy. Note that Eq. 8-21 maintains the overall mass and charge balance. Hence, volume changes corresponding to the defect species due to the reference state \((\Omega^0)\) exactly cancel out, as previously shown in Eq. 8-11 and \(\Delta \Omega_X\) is directly obtained from the DFT calculations as defined in Eq. 8-9. Considering a defect reaction involving charged oxygen interstitial plus two holes, it can be shown that the corrections in the relaxation volumes of individual components roughly cancel out when summed over for a charge neutral defect reaction. The defect reaction is given as

\[
\frac{1}{2}O_2(g) + V^X_i + 2V^X_{\bar{U}} \rightleftharpoons O''_{i'} + 2h^i
\]  

(8-22)
Table 8-5 Defect formation volume $\Delta \Omega^f$ for charged defects calculated from DFT compared with their relaxation volume $\Delta \Omega$ from DFT as well as empirical potential. (OS) stands for a calculation in which all of the corresponding defects were placed in one supercell in the DFT calculation.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$\Delta \Omega$ (A$^3$)</th>
<th>$\Delta \Omega^f$ (A$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>LAMMPS</td>
</tr>
<tr>
<td>$V''''_U$</td>
<td>40.11</td>
<td>22.5</td>
</tr>
<tr>
<td>$V''_O$</td>
<td>-18.5</td>
<td>-1.24</td>
</tr>
<tr>
<td>$O''_i$</td>
<td>20.37</td>
<td>8.15</td>
</tr>
<tr>
<td>$V_O - O_i(OS)$</td>
<td>3.62</td>
<td>7.39</td>
</tr>
<tr>
<td>$V''_O + O''_i$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V''_O + O''_i$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_U - 2V_O(OS)$</td>
<td>2.28</td>
<td>19.51</td>
</tr>
<tr>
<td>$V''''_U + 2V''_O$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V''''_U + 2V''_O$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The corresponding formation volume $\Delta \Omega^f(O''_i)$ of the reaction can be written in terms of its constituent relaxation volumes $\Delta \Omega_X$ and the associated error in relaxation volume $\Delta \Omega_X^{error}$ due to charged supercells in the DFT calculations, as

$$\Delta \Omega^f(O''_i) = [\Delta \Omega_{O_i} + \Delta \Omega_{O_i}^{error}] + 2[\Delta \Omega_{h^i} + \Delta \Omega_{h^i}^{error}]$$

(8-23)

where $\Delta \Omega_X^{error}$ can be broken into different correction volumes due to corresponding energy correction terms mentioned in Eq.8-13 and discussed in Sec. 8.3.2 as

$$\Delta \Omega_X^{error} = \Delta \Omega_X^{image} + \Delta \Omega_X^{align} + \Delta \Omega_X^{Bkgd}$$

(8-24)

Here, $\Delta \Omega^{image}$ is the volume correction due to the defect charge image energy correction. As discussed in Sec. 8.3.2, the image correction only depends on the magnitude of the charge and the properties of the lattice like Madelung constant and does not depend on the nature of the defect. Both $\Delta \Omega^{image}$ and $\Delta \Omega^{align}$ as shown in Table 8.3 are negligible when compared to the relaxation volume of charge defects.

However, although $\Delta \Omega^{Bkgd}$ is not negligible, it will exactly cancel out for $O''_i$ and $2h^i$ as it
scale linearly with the magnitude and sign of charge and is independent of the nature of the defect. Therefore the formation volume of defect reaction involving oxygen interstitial plus two holes, effectively reduces to

$$\Delta \Omega_f (O^{''}_{i}) = \Delta \Omega_{O_i} + 2 \Delta \Omega_{h^\ast}$$  \hspace{1cm} (8-25)

The defect reaction for the uranium vacancy (given in Eq. 8-20) simplifies to

$$O_2 + 2e^\ast \rightleftharpoons V''_{U} + 2h^\ast + 2O^\ast_0$$  \hspace{1cm} (8-26)

and the reaction volume (given in Eq. 8-21) can be written in term of individual relaxation volumes as

$$\Delta \Omega_f (V''_{U}) = \Delta \Omega_{V''_{U}} + 2 \Delta \Omega_{h^\ast} - 2 \Delta \Omega_{e^\ast}$$  \hspace{1cm} (8-27)

The values of the defect reaction volumes for charged defects obtained from the defect reactions are reported in Table 8-5. The magnitude of the resulting defect reaction volumes for the defect reactions seems more reasonable than the magnitude of the corresponding relaxation volume for the individual charge defects. For example, the volume of the Schottky defect cluster using charged individual components is estimated to be 6.6 Å³, which is similar to the value of 5.93 Å³ by Thompson and Wolverton²²⁰ using 96 atom UO₂ supercell with collinear AFM ordering for defect calculations using DFT. The average atomic volume in a 12 atom cubic UO₂ unit cell, based on the lattice parameter of 5.45 Å, is about 13.5 Å³ and for a UO₂ formula unit is about 40.4 Å³. This tells us that it may not be reasonable to compare the magnitude of formation and relaxation volumes directly with the average volumes for an atom or a formula unit in ionic system. This is understandable as formation and relaxation volumes reflect the change in volume of the system caused by the atomic relaxations surrounding the defect site and not the volume of the defect site.
Interestingly, if one considers the relaxation volume for a charge neutral defect, such as the oxygen Frenkel pair, the net relaxation volume calculated for the defect pair in one supercell (3.62 Å³) agrees well with that obtained for the two charged species calculated in separate supercells and added together (\(V_0^{\circ} + O_i^{\circ}; 3.26 \, \text{Å}^3\)). This indicates that (a) while the relaxation volume of each charged defect, as calculated using charged DFT supercells, seems unphysically large, there is an opposite physically effect in volume change, which goes to zero for a overall charge neutral reaction, and (b) the charge transfer reactions are different for the neutral and charged cases. It has been observed experimentally\(^{197,198}\) that both Frenkel and Schottky defects in ionic crystals result in an expansion of lattice, which is in line with the calculated reaction volumes, if both Frenkel and Schottky defects are considered to be formed by the charged constituents rather than the neutral counterparts.

8.4 Summary and Conclusions

In this study we have shown that there are discrepancies associated with calculation of relaxation volumes of individual charged defects via DFT calculations. Energy corrections terms to the defect formation energy of charge defects such image correction and alignment correction are shown to have a very small contribution to overall relaxation volumes as against the background energy correction term. The reasons for the strong scaling in the magnitude of the relaxation volume with the charge state of the defect are still not clear and require further investigations. Incorporating the effect of energy correction terms on relaxation volumes definitely scales down the magnitude of the relaxation volumes for these charged defects as compared to relaxation volumes with no correction. However, the defect formation volumes obtained from the overall charge neutral defect reaction model are not only reasonable in
magnitude but also the sign of the formation volumes compares very well with some of the other computational and experimental information available on overall neutral Schottky and Frenkel defects.
CHAPTER 9
CONCLUSION AND FUTURE WORK

9.1 General Implications

This work addresses the issue of ionic transport in strained oxide materials, using UO$_2$ as a prototypical material, both because of its importance in the current generation of nuclear reactors but also because its structure, fluorite, is common to many technologically important materials. Thus, our results have implications beyond the specific material studied, in particular for the transport properties of various other ionic fluorite-structured materials. Such as complex oxide hetero-structures\textsuperscript{221,222}, strained oxide thin films\textsuperscript{223,224}, and CeO$_2$ and stabilized ZrO$_2$ (YSZ)\textsuperscript{225–227} which are commonly used in solid oxide fuel cells, as well as sintering and creep properties of zirconia and hafnia based thermal barrier coatings\textsuperscript{228,229}. In many of these applications, the presence of strain can alter atomic scale events and the overall evolution of the system. Therefore our work provides the foundation for an \textit{ab initio} informed kMC approach and can be extended to any system where strain influences mobility.

The dipole tensor approach presented here can easily be extended to measure the effect of any arbitrary strain state on diffusivity, as long as the applied strains are small enough to not change the migration topology of the defect. In this work, applied strains were up to the relatively large value of 2\%, because the thermal gradients that develop within the fuel during operation can easily lead to such magnitudes of strain\textsuperscript{1,230–232}. Our results show that strain has a significant effect on the diffusivity, especially at low temperatures, with compressive strain leading to lower diffusivity and tensile strain to higher diffusivity. Our results show that the coupling between strain and diffusion can be rather complex, with significant changes in mobility in directions.
perpendicular to the applied strains. This has implications in epitaxial thin film composites\textsuperscript{223} where vertical strains dominate the overall strain state with thickness over 20 nm, promising greater control of functional properties beyond those typical of the lateral strains in such films.

This work provides the foundation to analyze defects (such fission products, fission gases) and their interaction with the much more complex strain fields associated with dislocations, grain boundaries and dislocation loops, and can be extended to microstructural features individually or in combination as function of temperature. For example, the strain field due to an edge dislocation can be easily implemented in our kMC simulations and can be used to examine the mobility of point defects such as a vacancy in its field. It would then be possible to compute much more accurate values of point defect absorption rates to edge dislocations without resorting to relying on parameters that are often derived from a much simplified model\textsuperscript{233}. Furthermore, it would also be possible to compute the portioning of point defect fluxes into different types of sinks, which have different and potentially interacting strain fields.

This work provides a link between atomistic simulations and mesoscale representations of the material. However, care must be taken to apply this model under conditions in which its assumptions are valid. The assumption that the elastic response of the defect environment can be approximated by that of the bulk is true only for dilute concentrations of defects. Changes in the potential energy landscape of the defect in presence of strain field should be made to acquire changes in barrier height and potential new minima.
To conclude the approach used in this study provides an extensive and systematic way of addressing multiscale problems by efficiently coupling the atomic scale DFT calculations with the mesoscale kMC simulations. This approach allows for incorporation of the effects of strain that affect defect mobility, and will yield much more physical and accurate results than if the strain effects are not accounted for. These results can be used as parameters for even higher length scale models to predict and understand fuel mechanical behavior.

9.2 Future Work on UO$_{2+x}$

The chemistry of an operating oxide fuel pin is complicated by the steep temperature gradient and the equilibrium pressure of oxygen in the gas phase within the fuel element. Fluorite structured UO$_2$ is a very stable compound that appears at O/U = 2.0, whereas at higher O/U ratio ordered compounds like U$_4$O$_{9-y}$ and U$_3$O$_7$ can also form$^{1,234}$. Deviation of uranium from exact stoichiometry is common because uranium can exist in number of different valence states such as U$^{4+}$, U$^{5+}$ and U$^{6+}$. It is important to study oxidation of UO$_2$ for predicting its thermodynamic behavior both during operating conditions and in the spent fuel stored in the repository.

Fluorite derived hyper-stoichiometric UO$_{2+x}$ is a complex binary material. As a consequence, the concentration of defects and defect structure is different in UO$_{2+x}$ compared to stoichiometric UO$_2$.$^{235-238}$ In UO$_{2+x}$ at low x values, the interstitial O atoms occur as isolated point defects. As x increases, individual defects interact with each other increasingly and form clusters. Various experimental and theoretical studies have shown that these clusters are not random but rather structured with well-defined configurations. A defect cluster model, the so-called 2:2:2 Willis type, was proposed for UO$_{2.11-2.13}$ over fifty years ago$^{234}$ and since then, has remained the dominant conceptual
model in the literature. However very recent first-principle molecular dynamics simulations at high temperature shows that the average structure of UO$_{2+x}$ involves a combination of defect structures including split quad and di-interstitial, di-interstitials, mono-interstitials and the Willis clusters$^{235,237–239}$.

Additionally the deformation behavior in single crystal UO$_{2+x}$ is found to be a strong function of stoichiometry and temperature. Keller et al.$^{100,240}$ reported that for UO$_{2+x}$ at temperature less than 873 K, glide become easier on the slip system $<110>$\(\{111\}\) compared to the primary $<110>$\(\{001\}\) and secondary $<110>$\(\{110\}\) slip systems. The dislocation substructures consist largely of screw dislocations, indicating that the screw dislocations controls deformation. It is likely that for higher O/U > 2.0, dislocation mobility is controlled by interactions between dislocations and oxygen defect clusters, sufficient to serve as obstacles to dislocation motion. Therefore some of the conclusions of this study are not directly applicable to UO$_{2+x}$ and will need additional investigations to incorporate dominant defects and build-up of local strain in fluorite structure to accommodate complex atomic defects in UO$_{2+x}$.

However, based on very recent studies on UO$_{2+x}$$^{235,237}$, the good news is that understanding of UO$_{2+x}$ can be built on the presented computational framework for UO$_2$ and there is no need to start from scratch. It has been shown that a DFT+U framework similar to that used in our study captures the electronic structure of U$_4$O$_9$ and U$_3$O$_7$ measured by X-ray absorption spectroscopy (XAS) very well$^{237}$. This indicates that application of U and J parameters derived for UO$_2$ to UO$_{2+x}$ is accurate enough to support qualitative conclusions derived for UO$_{2+x}$ and at this point the best possible.
APPENDIX A
TENSOR OPERATIONS

A single uranium vacancy can migrate to its twelve nearest neighbors along <110>. As discussed in the main text, the uranium vacancy migration path is complicated, involving two saddles (S1 and S2 in figure A1) along a curved path (Fig. 6-4), rather than a simple transition between nearest uranium sites along <110> directions. Given two-fold symmetry along <110> direction and the curved migration path, each migration direction actually consists of four paths, making for a total of forty-eight possible paths for a uranium vacancy to migrate to its nearest neighbor positions along <110> directions. To obtain a full KMC catalog of dipole tensors for single uranium vacancies (involving forty-eight paths and ninety-six saddles, as each path has two saddles), we performed symmetry operations on the dipole tensor of the saddle from the DFT calculations, to obtain dipole tensors for all other symmetrically equivalent paths. These symmetry operations can be characterized by performing simple tensor operations, defined as

\[ \bar{A} = RAR^T \]

where \( A \) is any second-rank tensor and \( \bar{A} \) is the final resultant tensor after applying the symmetry operation. \( R \) is the reflection or rotation matrix depending on the specific symmetry operation and \( R^T \) is its corresponding transpose. In our calculations, the general form of matrix \( R \), involving rotation about an axis oriented along a arbitrary unit vector \( \langle u, v, w \rangle \) by angle \( \theta \) is given by\(^{241}\)

\[
R = \begin{bmatrix}
    u^2 + (1-u^2)\cos\theta & uv(1-\cos\theta) - w\sin\theta & uv(1-\cos\theta) + w\sin\theta & 0 \\
    uv(1-\cos\theta) + w\sin\theta & v^2 + (1-v^2)\cos\theta & vw(1-\cos\theta) - usin\theta & 0 \\
    uv(1-\cos\theta) - w\sin\theta & vw(1-\cos\theta) + usin\theta & w^2 + (1-w^2)\cos\theta & 0 \\
    0 & 0 & 0 & 1
\end{bmatrix}
\]
Figure A-1  Schematic of four equivalent paths along one particular [110] direction and steps on how to obtain the dipole tensors for four paths along a specific [110] direction.

First, the symmetry operations are applied to obtain dipole tensors for both saddles for the four-degenerated path along a single [110] direction, followed by symmetry operations to obtain the saddle for all the remaining in-plane and out-of-plane directions. As shown in Figs. A1A and A1B, paths 1, 2, 3 and 4 corresponds to transitions from the initial state M0 to final state M1 along [110]. Dipole tensors for path 1 when reflected through the (-110) and (001) planes give dipole tensors for path 2 and 3, respectively, and the dipole tensors for path 4 can be obtained by reflection of path 2 across the (001) plane. In-plane dipole tensors along [1-10] (M0 → M2), [-1-10] (M0 → M3) and [-110] (M0 → M4) are obtained by rotating path 1 (M0 → M1) by 90°, 180° and 270°, respectively around the [001] axis, followed by the same set of reflections as for [110] (M0 → M1), to obtain dipole tensors for all equivalent paths along those directions. Out-of-plane dipole tensors, i.e. for planes (100) and (010), are obtained by 90° clockwise rotation of [110] (M0 → M1) around [010] and 90° anticlockwise rotation of [110] (M0 → M1) around [100], respectively.
APPENDIX B
CHARGE DEFECT ALIGNMENT CORRECTION

The general FNV formalism for potential alignment correction is described in references\(^6^8\),\(^6^9\). The three-dimensional model charge density is taken of the Gaussian form, given as

\[
\rho_{\text{model}}(r) = \frac{q}{\sigma^3 \sqrt{2\pi}} \exp \left( -\frac{r^2}{2\sigma^2} \right) \tag{B-1}
\]

where, \(r\) is the atomic position in real space, \(\sigma\) is the width of the Gaussian, taken in Å, and \(q\) is the total charge in eV. In the reciprocal space, using a discrete Fourier transform\(^2^4^2\) it reads as

\[
\rho_{\text{model}}(G) = \frac{q}{N} \exp \left( -\frac{G^2}{2\sigma^2} \right) \tag{B-2}
\]

where, \(G\) is the reciprocal space vector and \(N\) is the Fourier normalization constant. The long-range electrostatic potential in reciprocal space is given as\(^6^9\)

\[
V_{\text{model}}(G \neq 0) = \frac{4\pi}{\sqrt{\Omega}} \frac{\rho_{\text{model}}(G)}{|G|^2},
\]

\[
V_{\text{model}}(G = 0) = 0 \tag{B-3}
\]

The real space model potential is obtained from inverse discrete Fourier transform, given as

\[
V_{\text{model}}(r) = \frac{1}{\sqrt{\Omega}} \sum_G V(G) \exp(iG \cdot r) \tag{B-4}
\]

Therefore equations B-1 – B-4 are useful to compute the \(V_{\text{model}}(r)\) and then use it to compute the alignment correction (\(\Delta V\)) using Eq. (8-15), by taking the difference between the DFT potential (\(V^{\text{DFT}} = V^{\text{DFT}}[\text{defect}] - V^{\text{DFT}}[\text{bulk}]\)) and the model charge long-range potential \(V_{\text{model}}(r)\). The potentials averaged over X-Y plane are plotted along the Z-axis as shown in Fig. B-1 and B-2, along with
their difference. The difference between the $V_{DFT}$ and $V_{model}$ reaches a plateau at $C = -\Delta V$. 

Figure B-1  Charge alignment correction of vacancy of Gallium (charge -3) in a 3x3x3 cubic GaAs supercell. The electrostatic potentials are averaged along X, Y-axes. The defect is located at $Z = 10.46$ Å.

Figure B-2  Charge alignment correction of Silicon interstitial (charge 1+) in a 2x2x2 cubic Si supercell. The electrostatic potentials are averaged along X, Y-axes. The defect is located at $Z = 4.96$ Å.
APPENDIX C
ENERGY VS. VOLUME USING DFT CALCULATIONS

The energy vs. volume (E-V) profile for both perfect crystal and for a defect (in this case a uranium vacancy) is obtained by performing energy minimization runs in VASP at set of different volumes. The shape and size of the supercell are kept fixed for a given volume and only the atomic positions are allowed to relax (ISIF= 2). The E-V calculations are performed starting from the converged wave functions (using WAVECAR file) for the minimized perfect and defect structure, respectively. This is done to avoid that the self-consistency loop in DFT getting stuck in a metastable configurations of the localized uranium f-electrons\textsuperscript{205}, as shown in Fig. C-1. The bulk modulus and lattice parameter (Table C1) are estimated by fitting the energy and volume data to the Birch-Murnaghan equation of state\textsuperscript{243}.

![Figure C-1](image)

**Figure C-1** Energy of the perfect UO\(_2\) obtained as function of volume, obtained volume for the minimum energy is 1944.36 Å\(^3\) and energy of the supercell with a single uranium vacancy (charge -4) as function of volume, the volume obtained at the energy minima is 1984.75 Å\(^3\).

**Table C-1** Computed lattice parameter and bulk modulus using Birch-Murnaghan equation of state fit to the energy-volume data, as shown in Fig. C-1.

<table>
<thead>
<tr>
<th></th>
<th>Perfect UO(_2)</th>
<th>Uranium vacancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter (Å)</td>
<td>5.451</td>
<td>5.487</td>
</tr>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>220.53</td>
<td>203.53</td>
</tr>
</tbody>
</table>
APPENDIX D
STRAIN FIELD OF DISLOCATIONS IN ANISTROPIC MEDIA

The analytical expressions for the isotropic strain and displacement field of edge and screw dislocations are well known. The general problem of strain field of a dislocation in anisotropic media, also known as the sextic anisotropic elasticity theory of straight dislocation, involves complex mathematics and most of the discussion on anisotropic analytical solutions is restricted to special dislocation orientations. The basic stress and strain relations are given as

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} ; \quad \varepsilon_{kl} = \frac{1}{2} \left( \frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right)$$  \hspace{1cm} (D-1)

For cubic symmetry (in the X, Y and Z coordinate system), the elastic constant matrix, $C_{ij}$, for fluorite-structured, UO$_2$ as calculated using the Grimes empirical potential is given as

$$C \ (GPa) = \begin{bmatrix}
524.13 & 147.24 & 147.24 & 0.0 & 0.0 & 0.0 \\
147.24 & 524.13 & 147.24 & 0.0 & 0.0 & 0.0 \\
147.24 & 147.24 & 524.13 & 0.0 & 0.0 & 0.0 \\
0.0 & 0.0 & 0.0 & 146.76 & 0.0 & 0.0 \\
0.0 & 0.0 & 0.0 & 0.0 & 146.76 & 0.0 \\
0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 146.76
\end{bmatrix}$$  \hspace{1cm} (D-2)

Figure D-1  Cubic axes, and orientation of (B) $\frac{1}{2}a<110>[001]$ edge dislocation, (C) $\frac{1}{2}a<110>[110]$ edge dislocation.
To analyze the strain and displacement field for dislocation, the reference axis should be oriented with respect dislocation axes (X’, Y’, and Z’). Figure D-1 shows the axes for the \( \frac{1}{2}a<110>\{001\} \) and \( \frac{1}{2}a<110>\{110\} \) dislocations in Fluorite structure. The elastic constant matrix, \( C_{ij}' \), in X’, Y’ and Z’ axes is given by tetragonal geometry and can be obtained by rotation of about 45° about the Z [001] axis.

\[
C'(\text{GPa}) = \begin{bmatrix}
C_{11}' & C_{12}' & C_{13}' & 0 & 0 & 0 \\
C_{12}' & C_{11}' & C_{13}' & 0 & 0 & 0 \\
C_{13}' & C_{13}' & C_{33}' & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44}' & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44}' & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}'
\end{bmatrix}
\]

\[
C_{11}' = 482.45 \\
C_{33}' = 524.13 \\
C_{44}' = 146.76 \\
C_{66}' = 188.45 \\
C_{12}' = 188.92 \\
C_{13}' = 147.24
\]

(D-3)

D.1 \( \frac{1}{2} a<110>\{110\} \) Edge Dislocation

For this edge dislocation orientation, the dislocation line is along Z’ [001] axis, and the Burgers vector is along X’ [110] axis. From elastic constant matrix, \( C_{ij}' \)

\[
\cos 2\phi = \frac{c_{12}'^2 + 2c_{12}'c_{66}' - c_{11}'}{2c_{11}'c_{66}'}
\]

(D-4)

\[
c_{11}' = (C_{11}'C_{22}')^{1/2}
\]

(D-5)

2\( c_{66}' + c_{12}' - c_{11}' > 0 \); The equation gives real angles \( \phi \), and the anisotropic solution to the displacement field due to the edge dislocation is given by \( (u_x, u_y, 0) \)

\[
u_x = -\frac{b_X}{4\pi} \left[ \left( \tan^{-1} \left( \frac{2xy\sin(\phi)}{x^2 - \lambda^2 y^2} \right) \right) + \left( \frac{c_{11}' - c_{12}'}{2c_{11}'c_{66}'\sin(2\phi)} \ln \frac{q}{t} \right) \right]
\]

(D-6)

\[
u_y = \frac{\lambda b_X}{4\pi c_{11}'\sin(2\phi)} \left[ (c_{11}' - c_{12}') \cos(\phi) \ln(qt) - (c_{11}' + c_{12}')\sin(\phi) \tan^{-1} \left( \frac{y^2\lambda^2\sin(2\phi)}{x^2 - \lambda^2 y^2\cos(2\phi)} \right) \right]
\]

(D-7)

Where,

\[
b_X = 3.86 \text{ Å} \quad \lambda = \left( \frac{c_{11}'}{c_{22}'} \right)^{1/4} = 1 \quad \cos(2\phi) = -0.236 \quad \phi = 51.82^\circ \text{ and,}
\]
\( q^2 = x^2 + 2xycos(\phi) + y^2; \ t^2 = x^2 - 2xycos(\phi) + y^2 \) 

(D-8)

Gives,

\[
\begin{align*}
 u_x &= -\frac{b_x}{4\pi} \left[ \left( tan^{-1} \frac{1.57xy}{x^2-y^2} \right) + \left( 0.87 \ln \frac{q}{t} \right) \right] \\
 u_y &= \frac{b_x}{4\pi + 314.7} \left[ 78.12 \ln(qt) - 409.81 tan^{-1} \left( \frac{0.972y^2}{x^2+0.236y^2} \right) \right]
\end{align*}
\]

(D-9)

(D-10)

And, strain field using Eq. (D-1) are given as,

\[
\begin{align*}
 e_{xx} &= \frac{\partial u_x}{\partial x}; \ e_{yy} = \frac{\partial u_y}{\partial y}; \ e_{xy} = \frac{1}{2} \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right) \\
 e_{xx} &= \frac{0.811x^6y^5+0.541x^4y^3+0.894x^2y^5+0.153y^7}{x^8+0.952x^6y^2+2.226x^4y^4+0.952x^2y^6+y^8} \\
 e_{yy} &= \frac{-0.7405x^6y^5-0.20875x^4y^3-0.668x^2y^5+0.1526y^7}{0.99x^8+0.958x^6y^2+2.229x^4y^4+0.958x^2y^6+y^8} \\
 e_{xy} &= \frac{-0.33x^{11}+0.017x^9y^2-0.423x^7y^4+0.420x^5y^6-0.023x^3y^8+0.33xy^{10}}{x^{12}+1.424x^{10}y^2+3.68x^8y^4+2.96x^6y^6+3.68x^4y^8+1.42x^2y^{10}+1.001y^{12}}
\end{align*}
\]

(D-11)

(D-12)

(D-13)

D.2 \( \frac{1}{2} a<110>{001} \) Edge Dislocation

For \( \frac{1}{2} a<110>{001} \) edge dislocation, the dislocation line is along \( Z'[-110] \) and the Burgers vector along \( X'[110] \), therefore in above expressions \( C'_{66} = C'_{44}, C'_{12} = C'_{13}, C'_{11} = C'_{11}, C'_{22} = C'_{33} \) with \( 2C'_{44} + C'_{13} - C'_{11} < 0 \) and \( \phi = \frac{\pi}{2} - \delta \), where \( \delta \) is real and given by

\[
Cosh 2\delta = \frac{\bar{C}_{11}^2 - \bar{C}_{13}^2 - 2\bar{C}_{13}C'_{44}}{2\bar{C}_{11}C'_{44}}
\]

(D-14)

\( \delta = 36.62 \text{ degrees or 0.639 radians} \)

The anisotropic solution to the displacement field due to the edge dislocation is given\(^99\) by \((u_x, u_y, 0)\)
\[ u_x = -\frac{b_x}{4\pi} \left[ \left( \tan^{-1} \frac{2xy\lambda \sin(\phi)}{x^2 - \lambda^2 y^2} \right) + \left( \frac{C_{11}^2 - C_{12}^2}{2C_{11}'C_{66}'\sin(2\phi)} \ln \frac{q}{t} \right) \right] \quad \text{(D-15)} \]

\[ u_y = \frac{\lambda b_x}{4\pi C_{11}' \sin(2\phi)} \left[ (C_{11}' - C_{12}') \cos(\phi) \ln(qt) - (C_{11}' + C_{12}') \sin(\phi) \tan^{-1} \left( \frac{y^2x^2\lambda^2 \sin(2\phi)}{x^2 - \lambda^2 y^2 \cos(2\phi)} \right) \right] \quad \text{(D-16)} \]

Where,

\[ q^2 = x^2 + i2xy\lambda \sinh(\delta) + y^2\lambda^2 = x^2 + 1.31ixy + 0.92y^2 \quad \text{(D-17)} \]

\[ t^2 = x^2 - i2xy\lambda \sinh(\delta) + y^2\lambda^2 = x^2 - 1.31ixy + 0.92y^2 \quad \text{(D-18)} \]

Gives,

\[ u_x = -\frac{b_x}{4\pi} \left[ \left( \tan^{-1} \frac{2.32xy}{x^2 - 0.922y^2} \right) + \left( 1.41 \tan^{-1} \frac{1.31xy}{x^2 + 0.922y^2} \right) \right] \quad \text{(D-19)} \]

\[ u_y = \frac{b_x}{4\pi + 605.84} \left[ 144.13 \ln(qt) + 297.76 \ln \left( \frac{x^2 + 0.25y^2}{x^2 + 2.31y^2} \right) \right] \quad \text{(D-20)} \]

Strain will be given as,

\[ e_{xx} = \frac{-1.281x^6y + 4.68x^4y^3 + 1.58x^2y^5 + 0.112y^7}{x^8 + 7.09x^6y^2 + 14.28x^4y^4 + 6.02x^2y^6 + 0.72y^8} \quad \text{(D-21)} \]

\[ e_{yy} = \frac{-0.664x^6y - 2.238x^4y^3 - 0.127x^2y^5 + 0.1024y^7}{x^8 + 7.12x^6y^2 + 14.33x^4y^4 + 5.96x^2y^6 + 0.70y^8} \quad \text{(D-22)} \]

\[ e_{xy} = \frac{-0.567x^{11} - 3.51x^9y^2 - 4.40x^7y^4 + 4.09x^5y^6 + 2.75x^3y^8 + 0.377xy^{10}}{x^{12} + 10.65x^{10}y^2 + 40.36x^8y^4 + 62.72x^6y^6 + 33.96x^4y^8 + 7.54x^2y^{10} + 0.59y^{12}} \quad \text{(D-23)} \]
LIST OF REFERENCES


192 E. Hartmann, An Introduction to Crystal Physics (University College Cardiff Press, 1984).


BIOGRAPHICAL SKETCH

Anuj Goyal was born in New Delhi, India. He received his Bachelor of Technology in Metallurgical and Materials Engineering from Indian Institute of Technology, Madras, in 2010. He joined Department of Materials Science and Engineering at University of Florida, in August 2010 and began his Ph.D. under supervision of Prof. Simon R. Phillpot in January 2011. He received Master of Science from the University of Florida in December 2012. During his doctoral research he spent roughly a year from fall of 2013 to summer of 2014 working with Dr. Blas P. Uberuaga and Dr. David A. Andersson in the Materials Science and Technology Division – 8 at Los Alamos National Laboratory. He is the member of Tau Beta Pi, Engineering Honor Society and was awarded Outstanding International Graduate Student Award at University of Florida in 2014. He received his Ph.D. from the University of Florida in August 2015.