AN OFF-LATTICE KINETIC MONTE CARLO METHOD FOR THE INVESTIGATION OF GRAIN BOUNDARY KINETIC PROCESSES

by

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ABSTRACT

Kinetic Monte Carlo (KMC) methods have the potential to extend the accessible timescales of off-lattice atomistic simulations beyond the limits of molecular dynamics by making use of transition state theory and parallelization. However, it is a challenge to identify a complete catalog of events accessible to an off-lattice system in order to accurately calculate the residence time for KMC.

Possible approaches to some of the key steps needed to address this problem are developed in this thesis. After validating these methods in the study of vacancy diffusion, we implemented our off-lattice KMC method to study the kinetic behavior of the $\Sigma 5 \ (210)$ grain boundary (GB) in copper. We found that the activation energy associated with intrinsic diffusion at this GB is between the activation energies of interstitial diffusion and vacancy diffusion. We have also measured GB mobility in this system and found the activation energy of GB migration to be similar to that of bulk diffusion. For comparison, we have performed a molecular dynamics study of this target GB and obtained diffusivity and mobility estimates that are sufficiently similar to our KMC results at high temperatures. At low temperatures, the molecular dynamics simulations did not yield meaningful predictions. The results of this case study indicate that the off-lattice KMC method developed herein may provide a means to study GB kinetic properties under conditions and timescales that were previously inaccessible.

Towards the end of developing predictive relationships to describe GB kinetic properties, we have begun to assess whether the normalized ground state residence time of a GB is a good predictor of kinetic behavior by analyzing several low-CSL GBs. We see a clear relationship between normalized ground state residence time and kinetic properties for the GBs considered so far. A more thorough investigation will be required to establish whether or not these preliminary findings indicate a more general relationship.
ACKNOWLEDGMENTS

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Collaboration with Dr. Mansoo Park provided an opportunity for an early demonstration and experimental validation of some of the methods employed in this thesis, and I am grateful for this partnership. Peter Mahler Larsen was a visiting member of the Schuh Group in the past year, and his work in developing a fast method for point registration was invaluable to this thesis. In the past two years, I have had the pleasure of working with Sabrina Ball, who has recently earned her Master’s Degree from the Mechanical Engineering Department at MIT. Sabrina worked on extending our understanding of how the behavior of kinetic events can change in the presence of an applied load. Her work has made a real contribution to the broader field, and I am grateful to have had the chance to work closely with her during her time here.

My advisor, Professor Schuh, provided the initial and continued vision for my thesis project and has been a consistent partner in problem solving for the duration of this work. He has always offered a rare combination of enthusiasm and encouragement paired with an unyielding commitment to scientific rigor, while demonstrating a genuine concern for my personal well-being and professional growth. I feel privileged to have had the opportunity to work with him.

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ACRONYMS

GB  Grain Boundary
LAE  Local Atomic Environment
MD  Molecular Dynamics
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<th>Acronym</th>
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<tr>
<td>KMC</td>
<td>Kinetic Monte Carlo</td>
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<td>ART</td>
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<td>GBE</td>
<td>Grain Boundary Engineering</td>
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<tr>
<td>FCC</td>
<td>Face Centered Cubic</td>
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<tr>
<td>CSL</td>
<td>Coincident Site Lattice</td>
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<tr>
<td>DSC</td>
<td>Displacement Shift Complete</td>
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<tr>
<td>L-J</td>
<td>Lennard-Jones</td>
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<tr>
<td>EAM</td>
<td>Embedded-Atom Method</td>
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<tr>
<td>LAMMPS</td>
<td>Large-Scale Atomic/Molecular Massively Parallel Simulator</td>
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<td>PES</td>
<td>Potential Energy Surface</td>
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<td>TST</td>
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Grain Boundaries (GBs) are controlling in many mechanisms of materials failure including corrosion cracking, thermal coarsening, creep, and brittle failure [1–31]. These failure mechanisms are the Achilles heel of many advanced materials such as nano-grained materials and materials designed for extreme environments as a result of their large volume fraction of GBs and high performance specifications. However, the properties of individual GBs that mediate these courses of failure (e.g. diffusivity, mobility, sliding rate) can vary by orders of magnitude [32–62]. Grain Boundary Engineering (GBE) techniques, which exploit these vast differences in GB behavior, have been shown to limit GB related failure by increasing the fraction of GBs with properties that are desirable for a given application [34, 63–85]. In spite of many promising case studies, systematic advancement in the field of GBE has been significantly constrained by the lack of predictive theories relating GB structure to kinetic and mechanical properties. Thus, the goal of this thesis is to develop a new set of tools that will provide a means to investigate the predictive GB structure-property relationships that will pave the way for the next generation of GBE.

The development of predictive GB structure-property relationships remains a challenging and unsolved problem largely as a result of the complexity of the GB space. In general, five macroscopic parameters are required to describe GB structure [86–93]. Thus, studies that sample a large number of GBs across the GB space are necessary to explore GB structure-property relationships. However, experiments that can probe the properties of individual GBs are time consuming, and often the interfaces studied in these experiments are poor representations of those that would occur in a real specimen [58, 60, 94, 95]. For these reasons, the study of GB structure-property relationships is well suited to a computational approach, as computational methods have advantages over their experimental counterparts both in terms of the throughput of GBs that can be tested and the flexibility in GB geometries that can be generated. To date, the most extensive attempts to systematically investigate GBs across the GB space have all been computational in nature [59, 96–99].

As of yet, even the largest studies have been unsuccessful in the development of predictive GB structure-property relationships. The reason for this is that current computational tools have not been designed for the investigation of GB kinetic properties. In particular, traditional computational simulations have gener-
ally been limited to modeling timescales of only a few hundred picoseconds [59, 100–103]. Conversely, physical experiments are often on the order of at least several hundred seconds, but can be much longer (days or weeks) depending on the properties being investigated [56, 66, 104–107]. In order for simulations to probe physically observed phenomena, this time-scale disparity has required the use of non-physical parameters in computational approaches, such as very high temperatures and driving-forces, possibly at the cost of producing meaningful results.

The work in this thesis was motivated by the hypothesis that an off-lattice Kinetic Monte Carlo (KMC) approach to investigating GB kinetic properties could provide a means for performing high-throughput computational studies of GBs under experimentally relevant conditions. If successful, such a method could allow for large-scale kinetic studies of GBs across the five-parameter space, opening the door for the determination of predictive relationships between GB structure and their kinetic and mechanical properties.

1.1 RESEARCH QUESTIONS ADDRESSED BY THIS THESIS

Having established the need for predictive GB structure kinetic-property relationships, and noting that the lack of well-suited methods for GB investigations that can both probe experimentally relevant conditions and scale across the 5-parameter space is largely responsible for the presence of this gap in the literature, the present thesis work, which develops an off-lattice KMC method, addresses the following questions:

• How can we ensure reliable calculation of residence times in off-lattice KMC simulations? How do we uniquely define Local Atomic Environments (LAEs) and kinetic events? How do we compare these events and effectively store their information? How can we efficiently calculate effective vibrational attempt frequencies of kinetic events?

• Can we simulate physically relevant processes with an off-lattice KMC method? What patterns and forms do GB energy landscapes take? Can we simulate GB kinetic processes with an off-lattice KMC method?

• What timescales and conditions can we simulate using our off-lattice KMC method? What are the limitations of this method? What areas of advancement will further improve this approach?

1.2 STRUCTURE OF THIS DOCUMENT

The content of this thesis is structured into five main chapters:
• Chapter 2: Relevant background information related to GB structure, GBE, the methods used to investigate GB properties in prior studies, and relevant computational approaches used in materials science are presented. This chapter is intended to introduce the general reader to the fields of GB science and computational materials science; it can be omitted without loss of continuity by anyone already versed in these topics.

• Chapter 3: The methods developed to build an off-lattice KMC algorithm that reliably calculates residence time are presented here.

• Chapter 4: The methods developed in the previous chapter are implemented and optimized for the reliable calculation of residence time.

• Chapter 5: The off-lattice KMC algorithm presented in this thesis is validated in the study of vacancy diffusion in copper. The time-scaling of the algorithm as a function of various parameters is characterized.

• Chapter 6: A number of case studies that make use of the algorithm developed here (or parts of it) are presented. These case studies include: the study of grain boundary energy landscapes in several copper GBs; the study of intrinsic diffusion and mobility in the Σ5 (2 1 0) GB in copper along with a comparison to Molecular Dynamics (MD) simulations; and the study of kinetic properties as a function of normalized residence time in a range of special copper GBs.

Following this, concluding remarks and the future directions of this work are discussed, and a number of appendices relevant to the main body of the work are included.
This chapter is intended to provide an introduction to the topics of GBs and computational materials science for those not already familiar with these fields. Those already acquainted with these areas may skip this entire chapter or individual sections within it without loss of continuity.

2.1 GRAIN BOUNDARY STRUCTURE

A GB is formed at the interface of two grains in a polycrystalline material. Each grain has an orientation that can be described by a rotation relating the grain to the canonical orientation of the unit cell, in which the axes of the unit cell are aligned with the Cartesian coordinate system. In Figure 1, two grains, A and B, are highlighted in the 2-D depiction of a polycrystalline specimen, and the parameters describing their geometry are shown.

Figure 1: Illustration of the crystallographic geometry associated with a grain boundary.

The rotations of A and B away from the canonical orientation can be described by the rotation matrices made up of the column vectors \( [x_A, y_A, z_A] \) and \( [x_B, y_B, z_B] \), respectively. Thus, grain A can be related to grain B by the product of the two rotation matrices that first rotate grain A to be coincident with the Cartesian axes,
and then rotate it to coincide with grain B. This product of two rotations generates a new rotation matrix with a corresponding axis and angle of rotation and is an important descriptor of GB geometry called the misorientation. Since the axis of rotation is a unit vector, only two parameters are needed to define it; thus, when the angle of rotation is accounted for, the complete misorientation relationship can be specified by three parameters. Due to crystallographic symmetry, numerous axis-angle pairs can be used to describe this rotational relationship; however, the pair that minimizes the rotation angle is conventionally used to describe a misorientation, with the minimum rotation angle often referred to as the disorientation angle.

In addition to the misorientation relating the grains, the crystallographic planes that meet at the interface must be specified in order to fully describe the geometry of a GB. As illustrated on the right side of Figure 1, the vectors $[hkl]_A$ and $[hkl]_B$ denote the direction normal to the interface for grains A and B, respectively. As unit vectors, these vectors can be specified by only two parameters. Additionally, if the rotational relationship between two grains is characterized by their misorientation, then one interface normal can be obtained by transforming the other through the rotation matrix. As such, five independent parameters (three to define the misorientation relation and two to define the interface normal) are required to specify macroscopic GB geometry.

At the atomic scale, an additional three parameters, $t_x$, $t_y$, $t_z$, are also required to describe the translational position of the GB along the GB plane. In a physical specimen, these microscopic parameters will take on whatever value will minimize the GB energy [108]; in computational models they must be directly accounted for when generating a ground state GB, as will be discussed later in this document. For practical purposes, the five macroscopic parameters previously mentioned, describing relative and absolute grain orientation, are required to specify a GB. For this reason, GBs are said to exist in a 5-dimensional or 5-parameter space, which will be discussed in greater detail in the next section.

There are a number of different standards by which these five parameters are delineated. The three parameters that describe the rotation $A \rightarrow B$ are most commonly reported as either an axis angle pair: $\theta [h k l]$ (as mentioned above), or as a set of Euler angles: $\varphi_1$, $\varphi_2$, $\Phi$ [108].

One special type of rotation in GB crystallography is the Coincident Site Lattice (CSL) misorientation for which all elements in the rotation matrix are rational numbers that share a least common denominator, $\Sigma$ [109]. $\Sigma$ has the property of
being equal to the reciprocal of the fraction of atoms that are coincident across a given GB. \( \Sigma \) can also be represented as a quaternion of integers \([86, 109]\):

\[
q/|q| = [\cos(\theta/2) \ n_1 \ \sin(\theta/2) \ n_2 \ \sin(\theta/2) \ n_3 \ \sin(\theta/2)]
\]  
(1)

where \( \theta \) and \( n \) correspond to the axis angle pair description mentioned above. The sum of squares of the integer components of \( q \) are equal to \( \Sigma, 2\Sigma, \) or \( 4\Sigma \) (where \( \Sigma \) is always an odd integer). This representation provides a powerful means to generate the parameters of all possible GBs with a given \( \Sigma \).

Another important aspect of GB crystallography derives from the periodic nature of GBs: the Displacement Shift Complete (DSC) lattice is the lattice that is defined by the translation vectors of the GB itself [87]. The DSC is a useful construct because it defines the size of the region that must be explored when optimizing the microscopic, translational parameters \((t_x, t_y, t_z)\) associated with the ground state configuration of a GB. For example, if the DSC lattice vectors have lengths of \( D_x, D_y, D_z \), then only combinations of values between \( 0 \) and \( D_i \) must be considered for each \( t_i \) (where \( i \in (x, y, z) \)), as all translations beyond this region are periodically related to configurations within it.

In addition to these mathematical descriptors of a GB in the 5-parameter space, there are a number of other structural metrics that are used to characterize GBs. For example, free volume, faceting periodicity, and similarity to the coherent twin [92] are all structural features that have been used to try and understand the relationship between GB structure and properties. Among these, free volume is a particularly important structural descriptor to take note of; it is the free volume within the GB that facilitates the occurrence of kinetic mechanisms such as atomic diffusion along and across the GB, which are key in the kinetic behavior of GBs and the failure processes that they control. However, as we will see shortly it is not just the magnitude of the free volume, but its distribution throughout the GB plane that influences GB kinetics.

2.2 GRAIN BOUNDARY SPACE

The symmetry-reduced set of GBs that can be generated by varying the five macroscopic parameters required to describe GB structure discussed in the previous section make up the GB space. Any study that successfully relates GB structure to properties must sufficiently sample the GB space. A number of methods have been used to sample from GB space in past studies including: sampling from the CSL GBs [110]; building all possible GBs with a DSC less than some specified value [59, 99] (this case accounts for the largest effort to probe GB space, to date, in...
which 388 Face Centered Cubic (FCC) GBs were studied); or sampling around the high-symmetry axes of a crystal system [93]. An alternative approach could make use of recent developments in EBSD technology wherein the grains visualized in an EBSD image can be color-coded [91] by orientation; under this approach grain orientation data from a physical specimen could be used to design a set of GBs to use in high-throughput studies.

Past efforts to develop predictive relationships between GB structure and properties have been undertaken, making use of the sets of GBs described above, the largest of which was a study of 388 FCC GBs [59, 99]. Examples of the results from this study are shown in Figure 2 from Ref. [99], where we note that only free volume shows a clear correlation with GB energy.

A recent study made use of the data from Ref. [99] in developing a relationship between GB energy and structural parameters [93]; however the usefulness of this relationship in predicting GB properties is somewhat questionable, as a set of 388 GBs cannot sufficiently survey $\mathbb{R}^5$. A plot of the predictive function developed in this study is shown in Figure 3.

More commonly, however, attempts to relate GB structure to properties show a lack of correlation between the structural parameters considered (such as disorientation angle, plane inclination, $\Sigma$, and free volume) and kinetic behavior. An example of the results found in [59], in which structural parameters were compared with GB mobility is reprinted from [59] in Figure 4. In this case, we see that mobility does not seem to correlate with any of the structural parameters considered here, including both free volume and energy. This result demonstrates the complexity associated with finding predictive relationships for GB kinetic properties. Intuitively, one might expect that GBs with higher energy (i.e. GBs that are less stable) or have more free volume might be more mobile, but the data in Figure 4 do not support such a conclusion.

It is the hypothesis of the present work that one reason the identification of predictive relationships for GB kinetic properties has been so difficult is that past studies have focused on global GB metrics (such as energy, free volume, and disorientation angle), rather than metrics that reflect the topographical diversity within the boundary. If we pursue GB descriptors that are reflective of their energy landscapes— the range of kinetic events accessible to a GB— it may be possible to shed new light on the problem of predicting GB properties.
Figure 2: Plots of GB energy vs. (a) disorientation angle (b) Σ and (c) excess (free) volume. Only in the case of free volume is there a clear correlation between GB energy and the structural parameter, in which GB energy is seen to follow an increasing trend with free volume. These graphs are reproduced here for pedagogical purposes and were originally published in Ref. [99].

2.3 GRAIN BOUNDARY ENGINEERING

Knowledge of GB space and predictive relationships between structure and properties are of such great interest due to the extensive variance in kinetic properties
among GBs of different geometry. For example, Figure 5 shows data comparing the intergranular corrosion depth in a copper specimen for GBs with different geometry [111]. Here, the structural metric used to specify a GB is the interplanar spacing associated with the GB plane, \( d \), normalized by the lattice constant, \( a \). From Figure 5, it can be seen that GBs with larger interplanar spacing tended to have higher corrosion resistance [111]. Additionally, some GBs showed almost no evidence of corrosion during the experiment (e.g. the \( \Sigma 3 \) and \( \Sigma 1 \) GBs with the largest \( d/a \)), while the most susceptible GBs exhibited a corrosion depth of over 0.25 \( \mu \)m (the \( \Sigma 3 \) GB with the smallest \( d/a \)) during the three hour exposure window.

This dramatic difference in GB properties begs the question: can we design a corrosion-resistant specimen by controlling the types of GBs in a material? As previously mentioned, the variation in properties between GBs of different geometry is seen across the spectrum of GB kinetic properties, including cracking, mobility, sliding, and diffusion, and is not limited to corrosion resistance. Additionally, many of the failure events mediated by these kinetic properties are percolative phenomena, i.e. they occur only when a connected path of failed GBs span the sample diameter. Thus, we can ask the broader question: can we control macroscale materials properties by controlling the types of GBs and their connectivity within a specimen?

The response to this question is the field of GBE— a now decades-old technique that seeks to exploit the differences in individual GBs across the GB space and the
Figure 4: Plot of GB mobility vs. (a) disorientation angle (b) Σ (c) excess (free) volume and (d) GB energy. There are no apparent trends relating GB structure to mobility from this data. These graphs are reproduced here for pedagogical purposes and were originally published in Ref. [59].

properties of the GB network in order to optimize for a given set of properties in a macroscopic specimen [80, 112]. The processing methods associated with GBE generally incorporate a regimen of thermomechanical cycling in which a specimen is iteratively cold-rolled and annealed, with the net result of generating a drastically increased fraction of interconnected Σ3n (twin) boundaries in the specimen, while having minimal effect on grain size or texture [80]. As the increased presence of specific GBs (initially thought to be any low-CSL GBs, but eventually understood to be largely twin boundaries) resulted in significant property improvements [78, 79], these GBs were often considered to be ‘special’. From this began a two-tiered classification convention in which GBs were categorized as either ‘special’ or ‘general’ with regard to a prescribed macroscopic behavior (e.g. resistance to intergranular cracking, superplasticity, corrosion resistance). The importance of Σ3n boundaries was often paramount in these studies, and, as such, GBE techniques have largely been limited to low-stacking-fault energy FCC alloys such as copper and nickel in which annealing twins readily form [80]. An example of a specimen that was engineered (via GBE) to have superior intergranular corrosion resistance
BACKGROUND

Figure 5: Plot of GB corrosion vs. normalized interplanar spacing of the GB plane $d/a$. There is a general trend indicating that larger interplanar spacing correlates with slower corrosion; the variation in behavior between these GBs of different geometry demonstrates the importance of understanding how the GB space maps to GB properties. This graph is reproduced here for pedagogical purposes and was originally published in Ref. [111].

is shown in Figure 6 [79].

Figure 6: Images of a Fe-35Ni-25Cr samples that underwent 120 hours of ASTM G28—a corrosion test in which the specimen is placed in a 50:50 mixture of boiling ferric sulfate and sulfuric acid. The image on the left shows a specimen with 44% ‘special’ boundaries, while the image on the right was processed to have 83% ‘special’ boundaries. From these optical micrographs it is clear that the non-GBE sample failed due to intergranular corrosion (i.e. along the GBs), while the GBE sample was resistant to corrosion. These images are reproduced here for pedagogical purposes and were originally published in Ref. [79].
As new perspectives on GB structure, crystallography and symmetry have developed [90–92, 113] and understanding of GB networks and connectivity has advanced [81, 82, 114–116], researchers in the field of GBE continue to explore both the limits of what property improvements can be achieved with GBE as well as how GBE materials can be processed to reach those limits beyond annealing twins and thermomechanical cycling alone. However, the theoretical limits of what GBE can attain is still largely a matter of speculation, bounded by our incomplete understanding of GB structure-property relationships.

2.4 GRAIN BOUNDARY KINETIC AND MECHANICAL PROPERTIES

The purpose of this thesis is to provide a new computational tool for studying GB kinetic properties such that predictive relationships between GB structure and kinetic and mechanical properties may be developed. As a result, it is useful to outline the scope and nature of the specific GB properties of interest. In general, GB kinetic and mechanical properties encompass all properties that govern dynamic GB behavior including how a GB moves through the bulk (mobility), how individual atoms or clusters diffuse across or along a GB (diffusivity), and the manner in which adjacent grains slide past one another (sliding). Each of these topics is briefly introduced below.

2.4.1 Grain Boundary Mobility

GB migration refers to the movement of a GB into a neighboring grain. Though it is central to GB kinetics, the true nature of GB migration is not well understood. In simple models of GB migration, in which migration of a GB is treated as arising from diffusive jumps of individual atoms across the boundary, driven by a free energy difference between two grains [95], velocity, \( v \), is found to be proportional to a driving force, \( p \), according to:

\[
v = M \cdot p
\]

where \( M \) is mobility, which is a property of the GB that follows an Arrhenius temperature dependence:

\[
M = M_0 \exp \left( -\frac{H_M}{k_B T} \right)
\]

where \( H_M \) is the activation energy of GB migration, \( M_0 \) is a pre-exponential factor related to vibrational frequency, and \( k_B T \) is the thermal energy. In Eq. (2), GB motion occurs as a result of a driving force, \( p \), which can originate from a number of sources, but the most relevant to this study are curvature-derived driving forces and magnetic field-derived driving forces [58, 60]. The simplicity of this
model requires that mobility will be the same for either direction of motion, which is not guaranteed [95], and generally predicts, since it relies on a diffusive model, that the upper bound for the activation energy for GB migration will be the activation energy for bulk diffusion. In spite of prior efforts [59], as of yet, there is no predictive theory relating GB mobility to structure.

2.4.2 Grain Boundary Diffusivity

In the most naïve treatments of diffusivity in polycrystalline materials, GBs are treated uniformly as fast-diffusion pathways that short-circuit diffusing atoms through the specimen when compared to bulk diffusion. It is, of course, the case that GB diffusion rates are highly dependent on GB structure [1], and the diffusion kinetics observed for a given polycrystalline specimen will depend strongly both on the types of GBs present in the system as well as their connectivity. Though the activation energies, $E_{m,gb}$, and preexponential factors, $D_0$, for diffusion amongst a given set of GBs will vary, the diffusivity has been observed in all cases to exhibit Arrhenius behavior, just as in the bulk:

$$D_{gb} = D_0 \exp \left( \frac{E_{m,gb}}{k_B T} \right)$$  \hspace{1cm} (4)

As a first approximation, it is often taken that the diffusion activation energy, $E_{m,gb}$, in the GB is on the order of 1/2 that observed in the bulk [1]. However, again, this is a very naïve approach that does not account for differences related to GB structure, which can lead to differences in diffusivities that span more than six orders of magnitude [117]. Attempts to relate GB structure with diffusivity have lead to the qualitative conclusion that there is a correlation between activation energy for GB diffusion with GB energy [117], but, as in the case of GB mobility, predictive theories are still lacking.

2.4.3 Grain Boundary Sliding

GB sliding encompasses a number of deformation mechanisms. Many of these mechanisms are fundamentally network dependent, such as grain rotation, triple junction migration, and coupled GB migration and rotation; however, the bicrystal sliding rate is network-independent, and, as with other GB kinetic properties, GB sliding is highly dependent on GB structure [6, 118].

Analytical models for GB sliding rate have been developed for boundaries with different macroscopic shapes (e.g. sinusoidal, saw-toothed, stepped) for sliding mediated by diffusional creep and ‘pure’ sliding—mediated by dislocation emission [6, 24]. Atomistic treatments of GB sliding have also been considered, and from these, a number of different atomistic mechanisms have been observed to
contribute to GB sliding including both correlated and uncorrelated atomic motion at the GB [118]. In the case of diffusional creep at a stepped boundary, GB sliding rate has been analytically found to follow [6]:

\[ \dot{U} = 4 \frac{\tau_a \Omega \delta}{kT} h^2 D_{gb} \]  

for a shear stress \( \tau_a \), a step height \( h \), GB width \( \delta \), and atomic volume \( \Omega \). In the case of pure GB sliding, mediated by dislocation emission, GB sliding has been found to follow an activated rate law of the form [24]:

\[ \dot{U} = A \sigma^n t^{m-1} \exp\left(-\frac{Q_s}{kT}\right) \]  

with sliding activation energy \( Q_s \), stress \( \sigma \), stress-sensitivity parameter \( n \), and geometric prefactor \( A \). However, these models have not been extended to finite GB structure, and, as of yet, predictive theories relating GB sliding rate to the 5-parameter space have not been developed.

2.5 METHODS TO STUDY GRAIN BOUNDARY PROPERTIES

As a result of their prevalence in virtually all engineering materials and their prominence in dictating materials failure, GBs have been studied for over half a century, and it has been known for almost as long that the properties of GBs vary drastically across the GB space [32, 38]. GBs have been studied theoretically, experimentally, and computationally, and though they are still among the least understood of all lattice defects [108], our current understanding of GB structure and properties is backed by six decades of research and investigation.

As the goal of this thesis is to develop a new tool that will help close the gap in the understanding of GB structure-property relationships, it is valuable to thoroughly consider the nature of experiments and computations that have been performed on GBs to date. Studies of GBs consider either static GB properties, such as structure, energy, and free volume, or kinetic GB properties, such as mobility, diffusivity, and sliding which were introduced in an earlier section. When the properties of distinct GBs are considered, efforts are made to relate the static or kinetic GB properties to descriptors of GB structure such as misorientation, disorientation angle, and inclination angle. As predictive relationships between GB structure and properties have often proven difficult to identify, correlations between static and dynamic GB properties (e.g., relating energy to free volume or energy to mobility) are also often considered.

A vast range of experimental and computational techniques have been developed or utilized for the study of GBs, and an exhaustive evaluation of each of these methods is beyond the scope of this document. However, a discussion of the most
notable techniques and methods used in the study of various GB properties is presented in the following along with comments, where appropriate, regarding their scope, successes, and drawbacks.

2.5.1 Grain Boundary Energy Methods

GB energy (which is sometimes referred to as GB excess energy or simply excess energy) is a measure of the excess energy in a system resulting from the presence of the GB. It is reported as an energy density (per unit area); in atomistic simulations of bicrystals, where the system energy, $E_{total}$, the number of atoms, $N_{atoms}$, and the energy per atom in a defect-free crystal, $e_{atom}$, are all known, the GB energy, $E_{gb}$, can be calculated according to:

$$E_{gb} = \frac{E_{total} - e_{atom} \cdot N}{A_{gb}}$$  \hspace{1cm} (7)

where $A_{gb}$ is the area of the GB plane in the simulation cell. Some of the earliest studies of GB energy were theoretical and computational in nature. As early as 1959, GB energy was estimated from a model in which the excess energy due to the presence of the GB was considered to come entirely from the redistribution of electrons as a result of a gap in the periodic structure of the crystal lattice [119]. Based on the atomic structure of the atoms in the material of interest and the width of the GB region, a solution to the one-dimensional Schrödinger Equation allowed for a first approximation of GB energies.

Later, atomistic computer simulations using first pair potentials and then many-body potentials, such as Embedded Atom Method (EAM) [120] and Finnis-Sinclair [121] potentials, were used to estimate GB energy in bicrystals. It is because of the development of these semi-empirical approaches to calculating energy that the field of atomistic simulation exists, as we know it. As such, the principles of these are briefly described below.

In solid state systems, an atom’s internal energy is dictated by the positions of the atoms surrounding it. Pair potentials approximate the internal energy of an atom as a sum of the energy contributions from interactions with neighboring atoms that are within a pre-specified cutoff distance. Thus, the internal energy of atom $i$ in a system can be approximated as:

$$E_i = \sum_{j=1}^{J} E_{ij}$$  \hspace{1cm} (8)
where \( J \) is the number of atoms within a cutoff distance of atom \( i \), and \( E_{ij} \) is the interaction energy between atoms \( j \) and \( i \). The function used to calculate the interaction energy, \( E_{ij} \), may take many forms, the most familiar of which is the Lennard-Jones (L-J) potential [122]:

\[
E_{ij} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]
\]  

(9)

in which \( r_{ij} \) is the distance between atoms \( i \) and \( j \), and \( \epsilon \) and \( \sigma \) are material-specific parameters, with \( \epsilon \) corresponding to the depth of the potential well when atoms \( i \) and \( j \) are optimally spaced and \( \sigma \) corresponding to this optimal spacing. This potential aptly describes the combination of attractive and repulsive forces that dictate atomic interactions at close and long range. However, the assumption that the internal energy of an atom is just a linear sum of its interaction energy with each surrounding atom is quite simplistic and poorly describes densely packed atoms in solid state systems. A more nuanced approach would account for the non-linearity in the contribution of each interaction energy to the total internal energy of an atom; such methods are called many-body potentials.

In this thesis, potentials employing the Embedded-Atom Method (EAM) approach to generating a many-body potential were used [120]. In this case, the internal energy of an atom is calculated according to:

\[
E_i = F_{\alpha} \left( \sum_{i \neq j} J \rho_{\beta} (r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} J \phi_{\alpha\beta} (r_{ij})
\]  

(10)

\( F \) is the embedding energy, and is a function of the electron density at the location of atom \( j \) if atom \( j \) were not present: \( \rho (r_{ij}) \). \( \phi \) is a pair potential interaction (with a functional form similar to that of the L-J potential, \( \alpha \) and \( \beta \) correspond to the element types of atoms \( i \) and \( j \), respectively, and \( J \) is again the total number of atoms within a pre-specified cutoff distance of atom \( i \).

Both pair and many body potentials are generated semi-empirically by fitting a combination of experimental and computational (from first-principles calculations) data. The total energy of an atomistic system, using either pair or many body potentials, is calculated as the sum over the internal energy of all atoms:

\[
E_{\text{total}} = \sum_{i=1}^{N} E_i
\]  

(11)
In atomistic simulations, GB energy is calculated using Eq. 7 on a bi-crystal of the desired geometry. Generation of the bicrystal itself, however, is a non-trivial task. Two grains of desired orientation are generated, constraining the five macroscopic degrees of freedom described in section 2.1. However, the translational degrees of freedom in GB structure (i.e. the variance in structures that can form if the grains are moved relative to one another along the GB plane) must be taken into consideration when generating a desired GB, as many possible variants will not yield the ground state GB that corresponds to its true, physical form.

Several methods for optimizing the translational degrees of freedom of a simulated bicrystal have been developed. These methods include generation of systems with no periodic boundary conditions, periodic boundary conditions only in the plane of the GB, and periodic boundary conditions in all directions. In the last case, two boundaries are generated and the resulting structure has no free surfaces, while in the first two cases, only one GB and two (or more) free surfaces are generated. In all cases, a series of static minimizations (generally utilizing conjugate-gradient or steepest-descent algorithms at 0 K) each using different translational vectors, allow for the determination the true, minimum energy GB structure for a given GB orientation [123]. Variations on this approach in which atoms are sometimes removed or added to the bicrystal, with the goal of minimizing the Grand-Canonical, rather than Canonical ensemble have been developed [124], sometimes using Monte Carlo techniques to search for the minimum energy structure. A number of commercial and open-source software packages are available for performing static atomistic minimizations of this nature. The open-source molecular dynamics software package: Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [125, 126] was used throughout this thesis. Example code for finding the ground state configuration of a GB that was used in this thesis is included in Appendix A.2.

Experiments designed to measure the relative energy of GBs with different orientation were first performed by applying hydrostatic pressure during annealing to sphere-on-plate specimens with known orientation distributions and analyzing the resulting X-ray spectra [127]. In these experiments, free energy was expected to correlate directly to free volume according to:

\[ G = F + pV_{\text{free}} \]  

(12)

where \( V_{\text{free}} \) is the free volume in the GB, \( p \) is the applied pressure, and \( F \) is the Helmholtz free energy of the boundary. Later experiments used thermal grooving techniques to measure GB energy [94]. In these studies, single-crystal specimens were cut along a specified plane and diffusion bonded in the desired orientation (with nature allowing the sample to relax to the optimal translational degrees of
freedom). The samples were then milled such that the GB of interest made a right angle with the free surface, and, after annealing, the angle of the groove formed at the intersection of the GB with the surface could be related to GB energy according to:

\[ \frac{E_{gb}}{\gamma_s} = \cos \Psi_1 + \cos \Psi_2 \]

(13)

with \( E_{gb} \) being the GB energy, \( \gamma_s \) being the energy of the free surface, and the angles \( \Psi_1 \) and \( \Psi_2 \) being the angles between the surface and surface normal on each side of the groove, as measured with an interference microscope [94]. Images from a GB grooving experiment and a schematic illustrating the terms in Eq. 13 are shown in Figure 7 (note that in this figure, \( \gamma_b \) corresponds to the GB energy that is referred to in this document as \( E_{gb} \)).

Figure 7: Left: Micrograph of a copper GB after a thermal annealing process where a groove at the interface is visible. Right: Schematic of the variables used to calculate GB energy in Eq. 13; note that, in this image GB energy corresponds to the \( \gamma_b \) variable. These images are reproduced here for pedagogical purposes and were originally published in Ref. [94].

In a recent study, a universal function relating GB energy to the 5-parameter GB space for FCC metals has been found [93]. In this study, previously determined GB energy data for 388 GBs [99] in Cu, Al, Ni, and Au was fit to a function with 43 parameters using an interpolation function [93]. As described in section 2.2, this development is the first comprehensive, predictive model of a GB property with respect to the 5-parameter space.
2.5.2  Grain Boundary Free Volume Methods

Few studies of GB properties and structure fail to mention GB free volume as an important GB characteristic. It is generally reported as a “free volume density”: excess volume per unit area, analogous to GB energy. GB free volume is most easily determined from a computational approach in, again, an analogous manner to GB energy. In an atomistic simulation, a minimized GB structure with periodic boundary conditions in all directions and volume $V$, the GB free volume, $V_{\text{free}}$, is:

$$V_{\text{free}} = \frac{V - v_{\text{atom}} \cdot N}{A_{gb}} \quad (14)$$

where, $v_{\text{atom}}$ is the volume per atom in a defect-free crystal and $A_{gb}$ is the grain boundary area in the system. If free surfaces are present in the structure, then the reconstructed lattice near the free surface will also contribute to the free volume calculated in Eq. 14, in which case the Voronoi volume of each atom in the system that is sufficiently far from a free surface can be used to calculate the GB free volume. The Voronoi volume associated with an atom is the volume of a polyhedron with faces made up of the perpendicular bisectors of all vectors between the central atom and its nearest neighbors. An open source software package with tools to quickly calculate these polyhedra and their volumes called Voro++ is useful for performing analysis of free volume in GBs and other complex atomistic defects [128].

Experimentally, GB free volume has proven difficult to quantify [129]. However, recent methods have been developed from which it is possible to measure GB free volume using the thermodynamic argument [129]:

$$V_{\text{free}} = \frac{\partial E_{gb}}{\partial p} \quad (15)$$

where, again $V_{\text{free}}$ is the GB free volume, $E_{gb}$ is the GB free energy, and $p$ is pressure. In this experimental setup, a triple junction with one low angle GB and two identical high angle GBs is grown from seed and the angle that the boundaries make at the triple junction allow for a determination of the GB energy (as described in section 2.5.1). When this experiment is performed at a number of annealing pressures, $V_{\text{free}}$ can be obtained from Eq. 15.

Though free volume is found to correlate with GB energy, there are, as of yet, no predictive models relating GB free volume to the 5-parameter GB space.
2.5.3 Grain Boundary Mobility Methods

As previously introduced, GB mobility is an important kinetic property that governs key microstructural processes such as grain growth and recrystallization. Early studies of GB migration and mobility consisted of measurements of strain-induced GB velocity in high-purity materials [38]. Subsequent studies have used many of the numerous driving forces from which GB motion can be induced, most notably including curvature or capillarity driven [57] and magnetically driven motion [58, 95]. It has been argued that magnetically driven GB motion, since it can be performed on planar GBs, offers a more accurate means of measuring GB mobility than methods that require curved GBs [58]. However, this method is limited to the study of materials with magnetic anisotropy. The advantages of magnetic driving force studies include the ability to calculate direct, rather than reduced, mobilities, and the aforementioned ability to study planar GB geometry, limiting complications that arise as a result of the presence of triple junctions and distortions in low angle GBs with more complex geometries [58]. In these magnetically driven experiments, mobility is determined from Eq. 2, where velocity can be determined by optical microscopy and $p$ is given by:

\[
p = \mu_0 \frac{\Delta \chi}{2} H^2 (\cos^2 \theta_1 - \cos^2 \theta_2)
\]  

(16)

with $\theta_1$ and $\theta_2$ being the angles between the magnetic field and the trigonal axis in each grain and $\Delta \chi$ being the difference in magnetic susceptibility parallel to and perpendicular to the trigonal axis [130]. In contrast, the driving force in capillary driven experiments is given by

\[
p = \frac{E_{gb} f}{a}
\]  

(17)

with $E_{gb}$ having the usual definition of GB energy, $f$ being a geometrical factor, and $a$ being displacement distance. Only a reduced mobility, $M \cdot E_{gb}$, can be derived from these experiments. However, in all experiments, it should be noted that the presence of impurities, even at very low concentrations, can have a very significant effect on the measurements taken. As a result of this, a number of models to treat GB mobility in the presence of solutes have been developed [95].

Most computational methods for studying GB mobility are based on MD approaches. Due to the time-scale limitations associated with MD (several hundred picoseconds, compared with minutes, hours, or longer in experimental studies), corroborating mobility values derived from simulation with experiments is generally not a straightforward endeavor [103, 131–133]. In general, the MD approaches
used fall into one of two classes: driven motion methods and fluctuating boundary methods.

In the first case, GB motion of planar bicrystals is driven by the application of a fictitious energy penalty applied to one side of the GB [59, 134]. The driving forces required to produce measurable GB velocities on MD timescales in this method can produce internal stresses on the order of several GPa, which is much higher than the regimes accessed experimentally, and produce GB velocities on the order of \( \text{m/s} \) while experimental studies generally probe GB motion on the order of \( \text{\mu m/s} \) [103]. As a result of this, the mobilities measured using this method are sometimes orders of magnitude higher than what is observed experimentally, and it is possible for the method to probe mobility outside of the regime in which the linear relation described by Eq. 2 is valid [103].

In the case of fluctuating boundary methods, traditionally, a GB is equilibrated at very high temperatures (on the order of \( 0.8\ T_m \)), and the average position of the GB is tracked over time. From this approach, the mobility of the GB can be determined from a random walk treatment where:

\[
D = \frac{d\langle \Delta^2 \rangle}{dt} \sim \frac{2MkT}{A} \tag{18}
\]

where \( D \) is diffusivity, \( \langle \Delta^2 \rangle \) is the mean-squared average displacement of the GB, and \( A \) is the interface area [102, 135]. This method has been adapted to effectively calculate GB mobility in the zero-driving force limit at much lower temperatures by using a statistical resampling analysis [102]. Deng, et al. adapted this method to incorporate a driving force, which has allowed for a new theory of GB migration to develop, including the demonstration of both diffusive and ballistic regimes of GB migration [101]. This recent work has shown that, at sufficiently high temperatures and pressures, a linear velocity-driving force relationship is not observed for GB motion [101]. The pressure-temperature regime in which Eq. 2 is valid was investigated for several example GBs; Figure 8, originally published in this study, illustrates the transition between mobility mechanisms as a function of temperature and pressure.

In addition to the challenges associated with the temperatures and pressures required to simulate GB motion, it has recently been shown that a system must be sufficiently large in order to accurately probe GB motion [136]. Specifically, it was shown that a key event in GB migration is the formation of an island or plateau of critical size (which is a function of driving force). If a simulation cell is too small, then island formation (and subsequent coalescence) will not be observed, and the simulated kinetic properties may not be valid. Figure 9 was originally published
2.5 METHODS TO STUDY GRAIN BOUNDARY PROPERTIES

Figure 8: A map of the mechanistic regimes of GB mobility for the Σ5 (130) GB in nickle, showing a transition between a diffusive mechanism (in which atom-hopping from one side of the GB to the other is the dominant process) and a ballistic regime (in which concerted motion of clusters of atoms drives GB motion). Only in the diffusive regime is Eq. 2 valid. This image is reproduced here for pedagogical purposes and was originally published in Ref. [101].

in this work: Ref. [136], and shows that there is a driving force-dependent critical system size that must be met in order for this meso-scale mechanism to be observed.

Thus, although a significant amount of work and progress has been made with regard to understanding GB migration and mobility, the complexity of the GB space, coupled with the plethora of possible driving forces that can cause GB motion, and the inherent timescale and size constraints associated with traditional MD approaches to computationally study GB motion, there does not exist a predictive theory relating GB structure with mobility.

2.5.4 Grain Boundary Diffusivity Methods

GB diffusivity is one of the most thoroughly studied properties of GBs, with comprehensive tables available for many pure materials and alloys having been pub-
Figure 9: Left: Motion of the $\Sigma 7 \ (321)$ GB in aluminum for two system sizes (left column of images: $340 \times 420 \ \AA^2$, right column of images: $170 \times 210 \ \AA^2$). Right: A map showing the critical island size and converged system size for GB motion studies as a function of driving force pressure. This image is reproduced here for pedagogical purposes and was originally published in Ref. [136].

lished for over 20 years [36]. Experimentally, GB solute- and self-diffusion can be studied via radiotracer experiments, in which a thin layer of tracer is plated at a surface that intersects a GB, and the concentration profile of tracer atoms along the GB is measured at a later time for a number of temperatures. From an Arrhenius treatment of the data, the effective diffusion activation energy and diffusion constants can be determined [2, 32].

Computationally, GB diffusion is generally studied with MD simulations, which have provided some insight into the atomistic nature of the GB diffusion process, including the extended understanding of the importance of correlation effects [1]. In a number of cases, KMC approaches have also been used to study GB diffusivity since comprehensive lists of possible transition events can be empirically developed for GB diffusivity in some well-ordered boundaries [137, 138]. However, in spite of the wealth of knowledge with regard to GB diffusivity, predictive relationships of GB diffusivity with respect to the 5-parameter GB space have not been developed.

2.5.5 Grain Boundary Sliding Methods

GB sliding has been treated theoretically and experimentally for almost 50 years on both bicrystal and polycrystalline specimens [6, 7, 139]. Experimentally, GB sliding has been measured by viewing or photographing a bicrystal in a hot-stage tensile setup through an optical microscope, which has allowed for observations of both GB migration and sliding. With this technique, the decoupled measure-
ment of GB sliding rates have been accomplished [24, 27]. As with other GB kinetic properties, the presence of solutes has a strong effect on observations of GB sliding.

Computationally, GB sliding has been studied much more rarely. When it has been modeled, MD has been used, and both bicrystal and polycrystalline systems have been considered [118]. As with GB diffusivity, these studies have greatly contributed to the understanding of the atomic-level mechanisms associated with GB sliding. However, these methods suffer the same timescale related drawbacks as MD studies of GB migration, with stresses on the order of several GPa being required to generate observable mechanical responses in the MD timeframe. As with the other GB dynamic properties discussed herein, these experiments have not, as of yet, lead to the development of a predictive framework relating GB sliding to the 5-parameter space.

2.6 THE COMPUTATIONAL TOOLBOX

In section 2.5 the experimental and computational methods used to study key GB static and dynamic properties were summarized, and it was repeatedly noted that predictive relationships describing a mapping between GB properties and structure have been notoriously hard to identify. With the exception of recent developments in obtaining a predictive relationship between GB structural parameters and GB energy, only limited trends have been identified. However, a comprehensive mapping between GB structure and kinetic properties is essential to the advancement of GBE and achieving potentially orders of magnitude property enhancements in materials used across the spectrum of engineering applications.

A notable limitation in the development of predictive relationships describing GB properties is that the vast size of the GB 5-parameter space requires a large number of GBs with known properties that span the crystallographic space. In considering the methods described in section 2.5, we note that physical experiments on bicrystals are time intensive, which virtually eliminates their applicability to high-throughput investigation. However, if computational methods are used, it must be possible to corroborate the results with experimental studies. Most of the computational methods described in 2.5 use temperature and pressure ranges that cannot be directly compared with experimental measurements (and are often not physically relevant). Thus, the computational tools currently available to study GBs are not well suited to the development of predictive GB structure-property relationships.
A schematic of the computational tools typically used in the materials science community is shown in Figure 10. As shown in the figure, each method has a range of spatial resolution and simulation times accessible to it. For example, Monte Carlo simulations can be used to simulate meso-scale to atomistic spatial resolution, but only at very long timescales (when a specimen is in its equilibrium state). Conversely, ab initio, or first principles, methods can be used to resolve electronic structure, but these computationally intensive simulations only allow for access of very short timescales, much like MD. Meso-scale methods, including on-lattice KMC methods (which will be introduced shortly), can be employed in the simulation of experimentally comparable timescales, at the cost of spatial resolution. From Figure 10, there is a clear need for a new set of tools that will allow for the computational study of atomistically resolved systems on experimental timescales.

Figure 10: Schematic of the computational tools typically used in computational materials science studies. Each method occupies a range of simulation times and spatial resolution. There is a clear gap in the capabilities of this tool set corresponding to atomistic resolution and experimentally relevant timescales, as indicated in the figure. Note that this figure is intended to be illustrative, rather than exhaustive; many computational methods are not specifically shown here, and a more nuanced consideration of each of them would necessarily deform and blur the edges of these categorizing blocks.

It is the premise of this thesis that one approach to meeting this need would make use of an off-lattice KMC algorithm. Due to their stochastic nature, it is possible for KMC methods to simulate rare events that occur at long timescales and are not typically accessible in dynamics simulations. In principle KMC methods evolve a system through a series of kinetic events and determine the physical time that passes during the course of this evolution by calculating the probabilities of each event. Transition State Theory (TST) provides the basis for the event
probability calculations and will be introduced in section 2.8.

In order to calculate accurate event probabilities and obtain meaningful approximations of kinetic processes, KMC methods require a complete knowledge of the target system’s energy landscape—i.e. the set of all possible kinetic events accessible to the target system (this concept is described in detail in section 2.7). In an on-lattice approach, space is approximated by a simulation grid, and all participating bodies (e.g. atoms if the system of interest is at the atomistic length-scale) occupy a discrete location on this grid. In this scenario, the complete energy landscape can be defined by identifying all the possible permutations of grid arrangements. For large, complex systems this can be an intensive process, but it is often computationally tractable at the scale of atoms.

The limitation of on-lattice KMC methods is that complex kinetic processes occur in a spatially continuous domain and are not well-approximated when superimposed on an atom-scale grid. Thus, accurate simulation of kinetic events at the atomistic length-scale would require a grid-resolution that is orders of magnitude smaller than the size of an atom, and permuting all possible arrangements on this refined grid would not be a computationally manageable option for the system sizes that are required to probe kinetic processes (i.e. thousands of atoms). Thus, a KMC method that does not constrain participating bodies (again, this would be atoms in the present context) to positions on an underlying grid, is necessary for pursuing the accurate simulation of complex kinetic processes.

Off-lattice KMC methods may offer a means of simulating atomistic-scale defects, including GBs, under experimentally relevant conditions; however, there are a number of challenges that have impeded their development and adoption in computational materials science. The first of these challenges relates to the need in off-lattice KMC approaches for a method to map a system’s energy landscape. Without the discrete grid used in on-lattice simulations, possible states cannot simply be permuted, but instead, must be explored on the continuous energy landscape. The second challenge is associated with the fact that, in order for the underlying assumptions of KMC methods (which will be described in section 2.8) to be fulfilled, all kinetically relevant transitions on the energy landscape must be known. Developing and optimizing methods that are able to overcome these challenges has been much of the work of this thesis and will described in detail in chapters 3 and 4.
2.7 GRAIN BOUNDARY ENERGY LANDSCAPES

As discussed in section 2.6, complete knowledge of the local energy landscape surrounding a target system is a prerequisite for all KMC methods, so developing methods to map the energy landscape of GB structures is central to the approach for investigating GB properties presented in this thesis. This section includes a brief overview of the definition and relevant terminology associated with energy landscapes in the context of KMC algorithm development and its application to GB systems.

An energy landscape is a $d \cdot N$ dimensional Potential Energy Surface (PES)—$N$ being the number of bodies (e.g. atoms) in a system, and $d$ being the dimensionality of the system. In other words, for every possible set of values that a system’s position vector: $(x_1, x_2, ..., x_{3N})$, can take, there is a corresponding associated energy, and it is the map of each energy with respect to all the $d \cdot N$ degrees of freedom of the system, that comprises the system’s energy landscape.

The Hessian matrix associated with a configuration is the matrix of second partial derivatives of the PES, evaluated at the configuration of interest, and it describes the change in the forces that each body experiences with changes in the position of any given body. Thus, for a PES of a three dimensional system with $N$ bodies described by the function $f(x_1, x_2, ..., x_{3N})$, the Hessian matrix, $H(f)$, is given by:

$$H(f) = \begin{bmatrix}
\frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_1 \partial x_{3N}} \\
\frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \cdots & \frac{\partial^2 f}{\partial x_2 \partial x_{3N}} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial^2 f}{\partial x_{3N} \partial x_1} & \frac{\partial^2 f}{\partial x_{3N} \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_{3N}^2} 
\end{bmatrix} \quad (19)$$

Stationary or critical points on the PES correspond to configurations where the force vector, $-\nabla f(x_1, x_2, ..., x_{3N})$, is zero. If at a given critical point all eigenvalues of $H(f)$ are positive (i.e. every curvature of the landscape is concave up), then that point corresponds to a local minimum on the PES. The global minimum, or ground state, of a system is the minimum with the lowest energy. Conversely, if all eigenvalues of $H(f)$ are negative, then the point corresponds to a maximum on the PES. A system can transition between two adjacent minima via a saddle point,
which is a critical point where $\mathcal{H}(f)$ has both positive and negative eigenvalues (i.e. one or more curvatures of the landscape are concave down). In general, it is accepted that kinetically relevant transitions correspond to first-order saddle points (also called transition states), wherein only one eigenvalue of $\mathcal{H}(f)$ is negative. A schematic of a potential energy landscape, projected from $3N$ dimensions onto two dimensions in configuration space, is shown in Figure 11.

![Figure 11: Schematic of an energy landscape projected onto two configurational dimensions [140]. Images of the $\Sigma_3 (\{111\}$ GB corresponding to each an absolute minimum, a transition state, and an adjacent minimum configuration are shown, where the atoms are colored according to centrosymmetry with the scale indicated, and only atoms in the boundary are shown. This schematic was originally published in [140] and is reproduced here as part of the body of work presented in this thesis.](image-url)

A GB energy landscape is the potential energy surface corresponding to a given GB structure. Since the GB structure is periodic in nature, it has the dimension of $3N$, where $N$ is the number of atoms in a repeat unit and has the same symmetry as the GB. For the purposes of kinetic investigations, the energy landscape is sufficiently described by a catalog or database containing the local minimum configurations that the structure can take and the transition pathways and saddle points connecting these minima. The maxima and higher order saddle points on the energy landscape do not contribute to kinetic events and can be neglected in an investigation of kinetic properties.
2.8 TRANSITION STATE THEORY

Transition State Theory (TST) is the backbone of KMC methods, treating the problem of calculating the rate at which events will occur based on their probability, so a foundational understanding of the principles and assumptions of this concept is essential to the work in this thesis. An excellent review of the origin and development of reaction-rate theory was published by Hänggi, et al. in 1990 and is a valuable reference for the interested reader [141].

The Van’t Hoff-Arrhenius law was empirically found to describe the rate of a reaction, $k$, with an associated activation barrier, $E_a$:

$$k = \nu^* \exp \left( -\frac{E_a}{k_B T} \right) \tag{20}$$

where $\nu^*$ is a prefactor related to the frequency with which the event is attempted, $T$ is temperature (in Kelvin), and $k_B$ is the Boltzmann constant ($k_B = 8.617 \cdot 10^{-5} \text{eV/K}$) [141]. The term, $k_B T$ is commonly referred to as the thermal energy of a system, as a system will have sufficient thermal energy available to activate processes with an activation energy satisfying: $E_a < k_B T$, and the system will be continuously converting back and forth between states connected by this low-energy path.

Later, an equation of the same form was derived from a statistical mechanics approach by Eyring, who incorporated the partition functions of the initial energy well, $Z_0$ and the activated state $Z^\dagger$ to obtain the TST rate, $k_{\text{TST}}$ [141]:

$$k_{\text{TST}} = \left( \frac{k_B T}{\hbar} \right) \frac{Z^\dagger}{Z_0} \exp \left( -\frac{E_a}{k_B T} \right) \tag{21}$$

where the prefactor: $\left( \frac{k_B T}{\hbar} \right) \frac{Z^\dagger}{Z_0}$ is the angular frequency at the bottom of the potential energy well, analogous to $\nu$ in Eq. 20. The assumptions of this theory are that (i) any system it applies to must be in thermodynamic equilibrium (ii) once the system passes through the transition state, it will not cross back [141]. Partition functions are statistical descriptors of a system; for a system that can be characterized by a canonical ensemble (also called the NVT ensemble—in which the temperature, volume, and the number of particles in the system remain constant throughout a process, but where heat can be exchanged with the surrounding environment), the partition function $Z$, is given by the weighted cumulative sum over each possible state $i$ (with corresponding energy $E_i$) a system can take:

$$Z = \sum_i \exp \left( -\frac{E_i}{k_B T} \right) \tag{22}$$
The temperature-dependent weighting factor: \( \exp \left( -\frac{E_i}{k_B T} \right) \) corresponds to the relative likelihood of each state according to a Boltzmann distribution. Thus, the probability that a system will occupy state \( i \) is given by:

\[
p_i = \frac{1}{Z} \exp \left( -\frac{E_i}{k_B T} \right)
\]  

(23)

The TST rate described in Eq. 21 was derived as the probability ratio of the system being in the initial state, indexed by 0, and the transition state, indexed by \( \dagger \), multiplied by a vibrational frequency factor, \( \left( \frac{k_B T}{h} \right) \):

\[
k_{\text{TST}} = \left( \frac{k_B T}{h} \right) \frac{p_0}{p^\dagger} = \left[ \left( \frac{k_B T}{h} \right) \frac{Z^\dagger}{Z_0} \right] \exp \left( -\frac{E_a}{k_B T} \right)
\]  

(24)

where \( E_a \) is the energy barrier: \( E^\dagger - E_0 \). It was shown by Vineyard that the frequency prefactor in Eqs. 21 and 24 can be calculated (making use of the harmonic approximation) as the ratio of all real vibrational frequencies at the initial state, \( \nu_i \), to all real vibrational frequencies at the saddle point, \( \nu_{i}^\dagger \), [142]:

\[
\nu^* = \frac{\prod_{i=1}^{3N} \nu_i}{\prod_{i=1}^{3N-1} \nu_{i}^\dagger}
\]  

(25)

Note that, due to the negative curvature at the saddle point state, there is one imaginary frequency in an activated state, so the product in the denominator of Eq. 52 is only over \( (3N - 1) \) terms. The vibrational frequency at a given state is related to the eigenvalues of the mass normalized Hessian matrix, \( \lambda_i \), described in section 2.7 by:

\[
\nu_i = \frac{1}{2\pi} \sqrt{\lambda_i}
\]  

(26)

This treatment of event probabilities is integral to KMC methods and will be relied upon in the forthcoming chapters of this document.
METHODS

3.1 KINETIC MONTE CARLO

As discussed in section 2.6, stochastic computational methods like KMC provide a powerful alternative to MD simulations since they offer a pathway to increasing simulation times by orders of magnitude. Additionally, the stochastic nature of KMC lends itself to efficient and straightforward parallelization, which allows for the optimized use of advanced computing resources. The reason for the timescale advantage of KMC methods derives from their use of a variable system residence time, rather than a timestep of pre-specified length. The KMC algorithm implemented in this thesis was introduced by Bortz, et al. in 1975 and calculates the residence time of a system, $\tau_R$, as the cumulative sum over the rates of all processes a system can undergo, according to [143]:

$$\tau_R \sim \left( \sum_{i=1}^{N} \sigma_i k_i \right)^{-1}$$  \hspace{1cm} (27)

where $N$ is the total number of possible kinetic events accessible to a system, $k_i$ is the rate corresponding to process $i$, and $\sigma_i$ is the degeneracy of event $i$. Substituting the Arrhenius rate law introduced in section 2.8 for the $k_i$ terms yields:

$$\tau_R \sim \left( \sum_{i=1}^{N} \sigma_i \nu_i^* \exp \left( \frac{-E_{a,i}}{kT} \right) \right)^{-1}$$  \hspace{1cm} (28)

Where, again, $\nu_i^*$ is the effective vibrational frequency associated with event $i$, $E_{a,i}$ is the activation energy required for event $i$, and $kT$ is the thermal energy.

The challenges in implementing KMC in off-lattice systems include the need for methods to (a) determine the kinetic processes accessible to a configuration (i.e. find the $E_{a,i}$ terms in Eq. 28) and (b) ensure that the catalog of $N$ events is sufficiently complete such that the sum in Eq. 28 does not miss critical contributing terms. Only when these criteria have been satisfied can the system kinetics calculated with a KMC method be considered meaningful.

The first of these challenges can be overcome by exploring the kinetic events accessible to a system using the Activation-Relaxation Technique (ART) (see section 3.2), which yields an energy landscape, including indexed information of

45
local minima and activated transitions that connect them. The kinetic Activation-Relaxation Technique (k-ART) is an adaptation of ART that takes advantage of this feature for the development of a KMC algorithm. In k-ART, ART is used to identify all the possible transitions that can occur in a given configuration. Though these configurations include off-lattice coordinates, they can be indexed using a topological approach, a technique that has been successfully demonstrated [144, 145], wherein the graph indexing program NAUTY [146], was utilized. This approach has a number of drawbacks which are discussed in detail in Chapter 4.

In traditional KMC algorithms (including the methods implemented in k-ART and this thesis) a KMC evolution event is enacted by selecting a random transition (weighted by its probability) amongst the accessible transitions identified, and the new configuration—corresponding to the final state of this randomly selected kinetic event—is adopted. The system time is then updated according to [143]:

\[ \Delta t = -\frac{\ln(\mu)}{\sum_i k_i} \] (29)

where \( \mu \) is a random number on the interval \([0, 1]\), and \( k_i \) is, again, the rate associated with a transition \( i \) given in Eq. 28. Following this method, the system is then evolved through many kinetic events, allowing simulations at arbitrarily long timescales to be performed.

### 3.2 The Activation Relaxation Technique (ART)

ART is an algorithm that was specifically developed to sample energy landscapes [144, 147, 148]. It has been successfully adapted to study defects in crystalline solids [149], organic and biological models [148], amorphous silicon [150], metallic glasses [151, 152], and for use in first principles calculations [153]. In the preliminary work for this thesis, ART was adapted to study grain boundary energy landscapes [140].

ART is an algorithm for finding transition states in a potential energy landscape when only the initial configuration is known [144, 147] and consists of each a perturbation, convergence, and relaxation phase. In the perturbation phase, the initial atomic configuration in a minimum energy state is locally perturbed until the lowest eigenvalue of the Hessian matrix, \( \lambda_{\text{min}} \), is less than a small negative number, \( \lambda_c = -1.0 \). The perturbation event consists of choosing a random atom in the vicinity of the defect and displacing it in a random direction by a random distance in the range \( 0.5 - 2.0 \) Å. An atom is deemed to be in the vicinity of the defect if its centrosymmetry parameter [154] is larger than a critical value of 0.1.
In the convergence phase of ART, the system is iteratively pushed along the eigenvector corresponding to the lowest eigenvalue of the Hessian matrix and relaxed in the hyperplane of this vector until either a transition state is converged upon or an alternative exit condition is met. A transition state has to meet the requirements: $\lambda_{\text{min}} < 0$ and $f_{\text{max}} < f_{\text{tol}}$, where $f_{\text{max}}$ refers to the maximum force in any direction on any atom, and here, $f_{\text{tol}} = 0.005 \text{ eV/Å}$ was used. Alternative exit conditions for the convergence phase of the algorithm included reaching either a configuration with $\lambda_{\text{min}} > 0$ or the maximum number of convergence steps, prescribed here as 75. If a transition state was found in the convergence phase, its connectivity to the initial minimum was then checked [152], and if it was determined that the transition state was connected to the initial minimum, the algorithm proceeded to the relaxation phase. If any of the requirements for a transition state were not met or the transition state was not found to be connected to the initial minimum, the search was deemed unsuccessful.

The relaxation phase of the algorithm consisted of a constant-stress conjugate gradient relaxation (with all elements of the stress tensor set to zero) from the transition state to an adjacent minimum, which was achieved by pushing the atomic configuration at the transition state slightly away from the initial minimum configuration prior to the minimization.

The minimum eigenvalue calculation in this method is approximated using the Lanczos method [149, 155] with a maximum number of iterations: $L_N = 15$. If $L_N$ Lanczos iterations are completed before other exit conditions of the algorithm are reached, convergence is tested by comparing the residual to a cutoff value, here: 0.1. If the convergence test fails, then the Lanczos method is implicitly restarted, where the most recently calculated eigenvector is used as the initial guess to initialize the method [155]. It should be noted that, in this discussion, the term ‘residual’ is a measure of the quality of the approximated eigenvalue-eigenvector pair and is calculated as: $|A\nu - \lambda\nu|$ for matrix $A$, approximate eigenvector $\nu$, and eigenvalue $\lambda$. This implicit restarting procedure is repeated until either the residual is lower than the specified value, or the Lanczos method has been attempted $L_N$ times.

Within the Lanczos method, it is possible to avoid explicitly calculating the Hessian matrix by instead approximating the product of the Hessian matrix, $H(x_n)$, with the $j^{\text{th}}$ vector of the Krylov subspace, $\nu_j$, using a second order finite difference approximation:

$$H(x_n)\nu_j \approx \frac{1}{2\epsilon} \left( \nabla f(x_n + \epsilon \nu_j) - \nabla f(x_n - \epsilon \nu_j) \right)$$ (30)
where \( f \) is the potential energy function and, consequently, \(-\nabla f\) is the 3N force vector for the system (\( N \) being the number of atoms present). This approach allows for significant improvements in computational efficiency compared with direct computation of the Hessian Matrix.

This ART procedure can be repeated many times with different random perturbations in order for the space of possible transitions accessible to the system to be explored.

3.3 Complete Energy Landscape Searches

Though ART provides us with a means with which to explore the energy landscape of a configuration, it does not offer any guidance as to how we might ensure the completeness of the energy landscape, which we have noted is a prerequisite for a KMC method. This is an often neglected topic in the off-lattice KMC space, with arbitrary metrics generally dictating the termination of an energy landscape search. This shortcoming of prior off-lattice KMC approaches is commonly cited as a reason for the skepticism that their results are met with and for their comparatively limited adoption.

For this reason, we have aimed to develop a deterministic search method, capable of quantitatively determining the completeness of an energy landscape search and providing convergence in the predicted residence time of a configuration. In the following sections, we describe methods for identifying distinct kinetic events, comparing kinetic events, performing a deterministic search, determining the criteria for terminating a search process, and identifying unique LAEs. Each of these topics are critical aspects of obtaining converged residence times for KMC methods.

Note that much of the content of this section is currently accepted for publication in:

3.3 COMPLETE ENERGY LANDSCAPE SEARCHES

3.3.1 Identifying Distinct Kinetic Events

The first step towards the goal of systematically mapping a configuration’s complete energy landscape is to define a means by which two independently identified kinetic pathways can be compared and identified as either equivalent or unique. Without such a comparison method, it is impossible to assess the completeness of an energy landscape and, in turn, ensure that we have identified the N possible kinetic events required to reliably calculate residence time in Eq. 28.

The difficulty associated with uniquely specifying a kinetic event lies in the numerical nature of computer simulations. An efficient saddle point search method, such as ART, must make use of numerical parameters to determine whether or not a saddle point has been identified in a given search and whether or not a minimum has been reached during the relaxation process. In particular, since transition states exist at points on a potential energy surface with a zero force vector, one must employ a cutoff force tolerance, \( f_{\text{tol}} \), below which the force is considered to be nominally zero. For our simulations that follow, we use a default value of \( f_{\text{tol}} = 0.005 \text{ eV/Å} \) (unless otherwise noted). If we perturb our ground state system in two slightly different ways that both result in convergence upon the same physical saddle point, the atomic configurations identified by the algorithm at the saddle point will not generally have numerically identical atomic positions when they reach the force cutoff.

The stricter we make the force tolerance parameter, the closer the saddle point configurations will be to one another. However, there is a steep computational penalty associated with a tightening of the force tolerance. We have found that saddle point searches with a decreased force cutoff of \( f_{\text{tol}} = 0.0009 \text{ eV/Å} \) can take 50% longer to converge than the same searches with a cutoff of \( f_{\text{tol}} = 0.005 \text{ eV/Å} \). In most cases, the transition state configuration found with the larger force tolerance differed from that found with the tighter force tolerance by less than 0.1 Å in all atomic positions. In a few rare cases, we observed the positional difference between configurations that were converged to each of these tolerances to be as large as 0.25 Å for the most deviant atomic position. Similarly, the uncertainty in atomic position at a minimum energy configuration is generally less than 0.01 Å, and occasionally as high as 0.025 Å (noting that, in this case, it is a much stricter set of cutoff parameters that terminate relaxation to a minimum). Thus, though it is computationally worthwhile to use the largest force tolerance that a method can accept (based on the required certainty for the activation energy), choosing to do so requires that the method used to compare transition states must be able to account for positional uncertainty of atoms that is generally on the order of 0.2 Å at the saddle point and 0.02 Å at a minimum configuration. In cases where even larger force tolerances have been used to converge to saddle points and adjacent
minima, e.g. [156], the method of comparing saddle point configurations must be able to account for even greater positional uncertainty. Bearing in mind this challenge, we next review several approaches that have been employed in prior studies characterizing off-lattice kinetic events.

### 3.3.1.1 Classifying and Comparing Kinetic Events

The simplest approaches to classifying kinetic events make use of individual macroscopic metrics such as the activation energy of an event and the relative energy of its adjacent minimum configuration [157], for example. However, these macroscopic values do not uniquely specify a given process, so researchers have turned to the use of more direct topological approaches.

Béland et al. used a graphical isomorphism approach, specifically making using of a program called NAUTY [158, 159], to specify unique kinetic processes [145]. In this approach, a center-point for each event must first be identified. A sphere with radius $R$ is then drawn around this center and the set of atoms that lie within this sphere then make up the nodes of a truncated graph. The edges of the graph are defined to connect any two nodes (atoms) that are closer than some edge cutoff distance, $a$, in the physical configuration. A two-dimensional example of how a graph is constructed in this fashion is shown in Figure 12. A kinetic event, using this approach, is then completely specified by three graphs, one for each of the initial configuration, the transition state configuration, and the adjacent minimum configuration. NAUTY, or a similar tool, can be used to analyze these graphs and assign a set of hex keys corresponding to the canonical representation of each one. From this, the set of three hex keys that identify the graphs at the initial, transition, and final states uniquely specify a kinetic process, and anytime an event is identified, its uniqueness can be determined by comparing the hex keys associated with its configurations to those that have been found previously.

This approach is powerful as it minimizes the amount of information that must be stored to fully specify a kinetic event and has a very straightforward comparison rule. However, it has a number of issues that make it ultimately unfavorable as a tool for uniquely specifying kinetic events. For example, the method is unable to account for the positional irregularities associated with the numerically converged configurations used in off-lattice methods. This results in either the false classification of two events as being distinct when they are, in fact, the same, or vice versa. In Figure 12 an example is shown demonstrating how a small, numerically-based irregularity in an atom’s position results in a graph with one additional edge and completely different graph hex keys. Additionally, the use of hex keys for transition state identification, though offering a simple means of defining kinetic processes, leaves the user no information with which to compare
3.3 COMPLETE ENERGY LANDSCAPE SEARCHES

Figure 12: Two-dimensional schematic of how a truncated graph is generated from a configuration of atoms given parameters $R$ and $a$. A hex key identifying the canonical labeling of the graph is generated by NAUTY. In this approach, minor perturbations in atomic position, such as the slight displacement of the atom outlined in black in the exploded view, results in the presence of a new edge, colored light blue. The hex keys generated for the graph with this additional edge share no resemblance to those corresponding to the unperturbed configuration.

the similarity between two events that were found to be distinct, making it difficult to validate and optimize the method.

An alternate topological approach developed by Nandipati et al. [160] that suffers from similar issues stores the transition state configuration as a binary number by overlaying a fine grid in the region central to the transition and assigning ones to the voxels of the grid that contain the center of mass of an atom and zeros to all other voxels. The grid is then unwrapped into a string of bits that make up a large binary number. This number can be conveniently stored and referenced. However, uncertainty of atomic position can, once again, confound this method, making it much too easy to store the same kinetic event multiple times due to minor perturbations in the atomic structure, complicating any attempt to determine the completeness of the energy landscape.

3.3.1.2 Method Developed for this Work

Due to concerns with the existing methods for uniquely specifying a kinetic process, we have pursued an alternate approach. Since our goal is to uniquely label atomic topologies without abstraction that would lose the physical features of the structure, we have chosen to work directly with atomic coordinates and trajecto-
ries. Furthermore, knowing the importance of uncertainty in atomic positions associated with numerical methods in general and with ART in particular, we hope to leverage that knowledge in event labeling. Specifically, we store atomic motion vectors associated with the transition. For each kinetic event found with ART, the $x$, $y$, and $z$ displacements of each atom are stored between both the initial state and the saddle point, and the initial and final states. A schematic illustrating an event in which 4 atoms are displaced is shown in Figure 13. In our method, the full vector description of each $t_i$ displacement is stored to uniquely specify the kinetic event.

![Figure 13: Schematic of a kinetic event in an FCC system. In this example, 4 atoms, originally located at the dotted circles, participate in the process. The kinetic event is defined according to the $x$, $y$, and $z$ components of the displacement vectors of these atoms ($t_1$, $t_2$, $t_3$, and $t_4$).](image)

The comparison of two kinetic processes can be conducted by comparing the $x$, $y$, and $z$ displacements of each atom in each of the events. If the difference between the displacements of any atoms in any direction is greater than a cutoff value $\epsilon$, which is chosen based on the known uncertainty associated with atomic position for the force tolerance being employed, then the events are taken to be unique. With a properly chosen value of $\epsilon$, atomic motions that are literally indistinguishable to within numerical uncertainty associated with the potentials and ART can be clearly identified; provided the uncertainty in atomic positions is deemed acceptable in the first place, the uncertainty in comparing and labeling events is guaranteed to be no worse. At first glance, this approach might seem unnecessarily cumbersome compared with some of the memory-leaner alternatives previously discussed, but it has several crucial advantages. To begin with, it uses the most basic definition of a kinetic event, i.e., the movements of atoms in the system, to define and distinguish kinetic events. Secondly, because it makes use of the known numerical uncertainty of atomic positions in distinguishing between events, it allows the user to choose convergence criteria that are logically consistent with an application without sacrificing the ability to compare events.
A comparison of the present method with previous approaches is presented later in Chapter 4 of this thesis.

If the information about each kinetic process is stored in a database, we can easily minimize the search space by performing comparisons with only the subset of events that have, e.g., activation energies within some tolerance of that found in the current search, or some other rapid screening criterion. This has the added advantage of allowing us to consider only the displacements between the initial and final configurations of a process, which halves the number of required comparisons by excluding the saddle point, which is associated with greater uncertainty in atomic position. Though it is possible for multiple activated states to lead to the same final state, we have not found these activated states to have similar enough activation energies so as to be confused with one another, at least in the system of our analysis.

3.3.2 Completeness of the Search

Assuming that we can reliably distinguish between two kinetic events, it is possible to determine whether an event has been previously identified or is new as the search of the energy landscape progresses. From this, it is possible to develop metrics for determining the completeness of an energy landscape search.

3.3.2.1 Search Termination Criteria

The simplest approach to terminating an ART search is to qualitatively deem the search to be complete after some arbitrary number of search attempts or successful searches [144, 152]. For example one could deem their search complete when \( n \) unique saddle points have been identified [152, 161], but \( n \) remains somewhat arbitrary. More sophisticated stopping criteria have been introduced, for example Fan et al. in Ref. [161] terminate a search if a newly found event has a kinetic probability that is less than 0.1% of the current residence time estimate. However, this approach still relies on arbitrary factors such as the order in which events are randomly identified. An improvement over arbitrary termination is to choose some property of the search or the energy landscape around which a statistical test can be built to determine the probability that the chosen property is sufficiently close to the true value. For example, in Ref. [157] we used the frequency of the most commonly found kinetic event as a metric for terminating the search. Specifically, we binned all the kinetic events found with random ART searches and tracked how the average frequency across the bins of the most commonly found saddle point, \( f_{max} \), changed with additional successful searches. We then used the sam-
ple mean of $f_{\text{max}}$ and its standard deviation, $s$, in a Student’s t-test to calculate the minimum sample size, $n_{\text{min}}$, that would be required to achieve the desired confidence that our calculated value was sufficiently close to the true value, and once our sample size exceeded $n_{\text{min}}$, we deemed our search complete.

The above proposal was presented in the context of a static energy landscape search, i.e., without connection to a KMC context or, indeed, any structural evolution. Since system kinetics are of prime interest to a KMC application, we presently suggest that a further improved approach would be to define a metric based on a kinetic property of the system, rather than a numerical one, as has been previously suggested [161]. Specifically, since an accurate calculation of the residence time, $\tau_R$, is our goal, we propose to use the convergence of $\tau_R$ to assess the completeness of an energy landscape search. The method used to establish convergence in our present approach is discussed below.

3.3.2.2 Deterministic Search Method

Whether one uses an arbitrary or quantitative approach to search termination, the random nature of the perturbations typically used in the search method are a common limitation. In either case, we cannot be sure that we have effectively searched the energy landscape, and, in either case, we must perform a large number of searches that, by definition, contain no new information in order to sufficiently characterize the energy landscape; this all results in an inefficient use of computational resources.

As an alternative to the stochastic search method, we employ a deterministic search method by applying a set of systematic perturbations (each of which separately initiates the ART algorithm) to one atom in the system at a time. The perturbations make up the points of a 3-dimensional mesh, with points that are uniformly spaced on concentric spheres with radii corresponding to the magnitude of the perturbation, $d_i$, and centered on the atom being investigated. The product of the number of directions on a perturbation sphere, $\rho$, and the number of shells in the radial direction of the mesh, $d$, is the total number of perturbations in the search of each atom. In Figure 14, perturbation meshes with several values for $\rho$ and a representative set of concentric shells (with $d = 4$) that are separated in the radial direction by a distance $\delta$, are shown to illustrate the nature of the perturbation space used in the deterministic search.

When $\rho$ and $d$ are made sufficiently large and $\delta$ is made sufficiently small, the systematic search can explore all the relevant kinetic pathways in a system. However, determining the critical values for $\rho$, $d$, and $\delta$ requires some optimization.
3.3 COMPLETE ENERGY LANDSCAPE SEARCHES

Figure 14: Perturbation meshes with increasing $\rho$ can be used to calculate a system’s residence time and determine the minimum required value of $\rho$. Each perturbation mesh is projected on a set of $d$ concentric shells, yielding the full set of perturbation vectors required for the systematic search. The $\rho$ points are placed approximately uniformly on the sphere according to the method described by Rusin [162].

By calculating the residence time for a system as a function of these parameters, a critical value—beyond which residence time is independent of $\rho$, $d$, and $\delta$ respectively—can be determined for each of them. One caveat important to the validity of this approach is that meshes of increasing $\rho$ or $d$ must not inherit all the same perturbation directions as the coarser meshes. This requirement removes the bias on $\rho$ and $d$ that is introduced if particular directions or radii in the coarse mesh are very advantageously aligned for searching certain atomic environments.

3.3.3 Uniquely Specifying Local Atomic Environments (LAEs)

The efficiency of our deterministic search method hinges on the need to only search for the kinetic events of atoms in unique LAEs; atomic environments that are sufficiently similar will produce the same set of kinetic events, and thus need not be searched again. If we have a means to specify a LAE, then we only need to perform this systematic search on one representative atom with each unique LAE. Particularly for the case of periodic defects such as GBs or defects that appear with many high-fidelity duplicates in the same system, like point defects, the consideration of only unique LAEs leverages the order in the structure to simplify the computational problem.
Throughout the literature, a number of parameters have been used to specify LAEs in off-lattice systems including the centrosymmetry parameter [154], the common neighbor analysis [163], and hex keys from graphical or topological approaches such as those presented in our discussion above [156, 160]. However, each of these approaches is limited in either its ability to uniquely specify LAEs (as in the first two cases), or in its ability to accommodate small perturbations in atomic structure (as in the latter cases), as described earlier. We therefore suggest a more exhaustive approach to labeling LAEs. Namely, we define an LAE by the set of vectors, $r_i$, denoting the $M$ closest neighbor positions relative to our target atom. An appropriate size for $M$ needs yet to be determined, and will depend on the complexity of the system being studied. However, we envision that at a minimum one would require the nearest-neighbor positions, which is illustrated as an example only for an FCC system in Figure 15, i.e., $M = 12$. Two atomic environments are deemed to be equivalent if the vectors to all the $M$ closest neighbors are the same to within $\epsilon$, where $\epsilon$ is again the uncertainty in atomic position, $0.025$ Å at minima on the potential energy landscape in our method. In an efficient application of this approach, a means to quickly identify if LAEs are rotationally or symmetrically equivalent should be implemented. One such method is presented in the next section.

![Figure 15: The vectors, $r_i$, locating the $M$ closest neighbors of a central atom are used to define its unique atomic environment, illustrated here for the case of $M = 12$.](image)

In addition to storing the $M$ closest neighbor vectors, the magnitude of the square of the vector sum of these vectors, $S^2$, can also be stored to facilitate screening the set of known LAE (where $r_{ij}$ indicates the $j^{th}$ component of vector $r_i$):

$$S^2 = \sum_{j=1}^{3} \left( \sum_{i=1}^{M} r_{ij} \right)^2$$ (31)

This permits the fewest possible comparisons to determine the uniqueness of a target LAE. In this scenario, only candidates with $S^2$ values that are within $\epsilon S^2$...
3.3 COMPLETE ENERGY LANDSCAPE SEARCHES

of the target LAE’s $S^2$ are compared, where $\epsilon_{S^2}$ is based on the propagation of uncertainty of $\epsilon$ [164]:

$$
\epsilon_{S^2} = 2\epsilon \sqrt{S^2} \tag{32}
$$

Given this approach, the challenge of specifying an atom’s LAE becomes the challenge of determining what value of $M$ is sufficient to uniquely specify a LAE for kinetic simulations, which is discussed in the 4 Chapter. The kinetic transitions that result from the perturbation of an atom with a given LAE can then be systematically searched according to the method described above. This also improves the performance of the method we have described for comparing kinetic events, because once an LAE has been searched, we no longer need to store all the information about its kinetic events. Instead, we can simply store the information about a perturbation that led to the event as well as the energetic information required for the residence time calculation. When implemented in a KMC algorithm, a kinetic event is selected from the catalog of possible events, and the system can be evolved by executing the perturbation and ART search that led to finding the event initially. This prevents the method from unintentionally forcing an event that is not physical and can accommodate elastic strains present in dynamic processes, as has been discussed in other KMC cataloging approaches [144].

3.3.4 Comparing Local Atomic Environments (LAEs)

The most naïve approach to comparing LAEs is to directly compare the 12 vectors locating the positions of the nearest neighbors. If the atoms neighboring atom A can be located with the same vectors (to within some $\epsilon$) as the neighbors of atom B, then we can conclude that atom A and B have the same LAE. However, in the worst case, this would require $3 \cdot 12! \approx 1.4$ billion comparisons for each pair of atoms. In practice we could screen which vectors to compare by their magnitude, which makes this problem tractable. However, this approach does not account for atoms with LAEs that are rotationally equivalent, introducing significant inefficiency into the method. As the most time-intensive aspect of the present algorithm is the process of searching an energy landscape.

The general problem of quickly trying to identify if two sets of points are related (where an atom and its surrounding neighbors define one set of points) is a non-trivial undertaking, where the brute force approach mentioned above. Peter Mahler Larsen, a visiting scientist to the Schuh Research Group during the Spring of 2016, has recently developed a method of this kind that was implemented in this thesis. Larsen’s method efficiently searches through permutation space to determine the optimal mapping of the atoms in one point set onto the atoms in

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the other set. Given this optimal mapping, the method then finds the delaunay triangulation of the point sets and determines the rotation and scaling required to relate them. This work is in preparation for publication; the interested reader should contact Peter Mahler Larsen (pmla@fysik.dtu.dk) for further details.
IMPLEMENTATION

Note that much of the content of this section is currently accepted for publication in:


4.1 AN EXAMPLE SYSTEM

In implementing the methods described in Chapter 3, we have studied a symmetric tilt grain boundary (GB) in copper, namely the Σ5 (2 1 0) grain boundary, as an example system. We consider grain boundaries as ideal target systems for off-lattice KMC, as they generally present a level of structural complexity that is beyond what can be analytically considered or treated with lattice KMC approaches [165], yet it is not so disordered, as in the case of a metallic glass [151], that the kinetic events of the system cannot be sufficiently tabulated.

The example GB was minimized with the LAMMPS [125, 126] molecular dynamics package using the static minimization technique described elsewhere [157] as a planar bicrystal with periodic boundary conditions in the plane of the GB and free surfaces in the direction perpendicular to the plane of the GB. This system is shown in Figure 16, which was generated with the Ovito Open Visualization Tool [166, 167] and shows atoms colored according to their centrosymmetry parameter [154]. The system contains 2040 atoms and is about 290 Å² in the plane of the GB. The embedded atom method (EAM) potential developed by Mishin et al. [168, 169] was used both for the minimization of the grain boundary structure in LAMMPS and with the ART method in the remainder of this chapter.

4.2 OPTIMIZING THE SEARCH PARAMETERS

We have implemented the methods introduced in Chapter 3 with the example system, the Σ5 (2 1 0) grain boundary in copper, and here we evaluate how well these methods allow us to reliably calculate residence time and achieve quan-
tifiable uncertainty. This process requires the optimization of several parameters including the best value of $\epsilon$ (the uncertainty in atomic position) to use to distinguish between kinetic events, the critical values of $\rho$, $d$, and $\delta$ (the number of perturbation directions on a perturbation sphere, the number of concentric perturbation spheres, and the radial distance between perturbation spheres, respectively) required to specify the deterministic search, and the number of atoms, $M$, necessary to sufficiently define a LAE. In the following analysis, we have calculated residence time at 773 K and approximated the vibrational frequency at each saddle point to be constant at $8 \cdot 10^{12}$ Hz, which we have found to be a good approximation for these kinetic processes. A more exhaustive study of the range of values of $\nu^*$ is presented in a later section.

4.2.1 Optimizing $\epsilon$

We consider values for $\epsilon$ in the range 0.010 – 0.050 Å based on our knowledge that atomic position has an uncertainty on the order of 0.01 Å, but can be as much as 0.025 Å in minimum energy configurations. To assess how the residence time is affected by $\epsilon$, we have calculated the residence time, according to Eq. 28, using our systematic search method for various choices of $\epsilon$ in this target range. Since the critical value of $\rho$ is initially unknown, we perform the systematic search for a range of $\rho$ values (with $d = 4$, $\delta = 0.5$ Å, and $d_1 = 0.75$ Å held constant), the results of which are shown in Figure 17.
4.2 Optimizing the Search Parameters

From Figure 17, we note that the calculated residence time seems to be relatively converged for about 500 perturbation directions (ρd); a more quantitative assessment of this is discussed below. As expected, larger values of ϵ result in larger residence times due to cases where distinct events are incorrectly identified as being the same, while the smallest values of ϵ result in the opposite effect, where the same kinetic event is incorrectly counted multiple times. The optimal value of ϵ is different for each event. Some kinetic events are somewhat sloppy, with the highest uncertainty in their atomic positions (±0.025 Å), for which a large ϵ is preferable, while many other events are much cleaner and a smaller ϵ could be used. However, for meshes with greater than 250 perturbation directions, the difference between the residence time calculated with the different choices of ϵ is, at most $7.9 \times 10^{-11}$ s. Thus, we take half this value, $4.0 \times 10^{-11}$ s, to be the uncertainty associated with the residence time we obtain with this method (shown as error bars in Figure 17) and choose an intermediate ϵ = 0.025 Å in future calculations.

At this point, it is important to recall that none of the exact points on the sparser meshes are inherently included in the denser meshes. Thus, it is possible to find
certain kinetic events with a sparser mesh that are then missed with the denser mesh. This prevents the determination of the minimal mesh size from being biased by a ‘lucky’ sparse mesh population that is inherited by all denser meshes and accounts for the non-monotonic behavior seen in Figure 17.

4.2.2 Optimizing Mesh Parameters

Using $\epsilon = 0.025$ Å, we can now optimize the mesh parameters required for a complete search of the energy landscape for our target system. From Figure 17 it appears that the critical value of $\rho$ may be around 150; however, it is possible that with different choices of $d$ and $\delta$ a more minimal perturbation sphere may be used. We proceed by optimizing the radial parameters of the mesh. After finding that no search converged to a saddle point when the initial perturbation was less than 0.75 Å in our implementation of ART, we define the space of possible radial perturbation distances as ranging from 0.75 – 2.25 Å. We consider shell spacing values of $\delta$ ranging between 0.1 – 1.0 Å. Setting $\rho = 328$, we investigate residence time as a function of $d$ and $\delta$, as shown in Figure 18.

Figure 18: Calculated residence time for the ground state configuration of the $\Sigma 5 \{210\}$ GB in copper as a function of radial shells, $d$, and shell spacing, $\delta$, for a perturbation mesh with $\rho = 328$. If $\delta$ is set to 0.15 Å, and $d_1 = 0.75$ then $d = 4$ is the minimal number of required shells in this system.
4.2 Optimizing the Search Parameters

From Figure 18, we note that the residence time is independent of $d$ so long as $d > 4$ and $\delta = 0.15 \text{ Å}$. As such, we have found that including perturbations with $d_i > 1.20 \text{ Å}$ did not affect the residence time calculation. Decreasing $\delta$ to 0.10 Å did not affect the residence time either. However, we note that the residence time did show sensitivity to the choice of the lowest $d_i$ value, $d_1$. Holding $d = 5$ and $\delta = 0.15 \text{ Å}$, we increased $d_1$ from 0.75 Å to 0.85 Å and observed an increase in residence time.

Having a sense of the optimal set of perturbation shells with $\rho$ held constant, we next need to determine the codependence of our mesh parameters. In Figure 19, we show the residence time as a function of $d$ for $\rho = 156$ and $\rho = 328$ with $\delta = 0.15 \text{ Å}$ and $d_1 = 0.75 \text{ Å}$ and error bars centered on data with $\rho = 328$. In Figure 19, it can be seen that the residence time vs. $d$ behavior is independent of the mesh density $\rho$, with both datasets converging to $d = 4$ as the minimal number of radial shells in the perturbation mesh.

![Graph](image)

**Figure 19:** Calculated residence time for the ground state configuration of the $\Sigma 5$ (210) GB in copper as a function of radial shells, $d$, in the perturbation mesh with $\rho = 156$ and $\rho = 328$ and $\delta = 0.15 \text{ Å}$.

Having established that the mesh parameters are independent, we can now revisit Figure 17 and determine the minimal mesh density, $\rho$, for this system. Noting that choosing a constant value for $\epsilon$ lead to an uncertainty in the residence time
of $4.0 \cdot 10^{-11}$ s, we can calculate the standard deviation of the residence time for the data shown in Figure 17 with $\epsilon = 0.025$ Å. By successively neglecting the data from the coarsest meshes, we obtain a series of standard deviation values, $s_{\tau_R,i}$, where $\tau_R,i$ is defined as the average residence time calculated using the set of meshes with $\rho \geq \rho_i$ and $\rho_P$ being the finest mesh:

$$\tau_{R,i} = \frac{1}{P-i} \sum_{j=i}^{P} \tau_{R,p,j}$$

We use the requirement that a minimally sufficient mesh must satisfy $s_{\tau_R,i} < 4 \cdot 10^{-11}$ s. In Figure 20 we plot $s_{\tau_R,i}$ as a function of $\rho$ (along with $\tau_R$ for illustrative purposes). The uncertainty associated with $\tau_R$ is shown as a horizontal black line; the point at which $s_{\tau_R,i}$ crosses below this line, at $\rho = 46$, is marked with a vertical dotted line, and we can take $\rho = 46$ to be minimally sufficient for the present system of study.

![Figure 20](image-url)
4.2.3 Labeling Kinetic Events

In Figure 21, we show several examples in which we have used NAUTY to identify unique kinetic events and LAEs for the energy landscape search of the $\Sigma 5\ (2\ 1\ 0)$ grain boundary for several example combinations of the R and $a$ parameters (recall that R is the radius of the truncated graph and $a$ is the cutoff distance for an edge). For the purposes of this comparison, we have only used meshes with $\rho$ in the most relevant range: 46–562. To allow for a direct comparison with the results of Figure 17, we have held $d = 4$, $\delta = 0.5$ Å, and $d_1 = 0.75$ Å constant.

From this figure we see, as was observed with our method above, that the residence time appears to converge for perturbation meshes with greater than about 500 directions. The sensitivity of the residence time to the choices of R and $a$ are notable, as the spread of calculated residence times in the converged region, $\sim 1 \cdot 10^{-10}$ s, is about the same as the residence time itself, and there is no obvious way of determining which combination of R and $a$ lead to the true residence time.
of this system.

In Figure 22, we plot the same data as shown in Figure 21 and compare it with the data from Figure 17 with $\epsilon = 0.025$ Å. From Figure 22, we note that residence time calculated using the present method lies within the same range as that calculated using NAUTY, but with a tighter uncertainty (under half). In all cases, the meshes with greater than 500 directions show a converged residence time behavior.

In addition to having a tighter uncertainty, our approach has the advantage of not depending on the arbitrary choice of parameters $R$ and $a$. Because it relies instead on the physical definition of a kinetic event (the displacement of atoms) in distinguishing between events, we believe it provides a reasonable means of determining the residence time in an off-lattice atomic configuration.
4.2.4 Local Atomic Environment Size

To determine the minimum number of closest neighbor atoms, $M$, required to specify a LAE for our system, we have calculated the residence time of our example system using values of $M$ ranging from 12 to 64. Only the atoms in or near to the grain boundary were of interest in the kinetic analysis, thus atoms more than one nearest neighbor spacing from the GB were not searched for kinetic events. In this highly ordered GB, the number of unique LAEs in the GB region ranged from 8 to 22 for the investigated values of $M$. The results are shown in Figure 23. The error bars denote the uncertainty in the residence time calculation. Due to the minimal fluctuation observed in the residence time across the full range of LAE sizes considered, we conclude that 12 closest neighbors is sufficient for the definition of the LAE in this case.

![Figure 23: Residence times for the ground state configuration of the $\Sigma 5 \ (210)$ GB in copper for increasing LAE sizes. Error bars based on uncertainty calculated from Figure 17 are overlain.](image)

4.3 Illustrating the Deterministic Search

In Figure 24 we show the perturbation directions that resulted in successfully finding a saddle point for three different LAEs for perturbation meshes with $\rho = 128$ and $\rho = 562$. Perturbations that led to a successful ART search are plotted on a
unit sphere, or ‘transition globe’, and colored according to the activation energy of the corresponding kinetic event. For clarity in visualization, perturbations of all magnitudes are collapsed onto a single globe.

From Figure 24, we see that in the cases where a denser mesh was used, there are ‘continents’ of perturbation directions that result in what appear to be the same kinetic event. In some cases, these continents are quite large, indicating that a broad range of perturbations will lead to convergence to the same saddle point. In other cases, only a narrow set of directions lead to a given event. It is these latter kinetic events, if sufficiently low in activation energy, that dictate the required mesh density of a system and which highlight the risks of declaring any search “complete”: there is always some chance of missing the critical perturbation that might find a low energy (highly kinetically significant) transition.

To investigate the potential relationship between the activation energy of a kinetic event and the ease with which it can be converged upon, in Figure 25 we plot the solid angle, in steradians, that a ‘continent’ on a transition globe occupies as a function of its activation energy. In general, we see that across the whole range of activation energies there are many events that will only be observed if triggered by a relatively localized perturbation. Conversely, there is a subset of transitions for which a broad range of perturbations will converge to what appears to be the same saddle point, as can be observed in Figure 24. There is a possible correlation between higher energy saddle points with larger continent areas. One explanation of this trend might be that higher energy saddle points are less likely to fall back down into the initial minimum state during convergence than lower energy activated states, so a wider set of initial perturbations can converge to the same saddle point in these cases.

4.4 EFFECTIVE VIBRATIONAL FREQUENCY

As discussed in section 2.8, Vineyard showed that, when the harmonic approximation is valid (i.e. when temperature is not near either absolute zero or the melting point of a material), the effective vibrational frequency associated with a kinetic event can be calculated according to Eq. 52 (reprinted below for clarity), where $\nu_i$ indicates the set of real vibrational frequencies associated with an atomistic configuration (which are related to the eigenvalues of the Hessian matrix by $\nu_i = \sqrt{\lambda_i}/2\pi$).
Example:

An atom with LAE 1 is perturbed along \( r \), and a transition state with \( E_a = 2.4 \text{ eV} \) is identified and mapped to the globe.

Figure 24: Perturbation directions that resulted in the identification of a saddle point are plotted on a unit sphere, colored according to the activation energy of their corresponding transition state, creating a ‘transition globe’. The transition globes of atoms in three different LAEs are shown for perturbation meshes with \( \rho = 128 \) and \( \rho = 562 \).
\[
\nu^* = \frac{3N}{3N-1} \prod_{i=1}^{3N} \nu_i \\
\]

This requires that the full spectrum of eigenvalues from both the initial state and the saddle point state be obtained in order to calculate \(\nu^*\). Due to the computational intensity of this task, in past studies, researchers have often made the simplifying assumption that \(\nu^*\) is approximately a constant on the order of \(10^{13} \text{ Hz}[145]\).

To test this assumption, the full eigenvalue spectrum of each unique saddle point identified for our example system was calculated. For this, the full Hessian matrix at each saddle point was calculated, and then the python \texttt{eigvalsh} function from the \texttt{numpy.linalg} package, which implements the LAPACK functions \texttt{_syevd} and \texttt{_heevd}, was used to obtain the eigenspectra. The eigenspectra at each saddle point as well as an exploded view of the 50 largest eigenvalues are shown in Figures 26 and 27, respectively. The lines are colored according to the activation energy of the event that each set of eigenvalues corresponds to, and the dotted, black line indicates the eigenvalue spectrum of the ground state system.
Figure 26: Each colored line shows the spectrum of eigenvalues of the Hessian matrix at a saddle point configuration, ordered from smallest to largest. The color of the line corresponds to the activation energy at the saddle point. The dotted, black line shows the eigenvalue spectrum of the ground state configuration.

Figure 27: An exploded view of the 50 largest eigenvalues of the Hessian matrix for each saddle point accessible to the $\Sigma 5 (2 1 0)$ GB in copper.

It is apparent from Figures 26 and 27 that the largest eigenvalue at each saddle point is greater than the largest ground state eigenvalue for this system. Addition-
ally, though there is a difference in the spectra at different saddle point states, the
ranges are notably similar (indicating that the use of a constant value for $\nu^*$ may
be justified). Since the variance among the eigenvalue spectra is greatest for the
largest values, and since methods of calculating eigenvalue spectra are also most
accurate for the largest eigenvalues, we evaluated the calculation of $\nu^*$ (from Eq.
52) by using progressively more terms in each product.

Figure 28 shows the value of $\nu^*$ when calculated using 1 – 500 terms in the
product. From Figure 28, it appears that $\nu^*$ takes on a stable value when only
a few terms are used from the eigenspectra, but as increasingly more terms are
used, the calculation becomes unstable, and $\nu^*$ either goes to zero or, in a few
rare cases, diverges. The reason for this numerical instability is the result of the
increasing uncertainty in the eigenvalues calculated far from the dominant modes
(due to the iterative nature of their determination), coupled with the nature of Eq.
52, which successively multiplies ratios of values that are going to zero. Figure 29
shows, again, an exploded view of $\nu^*$ when the product in Eq. 52 was truncated
after 1 – 50 terms. Here, again, the divergence in the calculation when more than
20 terms have been included, is clear.

Figure 28: $\nu^*$ calculated from increasing numbers of eigenvalues from the spectra shown
in Figure 26. This calculation appears to be stable for only the first few terms.

Finally, we see how using $\nu^*$, truncated at different points in the product, af-
ficts the calculated value of residence time from Eq. 28. Figures 30 and 31 show
residence time as a function of the number of terms included in the $\nu^*$ product,
4.4 Effective Vibrational Frequency

![Graph showing vibrational frequency and activation energy]

Figure 29: An exploded view of $\nu^*$ from Figure 28 calculated with between 1 – 50 of the largest eigenvalues.

with Figure 31 showing an exploded view of the first 50 terms from Figure 30.

From Figure 31, we see that even if only the largest eigenvalues (i.e. the two largest eigenvalues from the ground state and the largest eigenvalue from the saddle point state) are used in calculating $\nu^*$, the residence time takes a stable value. Thus, the approximation of $\nu^*$ used in this work is:

$$\nu^* = \frac{\nu_1 \nu_2}{\nu^*_1}$$  \hspace{1cm} (34)

in which $\nu_1$ and $\nu_2$ are the two largest vibrational frequencies in the ground state configuration, and $\nu^*_1$ is the largest vibrational frequency at the saddle point. This approximation accounts for the variance in vibrational frequencies associated with different kinetic events while requiring only minimal computational cost; to obtain the largest eigenvalues of the Hessian matrix, we have again used Lanczos method with an implicitly defined Hessian matrix (as discussed previously, though, in this case iterating to find the largest eigenvalues rather than the smallest) to quickly identify the largest eigenvalues in a system. The impact of calculating $\nu^*$ in this manner on the computation time of the method will be discussed and compared with using a constant value for $\nu^*$ in section 5.2.3.
4.5 DEGENERACY

The degeneracy, $\sigma_i$, in Eq. 28 associated with kinetic event $i$ relates to the symmetry of the system of interest. In this implementation, $\sigma_i$ is simply equal to the number of atoms in the target system that have the same LAE as the atom whose perturbation initiated the search for event $i$. For example, if event $i = 12$ was identified by first perturbing an atom indexed with id $= 520$ with LAE 92, then $\sigma_{12}$ in Eq. 28 would be equal to the total number of atoms in the system with LAE 92. If only atom 520 is in LAE 92, then $\sigma_{12} = 1$; if five atoms are in LAE 92, then $\sigma_{12} = 5$, and so on.

4.6 COMPUTATIONAL METHOD

The methods described in this document were coded in C++, the code from which is available upon request. An overview of the flow of the method is shown below. The catalog used to store kinetic events was implemented in a PostgreSQL Database which interfaced with the main C++ algorithm using the pqxx library.
The structure of the database is described briefly in section 4.6.2, and the structure of the important database tables are presented in section A.3 of the Appendix.

4.6.1 Algorithm Framework

A flowchart of the off-lattice KMC method developed here is shown in Figure 32. The flow of the algorithm starts from the top-left corner of the chart with the identification of all the unique LAEs in a structure. The method then proceeds to perform a complete energy landscape search of each LAE following the flow of the blue boxes. When the search of the energy landscape is complete, the method proceeds to the KMC evolution steps in which an event is randomly selected. The system is evolved through the selected process and the simulation time is updated according to Eq. 29 after selecting another random number. Boxes connected by multiple arrows indicated parallel processes. Note that DB is the abbreviation for database and tx is the abbreviation used for transition in this work.
Algorithm Structure

For each new, unique LAE, run ART searches initiated by the perturbation set.

Search done?

Store in DB

Saddle point?

Choose event and evolve

Calculate residence time

Iter:\n
N

Y

New tx?

Relax to adjacent state

Assign a LAE ID to each atom in the defect region

Figure 32: Flowchart of the off-lattice KMC method developed for this work is shown here. The method starts from the oval at the top-left of the chart, by identifying all the unique LAEs in a structure. Items colored blue correspond to steps in the method related to using ART for searching the energy landscape of an LAE while green colored items correspond to KMC evolution steps.

4.6.2 Database Structure

A schematic of the database structure used in the present method is shown in Figure 33. Each box corresponds to a different table of information, and, analogous to Figure 32, tables colored blue store information related to the completeness of the energy landscape search while tables colored green store information related to the KMC evolution of the system. The variable names shown below each table name are the names of the columns that each row of input data will have. Thus, in configs_table, each row will correspond to a unique LAE and have an associated id; the sum term holds the result of Eq. 31, searched stores a boolean value indicating whether or not that LAE has been fully searched, followed by 48 columns of information locating the 12 nearest neighbor atoms (and their euclidean distance from the central atom), and the last column contains a time_stamp of when the entry was made.

The transitions_table stores a unique id and kinetic information about each unique kinetic event including the energy of the adjacent minimum configuration (min_eng), its associated activation energy (sp_eng), the effective vibrational frequency of the event (nu_star), the id of the LAE of the atom whose perturbation lead to identifying the event (configid, this is a foreign key), and the perturba-
4.6 Computational Method

tion parameters associated with finding the event.

Database Structure

![Diagram of database structure]

As mentioned, the tables listed in blue boxes in Figure 33 contain information about the energy landscape search process. They are also important for tracking the information about each processor’s configuration in a parallel simulation. For example, there is one `num_x` table per processor used in the simulation, and it stores how many atoms (`num_atoms`) are in each LAE (configid) in its current configuration. Similarly, the `pxcy` tables store the `atomid` of each atom in LAE `y` in processor `x`’s current configuration. Lastly, there is one `txid` table for each transition that corresponds to a LAE that is actively being searched. It stores the `x`, `y`, `z` displacements of every atom that moved more than `\epsilon = 0.025 \text{Å}` in the course of a kinetic event. Further description of the structure of the database is included in Appendix A.3.
5.1 Vacancy Migration in Copper

To validate the off-lattice KMC method developed in this thesis, we have implemented the method in the study of a vacancy migration event in copper. We have considered systems with both 499 and 2047 atoms, each with a single vacancy, and calculated vacancy diffusion and self-diffusion at 500 °C. Images of the two systems are shown in Figure 34.

![Figure 34: Systems with 499 and 2047 atoms, each with a single vacancy, were used to validate the off-lattice KMC method developed in this work. Atoms are colored according to their centrosymmetry parameter [154].](image)

The rate of self diffusion was calculated from the mean square displacement of atoms at each time interval according to the three-dimensional isotropic diffusion equation [170]:

\[
D_s = \frac{\langle (x-x_0)^2 \rangle}{6t} \exp \left( - \frac{E_v^\gamma}{k_B * T} \right) \left( \frac{N}{T} \right)
\]

Where \( E_v^\gamma \) is the vacancy formation energy in copper (1.27 eV), \( t \) is the time interval during which the atom moved from position \( x_0 \) to position \( x \), and \( N \) is the number of atoms in the system. The \( \exp \left( - \frac{E_v^\gamma}{k_B * T} \right) \left( \frac{N}{T} \right) \) term adjusts the calculated self-diffusivity by the expected vacancy fraction at the simulated temperature, correcting for the artificially-high vacancy fraction present in the simulation cell.
The displacement average is taken over all atoms in the system, and the time intervals can be re-sampled in a manner similar to the method described in [102] to tighten the uncertainty of the calculation. The rate of vacancy migration was similarly calculated according to:

\[ D_v = \frac{(x - x_0)^2}{6t} \]  

(36)

where the angle brackets indicating the sample mean have been omitted since vacancy displacement at each time interval cannot be averaged over the system (there is only one vacancy present in the simulation cell), and the vacancy fraction does not need to be corrected since, unlike atoms in the bulk, the vacancy always has available migration sites. A summary of the self-diffusion and vacancy diffusion coefficients determined using the off-lattice KMC method from this thesis are shown in Table 1 along with representative experimental data for the same system and temperature (500 °C) from Ref. [171].

<table>
<thead>
<tr>
<th>Method</th>
<th>( D_v ) [m²/s]</th>
<th>( D_s ) [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Thesis 499 atoms</td>
<td>( 1.0 - 19 \cdot 10^{-12} )</td>
<td>( 0.8 - 1.1 \cdot 10^{-19} )</td>
</tr>
<tr>
<td>This Thesis 2047 atoms</td>
<td>( 0.7 - 98 \cdot 10^{-12} )</td>
<td>( 0.4 - 1.1 \cdot 10^{-19} )</td>
</tr>
<tr>
<td>Tracer Experiments [171]</td>
<td>( 3.0 \cdot 10^{-12} )</td>
<td>( 3.9 \cdot 10^{-19} )</td>
</tr>
</tbody>
</table>

Table 1: The vacancy and self-diffusion in copper calculated with the off-lattice KMC method presented in this thesis for a system with 499 atoms and a system with 2047 atoms. Calculations were made at 773 K. For comparison, experimental data on the same system from Ref. [171] is shown.

From Table 1, it can be seen that the off-lattice KMC method implemented here provides a good match to the experimentally measured values of \( D_s \) and \( D_v \) in copper for both system sizes. However, it should be noted that the uncertainty associated with the calculated \( D_v \) values is much greater than for the \( D_s \) values. This is to be expected as ensemble averaging could not be used to calculate the vacancy diffusion rate, so a larger set of raw data would be required to achieve the same uncertainty as the self-diffusion calculation.

5.2 CHARACTERIZATION

Having shown that the off-lattice KMC method developed in this thesis is capable of reproducing diffusion behavior in a bulk copper system, it was desirable to characterize the scaling properties of the algorithm and identify and optimize op-
opportunities for efficiency improvements. In the remainder of this chapter, we con-
sider the calculation-time effects of system size, number of terms used to define a 
\textit{LAE}, the method of calculating $\nu^*$, and system complexity. In the final section 
of this chapter, we briefly compare the performance of the present method with an 
\textit{MD} implementation.

5.2.1 \textit{System Size}

In Figure 35, the number of \textit{KMC} evolution steps taken during a simulation as a 
function of the wall-clock time for a vacancy in a system of 499 and 2047 atoms is 
shown.

Figure 35: Number of \textit{KMC} evolution steps as a function of wall-clock time for vacancy 
systems of two different sizes. Both the gold and black lines correspond to 
systems with 499 atoms, as indicated by the arrows, while the cyan and red 
lines correspond to systems with 2047 atoms. The step-like behavior of the red 
simulation is due to the fact that this simulation made use of a pre-initialized 
database, unlike the other three simulations.

In Figure 35, both the gold and black lines correspond to systems with 499 
atoms, as indicated by the arrows, while the cyan and red lines correspond to 
systems with 2047 atoms. The step-like behavior of the red simulation is due to 
the fact that this simulation made use of a pre-initialized database, unlike the 
other three simulations. It can be seen that, though the systems with 2047 atoms 
run slower, they are not slower by a factor of 4, but rather approximately a factor
of 2. The slow down is almost entirely due to an increased number of atoms in the force calculation.

5.2.2 LAE Size

Next we consider how the number of terms in the LAE affects the computational cost of the method. Though it was found for the example system that an LAE with $M = 12$ neighboring atoms was sufficient, it has been reported that for some multicomponent systems (with long-range electrostatic interactions) LAEs with more than $M = 200$ neighboring atoms were required [165]. Thus, it is worthwhile to investigate the scaling of the computation time with this parameter to explore the applicability of this method for potential future applications. In Figure 36 the number of KMC evolution steps taken as a function of wall-clock time is shown for a system with 499 atoms and an LAE size of each 12 and 24 atoms.

![Figure 36: Number of KMC evolution steps as a function of wall-clock time for vacancy systems with two different LAE sizes. For comparison, data from a simulation with an LAE size of 12 and 2047 atoms is shown.](image)

We note that the simulation using $M = 24$ is slower than the simulation in which $M = 12$; however, it is about $1.5 \times$ slower, which is still faster than the system with 2047 atoms and $M = 12$, which was $2 \times$ slower than the simulation with 499 atoms and $M = 12$. This scaling should be taken into account in designing simulations for systems that require a larger LAE than the example system used in this thesis.
5.2.3 Calculation of ν*

As discussed in section 4.4, ν* in Eq. 28 is often taken to be a constant on the order of $10^{13}$ Hz. However, we have developed an approximation for ν* that does not require the calculation of the full eigenspectra of the ground state and each saddle point, but instead, uses only the two largest eigenvalues from the Hessian matrix corresponding to the ground state system and the single largest eigenvalue from the saddle point system. In Figure 37, we compare the computation time of simulations in which ν* is calculated with our approximation (Eq. 34), and in which it is assumed to be constant with ν* = 6 THz, which is approximately the average of the vibrational frequencies we found for these vacancy systems.

The data in Figure 37 is the same as in Figure 36; however the notations regarding the simulation parameters are different. In this case, it has been noted that both the gold and cyan simulations correspond to calculated values of ν* while the black and red simulations correspond to simulations in which ν* is assumed to be constant.

From Figure 37, we see that the computational cost of calculating ν* is essentially negligible for this system. Thus, although the values of ν* may be well approximated by a constant value for some systems, since there is no added cost to including the direct calculation of ν* via Eq. 34, it is worth including it in KMC methods.

5.2.4 System Complexity

Having considered the algorithm scaling of several vacancy systems with various parameters, we now turn to the example GB system used in the optimization of the present methods, namely, the Σ5 (2 1 0) GB in copper. Figure 38 shows the number of KMC steps taken with respect to the wall-clock time for this GB (with 2040 atoms) as well as the simulation of a vacancy with 2047 atoms.

From Figure 38, it is clear that the added complexity of the GB system, for which the defect has a much larger spatial extent than the vacancy, results in a significant increase in computational cost. After this initial, relatively simple, ground state structure has been characterized and the GB begins to evolve, the method very quickly becomes overloaded with new LAEs to search, resulting in a simulation drastically slower than the vacancy. After 65 hours of wall-clock time, the GB system has only taken about 100 KMC steps, while the vacancy system has taken almost 600 steps. In an optimized version of the method (which changes
Figure 37: Number of KMC evolution steps as a function of wall-clock time for vacancy systems of two different sizes in which $\nu^*$ was either calculated using Eq. 34 or assumed to be constant with a value of 6 THz. The data in this figure is the same as in Figure 36; however the notations regarding the simulation parameters are different. In this case, it has been noted that both the gold and cyan simulations correspond to calculated values of $\nu^*$, while the black and red simulations corresponds to simulations in which $\nu^*$ is assumed to be constant. As mentioned with regard to Figure 35, the step-like behavior of the red simulation is due to the fact that this simulation made use of a pre-initialized database, unlike the other three simulations.

the algorithm behavior in the case of a failed evolution event—this topic will be discussed in Chapter 7), the vacancy simulation of 2047 atoms takes over 13,000 KMC steps in just 24 hours (see section 5.2.5), while the GB simulation takes between 200 and 300 steps in the same timeframe, meaning the GB simulation is on the order of $50\times$ slower than the vacancy simulation.

5.2.5 Comparison with Molecular Dynamics

Though the GB simulation is drastically slower than the vacancy simulation, the 100 KMC steps taken in the simulation shown in Figure 38 correspond to a cumulative simulation time of almost 100 ns, which is a timescale that is virtually unreachable in a MD simulation of a comparable system. This simulation, which took just under 3 days, was performed at 773 K, and as lower temperatures are in-
investigated, the simulation time increases exponentially. This essentially provides a proof-of-concept that the methods developed in this thesis may provide a means to investigate kinetic behavior of complex defects such as GBs.

However, even for simple systems such as vacancies there are advantages to the present method over an MD approach. In Figure 39 we show the number of KMC evolution steps taken with respect to wall-clock time for an improved implementation of the algorithm (compared with sections 5.2.1–5.2.4), in which the algorithm behavior in the case of a failed evolution event was altered (see Chapter 7 for further discussion). For a 499 atom system, the cumulative simulation time was more than 2 µs during a 3 hour simulation (using 60-cores on a workstation computer). Simulating diffusion with MD using the LAMMPS simulation package in a comparable system with 499 atoms required about 1 hour to simulate 3 ns using 6-cores (the maximum number that could efficiently be used on a system of this size. Thus, the KMC method developed here offers a $20 \times$ speed-up in comparison with MD on a per-processor basis, or a $200 \times$ speed-up in terms of wall-clock time at 773 K. Once again, as lower temperatures are investigated, this advantage becomes exponentially more pronounced.

At high temperatures, the simulated time decreases exponentially; however, MD already provides a sufficient means for investigating the kinetic behavior of atomistic materials at high temperatures.
Figure 39: Number of KMC steps taken with respect to wall-clock time for vacancy systems with 499 and 2047 atoms. The steep curves correspond to an improved version of the algorithm in which the method of responding to failed evolution steps is altered (see Chapter 7 for further discussion of this topic).
In this chapter, the methods developed and implemented in the course of this thesis are applied to various case studies of GB kinetic processes. In addition to the case studies presented below, some of the methods described herein were used in the study of tungsten diffusion in chromium in a joint computational and experimental collaboration. As this study provides an interesting perspective on the prospective applications of the methods used in this thesis to broader materials systems and defects and provides the opportunity to directly compare simulation results with experiments, it is worth including in this thesis. However, since it does not directly relate to kinetic processes at GBs it has been placed in Appendix section A.1 rather than in the present chapter.

As in other parts of this thesis, some of the case studies presented here have been published independently. Where applicable this is noted at the beginning of the case study along with a description of the contributions made by each of the authors.

6.1 GRAIN BOUNDARY ENERGY LANDSCAPES

Note that this case study was originally published in Ref. [140]:


Grain boundaries (GBs) govern many materials properties such as plasticity, intergranular and fatigue cracking, corrosion, creep, and thermal coarsening [35, 49, 65, 111, 172, 173]. The kinetic properties of individual GBs that drive such macroscopic behavior can vary by orders of magnitude from one GB to the next [50, 56, 61, 83], and, as such, the macroscopic properties of materials are significantly impacted by the collection of individual grain boundaries in a specimen [81, 83, 174]; the practice of “grain boundary engineering” relies heavily on this concept and has led to some remarkable property enhancements [81–83, 174]. However, predictive relationships between GB structure and kinetic properties remain elusive. This is at least in part because the number of possible GB configurations across the full five-parameter GB crystallographic space is vast [91]. Over the years, a number of investigations of GB properties across the five-parameter space have
been undertaken [59, 99, 110, 175]. However, the major focus of most such work has been on the absolute excess energy of GBs, while the kinetic properties of GBs across the space have been substantially less studied.

It is the premise of our investigation that grain boundary engineering, by virtue of its dependence upon GB kinetic properties, does not necessarily require information about the excess energy of GBs, but rather needs input on the shape and structures of GB energy landscapes—the series of local stable and metastable GB configurations and the pathways and activated states between them. It is the depth or shallowness of the potential well that an individual GB sits in relative to other nearby configurations, rather than the absolute position of that well on the energy scale, that will determine the stability and evolution of a GB. Yet to our knowledge, there are no prior studies revealing the energy landscape of any given GB. It is our purpose here to do so for a few coincidence boundaries to establish the importance of such data for grain boundary engineering.

GB potential energy landscapes in this study were investigated using the activation-relaxation technique (ART) [144, 148]. ART is an efficient saddle point finding algorithm consisting of three phases: perturbation, convergence and relaxation. The initial grain boundary configurations were generated, using the LAMMPS molecular dynamics simulation package [125, 126], from two individual grains oriented according to the desired final configuration and separated by a small distance of \( \sim 1 \) Å. Using the embedded atom method [176] potential developed by Mishin et al. [168, 169], a conjugate gradient minimization was performed on the two-grain system, resulting in a minimum energy GB configuration. The conjugate gradient relaxation was performed at zero pressure in a region within a cutoff distance of the boundary. In some cases, numerous initial configurations were required in order to generate the ground state structure, as discussed in the appendix of this thesis. Three symmetric tilt GBs were investigated here:

- \( \Sigma 5 \ (1\overline{1}0) \) (905 mJ/m\(^2\), 3232 atoms)
- \( \Sigma 5 \ (2\overline{1}0) \) (952 mJ/m\(^2\), 2040 atoms)
- \( \Sigma 3 \ (111) \) coherent twin (23 mJ/m\(^2\), 5850 atoms)

System size and GB-region cutoff were optimized in the initial stages of the investigation by considering systems ranging from less than 1000 atoms to greater than 10,000, and varying the GB-region cutoff distance.

In the implementation of ART used in this study, ART was initiated by perturbing a random GB atom, identified as one with a centrosymmetry parameter greater than 4.0 [154], by a distance \( \alpha_0 = 1.3 \) Å in a random direction. The perturbation phase followed Ref. [152], with \( N_R = 2 \) steps of modified conjugate

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gradient relaxation for each perturbation, and $\lambda_c = -1.0$, the cutoff value the minimum eigenvalue had to be less than in order to proceed to the convergence phase of the algorithm. The lowest eigenvalue of the system was calculated using the Lanczos algorithm with $L_N = 15$ Lanczos iterations, where the product of the Hessian matrix with the $j^{th}$ vector of the Krylov subspace was calculated using a second-order finite-difference approximation. If, after $L_N$ Lanczos iterations, the residual (i.e. the difference $|\lambda v - \lambda v|$ for a matrix $\lambda$, eigenvalue $\lambda$ and approximate eigenvector $v$) was greater than 0.1, the Lanczos algorithm was implicitly restarted using the most recently approximated eigenvector as the initial guess until the residual was less than 0.1 or the Lanczos method had been attempted $L_N$ times [155]. The convergence phase again followed Ref. [152] with $\alpha_{\text{max}} = 0.5$ Å, the largest distance any atom could move for a given convergence step, $f_{\text{tot}} = 0.005$ eV Å, the maximum value any component of the force vector could have for a transition state to be identified, and $N_{\text{max}} = 50 - 75$, the maximum number of convergence steps.

The requirements for successful saddle point identification were $\lambda_{\text{min}} \leq \lambda_{\text{cf}} = -0.001$ and $f_{\text{max}} \leq f_{\text{tot}}$. If these were satisfied, the connectivity checking phase of the algorithm was entered. Following Ref. [152], connectivity was verified if a constant strain conjugate gradient minimization of the saddle point configuration resulted in a maximum deviation from the initial configuration, $\Delta x_{\text{max}} \leq \Delta x_{\text{tot}} = 0.5$ Å. The adjacent minima to connected saddle points were identified using a conjugate gradient minimization in LAMMPS with all stress components zero. Transitions for which the adjacent minimum was sufficiently similar to the saddle point (within 0.05 eV of the saddle point energy and with $\Delta x_{\text{max}} \leq \Delta x_{\text{tot}}$) were excluded as these are not kinetically viable pathways.

As the algorithm ran, saddle points were binned into groups of five according to the order in which they were found, and frequencies and standard deviations of their occurrence were determined. The t-statistic was then used to calculate the total number of saddle points required to achieve a desired confidence interval (95%, two-sided, within 10% of the true mean) for the frequency of each saddle point. If the number of saddle points found was greater than what was required for the confidence interval for the most frequently occurring saddle point, the program was stopped, and the space was deemed sufficiently explored. It should be noted that the choice of parameters used in ART, most importantly $\alpha_0$ and $\lambda_c$, can affect the distribution of saddle points found in the search; however, we have found that the specific transitions revealed are independent of these parameters, with the exception of very extreme choices. For this reason, parameters that minimized the time required to find a saddle point were used.
The present implementation of ART was validated through investigation of vacancy migration in copper, yielding excellent agreement with expectations (i.e. a single prominent event with activation energy of 0.68 eV, compared to 0.71 eV from experiments and within 0.01 eV of other simulation results for copper [168]). The precision of the saddle points found by the algorithm was thus taken to be 0.01 eV, limited by $f_{\text{tol}}$, while the accuracy was limited by the potential used and was taken to be 0.03 eV. As our interest is in energy differences rather than absolute energies, the precision drives the uncertainty in this investigation.

From the output of ART, the energy landscapes governing the kinetic behavior of GBs are obtained, and a graphical representation of this data is shown in Figure 40 for the three GBs studied here. The nodes of each graph correspond to accessible states (minima and transition states) and are positioned with respect to the vertical energy axis shown. Multiple nodes with very similar energies were combined together to generate the pictorial representation in Figure 40 and are larger in size than uncombined nodes. The edges connecting the nodes correspond to the trajectories (initial configuration to transition state to adjacent minimum) found for each GB and are shown as curved arrows. Examples of the atomic configurations of a transition are shown in the figure and correspond to the shaded nodes. Several noteworthy features of these energy landscapes can be observed directly from Figure 40.

Figure 40: Graphs of the energy landscape of grain boundaries in copper. The nodes show accessible states to each GB, ranging from the equilibrium configuration (left) over activated states (middle) to adjacent basins (right). For clarity, nodes of very similar energy are shown as single large nodes. The black lines correspond to the lowest-energy symmetric transition. Atomic configurations corresponding to the shaded nodes are shown in the figure. Atomic configuration images were generated with AtomEye [177] and are colored according to centrosymmetry. Only non-fcc-coordinated atoms are shown. The largest eigenvalue of the adjacency matrix, $\lambda$, and the normalized degree heterogeneity, $\Delta$, of each graph are shown in the subcaptions.
First, Figure 40 provides an intuitive illustration of the kinetic transitions accessible to each GB. A discrete set of transitions is accessible to each GB which leads to a final structure that is either locally perturbed from the ground state or structurally identical to the ground state but atomically distinct. For both of the \( \Sigma 5 \) GBs, locally perturbed transitions disrupted the order in the plane of the GB and used the GB free volume to accommodate the disturbance. However, for the \( \Sigma 3 ( 1 1 1 ) \) GB, for which there is no excess free volume in the GB, the perturbation was out of the plane of the GB and resembled the formation of a Frenkel pair, which is why these transitions are so much higher in energy than those in the two \( \Sigma 5 \) GBs. Additionally, it can be seen from Figure 40 that the transitions with activation energy less than 1.0 eV in the \( \Sigma 5 ( 2 1 0 ) \) GB have very low energy barriers for the reverse process (0.04 – 0.08 eV). These transitions will be frequent, but primarily transient as the reverse transition energy barrier is so low. Conversely, similar low-energy transitions in the \( \Sigma 5 ( 2 1 0 ) \) GB have relatively higher barriers for the reverse process (0.1 – 0.25 eV), so it is expected that these low-energy transitions will have a greater impact on the kinetic behavior of this GB.

Another interesting feature of these energy landscapes is that in all three cases “symmetric” transitions were found that returned the GB to a ground state configuration, but one distinct from the initial state; the lowest-energy symmetric transition for each GB is designated by black curved arrows in Figure 40. For the \( \Sigma 5 \) GBs, these events correspond to the shear sliding of the two grains past one another along the plane of the GB. The minimum activation energy for sliding for the \( \Sigma 5 ( 1 3 0 ) \) GB is 1.70 eV and is 2.10 eV for the \( \Sigma 5 ( 2 1 0 ) \) GB (in the absence of biasing stress, which could lower this value). This disparity is particularly noteworthy as the ground state energies of these two GBs differ by only about 5% and they have the same misorientation. Only the plane inclination of these boundaries is different, and whereas the plane has little effect on the GB energy, it has a remarkable effect on the kinetic properties. If we consider the symmetric transitions for these two GBs at 200 °C, transition state theory would suggest that sliding in the \( \Sigma 5 ( 2 1 0 ) \) GB would be 4 orders of magnitude slower (i.e. \( e^{\Delta E_a/k_B T} \approx 10^4 \), where \( \Delta E_a = 0.40 \) eV is the difference in activation energies, \( T \) is the temperature, and \( k_B \) is Boltzmann’s constant). Similarly, the relative sliding rates would be expected to differ by more than 6 orders of magnitude at room temperature.

Another noteworthy result from Figure 40 is that the lowest-energy transition observed for the \( \Sigma 3 ( 1 1 1 ) \) coherent twin is \( \sim 6 \) times higher than either of the \( \Sigma 5 \) GBs. The symmetric transition in the \( \Sigma 3 ( 1 1 1 ) \) GB does not lead to macroscopic sliding, but rather consists of the local interchange of several atoms in the GB plane without sliding. Nevertheless, if we follow the kinetic analysis above for \( T = 200 \) °C, we find the rate of the symmetric transition in the \( \Sigma 3 ( 1 1 1 ) \) GB is expected to be 27 orders of magnitude slower than in the \( \Sigma 5 ( 1 3 0 ) \) GB.
and 23 orders of magnitude slower than in the $\Sigma 5\,(210)$ GB. Although the much lower energy of the coherent twin is its best-known distinguishing feature (~0.5% of the energy of the $\Sigma 5$ GBs), we view the very dramatic difference in the energy landscape and its effect on kinetic properties as being of primary importance.

The graphs in Figure 40 offer a unique description for the energy landscape about the minima of each GB; they can be regarded as kinetic fingerprints for the GBs they correspond to, and their properties as graphs may also be worthy of analysis. In an initial characterization of these graphs, we consider the largest eigenvalue of the adjacency matrix, $\lambda$, and the normalized degree heterogeneity, $\Delta$, of each graph (unweighted and undirected in this analysis), as shown in the subcaptions of Figure 40. $\lambda$, also called the spectral radius, is important in calculating graph invariants and scales with network size; it is largest for the $\Sigma 5\,(210)$ GB and decreases slightly for the $\Sigma 5\,(130)$ GB and again for the $\Sigma 3\,(111)$ GB. The degree of heterogeneity, $\Delta$, is a metric that varies from zero, for a regular graph, to one, for a star graph, and is calculated by normalizing the Randić index [178]. It is largest for the $\Sigma 3\,(111)$ GB and is very similar for the two $\Sigma 5$ GBs. Together, these metrics indicate that the energy landscape networks for the $\Sigma 5$ GBs are larger and more regular than the network of the $\Sigma 3\,(111)$ GB, features which may correlate with the formation of complex dynamic GB structures during GB evolution.

In summary, the activation-relaxation technique has been employed to determine a first view of grain boundary energy landscapes in face-centered cubic copper. Each GB has a characteristic energy landscape with unique, relatively small set of transitions available to it. We suggest that this energy landscape, rather than absolute energy, will play a primary role in governing GB properties. For the few select coincidence boundaries examined here, we have found activation energy differences for symmetric transitions ranging from 0.40 to 2.56 eV with GB plane and misorientation, which correspond to differences in kinetic activation rates of up to 27 orders of magnitude at 200 °C.

6.2 KINETIC PROPERTIES OF THE $\Sigma 5\,(210)$ GRAIN BOUNDARY IN COPPER

The development of the off-lattice KMC method that has been the work of this thesis was motivated by the need to simulate the kinetic properties of atomistic-scale defects such as GBs under experimentally relevant conditions. In this case study, we consider the kinetic properties of the $\Sigma 5\,(210)$ GB, which was used to parameterize and optimize the present method.
The off-lattice KMC method developed in this thesis was employed in the study of our example GB at temperatures ranging from 298 – 1173 K. Simulations were run for about 24 hours at each temperature, resulting in 200 – 400 KMC evolution steps and simulated times as long as 0.762 s for the lowest temperature simulations or as short as 0.16 ns for the highest temperature simulations. We note that typical KMC simulations often report thousands of evolution steps; however, due to some of the limitations of the present method (which will be discussed in more detail in Chapter 7), we were bound to this relatively small number of evolution events.

Images of our example GB before and after a representative kinetic process are shown in Figure 41. These images are from a simulation at 1173 K, so the timescale for the event is on the order of 2fs. A similar event occurring at a lower temperature would have a timescale that is orders of magnitude longer. In Figure 41 we can see that the kinetic event resulted in a localized disruption of the GB plane and a localized widening of the GB-region. This is typical of the kinetic events observed in this study.

Using the data from these simulations, we were able to estimate several important properties in this defect-free GB: intrinsic diffusion at the GB both out of the plane of the GB and within the GB-plane as well as the GB mobility. For comparison, we have also analyzed intrinsic diffusion and mobility in our example GB using MD at several representative temperatures. In the following, the analysis methods and results are presented and discussed for both intrinsic diffusion and mobility. We then present the simulation and analysis methods used for the MD study, followed by a discussion comparing the results of the KMC and MD approaches. Finally, we explore the nature of the kinetic events that take place during the KMC evolution process.

Throughout this document, the term, intrinsic GB diffusion or intrinsic diffusion, refers to the diffusion of copper atoms, unassisted by the presence of vacancies or other point defects, at the GB. In-plane diffusion, or diffusion within the GB plane, is denoted by $D_\parallel$, and out-of-plane diffusion, i.e. diffusion perpendicular to the boundary plane, is denoted by $D_\perp$. For this work, we have assumed the diffusion in the plane is isotropic.
6.2.1 Intrinsic Diffusion

The intrinsic diffusion can be calculated according to:

\[ D_\parallel = \frac{\langle (x_\parallel - x_0)^2 \rangle}{4t} \]  
\[ D_\perp = \frac{\langle (x_\perp - x_0)^2 \rangle}{2t} \]

(37)  
(38)

where the factor of 2 difference in the denominator of these two equations relates to the fact that in-plane GB diffusion is two-dimensional, while out-of-plane diffusion is one-dimensional. \( x_\parallel \) and \( x_\perp \) correspond to the projection of the atomic position within and out of the GB plane, respectively, for a given atom relative to
its initial position, $x_0$. The angle brackets indicate that the mean of the projected square displacements of all atoms in the GB region must be taken to estimate the diffusivity. It should be noted that the two-dimensional model of diffusion used in Eq. 37 assumes that diffusion within the boundary plane is isotropic.

However, analyzing kinetic parameters such as intrinsic diffusivity from a KMC simulation is not quite as straightforward as fitting a line to the mean-square displacement vs. time data. This is because the stochastic nature of the simulation incorporates a random number in each timestep’s calculation (see Eq. 29). As such, it is only in the context of the ensemble average of all the evolution events that kinetic parameters can be calculated. To illustrate this point, the mean-squared displacement both in and out of the GB plane is plotted with respect to time both at 298 and 1173 K in Figures 42 and 43, respectively. In Figures 42 and 43, the KMC simulation data has been resampled such that, for a trajectory with $N$ KMC evolution steps, local estimates for $D_\parallel$ and $D_\perp$ could be made for each $ij$-interval, where $i \in [0...N]$ and $j \in [(i+1)...N]$. Note that the raw data for the simulations not shown here is included in Appendix A.4.

![Figure 42: Mean-square displacement vs. time for a KMC simulation at 298 K in the Σ5 (210) GB in copper both in and out of the GB plane.](image)

From Figures 42 and 43, it can be seen that the square-displacement vs. time data follow a very broad distribution, and it is only from considering the properties of this distribution as a whole that we can estimate the intrinsic diffusion of the system. In Figures 42 and 43, each data point $(\Delta x^2_{\perp,n}, t_{\perp,n})$ or $(\Delta x^2_{\parallel,n}, t_{\parallel,n})$ can provide us with an estimate of the intrinsic diffusivity, $D_{n,\perp}$ or $D_{n,\parallel}$, respectively.
Figure 43: Mean-square displacement vs. time for a KMC simulation at 1173 K in the \( \Sigma 5 \) (210) GB in copper both in and out of the GB plane.

Where, in the form of Eqs. 37 and 38:

\[
D_{n,\parallel} = \frac{\Delta x^2_{\parallel,n}}{4t_{\parallel,n}} \tag{39}
\]

and

\[
D_{n,\perp} = \frac{\Delta x^2_{\perp,n}}{2t_{\perp,n}} \tag{40}
\]

Our estimate of \( D_{\parallel} \) and \( D_{\perp} \) can then be determined from the mean of all the \( D_{n,\parallel} \) and \( D_{n,\perp} \) values from the data set. If we have \( M \) total data points, then:

\[
\bar{D}_{\parallel} = \frac{1}{M} \sum_{n=1}^{M} \frac{\Delta x^2_{\parallel,n}}{4t_{\parallel,n}} \tag{41}
\]

and

\[
\bar{D}_{\perp} = \frac{1}{M} \sum_{n=1}^{M} \frac{\Delta x^2_{\perp,n}}{2t_{\perp,n}} \tag{42}
\]
To calculate a more robust estimate of the mean of our distribution of $D_{n,\parallel}$ and $D_{n,\perp}$ and obtain meaningful confidence bounds on our estimate, we have used a bootstrapping approach to calculate intrinsic diffusivities from our data. Namely, instead of taking the average over all data points in our sample, we take an average over a new sample, of the same size as the original sample, but generated by randomly selecting $D_{n,\parallel}$ or $D_{n,\perp}$ terms from the data set with replacement, which gives an estimate of the modified data set: $\tilde{D}'_{\parallel,k}$ and $\tilde{D}'_{\perp,k}$. We perform this random sampling with replacement on our data set repeatedly and calculate $K = 1000$ different $\tilde{D}'_{\parallel,k}$ and $\tilde{D}'_{\perp,k}$'s, from which our final estimate of the sample mean can be obtained as:

$$D_{\parallel} = \frac{1}{K} \sum_{k=1}^{K} \tilde{D}'_{\parallel,k}$$

(43)

and

$$D_{\perp} = \frac{1}{K} \sum_{k=1}^{K} \tilde{D}'_{\perp,k}$$

(44)

By arranging all our $\tilde{D}'_{\parallel,k}$ and $\tilde{D}'_{\perp,k}$ terms in ascending order, we can obtain 95% confidence bounds on our estimate from the $k = 50$ and $k = 950$ terms in our $\tilde{D}'$ distribution.

The diffusion rates calculated at each temperature according to this method are shown in an Arrhenius plot in Figure 44 along with the best-fit equations for each dataset, indicating both the activation energy for intrinsic diffusion as well as the diffusion coefficient. The error bars with 95% confidence intervals on each of the diffusivity estimates according to the method described above are about the same size as the data points themselves.

From Figure 44 we note that the activation energy of out-of-plane intrinsic diffusion is about 0.66 eV and the activation energy of in-plane intrinsic diffusion is about 0.67 eV, these values are very similar to the migration energy of bulk diffusion in copper (via a mono-vacancy mechanism), which has a migration energy of 0.69 eV with this EAM potential.

Intrinsic diffusion is not easily measured for complex defects such as GBs; however, interstitial and vacancy diffusion at this GB have previously been investigated in a combined MD-KMC approach in which all kinetic events were manually identified from an MD simulation in Ref. [137]. A comparison of the intrinsic and
Figure 44: Intrinsic diffusion both parallel to and perpendicular to the GB plane in the \( \Sigma 5 (210) \) GB in copper is shown for several temperatures in an Arrhenius plot. The resulting line from a linear fit of the data is overlain along with the corresponding diffusion equations. The error bars show the 95\% confidence intervals on each of the diffusivity estimates.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Diffusion</th>
<th>Intrinsic</th>
<th>Interstitial</th>
<th>Vacancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{\perp} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_{a\perp} ) eV</td>
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<td>0.867</td>
<td>0.564</td>
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<td>( D_{0\perp} ) m(^2)/s</td>
<td>5.85 ( \times ) 10(^{-6})</td>
<td>1.34 ( \times ) 10(^{-7})</td>
<td>2.97 ( \times ) 10(^{-6})</td>
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<table>
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<th>Parameters</th>
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<th>Intrinsic</th>
<th>Interstitial</th>
<th>Vacancy</th>
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<tr>
<td>( D_{\parallel} )</td>
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<td></td>
</tr>
<tr>
<td>( E_{a\parallel} ) eV</td>
<td>0.67 ± 0.08</td>
<td>0.741</td>
<td>0.567</td>
<td></td>
</tr>
<tr>
<td>( D_{0\parallel} ) m(^2)/s</td>
<td>6.54 ( \times ) 10(^{-6})</td>
<td>0.75 ( \times ) 10(^{-7})</td>
<td>1.71 ( \times ) 10(^{-6})</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Diffusion at the \( \Sigma 5 (210) \) Grain Boundary in Copper. \( \dagger \) Literature values from Ref. [137]

defect diffusion mechanisms at this GB are shown in Table 2.
6.2 Kinetic Properties of the $\Sigma 5\{210\}$ Grain Boundary in Copper

From Table 2, we note that, in the presence of point defects, diffusion out of the plane of the GB has a higher activation energy than diffusion in the plane of the GB, while these mechanisms have very similar activation energies in the intrinsic case. The activation energy of intrinsic GB diffusion (in any direction) calculated in this work is in between the activation energy of interstitial and vacancy migration. For this GB, since the activation energy of vacancy migration at the GB is lower than either of the other mechanisms, it is assumed that vacancy migration will generally dominate GB diffusion. It has been found that intrinsic diffusion can dominate kinetic processes such as diffusion at a dislocation core [179]; thus, it is possible that GB intrinsic diffusion may be an important kinetic property for some GBs, and this method provides a straightforward approach for accessing this property.

6.2.2 Mobility

The mobility of our example GB can also be estimated from the simulation data using the framework of the fluctuating boundary method, as modified in Ref. [102]. In this analysis, mobility is related to the change in average position of the GB plane, $\bar{z}$, according to:

$$M = \frac{(\bar{z} - \bar{z}_0)^2}{t} \cdot \frac{A}{2k_B T}$$  (45)

where $A$ is the area of the GB plane and $k_B T$ is, again, the thermal energy of the system. Analogous to the case of intrinsic diffusion, mobility in a KMC simulation cannot be directly determined from a linear fit of $\Delta \bar{z}^2$ as a function of $t$, but rather, must be determined from an analysis of the distribution of $A\Delta \bar{z}_i^2 / 2k_B T t_i$ terms that are obtained by considering each of the data points in the sample. The mean-squared displacement of the GB interface (calculated as the average $z$-component of all atoms in the GB region) is plotted with respect to time both at 298 and 1173 K in Figures 45 and 46, respectively. In Figures 45 and 46, the KMC simulation data has again been resampled. Thus, for a KMC evolution series with $N$ steps, we obtain mobility estimates for each $ij$-interval with $i \in [0...N]$ and $j \in [(i+1)...N]$. Note that the raw data for the simulations not shown here is included in Appendix A.4.

Using the same bootstrapping approach as described in the discussion of intrinsic diffusion at each temperature, we can calculate a mobility estimate from the ensemble average of the sample and corresponding confidence bounds. Figure 47 shows the results of this analysis on our example GB at the temperatures consid-
A linear-fit of the data shown in Figure 47 predicts an activation energy of $G_B$ migration of $0.72 \pm 0.08$ eV and a mobility prefactor of $8.03 \cdot 10^{-3}$ m$^4$/J·s. We note that this is only slightly higher than the activation energies found for both in and out-of-plane diffusion at the GB previously discussed, though still quite similar to
the activation energy of the mono-vacancy migration mechanism in copper.

Though mobility of the $\Sigma 5$ (2 1 0) GB in copper has not been specifically studied experimentally, we can consider the results from a range of computational and experimental studies of GB mobility in copper to contextualize this work. Vandermeer, et al. found the mobility of the GB network in a copper sample undergoing recrystallization to be $6.3 \cdot 10^{-10} \text{ m}^4/\text{J} \cdot \text{s}$ at 394 K [180]. This is several orders of magnitude faster than the prediction of the present model; however, since the example GB in this study is quite well ordered, we might expect it to have a lower mobility than the overall network. Conversely, Viswanathan, et al. found the activation energy of GB migration in [0 0 1] tilt and mixed GBs in copper to be 1.30 eV, which would predict drastically slower GB mobility than the present study [181]. However, this is again, not a direct comparison. Computational studies of copper GBs often find activation energies of GB migration on the order of 0.2 eV, as in Ref. [182], which results in drastically faster GB motion than is predicted by the present model and not corroborated by experimental evidence.

Given this picture of the landscape of GB mobility results, we consider the predictions of the off-lattice KMC method presented in this thesis to indicate that we
may have a promising method for calculating GB mobilities that can be experimentally confirmed.

### 6.2.3 Comparison with Molecular Dynamics Simulations

MD simulations were performed on our example GB with the same geometry as has been previously described using the LAMMPS open-source software package and the same EAM potential developed by Mishin, et al., [168] as was used in our KMC simulations. The simulation cell was annealed at temperatures in the range 298 – 1173 K. The system was brought to the target temperature by a staged equilibration process in increments of 300 K for 300 picoseconds each, with a timestep of 1 femtosecond, temperature and pressure held constant, and an additional Berendsen barostat used to moderate the pressure [183]. After equilibrating in this manner at the target temperature, the simulation was run for 10 nanoseconds, with a timestep of 1 femtosecond, at constant temperature and volume, again with a Berendsen barostat. At each stage, the target pressure in the system was set to zero.

During the final stage of the MD simulation, the displacement of all atoms was tracked at every 10,000 steps. When this data was post-processed, resampling was achieved by treating each step in the simulation as its own initial configuration so that a mean square displacement for each possible time interval could be calculated. Diffusivity and mobility were then calculated using the Eqs. 37, 38, and 45; however, in this case, we can estimate our kinetic parameters using a least-squares fit of the data since it is not a stochastic sample. The slope of the mean squared displacement curve vs. time for each of the projections in the plane of the GB and out of the plane of the GB and for the GB interface was analyzed at each temperature investigated to proved estimates of the kinetic parameters of interest.

#### 6.2.3.1 Molecular Dynamics Results

Images of the simulation cell at 1173 K at the beginning and end of the 10 ns simulation are shown in Figure 48. We note that the entire simulation cell is much more disordered than the cell used in the KMC simulation. Additionally, we note that the GB has migrated, noticeably from its initial position during the course of this simulation.

In Figures 49–56 we show the raw data of our diffusion and mobility analysis for simulations at 1173, 973, 573, and 298 K.
Due to the fact that the GB moved so much during the course of the simulation, analysis of the intrinsic diffusion was quite difficult, as the atoms involved in the GB region are constantly changing, so determining the displacements of atoms that moved within the GB plane or perpendicular to the GB plane often involves comparing an atom’s current position to its position prior to being part of the GB region. Some correction can be made for this, such as only considering displacements from configurations that are not too distant, i.e. within the last 100 snapshots. We have incorporated this into our analysis, but the impact of this challenge cannot be fully mitigated, and for this reason, we expect these estimates of intrinsic diffusivity to be lower than their true values (based on the assumption that we expect GB intrinsic diffusivity to be higher than bulk diffusivity in the absence of vacancies).

Since each data point we have for the position of the interface with respect to time relies on only a single input, rather than an average over the displacements
Figure 49: Intrinsic Diffusion from Molecular Dynamics at 1173 K.

$$D_{\parallel} = 9.39 \times 10^{-11} \pm 6.85 \times 10^{-13} \text{ m}^2/\text{s}$$
$$D_{\perp} = 2.41 \times 10^{-11} \pm 1.62 \times 10^{-13} \text{ m}^2/\text{s}$$

Figure 50: Intrinsic Diffusion from Molecular Dynamics at 973 K.

$$D_{\parallel} = 2.20 \times 10^{-11} \pm 1.78 \times 10^{-13} \text{ m}^2/\text{s}$$
$$D_{\perp} = 3.87 \times 10^{-12} \pm 2.80 \times 10^{-14} \text{ m}^2/\text{s}$$
6.2 KINETIC PROPERTIES OF THE $\Sigma 5\ (210)$ GRAIN BOUNDARY IN COPPER

Figure 51: Intrinsic Diffusion from Molecular Dynamics at 573 K

Figure 52: Intrinsic Diffusion from Molecular Dynamics at 298 K
Figure 53: Mobility from Molecular Dynamics at 1173 K

$M = 5.63 \times 10^{-8} \pm 1.34 \times 10^{-8} \text{[m}^4/\text{Js]}$

Figure 54: Mobility from Molecular Dynamics at 973 K

$M = 3.29 \times 10^{-8} \pm 3.22 \times 10^{-9} \text{[m}^4/\text{Js]}$
6.2 KINETIC PROPERTIES OF THE $\Sigma 5 \{210\}$ GRAIN BOUNDARY IN COPPER

Figure 55: Mobility from Molecular Dynamics at 573 K

\[ M = 1.13 \times 10^{-08} \pm 2.33 \times 10^{-09} \text{ [m}^4/\text{Js]} \]

Figure 56: Mobility from Molecular Dynamics at 298 K

\[ M = 1.19 \times 10^{-09} \pm 1.92 \times 10^{-08} \text{ [m}^4/\text{Js]} \]
of all atoms in the GB region, we use only displacement measurements that correspond to intervals that are less than 10% of the total simulation time, because these intervals are accessed most in the resampling process.

6.2.3.2 Comparison of MD and KMC Results

The intrinsic diffusion and mobility values determined from MD simulations are overlain on the plots obtained from our KMC investigation (Figures 44 and 47) in Figures 57 and 58.

![Figure 57: Intrinsic diffusion both in the plane of and out of the plane of the GB in the Σ5 (210) GB in copper is shown for several temperatures in an Arrhenius plot. The resulting line from a linear fit of the data is overlain along with the corresponding diffusion equations. The error bars show the 95% confidence intervals on each of the diffusivity estimates. Open data points correspond to KMC simulations and colored data points correspond to MD simulations.](image)

At high temperatures, we see that the MD estimates of the diffusivities and mobilities are several orders of magnitude lower than the values determined with our KMC method, while, at lower temperatures, the values are drastically higher. The estimates of GB mobility and in-plane diffusion are particularly strong examples of this behavior. Conversely, the measurement of out-of-plane diffusion at 298 K is in good agreement with the KMC simulations.
6.2 Kinetic Properties of the $\Sigma_5$ (210) Grain Boundary in Copper

Figure 58: Mobility of the $\Sigma_5$ (210) GB in copper is shown for several temperatures in an Arrhenius plot. The resulting line from a linear fit of the data is overlain along with the corresponding diffusion equations. The error bars show the 95% confidence intervals on each of the mobility estimates. Open data points correspond to KMC simulations and colored data points correspond to MD simulations.

In the case of intrinsic diffusion, the general slope of the MD diffusion data seems to be similar to the high temperature slope of the KMC data. The trend in the MD mobility data seems to be much more shallow than the KMC data at all temperatures. However, it is difficult to directly compare the results of these methods, as we expect our kinetic parameter estimates to be poor at high temperatures with our KMC approach—where less than 10 ps were simulated at 1173 K. Likewise, we expect the MD simulations to provide poor estimates at low temperatures, where little measurable activity is expected to occur in the 10 ns window. In agreement with our expectation, we note that the intrinsic diffusivities calculated with MD are lower than those observed with KMC at high temperatures. We expect this to be the case due to both the challenge associated with analyzing intrinsic diffusivity in our MD specimen, and due to the fact that our simulation cell is still largely in the ground state during the simulation, which we do not expect to be the case at this high temperature.
Though the MD results do not match completely with the KMC results, considering the drastic differences in the simulation conditions of a ground state GB and a roughened GB equilibrated at high temperatures, they are sufficiently similar so as to provide a measure of validation for the methods developed in this work. That said, we note that the MD simulations each took only about 12 hours using 8 processors. Thus, the computational load was about $15 \times$ lower than for the KMC simulations, so, at high temperatures, the MD approach is far superior to the KMC method.

### 6.2.4 The Nature of the KMC Evolution Process

Having analyzed the kinetic parameters of this system from both the KMC method and compared that with a MD approach, we can consider directly the evolution behavior predicted by our KMC method. First, we consider the distribution of activation energies for the events that occurred during our KMC simulations. In Figure 59, the cumulative frequencies of the activation energy distributions are plotted for the six temperatures considered in this study.

![Figure 59](image)

Figure 59: The distribution of activation energies from the KMC evolution simulations of the $\Sigma 5 \ (210)$ GB in copper at six different temperatures.

From Figure 59, as we might expect, we see that the higher temperature simulations generally access a few high energy events $\sim 1 - 1.2 \text{ eV}$ that the lower temperature simulations do not access. Additionally, we see that there are two
main populations of events, happening at just over 0.2 eV and 0.8 eV. To further understand this behavior, we consider the maximum displacement of an atom during an evolution event (both within the GB plane and out of the GB plane) as a function of activation energy as well as the relative energy of the minimum configuration at the end of the event, which are shown in Figures 60 and 61, respectively. In this case, we have considered only the data from a representative temperature: 773 K and only ij-adjacent intervals, sampled with $i \in [0...N]$ and $j = i + 1$ (where $N$ is the total number of evolution steps in a given trajectory).

In figure 60 we see, again, two main populations of events occurring at about 0.2 eV and 0.8 eV. The maximum displacement of an atom does not seem to depend on the activation energy of an event. However, we note that, in general, the maximum in-plane displacement can be much greater than the out of plane displacement, reaching as far as almost 4 Å in some cases.

In Figure 61 it can be seen that the displacement of atoms does not seem to be a function of the energy of the adjacent minimum state. Additionally, we see that, for the events explored in this simulation, the adjacent minimum configuration tends to have an energy in one of three populations: about 0.5 eV above the previous state, about the same as the previous state, or about 0.5 eV below the previous
Figure 61: The maximum displacement of an atom during a kinetic event (both in plane and out of plane) is shown as a function of the energy of the minimum configuration converged upon at the end of the event for the KMC evolution simulation of the $\Sigma 5 \ (210) \ GB$ in copper at 773 K.

state. To get a sense of how a system evolves through these energy states during the simulation, we consider both the activation energy and adjacent minimum energy as a function of the number of KMC steps that the system has evolved away from the initial, ground state configuration in Figure 62. To preserve the trajectories of these systems, no resampling was performed in generating this figure.

In Figure 62, we see that the first evolution event away from the minimum energy configuration consistently involved an activation energy of $\sim 0.8 \ eV$ and resulted in an adjacent energy configuration about $0.5 \ eV$ above the ground state configuration. After this initial disruption of the ground state, events of much lower activation energy $\sim 0.2 \ eV$ were accessible, which included events that would return the system to the ground state configuration (i.e. events with a negative adjacent minimum energy). We see that, after the first displacement from the ground state configuration, the distribution of activation energies and adjacent minima accessed is consistent for the remaining evolution steps, indicating that critical new mechanisms are not being identified with each evolution step.

Next we consider how the maximum displacement of atoms depends on the KMC evolution step, again neglecting any resampling in this analysis to preserve
Figure 62: The activation and adjacent minimum energies as a function of evolution steps from the ground state configuration from the KMC simulation of the \( \Sigma 5 (210) \) GB in copper at 773 K.

The independent trajectories. This behavior is shown in Figure 63.

In Figure 63, we again see that in-plane displacements can be much larger than out-of-plane displacements. We note that the range of observed maximum displacements does not seem to depend on the evolution steps from the ground state configuration. However, we note that, of the four trajectories that evolved beyond 7 steps, the in-plane and out-of-plane displacements of the events observed were about 1.25 Å. The preference for these events is at least partially an artefact of the simulation method, indicating that this series of events has a high probability, but not that they are the only possible series of events.

Lastly, we consider the in-plane maximum displacement as a function of the maximum out-of-plane displacement for the same event to learn more about the mechanistic nature of these events. This comparison is shown in Figure 64 for the simulation data at 773 K, where again, no resampling has been performed on the data.

From Figure 64 we note that there is no general trend relating events with large in-plane displacements to their expected out-of-plane displacements, but rather,
that a rich population of possible events exists, with a range of possible displacement combinations.

6.3 PREDICTING KINETIC BEHAVIOR IN GRAIN BOUNDARIES

The off-lattice KMC method that has been introduced in this thesis provides a promising framework for estimating GB kinetic properties such as diffusivity and mobility. However, it is not a high-throughput method, and after several evolution steps on the small, simple example GB considered in our case study, the method is so bogged down with searching new LAEs for kinetic events that GB evolution slows to a crawl. As demonstrated above, it is still possible to estimate kinetic properties using this method. However, towards the end of developing predictive relationships between GB structure and properties, many thousands of GBs will need to be studied—a proposition for which this method is not well-suited in its current form.

However, calculation of the ground state residence time of a GB structure is a relatively fast process (depending on the number of unique LAEs in the target GB) that could lend itself to a high-throughput approach. As such, we have asked the question: how much can we infer about GB kinetics from normalized ground state
residence time alone? If GB kinetics are controlled by the process of disrupting the ground state configuration of the GB, then the ground state residence time of a GB would be expected to correlate with other GB kinetic properties. To determine the validity of this line of thinking, we have begun to analyze the kinetic properties of a number of GBs using the methods described in section 6.2.

We have begun our analysis by considering several Σ5 and a number of Σ3 GBs each at 773 K. Figure 65 shows the data from the beginning of this analysis, in which the following GBs have been considered:

- Σ5 (210)
- Σ5 (130)
- Σ3 (111)
- Σ3 (112)
- Σ3 (110)
- Σ3 (221)
- Σ3 (111) (617)
From Figure 65, there is a clear correlation between the ground state residence time (normalized by GB area) and the calculated intrinsic diffusivities and mobilities. Sufficient data has not yet been collected with which it would be possible to say that normalized ground state residence time is a good predictor of GB kinetics and will be valuable in developing predictive GB structure-property relationships; however, it appears to be worth pursuing.
CONCLUSIONS AND FUTURE WORK

7.1 SUMMARY

Towards the goal of performing reliable Kinetic Monte Carlo (KMC) simulations on off-lattice systems, we have shown that it is possible to calculate the residence time of a system by deterministically searching the events accessible to atoms in unique Local Atomic Environments (LAEs). If a sufficiently dense set of perturbations are used in the search, a full set of kinetically relevant activated pathways accessible to a system can be cataloged. In order to achieve this goal, this thesis presented discussion of several key ingredients:

- Distinguishing kinetic events: we presented an exhaustive approach to defining kinetic events by the displacements of atoms and used the numerical uncertainty in atomic position to differentiate between events. We compared this method to a previously developed topological approach.

- Performing complete searches on an energy landscape: we presented a deterministic search method for achieving a converged residence time calculation that made use of an optimizable 3D mesh of perturbation directions, rather than random perturbations, to initiate energy landscape searches.

- Specifying Local Atomic Environments (LAEs): we defined a LAE by the positions of its neighbors and showed that, for the relatively simple system being considered here, the positions of the 12 nearest neighbors were sufficient to define a unique LAE.

In demonstrating the effectiveness of this method, we have mapped the energy landscape of the ground state $\Sigma 5$ (210) GB in copper, a simple, symmetric-tilt GB. We have shown that residence time calculated for this system converges independently with each of the mesh parameters of the deterministic search. We have shown that the previously implemented topological method used to identify unique kinetic events and the present method result in similar residence time calculations and similar convergence behavior with the perturbation mesh parameters. However, the present method’s uncertainty in the residence time is less than half that of the topological approach. Additionally, since our method makes use of the physical definition of a kinetic process (the displacement of atoms) in comparing kinetic events, we have improved confidence in our calculation of residence time over the previous approaches, which rely on the selection of arbitrary
parameters.

After validating this method in the study of vacancy diffusion, we have characterized the scaling behavior of the algorithm with various parameters including system size and number of terms in the LAE definition. We have found that the method is quite sensitive to system complexity, wherein a GB system with the same simulation cell size as a system with a vacancy was more than an order of magnitude slower to undergo KMC evolution. In spite of this, we demonstrated that the present method provides a means with which to study kinetic behavior that is inaccessible using MD methods at low-temperatures.

We have implemented the off-lattice KMC method to study the kinetic behavior of the Σ5 (210) GB in copper. First, we have mapped its ground state energy landscape and noted that sliding events can be initiated with a local, thermal activation with an activation energy of 2.10 eV for this GB. We have then made use of the full off-lattice KMC framework to study the intrinsic diffusivity and mobility of this example GB system. We have found that the intrinsic diffusivity has an activation energy that is in between that of interstitial diffusivity and vacancy diffusivity at this GB. We have measured mobility at this GB. Though it is difficult to corroborate the mobility estimate with past studies, we have found the activation energy of the process to be only slightly higher than for bulk diffusion in copper at 0.72 eV, compared with 0.69 eV for diffusion in the bulk (which is often thought to dominate GB mobility). These results encourage the possibility that the present method will provide a powerful means of accessing GB kinetic properties. We have performed MD simulations on this GB to compare with our KMC method and found that, though the diffusivity and mobility values do not perfectly match, they are sufficiently similar to convince us that our KMC method can provide meaningful results, particularly at low temperatures.

With the goal of developing predictive relationships to describe GB kinetic properties, we have noted that the off-lattice KMC method, in its current form, does not provide an overwhelmingly high-throughput solution for studying GB kinetic properties. However, we have begun to assess whether it is possible that the normalized ground state residence time is a good predictor of kinetic behavior. We have analyzed several low-CSL GBs and seen a clear relationship between normalized ground state residence time and kinetic properties like intrinsic diffusivity (both in and out of the GB plane) and mobility. A more thorough investigation will be required to establish whether or not the preliminary findings reported in this document indicate a more general relationship.
7.2 FUTURE WORK

There are a number of areas of future work which may follow from the progress made in thesis. These topics fall into two categories as they relate to either (1) further developments and improvements of the off-lattice KMC algorithm or (2) new systems and that can be studied with the present method.

In the former case, the following specific next steps are recommended:

- Troubleshoot evolution steps that fail: in a typical KMC simulation employing the present method, about 1/3 of the attempted evolution steps fail. Originally, it was interpreted that this was due to an insufficiently searched LAE, and so, regardless of the LAE that the perturbed atom corresponded to, it was given an new LAE id and searched again. However, when it was observed that this course of action did not increase the evolution success rate, and, instead, drastically decreased the speed of the algorithm, the new course of action was established in which, after a failed attempt at an evolution step, a new evolution event is randomly chosen, and the failed step is ignored. One possible development that may lower the failure rate would be to store a larger set of successful perturbations (rather than only the one corresponding to the fewest number of convergence iterations) in the database. If a given perturbation failed, then all of the other possible perturbations could be attempted before ignoring the failed event.

- Analyze contribution from entropy: the present method was developed with the intention of studying low-temperature GB kinetic processes; as such, it was assumed that the entropic contribution to the free energy of these events could be neglected. However, entropy can be strictly included in the calculations, and it is worthwhile to establish the contribution of entropy to the low-temperature kinetics described here.

- Implement supercomputer parallelization: due to the stochastic nature of evolution in KMC simulations, the availability of additional computing power will allow for the study of systems with greater complexity or longer timescales.

In the latter, future areas of study may include:

- Expand GB kinetic parameter study: additional copper GBs can be investigated to determine whether normalized ground state residence time is a good predictor of GB kinetic behavior.

- Consider other defect systems: the off-lattice KMC method described here is equally applicable to the study of other atomistic scale defects, from point defects and clusters, to dislocations and surfaces.
• Consider other materials systems: the present method can naturally extend to the study of systems of other pure metals. Extension to multi-component systems will likely require a much larger definition of LAE; however, if the present method is successfully implemented on a supercomputer framework, studying these complex systems with long-range interactions may be tractable.
A.1 TUNGSTEN DIFFUSION IN CHROMIUM

Note that this case study was originally published in Ref. [184]:


This work was performed in collaboration with Dr. Park; Dr. Park performed all of the experimental work in this study and documented that contribution, while the present author performed the computations and was responsible for writing the remainder of the document.

The solute diffusion of tungsten at low concentrations in chromium has been investigated both by experiments and computational methods. From finite-source diffusion experiments measured with an Electron Probe Micro Analyzer at temperatures from 1526 – 1676 K, it was found that the diffusivity of tungsten in chromium follows the Arrhenius relationship $D = D_0 \exp\left(-\frac{Q}{RT}\right)$, where the activation energy was found to be $Q = 386 \pm 33$ kJ/mol. Diffusion of tungsten in chromium was investigated computationally with both the activation-relaxation technique (ART) and molecular dynamics (MD) using a hybrid potential. From ART, the effective diffusion activation energy was determined to be $Q = 315 \pm 20$ kJ/mol based on a multi-frequency model for a monovacancy mechanism. From MD, the square displacement of tungsten was analyzed at temperatures between 1200 and 1700 K, and the diffusion activation energy was determined to be $Q = 310 \pm 18$ kJ/mol. In spite of possible complications arising due to experimental compositions away from the dilute limit, the agreement between experiments and simulations falls within the calculated uncertainties, supporting a monovacancy mechanism for diffusion of tungsten in chromium.

Because it is often used at elevated temperatures, diffusion in chromium (Cr) has been studied experimentally, theoretically, and computationally for decades [121, 185–198]. Although there were some early discrepancies regarding the mechanisms and activation energy of Cr self-diffusion [185, 193–195], these were eventually resolved and Cr self-diffusion is now believed to follow the normal mechanisms identified for other BCC metals [185, 193], namely, monovacancy diffusion.
at lower temperatures, with a contribution from divacancy diffusion at higher temperatures (generally above about 1700 to 2000 K [188, 197]). Additionally, there exists a large body of work regarding diffusion in a number of Cr-alloys [192, 199–205]. Diffusion in chromium-tungsten (Cr-W) alloys is among the least studied of these binary systems, with Ref. [206] providing the only discussion of it of which we are aware, and that being a qualitative analysis of Cr-W grain boundary diffusion.

As tungsten (W) is only mildly soluble in Cr, it is not surprising that this couple has not previously been given much attention. However, recent work on the stability of nanocrystalline alloys [173, 207] indicates that Cr-W is a good candidate system to form stable nanocrystalline phases [173]. The possibility of fabricating nanocrystalline alloys with superior strength, hardness, and thermal stability in the Cr-W system is compelling, and our group’s unpublished work on the processing of such alloys also led us to appreciate the need for a better understanding of the kinetics of the system. It is therefore our purpose in the present case study to address the gap in kinetic data in the literature for the diffusion of W in Cr. In this study, Cr-W diffusion was investigated experimentally at temperatures in the range 1526 – 1676 K in the low-concentration solid solution regime (i.e., W content below the solubility limit of ~ 30%) that is most relevant to applications of the Cr-W system. To complement this experimental work and more explicitly connect to the dilute limit, computational studies of dilute Cr-W systems were also performed.

The activation-relaxation technique (ART) [144, 147] was used to investigate the energies of the accessible atomic structure transitions at a vacancy in a Cr-W system. Additionally, the diffusion of a single W atom in Cr was investigated with molecular dynamics simulations at temperatures between 1200 and 1700 K.

A.1.1 Experiments

Chromium discs (99.9% purity, 10 mm diameter, 5 mm thickness, from Alfa Aesar) were ground flat and parallel. To induce grain growth, the specimens were annealed at 1675 K for 24 hours. The final grain size was about 350 – 400 µm. A thin film (~ 1 µm) of high-purity tungsten (99.95%, from Alfa Aesar) was deposited on each disc by physical vapor deposition for 3 hours using an in-house sputter system operated under 155 W of RF power (from CESAR), while flowing 10 sccm Ar gas, with the chamber vacuum maintained below 10^{-7} Torr.
Each specimen was sealed in a quartz tube, first evacuated to $10^{-6}$ Torr using a turbo pump, and then backfilled with high-purity argon gas to 120 Torr. The sealed specimen was annealed in a furnace and exposed to temperatures of 1526, 1550, 1576, 1627, and 1676 K for 398, 212, 120, 48, and 22 hours, respectively. The diffusion depth in all cases was around 40 µm. After annealing, each specimen was laid on its side, embedded in an electrically conductive resin, and ground through half of its full width using an automatic polisher (TegraForce-5 from Struers) to expose the diffusion cross-section. A right angle between the side and top surface was achieved to within 0.2°. An Electron Probe Micro Analyzer (EPMA, JXA-8200 from JEOL) was then used to obtain depth profiles of tungsten concentration in chromium. For each specimen, 5 – 12 concentration profiles were acquired, spaced at least 20 µm apart.

A cross section of a chromium disc after tungsten diffusion is shown in 66, where the image contrast from backscattered electrons and the inset energy-dispersive spectroscopy (EDS) map show the local tungsten content. The tungsten diffusion profile is uniform along the long axes of the specimen and approximates one-dimensional diffusion well.

![Figure 66: Scanning electron microscopy (SEM) image taken in backscatter mode, for a chromium disc cross section after annealing at 1526 K. A tungsten elemental map from EDS is shown in the inset.](image)

Tungsten concentration as a function of diffusion depth at five different temperatures measured using EPMA is shown in 67. The diffusion of W into Cr in this experimental setup follows that for a semi-infinite one-dimensional solution of Fick’s second law with a limited diffusant source:

$$C(x, t) = \frac{M}{\sqrt{\pi Dt}} \exp \left( -\frac{x^2}{4Dt} \right)$$  \hspace{1cm} (46)
Here, \( C \) is the concentration of tungsten at a distance \( x \) from the initial Cr-W interface after diffusion time \( t \), and \( M \) is the total amount of deposited tungsten. \( D \) is the solute self-diffusion coefficient of tungsten in chromium. Concentration was converted to specific activity and is plotted vs. \( x^2 \) in Figure 68. Specific activity was obtained from concentration through division by the specimen density in any convenient units; for the data in Figure 68, the units of density were chosen for each profile so as to provide uniform separation of the curves. From a fit of Eq. 46 to the data in Figure 68 (with \( M \) treated as an unknown fitting parameter at each temperature), the diffusion coefficient was determined for each specimen (correlation coefficients \( R^2 > 0.98 \) were obtained for each profile), as listed in Table 3, and an Arrhenius plot of \( \ln D \) vs. \( 1/T \) is presented in Figure 4. In Eq. 46, \( D \) is assumed to be independent of concentration; the use of this equation is valid in the present study because \( \log(\text{activity}) \) vs \( x^2 \) was found to be linear and the thickness of the deposited solute layer was less than 1 \( \mu \)m, which is much less than \((Dt)^{1/2}\) for every investigated temperature.

![Figure 67: Tungsten concentration versus penetration-distance at five different temperatures from EMPA measurements in a Cr-W diffusion. The diffusion length is zeroed at the initial Cr-W interface.](image)

The equation for the solute diffusion of tungsten in chromium can be described by an Arrhenius relationship:

\[
D = D_0 \exp \left(-\frac{Q}{RT}\right)
\] (47)

A least squares regression analysis of the data from Figure 69 yields the activation energy, \( Q = 386 \pm 33 \) kJ/mol and the diffusion prefactor, \( D_0 = \Lambda_0 \exp (-6.8 \pm 2.5) \) m\(^2\)/s where \( \Lambda_0 \) is the unit measure of diffusivity: 1 m\(^2\)/s, and the reported uncertainty ranges correspond to 95% confidence bounds.
Figure 68: Specific activity versus square-penetration-distance at five different temperatures, presented on a logarithmic scale.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>D [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1526</td>
<td>5.27 \times 10^{-17}</td>
</tr>
<tr>
<td>1550</td>
<td>1.17 \times 10^{-16}</td>
</tr>
<tr>
<td>1576</td>
<td>2.24 \times 10^{-16}</td>
</tr>
<tr>
<td>1627</td>
<td>3.74 \times 10^{-16}</td>
</tr>
<tr>
<td>1676</td>
<td>1.08 \times 10^{-15}</td>
</tr>
</tbody>
</table>

Table 3: Measured solute diffusivity of tungsten in chromium at five temperatures

A.1.2 Computations

A.1.2.1 Cr-W Potential and Vacancy Structure

The initial configuration, generated with the open-source Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package [125, 126], was a pure, single crystal of BCC Cr with periodic boundary conditions in all directions and initial geometry minimized according to the concentration-dependent embedded atom method (CD-EAM) potential developed by Stukowski et al. [120, 169, 208]. This potential was developed to study BCC Fe-Cr alloys throughout the full compositional range and was verified to satisfactorily reproduce the self-diffusion behavior of pure chromium with a monovacancy migration energy of 0.99 eV [190].

One atom was removed from the single-crystal structure of pure Cr to generate a vacancy, and the system geometry was minimized again with the Stukowski CD-EAM potential. The vacancy formation energy in Cr was determined to be
A binding energy between W and the vacancy was observed. When the vacancy was separated from the W, the system was found to be 0.66 eV higher in energy than when W was bound to the vacancy. Images of the configurations of
the vacancy structure when bound to a W atom and sufficiently removed from the W atom are shown in Figure 70. Atoms that were not in the vacancy structure were excluded from this figure. Atoms are colored according to centrosymmetry [154] with the scale shown.

![Vacancy Structures](image)

Figure 70: Vacancy structures for the bound and free states found in this study. The image containing W in the vacancy structure (left) is 0.66 eV lower in energy than the free vacancy structure with the W atom in the bulk (right). Atoms with centrosymmetry parameter $< 0.5$ were excluded from the image for clarity. The images were generated with AtomEye [177].

From Figure 70, it is apparent that the W atom introduces an asymmetry into the vacancy structure that is not present in the unbound vacancy. Intermediate structures with intermediate energies (0.54 and 0.59 eV above the minimum energy structure) were found for the cases where W was a nearest neighbor and next-nearest neighbor to the vacancy. A schematic showing all relevant locations of the W atom with respect to the vacancy is shown in Figure 71, and their relative energy levels are presented in Table 4.

A.1.2.2 Local Transitions at a Vacancy

A schematic relevant to solute diffusion in dilute alloys is presented in Figure 71 and will be useful in discussing the results of ART. The post-processed data from ART is summarized in Table 4 including the type of transition corresponding to Figure 71, the activation energy of the transition, and the final energy of the configuration after the transition, both relative to the lowest energy structure. Although multiple mechanisms were found for some transitions, all activation energies reported in Table 4 correspond to the lowest energy mechanism found. It should be
Figure 71: Schematic of the possible jumps relevant to solute diffusion. The vacancy is initially at point 1 and the solute is located in the site marked with the W. Sites of unique vacancy jumps are numbered. Jump frequency from site i to site j is indicated by $\omega_{ij}$ and is proportional to the exponential of the activation energy required for the jump. If the forward and reverse activation energies identified by ART were identical for a given transition, then only $\omega_{ij}$ is shown in the schematic. This schematic is modeled after Ref. [198].

<table>
<thead>
<tr>
<th>Transition</th>
<th>$E_a$ [eV]</th>
<th>$E_{adj}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{1W}$</td>
<td>0.55</td>
<td>0.0</td>
</tr>
<tr>
<td>$\omega_{11}$</td>
<td>4.24</td>
<td>0.0</td>
</tr>
<tr>
<td>$\omega_{12}$</td>
<td>1.73</td>
<td>0.73</td>
</tr>
<tr>
<td>$\omega_{13}$</td>
<td>1.03</td>
<td>0.59</td>
</tr>
<tr>
<td>$\omega_{14}$</td>
<td>4.02</td>
<td>0.66</td>
</tr>
<tr>
<td>$\omega_{15}$</td>
<td>0.96</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 4: Transition energies for solute diffusion in a Cr-W alloy
noted that only the jump corresponding to $\omega_{1W}$ results in any motion of the tungsten atom. However, the relative jump frequencies of all the events accessible to the bound vacancy must be considered in correctly analyzing the solute diffusion of W in Cr. In particular, these other frequencies are important in determining the correlation coefficient and vacancy escape frequency [198, 209] as discussed below. The activation energies for the reverse jumps can be calculated from Table 4 as the difference: $E_{rev} = E_a - E_{adj}$.

The transition in which the vacancy moves to position 4 in Figure 71 corresponds to the separation of the vacancy from the tungsten, such that the final structure is 0.66 eV higher in energy than that of the bound structure. Additionally, when the vacancy moves to position 2 in Figure 71, the total energy of the structure is actually higher in energy than the unbound state by 0.07 eV, resulting in a repulsive interaction between the W and the vacancy.

A visual summary of all the transitions found with ART for this system, once again including only the lowest energy mechanisms, is presented in Figure 72, plotted as an energy landscape graph [157]. Important features of these transitions including the energy at the transition state, $E_a$, and the energy of the adjacent minimum configuration, $E_{adj}$ (both shown in eV relative to the initial minimum), can be read directly from Figure 72. For clarity, the transitions have each been labeled to correspond to the jump frequencies in Figure 71.

A.1.2.3 Determination of Diffusivity from ART Transitions

Solute diffusivity, $D_S$, can be calculated from the jump frequencies in Figures 71 and 72 according to:

$$D_S = a^2 f_S \omega_S \exp \left( -\frac{G_f^v - G_b^v}{kT} \right)$$ (48)

Where $a$ is the lattice parameter, $\omega_S$ is the jump frequency for the solute to exchange with the vacancy ($\omega_{1W}$ in our model), $G_f^v$ is the formation energy of a vacancy in pure Cr (2.56 eV), and $G_b^v$ is the binding energy of the solute atom with the vacancy, which is negative when attractive, ($-0.66$ eV for W in Cr). The correlation factor, $f_S$, depends on the other jump frequency terms in Figure 71 according to an equation developed by Manning [209] for dilute BCC systems:

$$f_S = \frac{7F \omega_{\beta m}}{2\omega_S + 7F \omega_{\beta m}}$$ (49)
Figure 72: Energy landscape graph of transitions relevant to the diffusion of tungsten in chromium found using ART, plotted on a vertical energy axis. Energy values are plotted relative to the initial minimum energy of the structure. The circles correspond to accessible configurations on the energy landscape and the lines correspond to the pathways connecting them. Forward progress in the transition corresponds to progress along the abscissa. The transitions have been labeled to correspond to the jump frequencies in Figure 71. Only a single label is necessary to denote the symmetric transitions.

\( \omega_{\beta m} \) is defined as the jump frequency for the vacancy to move between the first- and third- or fifth- nearest neighbor site with respect to the solute atom, and \( 7F \) is defined by Manning [209] as:

\[
7F = \frac{331.14 \left( \frac{\omega_{14}}{\omega_{15}} \right)^2 + 857.93 \left( \frac{\omega_{14}}{\omega_{15}} \right) + 409.95}{165.57 \left( \frac{\omega_{14}}{\omega_{15}} \right) + 134.21}
\]  

(50)

With \( \omega_{1\beta} \) being the jump frequency for the vacancy to move from a second- to a first- nearest neighbor position and \( \omega_{1m} \) being the jump frequency for the vacancy to move from a second- to a fourth- nearest neighbor position with respect to the W atom.

In the present analysis, instead of using the traditional geometrical definition of nearest neighbor based on the shortest Cartesian distance, we choose the site with the lowest activation barrier as the ‘nearest neighbor’ in order to accurately
determine the escape frequency. Similarly, the second- and third- nearest neighbors are those with increasingly higher activation barriers. We note that the geometry and symmetry arguments used to develop Eqs. (49-50) assumed both that the traditional nearest neighbor definition was used and that the binding of the second-nearest neighbor was much stronger than for the third- or fifth- nearest neighbors. The approach used here conforms to the latter assumption, and usually also yields neighbor orderings consistent with the geometrical approach as well.

Thus, in the calculations performed here: \( \omega_{j\beta} = \omega_{51} \), \( \omega_{jm} = \omega_{54} \) (where \( E_{a,jm} = E_{a,54} = 0.89 \text{ eV} \) was found with ART), and \( \omega_{m} = \omega_{12} \). In all cases, jump frequency was related to the activation energy of the transition by:

\[
\omega_{ij} = \nu_{ij}^* \exp\left(-\frac{E_{a,ij}}{kT}\right)
\]

(51)

Where \( \nu_{ij}^* \) is the effective frequency for a transition from position \( i \) to position \( j \). This value is defined by Vineyard [142] as the ratio of the products of all real vibrational frequencies in the initial state to all the real vibrational frequencies in the transition state:

\[
\nu^* = \left( \prod_{i=1}^{N} \nu_i \right) \left( \prod_{i=1}^{N-1} \nu_i' \right)
\]

(52)

Under the harmonic approximation, the vibrational modes themselves can be calculated from the eigenvalues of the mass-normalized Hessian matrix (i.e. \( H_{ij}^m = H_{ij}/\sqrt{m_im_j} \)). Thus, for each transition of interest, the mass-normalized Hessian matrix was calculated using a centered difference approximation with the potential described above. The eigenvalues, \( \lambda_i \), of the normalized Hessian matrix for both the initial configuration and saddle point were then determined using standard LAPACK routines [210]. From the eigenvalues, the vibrational modes were calculated according to:

\[
\nu_i = \frac{1}{2\pi} \sqrt{\lambda_i}
\]

(53)

All real vibrational modes were then used in Eq. (52) to determine the effective transition frequency, \( \nu^* \). The effective transition frequency for each of the transitions required in order to calculate \( D_S \) are shown in Table 5.
Using the values in Tables 4 and 5, $D_S$ was calculated according to Eq. (48) at temperatures between 1200 and 1700 K. An Arrhenius fit of the data is presented in Figure 73.

![Figure 73: Solute diffusion of W in Cr as generated from Eq. (48), using activation energies determined with ART.](image)

From a linear fit of the data in Figure 73, we find that the effective activation energy for W diffusion in Cr given a monovacancy mechanism is $Q = 315 \pm 20$ kJ/mol, and the pre-exponential term is $D_0 = \Lambda_0 \exp(-11 \pm 2.5) \text{ m}^2/\text{s}$, where $\Lambda_0$ is again the unit measure of diffusivity: 1 m$^2$/s. Uncertainty associated with these values derives both from the inherent uncertainties in the potentials used.
to model the system as well as from the assumptions that lead to the calculation of the correlation factor including consideration of only mechanisms within a traditional ‘single-jump’ distance and the use of the harmonic approximation. We estimate these uncertainties as amounting to perhaps ±20 kJ/mol in the activation energy and ±2.5 in the constant of the linearized Arrhenius model based on the range of values these terms can take when the input activation energies in Eq. 48 are varied (individually) by 0.2 eV— a reasonable assumption of the error associated with the potential.

A.1.2.4 MD of Many Transitions

The system, generated as described previously, was annealed at temperatures in the range 1200 – 1700 K. The system was brought to the target temperature by a staged equilibration process in increments of 300 K for 300 picoseconds each, with a timestep of 1 femtosecond, temperature and pressure held constant, and an additional Berendsen barostat used to moderate the pressure [183]. After equilibrating in this manner at the target temperature, the simulation was run for 100 nanoseconds, with a timestep of 1 femtosecond, at constant temperature and volume, again with a Berendsen barostat. At each stage, the target pressure in the system was set to zero.

During the final stage of the MD simulation, the displacement of all atoms was tracked at every 10,000 steps. When this data was post-processed, resampling was achieved by treating each step in the simulation as its own initial configuration so that a mean square displacement for each possible time interval could be calculated. Diffusivity was then calculated based on the relation: \( \langle (x - x_0)^2 \rangle = 6Dt \), which assumes an isotropic diffusion model. The slope of the mean squared displacement curve vs. time was then taken as an estimate of the diffusivity of W in Cr at each temperature investigated.

It should be noted that the slope of the mean squared displacement least-squares fit had to be rescaled to account for a discrepancy between the expected vacancy fraction in a physical specimen of Cr at the temperature of interest and the vacancy fraction in the system generated for this simulation. Namely, the correction: \( D' = f_{\text{actual}}/f_{\text{simulation}}D \), was used, where the vacancy fraction follows the Arrhenius form: \( f = \exp(-G_v/kT) \).

The activation energy for diffusion of W in Cr was estimated from the MD data (based on an enforced monovacancy mechanism) in the same fashion as the experimental data analysis presented above. The Arrhenius representation of the diffusivities determined at 11 different temperatures between 1200 and

133
1700 K is presented in Figure 74. From this treatment, it was calculated that $Q = 310 \pm 18 \text{ kJ/mol}$ with 95% confidence bounds and $D_0 = A_0 \exp(13.7 \pm 1.5) \text{ m}^2/\text{s}$, with $A_0$ the unit measure of diffusivity: 1 m$^2$/s.

![Figure 74: Arrhenius diffusion data for solute diffusion of W in Cr from MD simulations. The dashed lines indicate the 95% confidence bounds for the value of D.](image)

A.1.2.5 Comparison of Computational and Experimental Results

A summary of the results for the activation energy and diffusion prefactor for diffusion of W in Cr as determined by all three methods is presented in Table 6. The activation energies determined with the computational results are in excellent agreement with one another. To some extent, this can be regarded as a validation of the methodology used in connection with Eqs. 49–50 and the use of an energy-based ordering of atomic neighbors, since the MD results do not depend on that analysis and return the same essential output with regard to the diffusion activation energy. However, the diffusion values predicted by these two approaches differ by about an order of magnitude due to the discrepancy in their diffusion prefactor estimates. This difference may be related to the harmonic approximation assumed in the multiple frequency analysis; i.e., anharmonic effects may be relevant in the present temperature range. However, since validation with a system containing 3455 atoms did not show significantly different diffusion behavior...
from the 431 atom system, we do not expect this to be a major factor at these temperatures. Alternatively, it may be an indication that the empirical values in Eqs. 49–50 are not optimized for diffusion in the Cr-W system.

<table>
<thead>
<tr>
<th>Method</th>
<th>( Q ) [kJ/mol]</th>
<th>( D_0 ) [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>386 ± 33</td>
<td>( A_0 \exp(-6.8 \pm 2.5) )</td>
</tr>
<tr>
<td>ART</td>
<td>315 ± 20</td>
<td>( A_0 \exp(-10.6 \pm 2.5) )</td>
</tr>
<tr>
<td>Molecular Dynamics</td>
<td>310 ± 18</td>
<td>( A_0 \exp(-13.7 \pm 1.5) )</td>
</tr>
</tbody>
</table>

Table 6: Summary of results for the diffusion of W in Cr determined with three different methods.

While there is a non-negligible difference between the computational and experimental activation energies of order 20%, this is an apparent inconsistency on the slope of the data and not of the diffusivity values themselves. This can be seen in Figure 75, where diffusivity data for all three methods has been overlaid, and the agreement is good within uncertainty. The experimental data lie between those of the models, and actually lie within the error bands of both of the two methods, which is encouraging.

A number of features of the computational approach may have contributed to the observed mild disagreement between the activation energies determined by the experimental results and models. These include the use of a highly-simplified model in which only monovacancy mechanisms were considered and W-W interactions were ignored. Additionally, the accuracy of both computational methods was highly dependent on the quality of the potential used to model the system, which is uncertain. Alternatively, whereas in a very dilute alloy the assumed simple monovacancy mechanism may be the only contributing mechanism to diffusion in this system, the experimental system in this study involved concentrations up to about 7 atomic % W, and W-W interactions may have played a role.

To investigate this last possibility, a computational system with multiple tungsten atoms was considered. In particular, a system was built as previously discussed, and then a Cr atom in the vacancy structure was replaced with a W atom, such that the final system contained two W atoms in the vacancy structure. The system was minimized using the hybrid potential described previously with the addition of another EAM potential to account for W-W interactions [211]. ART was then performed on this system in order to find the transitions accessible to a vacancy with two adjacent W atoms as well as the binding energy of the vacancy to the tungsten pair. Additionally, the importance of W-W clusters was consid-
Figure 75: Arrhenius diffusion data for diffusion of W in Cr from experiments, MD simulations, and ART. The blue, dashed lines and black error bars indicate the 95% confidence bounds for the value of $D$ from MD and experiments, respectively.

considered by comparing the relative energy of a system with adjacent W atoms to a system with two separated W atoms.

From these simulations, it was found that separation of the two W atoms resulted in an energy penalty of $5.05 \text{ eV}$, which indicates a strong likelihood that the W atoms would be found in pairs or possibly clusters of higher order in a non-dilute alloy. Additionally, it was found that the binding energy of a vacancy to the W atom pair was $-0.54 \text{ eV}$, which is $0.12 \text{ eV}$ less attractive than the interaction between a single W atom and a vacancy. From these features, one could conjecture that the diffusivity of W in this system may involve a contribution from W-W interactions, and this may in turn account for some of the minor discrepancies amongst the data series in Fig. 75.

A.2 GENERATING INITIAL STRUCTURES

To generate an initial GB structure we create two grains with the desired orientation and then minimize the bicrystal to a local minima. In our simulations, we re-
quire periodic boundary conditions in all three directions, but we do not want to create two GB interfaces, so we add a section of empty space above and below the top and bottom surfaces so that the simulation cell is periodic in the z-direction, but no secondary interface is formed. To limit the effects of the top and bottom surfaces on the behavior of the GB, we also include blocks of atoms between each surface and the dynamic region of the simulation which are forced to be frozen. The following LAMMPS input script accomplishes this:

```plaintext
# LAMMPS Input File for Grain Boundary generation in copper
# Kathleen Alexander, Jun2012
# This file will generate a single Sigma 3 (1 1 1) symmetric twin grain boundary
# Note that the z direction is normal to the grain boundary plane

# ------------ Original Development -------------------
# Header from the original file developed by Mark Tschoop
# LAMMPS Input File for Grain Boundaries
# Mark Tschoopp, Dec2009

#--------- Define System Variables ---------------------------
# The following variables pertain to copper
variable latparam equal 3.6099999 # lattice parameter for copper: previously calculated
variable minimumenergy equal -3.53999 # energy of a completely coordinated atom in the lattice: previously calculated
variable NN equal 1.28 # Nearest neighbor distance in copper, same as metallic radius
# The following variables are general
variable eVAtomJm equal 16021.7646 # conversion from eV/A^2 to mJ/m^2
variable sigma equal 5 # CSL sigma value for the system of interest
variable DSCcuts equal 8 # number of cuts in the DSC lattice to translate the grains by
variable dirname index Cu_Sigma5_130_ppp

#--------- Define Geometry Variables -------------------------
# The following 9 variables describe the GB normals in grains 1 and 2
variable x11 equal 1.0
variable x12 equal 0.0
variable x13 equal 0.0
variable x21 equal 1.0
variable x22 equal 0.0
variable x23 equal 0.0
variable y11 equal 0.0
variable y12 equal 3.0
variable y13 equal 1.0
variable y21 equal 0.0
variable y22 equal 3.0
```
variable y23 equal -1.0
variable z11 equal 0.0
variable z12 equal -1.0
variable z13 equal 3.0
variable z21 equal 0.0
variable z22 equal 1.0
variable z23 equal 3.0

#---------------- Define Simulation Variables ------------------------
# The following variables effect the nature of the simulation
variable CSLplanes equal 5 # the number of CSL lattice vector translates in the plane
variable overlapfactor equal 0.1 # Fraction of NN that will be the overlap cutoff
variable etol equal 1.0e-25 # Energy tolerance to exit minimization
variable ftol equal 1.0e-25 # Force tolerance to exit minimization
variable maxiter equal 10000 # Maximum number of iterations to exit minimization
variable maxeval equal 20000 # Maximum number of force evaluations to exit minimization

#---------------- Define Dependent Variables ---------------------------
# The following variables depend on other variables that are previously defined
variable xrep equal ${latparam}*sqrt(${x11}^2+${x12}^2+${x13}^2) # repeat distance in the x direction
variable yrep equal ${latparam}*sqrt(${y11}^2+${y12}^2+${y13}^2) # repeat distance in the y direction
variable zrep equal ${latparam}*sqrt(${z11}^2+${z12}^2+${z13}^2) # repeat distance in the z direction
variable xinc equal ${latparam}/sqrt(${x11}^2+${x12}^2+${x13}^2) # repeat distance in the x direction
variable yinc equal ${latparam}/sqrt(${y11}^2+${y12}^2+${y13}^2) # repeat distance in the y direction
variable zinc equal ${latparam}/sqrt(${z11}^2+${z12}^2+${z13}^2) # repeat distance in the z direction
variable xdelta equal 2*${xinc} # interplanar spacing in the z direction
variable ydelta equal 2*${yinc} # interplanar spacing in the z direction
variable zdelta equal 2*${zinc} # interplanar spacing in the z direction
variable overlapcut equal ${overlapfactor}*${NN} # overlap cutoff distance

# Simulation cell size
# specifically, the number of planes in the given crystallographic direction
variable xreps equal 25
variable yreps equal 3
variable zreps1 equal 3
variable zreps2 equal 3
variable block_planes equal 1
variable nzdelta equal -1*${zdelta}
variable extra_height equal 1
variable eps equal 0.0

#------------------ Counter Loops and Make Directory -------------------
shell mkdir ${dirname}
shell mkdir ${dirname}/Pics
shell mkdir ${dirname}/Pics/Min1
shell mkdir ${dirname}/Pics/Min2
shell mkdir ${dirname}/Pics/Run
shell cp A ${dirname}/Pics/Min1
shell cp A ${dirname}/Pics/Min2
shell cp A ${dirname}/Pics/Run

# ---------- Initialize Simulation ---------------------
clear
units metal
dimension 3
boundary p p p
atom_style atomic

# ---------- Create Atomistic Structure ---------------------
# The following creates two grains according to the parameters defined above
lattice fcc ${latparam}
variable X equal (${xreps}*${xrep})
variable X1 equal ${eps}*${X} #${xdelta}
variable X2 equal ${X}-${eps}*${X} #${X}-${xdelta}
variable x_len equal ${X2}-${X1}
variable Y equal (${yreps}*${yrep})
variable Y1 equal ${eps}*${Y} #${ydelta}
variable Y2 equal ${Y}-${eps}*${Y} #${Y}-${ydelta}
variable y_len equal ${Y2}-${Y1}
variable Z1 equal -1*(${zreps2}+${block_planes})*${zrep}+${zdelta}
variable Z2 equal (${zreps1}+${block_planes})*${zrep}+${zdelta}
variable Z_bottom equal ${Z1}-${extra_height}*${zrep}
variable Z_top equal ${Z2}+${extra_height}*${zrep}
variable Zblock equal (${Z2}-${block_planes}*${zrep})
variable nZblock equal ${Z1}+(${block_planes}*${zrep})
variable Zblock_delta equal ${Zblock}+${zinc}*0.5
variable nZblock_delta equal ${nZblock}-${zinc}*0.5
region whole block 0.000000 ${X} 0.000000 ${Y} ${Z_bottom} ${Z_top} units box
create_box 2 whole
region top block INF INF INF INF ${zdelta} ${Z2} units box
region top_block block INF INF INF INF ${Zblock_delta} ${Z2} units box
region gb_upper_dynamic block INF INF INF INF \{zdelta\} \{Zblock\} units box
region gb_upper block \{X1\} \{X2\} \{Y1\} \{Y2\} \{zdelta\} \{Zblock\} units box
lattice fcc \{latparam\} orient x \{x11\} \{x12\} \{x13\} orient y \{y11\} \{y12\} \{y13\}
create_atoms 1 region top

region bottom block INF INF INF INF \{Z1\} \{nzdelta\} units box
region lower_block block INF INF INF INF \{Z1\} \{nZblock_delta\} units box
region gb_lower_dynamic block INF INF INF INF \{nZblock\} \{nzdelta\} units box
region gb_lower block \{X1\} \{X2\} \{Y1\} \{Y2\} \{nZblock\} \{nzdelta\} units box
lattice fcc \{latparam\} orient x \{x21\} \{x22\} \{x23\} orient y \{y21\} \{y22\} \{y23\}
create_atoms 2 region bottom

# ---------- Define Interatomic Potential ---------------------
pair_style eam/alloy
pair_coeff * * Cu01.eam.alloy Cu Cu
neighbor 2.0 bin
neigh_modify delay 10 check yes

# ---------- Displace atoms and delete overlapping atoms ---------------------
delete_atoms overlap \{overlapcut\} all all

# ---------- Define Settings ---------------------
compute csym all centro/atom fcc
compute 1 all property/local natom1 natom2
compute 2 all property/local patom1 patom2

# ---------- Run Minimization 1---------------------
shell cd \{$dirname\}/Pics/Min1
reset_timestep 0
thermo 10
thermo_style custom step pe lx ly lz press pxx pyy pzz
dump 1 all cfg 25 dump.min_*.cfg mass type xs ys zs c_csym fx fy fz
dump_modify 1 element Cu Cu
min_style cg
min_modify dmax 0.01
minimize \{etol\} \{ftol\} \{maxiter\} \{maxeval\}
undump 1
shell cd ../..//

#---------- Assign GB and Dynamic Groups ---------------------
region r_dynamic block INF INF INF INF \{nZblock\} \{Zblock\} units box
region r_gb block \{X1\} \{X2\} \{Y1\} \{Y2\} \{nZblock\} \{Zblock\} units box
# A.2 generating initial structures

group dynamic_1 region gb_upper_dynamic
group dynamic_2 region gb_lower_dynamic
group dynamic region r_dynamic
group gb_1 region gb_upper
group gb_2 region gb_lower
group gb region r_gb

#---------- Define GB Energy Computes -----------------------------
compute eng gb pe/atom
compute eatoms gb reduce sum c_eng

#---------- Run Minimization 2---------------------
# Now allow the box to expand/contract perpendicular to the grain boundary
shell cd ${dirname}/Pics/Min2
reset_timestep 0
thermo 10
thermo_style custom step pe lx ly lz press pxx pyy pzz c_eatoms
dump 1 all cfg 25 dump.min_*.cfg mass type xs ys zs c_csym c_eng fx fy fz
dump_modify 1 element Cu Cu
fix 1 dynamic box/relax aniso 0.0
min_style cg
min_modify dmax 0.1
minimize ${etol} ${ftol} ${maxiter} ${maxeval}
unfix 1
undump 1
shell cd ../../../

#---------- Calculate GB Energy ---------------------
variable esum equal "v_minimumenergy * count(gb)"
variable xseng equal "c_eatoms - (v_minimumenergy * count(gb))"
variable gbarea equal ${x_len}*${y_len}
variable gbe equal "(c_eatoms - (v_minimumenergy * count(gb)))/v_gbarea"
variable gbemJm2 equal $(gbe)*${eVAtomJm2}
variable gbernd equal round(${gbemJm2})
print "GB energy is ${gbemJm2} mJ/m^2"

#---------- Dump data into Data file ---------------------
shell cd ${dirname}
reset_timestep 0
timestep 0.001
fix 1 dynamic box/relax aniso 0.0
The above method can converge a bicrystal to a local minimum configuration; however, in order to find the global minimum structure of the bicrystal, we must explore its microscopic degrees of freedom. To accomplish this, we repeat the previous minimization on bicrystal structures that are slightly translated with respect to one another. The following bash script repeatedly updates the LAMMPS input script with new translational positions and initiates the LAMMPS program while keeping track of the lowest energy structure found during the search process:

```bash
#!/bin/bash

INP_FILE=('Cu_repeat_distance_ppp_130.in')
NEW_DIRECT=('Cu_Sigma5_130_ppp')
MAXX=38
MAXY=21
MAXZ1=20
MAXZ2=20
MINGBENG=10000

mkdir MIN-GB-DATA

FILES=${#INP_FILE[*]}

print "All done"
```
for ((i=0; i < FILES; i++))
do
  for zplanes1 in $(eval echo \"{17..17}\")
do
    for zplanes2 in $(eval echo \"{17..17}\")
do
      for yplanes in $(eval echo \"{21..\${MAXY}}\")
do
        for xplanes in $(eval echo \"{38..38}\")
do
          sed -i 's/variable zplanes1 equal.*/variable zplanes1 equal \${zplanes1}/g' ${INP_FILE}
sed -i 's/variable zplanes2 equal.*/variable zplanes2 equal \${zplanes2}/g' ${INP_FILE}
sed -i 's/variable xplanes equal.*/variable xplanes equal \${xplanes}/g' ${INP_FILE}
sed -i 's/variable yplanes equal.*/variable yplanes equal \${yplanes}/g' ${INP_FILE}
sed -i 's/variable xmove equal.*/variable xmove equal \${xtrans}\*$\{xinc\}/g' ${INP_FILE}
sed -i 's/variable ymove equal.*/variable ymove equal \${ytrans}\*$\{yinc\}/g' ${INP_FILE}
          rm -rf ${NEW_DIRECT\[$i\]}/
        done
      done
    done
  done
done
  rm log.lammps
mpirun -np 6 lmp_openmpi < ${INP_FILE\[$i\]}

cd ${NEW_DIRECT}

gbenergy=$(echo $(echo dump.final_*.txt | grep -oE \[0-9\]\{4\}\))
echo dump.final_*.txt | grep -oE \[0-9\]\{4\}\ if [ $? -ne 0 ]; then
  unset gbenergy
gbenergy=$(echo $(echo dump.final_*.txt | grep -oE \[0-9\]\{3\}\))
echo dump.final_*.txt | grep -oE \[0-9\]\{3\}\ if [ $? -ne 0 ]; then
  unset gbenergy
gbenergy=$(echo $(echo dump.final_*.txt | grep -oE \[0-9\]\{2\}\))
echo dump.final_*.txt | grep -oE \[0-9\]\{2\}\fi
fi
cd ../

echo \"\${gbenergy}\" >> gb_data.txt
if [ $(eval echo \"\${gbenergy}\") -lt $(eval echo \"\${MINGBENG}\") ]; then
  unset MINGBENG
MINGBENG=$(\"\${gbenergy}\")
mv log.lammps ${NEW_DIRECT}
APPENDIX

```bash
cp ${INP_FILE} ${NEW_DIRECT}
mv ${NEW_DIRECT}/ MIN-GB-DATA/${NEW_DIRECT}_${MINGBENG}
fi
done
done
done
done

done
done
done

rm *
exit 0
```

A.3 DATABASE STRUCTURE

The PostgreSQL database used to store the KMC catalog information was populated with the following tables:

A table to store the configuration information of each unique LAE:

```sql
CREATE TABLE configs_table (  
id SERIAL PRIMARY KEY,  
sum real,  
num_atoms integer DEFAULT 0,  
searched integer DEFAULT 0,  
_1 real,  
_1_1 real,  
_1_2 real,  
_1_3 real,  
_2 real,  
_2_1 real,  
_2_2 real,  
_2_3 real,  
_3 real,  
_3_1 real,  
_3_2 real,  
_3_3 real,  
_4 real,  
_4_1 real,  
_4_2 real,  
_4_3 real,  
_5 real,
```

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As well as a table to store the event information associated with each unique kinetic process identified in the deterministic search process:

CREATE TABLE transitions_table (  
id SERIAL PRIMARY KEY,  
min_eng real,  
sp_eng real,  
nu_star real,  
configid integer,  
time_stamp timestamp with time zone DEFAULT now()  
);

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APPENDIX

p_dist real,
p_x real,
p_y real,
p_z real,
iterations integer,
time_stamp timestamp with time zone DEFAULT now();

Additional tables are dynamically created and destroyed throughout the KMC method that store information about the numbers of atoms in each LAE on each processor.

A.4 SQUARE DISPLACEMENT VS. TIME DATA FROM KMC SIMULATIONS

Figures 76 through 89 show the square displacement vs time data for the KMC simulations on the Σ5 (210) GB presented in section 6.2 for all temperatures investigated in this study. All values of diffusivity and mobility were calculated using the bootstrapping approach described in section 6.2.

![Figure 76: Mean-square displacement vs. time for a KMC simulation at 298 K in the Σ5 (210) GB in copper both in and out of the GB plane.](image)

Figure 76: Mean-square displacement vs. time for a KMC simulation at 298 K in the Σ5 (210) GB in copper both in and out of the GB plane.
Figure 77: Mean-square displacement vs. time for a KMC simulation at 373 K in the \( \Sigma 5 (210) \) GB in copper both in and out of the GB plane.

Figure 78: Mean-square displacement vs. time for a KMC simulation at 573 K in the \( \Sigma 5 (210) \) GB in copper both in and out of the GB plane.
Figure 79: Mean-square displacement vs. time for a KMC simulation at 773 K in the Σ5 (210) GB in copper both in and out of the GB plane.

Figure 80: Mean-square displacement vs. time for a KMC simulation at 973 K in the Σ5 (210) GB in copper both in and out of the GB plane.
Figure 81: Mean-square displacement vs. time for a KMC simulation at 1173 K in the $\Sigma 5 (210)$ GB in copper both in and out of the GB plane.

Figure 82: Mean-square displacement vs. time for a KMC simulation at 1173 K in the $\Sigma 5 (210)$ GB in copper both in and out of the GB plane.
Figure 83: Mean-square interface displacement vs. time for a KMC simulation at 298 K in the Σ5 (210) GB in copper.

Figure 84: Mean-square interface displacement vs. time for a KMC simulation at 373 K in the Σ5 (210) GB in copper.
Figure 85: Mean-square interface displacement vs. time for a KMC simulation at 573 K in the Σ5 (210) GB in copper.

Figure 86: Mean-square interface displacement vs. time for a KMC simulation at 773 K in the Σ5 (210) GB in copper.
Figure 87: Mean-square interface displacement vs. time for a KMC simulation at 973 K in the $\Sigma 5 \{210\}$ GB in copper.

Figure 88: Mean-square interface displacement vs. time for a KMC simulation at 1173 K in the $\Sigma 5 \{210\}$ GB in copper.
Figure 89: Mean-square interface displacement vs. time for a KMC simulation at 1173 K in the Σ5 (210) GB in copper both in and out of the GB plane.
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