A First Principles Study of Pipe Diffusion in Nickel

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A FIRST PRINCIPLES STUDY
OF PIPE DIFFUSION IN NICKEL

A dissertation submitted in partial
fulfillment of the requirements for the degree of
Doctor of Philosophy

By

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ABSTRACT


Vacancy-mediated diffusion along dislocations, often referred to as pipe diffusion, can contribute to creep deformation of metals in many engineering applications. This process is studied along an \( \frac{a}{2}(1\bar{1}0) \) screw dislocation in fcc Ni using a density functional theory approach. An accurate geometrical configuration of the screw dislocation core, dissociated into Shockley partial dislocations and separated by a stacking fault, was previously derived using a lattice Green’s function technique. Activation energies and frequencies are calculated for atom-vacancy exchanges that contribute to diffusion around and along one of the partial cores. This analysis reveals the significant role of the sites within the compressive component of the dislocation, the dominant contribution of the hops around the screw geometry rather than directly along the dislocation line, and the importance of including the stacking fault sites. Kinetic Monte Carlo simulations use these frequencies to generate diffusion coefficients that account for correlation effects. Near 80% of the melting temperature \( T_m \), these pipe diffusivities are an order of magnitude higher than those found in fcc regions, and they are eight orders higher at room temperature. Calculations are compared to experimental results and the differences are discussed. While pipe diffusion is unlikely to contribute to isotropic mass flux at low dislocation densities, it will accelerate dislocation mechanisms controlling creep, particularly when alloying elements are involved. To
quantify the effects of chemistry on diffusivity in addition to geometry, the described techniques also analyze the pipe diffusivity of several important alloying elements to Ni-base superalloys: Co, Cr, Al, Ti, Mo, W, and Re. Calculations quantify how the partial core enhances diffusivities of each element relative to isotropic diffusion in fcc Ni.

Advances in first principles methods provide a means to explore the rate constants of mechanisms that constitute diffusion with molecular dynamics. We apply these to select atom-vacancy exchanges near the same screw dislocation partial core in fcc Ni at 1000 and 1400 K. Intrinsic properties of this dynamic approach contrast limitations of the widely used harmonic transition state theory (HTST) approximations that were previously applied, revealing direction-dependent free energy profiles and temperature-dependent correlation effects. In contrast to static HTST, the dynamic approach reveals an asymmetry in mass transport that is related to the edge character of the partial dislocation. This arises from different philosophies underlying the two methodologies. The absolute values of the rate constants, however, are within the same order of magnitude, with the HTST method generally underestimating rates by a factor of 2-5. Combined with a twofold increase in rates due to thermal expansion at high temperatures, this partially explains why our kinetic Monte Carlo simulations yield lower diffusivities for pipe diffusion than experiments observe.
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Chapter 3 is based on “First-principles kinetic Monte Carlo study of substitutional solute pipe diffusion in fcc Ni,” by Luke J. Wirth, Amir A. Farajian, and Christopher Woodward, which will be submitted to a journal soon.

Chapter 4 is based on “Ab initio molecular dynamics of pipe diffusion in fcc Ni beyond transition state theory,” by Luke J. Wirth, Christopher Woodward, and Amir A. Farajian, which is currently undergoing peer review.

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Chapter 1. Introduction

Dislocations in metal materials provide high-diffusivity pathways for mass transport. Diffusion along these dislocations, known as pipe diffusion, has important implications on the deformation of engineered metal materials during high-temperature operating conditions. In Ni-base superalloy turbine components like blades and discs, pipe diffusion can be the rate-limiting mechanism of plastic creep deformation in certain contexts. Modern simulation methodologies allow for accurate study of the individual atom-vacancy exchanges that compose pipe diffusion from first principles via density functional theory (DFT). These simulations account for quantum mechanical interactions between particles and do not depend on any empirically obtained information as input. Here, we use a static DFT methodology based on harmonic transition state theory (HTST) to study vacancy-mediated self- and substitutional solute pipe diffusion along an $\frac{a_0}{2}(1\bar{1}0)$ screw dislocation core in fcc Ni. We then use a pair of ab initio molecular dynamics techniques to study several atom-vacancy exchanges at elevated temperatures while accounting for free energy contributions to diffusion and the presence of barrier recrossings.

1.1 Materials Context

$\gamma$-$\gamma'$ Ni-base superalloys are capable of withstanding operating temperatures above 800°C. Resultantly, they commonly compose turbine blades and discs in jet engines. The $\gamma$ phase is an fcc Ni matrix that contains various alloying elements, and the $\gamma'$ phase is an intermetallic, which is usually Ni$_3$Al. High volume fractions of $\gamma'$ provide strength; these are
ideally around 70%. Such fractions are attainable at 100-150 °C below the solvus temperature of a particular superalloy \([2]\), e.g., 1298 °C for CMSX-4 \([3]\). High concentrations of Al and Ti allow these high volume fractions to exist, while other elements like Co, Cr, Mo, W, Ta, or other refractory elements promote solution strengthening \([1]\). The presence of Cr also resists corrosion, but too high a concentration of it (or of the other alloying elements) can cause unwanted phases to form, weakening the superalloy.

Dislocations are linear defects in crystalline structures, like the fcc \(\gamma\) matrix or the L1\(_2\) ordered \(\gamma'\) phase of the Ni-base superalloys. A dislocation is characterized by a dislocation line, which extends over some distance through a material, and a Burgers vector \(b\) that describes the distortion of the crystal lattice by the dislocation. The dislocation line lies in a plane called the slip plane, which it can move along to accommodate applied shear stresses. One fundamental type of dislocation is the edge dislocation, which consists of an extra half plane of atoms on one side of the slip plane along the dislocation line, with that dislocation line running perpendicularly to the Burgers vector. The other fundamental type is the screw dislocation, where the dislocation line and Burgers vector are parallel, and the distorted geometry around the dislocation line adopts a helical character. Most realistic dislocations aren’t perfectly straight and can’t be neatly categorized as one or the other, so they are said to consist of mixed edge and screw components. It is often energetically favorable for dislocations to dissociate into partial dislocations like so:

\[
\frac{a_0}{2} \langle 1\bar{1}0 \rangle \rightarrow \frac{a_0}{6} \langle 2\bar{1}1 \rangle + \frac{a_0}{6} \langle 1\bar{2}\bar{1} \rangle
\]  

(1.1)

This describes dissociation of a screw dislocation in an fcc crystal. \(a_0\) is the lattice parameter (3.52 Å in fcc Ni \([4]\)) and \(\langle 1\bar{1}0 \rangle\) is the direction of the dislocation line. The two partial dislocations are separated by an hcp stacking fault, and the plane normal to the dislocation line has features that are illustrated in Fig. 1.1.
Dislocations in deformed materials form pathways that provide enhanced diffusivities for mass transport relative to crystalline regions. These pathways are predominantly one-dimensional with small cross-sectional areas relative to long extensions in the dislocation line direction, which is why this phenomenon has historically been called “pipe diffusion.” Because of the absence or diminished presence of grain boundaries in “single crystal” Ni-base superalloy turbine blades, pipe diffusion is of particular concern relative to traditional polycrystalline materials, where grain boundary diffusion might be of greater interest. While pipe diffusion has been discussed in the body of scientific literature for quite some time, only recently have direct observations of the effects been possible. One transmission electron microscopy (TEM) study observed pipe diffusion increasing the diffusivity of impurities in aluminum by three orders of magnitude near 600 K [9]. Another more recent work captured images of the phenomenon in a superlattice with atomic resolution [10]. In commercial applications such as Ni-base superalloy turbine blades and discs, pipe diffusion is primarily of concern because it enables diffusion-limited deformation processes, e.g. creep at high temperatures, to proceed at faster rates than would occur in the
presence of only bulk diffusion [11]. Creep consists of the time-dependent plastic deformation of a material when exposed to a sustained stress especially at elevated temperatures, and is a primary contributor to failures in technologies that operate at high temperatures and experience sustained stresses, like blades in gas turbines [12]. Pipe diffusion can indirectly affect creep via its contributions to diffusion-induced grain boundary migration or slip [13]. In emerging technologies that are engineered at the nanoscale, creep can be encountered even more frequently and at lower temperatures [14].

1.2 Computational Approach

Because of the charge transfer that occurs when an atom moves from one site to another and passes its neighbors, diffusion is more accurately modeled with quantum mechanical techniques than within the hard-sphere approximation of classical mechanics. A fundamental equation governing quantum mechanical behavior is the Schrödinger equation, which in its simplest, time-independent form can be expressed as an eigenvalue problem:

\[ H\Psi = E\Psi, \quad (1.2) \]

where \( H \) is the Hamiltonian operator, \( \Psi \) is the wave function of a system, and \( E \) is the total system energy. This equation describes the quantum behavior of a system like Newton’s laws describe the classical behavior of a system, but solving it for realistic many-atom systems is impracticable. By making a series of simplifying approximations that have been developed over the years, it is possible to balance accuracy and efficiency to quantum mechanically describe systems of interest through density functional theory (DFT).

First, electrons and ions are handled separately within this framework according to the Born-Oppenheimer approximation, where the electrons rapidly react to any changes in the external potential created by the presence of the ions, which are considered to be fixed within a given state. This allows for terms of the Hamiltonian to be separated based
on whether they concern either electron-electron or electron-ion interactions, simplifying calculations. Next, the Hohenberg-Kohn theorems state that the energy of a given system is a functional of its electron density, and that the ground state energy is a unique functional of the ground state electron density [15]. Kohn and Sham devised such a functional for use in systems where each electron is described by its own Schrödinger-like equation existing within an effective potential representing the ions and other electrons [16]. In a system of $N$ electrons, each of these Kohn-Sham equations takes the following form [17]:

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) + V_H(\mathbf{r}, \rho) + V_{XC}(\mathbf{r}, \rho) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}),$$

(1.3)

where the terms in the equation (from left-to-right) represent the electron kinetic energy, the ion-electron interaction potential, the Hartree potential or Coulombic interaction between electron $i$ and the electron density $\rho$ of all electrons present, and the exchange-correlation functional; $\phi_i$ is the single-electron wavefunction, and $\epsilon_i$ is the single-electron energy. While this approach makes quantum mechanical calculations computationally feasible, it necessitates approximation of the exchange-correlation functional to account for exchange and correlation energies. The former includes contributions that arise from the antisymmetric nature of the overall wavefunction, while the latter accounts for the difference between the Hamiltonians of the interacting electrons and non-interacting, electron-like particles (excluding the exchange and Hartree contributions). Two common classes of these functionals employ local density approximations (LDA) based on the electronic density at each point in space or generalized gradient approximations (GGA) which also include information on the density gradient.

Through iterative calculations, one can obtain the ground state electron density for a particular configuration of ions. Given an initial electron density, Eq. (1.3) is solved to obtain a set of single-electron wavefunctions. These are then used to generate a new electron density:
\[ \rho(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}), \quad (1.4) \]

where \( \phi_i^*(\mathbf{r}) \) is the complex conjugate of \( \phi_i(\mathbf{r}) \). This density is inserted back into Eq. (1.3) until a self-consistent solution sees the input and output densities agree. To relax an atomic geometry, ions move (most commonly according to a conjugate gradients algorithm) to minimize Hellmann-Feynman forces based on the calculated ground state density. This process repeats until all forces felt by ions are less than some desired tolerance, at which point the system is considered to be optimized and further study of its properties may be expected to reveal meaningful information. Efficient iterative matrix diagonalization techniques help to make these calculations practical on contemporary supercomputers for systems containing hundreds of atoms [18]. Iterative diagonalization methods were developed to improve the efficiency of pseudopotential plane wave methods, and over the last 20 years have become popular for modeling defects in a wide variety of materials. Central to these methods, pseudopotentials describe the behavior of non-valence electrons, which are generally relatively less important in determining the physical properties of a material, thus speeding up calculations considerably. Further details concerning DFT in general are readily available in the literature [17–20], and the parameters and settings used for calculations here are discussed in the methodology sections of Chapters 2-4.

1.3 Scope

The next three chapters of this work each provide study of a different aspect of diffusion along a screw dislocation partial core. Each chapter is largely self-contained with an introduction, literature review, description of methodology, and discussion of results, though some of the fundamental literature and methodologies discussed within Chapter 2 are relevant to all chapters.

Chapter 2 considers vacancy-mediated self-diffusion of Ni along the partial core.
A harmonic transition state (HTST) framework uses DFT-generated nudged elastic band (NEB)-calculated migration energy barriers and Vineyard attempt frequencies. These provide rate constants that describe the frequency with which a vacancy hops along each of many activation pathways in and around the core. A kinetic Monte Carlo (KMC) model uses these rates to generate Ni diffusivities along the core over a range of temperatures. By comparing these values to those in fcc Ni, we quantify the magnitude by which the dislocation core enhances diffusivities relative to those occurring in bulk regions.

Chapter 3 builds on the study of Chapter 2 by extending the analysis to consider a variety of alloying elements that are important to Ni-base superalloys: Co, Cr, Al, Ti, Mo, W, and Re. DFT calculations identify the rate constants of solute-vacancy exchanges along many important pathways near the core, which are input into the KMC model to generate diffusivities of each solute in the dilute case. Results allow comparisons of diffusivities to be made with both respect to chemistry as well as geometry, and the reported activation energies could potentially be used as input into creep rate models.

Chapter 4 introduces an ab initio molecular dynamics (MD)-based methodology to calculate several rate constants within a framework that includes information which is invisible to the static approach. Constrained MD simulations generate free energy gradients along a reaction pathway, which are then integrated to obtain free energy barriers for several atom-vacancy exchanges at 1000 and 1400 K. Followup unconstrained MD simulations assess the likelihood of failed atom-vacancy exchanges once the diffusing atom crosses the saddle point, which are omitted from transition state theory. The resultant rate constants suggest asymmetries along several pathways that oppose those observed statically, while also suggesting that the HTST approach consistently underestimates the rate constants by a factor of 2-5.

Appendix A introduces the consideration of pipe diffusion in the more complicated ordered geometry of Ni₃Al, which composes the γ’ precipitates of Ni-base superalloys. On-the-fly KMC simulations utilize classical mechanics-based atomistic modeling to provide
insights on which series of activation pathways may be important in characterizing diffusion along a partial dislocation core and within its neighboring complex extrinsic stacking fault (CESF). Diffusion in the CESF is of interest because it can reorder the fault to a lower energy configuration, enabling microtwinning mechanisms. Appendices B-D provide additional details on the calculations and results of Chapters 2-4.
Chapter 2. Vacancy-Mediated Self-Diffusion along an $\frac{a}{2}(110)$

**Screw Dislocation in fcc Ni**

This chapter considers the problem of vacancy-mediated self-diffusion (i.e., of Ni atoms) along and around one partial core of a screw dislocation in fcc Ni, and is based on a paper we published in *Physical Review Materials* [21]. The pure Ni case here represents and should inform expectations on diffusive mechanisms in the $\gamma$ phase of Ni-base superalloys. A discussion of previous experimental and theoretical work provides context for the work done here as well as that of later chapters. A geometry suitable for study of diffusion is prepared within a DFT framework, and calculations provide harmonic transition state theory (HTST) rate constants for many individual atom-vacancy exchanges within the core structure. These rates are input to kinetic Monte Carlo simulations, which lead the vacancy on probability-weighted random walks throughout the structure, enabling calculations of diffusion coefficients through the tracking of atomic behavior. A few particularly important pathways with relatively low migration energy barriers emerge as significant contributors to mass transport along the partial core. Diffusivities in both the fcc Ni and dislocation cases are fit to Arrhenius parameters for comparison with experimental findings, and differences between the studies are discussed.

### 2.1 Introduction

Microstructures of most Ni-based superalloys exhibit $\gamma$-$\gamma'$ ordering, consisting of a disordered fcc $\gamma$ matrix with ordered $L1_2$ $\gamma'$ $\text{Ni}_3(\text{Al},\text{Ti})$ precipitates. These precipitates optimally
make up ~55-70% of the volume fraction of the material \[22\] and form largely coherent interfaces with the $\gamma$ phase. Creep resistance derives from both precipitation-hardening and solution strengthening in the $\gamma$ matrix \[1\]. Historically, the general role of diffusion along dislocations in creep has been subject to spirited debate \[23-25\]. Lattice diffusion is commonly assumed to replace pipe diffusion as the rate-limiting process for creep in metals above ~60% of the melting temperature \[1\], or above about 1040 K in Ni, but the localized effects of pipe diffusion mean that it can undermine strengthening mechanisms in a variety of ways.

Experimental works on nickel have provided Arrhenius parameters for pipe diffusion along an edge dislocation using a surface counting technique at low temperatures \[26\] and in screw and edge dislocations using a more precise radiography approach. \[27\] A study using a serial sectioning method suggested that dislocations act as “isolated high-diffusivity pipes” at low temperatures where lattice diffusion is effectively frozen out, and that arrays of dislocations compose regions where diffusion tends to occur at high temperatures \[28\]. Ballufi and Granato provide a review of similar studies in a variety of metals \[29\]. Beyond the context of Ni-based superalloys, representative experimental works from the literature identify pipe diffusion as the rate-limiting mechanism for low-temperature climb behavior in Mg-Al-Zn alloys \[30\], measure high-temperature pipe diffusivities of yttrium in yttria-stabilized zirconia (YSZ) that are 5-6 orders of magnitude larger than those in the bulk \[31\], provide TEM images showing the progression of pipe diffusion in a metal/semiconductor superlattice \[10\], and reveal atomic segregation due to pipe diffusion along semiconductor heterostructures \[32\].

A number of theoretical works have also simulated pipe diffusion in different materials using various methods. Embedded-atom method (EAM) potentials have been applied to self-diffusion in Al \[33\] and Mg diffusion in Al-rich Al-Mg \[34\], and resonant model pseudopotentials have been used to study self-diffusion in Cu \[35\]. Interstitial Si diffusion at dislocations in Al has been studied using paired quantum and molecular mechanics
(QM/MM) with orbital-free density functional theory (DFT) to resolve long-range elastic fields of the dislocations [36]. Here, pipe diffusion is modeled along a partial dislocation core in fcc Ni using a fully quantum mechanical approach. This offers a unique opportunity for advancing our understanding of pipe diffusion by comparing direct simulation with emerging experimental results. While the numbers generated by these different methodologies cannot always be directly compared, their findings complement one another in describing how diffusion mechanisms operate. For instance, in many experimental results, diffusion in fcc regions cannot be isolated from that which takes place along dislocation pipes or in grain boundaries within experimental samples [37]. This is not an issue in simulations where defects can be introduced and modeled independently. Through this work, we can quantify how pipe diffusion behaves relative to diffusion within the crystalline fcc Ni lattice, which has been studied extensively experimentally [37–40] and with first principles techniques [41–45].

An \( \frac{1}{2}(1\bar{1}0) \) screw dislocation in fcc Ni, dissociated into Shockley partial dislocations, was prepared using Density Functional Theory and a lattice Green’s function (LGF) embedding method. This technique is well documented [46], and the specific calculations for the screw dislocation in fcc Ni are described in the literature [5]. Migration energy barriers and attempt frequencies for many vacancy-atom exchanges that compose pipe diffusion are then calculated within the equilibrium geometry of one of these partial cores. This information is the basis for kinetic Monte Carlo (KMC) simulations of vacancy-mediated mass transport through a dislocation system while accounting for correlation effects. This unique combination of methodologies provides insights into the geometrical and local strain effects that accelerate diffusion in or near the partial dislocations. Of particular interest are the low migration energy barriers around the screw component of the partial dislocation core, on the side of the partial dislocation containing the compressive side of its edge component, and between atomic sites that are adjacent to the partial dislocation core and those which lie in the stacking fault.
2.2. Methodologies

2.2.1 Geometry Preparation

Calculations were performed using the Vienna Ab Initio Simulation Package (VASP) \cite{vasp} with generalized gradient approximation projector augmented wave (GGA-PAW) pseudopotentials \cite{ggapaw1,ggapaw2}. All calculations were spin-polarized with a plane wave basis cutoff of 400 eV, a force tolerance of 0.005 eV/Å, and following convergence testing, Methfessel-Paxton smearing of 0.25 eV \cite{ggapaw3}. The spin polarized GGA-PAW approach predicts lattice and elastic constants ($a_0=3.5219\text{Å}$, $C_{11}=2.70$, $C_{12}=1.56$, $C_{44}=1.29$ Mbar) that are in good agreement with measured values \cite{expt}.

In previous work an $a_0/2\langle1\bar{1}0\rangle$ screw dislocation was relaxed using the 2 dimensional lattice Green’s function (LGF) method and the VASP package \cite{lgf}. This approach produces an isolated dislocation by accounting for the effects of its long-range strain fields on its local geometry \cite{lgf1,lgf2,lgf3}. This leads to an accurate description of the dissociated core structure. The LGF cell consisted of a parallelepiped of 620 atoms, with one periodic unit along the dislocation line, and $20a_0/2\langle111\rangle$ by $31a_0/2\langle1\bar{1}2\rangle$ lattice vectors normal to the line direction. Upon relaxation, the $a_0/2\langle1\bar{1}0\rangle$ dislocation dissociates into $a_0/6\langle1\bar{2}1\rangle$ and $a_0/6\langle2\bar{1}1\rangle$ Shockley partial dislocations, which are separated by a stacking fault that is approximately 4b wide where b is the 2.49 Å length of the Burgers vector. This is in good agreement with the separation width reported by another DFT study using the Peierls-Nabarro approximation as well as the analytic value using anisotropic elasticity theory \cite{strain}. Within the LGF-generated geometry, when the origin is placed at the center of the stacking fault, the symmetry operation $(x, y, z) \rightarrow (-y, -x, -z)$ permutes any atomic site to its counterpart on the opposite side within $< 0.004$ Å. Resultantly, only the $a_0/6\langle1\bar{2}1\rangle$ partial core is analyzed, as this degree of symmetry justifies assuming equal and opposite behavior in and along the
$\alpha_6 \langle 2\overline{1}\overline{1} \rangle$ partial.

Hexagonal sections around the $\frac{2}{3} \langle 121 \rangle$ Shockley partial are extracted from the LGF-generated geometry so that vacancies can be inserted near the dislocation. A representative example of one such section is shown in Fig. 2.1 where sites that are relaxed following vacancy insertion are shown in white while sites in the surrounding, shaded region are fixed. The latter region maintains the structure of the partial dislocation core across relaxations and isolates the core from any effects of proximity to its neighboring periodic images during analysis in \textsc{vasp}. The sites labeled A-E, I, and J in the white region indicate where vacancies could be inserted into the A-centered hexagon in the figure, while the remaining lettered sites indicate where vacancies could be inserted into cells with different centers. Hexagonal cells centered on sites B, C, F, P, and S were also used. The slab of atoms in the figure has a depth of $b$ and is repeated four times in the $\langle 1\overline{1}0 \rangle$ direction of the dislocation line. So, when periodic boundary conditions are applied in this direction, the single vacancy is separated from its periodic image by $4b$, and their interactions with one another are assumed to be negligible. Periodic boundary conditions are also applied within the $(1\overline{1}0)$ plane of Fig. 2.1 such that neighboring hexagonal cells meet at the dashed perimetral line to fill the plane continuously with atoms.

Prior to vacancy insertion, positions of atoms at the 76 sites within the relaxation region were optimized within the confines of the fixed boundary. Residual forces were on average $\sim 0.002$ eV/Å with a total energy change of $\sim 10^{-4}$ eV/atom on relaxations. In one of the hexagonal cells used, this second relaxation causes the interatomic distances between pairs of stacking fault atoms that lie on opposite sides of the border between free and fixed regions to change by 0.1, 0.2, 0.9, and 1.6\% of their LGF-identified distances. This suggests that the structure of the partial core within the hexagonal supercell is well-preserved despite the elastic attraction between the single partial and the stacking fault. One vacancy was inserted in each cell, and the 76 free sites of each cell (now containing 75 atoms and the vacancy) were relaxed again. These configurations were used as initial and
final geometries for vacancies moving between adjacent sites. Throughout this process, vacancies were never introduced at sites that bordered a fixed boundary region. Γ-centered $3 \times 3 \times 5 \ k$-meshes were used for these relaxations following convergence testing. Because of the presence of the dislocation and stacking fault in the otherwise fcc geometry, there are geometrical mismatches where the hexagon borders meet one another. Three checks confirmed that the supercells were large enough to confine the significant effects of this mismatch within the fixed boundary region in order to not significantly affect vacancy behavior near the center of the relaxation region; details are provided in Appendix B on p. A purely fcc Ni cell was also prepared for comparison with the dislocation core. This supercell was cubic with 108 atomic sites and all atoms free to move, and was prepared with a $5 \times 5 \times 5 \ k$-mesh.
2.2.2 Nudged Elastic Band (NEB)

Reaction pathways were identified using a nudged elastic band (NEB) method. In this approach, intermediate images discretely represent a minimum energy path (MEP) between two known states of a system. Here, these states are two relaxed configurations of one hexagonal cell with vacancies at adjacent sites, e.g., at sites A and B in Fig. 2.1. The vacancy migration energy barrier is calculated by:

\[ E_{m,v_0\rightarrow v_f} = E_{saddle,v_0\rightarrow v_f} - E_{v_0} \]  

where \( E_{m,v_0\rightarrow v_f} \) is the migration energy for the vacancy to move from site 0 to site \( f \), \( E_{saddle,v_0\rightarrow v_f} \) is the NEB-calculated energy of the saddle point of the vacancy transition from
site 0 to site \( f \), and \( E_{i0} \) is the energy of the cell when the vacancy is at initial site 0. All of these energies are obtained through electronic structure calculations. Each saddle point provides two \( E_m \) values, e.g., \( E_{m,A\rightarrow B} \) and \( E_{m,A\leftarrow B} \) where the arrow indicates the direction of the vacancy. These vary as \( E_{vA} \) and \( E_{vB} \) are not equal for most pairs of sites. An initial configuration of each image is linearly interpolated from the geometries of the cell with its vacancy at initial site 0 and final site \( f \). Then, atoms in each image are relaxed along NEB forces:

\[
F_i^{\text{NEB}} = F_i^\perp + F_i^{\parallel}
\]

(2.2)

where \( F_i^\perp \) is the component of the potential force on image \( i \) that is perpendicular to the tangent of the NEB path and \( F_i^{\parallel} \) is a force parallel to that path, which originates from imaginary springs that keep the images separated from one another:

\[
F_i^\perp = -\nabla E(R_i) + \nabla E(R_i) \cdot \hat{\tau}_i \hat{\tau}_i
\]

(2.3)

\[
F_i^{\parallel} = k(|R_{i+1} - R_i| - |R_i - R_{i-1}|)\hat{\tau}_i
\]

(2.4)

where \( \nabla E \) is the energy gradient, \( R_i \) is the configuration of image \( i \), \( \hat{\tau}_i \) is the tangent to the NEB path at image \( i \), and \( k \) is a spring constant [59], which here is 5.0 eV/Å². Images are prepared using a conjugate gradient optimizer based on forces rather than energy, necessitated by the force projection scheme of the NEB method [62]. As the intermediate images converge on the MEP, the perpendicular force defined in Eq. 2.3 approaches zero [59].

For exchanges with migration barriers \(< 0.8\) eV, more accurate climbing image NEB (CNEB) simulations rigorously converged on the saddle points of these particularly significant jumps [60]. This threshold was originally chosen because it includes all vacancy hops between sites that are adjacent to the partial core as well as hops between those sites and sites that lie in the stacking fault. (A later revisitation of this assumption found that omis-
sion of the CNEB step fortunately resulted in errors of less than 0.01 eV for each migration energy barrier calculated this way and input into the rate catalog used here. Because of the imaginary spring forces acting on the saddle point geometry within standard NEB, it is generally good practice to always perform the CNEB step.) In the CNEB approach, the highest energy image \( j \) is freed from the neighboring spring forces and feels an enhanced force perpendicular to its path:

\[
F_{Cl}^j = -\nabla E(R_j) + 2\nabla E(R_j) \cdot \hat{\tau}_j \hat{\tau}_j
\]

For each vacancy exchange, a standard NEB calculation was performed to identify a reaction pathway, with the CNEB method following. A trial that looked at a vacancy exchange between two sites near the partial core that were in each others’ second shells of neighbors saw the reported saddle point energy rise by 0.07 eV after the CNEB method was applied. However, the resultant \( E_m \) value of 1.95 eV was high enough that this exchange and others involving comparable interatomic distances were assumed to be energetically unfavorable enough to be negligible. Using one intermediate image was sufficient to study each path, with nearly identical saddle point energies calculated in another trial that used one, three, and seven images to analyze one vacancy exchange. A similar single-image approach has been taken by other authors studying diffusion with similar methodologies \[63, 64\].

### 2.2.3 Vineyard Attempt Frequencies

To provide the model with vibrational information that affects hop rates, the Vineyard attempt frequency \( \nu'^* \) was calculated for significant jumps \[65, 66\]:

\[
\nu'^* = \frac{\prod_{i=1}^3 \nu_i}{\prod_{i=1}^2 \nu'_i}
\]

where \( \nu_i \) are the vibrational frequencies of an atom at its equilibrium position prior to a hop.
and $\nu_i'$ are its non-imaginary frequencies when it is at the saddle point along the hop. A previous study found that including only frequencies of the hopping atom produces values that can be expected to agree quite well, within a factor of $\frac{2}{3}$ to $\frac{3}{2}$ of the more accurate value that one would obtain by including the vibrational modes of other nearby atoms in the product terms [64]. These attempt frequencies were calculated for hops with energy barriers $< 0.8$ eV, while otherwise the fcc value was used to provide an estimate. These attempt frequencies along with the NEB-generated migration energies were then used to calculate the frequency or rate constant $k$ of each vacancy hop:

$$ k = \nu' \exp\left(-\frac{E_m}{k_B T}\right)$$

(2.7)

2.2.4 Kinetic Monte Carlo (KMC) Methodology

Jump frequencies for all possible vacancy hops within the system were included in a catalog of rate constants for the KMC code, which moves a single vacancy through a system of atomic coordinates according to the Bortz-Kalos-Lebowitz algorithm, also known as the N-fold way [67–69]. A vacancy at a given site has $N$ neighbors within some cutoff distance and a hop rate $r$ to each neighbor. In fcc Ni, the cutoff distance is chosen to be the nearest neighbor distance of 2.49 Å. Within the dislocation cell, it is set slightly higher to accommodate possible vacancy hops within the distorted geometries of the first shells of nearest neighbors of various sites, as discussed later. These neighbors are referred to as “nearby neighbors” of a given site in this work.

In the KMC algorithm, rates $r_1, r_2, \ldots, r_N$ are summed and partitioned, with each partition corresponding to a rate such that the fastest rates have the largest partitions and their corresponding hops are most likely to occur. A random number is generated to identify the partition that represents one hop, and that hop is then implemented. This is determined by evaluating which site index satisfies [69]:

18
\[ \sum_{i=0}^{m-1} r_i \leq \rho_1 \sum_{j=0}^{N} r_j < \sum_{k=0}^{m} r_k \quad (2.8) \]

where \( i, j, \) and \( k \) are summation indices for sums of the jump rates \( r \) that describe the hops available to a vacancy, \( m \) is the index of a possible hop site under consideration in a given step of evaluation, \( \rho_1 \) is a randomly distributed number on the interval \([0,1)\), \( N \) is the total number of hops that are possible, and \( r_0 \) is defined as 0. Rates are summed in some arbitrary order and evaluation begins at \( m = 1 \), continuing until \( m \) is identified with a maximum value of \( m = N \). After each successful identification of \( m \), the simulation time \( t \) is advanced by: \[ \Delta t = -\frac{\ln(\rho_2)}{\sum_{j=1}^{N} r_j} \quad (2.9) \]

where \( \rho_2 \) is a uniformly distributed random number on the interval \((0,1)\). Although this time is independent of the hop that is chosen, overall simulation results are equivalent to those that can be obtained through a less efficient algorithm that does relate each increment of elapsed time to each particular hop \([67, 70]\).

At each temperature studied, a vacancy made \( k \) random walks through the KMC cell, where each walk consisted of \( 1000N \) hops with \( N \) being the number of atoms in the system. During each walk, one atom in the cell is selected to be a tracer atom, and its behavior is tracked to generate a diffusion coefficient \( D_{KMC} \):

\[ D_{KMC} = \frac{\sum_{i=1}^{k} [z_i(t_i)]^2}{2nt} \quad (2.10) \]

where \( z_i(t_i) \) is the displacement of the tracer atom over the time \( t_i \) elapsed on walk \( i \), \( n \) is the dimensionality of the system, and \( t \) is the total time of all walks. In the dislocation system, \( z \) is the component of displacement in the direction of the dislocation line and \( n = 1 \). Since the tracer atom relies on the vacancy to move and the vacancy remains in the
vicinity of the tracer atom after moving it “forward” in some diffusion direction, correlation effects emerge as the vacancy has some probability of moving the tracer atom “backward,” whether on its next hop or after making several hops. One major advantage of the KMC method is that these effects are automatically included, provided that the vacancy’s rate catalog is well-constructed. A correlation factor that describes this behavior can be calculated as follows: [65]

\[
f_i = \frac{[z(t_i)]^2}{\sum_{j=1}^{k} \lambda_k^2}
\]

(2.11)

\[
f = \langle f_i \rangle
\]

(2.12)

where \( k \) is the number of hops that the tracer atom makes during the \( i \)th vacancy walk, \( \lambda_k \) is the tracer’s displacement during hop \( k \), and \( \langle f_i \rangle \) is the mean value of \( f_i \). In the dislocation system, \( \lambda_k \) is the component of displacement along the direction of the dislocation line.

Diffusion coefficients were scaled by the number of vacancies expected within the KMC cell at equilibrium, \( N_v \):

\[
D = D_{KMC} N_v
\]

(2.13)

\[
N_v = \sum_{i=1}^{N} \exp \left( - \frac{E_{v,i}}{k_B T} \right)
\]

(2.14)

\[
E_{v,i} = (E_{cell,vi} + \mu_N) - E_{cell}
\]

(2.15)

\[
\mu_N = \frac{1}{N} E_{fcc}
\]

(2.16)
where $E_{vf,i}$ is the energy of vacancy formation at site $i$, $E_{cell,vi}$ is the vasp-calculated electronic energy of a supercell containing a vacancy at site $i$, $\mu_{Ni}$ is the chemical potential of Ni (-5.46 eV/atom), $E_{cell}$ is the energy of the supercell with no vacancy, and $N$ is the number of atoms in a defect free fcc supercell with energy $E_{fcc}$. In Eq. 2.15, the dislocation, stacking fault, and same fixed boundary region are present in both of the supercell configurations that have $E_{cell,vi}$ and $E_{cell}$. The energy difference that is not accounted for by the chemical potential of the missing Ni atom is therefore the energy of vacancy formation at site $i$. [71]

$E_{vf,i}$ at a given site could fluctuate < 0.02 eV when a particular vacancy was considered in different hexagonal cells. This effect arose because different hexagonal cells contained different proportions of the three possible types of sites: partial core-adjacent, stacking fault, and fcc. For instance, the cell centered on site F contained more stacking fault sites than the cell centered on site A shown in Fig. 2.1. These variations could slightly change the volume of the relaxation region. In these cases, the lowest $E_{vf,i}$ value that was calculated for a particular site $i$ was used in later calculations, under the assumption that the higher energies corresponded to vacancies and their surrounding atoms being unable to completely relax because of the boundary conditions of the specific hexagonal cell choice. Differences in migration energies from different cells were similarly < 0.02 eV. This is within the predicted margin of error given that DFT calculations are generally accurate to approximately 2-3 meV/atom.

2.2.5 KMC Geometry

KMC simulations of diffusion in the partial dislocation core took place in a cell generated from atomic coordinates, derived by the LGF approach, repeated ten times along the dislocation line and with periodic boundary conditions applied in the direction of the dislocation line. This cell is depicted in Fig. 2.2. Migration energy barrier calculations informed the choices of these sites, as is discussed in Section IIB. Simulations in the 350-atom dis-
location core cells consisted of at least 100,000 walks or about $3 \times 10^{10}$ steps. Separate simulations of an 864-atom fcc Ni cell were also performed with 4,000 walks or about $3 \times 10^9$ steps. The fcc cell was larger to provide the vacancy with enough separation from its images in neighboring supercells in all three dimensions in order to more accurately describe correlation effects. Fewer total steps were required for these results to converge due to symmetry.

In all cases, tracer atoms and vacancies were inserted randomly throughout the cell. This was done to avoid biased sampling of particular diffusion pathways. Each simulation was tested for convergence through an analysis of the squared displacement of the tracer atom on each walk. Calculating the standard error $s/\sqrt{k}$ of that displacement, where $s$ is the standard deviation and $k$ is the number of walks, confirms that it was less than 1% of the mean squared displacement at each temperature.

Upon initialization of a KMC simulation, nearby neighbors of all potentially vacant sites are identified and jump rates to each of them are calculated. An example of the possible vacancy destinations from an “A” site hop, viewed from within the plane normal to the dislocation line, is illustrated in Fig. 2.3. Hops into the perimeter boundary region of Fig. 2.2 are assumed to behave like those in the pure fcc case. Upon a vacancy entering this region, it is randomly returned to another site that borders the boundary. This allows the model to account for the effects of a vacancy randomly wandering from and to the core, assuming this is an isotropic process. If the vacancy hopped along the stacking fault in the direction of the other partial core, e.g., from an M site to an O site in Fig. 2.1, it was returned to an N site as though it had migrated from the equal and opposite counterpart partial core. Vacancy diffusion from one partial to the other was also assumed to be isotropic. Results are scaled with the equilibrium vacancy concentration term of Eq. 2.13 and effects of vacancy buildup or depletion are omitted as only one isolated vacancy is ever considered. This assumption is validated by the equilibrium concentration of vacancies at the highest temperature of 1400 K being about one per 230 KMC cells or $4 \times 10^4$ sites.
Figure 2.2: View of the cell used for the KMC simulation normal to the dislocation line, visualized in and with the dislocation core identified using the dislocation extraction algorithm (DXA) of the Open Visualization Tool ovito [6–8]. White (near core) sites surround the partial dislocation core, red sites lie in the stacking fault, and green sites have strained fcc ordering. The white perimeter sites compose an fcc boundary condition region and the dark blue sites indicate a stacking fault boundary condition region.

Figure 2.3: In-plane view of possible vacancy hop destinations when a vacancy is at the central A site. Perspective is exaggerated to indicate distribution of the sites in the ⟨001⟩ direction; sites B and C neighbor the stacking fault, while sites I and D are farther from it. Atomic sites are shifted from their fcc positions because of the partial dislocation, which runs vertically between the A, B, and C sites. Eleven nearby neighbors are depicted rather than the twelve nearest neighbors that a normal fcc site would have. In this example, the 12th nearest site is a second “C” atom with a migration energy barrier that is high enough that the probability of the vacancy hopping there is negligible.
The kinetic Monte Carlo code was verified by comparing its diffusion coefficients and correlation factors for fcc Ni and a (210) Cu grain boundary (GB) to other studies. In the case of fcc Ni, we found excellent agreement with the known fcc correlation factor of 0.78145 \[72\] and with Arrhenius diffusion parameters calculated by another study that operated in a similar GGA framework but with analytical equations in lieu of KMC simulations \[45\]. While the geometry for the Cu GB comparison was taken from a different dataset \[73\] than that used by the KMC study, the activation energy reported by our code was in excellent agreement and the diffusion prefactor in good agreement with those of the KMC study \[74\]. The authors of the Cu GB study used a different methodology for calculating the correlation factor than our Eq. 2.11 which incorporated formation energy effects that depended on vibrational contributions in their case. By including their numbers for these, the correlation factors generated by the present code could be brought into better agreement with their results.

2.3 Self-Diffusion

2.3.1 Electronic Structure Calculations

Vacancy migration energy barriers \(E_{m}\) between adjacent sites, which were used as input for the KMC simulations, are provided in Fig 2.4(a). There, they are organized by intersite distance and categorized by the type of site that the vacancy hops from. Each intersite distance is defined as the distance between a pair of atoms in the LGF-produced geometry, before any vacancies are inserted. The distorted geometry near the dislocation causes the nearby intersite distances to vary around the 2.49 Å distance seen in defect-free fcc Ni. Many of the migration energies near the dislocation core and in the stacking fault are significantly less than the fcc value, and a trend towards restoring the fcc behavior is observed as these distortions diminish. Increasing this distance does not have a one-to-one correspondence
with increases in migration energy for two reasons. The geometries of atoms that surround two pairs can be different depending on location. For example, an F site has two H-type neighbors that are both 2.47 Å away, but the vacancy migration energy barriers of the two F→H hops are 0.74 and 1.17 eV. Second, the energy of a vacancy hop calculated using Eq. 2.1 can vary with the direction of the hop between two sites. For instance, an A site has an E neighbor that is 2.51 Å away, and the barrier for that A→E vacancy hop is 1.04 eV even though the intersite distance is greater than that seen in fcc Ni. The counterpart A←E hop has a barrier of 1.15 eV.
Figure 2.4: (a) Migration energy barriers and (b) jump attempt frequencies for all analyzed jumps in the dislocation system, which mostly take place within the bounded region depicted in the inset of panel (a), though a few cross the boundary that separates the partial dislocation from its counterpart. Colors and shapes correspond to the site that the vacancy initiates its hop from. The distance on the x-axis is that between atomic sites in the LGF-prepared geometry before a vacancy is introduced.

Many of the lowest energies are near the partial core, e.g., a vacancy hopping from an A
site to a B site in Fig. 2.3. In Fig. 2.4(a), all neighbors of core-adjacent sites within their
distorted first shell of nearby neighbors up to 2.63 Å are included, while otherwise a cutoff
distance of 2.50 Å is applied. All jumps were analyzed with at least NEB accuracy with
the exception of some jumps involving the “R” and “S” sites in the fcc region adjacent
to the stacking fault, which were approximated using representative values from nearby
exchanges. Beyond the cutoff distance and outside the core region, migration energies be-
come sufficiently large that one can assume their probabilities of occurrence are negligible.
Two pairs with intersite distances near 2.6 Å, which both involve a “C” site, are the most
extreme examples of this behavior deviating near the core. The tensile side of the edge
component of the partial dislocation causes these greater distances to be seen only around
this site, and the low migration energy barriers arise from the softened structure of this
region, even though the intersite distance is considerably larger than the fcc value.

Since the migration energies contribute to the exponential term in Eq. 2.7, the
energy differences observed throughout this range are the dominant contributors in deter-
mining the actual hop rates of the transitions. The attempt frequencies calculated using Eq.
2.6, which are plotted in Fig. 2.4(b) for each hop, are mostly near the fcc value of 4.4 THz.
These values were only calculated for particularly significant jumps with migration barriers
of < 0.8 eV. For the most part, these are slightly diminished near the dislocation core and
in the stacking fault relative to the value in fcc Ni.

After inserting vacancies at the sites shown in Fig. 2.1, the vacancy formation en-
ergy $E_{\text{vf},i}$ is calculated at each site $i$ using Eq. 2.15, as shown in Table 2.1. The three most
favorable sites for vacancy formation (A, B, and F in Fig. 2.1) are on the side of the cell that
contains the compressive side of the edge dislocation component of the partial dislocation,
as illustrated in Fig. 2.5 and labeled C1, C2, and C3 respectively. Table 2.2 provides the
average distance to the nearby neighbors of each of these sites in particular; formation of
vacancies on the compressive side is energetically favorable as their insertion relieves some
of that compression. The directional differences in migration energy, discussed above and
shown in Fig. 2.4(a), are reflected in the varying formation energies at each site.

\[
\begin{array}{ccc}
\text{Near Partial} & \text{In Fault} & \text{Surroundings} \\
A & 1.17 & F & 1.20 & D & 1.27 \\
B & 1.15 & G & 1.35 & E & 1.29 \\
C & 1.36 & M & 1.29 & H & 1.31 \\
N & 1.34 & I & 1.30 & \\
O & 1.33 & J & 1.39 & \\
P & 1.29 & K & 1.42 & \\
L & 1.41 & \\
Q & 1.33 & \\
fcc & 1.38 & \\
\end{array}
\]

Table 2.1: Vacancy formation energies (eV) at sites around a partial dislocation core of the \( \frac{2}{3} \langle 1\bar{1}0 \rangle \) screw dislocation. Labels correspond to atomic positions shown in Fig. 2.1.

Figure 2.5: Atomic sites in the vicinity of the partial screw dislocation core, visualized in ovito [6]. White sites neighbor the partial core, red sites lie in the stacking fault, and green sites are strained fcc. Labels indicate whether atoms exhibit more compressive (C) or tensile (T) character relative to unstrained fcc atoms, based on distances to their nearest neighbors. Labels f_C or f_T denote sites in the strained fcc region that border the compressive or tensile sites. Table 2.2 provides the average distances to the nearest neighbors of all labeled atoms.
<table>
<thead>
<tr>
<th>Site</th>
<th>Average Distance to Nearest Neighbors (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁ (A)</td>
<td>2.465</td>
</tr>
<tr>
<td>C₂ (B)</td>
<td>2.465</td>
</tr>
<tr>
<td>C₃ (F)</td>
<td>2.474</td>
</tr>
<tr>
<td>T₁ (J)</td>
<td>2.496</td>
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<tr>
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<tr>
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<td>2.483</td>
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<tr>
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<tr>
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<td>2.501</td>
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<tr>
<td>fT₂ (L)</td>
<td>2.500</td>
</tr>
<tr>
<td>unstrained fcc</td>
<td>2.489</td>
</tr>
</tbody>
</table>

Table 2.2: Average distances to nearest neighbors of each site labeled in Fig. 2.5 as originally prepared [5] prior to vacancy insertion. Atoms at compressive and tensile sites have 11 nearest neighbors at a variety of distances within a cutoff radius of 2.65 Å, while atoms at both neighboring and unstrained fcc sites have 12 nearest neighbors. Unstrained fcc atoms are equidistant from all nearest neighbors. Values have mÅ precision to avoid roundoff errors that could be on the 0.01 Å order of magnitude that differentiates the compressive, tensile, and fcc regions from one another. The average-neighbor-distance values of sites C₁, C₂, and C₃ in the hexagonal supercells used in this work agree with the values from the original cell within ±0.001 Å.

By summing the energies of vacancy formation and migration, effective activation energies \( Q = E_m + E_{vf} \) can describe the diffusive behavior of one particular vacancy hop. For instance, \( E_{vf,A} \) and the \( E_m \) value of the A → A hop provide \( Q_{⟨110⟩} = 1.94 \text{ eV} \). This could be applied to describe vacancy diffusion specifically along A sites in that direction. Insertion of these energies into the KMC model is necessary to describe the collective mass transport that depends on many different jumps taking place and interacting in ways that could not be determined \textit{a priori}. Qualitatively, one can note that \( Q_{⟨110⟩} \) values near the core are significantly less than the fcc value, which is restored as site distance from the core increases.
2.3.2 Kinetic Monte Carlo Simulations

Diffusivity in a real material as a function of distance to an isolated dislocation is a continuous function that has a maximum near the core and decays to the bulk value as that distance increases [33]. Practically, an effective dislocation radius is typically assigned such that diffusion within that cross-sectional area can be described with one dislocation diffusion coefficient, while outside of that radius, diffusion is assumed to behave like it does in the bulk lattice. Changing the radius of the KMC supercell that contains the dislocation core effectively determines the dislocation density of the KMC simulation, which directly affects the calculated diffusion coefficient. Increasing this radius and therefore the number of fcc sites that lie in the plane that cross-sections the dislocation line causes the diffusion coefficient to diminish at a given temperature, both because hops in fcc regions take longer than those that are near the dislocation core and because increasing this area introduces more possibilities for diffusion perpendicular to the dislocation line. Classically, this radius has traditionally been assumed to be well approximated by twice the Burger’s vector \((\sim 5 \text{ Å})\) [29, 33]. A molecular dynamics study of dislocation cores in Al plotted \(D\) values as a function of simulation radius and used a curve-fitting technique to identify the radius of their core as approximately 6 Å [33]. In another study Lu and co-workers found that exchanges involving stacking fault sites are particularly important in describing diffusion near the core [36]. The migration energy results plotted in Fig. 2.4 suggest that some jumps from the core-adjacent sites to surrounding ones can have high probabilities, for example, \(E_{m,A\rightarrow D} = 0.63 \text{ eV}\). For the pure Ni system, omitting these would hamper the accurate description of vacancy behavior in this region. In another system with vacancies more tightly bound to the dislocation core, this might not be the case. With this in mind, sites under consideration here lie within \(2b\) or 4.98 Å of the imaginary line in the \([\bar{1}\bar{1}2]\) direction on the \((1\bar{1}0)\) plane that originates at the partial core and lies in the plane of the stacking fault as shown in Fig. 2.2. This is effectively equivalent to the 5 Å radius assumed for experiments.
and is also the closest integer multiple of \( b \) to the value from the MD study; each multiple corresponds to one perimetral layer seen in Fig. 2.2.

While the primary goal of the KMC model is to calculate diffusion coefficients, one can also extract from it information on the correlation effects that it automatically accounts for as it moves the vacancy through the cell. Correlation factors \( f \) for the dislocation core system are calculated using Eq. 2.12 and plotted as a function of temperature in Fig. 2.6. These values are consistently lower than the fcc value of 0.78145 [72] due to the vacancy’s tendency to oscillate along low-energy pathways between pairs of sites. In an fcc crystal, jumps to any of a vacant site’s twelve nearest neighbors are equally energetically favorable. This symmetry causes the vacancy to tend to diffuse through the crystal rather than oscillate along a particular pathway, and also causes the correlation factor to be temperature-independent. For the results depicted in Fig. 2.6, correlation factor values near room temperature particularly pronounce this effect; most of the time, there isn’t enough kinetic energy in the system to initiate a series of jumps that produces more efficient transport along the dislocation line. As temperature increases, \( f \) rises with exponential behavior at the lowest temperatures, adopts a linear trend, and then begins to level off as it approaches the high temperature regime where this analysis stops due to the expected emergence of other diffusion mechanisms [38] and anharmonic effects.
Figure 2.6: Correlation factor $f$ in $\frac{2}{6}(\bar{1}\bar{2}1)$ Ni partial screw dislocation core as a function of temperature. Low values at low temperatures are due to the vacancy tending to oscillate along low-energy pathways.

Hops that occur most often in the dislocation region can be identified by tracking the behavior of the vacancy or tracer atom throughout the KMC simulations. Combining this information with the projected distance along the dislocation line of each hop provides a means for calculating the relative contributions of each hop to the total distance traversed during the tracer atom’s random walk at a given temperature. The contributions of the pairs with the ten most common hops at two representative temperatures are presented in Table 2.3, with both directions accounted for in the reported percentages of the random walk. These compose 93.4 and 69.0 % of the cumulative distance traversed by the tracer atom’s total walk through the cell in Fig. 2.2 at 700 and 1400 K, respectively. All ten of these exchanges include at least one A, B, or F site that is located on the side of our cell that contains the compressive side of the edge component of our partial dislocation. Many of these exchanges, including A$\leftrightarrow$B and B$\leftrightarrow$F, which make the two largest contributions, are distributed around the screw geometry of the core rather than directly along its dislocation line. At the lower temperatures (700 K), most exchanges occur along a small number of low-energy pathways, while at higher temperatures jumps like B$\leftrightarrow$B and F$\leftrightarrow$F are active.
more often. These latter jumps are parallel to the diffusion direction, so their more common occurrences contribute to atoms diffusing greater distances at higher temperatures. The importance of including stacking fault sites in our analysis, especially F but also G, M, and N, can be seen from this table. The F↔N exchange is almost normal to the diffusion direction, and directly contributes very little to diffusion despite its common occurrence. Nonetheless, implementing jumps like this is important in order to accurately describe the behavior of the vacancy within our cell.

<table>
<thead>
<tr>
<th>Exchanges</th>
<th>( r_{(1\bar{1}0)} ) [Å]</th>
<th>700 K</th>
<th>1400 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ↔ B</td>
<td>1.09</td>
<td>41.7</td>
<td>16.4</td>
</tr>
<tr>
<td>B ↔ F</td>
<td>1.10</td>
<td>26.6</td>
<td>13.7</td>
</tr>
<tr>
<td>A ↔ D</td>
<td>1.14</td>
<td>6.8</td>
<td>6.6</td>
</tr>
<tr>
<td>B ↔ G</td>
<td>0.44</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td>F ↔ N</td>
<td>0.19</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>F ↔ M</td>
<td>1.14</td>
<td>2.9</td>
<td>5.0</td>
</tr>
<tr>
<td>B ↔ E</td>
<td>1.22</td>
<td>2.9</td>
<td>4.5</td>
</tr>
<tr>
<td>A ↔ I</td>
<td>1.17</td>
<td>2.3</td>
<td>3.9</td>
</tr>
<tr>
<td>B ↔ B</td>
<td>2.49</td>
<td>4.8</td>
<td>8.8</td>
</tr>
<tr>
<td>F ↔ F</td>
<td>2.49</td>
<td>3.3</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table 2.3: Contributions of the ten most common tracer-vacancy exchanges to the total random walk of the tracer atom along the partial dislocation core at 700 and 1400 K. These are representative examples and no particular trend is expected based on the temperature difference other than higher energy jumps activating more frequently at the higher temperature. Sites are labelled in Fig. 2.1. \( r_{(1\bar{1}0)} \) values are the displacements between sites projected onto the \( (1\bar{1}0) \) direction. Exchanges are listed in descending order of how frequently they occur at 700 K. The same exchanges are the ten most common at both temperatures.

### 2.3.3 Diffusion Coefficients and Arrhenius Parameters

The KMC-generated diffusion coefficients for bulk Ni are in good agreement with those reported by Wu and co-workers using GGA pseudopotentials within \texttt{vasp} \[^{[45]}\]. The Arrhenius parameters are listed along with these results in Table 2.4. Minor differences between the two results can be attributed to slight variations in methodology. Also listed are exper-
imental results from one particularly relevant study by Maier [37], which used a relatively accurate direct sectioning technique at comparable temperatures of 813-1193 K while taking measures to omit any contributions from pipe diffusion to their final results.

Multiple factors contribute to the disagreement between the simulation results and the experimental ones. To explain the difference in activation energy, there is an established error in DFT calculations in systems that contain a vacancy. Mattsson and Mattsson have shown that the internal surface area surrounding a vacancy (e.g. a low electron density region) leads to calculated $E_{av}$ values from Eq. 2.15 that systematically underestimate experiment [75]. Using local density approximation (LDA) pseudopotentials can lead to some cancellation of this error (in this case, at the expense of underestimating the lattice constant of Ni), but as Wu, et al. point out, correctional terms would be needed regardless of the choice of exchange-correlation functional or pseudopotential to closely match experimental results [45]. They offer correctional shift terms $A_{shift}$ and $E_{shift}$ for $D_0$ and $Q$, which have not been applied to the values reported here, but could be applied if desired. One means of bringing the diffusion prefactor into better agreement with experimental results would be to include vibrational contributions to the equilibrium number of vacancies calculated with Eq. 2.15. These are highly temperature dependent and accurately calculating them in the dislocation system goes beyond the scope of the current study. Recent ab initio work investigating this topic in detail for fcc Ni is available in the literature [76].

<table>
<thead>
<tr>
<th>System</th>
<th>$D_0$ (m$^2$/s)</th>
<th>$Q$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc</td>
<td>$4.30 \times 10^{-7}$</td>
<td>2.43</td>
</tr>
<tr>
<td>Other simulation [45]</td>
<td>$4.29 \times 10^{-7}$</td>
<td>2.48</td>
</tr>
<tr>
<td>Experiment [37]</td>
<td>$9.2 \times 10^{-5}$</td>
<td>2.88</td>
</tr>
</tbody>
</table>

Table 2.4: A comparison of Arrhenius diffusion parameters for fcc Ni from the current study, another DFT study, and experimental observation.

With this context for interpreting the results in place, diffusion coefficients from the partial dislocation cell are compared with the fcc values. Diffusion coefficient plots for both
systems, along with Maier’s experimental data for fcc Ni [37], are plotted in Fig. 2.7. The
diffusivities within the partial dislocation system are consistently higher than those found
in the fcc system. These values are about one order of magnitude higher at the very highest
temperature of 1400 K, and eight orders of magnitude higher near 300 K. For the sake of
comparing with other data, Arrhenius parameters have been fit to this pipe diffusion data
and are compiled in Table 2.5. Because of the previously discussed temperature effects on
correlation factor and hop activity, fits have been made to the entire range as well as in the
regions where \( f \) displays its approximately pre-linear and linear behavior. The traditional
\[ D = D_0 \exp\left(-\frac{Q}{k_B T}\right) \] formalism wraps \( f \) up in \( D_0 \), which is better suited for describing
symmetrical systems like the fcc lattice with temperature-independent \( f \) values. Regard-
less, the activation energies of the fits to the dislocation system data are consistently less
than the fcc values, which is to be expected given the lowered vacancy migration energy
barriers and comparable formation energies in the near-core region. In the low temperature
dislocation Arrhenius fit, the diffusion prefactor \( D_0 \) is suppressed due to correlation effects.
At higher temperatures, \( Q \) rises because jumps that require more thermal energy are more
active.
Figure 2.7: A comparison of KMC simulation-generated diffusion coefficients in the dislocation cell and in fcc Ni. Experimental data for the fcc case is included from a study that focused on the monovacancy diffusion mechanism in the Ni lattice at comparable temperatures [37], and experimental pipe diffusion results are from a study that considered partial screw dislocations prepared in a grain boundary in fcc Ni [27].

<table>
<thead>
<tr>
<th>Fit Temperature Range</th>
<th>$D_0$ (m$^2$/s)</th>
<th>$P_0$ (m$^4$/s)</th>
<th>Q (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300-1400K</td>
<td>$6.89 \times 10^{-8}$</td>
<td>$7.26 \times 10^{-26}$</td>
<td>1.93</td>
</tr>
<tr>
<td>300-700K</td>
<td>$4.28 \times 10^{-8}$</td>
<td>$4.51 \times 10^{-26}$</td>
<td>1.91</td>
</tr>
<tr>
<td>800-1400K</td>
<td>$1.28 \times 10^{-7}$</td>
<td>$1.35 \times 10^{-25}$</td>
<td>1.98</td>
</tr>
<tr>
<td>Experiment [27, 29]</td>
<td>$2.6 \times 10^{-4}$</td>
<td>$6.6 \times 10^{-23}$</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Table 2.5: Arrhenius diffusion parameters and integrated flux coefficient, $P_0$, for an $\frac{2}{6}(1\bar{2}1)$ Shockley partial screw dislocation in fcc Ni, obtained by fitting the data at different temperature ranges.

By multiplying the diffusion coefficient of the dislocation cell by its area, which is approximately $17b^2$, the integrated flux ($P$) can be calculated through the dislocation region. This term, “integrated flux,” is in use for consistency with previous literature. For the simulated
data, this term is a proportionality constant such that the ratio of flux through different regions, each with some known $P_i$, can be quickly assessed, and comparisons with experiment can be readily made. The integrated flux was traditionally measured in experiments and used to derive the diffusion coefficient by making an assumption about the area of the diffusion pipe radius as discussed above. This quantity can be fit to temperature to produce an integrated flux coefficient, $P_0$, which is analogous to the Arrhenius prefactor, $D_0$.

In Fig. 2.9(a), the integrated flux through the system is plotted as a function of temperature, along with that which was observed experimentally using radiotracers in a dissociated $\frac{a}{2}(1\overline{1}0)$ screw dislocation in fcc Ni [27]. (To our knowledge, this is the only experimental work available that specifically considered a screw dislocation in Ni.) The calculated and experimental activation energies, which are listed in Table 2.5, are in good agreement with one another with a difference of $< 0.05$ eV, which is significantly less than the deviation between simulated and experimental fcc Ni ($\sim 0.4$ eV). Like in the fcc case, the intercept or prefactor of the experimental data is significantly higher than the simulated value, but in the case of the dislocation this difference becomes even more pronounced. One factor that helps to explain this discrepancy is that the experimentally observed screw dislocations were prepared in a grain boundary (GB), and the entropies of vacancy formation, $S_f$, in such a geometry can increase $D_0$. Another theoretical study found $S_f/k_B$ of up to 5.13 at sites in Cu GBs [74]. Given that $D_0$ is directly proportional to $\exp(S_f/k_B)$, this effect could contribute significantly to an increase in the equilibrium vacancy concentration. Additionally, the experiment operated at 873-1243 K and its findings were extrapolated to the entire temperature range. Fig. 2.8 provides a direct comparison of the simulated diffusivities with the individual data points collected in the experimental studies.
Figure 2.8: A comparison of KMC simulation-generated diffusion coefficients with the individual data points collected experimentally by Maier in the fcc case [37] and by Canon for the dislocation core [27].
2.3.4 Dislocation Density Analysis

Figure 2.9: (a) Critical dislocation densities for pipe diffusion and fcc diffusion to contribute equally to diffusive flux, compared to numbers derived from experimentally determined Arrhenius parameters assuming an effective dislocation area of $\pi (5 \text{ Å})^2$ [27, 37]. Ultrafine grain material information is from [77]. (b) Schematic of the two areas being compared.

In a deformed bulk sample that includes regions of high and low dislocation density, a critical dislocation density can be defined so that the diffusion flux through these two regions is the same. To calculate the critical density, an fcc cross section area is calculated such that its flux is equal to the flux through the dislocation cross section area depicted in Fig. 2.2. Dividing the number of dislocations, 1, by the sum of these two cross section areas gives the corresponding critical dislocation density, which is depicted in Fig. 2.9(b). The deformed bulk, having this density, is assumed to contain only parallel screw dislocations and no other debris. The calculated dislocation density therefore is a threshold, above which diffusion through dislocations would be the dominant contributor to overall diffusion. The dislocation density of a well-annealed fcc crystal is about $10^{10}$ m$^{-2}$ [78], while a recent plastic deformation study suggested a saturation density of about $3 \times 10^{14}$ m$^{-2}$ to $2 \times 10^{15}$ m$^{-2}$ in Ni, depending on the measuring method [77]. The well-annealed
value is significantly less than the theoretical ones plotted in the figure, but the necessary density could be present in the deformed sample at low temperatures up to around 700 K. Theory and experiment agree that pipe diffusion could be the primary means of mass transport that occurs in emerging ultrafine-grain (UFG) materials that have dislocation densities at these levels, though the experimentally suggested threshold density is much lower. The disagreement between experimental and calculated diffusion coefficients for pipe diffusion [reflected in Fig. 2.9(a)] results in the separation of the two curves in Fig. 2.9(b) by several orders of magnitude. If a correctional term was applied to account for this, these two lines would intercept one another at high temperature. Another reason for the disagreement between reported thresholds is the significantly greater experimentally reported activation energy for fcc diffusion (seen in Table 2.4), which causes the experimental curve in Fig. 2.9(b) to decrease more sharply than the theoretical curve as temperature decreases. (The comparison of data from the two experimental studies is not perfect due to the different methodologies and extrapolation of higher temperature Arrhenius parameters to calculate $D$ values near room temperature.)

Considering Figs. 2.7 and 2.9(b), pipe diffusion is not the dominant isotropic bulk diffusion mechanism in well-annealed fcc Ni, which is in line with expectations. However, the local effects of pipe diffusion on deformation will be quite significant, since pipe diffusion consistently provides greater diffusivities than would otherwise exist in fcc Ni. One could expect pipe diffusion to be the rate limiting process for diffusion controlled dislocation motion over a wide range of dislocation densities. Also, these results provide support for the proposed idea that pipe diffusion makes grain boundary sliding possible in these UFG materials at low temperatures where deformation is assumed to be negligible in traditional metals [79].
2.4 Conclusions

Pipe diffusion was analyzed along a partial screw dislocation in fcc Ni using a first principles approach. Diffusion coefficients describing monovacancy-facilitated diffusion along a dislocation line were calculated for a temperature range of 300-1400 K. These values are consistently significantly higher than those calculated in crystalline fcc Ni, even when correlation effects made mass transport along the dislocation core inefficient at low temperatures. This diffusion depends significantly on vacancies hopping to and from stacking fault sites as well as those that were adjacent to the core. Comparisons were made to experimental findings, and limitations of directly comparing the two approaches were discussed. Pipe diffusion is likely to contribute to localized creep mechanisms that involve mass transport near or along dislocations. Finally, integrated fluxes across the core structure were calculated to assess the critical dislocation density required to exceed conventional (bulk) mass transport. We observe that the required dislocation densities are achieved in stage II-III deformed metals and are also likely to be encountered in ultrafine grain materials at low temperatures.
Chapter 3. Pipe Diffusion of Substitutional Solutes in Nickel

This chapter builds on the analysis of Chapter 2 by studying how solute elements diffuse along the core in dilute solid solutions. The solutes considered are of importance to Ni-base superalloys: Co and Cr help to stabilize the γ phase and are often present in these alloys in concentrations of around 10 wt.% [1], Al and Ti promote the formation of the γ’ precipitates, and the refractory elements Mo, W, and Re provide solution strengthening. This extension enables quantification of the effects of chemistry in addition to geometry on diffusivities along the core. The resultant values may be of interest in creep rate models when pipe diffusion of a particular solute may be the rate-limiting step in a creep mechanism or means of γ’ precipitate dissolution.

3.1 Introduction

A general introduction to pipe diffusion in nickel is provided in the introduction to Chapter 2, where it is noted that conventional wisdom assumes that lattice diffusion replaces pipe diffusion as the rate-limiting process for creep in superalloys above ~60% of the melting temperature [1], but that particular creep mechanisms may still have pipe diffusion as their rate limiting step. This is particularly true when considering solute elements; e.g., because of the higher energy barriers to Re transport relative to Ni self-diffusion, pipe diffusion may continue to govern the high temperature diffusive behavior of Re, which is of note as it appears in third-generation superalloys in concentrations of 5.0+ wt.% [80].

Experimental studies specifically focusing on solute pipe diffusion in fcc metals
are fairly limited in the literature, though one considers the diffusion of Si and Ge along edge dislocations in Cu \[81\], and in 2008, Legros and coworkers directly observed pipe diffusion of Si along a dislocation in an Al thin film enhancing the diffusivity by several orders of magnitude relative to that in bulk regions \[9\]. Other experiments identify different phenomena occurring at the microscale of Ni-based superalloys that are best explained by pipe diffusion. Smith, et al., used transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy to reveal Co and Cr Cottrell atmospheres in the vicinity of Shockley partial dislocation cores at a $\gamma'$-microtwin interface, and suggested that in that case, pipe diffusion was responsible for the creation of the atmospheres, even if not for their long term growth or Cottrell atmosphere formation in general \[82\]. Another TEM/EDX work found Re segregation at a dislocation core along a $\gamma - \gamma'$ interface, also suggesting pipe diffusion as the likely cause \[83\]. Atom probe tomography (APT) identified pipe diffusion-caused segregation of the $\gamma$-stabilizers Co and Cr in another dislocation core at a $\gamma - \gamma'$ interface, leading to directional coarsening (rafting) \[84\].

Pipe diffusion has long been proposed to play a role in dynamic strain aging (DSA), and the authors of a recent study observed an activation energy for serrated flow that agreed well with their estimate for diffusion of Mo along dislocations, which they consider to be responsible \[85\]. An example of a strategy for avoiding DSA caused by pipe diffusion of carbon is to additively manufacture Ni-based superalloys to introduce secondary phases that leach C atoms from arrested mobile dislocations, thus preventing the buildup of Cottrell atmospheres \[86\]. A number of experimental contributions to the literature identify pipe diffusion as the rate-limiting mechanism for low-temperature creep behavior in a variety of alloys. Under certain stress and temperature conditions described in greater detail in these papers, representative works attribute pipe diffusion to be a rate limiting step in climb in several Mg-Al-Zn alloys \[30\], within grain boundaries to be a rate-controlling step in a coarse-grained Al-Cu-Mn alloy \[87\], and to potentially be the rate-controlling mechanism in a Mg-Gd alloy \[88\]. The enhanced diffusivities of pipe diffusion may also
be advantageous in certain circumstances. Wang, et al. observe expedited growth of T₁ (Al₂CuLi) precipitates in an Al-Cu-Li-Mg-Ag alloy sample that was pre-stretched prior to precipitation hardening [89], which they attribute to pipe diffusion of Cu and Li along the dislocations that the stretching introduced. Beyond alloys, experimental works measure high-temperature pipe diffusivities of yttrium in yttria-stabilized zirconia (YSZ) that are 5-6 orders of magnitude larger than those in the bulk [31], provide TEM images showing the progression of pipe diffusion in a metal/semiconductor superlattice [10], reveal atomic segregation due to pipe diffusion along semiconductor heterostructures [32], and observe, via TEM/EDX, Sn-enriched filaments in GeSn providing evidence of pipe diffusion during epitaxial growth having enabled phase separation by carrying Sn solutes to the surface where they accumulate and form droplets [90].

A density functional theory (DFT) study of solute diffusion in fcc Ni revealed that atoms with larger atomic radii, which were traditionally assumed to be slow diffusers, actually have lower energy barriers to diffusion because of the directional bonding characteristics of their d electrons to their neighbors in the host Ni lattice [41]. Hargather and co-workers recently prepared a DFT study of dilute solute diffusivities in fcc Ni along with a comprehensive compilation of the Arrhenius parameters generated by many first-principles and experimental studies throughout the literature [91]. Other first principles studies considering solute diffusion are also available, including a five-frequency model study of diffusion in fcc Al [63] and a high-throughput database of solute diffusion in a variety of metals [45]. In the context of dislocations, a paired quantum mechanics/molecular mechanics (QM/MM) methodology identified enhanced diffusivities of an interstitial Si atom along an edge dislocation in Al, particularly along the associated stacking fault ribbon [36]. Other studies have used QM/MM to quantify the energy barriers to diffusion of H in a screw dislocation in W [92] and used DFT-informed calculations to quantify the acceleration of H diffusion in fcc Al by an edge dislocation [93].
3.2 Methodology

Electronic structure calculations take place within \texttt{vasp} using the same settings and hexagonal cell introduced in Section 2.2.1. Solute-vacancy rate constant $k$ calculations use Eq. \ref{eq:k}, where nudged elastic band (NEB) simulations provide $E_m$ (see Section 2.2.2) and the hopping atom approximation provides the Vineyard attempt frequency $\nu^*$ (Section 2.2.3). Kinetic Monte Carlo (KMC) simulations (Section 2.2.4) keep track of the dilute solute atom as a vacancy propagates through the same kind of cell described in Section 2.2.5.

The study of self-diffusion along the dislocation core in Chapter 2 informed the construction of rate catalogs here. There, $E_m$ for 116 vacancy hops in two directions along each of 58 pathways were calculated near the partial core. Vacancies could hop between sites without a specifically calculated $E_m$ with the fcc value if they were within $\leq 2.50$ Å of one another. The cutoff distance for manually calculated pathways was 2.63 Å to accommodate the tensile side of the edge component present on one side of the partial screw core. Second nearest-neighbor hops were excluded because a trial calculation revealed $E_m$ of one near the core to be 1.95 eV, well above the fcc value. The attempt frequencies of hops with $E_m < 0.8$ eV were calculated with Eq. \ref{eq:2.6} while the rest were approximated with the fcc value.

Here, $E_m$ barriers to solute hops in the dislocation system are calculated with the NEB method for 34 jumps along pathways that have at least one exchange with $E_m < 0.8$ eV in the self-diffusion case. Because of the prohibitive computational cost of analyzing all solute jumps in all systems, these particularly relevant jumps are accurately defined while the remainder are estimated. Estimates are produced by categorizing the remaining 82 self-diffusion values based on their location in the cell, and modifying them by the average difference between self-diffusion and solute-diffusion $E_m$ values in that category for the NEB-analyzed jumps for that solute. The four categories of vacancy-solute hop used in these modifications are: between a near core site and a site in the stacking fault, be-
tween either of a near core or stacking fault site and one in the surrounding strained fcc region, entirely within the stacking fault, or entirely within the surrounding strained fcc region. Jumps between sites without specifically assigned energy barriers but within the cutoff distance may hop with the solute $E_m$ value as calculated using the fcc cell, while KMC simulations exclude jumps between pairs separated by more than the cutoff distance. Because testing suggests that calculating $\nu^*$ values for the solute jumps in the dislocation geometry is not expected to change the resultant diffusivities by more than 25 % (see Section 3.3.4), all solute hops are assigned the $\nu^*$ value of the solute hopping in fcc Ni.

Pipe diffusion simulations take place in a KMC cell that contains periodic repetitions of a (1\,\bar{1}0) slab of atoms. Each slab contains all sites within approximately $2b$ of the dislocation core or the stacking fault, as long as they are closer to the $\frac{\mathbf{c}_0}{6} (1\bar{2}1)$ partial core than they are to its counterpart. The slab is repeated ten times in the dislocation line direction before periodic boundary conditions are applied. (They are repeated thirty times to study Al and Ti at 300-600 K because convergence testing suggested that the faster diffusers need larger cells at lower temperatures.) Each slab contains three core-adjacent atomic sites, four that lie in the stacking fault, and ten surrounding strained fcc sites. If the vacancy hops out of this fcc region, it is assumed to wander off into the surrounding fcc lattice and is randomly returned to another strained fcc site, replacing a Ni atom. If it hops along the stacking fault towards the other partial core, it similarly is assumed to wander to that core and then randomly replaces a Ni atom at another stacking fault site on the border to simulate its having wandered back. KMC simulations of the solutes in fcc Ni are handled according to LeClaire and Lidiard’s five frequency model for solute diffusion \cite{94,95}, which results in modifications of the $E_m$ and $\nu^*$ values of Ni hops that occur in the first shell of neighbors of the solute, as well as those that dissociate or associate the vacancy-solute pair. These modifications are omitted in the dislocation case because they can not be systematically described in the asymmetric geometry of the core, as discussed in detail in Section 3.3.5.
A total of $3.5 \times 10^9$ vacancy hops take place for each solute at each temperature in both dislocation and fcc cells. For the self-diffusion case along the core, when diffusivities are fit to Arrhenius parameters and compared to those produced by taking ten times as many steps, the $D_0$ values agree within 1.4% and the $Q$ values agree to the 0.01 eV degree of precision reported here, justifying the use of this number of steps. Starting configurations of each walk see the tracer atom and vacancy inserted randomly into the KMC cell. Simulations in the fcc geometry adopt a larger 864-atom KMC cell to separate the vacancy from its periodic image in all three dimensions.

3.3 Results and Discussion

3.3.1 Migration energies

Fig. 3.1 displays the energy barriers to atom-vacancy exchanges for each type of diffuser in (a) fcc Ni and (b)-(f) along representative pathways in the dislocation cell, which are all in the immediate vicinity of the partial core and resultantly consistently have lower migration energy barriers than those in the fcc case. For the dislocation exchanges, two sets of energies are plotted within each set of vertical lines; these concern a jump between the same pair of sites in opposite directions. The two directions share an NEB-generated saddle point configuration and energy, but the equilibrium configurations prior to or after the hop can have different energies, resulting in asymmetries. Panel (b) is a jump in the $[1\bar{1}0]$ direction of the dislocation line between sites that express compressive character due to the edge component of the partial core, while panel (c) is for a jump in the same direction on the tensile side of the partial. These sites are designated as compressive and tensile because they have average distances of 2.465 and 2.503 Å to their 11 nearest neighbors, relative to the 2.490 Å nearest-neighbor distance in unstrained fcc Ni. Minor directional effects emerge for these two hops when it is energetically favorable for the vacancy-solute pair to be aligned in one way prior to or after the hop, e.g., a configuration where a W atom
appears before a vacancy in the [1\bar{1}0] direction, when both defects are at adjacent sites with tensile character, has an energy that is 0.02 eV lower than a configuration with the opposite ordering. Panel (d) provides barriers for a hop around the screw geometry of the partial core between two compressive sites, and panel (e) concerns another jump around the screw geometry but between a compressive site and a tensile site. For each solute, the barrier for an atom to hop into the tensile site when the vacancy moves into the compressive site [the first column of panel (e)] is consistently lower than those that are the other way around. Panel (f) shows energy barriers for a hop between a compressive partial-core adjacent site and a site in the stacking fault (also on the compressive side with 2.474 Å average distance to nearby neighbors). Exchanges that install the vacancy in the core-adjacent site and the atom in the stacking fault site are consistently more favorable than those in the opposite direction.

![Energy barriers graph](image)

Figure 3.1: Energy barriers to atom-vacancy exchanges for each type of atom in fcc Ni and along five pathways near the partial dislocation core. Pairs of energies grouped together within vertical lines are in different directions between the same pair of sites.

With regard to solute type, the Ni\textsubscript{3}(Al,Ti) \(\gamma'\) stabilizers Ti and Al consistently en-
counter the lowest barriers to migration, with Ti hops being 0.04-0.18 eV more favorable than their Al counterparts for the jumps calculated here. Re always has the largest barrier, usually followed by W. The three refractory elements display hierarchal behavior, with barriers to Re-vacancy exchanges 0.15-0.21 eV higher than those of W along each pathway, which are correspondingly 0.11-0.17 eV higher than those to Mo hops. Co consistently sees higher energy barriers than those of Ni self-diffusion, and its higher barriers frequently overlap with the refractory sequence. Mo or Ni may have a higher energy barrier depending on the activation pathway, while Cr consistently sees barriers that are lower than any of Co, Mo, or Ni, but higher than those of the γ’ stabilizers.

In a pair of DFT studies, Reed and coworkers identified that the two most important determinants of the energy barrier of a solute atom hopping in fcc Ni are magnetism and solute compressibility, which is related to the directional bonding of a solute’s d electrons to its Ni neighbors [41,42]. These effects overwhelm any contributions from strain effects emerging from solute-host radius mismatch, which was traditionally assumed to be the dominant factor. An alternative interpretation, using arguments from quantum chemistry in support of the same conclusions, suggests that the atoms being referred to as “compressible” instead have more freedom to re-orient their non-spherical orbitals when passing by the surrounding Ni atoms at the saddle point, which the “non-compressible” elements have less freedom to do because of their less directional bonds. Regardless of whether one prefers the compression or reorientation argument, both link d electron bonding characteristics to diffusion barriers of different solutes, providing plausible arguments for the ranking of diffusion barriers for various elements. Trends observed here in the dislocation system are consistent with these observations. For instance, the energy barriers of hops in the dislocation line direction of Re, which exhibits pronounced directional bonding, are consistently higher along the tensile side of the core [Fig. 3.1(c)] relative to those along the compressive side [Fig. 3.1(b)]. This is because the Re atom begins in a more energetically favorable position on the tensile side, and to compress it within the saddle point configu-
ration, more energy must be input than if it had began in a higher-energy, pre-compressed site.

Magnetic properties also affect the diffusive behavior of ferromagnetic Ni and Co and antiferromagnetic Cr relative to one another along different pathways. Cr atoms can hop in fcc Ni with an energy barrier that is 0.22 eV less that of a Ni atom making a hop, but in the dislocation system, Cr doesn’t hop with quite as much relative ease, having energy barriers that vary from those of Ni by -0.14 to +0.02 eV. In the ground state configuration of Cr in fcc Ni, the magnetic moments of all atoms are aligned with one another. If calculations begin with the spin of the Cr atom aligned opposite to that of its Ni neighbors, they converge upon a state with a higher energy of 1.12 eV relative to the 0.84 eV energy found when the spins are initially aligned. This finding is consistent with the results of a neutron scattering experiment that found that the magnetic moment of a dilute Cr solute in Ni has a similar magnetic moment to the host Ni atoms, while the moments of the Ni atoms that neighbor the solute are reduced relative to pure Ni [96].

Two sets of calculations relaxed twenty pre-hop configurations containing a Cr-vacancy pair of neighbors within the partial core geometry. In one set, the spin of the Cr atom was initialized as parallel to the Ni atoms, while in the other, it was initialized to be antiparallel. In nineteen cases, the calculation with an initially antiparallel Cr atom converged to an energy 0.065-0.105 eV lower than that of the initially parallel calculation, while in the one remaining sample, both calculations converged to the same energy. After four ionic steps of calculations considering the other fourteen equilibrium sites with Cr-vacancy pairs, all parallel calculations appeared to be converging towards higher energies. NEB calculations preparing each of the seventeen saddle point geometries also appeared after four ionic steps to be converging to the same energy regardless of spin initialization. This is sufficient evidence to support the claim that calculations within the partial core with the spin of the Cr atom initialized as antiparallel to the ferromagnetic Ni atoms will converge to the ground state energy, and converged versions of these calculations provide
all such reported energies here. Zhang and Lu previously reported that the magnitude of the magnetic moment of a Cr atom near an edge dislocation in α-Fe varies depending on whether it is at a compressive, tensile, or equilibrium atomic site, finding that the spin of the Cr atom was in all cases antiferromagnetic relative to its neighbors [97].

### 3.3.2 Diffusivities

To establish a context for interpreting the pipe diffusivity results, Table 3.1 compares the activation energies of diffusion in fcc Ni for different types of atoms as calculated here (the “KMC” column) with values produced by four other DFT studies. Variations in methodologies cause the observed differences between values for each type of diffusing atom. Wu, Janotti, and Hargather use five frequency model equations to calculate diffusivities, while this work and Schuwalow use KMC simulations. To better enable comparison to the other values here, Wu’s numbers are presented free of the correctional factors that the authors introduce to bring their DFT calculations into agreement with experiment. Janotti’s values were interpreted from a figure rather than a table, which may have introduced error of approximately ±0.05 eV. Wu and Schuwalow use differently parameterized GGA exchange-correlational functionals than those used here, while Hargather and Janotti both use local density approximation (LDA) functionals. Hargather uses a quasi-harmonic Debye model [43] to calculate entropic effects, while the other studies account for these with the Vineyard attempt frequency [66]. Schuwalow notably incorporates solute-vacancy binding information for vacancies within the six nearest neighbor shells of each solute, finding that the energies are distributed through the range of ±0.05 eV [98]. Our KMC-generated values based on the five frequency model agree well with theirs, despite omitting that information. The ~0.1 eV difference between the activation energies reported for Re is comparable to the differences Agarwal and Trinkle found for solute diffusion in hcp Mg when comparing activation energies generated by an 8-frequency model with those calculated by an exact Green’s function approach [99]. Hargather’s review also compiles experimentally
observed diffusivities of all elements considered here in fcc Ni \cite{91}. Broadly speaking, the GGA-calculated activation energies $Q$ tend to be lower than either the LDA values or those observed experimentally, though $Q$ for Al and Ti are even lower in the LDA approach.

<table>
<thead>
<tr>
<th>Diffuser</th>
<th>KMC</th>
<th>Wu \cite{45}</th>
<th>Schuwalow \cite{98}</th>
<th>Janotti \cite{41}</th>
<th>Hargather \cite{91}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2.43</td>
<td>2.48</td>
<td>–</td>
<td>2.90</td>
<td>2.85-3.03</td>
</tr>
<tr>
<td>Co</td>
<td>2.57</td>
<td>2.60</td>
<td>–</td>
<td>3.06</td>
<td>3.07</td>
</tr>
<tr>
<td>Cr</td>
<td>2.34</td>
<td>2.45</td>
<td>–</td>
<td>3.11</td>
<td>3.06</td>
</tr>
<tr>
<td>Al</td>
<td>2.42</td>
<td>2.47</td>
<td>–</td>
<td>–</td>
<td>2.36</td>
</tr>
<tr>
<td>Ti</td>
<td>2.43</td>
<td>2.45</td>
<td>–</td>
<td>2.12</td>
<td>2.17</td>
</tr>
<tr>
<td>Mo</td>
<td>2.45</td>
<td>2.52</td>
<td>2.44</td>
<td>2.75</td>
<td>2.93</td>
</tr>
<tr>
<td>W</td>
<td>2.69</td>
<td>2.73</td>
<td>2.66</td>
<td>3.06</td>
<td>3.14</td>
</tr>
<tr>
<td>Re</td>
<td>3.00</td>
<td>2.99</td>
<td>2.91</td>
<td>3.47</td>
<td>3.58</td>
</tr>
</tbody>
</table>

Table 3.1: Activation energies $Q$ (eV) for solute diffusion in fcc Ni from this kinetic Monte Carlo (KMC) study compared with others. Values provided here are from Arrhenius fits over the full 300-1500 K temperature range.

Fig 3.2 provides Arrhenius plots of all solutes along the dislocation pipe as well as in fcc Ni. Individual points come from KMC simulations, while lines are plotted according to:

$$D = D_0 \exp \left( \frac{-Q}{k_B T} \right), \quad (3.1)$$

where the diffusion prefactor $D_0$ and activation energy $Q$ are found by fitting the individual data points over the depicted temperature range. Panel (a) provides a view over all temperatures considered here. Two sets of slopes or activation energies clearly emerge: the gentler slopes of the solid lines correspond to pipe diffusivities along the partial core, while the steeper slopes of the dashed lines correspond to diffusion in fcc Ni. Within the traditional Arrhenius formalism for self-diffusion in fcc metals, a temperature-independent correlation factor $f$ contributes to $D_0$. This becomes a temperature-dependent quantity during solute diffusion because solute-vacancy interactions affect nearby Ni-vacancy exchanges; this results in the effects of $f$ being distributed among both $D_0$ and $Q$ during a fit. $f$ for a solute diffusing through an fcc lattice can be calculated within the five-frequency model using
a formula derived by Manning [100]. Within the complex geometry of the partial core, the KMC method automatically includes vacancy correlation effects as the vacancy travels throughout many different combinations of activation pathways in the cell. This causes some data points to visibly deviate from their corresponding fitted line, because at low temperatures the vacancy tends to oscillate along low-energy pathways which aren’t conducive to mass transport, while at high temperatures more energetically expensive jumps activate, increasing the slope. This effect is distinct from curvatures that emerge in experimental studies of diffusion in Ni due to different mechanisms emerging, like the curvature of self-diffusion in fcc Ni from 1253-1673 K attributed by Bakker to di- and tri-vacancy mechanisms [38]. It is also worth noting that Re diffusivities in fcc Ni are omitted below 600 K because of the rare occurrence of Re-vacancy exchanges. One Re hop occurred in $3.5 \times 10^9$ KMC steps or $\sim 2$ years within the simulation at 500 K, and zero hops took place in as many steps at 300 and 400 K).
Figure 3.2: KMC-simulated diffusivities and lines fit to produce Arrhenius parameters for each type of atom in the fcc and partial screw dislocation core cells from (a) 300-1500 K and (b) 1000-1500 K.

Fig. 3.2(b) provides a clearer view of the temperature range where the pipe and bulk diffusivities of different elements span approximately four orders of magnitude. Differences
between the two sets of slopes are not as visually evident within this perspective, but the activation energies provided in Table 3.2 clearly indicate significant variations. Over this range, agreements between the data points and their fitted lines are much better than those over the full temperature range because most of the pathways available to the vacancy at 1500 K are at least non-negligible at 1000 K. Cr data points demonstrate the greatest deviation from the fitted line, ranging from +6.1% to -2.2% of the fit-generated values, suggesting that the Arrhenius parameters provided in Table 3.2 can produce pipe diffusivities that reliably represent KMC-generated ones over this range of high temperatures. The data points of Fig. 3.2 omit error bars because they are small relative to the range of values spanned by the logarithmic axis; the relative standard error due to KMC simulation convergence is <2% for each point in Fig. 3.2(b).

<table>
<thead>
<tr>
<th></th>
<th>Along partial core</th>
<th>In isotropic fcc Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_0$ (m$^2$/s)</td>
<td>$Q$ (eV)</td>
</tr>
<tr>
<td>Ni</td>
<td>$1.45 \times 10^{-7}$</td>
<td>1.99</td>
</tr>
<tr>
<td>Co</td>
<td>$1.48 \times 10^{-7}$</td>
<td>2.04</td>
</tr>
<tr>
<td>Cr</td>
<td>$1.46 \times 10^{-7}$</td>
<td>2.00</td>
</tr>
<tr>
<td>Al</td>
<td>$2.87 \times 10^{-7}$</td>
<td>1.96</td>
</tr>
<tr>
<td>Ti</td>
<td>$7.61 \times 10^{-7}$</td>
<td>2.02</td>
</tr>
<tr>
<td>Mo</td>
<td>$3.70 \times 10^{-7}$</td>
<td>2.14</td>
</tr>
<tr>
<td>W</td>
<td>$2.48 \times 10^{-7}$</td>
<td>2.23</td>
</tr>
<tr>
<td>Re</td>
<td>$1.13 \times 10^{-7}$</td>
<td>2.29</td>
</tr>
</tbody>
</table>

Table 3.2: Arrhenius diffusion prefactors $D_0$ and activation energies $Q$ for solute diffusion along the partial dislocation core and in bulk fcc Ni over the range of 1000-1500 K.

The previously mentioned argument of Reed and coworkers that explains activation energies as depending on the bonding characteristics of valence electrons rather than the atomic radius appears to hold in the dislocation geometry as well. Table 3.3 compiles information relevant to the Hume-Rothery rules, which use these radii and some other physical qualities to empirically describe the solubility of an alloying element in a solid solution. Magnetic ordering information is also provided for each solute along with KMC-generated diffusivities at 1000 K, which are intended to be representative examples of diffusivities that can be
considered without making reference to the separated $D_0$ and $Q$ terms. Co is listed as fcc because, despite its frequent categorization as an hcp material, its crystal structure depends on grain size and temperature. For small grains at low temperatures, it adopts the fcc structure $[101]$. Since the DFT calculations here are performed at 0 K and the grain size can be taken to be the size of the supercell, Co is expected to be fcc in this context. The variations in diffusivities with chemistry do not appear to be a function of any of the listed properties.

<table>
<thead>
<tr>
<th>Element</th>
<th>$r$ (Å)</th>
<th>Structure</th>
<th>Valence</th>
<th>EN</th>
<th>Magnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.25</td>
<td>fcc</td>
<td>2 or 10</td>
<td>1.8</td>
<td>ferro-</td>
</tr>
<tr>
<td>Co</td>
<td>1.25</td>
<td>fcc</td>
<td>4</td>
<td>1.8</td>
<td>ferro-</td>
</tr>
<tr>
<td>Cr</td>
<td>1.29</td>
<td>bcc</td>
<td>6</td>
<td>1.6</td>
<td>antiferro-</td>
</tr>
<tr>
<td>Al</td>
<td>1.43</td>
<td>fcc</td>
<td>3</td>
<td>1.5</td>
<td>para-</td>
</tr>
<tr>
<td>Ti</td>
<td>1.47</td>
<td>hcp</td>
<td>4</td>
<td>1.5</td>
<td>para-</td>
</tr>
<tr>
<td>Mo</td>
<td>1.39</td>
<td>bcc</td>
<td>6</td>
<td>1.8</td>
<td>para-</td>
</tr>
<tr>
<td>W</td>
<td>1.41</td>
<td>bcc</td>
<td>6</td>
<td>1.7</td>
<td>para-</td>
</tr>
<tr>
<td>Re</td>
<td>1.37</td>
<td>hcp</td>
<td>7</td>
<td>1.9</td>
<td>para-</td>
</tr>
</tbody>
</table>

Table 3.3: Hume-Rothery rule information and magnetic ordering of selected solutes, compared to representative diffusivities for pipe and bulk diffusion at 1000 K. The radii ($r$) are metallic and electronegativities (EN) are Pauling values.

Over the high temperature range of Fig. 3.2(b), Ti, Al, Ni, Cr, and Mo have higher diffusivities along the dislocation pipe than any type of atom does in fcc Ni. The diffusivity of Ti in fcc Ni just overtakes the pipe diffusivity of Co at the highest temperature considered here of 1500 K. Al and Ti in the bulk both diffuse faster than W along the core, and Re pipe diffusivities are comparable to those of Ni and Mo in fcc Ni. To more readily assess how the geometry of the partial core affects the diffusivity of each species of solute relative
to diffusion in fcc Ni, Fig. 3.3 provides the ratios of $D$ along the partial to $D$ in fcc Ni for each diffusing atom, using the KMC-generated values at each temperature. The dislocation pipes consistently enhance the transport of Re to a greater degree than any other solute and in many cases by at least an order of magnitude. The diffusion of Co and W are both enhanced more than the self-diffusion of Ni, as these two solutes encounter relatively high barriers relative to self-diffusion in fcc Ni as seen in Fig. 3.1(a), but have barriers comparable to self-diffusion for some hops in the core, as shown in Fig. 3.1(b). Mo diffusivity is consistently enhanced less than Ni; while the two often have similar energy barriers, it tends to be energetically expensive to move a Mo atom out of certain sites with tensile character near the partial, as shown by two migration energies in Fig. 3.1(c) and one in Fig. 3.1(e) being over 0.1 eV greater than the Ni self-hop energy along the same pathway. Al and Ti are less enhanced because their energy barriers are already low in the fcc case so the lower energy barriers of the pipe don’t offer as much opportunity for enhancement. For instance, a comparison of $\exp(-E_m/k_B T)$ for the fcc jump of Fig. 3.1(a) with the extreme lowest energy barriers in Fig. 3.1(d) at 1000 K suggests that a Ni atom would hop about 675 times faster along the pathway in the pipe than it would in fcc Ni, while a Ti atom in the same circumstances would hop only 140 times faster than in fcc Ni, even though that particularly low energy barrier falls below 0.1 eV. Finally, the diffusivity of Cr is least enhanced by the dislocation pipe at all temperatures considered, since as discussed above due to its magnetic characteristics, energy barriers to Cr hops are significantly less than those to self-diffusion in fcc Ni, while Cr behaves more like Ni in the partial core.
Figure 3.3: Relative enhancement of the diffusivity of each type of atom along the partial core, calculated as the ratio $D_{\text{pipe}} / D_{\text{fcc}}$ where $D_{\text{pipe}}$ is the pipe diffusion coefficient and $D_{\text{fcc}}$ is the diffusion coefficient in bulk fcc Ni.

### 3.3.3 Implications for engineering superalloys

Diffusivities calculated with these parameters could be used to calculate creep rates using various models. For instance, Evans and Knowles provide a formalism for creep rate due to climb that takes lattice and pipe diffusivities as input [105]. While the diffusivities reported here concern the partial core of a screw dislocation, one could obtain an approximate edge diffusivity by considering Canon and Stark’s experimental finding that $D_0$ and $Q$ for diffusion in a tilt grain boundary in Ni (along edge dislocations) are about 10 and 15 % less, respectively, than those that describe diffusion in a twist boundary (along screw dislocations) [27]. For a given solute, pipe and lattice diffusivities could be used to prepare effective diffusion coefficients at a given dislocation density and temperature, which could then go into the model recently presented by Hargather and coworkers to calculate the relative creep rate of a Ni-X alloy as a function of solute concentration, as compared to the pure
Ni case [91]. In a real engineered material, one might expect additional creep resistance to emerge due to the presence of a slowly diffusing atom like Re in the dislocation core. This could impede transport of other atoms/vacancies along the core both because the Re atom occupies a spot that it is unlikely to hop out of, but which would otherwise be available for other atoms/vacancies to pass through, and also because it may affect the behavior of other atoms in its vicinity, e.g., to suppress the rate constants of atoms hopping past it. Here, for a vacancy and Ni atom to exchange places within the nearest neighbor shell of a dilute Re atom ($w_1$ in the five frequency model), the energy barrier is 0.06 eV greater than that of a Ni atom-vacancy exchange in pure Ni. A recent theoretical work reports that for a dislocation pinned at a nanovoid in fcc Al, pipe diffusion enables the void to emit vacancies until the dislocation becomes unpinned [106]. It is reasonable to expect that the presence of Re along the dislocation core would impede this process, particularly if it segregates to the dislocation or the dislocation/void interface.

Given the potential roles of pipe diffusion as the rate limiting process within more complicated sequences within Ni-base superalloys, one might want to compare the activation energies predicted here with those of creep observed experimentally in some context. Although pipe diffusivities of five of the elements have similar activation energies within the range of 1.96-2.04 eV, these results could provide support for either pipe diffusion in general or pipe diffusion of one of the more distinct refractory elements being the rate-limiting process. If extrapolating these results to different contexts, there are a few important considerations that one should keep in mind. The static calculations employed here do not account for the entropy of vacancy formation, which is expected to play a significant role in the free energy of vacancy formation in reality [76], or for the free energy of vacancy migration, which results in the Vineyard harmonic transition state theory approach of Eq. 2.7 underestimating the rate constants of several self-diffusion exchanges in the dislocation cell at elevated temperature by factors of 2-5 [107]. These calculations also omit the effects of thermal expansion, which can result in lower barriers at higher temperatures
that ultimately lead to a further underestimate of each $k$ value by a factor of $\sim 2$ at 1400 K within the GGA-PAW framework used here [107]. Mantina and coworkers provide a more in-depth discussion of how thermal expansion within the quasiharmonic approximation (QHA) affects the entropy and enthalpy of vacancy formation and migration relative to the expansion-independent harmonic approximation (HA) in the case of fcc Al [108].

To directly compare our values with experiment, one may need to account for the DFT underestimate of vacancy formation energy described by Mattsson and Mattsson [75]. Wu and coworkers provide correctional factors to convert GGA-PAW-generated $D_0$ and $Q$ values to match experimental ones [45], which one could apply to the values provided here to produce an estimate of how pipe diffusion may behave under the set of assumptions that would govern the use of the same correctional factor for both the fcc and partial core cases.

### 3.3.4 Estimating attempt frequencies

The Vineyard attempt frequency $\nu^*$ [66] contributes to defining the rate constant $k$ of each atom-vacancy exchange. Because these attempt frequencies are consistently on the order of THz, their variations between different hops affect the magnitude of $k$ for a given hop significantly less than variations in migration energy barriers between hops, which contribute to the exponential term of Eq. 2.7. DFT calculations of $\nu^*$ via Eq. 2.6 require significant computational resources even within the hopping atom approximation. To assess the appropriateness of approximating $\nu^*$ for the many possible solute hops in the dislocation cells by using the attempt frequency that the solute hops with in fcc Ni, $\nu^*$ values were calculated in both directions along two activation pathways near the screw geometry of the partial core for several solutes and compared with the values from within fcc Ni, as shown in Table 3.4.

The Core⊥ hop is around the screw geometry of the core, with the atom hopping from a site expressing tensile character to one expressing edge character in the F or forward direction and vice versa in the R or reverse direction; the Core∥ hop is between periodically repeated sites on the compressive side of the edge component of the screw partial core, with the
Table 3.4: Attempt frequencies (THz) of atom-vacancy exchanges in fcc Ni and along two pathways near the partial core in both directions.

<table>
<thead>
<tr>
<th>Atom</th>
<th>fcc</th>
<th>Core^F_∥</th>
<th>Core^R_∥</th>
<th>Core^F_⊥</th>
<th>Core^R_⊥</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>4.42</td>
<td>4.26</td>
<td>4.05</td>
<td>3.26</td>
<td>4.80</td>
</tr>
<tr>
<td>Co</td>
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<td>3.54</td>
<td>3.17</td>
<td>3.49</td>
<td>3.93</td>
</tr>
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<td>3.30</td>
<td>3.99</td>
</tr>
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<td>3.25</td>
<td>2.77</td>
<td>3.19</td>
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</tr>
<tr>
<td>Ti</td>
<td>4.20</td>
<td>4.09</td>
<td>3.91</td>
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</tr>
<tr>
<td>Mo</td>
<td>4.35</td>
<td>3.84</td>
<td>3.92</td>
<td>3.23</td>
<td>3.86</td>
</tr>
</tbody>
</table>

atom hopping in the [1\Bar{1}0] dislocation line direction within the \(\frac{a_0}{6}(\Bar{1}21)\) partial core in the F case and in the [\Bar{1}10] direction in the R case.

The most extreme difference from the fcc value is seen in Al, where the Core^R_∥ hop has an attempt frequency that is approximately half of the fcc value. KMC-generated pipe diffusivities from a set of KMC simulations that use the fcc \(\nu^*\) of 5.45 THz for all Al hops are compared to those from a set that uses the slowest value of 2.77 THz for all Al hops in Fig. 3.4. These results suggest that the variation in attempt frequency has a minor effect on the overall outcome of the simulations. Fitting the data using the slower frequency over the range of 1000-1500 K produces a \(D_0\) that is 64% of the value using the fast frequency, along with a \(Q\) that is actually 0.02 eV lower, offsetting some or all of the decrease from the diminished \(D_0\) depending on the temperature. Directly comparing the KMC-generated diffusivities reveals that the slower frequency produces a \(D\) that ranges from 112% of the faster one at 300 K to 78% at 1500 K. The counterintuitive increase at 300 K can be explained by the slower attempt frequency increasing the correlation factor at that temperature by making Ni-vacancy exchanges more likely; these are necessary for net transport of the Al atom to take place. These variations are relatively minor and justify the use of approximating all solute hop attempt frequencies by the fcc value.
3.3.5 Considering solute-vacancy interactions within KMC simulations

LeClaire and Lidiard’s five frequency model [94, 95] identifies five types of hop frequency in the case of a dilute solute atom diffusing in an fcc crystal. \( w_0 \) is a pure solvent hop in the absence of a solute, \( w_1 \) is a solvent hop within the nearest neighbor shell of the solute, \( w_2 \) is a hop of a solute, \( w_3 \) is a solvent hop that sees the vacancy move out of the nearest neighbor shell of the solute, and \( w_4 \) is a solvent hop that instead brings the vacancy into this shell. For the sake of simplicity, the \( w_3 \) and \( w_4 \) frequencies are assumed to be equivalent for any type of hop in and out of the nearest neighbor shell. Calculations in this work consider a hop between an \((\frac{a_0}{2}, \frac{a_0}{2}, 0)\) site and an \((a_0, 0, 0)\) site where \(a_0\) is the cubic lattice constant and the single solute atom is at \((0, 0, 0)\).

In the dislocation cell, Ni hops do not always neatly fit into one of these categories, because the strained geometry causes the interatomic distances between an atom and its nearest neighbors to differ from one another. With 19 unique types of sites in the KMC cell each having up to 12 distinct nearest neighbor sites that a vacancy could be situated.
at, the number of solute-vacancy combinations and possible Ni atom-vacancy exchanges within each one mean that it would be infeasible to evaluate all possibilities within a DFT framework. Because the existence of an incomplete KMC rate catalog could introduce pronounced inaccuracy into its results [67], an investigation was carried out to assess whether some energy barriers to Ni atom-vacancy exchanges in the vicinity of a solute atom in the dislocation cell could be approximated by combining information from the five frequency model for that solute with the energy barrier of the Ni atom hopping in the pure Ni case. The energy barriers of twelve Ni hops in the vicinity of a dilute Co or Al atom were prepared in three different ways: as accurate $E_m$ values calculated with the NEB method, self-diffusion values $E_{m,\text{self}}$ that ignore the presence of the solute, and modified values $E_{m,\text{mod}}$ that use fcc five frequency information to approximate solute-vacancy interaction effects in the dislocation system. These are calculated as $E_{m,\text{mod}} = E_{m,\text{self}} + E_i$, where $E_i = E_{m,w_i} - E_{m,w_0}$ for $i = 1, 3, 4$ from the five frequency model depending on the location of the vacancy relative to the solute before and after each jump. These Ni-vacancy exchanges take place in the immediate vicinity of a solute in each direction along three pathways: along $\langle 1\bar{1}0 \rangle$ on the compressive side of the core, along $\langle 1\bar{1}0 \rangle$ on the tensile side of the core, and between sites that lie on the compressive and tensile sides. One set of these jumps sees a solute atom positioned on the compressive side and neighboring each exchange, while another sees a solute on the tensile side neighbor each one. Fig. 3.5 presents these values.
Figure 3.5: Comparison of methods to calculate solvent Ni atom-vacancy exchange energy barriers near the partial core in the vicinity of (a) a Co solute atom and (b) an Al solute atom. NEB values are presumed to be accurate, \( E_{m,\text{self}} \) values ignore the presence of the solute, and modified \( E_{m,\text{mod}} \) values are in each case the self-diffusion value adjusted according to the fcc five frequency model.

A simple analysis of the error of each approximation considers the sum of the squares of the differences of each predicted value (SSE) relative to the accurate NEB value. In the Co case, the \( E_{m,\text{self}} \) SSE is 26% less than the \( E_{m,\text{mod}} \) value, while in the Al case the \( E_{m,\text{mod}} \) approximation produces 4% less SSE than \( E_{m,\text{self}} \). These results justify use of the simpler \( E_{m,\text{self}} \) approximation. Based on the literature cited [98, 99] in the discussion of Section...
3.3.2, the omission of solute-vacancy interaction effects likely results in an error in the reported activation energies that has an upper bound of $\sim 0.1$ eV.

### 3.4 Conclusions

We studied diffusion along a partial core of an $\frac{a_0}{3}(1\bar{1}0)$ screw dislocation in fcc Ni. A nudged elastic band scheme within a DFT framework generates activation energies of various atom-vacancy exchanges in and around the partial core for each of seven solutes. A general trend emerges along each activation pathway, where the migration energy barriers rank in the following descending order: Re, W, Co, Mo or Ni, Cr, Al, Ti. These energy barriers contribute to the calculation of harmonic transition state theory-based rate constants that describe the frequency at which each solute-vacancy exchange takes place in the dilute solute case. In conjunction with a rate catalog describing Ni atom hops, a kinetic Monte Carlo (KMC) model leads the vacancy on a probability-weighted random walk, during which the behavior of the solute atom is tracked to generate a diffusivity at each temperature over the range of 300-1500 K in 100 K increments. The resultant values quantify the effects of geometry and chemistry on diffusivity for the chosen systems and can lead to useful comparisons, e.g., the diffusivity of Re along the dislocation pipe at 1300-1500 K is predicted to be slightly lower than that of isotropic self-diffusion in fcc Ni over the same range. The activation energies and diffusivities reported here could be used as input into creep rate models or may be able to suggest that pipe diffusion of a certain element is the rate-limiting factor of a particular creep mechanism in a given context.
Chapter 4. *Ab initio* molecular dynamics of pipe diffusion in fcc Ni beyond transition state theory

In this chapter, we model the rate constants of several atom-vacancy exchanges with a dynamic approach that is completely different from the harmonic transition state theory (HTST) method used in Chapters 2 and 3. A combination of molecular dynamics (MD) techniques generate the rate constants at finite temperatures rather than at 0 K, with constrained MD simulations producing free energy profiles along the reaction coordinate and unconstrained MD simulations investigating the effects of barrier recrossings omitted by TST. The resultant values suggest that HTST systematically underestimates the rate constants due to omission of the dynamically observable effects by factors of 2-5.

4.1 Introduction

4.1.1 Context

A downside to the static calculation of energy barriers considered in Chapters 2 and 3 is that diffusion is inherently kinetic, and in reality it may not unfold according to the assumptions that govern static simulations. Several previous studies have investigated pipe diffusion using molecular dynamics (MD) techniques. An early classical MD study, using the Embedded Atom Method, reported that vacancies, interstitials, and diffusion in the stacking fault ribbon between dissociated partial dislocation cores all contribute to pipe diffusion in fcc Cu [35]. Similar works used classical MD (i.e., EAM) to calculate vacancy-
mediated self-diffusion migration energies along dislocation pipes in Cu, Ag [109], and Al [110]. To demonstrate this, Purja Pun and Mishin used classical MD to study dislocation self-diffusion in fcc Al in the intrinsic case with no point defects initially inserted into the simulation supercell [33]. At homologous temperatures of 0.72-0.96T_{m} (where T_{m} is the melting temperature), they found that screw dislocation cores generate Frenkel pairs, resulting in a mechanism that dominates contributions to diffusion over the equilibrium-scaled vacancy or interstitial mechanisms. Later MD studies considering the intrinsic mechanism found that it can also occur in Ni [111] and that the generation of point defects arises from constriction of the separated partial cores at high temperatures [112], which static methods would be unable to account for. Another recent classical MD study on pipe diffusion in bcc metals found that vacancies may dissociate and disperse along the dislocation line, which could give rise to new mechanisms to facilitate pipe diffusion [113]. A disadvantage of the atomistic potential approach is that it does not accurately account for the effects of charge transfer as an atom diffuses. While MD simulation cells containing long portions of the dislocation line are currently inaccessible to DFT, ab initio MD simulation cells containing hundreds of atoms do allow dynamic quantum mechanical investigations of individual exchanges that may contribute to pipe diffusion.

4.1.2 Approach

Here, we utilize an alternative kinetic method, based on a combination of ab initio constrained and unconstrained molecular dynamics (CMD and MD), to calculate the rate constants k of atom-vacancy exchanges along three diffusion pathways near a partial screw dislocation core in fcc Ni. This approach offers three advantages: simulations occur at realistic operating temperatures with no extrapolation from 0 K, it includes entropic contributions to free energy barriers of vacancy migration without relying on harmonic or quasi-harmonic approximations, and correlation effects from barrier recrossings can emerge in the dynamic simulations. The guiding principle of this methodology is that one can model
the time-independent rate constants of particular atom-vacancy exchanges by performing
dynamic simulations over short lengths of time at the nanoscale. This idea originally devel-
oped in a series of works by Bennett and Chandler [114,117] and led to the highly practical
relation for the rate constant [118, 119]:

\[
k = P_0 R(t),
\]

(4.1)

where \( P_0 \) represents the probability density that the diffusing atom is at \( q^* \), the top of the
energy barrier along a reaction coordinate relative to an initial state, and \( R(t) \) represents the
particle flux along the reaction coordinate through a dividing surface that includes \( q^* \) and
separates the coordinate into initial and final states.

Calculations of \( P_0 \) here employ thermodynamic integration of free energy gradi-
ents obtained through CMD simulations, which allow the study of rare events like diffu-
sion hops on timescales not typically available to conventional MD. Carter and coworkers
named this context the “blue moon ensemble” in a foundational paper that describes how
to remove constraint-induced bias to obtain physically meaningful information for realistic,
unconstrained cases where these events happen [120]. Later works from a variety of
groups [118,121–123] generalize the calculation of these free energy gradients, which one
can now compute using software like the Vienna \textit{ab initio} simulation package (\textit{vasp}) [124].
The \( R(t) \) term of Eq. (4.1) incorporates the effects of barrier recrossing that traditional TST
omits.

Applications of this methodology in the relatively recent literature tend to involve
systems with many degrees of freedom such as ring closure in dioxin formation [125], hy-
drocarbon conversion [126], or loading-dependent hydrocarbon diffusion in zeolites [127].
They may also concern cases with high rates of barrier recrossing like solid-liquid or liquid-
gas nucleation [128,129]. However, Bennett’s first work on recrossings was in the context
of diffusion in solids studying vacancy migration in fcc Ar [114], which another group
later revisited within the blue moon ensemble [130]. In a study with similarities to that
conducted here, Gillan and coworkers considered recrossings during vacancy diffusion in CoO [131]. Major differences between our work and theirs include: methodologies of free energy calculations, rigid-ion potentials instead of DFT, ionic ceramic chemistry versus the metallic environment considered here, and their rock-salt crystalline lattice structure instead of a partial dislocation core. To our knowledge, the techniques used here have not been applied to the study of defect migration in engineering materials or within a first principles context to vacancy migration in general.

As was the case in Chapters 2 and 3, calculations of migration rate constants in solids typically approximate entropic contributions, most commonly with Vineyard’s harmonic transition state theory (HTST) [66], which estimates entropic effects in an attempt frequency term, $\nu^*$, which is neatly calculated within the hopping atom approximation [64]:

\[
k = \nu^* \exp \left( \frac{-E_m}{k_B T} \right),
\]

\[
\nu^* = \frac{\Pi_{i=1}^{3} \nu_i}{\Pi_{i=1}^{2} \nu'_i}.
\]

$E_m$ is the potential energy barrier to migration, $k_B$ is the Boltzmann constant, $T$ is the temperature, $\nu_i$ are vibrational frequencies of a hopping atom at its equilibrium position pre-hop, and $\nu'_i$ are its two real vibrational frequencies at the static saddle point. This approximation assumes harmonicity, which may be invalid at high homologous temperatures and is not particularly well-suited for the asymmetric geometry of the dislocation, especially within a supercell with fixed boundary conditions. A second downside is that the approximation discards all information on the unstable vibrational mode at the transition state, which may be particularly important in the context of dislocations because of the soft phonon modes along their cores. One first principles technique provides a means for calculating the contribution of the unstable mode to the free energy of migration [132], but it also uses a harmonic framework and is best suited for crystalline geometries. The approach of Eq. (4.1) avoids these approximations and enables construction of more accurate
rate constants concerning pipe diffusion in particular, while also providing the benefits that come with accounting for finite temperature effects and barrier recrossings.

Rate calculations here consider three atom-vacancy exchange pathways near the screw dislocation partial core, indicated by the arrows in Fig. 4.1(a). The view of the figure bisects the stacking fault and partial core to show the plane containing the compressive side of the edge component of the screw partial; the (111) slab of atoms just above the plane of the page contains the tensile side. In Chapter 2, we identified hops along these three pathways as some of the most significant contributors to pipe diffusion using Eq. (4.2). The activation pathway $Q_\parallel$ is parallel to the [1\(ar{1}0\)] direction of the dislocation line, while $Q_N$ wraps around the screw geometry of the partial core with a large component normal to the dislocation line, and $Q_{P-SF}$ is between a partial core-adjacent site and a site in the hcp stacking fault between the partial core and its counterpart. “Sites” here refer to unique atomic equilibrium positions in the (1 \(ar{1}0\)) slabs that run normal to the dislocation line. These sites repeat periodically along the dislocation line direction. Atomic hops along each pathway are analyzed in both directions, with a superscript “F” or “R” indicating whether the component of the atom’s displacement in the [1\(ar{1}0\)] direction is positive (forward) or negative (reverse). Each hop is studied at two temperatures: 1000 K, which is about 0.6 times $T_m$ of the Ni-base superalloys and marks the onset of high-temperature operation [1], and 1400 K, which is between the approximate average operating and hot spot temperatures of Ni-base superalloy components [80].
Figure 4.1: Illustration of the local geometry that surrounds the atom-vacancy exchange pathways considered here. (a) The partial screw dislocation core resides between an hcp stacking fault and surrounding strained fcc Ni, as visualized in ovrro [6–8]. Arrows indicate the particular pathways for which vacancy hop rates are calculated. (b) Schematic of the constraint system used in simulations of hops along the $Q_{\parallel}$ pathway, which is indicated by the blue arrow in panel (a). Illustrations of atoms here have smaller radii to depict the center of the diffusing atom as it travels through 17 discrete points along its diffusion pathway.

To construct free energy profiles of each jump, we perform CMD simulations to calculate free energy gradients when the diffusing atom is constrained to each one of 17 discrete points along each pathway. These points fall along two line segments that connect an initial equilibrium position $q_0$ to the saddle point $q^*$, and then connect $q^*$ to the final equilibrium position $q_f$. Together, these segments define the reaction coordinate of one atom-vacancy exchange. During MD, constraints fix the distances between the diffusing atom and each of the two terminals of the line segment containing the discrete point of interest. Because the partial screw dislocation core doesn’t dramatically strain the fcc geometry, these anchor points are closely approximated by the midpoints between pairs of nearby atoms, which therefore define the constraints. Fig. 4.1(b) illustrates the discrete points along the diffusion pathway, the three anchors (black dots), and the constraint-defining atoms (connected by dashed lines) for the jump along the $Q_{\parallel}$ pathway. Integrating the free energy gradients produced by these simulations produces the $P_0$ term of Eq. (4.1). Followup unconstrained MD simulations, beginning with the diffusing atom atop the energy barrier, enable study of
barrier recrossings and calculation of $R(t)$.

4.2 MD Methodology

4.2.1 Geometry preparation

This study takes place using VASP within the same hexagonal supercell geometry prepared within the same set of settings that was outlined in Section 2.2.1. To prepare for constrained molecular dynamics simulations where the diffusing atom is tethered to a fractional value of the reaction coordinate, geometries are interpolated from the NEB geometries that consist of converged initial equilibrium, saddle point, and final equilibrium configurations. A 7-image NEB calculation between the initial and saddle points of one jump validated this approach by identifying that the linearly interpolated location of the diffusing atom strays from the NEB-identified path by $< 0.5\%$ of the distance between endpoints; details concerning this analysis are presented in Appendix C.

4.2.2 Molecular dynamics simulations

A Nosé-Hoover thermostat [133, 134] controls the velocities of the atoms during CMD simulations such that sampled states correspond to an equilibrium distribution drawn from a canonical ensemble. Two trial simulations, each with the diffusing atom constrained halfway between its initial equilibrium position and the saddle point along the jump in the dislocation line direction, ran with time steps of 1.0 and 2.0 fs but otherwise identical settings including initial atomic velocities at 1400 K. Resultant forces on the constrained atom evolve qualitatively in the same way over the full 2.5 ps of each trial, with the total average force on the constrained atom differing between the two cases by $< 2\%$. A time step equal to 2.0 fs was therefore adopted for MD simulations. Each temperature oscillates around its fixed value with a period of 20 fs, which at 50 THz is on the same order of magnitude as the Debye frequency of Ni, which is $\sim$10 THz. Four simulations at each
point randomly initialize the velocities of all particles according to a Maxwell-Boltzmann distribution at the specified temperature. This breadth of sampling reduces the effect that an unrepresentative initial set of velocities would have on the free energy gradient, since averages over the multiple samples are intended to approximate an ensemble average. Each simulation runs for 4200 fs with data from the first 200 fs of each simulation omitted from calculations to allow temperature oscillations to stabilize following initialization. This short stabilization period is enough to ensure that temperature fluctuations are within ±7% of the desired target temperature over the remainder of each simulation. The SHAKE algorithm constrains the diffusing atom to a discrete point along its path \[^{135}\]. Simulation settings are identical to those used for optimization, except that MD simulations employ a single k-point (Γ).

The constrained MD simulations also generate initial configurations of atoms for the unconstrained MD simulations, which begin with the diffusing atom atop the energy barrier. Extractions occur each time the diffusing atom crosses through the plane that is normal to the reaction coordinate and contains the NEB-identified saddle point location of the diffusing atom. These configurations are separated from one another by at least 50 fs, which is the approximate correlation time of the sum of atomic energies during the constrained simulations. Fifty geometries are used for each jump at each temperature, with initial velocities drawn from a Maxwell-Boltzmann distribution. Each geometry is used twice, once with a positive and once with a negative initial velocity along the reaction coordinate. Initial velocities are assigned such that the average velocities of the diffusing atom in particular over the fifty unconstrained simulations in each of the positive and negative directions equals the expected average velocity from the Maxwell-Boltzmann distribution. Unconstrained MD simulations used the same settings as the constrained ones and ran for at least 400 fs, continuing longer when necessary to allow the diffusing atom to reach an equilibrium position on the reaction coordinate.
4.2.3 Rate constant calculations

Calculations of the free energy gradients from CMD simulations \cite{120, 122, 123, 136} rely on Bucko’s implementation of the technique in \emph{vasp} \cite{124}. The net free energy gradient at each point of constraint $q_j$ along a reaction coordinate $q$ is defined:

\[
\left( \frac{\partial A}{\partial q} \right)_{q_j} = \frac{\left\langle |Z|^{-1/2} \left( \frac{\partial A}{\partial c_1} \cdot \frac{q_j}{||q||} + \frac{\partial A}{\partial c_2} \cdot \frac{q_j}{||q||} \right) \right\rangle}{\left\langle |Z|^{-1/2} \right\rangle},
\]

(4.4)

where $A$ is the Helmholtz free energy, $Z$ is a mass metric tensor that here removes bias introduced by the constraints \cite{120}, $\frac{\partial A}{\partial c_i}$ is the free energy gradient along constraint $i$, and $||q||$ is the length of reaction coordinate $q$. Dot product operations project the free energy gradient vectors onto the direction of the reaction coordinate. This projection is necessary because the instantaneous orientations of these vectors in space move around during the dynamic simulations and are not always collinear with the reaction coordinate, particularly during simulations that constrain the atom near one terminal of the reaction coordinate when one constraint is necessarily short ($\sim$0.1 Å). Angle brackets represent canonical ensemble averages, where each data point contributing to the ensemble average consists of the average value of a bracketed term over a single correlation time of 50 fs. Thermodynamic integration of these gradients provides free energy profiles along each pathway:

\[
\Delta A = \int_{q_0}^{q^*} \left( \frac{\partial A}{\partial q} \right)_{q_j} \cdot dq,
\]

(4.5)

where $q_0$ and $q^*$ are the terminals of one line segment of a reaction coordinate and $dq$ is the distance between points where the diffusing atom is constrained, as illustrated in Fig. 4.1(b). In this case, integration proceeds from an initial equilibrium position $q_0$ to $q^*$; integrations are also performed from final equilibrium positions $q_f$ to $q^*$ along each pathway. The gradient at the saddle point projected onto the corresponding reaction-coordinate segment is calculated separately for each of these integrations, once using the set of constraints
corresponding to the line segment that spans $q_0$ to $q^*$ and once with those corresponding to the line segment connecting $q_f$ to $q^*$.

The modified trapezoidal rule with coefficients suggested by den Otter and Briels [122] evaluates the integral:

$$f(x + h) = f(x) + \frac{h}{24} \left[ -f'(x - h) + 13f'(x) + 13f'(x + h) - f'(x + 2h) \right],$$

where $f'$ is the derivative of $f$ and $h$ is the integration step size. Near the terminals of the reaction coordinate, evaluation of the integral omits any terms that lay outside of the diffusion pathway with the leading coefficient of $\frac{1}{24}$ adjusted to properly weigh the remaining contributions. Free energy values from these profiles contribute to the $P_0$ term of the rate constant Eq. (4.1) [118, 119]:

$$P_0 = \frac{\exp\left[ -A(q^*)/k_B T \right]}{\int_{q_0}^{q^*} \exp\left[ -A(q)/k_B T \right] dq}.\quad (4.7)$$

The other component of Eq. (4.1) describes the flux of the diffusing atom along the reaction coordinate through the dividing surface that separates its equilibrium states and includes its saddle point [118]:

$$R(t) = \frac{\delta(t) [q^* - q(0)] \theta[q(t) - q^*]}{\left\langle [q^* - q(0)] \right\rangle} \quad (4.8)$$

where $\dot{q}(0)$ is the velocity of the diffusing atom along the reaction coordinate at $t = 0$, $\delta$ is the Dirac delta function, $\theta$ is the Heaviside step function, which here identifies whether the system is in its initial or final state based on which side of the dividing surface the diffusing atom is on, and the angle brackets indicate canonical ensemble averages. $R(t)$ is calculated
by taking the average value of many samples of \( \dot{q}(0) \theta[q(t) - q^*] \) from unconstrained simulations that begin with the initial condition \( q(0) = q^* \) \(^{[119, 127]} \). To calculate, for instance, the \( R(t) \) term that contributes to the rate constant of the \( Q_{P-SF}^F \) hops, each atomic trajectory beginning with an initial velocity from the near partial site (P) towards the vacant stacking fault site (SF) that ultimately equilibrates there will make one positive contribution to the numerator of Eq. (4.8). If the diffusing atom in such a case makes several intermediate crossings (with positive velocity at \( q^* \)) and recrossings (with negative velocity at \( q^* \)), only one positive term contributes to the average because the preceding crossings and recrossings cancel one another out \(^{[137]} \). Trajectories that begin with an initial velocity towards the P state but return to equilibrate in the SF state contribute zero to the average because they have an inherently equal number of crossings and recrossings, which also cancel one another. P to P and SF to P trajectories contribute zero to the average because the step function is zero when the system equilibrates in the P state. The velocity \( \dot{q}(0) \) at simulation initialization contributes to the average for all crossings/recrossings along a particular trajectory, because the initial velocity corresponds to a Maxwell-Boltzmann distribution at the temperature of interest. Atomic collisions that lead to recrossings alter the velocity of the diffusing atom such that it may no longer correspond to the relevant distribution. The use of a finitely sized sample of these reset velocities to calculate \( R(t) \) would produce a rate constant \( k \) that is not directly comparable to those calculated with the TST and HTST methodologies. Ensemble averages are taken over the one hundred sets of initial conditions for each jump at each temperature, with fifty trajectories initially pointed towards each of the two equilibrium states.

Calculations of the standard error on the difference between \( R(t) \) and \( R(t)_{TST} \) consider the quantity \( \dot{q}(0) \left[ \theta[q(t) - q^*] - \theta[q(0^+) - q^*] \right] \), since in the TST approximation, the step function at time \( 0^+ \) is equivalent to that at time \( t \) due to the absence of recrossings. \( R(t) \) values reach plateaus on timescales \( \tau_{cross} < t < \tau_{hop} \), where \( \tau_{cross} \) is the time it takes the atom to move to one equilibrium position from the top of the barrier and \( \tau_{hop} \) is the average
time it takes for an atom-vacancy exchange to spontaneously occur from an equilibrium state [117]. This plateau value allows the time-dependent $R(t)$ term to contribute to the calculation of time-independent rate constants. In some contexts with high recrossing rates, Eq. (4.8) may have a large relative error or the Heaviside step function may be poorly suited to describe the state of the system [118]. Neither of these conditions exist in the current study, as the atom-vacancy exchanges considered here have recrossing rates of $\leq 30\%$ and atoms in the unconstrained MD simulations consistently move to one equilibrium position or the other along the reaction coordinate. Resultantly, this approach is a valid means for calculating $k$ in this context.

4.3 Results and discussion

4.3.1 Free energy profiles

Fig. 4.2(a) provides an example of the free energy gradients calculated at the fifth point along the $Q_{p-SF}^R$ activation pathway. To reduce the bias imposed by initial conditions and encourage better sampling of the phase space, four samples begin with different sets of initial velocities. As seen in the figure, different simulations generate cumulative average gradients that converge to slightly different plateaus. Those calculated at lower temperatures tend to be greater than those at higher temperatures, consistent with expectations. Standard error ($s/\sqrt{n}$ where $s$ is the sample standard deviation and $n$ the number of samples) calculations take the average free energy gradient over each 50 fs block of time to be one data point. This is the approximate correlation time of the sum of the kinetic and potential energies of all moving atoms during CMD simulations identified by a reblocking approach [138]. This error is statistical rather than an inherent byproduct of the methodology, and the $\sim 10\%$ error bars observed in the free energy profiles of Fig. 4.2(b-c) would drop to $5\%$ with a fourfold increase in the number of samples, consistent with the definition of standard error. In some simulations, the vacancy exchanged places with another of its
unconstrained neighbor atoms. While unsurprising because of low energy barriers relative to the temperatures (the probability of a particle drawn from a Boltzmann distribution having at least 0.5 eV at 1400 K is $\sim 1.6\%$), such exchanges destroy the constraint systems and are not relevant to study of the reaction coordinates of interest. In situations where these jumps are unavoidable, one strategy is to introduce harmonic springs with varying spring constants that restrict those neighboring atoms to their equilibrium positions, then extrapolate results as the spring constants go to zero [130]. Because the jumps here are not so common, data from the cases where they do occur is simply excluded and the error for that gradient is higher because of the diminished number of samples.

Integrating the free energy gradients produces migration energy profiles for each exchange, as shown in Fig. 4.2 panel (b) for the $Q_{P-SF}$ and (c) $Q_{\parallel}$ pathways. Integrations take place with reference to the saddle point energy to allow for comparisons of barriers calculated using different methodologies and in different directions along the reaction coordinate. Fig. D.1 provides similar profiles for the other two jumps. Free energy barrier heights are generally below the NEB-generated potential energy barriers; the sole exception to this is for the $Q_{P-SF}^F$ jump depicted in Fig. 4.2 (b) at 1000 K, where the dynamically generated free energy barrier height when the atom hops from left to right is 0.007 eV greater than the static $E_m$. In all cases, free energy barriers are lower at 1400 K than at 1000 K. Table D.1 provides details on the contributions of energy barriers and profiles via Eq. (4.2) and $P_0$ to rate constants $k$ for each method and temperature.

Asymmetries along $Q_{P-SF}$ exist in opposite directions depending upon which method is used, as shown in Fig. 4.2 panel (b). Both atomic sites along the pathway express compressive character due to the edge component of the screw partial core. The near core site has an average distance to its nearest neighbors, or $d_{NN}$, of 2.465 Å, making it slightly more compressive than the site in the stacking fault that has $d_{NN}$ of 2.474 Å. These distances are taken from the originally prepared dislocation geometry [5] before any vacancy is inserted. Fig. 2.5 illustrates which sites in the vicinity of the pathways considered here are more
Figure 4.2: Free energy gradients calculated with the diffusing atom constrained at one point along the $Q_{P-SF}$ pathway along with the resultant free energy profiles from integrating gradients from all points of constraint along a reaction coordinate. (a) Different line textures represent the cumulative net free energy gradient in each of four samples taken at each temperature. Free energy profiles for the (b) $Q_{P-SF}$ and (c) $Q_{R}$ hops are compared with nudged elastic band-generated energy barriers. Error bars display the integrated absolute standard error of the convergence of the gradients due to sample size.
compressive or tensile relative to fcc Ni, which has a nearest neighbor distance of 2.490 within the spin-polarized GGA-PAW approach [4]. Table 2.2 provides the average nearest neighbor distance for each of these sites. Static calculations report that a hop along $Q_{P-SF}^F$ is 0.051 eV more favorable than one along $Q_{P-SF}^R$, suggesting that it is energetically favorable to install the vacancy in a site that expresses more pronounced compressive character, presumably to reduce the elastic energy. At 1.15 eV, this more compressive near core site has the lowest statically calculated vacancy formation energy of 17 sites considered near the core in Chapter 2. In contrast, the dynamic simulations indicate lower free energy barriers in the opposite direction along this pathway, suggesting that it is instead easier for the atom to hop into the more compressive site than out of it at elevated temperatures. A $Q_{P-SF}^R$ hop is 0.026 and 0.039 eV more favorable than a $Q_{P-SF}^F$ one at 1000 and 1400 K. These asymmetries demonstrate that configurations sampled by the dynamic technique are necessary to account for the energetically preferable condition of the dislocation at elevated temperatures to accurately describe diffusion processes.

The NEB-calculated energy barriers to diffusion along $Q_{//}$ are direction-independent, because in either case $E_m$ is equal to the difference in energy at the saddle point connecting the two equilibrium configurations from the energy of either of those configurations that see one vacancy at one of two neighboring sites. In the static case, these sites along the $\langle 1\overline{1}0 \rangle$ direction are effectively periodic within the supercell used here that has a depth of 4b. The relaxed configurations of atoms around a vacancy at these effectively periodic sites are very similar; for instance, the remaining three atoms that are distributed in the $\langle 1\overline{1}0 \rangle$ column of atoms containing the vacancy see the distances to each of their respective neighbors vary by $\leq$ 1 mÅ, ultimately resulting in the energies of the different configurations agreeing within 1 meV of one another as well. In contrast, this degree of symmetry is not observed during dynamic simulations, as atoms that neighbor the vacancy behave differently when the vacancy is at different sites that could be assumed to be periodic in the static case. For instance, during dynamic simulations of $Q_{//}$ at 1400 K and making reference to the labels
of Fig. 2.1, an atom at a “B” site that is just ahead of a “B” vacancy in the [110] direction tends to be about 0.1 Å closer to either of its “A” atomic neighbors in the \(q_f\) configuration when compared to the \(q_0\) one. This is the most dramatic variation observed among any of the “B” atoms and their neighbors; these differences range from 0.001 to 0.1 Å, in some cases exceeding the standard error of ~0.02 Å of most correlation time-averaged distances. These variations suggest rearrangements of the atoms within the cell during the dynamic case.

Contributing factors to this rearrangement during high-temperature dynamic simulations may include the depth of the supercell or differences in how constraint points are defined as illustrated in Fig. 4.1(b), where one constraint system defines the diffusion path from \(q_0\) to \(q^*\) and a second constraint system defines the path from \(q_f\) to \(q^*\). Fig. 4.3 and Table 4.1 provide a comparison of the average interatomic distances between the three atoms in the \langle 110 \rangle row containing both the diffusing atom and the vacancy. This analysis indicates smaller mismatch (up to 0.015 Å) at the saddle point as a function of constraint system relative to the mismatches observed between the \(q_0\) and \(q_f\) states (up to 0.077 Å). This suggests that rearrangements within the supercell under high temperature dynamics might be the reason for the observed initial/final site asymmetry that is not observed in the static case. Increasing the number of sample systems to decrease the uncertainty of the integrated free-energy results could give rise to a more accurate comparison. Ultimately, this results in the dynamic approach identifying barrier heights that are lower along \(Q^R_{\|}\) than \(Q^F_{\|}\) by 0.052 and 0.074 eV at 1000 and 1400 K, as shown in Fig. 4.2 panel (c). These barriers are expected to represent upper bounds on the true free energy barriers for either hop in case the factors that cause rearrangements within the supercell also cause the diffusing atom to stray from its minimum energy path. We do not expect these direction-dependent free energy barriers to result in a net mass flux or effective chemical potential along the dislocation line direction in reality, because these intra-cell biases should be offset by free energy contributions making vacancy formation increasingly favorable in the site that sees
a higher barrier to escape. Furthermore, strict periodicity is still imposed with a period of 4b that eliminates any overall inter-cell bias parallel to the dislocation core.

\[
\begin{align*}
\text{(a)} & \quad q_0 \quad q_f \\
\text{(b)} & \quad q^* \\
\end{align*}
\]

Figure 4.3: Illustration of the \langle 1\bar{1}0 \rangle row of atoms containing both the vacancy and diffusing atom for the \( Q_{\parallel} \) pathway, where vertical dashed lines indicate periodic boundary conditions, at (a) equilibrium positions \( q_0 \) and \( q_f \) and (b) the saddle point configuration \( q^* \). Table 4.1 provides the average dynamic interatomic (I) and cross-void interatomic (C) distances indicated here.

<table>
<thead>
<tr>
<th>Distance</th>
<th>( q_{0,LHS} )</th>
<th>( q_{f,RHS} )</th>
<th>Difference</th>
<th>Distance</th>
<th>( q_{i,LHS} )</th>
<th>( q_{i,RHS} )</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_1 )</td>
<td>2.581</td>
<td>2.529</td>
<td>-0.052</td>
<td>( I )</td>
<td>2.640</td>
<td>2.625</td>
<td>-0.015</td>
</tr>
<tr>
<td>( I_2 )</td>
<td>2.528</td>
<td>2.605</td>
<td>0.077</td>
<td>( C_1 )</td>
<td>3.739</td>
<td>3.743</td>
<td>0.003</td>
</tr>
<tr>
<td>( C )</td>
<td>4.853</td>
<td>4.828</td>
<td>-0.025</td>
<td>( C_2 )</td>
<td>3.583</td>
<td>3.595</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 4.1: Average interatomic distances indicated in Fig. 4.3 during constrained MD simulations along \( Q_{\parallel} \) at 1400 K. Statistical uncertainty on the position of each atom according to correlation time averaging is \( \sim 0.02 \) Å. Subscripts on \( q \) terms indicate use of either the left hand side (LHS) or right hand side (RHS) constraint system depicted in Fig. 4.1(b).

### 4.3.2 A note on the effects of thermal expansion

DFT studies often omit the effects of thermal expansion because of the high computational costs of expanding the supercell at different temperatures and repeating all geometry relaxations and calculations within each expanded cell. When expansions are applied, they typically rely on the quasiharmonic approximation (QHA), which as discussed above has disadvantages for studying dislocations. As the original dislocation geometry was prepared at 0 K [5], and because our previous HTST study of Chapters 2 and 3 did not employ
expanded supercells, most of the dynamic calculations here also do not take place in expanded cells, thus allowing direct comparison of the dynamic and static methodologies. Nonetheless, to investigate expansion-dependent entropic effects, one set of calculations in the present study considering $Q_{\parallel}$ does take place in an expanded geometry consistent with 1400 K. These supercells are expanded by the empirical linear thermal expansion coefficient of Ni of 13.4 $\mu$m/K·m \cite{39}, which is within 5% of the value calculated by the software PHONOPY \cite{40,41} within the QHA for a 32-atom fcc Ni cell prepared with the same parameters as the other geometries used here. Both the statically and dynamically calculated energy barriers drop relative to those from the unexpanded cell, as can be seen by comparing the barriers of Fig. 4.2(c) with those of Fig. D.1(b). Calculations in the expanded cell cause the exponential term of Eq. (4.2) in the static case at 1400 K to rise by a factor of 1.6 relative to the unexpanded one, while the dynamic $P_0$ term increases by factors of 2.4 for $Q_F^{\parallel}$ and 1.6 for $Q_R^{\parallel}$ following expansion. These observations suggest that thermal expansion similarly affects both dynamic and static simulation results, increasing the rate constant along any given pathway by a factor of about two at 1400 K. Asymmetries in the free energy profiles cause $Q_R^{\parallel}$ hops to be energetically preferred over those along $Q_F^{\parallel}$ in both the unexpanded and expanded dynamic cases.

4.3.3 Barrier recrossings

Unconstrained MD simulations that follow generation of the free energy profiles see recrossings along all pathways after the diffusing atom is placed atop the energy barrier and freed to move. Fifty trajectories begin with the atom moving along each direction of the reaction coordinate of each pathway at each temperature. Fig. 4.4(a) provides a representative example of this behavior along the $Q_{P-SF}$ pathway at 1400 K, and Fig. D.2 provides plots for the other jumps. Cyan lines plot trajectories of the diffusing atom along the reaction coordinate beginning with a forward velocity component along [110] while magenta velocities are initially in a reverse direction. The atom proceeds to its initial destination.
more often than not, but some recrossings take place in both directions. Table 4.2 provides the numbers of completed recrossings for each jump and direction. Most simulations see the atom reach an equilibrium position within 400 fs, but in some cases the atom hangs near the top of the barrier and needs more time; one such case is visible in Fig. 4.4(a) as the magenta line that is consistently near $q^*$. Occasionally, the atom has time to reach an equilibrium position and then hop back out. Because spontaneous hops at this temperature are not particularly rare as discussed above, these do not count as additional barrier recrossings as long as the atom had already crossed the dashed line of the figure. Over all unconstrained MD simulations, the atom returns to the initial position it is initially moving away from in 14 and 19% of cases at 1000 and 1400 K, respectively. This suggests that at elevated temperatures, correlation effects from barrier recrossings can become as significant as the geometrical correlation factor for vacancy-mediated diffusion in fcc crystals, which suppresses diffusivities by about 21.9% [72].

Recrossings diminish each $R(t)$ contribution from its TST-predicted value, which when assuming Maxwell-Boltzmann statistics is simply $R(t) = \langle \frac{1}{2} |\dot{q}| \rangle = \sqrt{\frac{k_B T}{2\pi m}}$, where $\dot{q}$ is the velocity of the diffusing atom along its reaction coordinate and $m$ is its mass [127]. $R(t)$ in a particular direction reduces gradually with each barrier recrossing by an atom initially heading in that direction, or increases with each recrossing cancellation, until it converges to a plateau value. Fig. 4.4(b) demonstrates this for the $Q_{P-SF}$ pathway at 1400 K, and Fig. D.3 provides similar plots for the rest of the jumps studied. In the expanded cell, recrossings diminish $R(t)$ from the uncorrected TST value by 7.1 and 12.2% along the $Q_{\parallel}^F$ and $Q_{\parallel}^R$ pathways, while in the unexpanded cell these values decrease by 8.3 and 15.0%. These agreements are within the margin of uncertainty for the differences in $R(t)$ and $R(t)_{TST}$ due to sample size at each temperature, suggesting that recrossing behavior is independent of cell expansion. It takes about 300 fs for the plateau values of $R(t)$ to emerge compared to ~150 fs in the unexpanded cell, because the additional volume available to each atom in the expanded cell increases the amount of time before collisions with neigh-
Figure 4.4: Behavior of the diffusing atom at the top of the energy barrier of the $Q_{P-S_F}$ reaction coordinate along with resultant effects on the associated hopping rates. (a) Movement of the diffusing atom from its beginning position $q^*$ atop the energy barrier during unconstrained MD simulations at 1400 K. Dotted cyan and solid magenta lines respectively represent fifty trajectories each where the diffusing atom begins with an initially forward or reverse velocity along $[1\bar{1}0]$. (b) Representation of particle flux along the reaction coordinate through the saddle point-containing dividing surface at 1400 K.
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Jump</th>
<th>$P_0$ ($\times 10^{-3}$ Å$^{-1}$)</th>
<th>$R(t)$ ($\times 10^{-3}$ Å/fs)</th>
<th>Recrossings</th>
<th>$k$ (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>$Q_{P-S_F}^F$</td>
<td>2.10</td>
<td>1.43</td>
<td>6</td>
<td>3.0</td>
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<tr>
<td></td>
<td>$Q_{P-S_F}^R$</td>
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<td>1.37</td>
<td>11</td>
<td>4.7</td>
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<tr>
<td></td>
<td>$Q_{N}^F$</td>
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<td>1.48</td>
<td>3</td>
<td>34</td>
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<td>$Q_{N}^R$</td>
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<tr>
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<td>14</td>
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<td></td>
<td>$Q_{P-S_F}^R$</td>
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<td>1.42</td>
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<tr>
<td>1400</td>
<td>$Q_{N}^F$</td>
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<td>$Q_{N}^R$</td>
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<tr>
<td></td>
<td>$Q_{N}^R$</td>
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<td>159</td>
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<td></td>
<td>$Q_{N}^R$</td>
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<td>1.62</td>
<td>14</td>
<td>126</td>
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<tr>
<td></td>
<td>$Q_{P-S_F}^F$</td>
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<td>1.64</td>
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<td>98</td>
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<tr>
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<td>$Q_{P-S_F}^R$</td>
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<td>1.71</td>
<td>5</td>
<td>125</td>
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<tr>
<td>1400 Expanded Cell</td>
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<td>1.65</td>
<td>8</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>$Q_{N}^R$</td>
<td>38.5</td>
<td>1.56</td>
<td>11</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 4.2: Information on the atom-vacancy exchanges studied in this work. $Q_{\parallel}$ is the activation pathway parallel to the dislocation line, $Q_N$ is around the core and approximately normal to the dislocation line, and $Q_{P-S_F}$ is between the partial core and the stacking fault. Superscripts $F$ and $R$ indicate the direction that the atom moves during each jump as forward or reverse with respect to the dislocation line direction of $[1\bar{1}0]$. $P_0$ represents the probability of finding the diffusing atom at the top of the energy barrier relative to finding it in its initial state. $R(t)$ represents the flux along the reaction coordinate through the energy barrier-containing dividing surface. Recrossing numbers indicate how many of 50 MD trajectories return to the equilibrium configuration they were initially pointed away from. $k$ values are rate constants.
boring atoms push the diffusing atom into an equilibrium position. Table 4.2 collects the $P_0$ and $R(t)$ information that leads to calculation of the rate constants $k$. Each $P_0$ term calculated by Eq. (4.7) depends on the height of the free energy barrier as well as its curvature, with flatness near the equilibrium positions causing it to diminish. Seemingly small asymmetries can cause notable changes in $P_0$ depending on direction, like the 62% variation for jumps along $Q_\parallel$ at 1000 K. Both $P_0$ and $R(t)$, and therefore $k$, generally increase with rising temperature irrespective of any specific hop and direction, consistent with basic physical expectations.

### 4.3.4 Rate constants

The sense of the partial screw dislocation and the distribution of its edge component affect the direction-dependence of the rate of each hop. In all three cases concerning $Q_\parallel$, $P_0^R$ is greater than $P_0^F$, but recrossings diminish $R(t)^R$ more than $R(t)^F$. When placed at the dividing surface for the unconstrained MD simulations, an atom making a $Q_\parallel^E$ hop has already reached the saddle point and is more likely to succeed to its destination; the inverse is true for $Q_\parallel^R$, $Q_N^E$, and $Q_{P-SF}^R$ have higher values of both $P_0$ and $R(t)$ than their counterparts $Q_N^R$ and $Q_{P-SF}^E$, with all biases encouraging the atom to situate on the same site, which exhibits the most pronounced compressive behavior of all sites in the LGF-prepared screw partial core geometry. The jumps along $Q_{P-SF}$ at 1000 K exhibit a greater reduction to $R(t)$ in the forward direction even though more recrossings occur in the reverse direction. This behavior arises from forward trajectories with higher initial velocities failing to equilibrate at their destination, indicating that the effects of these directional biases on $R(t)$ can supersede the tendency of an atom with more initial kinetic energy to be more likely to successfully cross the barrier.

Combining $P_0$ and $R(t)$ reveals that atomic hops along $Q_\parallel^R$, $Q_N^E$, and $Q_{P-SF}^R$ have higher rate constants $k$ than those in the opposite directions along each pathway, regardless of temperature or cell expansion. This direction-dependence suggests that each hop mech-
anism contributes an asymmetry to mass transport along the dislocation line, which could also possibly affect movement of the dislocation on a larger scale. By taking the standard error bars of Fig. 4.2(b) and Fig. D.1 to represent the standard deviations of each free energy barrier height, a one-tailed t-test analysis indicates a statistical certainty of 77% that the asymmetry along $Q_{\parallel}$ at 1400 K is in the reverse direction. Certainties for biases along the other two pathways at the same temperature are 57% along $Q_{N}$ and 71% along $Q_{P-SF}$.

It is reasonable to expect that based on geometrical symmetry, diffusion along the counterpart partial core would exhibit opposite directional-dependence. Depending on the sense of rotation of the original screw dislocation and its context within a material, diffusion along one partial may prevail and result in a net directional diffusion bias.

4.3.5 Comparisons with other approaches

Fig. 4.5(a) compares the rates calculated here, denoted $k_{\text{Exact}}$, with those calculated by recrossing-excluding dynamic TST and static HTST approaches to assess differences among results produced by the three methodologies. The figure includes rates from both temperatures. Fig. 4b provides uncertainties in the differences between $k_{\text{TST}}$ and $k_{\text{Exact}}$ due to finite sample size. These reflect the standard error, relative to the magnitude of $k_{\text{Exact}}$, on the difference between the contributions to $R(t)$ and $R(t)_{\text{TST}}$ due to recrossings occurring in some of the 100 unconstrained simulations along each pathway. This uncertainty is typically 2-4% and independent of rate constant magnitude. Errors in the free energy profiles that affect both $k_{\text{Exact}}$ and $k_{\text{TST}}$ are reported elsewhere in Figs. 4.2 and D.1. Calculations detailed in Appendix B identified the error in the HTST energy barrier that originates from the use of a single image for an NEB calculation to be insignificant, on the order of $10^{-5}$ eV when compared to a more expensive 7-image calculation. Calculations of $\nu^{*}$ using Eq. (4.3) for a hop between identical sites along the dislocation direction could disagree with one other by up to 5.4% due to inaccuracies in calculating the vibrational frequencies of the diffusing atom at equivalent initial positions along the dislocation line. These inaccura-
cies appear even in calculations in the crystalline fcc case, and error bars on $k_{HTST}$ in Fig. 4.5 reflect the maximum previously observed deviation near the partial core. These error bars also omit DFT-induced error, on the order of 1 meV/atom, because all methodologies use the same simulation parameters and supercells (aside from finer $k$-grids for the static calculations), and the intention is to compare methodologies within the same framework.

The absolute values of all rates presented in Fig. 4.5 are provided in Table D.2.

The dynamic TST approach overestimates the rate constants by up to 18% as a consequence of omitting the effects of barrier recrossing. Trajectories with lower initial velocities are generally more likely to recross the barrier, so reductions from $k_{TST}$ to $k_{Exact}$ are less than the percentages of trajectories that recross the barrier, which have a maximum of 30%. Static HTST values systematically underestimate $k$, with values in all 14 cases calculated to be $\leq 70\%$ of $k_{Exact}$. This upper limit comes from the $Q_{P-SF}$ case at 1000 K, where the dynamic free energy profile height is greater than the NEB-calculated barrier. Because free energy profile curvature as well as height both affect $P_0$, $k_{Exact}$ is higher than $k_{HTST}$ despite the difference in energy barriers and presence of dynamic recrossings. Comparisons of the rate constants calculated using the expanded supercell blend in with the others plotted in Fig. 4.5 (near 60 GHz), providing evidence that the use (or lack thereof) of a thermally expanded supercell does not affect how the two methodologies behave relative to one another.

Our static study of diffusion along this partial core from Chapter 2 produced diffusivities that were fit to Arrhenius parameters $D_0$ and $Q$ (diffusion prefactor and activation energy) for comparison with an experimental study that took place from 873-1243 K [27]. Parameter-generated diffusivities for the core match kinetic Monte Carlo (KMC)-generated values within $\pm 21\%$, suggesting that the fits are accurate enough that comparing them to others can yield meaningful observations concerning the diffusivities. The activation energies agree rather well, but the simulated data points from 800-1400 K produce underestimates of the experimental data points and prefactor by about three orders of magnitude. A
Figure 4.5: (a) Comparison of the rate constants computed here, $k_{\text{Exact}}$, with dynamic TST calculations that omit recrossings, $k_{TST}$, and those from static calculations that use Vineyard’s theory, $k_{HTST}$. Error bars for $k_{HTST}$ reflect the inaccuracy of calculating the Vineyard attempt frequency $\nu^*$. In lieu of error bars on $k_{TST}$, panel (b) shows the relative standard error, as a percentage of $k_{\text{Exact}}$, in the difference between $k_{TST}$ and $k_{\text{Exact}}$ due to recrossings observed in 100 MD simulations along each pathway.
motivator for this work was to investigate whether the inclusion of entropic and temperature effects would lead to better agreement with experiment by identifying faster hopping rates $k$ that would lead to a systematic enhancement of the overall diffusivity relative to static calculations. The dynamic methods used here are too expensive to populate an entire KMC rate catalog to generate diffusivities at many temperatures to produce fitted parameters like in the static study, but these calculations indicate $k_{HTST}$ underestimates the rate by a factor of 3.6 on average. In combination with the omission of thermal expansion, we suggest that these sources of error in the statically calculated rate constants lead to an underestimate of the diffusion coefficient by a factor of $\sim$7 at 1400 K. Causes of the remaining disagreement between theory and experiment may include entropic contributions to vacancy formation [76] or lowered free energies of vacancy formation or migration because the experimentally studied screw dislocations were situated in a grain boundary rather than isolated in a surrounding strained fcc geometry. Some of this error may have been fortuitously cancelled by the systematic underestimation of vacancy formation energies by DFT [75]. One can compare our results to the opposing conclusion of Gillan and coworkers, who found that the Vineyard estimate typically overestimates the rate constant of vacancy hops in cobalt oxide while remaining on the same order of magnitude [131]. The difference in conclusions between our work and theirs could be due to geometry, chemistry, their use of umbrella sampling instead of the blue moon approach to calculating free energy barriers, or their use of classical potentials as opposed to DFT.

4.4 Conclusions

In light of the philosophies behind the methodologies of Eqs. (4.1) and (4.2) being quite different from one another, the dynamically calculated rate constants reveal preferred diffusion directions that are mostly opposite to the ones determined by the static, harmonic transition state theory (HTST). Nevertheless, it is remarkable that they consistently pro-
duce rates on the same order of magnitude that effectively validate one another. Although $k_{HTST}$ consistently underestimates the true value, it still provides a reasonably accurate prediction that here is usually 20-50% of $k_{Exact}$. While the computational costs of calculating the free energy gradients and barrier recrossings vary slightly from system to system, it is approximately 30 times more expensive to run the 17×4 constrained molecular dynamics simulations required to produce a free energy profile and dynamic $k_{TST}$ rate constant than it is to perform the nudged elastic band and Vineyard attempt frequency calculations. Adding 100 unconstrained MD simulations to analyze barrier recrossings and obtain $k_{Exact}$ brings the relative computational cost up to ∼35 times that of calculating the static $k_{HTST}$. This result bolsters the appeal of the harmonic Vineyard approximation. We note that the qualitative advantages of the dynamic approach, particularly the direction-dependent free energy profiles and diffusion rates along each hop, are intrinsically beyond the reach of the static approach.
5. Conclusions

5.1 Summary

We studied vacancy-mediated diffusion along a partial $\frac{3}{2}(\overline{1}0)$ screw dislocation core in fcc Ni by investigating individual atom-vacancy exchange pathways using first principles techniques. A kinetic Monte Carlo (KMC) model generated self-diffusivities over a range of temperatures using density functional theory (DFT)-calculated harmonic transition state theory (HTST)-based rate constants to describe each individual exchange within the geometry of the partial core. Each rate constant is informed by a nudged elastic band-generated migration energy barrier and a Vineyard attempt frequency. Exchanges between sites that lie on the compressive side of the edge component of the screw dislocation partial core tend to have lower barriers; these include pathways around the core and one that connects a core-adjacent site with one in the stacking fault. The Arrhenius parameters calculable as a result of this work were compared with experimentally observed ones and comparisons were made between the two.

An extension of the HTST-informed KMC model analyzed the diffusion of dilute substitutional solutes along the partial core. These are important to $\gamma - \gamma'$ Ni-base superalloys for a number of reasons: Co and Cr help form the $\gamma$ phase, Al and Ti enable high volume fractions of intermetallic $\gamma'$ precipitates, and the refractory elements Mo, W, and Re provide solution strengthening. Differences in diffusivity due to geometry and chemistry are both quantified. Pipe diffusivities of the individual solute elements are of interest.
because they may describe the rate limiting step in a particular creep mechanism. The resultant activation energies could be input into creep rate models in order to weigh the contributions of solute pipe diffusion in a multi-step creep system of interest.

The HTST approach is popular because of its efficiency, but its 0 K, static nature means that it is quite approximation-dependent. We applied a molecular dynamics technique, rooted in the Bennett-Chandler formalism, to reobtain rate constants for a few atom-vacancy exchanges near the partial core that were indicated as particularly significant by the HTST study. These simulations took place at more realistic operating temperatures of 1000 and 1400 K, and allow for calculation of the free energy of migration through constrained molecular dynamics, while unconstrained molecular dynamics simulations also probe the likelihood of exchanges that proceed to the saddle point but fail to ultimately equilibrate at their destination. A qualitatively significant finding of this work is that it suggests energy profiles along certain activation pathways are more favorable in the opposite direction than the static simulations indicated. Our findings suggest that the HTST formalism consistently underestimates individual rate constants by factors of 2-5; running the calculations in a thermally expanded cell at 1400 K rather than the 0 K equilibrium one adds an additional factor of two to this underestimate. These results help to provide context for interpreting HTST-generated rates, and contribute to explaining why their associated diffusivities are consistently orders of magnitude lower than those observed experimentally.

5.2 Limitations and avenues for future work

One limitation of this work is that its analysis is confined to a set of pathways around the partial core. This is suitable for providing an effective diffusion coefficient within the cross-sectional area considered here, but a more complete picture of diffusion could be formed by considering how the vacancy diffuses throughout the long range strain field of the core. While the energy barriers for individual jumps quickly reapproach the value seen in fcc Ni
as one moves away from the core, individual variations among these could lead to some sort of collective emergent vacancy flow behavior around the partial, which cannot be accounted for within our approximation that the vacancy wanders to/from all neighboring sites isotropically. In pursuit of a more geometrically comprehensive description of diffusion along and around the core, one might also choose to calculate an activation energy tensor \[57\] rather than obtaining a simple one-dimensional \( D \) or \( Q \) scalar like those reported here.

The current study also considers a screw dislocation and seeks to contextualize its results in engineered materials by making reference to effects that dislocations may have on creep mechanisms including climb, while climb is associated with edge rather than screw dislocations. (A recent discrete dislocation dynamics paper reports including climb of dislocations with mixed character above a cutoff of 15° \[142\].) A future study may want to consider diffusion along an edge dislocation; depending on the degree of strain present in the edge partials, such a study could conceivably need to include a larger cross-sectional area to capture all relevant nearby activation pathways. A discussion on the effects of compressive/tensile character on energy barriers in a dissociated edge partial core as compared to the partial cores of the screw dislocation considered here would be of interest.

The MD techniques of Chapter 4 provide new insight on individual exchanges, but are too computationally expensive to populate a KMC rate catalog to generate diffusivities. Intuitively, the rate constants tending to be 2-5 times greater than those from HTST seems to suggest that the diffusivities observed in a KMC simulation would also be 2-5 times greater. However, such a result might not manifest neatly within the Arrhenius formalism as a two to fivefold increase in the diffusion prefactor \( D_0 \), and this variation could also lead to some multi-hop pathways emerging during KMC that behave in unanticipated or even counterintuitive ways.

Pipe diffusion in the \( \gamma' \) precipitates also has implications on the plastic deforma-
tion of engineered Ni-base superalloy materials. The ordered structure of Ni$_3$Al makes such study more complicated, as there are many more activation pathways available for the vacancy to hop along, and the distribution of pathways changes with time as antisite defects are created and annihilated. The partial cores of a superdislocation may also border different types of stacking faults where diffusion could be of even greater significance to deformation than the pipe diffusion itself. For instance, reordering of a superlattice complex extrinsic stacking fault (SECF) into a superlattice complex stacking fault (SCF) is proposed to be the mechanism that enables partial cores to carry out microtwinning in Ni$_3$Al [143].

A preliminary investigation of this subject using atomistic methods and an on-the-fly KMC model is presented in Appendix A. Future study of this problem using DFT would need to be carefully crafted to ensure that study of all significant diffusive/reordering mechanisms takes place.
Appendix A: Planar and Pipe Diffusion in Ni₃Al

A.1 Background

Previous chapters considered diffusion in a pure Ni environment to better understand how pipe diffusion may occur in the γ matrix of Ni-base superalloys. Pipe diffusion within the intermetallic Ni₃Al γ′ phase is also of interest, but the high number of activation pathways present within the complicated geometry in the vicinity of a partial core in Ni₃Al precludes the straightforward preparation of a kinetic Monte Carlo rate catalog using DFT. A preliminary exploration of these pathways using simpler methodologies rooted in classical mechanics will serve as a guide for later DFT studies by identifying which exchanges or multi-jump mechanisms are of significance to diffusion there. The structure that this study takes place in was prepared previously by Rao, et al. [143], and is depicted in Fig. A.1. Unlike the symmetric screw partial dislocations separated by an hcp stacking fault considered previously, here a series of differentpartials is separated by different types of stacking faults. Leading partials that sweep through the material cause the emergence of a complex stacking fault (CSF) followed by a complex extrinsic stacking fault (CESF). “Complex” here indicates that an anti-phase boundary (APB) exists in conjunction with the planar defect of the stacking fault. Different types of planar defects that can occur in Ni₃Al and the displacement vectors that cause them are discussed in detail by Voskoboinikov [144]. Diffusion within the CESF is of particular interest because this can lead to it being reordered into a lower energy superlattice extrinsic stacking fault (SESF), thus enabling the partials to continue moving through the γ′ structure, causing microtwinning and defeat of
Figure A.1: Series of partial dislocation cores and stacking faults resulting from dissociation of an $a\langle112\rangle$ edge dislocation in Ni$_3$Al [143]. (a) A complex stacking fault (CSF) lies between the leading $\frac{a}{6}\langle1\bar{1}2\rangle$ partial (on the right) and the central $\frac{a}{6}\langle1\bar{1}2\rangle$ partial, with a complex extrinsic stacking fault (CESF) between that central partial and the $\frac{a}{6}\langle12\bar{1}\rangle$ partial on the left. Other partials far to the left are omitted from view. Panel (b) presents the same view but with atoms colored according to type, with Ni atoms colored red and Al atoms colored blue. Visualizations are prepared with ovito [6–8].

Harris and co-authors studied diffusion in cubic Ni$_3$Al [145], considering the tracer diffusivity of Ni and Al atoms within a kinetic Monte Carlo model as a function of Ni concentration using atomistic potentials. They report relatively good agreement of their Ni tracer activation energies with those observed experimentally by Shi, et al. [146]. They also considered the vacancy-mediated motion of a (100) APB through the crystal, finding that its reordering tends to occur by a vacancy accomplishing a small amount of reordering at once then wandering away, as opposed to a fast “zipper” reordering where many antisite defects are reordered one after another. The possibility of this type of behavior existing in the CESF between partial dislocation cores was a motivation for the current study. A DFT study also reports NEB-generated energy barriers to self- and solute diffusion in Ni$_3$Al [147]. The authors discuss two mechanisms necessary for net mass transport that consist of multiple
jumps: a two-jump antisite-assisted mechanism and a six-jump cycle that creates disorder with its first free jumps and restores order with the next three. Because these sequences rely on the presence of antisite defects, the number of activation pathways to be considered for a full analysis of all possibilities becomes quite high. This is particularly true in cases where a vacancy creates (or reverses) an antisite defect and then wanders away; the geometrical asymmetry of the atoms depicted in Fig. A.1 makes this an even larger obstacle to creating a complete rate catalog in the pipe/CESF diffusion case.

A.2 Methodology

An on-the-fly (OTF) kinetic Monte Carlo model allows a vacancy to wander throughout the structure to probe how the vacancy behaves in the partial cores and stacking faults. The KMC models of Chapters 2 and 3 used rate catalogs that were fully predefined before any KMC simulations began. These were suitable for study of self-diffusion along the partial core in Ni because of the localized region where low energy barriers of interest are concentrated, but general disadvantages of such catalogs are that they are limited by the human imagination and require the rate constants of each individual exchange to be processed manually. In contrast, the OTF model provides for the automatic calculation of all relevant atom-vacancy rate constants for a given configuration, thus providing the vacancy more freedom to wander than it would have with a finite rate catalog. By keeping track of the vacancy’s behavior while on such a walk, we can identify emergent pathways that are significant for either pipe/fault diffusion or CESF reordering. In future work, these can be studied in greater detail with DFT, but at this point classical atomistic simulations are used to more efficiently explore the great number of possibilities. The OTF KMC program propagates a vacancy throughout the Ni$_3$Al system depicted in Fig. A.1 according to the flow chart of Fig. A.2. The vacancy can initially be inserted at any site; future enhancements may wish to weigh this according to vacancy formation energies. All neighboring sites within some cutoff radius are considered as possible destinations for vacancy hops.
The cutoff radius here is set to be 3 Å, which generally includes the 12 nearest neighbors of the vacancy, though some sites may have slightly fewer or more neighbors due to various combinations of defects.

![Diagram](image)

Figure A.2: Process for implementing the on-the-fly kinetic Monte Carlo model. This allows the vacancy to wander throughout the ordered, defected geometry of concern without the need to handcraft and store a rate catalog.

Each new geometry is optimized within the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [148] using Purja Pun and Mishin’s Ni-Al embedded atom method (EAM) potential [149]. The supercell, carved out of the original geometry [143], is approximately $20 \times 70 \times 100 \text{ Å}$ with periodic boundary conditions applied in the direction of the dislocation line (the 20 Å dimension). The rates of each hop are obtained within the Vineyard harmonic transition state theory approximation (Eq. 2.7). Nudged elastic band (NEB) simulations [59–61] take place to provide the migration energy barrier $E_m$ of each possible vacancy jump. NEB forces apply to all atoms within a $20 \times 30 \times 30 \text{ Å}$ region centered on the vacancy, with a force convergence criterion of 0.01 eV/Å and spring constants of 5.0 eV/Å$^2$ applied along the band. Each NEB simulation includes 13 images along the band including the initial and final equilibrium configurations, with a climbing-image NEB calculation following convergence of the initial one. The attempt frequency of each jump
is set to the arbitrarily chosen constant value of 4.0 THz. During future DFT work, it may be more suitable to use the attempt frequencies of Ni and Al in cubic Ni$_3$Al, based on the attempt frequency analysis of solutes diffusing in Ni in Chapter 3, which indicated that the attempt frequencies in cubic Ni are similar in magnitude to those observed near a dislocation.

A.3 Results

A.3.1 Energy Barriers

While the primary goal of this work is to identify and analyze collective trends that contribute to diffusion or APB reordering, the energy barriers of activation pathways in L1$_2$ Ni$_3$Al can be compared with some representative pathways in the more complicated system in order to inform expectations on how, e.g., the presence of a partial core may affect diffusivities. In Fig. A.3, NEB-calculated energy barriers are provided for a number of atom-vacancy exchanges in (a) the crystalline system as well as (b) along the dislocation line direction between sites bordering the central partial depicted in Fig. A.1. In contrast to the pronounced softening and lower energy barriers within the partial in pure Ni relative to the fcc case discussed in earlier chapters, many of these jumps actually have higher barriers than those in the cubic case, likely due to the interactions with atoms lying in the two neighboring stacking faults. Of the sites that neighbor the CESF [on the left side of Fig. A.3 panel (b)], there is a lower energy barrier for an Al atom to hop out of its starting position and into a $v_{Ni}$ site than for a similar exchange in the cubic case. This could possibly contribute to a multi-jump mechanism that leads to reordering, though this would depend on the barriers to any additional involved jumps as well as the competing ones at each vacancy location.
Figure A.3: Energy barriers to atom-vacancy exchanges in Ni₃Al. (a) Barriers in crystalline L1₂ Ni₃Al. Each arrow indicates the direction that an atom travels towards the initial position of the vacancy, which the arrow points to. (b) Representative barriers to atom-vacancy exchanges along the central partial core of Fig. A.1.

An example of a multi-jump sequence that could occur within this system is shown in Fig. A.4(a), where six vacancy hops around the partial core cause a Ni atom and a vacancy to exchange places. Panel (b) depicts the energy profile along the reaction coordinate consisting of all six exchanges, and the maximum energy along the sequence is 2.10 eV higher than that of the initial configuration. This value can’t be used to straightforwardly obtain a rate constant because at each local energy minimum, the vacancy has a chance to move backwards along the reaction coordinate or to swap places with any of its ~10 other nearest neighbors, which may lead it into some other cycle. The possibility of antisite defects existing at any of those sites or at other nearby sites underlies the need for an on-the-fly rate catalog rather than a handcrafted one. The depicted six-jump sequence, which one might say is intuitively likely to be significant to mass transport based on the enhanced pipe diffusion discussed in Chapters 2 and 3, turns out to be rather improbable based on the combination of high energy barriers for the first step in either direction along the reaction coordinate with low barriers leading to the immediate reversal of either step.
Figure A.4: Example of a six-jump cycle around the central partial core of Fig. A.1. (a) The six jumps sequentially allow a vacancy on one side of the partial to exchange places with a Ni atom on the other side. (b) The energy of the system during all six NEB calculations is plotted as a function of reaction coordinate.

A.3.2 On-the-fly kinetic Monte Carlo calculations

In its current state, the on-the-fly KMC program leads the vacancy on about ten steps per hour within a simulation running on 132 CPUs. Future optimizations and developments, such as implementing the capability to catalog the history of all states that have been visited in case they are returned to, may enable the code to run much faster and eventually generate converged diffusivities for pipe and planar diffusion of Ni and Al within the structure. For now, the simulations provide insight on which linear or planar defect the vacancy tends to hop within following initial insertion near the central partial core. Based on eight simulations at 1000 K that each begin with the vacancy inserted at one of the unique sites near the partial of interest, the vacancy most commonly tends to make most of its hops within the stacking fault that it initially neighbors. Fig. A.5 illustrates the path that a vacancy takes over ~300 hops as it mostly wanders through the CSF after insertion at an adjacent Ni site. Most hops are within the two planes of the stacking fault, though a number of excursions to and from neighboring (111) planes are visible. The illustration is representative of the behavior of the vacancy following all eight initializations; it tends to hop into the closer of the CESF or CSF. In one case (out of about 2350 hops elapsed over all simulations), the va-
cancy escaped from the defect network and wandered off into the surrounding bulk Ni$_3$Al. Ni vacancies tended to exchange places with Ni atoms; in each run where the vacancy began at a Ni site, any later $v_{Ni} \leftrightarrow Al_{Al}$ exchanges were reversed on the next step.

![Figure A.5: Illustrations of the vacancy’s path (in black) as it wanders at 1000 K through the structure after being inserted at one of the Ni sites that lies to the upper right of the core in the view of panel (a). Periodic images along the dislocation line are omitted for clarity and some atoms were removed for the visualization of panel (b).](image)

More vacancy-Al exchanges took place during the simulations that began with a vacancy at an Al site, but again most of these jumps quickly reverted. A higher temperature simulation at 1500 K analyzed the case following insertion of the vacancy at an Al site that borders the CESF. This run saw the reordering of two Ni-Al pairs within two planes of the CESF, as depicted in Fig. [A.6](image). These atoms remained in their new configurations even after the
vacancy wandered out of their vicinity. This type of reordering is consistent with Harris and co-authors’ observation in the cubic Ni$_3$Al case of the vacancy accomplishing only a minor amount of reordering within an APB at a time [145]. One accelerated KMC simulation ran at the higher temperature of 3000 K to assess whether some important mechanisms within the fault were out of reach of the temperature/timescale in use. Such a run is made possible above the melting temperature by the fact that in this approximation of the rate constants, temperature only features into the exponential term and does not affect calculations of individual energy barriers. However, the additional thermal energy just allowed the vacancy to spend more time in surrounding bulk regions rather than in the faults and partial cores. An issue across all simulations is that when the vacancy wanders into the left partial core on the other side of the CESF, which has more open space in the center of it than the other partials, the KMC program as currently designed to study vacancy-mediated diffusion could run into issues. The relaxation of some post-hop configurations returns the pre-hop configuration, and NEB calculations in some cases diverge in the search for a saddle point. Solutions may apply NEB forces to fewer atoms or consider other mechanisms that involve substantial reorientation of several atoms instead of just one.
Figure A.6: View demonstrating reordering of two Ni-Al pairs in the CESF. Atoms have plotted radii of 0.2 Å and the orientation of the figure is similar to that in Fig. A.5a) but rotated; the green line indicating a partial core, which here is the leftmost one from Fig. A.1, runs along \(\langle 1\overline{1}0\rangle\). Initial and final configurations of the atoms during the 1500 K KMC simulation are here visualized simultaneously. Circled sites that see reordering are evident as atoms of both types appear at them. The reordering in the \(\langle 1\overline{1}0\rangle\) direction creates Al-Al and Ni-Ni nearest neighbor pairs in the Ni$_3$Al row of atoms, while the other one introduces an Al atom to a row that is otherwise all Ni atoms.

A four-jump cycle that leads to the formation of the Ni-Ni and Al-Al atom pairs in the Ni$_3$Al row of atoms is illustrated in Fig. A.7, which also provides the energy barriers for all possible vacancy exchanges within each configuration (up to 1.5 eV to exclude unlikely possibilities). In each case, the jump that contributes to reordering has an energy barrier that is among the three or four lowest out of those possible and always within about 0.1 eV of the lowest. These \(\sim 0.1\) eV differences at 1500 K mean that the exchanges required in this cycle are about half as likely as each of the most common jumps. The full reordering process remains somewhat less common because four of these moderately likely jumps (which are competing with several other significant possibilities) need to happen sequentially, and then the vacancy needs to wander away without first reversing this reordering. A simpler two-jump process led to the introduction of the Al atom in the Ni row about 50 steps later. This process is a little simpler: the Al atom hops into the Ni row, another Ni atom fills the \(v_{Al}\), and then the vacancy wanders off. Energy barriers in this case are similar to those seen during the four-jump sequence. It is also worth mentioning that on the first step of this run
when the vacancy is adjacent to the partial core, the energy barrier for it to hop away from the partial to exchange places with an Al atom in the CESF is about 0.59 eV, while the next lowest barrier is 0.93 eV. Notably, this difference makes it more than an order of magnitude more likely for the vacancy to hop out of the partial than for the next-most likely pipe diffusion jump to take place. This gap would become even wider at lower temperatures.
Figure A.7: Illustration of a four jump cycle that leads to reordering in the Ni$_3$Al complex extrinsic stacking fault. Each panel (a)-(e) shows the configuration of portions of three $\langle 1\bar{1}0 \rangle$ rows of atoms at a sequential step during the KMC simulation. Arrows in (a)-(d) indicate which atom is going to hop into the vacancy next, and the line plots below the configurations display the energy barriers of possible jumps (occasionally staggered for visibility and with only barriers under 1.5 eV depicted). The red diamond corresponds to the energy of the jump that actually takes place in the reordering sequence.
A.4 Conclusion

Findings to this point suggest that vacancy diffusion in Ni$_3$Al is faster within the complex extrinsic stacking fault and complex stacking fault than along the partial dislocation core between the faults. The introduction of an Al vacancy appears to make reordering mechanisms more likely to emerge relative to that of a Ni vacancy. These reordering processes consist of relatively probable multi-jump cycles that occur somewhat sporadically as the vacancy travels along its weighted random walk. It remains possible that a more efficient mechanism emerges once a certain amount of reordering has taken place, but if aiming to quantify diffusivities or reordering rates, future study should continue exploring Al vacancy diffusion within the CESF. Four- and two-jump mechanisms like the ones observed here would be reasonable starting points, though one should be careful not to neglect consideration of the energy barriers of other feasible vacancy hops within relevant configurations.
Appendix B: Validation of Hexagonal Supercell to Isolate Dislocation

Supercell validity checking details:

Three checks were performed to ensure that the supercells chosen were large enough to restrict the effects of geometrical mismatch occurring within the fixed boundary regions from affecting vacancy behavior near the center of the relaxation region.

First, the average forces induced on atoms within the internal relaxation region by the introduction of a vacancy (before subsequent relaxation) were calculated for several supercells. Those forces in a hexagonal cell with 76 sites were found to be comparable to those in a larger cell, as shown in Table B.1.

<table>
<thead>
<tr>
<th>Cell Shape</th>
<th># Relaxation Sites</th>
<th>Average Force (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal</td>
<td>28</td>
<td>0.151</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>76</td>
<td>0.068</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>148</td>
<td>0.044</td>
</tr>
<tr>
<td>Square</td>
<td>64</td>
<td>0.077</td>
</tr>
</tbody>
</table>

Table B.1: Average forces felt within the relaxation regions of different supercells upon vacancy insertion.

Second, atoms at various sites within the relaxation region were perturbed 0.05 Å in the direction of the dislocation line. The forces that these perturbations induced on an atom in the fixed boundary region were measured, and were found to be insignificant when atoms in the center site or adjacent to the center site were perturbed. These forces are provided in Table B.2. Only atomic sites that were centrally located or adjacent to the center site were used in later NEB calculations.
### Table B.2: Forces felt by a fixed boundary atom following perturbation of an atom in the relaxation region.

<table>
<thead>
<tr>
<th>Perturbed Atom Location</th>
<th>Force (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center</td>
<td>0.008</td>
</tr>
<tr>
<td>Adjacent to Center</td>
<td>0.006</td>
</tr>
<tr>
<td>Adjacent to Center</td>
<td>0.006</td>
</tr>
<tr>
<td>Adjacent to Fixed Boundary</td>
<td>0.009</td>
</tr>
<tr>
<td>Adjacent to Fixed Boundary</td>
<td>0.061</td>
</tr>
</tbody>
</table>

Third, several energies were calculated in different supercells to test whether supercell choice significantly affected their values. These were the vacancy migration energy, $E_m$, of the $F \rightarrow B$ vacancy hop and the vacancy formation energy, $E_{vf}$, at the $B$ site. (Site indices are identified in Fig. 2.1) Calculations were made in two different hexagonal cells centered on sites B and F, with 76 sites free to relax and the remaining sites fixed within the boundary condition region. A larger “rectangular” cell was also used, containing 360 atomic sites in total, with 120 free to relax in a central $5 \times 6 \times 4$ atomic arrangement. This cell was centered between the B and F sites.

### Table B.3: Vacancy migration and formation energies as a function of supercell choice.

<table>
<thead>
<tr>
<th>Cell</th>
<th>$E_{m,F\rightarrow B}$ (eV)</th>
<th>$E_{vf,B}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-centered hexagon</td>
<td>0.555</td>
<td>1.147</td>
</tr>
<tr>
<td>F-centered hexagon</td>
<td>0.570</td>
<td>1.164</td>
</tr>
<tr>
<td>BF-centered rectangle</td>
<td>0.565</td>
<td>1.143</td>
</tr>
</tbody>
</table>
Appendix C: Validation and Convergence Testing of Constrained Molecular Dynamics Simulation (CMD) Parameters

Molecular dynamics simulations in the canonical ensemble:

To simulate the behavior of a system within the canonical ensemble (or the NVT ensemble where the number of particles in a system, volume of the system, and temperature of the system are held constant), one needs to control the temperature of that system so it does not diverge from some fixed value. In practice, this means that the kinetic energies of particles in a system should have a Boltzmann distribution around the desired temperature value, so that:

\[ k_B T = m < v^2 > \] (C.1)

where \( k_B \) is Boltzmann’s constant, \( T \) is the constant temperature, \( m \) is the mass of a particle, and \( < v^2 > \) is its mean velocity [119]. In order to be practically useful, a scheme for fixing the temperature must not cause the system to behave in a non-physical manner. Realistically, the deviations from physical behavior caused by a particular method should factor into the decision on which method is chosen. Two methodologies, both well-discussed in the scientific literature, are implemented in VASP for constrained MD simulations: the Andersen and Nosé-Hoover thermostats.
**Andersen thermostat:**

The Andersen thermostat is a stochastic method for fixing the temperature, wherein impulsive forces act on an atom to randomly set its velocity to one from the Boltzmann distribution of velocities at that temperature \([119][150]\). The user chooses the frequency that atoms collide with the thermostat, typically by identifying the probability that any given atom’s velocity changes on a single MD step. Between collisions, atoms remain on unperturbed trajectories. Frenkel and Smit write that a weakness of the method is that its stochastic nature non-realistically disturbs a system’s dynamics by randomly decorrelating particle velocities, making it ill-suited to obtain dynamic properties like diffusion coefficients \([119]\). In the case of the diffusion coefficient, this is because the mean-squared displacement of an atom is dependent on the collision probability. Allen and Tildesley point out that if the collision probability is too high, then the system is prone to slowly explore its configuration space because the collisions will actually dominate how it behaves; too low of a collision probability will see the canonical distribution of energies explored slowly \([150]\). An advantage of this method is its ability to accommodate ergodic system behavior.

**Nosé-Hoover thermostat:**

The Nosé-Hoover thermostat is a deterministic method of fixing the temperature, wherein terms with artificial coordinates and velocities are added to the Lagrangian, which is used to write the equations of motion for the system \([119][150]\). An effective Hamiltonian term, \(H'_{\text{Nose}}\) is conserved, though this is not a true Hamiltonian because one cannot derive the equations of motion from it. This kind of approach is analogous to controlling the volume of a system with a piston \([150]\). In contrast to the Andersen thermostat, the Nosé-Hoover model describes dynamic properties like diffusion coefficients well, while a drawback is its
inability to account for ergodicity.

A 2018 work, also conducted in VASP, considered the effects of thermostat choice on the anharmonic free energy of fcc Al at high temperatures and pressures [151]. The authors found that the Andersen thermostat produced inaccurate anharmonic free energies when time steps greater than 0.5 fs were used, though it’s worth noting that they were operating at 4000 K. They note that their Nosé-Hoover simulations were not ergodic because phonons were unable to interact with one another, resulting in generation of ensembles that were not canonical.

For testing in the present case, energies, temperatures, and average force components as a function of time step were analyzed for each thermostat at 5 and 300 K. In both Nosé-Hoover thermostat cases, the temperature oscillated with a period of 80 fs. Probabilities of 0.1 and 0.9 collisions per atom per time step were used for the Andersen case. These energies and temperatures are plotted in Fig. C.1 and Fig. C.2. The energies in Fig. C.1 are nearly constant in the Nosé-Hoover case because they include the energy accumulated in the thermostat over time, so variations are due to numerical drift. Fluctuations in the Andersen case are more pronounced since the thermostat energy isn’t tracked and system energy is not held constant in the canonical ensemble. The magnitudes of temperature fluctuations are fairly consistent across thermostats/parameters, with the greater probability of collisions in the Andersen case resulting in a more frequently changing temperature as atoms are consistently assigned new velocities.
Figure C.1: System energies and temperature as a function of time computed using different thermostats and at different temperatures. (a) Nosé-Hoover thermostat at 5 K, (b) Nosé-Hoover thermostat at 300 K, (c) Andersen thermostat at 5 K and \( P = 0.1 \), where \( P \) is the probability of a particle-thermostat collision per time step, (d) Andersen thermostat at 300 K and \( P = 0.1 \), (e) Andersen thermostat at 5 K and \( P = 0.9 \), (f) Andersen thermostat at 300 K and \( P = 0.9 \).
Figure C.2: Cumulative average force components on a constrained atom as a function of time computed using different thermostats and at different temperatures. (a) Nosé-Hoover thermostat at 5 K, (b) Nosé-Hoover thermostat at 300 K, (c) Andersen thermostat at 5 K and $P = 0.1$, where $P$ is the probability of a particle-thermostat collision per time step, (d) Andersen thermostat at 300 K and $P = 0.1$, (e) Andersen thermostat at 5 K and $P = 0.9$, (f) Andersen thermostat at 300 K and $P = 0.9$.

The behavior of forces in Fig. C.2 shows qualitatively different behavior in the Andersen cases with the high collision probability of 0.9 per atom per time step. The forces are far from convergence over the time scales pictured at both 5 and 300 K in panels (e) and (f), because the system behavior is dominated by the tight coupling of each atom.
to the thermostat. The forces in the 0.1 collision probability cases are much closer to those obtained with the Nosé-Hoover thermostat, as can be seen by comparing the pairs of panels (a)-(c) and (b)-(d). For instance, at 5 K, the qualitative order of the x, y, and z force lines are the same using both thermostats. Because the Nosé-Hoover forces tended to stabilize with fewer time steps and the Andersen simulations were approximately three times as resource-intensive, the Nosé-Hoover thermostat was adopted for all simulations. (Nosé-Hoover runs would see about 6 self-consistent electronic steps for each ionic step, while the frequent velocity reassignments in the Andersen case caused around 20 SC steps to regularly be necessary.)

Fig. C.2 displays cumulative average force components on a constrained diffusing atom in a test case, as determined by each thermostat at 5 K (left column) and 300 K (right column). Panels (a) and (c) suggest that the two thermostats will eventually agree with one another, as the variations are on the same order of those observed by changing different parameters within the Nosé-Hoover framework, shown below in Figs. C.6, C.8, and C.9. When the Andersen thermostat was tested with a collision probability of 0.9 per atom per time step, as shown in panels (e) and (f), the high probability of collisions caused the average force to be far from convergence at the end of the trial runs. The additional time requirements of the Andersen simulations become even more pronounced at higher temperatures, causing the results in panel (f) to be cut off. Based on this discussion and testing, the Nosé-Hoover thermostat is adopted for all calculations.

a. **Time step**: Trial simulations, each beginning with the same set of randomized initial atomic velocities but using different time steps, calculated forces on an atom as it was constrained to its location in the saddle point geometry. In Fig. C.3(a), time steps greater than 2 fs display an inability to accurately reproduce the forces calculated with smaller time steps. Fig. C.3(b) takes place over a longer time period and confirms that choosing either a time step of 1 fs or 2 fs does not cause significantly different results to be calculated.
Resultantly, calculations use a time step of 2 fs.

Figure C.3: Total force felt on an atom constrained to its saddle point location as a function of time step and elapsed time at 5 K.

Due to concerns that the 5 K test may not hold at higher temperatures, the test was repeated at 1400 K. Some numerical disagreement is observed near local minima and maxima, but the steps of 1 fs and 2 fs continue to produce data that agrees well:

Figure C.4: Total force felt on an atom constrained to its saddle point location as a function of time step and elapsed time at 1400 K.
b. Initialization: Early in the MD simulations, a temperature spike is observed before more representative temperature oscillations begin. This spike is associated with a drop in the energy of the system + thermostat, as shown in Fig. C.5 for a constant 300 K trial. To avoid any unrealistic effects of this behavior on reported values, the first 200 fs of all runs are discarded. No other artifacts demanding an initialization/thermalization period are observed, which may be because the initial geometries were already optimized through the nudged elastic band (NEB) method.

Figure C.5: Total system plus thermostat energy and temperature as a function of time immediately following initialization of a CMD trial.

c. Temperature oscillation period: A general rule of thumb is that temperature fluctuations during Nosé-Hoover dynamics should not occur at a frequency with an order of magnitude higher than that of the Debye frequency, which in Ni is $\sim 10$ THz. Here, a period of 80 fs is used, near the approximate Debye period of 100 fs. A test run confirmed that the forces on an atom constrained to its saddle point location are comparable to those felt when a longer period of $\sim 600$ fs is used, as shown in Fig. C.6.
Figure C.6: Cumulative averages of x, y, and z force components on a constrained diffusing atom with the temperature fluctuating around 5 K with a period of a) 80 fs and b) 620 fs.

d. Electronic self-consistency (SC) loop break condition: To ensure that appreciable numerical error would not accumulate as a result of the many self-consistent and ionic steps over the course of the MD simulations, the same framework calculated the forces on the constrained diffusing atom when different SC break conditions were used, as shown in Fig. C.7. While the forces reported with various break conditions are qualitatively comparable on a large scale, the $10^{-6}$ eV choice most accurately reproduces the force calculated using $10^{-7}$ eV, as shown in the inset of Fig. C.7(a). A more noticeable effect is in the system + thermostat energy shown in panel (b), where significant drifts are observed with less restrictive break conditions. These calculations used a time step of 1 fs; because of this, numerical error as a function of time with a step of 2 fs will be slightly less than that which is depicted. The reduction in error from the reduction in time steps per total length of time will outweigh the associated increase in number of SC steps per ionic step, which does not scale linearly with time step.
Figure C.7: Effect of self-consistent step convergence criterion [eV] on (a) the force on the constrained diffusing atom calculated from the cumulative averages of its component forces over each simulation and (b) the total energy of the simulation, considering kinetic and potential energies of atoms in addition to the energy of the thermostat. $10^{-7}$ eV values are cut off due to the calculations being too resource-intensive to finish within the allocated ten hours of simulation time.

e. Constraint choice: When identifying a midpoint of two atoms to constrain the diffusing atom to, there are often multiple midpoints with comparable distances to the desired point in space that the chosen midpoint should represent. To confirm that this choice would not have a significant effect on observed properties, a test run considered the forces experienced by the diffusing atom when one of the two midpoint constraints was replaced by another one. Force behavior is qualitatively similar as shown in Fig. C.8. Quantitative differences may be because a longer run would be needed to bring the standard error within a range used for reported averages.
f. **Average forces on an atom when constrained at its saddle point location:** Initial expectations supposed that the diffusing atom, when constrained to its saddle point location, would experience the total average force, calculated from the cumulative average component forces to account for direction, to be zero (i.e., less than the force tolerance of 0.005 eV/Å used for optimization). Fig. C.8(a) shows that even at the low temperature of 5 K, this approach calculated a force of around 0.01 eV/Å, or twice the optimization force tolerance. A few factors may contribute to the observed discrepancy. The energy landscape around the saddle point could be asymmetric, e.g., it may be energetically favorable for the constrained atom to bow into the tensile side of the edge component of the screw dislocation, causing the forces experienced in this region to dominate the averaged quantities. The NEB method, as implemented in the VASP transition state theory (VTST) toolkit, uses a force-based optimizer that moves the atoms along specifically-defined NEB forces; the forces and configuration of minimum energy state as calculated by a different methodology may differ slightly. Finite temperature effects may play a role, as the NEB optimization also took place at 0 K. An analysis of the position of the transitioning atom over the course of simulations at different temperatures found that its average location differs from that in the NEB-generated saddle point geometry. Table C.1 reports these differences.
Table C.1: Absolute difference of average constrained atom location coordinates from NEB-generated saddle point values, for test runs spanning at least 2000 fs. The first 200 fs are omitted in each case, and the z direction corresponds to the dislocation line direction.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>x [Å]</th>
<th>y [Å]</th>
<th>z [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>&lt; 10^{-5}</td>
<td>0.012</td>
<td>&lt; 10^{-3}</td>
</tr>
<tr>
<td>300</td>
<td>0.004</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>600</td>
<td>&lt; 10^{-3}</td>
<td>0.013</td>
<td>0.004</td>
</tr>
</tbody>
</table>

**g. Γ-point only k mesh:** In validating whether a 1×1×1 k-mesh would accurately calculate forces on the constrained atom, trial simulations calculated the forces felt by such an atom at 5 K using 1×1×1 and 1×1×3 k meshes, as depicted in Fig. C.9. The z direction and third translation vector of the supercell both correspond to the direction of the dislocation line, along which the effects of the finer mesh are felt. The magnitude of the total force from components is about 0.01 eV/Å in both cases. Although the sign of the average z-component of the force changes from one case to the next, no positive or negative bias is expected along the z direction. Numerous reasons why the average force may exceed the optimization force tolerance are discussed in the previous section. Since the finer k-mesh doesn’t bring the average force within the optimization force tolerance of 0.005 eV/Å, calculations employ a 1×1×1 k-mesh.

![Figure C.9](image1.png)

Figure C.9: Cumulative average force components on a constrained atom as a function of time using a). 1×1×1 and b). 1×1×3 k meshes.

**i. Linear interpolation to obtain points along minimum energy path (MEP): VASP**
calculations previously prepared geometries of the initial/final endpoints of vacancy diffusion and the single-image CNEB method prepared static saddle point configurations. Both of these composed the first, middle, and final geometries along each reaction coordinate for the CMD simulations. To see if a more detailed NEB run would be needed to populate the path, a 7-image NEB simulation calculated intermediate images between the initial and saddle point geometries of the $Q_N$ atom-vacancy exchange. A comparison of the diffusing atom’s position in these images with its position in linearly interpolated non-optimized images revealed the two to be very similar. This is visualized in Fig. C.10, where the linearly interpolated positions are each about 0.01 Å or 0.4% of the length of the reaction coordinate away from the NEB-calculated MEP. Resultantly, all CMD calculations with the diffusing atom at intermediate positions used linearly interpolated initial geometries between the previously obtained initial/saddle or saddle/final points. Preparing the central geometry with NEB was important because the pathway of the diffusing atom was bowed, though approximately linear to and from the saddle point location. Table C.2 lists the absolute and relative magnitudes of these deviations from linearity.

![Figure C.10: Representative example of the difference in location of the diffusing atom between linearly interpolated and NEB-calculated images, visualized in OVITO. The initial point and saddle point atoms are in exactly the same place for both the linear interpolation and NEB preparations. Atoms in the illustration have radii of 0.02 Å for visual clarity.](image)
Table C.2: Comparison of diffusing atom location at the CNEB-generated geometry, compared to a linearly interpolated value between initial and final points, for three diffusion pathways between neighboring sites. Relative distance is a percentage of the linearly interpolated distance from initial to final point. Reaction coordinates are less than the \( 2.49 \text{ Å} \) magnitude because the atom relaxes into its vacant neighbor site before and after each exchange.

### j. Convergence of the terms in the equation that \textsc{vasp} uses to calculate the free energy gradients:

Fig. C.11 plots the evolution with time of each term in the following equation for one constrained MD sample:

\[
\left( \frac{\partial A}{\partial q} \right)_{q_j} = \frac{1}{|Z|^{-1/2}} \left\langle |Z|^{-1/2}[\lambda_k + Gk_BT] \right\rangle_{q_j} 
\]  

(C.2)

where \( Z \) is a mass metric tensor, \( \lambda_k \) is the Lagrange multiplier along constraint \( k \) in the CMD simulation, \( G \) represents contributions to the free energy gradient beyond those accounted for within the Lagrange multiplier, and the angle brackets \( \langle \rangle \) represent an ensemble average, where each contribution to the ensemble average is the average over one correlation time. These tests concern one sample of the \( Q_N \) exchange at 1400 K. \( \lambda \) values appear to be drifting slightly upwards with simulation time, but it is the difference between these two that is most important. The total system behavior including all of these individual components is provided for a representative constraint point along the \( Q_{P-S_F} \) exchange at both temperatures in Fig. 4.2(a).
Figure C.11: Convergence of the components of Eq. C.2 in one sample.
Appendix D: Extended Results of Molecular Dynamics Simulations

Figure D.1: Comparison of migration energy barriers calculated with static techniques at 0 K with free energy barriers from dynamical techniques at higher temperatures. Moving from left to right on the x-axis of each plot corresponds to moving in the positive [110] direction, or from left to right in Fig. 4.1(a). (a) Atom-vacancy exchange $Q_N$ around the partial dislocation core. (b) $Q_{ij}$ in a cell that has been expanded according to the empirical thermal expansion coefficient for Ni of 13.4 $\mu$m/K-m [139].
Table D.1: Comparison of how temperature variations affect the energetic contributions to $k$ for each jump when calculated in the static HTST framework and in the dynamic approach. While the heights of the free energy barriers decrease with temperature in contrast to the constant static energy barrier, the changing curvature of the free energy profile results in $P_0$ increasing with temperature by a factor that is generally slightly less than that observed in the HTST case.

<table>
<thead>
<tr>
<th>Jump</th>
<th>$\exp\left(\frac{-E_{m}}{k_B \times 1000 K}\right)$</th>
<th>$\exp\left(\frac{-E_{m}}{k_B \times 1400 K}\right)$</th>
<th>$\exp\left(\frac{-E_{m}/k_B}{1400 K}\right)$</th>
<th>$P_{0,1000K}(\times10^{-3}\text{Å}^{-1})$</th>
<th>$P_{0,1400K}(\times10^{-3}\text{Å}^{-1})$</th>
<th>$\frac{P_{0,1400K}}{P_{0,1000K}}$</th>
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<td>0.00247</td>
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<td>2.10</td>
<td>13.9</td>
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Figure D.2: MD behavior of diffusing atoms along the reaction coordinates of different hops following placement at and then release from $q^*$, the top of the energy barrier. Cyan lines indicate initial forward velocities along $[110]$ towards equilibrium position $q_f$ while magenta ones are initially in the reverse direction towards $q_0$. Plots are along $Q_{∥}$ (a) at 1000 K and (b) 1400 K, $Q_N$ at (c) 1000 K and (d) 1400 K, (e) $Q_{P−S_F}$ at 1000K, and (f) $Q_{∥}$ in the thermally expanded supercell at 1400 K.
Figure D.3: Comparison of flux across the top of the energy barrier for various jumps when recrossings are accounted for (solid lines) versus the traditional TST value where they are not (dashed lines). Plateau values are valid on timescales greater than the time it takes the atom to relax to an equilibrium position from the top of the barrier but less than the time it would take the atom to spontaneously hop out of that equilibrium position. Plots concern the $Q_{\parallel}$ pathway (a) at 1000 K and (b) 1400 K, $Q_N$ at (c) 1000 K and (d) 1400 K, (e) $Q_{P-SF}$ at 1000K, and (f) $Q_{\parallel}$ in the thermally expanded supercell at 1400 K.
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Jump</th>
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<th>$k_{HTST}$</th>
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Table D.2: Rate constants calculated with exact, transition state theory (TST), and harmonic transition state theory (HTST) methodologies for all hops analyzed, along with ratios relating $k_{Exact}$ to the other two. Median and mean ratios of $k_{Exact}$ to $k_{TST}$ and $k_{HTST}$ provide simple quantifications of how reported rates generally differ based on methodology. Values of $k_{Exact}$ for $Q_\parallel$ in the thermally expanded cell at 1400 K increase by a factor of 2.40 or 1.62 relative to the unexpanded cell.
References


