A FIRST PRINCIPLES STUDY OF DEFECTS IN TITANIUM: INTERACTION OF TWIN BOUNDARIES WITH DISLOCATIONS AND OXYGEN INTERSTITIALS

BY

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DISSERTATION

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Abstract

Interaction between gliding dislocations and twin boundaries affects the plastic deformation of hcp metals such as titanium. In addition, oxygen greatly affects both strength and twinning in titanium. Predictive models of strength and twinning rely on understanding of the underlying atomic scale mechanisms which are best captured through computer simulations. While recent first-principles methods predict dislocation core structures and boundary geometries and energies, modeling a dislocation near a boundary requires new techniques to treat the long range strain field of the dislocation near a boundary. Using flexible boundary conditions with a new method to compute the lattice Green’s function for crystals containing a planar interface, we present a general method to study line defects interacting with interfaces with a tractable number of atoms. This method is general in the sense that it can consider long range atomic interactions and reconstructions near the interface. We use the interfacial lattice Green’s function to model a screw dislocation interaction with Ti (10\bar{1}2) twin boundary for the first electronic structure prediction of a dislocation in a boundary. We predict the dislocation core geometry in the twin boundary and compare with the core structure in bulk titanium. The first principles nature of this study makes it possible to consider interactions with solutes. The interaction energy of an oxygen interstitial with the Ti (10\bar{1}2) is also computed. While we applied our method to a systematic study of defects interactions in titanium, the method is general and opens up the possibility of investigating line defects/interface interactions with chemistry changes in arbitrary systems.
To my family

and

to Artan
Acknowledgments

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Chapter 1

Introduction

Crystals are like people; It’s the defects in them that make them interesting.

Sir F. Charles Frank

A perfect crystal is an infinite continuation of repeating units in all directions. In reality, disturbances in reference configuration, known as defects, deviate the crystal from the ideal regularity. Defects are broadly categorized based on their geometric dimensionality: point defects— vacancies, interstitials— decay in spatial extent in all directions, line defects — dislocations, crack tips— thread along a one-dimensional curve and planar defects —free surfaces, grain boundaries, stacking faults, bicrystal interfaces — can be treated as mathematical surfaces. Defects control the mechanical properties of materials such as strength and ductility. Accurate study of defect geometry is the first step in exploring how they change the material properties. Long-range behavior of many defects is well explained by anisotropic elasticity. However, the continuum description often diverges near the center of the defect in atomic scale. In many cases the core of the defect is difficult to investigate experimentally and is best captured through computer simulations. Here, we focus on developing an accurate and quantitative method for modeling straight line defects in planar interfaces with possibility of chemistry change and apply our method to the case of screw dislocations in twin boundaries in α-Ti.
1.1 Defects and deformation modes in titanium

α phase of titanium has a hexagonal close-packed (hcp) crystal structure with experimental room temperature lattice parameters \(a=2.95\text{Å}\) and \(c=4.68\text{Å}\). The consequent \(c/a\) ratio for pure α-Ti is 1.587, is smaller than the ideal \(c/a\) ratio of 1.633 for the hcp structure. Plastic deformation is controlled by glide of dislocations on possible slip systems of the crystals. Figure 1.1 shows the slip systems (planes and directions) in the hcp Ti. The main slip directions are along the three close-packed directions \(\langle11\bar{2}0\rangle\) introducing \(\vec{a}\) -type Burgers vectors. Slip planes containing these type of Burgers vectors are the basal \((0001)\) plane, three \(\{10\bar{1}0\}\) prism planes and six \(\{10\bar{1}1\}\) pyramidal planes leading to a total of 12 slip systems out of which 4 are independent. Von Mises criterion requires at least 5 independent slip systems for a homogeneous plastic deformation of polycrystals. The limitation in the number of independent slip systems is addressed by activation of \(\vec{c}\) or \(\vec{c} + \vec{a}\) type Burgers vectors and deformation twinning. The non-basal Burgers vectors slip systems are not sufficiently active.

Figure 1.2 shows the critical resolved shear stress (CRSS) for slip with \(\vec{a}\) and \(\vec{c} + \vec{a}\) Burgers vectors as a function of temperature in single crystal Ti-6.6Al[2]. CRSS is the slip-plane-resolved component of the applied stress that moves the dislocation and is a measure of activity of a slip system. The CRSS for \(\vec{c} + \vec{a}\) slip is significantly higher than \(\vec{a}\)-type slip. For \(\vec{a}\)-type slip, prism planes are the dominant slip planes in Ti followed by pyramidal and basal planes.

At low temperatures, twinning plays a key role in plastic deformation and ductility of titanium. The classical theory of deformation twinning describes the twin lattice by a simple shear of the original (matrix) lattice points. The invariant plane of this shear (twin habit plane) and the shear direction are called \(K_1\) and \(\vec{n}_1\); the second invariant or the conjugate plane is named \(K_2\). The plane containing shear direction \(\vec{n}_1\) and normals to \(K_1\) and \(K_2\) is the plane of shear \(P\) and the intersection of \(P\) and \(K_2\) gives the conjugate shear direction \(\vec{n}_2\). Figure 1.3 shows these twinning elements. The main twinning modes in Ti are \(\{10\bar{1}2\}\),

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Figure 1.1: Slip systems in the hcp Ti. The main slip direction is along the close-packed directions $<1\bar{1}20>$ ($\alpha$-type slip). Prismatic slip is dominant followed by pyramidal and basal systems respectively.

Figure 1.2: CRSS for slip with $\vec{a}$ and $\vec{c}$ + $\vec{a}$ Burgers vectors as a function of temperature in single crystal Ti-6.6Al [Lutjering and Williams, 2007].
Figure 1.3: Crystallographic twinning elements (a) and twinning elements for (10\bar{1}2) twin boundary in the hcp lattice. The unit cell defined by $\vec{\eta}_1, \vec{\eta}_2, \vec{P}$ in the matrix is sheared to $\vec{\eta}_1, \vec{\eta}_2', \vec{P}$ in the twin.

$\{11\bar{2}1\}$ and $\{11\bar{2}2\}$. The twinning elements for these modes are presented in Table 1.1.

<table>
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<th>Twinning plane ($K_1$)</th>
<th>Twinning shear ($\vec{\eta}_1$)</th>
<th>Conjugate plane ($K_2$)</th>
<th>Conjugate shear ($\vec{\eta}_2$)</th>
<th>Shear plane ($P$)</th>
<th>Magnitude of twinning shear</th>
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<tr>
<td>${10\bar{1}2}$</td>
<td>$\langle 10\bar{1}1 \rangle$</td>
<td>${1012}$</td>
<td>$\langle 101\bar{1} \rangle$</td>
<td>${1\bar{2}10}$</td>
<td>0.167</td>
</tr>
<tr>
<td>${11\bar{2}1}$</td>
<td>$\langle 11\bar{2}6 \rangle$</td>
<td>$\langle 11\bar{2}0 \rangle$</td>
<td>$\langle 1100 \rangle$</td>
<td>0.638</td>
<td></td>
</tr>
<tr>
<td>${11\bar{2}2}$</td>
<td>$\langle 11\bar{2}3 \rangle$</td>
<td>${1124}$</td>
<td>$\langle 2243 \rangle$</td>
<td>${1100}$</td>
<td>0.225</td>
</tr>
</tbody>
</table>

Twinning is specially important if stress is applied parallel to $c$ axis and dislocations with non-basal Burgers vectors cannot move. This case activates $\{10\bar{1}2\}$ and $\{11\bar{2}1\}$ modes during tension. $\{10\bar{1}2\}$ mode is the most frequently observed. Under compression $\{11\bar{2}2\}$ twins are activated. $\{10\bar{1}1\}$ twins are also observed only at high temperatures. Twinning is highly affected by the presence of solutes. In titanium high concentrations of oxygen decreases the occurrence of twins.
In addition, Ti strength is significantly increased by the interstitial solute oxygen. Figure 1.4 shows the effect of oxygen content on the yield stress of titanium wire specimens obtained from experiments[3]. At 77K the curve is parabolic but becomes almost linear in higher temperatures. In addition, the rate of solid solution strengthening increases with decrease in temperature. The oxygen content of commercial titanium alloys range between 0.08% to 0.20% depending on the alloy type. The $\alpha$ phase of titanium is also hardened by substitutional solutes Al, Sn and Zr which have large size misfit and high solubility in Ti.

Figure 1.4: Effect of oxygen on the yield stress of Ti wire specimens[Conrad, 1981].

The interplay between slip, twinning and solutes is the key to understanding and controlling mechanical behavior of titanium. The motivation behind this thesis work is to provide a systematic framework capable of accurate and quantitative description of the interaction between various lattice defects: dislocations interacting with planar defects with chemistry
changes due to solutes.

1.2 Dislocation/twin boundary interactions in Ti

Interaction of twin boundaries with glide dislocations affects the mechanical property from different aspects. Twin boundaries may impede dislocation motion and cause strengthening. On the other hand, dissociation of perfect dislocations absorbed in the boundary nucleates twinning dislocations that govern twin growth. Finally, allowing for the motion of dislocations in the boundary increases the plastic deformation accommodation and enhances ductility. Yoo[4] did a thorough review of the interaction of perfect glide dislocations and twin boundaries in hcp metals from a crystallography and elasticity point of view. This review covers $\frac{1}{3}(1\bar{1}20), [0001]$ and $\frac{1}{3}(1\bar{1}23)$ dislocations interacting with $\{10\bar{1}1\}$, $\{10\bar{1}2\}$, $\{1\bar{1}21\}$ and $\{11\bar{2}2\}$ twin boundaries. He identified twenty six distinct types of possible interactions and used an energy criterion to examine the energetic feasibility of those interactions. The results indicate that a screw dislocation parallel to the twin boundary can cross slip at the interface under applied stress. Moreover, basal mixed dislocations are attracted by the $(10\bar{1}2)$ twin boundary in cadmium and zinc implying that incorporation of these dislocations into the twin boundary is energetically feasible. On the other hand, the interaction between both basal and prism mixed dislocations and $(10\bar{1}2)$ twins are found to be repulsive in Ti, Zr and Mg.

However, motion of dislocations through or along a boundary depends on the atomic structure of the interface and core geometry of the dislocation that cannot be treated by continuum descriptions alone and are also difficult to measure experimentally. Serra and Bacon have done extensive atomistic simulations of various matrix dislocations impinging on twin boundaries in hcp metals[5, 6, 7]. They observed three broad classes of interactions: transmission of dislocations through the interface, complete absorption of dislocations in the boundary that causes the dislocation to undergo core reconstructions and finally dissociation.
of the matrix dislocation into interfacial defects which may subsequently move along the twin boundary. The latter suggests a new mechanism for nucleation of twinning dislocations from a perfect lattice dislocation.

In the case of an \( \langle a \rangle \)-type screw dislocations interacting with (10\( \overline{1} \)2) twin boundary under applied stress, Serra and Bacon observed that the dislocation always crosses the interface by cross-slip; either transmitting through or reflecting from the boundary without dissociating into partial defects. This is contrasted to the case of (10\( \overline{1} \)1) twin boundary where the dislocation is absorbed into the interface by decomposing into twinning dislocations\[5\].

Interaction of the basal \( \langle a \rangle \)-type mixed dislocation with (10\( \overline{1} \)2) is more complicated. According to Serra and Bacon\[6\], the dislocation becomes trapped in the boundary by decomposing into twinning dislocations and interfacial defects. The final geometry depends on the Burgers vector sign and the order of leading and trailing partials of the original mixed dislocation.

In addition, Pond et. al\[7\] studied the mobility of interfacial defects in (10\( \overline{1} \)2) twins under applied stress. They found that defects with Burgers vectors parallel to the interface (twinning dislocations) are mobile only when their step height \( h \) is small. On the other hand, for large \( h \) defects, the applied stress often reconstructs their narrow core structure and emits partial dislocations from the boundary.

1.3 Computational concerns

All of the simulations mentioned in Section 1.2 are based on classical interatomic potentials where a functional form for energy is fitted to a number of bulk material properties such as the lattice parameters and elastic constants. However, the prediction of these potentials for defect properties like stacking fault energies and defect formation energies are often inconsistent with reported experimental values. The inconsistency arises because classical potentials do not describe the electronic nature of bonding in metals. The inability to
describe atomic bonding also restricts classical potentials from considering chemistry changes in the presence of solutes. Therefore, classical atomistic studies are limited by the accuracy of their interatomic potential; yet they have the advantage of being computationally cheap with the ability to do million atom simulations.

To have a more accurate account for defect properties and the ability to consider chemistry changes, we primarily use density functional theory (DFT). DFT is a very popular and successful quantum mechanical approach to describe electronic structure of materials. In quantum mechanics, all the information about a given system is contained in the system’s wave function which solves the Schrödinger’s equation. Within Born-Oppenheimer approximation, the many-electron non-relativistic Schrödinger’s equation is written as

\[
-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{\text{ext}}(\vec{r}_i) + \sum_{i \neq j} U(\vec{r}_i, \vec{r}_j) \right] \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = E \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)
\]

where the first term gives the kinetic energy of electrons, second term is the external potential from nuclei acting on electrons and the last term accounts for the electron-electron interactions. Solution of this equation gives the many-electron wave function \( \Psi \) and the energy \( E \). The objective is to replace the many-body electron wave functions with the ground state electronic charge density as the basic variable. This idea originates from Hohenberg-Kohn theorems\[8\] stating that the ground state charge density determines the external potential uniquely, except for a constant and that the total energy of the system can be defined as a functional of the charge density where the ground state charge density minimizes total energy for any external potential. Kohn and Sham\[9\] proposed an approach to determine the ground state charge density and the ground state energy by replacing the original many-body problem of interacting electrons in an external potential with an auxiliary problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential for the non-interacting electrons and an exchange-correlation functional for all the many-electron effects. DFT is a first principles method in the sense that once
the atom positions and chemical identities are defined, the total energy can be calculated by solving Kohn-Sham equations without the need to fit materials properties. But this level of accuracy comes at an expensive computational cost. With modern supercomputers, DFT is able to simulate up to 1000 atoms. Moreover, use of plane wave basis functions to calculate the independent-particle electronic states imposes periodic boundary conditions.

The long-range (elastic) fields of an isolated dislocation are not compatible with the periodic boundary conditions typically used in DFT. Fixed boundary conditions require simulation sizes large enough for the elastic solution to be accurate—a size beyond modern DFT. Flexible boundary conditions avoid these issues by relaxing the atoms away from the defect core through lattice Green’s function (LGF) as if they are embedded in an infinite harmonic medium. Flexible boundary conditions use the perfect lattice Green’s function corresponding to the specific geometry of the problem. For instance, line defects in the presence of interfaces require interfacial lattice Green’s function (ILGF). In order to extend the applicability of DFT to isolated defects/boundary interactions, we present a general and accurate method to compute ILGF for all types of crystal structures and interface orientations. We use ILGF to develop a DFT-flexible boundary conditions approach for interfaces. The end result is the first DFT study of line defects in interfaces and paves the way to investigate a wide range of interesting problems in the field of defects research.

1.4 Scope

The following chapters develop a systematic framework for accurate and quantitative description of defects interactions in Ti. We present a general—for all types of interactions and crystal structures—method to study line defects in interfaces through direct calculation of interfacial lattice Green’s function. The interfacial lattice Green’s function is the cornerstone of flexible boundary condition methods that are suitable to use with DFT. The method is applied to the study of a [1210] screw dislocation interaction with a Ti (1012) twin boundary.
Core structure of the the [1210] screw dislocation in bulk Ti is also modeled through DFT flexible boundary conditions and compared to the screw dislocation in twin boundary. The quantum mechanically informed method opens up the possibility of interactions with solutes as well.

Chapter 2 explains the new procedure for computing interfacial lattice Green’s function by coupling the interface region to two semi-infinite bulk regions. Specifically, this method is applicable to studies of line defects interactions with planar interfaces such as dislocations or crack tips interacting with grain boundaries and two phase interfaces and interface disconnections (defects with both dislocation and step character).

Chapter 3 studies the screw dislocation core geometry in bulk Ti with MEAM and DFT. Two metastable core structures are observed depending on the initial position for the origin of the elastic displacement field for a perfect screw dislocation. The higher energy core always transforms to the lower energy core under sufficient stress. The transition from low to high energy core was never observed suggesting that only the dominant core needs to be considered. The ground state core splits into two mainly screw character partials separated by a region of prismatic stacking fault.

Chapter 4 applies the ILGF computation method to the specific case of a [1210] screw dislocation in a Ti (1012) twin boundary. First, the method is verified using a classical potential study. It is shown that flexible boundary conditions are essential in getting meaningful results for the core structure with a tractable number of atoms. The stress to transmit the dislocation through the boundary is also computed. The screw dislocation always cross slips across the twin boundary. Once the method is verified, it is used to study the same dislocation boundary system with DFT. The predicted core structures are compact and trapped in the twin boundary.

Chapter 5 investigates the interaction of oxygen interstitials with planar faults in Ti: (1012) twin boundary and prismatic stacking faults. The energetics of interstitial sites at the twin geometry are compared with the bulk octahedral site. We show that the oxygen is
attracted to the twin boundary. This fact is an important piece of information that should be considered in future studies of twin growth. In addition, oxygen increases the prismatic stacking fault energy in Ti and is repelled by the faulted area. The interaction energy between a bulk screw dislocation and the oxygen interstitial is approximated in terms of a volumetric size misfit. Although there is no long-range dilatation in the screw dislocation field, the volumetric strain and consequently interaction energy is nonzero inside the core region.

Appendix A introduces the internal relaxations that arise upon applying a uniform strain to the hcp lattice. In the hcp structure the primitive unit cell consists of two atoms. Displacements that break the hexagonal symmetry of the lattice create unbalanced forces that lead to internal relaxations inside the unit cell. Internal relaxations change the computed elastic constants and affect the convergence of flexible boundary conditions. Flexible boundary conditions start by displacing all of the atoms according to the elastic displacement field of an isolated dislocation. The strain associated to this displacements creates unbalanced forces on atoms that should be removed by adding the internal displacements. We show that ignoring the additional displacements breaks the convergence of flexible boundary condition methods.

Appendix B compares the efficiency of three methods to compute the lattice Green’s function. Inversion of the force constant matrix for the LGF requires Fourier techniques to project out the singular subspace, corresponding to uniform displacements and forces for infinite lattice. Efficiency of three techniques—relative displacement, elastic Green’s function correction and discontinuity correction—is computed for both elastically isotropic and anisotropic cases and compared to the analytic results. Our results verify that the discontinuity correction is the most computationally efficient method. In addition, while the convergence trends generally match the analytically predictions, there is an unusually improved convergence for lattices with elastic isotropy. This connects the anisotropy of the material to the efficiency of the computational method used in Green’s function calculations.
Chapter 2

Lattice Green’s function for crystals containing a planar interface

In this chapter, we present a method to compute the lattice Green’s function for a planar interface with arbitrary atomic interactions suited for the study of line defect/interface interactions. The interface is coupled to two different semi-infinite bulk regions, and the Green’s function for interface-interface, bulk-interface and bulk-bulk interactions are computed individually. The elastic bicrystal Green’s function and the bulk lattice Green’s function give the interaction between bulk regions. We make use of partial Fourier transforms to treat in-plane periodicity. Direct inversion of the force constant matrix in the partial Fourier space provides the interface terms. The general method makes no assumptions about the atomic interactions or crystal orientations and extends the application of flexible boundary condition methods to modeling defect/interface interactions from first principles.

2.1 Flexible boundary conditions

Geometry of an isolated dislocation breaks the periodicity of the lattice in the plane perpendicular to the dislocation line. This is not compatible with the periodic boundary conditions that are typically used in supercell methods. Alternatively, atomistic simulations cut out a box of atoms surrounding the defect and fix a few outer layers of atoms to the positions obtained from elasticity and relax the atoms inside. The stress field of an edge or screw dislocation is proportional to the inverse of the distance from the dislocation center. Therefore, cutting out the simulation box results in non zero tractions at the box surfaces requiring a large buffer region (\(\sim 10^4\) atoms) to protect the defect core. Such large simulations are
not feasible via computationally expensive methods such as density functional theory. Flexible boundary condition methods avoid these issues by relaxing the atoms away from the defect core through lattice Green’s function (LGF) as if they are embedded in an infinite harmonic medium. Hence, the atomic scale geometry of the defect core is coupled to the long-range strain field in the surrounding medium. Flexible boundary conditions were first introduced by Sinclair et al. to model defects in bulk materials[10] and then redeveloped to study cracks[11, 12], dislocations[13, 14, 15, 16], vacancies with classical potentials and isolated screw or edge dislocations with density-functional theory[17, 18, 19, 20]. Introducing a threading direction for the line defect keeps the periodicity of the lattice in this direction. The first step in a flexible boundary conditions scheme is to generate an array of atoms with one crystallographic repetition along the dislocation line. In the plane perpendicular to the threading direction, the dimensions should be large enough to incorporate the regions around the dislocation. The initial dislocation configuration is introduced by displacing all the atoms according to the anisotropic elastic displacement of the isolated dislocation. The dislocated geometry is then divided into three regions as shown in Figure 2.1. Region I contains the nonlinear core geometry. The atoms (in fact atom rows along the threading direction) in this region are relaxed independently from the other regions. Interaction between these atoms is obtained from a chosen interatomic potential or DFT. An energy minimization technique such as conjugate gradient is used to optimize the positions. Atoms in regions II and III interact through the same interatomic rule but are only displaced collectively through the lattice Green’s function. Region (II) contains all the atoms on which forces are built up during the optimization of region I while region III is a portion of the crystal that is necessary to start with zero forces on region II atoms.

First, atoms in region I are allowed to relax towards their minimum energy configuration. This process generates forces on region II atoms due the fact that their positions are not optimized yet. These forces are used to generate a corrective displacement filed on atoms of all three regions (and implicitly the infinite crystal). The additional displacement field
Figure 2.1: Schematic simulation cell for modeling an isolated dislocation with flexible boundary conditions. The cell is divided into three regions: region I (core), region II (transition) and region III (buffer).

is obtained from a superposition of lattice Green’s functions. The lattice Green’s function gives the discrete displacement field of a crystal in response to a unit line force applied on one of the atoms. Alternatively, the same corrective displacements cancel an internal force built up on an atom. Since, region I is nonlinear, LGF– valid in the harmonic response limit– cannot produce the exact equilibrium state. Therefore, iteration of the final two steps is required until zero forces are achieved in regions I and II. Note that the initial forces in region III caused by breaking the atomic bonds during creation of the supercell are ignored. No forces should develop in region III during the entire process.


## 2.2 Harmonic response

Harmonic response is characterized by a linear relationship between forces and displacements[21]. Lattice Green’s function \( G(\vec{R}, \vec{R}') \) relates the displacement \( \vec{u}(\vec{R}) \) of atom \( \vec{R} \) to the internal forces \( \vec{f}(\vec{R}') \) on another atom \( \vec{R}' \) of the crystal through

\[
\vec{u}(\vec{R}) = -\sum_{\vec{R}'} G(\vec{R}, \vec{R}') \vec{f}(\vec{R}').
\] (2.1)

Conversely, the forces on an atom can be expressed in terms of displacements through the force constant matrix \( D(\vec{R}, \vec{R}') \) by

\[
\vec{f}(\vec{R}) = -\sum_{\vec{R}'} D(\vec{R}, \vec{R}') \vec{u}(\vec{R}').
\] (2.2)

Figure 2.2 shows the harmonic response schematically. The static LGF can also be viewed as the zero frequency limit of the dynamical Green’s function[22]. Translational invariance of an infinite crystal makes \( G \) and \( D \) functions of the relative positions of the atoms. Substituting Eqn. (2.2) into Eqn. (2.1) gives \( \sum_{\vec{R}'} G(\vec{R} - \vec{R}') D(\vec{R}') = 1 \delta(\vec{R}) \), where \( \delta(\vec{R}) \) is the Kronecker delta function. A constant shift in atom positions does not produce internal forces; hence, \( \sum_{\vec{R}} D(\vec{R}) = 0 \), and so \( G(\vec{R}) \) is the pseudo inverse of \( D(\vec{R}) \) in the subspace without uniform displacements or forces. In a bulk geometry, the Fourier transform of the lattice functions are defined as

\[
G(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} G(\vec{R}), \quad G(\vec{R}) = \int_{BZ} \frac{d^3 k}{(2\pi)^3} e^{-i\vec{k} \cdot \vec{R}} G(\vec{k})
\]

where the summation is over lattice points[23]. In reciprocal space, the matrix inverse relation \( G(\vec{k}) D(\vec{k}) = 1 \) and the sum rule \( D(\vec{0}) = 0 \) require that \( G(\vec{k}) \) has a pole at the \( \Gamma \)-point. While computation of the force constant matrix \( D(\vec{R}) \)—and subsequently \( D(\vec{k}) \)—is straightforward, \( G(\vec{R}) \) can not be computed directly due to its long range behavior. Instead, we invert \( D(\vec{k}) \) to get \( G(\vec{k}) \) and then perform an inverse Fourier transform. Convergence of
Figure 2.2: Schematics of the harmonic lattice response. Displacing an atom produces internal forces on the neighboring atoms. These forces are given by the force constant matrix for small displacements. Conversely, a force on an atom induces displacements on other atoms of the lattice. Lattice Green’s function gives these displacements for small forces.

the inverse Fourier transform requires an analytical treatment of the pole at the Γ-point\cite{24, 25}. In an interface geometry, translational invariance is broken in the direction perpendicular to the interface; we use Fourier transforms in the interface plane only. This produces an infinite dimensional dynamical matrix that can not be simply inverted, but requires a more complex computational approach.
2.3 Computation of lattice Green’s function for a planar interface

In our approach, the interface is coupled to two different semi-infinite bulk regions. The Green’s function for interface-interface, bulk-interface and bulk-bulk interactions are computed separately. We approximate the long-range bulk-bulk interaction of the discrete interfacial lattice Green’s function (ILGF) with the continuum bicrystal Green’s function based on the assumption that just like the perfect bulk LGF asymptotically matches the continuum Green’s function, the interfacial LGF matches the continuum “interfacial” Green’s function. The ILGF for atoms in the same bulk regions is given by the bulk LGF of each region plus an elastic correction caused by the interface. The Green’s functions for the interface are obtained from direct inversion of the force constant matrix using a partial Fourier transform to account for translational invariance.

Figure 2.3a shows two lattices, \( \lambda \) and \( \mu \) joined at a planar interface. Each set of vectors \( \vec{a}_1^{\lambda,\mu}, \vec{a}_2^{\lambda,\mu} \) and \( \vec{a}_3^{\lambda,\mu} \) give the periodic directions in their corresponding lattice. We introduce integer matrices \( M^\lambda \) and \( M^\mu \) and deformation operators \( F^\lambda \) and \( F^\mu \) so that

\[
F^{\lambda,\mu} [\vec{a}_1^{\lambda,\mu}, \vec{a}_2^{\lambda,\mu}, \vec{a}_3^{\lambda,\mu}] M^{\lambda,\mu} = [\vec{T}_1^{\lambda,\mu}, \vec{T}_2^{\lambda,\mu}, \vec{T}_3^{\lambda,\mu}]
\]  

(2.3)

to define the supercell. We use \( \vec{T}_1^{\lambda} = \vec{T}_1^{\mu} = \vec{t}_1 \) and \( \vec{T}_2^{\lambda} = \vec{T}_2^{\mu} = \vec{t}_2 \) as nonparallel vectors to define the interface plane where \( \vec{t}_2 \) will be the periodic threading vector for a line defect in the interface. The combined lattice has translational invariance in \( \vec{t}_1 \) and \( \vec{t}_2 \) directions in the interface plane while the periodicity is broken in directions outside the plane. Introducing a threading direction reduces the problem to 2D (i.e plain strain or anti-plane strain conditions). We confine our calculations to the plane orthogonal to \( \vec{t}_2 \) and define the Cartesian coordinate \( \hat{x}, \hat{y}, \hat{z} \) so that \( \vec{t}_1 \cdot \hat{x} = a_0, \vec{t}_2 = |\vec{t}_2| \hat{y} \) and \( \hat{z} = \hat{x} \times \hat{y} \). Note that in general \( a_0 \neq |\vec{t}_1| \) because \( \vec{t}_1 \) and \( \vec{t}_2 \) can be nonorthogonal. Specifically, the lattice positions, \( \vec{R} = x\hat{x} + z\hat{z} \) and
the Fourier vectors, $\vec{k} = k_x \hat{x} + k_z \hat{z}$, will be 2D vectors throughout this chapter and

$$D_{\alpha \alpha'}(\vec{R}, \vec{R}') = D_{\alpha \alpha'}(x - x'; z, z')$$

with $\alpha$ and $\alpha'$ identifying the $xyz$ components of the second rank tensor $D$ in Cartesian coordinates. We index atoms in our computational cell with integer $l$ at position $(x_l, z_l)$; due to periodicity in the $\hat{x}$ direction, each atom also occurs at $x_l + n a_0 \hat{x}$ for integer values of $n$. The partial Fourier transform is

$$D_{\alpha \alpha'}(x_l - x_{l'} + n a_0; z_l, z_{l'}) = a_0^2 \pi \int_{-\pi/a_0}^{\pi/a_0} e^{-ik_x(x_l - x_{l'} + n a_0)} D_{\alpha \alpha'}(k_x) dk_x$$

(2.4)

for all pairs $l, l'$. Note that "l" indexes layers of atoms with particular $z$ values. There may be two different layers that have equal $z$: $z_l = z_{l'}$ while $l \neq l'$. $D(k_x)$ is infinite dimensional due to infinite values of $l$.

To avoid the inversion of infinite dimensional $D(k_x)$, the geometry is divided into two semi-infinite bulk regions coupled with an interface region. Figure 2.3b shows the schematic divisions of the regions in an interface geometry consisting of lattices $\lambda$ and $\mu$. The "bulk" regions represent layers of atoms that are far from and affected only through an elastic field by the interface. The atomic scale interaction between atom pairs are as if they were in their corresponding bulk geometry. Bulk $\lambda$ and bulk $\mu$ are symbolized by (+) and (−) in our notation. The remaining layers, affected by the reconstructions near the interface, are included in the "interface" region (I). We define the interface region as atoms where the force constant matrix differ from those in the bulk lattice. For specific geometries, additional bulk layers may be included in the interface to insure a smooth transition between the regions. We block partition the infinite dimensional $D_{\alpha \alpha'}(k_x)$ and $G_{\alpha \alpha'}(k_x)$ based on the atom
Figure 2.3: Bicrystal $\mu$ and $\lambda$ (a), separation into bulk and interface regions (b) and the Ti (1012) twin boundary (c). Two different lattices, $\lambda$ and $\mu$ are connected through a planar interface. The unit cells of $\lambda$ and $\mu$ are given by $\vec{a}_{1,\lambda,\mu}$, $\vec{a}_{2,\lambda,\mu}$ and $\vec{a}_{3,\lambda,\mu}$—all of which must be lattice vectors in $\lambda$ and $\mu$. The combined lattice has the periodicity of the interface in $\vec{t}_1$ and $\vec{t}_2$ directions. Introducing a line defect threading direction $\vec{t}_2$ reduces the problem to 2D in the plane normal to $\vec{t}_2$. In (b), the crystal is divided into two semi-infinite bulk regions, bulk $\lambda$ and bulk $\mu$ symbolized by (+) and (−) respectively, coupled with an interface region (I). The bulk regions are far from and affected only through an elastic effect by the interface. The force constant matrix between atom pairs in the bulk is not affected by the interface. The remaining layers are included in (I). (c) shows the periodicity vectors for the Ti (1012) twin boundary. The interface is defined by $\vec{t}_1 = \sqrt{3}a^2 + c^2 \hat{x}$ and $\vec{t}_2 = a\hat{y}$ where $a$ and $c$ are the hcp unit cell parameters in Ti for both $\lambda$ and $\mu$. $\mu$ is the reflection of $\lambda$ about the interface plane. Ti (1012) twin boundary is chosen to demonstrate the application of our method in Chapter 4.
region (+, −, or I) of indices \( l \) as

\[
D(k_x) = \begin{pmatrix}
D_{II}(k_x) & D_{I-}(k_x) & D_{I+}(k_x) \\
D_{-I}(k_x) & D_{--}(k_x) & D_{+-}(k_x) \\
D_{+I}(k_x) & D_{+-}(k_x) & D_{++}(k_x)
\end{pmatrix}
\] (2.5)

where \( l > l_+ \) belong to (+) region, \( l < l_- \) belong to (−) region and the finite-dimensional region is (I). \( D(k_x) \) and \( G(k_x) \) are Hermitian and satisfy

\[
\sum_{\alpha''} D_{\alpha l, \alpha'' l'}(k_x) G_{\alpha'' l', \alpha' l}(k_x) = \delta_{\alpha \alpha'} \delta_{ll'}.
\] (2.6)

We construct \( D(k_x) \) by direct calculation of \( D_{\alpha l, \alpha'' l'}(x_i - x_i' + na_0; z_l, z_l') \) followed by a partial Fourier transform according to Eqn. (2.4) and block partitioning as in Eqn. (2.5). Note that due to the finite number of interface layers and decay of the force constant matrix, the infinite dimensional non-zero sections of \( D(k_x) \) consists of −−, −+ and ++ interactions (bulk-like regions with themselves) which we explicitly avoid in our approach.

The infinite dimensional blocks of \( G(k_x) \) are known from bicrystal elastic and bulk lattice calculations. The distance between + and − is large enough for the elastic Green’s function to be applicable; the real space solution of \( G^{-+} \) is calculated from the bicrystal elastic Green’s function in both plane strain and anti-plane conditions proposed by Tewary et. al[1]. We partially Fourier transform the real space solution by a continuum version of Eqn. (2.4),

\[
G^{-+}_{\alpha l, \alpha' l'}(k_x) = \int_{-\infty}^{\infty} G^{-+}_{\alpha \alpha'}(x; z_l, z_{l'}) e^{ik_x x} dx.
\] (2.7)

\( G^{-+} \) is the conjugate transpose of \( G^{-+} \) due to \( G(k_x) \) being Hermitian. The functional form of \( G^{-+}(x; z_l, z_{l'}) \) consists of real parts of \( \ln(x + p^\lambda_q z_l + p^\mu_{q'} z_{l'}) \) where \( p^\lambda_q \) and \( p^\mu_{q'} \) are the complex roots of the sextic equation of anisotropic elasticity for bicrystal \( \lambda \mu \) and \( q, q' = 1, 2 \) in plain
strain and 1 in anti-plane conditions [1]. We rewrite $\ln(x + \gamma_{\alpha\alpha}'\gamma_{\alpha\alpha}' + i\beta_{\alpha\alpha}')$ with

$$\gamma_{\alpha\alpha}' = \Re(p^\lambda_q z_l + \Re(p^\mu_q z')_l), \beta_{\alpha\alpha}' = \Im(p^\lambda_q z_l + \Im(p^\mu_q z')_l).$$

The Green’s function in real space is the real part of the complex logarithm with the form

$$G^{-+}_{\alpha\alpha'}(x; z_l, z') = \sum_{q,q'} a^{qq'}_{\alpha\alpha'} \ln \left| (x + \gamma_{\alpha\alpha}'\gamma_{\alpha\alpha}')^2 + (\beta_{\alpha\alpha}')^2 \right| + b^{qq'}_{\alpha\alpha'} \arctan \left( \frac{\beta_{\alpha\alpha}'x}{x + \gamma_{\alpha\alpha}'} \right)$$

(2.8)

where $a^{qq'}_{\alpha\alpha'}$ and $b^{qq'}_{\alpha\alpha'}$ are real valued coefficients of the term $qq'$. Eqn. (2.8) is obtained by rewriting Eqn. (60) in [1]. The partial Fourier transform is

$$G^{-+}_{\alpha\alpha'}(k_x) = -\pi \frac{t_2}{|t_2|} \sum_{q,q'} a^{qq'}_{\alpha\alpha'} e^{-i\gamma_{\alpha\alpha}'(k_x)} e^{-i\beta_{\alpha\alpha}'(k_x)} + b^{qq'}_{\alpha\alpha'} \frac{k_x}{|k_x|} e^{-i\gamma_{\alpha\alpha}'(k_x)} e^{-i\beta_{\alpha\alpha}'(k_x)}$$

(2.9)

with a first order pole at $k_x = 0$. The $1/|t_2|$ prefactor is required for the elastic and lattice Green’s functions to have consistent units of (length$^2$/energy). We separate the pole from the remainder of the Green’s function

$$G^{-+}_{\alpha\alpha'}(k_x) = \frac{\hat{G}_{\alpha\alpha'}^{-+}(k_x)}{|k_x|} + \check{G}_{\alpha\alpha'}^{-+}(k_x).$$

(2.10)

The pole with a constant coefficient $\hat{G}_{\alpha\alpha'}^{-+} = -\frac{\pi}{|t_2|} \sum_{q,q'} a^{qq'}_{\alpha\alpha'}$ will be treated analytically while the nonsingular remainder $\check{G}_{\alpha\alpha'}^{-+}(k_x)$, will be treated numerically.

The $G^{-+}(k_x)$ and $G^{++}(k_x)$ blocks in Eqn. (2.5) are obtained from the bulk lattice Green’s function of $\lambda$ and $\mu$ lattices plus an elastic term due to the presence of the interface. The full Fourier transform of the bulk LGF $G^{\sigma\sigma}(\vec{k})$ is the inverse of the bulk dynamical matrix. The partial inverse Fourier transform gives the Green’s function in terms of $k_x$ and atom indices

$$G^{\sigma\sigma}_{\alpha\alpha'}(k_x) = \frac{1}{A_BZ} \int_{k_i(k_x)}^{k_f(k_x)} G^{\sigma\sigma}_{\alpha\alpha'}(\vec{k}) e^{-i\vec{k}(z_l - z')} dk_z$$

(2.11)
for $\vec{k} = (k_x, k_z)$ in the Brillouin zone (BZ), $A_{BZ}$ the area of the BZ and $k_i(k_x)$ and $k_f(k_x)$ showing the initial and final values of $k_z$ at each $k_x$. $\mathcal{G}_{\alpha\alpha'}^\sigma(\vec{k})$ has a second order pole at $k = \sqrt{k_x^2 + k_z^2} = 0$ which is responsible for the logarithmic long range behavior of LGF in real space. The LGF in reciprocal space is

$$G_{\alpha\alpha'}^{\sigma\sigma}(\vec{k}) = \frac{\hat{G}_{\alpha\alpha'}^{\sigma\sigma}(\vec{k})}{k_x^2 + k_z^2} f_c(k_x) + \hat{G}_{\alpha\alpha'}^{\sigma\sigma}(\vec{k})$$

where $\hat{G}_{\alpha\alpha'}^{\sigma\sigma}$ is the $\vec{k}$ direction-dependent elastic Green’s function and $f_c(k)$ is a cutoff function that vanishes smoothly at the edges of the BZ. In general anisotropic cases, $\hat{G}_{\alpha\alpha'}^{\sigma\sigma}(\vec{k})$ is represented by a Fourier series expansion as $\hat{G}_{\alpha\alpha'}^{\sigma\sigma}(\vec{k}) = \sum_{n=0}^{N_{max}} \hat{G}_{\alpha\alpha'}^{\sigma\sigma,n} e^{i n \phi_k}$ where $\phi_k$ is the angle of $\vec{k}$ relative to an arbitrary in-plane direction and the truncation $N_{max}$ is sufficiently large[24].

The integrand in Eqn. (2.11) is not singular for $k_x \neq 0$ however the $k^2$ pole in $G_{\alpha\alpha'}^{\sigma\sigma}(\vec{k})$ results in a pole of order $|k_x|$ in $G_{\alpha\alpha'}^{\sigma\sigma}(k_x)$. To treat the small $k_x$ behavior analytically, we integrate Eqn. (2.11) as four terms

$$\int_{k_i(k_x)}^{k_f(k_x)} G_{\alpha\alpha'}^{\sigma\sigma}(\vec{k}) e^{-ik_x(z_l-z_{l'})} dk_z = \int_{k_i(k_x)}^{k_f(k_x)} G_{\alpha\alpha'}^{\sigma\sigma}(\vec{k}) (e^{-ik_x(z_l-z_{l'})} - 1) dk_z + \int_{k_i(k_x)}^{k_f(k_x)} G_{\alpha\alpha'}^{\sigma\sigma}(\vec{k}) \frac{\hat{G}_{\alpha\alpha'}^{\sigma\sigma,0}}{k_x^2 + k_z^2} f_c(k_x, k_z) dk_z$$

$$+ \int_{k_i(k_x)}^{k_f(k_x)} \frac{\hat{G}_{\alpha\alpha'}^{\sigma\sigma,0}}{k_x^2 + k_z^2} (f_c(k_x, k_z) - 1) dk_z + \int_{k_i(k_x)}^{k_f(k_x)} \frac{\hat{G}_{\alpha\alpha'}^{\sigma\sigma,0}}{k_x^2 + k_z^2} dk_z$$

where $\hat{G}_{\alpha\alpha'}^{\sigma\sigma,0}$ is the $n = 0$ coefficient in Fourier expansion of $\hat{G}_{\alpha\alpha'}^{\sigma\sigma}(\vec{k})$. The first three terms
in Eqn. (2.12) are evaluated numerically while the last integral is
\[
\int_{k_i(k_x)}^{k_f(k_x)} \frac{\hat{G}^{\sigma\sigma,0}_{\alpha\alpha'}}{k^2_k + k^2_z} dk_z = \frac{\pi \hat{G}^{\sigma\sigma,0}_{\alpha\alpha'}}{|k_x|} + \hat{G}^{\sigma\sigma,0}_{\alpha\alpha'} \left( \frac{\arctan(k_f(k_x)/k_x) - \arctan(k_i(k_x)/k_x)}{k_x} - \frac{\pi}{|k_x|} \right)
\]  
(2.13)
where \(\frac{\pi \hat{G}^{\sigma\sigma,0}_{\alpha\alpha'}}{|k_x|}\) is the pole and the remaining terms are added to the numerically evaluated part. Note that the direction dependent terms in \(\hat{G}^{\sigma\sigma}_{\alpha\alpha'}(k)\) expansion do not contribute to the pole in \(k_x\) and are included in the second integral of Eqn. (2.12). We add an elastic correction term to \(\hat{G}^{\sigma\sigma}_{\alpha\alpha'}(k_x)\), due to the interface obtained from Eqn. (59) in [1]. Combining Eqn. (2.13), Eqn. (2.12), and Eqn. (2.10) produces
\[
\hat{G}^{\sigma\sigma'}_{\alpha l,\alpha l'}(k_x) = \hat{G}^{\sigma\sigma'}_{\alpha\alpha'}(k_x) + \tilde{G}^{\sigma\sigma'}_{\alpha l,\alpha l'}(k_x).
\]  
(2.14)

Eqn. (2.5) has unknown blocks \(\hat{G}^{II}(k_x), \hat{G}^{I\sigma}(k_x)\). Direct substitution of the block partitions gives
\[
\hat{G}^{I\sigma}(k_x) = -(\hat{D}^{II}(k_x))^{-1} \sum_{\sigma' = \pm} \hat{D}^{I\sigma'}(k_x) \hat{G}^{\sigma\sigma}(k_x) \\
\hat{G}^{II}(k_x) = (\hat{D}^{II}(k_x))^{-1} \sum_{\sigma'\sigma = \pm} (\hat{D}^{II}(k_x))^{-1} \hat{D}^{I\sigma}(k_x) \hat{G}^{\sigma\sigma}(k_x) \hat{D}^{I\sigma'}(k_x) (\hat{D}^{II}(k_x))^{-1}
\]  
(2.15)  (2.16)

Note that by choosing the appropriate set of independent equations we manage to avoid the calculation of the infinite dimensional \(\hat{D}^{\sigma\sigma'}(k_x)\). The finite range of \(\hat{D}^{I\sigma}(k_x)\) means that only a finite subset of atoms in each semi-infinite \(\pm\) region are considered for \(\hat{G}^{\sigma\sigma'}(k_x)\). To treat the poles in \(\hat{G}^{II}(k_x)\) and \(\hat{G}^{I\sigma}(k_x)\) analytically, we use a \(k_x\) expansion of \(\hat{D}(k_x) = \hat{D} + \hat{\mathbf{D}}(k_x)\) derived from Eqn. (2.4) where \(\hat{\mathbf{D}}(k_x) = \hat{D}^{(1)}k_x + O(k_x^2)\). Therefore, for small \(k_x\)
\[
(\hat{D}(k_x))^{-1} = \left[\hat{D} + \hat{\mathbf{D}}(k_x)\right]^{-1} \\
= \hat{D}^{-1} \left[\mathbf{I} + \hat{\mathbf{D}}(k_x)\hat{D}^{-1}\right]^{-1} \\
= \hat{D}^{-1} - k_x \hat{D}^{-1} \hat{D}^{(1)} \hat{D}^{-1} + O(k_x^2).
\]  
(2.17)
Using the small $k_x$ expansions for the bulk Green's functions with Eqn. (2.15) and Eqn. (2.16) gives

$$G^{I\sigma}(k_x) = \frac{1}{|k_x|} \hat{G}^{I\sigma} + \hat{G}^{I\sigma}(k_x) \quad \text{and} \quad G^{II}(k_x) = \frac{1}{|k_x|} \hat{G}^{II} + \hat{G}^{II}(k_x)$$  \hspace{1cm} (2.18)

where

$$\hat{G}^{I\sigma} = - (\hat{D}^{II})^{-1} \sum_{\sigma' = \pm} \hat{D}^{I\sigma'} \hat{G}^{\sigma'\sigma} \quad \text{and} \quad \hat{G}^{II} = (\hat{D}^{II})^{-1} + \sum_{\sigma,\sigma' = \pm} (\hat{D}^{II})^{-1} \hat{D}^{I\sigma} \hat{G}^{\sigma'\sigma} \hat{D}^{\sigma'I} (\hat{D}^{II})^{-1}$$

are the constant coefficients of the pole and $\hat{G}^{I\sigma}(k_x)$ and $\hat{G}^{II}(k_x)$ include the remaining nonsingular terms. $\hat{G}^{II}(k_x)$ and $\hat{G}^{I\sigma}(k_x)$ have a cusp approaching $k_x = 0$ and the value at $k_x = 0$ is

$$\hat{G}^{I\sigma}(0) = -(\hat{D}^{II})^{-1} \sum_{\sigma' = \pm} \hat{D}^{I\sigma'} \hat{G}^{\sigma'\sigma}(0)$$  \hspace{1cm} (2.19)

$$\hat{G}^{II}(0) = (\hat{D}^{II})^{-1} + \sum_{\sigma,\sigma' = \pm} (\hat{D}^{II})^{-1} \hat{D}^{I\sigma} \hat{G}^{\sigma'\sigma}(0) \hat{D}^{\sigma'I} (\hat{D}^{II})^{-1}. \hspace{1cm} (2.20)$$

Depending on the relative values of $\sigma$ and $\sigma'$, $\hat{G}^{\sigma\sigma'}(0)$ is calculated as the following:

**Case 1: $\sigma = \sigma'$**

$\hat{G}^{\sigma\sigma}_{a_l,a_l'}(k_x = 0)$ is obtained by taking the limit of Eqn. (2.12) and Eqn. (2.13) as $k_x \to 0$:

$$\hat{G}^{\sigma\sigma}_{a_l,a_l'}(k_x = 0) = \int_{k_x(0)}^{k_f(0)} G^{\sigma\sigma}(k_x \hat{z})(e^{-ik_x(z_l - z_{l'})} - 1) dk_x$$

$$+ \int_{k_x(0)}^{k_f(0)} G^{\sigma\sigma}(k_x \hat{z}) - \frac{\hat{G}^{\sigma\sigma}}{k_x^2} f_c(k_x) dk_x$$

$$+ \int_{k_x(0)}^{k_f(0)} \frac{\hat{G}^{\sigma\sigma}}{k_x^2}(f_c(k_x) - 1) dk_x$$

$$+ \lim_{k_x \to 0} \hat{G}^{\sigma\sigma} \left( \frac{\arctan(k_f(k_x)/k_x) - \arctan(k_i(k_x)/k_x)}{k_x} - \frac{\pi}{|k_x|} \right). \hspace{1cm} (2.21)$$
Note that since \( \vec{k} = k_z \hat{z}, \), \( \hat{G}^{\sigma \sigma} (\vec{k}) \) is evaluated along a constant \( \hat{k} \)-direction and therefore is a constant. The cut off function is

\[
f_c(k_z) = \begin{cases} 
1 & 0 < |k_z| < 0.5 k_{z,\text{max}} \\
\frac{12(1 - |k_z|)^2 - 16(1 - |k_z|)^3}{12} & 0.5 k_{z,\text{max}} < |k_z| < k_{z,\text{max}}
\end{cases}
\]

where \( k_{z,\text{max}} \leq \text{Min}(|k_i(0)|, k_f(0)) \) to insure that \( f_c(k_z) = 0 \) at the Brillouin zone boundary. We isolate the \( k_z = 0 \) point by dividing the integration path in Eqn. (2.21), Eqn. (2.22) and Eqn. (2.23) into three intervals

\[
[k_i(0), k_f(0)] = [k_i(0), -\epsilon/2) \cup [-\epsilon/2, \epsilon/2] \cup (\epsilon/2, k_f(0)]
\]

where \( \epsilon \) is sufficiently small. The first and third intervals do not contain the \( \Gamma \)-point and therefore their corresponding integrals are evaluated numerically without special treatments.

To evaluate the integrals in Eqn. (2.21) and Eqn. (2.22) over \([-\epsilon/2, \epsilon/2]\), we use the small \( k_z \) leading order terms of \( \hat{G}^{\sigma \sigma} (\vec{k}) \) \([24]\) and the exponential term

\[
\int_{-\epsilon/2}^{\epsilon/2} G^{\sigma \sigma} (k_z \hat{z})(e^{-ik_z(z_l - z_{l'})} - 1) dk_z = \\
\int_{-\epsilon/2}^{\epsilon/2} \left( \frac{\hat{G}^{\sigma \sigma}}{k_z^2} + \frac{i G^{\sigma \sigma,i}}{|k_z|} \frac{k_z}{|k_z|} + \hat{G}^{D} (k_z) \right) \left( -ik_z(z_l - z_{l'}) - k_z^2 \frac{(z_l - z_{l'})^2}{2} \right) dk_z = \\
\left( G^{\sigma \sigma,i}(z_l - z_{l'}) - \hat{G}^{\sigma \sigma} \frac{(z_l - z_{l'})^2}{2} \right) \epsilon
\]

and

\[
\int_{-\epsilon/2}^{\epsilon/2} G^{\sigma \sigma} (k_z \hat{z}) \frac{\hat{G}^{\sigma \sigma}}{k_z^2} f_c(k_z) dk_z = \int_{-\epsilon/2}^{\epsilon/2} \left( \frac{G^{\sigma \sigma,i}}{k_z} \frac{i \hat{G}^{\sigma \sigma}}{|k_z|} + \hat{G}^{D} (k_z) \right) dk_z = \hat{G}^{D} (0) \epsilon.
\]

\( \hat{G}^{\sigma \sigma} / k_z^2 \) and \( \hat{G}^{D} (k_z) \) are the elastic and discontinuity corrections and \( i G^{\sigma \sigma,i} / k_z \) appears only in the case of a multi atom basis. \( \hat{G}^{\sigma \sigma} \) and \( G^{\sigma \sigma,i} \) are constants here\([24, 25]\). Also note that \( f_c(k_z) = 1 \) over \([-\epsilon/2, \epsilon/2]\); hence the integral in Eqn. (2.23) equals zero over this interval.
Taking $\epsilon$ to be $\frac{k_f(0) - k_i(0)}{N_{\text{div}}}$ where $N_{\text{div}}$ is the number of divisions in the discrete $k_z$ mesh we have

$$
\tilde{G}_{\alpha\alpha',\sigma\sigma'}(0) = \frac{k_f(0) - k_i(0)}{N_{\text{div}}} \left[ \sum_{k_z \neq 0} \left( \tilde{G}_{\alpha\alpha'}^{\sigma\sigma}(k_z \hat{z}) e^{-ik_z(z_l - z_{l'})} - \frac{\tilde{G}_{\alpha\alpha'}^{\sigma\sigma}}{k_z^2} \right) + \tilde{G}_{\alpha\alpha'}^{\sigma\sigma}(z_l - z_{l'}) - \frac{\tilde{G}_{\alpha\alpha'}^{\sigma\sigma}(z_l - z_{l'})}{2} + \tilde{G}_{\alpha\alpha'}^{\alpha\alpha}(0) \right] + \tilde{G}_{\alpha\alpha'}^{\sigma\sigma} \left( \frac{1}{k_i(0)} - \frac{1}{k_f(0)} \right).
$$

The first summation

$$
\frac{k_f(0) - k_i(0)}{N_{\text{div}}} \sum_{k_z \neq 0} \left( \tilde{G}_{\alpha\alpha'}^{\sigma\sigma}(k_z \hat{z}) e^{-ik_z(z_l - z_{l'})} - \frac{\tilde{G}_{\alpha\alpha'}^{\sigma\sigma}}{k_z^2} \right) = \frac{k_f(0) - k_i(0)}{N_{\text{div}}} \sum_{k_z \neq 0} \left[ (\tilde{G}_{\alpha\alpha'}^{\sigma\sigma}(k_z \hat{z})(e^{-ik_z(z_l - z_{l'})} - 1)) + (G_{\alpha\alpha'}^{\sigma\sigma}(k_z \hat{z}) - \frac{G_{\alpha\alpha'}^{\sigma\sigma}}{k_z^2} f_c(k_z)) + \left( \frac{\tilde{G}_{\alpha\alpha'}^{\sigma\sigma}}{k_z^2} (f_c(k_z) - 1) \right) \right]
$$

is the numerical integration of all three integrals in Eqn. (2.21)-(2.23) over $[k_i(0), -\epsilon/2) \cup (\epsilon/2, k_f(0)]$. The last term $\tilde{G}_{\alpha\alpha'}^{\sigma\sigma} \left( \frac{1}{k_i(0)} - \frac{1}{k_f(0)} \right)$ is the evaluation of Eqn. (2.24).

**Case 2: $\sigma \neq \sigma'$**

$G_{\alpha\alpha'}^{\sigma\sigma'}(k_z = 0)$ is obtained from the small $k_z$ expansion of Eqn. (2.9) and removing the $k_z^{-1}$ term

$$
G_{\alpha\alpha'}^{\sigma\sigma'}(0) = \frac{\pi}{|t_2|} \left( 2a_{\alpha\alpha'}^{qq'} |\beta_{l,l'}^{qq'}| - b_{\alpha\alpha'}^{qq'} \gamma_{l,l'}^{qq'} \right).
$$

(2.25)

To ensure a smooth transition between interface and bulk regions, we compare the pole terms and the cusps for atom indices at the boundary between the regions (i.e $l_+$ and $l_-$). Labeling $l_\sigma$ as $\sigma = \pm$ or (I) does not change the material response. Specifically we should
have

\[
\hat{\mathcal{G}}^{II}_{\alpha l, \alpha' l'} = \hat{\mathcal{G}}^{\sigma \sigma}_{\alpha \alpha'}, \quad \hat{\mathcal{G}}^{II}_{\alpha l, \alpha' l'}(0) = \hat{\mathcal{G}}^{\sigma \sigma}_{\alpha l, \alpha' l'}(0) \tag{2.26}
\]

Eqn. (2.26) determines the finite size effect in the interface. Note that once the bulk force constant matrix is known, identifying atoms in the interface region does not require additional computation effort.

Evaluating the Green’s function in real space between to atoms \((x_l + na_0, z_l) \) and \((x_{l'}, z_{l'})\) requires a partial inverse Fourier transform over Eqn. (2.18),

\[
\mathcal{G}^{I\sigma}_{\alpha \alpha'}(x_l - x_{l'}, n a_0; z_l, z_{l'}) = \int_{-k_{\text{max}}}^{k_{\text{max}}} \mathcal{G}^{I\sigma}_{\alpha l, \alpha' l'}(k_x) e^{-i k_x (x_l - x_{l'} + n a_0)} \, dk_x \tag{2.27}
\]

and

\[
\mathcal{G}^{II}_{\alpha \alpha'}(x_l - x_{l'}, n a_0; z_l, z_{l'}) = \int_{-k_{\text{max}}}^{k_{\text{max}}} \mathcal{G}^{II}_{\alpha l, \alpha' l'}(k_x) e^{-i k_x (x_l - x_{l'} + n a_0)} \, dk_x. \tag{2.28}
\]

The \(\hat{\mathcal{G}}\) term in Eqn. (2.18) is treated analytically via

\[
\int_{-\infty}^{\infty} \frac{1}{|k_x|} e^{-i k_x x} \, dk_x = -2 \ln |x|.
\]

Therefore

\[
\int_{-k_{\text{max}}}^{k_{\text{max}}} \frac{1}{|k_x|} e^{-i k_x x} \, dk_x = -2 \ln |x| + 2 \text{Ci}(k_{\text{max}} x). \tag{2.29}
\]

Note that \(\lim_{x \to 0} -2 \ln |x| + 2 \text{Ci} = 2 \gamma + 2 \ln(k_{\text{max}})\) where \(\gamma \approx 0.577215\) is the Euler constant.

The partial inverse Fourier transform for \(\hat{\mathcal{G}}\) terms are evaluated numerically over a discrete \(k_x\) mesh of size \(N_{k_x}\)

\[
\hat{\mathcal{G}}^{I\sigma}_{\alpha \alpha'}(x_l - x_{l'}, n a_0; z_l, z_{l'}) = \frac{1}{N_{k_x}} \sum_{k_x} \hat{\mathcal{G}}^{I\sigma}_{\alpha l, \alpha' l'}(k_x) e^{-i k_x (x_l - x_{l'} + n a_0)} \tag{2.30}
\]
and
\[ \tilde{G}_{\alpha\alpha'}^{II}(x_i - x_{i'} + na_0; z_l, z_{l'}) = \frac{1}{N_{k_x}} \sum_{k_x} \tilde{G}_{\alpha\alpha'}^{II}(k_x)e^{-ik_x(x_i - x_{i'} + na_0)}. \] (2.31)

Table 2.1: Summary of the procedure for ILGF computation. Regions (+, −, and I) are defined in Figure 2.3b. \( G_{-}^{\pm}(x; z, z') \) is the elastic Green’s function for a bicrystal computed by Tewary et al.\[1\]. \( G_{\sigma\sigma}(\hat{k}) \) is the LGF in bulk \( \sigma = \pm \). FT prefactors required to maintain the consistency between elastic bicrystal GF and bulk LGF solutions are also listed.

1. Compute \( D_{\alpha\alpha'}(x_i - x_{i'} + na_0; z_l, z_{l'}) \) directly. Divide the geometry into −, I, + regions.
2. \( D_{\alpha\alpha'}^{I\sigma}(k_x) = \sum_{n=-\infty}^{\infty} e^{ik_x(x_i - x_{i'} + na_0)} D_{\alpha\alpha'}(x_i - x_{i'} + na_0; z_l, z_{l'}) \), \( a_0 \) = periodicity in \( x \) direction and \( \sigma = \pm, I \). Eqn. (2.4)
3. \( G_{\alpha\alpha'}^{\pm}(k_x) = \frac{b_{h_1}}{2\pi|x_1|} \int_{x_{i}'}^{\infty} G_{\alpha\alpha'}^{\pm}(x; z_l, z_{l'})e^{ik_x x} dx \), \( b_1 = \frac{2\pi}{a_0}, b_1b_2 = A_{BZ} \). Eqn. (2.7)
4. \( G_{\alpha\alpha'}^{\sigma\sigma}(k_x) = \frac{1}{L} \int_{k_x}^{k_x} G_{\alpha\alpha'}^{\sigma\sigma}(k_x; k_x)e^{-ik_x(z_l - z_{l'})}dk_x \). Eqn. (2.11)
5. \( G_{\alpha\alpha'}^{\sigma\sigma}(k_x) = \frac{G_{\alpha\alpha'}^{\sigma\sigma}}{|k_x|} + \tilde{G}_{\alpha\alpha'}^{\sigma\sigma}(k_x) \). Eqn. (2.14)
6. \( D_{\alpha\beta n}(k_x)G_{\beta n,\alpha'}^{l\sigma}(k_x) = \delta_{\alpha\alpha'}\delta_{l'l} \rightarrow G_{\alpha\alpha'}^{l\sigma}(k_x) = \frac{G_{\alpha\alpha'}^{l\sigma}}{|k_x|} + \tilde{G}_{\alpha\alpha'}^{l\sigma}(k_x), (\sigma = \pm, I) \). Eqn. (2.15)-(2.18)
7. \( G_{\alpha\alpha'}^{l\sigma}(x = x_i - x_{i'} + na_0; z_l, z_{l'}) = \frac{\tilde{G}_{\alpha\alpha'}^{l\sigma}}{b_{h_1}} (-2\ln|x| + 2\text{Ci}(\frac{b_{h_1}}{2}x)) + \frac{1}{N_{k_x}} \sum_{m=1}^{N_{k_x}} \tilde{G}_{\alpha\alpha'}^{l\sigma}(\frac{mb_{h_1}}{N_{k_x}}) e^{-\frac{mb_{h_1}}{N_{k_x}}x} \). Eqn. (2.29)-(2.31)

2.4 Summary

We developed an automated computational approach to calculate the lattice Green’s function of crystals containing planar interfaces for arbitrary force constants and interface orientations. This method is general in the sense that it can consider long range atomic interactions and reconstructions near the interface. Table 2.1 summarizes the steps involved in the
method. The end result is a computationally tractable approach suited for studies of defects in interfaces. We use this method to study the interaction of a Ti (10\bar{1}2) twin boundary with a screw dislocation in Chapter 4.
Chapter 3

Core structure of a screw dislocation in Ti from first principles and classical potentials

Core structure and mobility of dislocations directly relate to mechanical properties of materials [26]. Accurate atomic scale studies of dislocation core geometry is specially important for high stacking fault materials such as Ti where the dislocation core is compact and therefore difficult to investigate by experiments. Classical potential studies predict both prismatic and basal core spreading for screw dislocations in Ti depending on the origin of the initial elastic displacement field[5]. The prismatic core is expected for Ti where slip on the prism planes is dominant. Recently, core geometry of 1/3[1210] screw dislocation in Ti has been studied in the cluster approach with DFT[27]. Those DFT calculations show two different metastable core structures depending on the origin for the elastic displacement field of the dislocation imposed before the relaxations. One of the cores is symmetrically prismatic while the other shows a combination of prismatic and pyramidal spreading. We revisit this problem to identify (a) if the existence of metastable cores is an artifact of the boundary conditions and (b) if the cores can be easily transformed from one to the other (e.g cross-slip or transition states). We model the isolated dislocation using flexible boundary conditions where lattice Green’s function couples the core to the far field harmonically responding medium, eliminating the spurious effects of free surfaces in the cluster approach. In addition to DFT, we use a modified embedded atom (MEAM) potential for Ti[28] to investigate the dependence of core geometry metastability on the potential and study the behavior under stress.
3.1 Computational method

Isolated dislocations are modeled using flexible boundary conditions\cite{10, 18, 20}. Periodic boundary conditions are applied along the dislocation line. Flexible boundary conditions relax atoms surrounding the dislocation core region with the lattice Green’s function (LGF) as if they are embedded in an infinite medium. The anisotropic elasticity solution for the perfect screw dislocation displacement field is applied to all atoms initially. Flexible boundary conditions method divides the simulation geometry into three regions: core (I), transition (II) and buffer (III). Force calculations are done with DFT throughout the whole geometry. Conjugate gradient method relaxes the atoms around the core (region I). Displacements in region I generate forces on atoms of the transition region (II). LGF removes the forces on region II by adding corrective displacements to all atoms. The outermost region (III) acts as a buffer to protect forces in regions I and II from the boundaries of the simulation cell. Atoms in the buffer region are only displaced by the corrective displacements of the LGF update stage. Relaxation in region I (conjugate gradient) and region II (LGF update) is iterated until forces in regions I and II are smaller than a chosen threshold.

First principles calculations are performed with \texttt{vasp}\cite{29, 30}, a plane wave based density functional code using projected augmented wave (PAW) method within generalized gradient approximation (GGA) \cite{31}. The 4s and 3d electrons in Ti are treated as valence electrons. A plane wave energy cut-off of 290 eV ensures energy convergence to 0.05 meV/atom. The k-point mesh consists of 16 k-points along the dislocation line and 1 k-points in each of the orthogonal directions in the plane perpendicular to the threading direction. This k-point mesh with Methfessel-Paxton smearing of 0.2 eV gives an energy accuracy of 0.1 meV/atom for bulk Ti. The screw dislocation supercell has 621 (I:41, II:196, III:384) atoms. We modeled the same screw dislocation in a 882 (I:162, II:286, III:434) atom supercell with MEAM instead of DFT.

Figure 3.1 shows the simulation cells used in DFT and MEAM calculations. The MEAM
supercell is terminated in vacuum. Classical potential relaxations are done using LAMMPS package[32]. Since we are interested in the solution only in regions I-III, including a vacuum region in DFT calculations is very inefficient. Also, the electrons tend to form a charge dipole at the metal surface and create image forces in region III. In case of screw dislocations, a periodic simulation simulation cell with domain boundaries at the edges of the cell can be used instead. Using domain boundaries lead to smaller charge density perturbations and smaller cell sizes[33].

3.2 Stacking fault energies

Prismatic stacking fault is the lowest in energy and has a geometry important in the dislocation core structure and mobility in Ti. In hcp structure, prism planes are separated by a/3 or 2a/3. Therefore, two types of prismatic stacking faults are possible: the “easy” and “hard” stacking faults which are created between a widely-spaced or a closely-spaced pair of prism planes respectively and both appear in the dislocation core. Figure 5.4 shows the generalized stacking fault energy (SFE) surface for easy prismatic stacking fault in Ti from DFT and MEAM. The generalized stacking fault energy for the prism plane is defined by displacing a single (10¯10) prismatic plane by a linear combination of [0001] and 1/3 [1¯210]. The faulted geometry is allowed to relax in the [10 ¯10] direction. Repeating this procedure for various displacement vectors gives the energy-displacement or the gamma surface. Our results show that MEAM stacking fault energy values generally agree well with those obtained from DFT. Stacking fault displacements along [1210] appear in the 1/3 ⟨1210⟩ screw dislocation core. Note that 1/6 [1210] is a local minimum (γ = 0.220 J/m²) with DFT and a saddle point (γ = 0.297 J/m²) with MEAM. Table 5.4 compares DFT and MEAM stacking fault energies at representative points. Easy and hard prismatic SFE and pyramidal SFE are evaluated at 1/6 [1210]. DFT and MEAM hard prismatic stacking fault energies are five times higher than the corresponding easy prismatic and pyramidal stacking fault energies.
Figure 3.1: Simulation cells used in DFT and MEAM calculations. Gray, blue and black correspond to regions I, II and III respectively. The DFT supercell has domain boundaries at the edges of the periodic cell. The MEAM supercell is embedded in vacuum and is not repeated in the plane perpendicular to the dislocation line. Both cells are periodic along the dislocation line into the plane of view along [1210].

Note that with DFT, basal I2 stacking fault energy is higher than the easy prismatic while with MEAM, basal SFE is the smallest.

Figure 3.3(a) shows the projection of the (10\bar{1}1) pyramidal gamma surface computed by MEAM. The fault displacement vector $\vec{t} = 1/2 [\bar{1}012] + 1/6 [1210]$ corresponds to a lattice
Figure 3.2: Generalized stacking-fault energy surface for (10\bar{1}0) prism plane in Ti from (a) DFT and (b) MEAM. Stacking fault displacements along [1\bar{2}10] appear in the 1/3(\bar{1}210) screw dislocation core. The point corresponding to 50% slip along [\bar{1}210] direction is a local minimum with $\gamma = 0.220 \text{ J/m}^2$ in (a) and a saddle point with $\gamma = 0.297 \text{ J/m}^2$ in (b).

Figure 3.3: Projection of the (10\bar{1}1) pyramidal plane generalized stacking fault energy for MEAM (a) and its cross section along 1/3[\bar{1}210] direction for MEAM and DFT (b). The white square is located at 1/2[\bar{1}012] + 1/6[\bar{1}210] which correspond to a zero SFE value. (b) shows the MEAM and DFT values of the stacking fault energy in the pyramidal plane along the white arrow.

vector and consequently gives a zero stacking fault energy (white square in Figure 3.3(a)). To compare with DFT, we computed the pyramidal stacking fault energy along the path
shown by a white arrow in Figure 3.3(a). Figure 3.3(b) shows that MEAM pyramidal SF energies are lower than DFT values.

Table 3.1: Stacking fault energies from DFT and MEAM. Easy and hard prismatic and pyramidal stacking fault energies $\gamma_{\text{easy}}$, $\gamma_{\text{hard}}$, and $\gamma_{\text{pyram}}$ are evaluated at $1/6[1\overline{2}10]$. $\gamma_{I2}$ corresponds to the metastable intrinsic stacking fault on the basal plane.

<table>
<thead>
<tr>
<th>(J/m$^2$)</th>
<th>$\gamma_{\text{easy}}$</th>
<th>$\gamma_{\text{hard}}$</th>
<th>$\gamma_{\text{pyram}}$</th>
<th>$\gamma_{I2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>0.220</td>
<td>1.185</td>
<td>0.689</td>
<td>0.292</td>
</tr>
<tr>
<td>MEAM</td>
<td>0.297</td>
<td>1.495</td>
<td>0.443</td>
<td>0.172</td>
</tr>
</tbody>
</table>

### 3.3 Dislocation core structures

Figures 3.4 and 3.5 show the core structure of the $1/3[1\overline{2}10]$ screw dislocation in Ti obtained from DFT and MEAM at two initial positions for the origin of the elastic solution for a perfect screw dislocation. The red squares indicate the initial centers; while the long-range solution is the same, there can be variations in the relaxed core geometry. Tarrat et al. considered five initial positions and reported the geometry of two different core structures. They compared the DFT core structures to the results from a EAM potential. In one case, both EAM and DFT gave a symmetric prismatic core. The other initial position caused the EAM core to spread on the basal plane while DFT showed a combination of prismatic and pyramidal spreading[27]. We consider positions 3 and 5 from[27] which correspond to our position 1 (Figure 3.4) and position 2 (Figure 3.5) respectively.

Figure 3.4(a),(b) and Figure 3.5(a),(b) show the differential displacement (DD) maps[34] of the cores. Each circle is a row of atoms along the dislocation threading direction (i.e. out of the plane), where an arrow between two rows of atoms corresponds to the relative displacement between the rows compared with the perfect crystal. The length of the arrow scales as the magnitude of the relative displacement between atom rows. A closed triad of arrows shows a Burgers vector displacement. Our results confirm the existence of metastable
core structures depending on the initial position of the dislocation line. In addition, MEAM and DFT core geometries agree very well in each case. We compute the excess energy between the two cores by subtracting the energies of region I atoms in each core using MEAM. We find that core 2 is about 12 meV/b higher in energy where b is the magnitude of the dislocation’s Burgers vector. Also, we study the structure of the partial dislocations for both cores. Figure 3.4 and Figure 3.5 (c)-(h) show the Nye tensor distribution[35] superimposed on the DD maps of the dissociated partials for cores 1 and 2 respectively. Color contours in Figure 3.4 and Figure 3.5 show the linear interpolation of Nye tensor density following the method of Hartley and Mishin[35]. Nye tensor’s screw component and edge components on basal and prism planes are plotted in each case. Partial dislocations are identified by local extrema in the Nye tensor distribution or a closed triad of atoms in DD maps. In these maps closed triads represent a half Burgers vector to identify the partials. Core 1 is dissociated into two screw character partials separated by less than 2c on the prismatic plane. Both MEAM and DFT give the same compact core with symmetrical prismatic spreading. Core 2 partials have both screw and edge character and form a non-planar core structure. Note that position 1 is located between a widely-spaced pair of prism planes and exactly on a basal plane. In this case, dislocation displacements tend to create an easy prismatic stacking fault in the core without a possibility of displacing basal planes. The low value of $\gamma_{\text{easy}}$ allows these displacements and creates a symmetric prismatic core. On the other hand, position 2 is located between closely-spaced prismatic planes and halfway between two basal planes. Here, the dislocation displacement field induces a hard prismatic stacking fault which requires a very high energy according to Table 5.4. Therefore, a combination of a basal followed by an easy prismatic fault creates the non-planar core.

We investigate the behavior of screw cores under applied stress. Since the prismatic plane is the dominant slip plane for the glide of the screw dislocation, we compute the stress required to move the dislocation by applying strain on the prism planes. In order to find the minimum stress, dislocation core geometry should be relaxed under several incrementally
Figure 3.4: Core structure of the dissociated 1/3 [1210] screw dislocation at position 1 (the lower energy core between two metastable configurations). The red square shows the origin of the elastic solution for the perfect dislocation. Contour plots of the screw and edge components of the Nye tensor are plotted. DD maps of the dissociated dislocations are superimposed. Partial dislocations are identified by local extrema in the Nye tensor distribution or a closed triad of atoms in DD maps. The core spreading onto the prism planes is similar between DFT and MEAM. Note the change of scale from screw component to edge component plots.

increasing strain values. These are computationally expensive calculations from DFT. On the other hand, MEAM potential predicts the stacking fault energies and dislocation core
Figure 3.5: Core structure of the dissociated 1/3 [1210] screw dislocation at position 2 (the higher energy core between two metastable configurations). The red square shows the origin of the elastic solution for the perfect dislocation. Contour plots of the screw and edge components of the Nye tensor are plotted. DD maps of the dissociated dislocations are superimposed. Partial dislocations are identified by local extrema in the Nye tensor distribution or a closed triad of atoms in DD maps. Both DFT and MEAM show similar non-planar core spreading. Note the change of scale from screw component to edge component plots.

geometries very well while being computationally cheap and thus is used to perform stress calculations. We found that core 1 starts to move under $\epsilon = 0.005$ prismatic strain. The
Figure 3.6: Screw dislocation MEAM cores under strain on the prism plane. (a) and (c) show cores 1 and 2 under zero applied strain respectively. Core 1 moves under $\epsilon = 0.005$ prismatic strain (b) while core 2 reconstructs into core 1 and moves at $\epsilon = 0.007$ (d).

Higher energy core 2 reconstructs into the lower energy core 1 and begins to move on the prismatic plane at $\epsilon = 0.007$. Since core 2 is non-planar, we also put the cores under strain $\epsilon'$ on the pyramidal plane for testing purposes. Core 1 begins to slip on the prism plane under $\epsilon' = 0.005$ pyramidal strain. At $\epsilon' = 0.012$ core 2 transforms into core 1 again and starts to slip on the prism plane. For completeness, we applied basal strains $\epsilon''$ to the cores as well. Core 1 starts to move along prismatic planes at $\epsilon'' = 0.012$ and Core 2 again transforms into Core 1 under $\epsilon'' = 0.015$ and moves on prismatic planes. This suggests that Core 1 is the ground state and is the dominant core configuration, even under stress. Core 2 is not expected to impact mechanical behavior of Ti; it appears to be a metastable “artifact” of relaxing the dislocation from the initial displacements due to anisotropic elasticity theory for a perfect dislocation.
3.4 Summary

We investigated the existence of metastable core structures for a 1/3[1210] screw dislocation in Ti using DFT and MEAM potential in a flexible boundary conditions framework. We confirmed that the metastable cores are not artifacts of the boundary conditions or the computational method. In addition, we studied the behavior of the two cores under applied strain and found that the higher energy core always reconstructs into the lower energy one independent of the applied stain direction. We did not observe the transformation from low to high energy core which rules out the possibility of having transition states. Both dislocations continued to slip on the prism plane under sufficient strain. We also showed that the MEAM potential agrees well with DFT in computing stacking fault energies and dislocation core structures. Note that although MEAM basal stacking fault energy is
lower than the prismatic value, the dislocation core structures still agree with DFT closely. Agreement of MEAM and DFT is an important result suggesting that the MEAM potential is a reliable approximation for DFT in modeling dislocations in Ti and can be used in calculations that require large numbers of atoms beyond the scope of DFT.
Chapter 4

Interaction of a Ti (10\overline{1}2) twin boundary with a screw dislocation

In this chapter, we apply the method introduced in Chapter 2 to the case of a Ti (10\overline{1}2) twin boundary interacting with a [1\overline{2}10] screw dislocation. We start by construction of the dislocation-free twin geometry and calculate the corresponding ILGF. We apply the computed ILGF to simulate the dislocation/boundary interactions by flexible boundary conditions with the Ti MEAM potential and density functional theory. We start with MEAM potential in order to be able to compare our flexible boundary condition results with those obtained from traditional fixed boundary conditions. We also use the MEAM potential to compute the stress required for moving the dislocation through the boundary and show that the twin boundary is acting as a barrier to the dislocation slip. Achieving the critical stress involves several simulations with incrementally increasing applied stress which is not practical to do with DFT. Finally, we study the core geometries using DFT which marks the first DFT study of dislocation/boundary interactions. The screw dislocation is shown to be trapped in the twin boundary with a compact core.

4.1 Construction of the (10\overline{1}2) twin boundary

Following the notation introduced in Eqn. (2.3) for the twin boundary, $F^\lambda\mu$ and $M^\lambda\mu$ matrices are

$$F^\lambda\mu = I, \quad M^\lambda = \begin{bmatrix} 2 & 0 & 0 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix}, \quad \text{and} \quad M^\mu = \begin{bmatrix} 2 & 0 & 0 \\ 1 & 1 & 0 \\ -1 & 0 & 1 \end{bmatrix}. $$

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The twin boundary is defined by \( \vec{t}_1 = \sqrt{3}a^2 + c^2 \hat{x} \) and \( \vec{t}_2 = a\hat{y} \) where \( a \) and \( c \) are the hcp lattice constants in Ti. Lattice \( \mu \) is the reflection of \( \lambda \) about the twin boundary plane. Figure 4.1 shows the MEAM and DFT simulation cells for computing the relaxed geometry. In both cases, periodic boundary conditions are applied in the interface plane. With MEAM, fixed boundary conditions are used in the direction perpendicular to the interface by freezing a few layers of atoms at the top and bottom of the cell. These layers are disturbed by the presence of free surfaces at the top and bottom and have non-zero forces at the beginning. Size of these frozen regions is controlled by the MEAM potential cut off distance of 5.5\( \text{Å} \). The geometry is allowed to relax until zero forces are achieved. We observe that MEAM potential breaks the mirror symmetry of the twin boundary. With DFT, the initial structure is constructed from the perfect Ti lattice. Then, the twin boundary is generated by applying mirror symmetry operation. In order for periodic boundary conditions to be valid in the direction normal to the boundary, two twin boundaries are created in the structure. All atom positions and the supercell dimension perpendicular to the twin boundaries are allowed to relax till the forces are smaller than 5 meV/\( \text{Å} \). Previous studies have shown that relaxing all degrees of freedom gives the accurate energies[4]. Bulk geometry is retrieved away from the interface and lattice structures on opposite sides of the boundary are related through mirror symmetry.

To help identify the structure of the interface region, we define a measure for volumetric strain at each Ti atom site, with respect to the bulk structure, based on averaging the nearest neighbor bond lengths:

\[
e_V(i) = \left( \frac{1}{N_i} \sum_{j=1}^{N_i} r_{ij} - r_0 \right) / r_0
\]

where \( e_V(i) \) is the volumetric strain at site \( i \), \( r_{ij} \) is the bond length between atom \( i \) and its \( j \)th nearest neighbor, \( N_i \) is the total number of nearest neighbors for atom \( i \) and \( r_0 \) is the average bond length in bulk Ti. Figure 4.2 shows the volumetric strain in the twin geometry with respect to bulk Ti. The volumetric strain alternates in sign at the boundary.
Figure 4.1: Simulation cells for construction of Ti (10\bar{1}2) twin boundary with DFT and MEAM. Gray and blue colors distinguish AB stacking in the hcp structure.

and quickly decays to zero away from the boundary. This also provides a geometric measure for the interface thickness which is about 13 atomic layers wide from Figure 4.2.

4.2 Lattice Green’s function for Ti (10\bar{1}2) twin boundary

We use the method introduced in Section 2.3 to compute the ILGF for a Ti lattice containing (10\bar{1}2) twin boundary. In addition, the notation of Section 2.3 is used throughout this
Figure 4.2: Volumetric strain in Ti (10\(\bar{1}2\)) twin boundary. Twin geometry and basal planes orientation are shown. Volumetric strain is highest at the boundary with alternating signs and is small elsewhere. Zero strain means that bulk geometry is recovered.

We test our Green’s function by computing the force constant matrices \(\overline{\mathbf{D}}(\mathbf{R})\) using \textsc{lammps} package\[32\] with the Ti MEAM potential and the maximum cut off distance of 5.5\(\text{Å}\)[28]. We start the verification using a classical potential because these computations are quick and allow us to focus on isolating and fixing the possible errors in the method. Besides, the general method makes no assumptions about the type of inter-atomic interactions. The partial FT in Eqn. (2.4) is done by a uniform discrete mesh of 40 \(k_x\) points over \((-\pi/a_0, \pi/a_0)\) where \(a_0\) is the periodicity of the geometry in \(x\) direction. The same \(k_x\) values must be used in (+), (−) and (I) regions. Limits of \(k_z\) in Eqn. (2.11) are then chosen so that the equivalent of \(A_{BZ}\) is covered in both (+) and (−). The first three integrals in Eqn. (2.12) are evaluated numerically over a uniform \(k_z\) mesh of 160 points at each \(k_x\). For \(|k_x| < 0.1\pi/a_0\), the density of \(k_z\) mesh is doubled to insure the convergence around the discontinuity at \(\Gamma\)-point[24, 25].

To determine the convergence with k-points, we computed the Green’s function \(G(0; z_l, z_l')\) for a \(l\) in (I) and another in (−) with different k-point meshes. Table 4.1 shows that our choice of k-points produces numerical errors of less than 2%.

Figure 4.3 shows the supercell with bulk (+/−) and interface (I) divisions and the paths along which LGF is evaluated for testing purposes. \(G_{xx}(x_l - x_{l'}; z_l, z_{l'})\) is plotted along a vertical and six horizontal paths in the supercell where the reference atom \(l'\) is the first atom.
Table 4.1: Green’s function $G(0; z_l, z_l)$ with different k-points meshes for atoms in interface (I) and bulk (−) regions. The Green’s function is in $\text{Å}^2/\text{eV}$. The $40 \times 160$ mesh produces numerical errors of less than 2%.

<table>
<thead>
<tr>
<th>$(k_x \times k_z)$</th>
<th>(I) $G_{xx}$</th>
<th>$G_{yy}$</th>
<th>$G_{zz}$</th>
<th>(−) $G_{xx}$</th>
<th>$G_{yy}$</th>
<th>$G_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$20 \times 80$</td>
<td>0.1778</td>
<td>0.0880</td>
<td>0.3114</td>
<td>0.1223</td>
<td>0.2993</td>
<td>0.1808</td>
</tr>
<tr>
<td>$40 \times 160$</td>
<td>0.1832</td>
<td>0.0885</td>
<td>0.3106</td>
<td>0.1233</td>
<td>0.3000</td>
<td>0.1794</td>
</tr>
<tr>
<td>$80 \times 320$</td>
<td>0.1852</td>
<td>0.0887</td>
<td>0.3105</td>
<td>0.1232</td>
<td>0.3000</td>
<td>0.1794</td>
</tr>
</tbody>
</table>

Figure 4.3: [1210] projection of the Ti supercell containing a (1012) twin boundary. The supercell is divided into bulk (+/−) and interface (I) regions. $y$ axis is pointing into the plane. Variation of the $G_{xx}$ component of the lattice Green’s function is plotted along six horizontal and one vertical paths. The reference atom $(x', z')$ is the first atom in horizontal paths and the atom right below the interface in the vertical path. Bulk behavior along the $z = z'$ paths is recovered away from the interface. The long range behavior of the LGF matches the EGF along the vertical path, while deviating for small $z - z'$.

$(x_l = 0)$ in the horizontal paths and the atom right below the interface in the vertical path.

Bulk response along $z_l = z_l'$ paths is gradually recovered as the paths get farther from the
interface and closer to the (−) region. In addition, it is worth noting that paths 1 and 2 are located in bulk and interface regions respectively. Therefore, the LGF is obtained from the bulk lattice Green’s function along path 1 and from the ILGF method along path 2. The good agreement between the response of these two paths verifies the smooth transition between the bulk-interface divisions. $G_{xx}(x - x'; z, z')$ as a function of $z$ is also plotted for atoms along the vertical line shown on the supercell in Figure 4.3. The reference atom is located on the vertical line at $x_v = x', z_v = z' = -1.413\text{Å}$ which is right below the interface. The long range behavior of the ILGF matches the elastic Green’s function (EGF).

Finally, we apply the ILGF method to compute the Green’s function for the DFT (10Ì2) twin boundary. Partial FT k-points mesh is the same as one we used with MEAM. The only difference is that the force constant matrix $D(\vec{R})$ is computed by DFT. Figure 4.4 shows nonzero components of the LGF along horizontal paths for adjacent interface and bulk layers computed by DFT. The horizontal paths are the same as red and black paths in Figure 4.3. Figure 4.4 verifies the smooth transition between bulk and interface response in the DFT calculations. We use the Green’s function to model an isolated dislocation interacting with the boundary in the following section.

4.3 Screw dislocation in the twin boundary: Classical potential study

4.3.1 Core geometry

We use a 652 atom supercell with 73 atoms in region I, 219 atoms in region 2 and 360 atoms in region 3. The number of atoms translates to radii of $R=5b$, $5b < R \leq 9b$ and $9b < R \leq 12b$ for regions I, II and III respectively; $b$ is the magnitude of the Burgers vector equal to $|\vec{t}_2|$ (Section 2.3) which is also the periodicity along the threading direction in case of the [Ì2Ì0] screw dislocation. To verify the results, we modeled the same dislocation/interface
Figure 4.4: Nonzero components of the LGF along horizontal paths for adjacent interface and bulk layers (red and black paths in Figure 4.3) computed using DFT. A smooth transition between bulk and interface response is verified.

geometry with fixed boundary conditions using supercell radii of 12–50b. Outer layers of atoms in a region of width 3b are frozen to elastic displacement field of the screw dislocation and the inner atoms are relaxed through the conjugate-gradient method using Ti MEAM. Large supercells are required to minimize the effect of free surfaces created by the fixed boundaries.

Figure 4.5 shows the differential displacement maps[34] of the screw dislocation core structure in the Ti (10\overline{1}2) twin boundary obtained by fixed and flexible boundary conditions. A closed triad of arrows shows a Burgers vector displacement. Fixed boundary conditions result in a finite-size effect that is removed with flexible boundary conditions, or with significantly larger calculations. For supercell radii $R \leq 17b$ ($R=17b$ corresponds to 1312 atoms relaxed), the dislocation center is trapped in the interface while for $R$ be-
Figure 4.5: Differential displacement maps of a screw dislocation core in Ti (10\overline{1}2) twin boundary computed by fixed and flexible boundary conditions. Fixed boundary conditions cause a supercell size effect which is evident from different core structures for radius $R$ smaller or larger than 17b (1312 atoms relaxed). Flexible boundary conditions give the same core structure as the large fixed boundary conditions supercell with significantly fewer atoms required to relax by energy minimization (i.e., 73 atoms in region (1) and 652 atoms total).

Between 18 and 50b—corresponding to 1474 and 11364 atoms respectively—the dislocation center moves out of the interface towards the bottom lattice. This is possible due to the broken mirror symmetry at the twin boundary for this MEAM potential. The core structure from flexible boundary conditions is in good agreement with large fixed boundary conditions results—hence the correct structure can be obtained using flexible boundary conditions with significantly fewer atoms than with fixed boundary conditions. In addition, there is no way to obtain the critical supercell size for fixed boundary conditions other than performing a series of simulations with different sizes and detect the one where a permanent core geometry change happens.
4.3.2 Behavior under applied stress

We study the behavior of the screw dislocation core at the twin boundary under applied stress. Stress is a continuum concept inherently and its definition at atomic scale is subject to ambiguity. On the other hand, strain has a geometric definition and depending on its definition can be applied to the points of a discrete lattice. We apply a uniform small strain field in a Lagrangian framework to measure the mobility of the screw dislocation at the boundary. In addition, we observe the slip path of the dislocation as it passes through the twin boundary under sufficient applied strain. Applying a strain field to the hcp lattice requires special care due to the internal relaxations explained in Appendix A.

At the (10 12) twin boundary, atoms are arranged at narrow and wide spaces as depicted in Figure 2.3c. In Figure 4.5 calculations, the dislocation line is centered in between a narrowly spaced pair of atoms at the boundary called “core N”. Choosing the wide space as the origin for the dislocation gives a different core geometry: core W. We calculate the optimized core geometry in both cases and subject them to incrementally increasing strain fields.

Figure 4.6 shows core N under $\epsilon_{xy}$ and $\epsilon_{yz}$ strains. The $xy$ is the twin boundary surface with $z$ along the plane normal. Dislocation line lies along $y$ direction. $\epsilon_{xy}$ and $\epsilon_{yz}$ have components along the basal and prismatic planes on each side of the boundary. The orientation of crystal coordinates and the reference coordinates is shown in Figure 4.6. The angle between basal planes and the twin boundary which is equal to the angle between $x'(x'')$ and $x$ is $\theta = \arctan(c/\sqrt{3}a)$. Given the fact that $c/a$ ration for Ti is 1.596 from MEAM, strain tensor can be rotated as

$$\epsilon_{xy} = 0.735\epsilon^p - 0.677\epsilon^b, \epsilon_{yz} = 0.735\epsilon^p + 0.677\epsilon^b$$

with $\epsilon^b$ and $\epsilon^p$ denoting basal and prismatic components of the strain tensor in the top crystal. The strain components in the bottom crystal follows from a mirror symmetry operation on
Figure 4.6: Screw dislocation— with origin in a narrow space (core N) at the twin boundary— under applied strain in the depicted coordinate frame. Outlines of the (10 12) twin boundary and the hexagonal hcp cell in the top and bottom lattice are shown. Dislocation line lies along the y (i.e [1 210]) direction. Both strains have components along the basal and prismatic planes. Red arrows show the slip path of the dislocation under sufficient strain.

the top crystal. At zero strain, the screw dislocation is located below the boundary due to the fact that the MEAM potential breaks the mirror symmetry of the twin. The screw dislocation first moves towards the twin boundary along the prism planes under $\epsilon_{xy} = 0.012$. Increasing $\epsilon_{xy}$ and $\epsilon_{yz}$ moves the dislocation along the prismatic and basal planes of the upper lattice respectively.

Figure 4.7 shows core W under $\epsilon_{xy}$ and $\epsilon_{yz}$ strains. In this case, the dislocation is trapped in the twin boundary under zero strain. Applying sufficiently large $\epsilon_{xy}$ moves the dislocation
Figure 4.7: Screw dislocation– with origin in a wide space (core W)– under applied strain in the depicted coordinate frame. Outlines of the twin boundary and the hexagonal hcp cell in the top and bottom lattice are shown. Notations are consistent with Figure 4.6.

along the prismatic planes of the upper lattice while $\epsilon_{yz}$ directs the slip path towards the basal planes of the bottom lattice. In addition, we applied a strain on the prism planes of the top lattice and obtained a critical value of 0.010 and 0.018 for cores N and W respectively. These values are higher than $\epsilon_{\text{bulk prism}} = 0.005$, the prismatic strain required to move the screw dislocation in bulk Ti. Therefore, the twin boundary is acting as a barrier to the motion of the screw dislocation.

Serra and Bacon studied the interaction between a screw dislocation and (10\(\overline{1}2\)) twin
boundary for model hcp systems using a many-body interatomic potential of the Finnis-Sinclair type for Ti[5]. This potential predicts two core structures for the screw dislocation in bulk Ti: prism and basal cores. In Chapter 3, we showed that only a symmetric prismatic core needs to be considered in studies of screw dislocations in bulk Ti. The the prism core is initially located away from the twin boundary for glide on both narrow and wide prismatic slip systems. The dislocations move towards the boundary under sufficient $\epsilon_{xy}$ and $\epsilon_{yz}$ strains and require more strain to pass through the boundary. Core N continues to glide on basal planes on the opposite side of the boundary (transmission) under $\epsilon_{xy} = 0.018$ and on the basal planes of the initial side (reflection) under $\epsilon_{yz} = 0.025$. On the other hand, core W glides on prism planes of the opposite side under $\epsilon_{xy} = 0.021$ and basal planes of the initial side under $\epsilon_{yz} = 0.01$. The strain values reported are the magnitude of the strain component. The sign is determined by the sense of the dislocation so that it starts to move towards the boundary at the beginning. They also applied a strain resolved on the prism planes where the dislocation is originally located and observed that both core N and core W became trapped in the boundary and required a critical value of $\epsilon_c = 0.013$ and $\epsilon_c = 0.022$ to pass through. The above results indicate that the twin boundary acts as a barrier to the dislocation slip.

Our results agree with[5] qualitatively in the sense that in both cases twin boundary acts as a barrier to slip of the dislocation and that dislocation cross-slips at the twin boundary. However, there are some disagreements in the choice of slip planes after dislocation leave the boundary. For core N, we observe transmission from prism to prism under $\epsilon_{xy}$ and prism to basal under $\epsilon_{yz}$ while Serra and Bacon reported a transmission from prism to basal under $\epsilon_{xy}$ and reflection from prism to basal under $\epsilon_{yz}$. Our results for core W show a transmission from prism to prism under $\epsilon_{xy}$ and a reflection from prism to basal under $\epsilon_{yz}$ compared to transmission from prism to prism and reflection from prism to basal under $\epsilon_{xy}$ and $\epsilon_{yz}$ predicted in[5].
4.4 Screw dislocation in the twin boundary: DFT calculations

DFT calculations are performed with vasp using PAW method within GGA approximation [31]. The 4s and 3d electrons in Ti are treated as valence electrons. A plane wave energy cut-off of 290 eV is used throughout the calculations. The supercell has 828 (I:72, II:264, III:492) atoms. A k-point mesh of $1 \times 1 \times 16$ is used with 16 k-points along the threading direction of the dislocation.

![Vacuum Simulation Cell](image)

Figure 4.8: Flexible boundary conditions simulation cell for dislocation/boundary geometry. Grey, cyan and black distinguish regions I, II and III which are embedded in vacuum.

Figure 4.8 shows the simulation cell used in flexible boundary conditions modeling of dislocation/twin boundary geometry. In order to isolate the geometry from its periodic images, we need to embed the regions in vacuum. The size of the vacuum region is determined by the distance over which charge density decays. The vacuum region should be large enough so that no charge interference is observed at the periodic boundaries and is determined
Figure 4.9: Charge density near a free surface in Ti. A $1 \times 1 \times 10$ supercell is used with a vacuum region of $13 \ c$ adjacent to the outermost basal planes. Only a section of the cell near the free surface is shown. Color code shows the distribution of the electronic charge density in logarithmic scale.

from a separate free surface calculation. In the case of PAW Ti, charge density typically drops several orders of magnitude over a distance of $2c$. Figure 4.9 shows the charge density distribution near a free surface on the basal planes.

We start by displacing all of the atoms according to the anisotropic elasticity solution for the displacement field of a screw dislocation at zero distance from the interface[36]:

$$u_z(x, y) = \begin{cases} \frac{b}{2\pi} \arctan \frac{C_{46}x - C_{44}y}{\sqrt{C_{44}C_{66} - C_{46}^2}} , & y \geq 0 \\ \frac{b}{2\pi} \arctan \frac{-C_{46}x + C_{44}y}{\sqrt{C_{44}C_{66} - C_{46}^2}} , & y < 0 \end{cases}$$

where the twin boundary is defined by $x$ and $z$, dislocation line is along $z$ and $y$ is normal to the twin boundary. $C_{ij}$ are the elastic constants of the top lattice in the chosen Cartesian coordinates. Elastic constants of the bottom lattice is given by a mirror operation about the twin boundary plane. Two nonequivalent positions for the origin of the displacement field corresponding to core N and core W in Section 4.3 are considered.

Figure 4.10 shows the differential displacements maps for the relaxed core structure of the
dislocation in the twin boundary with two initial positions (narrow and wide sites) for the dislocation line. In both cases, core geometry is compact and confined to the twin boundary. In the narrow site core, comparable differential displacements are observed at the adjacent wide site of the twin boundary.

Figure 4.10: Differential displacements maps of a 1/3 [1210] screw dislocation in Ti (1012) twin boundary with two initial positions for the dislocation line.

Figure 4.12 shows the linear interpolation of the Nye tensor’s density. Differential displacement maps[34] of the core structure are also superimposed. In these maps closed triads represent a half Burgers vector to identify partials. DD maps show two close mirror triads in both cores located immediately above and beneath the boundary. However, Nye tensor distribution does not show separate peaks at these sites. Edge components are an order of magnitude smaller than the screw component for the narrow core and even smaller for the wide core.

In addition, we analyze the core geometry to get the local volumetric strain- a quantity essential in computation of dislocation interactions with solutes. The local volumetric strain at each atomic site in the dislocation geometry is defined from the nearest neighbor positions as[35]

\[
e_V = \left[ \frac{\det \{ \sum_{\mathbf{x}_i} \mathbf{x}_i \mathbf{x}_j \}^1}{\det \{ \sum_{\mathbf{x}} \mathbf{x}_i \mathbf{x}_j \}^1} \right]^{-1} - 1
\]  

(4.1)
Figure 4.11: Core structure of a 1/3 [1210] screw dislocation in Ti (10\12) twin boundary with two initial positions for the dislocation line. Screw and edge components of the Nye tensor is superimposed on the differential displacement maps of the core. Magenta squares show the initial positions of the dislocation line. Note the scale change from screw component to edge components plots.
where $\vec{x}'$ are the vectors from an atom to its nearest neighbors at each site in the dislocation geometry and $\vec{x}$ are the corresponding nearest neighbor vectors in the dislocation-free twin geometry.

Figure 4.12: Local volumetric strain in the dislocation geometry for the wide-site (left) and narrow-site (right) core.

A screw dislocation does not have a far field dilation due to the fact that only shear components of its elastic strain tensor are nonzero. However, we find that there is a significant tensile volumetric strain at the core region. The tensile region of the narrow-site core is more spread out compared to the wide-site core. High volumetric strain spots identify places where solutes have the largest interactions with the dislocation.

### 4.4.1 Density of states

Electronic density of states (DOS) is one of the primary quantities used to describe the electronic structure of a material. DOS gives the number of electronic states per energy interval at each energy level and is averaged over the space for the entire solid. To interpret the effect of changes in environment (i.e., defects), it is often useful to understand the density of states in the vicinity of specific atoms. One standard way to this is to use the local density of states (LDOS) which is the space-resolved DOS defined as the number of electronic states at a certain energy level weighted by the fraction of the total electron density for those states.
within a specified volume around each nuclei. Each LDOS can be further projected onto atomic orbitals of each atom to show each orbital’s contribution.

First, we quantify the effect of strain on the LDOS by applying volumetric and shear strain of 1% to a bulk Ti unit cell. The calculations are done using a $16 \times 16 \times 12$ k-points mesh. Figure 4.13 shows that the bulk LDOS is not changed by a volumetric or shear strain.

![Figure 4.13: Effect of strain on electronic density of states for s, p and d states in bulk Ti. A 1% volumetric strain ($e_{V}$) and shear strain ($e_{23}$ in the hcp cell coordinates) are applied to the unit cell in separate calculations. Energies are shifted with respect to the Fermi energy.](image)

Next, we study the LDOS for chosen atoms in the twin geometry before introducing the dislocation and compare with bulk. These calculations are done with the DFT supercell in Figure 4.1 and a k-points mesh of $6 \times 1 \times 16$ and a smearing of 0.2 eV. We label the chosen atoms in terms of the number of atomic planes from the boundary. Two nonequivalent atom types at the boundary (zero distance) are named 0A and 0B. We choose both atom types
Figure 4.14: LDOS for twin boundary geometry. Density of s, p and d states of atoms shown in the legend is plotted. DOS for s states remains almost the same throughout the geometry. The biggest discrepancy occurs between the p and d states of twin boundary atoms and bulk. Note the scale change in the d plots. Energies are shifted with respect to the Fermi energy.

A and B at the boundary and the atom immediately below the narrow site of the twin boundary. An atom far from the boundary is chosen as a bulk reference. Chosen atoms and their corresponding LDOS is shown in Figure 4.14. Density of the s states remains almost
the same for atoms near the twin boundary and the bulk atom. The biggest discrepancy occurs between the p and d states of twin boundary atoms and bulk.

Figure 4.15: Electronic density of states for Ti s, p and d states in and outside of the screw dislocation core trapped at (10\overline{1}2) twin boundary. Relative positions of the chosen atoms in the twin geometry are shown. C and TB label atoms inside the dislocation core and outside the core and close to the twin boundary respectively. The biggest discrepancy occurs in the density of d states inside the dislocation core. Note the change of scale in the d plots. Energies are shifted with respect to the Fermi energy.

To understand the changes in LDOS caused by the dislocation, we compute the local density of states for the twin boundary atoms in Figure 4.14 in the core of dislocation and compare with equivalent atoms outside the core. Figure 4.15 shows the density of states plots and the choice of atoms. Effect of the dislocation core is specially revealed by comparing the dashed and solid lines of the same color in Figure 4.15. The change is more pronounced in the density of d states inside the dislocation core. Since, strain does not affect the LDOS, we attribute all of this change to the geometry of the boundary dislocation.
4.5 Summary

We computed the ILGF for a Ti (10\text{I}2) twin boundary with both MEAM potential and DFT and studied the screw dislocation/twin boundary interaction using flexible boundary conditions. MEAM calculations verified that flexible boundary conditions remove the final size effect created by using fixed boundary conditions with significantly fewer atoms. In addition, we studied the behavior of boundary/dislocation under applied stress and confirmed that the screw dislocation cross slips at the twin boundary. The strain required to move the dislocation through the boundary is higher than the Peierls strain, confirming that the twin boundary acts as a barrier to the motion of the dislocation. Finally, we modeled the same dislocation geometry using ILGF method with DFT for the first electronic structure prediction of a dislocation in a boundary. We showed that the screw dislocation was trapped in the boundary with a compact core geometry. The change in density of states near the twin boundary in and out of the dislocation core region was also shown.
Chapter 5

Interaction of oxygen interstitials with lattice faults in Ti

We investigate the interactions of oxygen with (10\(\bar{1}2\)) twin boundary and (10\(\bar{1}0\)) prism plane stacking fault. The energetics of four interstitial sites in the twin geometry are compared with the bulk octahedral site. We show that two of these sites located at the twin boundary are more attractive to oxygen than bulk while the sites away from the boundary are repulsive. We approximate the interaction energy of oxygen with a dislocation in terms of a volumetric size misfit and a chemical misfit manifested in a prismatic stacking fault. We show that oxygen increases the stacking fault energy and therefore is repelled by the faulted geometry. Also, despite zero long-range dilatation in the elastic field of the screw dislocation, there is a weak attraction between oxygen and dislocation inside the core.

5.1 Computational method

DFT calculations of oxygen in Ti are performed with 	exttt{vasp} using PAW method within GGA. Ti 4s and 3d electrons are considered as valence electrons. A plane wave energy cut-off of 500 eV is used throughout the calculations. A k-points mesh of 16\(\times\)16\(\times\)12 with a smearing of 0.2 eV is used for a Ti unitcell and is adjusted for each geometry accordingly. Table 5.1 compares the lattice and elastic constants and planar fault energies obtained from PAW, ultra-soft pseudo potentials (USPP) with p electrons treated as valence and experiments. Lattice parameters and twin boundary energies from PAW and USPP are almost identical. The elastic constants differ within 12\% and the prismatic stacking fault energy is approximately 20\% higher for USPP. Both PAW and USPP agree well with experiments.
Table 5.1: Comparison of lattice and elastic constants and planar fault energies for PAW with USPP and experiments.

<table>
<thead>
<tr>
<th></th>
<th>lattice constants</th>
<th>elastic constants (GPa)</th>
<th>fault energies (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a(A)</td>
<td>c/a</td>
<td>C_{11}</td>
</tr>
<tr>
<td>PAW</td>
<td>2.9197</td>
<td>1.581</td>
<td>169</td>
</tr>
<tr>
<td>USPP</td>
<td>2.9486</td>
<td>1.580</td>
<td>164</td>
</tr>
<tr>
<td>Experiment</td>
<td>2.95</td>
<td>1.587</td>
<td>176</td>
</tr>
</tbody>
</table>

5.2 Twin boundary

Figure 5.1 shows the supercell for modeling the (10\overline{1}2) twin boundary. We choose four interstitial sites (pos 1-4) near the interface to put the oxygen. Pos 0 corresponds to the octahedral site for interstitials in the bulk lattice. To study the effect of periodic images of the oxygen interstitial, we double the original DFT unit cell along [10\overline{1}1] and consider three out of the plane dimensions (a, 2a, 3a) for the supercell along 1/3 [1\overline{2}10] where a=2.948 Å is the lattice parameter. Table 5.2 shows the energy difference between putting oxygen at twin boundary interstitial sites pos 1-4 and the bulk octahedral site pos 0. At each site i, energy difference $\Delta E(pos\ i)$ is defined as $E(pos\ i) - E(pos\ 0)$. For all supercell dimensions, pos 1 and 4 located exactly at the boundary are more attractive for the oxygen than the bulk octahedral site while pos 2 and 3 are repulsive.

Table 5.2: Oxygen energy at twin boundary interstitial sites. Table entries show the energy difference at site i, $\Delta E(pos\ i)$ defined as $E(pos\ i) - E(pos\ 0)$ and are expressed in meV units. For all supercell dimensions, pos 1 and 4 located exactly at the boundary are more attractive for the oxygen than the bulk octahedral site while pos 2 and 3 are repulsive.

<table>
<thead>
<tr>
<th>Dimension along 1/3 [10\overline{1}2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
</tr>
<tr>
<td>pos 1</td>
</tr>
<tr>
<td>pos 2</td>
</tr>
<tr>
<td>pos 3</td>
</tr>
<tr>
<td>pos 4</td>
</tr>
</tbody>
</table>
Figure 5.1: Oxygen sites at the twin boundary. Four interstitial sites (pos 1-4) in the (10\{1\}2) twin geometry are considered and compared with the octahedral site in bulk (pos 0). Interstitials on and below the interface are chosen. Top part of the twin boundary is related to the bottom part by mirror symmetry. Bulk geometry is retrieved away from the interface. To study the effect of periodic images of oxygen interstitial, three supercell dimensions a, 2a and 3a in \(1/3\{1\bar{2}10\}\) direction (out of the plane) are considered where a=2.948 is the lattice parameter of Ti.

Figure 5.2a shows the geometry of three interstitial sites. Pos 0 serves as a baseline for comparison with an attractive site, pos 1 and a repulsive site pos 2. Atoms at both pos 1 (attractive) and pos 2 (repulsive) sites undergo relaxations to approach pos 0 geometry. Figure 5.2b shows the electronic density of oxygen s and p states. Attraction or repulsion of sites are manifested as shifts in the density of states plots.
Figure 5.2: Geometric analysis of pos 0, pos 1 and pos 2 interstitial sites (a) and electronic density of states for oxygen s and p states at each site (b). Pos 0, corresponding to the bulk octahedral site, serves as a baseline for comparison. According to (a) atoms at both pos 1 (attractive) and pos 2 (repulsive) undergo relaxations to approach pos 0 geometry. The numbers in parenthesis show dimensions before relaxation. Distances are in Å. In (b), the zero energy corresponds to the Fermi energy. Attraction or repulsion of sites are manifested as shifts in the density of states plots.

In addition, we can extract some information about the oxygen-oxygen pair interactions at each site by comparing data from different supercells where periodic images of oxygen are located at distances a, 2a and 3a. Table 5.3 shows the change in oxygen binding energy as
the distance between oxygen atoms changes. At each site, the difference in binding energy as oxygen-oxygen distance goes from $d_1$ to $d_2$ is defined as

$$\Delta E^b(d_1, d_2) = [E(S_{d_2} + O) - E(S_{d_2})] - [E(S_{d_1} + O) - E(S_{d_1})]$$

where $S_{d_1}$ and $S_{d_2}$ denote the supercells with dimensions $d_1$ and $d_2$ respectively and $E(S_{d_i} + O)$ is the energy of supercell $S_{d_i}$ with an oxygen at the corresponding interstitial sites. At the bulk site, pos 0, the oxygen binding energy decreases when the distance between oxygen atoms doubles suggesting that there is a repulsive oxygen-oxygen interaction at distance $a$. Also, increasing the distance to $2a$ does not affect the binding energy significantly implying that the oxygen-oxygen interaction is already weak at distance $2a$. This is consistent with a previous study of oxygen-oxygen pair interaction in Ti[37]. At pos 1, distancing oxygen pairs from $a$ to $2a$ costs 37 meV showing an attractive interaction between oxygen pairs at distance $a$. The energy goes down when moving the atoms from $2a$ to $3a$ implying that the interaction is repulsive at $2a$ although the change in binding energy of oxygen pairs is still positive. At pos 2, oxygen pair interactions are repulsive at distance $a$ and attractive at $2a$.

Table 5.3: Change in oxygen binding energy with oxygen-oxygen distance. $\Delta E^b(a, 2a)$ is the difference in binding energy as the oxygen-oxygen separation goes from $a$ to $2a$. The energy values are expressed in meV.

<table>
<thead>
<tr>
<th>pos</th>
<th>$\Delta E^b(a, 2a)$</th>
<th>$\Delta E^b(a, 3a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-117.7</td>
<td>-116.7</td>
</tr>
<tr>
<td>1</td>
<td>37</td>
<td>16.5</td>
</tr>
<tr>
<td>2</td>
<td>-49.1</td>
<td>19.5</td>
</tr>
</tbody>
</table>


5.3 Stacking fault

Figure 5.3 shows the cross section of the (10\bar{1}0) prismatic plane gamma surface along 1/3[\bar{1}210]. Since, prismatic slip is the dominant mode in Ti, prismatic stacking faults are instrumental in studying core structure of dislocations in Ti. DFT calculations give a metastable stacking fault at 50% along 1/3[\bar{1}210]. The fault displacement and the corresponding stacking fault energy are a/2 and 0.220 J/m$^2$ respectively.

![Stacking fault energy graph](image)

Figure 5.3: Cross section of the (10\bar{1}0) prismatic plane gamma surface along 1/3[\bar{1}210] computed by DFT with PAW pseudopotentials. DFT calculations give a metastable stacking fault at 50% along 1/3[\bar{1}210].

Figure 5.4 shows the geometry of an oxygen interstitial in the prismatic stacking fault before and after applying the a/2 displacement along [1\bar{2}10]. Since this is a metastable stacking fault, we allow for relaxations in all directions after introducing the oxygen. Structure of the faulted region locally changes from hcp to a bcc-like structure. Our calculations show that oxygen, initially at the bulk hcp octahedral site, moves to the faulted region bcc octahedral site as shown in Figure 5.4. Since oxygen is an α stabilizer, it is expected to have higher energy in the bcc structure and therefore should increase the stacking fault energy[3]. To quantify the effect of oxygen on the prismatic stacking fault, we used 10\times1\times2 (40 atoms) and 10\times2\times2 (80 atoms) Ti supercells with one and two lattice vectors dimensions along [\bar{1}210] respectively. Using two sizes provides an understanding of the size effect resulted
by having periodic images of the oxygen interstitial. Table 5.4 compares the stacking fault energies before and after introducing the oxygen interstitial to each supercell. Oxygen increases the stacking fault energy as expected. In addition doubling the supercell dimension results in a 6% difference in the computed stacking fault energy value. We also studied the oxygen-oxygen pair interaction at the stacking fault following the method we used for the twin boundary. The oxygen binding energy is defined as

$$E_{\text{bind}}(O) = [E^{\text{fault}}(Ti + O) - E(Ti + O)] - [E^{\text{fault}}(Ti) - E(Ti)].$$

Table 5.4 shows that the oxygen binding energy increases as the oxygen-oxygen distance doubles leading to the fact that oxygen pair interactions at distance $a$ is attractive.

Table 5.4: Effect of oxygen on the stacking fault energy. The prismatic stacking fault energy at 50% along [1210] is calculated for pure Ti and two Ti supercells with an oxygen interstitial. $E_{\text{bind}}(O)$ is equal to $[E^{\text{fault}}(Ti + O) - E(Ti + O)] - [E^{\text{fault}}(Ti) - E(Ti)]$

<table>
<thead>
<tr>
<th></th>
<th>SF energy (J/m²)</th>
<th>$E_{\text{bind}}(O)$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure Ti</td>
<td>0.220</td>
<td>-</td>
</tr>
<tr>
<td>40 Ti+O</td>
<td>0.278</td>
<td>98.84</td>
</tr>
<tr>
<td>80 Ti+O</td>
<td>0.262</td>
<td>145.28</td>
</tr>
</tbody>
</table>

5.4 Screw dislocation

To approximate the volumetric misfit contribution to the interaction energy between an oxygen interstitial and a dislocation, we quantify the change in binding energy of oxygen in Ti as a function of volumetric strain. We take a 4×4×3 Ti supercell with 96 Ti atoms and 1 oxygen atom at an octahedral site and subject it to several tensile and compressive volumetric strains. The change in oxygen binding energy is defined as

$$\Delta E_{\text{bind}}(O; e_V) = [E(96Ti + O; e_V) - E(96Ti + O; 0)] - [E(96Ti; e_V) - E(96Ti; 0)].$$
Figure 5.4: Geometry of an oxygen interstitial in the prismatic stacking fault. Structure of the faulted region locally changes from hcp to a bcc-like structure. Oxygen moves from bulk hcp octahedral site to the bcc octahedral site and increases the prismatic stacking fault energy.

where $E(X; e_V)$ is the energy of a supercell with atoms X under a volumetric strain of $e_V$. Figure 5.5 shows the change in binding energy with volumetric strain.

To determine the dislocation/oxygen interaction energy, we compute the local volumetric strain at the interstitial sites in the dislocation geometry. We choose the minimum energy core for the [1210] screw dislocation in bulk Ti shown in Figure 3.4. Local volumetric strain definition is similar to Eqn. (4.1) repeated here:

$$e_V = \left[ \frac{\det \{ \sum_{x'} x'_i x'_j \}^{1/2}}{\det \{ \sum_{x} x_i x_j \}} \right]^{1/2} - 1$$

with the difference that $\vec{x}'$ and $\vec{x}$ are defined between an octahedral interstitial site and its
Figure 5.5: Change in binding energy of an oxygen interstitial in bulk Ti as a function of volumetric strain.

Figure 5.6: Interaction energy between an oxygen interstitial and screw dislocation in bulk Ti.

nearest neighbor sites in the dislocation and reference geometry respectively. Mapping the change in binding energy with $e_V$ onto the local $e_V$ in the dislocation geometry leads to an interaction energy map between oxygen and the screw dislocation shown in Figure 5.6.
There is no long-range dilation in the screw dislocation’s elastic field. However, there is an attractive interaction of approximately 6 meV inside the dislocation core.

## 5.5 New interstitial sites in the dislocated twin boundary

Figure 5.7 shows the geometry of the twin boundary interstitial cages before and after applying the dislocation displacement field. The atomic positions are obtained from the relaxed dislocation geometry with DFT. Atoms are labeled according to the convention used in the plots of Figure 4.14. Dislocation initial position is half way between 0B and 0A (wide spacing) and the red atom shows the schematic position of oxygen interstitial. The cage containing the dislocation changes drastically with a different number of possible interstitial neighbors. The other cage, located immediately below the boundary, undergoes a shear without any changes in the number of interstitials neighbors.

The ultimate goal is to compute the energetics of oxygen in each of these new sites to obtain the interaction energy between the twin boundary dislocation and oxygen. However, putting the oxygen atom in each of these sites creates an infinite array of oxygen atom images along the dislocation line due the periodic boundary conditions in this direction. One way to approximate the dilute limit is to increase the periodicity in the threading direction. Our calculations of oxygen in Ti twin boundary in Section 5.2 show that changing the distance between periodic images of oxygen affects the energy values significantly. On the other hand, even doubling the dimension of our current dislocation/twin boundary supercell requires considering 1656 atoms. A DFT computation of this size is extremely expensive and not possible with our current computational resources and remains an area of future work.
Figure 5.7: Geometry of the interstitial sites at the twin boundary before and after applying the dislocation displacement field. Red atoms show the schematic positions of an oxygen interstitial. Atoms are labeled according to their distance from the twin boundary; cf. Figure 4.14. The dislocation line lies at the center of the top site which is located at the twin boundary. The dislocation displacement field transforms the initial cage into a more complex one with seven possible oxygen neighbors instead of the original six. The bottom site is located just below the boundary and is merely sheared by the dislocation field without a change in the oxygen neighbors.

5.6 Summary

We studied the energetics of oxygen interstitial interactions with (10\overline{1}2) twin boundary. Four interstitial sites in the twin geometry are compared with the bulk octahedral site. We show that two of these sites located at the twin boundary are more attractive to oxygen than bulk while the sites away from the boundary are repulsive. In addition, we compared the oxygen-
oxygen pair interactions at each site for different distances between periodic images of the oxygen atom. We observed that oxygen pairs repel/attract each other when separated by a single lattice parameter at the bulk/twin boundary site. Moreover, we study the interaction of oxygen with prismatic stacking fault to approximate oxygen-dislocation interaction. We show that oxygen increases the stacking fault energy and therefore is repelled by the faulted geometry and consequently a dislocation core. The volumetric misfit leads to an attractive interaction inside the screw dislocation core which is approximately 5% of the repulsion by stacking fault.
Chapter 6

Conclusion

The objective of this work is to study the interaction between different lattice defects in Ti with DFT. The results can be viewed from two angles: method development and application. We developed a new and direct method to compute the interfacial lattice Green’s function that extends the DFT-flexible boundary conditions methods to study of line defects in interfaces. With this general method, we can now predict the core geometry of line defects near and inside any planar interface with chemical accuracy. The method is applied to the study of a [1\(\bar{2}10\)] screw dislocation interacting with a Ti (10\(\bar{1}2\)) twin boundary. Core geometry of the screw dislocation in bulk Ti and interaction of oxygen interstitials with the twin boundary are also studied.

6.1 Summary of Results

We developed a new computational approach to compute the lattice Green’s function for crystals containing a planar interface for arbitrary force constants and interface orientations. This method is general in the sense that it can consider long-range atomic interactions and reconstructions near the interface. We used this method to study the interaction of a [1210] screw dislocation with a (10\(\bar{1}2\)) twin boundary in Ti. We computed the ILGF for the twin boundary with both MEAM and DFT and applied it to the study of dislocation/boundary interaction in a flexible boundary conditions framework. MEAM calculations verified that flexible boundary conditions remove the finite-size effect created by using fixed boundary conditions and require significantly fewer atoms. In addition, we showed that the screw
dislocation cross slips at the twin boundary under applied stress. Finally, we studied the same system with DFT for the first electronic structure prediction of a dislocation core in an interface. We show that the screw dislocation is trapped in the boundary with a compact core.

We studied the core structure of the $[1\bar{2}10]$ screw dislocation in bulk Ti as a baseline for comparison with dislocation/boundary geometry. We used both MEAM and DFT and confirmed the existence of two metastable core geometries. The metastable cores are not artifacts of the computational method or boundary conditions and depend on the position of the origin for the elastic displacement field of the perfect dislocation. A MEAM potential computed the relative core energies and showed the behavior of both cores under applied stress. We found that the higher energy core always reconstructed into the lower energy one independent of the stress component direction. Transformation from low to high energy core was not observed. Therefore, the higher energy core is not a transition state and future studies only need to consider the lower energy core. The ground state core geometry is compact and dissociates into two mainly screw character partials separated by less than 2c along the prism plane.

We investigated the interaction of oxygen with (10$\bar{1}$2) twin boundary and (10$\bar{1}$0) prismatic stacking fault. Four interstitial sites in the twin geometry are compared with the bulk octahedral site. We show that two of these sites located at the twin boundary are more attractive to oxygen than bulk while the sites away from the boundary are repulsive. In addition, we compared the oxygen-oxygen pair interactions at each site for different distances between periodic images of the oxygen atom. We observed that oxygen pairs repel/attract each other when separated by a single lattice parameter at the bulk/twin boundary site. We approximate the interaction energy of oxygen with a dislocation in terms of a volumetric size misfit and a chemical misfit manifested in a prismatic stacking fault. We show that oxygen increases the stacking fault energy and therefore is repelled by the faulted geometry. Also, despite zero long-range dilatation in the elastic field of the screw dislocation, there is a weak
attraction between oxygen and dislocation inside the core.

6.2 Limitations

Despite the generality of ILGF computation method in considering arbitrary crystal orientations for the interface, the method inherently assumes that the line defect’s threading direction lies in the interface plane. Therefore, problems in which line direction and the interface intersect at a nonzero angle are beyond the scope of the present method. In addition, all of the twin boundary interactions with dislocations or oxygen interstitials are based on the existing twins. While these interactions are essential in understanding twinning growth mechanisms, they do not address the effects of lattice dislocations or oxygen on nucleation of twins. Finally, the interaction between all three defect types—dislocation, twin boundary and oxygen—at the same time is missing from this study. The ultimate goal is to compute the energetics of oxygen in each of the new interstitial sites introduced in Section 5.5 to obtain the interaction energy between the twin boundary dislocation and oxygen. However, putting the oxygen atom in each of these sites creates an infinite array of oxygen atom images along the dislocation line due the periodic boundary conditions in this direction. One way to approximate the dilute limit is to increase the periodicity in the threading direction. Our calculations of oxygen in Ti twin boundary show that changing the distance between periodic images of oxygen affects the energy values significantly.
Appendix A

Internal relaxations in the hcp lattice

In this chapter, we discuss the problem of applying a continuum strain field to a hcp lattice. Applying a homogeneous strain field to multiple atom lattices requires special care. In monoatomic lattices, all of the atoms are equivalent and move according to the displacement field associated with the prescribed homogeneous strain. In the hcp structure, the primitive unit cell consists of two atoms. Displacement fields that break the hexagonal symmetry of the lattice create unbalanced forces that lead to internal relaxations inside a unit cell. We show that ignoring these relaxations affects elastic constant calculations and interferes with the convergence of the flexible boundary conditions methods applied to strained geometries.

A.1 Examples of internal relaxations in hcp Ti

Figure A.1 shows the internal relaxations caused by a uniform $\epsilon_{xy}$ shear strain in a hcp lattice. Solid circles show the initial positions. Blue and red distinguish two nonequivalent types of atoms in the lattice. Empty circles show the atoms displaced according to the strain field. After applying the strain, blue atoms are fixed and red atoms are allowed to relax. Diamond symbols show the atom positions after internal relaxations. For all of the red atoms, the internal relaxation is along y direction under $\epsilon_{xy}$.

In our calculations, there are two types of problems that are greatly affected by internal relaxations: elastic constant computations and flexible boundary conditions for the hcp lattice. Elastic constants are obtained by applying a series of homogeneous strains to a lattice unit cell and obtaining the energy-strain or stress-strain plots. The energy or stress
Figure A.1: Positions of atoms in a hcp lattice under a uniform $\epsilon_{xy}$ shear strain before (circles) and after (diamonds) internal relaxations. Solid circles show the initial positions. Blue and red distinguish two nonequivalent types of atoms in the lattice. Empty circles show the atoms displaced according to the strain field. After applying the strain, blue atoms are fixed and red atoms are allowed to relax. Diamond symbols show the atom positions after internal relaxations.

Value can drastically change if internal displacements are allowed. Table A.1 shows that $C_{11}$ and $C_{12}$ change by relaxing the atomic positions.

Table A.1: Elastic constants for hcp Ti in (GPa) units. MEAM values for elastic constants, with and without allowing the internal relaxations, are compared with the experimental values. Only $C_{11}$ and $C_{12}$ are affected by the internal relaxations.

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEAM (not relaxed)</td>
<td>194</td>
<td>74</td>
<td>72</td>
<td>192</td>
<td>58</td>
</tr>
<tr>
<td>MEAM (relaxed)</td>
<td>174</td>
<td>95</td>
<td>72</td>
<td>192</td>
<td>58</td>
</tr>
<tr>
<td>Experiments</td>
<td>176</td>
<td>87</td>
<td>68</td>
<td>191</td>
<td>51</td>
</tr>
</tbody>
</table>

Magnitude of the internal displacements is comparable to the displacements caused by the homogeneous strain field. We studied the relationship between the internal relaxations and strain for shear strains $\epsilon_{xy}$ and $\epsilon_{yz}$.

Figure A.2 shows the dependence of the internal displacements magnitude on applied
Figure A.2: Internal displacement as a function of the applied strain. The internal shift linearly increases with $\epsilon_{xy}$. This strain breaks the hexagonal symmetry of the lattice. There is no first order linear dependence between the internal relaxations and $\epsilon_{yz}$ that preserves the hexagonal symmetry of the close packed planes.

Shear strains $\epsilon_{xy}$ and $\epsilon_{yz}$. The internal shift linearly increases with $\epsilon_{xy}$. This strain breaks the hexagonal symmetry of the lattice. There is no first order linear dependence between the internal relaxations and $\epsilon_{yz}$ that preserves the hexagonal symmetry of the close packed planes. The linear dependence between the internal displacements and strain is analogous to piezoelectricity where the polarization is $\vec{P} = \mathbf{d} : \sigma$. The piezoelectric modulus $\mathbf{d}$ is a third rank tensor that connects the polarization to the applied stress $\sigma$. The linear dependence of the internal relaxations $\vec{u}^{rel}$ on the strain $\epsilon$ can be expressed via a third rank tensor $\eta$[38];

$$\vec{u}^{rel} = \eta : \epsilon. \tag{A.1}$$

It is interesting to note that the third rank tensor $\eta$ and consequently internal displacements $\vec{u}_r$ are only nonzero in the case of non centrosymmetric lattices such as hcp.

A uniform shear strain creates equal and opposite forces on the two atoms in the hcp forces that tend to cause the internal relaxations. The strain components of a screw dislocation are

$$\epsilon_{xy} = -\frac{b}{2\pi} \frac{\sin(\theta)}{r}, \epsilon_{yz} = \frac{b}{2\pi} \frac{\cos(\theta)}{r}.$$
Figure A.3: Atomic forces in (meV/Å) in the dislocation field before and after applying a corrective internal relaxation displacement field. The small magenta squares show the position of the dislocation. The internal forces are considerable even beyond the nonlinear core region outlined by the black squares. Adding the corrective internal displacements significantly reduce the forces. The linear relationship between strain and internal shifts is not valid inside the nonlinear core. Therefore, the corrective internal displacements obtained from Eqn. (B.1) should not be expected to reduce the forces in the nonlinear region.

As depicted in Figure A.2, $\epsilon_{xy}$ is the dominant strain component in inducing internal shifts. Also, our calculations show that this strain induces the internal relaxations in the y direction which coincides with the dislocation threading direction in Figure A.3. To compute the internal displacement field in response to the dislocation stain field, we calculate the dominant component of $\eta$ (i.e $\eta_{yxy}$). Using Eqn. (B.1) gives

$$\vec{u}_{rel} = 2\eta_{yxy} \epsilon_{xy}.$$

Note that in the general case, other components of the $\eta$ tensor might be required depending on the geometry and the external strain field.

Figure A.3 shows the y component of forces on atoms before and after applying the inter-
nal displacement field. Layers of atoms separated by a $c/2$ distance correspond to different atom types and the internal forces change sign from one atom type to the other. Force magnitudes are considerable even outside the nonlinear core region and reduce significantly after the corrective internal displacements are applied. The linear relationship between strain and internal shifts is not valid inside the nonlinear core. Therefore, the corrective internal displacements obtained from Eqn. (B.1) should not be expected to reduce the forces in the nonlinear region. We found that it is more practical to apply the internal displacements only to the atoms outside the core region due the fact that the invalid additional displacement may affect the core structure. Besides, the nonlinear region is always fully relaxed through energy minimization.

A basic requirement for flexible boundary conditions to work is to begin with zero forces in regions II and III. LGF is computed for the multiple atom lattice and updates are applied to remove any forces that develop in region II only. Therefore, the oscillating forces in region II relax after the first LGF update. However, having nonzero forces built up in region III is violating the assumption that no forces should develop in this region during the relaxation process. We found that ignoring the internal relaxations interferes with the convergence of flexible boundary conditions method in some cases. The problem is especially pronounced in case of applied strains where the strain field – and consequently internal relaxations – do not drop with the distance from the core and are considerable in region III.

Calculation of internal relaxations for the interface geometry requires additional care. The atomic geometry close to the interface is different from that of bulk due to the relaxations near the interface. The relaxations are significant in a few atomic layers and the bulk geometry is retrieved at farther distances. To find the internal displacements in response to a uniform strain, we apply the strain to an interface unit cell. The unit cell consists of one crystallographic repetition along each periodic direction in the interface plane and contains all of the atomic layers in the direction normal to the interface until the geometry is bulk-like. The bulk response is applied to the bulk-like regions. Then, we relax the atomic
positions under the applied strain and index the internal displacements according to the
distance of the atom from the interface. Finally, we map this information to the desired
gometry, calculate the local strain at each atom site and use Eqn. (B.1).

Figure A.4: Effect of internal relaxations on the convergence of the flexible boundary con-
dition method. The method is used to study the response of a screw dislocation in the Ti
(10\bar{1}2) twin boundary (core N) under applied strain. The 1.5 % strain induces shear on the
prismatic planes on lower side of the twin boundary. This strain is not big enough to transfer
the dislocation through the boundary. Changes in maximum force in region II as a function
of number of flexible boundary method cycles is chosen as a measure for convergence. The
method converges after 7 cycles if internal relaxations are applied. Ignoring the internal
displacements breaks the convergence. The geometry does not change in both cases.

Figure A.4 shows an example of the effect of internal relaxations on the convergence
of flexible boundary conditions used in modeling a twin boundary dislocation response to
applied strain. A 1.5 % strain induces shear on the prismatic planes on lower side of the twin
boundary. This strain is not big enough to transfer the dislocation through the boundary.
Maximum force in region II is monitored at the end of each flexible boundary method cycle
and is used as a measure for convergence. The convergence is achieved after 7 cycles if internal
relaxations are applied. However, ignoring the internal shifts breaks the convergence.

A.2 Summary

Displacement fields that break the hexagonal symmetry of the hcp lattice lead to internal relaxations inside a unit cell. We computed the internal relaxations caused by applying a continuum strain field to hcp Ti using MEAM and presented examples of the cases where ignoring these relaxations affected the results. We showed that not allowing for relaxations during elastic constant calculations overestimates $C_{11}$ and underestimates $C_{12}$. In addition, we observed that the internal displacements have a linear relationship with the magnitude of shear strain on the prism planes and a second order relationship with the basal shear strain. Finally, we showed that precluding the internal relaxations lead to a divergence in flexible boundary conditions procedure for strained geometries.
Appendix B

Convergence rate for numerical computation of the lattice Green’s function

The inversion of the force constant matrix for the lattice Green’s function requires Fourier techniques to project out the singular subspace, corresponding to uniform displacements and forces for the infinite lattice. Three different techniques—relative displacement, elastic Green’s function, and discontinuity correction—have different computational complexity for a specified numerical error. We calculate the convergence rates for elastically isotropic and anisotropic cases and compare them to analytic results. Our results confirm that the discontinuity correction is the most computationally efficient method to compute the lattice Green’s function.

B.1 Background

The lattice Green’s function $G^L(\vec{R} - \vec{R}')$ and the force constant matrix $D(\vec{R} - \vec{R}')$ relate the internal displacements $\vec{u}(\vec{R})$ and forces $\vec{f}(\vec{R}')$ of atoms $\vec{R}$ and $\vec{R}'$ of the lattice through $\vec{u}(\vec{R}) = \sum_{\vec{R}'} G^L(\vec{R} - \vec{R}') \vec{f}(\vec{R}')$ and $\vec{f}(\vec{R}) = -\sum_{\vec{R}'} D(\vec{R} - \vec{R}') \vec{u}(\vec{R}')$. Translational invariance of an infinite lattice makes $G^L$ a function of the relative positions of two atoms. Substituting one of the above relations into the other gives $\sum_{\vec{R}'} G^L(\vec{R} - \vec{R}') D(\vec{R}') = -\delta(\vec{R})$, where $\delta(\vec{R})$ is the Kronecker delta function. A constant shift in the atoms positions does not produce internal forces, giving the sum rule $\sum_{\vec{R}} D(\vec{R}) = 0$ and making $G^L(\vec{R})$ the pseudoinverse of $D(\vec{R})$ in the subspace without uniform displacements or forces. Fourier transform of the lattice functions are defined as $G^L(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} G^L(\vec{R})$, $G^L(\vec{R}) = \int_{BZ} \frac{d^3 k}{(2\pi)^3} e^{-i\vec{k} \cdot \vec{R}} G^L(\vec{k})$ for $\vec{k}$ in the Brillouin zone (BZ). The integral can be approximated by a discrete sum of $N_k$ points.
Figure B.1: Integrand of the inverse Fourier transform for (a) LGF, (b) relative displacement method, (c) EGF correction and (d) discontinuity correction at $\mathbf{R} = (1, 1)$. $\mathcal{G}_L^{\bar{k}}$ has a second order pole at the $\Gamma$-point. The relative displacement method avoids the pole by considering only the displacements relative to a fixed point. The EGF correction removes the second order pole by subtracting a cutoff elastic Green’s function. Removal of the pole creates a discontinuity independent of $|\bar{k}|$ at the $\Gamma$-point. The discontinuity correction removes the discontinuity created by EGF correction. The remaining part of the integrand is smooth in the entire Brillouin Zone. The bottom row shows the variation of the integrand as a function of $|\bar{k}|$ when the origin is approached from different angles $\theta = \tan^{-1}(k_y/k_x)$. The discontinuity created at the $\Gamma$-point by the relative displacement method and EGF correction is independent of $|\bar{k}|$ but depends on the direction of approaching the origin. N.B.: the vertical scale changes from LGF to relative displacement and EGF correction to discontinuity correction.

as $\mathcal{G}_L^{\bar{k}}(\mathbf{R}) = \frac{1}{N_k} \sum_{\bar{k}} e^{-i\bar{k}\cdot\mathbf{R}} \mathcal{G}_L^{\bar{k}}$. In reciprocal space, the matrix inverse relation and the sum rule are $\mathcal{G}_L^{\bar{k}} \mathcal{D}(\bar{k}) = 1$ and $\mathcal{D}(\bar{0}) = 0$ respectively. For a single atom crystal basis, $\mathcal{D}(\bar{k})$ expands for small $\bar{k}$ as $\mathcal{D}(\bar{k}) = \sum_{\mathbf{R}} \mathcal{D}(\mathbf{R})[1 - \frac{(\mathbf{R}\cdot\mathbf{R})^2}{2!} + \cdots] \simeq -\frac{1}{2} \sum_{\mathbf{R}} (\bar{k} \cdot \mathbf{R})^2 \mathcal{D}(\mathbf{R})$, due to the inversion symmetry of $\mathcal{D}(\mathbf{R})$. At the $\Gamma$-point, $\mathcal{D}(\bar{k})$ is of the order $k^2$, so $\mathcal{G}_L^{\bar{k}}$ has a second order pole. Due to this singularity, the 3D inverse Fourier transform of $\mathcal{G}_L^{\bar{k}}$ converges very slowly while the 2D version does not converge at all. Different behavior of 3D and 2D integrals lies in the integration factors which are proportional to $k^2$ and $k$ respectively. The 3D integration factor cancels out the second order pole leaving a discontinuity in the $\Gamma$-point that causes a poor convergence. The 2D integrand is still singular which results in a non-convergent integral.
Fig. B.1 shows the relative displacement method, elastic Green’s function correction and discontinuity correction which are used to avoid the singularity in LGF.

### B.2 Relative displacement

Rigid body translations leave the potential energy of the lattice unchanged. Choosing an arbitrary atom as an undisplaced origin for the relative displacements of atoms requires calculation of

\[ G_L^L(\vec{R}) - G_L^L(\vec{0}) = \frac{1}{(2\pi)^3} \int G_E^E(\vec{k}) e^{i\vec{k} \cdot \vec{R}} - \frac{1}{(2\pi)^3} \int G_L^L(\vec{k}) e^{i\vec{k} \cdot \vec{0}} \]

which reduces to

\[ G_L^L(\vec{R}) - G_L^L(\vec{0}) = \int G_L^L(\vec{k})(\cos(\vec{k} \cdot \vec{R}) - 1) d\vec{k}, \tag{B.1} \]

due to the sum rule and inversion symmetry. For small \( k \), \( \cos(\vec{k} \cdot \vec{R}) - 1 \) is of the order \( k^2 \) which cancels out the second order pole in \( G_L^L(\vec{k}) \) leaving a \( \vec{k} \)-direction dependent discontinuity at the \( \Gamma \)-point. The discretized version of eqn. (B.1) is \( \frac{1}{N_k} \sum_k (\cos(\vec{k} \cdot \vec{R}) - 1) G_L^L(\vec{k}) \)[11, 39, 40, 41].

### B.3 Elastic Green’s function correction.

Following the procedure and notations of [24], \( G_L^E(\vec{k}) \) for small \( k \) expands as

\[ G_L^E(\vec{k}) = [\tilde{D}(\vec{k})]^{-1} = k^{-2}[\tilde{\Lambda}^{(2)}(\vec{k})]^{-1} + [\tilde{\Lambda}^{(2)}(\vec{k})]^{-1}\tilde{\Lambda}^{(4)}(\vec{k})[\tilde{\Lambda}^{(2)}(\vec{k})]^{-1} + O(k^2) = \tilde{G}_E^E(\vec{k}) + G_{dc}^E(\vec{k}) + O(k^2), \]

where \( k^2\tilde{\Lambda}^{(2)}(\vec{k}) \) and \( k^4\tilde{\Lambda}^{(4)}(\vec{k}) \) are the second and fourth order terms in a small \( k \) expansion of \( \tilde{D}(\vec{k}) \). The Fourier transform of the elastic Green’s function \( \tilde{G}_E^E(\vec{k}) \) is the second order pole and \( G_{dc}^E(\vec{k}) \) is a \( \vec{k} \)-direction dependent discontinuity[24]. The elastic part \( \tilde{G}_E^E(\vec{k}) \) should be inverse Fourier transformed analytically and the remaining part which no longer has a pole (it still has a discontinuity) can be inverse transformed numerically by

\[ \frac{1}{N_k} \sum_k \cos(\vec{k} \cdot \vec{R})(G_L^L(\vec{k}) - \tilde{G}_E^E(\vec{k}) f_{cut}(\vec{k})) \]

where \( f_{cut} \) is a cutoff function that smoothly vanishes on the Brillouin zone edges. Removal of the second order pole by subtraction of a cutoff version of elastic Green’s function is used in the semicontinuum method of Tewary[42].
B.4 Discontinuity correction

To further improve convergence, the discontinuity correction treats the $G^{dc}(\vec{k})$ part analytically [24]. The remaining portion of $G^L(\vec{k})$ given by $\frac{1}{N_k} \sum_k \cos(\vec{k} \cdot \vec{R}) (G^L(\vec{k}) - (\hat{G}^E(\vec{k}) + G^{dc}(\vec{k})) f_{cut}(\vec{k}))$ is smooth and can be integrated numerically more efficiently.

We expect the convergence rate of the discontinuity correction method to be consistent with the results for integration of smooth periodic functions, while the convergence of relative displacement and elastic Green function correction methods should be dominated by the discontinuity. For $N_{\text{div}}$ partitions in each direction, mid-point rule gives a $N_{\text{div}}^{-4}$ scale for convergence rate of such integrals in all dimensions[43, 44]. The number of $k$ points $N_k$ is $N_{\text{div}}^d$ for dimensionality $d = 1, 2, 3$; therefore, the convergence rate of the mid point rule scales as $N_k^{-4/d}$. In the EGF correction and relative displacement method the integrand is smooth everywhere except the $\Gamma$-point so we expect the error to be dominated by the area/volume around $\Gamma$-point and therefore be of the order of $N_k^{-1}$ or $N_{\text{div}}^{-d}$.

We check the predictions of convergence for the three methods using (1) a simple cubic nearest neighbor model and (2) FCC Al. First, as a simplified case we consider a square (cubic in 3D) elastically isotropic lattice with nearest neighbor interactions and lattice constant $a_0 = \pi$. The nonzero component of the LGF matrix is $G^L(k_x, k_y) = [\sin^2(\pi k_x/2) + \sin^2(\pi k_y/2)]^{-1}$. The second order pole is given by the elastic Green’s function $G^E(k_x, k_y) = 4/(\pi|\vec{k}|^2)$ which is multiplied by a cutoff function to vanish smoothly at the BZ edges. The discontinuity correction is given by $G^{dc}(k_x, k_y) = (\hat{k}_x^4 + \hat{k}_y^4)/3|\vec{k}|^2$ which is also multiplied by the cutoff function. The three dimensional $G^L$, $G^E$ and $G^{dc}$ are obtained by replacing the 2D vector $\vec{k} = (k_x, k_y)$ with $\vec{k} = (k_x, k_y, k_z)$. For the elastically anisotropic Al, we obtain the force constant matrix $D(\vec{R})$ from DFT (ultrasoft pseudopotentials with GGA[20]). Numerical integration over the BZ is done with a uniform mesh evaluating the integrand at the midpoints. Even and odd values of $N_{\text{div}}$ give meshes that include or avoid the $\Gamma$-point—what we call $\Gamma$ and non-$\Gamma$ centered meshes respectively. When applying the
relative displacement method and EGF correction, the value of the integrand—which is discontinuous at $\Gamma$—is assigned zero at the $\Gamma$-point. We calculate the numerical error as a function of $N_k$ and $N_{\text{div}}$ to compare the efficiency of the three methods.

Fig. B.2 shows the convergence rates of relative displacement method, EGF correction and discontinuity correction in the square lattice case. The discontinuity correction and EGF correction scale as $N_k^{-2}$ and $N_k^{-1}$ respectively as expected. The value of $\vec{R}$ does not affect the power law scalings of the convergence but the prefactors are changed in the relative displacement method and are of the same order in EGF and discontinuity corrections. While the $N_k^{-1}$ convergence for relative displacement method obtained by a $\Gamma$ centered mesh is in accordance with the analytical predictions, use of a non-$\Gamma$ centered mesh produces a convergence faster than expected for this method. This is an artifact of the isotropy of the EGF.

The integrand in the relative displacement method is

$$I(\vec{k}) = (\cos(\vec{k} \cdot \vec{R}) - 1) \tilde{G}_L^E(\vec{k})$$

Near the $\Gamma$-point, $G_L^E(\vec{k})$ matches $\tilde{G}_E^E(\vec{k})$ and the leading term in the integrand is $I(\Gamma)(\vec{k}) = -k^2 R^2 (\vec{k} \cdot \vec{R})^2 \tilde{G}_E^E(\vec{k})/2k^2$. For an isotropic EGF, $\tilde{G}_E^E(\vec{k})$ is constant, so

$$I_{\text{iso}}^{(\Gamma)}(\vec{k}) = -\frac{1}{2} \tilde{G}_E^E R^2 \cos^2(\theta_{\vec{k}, \vec{R}})$$

where $\theta_{\vec{k}, \vec{R}}$ is the angle between vectors $\vec{k}$ and $\vec{R}$. The value of the integral over a square $k_0 \times k_0$ region around $k = 0$, for small $k$ is

$$\int_{k_0^2} I_{\text{iso}}^{(\Gamma)}(\vec{k}) d^2k = -\int \int_{k_0^2} \tilde{G}_E^E R^2 \cos^2(\theta_{\vec{k}, \vec{R}}) \frac{dk_x dk_y}{2} = -\frac{k_0^2}{4} \tilde{G}_E^E R^2.$$  \hspace{1cm} (B.2)

The midpoint rule integration of the same region with a non-$\Gamma$ centered mesh uses the $k$ points $\vec{k}_1 = (k_0/2, k_0/2)$, $\vec{k}_2 = (-k_0/2, k_0/2)$, $\vec{k}_3 = (-k_0/2, -k_0/2)$ and $\vec{k}_4 = (k_0/2, -k_0/2)$ each contributing area $k_0^2/4$. The angle between each $\vec{k}_i$ and $\vec{R}$, are $\theta_1$, $\theta_2 = \theta_1 + \pi/2$, $\theta_3 = \theta_1 + \pi$ and $\theta_4 = \theta_1 + 3\pi/2$. Therefore, the numerical approximation for the integral
Figure B.2: Convergence rate with number of k-points of the relative displacement method, EGF correction and discontinuity correction in a 2D square lattice. We expect $N_k^{-2}$ convergence for discontinuity correction and poorer $N_k^{-1}$ convergence for EGF correction and relative displacement method. Using a non-$\Gamma$ centered mesh (left) causes an unusually fast convergence for the relative displacement method in elastically isotropic materials. The exponents in the power law scalings are not affected by the value of $\vec{R}$, while prefactors are changed in relative displacement method and are of the same order in EGF and discontinuity corrections.
which is equal to the exact value of the integral around Γ-point given by eqn. (B.2). To avoid the effect of the discontinuity at the origin using a Γ centered mesh, the Γ-point contribution to the integral is considered zero while its actual value is given by eqn. (B.2). This is the source of the dominant error in relative displacement method on a Γ centered mesh, and accounts for the $R^2$-dependence of the error. This dependence is verified by comparing the ratio of prefactors of the relative displacement convergence laws for different $R$ values and the corresponding $R^2$ in Fig. B.2 which are both approximately 27. On the other hand, the non-Γ centered mesh automatically gives the exact value of the integral around the origin based on eqn. (B.3) and thus produces a faster convergence limited only by the convergence of smooth periodic functions. For elastically anisotropic materials, $\hat{G}_{\Gamma}(\hat{k})$ depends on $\hat{k}$, and the numerical integration around Γ will not equal the analytic value—eliminating the special convergence for non-Γ meshes.

Fig. B.3 shows that the 3D results follow the same trend as the 2D ones in accordance with the expected values. Both Γ centered and non-Γ centered meshes give $N_k^{-4/d}$ ($d = 3$) and $N_k^{-1}$ scale for the convergence rate of discontinuity correction and EGF correction respectively. Similar to the trend observed in 2D case the Γ centered mesh produces the expected $N_k^{-1}$ scale for the convergence of relative displacement method and the non-Γ centered mesh produces faster convergence due to the isotropy of the elastic Green’s function.

Fig. B.4 shows that convergence trends are unchanged for anisotropic long range interactions in FCC Al except for relative displacement method. The lattice is periodic in the threading direction [110], appropriate for screw dislocations in FCC. With a non-Γ centered mesh, the anisotropy of the elastic Green’s function eliminates the fast convergence of the relative displacement method. The convergence trends of the three methods show that these
Figure B.3: Convergence rate with number of k-points of the relative displacement method, elastic GF correction and discontinuity correction in a 3D cubic lattice. The error for discontinuity correction method scales as $N_k^{-4/d}$ with dimension $d$ equal to three. Note that using a non-$\Gamma$ centered mesh creates a faster convergence for the relative displacement method as observed in the 2D case.

trends are not specific to the simplifying assumptions of isotropy or short range interactions and therefore can be trusted in realistic calculations.

Figure B.4: Convergence rate with number of k-points of the relative displacement method, elastic Green’s function correction and discontinuity correction in computation of the $G_{11}$ component of a 2D LGF in Al. The convergence of LGF calculations in a FCC lattice is the same as the one observed in the simplified problem in agreement with the expected values. Note that use of the non-$\Gamma$ centered mesh does not cause a fast convergence for relative displacement method due to the anisotropy of the elastic Green’s function.
Table B.1: Effect of dimension on the convergence rate with number of k-points and number of divisions for the relative displacement method, EGF correction and discontinuity correction. \(N_{\text{div}}\) is proportional to \(1/h\), the inverse grid spacing and \(N_k = N_{\text{div}}^d\).

<table>
<thead>
<tr>
<th>Power law scaling of error</th>
<th>2D</th>
<th>3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disc correction</td>
<td>(-2)</td>
<td>(-4/3)</td>
</tr>
<tr>
<td>EGF correction</td>
<td>(-1)</td>
<td>(-3)</td>
</tr>
<tr>
<td>Rel. displacement</td>
<td>(-1)</td>
<td>(-3)</td>
</tr>
</tbody>
</table>

Table B.1 summarizes the convergence results for the three methods. The expected convergence rate for a numerical integral of a smooth periodic function evaluated by mid-point rule is \(N_{\text{div}}^{-4}\). When expressed in terms of the number of \(k\)-points \(N_k\), the convergence rate would be proportional to \(N_k^{-4/d}\). Since the discontinuity correction leaves a smooth periodic part of the integrand, it follows the above convergence rate. The EGF correction and relative displacement method also converge with the scale of \(N_k^{-1}\) or \(N_{\text{div}}^{-d}\). The convergence rates imply that a certain amount of error is achieved with less \(N_k\) by discontinuity correction method compared to EGF correction or relative displacement method which means that the discontinuity correction requires the least computational effort. Although the EGF correction and relative displacement method require comparable computational effort, the \(R^2\) dependence of the error suggests that the relative displacement method takes even more \(k\)-points than the EGF correction. Also note that there is a trade-off between less computational effort and more complex algorithms. EGF and discontinuity corrections calculate the elastic Green’s function and discontinuity correction parts of the LGF analytically while relative displacement method does not require additional analytic evaluations.

The relative displacement method, elastic Green’s function correction and discontinuity correction have all been used in different calculations. These computational methods improve the slow rate of convergence for 3D and eliminate numerically divergent terms for 2D calculations. We find the discontinuity correction to be the most efficient method—improving the convergence rate to quadratic convergence for 2D over linear convergence for
the relative displacement and elastic Green’s function correction. The discontinuity correction method is general, applicable to any monatomic lattice, and can be generalized to any crystal. Beyond the monatomic case, the leading terms of $G^L(\vec{k})$ expansion for small $k$ include an extra term of the order $i/k$ without inversion symmetry. This term should be subtracted from $G^L(\vec{k})$ in addition to the $k^{-2}$ elastic contribution before applying the discontinuity correction. Finally, while the convergence trends match the analytical values, there is an unusual exception for lattices with isotropic elastic Green’s function. This connects the elastic anisotropy of a material to the efficiency of the computational methods used in Green’s function calculations.
References


