# The motion mechanism and thermal behavior of sigma 3 grain boundaries

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## Abstract

 $\Sigma$ 3 grain boundaries play a large role in the microstructure of FCC materials in general, and particularly so in grain boundary engineered materials. A recent survey of grain boundary properties revealed that many of these grain boundaries possess very large mobilities, and that these mobilities increase at lower temperature, contrary to typical models of thermallyactivated grain boundary motion. Such boundaries would have a tremendous mobility advantage over other boundaries at low temperature, which may explain some observed instances of abnormal grain growth at low temperature. This work explains the boundary structure and motion mechanism that allows for such mobilities, and explores several of the unique factors that must be considered when simulating the motion of these boundaries. The mobilities of a number of boundaries, both thermally-activated and antithermal, were then calculated over a wide temperature range, and several trends were identified that relate boundary crystallography to thermal behavior and mobility. An explanation of the difference in thermal behavior observed in  $\Sigma$ 3 boundaries is proposed based on differences in their dislocation structure.

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- 1. J. Humberson and E.A. Holm. Anti-thermal mobility in the  $\Sigma 3$  [111] 60° (11 8 5) grain boundary in nickel: Mechanism and computational considerations. Accepted with minor revisions by *Scripta Materialia*.
- 2. J. Humberson and E.A. Holm. Computing the free energy and mobility of a curved grain boundary. In preparation for *Applied Physics Letters*.
- 3. J. Humberson and E.A. Holm. The mobility and thermal behavior of  $\Sigma$ 3 grain boundaries in FCC metals. In preparation for *Acta Materialia*.

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## CHAPTER I

## Background

## 1.1 Grain boundaries

For crystalline materials, it is rarely the case that the entirety of a macroscopic sample will consist of a single crystal with a uniform crystallographic orientation. Rather, nearly every bulk sample of material is composed of smaller crystallites of varying orientations, called grains, separated by interfaces, or grain boundaries (GBs), at which there is a mismatch between their crystal structures caused by the difference in their orientations. These GBs are a class of defects important to determining the macroscopic properties of materials, because they affect the electrical [1–6], thermal [7–10], and chemical [11–19] properties of the bulk material, they provide fast routes for diffusion [20–23], and by serving as a barrier to dislocation motion they increase the yield strength of the material [24–28], as described in the Hall-Petch relationship [26, 27], though the emergence of different mechanisms of deformation cause this trend to reverse when the grain diameter drops to the low tens of nanometers [24, 28–30]. Understanding precisely how GB structure relates to these changes and how the network of GBs within a material, or its microstructure, evolves over time is crucial to predicting and controlling the properties of bulk materials.

#### 1.1.1 Grain boundary energy

Grain boundaries are the result of a mismatch between two identical crystal structures of differing crystallographic orientation; this mismatch creates a disordered region at the GB, in which the bonding of the atoms at the boundary is disrupted from the ideal bonding seen in the bulk crystal. This disruption of bonding results in atoms at the GB being higher in energy than their counterparts in the bulk, and so a GB carries with it a certain excess free energy per unit area  $\gamma$ , defined by Cahn in terms of the change in energy associated with the growth of the planar interface of a bicrystal from material reservoirs in equilibrium with the bicrystal.

$$\gamma = \left[\frac{\partial G}{\partial A}\right]_{T,P,N_i} \tag{1.1}$$

Here, G is the Gibbs free energy, A is the interfacial area, T is the temperature, P is the pressure, and  $N_i$  is the amount of component *i*. The GB energy has a considerable impact on the microstructure of materials, with lower-energy boundaries being much more prevalent than higher-energy boundaries [31–37]. As we will see later in section 1.1.3, the GB energy also influences the rate at which GBs move under a curvature-based driving force, and thus the rate at which the microstructure evolves [38].

Grain boundary energies are, in general, difficult to predict precisely, but for certain subsets of boundaries there exist models to describe how the energy varies with certain parameters. By far the most well-known model for predicting GB energies is the Read-Shockley model for low-angle GBs [39], which is applicable to GBs with a small (typically  $< 15^{\circ}$ ) misorientation (as will be discussed in section 1.1.2). By regarding a low-angle boundary as an array of evenly spaced dislocations, Read and Shockley [39] determined the energy of the dislocation array to be

$$\gamma(\theta) = \frac{\mu b}{4\pi (1-\nu)} \theta(A - \log \theta) \tag{1.2}$$

Here  $\theta$  is the misorientation angle,  $\mu$  is the shear modulus,  $\nu$  is Poisson's ratio, and A is a constant that depends on the properties of the dislocation cores. This model has shown excellent agreement with experimental and computational studies of the energy of low-angle GBs [39–43], and has become a standard model for describing these boundaries .

The Read-Shockley model was later extended by Wolf [44] to higher-angle boundaries, albeit in a strictly empirical way. Wolf found that the "plateau" in GB energy in the high-misorientation regime could be well-modeled by replacing  $\theta$  with sin  $\theta$ .

$$\gamma(\theta) = \gamma_0 \sin \theta (A - \log(\sin \theta)) \tag{1.3}$$

Here both  $\gamma_0$  and A are used as fitting parameters to the GB energies, and  $\theta$  is scaled to reflect the symmetry of the rotational axis common to both grains. Again, there is no theoretical basis for this model, as there is for the Read-Shockley model, but it has empirically shown very good agreement with GB energies calculated for sets of crystallographically similar boundaries across the entire misorientation range [44].

## 1.1.2 Description of grain boundaries

In order to talk about the properties of different GBs, we must have a way of unambiguously identifying them. To do so, we must be able to describe both the rotation required to bring the two crystal lattices into coincidence, called the misorientation between the two grains, and the plane of the boundary that separates them.

## Grain boundary misorientation

There are many ways of describing the rotation that transforms one crystal orientation into another, but perhaps the most intuitively simple approach is the so-called axis-angle description [45, 46]. In this, we specify the misorientation between the grains by finding a unit vector that has the same orientation in both crystals' lattice coordinates, which can be shown to always exist for any pair of crystal orientations, and giving the rotation required to bring the two lattices into coincidence. Specifying this unit vector requires two degrees of freedom, and the rotation requires an additional one, for a total of three rotational degrees of freedom. This approach to describing misorientation has the benefit of highlighting important, high-symmetry directions in the crystal that may have relevance to the boundary, such as describing the misorientation of a certain boundary as  $60^{\circ}[111]$ .

Within this three-dimensional misorientation space, there are some misorientations that hold special significance for GB properties. This is because certain rotations of one crystal relative to another result in some fraction of the lattice sites being common to both crystals, i.e. an atom on such a lattice site "belongs" equally well in either grain. The lattice consisting of such sites is called the coincidence site lattice (CSL), and the GB separating the grains is called a CSL boundary. The type of CSL is typically described in terms of  $\Sigma$ , the inverse density of coincidence sites in the lattice. For example, a  $\Sigma$ 3 misorientation means that a crystal shares one out of every three of its lattice sites with the other crystal. An example of this is shown in a dichromatic pattern in figure 1.1. In this depiction, filled and hollow symbols represent lattice sites in the first and second grain, respectively, and circles and triangles are offset from each other by  $\frac{a_0}{2} \langle 110 \rangle$ , which is directed into the plane of the image. At every third {111} plane, all the lattice sites of the two grains coincide, producing the  $\Sigma$ 3 relationship between the grains. A CSL unit cell is outlined in the center. An atom on a coincidence site in a grain boundary has its nearest-neighbor bonds disrupted less than other atoms in the boundary, and so may contribute to a lower grain boundary energy. Indeed, many low energy boundaries do have a low  $\Sigma$  (high density of coincidence sites) relationship between the grains [45, 47, 48], but the inverse is not always true; many CSL boundaries do not have properties that differ significantly from general GBs, and in their landmark review of geometric criteria for low interfacial energy, Sutton and Balluffi found that CSL alone was insufficient to reliably predict low energy interfaces [49].

#### Grain boundary plane

Historically, much of the research of characterizing the anisotropy of GB energy and its effect on microstructural evolution has focused on the misorientation between neighboring grains. More recently, however, advances in the acquisition of microstructural information have spurred more research into the effects of the GB plane orientation on boundary properties. This boundary plane anisotropy has been found to be at least as important a factor as misorientation anisotropy in determining GB energies, and in some cases it is a much larger factor [31,32,50–54]. One prominent example is the set of boundaries with a  $\Sigma$ 3 misorientation. Within this misorientation the boundary with {111}/{111} boundary planes, known as the coherent twin boundary (CTB), has an exceptionally low energy, and is correspondingly very common in FCC materials, though  $\Sigma$ 3 boundaries with boundary planes far away from {111} have energies typical of general high-angle boundaries [32,33,51,52,55–58]. As we will see in coming sections, the strong effect of boundary plane orientation is not limited to boundary energy, but also influences how rapidly GBs move.

Figure 1.1: Dichromatic pattern for a  $\Sigma 3$  misorientation, viewed in the  $\langle 110 \rangle$  direction with a CSL unit cell outlined, as described in the text



## 1.1.3 Grain boundary migration

In addition to static GB properties such as GB energy, for a thorough understanding of the role GBs play in materials we must also consider dynamic properties, such as the motion of GBs through a material. This is of particular practical importance, because the ability to understand how the GB network changes over time during processing is key to the ability to control the resulting microstructure, and thus the properties of the material. Here, we discuss several aspects of GB migration, including the forces that motivate such motion and the rate at which it occurs.

#### Driving forces for grain boundary migration

Generally speaking, GB migration may occur in cases where a material may decrease its free energy through the motion of a GB, often due to some asymmetry between the grains abutting the GB. The source the decrease in free energy may take many forms, among them the reduction of interfacial area [38, 46, 59], elastic strain energy [46, 60–65], magnetic energy [46, 66–70], elimination of strain in a plastically deformed grain [46, 71–82], dislocation motion under shear stress [46, 83–96], and even the entropically-driven motion up a temperature gradient [46, 97]. This decrease in free energy as the boundary migrates is often referred to as a "driving force", though this is used in the sense of a thermodynamic driving force rather than a literal force; a driving force for grain boundary migration has dimensions of energy per unit volume. Here, we outline in greater detail two driving forces that will be particularly relevant.

An especially important driving force is that which is exerted on a curved GB as a result of its interfacial energy, termed the capillary force. A GB carries with it a certain energy per unit area, and so there is a general drive for systems to eliminate as much of the interfacial area as possible. Flat GBs cannot move to eliminate any interfacial area, but curved GBs can do so by moving toward their local center of curvature. Cahn and Hoffman [38, 59] analyzed the capillary force on a GB resulting from this curvature, and found it to depend on both the local curvature and the energy of the GB.

$$p = (\gamma + \frac{\partial^2 \gamma}{\partial^2 \theta_1})\kappa_1 + (\gamma + \frac{\partial^2 \gamma}{\partial^2 \theta_2})\kappa_2$$
(1.4)

Here, p is the force driving grain boundary motion,  $\gamma$  is the GB free energy,  $\kappa_1$  and  $\kappa_2$  are the principal curvatures, and  $\theta_1$  and  $\theta_2$  are the inclinations of the GB along the directions corresponding to those principal curvatures. This is sometimes written more succinctly as  $p = \Gamma \kappa$ , in which  $\Gamma$ , called the stiffness of the boundary, incorporates both the free energy and its second derivative with respect to inclination, and the equation is understood to refer to both directions of principal curvature. For simplicity, some authors disregard the derivative of the free energy and use only  $\gamma$ . This is understandable, as exploring the variation of free energy with boundary inclination is difficult, but those studies which have done so [60,98,99] have found that those second derivatives of boundary free energy make a large contribution to the GB stiffness, and that a complete description of capillary-driven GB motion must incorporate this.

The capillary force may be used to drive the motion of any boundary with curvature, and researchers have created several grain boundary geometries that produce capillary forces of known magnitudes, such as capillary wedges [100–103], quarter- and half-loops [70,85,102, 104–109], and cylinders [60,110–112].

In the case of a flat GB, there will of course be no capillary force, but boundary motion can still be driven by a bulk energy difference in the two grains separated by the boundary. The two driving forces of this type that are most relevant for our purposes come from a difference in either elastic energy density or magnetic energy density across the boundary.

In the case of the elastic energy driving force, if a strain is applied to both grains, it will produce an elastic strain energy  $E_{elastic}$  in each grain of

$$E_{elastic} = \frac{1}{2} C_{ijkl} \epsilon_{ij} \epsilon_{kl} \tag{1.5}$$

Here,  $C_{ijkl}$  is the stiffness tensor for the material,  $\epsilon_{ij}$  and  $\epsilon_{kl}$  are strains, and the Einstein summation convention is used. If the orientation of the grains differs in such a way that the strain applied to both grains produces strains in different crystallographic directions in each grain, there is a difference in the elastic strain energy density across the boundary. This bulk energy difference drives the motion of the boundary with driving force  $p = \Delta E_{elastic} = E_{elastic}^{grain \ 1} - E_{elastic}^{grain \ 2}$ .

This driving force has been employed to study the motion of GBs using bicrystal systems, and formed the basis for many of the early investigations of GB motion via molecular dynamics [60–65], but it does have limitations. The ability of this method to drive boundary motion requires the strains produced in each grain to differ. For certain higher-symmetry boundaries, such as symmetric tilt GBs, in which the boundary is a mirror plane between the two grains, compressive and tensile strains either in the plane of the boundary or normal to it produce the same elastic strain energy density in both grains, and so do not move the boundary.

 $\gamma$ 

The magnetic energy driving force operates in a similar manner, but uses magnetic anisotropy under an applied magnetic field in place of elastic anisotropy under an applied strain field. When a magnetic field is applied to a bicrystal of a magnetically anisotropic material such as Bi, which has a rhombohedral crystal structure, it produces an driving force of [46, 113]

$$p = \frac{\mu_0 H^2 \Delta \chi}{2} (\cos^2 \theta_1 - \cos^2 \theta_2)$$
(1.6)

Here,  $\mu_0$  is the vacuum permeability, H is the applied magnetic field,  $\Delta \chi$  is the difference in magnetic susceptibility parallel and perpendicular to the trigonal axis of Bi, and  $\theta_i$  is the angle between the applied magnetic field and the trigonal axis in grain *i*. The ability to precisely control the magnitude of the magnetic driving force by tailoring the strength of the applied magnetic field makes this method especially useful experimentally, and it was used to produce the first determinations of the absolute mobility of GBs with large misorientations [66–68, 70, 113]. The magnetic driving force has a symmetry restriction similar to that of the elastic driving force, namely that the angles  $\theta_1$  and  $\theta_2$  must be different in the two grains to produce an energy difference. This is less of a practical restriction than for the elastic driving force, though, because of the greater ease and flexibility of applying the magnetic field in the desired direction.

#### Kinetics of grain boundary migration

Any of the above-mentioned driving forces will cause a grain boundary to migrate, but not all will move at the same rate under the same driving force. The canonical picture of the energetics of grain boundary migration is illustrated in figure 1.2. From the initial GB configuration, the perturbation of GB structure that allows the GB to advance in a given direction carries with it an increase in GB energy, leading to an activation barrier  $E_a$ . The nature of this perturbation depends on the GB in question. In highly disordered GBs, the mechanism responsible for boundary motion may be the diffusive motion of individual atoms; in more structured GBs, the process of crossing the energy barrier may correspond to the coordinated motion of groups of atoms [45, 46, 63, 64, 71, 114–117].



Figure 1.2: Schematic depiction of the energy barrier to grain boundary migration

When there is no driving force for GB motion, a GB is equally likely to move in either direction, and thus behaves like a random walker. This is the basis for techniques that extract the mobility of a GB (a measure of the migration velocity produced by a given driving force; defined more precisely in equation (1.9)) from simulations at nonzero temperature with no applied driving force [61, 118–122]. If, however, there is a driving force for GB motion, it will produce an energy difference  $\Delta E$  between the initial and final GB states, and will typically also lower the energy of the transition state by some amount  $\Delta E_a$ . The overall rate of boundary migration is then determined by the relative rates of forward and backward steps of the boundary, as in equation (1.7).

$$v = f_0 \exp(S_a(\Delta E)) l[\exp(-(E_a - \Delta E_a)/k_B T) - \exp(-(E_a - \Delta E_a + \Delta E)/k_B T)]$$
  
=  $f_0 \exp(S_a(\Delta E)) l \exp(-(E_a - \Delta E_a)/k_B T) [1 - \exp(-\Delta E/k_B T)]$  (1.7)

Here, v is the overall boundary velocity,  $f_0$  is an attempt frequency (typically taken to be on the order of the Debye frequency),  $S_a(\Delta E)$  is the activation entropy, which may generally depend on the driving force that produces the energy difference  $\Delta E$ , l is the distance the boundary moves with each step,  $k_B$  is the Boltzmann constant, and T is temperature. Here we will consider three combinations of activation energy and driving force that lead to very different thermal behavior.

In experimental studies of GB migration, the driving forces are typically small compared with the thermal energy, such that  $\Delta E \ll k_B T$ . This leads to  $\exp(-\Delta E/k_B T)$  being expanded to first order as  $\exp(-\Delta E/k_B T) \approx 1 - \Delta E/k_B T$ , which leads to a proportionality between the GB velocity v and the energy difference  $\Delta E$ .

$$v = [f_0 \exp(S_a(\Delta E))l \exp(-(E_a - \Delta E_a)/k_B T)/k_B T]\Delta E$$
(1.8)

This relation leads to the commonly used description of grain boundary mobility Mas the constant of proportionality between the GB velocity and the energy difference  $v = M\Delta E$ , or, expressed in terms of the driving force p (they differ by a factor of the atomic volume  $\Omega$ ), v = Mp. So long as  $\Delta E \ll k_B T$  holds (and as a result  $\Delta E_a \ll E_a$  also holds, because  $\Delta E_a < \Delta E$  and activation energies are on the order of an eV), this is a reasonable approximation. This leads to the typical thermally-activated variation of mobility with temperature, in which the mobility varies with  $\exp(-E_a/k_B T)$ , such as the blue curve in figure 1.3 with an activation barrier of 1.0 eV and a driving force producing an energy difference of 0.01 eV. The legitimacy of determining the GB mobility in molecular dynamics simulations by assuming this proportionality has come into question [114,115], as the driving forces used are often large enough to invalidate the assumption that  $\Delta E \ll k_B T$ , but the mobility may be defined more generally as the ratio of the GB velocity to applied driving force in the low driving force limit.

$$M = \lim_{p \to 0} \frac{v}{p} \tag{1.9}$$

Thermally-activated boundary motion is the most commonly observed way GB mobility varies with temperature, but the migration rate given in equation (1.7) can show other thermal behaviors, depending on the relative magnitudes of the activation energy and driving force.

Suppose the activation barrier is small, and the driving force is somewhat smaller than The motion mechanism and thermal behavior of sigma 3 grain boundaries J.D. Humberson the activation barrier. In that case, the barrier  $E_a - \Delta E_a$  to forward motion is very small, and so the rate of forward steps will show little variation with temperature, but the barrier  $E_a - \Delta E_a + \Delta E$  to backward motion is larger, and so the rate of backward steps increases with temperature. The net effect of this is that the boundary motion is slower at higher temperatures, termed antithermal behavior. An example is given by the green curve in figure 1.3 with an activation barrier of 0.01 eV and a driving force producing an energy difference of 0.001 eV.

If the activation barrier is small, but the driving force is considerably larger than the activation barrier, then the rate of forward steps will be the same as the antithermal case, and will not show much variation with temperature. The rate of backward steps, however, will also show little variation with temperature, but for the opposite reason. Rather than the barrier being so low that most attempts to cross it are successful, the barrier for the backward motion  $E_a - \Delta E_a + \Delta E$  is made so large by the excessive driving force that motion in the reverse direction does not occur, even at high temperatures. The result is that the boundary velocity stays roughly constant with temperature, called athermal behavior. An example is given by the red curve in figure 1.3 with an activation barrier of 0.01 eV and a driving force producing an energy difference of 0.5 eV.

Figure 1.3: Example boundary velocities calculated by equation (1.7) over a range of temperatures for a number of activation energies and driving forces. All velocities normalized by maximum velocity for ease of comparing thermal behaviors



## 1.2 Molecular dynamics

As computational resources have increased in power and decreased in cost, several methods of computer simulation have arisen that allow researchers to investigate aspects of materials behavior that are as yet impossible to probe by experimental means. At the smallest length and time scales, density functional theory (DFT) calculations provide insight into the energetics and electronic structure of grain boundaries given no more input than the elements and positions of the atoms involved [123–128]. At much larger length and time scales, coarse-grained methods such as the Monte Carlo Potts model (MCPM) enable the simulation of GB motion at the microstructural level [129–136]. Between these length and time scales, however, lies molecular dynamics (MD), a semiempirical model based in classical mechanics that has been the foundation of most computational research into GB properties, particularly studies of GB motion. We will outline here the broad strokes of the MD approach, and go into greater detail as it relates to GB migration.

## 1.2.1 Molecular dynamics algorithm

The method of molecular dynamics is based on the numerical integration of the equations of motion of classical mechanics, such as equation (1.10).

$$\frac{d^2 \vec{r_i}}{dt^2} = -\frac{1}{m_i} \frac{\partial V(\vec{r})}{\partial \vec{r_i}} \tag{1.10}$$

Given a potential energy function  $V(\vec{r})$  (discussed further in section 1.2.2) that gives the energy of the system for a set of atom positions  $\vec{r}$ , MD algorithms calculate the evolution of a system of atoms with time by calculating the acceleration  $\vec{a}$  of atoms with mass m from the gradient of the potential energy function and advancing the positions  $\vec{r}$  and velocities  $\vec{v}$ with each increment of time  $\delta t$ . There are several methods for performing this integration [137–139], but the most popular is a variation on the integrator used by Verlet [139], outlined in algorithm 1.

## Algorithm 1 Outline of velocity Verlet algorithm for molecular dynamics

```
1: t \leftarrow 0
  2: for i = 0, i < \text{num\_atoms}, i + + do
               \vec{r}_i(t) \leftarrow \vec{r}_{i,0}
  3:
               \vec{v}_i(t) \leftarrow \vec{v}_{i,0}
  4:
               \vec{a}_i(t) \leftarrow \frac{-1}{m_i} \frac{\partial V(\vec{r})}{\partial \vec{r}_{i,0}}
  5:
  6: end for
  7: while t < t_{max} do
               for i = 0, i < \texttt{num\_atoms}, i + + do
  8:
                      \vec{r_i}(t+\delta t) \leftarrow \vec{r_i}(t) + \vec{v_i}(t)\delta t + \frac{1}{2}\vec{a_i}(t)\delta t^2
 9:
               end for
10:
               \begin{array}{l} \mathbf{for} \; i=0, \, i < \texttt{num\_atoms}, \, i+ + \; \mathbf{do} \\ \vec{a}_i(t+\delta t) \leftarrow \frac{-1}{m_i} \frac{\partial V(\vec{r})}{\partial \vec{r}_i}(t+\delta t) \end{array}
11:
12:
               end for
13:
14:
               for i = 0, i < \text{num\_atoms}, i + + do
                      \vec{v}_i(t+\delta t) \leftarrow \frac{1}{2}(\vec{a}_i(t+\delta t)+\vec{a}_i(t))\delta t
15:
               end for
16:
               t \leftarrow t + \delta t
17:
               for i = 0, i < \text{num\_atoms}, i + + do
18:
                      \vec{r}_i(t) \leftarrow \vec{r}_i(t+\delta t)
19:
                       \vec{v}_i(t) \leftarrow \vec{v}_i(t+\delta t)
20:
                       \vec{a}_i(t) \leftarrow \vec{a}_i(t+\delta t)
21:
22:
               end for
23: end while
```

This algorithm simulates a system at a constant number of particles, volume, and en-

ergy, also called the NVE ensemble or the microcanonical ensemble. As a consequence of having fixed energy and volume, the temperature and pressure of the microcanonical ensemble fluctuate; however, the systems we typically wish to simulate possess well-defined temperatures and pressures. To address such systems, several methods have been developed that modify the equations of motion to control the temperature and pressure over the course of a simulation. One such example is the Nosé-Hoover [140, 141] thermostat, which guides the system toward a target temperature by coupling the atoms to a fictitious heat bath, reflected in the equations of motion in equation (1.11).

$$\frac{d^{2}\vec{r}_{i}}{dt^{2}} = -\frac{1}{m_{i}}\frac{\partial V(\vec{r})}{\partial\vec{r}_{i}} - \zeta\vec{v}_{i} 
\frac{d\zeta}{dt} = \frac{1}{Q} \Big[\sum_{i=0}^{N}\frac{1}{2}m_{i}v_{i}^{2} - \frac{3N+1}{2}k_{B}T\Big]$$
(1.11)

Here,  $\zeta$  represents a frictional force that speeds up or slows down atoms based on how far the system is from the target temperature T, and Q is a parameter that represents the strength of the coupling between the system and the heat bath. These equations of motion produce a system similar to the microcanonical ensemble, but which has a fixed temperature rather than energy, called the NVT or canonical ensemble. Analogous, though more complicated, barostats exist to drive systems toward target pressures or stress states [142, 143].

#### **1.2.2** Interatomic potentials

Everything in the previous section rests on the existence of a potential energy function, or interatomic potential, that describes the interaction between atoms in the material to be simulated. The accuracy of such potentials is one of the principal factors limiting the validity of MD as a tool to investigate materials systems, and as such the development and dissemination of high quality interatomic potentials is an active area of research. The style and complexity of interatomic potentials ranges from simple pairwise potentials , which only consider the distance between atoms and are well-suited to materials such as noble gases for which the directionality of bonding is less important, to more complicated many-body potentials that are better-suited to the modeling of covalently bonded materials such as silicon. For FCC metals, our materials of interest here, an interatomic potential that has been used extensively is the embedded atom method (EAM) [98, 144–156]. The energy per atom *i* for the EAM potential is given in equation (1.12), where *U* is a pairwise term describing the electrostatic interactions between the cores of atom *i* and another atom *j*,  $\rho_{\beta}$ is the electron density at the position of atom *i* contributed by another atom *j* of element  $\beta$ , and  $G_{\alpha}$  is an embedding function that gives the energy of embedding atom *i* of element  $\alpha$  into a total electron density from other atoms *j* of  $\sum_{i\neq i} \rho_{\beta}(\vec{r}_{ij})$ .

$$E_i = G_\alpha \Big(\sum_{j \neq i} \rho_\beta(\vec{r}_{ij})\Big) + \frac{1}{2} \sum_{j \neq i} U(\vec{r}_{ij})$$
(1.12)

This form for the energy per atom reflects the delocalized nature of the bonding of valence electrons in metals. The precise form of the pairwise potential, electron density, and embedding functions vary with the implementation of the EAM potential, but typically are either empirical or analytical functions that incorporate several fitting parameters. The process of ensuring the EAM potential is as accurate as possible then consists of a nonlinear least squares fitting of the functions to a combination of experimentally obtainable material properties such as elastic constants and data derived from *ab initio* methods like DFT, such as the energies of unstable crystal structures. EAM potentials fitted in this manner have proved to be very successful in recreating experimentally observed properties of many FCC metals, though studies of EAM potentials highlight the importance of ensuring that the potentials are fit to data relevant to the phenomena under study [152–154]. In this case, the dislocation structure of  $\Sigma$ 3 boundaries makes the reproduction of stacking fault energies particularly important. Thus, we use in this work the EAM potential for Ni developed by Foiles and Hoyt [98], as was used in the survey by Olmsted et al. [52, 157], which accurately reproduces the stable stacking fault energy of Ni.

### 1.2.3 Grain boundary motion in molecular dynamics

The length and time scales accessible by MD make it well-suited to the simulation of GB motion, and MD has served as an important complement to experimental studies, particularly for the control it offers the researcher over the crystallography of the simulated boundaries, and for the ability to look in detail at the atomic mechanisms responsible for boundary motion. We will separate MD studies of GB motion into three categories: curved GBs driven by a capillary driving force, flat GBs driven by elastic strain, and flat GBs driven by artificial driving forces.

## Molecular dynamics simulation of capillary-driven boundaries

The earliest studies of GB motion by MD used the capillary force exerted on a curved GB to drive its motion, and were often structured similarly to experiments. The most popular geometries for producing capillary motion in MD simulations are the half-loop [104–106], shown in figure 1.4, and the cylinder [60, 110–112], shown in figure 1.5. These essentially two-dimensional geometries have the convenient property that their shapes remain self-similar as the curved boundary moves, and the rates of decrease of their areas (given in equations (1.13) and (1.14)) can be related directly to the reduced mobility  $M^*$ , the product of the mobility M and the GB stiffness  $\Gamma$ .

$$\frac{dA_{loop}}{dt} = -2M\Gamma = -2M^* \tag{1.13}$$

$$\frac{dA_{cyl}}{dt} = -2\pi M\Gamma = -2\pi M^* \tag{1.14}$$

This is also a major limitation of curvature-based studies of GB motion. The reduced mobility may be determined easily, but such simulations offer no way of independently determining the absolute GB mobility and stiffness. However, one study by Zhang et al. [60] has combined curvature-based simulations to determine the reduced mobility of a cylindrical boundary with elastically-driven simulations of flat GB motion to determine the stiffness of a series of asymmetric  $\Sigma 5$  GBs at various inclinations lying tangent to the cylinder. The authors found the GB stiffness to vary by approximately a factor of three over the studied inclinations, a much greater variation than the GB enthalpy. This underscores the importance of the full GB stiffness, not just the energy alone, in determining the capillary driving force. Figure 1.4: Schematic representation of half-loop geometry for capillary-driven grain boundary motion, reproduced from Upmanyu et al. [106]



Figure 1.5: Example of cylindrical geometry for capillary-driven grain boundary motion. System shown is a cylindrical  $30^{\circ}$  [100] tilt GB, atoms colored by ECO order parameter



### Molecular dynamics simulation of elastically-driven grain boundaries

To drive the motion of a flat GB, some type of bulk driving force must be used. As described previously in section 1.1.3, a magnetic driving force has been used in bicrystal experiments,

but the difficulty of incorporating magnetic effects into MD simulations [158–160] makes this impractical. Instead, the first such driving force used in MD was based on elastic strain energy [161], which is comparatively easy to apply in MD simulations because imposing a strain on a simulated bicrystal only requires a change in one or more of the dimensions of the simulation cell. MD studies using an elastic driving force have investigated the mobility and motion mechanism of a number of boundaries [60–65], but, as mentioned in section 1.1.3, symmetry considerations limit the types of boundaries that can be studied. The desire for a driving force that may be used on boundaries of any crystallography motivated the development of a new class of driving force.

## Artificial driving forces for grain boundary motion

The previous examples were physical driving forces that may be used in experimental systems to produce GB motion. However, one of the advantages of the MD method is the level of control afforded to the researcher over the system being simulated. This direct control allows for the creation of a new, artificial driving force, similar in concept to elastic strain energy or magnetic energy driving forces, but based solely on the local crystallographic orientation around each atom. By adding an additional energy to atoms with a chosen local crystallographic orientation, a bulk driving force for GB motion is imposed that results in the GB moving to consume the higher-energy grain. Such an artificial driving force enables the researcher to simulate the motion of GBs of arbitrary crystallography, without the practical limitations that arise when using driving forces that depend on an anisotropy in the material. Here, we will give a description of the implementations of these artificial driving forces, discuss their validity for use in MD simulations of GB motion, and describe some of the uses to which they have been put.

The first such artificial driving force was implemented by Schönfelder et al. [162], who termed it an "orientation-correlated driving force" (OCDF) and based the added energy on the structure factor for a particular crystallographic orientation. The form of the added energy  $E_{OCDF}$  is given in equation (1.15), where N is the number of atoms in the system,  $\vec{k}_{\alpha}$  is the reciprocal lattice vector corresponding to a crystallographic orientation  $\alpha$ ,  $|S(\vec{k}_{\alpha})|^2$ is the structure factor for that orientation,  $\vec{r}_m$  is the real space vector of atom m, and  $a_1$  and  $a_2$  are parameters that determine the amount of energy per atom added to grains 1 and 2.

$$|S(\vec{k}_{\alpha})|^{2} = \frac{1}{N^{2}} \sum_{m=1}^{N} \sum_{l=1}^{N} \exp(i\vec{k}_{\alpha} \cdot (\vec{r}_{m} - \vec{r}_{l}))$$

$$E_{OCDF} = \sum_{j=1}^{N} a_{1} |S(\vec{k}_{1})|_{j}^{2} + a_{2} |S(\vec{k}_{2})|_{j}^{2}$$
(1.15)

By choosing  $a_1$  and  $a_2$  to be different, a bulk energy difference is created between the grains, which drives the motion of the boundary separating them. Schönfelder et al. compared the rate of motion induced in [001] twist GBs by the OCDF to that induced by an elastic driving force, and found the two to produce identical GB mobilities and activation parameters. Additionally, they noted that the OCDF was able to continuously drive the motion of the [001] tilt boundaries in their study, whereas using the elastic driving force resulted in GB sliding events that did not produce a steady rate of motion. The nominal magnitude of the energy added by the OCDF is determined by  $a_1$  and  $a_2$ , but two other factors affect how much of this energy actually produces a driving force on the boundary. The first of these is the temperature of the simulation; as the temperature increases, thermal fluctuations in the atom positions result in a reduction of the energy applied to each grain, and an accompanying reduction in the driving force. The other is the misorientation between the grains; as the misorientation grows small, the reciprocal lattice vectors  $\vec{k_1}$  and  $\vec{k_2}$  grow increasingly close together, and the difference in the energy added to each grain shrinks to zero. This effect of decreasing driving force with increasing temperature and decreasing misorientation is common to all artificial driving forces that use local crystallographic orientations to assign extra energy, and methods of mitigating this decrease have been incorporated into subsequent implementations.

The next major development in artificial driving forces was published by Janssens et al. [163], and featured the creation of a per-atom order parameter that describes the local crystallographic orientation. The Janssens driving force begins with two sets of reference vectors  $\vec{r}_j^I$  and  $\vec{r}_j^J$ , 12 for an FCC crystal, that give the ideal vectors from an atom to each of its nearest-neighbors j in crystals with a favored orientation I and an unfavored orientation

J. These reference vectors are then used to define a number of order parameters, given in equations (1.16).

$$\begin{aligned} \xi_i &= \sum_j |\vec{r_j} - \vec{r_j}^I| \\ \xi_{ij} &= \sum_j |\vec{r_j}^J - \vec{r_j}^I| \\ \xi_l &= f\xi_{ij} \\ \xi_h &= (1 - f)\xi_{ij} \end{aligned}$$
(1.16)  
$$\omega_i &= \begin{cases} 0 & \xi_i \leq \xi_l \\ \frac{\xi_i - \xi_l}{\xi_h - \xi_l} & \xi_l \leq \xi_i \leq \xi_h \\ 1 & \xi_h \leq \xi_i \end{cases} \end{aligned}$$

 $\xi_i$  represents the deviation of atom *i* from crystallographic orientation *I*, and  $\xi_{ij}$  is the expected order parameter for an atom in the grain with orientation *J*.  $\xi_{ij}$  is then used to define two threshold values  $\xi_l$  and  $\xi_h$  based on a thresholding parameter *f* (taken to be 0.25 in Janssens et al. [163]), the purpose of which is to reduce the effect of thermal vibrations on the normalized order parameter  $\omega_i$ , which varies between 0 in the grain *I* to 1 in the grain *J*. This normalized parameter  $\omega_i$  is then used to apply the artificial energy  $u_{\xi}(\vec{r_i})$  to the atom *i*, based on equation (1.17), with the intent that the added energy vary smoothly from 0 for atoms in grain *I* to  $u_0$  for atoms in grain *J*.

$$u_{\xi}(\vec{r}_i) = \frac{u_0}{2} (1 - \cos(\pi \omega_i)) \tag{1.17}$$

This energy difference then produces GB motion with a nominal driving force of  $u_0/\Omega$ , where  $\Omega$  is the atomic volume. The actual driving force, however, may be less than this, because even with the effect of the thresholding parameter f thermal fluctuations may still be large enough to cause atoms in grain I to have an order parameter greater than 0, or atoms in grain J to have an order parameter less than 1. This causes the average energy change as an atom's local orientation changes from I to J to be less than  $u_0$ . As with the OCDF of Schönfelder et al., this effect is more pronounced at high temperature and when the misorientation between the grains is small. To accurately determine the true driving force, thermodynamic integration may be used to calculate the amount of free energy per atom added to each grain by the artificial driving force for a given temperature and misorientation, with the difference in these free energies per atomic volume giving the actual driving force [157].

The artificial driving force by Janssens et al. grew rapidly in popularity as a result of the ease of applying it to drive the motion of boundaries of arbitrary crystallography, and because of its implementation in LAMMPS, a popular program for performing MD simulations [164]. In the decade since its introduction, the Janssens driving force, and others very closely related, have been used to study a wide variety of GBs in FCC materials [84,109,114,115,121,122,157,163,165-169]. This extensive use inspired a study by Coleman et al. [166] that compared the motion of GBs driven by this artificial driving force to motion driven by shear coupling, to verify that the artificial nature of the driving force does not affect GB motion. This study employed slip-vector analysis and a number of continuum-based deformation metrics to examine the atomic displacements in the wake of the moving boundary, and found that the result of artificially-driven boundary motion was indistinguishable from that of shear-coupled motion. Additionally, climbing image nudged elastic band (CINEB) calculations were performed to compare the transition path and energy barriers between the artificially-driven and shear-coupled motion, and the resulting energy landscape was again found to be essentially unchanged by the artificial driving force, as shown in figure 1.6. This detailed comparison of artificially driven and shear-coupled motion gives a firmer basis to the interpretation of the artificial driving force as being not only qualitatively, but also quantitatively similar to real driving forces.

Despite this careful analysis, there remains one way in which the Janssens driving force shows unphysical behavior, which was first pointed out by Ulomek and Mohles [168] and later addressed by Ulomek et al. [170]. The Janssens driving force determines the order parameter  $\xi_i$  based on the vectors  $\vec{r}_{ij}$  from atom *i* to each of its 12 nearest neighbors *j*. So long as the local environment around atom *i* is well-behaved, this produces an order parameter, and thus also an energy, that varies smoothly and provides the intended driving force. In the disordered region of a GB, however, there may exist local environments

Figure 1.6: Results of nudged elastic band calculations comparing the motion of a  $\Sigma 37$  symmetric tilt grain boundary driven by artificial and shear-coupled driving forces, reproduced from Coleman et al. [166]



such that an atom experiences a local minimum in the artificial energy, where no such minimum is desired. This is illustrated in figure 1.7, which shows the variation in energy added to an atom by the Janssens driving force as the atom is displaced across a grain boundary. More concerningly, when the atom moves far enough that the identity of one or more of its nearest neighbors changes, this causes an abrupt shift in the order parameter and a corresponding discontinuous change in the energy, which is clearly unphysical. This reneighboring process is expected to happen frequently as a GB moves through a volume of material and the local orientation around each atom changes from that of one grain to the other. The resulting discontinuous changes in the artificial energy violate conservation of energy in the simulation, and cause a large, systematic drift in the total simulation energy. MD simulations of GB motion are typically thermostatted to a target temperature, which mitigates the energy drift but does not address the problem of how the energy discontinuities may affect the dynamics of the moving boundary.

To correct this undesired behavior, Ulomek et al. developed a new artificial driving

force, which they called the energy conserving orientational (ECO) driving force [170]. This driving force defines an order parameter  $\chi_j$  for each atom j based on equation (1.18), where  $\vec{R}_{jk}$  is the vector from atom j to its neighbor k,  $\vec{Q}_{\alpha}$  and  $\vec{Q}_{\beta}$  are reciprocal lattice vectors for the two crystal orientations, and N is a normalization constant chosen so that  $chi_j$  varies from -1 to +1 at 0 K.

$$\chi_j = \frac{1}{N} \left[ \sum_{\alpha} \left| \sum_k w(|\vec{R}_{jk}|) \exp(\mathrm{i}\vec{Q}_{\alpha}\vec{R}_{jk}) \right|^2 - \sum_{\beta} \left| \sum_k w(|\vec{R}_{jk}|) \exp(\mathrm{i}\vec{Q}_{\beta}\vec{R}_{jk}) \right|^2 \right]$$
(1.18)

$$w(|\vec{R}_{jk}|) = \begin{cases} \frac{|\vec{R}_{jk}|^4}{R_{cut}^4} - 2\frac{|\vec{R}_{jk}|^2}{R_{cut}^2} + 1 & |\vec{R}_{jk}| \le R_{cut} \\ 0 & |\vec{R}_{jk}| > R_{cut} \end{cases}$$
(1.19)

 $w(|\vec{R}_{jk}|)$  is an envelope function, given in equation (1.19), designed to make the contribution of each neighbor k to  $\chi_j$  go smoothly to zero as the neighbor distance approaches a cutoff radius  $R_{cut}$ . This ensures that the reneighboring process does not cause a discontinuous change in the order parameter, and therefore appropriately conserves the added artificial energy as the Janssens driving force does not. The cutoff radius  $R_{cut}$  is adjustable in the ECO driving force, which allows for the order parameter to be calculated based on neighbors beyond just the 12 nearest neighbors. When additional neighbors are included in the order parameter calculation, the ability of the order parameter to distinguish between similar orientations is improved, which allows the use of the ECO driving force on bicrystals with a smaller misorientation than would otherwise be possible, at the expense of greater computation time. An artificial energy  $u_j$  is then assigned to each atom based on its order parameter  $\chi_j$  according to equation (1.20), where  $\eta$  is a thresholding parameter to suppress thermal fluctuations in  $\chi_j$ , similar to f in the Janssens driving force.

$$u_{j}(\chi_{j}) = \frac{u_{0}}{2} \begin{cases} 1 & \chi_{j} > \eta \\ \sin\left(\frac{2\pi}{\eta}\chi_{j}\right) & -\eta \le \chi_{j} \le \eta \\ -1 & \chi_{j} < \eta \end{cases}$$
(1.20)

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These modifications collectively ensure that the artificial energy an atom experiences varies smoothly as its local orientation changes, as shown in figure 1.7. The ECO force was also tested against a standard reference case for GB migration proposed by Mendelev et al. [61], and was found to yield a mobility consistent with the mobilities from both elastically-driven boundary motion and a fluctuation-based method with no applied driving force [170].

Figure 1.7: Comparison of the artificial energy added to an atom by the Janssens and ECO driving forces as the atom is displaced across a grain boundary, reproduced from Ulomek et al. [170]



# 1.2.4 Investigating mechanisms of grain boundary motion with molecular dynamics

One of the largest benefits offered by MD for the investigation of GB motion is that because the positions of the atoms can be stored at every timestep of the simulation, the atomic displacements that occur as the boundary moves through a volume of material may be analyzed after the simulation, and the mechanism by which a boundary migrates may be deduced. This provides an advantage over experimental observations of boundary motion, which are unable to follow individual atoms, and has lead to the use of MD to study the

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mechanisms of GB motions for several categories of boundaries.

The first MD study to point to the role of collective motions of atoms in GB migration was performed by Jhan and Bristowe [116], who simulated the elimination of a roughly hemispherical perturbation of an otherwise flat boundary for  $\Sigma 5$ ,  $\Sigma 13$ ,  $\Sigma 17$ , and  $\Sigma 29$  [100] twist GBs in Au. They noted that the capillary-driven motion of the  $\Sigma 5$  boundary occurred by the collective shuffle of groups of four atoms within the CSL unit cell, which rotated about the misorientation axis to convert from the orientation of one grain to that of the other, shown in figure 1.8. Schönfelder et al. [171] later identified that the motion of low-angle [100] twist boundaries in Cu occurred by the motion of a network of screw dislocations in the plane of the boundary, while higher-angle boundaries moved via the above atomic shuffles. Yan and Zhang [65] later expanded the analysis of the motion of [100] twist boundaries in Ni by incorporating statistical measures of coordinated atomic motion, such as the self-part of the van Hove correlation function and an algorithm developed by Zhang et al. [172] for identifying the collective motion of "strings" of atoms. In agreement with previous studies, they found the  $\Sigma 5$  boundary to migrate principally by four-atom shuffles, while the  $\Sigma 13$  was found to migrate by the string-like motions of groups of atoms along the screw dislocation network. Interestingly, a non-CSL high-angle boundary was found not to show atomic displacements of less than the nearest-neighbor distance during boundary motion, unlike the shorter displacements associated with the motion of the  $\Sigma 5$  and  $\Sigma 13$  boundaries. This suggests that the lack of available smaller displacements within the CSL unit cell may be the cause of the lower mobility observed for the non-CSL boundary compared to the  $\Sigma 5$ and  $\Sigma 13$ .

Analogously, Zhang and Srolovitz [64] analyzed atomic displacements in the migration of asymmetric  $\Sigma 5$  [100] tilt boundaries in Ni, and Zhang et al. [172] applied the abovementioned statistical methods to those displacements. Similar behavior to the [100] twist boundaries was seen, in that both local shuffling of atoms within the CSL unit cell and larger-scale collective string-like motion were observed as the boundary migrated. Crucially, however, the shuffling process, which is the principal mechanism by which the boundary migrates, was found to depend upon the string-like motion of atoms along the tilt axis of the boundary. The authors identified three processes involved in boundary migration: first, Figure 1.8: Example of the collective shuffle of atoms observed in the migration of a  $\Sigma 5$  [100] twist boundary in Au by Jhan and Bristowe, figure reproduced from ref. [116]. A section of (100) boundary plane is shown, with empty circles representing atoms in one grain and filled circles representing atoms in the other.



a fluctuation of excess volume somewhere in the boundary; second, the string-like collective motion of groups of atoms along the tilt axis, which effectively transports the free volume from the first step elsewhere along the boundary; third, the shuffling of atoms within the CSL cell, which was found to occur between the string-like displacements of the second step. This sequence of events highlights the importance of the string-like displacements in the overall mechanism of boundary motion, despite the fact that those displacements do not directly move the boundary in the direction normal to its boundary plane. Zhang et al. [63] later expanded this to asymmetric non-CSL high-angle [100] tilt boundaries in Ni, where they again found a combination of string-like collective motion and individual atomic hops, though in the non-CSL boundaries the string-like motion was not limited to lie along the tilt axis, as it was in the  $\Sigma$ 5 boundaries. The authors also used the mean first-passage time, a measure of the mean time it takes an atom to move a certain distance away from its initial position, to find a characteristic time scale for the individual atomic hops, which is roughly an order of magnitude greater than the characteristic time scale for string-like motion.

In contrast to the complex migration mechanisms seen in the lower-symmetry boundaries discussed above, the more regular structure of symmetric tilt boundaries leads to a much more orderly mechanism of motion [94, 173], based on the distortion of lattice structural units to the corresponding GB structural units, often referred to as "kite structures". A
representative example is shown in figure 1.9. The relative simplicity of this mechanism also makes it possible to study the energy barrier to boundary motion in greater detail [166] and develop analytical models to describe the boundary motion in various driving force regimes [174]. Notably, the translation of the grains that accompanies GB motion means the boundaries may be driven by shear stresses in the plane of the boundary, and a sufficiently large stress completely eliminates the energy barrier to boundary motion, representing one of the rare circumstances that can give rise to athermal boundary motion.

Figure 1.9: Atomic mechanism of motion for a  $\Sigma 17$  symmetric tilt grain boundary given by Suzuki and Mishin, reproduced from ref. [173]. Filled and empty circles correspond to atoms in different {100} planes.



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#### 1.2.5 A survey of grain boundary mobilities in fcc metals

One of the advantages of simulation for calculating grain boundary properties is the ability to set up large-scale, high-throughput automated calculations that span large sections of the five-parameter GB space [50,52,157,175–177]. One recent example is the work of Olmsted et al., who performed a series of molecular statics and molecular dynamics simulations to determine the GB energy and mobility for a set of 388 CSL boundaries in FCC materials [52, 157]. This boundary survey, the largest of its kind at the time, is notable for its thorough sampling of GBs across a wide crystallographic range; the authors chose to simulate every CSL boundary that could be accommodated within a simulation box of a certain size. Typical computational studies of GB properties limit their scope to a set of boundaries that differ crystallographically in only one regard, such as a series of symmetric tilt GBs with varying misorientation. In contrast, this inclusive criterion allowed the authors to search for trends in a much more diverse set of boundaries, including many that had not been simulated previously. The results of the survey, particularly the portion focusing on GB mobilities, highlight the great anisotropy of GB properties. Within a particular class of boundary, such as symmetric tilt boundaries sharing a common tilt axis, the calculated mobility may be found to vary smoothly and in a way that can be easily related to the boundary crystallography. However, across the entire five-parameter GB space there are no simple, universal predictors of boundary mobility, similar to boundary energy [49]. This may be seen in the variation of the mobilities calculated by Olmsted et al. with boundary disorientation, shown in figure 1.10. The authors explored correlations between mobility and several other boundary properties, such as disorientation,  $\Sigma$  value, energy, and excess volume; in each case, certain crystallographically similar subsets of GBs showed systematic variations, but there was no apparent global correlation. Another surprising finding of the survey was the rich variety of thermal variation of mobility seen in the studied boundaries. Contrary to conventional wisdom, which regards GB mobility as nearly always a thermally-activated process, a number of different thermal trends were observed in the simulated boundaries [157, 167], among them thermally-activated, antithermal, athermal, and thermally-damped behaviors. The range of thermal trends reflects the fact that the selection criterion that yielded the set of 388 GBs included several regions of crystallographic space that have not been well-studied previously. The atypical behavior of some of these boundaries has spurred further research into their properties [84,114,115,166,167,178,179].





Among the most surprising behaviors seen by Olmsted et al. were the varied thermal trends in the mobility of  $\Sigma$ 3 boundaries. The coherent twin did not move under the driving force magnitudes used, as is to be expected from its structure, but  $\Sigma$ 3 boundaries with other boundary plane orientations migrated, often with very high mobilities. More surprisingly, some of the  $\Sigma$ 3 boundaries obeyed the Arrhenius kinetics expected of thermally-activated GB motion, as described in section 1.1.3, while others moved antithermally, with higher mobilities at lower temperatures. To illustrate the relationship between boundary plane and thermal behavior, we will make use the method and results of Homer et al. [178] for the representation of grain boundary plane orientations. In this method, symmetry operations for a given misorientation are used to represent the orientation of a GB plane in a subset of the full stereographic projection corresponding to all possible GB plane orientations, which the authors call a grain boundary plane orientation fundamental zone [178, 180]. This

method of visualization allows for the compact representation of the results of bicrystal experiments, and can reveal trends in GB properties with boundary plane orientation. Homer et al. used this method to represent the thermal behavior of the  $\Sigma$ 3 boundaries reported in the Olmsted survey, shown in figure 1.11. In this figure, a red triangle indicates the orientation of a boundary that showed thermally-activated motion, and a blue circle indicates the orientation of a boundary that showed antithermal motion. With the mobility data represented in this way, it becomes clear that the thermally-activated boundaries all have orientations lying between the coherent twin with a {111} boundary plane and the symmetric incoherent twin with a {112} boundary plane, and therefore they share a common  $\langle 110 \rangle$  tilt axis. For further explanation of the crystallography of these boundaries, see section 3.1.

Figure 1.11: Thermal behavior of the  $\Sigma 3$  boundaries simulated by Olmsted et al. [157], using the grain boundary plane orientation fundamental zone of Homer et al. [178], reproduced from Homer et al. [178]



The boundary survey by Olmsted et al. provides a striking example of how GB plane orientation can affect boundary properties. The  $\Sigma$ 3 boundaries found to move antithermally were also found to have very high mobilities, which would give them a tremendous mobility advantage over thermally-activated boundaries at low temperatures. While the Olmsted survey established this behavior, it did not explain the mechanism responsible, nor did it explain why the boundaries with a  $\langle 110 \rangle$  tilt axis were the only  $\Sigma$ 3 boundaries found to be thermally-activated. In chapter II, we will describe the mechanism of motion that gives rise to this antithermal behavior, and describe some consequences of this mechanism for the simulation of these boundaries. Then, in chapter III, we will explore two important subsets of the  $\Sigma$ 3 boundaries, identify trends within each, and present a justification for the thermal behavior of the  $\langle 110 \rangle$  tilt boundaries.

#### CHAPTER II

# Computational considerations in the simulation of $\Sigma 3$ grain boundaries

#### 2.1 Background

As discussed in section 1.2.5, the recent survey of GB mobilities by Olmsted et al. featured several surprising findings, among them that only 221 (57%) of the studied boundaries had mobilities that varied with temperature in a thermally-activated manner. The remainder of the studied boundaries showed a variety of thermal behaviors that are not well-described by conventional models of GB motion [167]. For example, a significant fraction of incoherent  $\Sigma$ 3 boundaries — typically the most prevalent grain boundaries in FCC metals [32,181,182] — showed anti-thermal behavior, where mobility increases as temperature decreases, in the range 600 K  $\leq T \leq$  1400 K. The boundary survey identified these deviations from thermally activated behavior, but did not attempt to characterize the mechanisms that cause them. Thus, here we investigate an incoherent  $\Sigma$ 3 boundary that displays anti-thermal behavior, in order to discover whether this behavior persists at low temperatures and to determine the anti- thermal motion mechanism.

# **2.2** The simulation of an example $\Sigma 3$ grain boundary

To investigate anti-thermal motion in a typical incoherent  $\Sigma 3$  boundary, we preferred a boundary that differs from the coherent twin in character, with high mobility, and zero shear coupling. One such boundary is the  $\Sigma 3 \langle 111 \rangle 60^{\circ}$  boundary with  $\{11 \ 8 \ 5\}$  boundary planes. This boundary is of mixed tilt and twist character, has a relatively low boundary energy of 0.384 J/M<sup>2</sup> at 0 K, a relatively high mobility of 638 m/(s · GPa) at 1400 K, and is boundary number 366 in the Olmsted survey.

All simulations were carried out using the LAMMPS molecular dynamics package [164], using the EAM potential for nickel developed by Foiles and Hoyt [98]. The system was maintained at the target temperature by a Nose-Hoover thermostat [140,141], and a timestep of 3 fs was used. The simulation cell is periodic in all three Cartesian directions, creating two grain boundaries in the bicrystal. In all simulations reported here, the length of the simulation cell normal to the boundaries was 218.6 Å; the dimensions in the plane of the boundary and the magnitude of ECO force varied as described later. To determine grain boundary mobility, the simulation box was divided in half at the midpoint, and the position of each boundary was tracked independently. In each half of the simulation cell, the displacement of the boundary  $\Delta x$  was calculated as  $\Delta x = \frac{L_x \Delta \overline{\chi}}{4}$  where  $L_x$  is the length of the simulation normal to the grain boundaries and  $\Delta \overline{\chi}$  is the average order parameter. As previous studies of boundary migration have pointed out, the definition of grain boundary position is somewhat arbitrary, but because we are principally interested in tracking the change in position over time, any self-consistent method for defining boundary position should yield reasonable results, so long as boundary motion is self-similar. From the displacement vs. time data for each boundary, we then calculate a mean and standard deviation for the boundary position using the bootstrap resampling technique described by Race [169], with a smoothing length of 5 ps and a block length of 100 ps. It should be noted, as Race did, that such techniques systematically underestimate the standard deviation, but that they allow for accurate estimation of grain boundary mobilities with comparatively little computational cost.

As shown in Figure 1(a), the

 $\Sigma_3 \langle 111 \rangle 60^\circ 11.85$  boundary adopts a fully faceted structure, with {111} coherent twin facets alternating with {110} facets. This pattern of  $\Sigma_3$  grain boundaries faceting along low-index planes — namely, {111} {110}, and {112} — that represent local energy minima in the  $\Sigma_3$  grain boundary energy landscape has been observed previously in both experimental [183, 184, 184–190] and computational [56–58, 191–194] studies, and recent work by Banadaki and Patala [194] suggests that this behavior is common to all  $\Sigma_3$  grain boundaries.

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Figure 2.1: Side view of the  $\Sigma 3$  11 8 5 boundary showing the faceting along {111} and {110} planes. Atoms colored by ECO order parameter.

As would be expected, the overall motion of the boundary occurs not by movement of the sections of coherent twin boundary, but by the movement of the much more mobile  $\{110\}$  facets. At these  $\{110\}$  facets, the misfit between the two crystals is accommodated by sets of three Shockley partial dislocations on each trio of planes, as illustrated in figure 2.2, where the sum of the Burgers vectors for each set of dislocations is zero. The collective glide of this set of three partial dislocations has the net effect of exchanging the FCC stacking order of the  $\{111\}$  planes that are not in registry across the  $\{110\}$  facet, thus converting the crystallographic orientation of the atoms from that of one grain to that of the other. This is directly analogous to the motion of the  $\{112\}$  incoherent twin boundary, which has



been studied extensively for its role in twinning and detwinning processes.

Figure 2.2: Dichromatic pattern illustrating the triplet of Shockley partial dislocations that forms the building block of the {110} facet

This structure and motion mechanism sharply contrast those seen in typical high-angle grain boundaries, which contain no structure too large to be captured at the scale of the coincident site lattice (CSL) unit cell, and which are assumed to move via uncoordinated diffusive atomic hops. Thus, these features produce complications that are not present in simulations of general high-angle boundaries, but that must be accounted for to ensure physically accurate simulations of grain boundary motion. We consider three important factors here: the two dimensions of the simulation in the plane of the grain boundary, and the magnitude of the force used to drive grain boundary motion.

#### 2.3 System size in the faceting direction

Faceting of the boundary along the  $\{111\}$  and  $\{110\}$  planes requires us to consider how the size of our simulations along the  $\langle 6 \ 2 \ 10 \rangle$  faceting direction may affect the motion of the boundary. Specifically, we must consider the effect of the interaction between the facet junctions. Where two GB facets meet, the junction they form will have a dislocationlike character if the rigid-body translations of the two facets are different. Hamilton et al. [124] examined grain boundary faceting via a continuum elastic model, and based on the dislocation-like interaction between facet junctions, they determined that the energy of interaction between facet junctions  $E_{junc}$  depends on the facet spacing L as

$$E_{junc} = \frac{A\log L + B}{L} \tag{2.1}$$

Here, A and B are constants related to the properties of the grain boundary facets that form the facet junctions and the elastic constants of the material. This dependence was corroborated by molecular statics calculations; we find a similarly good fit to molecular statics calculations for our boundary, as seen in figure 2.3.



Figure 2.3: Excess energy of facet junction interaction as a function of facet length. The blue curve is the best fit of the model in equation (??), developed by Hamilton et al.

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The interaction between facet junctions sets the simulation length scale in the  $\langle 6\ 2\ 10 \rangle$  faceting direction; if this length is too small, the facet will interact with its own duplicates in neighboring periodic images, which may change the dynamics of the moving boundary. To ensure that the simulation captures realistic facet interactions in this direction, we determined boundary mobility using simulations with varying lengths along the  $\langle 6\ 2\ 10 \rangle$  direction, as shown in figure 2.4.



Figure 2.4: Variation of calculated mobility for the  $\Sigma 3$  11 8 5 boundary with system size in the  $\langle 6$  2 10  $\rangle$  direction at 700 K

For smaller system sizes, interactions between facet junctions produce a significant, systematic variation in boundary mobility. Because the grain boundary mobility survey by Olmsted et al. used a system size of 46.4 Å, or two repeats of the boundary period in this direction, it operated in a regime in which facet junction interactions markedly change the calculated mobilities. In contrast, though there is some fluctuation in mobility for larger system sizes, there is no systematic variation, and the mobilities do not differ outside the bounds of simulation error estimates.

# **2.4** System size along the $\langle 112 \rangle$ tilt axis

Next, we must consider the size of the simulation along the high-symmetry tilt axis of the boundary, i.e. the  $\langle 112 \rangle$  direction in the crystal. The mechanism of motion depends

on the glide of partial dislocations with sense vectors that point in this direction, and so we must ensure that any simulation is large enough to accurately capture the behavior of these dislocations. An additional complication arises because the {110} boundary prefers, below a certain temperature, to form a series of facets with {112} orientation rather than a flat boundary of {110} orientation. This faceting transition occurs because in FCC metals {112} boundaries have lower energy than {110} boundaries, and a {110}boundary may facet into {112} sections by rotating about the  $\langle 111 \rangle$  tilt axis common to both boundaries. This behavior has been observed experimentally by Hsieh and Balluffi as the reversible faceting/de-faceting transition of a {110} boundary in Al , and has been examined in more detail by Daruka and Hamilton using a combination of MD and Monte Carlo techniques. The length of the simulation box along the  $\langle 112 \rangle$  tilt axis of the bicrystal imposes an upper limit on the {112} facet length. If this length is too small, interactions between the facet junctions will artificially raise the energy of the faceted boundary relative to its unfaceted form. This, in turn, lowers the temperature at which the boundary undergoes the faceting transition.

To estimate the effect of the simulation size in the  $\langle 112 \rangle$  direction, we attempted to observe the faceting/defaceting transition in a manner similar to Hamilton and Daruka by creating a planar {110} boundary, cooling it below the presumed faceting transition temperature, heating above said temperature, and observing the faceting transition. However, when we cooled a planar {110} boundary of Foiles-Hoyt nickel, we observed no faceting even at 100K, far below the presumed transition temperature. We hypothesize that this is caused by a difference in the energy barrier for the faceting transition, since the energies of the {110} and {112} boundaries, as well as the energy of the transition state between the two, are material-dependent properties.

Working under the assumption that the unfaceted-to-faceted transition is more difficult than the faceted-to-unfaceted transition, we then generated bicrystals containing boundaries with average orientations of  $\{110\}$ , but which were faceted into  $\{112\}$  planes with as large a facet length as the simulation box could accommodate, as in figure 2.5a. These boundaries were checked for defaceting after 1 ns at a constant temperature, such as is shown in figure 2.5b. We operationally defined the faceting transition temperature as the lowest temperature at which at least one grain boundary transitions from faceted to defaceted. It should be emphasized that this is in no way a rigorous definition of the faceting transition temperature, but rather is a rough upper bound on it. At each system size and temperature, it is possible that defaceting might occur if the system were simulated for a longer time. However, in acknowledgment of computational limitations, we approximate the faceting temperature as the limit of the transition temperatures as the system size along the  $\langle 112 \rangle$ direction increases. As seen in figure 2.6, this limit appears to be approximately 600K.

The secondary faceting of this boundary has a drastic effect on the boundarys mobility, because {112} facets have a lower mobility than the {110} facets. The reasons for this difference in mobility, along with its implications for general  $\Sigma$ 3 boundaries, will be explored in subsequent work. Within the scope of this study, however, the observation of secondary faceting means that we must consider the roles of both {110} and {112} boundary facets. Clearly, the {110} faceted boundary will be the principal form of the boundary above the {110} faceting transition temperature. However, the combination of the driving force for boundary migration and fluctuations at the {112} facet junctions can extend this regime by causing kinetically-driven defaceting even below the nominal faceting transition temperature; thus, we will also report the mobilities of the {110} faceted boundary for temperatures down to 400 K. Because the activation energy for motion of the {112} facets is relatively large and the relevant temperatures are low, the mobility of the {112} faceted boundary is very small and cannot be resolved on MD time scales.

- Figure 2.5: Initial and final structures of a boundary with average {110} orientation simulated at 560 K with a facet length of 137.95 Å, or 32 repeats of the boundary period. Atoms colored by centrosymmetry parameter
  - (a) Boundary with average  $\{110\}$  orientation, initially faceted along  $\{112\}$  planes



(b) Boundary with  $\{110\}$  orientation, having defaceted after 1 ns



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Figure 2.6: Variation of defaceting temperature with system size in the  $\langle 112\rangle$  direction, as described in the text

## 2.5 Driving force magnitude

Finally, we must consider the effect of the magnitude of the ECO force used to drive the motion of the boundary. Because most boundaries move by a thermally activated mechanism, MD driving forces are generally several orders of magnitude larger than typical experimental driving forces in order to achieve significant motion within the MD timeframe. In this case, however, the boundary motion mechanism is the glide of partial dislocations on {111} planes, and so the energy barrier is expected to be very low. Thus, the driving force can and should be considerably smaller than that used in typical MD simulations to avoid overdriving the boundary. This motivates us to test the nominal mobility calculated for this boundary as a function of the ECO driving force applied.

For comparison purposes, we also wish to determine the boundary mobility in the zerodriving-force limit through the use of GB fluctuation methods, to ensure that the mobility calculated from driving boundary motion agrees. Such fluctuation methods use the fact that the average position of a flat GB will undergo a random walk at finite temperature, and the mean square displacement of the boundary increases linearly with time at a rate that depends in part on the GB mobility, as in equation (2.2).

$$\langle \overline{h}^2 \rangle = \frac{2Mk_BT}{A}t \tag{2.2}$$

Here,  $\langle \overline{h}^2 \rangle$  is the mean square displacement, M is the GB mobility,  $k_B$  is the Boltzmann constant, T is temperature, A is the GB area, and t is time.

We choose the AIRwalk method developed by Deng and Schuh [121, 122], which uses resampling of the interface's random walk to reduce noise in the mean square displacement. We apply no driving force to the boundaries, perform 20 replicate 1 ns simulations of boundary fluctuation at 1000 K, and use a sample length of 400 ps, as described in [121]. The resulting mean square displacement as a function of time, from which the mobility is calculated, is shown in figure 2.7. Figure 2.8 compares the mobilities calculated by driving boundary motion to the boundary mobility calculated by the AIRwalk method.

At very low driving forces (less than about 0.25 meV/atom), the boundary moves such a small amount during the simulation and the thermal noise becomes so significant that the



Figure 2.7: Variation of mean square boundary displacement with time at 1000 K as produced by the AIRwalk method of Deng and Schuh [121] with no applied driving force

calculated mobility becomes increasingly inaccurate. In contrast, very high driving forces (greater than 3 meV/atom) overdrive the grain boundary so strongly that the boundary does not experience the full effect of the driving force. (It should be noted that this high driving force regime is standard for MD simulations of grain boundary motion, and includes the driving forces used in the boundary survey by Olmsted, et al.) Because overdriving the boundary essentially reduces the energy barrier for forward motion to near zero, at low temperatures that freeze the backwards motion of the boundary, overdriven boundary mobility would appear not to vary with temperature, i.e. would be identified as athermal. Likewise, at temperatures high enough to enable the backwards motion of the boundary, the mobility of an overdriven boundary would decrease with increasing temperature, i.e. would be identified as antithermal. The result is that boundary mobilities that are calculated using driving forces that are too small or too large do not represent physically realistic situations.

Between the extremes, though, there is a region of driving forces for which the nominal mobilities agree with the true mobility calculated by fluctuation simulations. This indicates that physically accurate mobilities can be obtained from simulations of driven boundaries at less computational cost than fluctuation-based methods. Furthermore, the driving forces



Figure 2.8: Variation of calculated mobility for the  $\Sigma 3$  {11 8 5} boundary with applied driving force at 700 K. The horizontal line represents the mobility determined by the AIRwalk method.

in this regime correspond to experimentally realistic driving forces.

# 2.6 Temperature dependence of mobility

Based on the factors discussed above, we selected a system size of 86.3 Å (ten repeats of the boundary period) in the  $\langle 112 \rangle$  direction, 104.5 Å (five repeats of the boundary period) in the  $\langle 6\ 2\ 10 \rangle$  direction, and a synthetic driving force of 1 meV/atom (14.7 MPa) to simulate the motion of the  $\Sigma 3$  {11 8 5} grain boundary over the temperature range 400 K  $\leq T \leq 1400$  K. The results are shown in figure 2.9. As has been seen in previous studies, the boundary mobility is high in an absolute sense and decreases as temperature increases in an antithermal manner. However, thermally damped behavior, in which the mobility scales inversely with temperature, is not observed. This is to be expected, since thermally damped motion is typical of the phonon- damped glide of isolated dislocations. In contrast, the mechanism of concerted glide of successive triplets of Shockley partial dislocations does not necessarily dictate that the boundary as a whole will move as would a lone dislocation. Nonetheless, the low energy barrier to the glide of these Shockley partial triplets implies that the mobility of the boundary should certainly be large and should decrease with increasing temperature, as we see here.



Figure 2.9: Variation of calculated mobility for the  $\Sigma 3$  11 8 5 boundary with temperature

As discussed above, at low temperatures (T < 400 - 600K) the boundary should adopt a structure that includes low mobility {112} facets. At this point, the mobility drops abruptly and becomes thermally activated such that mobility decreases as temperature decreases. Furthermore, because the activation energy is significant and the temperature is low, boundary motion becomes too slow to capture in MD simulations.

# 2.7 Conclusions

In this work we have described the structure and motion mechanism of the  $\Sigma 3 \langle 111 \rangle 60^{\circ} \langle 118 5 \rangle$  grain boundary in nickel, and how MD simulations must take these factors into account. The mechanism by which this boundary moves, namely by the motion of triplets of Shockley partial dislocations, explains the large absolute mobilities observed, as well as the antithermal variation of boundary mobility with temperature. The faceting transition of the mobile {110} facet limits the temperature range for antithermal mobility. We note that boundaries with very large mobilities can drastically influence microstructural evolution. Thus, this new description of the motion of this incoherent  $\Sigma 3$  boundary, which illustrates how a certain type of boundary may move rapidly at relatively low temperatures, provides key parameters required for accurate mesoscale models of microstructural evolution.

#### CHAPTER III

#### Behavior of incoherent $\Sigma 3$ boundaries

## 3.1 Crystallography of the studied boundaries

We will begin by defining the subsets of  $\Sigma 3$  boundaries of interest to us here. Within the  $\Sigma 3$  misorientation, the orientation of the grain boundary plane has a particularly strong influence on the properties of the boundary, because of the exceptionally low energy and mobility of the coherent twin boundary (CTB). The ubiquity of this boundary makes it a convenient reference point from which to start. If we begin with the coherent twin with (111) boundary plane orientation, we have two orthogonal directions in the plane of the boundary that have particular importance,  $[1\overline{1}0]$  and  $[11\overline{2}]$ , which correspond to the directions with the first- and second-highest atomic densities in the (111) plane. If we take that boundary in the (111) plane and rotate it about the  $[1\overline{1}0]$  direction, we will create a series of grain boundaries that share a common [110] tilt axis, until we have rotated the boundary by  $90^{\circ}$ to a (112) orientation, a so-called "symmetric incoherent twin boundary" (SITB). Similarly, if we begin with the (111) boundary and rotate it about the  $[11\overline{2}]$  direction, we create a series of boundaries with a common  $[11\overline{2}]$  tilt axis, until another 90° rotation brings us to the (110) orientation, another SITB, though one far less studied than the (112) SITB. Lastly, if we begin with the  $(11\overline{2})$  and rotate it about the [111] direction that lies in the boundary plane, we create a series of boundaries that share a common [111] tilt axis, and after a  $90^{\circ}$ rotation we arrive again at the  $(1\overline{1}0)$  plane. These processes, along with the relationship between these planes, are illustrated in figure 3.1. These three sets of tilt boundaries represent important subsets of  $\Sigma$ 3 boundaries, because they represent paths between the three highest-symmetry boundaries in the  $\Sigma 3$  misorientation, namely the CTB and the two SITBs. Researchers such as Banadaki and Patala [194] and Wang et al. [190, 193] have shown that these boundaries represent local energy minima in the  $\Sigma$ 3 boundary plane space (disregarding for the moment the effects of grain boundary dissociation in low stacking fault energy materials such as Cu, which will be discussed in greater depth later), and that the structure and energy of general  $\Sigma$ 3 boundaries are well-represented by a model in which the boundaries facet along those low-index planes. Thus, studying the behavior of the boundaries along these axes gives us insight into the behavior of more general  $\Sigma$ 3 boundaries. In this work, we will principally be concerned with those boundaries lying along the [110] and [112] tilt axes, though we will include one example of a boundary along the [111] tilt axis.

Figure 3.1: Schematic illustration of the relationship between the grain boundary planes described in the text  $\mathbf{x}$ 



## 3.2 Faceting behavior of the studied boundaries

As mentioned previously, the drastically lower energy of the coherent twin has a large impact on the structure of  $\Sigma 3$  boundaries, and this causes these boundaries to facet in order to maximize the length of the coherent twin along the boundary. To consider the faceting behavior of these boundaries, it is useful to construct the boundaries in an initially flat configuration, then allow the boundary structure to evolve by running an MD simulation at finite temperature and observing how the faceted structure of the boundary emerges. We can compare the results of this process for both  $\langle 110 \rangle$  and  $\langle 112 \rangle$  tilt boundaries, using a boundary close to the inclination of the coherent twin and one that is farther away. In each case, the boundary is initially planar, and is cooled from 1000 K to 0 K over the course of 1 ns. This cooling rate is certainly far too great to reliably produce the equilibrium structure of each boundary, but this will still provide a useful qualitative view of the differences in structure between these boundaries.

Examining the structures that result from applying this process to a number of  $\langle 112 \rangle$ tilt boundaries in figure 3.2, which lie at a range of angles to the coherent twin, we observe a striking difference between those boundaries close to the coherent twin and those farther away. The two boundaries closest to the coherent twin (inclined at  $\leq 31.5^{\circ}$ ) have completely faceted along the coherent twin plane, while the boundaries farther from the coherent twin (inclined at  $\geq 50.7^{\circ}$ ) instead form a series of atomic-scale twin facets along their length. This difference in structure stems directly from the difference in inclination angle, because the angle each boundary makes with the coherent twin determines the relative amounts of CTB and {110} SITB in its fully faceted form. The large CTB content of these boundaries close to the coherent twin provides a strong energetic incentive for the boundary to maximize the amount of contiguous CTB. Boundaries far away from the coherent twin, however, have less CTB content, which lowers the energy benefit to aggregating the CTB sections. These factors combine to make boundaries at a large inclination to the coherent twin less likely to show persistent faceting during motion. It is worth noting, however, that when we create these high inclination boundaries in an initially fully faceted form, we do not see a difference in the rate of motion of the boundary from the unfaceted form. This again reflects that the motion of the boundary is controlled by the glide of the dislocation triplets, whether they have aggregated into a single facet or remain distributed throughout the boundary.

When we apply this process to a number of  $\langle 110 \rangle$  tilt boundaries, as in figure 3.3, we see the same relation between the boundaries as in the  $\langle 112 \rangle$  tilt case. The boundaries closer to the coherent twin (inclined at  $\leq 35.2^{\circ}$ ), with their greater CTB content, readily facet into large CTB and {112} sections; the boundaries farther away (inclined at  $\geq 43.3^{\circ}$ ), with less CTB content, show progressively finer facets.

Comparing the  $\langle 110 \rangle$  tilt boundaries to the  $\langle 112 \rangle$  tilt boundaries of similar inclination, we can see that the lowest inclination  $\langle 110 \rangle$  tilt boundary shows several smaller {112} SITB facets, whereas in the lowest inclination  $\langle 112 \rangle$  tilt boundary all the facets have aggregated together. In the larger inclination cases, the rapid cooling has trapped the  $\langle 110 \rangle$  tilt bound-

Figure 3.2: Faceting of initially flat  $\langle 112 \rangle$  tilt boundaries cooled from 1000 K. Atoms colored by common neighbor analysis, with red atoms indicating atoms in a local twin environment. For each boundary, the boundary planes and the angle to the coherent twin are given.



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aries in non-planar configurations, while the  $\langle 112 \rangle$  tilt boundaries returned to planar shapes. In both cases, this represents the lower mobility of the triplets of partial dislocations that make up the {112} SITB facets of the  $\langle 110 \rangle$  tilt boundaries relative to the triplets that make up the {110} SITB facets of the  $\langle 112 \rangle$  tilt boundaries. This difference in mobility has not been the subject of previous study, but was qualitatively observed by Wang et al., though the authors did not choose to comment on it [193]. The factors that give rise to this mobility difference will be explored in greater depth later. Figure 3.3: Faceting of initially flat  $\langle 110 \rangle$  tilt boundaries cooled from 1000 K. Atoms colored by common neighbor analysis, with red atoms indicating atoms in a local twin environment. For each boundary, the boundary planes and the angle to the coherent twin are given.



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#### 3.3 Parameters for boundary simulation

As we saw in chapter II, the appropriate choice of simulation parameters, specifically the simulation dimensions in the grain boundary plane and the magnitude of driving force used, is crucial for the most physically accurate simulation of boundary motion possible. To this end, we consider how the results of chapter II may tell us appropriate parameters to use in the simulation of these larger sets of boundaries.

For the simulation length in the principal faceting direction, i.e. the dimension that determines the maximum size of the CTB facet, we must consider both the interaction between the facet junctions and the number of dislocation triplets that make up the mobile facet, whether {110} or {112} planes. As discussed in chapter II, the number of dislocation triplets seems to be the more important of these two factors, and so in each case we choose a simulation size in this direction sufficient to yield at least five repeats of the grain boundary period.

We saw in chapter II that the simulation length along the tilt axis of  $\langle 112 \rangle$  tilt boundaries determined the maximum possible facet length when the mobile  $\{110\}$  section faceted into  $\{112\}$  sections, and that this affected the temperature at which the faceting transition occurred. However, given the apparent difficulty of observing the  $\{110\}$  to  $\{112\}$  faceting transition in our system, we will adopt the same approach as in chapter II. Namely, we will choose a simulation size along the  $\langle 112 \rangle$  direction to give at least six repeats of the grain boundary period, found to be free of size effects above the faceting transition temperature. We will then run simulations to determine the grain boundary mobility down to 400 K, with the knowledge that at some temperature below 600 K the  $\{110\}$  sections will facet along  $\{112\}$  planes, and the mobility will drop abruptly. We use the same condition to determine the size for the  $\langle 110 \rangle$  tilt boundaries, though it should be noted that no faceting transition will occur for these boundaries, because the mobile facet is already the lower energy  $\{112\}$ boundary.

To determine appropriate driving forces to use in the simulations, we note that all of the boundaries sharing a  $\langle 112 \rangle$  tilt axis move via the glide of dislocation triplets that make up the {110} facet, as the boundary in chapter II. Because these boundaries all share a common motion mechanism, we choose the driving force found in chapter II to yield a mobility consistent with that given by zero-driving-force fluctuation methods, 1 meV/atom (14.7 MPa), for all the  $\langle 112 \rangle$  tilt boundaries. For the  $\langle 110 \rangle$  tilt boundaries, however, the dislocation triplets that make up the {112} facet have a much lower mobility than those in the {110} facet, and so require a correspondingly higher driving force. To determine an appropriate driving force for these boundaries, we took a representative  $\langle 110 \rangle$  tilt boundary with {5 5 2}/{2 1 1} boundary normals and simulated the motion of the boundary at 700 K using a range of driving forces, the results of which are shown in figure 3.4. At high driving forces, there is a strong, systematic variation in mobility with driving forces, similar to that seen in other MD studies of grain boundary motion [114,115]. At low driving forces, the {5 5 2}/{2 1 1} boundary moves so little over the course of the simulation that the calculated mobility is not significantly different from zero. In the range of 5 meV/atom to 10 meV/atom, however, the mobility of the boundary does not change with driving force, and so we choose 10 meV/atom (147 MPa) as the driving force for the  $\langle 110 \rangle$  tilt boundaries in the interest of moving the boundary as far as possible during the simulation.





Apart from these parameters, in each simulation the ECO driving force [170] was used to drive the motion of the grain boundaries. A cutoff radius of 1.1 lattice parameters The motion mechanism and thermal behavior of sigma 3 grain boundaries J.D. Humberson (3.872 Å) was used, sufficient to include both first- and second-nearest neighbors. This cutoff was found to properly distinguish between atoms in each grain up to the maximum temperature of 1400 K, ensuring that the nominal applied driving force was representative of the actual driving force on the boundary. A order parameter cutoff value of  $\eta = 0.25$  was used. The systems were maintained at their target temperature by a Nosé-Hoover thermostat [140, 141], and maintained at zero pressure by a Parrinello-Rahman barostat with the modifications of Martyna, Tobias, and Klein [143]. For the error estimation by bootstrap resampling [169], a smoothing window of 5 ps and a sample window of 20 ps were used.

#### **3.4** Thermal behavior of $\langle 112 \rangle$ tilt boundaries

With the appropriate parameters in place, we may simulate the motion of a series of  $\langle 112 \rangle$  tilt boundaries over a range of temperatures and determine how the mobility of these boundaries varies with temperature. The boundaries to be simulated are summarized in table 3.1. For each boundary, motion is simulated at temperatures from 400 K to 1400 K at intervals of 100 K. The results of these simulations are given in figure 3.5.

Boundary planes	Angle relative to coherent twin	Index used by Olmsted et al.
${11 8 5}/{11 8 5}$	$17.0^{\circ}$	366
${7 4 1}/{7 4 1}$	31.5°	45
$\{5\ 2\ 1\}/\{5\ 2\ 1\}$	$50.7^{\circ}$	11
${6 2 2}/{6 2 2}$	$58.5^{\circ}$	47
${8 4 2}/{8 4 2}$	$67.8^{\circ}$	78
${1172}/{1172}$	$74.8^{\circ}$	258
${110}/{110}$	90.0°	5

Table 3.1: Crystallographic details of simulated  $\Sigma 3 \langle 112 \rangle$  tilt boundaries

The most immediately striking feature of these results is the similarity in the variation of mobility with temperature across all the boundaries, a reflection of the dislocation triplet motion mechanism common to these  $\langle 112 \rangle$  tilt boundaries. In each case, we see a strongly antithermal trend in the mobility, with mobilities for many boundaries at low temperature reaching several thousand m/(s · GPa). It should be reiterated that we expect the mobile {110} facet to undergo a faceting transition at some temperature below 600 K, at which point the mobility of the boundary is expected to drop abruptly. Nonetheless, at tempera-

Figure 3.5: The variation of mobility with temperature for several  $\Sigma 3 \langle 112 \rangle$  tilt boundaries. The inset gives the angle in degrees each boundary makes with the coherent twin.



tures somewhat above 600 K these boundaries would have a tremendous mobility advantage over other boundaries in a polycrystal. At the upper end of the temperature range, several boundaries show a drop in mobility below what would be expected from the trend up to that temperature. The reason for this is unknown, but as the temperature approaches the melting point (1400 K is  $0.9T_m$  for the EAM Ni potential used here), there may be additional impediments to the coordinated glide of dislocation triplets, disrupting the trend seen at lower temperatures.

To understand the antithermal trend observed in these  $\langle 112 \rangle$  tilt boundaries, we may start by considering the thermal behavior of the motion of a single dislocation. As the dislocation glides through a crystal, scattering of thermal phonons by the dislocation results in a damping of its motion such that, all else held constant, the velocity of the dislocation scales inversely with temperature [195–197], i.e.  $v_{dis} \propto T^{-1}$ . Our system is certainly more complicated than this single dislocation, but to compare the thermal behavior of our boundaries to this example case we can plot the logarithms of temperature and mobility and determine what power law, if any, applies. The results of this are shown in figure 3.6. To avoid the drop in mobility at high temperatures mentioned previously, linear regression was performed only on points at 1200 K and below.

Figure 3.6: The logarithm of mobility vs logarithm of temperature for several (112) tilt boundaries. The linear fit is to data points at 1200 K and below. The inset gives the angle in degrees each boundary makes with the coherent twin.



In each case, the logarithm of the data was found to be linear over the large majority of the temperature range, indicating that the thermal behavior of these boundaries is welldescribed by a power law in T. Similar slopes are seen for all the boundaries, which is again a result of the mechanism of motion these boundaries share. Referring to the values of the slopes given in table 3.2, we see that they fall roughly in the range of -0.7 to -0.9. This does not match the theoretical value of -1 for the lone dislocation, but again there are more factors affecting the rate of motion of our boundary than for the single dislocation. The ability of an individual dislocation in the boundary to advance is not only determined by the lattice through which it moves, but also by the requirement that the dislocations in a given triplet move together, and beyond that by the relative position of neighboring dislocation triplets. In light of this, it is unsurprising that we see results that look qualitatively similar to, but are quantitatively different from, the results expected for a single dislocation.

Angle relative to coherent twin	Slope of best-fit line in figure 3.6	$r^2$
$17.0^{\circ}$	-0.699	0.981
$31.5^{\circ}$	-0.817	0.971
$50.7^{\circ}$	-0.792	0.981
$58.5^{\circ}$	-0.849	0.942
$67.8^{\circ}$	-0.814	0.952
74.8°	-0.686	0.986
90.0°	-0.900	0.968

Table 3.2: Slopes of best-fit lines from figure 3.6

# **3.5** Angular variation of $\langle 112 \rangle$ tilt boundary mobility

In addition to considering how the mobility varies with temperature across a series of boundary inclinations, as we did above, we may also consider the complementary question of how mobility varies with the inclination of those boundaries at a number of different temperatures. In each of these  $\langle 112 \rangle$  tilt boundaries, we recall that the boundary motion occurs by motion of the  $\{110\}$  facets, while the CTB facets remain immobile. Thus, a natural expectation would be that as the angle a boundary makes with the coherent twin increases, the length of CTB facets decreases and the length of {110} facets increases, and this should produce a corresponding increase in the boundary mobility. We plot the data in this fashion in figure 3.7, and observe that this trend generally holds true, with the exception that in every case the  $\{110\}/\{110\}$  SITB (inclined at 90.0° to the coherent twin) has a mobility considerably lower than the trend would suggest. This may be understood by considering the difference in structure between the  $\{110\}/\{110\}$  boundary and the rest of the  $\langle 112 \rangle$  tilt boundaries. For the  $\{110\}/\{110\}$  boundary to move forward from its initially planar state, one of the dislocation triplets from which it is formed must first advance alone. For this triplet to move ahead of the rest of the boundary, however, requires the formation of new sections of CTB, which raises the energy barrier to this first step of forward motion. In contrast, a boundary with an amount of geometrically necessary CTB content always has a junction between the CTB and  $\{110\}$  facets (specifically, the junction that is concave with respect to the direction of boundary motion), at which the advance of a dislocation triplet does not require the creation of any CTB, and therefore that boundary has a much lower energy barrier to forward motion and a higher mobility.

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Figure 3.7: The variation of mobility of  $\langle 112 \rangle$  tilt boundaries with inclination to the coherent twin. The inset gives the temperature for each series.



The idea that the mobility of a  $\langle 112 \rangle$  tilt boundary is tied to the relative amounts of CTB and  $\{110\}$  facet that comprise the boundary motivates us to ask if there is a straightforward model to capture this dependence of mobility on boundary inclination. Previous authors have had great success in describing the variation of energy with boundary inclination using simple geometric models. Tschopp and McDowell [55–58] computed the energies of a series of  $\Sigma 3 \langle 110 \rangle$  tilt boundaries in Cu and Al, and found that the energies were well-described by a model of the form

$$E_{boundary} = E_{\{111\}} cos(\theta) + E_{\{112\}} sin(\theta)$$
(3.1)

where  $E_{111}$  is the energy of the coherent twin,  $E_{\{112\}}$  is the energy of the  $\{112\}/\{112\}$ SITB, and  $\theta$  is the angle the boundary makes with the coherent twin. This model simply regards the contributions of CTB and  $\{112\}$  boundary to the total boundary energy independently, and shows excellent agreement with the calculated energies over the entire inclination range, apart from the region corresponding to extensive formation of the 9R phase in Cu. Banadaki and Patala [194] generalized this idea, calculating the energies of  $\Sigma 3$  boundaries across the entire inclination space and using a geometric faceting model based on the energies of the CTB, {112} SITB, and {110} SITB. They also found good agreement for  $\langle 110 \rangle$  and  $\langle 112 \rangle$  tilt boundaries, though poor agreement for  $\langle 111 \rangle$  tilt boundaries. Nonetheless, in analogy with Tschopp and McDowell we attempt to create a geometric model for the mobility of a  $\langle 112 \rangle$  tilt boundary as a function of its inclination  $\theta$  to the coherent twin. To do so, we note that the motion of the boundary as a whole is determined by the motion of the mobile {110} SITB facet; the CTB remains sessile at the magnitude of driving force used. The rate of motion of the boundary, then, is simply given by the projection of the rate of motion of the {110} SITB facet onto the direction normal to the overall boundary, which is given by  $\sin(\theta)$  (recall that  $\theta$  is the angle the boundary normal makes with the coherent twin; the angle the {110} SITB facet makes with the boundary normal is therefore 90° –  $\theta$ ). Our resulting geometrical model has the form given in equation (3.2), where  $M_{\{110\}}$  is the mobility of the {110} boundary.

$$M_{boundary}(\theta) = M_{\{110\}}\sin(\theta) \tag{3.2}$$

This poses a problem, however, because as we saw in figure 3.7, the actual mobility of the {110} boundary is much lower than the angular trend would predict. Thus, rather than using the mobility of the {110} boundary, we regard that as an adjustable fitting parameter and attempt to fit the data up to, but not including, the {110} boundary. This is analogous to Tschopp and McDowell's use of a "hypothetical, unrelaxed" {112} boundary energy for a Cu boundary that undergoes no dissociation [56]. The results of fitting equation 3.2 to the data in figure 3.7 using an adjustable parameter for  $M_{\{110\}}$  are shown in figure 3.8. The agreement is generally poor. While some aspects seem to be well-described, such as the roughly linear increase in mobility with inclination angle at low angles, the simple geometric model fails to accurately predict the mobility of the boundary at an inclination of 74.8°, instead consistently predicting a mobility higher than that which was calculated. This occurs because as the boundary inclination approaches the 90° inclination of the {110} SITB, we do not expect an abrupt, step-like drop in mobility. Rather, we expect a region in which the mobility steadily drops as the CTB content of the boundary drops to zero, and a geometric model with a single fitting parameter cannot capture this behavior. Thus, we conclude that a simple geometric model of the kind that proved successful in describing the energies of  $\Sigma 3$  grain boundaries is insufficient to describe their mobilities; any model attempting to do so must at least incorporate a term accounting for the decrease in mobility as the boundary inclination approaches that of the {110} SITB.

Figure 3.8: As figure 3.7, with best-fit curves as described in the text.



# **3.6** Thermal behavior of $\langle 110 \rangle$ tilt boundaries

We now turn our attention to the other subset of  $\Sigma 3$  boundaries principally of interest: the  $\langle 110 \rangle$  tilt boundaries. The structures and energies of  $\Sigma 3 \langle 110 \rangle$  tilt boundaries have been well-investigated in a number of materials, particularly the {112} SITB, which plays a large role in twinning and detwinning processes. Here, as we did for the  $\Sigma 3 \langle 112 \rangle$  tilt boundaries, we simulate the motion of  $\langle 110 \rangle$  tilt boundaries at a number of inclinations to the coherent twin, over a range of temperatures. The boundaries to be simulated are summarized in table 3.3. Owing to the lower mobility of these  $\langle 110 \rangle$  tilt boundaries relative to the  $\langle 112 \rangle$  tilts, we will concern ourselves with the thermal behavior of these boundaries in the range of 800 K - 1400 K. Even within this range, several boundaries show so little motion at low temperatures that we cannot be confident that the mobilities calculated from accessible time scales are accurate, and so we disregard any mobility found to be below 20 m/(s  $\cdot$  GPa). Notably, the {112} SITB, at an inclination of 90° to the coherent twin, was found to be immobile with the selected magnitude driving force at temperatures below 1200 K, and so for that boundary we simulate its motion at increments of 50 K, rather than the increment of 100 K used throughout the rest of this work. The results of these simulations are shown in figure 3.9.

Boundary planes	Angle relative to coherent twin	Index used by Olmsted et al.
${552}/{211}$	$19.7^{\circ}$	119
${10 4 4}/{8 8 2}$	$25.2^{\circ}$	159
${4 1 1}/{1 1 0}$	35.2°	20
${14 2 2}/{10 10 2}$	43.3°	333
${8 1 1}/{5 5 4}$	64.6°	163
${1 1 2}/{1 1 2}$	90.0°	4

Table 3.3: Crystallographic details of simulated  $\Sigma 3 \langle 110 \rangle$  tilt boundaries

Figure 3.9: The variation of mobility with temperature for several  $\Sigma 3 \langle 110 \rangle$  tilt boundaries. The inset gives the angle in degrees each boundary makes with the coherent twin.



The qualitative difference between the thermal behavior of these  $\langle 110 \rangle$  tilt boundaries and that of the  $\langle 112 \rangle$  tilts is immediately apparent. Whereas the  $\langle 112 \rangle$  tilt boundaries The motion mechanism and thermal behavior of sigma 3 grain boundaries J.D. Humberson uniformly showed a strong antithermal trend and exceptionally large mobilities, these  $\langle 110 \rangle$  tilts show a thermally-activated trend, with several boundaries approaching the limit of mobilities discernible at MD timescales even at 800-900 K. The magnitudes of the mobilities observed here are correspondingly more modest, though it should be noted that mobilities at the upper end of the range  $10^2 - 10^3$  m/(s · GPa) at 1400 K are still higher than those for many other types of grain boundaries, as noted by Olmsted et al. [157], and so these boundaries would still have a mobility advantage over general boundaries.

The observation that the  $\langle 110 \rangle$  tilt boundaries show thermally-activated behavior prompts two questions: is this thermal behavior a strict Arrhenius-type, and if so how do the prefactors and activation energies of these boundaries compare to those of other boundaries? To determine this, we plot the logarithm of the mobility against inverse temperature in figure 3.10. We summarize the results of the linear fits to the Arrhenius plots in table 3.4. For boundaries with multiple apparent linear regions, we report the prefactor and activation energy for high- and low-temperature regions separately. Plots of the fits to each boundary's data may be found in appendix B.

Figure 3.10: The variation of log mobility with inverse temperature for several  $\Sigma 3 \langle 110 \rangle$  tilt boundaries. The inset gives the angle in degrees each boundary makes with the coherent twin.



While the  $\{112\}$  SITB shows a single linear dependence of log mobility on inverse temperature across the entire temperature range, the other  $\langle 110 \rangle$  tilt boundaries show multiple linear regions with different slopes, such as shown in figure 3.11. This behavior has been observed previously, where the change in slope implies a change in the activation energy for the thermally-activated process, presumed to correspond to a change in atomic motion mechanism. Here, we see a decrease in activation energy at higher temperatures. At higher temperatures, the activation energies for boundaries other than the  $\{112\}$  SITB are found to be in the range 0.24 eV - 0.39 eV, with an average activation energy of 0.33 eV; at lower temperatures, the activation energies are found to be in the range 0.57 eV - 0.97 eV, with an average of 0.71 eV. The change in activation energy is found to occur at 1000 K in one boundary, 1100 K in three of the boundaries, and 1200 K in the remaining boundary. It is unclear why the transition temperature would vary between boundaries, as it does not appear to do so in a systematic manner with respect to inclination angle (or, equivalently,  $\{112\}$  SITB boundary content). Boundary motion was simulated at increments of 100 K, which suggests that the actual transition temperature may be near 1100 K, and that the observed differences are a result of the combination of experimental error and the coarseness of our sampling. If this is the case, then a study of the 1000 K - 1200 K range with longer simulated trajectories of boundary motion and a finer temperature increment would produce a more accurate transition temperature.

The {112} SITB stands out from the rest of the  $\langle 110 \rangle$  tilt boundaries in that the activation energy seen for that boundary in the high-temperature region is considerably larger than that of any of the other boundaries. This stems from the same cause as the lower mobility of the {110} SITB relative to the other  $\langle 112 \rangle$  tilt boundaries seen in section 3.4. The rate-limiting step for motion of the {112} SITB is the breaking of one dislocation triplet away from from the boundary's initial planar state, which requires the formation of additional CTB sections on the {111} planes bounding the dislocation triplet, and so comes with a larger energy barrier than the motion of a dislocation triplet at a junction between CTB and {112} SITB sections. Lastly, we note that the {112} SITB was found to be immobile at MD time scales below 1200 K; this corresponds to the upper end of the observed transition, temperature range, which suggests that this boundary may undergo a similar transition,
but that the resulting mobility is so low that simulating the motion of the boundary is outside of the time scale feasibly accessible by MD.

Figure 3.11: The variation of log mobility with inverse temperature for a  $\Sigma 3 \langle 110 \rangle$  tilt boundary with  $\{10 \ 4 \ 4\}/\{8 \ 8 \ 2\}$  normals,  $25.2^{\circ}$  from the coherent twin. Also shown are the linear fits to high- and low-temperature regions.



Boundary planes	Angle relative to	Temperature	Logarithmic prefactor	Activation
	coherent twin	range (K)	$(\log m/(s \cdot GPa))$	energy (eV)
$\{5\ 5\ 2\}/\{2\ 1\ 1\}$	$19.7^{\circ}$	$\leq 1200$	12.29	0.707
${552}/{211}$	$19.7^{\circ}$	$\geq 1200$	7.73	0.243
${10 4 4}/{8 8 2}$	$25.2^{\circ}$	$\leq 1000$	11.81	0.575
${10 4 4}/{8 8 2}$	$25.2^{\circ}$	$\geq 1000$	9.05	0.338
${4 1 1}/{1 1 0}$	$35.2^{\circ}$	$\leq 1100$	11.89	0.569
${411}/{110}$	$35.2^{\circ}$	$\geq 1100$	9.61	0.360
${14 2 2}/{10 10 2}$	43.3°	$\leq 1100$	13.67	0.729
${14 2 2}/{10 10 2}$	43.3°	$\geq 1100$	9.07	0.298
${8 1 1}/{5 5 4}$	$64.6^{\circ}$	$\leq 1100$	16.07	0.973
${8 1 1}/{5 5 4}$	64.6°	$\geq 1100$	9.87	0.394
${1 1 2}/{1 1 2}$	90.0°	$\geq 1200$	20.33	1.728

Table 3.4: Values calculated from linear fits to Arrhenius plots of  $\Sigma 3 \langle 110 \rangle$  tilt boundaries

Lastly, the calculation of the activation energies and prefactors in table 3.4 allows us to check for the existence of a compensation effect [46, 108, 198], in which the two quantities are linearly related. The values from table 3.4 are plotted in figure 3.12. With the exception

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of the values for the  $\{112\}$  SITB, which presumably deviate from the rest because of the above-mentioned difference in motion mechanism, the data from both the high- and lowtemperature regimes fall along the line  $E_a = 0.0915M_0 - 0.49759$ . This gives a compensation temperature, at which all processes occur at the same rate, of  $T_c = 1063$ K, which agrees well with the transition temperatures observed for each boundary given above. However, for processes that show a compensation effect, the process with the lowest activation energy is fastest below the compensation temperature, and the process with the highest activation energy is fastest above it [198]. This is the opposite of the effect we see in table 3.4, so this is not a typical compensation effect in the sense of being a competition between the rates of processes with different activation energies. Rather, it is likely this effect indicates a structural transition in the mobile  $\{112\}$  SITB facet, which produces the change in activation energy. Such transitions have been observed previously in  $\Sigma 5$  and  $\Sigma 29$  twist boundaries, for which both GB migration and GB diffusion show different activation energies above a certain temperature, which coincides with the emergence of diffusive atomic motion out of the boundary plane [171]. This structural transition is an instance of the roughening transition in GBs, in which the mobility is found to increase drastically above a characteristic temperature [199]. To investigate the specific changes in atomic motion responsible for this transition, the statistical tools developed by Zhang et al. for characterizing the collective motions of atoms [172] may be employed.





#### **3.7** Angular variation of $\langle 110 \rangle$ tilt boundary mobility

Having examined the dependence of  $\langle 110 \rangle$  tilt boundary mobility on temperature, we now wish to follow the same path as in section 3.5 and examine how those mobilities vary with the inclination angle of each boundary to the coherent twin. The data are presented in figure 3.13. We observe a trend qualitatively similar to the one seen in figure 3.7 for  $\langle 112 \rangle$ tilt boundaries, where the boundary mobility initially increases with inclination as would be predicted by a geometric model, but drops off quickly as the inclination approaches 90°. Here, the drop in mobility for the {112} SITB is larger than the corresponding drop for the {110} SITB in figure 3.7, as a result of the factors discussed in section 3.6 regarding the lower mobility of the {112} SITB. We thus reach a conclusion analogous to the one in section 3.5: that a simple geometric model is insufficient to capture the variation of mobility with boundary inclination for  $\langle 110 \rangle$  tilt boundaries. Figure 3.13: The variation of mobility of  $\langle 110 \rangle$  tilt boundaries with inclination to the coherent twin. The inset gives the temperature for each series.



# **3.8 Differences in thermal behavior between** $\langle 110 \rangle$ tilt and $\langle 112 \rangle$ tilt boundaries

An apparent incongruity exists between the thermal behavior of the  $\langle 112 \rangle$  tilt boundaries presented in section 3.4 and that of the  $\langle 110 \rangle$  tilt boundaries presented in section 3.6. The two types of boundaries have much in common structurally. Both facet strongly along the CTB and a SITB, and motion of the boundary as a whole occurs by motion of the much more mobile SITB facet. The structure of the {110} SITB and the {112} SITB consist of the same triplets of Shockley partial dislocation. Why, then, is there such a striking difference, not only in the magnitudes of their mobilities, but even in the variation of those mobilities with temperature?

A productive first step to answering this question is to consider the dislocation structure of each of the SITBs. The dislocations in each case are the same, but their line vectors (sometimes called sense vectors) are different, which will lead to different dislocation character in the two boundaries. Dislocation mobility is affected by dislocation character, with screw dislocations having a lower mobility than edge dislocations, and so we might think at first glance that this will explain the observed difference in boundary mobility. Unfortunately, this is not the case. The partial dislocations in both boundaries have Burgers vectors  $\mathbf{b_1} = \frac{a_0}{6} [\bar{1}2\bar{1}]$ ,  $\mathbf{b_2} = \frac{a_0}{6} [2\bar{1}\bar{1}]$ , and  $\mathbf{b_3} = \frac{a_0}{6} [\bar{1}\bar{1}2]$ , or  $A\delta$ ,  $B\delta$ , and  $C\delta$  on the Thompson tetrahedron [195]. In the {112} SITB, all the dislocations point in a  $\langle 110 \rangle$  direction, which we will take to be  $[1\bar{1}0]$  for convenience. This means that the dislocation with Burgers vector  $\mathbf{b_3}$  will be a pure edge dislocation, and the other two will be mixed 30° dislocations. On the other hand, in the {110} SITB the dislocations lie in a  $\langle 112 \rangle$  direction, which we take to be  $[\bar{1}\bar{1}2]$ . Thus, the dislocation with Burgers vector  $\mathbf{b_3}$  is a pure screw dislocation, and the other two are mixed 60° dislocations. Based solely on the characters of these dislocations, we would expect the {110} SITB to have a lower mobility than the {112} SITB, but this is the opposite of what we observe. Clearly, dislocation character alone does not explain the marked difference between the {110} and {112} SITBs. We thus continue with our consideration of the dislocation structure of the boundaries, and address three ways in which these boundaries differ.

#### 3.8.1 Peierls energy and stress

Simply examining the character of the dislocations in each boundary offered no insight into their mobility difference, but it is useful to consider the source of our understanding of how dislocation character affects mobility. As mentioned before, we typically regard screw and dislocations to be less mobile than edge dislocations. However, this understanding comes from experiments and simulations that observe the behavior of perfect dislocations, albeit perfect dislocations that have dissociated into Shockley partial dislocations, as is typical in FCC materials. In FCC materials, a perfect dislocation has a Burgers vector of the type  $\frac{a_0}{6} \langle 110 \rangle$ ; as a consequence, screw and 60° mixed dislocations with these Burgers vectors must point along  $\langle 110 \rangle$  directions, the most closely-packed direction in the {111} planes. Correspondingly, edge and 30° mixed dislocations must point along  $\langle 112 \rangle$  directions, which are the second most closely-packed directions in these planes. This prompts us to ask if there is an effect on dislocation mobility, separate from the effect of dislocation character, that arises from the orientation of a dislocation's line vector in the {111} plane. Such an effect would presumably arise from the difference in the Peierls stress and energy of dislocations with different orientations, as a result of the different atomic packing along different directions. If this is the case, this effect would help to explain the observed difference in boundary mobility; as mentioned above, the partial dislocations in the  $\{110\}$  SITB all point in the second most closely-packed  $\langle 112 \rangle$  directions, whereas the partial dislocations in the  $\{112\}$  SITB all point in the most closely-packed  $\langle 110 \rangle$  directions.

Directly testing the effect of dislocation orientation on the properties of a partial dislocation is difficult. A lone partial dislocation must lie along the boundary of a stacking fault, which must in turn terminate at either another dislocation or the surface of the crystal. The presence of the stacking fault presents practical problems for the simulation of the dislocation, because of the strong driving force in such a system to eliminate stacking fault area by moving the partial dislocation. This makes previously established techniques for determining the Peierls stress of perfect dislocations unfeasible, as they require establishing a fine balance between forces on the dislocation. We may attempt to infer an effect of dislocation orientation on the Peierls stress and energy by looking for supporting evidence in studies on perfect dislocations. However, the bulk of detailed computational research into dislocation properties focuses on dislocations in BCC materials, because the greater number of slip systems and the lack of close-packed planes in BCC materials makes dislocation dynamics comparatively complicated. Even within those studies that look at dislocations in FCC materials, the bulk of the available research deals solely with edge and screw dislocations. Nonetheless, there are some studies in the literature that allow us to explore the effect of dislocation orientation, and we summarize three relevant results here.

Firstly, Schoeck and Krystian [200] used numerical calculations in the Peierls-Nabarro model to determine the Peierls energies for dissociated screw,  $30^{\circ}$ ,  $60^{\circ}$ , and edge dislocations in Cu. Their results are presented in table 3.5. The two values of the stacking fault energy for the screw and  $60^{\circ}$  dislocations are because the authors chose to investigate the effect of different stacking fault energies on the energy and separation of the dissociated partial dislocations produced by their Peierls-Nabarro calculation. Notable here is that the screw and  $60^{\circ}$  dislocations, which lie along the  $\langle 110 \rangle$  direction (the most close-packed direction in  $\{111\}$  planes), both have Peierls energies much higher than those of the edge and  $30^{\circ}$  dislocations, which lie along the  $\langle 112 \rangle$  direction (the second most close-packed

direction in  $\{111\}$  planes). The 60° dislocation having a larger Peierls energy than the screw dislocation is unexpected; the authors interpreted this as a result of the dissociation of the 60° dislocation into unequal partials with different Peierls barriers.

Dislocation type	Stacking fault energy $(J/m^2)$	Peierls energy $(eV/b)$
Screw	0.05	0.0019
Screw	0.045	0.0013
60°	0.05	0.0028
$60^{\circ}$	0.047	0.0030
$30^{\circ}$	0.05	0.0006
Edge	0.05	0.00002

Table 3.5: Peierls energies of dislocations calculated in the Peierls-Nabarro model. Data reproduced from Schoeck and Krystian [200]

Secondly, Lu et al. [201] used both density functional theory (DFT) and EAM calculations to construct generalized stacking fault (GSF) surfaces, as proposed by Vitek and Cockayne [202,203]. These GSF surfaces were then used in a modified version of the Peierls-Nabarro model, developed by the authors, to determine Peierls stresses for the screw,  $30^{\circ}$ ,  $60^{\circ}$ , and edge dislocations. Their results are given in table 3.6. Similarly to Schoeck and Krystian, the authors found the Peierls stresses of the screw and  $60^{\circ}$  dislocations to be considerably higher than those of the edge and  $30^{\circ}$  dislocations. There is some discrepancy between the results from the GSF surface calculated by DFT and the one calculated by EAM, though the authors note that the dislocation dissociation observed in the DFT calculations shows better agreement with experiment, which suggests that those results be given more weight.

Dislocation type	Peierls stress from DFT	Peierls stress from EAM	
	calculations $(meV/Å^3)$	calculations $(meV/Å^3)$	
Screw	1.60	0.55	
60°	0.61	0.28	
30°	0.33	0.21	
Edge	0.02	0.15	

Table 3.6: Peierls stresses of dislocations calculated in a modified Peierls-Nabarro model. Data reproduced from Lu et al. [201]

Lastly, and most strikingly, Szelestey et al. [204] performed a series of MD simulations in which a dislocation of either edge or screw character, dissociated into its component partial dislocations, was placed in a system with fixed simulation boundaries in the direction of *The motion mechanism and thermal behavior of sigma 3 grain boundaries J.D. Humberson*  dislocation glide. These fixed boundaries exert a repulsive image force on the dislocation, the net effect of which may be approximated as varying linearly with the displacement of the dislocation, so long as the dislocation is sufficiently close to one of the fixed boundaries [204–206]. If a stress is applied to the simulation box to produce a Peach-Koehler force opposing the image force on the dislocation, the equilibrium position of the dislocation may be related to the applied stress by equation (3.3).

$$\tau_{ext} = Ku + \tau_1 \sin \frac{\pi u}{a'} + \tau_2 \sin \frac{2\pi u}{a'}$$
(3.3)

Here,  $\tau_{ext}$  is the external stress applied, u is the displacement of the dislocation, K is an elastic constant representing the linearization of the image force,  $\tau_1$  and  $\tau_2$  are the maximum amplitudes of the stress exerted by the Peierls energy landscape, and a' is the spacing between atomic rows in the glide direction. By applying a range of external stresses and determining the positions of the partial dislocations as the peaks of the atomic misfit function, the authors were able to track how the equilibrium position of each partial dislocation changed as a function of applied external stress. Then, by subtracting the part of the external stress required to counter the image force, the variation of the stress acting on each partial dislocation from the Peierls energy landscape may be recovered, and the Peierls stress determined. The authors' results are given in figure 3.14.

It should be noted that the partial dislocations in figures 3.14a and 3.14b have the same Burgers vectors; in both cases, the partial dislocations are the result of the dissociation reaction:

$$\frac{a_0}{2}[\bar{1}01] \to \frac{a_0}{6}[\bar{1}\bar{1}2] + \frac{a_0}{6}[\bar{2}11] \tag{3.4}$$

The only difference in the screw case of figure 3.14a and the edge case of figure 3.14b is the orientation of the dislocations. In keeping with the results of the other two studies, when the partial dislocations are oriented along the close-packed  $\langle 110 \rangle$  direction, as in the screw case, the resulting Peierls stress is over an order of magnitude higher than when they are oriented along the  $\langle 112 \rangle$  direction, as in the edge case. Additionally, note that the difference in Peierls stress from partial dislocation orientation is even higher than might be

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## 3.8. DIFFERENCES IN THERMAL BEHAVIOR BETWEEN (110) TILT AND (112) TILT BOUNDARIES

Figure 3.14: Variation of stress from Peierls energy landscape with partial dislocation displacement. Figures reproduced from Szelestey et al. [204]

(a) Stress from Peierls landscape on partial dislocations dissociated from a screw dislocation.  $u_1$  and  $u_2$  are the displacements of the two partial dislocations, and  $u_c$  is the displacement of the center of the dissociated dislocation.



(b) Stress from Peierls landscape on partial dislocations dissociated from an edge dislocation.  $u_1$  and  $u_2$  are the displacements of the two partial dislocations.



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inferred from the effective Peierls stresses of the edge and screw dislocations. This is a result of the separation of partials for the screw dislocation not being an integer multiple of the atomic spacing, leading to a partial cancellation of the Peierls stresses of the partials as one partial "helps" the other over the Peierls barrier, which produces a lower effective Peierls stress for the dissociated dislocation. In the edge dislocation, the separation of partials is approximately an integer multiple of the atomic spacing, and so the two partials move in phase and no cancellation occurs.

In summary, we have touched upon three studies that show a large effect on the Peierls stress or energy stemming from the orientation of dislocations, independent of their character. This is not to say that dislocation character has no effect on these properties, of course; the works of Schoeck and Krystian [200] and of Lu et al. [201] both show differences between screw and  $60^{\circ}$  dislocations and between edge and  $30^{\circ}$  dislocations, and these differences presumably stem from the characters of these dislocations. Nonetheless, the results of these studies unanimously indicate that dislocations oriented along a  $\langle 110 \rangle$  direction, even partial dislocations, have a considerably higher barrier to motion than those oriented along a  $\langle 112 \rangle$  direction.

#### 3.8.2 Partial dislocation triplet interactions

As discussed above, the character of the partial dislocations in the  $\{110\}$  and  $\{112\}$  boundaries cannot explain the difference in their mobilities by the typical notion that screw dislocations are less mobile than edge dislocations. However, the character of the partials still has an effect on their interaction, and on the interaction between the triplets of partials that make up the boundaries, as indicated by the schematic depiction of the interactions between the edge and screw components of each partial in tables 3.7 and 3.8. In these tables, the relative orientation of the screw and edge components of each partial dislocation in a triplet of partials are given such that, for example, two partials with an edge component marked as "-" have the Burgers vectors of their edge components oriented in the same direction, whereas a partial with an edge component marked "+" and one with an edge component marked "-" have those components oriented in opposite directions. Let us now consider the effects of the interactions between each component, beginning with the  $\{112\}$ 

Burgers vector	Dislocation character	Direction of edge	Direction of screw
		component	component
$\mathbf{b_1} = \frac{a_0}{6} [11\bar{2}]$	Edge	+	0
$\mathbf{b_2} = \frac{a_0}{6} [1\bar{2}1]$	$30^{\circ}$ mixed	-	+
$\mathbf{b_3} = \frac{a_0}{6} [\bar{2}11]$	$30^{\circ}$ mixed	-	-

Table 3.7: Description of the relative orientation between screw and edge components of partial dislocations for a dislocation triplet in a (112) SITB. The sign of each component indicates its orientation relative to the same component of the other dislocations, as described in the text.

Looking first at the edge components of the partials in the  $\{112\}$  SITB, in table 3.7, we note that the edge component of the pure edge partial  $\mathbf{b_1}$  is opposite that of the mixed  $30^{\circ}$  partials  $\mathbf{b_2}$  and  $\mathbf{b_3}$ . As  $\mathbf{b_1}$  is on a separate glide plane from  $\mathbf{b_2}$  and  $\mathbf{b_3}$ , there will be a repulsive interaction between them at close range, and a vertical arrangement of these dislocations will be unstable [195, 196]. This repulsive interaction drives  $\mathbf{b_1}$  to separate from  $\mathbf{b_2}$  and  $\mathbf{b_3}$  by a distance of approximately 4 Å, as seen in figure 3.15a. This is the same repulsion that leads to the dissociation of the  $\{112\}$  SITB and the formation of the 9R phase in metals with a lower stacking fault energy (SFE), such as Cu, Au, and Ag [56–58, 189–193, 207–211]. In Ni, however, the higher SFE prevents such an extensive dissociation, and the 9R phase is not seen. Also note that this dissociation occurs in a fully relaxed {112} SITB, which involves a rigid translation of the grains of approximately  $\frac{a_0}{c_0}$ [111]. In boundaries consisting of both CTB and SITB facets, the CTB facets suppress the translation at the SITB facets, constraining the SITB facet closer to the mirror-image boundary structure [183, 184]; this will be discussed more in section 3.8.3. The screw components of  $\mathbf{b_2}$  and  $\mathbf{b_3}$  are of opposite sign and on separate glide planes, and so there is an attractive interaction between them such that they retain their vertical alignment [195, 196]. Thus, as the {112} SITB migrates, within each triplet of Shockley partial dislocations there is a repulsion between  $\mathbf{b_1}$  and the pair of  $\mathbf{b_2}$  and  $\mathbf{b_3}$ , which hinders the ability of the triplet to glide in a coordinated fashion.

Next, looking at the dislocations in the  $\{110\}$  SITB, we note that  $\mathbf{b_1}$  is now a pure screw dislocation, and that its screw component is opposite that of  $\mathbf{b_2}$  and  $\mathbf{b_3}$ . In this case, these opposite screw components result in an attractive force between  $\mathbf{b_1}$  and  $\mathbf{b_2}$  and between  $\mathbf{b_1}$  and  $\mathbf{b_3}$ , which would tend to keep the partial dislocations close together and

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Burgers vector	Dislocation character	Direction of edge	Direction of screw
		component	component
$\mathbf{b_2} = \frac{a_0}{6} [1\bar{2}1]$	$60^{\circ}$ mixed	+	-
$\mathbf{b_1} = \frac{a_0}{6} [11\bar{2}]$	Screw	0	+
$\mathbf{b_3} = \frac{a_0}{6} [\bar{2}11]$	$60^{\circ}$ mixed	-	-

Table 3.8: Description of the relative orientation between screw and edge components of partial dislocations for a dislocation triplet in a  $(1\overline{1}0)$  SITB. The sign of each component indicates its orientation relative to the same component of the other dislocations, as described in the text.

aligned vertically. However,  $\mathbf{b_2}$  and  $\mathbf{b_3}$  have opposite edge components and identical screw components, both of which would repel each other. A balance between the attraction of  $\mathbf{b_2}$ and  $\mathbf{b_3}$  to  $\mathbf{b_1}$  and the repulsion between  $\mathbf{b_2}$  and  $\mathbf{b_3}$  results in the structure seen in figure 3.15b, in which the dislocation triplets stay together, but  $\mathbf{b_2}$  and  $\mathbf{b_3}$  shift slightly away from each other, resulting in each triplet skewing slightly to one side. A similar structure was observed in molecular statics simulations of Cu by Wang et al. [193] As the {110} SITB migrates, each dislocation triplet is held together by the attractive interactions between the screw components of the partials, but each triplet has a repulsive interaction with adjacent triplets, which may lower the energy barrier for the advance of one triplet ahead of its neighbor.

#### 3.8.3 Relative grain translations

Frequently, the lowest energy structure of a grain boundary will involve the translation in the plane of the boundary of one grain relative to the other. When grain boundaries facet, if the translation vectors corresponding to the two facets are different there exists an elastic distortion at the junctions between facets, which can be modeled as a dislocation with a Burgers vector equal to the difference in translation vectors for the two facets [45, 124, 212, 213]. In the case of the {112} SITB, the lowest energy configuration involves a translation of one grain in the  $\langle 111 \rangle$  direction by approximately half of the {111} planar spacing [128, 183–185, 190, 191, 193, 208, 212], depending on the material, but the CTB has no such translation vector. Thus, the junction between the CTB and the {112} SITB must accommodate this mismatch in preferred translation states. The difference in translation vectors for the two facets gives a Burgers vector of  $\frac{a_0}{6}\langle 111 \rangle$  which prompts us to compare this facet junction to the junction between CTB and {110} SITB facets, to see if there is a difference between the two that may explain the difference in the mobilities of the  $\{112\}$  and  $\{110\}$  facets. If the relaxed configuration of the  $\{110\}$  SITB has no translation vector, or has a smaller translation vector than the  $\{112\}$  SITB, then less elastic distortion is associated with the facet junction, presumably leading to a lower barrier to facet motion.

To determine if this is the case, we began by relaxing a  $\{110\}$  SITB and checking for relative displacement of the grains in the  $\langle 111 \rangle$  direction. The relaxed structure may be seen in figure 3.15b, clearly showing the shift of the  $\{111\}$  planes. To compare the displacement of the  $\{110\}$  SITB to that of the  $\{112\}$  SITB, we then performed climbing image nudged elastic band (CINEB) calculations [214, 215] to determine the energy difference between the relaxed, offset configuration and the higher-energy, mirror-symmetry configuration for each boundary. In each case, the initial and final images for the CINEB calculation were the relaxed configurations corresponding to equal offsets in  $\pm \langle 111 \rangle$  directions. 18 images were used for the  $\{112\}$  SITB, 16 were used for the  $\{110\}$  SITB, and an inter-image spring constant of 10 eV/Åwas used for both. The results of the CINEB calculations are given in figure 3.16. Surprisingly, not only does the  $\{110\}$  SITB prefer the offset configuration, it actually has a larger energy difference between the offset and mirror-symmetry configuration than the  $\{112\}$  SITB does  $(87.2 \text{ mJ/m}^2 \text{ vs. } 45.6 \text{ mJ/m}^2)$ . The extent of the offset of the  $\{111\}$  planes near the facet junction is, in part, a function of this energy difference [183, 184], and so the the junction of a CTB and a  $\{110\}$  SITB would be predicted to have a greater elastic distortion than the junction of a CTB and a  $\{112\}$  SITB. Therefore, the difference in mobility between  $\langle 112 \rangle$  and  $\langle 110 \rangle$  tilt boundaries cannot be explained by this difference in the facet junctions they form.

Figure 3.15: Comparison of the relaxed structures of the  $\{112\}$  SITB and the  $\{110\}$  SITB at 0 K.

(a) Relaxed structure of the {112} SITB showing the dissociation of the Shockley partial with pure edge character from the  $30^\circ$  partials



(b) Relaxed structure of the {110} SITB showing the skewed orientation of the Shockley dislocation triplets



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Figure 3.16: Nudged elastic band calculations for sliding the {112} SITB and the {110} SITB in the  $\langle 111\rangle$  direction

(a) Calculated energy profile for the  $\{112\}$  SITB. The blue line is a cubic spline interpolation.



(b) Calculated energy profile for the  $\{110\}$  SITB. The blue line is a cubic spline interpolation.



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#### **3.9** A $\langle 111 \rangle$ tilt grain boundary

Here, we will examine an example of the set of (111) tilt boundaries simulated in the survey by Olmsted et al. [157] We choose a boundary with {3 2 1} boundary normals, number 30 in the Olmsted survey. As we did with the  $\langle 110 \rangle$  and  $\langle 112 \rangle$  tilt boundaries, we begin with an initially flat boundary to determine the faceting behavior of this  $\langle 111 \rangle$  tilt boundary. In keeping with the pattern seen in section 3.2, as well as the results of Banadaki and Patala [194], the  $\langle 111 \rangle$  tilt boundary facets along planes that represent local minima with respect to boundary plane orientation. In this case, because no coherent twin plane is readily accessible to the boundary, it instead facets along the  $\{112\}$  and  $\{110\}$  SITBs, as seen in figure 3.17a. Similarly to the (110) and (112) tilt boundaries, one facet (the  $\{110\}$ SITB) is much more mobile than the other, and motion of the boundary proceeds via the motion of this mobile facet. Note that the boundary is composed of {112} and {110} SITB facets, and those facets contain the same dislocations with different orientations. Thus, the motion of this boundary is similar to the motion of persistent dislocation kinks. As discussed in section 3.8.3, the relaxed structures of both the  $\{112\}$  and  $\{110\}$  SITBs feature a relative grain translation in the  $\langle 111 \rangle$  direction, and we see the same behavior in this boundary, as shown in figure 3.17b. As before, we now determine appropriate parameters for the simulation of this  $\langle 111 \rangle$  boundary.

The similarity of the motion of this boundary to the propagation of kinks along dislocations suggests that the energy barrier to boundary motion will be small, and so we must determine the effect of the magnitude of driving force on the boundary mobility. The calculated mobilities for a range of driving forces are shown in figure 3.18. At higher driving forces, the boundary is overdriven and the full effect of the driving force is not seen, resulting in a decrease in calculated mobility. Below a driving force of 1 meV/atom, the boundary moves so little that the error estimates quickly dwarf the mobilities. Based on this, we choose a magnitude of 1 meV/atom to drive the boundary.

We must also consider the size of the simulation in the  $[\bar{1} \ 4 \ 5]$  direction, the direction along which the boundary facets into {112} and {110} SITBs. Rather than determining the number of dislocation triplet units in the mobile facet, as was the case for the  $\langle 110 \rangle$  and  $\langle 112 \rangle$  tilt boundaries, here the size of the simulation in the faceting direction determines the length of the mobile kink in the dislocations. The variation of calculated mobility with system size in this direction is shown in figure 3.19. A modest effect of size on mobility is evident at small system sizes. Thus, we choose a length of 10 GB periods, or approximately 114 Å, in the  $[\bar{1} \ 4 \ 5]$  direction. Along the tilt axis, in the  $\langle 111 \rangle$  direction, we choose a length of 6 periods, or 18.4 Å. It should be noted that the length along the tilt axis does not influence the faceting behavior of the boundary, as it does for the  $\langle 112 \rangle$  tilt boundaries. However, we do expect a similar faceting transition in this boundary, with the {110} SITB facet breaking up into {112} SITB facets, though the difference in boundary structure may cause this transition to occur at a different temperature.

With these simulation parameters in place, we proceed to determine the mobility of the  $\langle 111 \rangle$  tilt boundary over the same temperature range as was used for the  $\langle 110 \rangle$  and  $\langle 112 \rangle$  tilt boundaries. The results are shown in figure 3.20. Strikingly, the boundary shows essentially no change of mobility with temperature over a range of 1100 K, though the mobility does drop by about 200 m/(s  $\cdot$  GPa) at 1400 K. Athermal boundary mobility is most commonly associated with a type of shear-coupled boundary motion, in which an external shear stress acts upon the dislocations in a low- or high-angle tilt boundary [84.85.87.89–91.94–96.167.173.216.217]. This stress can cause boundary migration through the collective motion of the GB dislocations, and, if the magnitude of the stress is sufficient, can eliminate the energy barrier and produce athermal motion, though this requires a large applied stress. Athermal motion has also been observed at high temperatures in a Zn bicrystal experiment with Bi solute [218], which the authors attributed to the boundary breaking away from the solute. In both of these cases, athermal behavior occurs because the local driving force for GB motion is large enough that it overwhelms the activation barrier, as described in section 1.1.3. Given that the  $\langle 111 \rangle$  tilt boundary motion is similar to kink propagation, we can expect a very small activation barrier, and so overdriving may be a problem here, as well. While our exploration of the effect of driving force on mobility in figure 3.18 did not suggest that 1 meV/atom would overdrive the boundary, it is nonetheless possible that reaching the regime in which the motion of the boundary is truly a biased thermal process would require even smaller driving forces. If this is the case, then, given the practical difficulties in determining a mobility from a boundary moving so slowly, zerodriving-force fluctuation-based methods would be the most appropriate to recover the true mobility.

- Figure 3.17:  $\langle 111\rangle$  tilt boundaries with {3 2 1} boundary normals, equilibrated at 600 K. Atoms colored by ECO order parameter.
- (a) Boundary viewed in  $\langle 111 \rangle$  direction with  $\{112\}$  and  $\{110\}$  SITB facets indicated



(b) Boundary viewed in  $[\bar{1} \ 4 \ \bar{5}]$  direction with  $\{111\}$  planes in profile to illustrate the relative translation of the grains in the  $\langle 111 \rangle$  direction



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Figure 3.18: Variation of calculated mobility of chosen  $\langle 111\rangle$  tilt boundary with applied driving force at 700  $_{\rm K}$ 



Figure 3.19: Variation of calculated mobility of chosen (111) tilt boundary with number of grain boundary periods in the  $[\bar{1} \ 4 \ \bar{5}]$  direction at 700 K

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Figure 3.20: Variation of calculated mobility of chosen (111) tilt boundary with temperature

#### 3.10 Conclusions

In this section, we have simulated the motion of a number of  $\Sigma 3$  GBs over a range of temperatures. In each case, the motion of the boundary was found to be controlled by a small number of low-index, high-symmetry boundaries: for the  $\langle 110 \rangle$  tilt boundaries, the CTB and the  $\{112\}$  SITB; for the  $\langle 112 \rangle$  tilt boundaries, the CTB and the  $\{110\}$  SITB; and for the  $\langle 111 \rangle$  tilt boundary, the  $\{112\}$  and  $\{110\}$  SITBs. The  $\langle 110 \rangle$  and  $\langle 112 \rangle$  tilt boundaries showed a strong dependence of mobility on the angle to the coherent twin, or equivalently on the orientation of the mobile facet relative to the overall direction of boundary motion. This similar dependence in both sets of boundaries reflects the fact that both sets migrate by the motion of a mobile facet perpendicular to the coherent twin. In thermal behavior, however, the two groups are drastically different. The  $\langle 112 \rangle$  tilt boundaries were all found to move antithermally in a way that was well-described by power laws with exponents in the range of -0.7 to -0.9. This is similar to the exponent of -1 expected for the thermally-damped glide of lone dislocations, as a result of the mechanism of motion for these boundaries, but it differs as a result of the more complicated dynamics of the movement of groups of three partial dislocations. It should be reiterated that the faceting transition discussed in chapter II will occur in all of these boundaries, as they all share the mobile {110} SITB facet. Nonetheless, above the faceting transition temperature their large mobilities and antithermal behavior give them a large mobility advantage over other boundaries. In contrast, the  $\langle 110 \rangle$  tilt boundaries all demonstrated thermally-activated motion. Two regimes of Arrhenius behavior were found for all boundaries except the  $\{112\}$  SITB, with a transition temperature of approximately 1060 K. This behavior points to an as-yet-uncharacterized structural transition in the mobile  $\{112\}$  SITB facet that affects the activation energy for facet motion. This difference in thermal behavior is surprising, given the apparent similarity in structure of the  $\langle 112 \rangle$  and  $\langle 110 \rangle$  tilt boundaries, but explanations for this difference are given based on differences in the dislocation structures of the two sets of boundaries.

#### CHAPTER IV

#### **Future work**

As with most research, the work presented here raises new, unexpected questions and suggests potential new areas of study. Here, we touch on several promising avenues of investigation.

# 4.1 Parameterization of a Monte Carlo model of boundary migration

Motion of the  $\langle 110 \rangle$  and  $\langle 112 \rangle$  tilt boundaries studied in this work is controlled by the mobile  $\{112\}$  and  $\{110\}$  facets, and these facets consist of individual triplets of Shockley partial dislocations. This suggests that we may be able to adopt a more coarsely-grained model for the motion of the boundary, one that reflects this structure, such as a kinetic Monte Carlo model. If each triplet of dislocations is represented separately in the Monte Carlo model, then the energy barriers to their motion and the energetics of their interaction can be determined by molecular statics and CINEB calculations, and be used to parameterize the model. This would allow the simulation of the  $\langle 110 \rangle$  and  $\langle 112 \rangle$  tilt boundaries at length and time scales more comparable to experiment, and would enable the use of experimentally accessible driving forces.

### 4.2 Changes in structure and energy from grain translation at large {112} and {110} facet lengths

As explored by Marquis et al. [183, 184], the constraint imposed at the junction between the coherent twin and the  $\{112\}$  or  $\{110\}$  facet results in the structure of the  $\{112\}$  or  $\{110\}$  facet varying along its length, with sections of the facet near facet junctions showing no grain translation, while sections of the facet far away from a junction show the relative translation in the  $\langle 111 \rangle$  direction preferred by the unconstrained boundary. While this has been observed experimentally in a {112} facet constrained by coherent twins, and a model developed that shows good agreement with observations, the analogous case with a {110} facet has not been observed. The incoherent twin boundary facets seen in experiment are typically above the length threshold given by Marquis et al. for predicted grain translation [184], which warrants an exploration of how the structure of {112} and {110} facets change at larger sizes (e.g. in the tens of nm), how this changes with temperature, and if this affects the motion of the boundary facet.

# 4.3 Changes in boundary structure with stacking fault energy

In metals with a low stacking fault energy (SFE), such as Cu, Au, and Ag, {112} SITBs are observed to dissociate into two walls of dislocations with a net tilt character, separated by the 9R phase that results from the glide of a Schockley partial dislocation on every third {111} plane [55–58, 191, 207, 219, 220]. The formation of the 9R phase is not observed in metals that have a higher stacking fault energy, such as Ni and Al, and so this was not a complication in our study. The questions of how the dissociation of the {112} SITB affects the motion of that facet, and of how the SFE affects the structure of the {110} boundary are still open, however, and must be addressed before the results of this work may be generalized to lower SFE FCC metals with confidence.

### 4.4 Development of an interpolative model for grain boundary mobility

Simple geometrical models were found to be insufficient to capture the variation of mobility with boundary inclination for the  $\langle 110 \rangle$  and  $\langle 112 \rangle$  tilt boundaries, but in both cases the mobility was found to vary smoothly with both inclination and temperature. This suggests that with a greater number of simulated boundaries, so that the boundary inclination space is more densely sampled, it should be possible to create a model that interpolates between the calculated mobilities to yield, for example, the mobility of a  $\langle 110 \rangle$  tilt boundary at any boundary inclination and temperature. Such a model is essential parametric input to mesoscale methods of simulating grain growth.

### 4.5 Determination of the effect of orientation on the Peierls barrier for Shockley partial dislocations

Though there exists evidence pointing to a higher Peierls barrier for partial dislocations oriented in  $\langle 110 \rangle$  directions than those oriented in  $\langle 112 \rangle$  directions, as discussed in section 3.8.1, a direct determination of this barrier would be preferable. Techniques that allow the calculation of the Peierls barrier for perfect dislocations [204, 206] cannot be applied directly to individual partial dislocations, because the stacking fault that must border such dislocations interferes with the balance of forces required to calculate the Peierls barrier. However, the application of an artificial driving force in such a way that, rather than driving GB motion, it instead artificially stabilizes the stacking fault in the simulation, offers a potential method for circumventing this problem. Preliminary efforts in this area have shown that it is possible to use the artificial driving force to stabilize the stacking fault, but that using this to calculate the Peierls barrier will require the delicate tuning of the driving force magnitude. If this can be achieved, it will provide direct evidence for the influence of partial dislocation orientation on the height of the Peierls barrier.

#### APPENDIX A

## Appendix A: Computing the free energy and mobility of a curved grain boundary

Current methods of calculating the free energy of grain boundaries are computationally expensive, and cannot be easily applied to boundaries with curvature. Here, we will outline a method for calculating both the free energy and mobility of a curved boundary, and briefly discuss how it may be generalized to other systems. This work does not follow the pattern of the main body of this dissertation, exploring the behavior of  $\Sigma$ 3 boundaries, but it is thematically similar in that it uses the artificial driving force to determine GB properties that would be difficult or impossible using existing methods.

Atomistic simulation methods have become powerful tools for determining not only the enthalpy of grain boundaries, but also their free energies, with techniques such as thermodynamic integration allowing for their calculation [221–224]. These techniques do have limitations, however. Current methods for determining grain boundary free energies require the boundary to have a constant area, at least on average, which makes them unsuitable for use on curved boundaries. Researchers have constructed atomistic simulations in which the curvature is known, allowing for the determination of the reduced mobility  $M^*$  [60, 104–106, 109–112]. However, there remains no method of determining the mobility and stiffness independently for a curved boundary. This is of particular practical importance because the migration of boundaries under this capillary pressure is one of the primary factors determining the interfacial structure of a material, and thus also its macroscopic properties. Here, we will show that a recently developed artificial driving force for driving grain boundary motion may be used to oppose the capillary pressure and allow for the determination of both the stiffness and mobility of a curved boundary. This is a new area of research not only because it is the first direct determination of the mobility and free energy of a curved boundary, but also because these properties are determined for a moving curved boundary. The properties of a curved boundary may be assumed to be related to the properties of the flat boundaries which lie tangential to it, but neither the way the flat boundaries contribute to the properties of the curved boundary nor the way these properties may change as the curved boundary moves and shrinks are well understood [109]. The capillary-pressure-induced motion of boundaries depends on the mobility and free energy of the moving boundary, and by providing the first way to directly determine these properties, this method provides the factors most relevant to predicting the evolution of grain boundary networks in real materials.

Cylindrical grains have been studied both theoretically and computationally for their favorable symmetry [60, 110–112]. We will use molecular dynamics simulations of a cylindrical grain here as a model system to demonstrate how the synthetic driving force can be used to oppose capillary pressure, allowing both free energy and mobility to be calculated.

A cylindrical grain will experience capillary pressure driving the grain to shrink. The surface of a cylinder of radius r has a curvature of 1/r everywhere, so the expression for the velocity of a cylindrical grain boundary of radius r solely from the capillary pressure takes on a simple form.

$$v = \frac{dr}{dt} = -\frac{M\Gamma}{r} = -\frac{M^*}{r} \tag{A.1}$$

This in turn leads to the customary parabolic grain growth equation

$$r^2 = r_0^2 - 2M^*t \tag{A.2}$$

By performing simulations in which a cylindrical grain is allowed to shrink freely, the reduced mobility may be determined, as has been done previously in the literature [60,110–112].

Note that both the mobility and the grain boundary stiffness may depend on both the misorientation between the cylindrical grain and the matrix grain, which will be the same at every point on the grain boundary, and the local boundary plane, which will vary around the boundary. This means that when we refer here to the mobility or stiffness of the boundary, what we are truly referring to is the average of that property over the boundary planes included on the surface of the cylinder. Also of note is that the grain boundary energy varies periodically around the cylinder, so the contribution of the second derivative of the grain boundary energy to the stiffness will average out to zero, leaving us with the only the energy itself, i.e. in this case  $\langle \Gamma \rangle = \langle \gamma \rangle$ .

Once the reduced mobility is known, another simulation may be performed with the artificial driving force applied to oppose the capillary pressure, i.e. to promote the growth of the cylindrical grain. Rather than using a artificial driving force of constant magnitude, as has been the case in its previous applications, we instead cause it vary inversely with the radius, i.e.  $u_0 = k/r$  for some constant k. This means the velocity of the grain boundary becomes

$$v = \frac{dr}{dt} = M(\frac{k}{\Omega r} - \frac{\Gamma}{r})$$
(A.3)

Correspondingly, the equation of motion becomes

$$r^2 = r_0^2 - 2M(\Gamma - \frac{k}{\Omega})t$$
 (A.4)

We choose here a value of k sufficient to slow down, but not stop, the shrinking of the cylinder. If we perform two simulations, one with this varying artificial driving force and one without, the rate of decrease of  $r^2$  follows eqs. (A.2) and (A.4), respectively, which yields a simple pair of equations that can be solved for M and  $\Gamma$ . An example of the parabolic kinetics of grain shrinkage over a range of artificial driving force constants is shown in figure A.1

All simulations were performed with the LAMMPS MD program [164], using the Foiles-Hoyt embedded atom potential for nickel [98], and temperature was maintained at 1000 K ( $0.64T_M$ ) by a Nosé-Hoover thermostat [140, 141]. The simulation box was periodic in all three Cartesian directions, measured 211.2 Åx 211.2 Åx 10.56 Å, and contained 43 200 atoms. Cylindrical grain boundaries were created by rotating a cylinder of the material of radius 52.8 Åabout the [001] direction, creating a [001] tilt boundary. Equations involving



Figure A.1:  $r^2$  against time for several magnitudes of artificial driving force opposing capillary force

the radius of the cylinder were recast in terms of the number of atoms in the cylinder N by assuming  $N\Omega = \pi r^2 h$ . The number of atoms in the cylinder was defined as the number of atoms with an order parameter less than 0. In simulations where the cylinder was shrinking, with or without a variable artificial driving force, the center of the cylinder was frozen to a radius of 10.6 Åto prevent the grain from rotating away from the chosen misorientation. As previous researchers have found, eliminating shear-coupled boundary motion in the form of grain rotation slowed the motion of the grain boundary.

As an example of this method, we have calculated the free energies and mobilities of a range of [001] tilt boundaries, shown in figures A.2 and A.3. The results are found to agree with the range of energies typically seen for general high angle grain boundaries, both experimentally and computationally determined. Of particular note is that previous computational studies of flat, general high angle tilt boundaries have shown a plateau in energy with misorientation at a smaller angle than is seen in our results [44]. A tentative explanation for this variation is that, unlike the typically studied flat boundaries, the fact that these boundaries are in constant motion means that they are unable to find the optimal accommodation for their constantly increasing dislocation density. If this is the case, it represents an important example of how the properties of a curved boundary - and thus also the behavior of that boundary as it moves through a polycrystalline material - can be affected by the fact that the boundary is in motion.



Figure A.2: Calculated energies for cylindrical [001] tilt boundaries over a range of misorientations

The use of the artificial driving force to calculate these energies and mobilities naturally raises the possibility of the presence of the driving force itself affecting the energy or mobility of a boundary. Previous studies which used the artificial driving force to calculate the mobilities of flat boundaries have not found evidence of any unphysical effects, and a recent in-depth comparison of artificially and mechanically-driven boundary motion found no difference between the two [166], but there is the chance that e.g. the addition of the extra energy could directly affect the free energy of the boundary. To ensure this is not the case, we also ran several series of simulations using the same initial setup with a range of values of k, producing different magnitudes of artificial driving force. The results are shown in figure A.4 The ability to calculate the energy and mobility using this method depends on the rate of shrinkage of the cylindrical grain being substantially different with and without the driving force. For low values of k, when the rates become too close together, we expect the calculated energies and mobilities to be unreliable. Regardless, because the mobility of a grain boundary is defined in the low driving force limit , the physically meaningful region is the plateau produced by the highest range of k values (i.e. the lowest net driving force)



Figure A.3: Calculated mobilities for cylindrical [001] tilt boundaries over a range of misorientations

that still allows the boundary to shrink.

We would also like to note that this approach may be generalized to other phenomena as well. By defining an appropriate order parameter and applying a known excess energy based on that parameter, the motion of many types of interfaces may be altered. This ability to influence the motion of a moving interface has the potential to offer insight into a number of open problems involving complex processes, such as the formation of dendrite structures in a supercooled unary system.

By applying an artificial energy penalty to a moving boundary, we are able to calculate the free energy and mobility of boundaries of practically arbitrary shape. So long as the local curvature can be calculated, and the rate of boundary motion may be determined both with and without a artificial driving force, then the free energy and mobility for that curved section of grain boundary may be determined.



Figure A.4: Variation of calculated free energy of cylindrical [001] tilt boundaries with magnitude of artificial driving force used

#### APPENDIX B

## Appendix B: Arrhenius plots for the thermally-activated $\Sigma 3$ $\langle 110 \rangle$ tilt boundaries

This appendix contains the plots of the logarithm of GB mobility against reciprocal temperature used to determine the mobility prefactors and activation energies for the studied  $\Sigma 3 \langle 110 \rangle$  tilt boundaries over various temperature ranges, as discussed in section 3.6, as well as the resulting data in tabular form.

Boundary planes	Angle relative to	Temperature	Logarithmic prefactor	Activation
	coherent twin	range (K)	$(\log m/(s \cdot GPa))$	energy (eV)
$\{5\ 5\ 2\}/\{2\ 1\ 1\}$	$19.7^{\circ}$	$\leq 1200$	12.29	0.707
${552}/{211}$	$19.7^{\circ}$	$\geq 1200$	7.73	0.243
${10 4 4}/{8 8 2}$	$25.2^{\circ}$	$\leq 1000$	11.81	0.575
${10 4 4}/{8 8 2}$	$25.2^{\circ}$	$\geq 1000$	9.05	0.338
${411}/{110}$	$35.2^{\circ}$	$\leq 1100$	11.89	0.569
${411}/{110}$	$35.2^{\circ}$	$\geq 1100$	9.61	0.360
${14 2 2}/{10 10 2}$	$43.3^{\circ}$	$\leq 1100$	13.67	0.729
${14 2 2}/{10 10 2}$	43.3°	$\geq 1100$	9.07	0.298
${8 1 1}/{5 5 4}$	64.6°	$\leq 1100$	16.07	0.973
$\{8\ 1\ 1\}/\{5\ 5\ 4\}$	64.6°	$\geq 1100$	9.87	0.394
${1 1 2}/{1 1 2}$	90.0°	Entire range	20.33	1.728

Table B.1: Values calculated from linear fits to Arrhenius plots of  $\Sigma 3$  (110) tilt boundaries

Boundary planes	Angle relative to	Temperature	Slope $(K)$	$r^2$
	coherent twin	range (K)		
${552}/{211}$	$19.7^{\circ}$	$\leq 1200$	-8202	0.995
${552}/{211}$	$19.7^{\circ}$	$\geq 1200$	-2820	0.836
${10 4 4}/{8 8 2}$	$25.2^{\circ}$	$\leq 1000$	-6676	0.999
${10 4 4}/{8 8 2}$	$25.2^{\circ}$	$\geq 1000$	-3923	0.983
${4 1 1}/{1 1 0}$	$35.2^{\circ}$	$\leq 1100$	-6608	0.992
${4 1 1}/{1 1 0}$	$35.2^{\circ}$	$\geq 1100$	-4177	0.975
${14 2 2}/{10 10 2}$	43.3°	$\leq 1100$	-8460	0.976
${14 2 2}/{10 10 2}$	$43.3^{\circ}$	$\geq 1100$	-3463	0.984
${8 1 1}/{5 5 4}$	$64.6^{\circ}$	$\leq 1100$	-11292	0.975
${8 1 1}/{5 5 4}$	$64.6^{\circ}$	$\geq 1100$	-4572	0.993
$\{1\ 1\ 2\}/\{1\ 1\ 2\}$	90.0°	Entire range	-20056	0.995

Table B.2: Linear fits to Arrhenius plots of  $\Sigma 3 \langle 110 \rangle$  tilt boundaries

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Figure B.1: Linear fits to Arrhenius plot of  $\Sigma 3 \langle 110 \rangle$  tilt boundary with {5 5 2}/{2 1 1} normals, inclined at  $19.7^{\circ}$  to the coherent twin



Figure B.2: Linear fits to Arrhenius plot of  $\Sigma 3$  (110) tilt boundary with {10 4 4}/{8 8 2} normals, inclined at  $25.2^{\circ}$  to the coherent twin

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Figure B.3: Linear fits to Arrhenius plot of  $\Sigma 3 \langle 110 \rangle$  tilt boundary with  $\{4 \ 1 \ 1\}/\{1 \ 1 \ 0\}$  normals, inclined at  $35.2^{\circ}$  to the coherent twin



Figure B.4: Linear fits to Arrhenius plot of  $\Sigma 3 (110)$  tilt boundary with  $\{14 \ 2 \ 2\}/\{10 \ 10 \ 2\}$  normals, inclined at  $43.3^{\circ}$  to the coherent twin

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Figure B.5: Linear fits to Arrhenius plot of  $\Sigma 3$   $\langle 110 \rangle$  tilt boundary with  $\{8\ 1\ 1\}/\{5\ 5\ 4\}$  normals, inclined at  $64.6^{\circ}$  to the coherent twin



Figure B.6: Linear fit to Arrhenius plot of  $\Sigma 3$  (110) tilt boundary with {1 1 2}/{1 1 2} normals, inclined at  $90^{\circ}$  to the coherent twin

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