A Grain Growth Study: the Five Parameter Grain Boundary Curvature Distribution and the Evolution of Grain Face Area

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Abstract

A distribution of grain boundary curvature as a function of five independent crystallographic parameters is proposed and tested on some simple geometries. The results show that the grain boundary mean curvature distribution (GBHD) is able to capture the curvature of a digitized microstructure though noise may arise from several sources.

The GBHD is measured in two sets of three-dimensional electron backscattered diffraction (EBSD) data collected in an austenitic and a ferritic steel. It is found that the grain boundary mean curvature varies with the boundary crystallography and is more sensitive to the grain boundary plane orientation than to the disorientation. The grain boundaries with the smallest curvatures also have low grain boundary energy and large relative areas while the curvature and energy of more general grain boundaries are, on average, inversely correlated.

The GBHD is also computed from a set of electron backscattered diffraction (EBSD) data collected from $SrTiO_3$ annealed at 1470 °C. Unlike the steels, the average grain boundary curvature is found to be directly correlated with the grain boundary energy, suggesting that the microstructure of $SrTiO_3$ at 1470 °C may contain many singular grain boundaries.

The integral mean curvature of grain faces (M_s) is analyzed for the grains in the steel samples and in SrTiO₃. Similar results are obtained in the three datasets. For a given grain, its M_s is closely related to its topological characteristics. Grains with a small number of faces have positive M_s and grains with many faces have negative M_s . The grains with zero M_s are those whose number of neighbors equal the average number of faces of their nearest neighbors.

Various geometric, topological, and mean-field features are hypothesized to capture the evolution of grain faces in a high purity Ni sample. The dataset was collected by the Suter group at Carnegie Mellon University using the high energy diffraction microscopy (HEDM) technique. It consists of two orientation maps of a given volume, one for the pre-anneal state and one for the after-anneal state between which the sample was annealed at 800 °C for 25 minutes. By fitting the various features with a few machine learning models, we show that curvature does affect the evolution of grain faces but the effect is not deterministic.

A face-averaged approximation is proposed to study the evolution of grain boundary properties. The effectiveness of this face-averaged assumption is validated by a comparison between the true GBHD and the face-averaged GBHD. The results show that the grain boundary area and curvature change vary with the grain boundary inclination systematically.

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1. Introduction

1.1 Motivation

Grain boundaries possess different properties than the bulk grains. For example, excess volume [1], reduced activation energy for diffusion [2] and large dielectric constant [3]. Moreover, the property of a specific grain boundary depends on the way the crystallites on the two sides meet. Dimos et. al. [4] found the critical current density of a superconductor depends on the lattice misorientation across boundary. Watanabe et. al. [5] demonstrated that the intergranular brittleness of the ordered intermetallic alloy Ni₃Al can be relieved by careful design of the grain boundary distribution inside the material and superplasticity can be achieved. Fujisaki et. al. [6] showed the coercivity of Nb-Fe-B sintered magnets depends on the grain boundary plane orientation via micromagnetic simulation. These observations about grain boundaries have helped us design materials with advantageous properties and benefited our everyday life.

However, we do not really understand grain boundaries systematically. Despite the clear evidence from experiments and simulations that grain boundary properties are closely related to grain boundary structures, we have only limited knowledge about the relative abundance and diversity of grain boundaries. The most important reason is that grain boundaries are inside dense solid materials, which makes them impervious to observation and measurement by most techniques. In addition, the number of distinguishable grain boundaries is large (> 10^4) at the relevant resolutions. Finally, the many grain boundaries within a bulk volume are not independent but are connected and form a network. The property of the network depends not only on the grain boundaries that constitute the network but also on the way they are connected within the network.

This thesis analyzes experimentally measured three-dimensional grain boundary networks. The focus is the grain boundary curvature, the grain boundary area change, and the grain boundary curvature change. Other aspects of the microstructures, like grain boundary energy and grain face topologies, are also evaluated and their correlations are studied.

1.2 Hypothesis

- I. Grain boundary curvature varies with grain boundary crystallographic parameters and is correlated with grain boundary energy. This correlation is inverse for non-singular boundaries and direct for singular boundaries, if there is an approximately constant chemical potential throughout the sample.
- II. There are correlations among the characteristics of grain faces, such as area and curvature, so that high temperature spontaneous changes can be predicted.
- III. Changes in the grain boundary population and grain boundary curvature are anisotropic.During grain growth, the population of low energy grain boundaries should increase.

1.3 Objectives

- I. Measure grain boundary curvature from digital three-dimensional orientation maps and plot grain boundary curvature as a function of the five crystallographic parameters.
- II. Apply the grain boundary curvature distribution to experimentally collected EBSD data and analyze the correlation between grain boundary curvature, energy and population.
- III. Measure integral curvature of grain faces (M_S) for the digital grains reconstructed from the experimental orientation maps. Analyze the correlation between M_S and the topological characteristics of a grain.
- IV. Track grain faces between two successively collected HEDM 3D orientation maps. Construct features to describe the geometric, topological and local mean-field features of grain faces.
- V. Analyze the correlation between different features of a grain face. Train machine learning models predict grain face area and the change of grain face area.
- VI. Study the anisotropy of grain face area and curvature change.

2. Background

2.1 Grain boundaries

Polycrystalline materials consist of small crystallites, or grains, in which atoms adopt a uniform crystal structure. When two grains meet, the periodicity of atomic positions is maintained within each grain until a few nanometers away from the grain boundary which can be thought of as a watershed [7]. The atoms sitting no more than a few nanometers away from the other grain are affected by it and their positions deviate from their ideal positions. The distorted regions are called grain boundaries.

In this chapter, the basic concepts that describe a single piece of grain boundary are introduced in Sections 2.1.1 and 2.1.2. Then some special grain boundaries and classic models that capture the essence of grain boundary structures are discussed in Section 2.1.3.

2.1.1 Parameterizations of grain boundary crystallographic parameters

Grain boundaries have five macroscopic degrees of freedom, two for the grain boundary plane orientation and three for the lattice misorientation between the two grains across the boundary [8]. The grain boundary plane orientation is usually given by the spherical angles θ and φ , as shown in Figure 2.1.



Figure 2.1. Illustration of spherical angles θ and φ . *n* is the grain boundary plane normal direction.

The misorientation is the rotation that can take the grain on one side of the boundary to coincidence with the grain on the other side. There are many ways to parameterize a

misorientation, including rotation matrices, axis-angle pairs, quaternions, Rodrigues vectors and Euler angles.

Rotation matrices (g) are 3×3 orthogonal matrices which express passive rotations following the convention of microstructure analysis [9]. In other words, a rotation matrix describes the rotation that take sample reference frame into the corresponding crystal reference frame. The rotation matrix of a cubic crystal can be written by putting direction cosines for [001], [010] and [100] directions as matrix rows. The advantage of the rotation matrix parameterization is that the combination of successive orientations can be computed easily by matrix multiplication. However, rotation matrices are kind of redundant. It takes nine numbers to write a rotation matrix while there are only three degrees of freedom for a rotation. In other words, the numbers in the rotation matrix are not independent.

From Euler's rotation theorem, there always exists an axis that remains unchanged after the rotation. In other words, there is always a direction [uvw] that has the same indices in the two crystal reference frames across the boundary. The axis-angle pair notation defines the rotation by specifying this common direction (rotation axis) and the corresponding rotation angle. The rotation axis and angle can be computed from the rotation matrix as following [10]:

$$\cos(\omega) = 0.5 \times (\operatorname{trace}(\boldsymbol{g}) - 1)$$
$$u = \frac{g_{23} - g_{32}}{2\sin(\omega)}, v = \frac{g_{31} - g_{13}}{2\sin(\omega)}, w = \frac{g_{12} - g_{21}}{2\sin(\omega)}$$
(2.1)

An alternative way to compute the rotation axis is from eigendecomposition of the rotation matrix. The rotation axis is the eigenvector of the rotation matrix which corresponds to the eigenvalue +1 [9]. The axis-angle notion is intuitive. Moreover, the misorientation angle is a simple but informative metric for the difference between two misorientations if the crystal symmetry, which will be discussed in detail in Section 2.1.2, is considered properly. The shortcoming of axis-angle notion is that the rotation axis will become indistinguishable as the misorientation angle approaches zero. Also, the combination of rotations in the axis-angle notion is not straightforward. To combine two orientations, one needs to convert the orientations to rotation matrices or quaternions to do the computation and then convert the result back.

Quaternions ($\mathbf{q} = [q_1, q_2, q_3, q_4]$) are four dimensional vectors. A unit quaternion can be written from the axis-angle pair notation following [11]:

$$q_1 = \cos\left(\frac{\omega}{2}\right), q_2 = u \times \sin\left(\frac{\omega}{2}\right), q_3 = v \times \sin\left(\frac{\omega}{2}\right), q_4 = w \times \sin\left(\frac{\omega}{2}\right)$$
 (2.2)

In which u, v, w are the components of the normalized rotation axis and ω is the rotation angle. The L2 norm of quaternions is 1, namely $q_1^2 + q_2^2 + q_3^2 + q_4^2 = 1$. Quaternion notion is compact and powerful because orientation combination follows the rule of complex number multiplication and is easy to compute [11]. The parameterization is getting more and more popular in various fields for fast and robust orientation conversion calculations [12], [13].

Rodrigues vectors $\mathbf{R} = [R_1, R_2, R_3]$ are also closely related to the axis-angle notation and contain three components. Rodrigues vectors can be calculated from axis-angle pairs as [9]:

$$R_1 = u \times tan\left(\frac{\theta}{2}\right), R_2 = v \times tan\left(\frac{\theta}{2}\right), R_3 = w \times tan\left(\frac{\theta}{2}\right)$$
 (2.3)

Notice Rodrigues vectors have length $\tan(\frac{\theta}{2})$. The advantage of the Rodrigues vector notion is related to the application of crystallographic symmetries and this will be discussed in detail in Section 2.1.2.

Euler angles describe the orientation by a successive set of rotations around a fixed set of axes. The set of axes can be used differently but the most popular convention is the Bunge Euler notion, in which the axis set is Z'X'Z' and rotation angles are $(\varphi_1, \Phi, \varphi_2)$. Note this axes set is defined in the current, not a fixed, reference frame. In other words, if there exists a fixed reference frame *XYZ*, the first *Z'* axis is the same as the *Z* axis but the second axis *X'* is φ_1 away from *X* since the coordinate frame has rotated around *Z'* for φ_1 in the first rotation. Similarly, the second *Z'* axis doesn't coincide with the *Z* axis. Rotation matrices can be written from Bunge Euler angle notation in the following way [9]:

$$\boldsymbol{g}_{\varphi_{1}}^{Z'} = \begin{bmatrix} \cos\varphi_{1} & \sin\varphi_{1} & 0\\ -\sin\varphi_{1} & \cos\varphi_{1} & 0\\ 0 & 0 & 1 \end{bmatrix}, \boldsymbol{g}_{\varphi}^{X'} = \begin{bmatrix} 1 & 0 & 0\\ 0 & \cos\varphi & \sin\varphi\\ 0 & -\sin\varphi & \cos\varphi \end{bmatrix}, \boldsymbol{g}_{\varphi_{2}}^{Z'} = \begin{bmatrix} \cos\varphi_{2} & \sin\varphi_{2} & 0\\ -\sin\varphi_{2} & \cos\varphi_{2} & 0\\ 0 & 0 & 0 \end{bmatrix}$$
$$\boldsymbol{g} = \boldsymbol{g}_{\varphi_{1}}^{Z'} \boldsymbol{g}_{\varphi_{2}}^{X'} \boldsymbol{g}_{\varphi_{2}}^{Z'}$$
(2.4)

 $g_{\varphi_1}^{Z'}, g_{\Phi}^{X'}$ and $g_{\varphi_2}^{Z'}$ are for the three successive rotations and g, the rotation (misorientation) of interest, is the matrix product of $g_{\varphi_1}^{Z'}, g_{\Phi}^{X'}$ and $g_{\varphi_2}^{Z'}$. The Euler angle convention is widely used to

record experimental data. [14, 15] Notice φ_1 and φ_2 will become indifferentiable when Φ is small.

2.1.2 Bi-crystal symmetry and the grain boundary fundamental zone

Parameterization of the five degrees of freedom enables us to define a grain boundary. However, two grain boundaries with different parameters are not necessarily unique because of symmetry. The symmetry of grain boundaries is defined in the context of two three-dimensional component crystals containing a unique interface, namely the boundary plane, and is referred to as bi-crystal symmetry [16].

Bi-crystal symmetry comes from the symmetry of the component crystals and is related to their relative orientations, or the misorientation, and the specific position of the boundary plane. While point symmetry always hold, there may or may not be one- or two- dimensional translation symmetry in the boundary plane depending on the misorientation and the plane normal [16], [17].

Because of the symmetry elements, it is possible that grain boundaries with different parameters are physically identical. It is well known that the crystallographic parameters have duplicates under crystal symmetry. For example, [100] and $[0\overline{1}0]$ are indistinguishable under cubic symmetry. The duplications produced by bi-crystal symmetry are similar to those produced by crystal symmetry but are more complicated and can result in unnecessary confusion in the analysis of grain boundaries. One way to avoid the duplication is to analyze only the grain boundaries in the fundamental zone (FZ), which originated from the concept of fundamental domain in topology.

The misorientation FZ is also referred as the set of disorientations. As discussed above, a misorientation can have many equivalent representations. Disorientation is the name of a special misorietation whose rotation angle is the minimum among its equivalent representations and whose rotation axis lies in the standard stereographic triangle. A physically distinct grain boundary can have many equivalent misorientation representations but one and only one of them lies in the FZ and can be called the disorientation. The Rodrigues vector is the best parametrization to visualize the misorientation FZ (Figure 2.2). With the Rodrigues vector, the geometry of FZ can be expressed neatly as [18]:

$$\sqrt{2 - 1} \ge R_1 \ge R_2 \ge R_3 > 0$$

$$R_1 + R_2 + R_3 \le 1$$
(2.5)

 R_1, R_2 and R_3 are the three components of the Rodrigues vector. In some other parameterizations like Euler angles, the misorientation FZs have distorted shapes and are difficult to illustrate.



Figure 2.2. The fundamental zone of cubic symmetry in Rodrigues space. (a) The outline of the truncated cube is the fundamental zone of orientation space. The red truncated tetrahedron is the fundamental zone of misorientation space, also known as the Mackenzie cell. (b) the Mackenzie cell. Figure reprinted from Reference [19].

Note that although we have just discussed the difference between the concept of misorientation and disorientation, many writers do not make this distinction and the term misorientation is often used to refer to disorientation. To be consistent with such convention, both misorientation and disorientation mean disorientation in the following document unless the term symmetrically equivalent misorientation is mentioned.

The grain boundary plane fundamental zone (GBPFZ) is associated with the common rotation axis and is more complicated. In centrosymmetric crystals, all rotation axes in the bicrystal frame have inversion symmetry and thus the GBPFZ is at most a half sphere. If the common rotation axis has extra symmetry, the GBPFZ will be reduced to a smaller region [9], [10].

The exact grain boundary fundamental zone can be obtained by combining the misorientation fundamental zone and the boundary plane fundamental zone. There is simulation evidence that the consideration of grain boundary plane fundamental zone reveals a stronger structure-property correlation than that of the misorientation fundamental zone [21]. However, usually only the misorientation fundamental zone is considered. One reason is that the grain boundary plane fundamental zone depends on the symmetry of the rotation axis and is different for each misorientation. Also, the duplications produced by in-plane symmetries are much fewer compared to those produced by lattice point group symmetries. In the following discussions, the fundamental zone stands for misorientation fundamental zone in Rodrigues vector space and grain boundary plane distributions will be plotted on a hemisphere, even if this is larger than the GBPFZ.

2.1.3 Classical models

General grain boundaries have complicated structures. Still, there are some simple but classical models that can help us build some intuition about the nature of grain boundary structures. In following section, we'll introduce tilt and twist boundaries, symmetric and asymmetric boundaries, low angle grain boundaries (LAGB) and high angle grain boundaries (HAGB), coherent and incoherent boundaries and the coincident site lattice (CSL) model.

Tilt and twist are two elementary grain boundary types defined by the relative position of the misorientation axis and the grain boundary plane. In tilt boundaries (Figure 2.3), the misorientation axis lies in the boundary plane. In twist boundaries (Figure 2.4b), the misorientation axis lies normal to the boundary plane.



Figure 2.3. Illustration of a low angle symmetry tilt grain boundary constructed by edge dislocations. Figure reprinted from Reference [22].

Note a problem with this classification is that the twist and tilt nature is not definite but depends on the parameters. Because one grain boundary can have different parameters due to

symmetry, it is possible that a grain boundary is classified as tilt by one set of parameter and twist by another set of parameter [23]. Also, natural grain boundaries are rarely perfect facets and have mixed tilt and twist characters. Nevertheless, some bi-crystal experiments, in which the tilt/twist character is carefully controlled, have indicated that the grain boundary of the same misorientation but different tilt/twist character have more than 10 times different mobility at the same temperature [2].

According to the misorientation angle, grain boundaries can be classified into low angle grain boundaries (LAGBs) and high angle grain boundaries (HAGBs). This classification is motivated by the assumption that small lattice mismatch, as in the case of LAGB, can be accommodated by dislocations. The grain boundary shown in Figure 2.3 is a tilt LAGB. Note that the set of dislocations in Figure 2.3 have the same Burgers vector and there is a reflection symmetry across the boundary. In this case, the grain boundary is actually a symmetric tilt LAGB. An asymmetric tilt LAGB is shown in Figure 2.4a, in which there exists another set of edge dislocation of a different Burgers vector and the reflection symmetry is broken. The grain boundary shown in Figure 2.4b constructed by two sets of crossing screw dislocations and has a twist character.



Figure 2.4. Illustration of (a) an asymmetric tilt grain boundary composed of two sets of edge dislocations and (b) a twist grain boundary composed of screw dislocations. Figure reprinted from Reference [22].

It's worth mentioning that the set of geometrically necessary dislocations needed to construct a LAGB boundary is determined by the lattice misorientation. For example, in Figure 2.3, the dislocation separation d is related to the misorientation angle θ and the dislocation Burgers vector **b** as $tan(\frac{\theta}{2}) = \frac{|\mathbf{b}|}{2d}$, which can be simplified to $\theta = \frac{|\mathbf{b}|}{d}$ for small θ [24]. The magnitude of Burgers vector, $|\mathbf{b}|$, depends on the lattice parameter and is relatively stable. As θ increases, the dislocations will be squeezed closer until their dislocation cores overlap and individual dislocations become indistinguishable. In such case, the lattice dislocation model can no long be applied and the grain boundary becomes a HAGB. The threshold misorientation angle that differentiates LAGBs and HAGBs is not deterministic, usually taken to be between 10° to 15° [19]. Some experiments have shown that there is a transition region between the highly ordered LAGB and the completely disordered general HAGB [2].

Not all HAGBs have completely disordered structure. Let's ignore the grain boundary atoms for a moment and think only about the lattice sites. When the two lattices meet at the interface, sometimes a portion of their lattice sites will overlap. An example is given in Figure 2.5, in which the two lattices are misorientated by 36.87@[100].



Figure 2.5. Different views of a CSL lattice with 36.87@[100] ($\Sigma5$) misorientation. Right side: interface parallel to paper plane. Left side: interface normal to paper plane. Red dashed line indicates a coherent boundary plane. Blue dashed line indicates a incoherent boundary plane. Reprinted from Reference [19].

There are 3 motifs in Figure 2.5, triangles, circles and triangles inside circles. The circle motif and the triangle motif stand for the two regular crystal lattice sites. The triangle inside

circle motif stands for the common sites shared by both lattices. Note the triangle inside circle motif forms a periodic lattice which has larger volume than the regular crystal lattices and is referred to as the coincident site lattice (CSL). CSL lattices are named by the inverse coincident sites density as Equation 2.6.

$$\Sigma = \frac{\text{volume of elementary CSL cell}}{\text{volume of elementary crystal lattice cell}}$$
(2.6)

The lattice in Figure 2.5 is assigned as a Σ 5 boundary. Actually, all misorientations can result in some level of lattice coincidence and can be assigned a Σ number given two infinite lattices. However, Σ numbers of the general HAGBs are very large thus are not really informative.

Remember the grain boundary type also depends on the boundary plane position. It can be seen easily from the left side of Figure 2.5 that the a grain boundary with its boundary plane lying along the red dashed line is different from one with its boundary plane lying along the blue dashed line. In the former case, the boundary is coherent as the two crystals match perfectly at the interface. In the latter case, the boundary is incoherent and the atomic structure at the interface is rather disordered.

Real atoms on grain boundaries are relaxed and generally won't sit on the exact perfect lattice position as in Figure 2.5. However, it's still legitimate to assume that atoms will stay close to the perfect lattice position, especially when the boundary plane is coherent and the coincident cite density is high. There has been plenty experimental evidence showing that low Σ CSL coherent boundaries have relatively low energy and small activation enthalpy, especially the Σ 3 in FCC material [25][26].

2.2 Grain boundary distributions

Like all high dimensional spaces, the 5D grain boundary space can't be presented directly in our 3D world with full details. The way to interpret the statistical information of grain boundary properties is to project them into lower dimension distributions. In the following section, some existing grain boundary property distributions will be introduced, including the grain boundary disorientation angle distribution, grain boundary plane distribution (GBPD), grain boundary character distribution (GBCD) and grain boundary energy distribution (GBED).

2.2.1 Grain boundary disorientation angle distribution

The simplest grain boundary distribution is the 1D disorientation angle (θ) distribution, for which the misorientation axes and grain boundary plane inclinations are ignored. There are two points about the disorientation angle distribution. The first one is that the largest disorientation angle is not 360° but varies for materials with different symmetry. This document will focus on cubic materials whose largest possible disorientation angle is 62.8°. The second point is that a random distribution of disorientation angles doesn't look uniform.

The random disorientation angle distribution was first presented by Mackenzie [27][28]. He showed that if a large number of points were sampled randomly in the grain boundary space, their disorientation angle distribution would peak at 45°, as show in Figure 2.6.



Figure 2.6. The grain boundary disorientation angle distribution sampled from random orientation distribution. Figure reprinted from Reference [26].

The shape of the disorientation angle distribution is associated with the shape of grain boundary fundamental zone Figure 2.2. The geometrical interpretation is as follows: if we intersect the FZ with a sphere of increasing radius, the intersections will correspond to contours of disorientation angles. The intersection area would increase with the sphere radius until the first corner of the FZ, which corresponds to $45^{\circ}/[100]$, is reached. The angle 45° stems from the 4-fold symmetry of the [001] axis. The intersection area will then start to decrease and reach zero when the last corner of the FZ is reached, which corresponds to a radius of $tan(\frac{62.8^{\circ}}{2})$. A sphere of even larger radius will then sweep out the fundamental zone.

2.2.2 Grain boundary plane distribution

The grain boundary plane distribution (GBPD) is the distribution of grain boundary area as a function of boundary plane, irrespective of the lattice misorientaions. The reference frame is the crystal frame and GBPDs are presented in standard stereographic triangles. Each grain boundary sits between two lattices and is converted to both crystal frames. Only the crystal lattice symmetry, not the bi-crystal symmetry, needs to be considered because misorientation is ignored in GBPDs. The distribution is normalized after all boundaries are counted to eliminate bias from the varying number of observations in different experiments. The unit is multiples of random distribution (MRD), which indicates the relative areas in a normalized distribution. The relative area expected in a random distribution is 1 MRD, higher and lower values correspond to boundaries that are over and underrepresented, respectively.

2.2.3 Grain boundary character distribution

The grain boundary character distribution (GBCD) is the distribution of grain boundary area as a function of the full five parameters. Due to the 2D space limitation of paper, it's usually presented as the grain boundary plane areas for a fixed misorientation. Unlike GBPDs, GBCDs counts for the full five parameters and needs to consider the bi-crystal symmetry. As mentioned in Section 2.1.2, there can exist some in-plane symmetry but it is fully enforced when computing the distribution and is obvious in the plots. As a result, GBCDs are always presented in the full stereographic projection circles. The unit is also MRD.

To compute the GBCD, one needs to first choose the parameterization for the five degrees of freedom. For the plane normal, the choice is fairly easy and is usually the spherical angles. For the misorientations, it's more complicated because of its 3D nature and the fact that one needs to take into account the bi-crystal symmetry. The Rodrigues vector is one choice but there are two problems with it. First, the partition of the parameters should be uniform but it's not easy to realize within the Rodrigues vector fundamental zone. The problem of segmenting the Rodrigues vector fundamental zone equally is essentially the same as dividing an irregularly shaped 3D object uniformly, for which there is no available analytic solution. Second, the misorientation axes of LAGBs are indifferentiable. Another choice is the Euler angles, first applied by Rohrer et. al. [29]. This is the convention that we are going to use for the grain boundary curvature distribution and it will be described in detail in Section 3.2.

It is worth noting that segmenting the full five parameters is not the only way to represent GBCD. As a matter of fact, the smoothness of GBCD is undermined due to the finite resolution of segmentation. Glowinski presented an alternative kernel based estimation of the GBCD [30] which surpasses the parameter segmentation by looking directly for grain boundary plane distributions of a fixed misorientation. The kernel based method shows better smoothness and sharper peaks for some small Σ CSL boundaries. However, the information in the full five parameter space is not integrated and the method can be slow if one is interested in many misorientations because the kernel based method searches for only a single misorientation each time. The qualitative trends in the distribution are consistent in the partition based and the kernel based method.

2.2.4 Grain boundary energy distribution

The grain boundary energy distribution (GBED) is the distribution of grain boundary energy, or more precisely the excess free energy associated with grain boundaries, as a function of the five crystallographic parameters. Grain boundary energy plays an important role in microstructure evolution since it provides the driving force for grain boundary migration [31][32].

It is well-accepted that the grain boundary energy is correlated to its crystallographic parameters [33]–[35]. Grain boundaries can be classified into two types depending on the local energy landscape: the singular boundaries, whose energy sits in local cusp, and non-singular boundaries, whose energy varies smoothly with the crystallographic parameters. The energy of singular boundaries is exceptionally low at its exact crystallographic parameters, and changes dramatically with any small deviation in the crystallographic parameters. In other words, the energy derivative is infinite, or un defined at the singular boundaries [31]. An example of singular boundaries is the coherent twins in FCC material [36].

There is no efficient way to estimate the energy of a grain boundary, unless it is a LAGB. The energy of LAGBs can be estimated directly from their misorientation angle, because a LAGB can be approximated by a set of dislocations, as shown in Section 2.1.3. The dislocation core energy can be calculated given the Burgers vector and number of dislocations can be estimated from the misorientation angle using the LAGB dislocation model. However, until now, there has been no simple deterministic model that can predict the energy of general HAGBs [32]. There are two ways to obtain the grain boundary energy data: experimental measurements and molecular-dynamics simulation.

The experimental measurement of relative grain boundary energy is based on the assumption that local equilibrium prevails during grain growth at high temperatures. As a result, when three grain boundaries meet at a triple junction, their tug of war results zero net force along the triple junction.

A simple case is illustrated in Figure 2.7b. If the vicinity of the grain boundary energy landscapes is smooth and the grain boundaries can't reduce a significant amount of energy by rotation, the force balance will then involve only the balance of grain boundary surface tensions, which can be described by Young's equations:

$$\frac{\gamma_1}{\sin\theta_{2,3}} = \frac{\gamma_2}{\sin\theta_{1,3}} = \frac{\gamma_3}{\sin\theta_{1,2}}$$
(2.7)

 γ is the magnitude of grain boundary energy. θ is the angle between the grain boundaries and is called the dihedral angle. The relative values of γ_1 , γ_2 and γ_3 can be decoded by measuring dihedral angles and applying Equation 2.7.



Figure 2.7. Illustrations of the balance of interfacial energies at triple junctions. (a) The full balance of surface tensions and torque forces. (b) The balance of surface tensions ignoring the torque forces. Reprinted from Reference [31].

However, the assumption that grain boundaries can't reduce a significant amount of energy by rotation is usually not valid. First, grain boundary energy is generally anisotropic so the tendency of a grain boundary to change its orientation, which can be quantified as its associated torque, is not rare. Second, the grain boundary energy landscape is not smooth. There exist cusps in the energy landscape which correspond to grain boundaries of exceptionally low energy. For example, the coherent twin boundary in FCC materials [32][37]. The grain boundaries sitting in the vicinity the cusps have a strong tendency to rotate themselves towards the low energy direction, which can result in torques of large magnitude. A complete description of equilibrium condition requires the balance of both surface tensions and torque forces and is given in the Herrings equation:

$$\sum_{i=1}^{3} \left(\gamma_i \boldsymbol{t}_i + \frac{\partial \gamma_i}{\partial \boldsymbol{t}_i} \right) = 0$$
 (2.8)

 t_i is the grain boundary trace direction in a plane normal to the triple junction. $\frac{\partial \gamma_i}{\partial t_i}$ is the direction orthogonal to both the boundary normal and the triple junction direction. This equation can be written more concisely with capillary vectors as:

$$(\xi_1 + \xi_2 + \xi_3) \times l = 0 \tag{2.9}$$

 ξ_1, ξ_2 and ξ_3 are the capillary vectors defined by Cahn and Hoffman [38], [39]

$$\boldsymbol{\xi} = \gamma \boldsymbol{n} + \left(\frac{\partial \gamma}{\partial \theta}\right)_{max} \boldsymbol{k}_0 \tag{2.10}$$

In which \boldsymbol{n} is the grain boundary normal direction. $d\theta$ is the orientation change in the boundary plane and \boldsymbol{k}_0 is the direction for which the angular rate increase of γ is the maximum.

Each triple junction gives one specific case of Equation 2.9. There are many triple junctions in a sample and the same grain boundary, or grain boundaries with the same crystallographic parameters, can appear in many triple junctions. Solving the equations simultaneously will then yield the relative grain boundary energy distribution in the sample [40]. Rohrer et al. have extracted grain boundary energy data from several materials via this approach [41]–[43].

Molecular-dynamics (MD) simulation is another approach to obtain grain boundary energy data. In theory, the analytic solution of a solid can be obtained by solving the corresponding many electron Schrodinger equation but the calculation is impedingly complicated. Practical calculations are based on models with reasonable assumptions and simplifications, among which the embedded atom method (EAM) is a popular one. The EAM model works well in systems with low symmetry, such as grain boundaries. Reference [44] is a good review paper on EAM and the points about the model is summarized below.

In a simple case, the EAM model makes the assumption that the total energy of solids can be approximated by an embedding energy plus an electrostatic interaction. The electrostatic interaction is basically a sum of all pair potentials as in the Lennard-Jones model. The embedding energy accounts for the interaction of an atom with the background electron gas provided by its neighbors. Its magnitude can be determined empirically by fitting experimental or DFT data. Put together,

$$E_{coh} = \sum_{j} G_{i} \left(\sum_{j \neq i} \rho_{j}^{a} \left(R_{ij} \right) \right) + \frac{1}{2} \sum_{i, j (j \neq i)} U_{ij} \left(R_{ij} \right)$$
(2.11)

 E_{coh} is the cohesive energy. *G* is the embedding energy. ρ^a is the spherically averaged atomic electron density. R_{ij} is the distance between atom *i* and *j*. *U* is the pair potential. With the EAM model, the system energy is written as a function of atom positions which can then be optimized simply. One thing to note about calculating grain boundary structure based on EAM and energy-minimization is that initialization is important. Though the grain boundaries are usually defined by the five macroscopic parameters, the five parameters are actually not enough to capture the full details of the exact grain boundary atomic structure because the microscopic shifts can still vary. Because energy-minimization techniques like conjugate gradient descent finds only local minima, different initializations which correspond to different microscopic shifts need to be tried for a given grain boundary to find an optimal minima.

The steps to compute the grain boundary energy using an EAM model are as follows. First, one needs to construct the atomistic structure of the grain boundary from its five macroscopic parameters by placing together two blocks of atoms following the given misorientation and boundary plane orientation. Atoms being too close to the boundary are deleted. Then the boundary conditions, which can be set as periodic in all directions or free surface parallel to the boundary plane, are specified. Finally, the energy minimization algorithm is specified and the structure is allowed to evolve by itself, during which the atoms sitting on the grain boundary are relaxed and can move around locally to approach the minimum energy configuration. Olmsted and Holm et al. investigated a large number of grain boundaries systematically by an EAM model with empirical interatomic potential [34][35]. Interestingly, the grain boundary energy

calculated by Olmsted and Holm et al., correlated well with the GBCD measured experimentally by Rohrer et al., [25][45].

2.3 Curvature basics

Curvature is an important concept in many fields. From a materials science point of view, curvature plays a key role in deriving the equilibrium condition in a system with interfaces [31], [46]. From a mathematic point of view, curvature captures the essence of a general geometric shape and lies at the heart of differential geometry. For example, two plane curves are congruent if and only if the signed curvature at all points of the two plane curves are equal [47]. In the following section, we'll first go over some basic concepts in differential geometry that are related to our interest, including plane curves, space curves, surfaces and curvatures. Then the interaction between curvature and other thermodynamic properties will be discussed.

2.3.1 Differential geometry basics

Differential geometry is a profound field which concerns the smoothness and properties of manifolds in high dimensions. To avoid unnecessary confusion, we'll restrict ourselves to 2D and 3D spaces in the following discussion. Let's begin with the simple case of a differentiable plane curves in two dimensions. A curve α can exist in arbitrary dimensions but essentially has only one degree of freedom, which we'll parameterize with *s*, the arc length of the curve. Note choosing of the parameter is not trivial because parameterization affects the numerical complexity of differential equation [48]. Arc length is the most elegant choice for the parameterized curve stays invariant. In three-dimensional Cartesian coordinates, the expression for the curve α is then $\alpha(s) = (x(s), y(s))$. The unit tangential vector of $\alpha(s)$ at *s* is then defined as $\mathbf{t}(s) = \alpha'(s)$, where the prime denotes derivative. The normal vector at *s* is defined as $\mathbf{n}(s) = \frac{\alpha''(s)}{||\alpha''(s)||}$, in which $||\alpha''(s)||$ denotes the norm of $\alpha''(s)$. $\mathbf{n}(s)$ is, of course, orthogonal to $\mathbf{t}(s)$.

A concept more relevant to our purpose of interest is the space curve on a surface. A surface is two dimensional and can be parameterized with two parameters, for which the convention is (u, v). A space curve embedded in the surface can still be parameterized with its arc length as $\alpha(s) = (u(s), v(s))$. For a space curve, apart from the tangent vector $\mathbf{t}(s)$ and the normal vector $\mathbf{n}(s)$, there is another important vector which is the binormal vector $\mathbf{b}(s)$, defined as $\mathbf{b}(s) = \mathbf{t}(s) \times \mathbf{n}(s)$. \times denotes cross product. The ordered triplet of unit vectors $(\mathbf{t}(s), \mathbf{n}(s), \mathbf{b}(s))$ is called the Frenet frame of α at $\alpha(s)$ [47] and their spatial arrangement is illustrated in Figure 2.8. The osculating plane is the plane spanned by $\mathbf{t}(s)$ and $\mathbf{n}(s)$. The tangent plane is the plane spanned by $\mathbf{t}(s)$ and $\mathbf{b}(s)$.



Figure 2.8. Illustration of (a) local Frenet frame. (b) osculating circle and radius of curvature. Reprinted from Reference [45].

A surface is usually denoted as $\mathcal{F}(u, v)$, which can be expressed as $\mathcal{F}(u, v) = (x(u, v), y(u, v), z(u, v))$ in 3D Cartesian coordinates. The surface properties of a surface are encapsulated its fundamental forms [49].

The first fundamental form captures the intrinsic property of the surface by expressing the square arc length between two infinitely close points $P(u_0, v_0)$ and $P'(u_0 + du, v_0 + dv)$ in terms of du and dv. Using first order approximation, $ds^2 = (\mathcal{F}_u du + \mathcal{F}_v dv)(\mathcal{F}_u du + \mathcal{F}_v dv) = \mathcal{F}_u \cdot \mathcal{F}_u du^2 + \mathcal{F}_u \cdot \mathcal{F}_v du dv + \mathcal{F}_v \cdot \mathcal{F}_v dv^2$, in which $\mathcal{F}_u = \frac{\partial \mathcal{F}(u_0, v_0)}{\partial u}$ and $\mathcal{F}_v = \frac{\partial \mathcal{F}(u_0, v_0)}{\partial v}$. The coefficients are denoted as E, F, G by convention:

$$E = \mathcal{F}_{u} \cdot \mathcal{F}_{u} = x_{u}^{2} + y_{u}^{2} + z_{u}^{2}$$

$$F = \mathcal{F}_{u} \cdot \mathcal{F}_{v} = x_{u}x_{v} + y_{u}y_{v} + z_{u}z_{v}$$

$$G = \mathcal{F}_{v} \cdot \mathcal{F}_{v} = x_{v}^{2} + y_{v}^{2} + z_{v}^{2}$$

$$(2.12)$$

The expression for the first fundamental form of \mathcal{F} is then:

$$I = Edu^2 + Fdudv + Gdv^2 \tag{2.13}$$

The second fundamental form captures the extrinsic property of the surface by expressing the distance from $P'(u_0 + du, v_0 + dv)$ to the tangential plane to $P(u_0, v_0)$, which gives us an idea of how curved the surface is. Here we need the second order approximation for the vector $\overrightarrow{PP'}$ between P and $P': \overrightarrow{PP'} = \mathcal{F}_u du + \mathcal{F}_v dv + \frac{1}{2}(\mathcal{F}_{uu} du^2 + 2\mathcal{F}_{uv} dudv + \mathcal{F}_{vv} dv^2)$. Project $\overrightarrow{PP'}$ onto the surface normal \mathbf{n} at P by taking the inner product and the terms containing \mathcal{F}_u and \mathcal{F}_v will then vanish: $\overrightarrow{PP'} \cdot \mathbf{n} = \frac{1}{2}(\mathcal{F}_{uu} \cdot \mathbf{n} du^2 + 2\mathcal{F}_{uv} \cdot \mathbf{n} dudv + \mathcal{F}_{vv} \cdot \mathbf{n} dv^2)$. Denote the coefficients by L, M, N and the second fundamental form of the surface is then:

$$II = Ldu^2 + Mdudv + Ndv^2 \tag{2.14}$$

From the coefficients of the two fundamental forms, we can write the Weingarten matrix:

$$\boldsymbol{W} = \begin{bmatrix} E & F \\ F & G \end{bmatrix}^{-1} \begin{bmatrix} L & M \\ M & N \end{bmatrix} = \begin{bmatrix} \frac{LG - MF}{EG - F^2} & \frac{MG - NF}{EG - F^2} \\ \frac{ME - LF}{EG - F^2} & \frac{NE - MF}{EG - F^2} \end{bmatrix}$$
(2.15)

The Weingarten matrix gives the relationship of two fundamental properties of the surface, the normal curvature and the tangent line direction.

Let's first step back to define the normal curvature of space curves. A simpler analogy of normal curvature, which is defined for space curve in 3D space, is the curvature of a plane curve defined in 2D space. The curvature of a plane curve at $\alpha(s)$, denoted as $\kappa(s)$, is given by $\alpha''(s) = \kappa(s)\mathbf{n}(s)$. The magnitude of the curvature is $||\alpha''(s)||$, which has an equivalent and more intuitive expression as the inverse radius of the osculating circle $\kappa(s) = \frac{1}{r}$, as illustrated in Figure 2.8b. Note that curvatures have signs, which are related to the direction of $\mathbf{n}(s)$. Similarly, normal curvature for a space curve in 3D space is defined as the component of $\alpha''(s)$ in the direction normal to \mathcal{F} . While a point on a 2D plane curve has only one definite curvature, a point on a 3D surface has a set of normal curvatures which correspond to the family of space curves intersecting at that point. On Figure 2.8, a space curve is the intersection of the surface and a given osculating plane. The family of space curves can be acquired by rotating the osculating plane around the plane normal for 180°. At a point (u_0, v_0) , given the tangent directions $(\mathcal{F}_u, \mathcal{F}_v)$ and the Weingarten matrix, the normal curvature can be written as:

$$\kappa_n = \begin{bmatrix} \mathcal{F}_u & \mathcal{F}_v \end{bmatrix} \boldsymbol{W} \begin{bmatrix} \mathcal{F}_u \\ \mathcal{F}_v \end{bmatrix}$$
(2.16)

The eigenvalues of the Weingarten matrix give the two extreme values of κ_n at (u_0, v_0) and the two extremals are called the principle curvatures. The corresponding eigenvectors give the principal directions.

The mean curvature *H* is the mean value of the two principal curvatures and the Gaussian curvature *G* is the product of the two principal curvatures. With the osculating circle radius notion, if the two principle curvatures at the point of interest are r_1 and r_2 then $H = \frac{r_1 + r_2}{r_1 r_2}$ and $G = \frac{1}{r_1 r_2}$. *H* and *G* can also be written from the trace and determinate of the *W*:

$$H = \frac{1}{2}tr(W) = \frac{1}{2}\frac{LG + NE - 2MF}{EG - F^2}$$

$$K = det(W) = \frac{LN - M^2}{EG - F^2}$$
(2.17)

2.3.2 Curvature in thermodynamic equilibrium

The equilibrium condition in a system containing a curved surface is related to the geometry of that surface because intensive surface properties interact with intensive volumetric properties through curvature. In this section, we'll follow the derivation in Reference [46]. First, the way curvature relates to different properties will be reviewed. Then an over simplified thermodynamic system will be analyzed to build some intuition about the importance of curvature.

The unit of surface energy is "per area", which is different from the "per volume" unit of other thermodynamic intensive variables. However, the two units can be related to one another with help of curvature. Consider an infinitely small smooth surface patch as in Figure 2.9. Then \boldsymbol{v} and \boldsymbol{u} are the two principal directions and r_1 and r_2 are the radii of the two principal curvatures. $d\varphi_1$ and $d\varphi_2$ are infinite small so the arc lengths are approximately $r_1d\varphi_1$ and $r_2d\varphi_2$. The area of the initial surface is $A_0 = r_1d\varphi_1r_2d\varphi_2$. Now move this surface along the normal direction (*n*) for an infinite small distance δn . Then the new surface area $A_1 = (r_1 + \delta n)d\varphi_1(r_2 + \delta n)d\varphi_2$ and the change in area is $\delta A = A_1 - A_0 = (r_1 + r_2)\delta n d\varphi_1 d\varphi_2 + O(\delta n^2)$. The second order
term $O(\delta n^2)$ can be neglected. Note the first order approximation for volume change is $\delta V = r_1 r_2 \delta n d\varphi_1 d\varphi_2$. Thus,

$$\delta A = \frac{(r_1 + r_2)}{r_1 r_2} r_1 r_2 \delta \mathbf{n} d\varphi_1 d\varphi_2 = 2H\delta V \qquad (2.18)$$

 δV is related to δA by the mean curvature *H*. The physical meaning of this expression is that the volume swept by a small patch of surface is related to its area change by its curvature.

Now we'll go through Gibb's derivation for the thermodynamic equilibrium for a system with a curved surface. Consider an isolated system that consists of two phases α , β and a curved surface *s* in the middle. Generally, the immediate volume beneath the surface will be affected by the surface and a transition region exists. Dealing with the transition region can be complicated so Gibbs imagined a hypothetical system in which there is no transition region and the interface is a straight dividing plane. All the extensive properties of the two phases are continuous and uniform until the dividing plane. Then all the excess properties associated with the transition region are assigned to the dividing plane as surface excess properties, so this hypothetical system has the same total properties as the original isolated system.



Figure 2.9. An infinite small patch of a smooth surface. \boldsymbol{n} is the plane normal direction. \boldsymbol{u} and \boldsymbol{v} are the principle directions. r_1 and r_2 are radii of curvature and the point *P*. Reprinted from Reference [45].

For above mentioned the system of α , β and *s*, the following conclusions can be reached following the first law of thermal dynamics in an isolated system:

$$dU_{sys} = dU^{\alpha} + dU^{\beta} + U^{s}dA = 0$$

$$dV_{sys} = dV^{\alpha} + dV^{\beta} + V^{s}dA = 0$$
(2.19)

$$dn_{k,sys} = dn_k^{\alpha} + dn_k^{\beta} + n_k^s dA = 0$$

U denotes internal energy. *V* denotes volume volume. *A* denotes area. n_k denotes the number of moles of component *k*. Note $V^s = 0$ because the surface is a dividing plane and has no volume. The equilibrium condition for this isolated system is maximum entropy (*S*), or equivalently, $dS_{sys} = dS^{\alpha} + dS^{\beta} + S^s dA = 0$. For each phase, $dS = \frac{dU}{T} + \frac{P}{T} dV - \sum_{k=1}^{c} \frac{\mu}{T} dn_k$ hold. *T* is temperature and *P* is preassure. We can then write all the properties of β in terms of α and *s* according to Equation 2.19, one can get:

$$dS_{sys} = \left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) dU^{\alpha} + \left(\frac{P^{\alpha}}{T^{\alpha}} - \frac{P^{\alpha}}{T^{\beta}}\right) dV^{\alpha} + \sum_{k=1}^{c} \left(\frac{\mu_{k}^{\alpha}}{T^{\alpha}} - \frac{\mu_{k}^{\beta}}{T^{\beta}}\right) dn_{k}^{\alpha} + \left(S^{s} - \frac{U^{s}}{T^{\beta}} - \sum_{k=1}^{c} \frac{\mu_{k}^{\beta}}{T^{\beta}} n_{k}^{s}\right) dA$$

$$(2.20)$$

Remember dA can be related to dV through Equation 2.18. The sign of curvature can be arbitrary but the convention is to define it as positive when the surface is convex relative to the β phase. Plug $dA = 2HdV^{\beta} = -2HdV^{\alpha}$ into Equation 2.20 and we'll get

$$dS_{sys} = \left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) dU^{\alpha} + \left(\left(\frac{P^{\alpha}}{T^{\alpha}} - \frac{P^{\alpha}}{T^{\beta}}\right) - 2H\left(S^{s} - \frac{U^{s}}{T^{\beta}} - \sum_{k=1}^{c} \frac{\mu_{k}^{\beta}}{T^{\beta}} n_{k}^{s}\right)\right) dV^{\alpha}$$

$$+ \sum_{k=1}^{c} \left(\frac{\mu_{k}^{\alpha}}{T^{\alpha}} - \frac{\mu_{k}^{\beta}}{T^{\beta}}\right) dn_{k}^{\alpha}$$

$$(2.21)$$

Remember the equilibrium condition is that the coefficients of dU, dV and dn all vanish such that $dS_{sys} = 0$. In other words, the thermal equilibrium, mechanical equilibrium and chemical equilibrium achieve at the same time so the system is in overall equilibrium. In Equation 2.21, we can see that the thermal equilibrium condition $T^{\alpha} = T^{\beta}$ and the chemical equilibrium condition $\mu_k^{\alpha} = \mu_k^{\beta}$ are the same as in a system without the surface. However, the mechanical equilibrium condition is changed due to the existence of the surface and curvature is the key to relate the surface and volumetric properties.

2.4 Grain boundary migration and grain growth

We have seen that the thermodynamic conditions of a system are changed by the presence of surface from a hypothetical isolated system in the previous section. Perfect global thermodynamic equilibrium can never be truly achieved in polycrystals because grain boundaries are not thermodynamic equilibrium structures [50]. Nevertheless, a legitimate assumption which laid the foundation of grain boundary migration analysis is that local equilibrium prevails in the system at high temperature. Note that all of the following discussions of local migration are restricted to the context of high temperature and no noticeable dragging effect so that the migration constraints are minimized [31]. In such a context, a small piece of smooth nonsingular grain boundary will migrate towards its local curvature center. Another important class of grain boundary is the singular boundaries, or facets. The migration of singular boundaries is different from that of the smooth boundary though the driving forces of both is same, which is the reduction in total grain boundary energy. Finally, grain boundaries don't stand alone but are connected in a network. The evolution of the network is affected by both the motion of individual grain boundaries and the topological constraints on connections. The spontaneous evolution of the grain boundary network at high temperature is also referred to as grain growth because the cooperative motion of all boundaries always results in an increase of the average grain size. In the following section, we'll first go over the local migration of the general smooth grain boundaries and then the motion of singular boundaries in Section 2.4.1. Then theories of individual grain growth and some classic models for collective growth of multiple grains are summarized in Sections 2.4.2 to 2.4.4.

2.4.1 Chemical potential in the vicinity of grain boundaries

The elementary process of the grain growth is the migration of atoms from one position to another following local energy variations. Thus, understanding the energy variation in polycrystalline materials is essential to understand microstructure evolution. But what's the source of energy variation during grain growth? The answer is: grain boundaries. Grain boundaries have anisotropic energy and their geometries (curvatures), inherited from the initial microstructure, are non-uniform. Herring realized the important role of grain boundaries in volumetric energy variations and derived the chemical potential for a small volume immediately beneath a grain boundary [31]. Note smooth boundaries and singular boundaries needs to be treated differently and we'll go through details of the general smooth boundaries only.

The system in Herring's derivation is a quasi-ideal crystal, which is an ideal solution of material atoms and point defects without dislocations. The fundamental assumption is that atoms move fast enough during grain growth so that thermodynamic equilibrium always holds within a small enough of region of the system. In other words, within an infinitely small region, the system is in its minimum energy state so the total energy change is zero with respect to any infinitely small property fluctuation. Now consider a small volume containing a piece of grain boundary. If an infinitely small hump is built on the grain boundary, there will be a small change in the boundary normal direction (δn) and a small change in the grain boundary area (δdS). The total energy change in grain boundary energy is given by $\delta \int \gamma(\mathbf{n}) dS = \int \delta \gamma(\mathbf{n}) dS_0 + \delta \int \gamma(\mathbf{n}) dS_0 dS_0$ $\int \gamma(\mathbf{n}) \delta dS$. The second term in this equation accounts for the energy contribution from area change assuming the grain boundary energy stays the same and is thus the same as the derivation in 2.3.2. The first term accounts for the fact that because grain boundary energy is a function of grain boundary crystallographic parameters, change of grain boundary normal direction n will result in a change of grain boundary energy. Note γ is generally a function of both misorientation and boundary normal direction but misorientation is fixed in current case. The value of the two terms are given by:

$$\int \gamma(\boldsymbol{n}) \delta dS = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \delta V$$

$$\int \delta \gamma(\boldsymbol{n}) dS_0 = \left(\frac{\partial^2 \gamma}{\partial \boldsymbol{n}_x^2} \frac{1}{R_1} + \frac{\partial^2 \gamma}{\partial \boldsymbol{n}_y^2} \frac{1}{R_2}\right) \delta V$$
(2.22)

Subscripts x and y denotes the principle directions at the point of interest. Detailed derivation can be found in [31]. This change in surface energy has to be balanced with a change in volume energy, which is given by.

$$-p\delta V + \mu_h \frac{\delta V}{\Omega_0} \tag{2.23}$$

In which *p* is the effective pressure caused by the surface tension of the grain boundary. μ_h is the chemical potential of point defects. Ω_0 is the atomic volume so $\frac{\delta V}{\Omega_0}$ is the number of migrated atoms. This pressure is not uniformly distributed in the crystal. Nevertheless, we'll assume that

it operates in a way similar to the hydrostatic pressure in the region immediately near the grain boundary. The second term arise from the fact that a change in the grain boundary shape is possible only if some atoms have migrated. The matter transportation mechanisms, volume diffusion and surface diffusion, are conservative so the migration of a set of atoms is equivalent to the migration of an equal amount of point defects in the opposite direction. Setting the sum of surface energy change and volume energy change to be zero and realizing that the grain boundary energy in the volume is given by $\mu = \mu_0 + p\Omega_0$, where μ_0 is the reference chemical potential, one gets the extra chemical potential in a volume immediately near the grain boundary:

$$\mu - \mu_h - \mu_0 = \left(\gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \frac{\partial^2 \gamma}{\partial \boldsymbol{n}_x^2} \frac{1}{R_1} + \frac{\partial^2 \gamma}{\partial \boldsymbol{n}_y^2} \frac{1}{R_2}\right) \Omega_0$$
(2.24)

The beauty of Equation 2.24 is that the extra chemical potential is completely determined from the local boundary geometry. Equation 2.24 is exact but the stiffness terms are difficult to measure in practice. A simplified expression which is more commonly used is $\mu = 2H\gamma$, in which $H = \frac{R_1 + R_2}{2R_1R_2}$ is the average mean curvature and the torque terms are ignored.

The above line of reasoning does not apply to singular boundaries, which are usually seen as facets in the microstructure. The reason is that the motion of facets is radically different from that of general boundaries. If an infinitely small hump were to appear on a perfect facet, the second derivative terms in Equation 2.24 would approach infinity as the size of the hump approaches zero. There is no way that the volumetric energy change can parallel this surface energy change. As a result, though in theory there exists a critical hump radius for which the associated surface energy and volume energy can balance each other, in practice the critical radius is so large that it can never be nucleated. Any smooth shape change on a facet will leads to an energy increase so a facet can only move parallel to itself.

Herring also derived an average chemical potential of a perfect facet on the free surface of a single crystal but the expression is probably less robust since realistic singular boundaries rarely correspond to perfectly flat facets but facets with steps [51]. Nevertheless, the conclusion is that the magnitude of the average chemical potential in the vicinity of a singular boundary is related to its energy, the energy of the nearby free surface, the intersection angles of the two surfaces and the perimeter of its facet.

2.4.2 Mechanisms for grain boundary motion

The grain boundary motion mechanism is related to the intrinsic boundary structure and we need to differentiate 3 types of grain boundaries here: the LAGBs, the general non-singular boundaries and the singular grain boundaries. Note LAGBs are likely to be non-singular since their energy changes smoothly, but they have attracted special attentions because of their well-defined structure.

Both LAGBs and general non-singular boundaries can be smooth and curved. However, as introduced in Section 2.1.3, LAGBs are comprised of dislocations so their primary motion mechanism is the glide and climb of grain boundary dislocations. On the other hand, the general non-singular boundaries are disordered regions and their motion mechanisms are mainly volume diffusion and surface diffusion. The singular boundaries often have facet shape, of which the structure is highly organized. The possible motion mechanisms include glide and climb of secondary grain boundary dislocations (SGBDs) and shuffling of pure steps.

The glide and climb of dislocations in LAGBs are not much different from the glide and climb of lattice dislocations except for the fact that the whole set of dislocations need to move collectively to avoid large curvatures and lengthen of the grain boundary. The diffusive motion of atoms near general non-singular boundaries is also similar to the diffusion inside the bulk lattice. The less well-known is probably the motion mechanism of the singular boundaries. In order to better illustrate that, we need to first further explore the structure of the singular boundaries.

Let's illustrate the singular boundaries with a coherent CSL boundary as we have seen in Figure 2.5. The boundary can be approximately by the periodic arrangement of a set of dislocations, which are called the structural dislocations or primary grain boundary dislocations (PGBDs). There is no essential difference between the PGBDs and the regular lattice. An ideal coherent CSL boundary constructed from PGBDs has perfectly ordered atomic structure and is likely to correspond to a deep energy cusp. However, in reality perturbations arise from one source or another. Most near-CSL boundaries don't have the perfect atomic arrangement but will always try to conserve the lowest energy structure as much as possible. This conservation is realized by introducing another set of dislocations, the secondary grain boundary dislocations (SGBDs), to ensure that the coincidence of lattice sites is maintained as much as possible in the presence of perturbations. SGBDs are differentiated from PGBDs mainly based on their different roles in

grain boundaries. In some sense, the adaptation of CSL boundaries to disturbance via the SGBDs is similar to the adaptation of bulk lattices to perturbations via the dislocations that constitutes LAGBs. By definition, SGBDs can have only very specific Burgers vectors and can reside only in the grain boundaries. The possible Burgers vectors for SGBDs include the smallest translation vectors that connect two different motifs (circles and squares in Figure 2.5) in the CSL lattice and zero. A SGBD can exist with zero Burgers vector because it has another character: the step height. The Burgers vector captures in-plane translations of the boundary and the step height captures normal to plane translations, as illustrated in Figure 2.10. A SGDB with zero Burgers vector is sometimes referred to as a pure step. SGDBs with non-zero Burgers vector and non-zero step are sometimes referred to as disconnections.



Figure 2.10 Illustration for the formation of grain boundary by bring two surfaces together. (a) Reference state with perturbations from dislocations. (b) A SGBD with non-zero Burgers vector and step height. (c) A SGBD with zero step height and non-zero Burgers vector. (d) A SGBD with non-zero step height and zero Burgers vector. Reprinted from Reference [52]

Now we can discuss the possible motion mechanisms for singular boundaries. The glide of the primary dislocations is unlikely because the spacing between the primary dislocations would generally be small and their simultaneous glissile motion would result in the intersection of different slip planes thus block each other. Then singular boundaries are also resistant to the simultaneous glide and climb because the such motion induce noticeable changes in the primary grain boundary dislocations thus perturbing the well-organized low energy structure of the boundary. However, the secondary dislocations can move laterally by glide and climb. More importantly, the presence of steps provides preferential sites that the atoms can transform from one crystal to another by local shuffling. In-situ TEM observation of a Σ 5 grain boundary contained in a thin-film Au bi-crystal confirmed that the primary motion mechanism of singular boundaries is the shuffling of atoms not the climb and glide of SGBDs [53]. Most recently, Zhang, Han and Srolovitz proposed that the existence of disconnections may be more universal that the community had expected, not only in singular boundaries but also in the general non-singular boundaries [54], [55]. They also argue that the motion mechanism of general non-singular boundaries is not diffusion but nucleation and propagation of disconnections. The theory remains to be examined by more experimental and computational works.

2.4.3 Grain boundary migration

Singular or non-singular, the migration of a piece of grain boundary can always be expressed at a high level as:

$$v = Mp \tag{2.25}$$

Where *v* is the grain boundary velocity. *M* is the boundary mobility. *p* is the pressure, or driving force. The mobility term usually takes the form of $M = A_0 \exp\left(\frac{-H}{kT}\right)$, in which *H* is the enthalpy barrier of migration and A_0 is a pre-exponential term containing the activation entropy, the attempt frequency, the number of active sites, the number of atoms transferred per diffusive process or shuffling and the atomic volume. The number of active sites term is important only when the migration mechanism is shuffling and corresponds to the number of steps. It's easy to notice that as temperature increases, *M* increases exponentially. This observation endorses our hypothesis that grain boundaries migrate rapidly in response to energy differences during grain growth because the temperature leads to large *M*. As all other grain boundary properties, *M* is also anisotropic and varies with the crystallographic parameters [2], [56].

2.4.4 Grain growth

We have explored mechanisms of the grain boundary migration process and will now proceed to the theories of normal grain growth. Such theories can be classified into two levels, the growth of a single grain and the increase of average grain size in a bulk volume. Grain boundary energy anisotropy is ignored in most available theories [57].

Under the assumption of isotropic grain boundary energy, the growth of a single grain is then decided by its integral mean curvature. The most famous theory is Mullins "n-6 rule", which

states that two dimensional grains with fewer than six sides will shrink and grains with more than six sides will grow and the growth / shrinkage rate depends on the number of sides [58]:

$$\frac{dA}{dt} = k\frac{\pi}{3}(n-6) \tag{2.26}$$

A similar equation for the integral mean curvature of grains in three dimensions was derived by and MacPherson and Srolovitz [59]:

$$\frac{dV}{dt} = -2\pi M\gamma \left(\mathcal{L}(\boldsymbol{D}) - \frac{1}{6} \sum_{i=1}^{n} e_i(\boldsymbol{D}) \right)$$
(2.27)

In which *M* is grain boundary mobility. γ is grain boundary energy. $\mathcal{L}(D)$ is a natural measure of the linear size of domain **D**. e_i is the edge length of triple line *i*.

Both the Mullins and the MacPherson-Srolovitz equations apply to individual grains. Theories for the collective grain growth inside an entire volume are much less exact. One of the earliest classic model in this field was brought up by Burke and Turnbull [60]. They assumed that the grain boundary energies are isotropic and the average grain boundary curvature is proportional to the average grain size, then $\frac{d\bar{R}}{dt} = C \frac{\gamma}{\bar{R}}$ where *C* is a constant and \bar{R} is the average grain size. Then $\bar{R}^2 + \bar{R}_0^2 \approx \bar{R}^2 = Kt$ in which *K* is a constant and the initial average grain size \bar{R}_0 is assumed to be small comparing to \bar{R} . This is known as the parabolic grain growth law, for which a more common form is

$$\bar{R} = Kt^n \tag{2.28}$$

n, the grain growth exponent, equals 2 in the above analysis but values ranging from 1 to 4 have be observed experimentally [57]. Smith realized that topological space filling requirements also play an important role during the normal grain growth procedure. For example, the coordination number *z*, defined as the number of edges meeting at one vertex, is fixed for any topologically stable structure. z = 3 in two dimension and z = 4 in three dimension, which agrees with the common observation of triple lines. Another example is that there is a constraint on *C*, the number of cells, *E*, the number of edges, *F*, the number of faces and *V*, the number of vertices in a dense volume filled by polyhedrons [57]:

$$-C + F - E + V = 1 \tag{2.29}$$

It's still not clear how such topological requirements come into play during the collective growth of many grains though it is well-accepted that grain growth is a cooperative procedure during which both the surface equilibrium and topological space-filling are important.

2.5 Experimental techniques

It wasn't possible to collect 3D orientation maps before the development of electron backscatter diffraction (EBSD) in the last twenty years. More recently, another emerging technique is high energy X-ray diffraction microscopy (HEDM), which collects the orientation maps non-destructively and made it possible to study the evolution of one microstructure throughout time. EBSD and HEDM are the two most popular techniques for measuring orientation maps.

2.5.1 Electron backscatter diffraction (EBSD)

Electron backscatter diffraction (EBSD) is a scanning electron microscopy (SEM) based technique that measures the crystallographic orientation of the sample surface. [14] In the experimental setup, the sample is placed beneath the electron beam and tilted 70° from the horizontal plane and a camera with a phosphor screen is placed in front of the sample. When the accelerated electrons hit the sample, they will enter the sample surface and be diffracted by the crystal lattice. The electrons that penetrate the sample surface by no more than a few nanometers have a high probably of escaping the sample, carrying the crystallographic information of the surface lattice. Many of these electrons will be collected by the nearby EBSD camera and the resultant diffraction pattern, also known as the Kikuchi pattern, can yield the lattice orientation after post processing. [14] Once the orientation of the current position is measured, the beam will move to the next position automatically and the process is repeated for the next position.

There are two main sources of noise in the EBSD data. The first source comes from the diffraction process and data collection. For example, if there were a lattice defect near the sample surface, the well-defined Bragg condition will be undermined, and electrons diffracted by the defect will then contribute to noise. Another example is the thermal vibration of the atoms, which is difficult to eliminate and also contributes to the background noise. The second source comes from the post-processing procedure. There is actually no way to resolve an accurate one-to-one correspondence between Kikuchi patterns and orientations because of the various noise of

the first kind. Experimentally, each collected Kikuchi pattern is processed by a technique called the Hough transformation and a voting mechanism is used to determine the best possible source orientation. The orientation with the most votes will be determined as the sample orientation and the reliability of this orientation is quantified from the difference between the votes of the best orientation and the votes of other orientations. Large differences indicate high reliability. This variable is named confidence index (CI) in the TSL software, which is the commercial software used to process our data. Noise arise from the fact that the voting result can be affected by the choice of parameters in Hough transformation.

The orientations maps for our analysis were collected by a serial section technique which works as follows. The electron beam will scan through a certain area of the sample surface following a pre-programed grid, which can be either hexagonal of cubic, and collect a slice of 2D data. Afterwards, the top layer of sample will be milled away uniformly by focused ion beam (FIB) and the new surface will be scanned again. This scan-mill cycle is repeated for tens of times for each orientation map. The scanned position and the milling distance is controlled precisely by the data collection software.

2.5.2 High energy X-ray diffraction microscopy (HEDM)

The physical principle underlying HEDM is similar to that of EBSD in the sense that orientation information is reconstructed from unique diffraction patterns in both cases. However, while EBSD (Kikuchi) patterns carry sample surface orientation information, HEDM patterns carry volumetric orientation information because the beam carries much higher energy and penetrates the entire sample. The beam size is also very different. While EBSD electron beams have rod shape and have nanometer-size [61], the HEDM X-ray beams have planar shape and can be as wide as one millimeter [62]. There are two classes of HEDM techniques and the one for orientation map collection is the near-field HEDM. A detailed description of the technique can be found in Reference [62] and is summarized below.

HEDM samples are usually rod shaped with a millimeter diameter. During the experiment, the high energy X-ray beam (50 - 100 keV) is focused into a planar shape with micron height and millimeter width which is slightly larger than the sample diameter and the sample is placed in the beam path. Because of the high beam energy, X-rays can penetrate through the sample and escape, carrying the lattice orientations of the illuminated sample volume. Diffraction patterns are collected by a CCD detector placed behind the sample for two or three detector

positions. For each illuminated area, the sample is rotated with a typically 1° interval for 180 continuous intervals, giving 360 (two detector positions) or 540 (three detector positions) diffraction patterns. The beam is then moved vertically for a fixed step size of a few microns and diffraction patterns of the next illuminated area are collected. The process is repeated for tens of times so that orientation information of a 3D volume is collected.

Sample orientations are resolved from the collected diffraction peaks with a forward modeling reconstruction (FMR) simulation technique. In the simulation, the illuminated sample area is meshed with equilateral mesh triangles and the orientation of each mesh triangle is searched and the optimal orientation is determined as the one for which the diffraction peak matches the experimentally detected diffraction peaks the best. The optimal orientation of each mesh triangle is determined independently. However, once all orientations of a layer are determined, initializing the neighboring layer's orientations with previous layer orientations will accelerate the process.

The biggest advantage of HEDM is that it is non-destructive. During the HEDM experiment, the vertical position of the beam is adjusted, and the sample is rotated to enable various angular diffraction geometries for each vertical position. Such diffraction measurements do no harm to the sample. As a result, one can anneal a sample and measure its orientation map several times during annealing intervals. The resulting data allows close examination of the sample microstructure evolution.

2.6 Machine learning basics

Machine learning models provide an effective way to analyze data correlations and have been proven useful in various fields [63]. As will be discussed in Section 3.1 and Chapter 6, it is possible to study the EBSD or HEDM collected 3D microstructures with the help of machine learning models. We introduce here the fundamental elements of a machine learning model and the typical workflow to build such a model. The 3D microstructure application and results are presented in Chapter 6 and Section 7.2.

2.6.1 Founding elements

What is machine learning? One concise definition is given by Mitchell [64]: "A computer program is said to learn from experience E with respect to some class of tasks T and

performance measure P, if its performance at tasks in T, as measured by P, improves with experience E."

A computer program, or machine learning model, can be considered as a function that takes some data as input and generates some target data as output. Specifying a model includes specifying the functional form of the model and specifying the exact parameters of this model. The functional form is an assumption that defines the underlying data distribution or how the input data (predictor variables, X) are related to the output data (response or target variable, y). Common functional forms include the linear relationship ($y = \beta X + \epsilon$) and the generalized linear relationships like that in the Gaussian distribution. Based on the functional form, or more general model assumptions, one can then determine an objective function, based on which model parameters can be learned from a given set of experience. The objective function is also known as the loss function or the cost function, and common examples include the mean squared loss (MSE = $\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n}$) for regression tasks and the logistic loss ($\sum_{i=1}^{n} -y_i log(\hat{y}_i) - (1 - y_i)log(1 - \hat{y}_i)$) for regression tasks, in which y_i is the true target variable value and \hat{y}_i is the model prediction.

The experience available to a machine learning model is the training data we provide it, which usually takes the form a 2D numerical matrix in the python convention. Each row of the matrix describes one data instance, and columns of the matrix correspond to feature vectors. Note that multi-dimensional data instances are allowed, but they are usually reshaped to one dimension during implementation for better computation performance. The way a model learns from experiences with respect to a given objective function is through some optimization techniques, among which iterative gradient descent is the most popular approach [65]. Other gradient-free optimization techniques include evolutionary algorithms [66] and Bayesian optimization [67].

Many possible tasks can be accomplished by machine learning models, including but not limited to classification, regression, clustering, and dimension reduction [68]. We are primarily interested in the regression task, in which the model needs to output a one-dimensional number $\hat{y}_i \in \mathbb{R}$ for each *n*-dimensional instance $X_i \in \mathbb{R}^n$. In other words, the model needs to solve a function *f* that takes X_i as input and produces $\hat{y}_i = f(X_i)$.

The model performance can be measured by the value of its objective function. However, the objective function values can be nonintuitive. For example, the value of MSE would depend

on the intrinsic scale of y. One intuitive evaluation metric for linear regression tasks is the R^2 score, which is defined as $R^2 = \frac{SSR}{SSTO} = 1 - \frac{SSE}{SSTO}$. $SSTO = \sum_{i=1}^{n} (y_i - \bar{y}_i)^2$ is the total sum of squares, denoting the total variance. $SSR = \sum_{i=1}^{n} (\bar{y}_i - \hat{y}_i)^2$ is the regression sum of squares, denoting the amount of variance explained by the model. $SSE = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2$ is the error sum of squares, denoting the amount of variance not captured by the model. The R^2 score provides a good performance reference for various kinds of tasks. However, note that R^2 should only be applied to linear models [69]. Also, note that the value of objective functions may include regularization terms (Section 2.6.2). One can report the final MSE or other metric values, like the mean absolute error (MAE $= \frac{\sum_{i=1}^{n} |y_i - \hat{y}_i|}{n}$), as the model performance regardless of the objective function [68].

2.6.2 Typical workflow

Real-word datasets usually have various kinds of problems, like incomplete entries and outliers, and the first step of building a model is to clean the data. Incomplete entries can be filled systematically, or one can simply disregard the corresponding instances. Outliers are trickier since the boundary between a useful data instance and an outlier is usually blurred [70] and are usually handled case-by-case depending on the problem and objective at hand. Examples of outliers in microstructure analysis include low confidence index (CI) pixels in orientation maps [61] and unrealistically extreme data value measurements. Other optional preprocessing steps include data transformation, which may improve model performance, and resampling, which is common in classifications with imbalanced datasets [71]. Exploratory data analysis [72] is often recommended if the expected trend within the dataset is unknown.

The next step is to select a model to fit the available data. The model should be selected based on the task (classification, regression, clustering) and the data at hand. Specifically, what is the expected relationship between the predictor and the response, and how many data instances are available? One should select a model with appropriate capacity, or complexity. For example, linear models can only capture linear relationships, thus have small capacities. Universal approximators like neural networks are, in theory, able to learn any kind of relationship, and thus have large capacities. Models with insufficient capacity are associated with large bias and small variance and may not be able to capture the true trend within data. This problem is known as underfitting. On the other hand, models with too large capacity are associated with small bias

but large variance, and may capture too many details, even noise, within the given training dataset. This is known as overfitting. Neither overfitting nor underfitting is wanted, but underfitting is generally worse because overfitting is more controllable. In the case of overfitting, methods like regularization or feature selection techniques can be applied to limit model capacity and improve performance [68]. Data availability is also often an issue when the model capacity is too large. The required number of training instances usually increases with the model capacity. Given limited training data, an under-trained complex model may perform worse than a well-trained simple model even if the complex model better describes the true trend. The general approach is to start with a complex model and tune the model compacity with regularization techniques.

Once the data is ready and a suitable model is picked, training can start. Training refers to the process of optimizing model parameters so that the model achieves a better objective function value when evaluated on a given set of training data. Popular gradient-based optimization techniques include gradient descent, stochastic gradient descent, accelerated gradient descent, and conjugate gradient descent [73]. Advanced implementations like Adam [74] is usually a mix of several such techniques. The model converges when the objective function stops improving, or the gradient update is too small, and the training process finishes. As mentioned in the previous paragraph, a common problem with the training process is overfitting, which is indicated by the fact that the model performs great on the given training data but generalizes poorly when evaluated on some unseen data. A well-trained model should be able to both fit the training data well and generalize to unseen data with good performance.

The model generalization performance cannot be interpreted from its training performance because of overfitting. A small portion of the available data should be separated from the training set for test purpose. If the model has hyperparameters, which differ from the usual parameters as they should be set by the user and not learnt from data, then a third set of data, known as a validation dataset, should be reserved for hyperparameter tuning. Examples of hyperparameters include the number of clusters in the k-means algorithm and the learning rate in neural networks [68]. In summary, given a model with hyperparameters, the available data should be divided into three sets: the training dataset, the validation dataset and the test dataset. The model is first trained with the training dataset and then tuned with the validation dataset, after which evaluated on the test dataset for an approximated true generalization error. The ratio

between the three datasets is usually around 6 : 2 : 2. Note that there may exist some randomness in the dividing of test and training datasets, and cross-validation [75] is usually applied for better reliability.

2.6.3 Correlation and causation

Note that most statistics and machine learning models solve only correlation, or association, but not causation. Pearl [76] differentiates the two as "An associational concept is any relationship that can be defined in terms of a joint distribution of observed variables, and a causal concept is any relationship that cannot be defined from the distribution alone." In other words, if X is said to cause Y, then different values of X may correspond to different distributions of Y, and the distribution of Y changes as the value of X varies [77]. Causation infers association, but the reverse is not true.

It is difficult to conclude causation because most research can be classified as observational studies, in which all not possible factors are collected and the treatment, or exposure, is not random, and the hidden variables, known as confounding variables, may affect the results. For example, in our research, stress accumulation near grain boundaries are not observed, and we simply observed the microstructures without trying to control them. Wasserman [77] summarizes the condition for reliable causal inference as "(i) the results are replicated in many studies, (ii) each of the studies controlled for plausible confounding variables, (iii) there is a plausible scientific explanation for the existence of a causal relationship."

There are two main frameworks to study causal relationships, which include the counterfactual model and the directed graphs [77]. We confine the focus of this research to correlations, though causal relationships can sometimes be argued for the impact of curvature.

3. The grain boundary curvature distribution

3.1 Data preparation

The experimentally collected 2D maps were processed using an open source software DREAM.3D [78]. In this chapter, we'll go over the structure of data in DREAM.3D, the data needed for the grain boundary curvature distribution, and the pipeline for data processing.

3.1.1 Data structure

DREAM3D files store data in the HDF5 structure [79], which is a well-developed data structure suitable for large datasets. As mentioned in 2.5.1, the raw EBSD data are collected as slices and one volume usually contain tens of slices. Each individual slice is virtually a three-dimensional matrix containing several types of data, including the coordinates of each scan position, the lattice orientation at that position, the reliability of the orientation and the material phase. Three-dimension because each type of data forms a two-dimensional matrix and the different data types gives the third dimension. The 3D matrices of the slices are concatenated and reshaped to yield an integrated four dimensional matrix in the HDF5 format [79]. Note that because each type of data has exactly the same size, the correspondence between difference data is implicit.

When the HDF5 file is written, both the data in the matrix and the size of the matrix are recorded. One can view, extract and even modify the data as long as the data size is consistent with the recorded matrix size. The benefit of the data size constraint is that the likelihood of messing up the data is minimized. In practice, one usually needs to manipulate the data in many ways and an operation often depends on another. If no constraint is enforced on the manipulation, a mistake can trigger a cascade a problem. Imagine one is only interest in the high-quality orientation data, so he / she filtered vertex orientations by the corresponding CI values but forgot to do so for the coordination data. If the orientations and Cis corresponds to the small CI voxels have been deleted without recording indexes of the deleted data, then there would be no way to trace the correspondence between the orientations and coordinates anymore. This problem can't happen to HDF5 file because the file won't allow writing of inconsistently shaped data.

From the 4D vertex data matrix one can then process the data and make other matrices to store intermediate data. We haven't really go into the topic of data process but the point is that

the matrices for data of the same level always have the same shape [78]. For example, vertex coordinate x and vertex coordinate y are both at the vertex level so they should have the same shape. The grain centroid and grain size are both at the grain level so they should have the same shape. This concept seems trivial but actually makes the data processing much easier.

3.1.2 Data process pipeline

The raw 2D orientation maps are available at the grain boundary data archive [80]. The first step of data processing with DREAM.3D was reading in the data, during which voxels with low image quality (≤ 120) or confidence index (≤ 0.1) were set as 'bad' data. Next, centroid and misorientation based algorithms were used to correct misalignments between the 2D sections. Then the volume was segmented into grains by examining the voxel orientations. The orientation of each voxel was compared to its neighbors and voxels with orientations that differed by $\leq 5^{\circ}$ were grouped together and assigned a unique grain identification (ID) number. Furthermore, grains had to have at least 100 voxels and at least two neighboring grains. After this process, the microstructure contained gaps created by groups of fewer than 100 voxels. The gaps were eliminated by dilating neighboring grains uniformly and the volumetric reconstruction was completed. Various properties, like grain size (from the number of voxels within the same grain and the voxel size) and grain orientation (from the average orientations of the voxels within the same grain) can then be calculated.

The voxels that make up the data create stair-stepped boundaries that must be smoothed to extract grain boundary plane and curvature distributions. Meshing algorithms were used to model the grain boundaries as triangular nets and two different smoothing algorithms, including a multi-material marching cube algorithm and a quick mesh algorithm, were used to create smoothly curved grain boundaries [81]–[83]. The details of the parameters and the effects of the meshing and smoothing procedures on the results are discussed in Section 3.3. At this stage, the reconstruction is complete and the microstructures are composed of discrete grains with unique identification (ID) numbers, bounded by a triangular mesh. Associated with each triangle in the mesh are the grain ID numbers on each side, the orientations of the grains on each side, the misorientation across the triangle, the surface normal, the area, and the curvature. This makes it possible to map these quantities locally and to define how they are distributed over the crystallographic and topological parameters.

3.2 Grain boundary curvature distribution

As a first step, grain boundary mean curvature was calculated locally for the triangles using a cubic-order algorithm derived by Goldfeather and Interrante [84]. For every triangle, a patch of its neighborhood was extracted and fit to a cubic order polynomial whose equation was established using the locations (centroid coordinates) and normal vectors of the triangles in this neighborhood. The size of the neighborhood patch was chosen to include the 2nd and 3rd nearest neighbors in our calculation. A least-square fit was used to solve for the coefficients of the polynomial and write the Weingarten matrix of this local surface patch. As mentioned in Section 2.3.1, Eigenvalues λ_1 and λ_2 of the Weingarten matrix correspond to the principle curvatures and the value of mean curvature was determined as $\frac{\lambda_1 + \lambda_2}{2}$. Signs of mean curvatures are usually defined as positive for convex and negative for concave and the sign of grain face curvatures followed this convention. However, notice only the absolute values of triangle mean curvatures were used in grain boundary curvature distribution as a function of crystallographic parameters. The reason lies in the exchange symmetry between neighboring grains. While convex and concave are explicit for an individual grain, there is no way to define such a property for the grain boundary network between grains.

After the calculation of curvature values, each triangle was then classified into a discrete distribution according to its crystallographic parameters using the same methods that have been used to compute the grain boundary character and energy distributions [85]–[87]. Briefly, the five grain boundary parameters are the three Euler angles ($\varphi 1, \Phi, \varphi 2$), specifying the lattice misorientation, and the two spherical angle, (θ, φ), specifying boundary normal direction. Because of bi-crystal symmetries, there are many indistinguishable representations of each boundary in the complete domain of boundary types. We used a sub-domain in which $\varphi 1, \Phi, \varphi 2$ range from 0 to 90 ° and θ, φ range from 0 to 90 ° and 0 to 360 °, respectively [8]. This sub-domain was the smallest regular-shaped volume whose parameters can be easily partitioned and contains an integer multiple of the fundamental zone.

This sub-domain was discretized into bins of equal volume such that there were 9 bins per 90°. In other words, $\varphi 1, \varphi 2$ and Θ were partitioned between 0-90° with 10° interval and $cos(\Phi)$, $cos(\varphi)$ were partitioned between 0-1 with a $\frac{1}{9}$ interval. The five parameters of every triangle were examined and its triangle curvature value was added to the corresponding bin in the sub-

domain. Symmetry operators were applied and it was also added to all bins corresponding to the indistinguishable representations. The number of triangles, or curvature values, in each bin was also tracked. With cubic symmetry, each triangle has 36 physically indistinguishable representations in this sub-domain. The number 36 is calculated as following. First, there is an exchange symmetry between the two lattices which has an order of 2. Then $\frac{48}{2}$, or 24, proper symmetry operators can be applied to both lattices and the triangle normal can be parameterized in either lattice. As a result, there are $2 \times 24 \times 24 \times 2 = 2304$ symmetrically equivalent parameterizations. The subdomain contains a $\frac{90}{360} \frac{90}{180} \frac{90}{360} \frac{90}{180} \frac{360}{360} = \frac{1}{64}$ of the full domain. So there are $\frac{2304}{64} = 36$ copies of each distinct boundary in the sub-domain [8].

Note the 36 representations can contain multiplicity, which is similar to that of the crystal symmetry: cubic symmetry has a symmetry order of 48 but a [100] orientation has only six different parameterizations: [100], [010], [001], [$\overline{1}00$], [$0\overline{1}0$], [$00\overline{1}$]. During the parameterization of misorientations, it's possible that one triangle is given the same parameters by *N* different symmetry operators and is putted into the same parameter box *N* times. However, multiplicity is not a problem because the curvature values in each bin are normalized by the number of values in that bin after all triangles are checked. This gave us the symmetry averaged mean curvature for the grain boundary mean curvature distribution (GBHD).

3.3 Validation of the method

It should be recognized that curvatures measured from discrete voxelized data are necessarily approximations of the true grain boundary curvature. Intuitively, the accuracy of this approximation should depend on the resolution of the data (the size of a voxel compared the size of a grain) and the way that the triangular mesh that represents the grain boundary is smoothed. Furthermore, when the curvature of an individual triangle is classified in the discrete five-parameter distribution, it will be averaged with boundaries that have similar parameters. Therefore, the symmetry averaged curvatures will also be affected by the discrete nature of the distribution. To understand how these factors influence the curvature measurement, we examined the effect of the data processing on the measured curvatures of simulated spherical grains. The data was processed with DREAM.3D version 4.2 [78]

Ten spheres were created and labeled with different resolutions. For example, S4 stood for a sphere with 4 voxels per radius. While it was arbitrary in these simulations, we selected a voxel size of $0.2 \,\mu m$. We constructed the spheres at the center of an assembly of eight other grains that all have the same disorientation (45°/[100]) with center grain. So while there are eight distinct grain boundaries surrounding the sphere, they have crystallographically indistinguishable misorientations. In the following tests, the meshing algorithm was chosen as the multi-material marching cube and the smoothing method was the Laplacian smoothing.



Figure 3.1. Shapes of S6 and S28 after different reconstruction procedures. (a) voxels of S6. (d) voxels of S38. (b) shape of S6 after smoothing with smoothing I. (e) shape of S28 after smoothing I. (c) shape of S6 after smoothing III. (e) shape of S28 after smooth.

Two of the spherical grains are illustrated in Figure 3.1. Figure 3.1a is an example of a lowresolution sphere (S6). In this case, there are six voxels per radius and the cube shaped voxels make a rather crude approximation for the sphere. Figure 3.1d shows a higher resolution sphere (S28) which has 28 voxels per radius and is more accurately reproduced. The triangular mesh has to be smoothed to remove stair-stepped structures. The parameters for the smoothing routine are the number of iterations and a weighting factor, λ , which controls how far a node moves on each iteration and varies between 0 (no smoothing) and 1 (maximum). For smoothing I, II, III, and IV, the values of λ /iterations were 0.05/50, 0.1/100, 0.2/200, 0.4/400, respectively, which results in increasingly strong smoothing. The effects of these different parameters are illustrated in Figure 3.1. With smoothing I, S6 (Figure 3.2(b)) is a fairly good approximation of a sphere. However, voxel-like steps can still be seen on the surface of the higher resolution sphere S28 (Figure 3.2(e)), indicating inadequate smoothing. When smoothing III was applied, the higher resolution sphere S28 (Figure 3.2(f)) became smooth and sphere-like while the lower resolution sphere, S6 (Figure 3.2(c)), was over-smoothed and is more like an octahedron than a sphere. This illustrates that fixed smoothing parameters are not be ideal for all grain sizes.

The results for the curvatures computed for the triangles associated with the different spheres and different smoothing processes are summarized in Figure 3.2.



Figure 3.2. Average triangle curvatures for spheres of different resolutions and smoothing parameters. The bars represent the standard deviations of triangle curvatures when spheres are smoothed with smoothing II.

The dashed line indicates the ideal curvature value calculated from sphere radius (R^{-1}) and the markers are the average values of the triangle curvatures for each sphere. The difference between a marker and the corresponding point on the dashed line measures the quality of the reconstruction. The smaller the difference, the better the reconstruction and the better the calculated curvature approximates the true curvature. From the plot, we can see that the optimal smoothing parameters are related to the resolution, which can be interpreted from feature size. Lower resolution spheres are smoothed better with smaller smoothing parameters while larger smoothing parameters worked better for the higher resolution spheres. This is consistent with the visual interpretation of Figure 3.1. The Laplacian smoothing method makes changes in the mesh nodes in proportion to local gradients. The low resolution sphere (S6) has larger gradients

between voxels and was therefore smoothed in a few iterations. The higher resolution sphere, S28, had smaller gradients, so more iterations and larger values of λ were required for optimal smoothing. The three exceptions to this trend in Figure 3.2 are S4, S6, and S9 with smoothing VI; in this case they were so over smoothed that their shapes were no longer stable.

As illustrated in Figure 3.2, the reconstruction quality and smoothing parameters affect the results and should be selected to best match the physical measurements. More precisely, we need to know the resolution of grain boundaries within our sample to properly mesh the data and measure the triangle curvatures. It is important to keep in mind that the resolution is not a single value, because there are both highly curved and very flat boundaries within the same microstructure. Also, unlike the ideal spherical geometries, grain boundary resolution is not linearly related to grain size. To understand the range of curvatures in our data, the distribution of triangle curvatures in the austenitic steel is plotted in Figure 3.3.



Figure 3.3. Triangle curvature frequency in the austenitic steel, produced with smoothing II.

Though the specific shape of the histogram depended on the smoothing parameters, results given by the four smoothing routines were similar and smoothing II was selected for this example. For reference to Figure 3.2, the ideal sphere resolutions, as log(number of voxels in volume), were calculated from the corresponding curvature values and labeled on the upper horizontal axis in Figure 3.3. It can be seen that the number of triangles with large curvatures is small compared to those with small curvatures. In both samples, more than half of the triangle

curvatures have absolute values less than $0.5 \ \mu m^{-1}$ (59.5 % for austenite, 55.6 % for ferrite). In other words, most of the grain boundaries in our microstructure maps were relatively flat and were comparable to the surfaces of the larger ideal spheres. Clearly the emphasis should be placed on getting accurate curvature values for the most populous, low curvature boundaries. For this reason, smoothing II was selected for the following study since it gave the best relative accuracy in the low curvature regime and acceptable accuracy for the higher curvatures.

When the curvature distribution is considered as a function of the crystallographic parameters, it is affected by the discrete binning and symmetry averaging procedures. When the discrete triangles are classified according to their crystallography, they are grouped into bins of finite width and averaged. When the curvature of a particular type of grain boundary is retrieved from these discrete bins, it is the average of 36 separate bins. Therefore, it is reasonable to expect there would be a disparity between triangle curvatures and symmetry averaged curvatures.



Figure 3.4. (a) Curvature distribution of S6, (b) Curvature distribution of S28.

The curvature distributions at the fixed misorientation between the center sphere and the surrounding grains were computed for the ten spheres and the distributions are plotted for S6 and S28 in Figure 3.4. For S6 (Figure 3.4a), the ideal curvature was $0.83 \ \mu m^{-1}$ and it should be uniform. The average curvature is somewhat lower ($0.65 \ \mu m^{-1}$), as expected from Figure 3.2, and the individual values vary from $0.22 \ \mu m^{-1}$ to $2.8 \ \mu m^{-1}$. For the higher resolution case represented by S28 (Figure 3.4b), curvature varied in a much smaller range (from $0.11 \ \mu m^{-1}$ to $0.26 \ \mu m^{-1}$) and the average value ($0.15 \ \mu m^{-1}$) was much closer to its ideal curvature ($0.16 \ \mu m^{-1}$). The symmetry averaged curvature distribution information for the other spheres are summarized in Figure 3.5, in which the mean triangle curvature and the ideal curvature are also shown for comparison. Based on these tests, we conclude that while high curvatures are underestimated, most curvatures are accurately reproduced.



Figure 3.5. Average curvature of the distribution for the 10 spheres when smoothing II is used for the reconstruction. The dots are mean symmetry averaged curvatures. The squares are mean triangle curvature. The error bars are standard deviations.

3.4 Conclusion

The mean curvature data quality depends on the microstructure resolution characteristic and the smoothing routine. The best smoothing routine should be chosen based on the resolution characteristic of the majority grain boundaries, though high curvatures are generally underestimated. With an appropriate smoothing routine, grain boundary mean curvatures can be accurately measured from discrete triangular mesh triangles and successfully reproduced by the symmetry averaged grain boundary curvature distribution (GBHD).

4. GBHD in the austenitic and ferritic steels

4.1 Material overview and statistics of the orientation map

The two steel samples had been studied for their grain boundary population and energy distributions. The data was collected by Beladi and detailed description of sample processing can be found in Reference [41], [42] and are summarized below.

The austenitic sample has face-centered cubic (FCC) structure and its composition was 0.6C–18Mn–1.5Al (wt.%). This composition belongs to the twinning-induced plasticity (TWIP) steel class in which the population of twin boundaries is large. The sample was produced by ~ 60 % cold rolling, followed by 1 min anneal at 800 °C. Its microstructure map covered $65 \times 40 \times 20$ µm³ volume and 3185 grains.

The ferritic sample has body-centered cubic (BCC) structure and its composition was 0.04 C–1.52 Mn–0.2 Si–0.22 Mo–0.08 Ti–0.033 Al (wt.%). The sample was hot rolled at temperatures between 1000 and 1200 °C to reduce 70 % of its height. It was then reheated to 1200 °C at rate of 5 °C s⁻¹ and was held for 300 s. Afterwards, it was cooled down to 890 °C, held for 20 s and then deformed to a strain of 1 at a strain rate of 1 s⁻¹. Finally, the sample was cooled to 650 °C at 10 °C s⁻¹ and held for 600 s, followed by water quenching. Two orientation maps was collected from different volumes of the ferritic steel. One was 40 × 35 × 14 µm³ and contained 1113 grains and the other was $30 \times 50 \times 22$ µm³ and contained 558 grains.

The grain size distribution is shown in Figure 4.1. There is an obvious cut-off in the grain size distributions, which resulted from the choice of minimum grain size in the reconstruction step. Note that this kind of cutoff is unavoidable in experimental data analysis for two reasons. One is that the experimental measurements have finite resolution and imperfect reliability. Any grain smaller than the map step size cannot be detected. Then it's difficult to differentiate between realistic tiny grains which are constituted by no more than a few voxels and small clusters of noise. The reason is that the density of grain boundary is high near small grains and the diffraction of electrons will be affected if there is a lattice defect, like a grain boundary, near the point of interest. As a result, voxels of small grains usually have low CI values in EBSD data. The other reason is that for a grain to be meshed properly and its properties, like curvatures, measured accurately, the grain needs to have a minimum size.



Figure 4.1. Log normalized grain size distribution of (a) austenitic steel, (b) ferritic steel. D in the x axis is grain diameter and < D > is the average grain diameter in the volume.

4.2 Integral mean curvature of grain faces

To analyze grain boundary curvature as a function of grain size and topology, we consider the curvature integrated over grain faces and entire grains. The integral mean curvatures of grain faces (M_S) for every reconstructed grain was calculated using Equation 4.1:

$$M_{S} = \sum_{j}^{n^{f}} \left(\sum_{i}^{n^{t}} H_{ij} \times A_{ij} \right)$$

$$(4.1)$$

where H_{ij} is the mean curvature of the ith triangle on the jth face of the grain and A_{ij} is the triangle area. The number of faces of the grain is n^f and the number of triangles on one face is n^t .

Note that the grains near the sample periphery were likely to be biased by the free surface. There are different criteria that can be used to remove biased grains. The most straightforward one is to remove all grains in contact with the free surface. However, that would result in a preferential removal of large grains. An alternative criterion suggested by Rowenhorst [88] is to remove all grains whose centroids fell within 2 < R > of the free surfaces of the sample where < R > is the average grain radius. The centroid grain removal criterion were applied to the austenite sample ($< R > = 1.2 \ \mu m$) and the larger volume of the ferrite sample ($< R > = 1.1 \ \mu m$). After this filtering, 1885 grains remained in the austenite and 538 grains remained in the ferrite.

Grains were categorized into topological classes according to their numbers of faces and the results are shown in Figure 4.2.



Figure 4.2. Integral mean curvature of grain faces (M_s) as a function of number of faces of grains (F). The markers represent average M_s for each grain class and the error bars show the standard deviation within the grain class. Only unbiased grains are included in the plot.

The domain of the horizontal axis was limited to 40 to emphasize the points near the zero crossing; this excludes only 3.4 % of the grains. The integral mean curvature was positive for grains with a smaller number of sides and negative for grains with a large number of sides. This is consistent with theories of grain growth that suggest grains with many sides grow and those with few sides shrink. Note that for grains within each class, M_s is a distribution rather than a constant. The ferrite data is noisier than the austenite data, especially for classes with a large number of faces (> 25). This is probably because there are fewer grains in the ferrite sample. For ferrite, the classes with F > 25 faces contain no more than 5 grains. Most of the grains with between 3 and 20 faces and have smaller standard deviations in both datasets. Note that the standard deviation increases again for grains with the fewest faces and the largest curvatures, as illustrated in Figure 3.2. The integral mean curvature crosses zero at about 17 grain faces for both the austenitic and ferritic steel. We tested different reconstruction procedures, such as using a minimum grain size of 16 voxels, but it did not alter the results.

Rowenhorst et al., [88] proposed that zero curvature grains were those whose numbers of faces (F) were the same as the average numbers of faces of their nearest neighbors, $\langle F_{NN} \rangle$. We tested the same idea on the austenitic steel data (Figure 4.3). The normalized integral mean

curvature of grain faces is calculated as $G' = M_s/R$, where *R* is the radius of the grain. The set of grains for this local topology analysis was limited to ones whose nearest neighbors also fall 2<*R*> from free surfaces of the sample, leaving 930 grains for analysis in austenite. The grey dots in Figure 4.3 are normalized grain curvatures of individual grains. Red squares are average normalized grain curvature for each $F - \langle F_{NN} \rangle$ class. The line for the average in each class passes almost exactly through the point with $F - \langle F_{NN} \rangle = 0$ and G' = 0. The results for the ferritic steel are not shown because after grains with incomplete neighbors were also removed, there were not enough grains left to support a statistical analysis.



Figure 4.3. Normalized integral curvature of grain faces (G') as a function of $F - \langle F_{NN} \rangle$ in austenite. $F - \langle F_{NN} \rangle$ is difference between number of faces of one grain (F) and the average number of faces of its nearest neighbors ($\langle F_{NN} \rangle$). Only grains that are unbiased themselves and have unbiased neighbors are included in the plot.

4.3 GBHD as a function of plane normal for fixed misorientations

In the remainder of this document, we refer to the symmetry averaged GBHD simply as the GBHD. From the previous study [41], [42] we know that Σ 3 boundaries have high population, which means that our measurements of these boundaries are the most reliable. Therefore, we examine the curvature as a function of the grain boundary plane orientation for grain boundaries with a 60° disorientation about the [111] axis (Σ 3) for the austenite and ferrite samples. In Figure 4.4, the curvature is plotted in stereographic projection with [001] and [100] pointing

normal to the plane of the paper and to the right, respectively. The grain boundary populations and relative energies, reported earlier [41], [42] are shown for comparison. Note that the grain boundary populations are not identical to those reported earlier because, in this case, they were computed using DREAM.3D [78].



Figure 4.4. Curvature, population, and energy distributions for austenite (a-c) and ferrite (d-f) for all grain boundaries with a $\Sigma 3$ (60°/[111]) disorientation. (a), (d) Grain boundary curvature. (b), (e) Grain boundary plane population. (c), (f) Grain boundary energy. In (a-c), the squares mark locations in the [111] zone. Each distribution is plotted in stereographic projection.

For the austenite sample, the most significant feature appears at the position of the coherent twin. This is the minimum curvature, maximum population, and minimum energy. This is the boundary that is terminated by (111) planes on both sides and is very flat. It is interesting to note that there is a maximum in curvature for boundaries that are 90° from the twin position and the maximum is reached at the positions of the (110) boundary planes. This is consistent with the observation that twins are usually plate shaped grains whose dominant surface plane is (111), but are bound by much smaller perpendicular surfaces. The high curvature results from the

geometric necessity of joining the two parallel (111) planes to bound the grain. Note that the population and energy distributions are relatively featureless for these orientations.

The distributions for the ferritic sample are nearly opposite that of the austenitic sample. The lowest curvatures occur in the [111] zone with the minimum curvature, energy, and maximum population occurring at the positions of the $(\overline{2}11)$, $(\overline{1}\overline{1}2)$, $(1\overline{2}1)$ symmetric tilt grain boundaries (these are indistinguishable grain boundaries). The maximum curvature $(1.0 \ \mu m^{-1})$ and minimum population occur at the position of the (111) twist grain boundary. It should also be pointed out that the range of the area distribution for the austenitic sample is much larger than for the ferritic sample, with a maximum population larger than 300 MRD for the austenitic steel but only about 9 MRD for the ferritic steel.



Figure 4.5. Curvature, population, and energy distributions for austenite (a-c) and ferrite (d-f) for all grain boundaries with a $\Sigma 9$ (38.9°/[110]) misorientation. (a), (d) Grain boundary curvature, austenite. (b), (e) Grain boundary plane population, austenite.

 Σ 3 boundaries are special for their low energy and large population. To better understand the distributions, a less unique misorientation (Σ 9 (38.9°/[110])) is also examined and the results are in Figure 4.5. For the Σ 9 boundaries, maximum grain boundary populations in both samples are

about 2 MRD, which are lower than 320 and 9 MRD of Σ 3 boundaries. At the same time, the energy is noticeably higher, especially for ferrite sample in which maximum energy increases by 50 %, from 0.8 r.u. of Σ 3 boundaries to 1.2 r.u. for Σ 9 boundaries. Maximum curvatures of Σ 9 boundaries are found approximately in the [114] zone for austenite and in [110] zone for ferrite. The minimum curvatures of Σ 9 boundaries lie on the [221] zone and near the (221) position in the ferrite sample but are rather spread out in the austenite sample.



Figure 4.6. Comparison of the curvature and relative energies of grain boundaries in the [111] zone of austenite, beginning at the $(1\overline{1}0)$ orientation. Because of bicrystal symmetry, the values repeat in periods of 60° .

When comparing the curvature, population, and energy distributions, it seems clear that for both samples, the curvature is correlated to the crystallography of the grain boundary, as hypothesized in Section 1.2. Furthermore, the comparison of curvature and energy shows systematic variations. The two boundaries thought to be singular, the (111) Σ 3 boundary in austenite and the ($\overline{112}$) Σ 3 boundary in ferrite, have the minimum curvature, minimum energy, and maximum population. This implies a direct correlation between curvature, energy, and population. However, this is not the case at all points. For example, if we compare the energy and curvature of the grain boundaries in the [111] zone for austentite (Figure 4.6) we see an inverse correlation between energy and curvature. Because these are among the highest energy and lowest population of the Σ 3 grain boundaries, we also assume that these are non-singular orientations.

4.4 Discussion

The results in Section 3.3 indicate that measuring curvatures from a discrete triangular mesh using the method of Goldfeather and Interrante [84] is accurate provided that there is sufficient resolution compared to the range of curvature to be measured. A basic limitation will always be that there is a wide range of grain sizes with different curvatures and no single smoothing procedure will be ideal for all grains. Fortunately, the largest fraction of boundaries has relatively low curvatures that are more accurately measured and these will dominate the distribution. For example, the curvatures of specific grain boundary types, as illustrated in Figure 4.4 to Figure 4.6, will be the average of values from the majority low curvature grain boundaries that are accurately measured and the minority high curvature boundaries whose curvatures are underestimated. So, the while the underestimated curvature of some boundaries will affect the results, the effect will be diluted by the majority boundaries that are measured more accurately.

Because the curvature-energy product is the driving force for grain growth, there is an extensive literature, dating back to the work of Smith [89], relating grain topology, integral mean curvature, and the tendency of grains to grow or shrink. Theoretical treatments of the problem led to the prediction that grains with more than 13 or 14 faces grow and those with fewer shrink [90]–[92]. Rowenhorst et al., reported that zero curvature grains had 15.5 sides [88] and in the current work we find it is about 17. The difference between the value we report and that reported by Rowenhorst et al., might not be significant. Note that while the data follow the trend of decreasing integral mean curvature with an increasing number of faces, the curvatures of grains with between 15 and 20 faces are less than the standard deviation, so the exact point where the curvature is zero is not clear. We note that the average numbers of sides per grain in the austenite and ferrite was 13.6 and 13.7, respectively, which are consistent with the number reported for β -Ti (13.7) [88].

MacPherson and Srolovitz [59], [93] recently showed that the number of sides alone does not determine the growth rate of a grain. Using data from more than 2000 β -Ti grains, Rowenhorst et al. [88] demonstrated the validity of the idea that zero curvature grains were those whose

numbers of faces (F) were the same as the average numbers of faces of their nearest neighbors, $\langle F_{NN} \rangle$. The fact that we get the same result from an austenitic steel (see Figure 4.3), which has a significantly different microstructure, suggests that this is a general feature of microstructures undergoing grain growth.

The observations reported in Figure 4.4 and Figure 4.5 provide clear evidence that the mean curvature of the grain boundary depends on its crystallographic parameters. In an isotropic system, one would expect the curvature be dictated by the size of the grain face. While it seems sensible that the grain and face size will still play a role, there is a clear effect of the grain boundary plane orientation (Figure 4.4 and Figure 4.6). In Figure 4.4a the curvature for the $60^{\circ}/[111]$ boundary in austenite varies from $0.3 \,\mu m^{-1}$ at the position of the (111) twist boundary to $1.2 \,\mu m^{-1}$ at the (110)-type positions 90° away. There are also significant curvature variations for the $60^{\circ}/[111]$ boundary in ferrite, even though the anisotropy in the grain boundary population is 30 times smaller.

The data in Figure 4.2 show that there is a strong correlation between curvature and the number of sides. Because it is known that grains with more sides are larger, there is also an intuitive correlation between curvature and grain size [29], [88], [94]. When the GBHD is computed, all grains are included. This means that for a single crystallographic type, triangles from small, higher curvature, shrinking grains are averaged together with triangles from large, lower curvature, growing grains. Despite this, there is still a crystallographic correlation. One might think this is because the GBHD is area weighted, so the larger grains have a more significant effect on the distribution than small grains. However, the large growing grains necessarily share boundaries with smaller shrinking grains, so one cannot attribute the distribution solely to the large grains.

While the GBHD is clearly sensitive to crystallography, there is no single correlation between curvature and energy or curvature and population. The one trend that is clear is that the lowest energy boundaries also have small curvature and large areas. If these boundaries are presumed to be singular and in contact the same mean-field chemical potential, then the curvature should be directly proportional the energy and inversely proportional to the area [95]. This is certainly obvious from the distributions plotted in Figure 4.4. However, there are also examples of opposite correlations. One example is illustrated in Figure 4.6. As noted in Section 2.4.1, non-singular boundaries in contact with a constant mean-field chemical potential should have curvatures that are negatively correlated to the energy.

Some of the preceding arguments are based on a mean-field chemical potential for the interfaces. It should be noted that each individual boundary is not assumed to have the same chemical potential. However, computing the curvature of a certain type of boundary involves averaging over many boundaries at different chemical potentials. The average curvature that results is therefore representative of mean chemical potential of the boundaries with the same crystallography.

The data in Figure 4.4 and Figure 4.6 show only a small portion of all grain boundary types. When the data is examined for all grain boundaries, the curvature is not strongly correlated to the population or energy, although the curvature and energy have a weak negative correlation. The absence of a strong correlation may be because of the competing behaviors of the singular and non-singular interfaces. Unfortunately, at the present time, is it not obvious how to classify the boundary types into these categories. It should also be pointed out that the lower the population of a boundary, the greater uncertainty there is in the curvature and energy measurement, so this may also play a role and mask any correlations that might exist. What we can say with confidence is that for the most commonly observed grain boundaries, the dominant trend is that low curvature boundaries have low energy and larger areas. However, there are no strong overall correlations between curvature and energy or area, similar to the area-energy correlation that was observed in many materials [96].

4.5 Conclusion

The curvatures measured for an austenitic steel and a ferritic steel show the expected trend that the integral mean curvature of the grains decreases as the number of grain faces increases. The curvatures are also related to grain topology. In austenite, when the number of faces on a grain is equal to the average number of faces of its neighbors, it has zero integral mean curvature. We find that the crystallography of the grain boundary strongly influences the curvature. The lowest curvature grain boundaries also have the lowest grain boundary energies and highest grain boundary areas. However, when all grain boundaries are considered, the curvature is not strongly correlated to energy or area and this might be the result of conflicting mechanisms that determine the curvatures of singular and non-singular boundaries.

5. GBHD in polycrystalline SrTiO₃

We apply the same techniques described in Chapters 3 and 4 to analyze the grain boundary curvature in a ceramic sample and explore in more detail the correlations among the grain boundary properties, including relative area, energy, and curvature.

SrTiO₃ is selected for this study for two reasons. First, we already have some knowledge of the types of grain boundaries that exist in SrTiO₃ and their energetics [87], [97]. Second, there is considerable current interest in grain boundary motion in SrTiO₃ because of the grain growth anomaly that occurs in the temperature range of 1350 °C to 1425 °C [98], [99]. In this region, the grain growth rate constant decreases by two orders of magnitude, while in most cases the grain growth rate constant is expected to increase with temperature [100]. The decrease in the rate constant is the result of an increasing concentration of relatively slowly moving grain boundaries. There is also a change in the distribution of grain boundary planes, with the fraction grain boundaries with the (100) orientation increasing in the region where the grain growth rate constant decreases [101]. In the same temperature range, there is a decrease in the grain boundary energy [102]. These observations have been interpreted as evidence for a grain boundary structural transition. However, microscopic studies of the boundaries do not provide strong evidence for such a transition [103]–[105]. Shih et al. [103] reported a tendency for larger grains to have atomically flat (100) oriented grain boundaries. Sternlicht et al. noted no difference in the structure of the fast moving and slower boundaries [105]. The same group reported that the boundaries move by the motion of steps and that on the microscopic level, the boundaries were made up of a limited number of low index atomically flat orientations [104], [105].

5.1 Material overview and statistics of the orientation map

The data was collected at Carnegie Mellon by Dillon [86]. A polycrystalline ceramic was prepared from commercially available SrTiO₃ powder (Sigma-Aldrich Corp., St. Louis, MO, 99 % pure). The powder was dry-ground for approximately ten minutes in an alumina mortar and uniaxially compacted at 1000 psi to form a 1/2" diameter pellet. The pellet was fired in air in a box furnace (Lindberg/Blue M 1700°C box furnace, Riverside, MI) according to the following heating schedule. The furnace was heated at 10 °C/min to 900 °C. After a 10 h dwell, it was
heated at 5 °C/min to 1340 °C. After another 10 h dwell, it was heated at 20 °C/min to 1470 °C, held at that temperature for 30 min, and then furnace cooled to room temperature.

Three-dimensional EBSD data was collected using procedures that have already been described in detail [86]. The sample was milled with a Ga⁺ ion focused ion beam (Nova 600, FEI Co., Hillsboro, OR) and the backscattered diffraction patterns were collected using an EBSD detector (Hikari, EDAX, Mahwah, NJ). The sample was ion milled 30 kV and 7 nA, and the EBSD data were acquired on a hexagonal grid using a 30 kV beam at a current of 9.5 nA. The in-plane EBSD resolution was 300 nm, and the spacing between layers was also 300 nm.

The design of the heat treatment and the choice of EBSD parameters were determined from the requirement that the data should cover thousands of grains, which is necessary for analyzing the distribution of grain boundary properties as a function of the five independent crystallographic parameters. To obtain data from this many grains in a reasonable period of time, one must consider the spatial resolution of EBSD orientation maps, the amount of time it takes to record the orientation maps, and the amount of time it takes to remove a layer of material by serial sectioning. The latter two parameters are characteristics of the instrument; for the instrument used for this study, we were limited to samples with average grain diameters between 1 and 5 μm (although for more modern instruments, the upper bound on the grain size has increased considerably). The limits arise because if the grains are too small, it is not possible to resolve the interface shapes and if the grains are too large, the rate of ion milling and data acquisition make the length of the experiment impractical. The in-plane EBSD resolution was 300 nm and the spacing between layers was also 300 nm. Two volumes were collected, one consisting of 36 layers and another consisting of 40 layers.

In the first step, the data was cropped and cleaned using the TSL OIM software. Each area in the two volumes was cropped to $69.3 \mu m \times 38.4 \mu m$ or $63.6 \mu m \times 76.8 \mu m$. The EBSD data were cleaned using two iterations of grain dilation with a minimum grain size of 10 pixels. This procedure considers any grouping with fewer than 10 pixels, or disorientations of $> 5^{\circ}$, to be insufficient to define a grain and assigns their orientation to match the orientation of an adjacent grain. A single average orientation was assigned to each grain, with an individual grain being defined as a set of pixels whose disorientations lie within 5° of one another. These maps, as shown in Figure 5.1, were used as the input for the remainder of the analysis.



Figure 5.1. Two volumes of SrTiO₃. (a) 69.3 $\mu m \times 38.4 \mu m \times 10.5 \mu m$ (b) 63.6 $\mu m \times 88.8 \mu m \times 11.7 \mu m$. In each case, the grains are colored by orientation, according to the color key.

The orientation maps were reconstructed using DREAM.3D version 6.4 [78], with procedures similar to that of the steel datasets. The misorientation threshold was 5°. The minimum grain size threshold was 100 pixels. Note different meshing technique, quick mesh instead of multi-material marching cubes, were used for mesh triangle generation. An example of a reconstructed grain, boundaries represented by the triangular mesh, is presented in Figure 5.2.



Figure 5.2. The mesh around a reconstructed grain, (a) colored by the absolute value of the mean grain boundary curvature, triangles with a larger than $0.5 \,\mu m^{-1}$ mean curvature were not shown. (b) The same grain in (a) but colored by the grain boundary normal direction.

There was a total of 3032 grains. The grain size distribution and the grain face distribution are shown in Figure 5.3. The average (spherical equivalent) grain diameter (*D*) was $3.3 \,\mu m$. The largest grain in the sample had an equivalent diameter of $14.5 \,\mu m$, which was about five times the average diameter. The average number of neighbors per grain (taken to be equivalent to the number of grain faces), was 11.9.



Figure 5.3. The distributions of diameters and numbers of faces for all grains in the two SrTiO₃ volumes. (a) Log of normal grain size distribution. < D > is averaged grain diameter. (b) Distribution of the number of grain faces. All grains are included for the plot.

As mentioned in Section 4.2, the grains near the sample free surface were probably biased. Different criteria can be applied to remove such grains. If we had removed all incomplete grains, which were in contact with the sample free surface, then there would be 1377 grains left in the two volumes. The remaining grains had an average equivalent diameter $\langle D \rangle$ of 3.1 μm and an average number of faces of 12.7. If grains were filtered according to their centroid positions and only the ones whose centroids fell more than $\langle D \rangle$ away from the free surface ($\langle D \rangle = 3.3 \mu m$) were kept, there would be 887 grains left. The average grain diameter $\langle D \rangle$ of the remaining grains was then 3.5 μm and the average number of grain faces was 14.2. It can be noticed that both criteria removed over 50 % grains in the volume. Nevertheless, neither criterion introduced substantial changes in the log normalized size distribution nor the number of faces distribution except for the tail of the largest grains. Most of the largest grains were removed by the shape completeness criterion. On the other hand, while the centroid criterion removed more grains than the complete shape criterion, the largest grains were more likely to be kept.

As one would expect, the topological characters (number of faces) of one grain is not independent of its size. The number of faces is plotted as a function of grain diameter in Figure 5.4, in which only the complete shape grains are included. It can be seen that small grains tend to have fewer faces, while large grains have more faces. However, the correlation is not deterministic. For example, there are two grains of very similar sizes but drastically different number of faces. One has 6.7 µm equivalent diameter and 38 faces. The other is slightly bigger in size, 6.9 µm equivalent diameter, but has only 13 faces.



Figure 5.4. The number of faces, F, plotted as a function of grain spherical equivalent diameter, D. The color bar indicates number of grains in the corresponding bin. Only complete grains are included in the plot.

5.2 Integral mean curvature of grain faces

The integral mean curvature of grain faces (M_s) was calculated according to Equation 4.1. We filtered the grains by their centroid positions in the analysis of M_s , after which 887 out of 3032 grains were left. The values of M_s for every grain have been classified by grain size and results are shown in Figure 5.5. Each point is the average of M_s in that size class and the bar shows the standard deviation of M_s within that size class (note that, for clarity, six grains with diameters larger than 10 μm were excluded from this plot).

A clear trend appears that smaller grains have positive curvatures (are convex) and larger grains have negative curvatures (are concave). The cross over from positive to negative curvature occurs for grains with diameters of about $3.8 \,\mu m$, which is greater than the mean diameter $(3.3 \,\mu m)$. With reference to Figure 5.3a, this shows that the majority of grains have positive curvature. Because grain boundaries move toward their centers of curvature, the smaller convex grains should tend to shrink and the larger concave grains should tend to grow. However, note that within each size class, there is a range of curvatures and in many cases the distribution spans positive and negative curvatures. This might arise from uncertainties in the measurement, but it also might arise from local fluctuations in curvature that depend on a grain's neighbors [88]. If so, then not all grains of the same equivalent diameter have the same sign of curvature. The largest grains have strongly negative curvatures and are expected to grow and consume the smaller grains.



Figure 5.5. Integral mean curvature of grain faces (M_s) as a function of number of faces of grains (F). The markers represent average M_s for each grain class and the error bars show the standard deviation within the grain class. Only unbiased grains are included.

Considering the relationship between the grain size and the number of grain faces illustrated in Figure 5.4, a similar relation between curvature and number of grain faces should be observed. Figure 5.6a shows the average and standard deviation of integral mean curvatures for grains with different numbers of faces (note that, for clarity, nine grains with more than 40 faces were excluded from this plot). The mean values of M_s are positive for grains with fewer than 16 sides and the mean values of M_s are negative for grains with 16 or more sides. However, as before, there are a range of classes (between 11 and 21 faces) where both positive and negative values fall within one standard deviation of the mean. The results in Figure 5.6a are consistent with the observation in the steal datasets (Figure 4.2), affirming the well-known connection between the number of grain faces and the curvature, that grains with few (many) faces have positive (negative) curvatures, are convex (concave), and are likely to shrink (grow) [58], [59], [90]. The distribution of integral mean curvatures in each topology class suggests that the number of grain faces alone does not uniquely determine the integral curvature for 3D grains. This is in contrast to a 2D isotropic model, where the number of neighbors determines the curvature.

The effect of nearest neighbors would have been clearer in a plot like Figure 4.3. As pointed out in reference [88], only grains whose nearest neighbors are all unbiased, namely centroids separated from the nearest free surface by more than the average grain diameter, should be considered in the analysis of $\langle F_{NN} \rangle$. However, when this condition was enforced, too few grains remained for this analysis. We conducted the $F - \langle F_{NN} \rangle$ analysis with the 887 grains used in Figure 5.5 and Figure 5.6a, which are unbiased themselves but may have biased neighbors.



Figure 5.6. (a) Integral mean curvature (M_s) of grain faces as a function of the number of grain faces, F, for each grain. For each category, the circle is the mean values and the line shows one standard deviation. (b) Normalized integral curvature of grain faces (G') as a function of $F - \langle F_{NN} \rangle$. $F - \langle F_{NN} \rangle$ is the difference between the number of faces of one grain (F) and the average number of faces of its nearest neighbors $(\langle F_{NN} \rangle)$. Only unbiased grains are included.

It is interesting to note that the correlation between G' and $F - \langle F_{NN} \rangle$ is actually robust even though biased neighboring grains were included. In Figure 5.6b, the individual grain data points are shown as grey circles, and the averaged values for each topology class ($F - \langle F_{NN} \rangle$) are shown as red squares. It can be seen that for the class averaged values, G' and $F - \langle F_{NN} \rangle$ are almost linearly correlated and a fitted line will pass through the origin almost exactly. We conclude that the close correlation between and $F - \langle F_{NN} \rangle$ previously observed in metals [88] (Figure 4.3) also occurs in this ceramic.

5.3 GBHD as a function of plane normal ignoring misorientations

The distributions of the relative areas of grain boundaries, their relative energies, and their curvatures, when classified by crystallography, show correlations. In Figure 5.7, the relative areas, energies, and mean curvatures are plotted as a function of the boundary plane orientation, ignoring the boundary misorientation.



Figure 5.7. Variations of grain boundary properties plotted as a function of grain boundary plane orientation (ignoring the grain boundary misorientation). (a) the absolute value of curvature, for which the unit is μm^{-1} ; (b) relative area, for which the unit is multiples of random distribution (MRD); (c) relative energy, for the which the unit is a procedure defined relative units (r.u.).

The distribution of grain boundary planes illustrated in Figure 5.7c shows a preference for grain boundaries with (100) orientations and the minimum is near (111). This is consistent with earlier measurements. [14, 18] The relative grain boundary energy was lowest near (100) and highest near (111). This inverse relationship with the relative grain boundary area is expected based on measurements in other systems. [3, 24, 25] The absolute value of the curvature also depends on the orientation of the grain boundary plane. In this case, the minimum curvature was at the (100) orientation and the maximum curvature was at the (111) orientation. These results show a direct correlation between the curvature and the energy and an inverse correlation between the curvature and the energy and an inverse correlation between the

curvature and the relative grain boundary area. As an example, faces of a single grain with these characteristics are shown in Figure 5.2. The black arrows indicate two grain faces with mostly (100) orientations and low curvature. Such flat (100) faces are common in the microstructure and have been observed in several experimental studies [103], [106]. The yellow arrow indicates a grain face with (110) orientations and relatively high curvature.

The correlations suggested by the results in Figure 5.7 can be tested. Specifically, we can determine the average value of one property for all of the boundaries that have a second property within a certain range. For example, when we average the energies of all grain boundaries that have relative areas within a 0.05 MRD range, the correlation in Figure 5.8a is obtained. Note that although there is some scatter, there is an inverse correlation between the quantities. When the curvatures of all boundaries within a 0.05 MRD range are averaged, there is also an inverse correlation (see Figure 5.8b). When the curvatures of all boundaries within a 0.05 r.u. range of the relative energy are averaged (Figure 5.8c), there is a positive correlation over the majority of the domain (> 0.8 r.u.). All three of these trends are consistent with the trends observed in Figure 5.7, though the standard deviations of these quantities are large compared to the variations among the mean values.



Figure 5.8. Correlations between average values of grain boundary properties. (a) The average energies of all boundaries in a 0.05 MRD range of relative area. (b) The average curvatures of all boundaries in a 0.05 MRD range of relative area. (c) The average curvatures of all boundaries in a 0.05 r.u. range of relative energy. In each plot, only averages determined from at least three observations are included. The standard deviations of the average energies in (a) and curvatures in (b) and (c) are 0.2 r.u., $0.12 \ \mu m^{-1}$, and, $0.08 \ \mu m^{-1}$, respectively.

5.4 GBHD as a function of plane normal for fixed misorientations

It is also possible to examine these grain boundary properties as a function of grain boundary plane orientation at a fixed misorientation and one example is illustrated in Figure 5.9. The

relative areas of different grain boundary planes are shown in Figure 5.9b. The maxima in the distribution are centered on the orientations of the symmetric tilt boundaries at (031) and ($\overline{013}$). The secondary maxima are at the (100) and ($\overline{100}$) orientations. Being perpendicular to the misorientation axis, they are twist boundaries. An energy minimum (see Figure 5.9c) is also at the symmetric tilt grain boundary position and there are other local energy minima near the twist grain boundary positions, consistent with the inverse correlations evident in Figure 5.7 and Figure 5.8. The low curvatures at the twist boundary positions and the symmetric tilt positions are consistent with the correlation to energy and inverse correlation to area in Figure 5.7 and Figure 5.8. The examination of the distributions at other misorientations (not shown) exhibit similar trends.



Figure 5.9. The (a) curvatures, (b) relative areas, and (c) relative energies as a function of grain boundary plane orientation for boundaries with a 40 ° misorientation around [100]. Each distribution is plotted in stereographic projection. The (031) and ($\overline{013}$) orientations are marked by black squares and the (100) and ($\overline{100}$) positions are marked with triangles. This is also the position of the misorientation axis.

5.5 Discussion

The integral mean curvature of grain faces (M_s) in SrTiO₃ follows a very similar trend to that of the austenite and ferrite data, suggesting that there are no significant differences in the relation between the neighborhood topology and curvature for metallic and ceramic polycrystals.

If one compares the distribution of grains as a function of the number of sides (Figure 5.3b) and the integral mean curvature as a function of the number of sides (Figure 5.6a), it is clear that far more grains have positive curvature than have negative curvature. Therefore, more grains are

convex and, presumably, shrinking than there are concave (negative curvature) growing grains. By conservation, all volume lost from shrinking grains must be gained by growing grains. Interestingly, when we plot the cumulative volume as a function of the number of sides (Figure 5.10) using all 3032 grains within the two sample volumes, we see that 50 % of the total volume is in grains with more than 16 neighbors. So, while there are fewer concave grains with more than 16 neighbors, they are on average larger than the grains with fewer than 16 neighbors.



Figure 5.10. The cumulative distribution of grain volume fraction as a function of grain faces (*F*), in which all grains are included. The dashed line corresponds to F = 16 and cumulative volume fraction = 0.5.

Given the relationships between grain size, number of neighbors, and integral mean curvature, one might assume that the correlation between curvature and grain boundary crystallography would be weak. However, Figure 5.7 and Figure 5.9 show that this is not the case. It is important to emphasize that the curvatures in these figures were classified only by crystallography, meaning that the value at every orientation is the average of data from grains of all sizes. In other words, grain boundaries with (100) orientations have lower curvatures (are flatter) on average then boundaries of (111) orientation, regardless of the size of the grain. Note that this is an unsigned curvature. Because of grain exchange symmetry, the sign of the boundary curvature is not unique. If a grain boundary is convex in the reference frame of one grain, it is concave in the indistinguishable reference frame of the other. The fact that the crystallographic correlation is independent of grain sizes arises because of the requirement that single boundaries join large and small grains.

As suggested in Section 4.4, one possible explanation for the relationship between a grain boundary's curvature and crystallography is the tendency of an interface to have a uniform chemical potential when local equilibrium occurs in the microstructure. Remember the chemical potential of a nonsingular interface [31] is expressed as $\mu = 2H\gamma$, if ignoring second derivatives (Equation 2.24). Assuming that there is a mean-field chemical potential, and individual interfaces have chemical potentials that approximate this value, then the curvature and the energy should be inversely related. This is reasonable, because curvature increases the interface area and the energy penalty for this curvature increases with the energy of the boundary. However, this is not consistent with the SrTiO₃ data, which shows curvature and energy to be directly proportional.

The observations that *H* and γ are not inversely related suggest that these boundaries may not be continuously curved surfaces. Evidence for the existence of facets can be found in Figure 5.9c, where there are abrupt minima in the grain boundary at the positions of the symmetric tilt and twist boundaries. If a grain boundary were made of singular interfaces, then there is a different prescription for determining the chemical potential, which was described by Herring [107] and Taylor [95]. For the case of singular interfaces, $\frac{1}{R}$ is undefined and γ is not differentiable, so Equation 2.24 is inoperable. When a singular (flat) interface moves along its normal, the change in energy occurs at the periphery of the facet and to the boundaries connected at the periphery, as illustrated schematically in Figure 5.11. We illustrate this point in the next paragraph.

Imagine a ridge that is infinitely long in the y-direction, as in Figure 5.11. We can describe its energy change per unit length in the y-direction when the flat top surface moves in the zdirection. As illustrated in Figure 5.11, this hypothetical ridge is bounded by three facets of two types. The top facet is of type 2. The left and right facets are of type 1. If the top facet in Figure 5.11a moves downward by Δz , its area increases by $A' - A = 2\delta\sigma_2$. At the same time, some area of the lateral type 1 facets $(2\delta\sigma_1)$ is eliminated. The exact energy change $(2\delta\sigma_2\gamma_2\Delta z \cot(\theta) - 2\delta\sigma_1\gamma_1\Delta z/\sin(\theta))$ depends on the energies of σ_1 and σ_2 (γ_1 and γ_2), the distance the facet moves (Δz) , and the angle between the facets (θ) . This illustrates the key difference between the energy changes that occur during the motion of a singular and nonsingular boundary. For the non-singular case, the energy change is determined completely by the radius of curvature and the energy of the grain boundary of interest. For the singular case, it is determined by the details of the specific geometry (θ in the simplified case illustrated in Figure 5.11) through the weighted mean curvature [95] and the boundary energy of both the boundary of interest and peripheral boundaries. In polycrystalline microstructures, a grain boundary, singular or non-singular, is usually connected to many different types of grain boundaries, although the types of these neighbors are not completely random [108]. Considering all of the possibilities for θ , γ_1 , and γ_2 , it is difficult to draw a general conclusion about the relation between measured curvature and energy in the presence of singular interfaces. If such boundaries are present in larger numbers, it is not surprising that the inverse correlation between curvature and energy is not observed.



Figure 5.11. Schematic of a ridge, assumed to extend infinitely in the + and – y directions, formed when two surfaces of type 1 meet a surface of type 2. (a) Initial position. (b) After surface 2 retracts by an amount Δz . (c) Illustration of the changes in the surface area.

If the $SrTiO_3$ grain boundary network were dominated by singular interfaces, we have a reasonable idea about what we would observe in our experiment. First, we will not measure zero curvature. The discretized nature of the data and the meshing of the boundary will lead to a minimum but finite curvature. Second, we would also measure energy minima at these orientations. In other words, low energy would correlate with low curvature, as we observe. Another consideration is that if the interfaces were mostly singular, one might expect a finite

number of interfaces, but instead we observe a continuous range of interface orientations. This difference can be reconciled if the boundaries are faceted on a length scale smaller than the resolution of the EBSD maps. In this case, we would see a continuous range of orientations, even if the boundaries were composed of different combinations of more elementary orientations. In fact, there is TEM evidence that is consistent with that idea. Sternlicht et al. [104], [105] reported that, regardless of the macroscopic boundary orientation, on the microscopic level grain boundaries in SrTiO₃ are made up of nanometer-scale flat terraces that mostly have $\{100\}$ and $\{110\}$ orientations separated by steps that also create $\{100\}$ and $\{110\}$ orientations. The steps in the micrographs are larger than the minimum possible step heights, usually by a small integer multiple, but it is not obvious that they could be considered facets. However, migration of such boundaries would require changing the areas of both the larger atomically flat terraces and the smaller multi-layer steps by a process analogous to that illustrated in Figure 5.11.

The observation that grain boundaries are microscopically made up of more elementary low index orientations is not inconsistent with surface observations. Relative surface energies are found to be reasonable predictors of relative grain boundary energies [109]–[111] and it has been reported that in this temperature range, SrTiO₃ surfaces are fully faceted and made up of low index orientations [101].

Finally, it is worth noting that these measurements are consistent with changes that are observed for $SrTiO_3$ grain boundaries in the so-called "anti-thermal" region where the boundaries migrate more slowly [100]. Measurements have shown that there is an increase in boundaries with low energy and with the (100) orientation [101], [102]. Here, we find these (100)-oriented, low energy boundaries also have a minimum curvature. Therefore, they have the lowest driving force for migration. While this does not explain why such low curvature, low energy boundaries form in this temperature range, it is consistent with the phenomenological observation of slower grain boundary migration.

5.6 Conclusion

Using 3D EBSD, we have measured the distribution of relative areas, energies, and curvatures in SrTiO3 annealed at 1470°C. The integral mean curvatures of grains vary such that small grains with fewer than 16 sides have positive curvatures and larger grains with more than 16 sides have negative curvatures. The number of excess neighbors correlates strongly with the normalized

integral mean curvature. The curvature is positive (negative) if a grain has fewer (more) neighbors than the average of its neighbors. The grain boundary curvature is inversely correlated to the grain boundary area, such that flat boundaries make up a relatively larger portion of the grain boundary area. Also, grain boundary curvature is correlated to grain boundary energy, such that lower energy boundaries are flatter and relatively larger. This latter correlation suggests that the grain boundary network is dominated by singular boundaries.

6. Grain face features from HEDM datasets

In the previous two chapters, we analyzed three sets of EBSD orientation maps and came up with three conclusions. First, the integral grain curvature is correlated with its topological character, like the number of faces, and a mean-field character, defined as $F - \langle F_{NN} \rangle$. Second, the different properties of grain boundaries, including population, energy, and curvature, are correlated. Third, the correlation between grain boundary energy and curvature is different for general boundaries, whose energy landscapes are smooth, and singular boundaries, whose energies sit in cusps. The validity of the third conclusion is not indisputable, since a robust and reliable discrimination of singular and non-singular boundaries is not yet available. Nevertheless, the first two conclusions are well-supported by experimental evidence. The various properties of a microstructure are clearly correlated.

However, direct evidence of how these properties affect the microstructure evolution was missing due to the destructive nature of the EBSD technique. The materials are milled away during the collection of orientation maps, so it is not possible to observe the evolution of microstructures via EBSD. This problem can be resolved with a non-destructive technique, like high energy diffraction microscopy (HEDM).

We will analyze two orientation maps collected via HEDM in the remainder of this document, which depict the before and after annealing state microstructures of a high purity Ni sample. Previous studies of these data have been published in references [112]–[114]. The focus of this research is the evolution of grain faces. Different grain face characteristics were first summarized as many numeric features, and these features were then analyzed with the help of machine learning models. Some grain face characteristics, like the crystallographic parameters, were not efficiently captured by our features and were analyzed separated.

This chapter intends describe the material in use (Section 6.1), the preprocessing concerns (Section 6.2), the feature engineering details (Section 6.3 - 6.7), and the machine learning models of choice (Section 6.8). Detailed sample statistics and analyses are presented in the following chapter (Chapter 7).

6.1 Sample overview

The sample in use is high purity Nickel. The diffraction experiment was conducted at the Advanced Photon Source at Argonne National Laboratory by Hefferan et al. [112]. A detailed description of the sample information and experimental set up can be found in Reference [115], and the most important points are summarized below.

The sample was machined to be a 1 mm diameter rod from a 99.999 % purity Nickel rod bought from Alfa Aesar. Before orientation map collection, the sample has been annealed at 750 °C for 2 hours to yield a fully recrystallized initial microstructure of appropriate grain size. The annealing atmosphere was 97 % N₂, 3 % H₂.

Six sets of nf-HEDM diffraction patterns of the same material volume were collected for six different anneal states, from which the microstructure map were resolved by a forward modeling technique [112]. The first set of diffraction patterns was collected for the 750 °C annealed sample, after which the sample was annealed again at 800 °C for about 30 minutes to enable microstructure evolution, and then followed by the collection of the second set of diffraction patterns. This anneal-measure cycle was repeated five times and six successive microstructures were collected. The anneal conditions are summarized in Table 6.1. In this research, we focus on the grain face evolutions in the last two states (anneal-state-4 and anneal-state-5).

Anneal State	Duration (min)	Temp (°C)	Environment
0	120	750	97%N ₂ , 3%H ₂
1	+23	800	97%Ar, 3%H ₂
2	+30	800	97% Ar, 3% H ₂
3	+25	800	$97\%N_2, 3\%H_2$
4	+35	800	$97\%N_2, 3\%H_2$
5	+25	800	$97\%N_2, 3\%H_2$

Table 6.1. Heat treatment history of Ni. Reprinted from Reference [112].

The orientation recovery process in HEDM is completely different from that in EBSD, but the recovered orientation data are both presented in the form of sequential map slices [61], [62]. The orientation maps were constructed from the data by Hefferan et al. [112], using a hexagonal grid of 2.0 μ m in-plane resolution and 4.0 μ m z-direction resolution. These map slices were converted to square grids (2.8 μ m by 2.8 μ m) and reconstructed to be 3D microstructures by Bhattacharya et al. [114], using DREAM.3D version 6.4 [78]. The misorientation threshold was 2° , and the smallest grain contained 27 voxels. In the as-collected maps, anneal-state-4 covers $395 \times 404 \times 84$ voxels, and the anneal-state-5 covers $398 \times 404 \times 104$ voxels.

This research is based on the grain tracking results from Bhattacharya et al. [114] A grain face is considered tracked if the grains on its two sides are tracked across the two anneal states. Detailed statistics of the tracked faces are given in Section 7.1.1.

6.2 Data preprocessing

Several processes need to be finished before good quality data can be retrieved from two sequential DREAM3D files, between which the tracking of grains has been solved. Specifically, a shared volume needs to be extracted between the two datasets. The data volumes need to be aligned. The experimentally measured grain faces should be examined and bad measurements, or outliers, should be excluded. Note we will not discuss recovering orientation maps from diffraction patterns, reconstructing 3D microstructures with DREAM.3D, or tracking grains. Please refer to references [112], [114], [115] for this information.

6.2.1 Datasets shared volume and alignment

The HEDM technique enables one to measure a sample volume repeatedly. However, if interruptions, like ex-situ heat treatments as in our case, happened during the measurements, then the measured sample volumes and the local coordinate system associated with each volume may not coincide exactly. Specifically, the anneal-state-5 covers a slightly larger volume ($398 \times 404 \times 104$) than anneal-state-4 ($395 \times 404 \times 84$). This volume difference may induce biases when analyzing grain faces near the sample boundary, so we decided to use only the volume covered, or shared, by both states.

The extraction of the shared volume is based on Bhattacharya's work of tracked grains. [114] The assumption is that grain growth is an approximately uniform process and the tracked grains should overlap the most in the shared volume. A coordinate descent algorithm was implemented accordingly. At the start of the algorithm, the two volumes were placed such that voxels at the (0,0,0) positions coincided. The grain ID of every voxel was compared, and the overlapping volume of the tracked grains was recorded (in voxels). Then the volume of anneal state four (V_{an4}) was shifted in the x-direction for a range of steps and the best x-shift that gave the largest overlapping volume, as well as the largest overlapping volume, was recorded. The shift range was decided from the sample size difference in x-direction (398 – 395 = 3) to be [-10 : 1 : 13]

(between -10 and 13 and with a step size of 1). Similar shifts were repeated in the y and z directions and then back to the x-direction. This x, y, z shift cycle ended when the largest overlapping volume did not change after a complete shift cycle, which indicated that the algorithm has converged. The shared volume was then calculated by comparing the best shifts and the sample dimensions.

In our datasets, the volume shared between V, the sample volume in anneal-state-4, and V', the sample volume in anneal-state-5, was calculated to be the same size as V, though the search algorithm did not force such a constraint, confirming a good experimental setup. Note if the experimentally measured volumes were far apart physically, the shift ranges need to be bigger. In all the following analyses, the volume of anneal-state-5 was cropped and only the shared volume was kept.

Note the volume of anneal-state-4 and the cropped volume of anneal-state-5 still sat in their local coordinate systems. The next step is to align their coordinates, which is important if one wants to track mesh nodes across different sample volumes directly for the purpose of measuring migration distance or mobility. We discuss two straightforward ways to align sample volumes here and leave the details of grain face migration until Section 6.6.

The best shift vector from the shared volume extraction process serves as the first method to align sample volumes. Another way is to take the average centroids shift from the tracked grains to be the shift between the two volumes. Similar to the first method, the underlying assumption is that the grain growth process is approximately random, or at least not strongly biased, in the x, y and z directions so the average shift of grain centroids should be zero if the two volumes are well aligned.

Neither of these two methods is perfect. The first method is straightforward, but the resolution is limited by the voxel size of the dataset. Sub-voxel alignments, in our case dimensions smaller than $2.8 \ \mu m \times 2.8 \ \mu m \times 4 \ \mu m$, are not achievable. The second method is not restricted by resolution, but the centroid shift of every tracked grain pair is considered as, probably unfairly, equally important. In our datasets, results from the two methods differed by $0.7 \ \mu m$, $0.7 \ \mu m$, and $2.8 \ \mu m$ in the x, y, and z directions respectively. We aligned the sample volumes following the second method. The second method can probably be improved by assigning a size-dependent weight factor to the shifts of tracked grains. Better alignment may also be achieved with the help of advanced machine learning models like the generative

adversarial neural network [116], [117]. However, detailed optimization on the alignment is out of the scope of this research.

6.2.2 Concerns about experimentally measured grain faces

To start with, we would like to point out that the focus of this and the following chapter is grain faces. The grain growth community has been traditionally more interested in grains, probably because the most fundamental insights about the evolution of microstructures, also known as the grain growth process, was inspired from the evolution of soap bubbles. For soap bubbles, it is natural to start the study with individual bubbles because bubble surfaces are isotropic and the driving force, pressure, is constant within each bubble. However, this situation does not apply to grain growth. Grain boundaries are anisotropic and local driving forces can vary significantly within one single grain [118], so we think grains are not the indisputable reasonable entity to start the analysis of microstructure evolution. To illustrate the point, the microstructure of anneal-state-4 is displayed as a voxel-based grain collection (Figure 6.1a) and as a mesh-based cellular network (Figure 6.1b). It can be seen that grain faces can also be considered as a basic element of the microstructure if one takes the point of view from a grain boundary cellular network, instead of a grain collection.

We are interested in grain faces because of this slightly different perspective they provide. Also, analyses of grain faces do not contradict analyses of grains. Some properties of grains, like integral curvature, which is believed to be correlated with the growth of grains [73, 97], are based on properties of grain faces.



Figure 6.1. Microstructure of anneal state 4, (a) as voxel-based grains and (b) as mesh-based grain boundary network.

Because of the discrete nature of the experimental method, measurements from the small grain faces are usually less reliable than measurements from larger faces. The reasoning is similar to that of the small (< 27) voxel groups, which are considered as noise rather than grains

during the DREAM.3D reconstruction. There are two main sources of small grain faces. One is the physically small grain faces, and the other is measurement artifacts. Remember that experimental measurements have finite resolution and accuracy so one should not try to interpret every detail in the dataset.

Some measurements, like mean curvature, depend on mesh quality. The meshes in this research are generated by the DREAM.3D quick mesh method and are smoothed using two different smoothing techniques, including DREAM.3D Laplacian smoothing [78] and a topology-faithful nonparametric smoothing method [119]. Neither of these smoothing techniques is perfect. Laplacian smoothing handles mesh triangles near triple lines poorly. Nonparametric smoothing generates overall smoother shapes but can produce more poorly shaped triangles on grain faces. Exact data values vary with smoothing methods, but the general trend is similar.

Another issue worth mentioning is the integrity of grain faces. We defined a grain face as the interface between two grains. Following this definition, it is possible that a grain face contains multiple isolated pieces. An example is shown in Figure 6.2, in which the two pieces are cut apart by another plate-shaped grain.



Figure 6.2. Example of a two-piece grain faces, (a) in the grain pair and (b) on individual grains.

The two pieces in Figure 6.2 represent the physical structure of the sample and are unlikely to be an artifact. In other cases, a grain face is composed of a large piece and some small satellite pieces which are likely to be artifacts of the reconstruction. We point out this problem because it causes problems when attempting to track mesh nodes, which will be discussed in detail later (Section 6.6.1).

6.2.3 Outliers

Data instances with extreme values are often considered to be different from those with moderate values and are called outliers. The interpretation and handling of outliers vary from case to case because outliers are usually associated with dual roles. Such unusual values may hold the key information of interest, or they may arise from noise that serves only to distort the underlying general trend [120]. The boundary is often blurred, and one needs to balance between the objective of capturing the central trend and the risk of ignoring informative critical events depending on the problem at hand.

Because this is the first time grain faces have been tracked, we had to develop a criterion to separate reliable data from outliers. A tracked grain face was determined as an outlier if any of the four conditions was satisfied: 1) $A < 20 \ \mu m^2$; 2) $A' < 20 \ \mu m^2$; 3) (A' - A) / A > 10; 4) (A' - A) / A < -0.9. A and A' stand for the area of a tracked grain face, in anneal-state-4 and anneal-state-5. The first two conditions require that grain faces are large enough in both states, in which $20 \ \mu m^2$ amounts to approximately four mesh triangles. The last two conditions are designed to filter out grain faces with dramatic area changes. Note the outlier thresholds are empirical. Some outlier grain faces probably result from imperfect measurements or data processing artifacts, but some are possibly good measurements of true grain faces. Similarly, not all non-outlier grain faces are necessarily good measurements with physical counterparts.

Elementary mesh triangles are also filtered. Unrealistic measurements, defined as the magnitude of triangle mean curvature value larger than $1 \,\mu m^{-1}$, or triangle area large than 7 μm^2 or triangle minimum interior angle smaller than 10° were not used in calculations of grain face features. The threshold values are determined by referencing the dataset resolutions and the 99 % or 1 % percentiles of the measurement distributions.

6.3 Crystallographic features

We start to discuss feature engineering for grain faces in this and the next few sections. A grain face is defined as the collection of grain boundary triangles that sit between the same two resident grains. Each characteristic of one grain face is summarized in one number, and a characteristic of all grain faces compose a data column, or feature.

6.3.1 Misorientation

The misorientation of a grain face is straight forward, identical to the misorientation of a grain boundary. We did not adopt the misorientation data as a feature directly. The reason is that, in the Euler angle convention, three numbers are needed to fully describe a misorientation, but we would like to confine features to be one number for each face. There are two reasons for this preference. The first one is that the interpretability of results, primarily feature importance, will be compromised if one-number features are mixed with multi-number features. Second, the available training data (at most tens of thousands of tracked grain faces) is limited and we do not plan to train models with huge capacities, such as neural networks. It is questionable that a moderate-capacity model can learn the multiple-number features properly when they are mixed with the one number-features in the full feature matrix.

The misorientation features are defined as distances from target misorientations, calculated following Equation 6.1, in which M_i stands for the misorientation of a grain face and M stands for the target misorientation. tr() is the trace operator [121], [122]. Note that before applying Equation 6.1, both M_i and M need to be converted to its representation within the fundamental zone. Proper crystallographic symmetries were applied on M_i and M, and the misorientation distance was determined as the smallest distance among the symmetrically equivalent copies. The most interesting target misorientation is $\Sigma 3$ (60° / [111]) [35], [123]. Some other low sigma misorientations, like $\Sigma 5$, $\Sigma 7$, $\Sigma 9$, may also be informative, but the general misorientations should be relatively featureless [19].

$$\beta = \arccos\left(\frac{\operatorname{tr}(M_i M^T) - 1}{2}\right) \tag{6.1}$$

6.3.2 Plane normal

Describing the plane normal of a grain face is much trickier since a grain face is usually composed of many grain boundary triangles, each with its own plane normal. The plane normal features are also distance-based. A few target plane normal directions were chosen: [111], [110], [100], [112]. For every grain boundary (mesh triangle), the distance between the triangle normal (n_i) and the target normal (n) is calculated following Equation 6.2. [121], [122]. Note both n_i and n should be given in crystallographic reference frames. Similar to the misorientation distances, proper symmetry operators were applied and the smallest one was determined as the

normal distance for a given grain boundary (η_{GB}) . Then the target normal distance of a grain face (η_{GF}) was determined as $\eta_{GF} = \sum_{j=1}^{J} (\eta_{GB}^{j}) / J$, in which *J* is the number of mesh triangles on the grain face. The standard deviations of the mesh triangle target normal distances were also recorded to characterize the variations of plane normal directions.

$$\eta = \sqrt{\frac{\zeta_1^2 + \zeta_2^2}{2}}, \qquad \zeta_k = \arccos(n_{i,k} \cdot n_k)$$
(6.2)

6.4 Geometric & topological features

The status of a grain boundary cellular network is described if the crystallographic information (namely what grain boundaries exist in this network), geometric information (namely what are the shapes of the boundary boundaries), and the topological information (namely how the grain boundaries are connected) are known. Combinations of these three fundamental types of information may also be useful.

A topology-faithful smoothing technique designed by Maddali et. al. [119] was applied to prepare the microstructure for features discussed in this section. The topology-faithful smoothing handles the smoothing of triple lines better than the DREAM.3D Laplacian smoothing method [82]. However, we note that the topology-faithful smoothing creates more poorly smoothed pits in the interior of grain faces. Such pits do not seem to have a significant effect on curvature calculations but can lead to noise in grain boundary plane normal related properties. As a result, we applied to topology-faithful smoothing to calculate grain face features and used DREAM.3D Laplacian smoothing for plane normal related calculations.

6.4.1 Geometric features

Three kinds of geometric features were designed: area (A), integral absolute mean curvature $(|\mathcal{H}|)$ and average absolute mean curvature $(|\mathbb{H}|)$. Note the absolute values of mean curvatures are used due to the switching symmetric, similar to what has been discussed for the GBHD (Section 3.2). The calculation of $|\mathcal{H}|$ is similar to the integral mean curvature of grain faces (Equation 4.1), except that absolute mean curvatures are used and there is no need to integrate over different grain faces. $|\mathbb{H}|$ is the average of absolute mean curvature, calculated as $|\mathbb{H}| =$

 $\sum_{j=1}^{J} (|H|^j) / J$. |H| is the unsigned triangle curvature and *J* is the number of triangles on the given grain face.

These features haven been measured for both the before-anneal dataset (anneal-state-4) and the after-anneal dataset (anneal-state-5). The change of a feature is always calculated as feature value in anneal-state-5 minus the feature value in anneal-state-4.

6.4.2 Topological features

Three types of topological features are calculated for each grain face, including the number of corners, the number of edges and the integral dihedral angles. Identifying corners in 3D microstructures is non-trivial. Sun et. al. [124] reported that discretization artifacts exist even in simulated 3D microstructures, which are generally considered to have high quality clean shapes. Our datasets were collected from experiments and enclosed many twins with complicated shapes, meaning there is probably many more noise and measurements are likely to be less reliable [113], [114]. Several corner and edge determination methodologies can be found from literature [124]–[126], among which Li et. al. [125] faced a situation similar to ours. Li et. al. [125] proposed the idea of canonical quadruple nodes, which do not necessarily have physical counterparts but are more robust to certain kinds of noise. The same approach was taken in by Liu et. al. [126].

We identified quadruple nodes by checking the connectivity of voxels. As shown in Figure 6.3, every grid position inside the sample volume has eight neighboring voxels, each with a grain ID (Section 3.1.2).



Figure 6.3. Illustration of voxels (the eight small cubes) and mesh grid positions (circular points sitting on the corners of voxels).

All mesh grid positions inside the sample volume were examined. If no less than four unique grain IDs were found among the eight voxels neighboring a mesh node, the set of unique grain IDs was recorded and served as identifiers of quadruple nodes. Note a unique set of grain IDs was recorded only once. Though some physical corners, which are enclosed in the same set of

four connected grains, are ignored in this approach, it is efficient since the majority grain ID set duplications have originated from discretization artifacts. There is no efficient way to differentiate the physical duplicated grain ID sets from the noise duplicated grain ID sets, so we decided to ignore all duplications.

Most of the grain ID sets have four members, consistent with what would be expected for quadruple nodes. However, larger grain ID sets, with five or six members, corresponding to quintuple or sextuple nodes, are also observed. The population of the quintuple nodes is small with respect to the population of quadruple nodes and the population of sextuple nodes are basically ignorable. These super nodes may have resulted from the limited experiment resolution. For example, a quintuple node might have resulted from a sub-resolution triple line and two quadruple nodes, as mentioned [125].

The number of corners (C) of a grain face was calculated by comparing the two resident grain IDs of a given face to the ID sets defining quadruple, or quintuple, nodes. If the two IDs labeling the grain face were found in one four grain set, C was increased by one. If the two IDs labeling the grain face were found in one five grain set, C was increased by two. Six grain sets were ignored since there were very few of them.

The number of edges was calculated from the connection of mesh triangles. DREAM.3D labels each mesh node with a unique ID and records the three nodes constituting each mesh triangle. These two data contain the full connection information of the mesh triangles. To find the triangles that share a common edge, one just needs to find the triangles containing the two corresponding mesh nodes. Edges shared by three mesh triangles were identified, and the three grains enclosing these edges, which can be found from triangle labels (Section 3.1.2), were recorded. Similar to the case of corners, it is assumed that an edge is defined by a unique set of three grain IDs. This assumption was shown to be effective by some random visual checks. However, a set of three grains might have defined more than one edges, or an edge might be shared by four grains. The latter two cases were relatively rare and were ignored in the current research.

The integral dihedral angles were also calculated from the connection of mesh triangles, and an illustration of the procedure is given in Figure 6.4. The transparent blue surface in Figure 6.4a depicts a grain face in anneal-state-4. Two other grain faces sharing a triple line with the blue face are shown in transparent red. A group of three mesh triangles sitting on this triple line is highlighted in non-transparent colors and magnified in Figure 6.4b. Dihedral angles were calculated within the three-triangle group, and were labeled as opposite, left or right based on the local arrangement of resident grains. The opposite dihedral angle is straight forward. The convention of left and right will be discussed in detail in Sections 6.6.4 and 6.7, where the motivation becomes more clear. In short, the choice of left and right is arbitrary but needs to be kept consistent once made. The calculation of dihedral angles was repeated in all group of three triangles sitting on edges of the objective grain face. Integral dihedral angles were then calculated from dihedral angles within these group of three triangles.



Figure 6.4. (a) Three grain faces enclosing a triple line. (b) A group of three mesh triangles on the triple line. (c) Simplified 2D illustration for the grain boundary (mesh triangle) of interest, the left and right nearest neighbor, or connected, boundaries, and dihedral angles formed by this group of three grain boundaries.

6.5 Mean-field features

We have seen that $F - \langle F_{NN} \rangle$, a mean-field defined by the nearest neighbors of a given grain, is highly correlated with G', the normalized integral curvature of grain faces, for a given grain (Figure 4.3 and Figure 5.5b). Are there similar kinds of correlations for grain faces? To answer this question, some mean-field features were designed for grain faces.

The mean-field features are based on differences between a grain face of interest and its nearest neighbors. The nearest neighbor grain faces refer to those connected to the grain face of

interest via shared triple lines and can be tracked by checking triple lines (Section 6.4.2). All geometrical and topological features can be used to design a corresponding mean-field feature.

More generally, a mean-field feature can be defined to capture all kinds of unusual events among the nearest neighbor faces. For example, we calculated the number of disappeared and appeared grains and grain faces within the nearest neighborhood of each grain face and recorded the number in fraction. The motivation behind these features is that the vanish of a grain is likely to induce a large perturbation in the local neighbor. The nucleation of new grains is usually thought to be rare but have been identified in the Ni datasets [127]. The extinction and nucleation of grains and grain faces may play the role of critical events and thus correlated with the evolution of grain faces.

6.6 Migration features

The migration distances of grain faces are of interest because migration distances combined with curvature data yields grain boundary mobility (Equation 2.25), which is an important grain boundary property (Section 2.4.3). To extract grain face migration distances, we first tracked the mesh nodes on the same grain face across the two datasets (Sections 6.6.1 and 0). However, the direct distances between tracked mesh nodes do not correspond to out-of-plane migration distances so it is necessary to use projections (Section 6.6.3). Finally, we also defined a local reference frame convention and extracted the migration direction of grain faces (Section 6.6.4).

6.6.1 An optimal-transportation-based algorithm for grain face tracking

In this section, the algorithm created by Maddali et al. [119] is briefly described. The problem context is that given the two sets of mesh nodes, capturing the before and after annealing shapes of a grain face, one needs to determine the displacement vectors. In other words, a mesh node in the before-anneal-state corresponds to which mesh node in the after-anneal-state or vice versa.

Maddali et al. designed this algorithm based on three assumptions. First, nodes in the beforeanneal-state follow the shortest possible path to complete the motion. Second, every node in the before-anneal-state has a correspondence in the after-anneal-state. Third, correspondences in the after-anneal-state are distributed as uniformly as possible. The linear optimization formulation of the problem is given by Equations 6.3 - 6.6. [119]

$$C_{ij} = \underset{\sigma_{ij}}{\operatorname{argmin}} \left\{ \sum_{i=1}^{M} \sum_{j=1}^{N} \sigma_{ij} |y_j - x_i|^2 \right\}$$
(6.3)

Such that

$$\sigma_{ij} \ge 0, \quad \forall \ i = 1, 2, ..., M \text{ and } j = 1, 2, ..., N$$
 (6.4)

$$\sum_{j=1}^{N} \sigma_{ij} = 1, \quad \forall i = 1, 2, \dots, M$$
(6.5)

$$\sum_{j=1}^{M} \sigma_{ij} = \frac{M}{N}, \quad \forall j = 1, 2, ..., N$$
(6.6)

 $\{x_i\}$ is coordinates of the set of mesh nodes in before-anneal-state. $\{y_j\}$ is coordinates of the set of mesh nodes in after-anneal-state. N and M are the number of mesh nodes in the beforeanneal-state and after-anneal-state. σ_{ij} is a weight matrix indicating the correspondence between $\{x_i\}$ and $\{y_j\}$. The objective function, Equation 6.3, is derived from the first assumption. Equation 6.5 and 6.6 are from the second and third assumptions.

This algorithm allows one to work with densities. In other words, one mesh node can correspond to multiple mesh nodes according the density matrix C_{ij} . Nevertheless, we constrain the elements of C_{ij} to be binary, taking the value of either zero or one, in our implementation. Direct application of this algorithm works well in general cases. An example of a tracked grain face in our dataset is given in Figure 6.5a, in which the blue surface depicts the grain face before annealing (anneal-state-4) and the yellow surface is the grain face after annealing (anneal-state-5). It can be seen that the black lines, which can be considered as the migration vectors of grain boundaries during annealing, look reasonable. However, not all tracking results look as good as Figure 6.5a. There remain at least two tricky problems.

The first problem is illustrated in Figure 6.5b, in which the grain face has two pieces in both anneal-state-4 and anneal-state-5. It is obvious that the long black lines connecting mesh nodes across the two pieces are not physical. This problem roots from the requirement that the correspondences to be evenly distributed (Equation 6.6) and is most serious for the multi-piece grain faces. One solution is to solve the correspondence of pieces first and then solve the correspondence of nodes within the paired pieces.



Figure 6.5. Examples of grain faces tracked following the algorithm designed by Maddali et al.. [119] Blue nodes and blue surface depicts the grain face in anneal-state-4. Yellow nodes and yellow surface depict the grain face in anneal-state-5. Black lines indicate the correspondence of mesh nodes.

The second problem resides in the intrinsic ambiguity of the term "grain boundary migration". Note the exact atoms constituting a piece of grain boundary change dynamically during the migration of a grain boundary [128], [129]. This problem is not obvious in traditional bi-crystal mobility experiments, in which the grain boundary shapes do not change throughout the experiment [19], [130]. However, the problem becomes significant when grain boundaries are examined in the context of real-word 3D polycrystalline materials, where grain boundary out-of-plane migration and in-plane shape change happen at the same time. The point can be illustrated with two simplified 2D examples in Figure 6.6.

The tracking is correct in the two examples of Figure 6.6. However, it is easy to notice that the length of the black lines, namely the direct migration distances, do not match the length of the green arrows, namely the out-ot-plane migration distances. Figure 6.6a illustrates the case of grain boundary area change, and an experimentally measured grain face example can be found in the left piece of Figure 6.5b. If a grain face goes through some area change during migration, both the area change and the out-of-plane migration (green arrow) will contribute to the direct migration distance (black line lengths). Figure 6.6b demonstrates the problem of shift, which is even more general, and a real grain face example can be find in Figure 6.5a. There are two possible sources for the shift. The first one is related to the finite resolution of our discrete data.

Any coordinates misalignment and any randomness in the mesh nodes sampling process can cause the discrete mesh nodes to mismatch, thus inducing some incorrect migration distances. The second possible source is physical shifts like grain boundary sliding [131], [132]. Note that we always keep the focus on out-ot-plane migration distances when discussing grain boundary migrations in this document. Grain face shape changes are left to be captured by geometric features like face area change (Section 6.4).



Figure 6.6. The blue nodes and lines depict a 2D grain boundary in the before-anneal-state. The yellow nodes and lines depict a 2D grain boundary in the after-anneal-state. The tracking results are indicated by the black lines. The out of plane migration distance is indicated by the green line.

One possible way to extract a more accurate out-of-plane migration distance is to track only the nodes in a shared area. Take the grain face in Figure 6.5a as an example. One can first project the 3D mesh nodes onto a 2D plane (Figure 6.7b). Work out a shared area in the 2D plane and which nodes reside in the shared 2D area (Figure 6.7c). Then the corresponding 3D nodes can be considered as residing in a shared area.



Figure 6.7. Illustration of identifying nodes in the shared area by projecting 3D mesh nodes to 2D. (a) The same grain face as in Figure 6.5a. (b) 2D projections of the mesh nodes. (c) Points that sit inside the shared area are now indicated by stars. Points outside are not shown.

Solid points in Figure 6.7b correspond to 3D mesh nodes that sit on boundary of the grain face, or triple lines. Hollow points correspond to mesh nodes sitting in the interior of grain faces.

Lines indicate boundaries of the 2D polygons, returned by MATLAB [133]. The 2D plane in Figure 6.7 was defined from the average normal of all mesh triangles and the centroid of all mesh nodes. The 2D intersections can be found with packages available in MATLAB [133]. Note this method would fail if the grain face has slid a large distance.

6.6.2 A nearest matching algorithm for grain face tracking

A second way to track mesh nodes is to consider a pair of mesh nodes tracked if they are the nearest neighbor of each other. Note that this nearest matching algorithm allows only 1-to-1 correspondence between mesh nodes so not all mesh nodes will be tracked. The optimal-transportation-based algorithm allows 1-to-N relationship so all nodes have at least one correspondence. Despite the simplicity, this nearest matching algorithm yields reasonable results, as can be seen in Figure 6.8.



Figure 6.8. (a) and (b) show examples of grain faces tracked following the nearest matching algorithm, similar to Figure 6.5. However, only mesh nodes that were tracked are shown. (c) Surfaces of the same grain face as in (b). The red arrows indicate a high curvature surface where mesh nodes are unlikely to be tracked.

Figure 6.8a illustrates the nearest matching result of the same face as in Figure 6.5b. It can be seen that the result is less sensitive to the area change problem mentioned in the previous section. However, the major drawback of this algorithm is that it biases against high curvature surfaces, as indicated in Figure 6.8b and Figure 6.8c by the red arrows.

6.6.3 Out-of-plane migration distance from tracked nodes

As discussed in Section 6.6.1, direct migration distances from tracked mesh node pairs are not equal to the out-of-plane migration distance. Though one can never fully recover the true out-of-

plane migration distances from datasets with a coarse time grid, such as the 25 min separated anneal-state-4 and anneal-state-5, a fair approximation of the values may be obtained by projecting migration distances from tracked mesh nodes along surface normals. For example, if the black lines in Figure 6.6 are projected along the surface normal, then they would have the same length as the green arrows. The surface normal directions of experimentally measured grain faces are usually less obvious than the case of Figure 6.6. Nevertheless, three kinds of projections have been tried.

A straight forward choice is to project migration distances along local surface normal directions. One mesh node is usually shared by several resident mesh triangles, each with a slightly different triangle normal. The surface normal at the mesh node can be calculated as the average of resident mesh triangles' normal directions.

However, as mentioned in Section 6.2.2, local triangle normal directions can be affected by mesh quality and may not be reliable, especially at positions near triple lines. A second projection method was designed to resolve this problem, in which a median plane is assumed to exist between before-anneal and after-anneal grain face pair. This median plane can be determined by fitting the mesh nodes with a linear regression model, or by training a supported vector machine (SVM) model to classify the before-anneal-state mesh nodes and the after-anneal-state mesh nodes. An example of an SVM median plane is given in Figure 6.9.



Figure 6.9. A pair of grain faces and a median plane solved by the SVM model. Blue surface depicts the grain face in anneal-state-4. Yellow surface depicts the grain face in anneal-state-5. Purple surface shows the median plane, whose normal direction is pictured by the purple arrow. (a) and (b) shows the same grain face pair from different views.

It can be seen that the normal direction of the median plane can approximate local surface normal directions well. Note that not all grain faces can be fitted by a single median plane. If both grain faces have highly curved shapes (Figure 6.10a), then multiple median planes are needed (Figure 6.10b).



Figure 6.10. (a) A highly curved grain face pair and (b) median planes fitted by the SVM model. Blue surface depicts the grain face in anneal-state-4. Yellow surface depicts the grain face in anneal-state-5. Different colors in (b) indicating different node clusters.

The median planes were fitted automatically in an iterative manner with the help of a goodmedian-plane criterion. The good-median-plane criterion was defined from the intuition that nodes from different mesh states should sit on different sides of the median plane, and the plane normal of the median plane should be close to at least one of the average triangle normal directions in the two states. In the beginning, a to-be-clustered pool of nodes was initialized with all mesh nodes on the tracked grain face pair. One median plane was fitted using the to-beclustered pool of nodes, and the good-median-plane condition was then checked. If the goodmedian-plane condition was not satisfied, then a K-means algorithm was run with the pool of nodes, and the nodes were then divided into two clusters. Next, one median plane was fit within each cluster. Once a good median plane was found for a cluster, all mesh nodes of this good cluster were removed from the to-be-clustered pool. The check-cluster-fit cycle was repeated until 90 % of the mesh nodes has been fitted with good median planes or the maximum number of clusters has been reached. Note the number of K-means clusters in each cycle is set as the number of bad clusters from the previous cycle plus one.

The third method is not a projection method. It is instead a decomposition method inspired from the idea that the height of a pillar becomes calculable if given the top and bottom surface areas and the volume of a pillar. In the context of tracked mesh nodes, the top and bottom surface areas are given by the triangle areas. The volume enclosed by a set of mesh nodes can be calculated from the associated convex hull [133]. The out-of-plane migration distance may then be approximated by pillar heights. One pillar is defined by six mesh nodes, three mesh nodes that form a mesh triangle on the before-anneal grain face and their correspondences on the after-anneal grain face. An example is shown in Figure 6.11.



Figure 6.11. Illustrations of pillars form by mesh nodes. Blue surface depicts the grain face in anneal-state-4. Yellow surface depicts the grain face in anneal-state-5. Pillar top surfaces are formed by mesh triangles in anneal-state-4. Pillar bottom surfaces are formed by the three correspondences, found by the optimal-transportation-based tracking algorithm, of the mesh nodes of the top surface. Pillar edges are shown by the blue and yellow lines.

We made an important assumption that $h = \frac{2V}{A_t + A_b}$, where V is the volume enclosed by a group of six mesh nodes. A_t is area of the top surface and was set to be the before-anneal (blue in Figure 6.11) mesh triangle area by convention. A_b is the area of the bottom surface and was set to be the yellow edge triangles in Figure 6.11. The average value of h, pillar heights, was taken to be the approximation for the migration distance of this grain face. Note the values of h depend pillar shapes so we include a pillar into the average only if both its top and bottom triangles have regular shapes, defined as the minimum interior angle larger than 10° .

6.6.4 Migration direction

Our interest in the grain face migration direction started with a simple question: is it true that a grain face always moves toward its curvature center? Answering this question requires access to the migration direction and the curvature sign of the objective grain face. We keep the focus on migration direction in this section and leave the topic of curvature sign, or more generally, curvature gradients, to the next section (Section 6.7).

First let us clarify the concept of migration direction within this research. It is defined within the pair of grains composing the grain face of interest, and is simplified to an indicator variable of three possible values {1, 0, -1}, describing whether if the grain face moved toward the left grain, did not move, or moved toward the right grain. It is defined this way because an indicator variable is simpler than a full three-dimensional migration vector, thus is probably more robust to various kinds of noise. As discussed in Section 6.6.1, our discrete measurements only allow for limited accuracy. Then the dimension of the indicator variable, one, is also consistent with that of the mean curvature. Of course, there is no natural way to differentiate left from right between two grains, but it is also not important. What matters is the relativity of left or right is always kept consistent across different datasets, including the before-anneal state (anneal-state-4) and the after-anneal state (anneal-state-5), and for different features. In this research, we defined the left and right grains arbitrarily in anneal-state-4 and then kept this convention consistent in anneal-state-5.

The migration direction of a grain face was extracted in two different ways. The first one was from the sign of the grain face out-of-plane migration vector, calculated as the average of the mesh node out-of-plane migration vectors, from all mesh nodes on the grain face of interest. The second was from the relative positions of the grain face centroid, the centroid of the left grain and the centroid of the right grain. The relative grain face position was calculated as $p = \frac{d_l}{d_l+d_r}$, where d_l and d_r are the distances between the grain face centroid, and the left and right grain centroids, for anneal-state-4 and anneal-state-5. The grain face was considered moved left if p, of anneal-state-4, was smaller than p', of anneal-state-5, by a threshold value (0.01).

6.7 Quasi curvature gradient features

Consistent with the migration direction (Section 6.6.4), quasi curvature gradients of a grain face were defined within the two grains composing the grain face. A gradient is introduced by a curved grain face, and the chemical potential in the vicinity of the convex side will be higher than that in the vicinity of the concave side (Section 2.4.1). Grain face integral curvature may serve as a reasonable descriptor for this curvature induced gradient. Note that the calculation of grain face integral curvature requires a reference grain to be defined, which was always chosen as the left grain in anneal-state-4, and was kept consistent with the definition of migration direction (Section 6.6.4), in this research.

We also calculated some quasi curvature gradients, inspired by questions such as if a grain face prefers to move toward the smaller grain. In other words, the size difference (V_diff) , or

even more generally, the number of faces difference (F_diff) , between the two grains were calculated as quasi curvature gradients.

6.8 Machine learning model choice

Each grain face feature, discussed in Sections 6.3 - 6.7, represents one physical property of a grain face. One way to check our understanding about a grain face property is to try predicting the corresponding feature from the other features. Many machine learning models in the regression analysis family can be applied for this kind of prediction: linear regression [77], support vector regression[134], regression trees [135], and neural networks [68]. Among these many choices, complicated models that are difficult to train, like neural networks, are not preferred because the available training data is limited, on the scale of $10^3 \sim 10^4$. The model of choice should be robust to feature correlated. The model should also support some kind of feature importance evaluation because we care about the interpretation of results. Accordingly, three models were selected, including a regular linear regression model and an XGBoost regressor [138]. All models were implemented with the scikit-learn python package [139].

6.8.1 Linear regression

Linear regression is one of the simplest, yet most fundamental models, in regression analysis and has a wide range of applications [77]. The linear regression model assumes that the onedimensional target variable $y \in \mathbb{R}^1$ is linearly correlated with the *p*-dimensional predictor $X \in \mathbb{R}^p$: $y = \beta X = \beta_0 + \beta_1 x_1 + \dots + \beta_p x_p + \epsilon$. $\beta \in \mathbb{R}^{p+1}$ is the slope coefficients that need to be determined, in which the extra dimension comes from the interception. ϵ stands for the error term that is not predicted by the model. One efficient way to solve for β is to consider the residual sum of squared errors (RSS), $||y - \beta X||_2^2$, as the objective function and solve the parameters iteratively via gradient descent. Second-order methods, which solve for β directly, were not used in this research since they are expensive and are more sensitive to correlated variables.

The slope coefficients β can be considered as a reference for relative feature importance if the predictor X is normalized. In this research, we normalized X within each column (feature) such that the feature values fall between zero and one. A large β_i then suggests that a small
difference in x_i can leads to a large change in y, and x_i can thus be considered as important. However, this reference is not perfectly reliable, as it is prone to multi-collinearity [140], [141]. We thus implemented two feature selection techniques, forward selection and LASSO regularization, to improve the interpretation, and possibly prediction, of the simple linear regression model.

6.8.2 Forward selection

Forward selection is a common wrapper method [136]. The model starts with no feature and works iteratively. A feature, which gives the most significant model performance improvement, is selected in each iteration and the process continues until a new feature no longer improves model performance, or all features have been selected. The model performance improvement was defined as an increasement in the adjusted R^2 score (R_{adj}^2) on the training data [142] in this research. $R_{adj}^2 = 1 - \frac{(1-R^2)(n-1)}{n-p-1}$, in which *n* is the number of training instances and *p* is the number of predictors. Note that useless predictors are compensated in R_{adj}^2 so the model will select a predictor only if it contributes a non-trivial R^2 score. The R^2 scores of the test datasets were not adjusted. Other comparable wrapper methods include backward elimination, stepwise regression, and best subset selection [136]

The models were trained with the RSS objective function, and the performance will be reported as (adjusted) R^2 scores, mean absolute error (MAE), and root mean square error (RMSE), evaluated following a five-fold cross-validation process. The relative feature importance can be interpreted from the selection order and the corresponding improvement in R^2_{adj} . The earlier a feature is selected, and the larger increase in R^2_{adj} it contributed, the more important the feature is.

6.8.3 LASSO regularization

Least absolute shrinkage and selection operator (LASSO) regularization is a common technique to prevent overfitting and perform feature selection [137]. A LASSO regularized linear regression model can be built from the vanilla linear regression by adding a L1 regularization term in the objective function and make it $||y - \beta X||_2^2 + \lambda ||\beta||_1$. The L1 regularization term enforces a constraint that the L1 norm of β is smaller than a fixed value, which is related to λ , thus forces some irrelevant coefficients of β to be zero and achieves feature selection. $\lambda \in$ $[0, +\infty)$, a large λ corresponds to strong parameter shrinkage. A zero λ enforces no shrinkage, and the resultant model is equivalent to a vanilla linear regression. An infinite λ shrinks every coefficient in β to zero. Other similar regularization techniques include the ridge regularization [143] and the elastic net regularization [144]. LASSO was chosen because it best meets our interest of feature selection, which is usually not achieved with ridge and elastic net regularization

In this research, the models were trained with the regularized RSS loss function. The model was trained following a nested cross-validation [145] procedure. In the first five-fold cross validation, the model selects the optimal hyperparameter λ from the best validation score. In the second five-fold cross validation, the dataset is shuffled and the model performance is be reported as the average test R^2 score, the average test MAE, and the average test RMSE. The optimal λ varied between [0.1, 10] for the different regression tasks in this research.

6.8.4 XGBoost

XGboost [138] is based on the decision tree algorithm, in which the assumptions lie in the tree structure. A tree is built greedily from top-down by asking Yes/No questions that lead to partition decisions. The questions are about feature values, and the choice of question is motivated by the reduction in the objective function or the information gain [135]. Each interior node of the tree corresponds to a question. Each leaf, or terminating node, corresponds to a cell of the partition and is associated with one value (if given a regression task) or one class label (if given a classification task) that applies to all instances within this partition. Note that unlike linear regression, decision trees have large model compacity and are not confined to linear relationships.

Decision trees can be sensitive to random noise in training examples, thus are usually combined with ensemble techniques, like bagging and boosting, to avoid overfitting. XGBoost takes the boosting approach. Many weak short trees are built sequentially, each trying to learn the error of the previous tree, and then combined in an additive way to yield the final prediction.

Relevant model parameters include the learning rate, the number of trees to build, the maximum depth of each tree, the minimum total instance weight needed in a child, the fraction of columns to be used by each tree, and the fraction of training instances available to a single tree. These parameters were tuned in a grid search style for each regression task. Two different losse

functions, MAE and RMSE, were tried and the model showed similar results. Similar to the case of Lasso regularized linear regression, the hyper parameters were tuned with a first five-fold cross validation and the model performances, as MAE and RMSE, were evaluated following a second five-fold cross validation. The tuned hyperparameters include the number of estimators, the learning rate, the fraction of training examples available to one tree, the fraction of features available to one tree, the minimum loss reduction required to make a further partition, and the minimum sum of instance weight needed in a child. Note that the R² score is not reported due to the non-linearity of XGBoost [69].

The relative feature importance can be evaluated in XGBoost by checking the interior nodes, and the corresponding features, of each tree. A feature is considered important if it is associated with a large gain in this research. Other alternative feature importance references include the training instances a feature splits and the frequency the feature appears in the trees.

6.9 Conclusion

In this chapter, we present preprocessing concerns and methodologies of grain face data feature engineering from two succeeding HEDM 3D microstructures. Various types of features are discussed, including crystallography, geometry, topology, mean-field, migration, and quasi-curvature gradient. Machine learning models that are suitable for the task are also reviewed. The results are presented in the next chapter.

7. Grain face evolution in polycrystalline Ni

The previous chapter (Chapter 6) has described what kind of grain face characteristics can be measured as numerical features for a pair of HEDM collected 3D microstructure and how the measurements were conducted. This chapter presents the results.

Similar to the analysis of grains (Sections 4.2 and 5.2), some grain face features are analyzed in pairs of two and as a function of each other (Section 7.1). The various features are then analyzed collectively with the help of machine learning models (Section 7.2). Some key evolution features, like area change and curvature change, are also plotted as a function of five crystallographic parameters and significant anisotropy is observed (Section 7.3).

7.1 Measurements on the evolution of grain faces

7.1.1 Statistics of the orientation maps

The volume of anneal-state-5 was cropped following the method described in Section 6.2.1 and only the volume common to both states, which covers $395 \times 404 \times 84$ voxels, was used. The tracking of the grains across the two volumes was accomplished by Bhattacharya et al. [114], using an algorithm that compares the grain misorientation, the grain size, and the grain centroid position in the two states.

The anneal-state-4 sample contains 2461 grains, in which 1357 grains are entirely enclosed in the sample volume and have complete shapes. The anneal-state-4 sample contain 2240 grains, in which 1165 grains are entirely enclosed in the sample volume. 2076 grains are tracked across the two anneal states, among which 1029 grains are fully enclosed in the volume in both states. The grain size and number of faces distribution for the tracked grains are shown in Figure 7.1.

The solid lines represent all tracked grains and the dash lines stand for the tracked complete grains which do not contact the sample free surface. X-axis of the figures is limited and a few grains with extremely large sizes or number of faces are not shown. To be specific, one big grain in anneal-state-4 and one big grain in anneal-state-5 has been excluded from Figure 6.1a. 38 tracked grains in anneal-state-4 and 40 tracked grains in anneal-state-5 have more than 40 faces. It can be noticed that the log size distribution of all tracked grains is approximately normal with a slightly negative mean value. The same distribution shifted more towards the negative side

when only the complete tracked grains are considered, indicating that large grains are preferentially removed.



Figure 7.1. The distributions of diameters and numbers of faces for the tracked grains in the two anneal states. (a) Log normalized grain size distribution. *D* is grain diameter. < D > is the averaged grain diameter. (b) Distribution of the number of grain faces (*F*).

More statistics about the grains and grain faces are summarized in Table 7.1. There are 14003 grain faces in anneal-state-4 and 12588 grain faces in anneal-state-5. 10913 grain faces are tracked across the two states, among which 6942 grain faces have complete shapes and are fully enclosed in the sample volume in both states.

	Anneal-State-4	Anneal-State-5
Annealing	120 min 750°C, 113 min 800°C	120 min 750°C, 113 + 25 min 800°C
Shared Volume (voxels)	$395 \times 404 \times 84$	$395 \times 404 \times 84$
# Grains	2461	2240
# Inner Grains	1357	1165
# Tracked Grains	2	2076
# Tracked Complete Grains	1	.029
# Grain Faces	14003	12588
# Tracked Faces	1	0913
# Tracked Complete Faces	6	5942

Table 7.1. Statistics of grains and grain faces in the two HEDM volumes.

Before getting into the data, we held three basic expectations about the evolution of the microstructure. The total grain boundary area should decrease, providing the driving force. The

number of grain faces should decrease while each grain face should grow larger. All three are generally true in our measurements. The total grain boundary area decreased during the annealing, from $14.3 \times 10^6 \,\mu m^2$ in anneal-state-4 to $13.7 \times 10^6 \,\mu m^2$ in anneal-state-5. The number of grain faces also decreased, from 14003 to 12588. The average grain face area increased, from 1023 μm^2 to 1086 μm^2 .

It is interesting to note the decrease in the total grain boundary area and the increase in the average grain face area are largely contributed by the untracked small grain faces. There are 3090 untracked grain faces in anneal-state-4 and 1675 untracked grain faces in anneal-state-5, which amount to only a small portion, 8.4 % and 4.1 % respectively, of the total grain boundary area in each state. However, 97.3 % of the net grain boundary area decrease is supplied by these untracked small faces. It is also noticed that the untracked grain faces are relatively small. The average size was $388.3 \ \mu m^2$ in anneal-state-4 and $335.2 \ \mu m^2$ in anneal-state-5.

As for the tracked faces, the average size of the tracked complete grain faces decreased slightly during the annealing, from 969.6 μm^2 to 960.0 μm^2 . On the other hand, the tracked incomplete grain faces, which contacted the sample boundary, have gained area from 1609.3 μm^2 to 1621.6 μm^2 . Note these trends match the reported evolution data of grains between anneal-state-4 and anneal-state-5, including a drop in the average volume of tracked bulk grains, and an increase in the average volume of the surface grains [114]. It is also worth mentioning that the magnitude of face area changes seems small not because grain faces are inactive, but because the growing and shrinking components tend to cancel each other. For example, the median area change among the tracked complete faces is $9.2 \ \mu m^2$ but the median area change among the tracked incomplete faces is $144.2 \ \mu m^2$.

In the following analysis, we focus on the tracked complete grain faces unless otherwise specified. These grain faces of interest are further filtered according to their size and the size change fraction (Section 6.2.3), and 6453 non-outlier tracked complete faces are left for analysis. Note unrealistic mesh triangle measurements on the 6453 faces are also filtered and extreme curvature values are removed (Section 6.2.3).

7.1.2 Grain face edges and corners

In theory, the number of edges should be precisely the same as the number of corners for a given grain face. In practice, there are various kinds of noise, arising from the constraints of the experiment measurements and the 3D reconstruction. The number of corners and number of edges were calculated following different routines discussed in Section 6.4.2 and the results are presented in Figure 7.2a, in which the x-axis is limited and a few data points are excluded. The maximum number of edges was 24, and the maximum number of corners was 42.



Figure 7.2. (a) The distribution of *E*, number of edges, as a function of *C*, number of corners. (b) The distribution of *E*, number of edges, as a function of \sqrt{A} , in which *A* is the grain face area. The color bar indicates number of grains in the corresponding bin. Only non-outlier tracked complete grain faces are included in the plot.

In Figure 7.2a, blocks with the darkest color sit along the diagonal line, suggesting that the C = E relationship holds for the majority of grain faces. There are more data points in the lower half of the plot, indicating that the number of corners (*C*) was generally measured to be larger than number of edges (*E*) for a given face. Based on some random visual checks, we noticed that the measurements on *E* are probably more reliable than that on *C*, but detailed quantification of the calculation errors is nontrivial and is out of the scope of this research.

We have seen that for grains, the number of faces is correlated to the grain diameter (Figure 5.4). For reference, the number of edges is plotted by a grain face length scale, \sqrt{A} , in Figure 7.2b and a clear linear correlation can be observed.

7.1.3 Grain face integral dihedral angle measurements

We measured the integral dihedral angles of a grain face, from triple line triangle groups, following a local resident grain pair reference frame (Section 6.4.2).

The results are presented in Figure 7.3. The distribution of three locally defined integral dihedral angles, DA_L , DA_R and DA_O , are very similar. The peaks are all found near 120°, consistent with the arrangement of equilibrium triple lines (Section 2.2.4), though the dispersions of the distributions are also significant. Some of the dispersion may have originated from grain boundary energy anisotropy, and some may have risen from artifacts in the meshing and smoothing routines. Changes of the dihedral angles, ΔDA_L , ΔDA_R and ΔDA_O , are generally small and the peaks are found near 0° (Figure 7.3b). The axis of Figure 7.3b is limited to 60°, according to which 9, 5, and 1 data points are excluded for ΔDA_L , ΔDA_R and ΔDA_O respectively.



Figure 7.3. Distributions of (a) integral dihedral angles, and (b) the change of integral dihedral angles, for the non-outlier tracked complete grain faces.

7.1.4 Grain face area and integral absolute curvature change

We are interested in predicting the grain face area change during annealing. For grains, it is well known that big grains tend to grow and small grains tend to shrink. Is there a similar trend for grain faces? To test this idea, we plotted the average grain face area change, defined as $\Delta A = A' - A$, for different size (A) classes. A' is the grain face area in anneal-state-5 (the after-annealing state), and A is the grain face area in anneal-state-4 (the before-annealing state). The results are presented in Figure 7.4a, in which size classes are drawn with a step size of 250 μm^2

and the x-axis has been cut, excluding about 0.5 % data points with extreme values. It can be seen that the correlation between ΔA and A is very weak. Standard deviations are large, thus not shown. For reference, the median standard deviation for the size classes in Figure 7.4a was $467.5 \ \mu m^2$.

The trend is much clearer when curvature is also considered. In Figure 7.4b, $\Delta |\mathcal{H}|$, the change of grain face integral absolute curvature, is binned and plotted as a function of $|\mathcal{H}|$, the grain face integral absolute curvature in anneal-state-4. Note the unsigned triangle curvatures were used because of switching symmetry (Section 6.4.1). Average data values in bins are indicated by black circles and stand deviations by the bars.



Figure 7.4. (a) Grain face area change (ΔA) as a function of the grain face area in the before annealing state (A). (b) Grain face integral absolute curvature change ($\Delta |\mathcal{H}|$) as a function of the grain face integral absolute curvature in the before annealing state ($|\mathcal{H}|$). Only non-outlier tracked complete grain faces are included in the plots.

7.1.5 Grain face mean-field and area change

 ΔA , the grain face area change, is also plotted as a function of $E - \langle E_{NN} \rangle$, a mean-field parameter defined by the grain face's nearest neighbors (Section 6.5). The results are presented in Figure 7.5, in a way similar to Figure 4.3 and Figure 5.5b. The correlation is very weak, though the faces with strong negative $E - \langle E_{NN} \rangle$ tend to grow and the faces with large positive $E - \langle E_{NN} \rangle$ tend to shrink. Also, note that this overall negative trend contrasts that for grains in Figure 4.3 and Figure 5.5b, where a positive G' or M_s corresponds to a trend of shrinking.



Figure 7.5. ΔA as a function of $E - \langle E_{NN} \rangle$. *E* is the number of edges of the grain face in anneal-state-4. $\langle E_{NN} \rangle$ is the average number of edges of the grain face's nearest neighbor faces in anneal-state-4. Only non-outlier tracked complete grain faces are included in the plots.

7.1.6 Grain face out-of-plane migration measurements

The out-of-plane migration measurements turned out to be uninformative. Various models have been fitted but the results are far from significant. The most important reason is probably that the distances traveled by the grain faces are too short to be measured accurately. The cumulative distributions of the out-of-plane migration distances, calculated from methods discussed in Section 6.6, are shown in Figure 7.6.

It can be noticed that results following different calculation routines differ from each other but are more or less similar, especially the results returned by the local normal projection method and the SVM projection method. However, the out-of-plane migration distances are generally small. Remember the sample resolution is 2.6 *um* in-plane and 4 *um* inter-plane. It can be seen that the majority of grain faces are associated with sub-resolution out-of-plane migration distances. This situation is tricky, especially considering that the two datasets were not perfectly aligned at a sub-resolution scale (Section 6.2.1).

All steps leading the way to the final measurement value, including data collection, discretization, meshing, sample alignment, tracking, and projection, introduce some level of uncertainty. Our migration distance values were small to start with, so the true trend was probably overshadowed by uncertainties from the various sources.



Figure 7.6. Cumulative distributions of the out-of-plane migration distances for non-outlier and non-piecewise tracked complete grain faces. The solid lines show results following and optimal transportation inspired tracking algorithm (Section 6.6.1). The dashed lines show results following a nearest matching algorithm (Section 6.6.2). The projection methods are specified in the legend.

7.2 Analyzing data with machine learning models

We have analyzed some features of grain faces in a pairwise style (Figure 7.4 and Figure 7.5). Though pairwise style analysis can be informative, as it allows direct two-dimensional visualization, it is not efficient. The number of possible analyses grows quadratically with the number of available features so one has to be careful about which features to check. This section presents results from three machine learning models, in which multiple features are evaluated together with much better efficiency.

The training and test data have been limited to the non-outlier tracked complete grain faces. However, note that our definition of outlier is empirical. The model performance varies with the exact data instances included in the training set. For better reliability, all models are fitted following a five-fold cross-validation process (Section 6.8), and the average test results are reported. In each prediction task, every predictor feature was normalize so that the values fall between zero and one while the target variable was left unchanged.

7.2.1 Feature summary

Table 7.2 presents a summary of features discussed in the previous chapter (Sections 6.3 - 6.6), in which the features are sorted into five blocks, corresponding to the crystallographic, geometric,

topological, mean-field, and quasi-curvature gradient feature types. Note properties of annealstate-4 are denoted without an apostrophe (e.g. A), and properties of anneal-state-5 are denoted with an apostrophe (e.g. A').

Feature Name	Feature Description
Dist_Σ3	Misorientation distance to $\Sigma 3$
Dist_111_Avg	Average normal direction distance to (111) direction
Dist_111_Std	Standard deviation of normal direction distances to (111) direction
Dist_110_Avg	Average normal direction distance to (110) direction
Dist_110_Std	Standard deviation of normal direction distances to (110) direction
Dist_100_Avg	Average normal direction distance to (100) direction
Dist_100_Std	Standard deviation of normal direction distances to (100) direction
Α	Grain face area in anneal-state-4.
$ \mathcal{H} $	Grain face integral absolute mean curvature in anneal-state-4.
HI	Grain face average absolute mean curvature in anneal-state-4.
ΔA	Grain face area change, from $A' - A$.
$arDelta \mathcal{H} $	Grain face integral absolute mean curvature change, $ \mathcal{H} ' - \mathcal{H} $.
$\Delta \mathbb{H} $	Grain face average absolute mean curvature change, $ \mathbb{H} ' - \mathbb{H} $.
С	Grain face number of corners in anneal-state-4.
Ε	Grain face number of edges in anneal-state-4.
DA_L	Grain face integral dihedral angle, along the local left side, in anneal-state-4.
DA_R	Grain face integral dihedral angle, along the local right side, in anneal-state-4.
DA_O	Grain face integral dihedral angle, along the local opposite side, in anneal-state-4.
ΔC	Grain face number of corners change, $C' - C$.
ΔE	Grain face number of edges change, $E' - E$.
ΔDA_L	Grain face integral dihedral angle change along the local left side, $DA_L' - DA_L$.
ΔDA_R	Grain face integral dihedral angle change along the local right side, $DA_R' - DA_R$.
ΔDA_O	Grain face integral dihedral angle change along the local opposite side, $DA_0' - DA_0$.

Table 7.2. Feature summary.

$E - \langle E_{NN} \rangle$	Difference between number of edges of a grain face, E , and the average number of edges of the grain face's nearest neighbor faces, $< E_{NN} >$, in anneal-state-4.		
$ \mathcal{H} - < \mathcal{H} _{NN} >$	Difference between integral absolute curvature of a grain face, $ \mathcal{H} $, and the average integral absolute curvature of the grain face's nearest neighbor faces, $< \mathcal{H} _{NN} >$, in anneal-state-4.		
NN_Pos_Frac	Fraction of nearest neighbor grain faces with positive integral mean curvature in anneal-state-4, curvature habitant grain as one of the two grains defining the grain face of interest.		
NN_Twin_Frac	Fraction of twins among nearest neighbor grain faces in anneal-state-4.		
NN_Grow_Frac	Fraction of the nearest neighbor grain faces with positive ΔA .		
NN_Ext_Frac	Fraction of the nearest neighbor grain faces that went extinct during annealing, which existed in anneal-state-4 but not in anneal-state-5.		
NN_Nuc_Frac	Fraction of the nearest neighbor grain faces that nucleated during annealing, which existed in anneal-state-5 but not in anneal-state-4.		
$sum(\Delta A_{NN})$	Total area changes, ΔA , of nearest neighbor grain faces.		
NNG_Ext_Frac	Fraction of the nearest neighbor grains that went extinct during annealing, which existed in anneal-state-4 but not in anneal-state-5.		
NNG Nuc Frac	Fraction of the nearest neighbor grains that nucleated during annealing,		
1110_1100_1100	which existed in anneal-state-5 but not in anneal-state-4.		
$max(\Delta F_{NNG})$	which existed in anneal-state-5 but not in anneal-state-4. The maximum number of faces change among nearest neighbor grains.		
$max(\Delta F_{NNG})$ $min(\Delta F_{NNG})$	which existed in anneal-state-5 but not in anneal-state-4. The maximum number of faces change among nearest neighbor grains. The minimum number of faces change among nearest neighbor grains.		
$max(\Delta F_{NNG})$ $min(\Delta F_{NNG})$ $< \Delta F_{NNG} >$	which existed in anneal-state-5 but not in anneal-state-4.The maximum number of faces change among nearest neighbor grains.The minimum number of faces change among nearest neighbor grains.The average number of faces change among nearest neighbor grains.		
$max(\Delta F_{NNG})$ $min(\Delta F_{NNG})$ $< \Delta F_{NNG} >$ $\Delta Dist_F_LG$	which existed in anneal-state-5 but not in anneal-state-4. The maximum number of faces change among nearest neighbor grains. The minimum number of faces change among nearest neighbor grains. The average number of faces change among nearest neighbor grains. The change of distance between the grain face centroid and the local left grain centroid, $Dist_F_LG' - Dist_F_LG$, given in fraction.		
$max(\Delta F_{NNG})$ $min(\Delta F_{NNG})$ $< \Delta F_{NNG} >$ $\Delta Dist_F_LG$ V_Diff	which existed in anneal-state-5 but not in anneal-state-4. The maximum number of faces change among nearest neighbor grains. The minimum number of faces change among nearest neighbor grains. The average number of faces change among nearest neighbor grains. The change of distance between the grain face centroid and the local left grain centroid, $Dist_F_LG' - Dist_F_LG$, given in fraction. Volume difference among the two resident grains, as $V_{left} - V_{right}$, in anneal-state-4.		
$max(\Delta F_{NNG})$ $min(\Delta F_{NNG})$ $< \Delta F_{NNG} >$ $\Delta Dist_F_LG$ V_Diff F_Diff	which existed in anneal-state-5 but not in anneal-state-4. The maximum number of faces change among nearest neighbor grains. The minimum number of faces change among nearest neighbor grains. The average number of faces change among nearest neighbor grains. The average number of faces change among nearest neighbor grains. The change of distance between the grain face centroid and the local left grain centroid, $Dist_F_LG' - Dist_F_LG$, given in fraction. Volume difference among the two resident grains, as $V_{left} - V_{right}$, in anneal-state-4. Number of faces difference among the two resident grains, as $F_{left} - F_{right}$, in anneal-state-4.		
$max(\Delta F_{NNG})$ $min(\Delta F_{NNG})$ $<\Delta F_{NNG} >$ $\Delta Dist_F_LG$ V_Diff F_Diff $F - < F_{NN} >$ $_Diff$	which existed in anneal-state-5 but not in anneal-state-4. The maximum number of faces change among nearest neighbor grains. The minimum number of faces change among nearest neighbor grains. The average number of faces change among nearest neighbor grains. The average number of faces change among nearest neighbor grains. The change of distance between the grain face centroid and the local left grain centroid, $Dist_F_LG' - Dist_F_LG$, given in fraction. Volume difference among the two resident grains, as $V_{left} - V_{right}$, in anneal-state-4. Number of faces difference among the two resident grains, as $F_{left} - F_{right}$, in anneal-state-4. Topological mean-field difference among the two resident grains, as $(F - \langle F_{NN} \rangle)_{left} - (F - \langle F_{NN} \rangle)_{right}$, in anneal-state-4.		
$max(\Delta F_{NNG})$ $min(\Delta F_{NNG})$ $< \Delta F_{NNG} >$ $\Delta Dist_F_LG$ V_Diff F_Diff $F - < F_{NN} >$ $_Diff$ M_s_Diff	which existed in anneal-state-5 but not in anneal-state-4. The maximum number of faces change among nearest neighbor grains. The minimum number of faces change among nearest neighbor grains. The average number of faces change among nearest neighbor grains. The change of distance between the grain face centroid and the local left grain centroid, $Dist_F_LG' - Dist_F_LG$, given in fraction. Volume difference among the two resident grains, as $V_{left} - V_{right}$, in anneal-state-4. Number of faces difference among the two resident grains, as $F_{left} - F_{right}$, in anneal-state-4. Topological mean-field difference among the two resident grains, as $(F - \langle F_{NN} \rangle)_{left} - (F - \langle F_{NN} \rangle)_{right}$, in anneal-state-4. Integral mean curvature of grain faces difference among the two resident grains, as $(M_s)_{left} - (M_s)_{right}$, in anneal-state-4.		

The correlation coefficients [77] between these features are plotted in Figure 7.7.



Figure 7.7. Feature correlations. Correlation coefficients are listed and are indicated by color, according to the color bar on the right.

It can be noticed that the average plane normal distance features ($Dist_111_Avg$, $Dist_110_Avg$, and $Dist_100_Avg$) are very weakly correlated with other features, indicating that this kind of normal distance feature design, which summarizes the non-uniform plane normal information of an entire grain face into one single number, is probably not sensitive enough and useful grain face plane normal characteristics are not captured. The standard deviations of plane normal distances ($Dist_111_Std$, $Dist_110_Std$, and $Dist_100_Std$) are better correlated with other features. For example, the correlation coefficient between $Dist_111_Std$ and $|\mathcal{H}|$ was 0.38. However, it is likely that there are not much useful crystallographic information within the standard deviation features, since the three standard deviation features, $Dist_111_Std$, $Dist_110_Std$, and $Dist_100_Std$, vary with similar trends

consistently. The correlations probably have stemmed from confounding factors [146]. For example, large highly curved grain faces are likely to be associated with large plane normal variations.

The quasi-curvature gradient features are also relatively undistinguished, suggesting that the evolution of a grain face is probably not biased by the relative size, or topological features, of the two resident grains defining this grain face.

The average plane normal distance features, the quasi-curvature gradient features, and some dihedral angle features are not going to be fed into the models (Sections 7.2.2 - 7.2.4), for they are generally associated with small correlation coefficients, or there exists no physical ground to differentiate left from right.

7.2.2 Grain face area

It has been seen in Figure 7.2b that \sqrt{A} , the square root of grain face area, is positively correlated with *E*, grain face number of edges. We now try to predict *A* with various other grain face features. One feature that is obviously closely correlated with *A* is $|\mathcal{H}|$, the integral absolute curvature of grain face, and has been removed from the pool of predictor features.

The result of a linear regression model, fitted gradually with the forward feature selection technique (Sections 6.8.1 and 6.8.2), is shown in Figure 7.8, in which the number of selected features is indicated in the lower x-axis and names of the selected features are shown in the upper x-axis. This simple linear regression model can predict *A* with an over 0.6 test averaged R^2 score following a five-fold cross-validation process. Considering that 3D microstructure data is always subject to various kinds of noises and the quantities we measure and try to predict have distributions (Chapter 4 - 5, Section 7.1), this result is reasonably good. In comparison to other measurements reported in literature [36], [43], [88], a 0.62 R^2 score is also significant. For reference, the best MAE is 576.10 and the RMSE is 887.01. 24 out of 26 features are selected, among which $|\mathcal{H}| - \langle |\mathcal{H}|_{NN} \rangle$, *E*, and $E - \langle E_{NN} \rangle$ can be considered as the most important predictors since they are the first three selected features and most of the model performance improvement is contributed by them. The rest of the features helped only marginally.

A $0.63 R^2$ score can be attained by the LASSO regularized linear regression model (Section 6.8.3). The best MAE is 570.74 and the best RMSE is 889.31. The slope coefficients are plotted in Figure 7.9a as a reference for feature importance (Section 6.8.1). Three features with the

largest slope coefficients include $|\mathcal{H}| - \langle |\mathcal{H}|_{NN} \rangle$, *E*, and $E - \langle E_{NN} \rangle$, which match the three most important features in the forward selection linear regression model exactly. However, note $E - \langle E_{NN} \rangle$ is assigned a negative slope coefficient, though it is positively correlated with *A* (Figure 7.7).



Figure 7.8. Regression results on *A*, returned by a linear regression model with forward feature selection. Training scores are given in adjusted R^2 . Test scores are given in R^2 .



Figure 7.9. Relative feature importance, indicated by bar lengths, for response *A*, returned by (a) a LASSO regularized linear regression model, and (b) a XGBoost regressor. Outward black bars in (a) correspond to positive slope coefficients. Inward white bars in (a) correspond to negative slope coefficients.

The XGBoost regressor (Section 6.8.4) reached a 419.99 RMSE and a 225.88 MAE, much smaller than that of the linear models. The relative feature importance (Section 6.8.4) is plotted in Figure 7.9b. Two features, $|\mathcal{H}| - \langle |\mathcal{H}|_{NN} \rangle$ and *E*, are identified to be most important by this model while $E - \langle E_{NN} \rangle$ is attributed an importance much smaller than that in the two linear models.

7.2.3 Grain face area change

We then tried to predict ΔA , the area change of a grain face, which is the most intuitive descriptor for the grain face shape evolution. $\Delta |\mathcal{H}|$, the integral absolute curvature change of grain faces, was highly correlated with ΔA and was removed from the pool of predictor features before fitting the model.

The results of the forward feature selection linear regression model are presented in Figure 7.10. 23 out of 26 features are selected, and a 0.24 R^2 score is reached. The best MAE is 179.37 and the best RMSE is 361.41. From the model R^2 score we see that ΔA is more difficult to predict than A. Note that the values of MAE and RMSE do not contradict this conclusion. MAE and RMSE are not scale invariant, so they can be used to compare models for the same task but cannot be used to compare different tasks given unnormalized target variables.



Figure 7.10. Regression results on ΔA , returned by a linear regression model with forward feature selection. Training scores are given in adjusted R^2 . Test scores are given in R^2 .

It is interesting to note that the model performance does not saturate after the selection of the first few features. This slow and graduate rise in R^2 score suggests that, unlike the case of *A*, the variance in ΔA cannot be explained by only a few key features.

The LASSO regularized linear regression model achieves a 0.25 five-fold cross-validation test R^2 score, and the slope coefficients are plotted in Figure 7.11a as a reference for the relative feature importance. The best MAE is 177.63 and the best RMSE is 361.32. It is seen again that features selected in an early stage of the forward selection process, for example, the first four selected features in Figure 7.10, correspond to the long bars in Figure 7.11a, though the bar length rank and the selection order does not match exactly.

The XGBoost regressor attains a 134.14 MAE and a 301.91 RMSE. The relative feature importance is given in Figure 7.11b. The longest two bars, ΔE and $\Delta |\mathcal{H}|$, correspond to the first two selected features in the forward selection model, while some other relatively long bars corresponded to features selected in a late stage, for example, NN_Nuc_Frac (21th).



Figure 7.11. Relative feature importance, indicated by bar lengths, for response ΔA , returned by (a) a LASSO regularized linear regression model, and (b) a XGBoost regressor. Outward black bars in (a) correspond to positive slope coefficients. Inward white bars in (a) correspond to negative slope coefficients.

7.2.4 Grain face integral unsigned mean curvature

It has been seen in Figure 7.4 that $\Delta |\mathcal{H}|$, the change of grain face integral absolute curvature, which is highly correlated with ΔA but contains extra information from curvature, is probably easier to predict than ΔA . We removed ΔA from the pool of predictors before predicting $\Delta |\mathcal{H}|$.

The results of the forward feature selection linear regression model are presented in Figure 7.12. 24 out of 26 features are selected, and a 0.34 R^2 score is achieved. The best MAE is 11.95 and the best RMSE is 21.74. The model performance improves most efficiently with the first three selected features: $|\mathcal{H}|$, A, and ΔE .



Figure 7.12. Regression results on $\Delta |\mathcal{H}|$, returned by a linear regression model with forward feature selection. Training scores are given in adjusted R^2 . Test scores are given in R^2 .



Figure 7.13. Relative feature importance, indicated by bar lengths, for response $\Delta |\mathcal{H}|$, returned by (a) a LASSO regularized linear regression model, and (b) a XGBoost regressor. Outward black bars in (a) correspond to positive slope coefficients. Inward white bars in (a) correspond to negative slope coefficients.

The LASSO regularized linear regression model achieves a 0.34 R^2 score. The best MAE is 11.89 and the best RMSE is 21.74. The slope coefficients are plotted in Figure 7.13a as a reference for the relative feature importance. The longest two bars agree with the two first selected features in the forward selection procedure ($|\mathcal{H}|$ and A). All other features, including ΔE , are assigned relatively small slope coefficients.

The XGBoost regressor attains a 9.96 MAE and a 19.40 RMSE. The relative feature importance is given in Figure 7.13b. $|\mathcal{H}|$ is again assigned large importance, but *A* is not anymore. On the other hand, some features that are not selected in an early stage in the forward procedure are now assigned relatively large importance, for example $|\mathcal{H}| - \langle |\mathcal{H}|_{NN} \rangle$ (12th selected).

7.2.5 Model performance summary

The performance of the prediction tasks (Sections 7.2.2 - 7.2.4) are summarized in Table 7.3.

	Forward Selection LR		LASSO LR		XGBoost				
	\mathbb{R}^2	RMSE	MAE	\mathbb{R}^2	RMSE	MAE	\mathbb{R}^2	RMSE	MAE
Α	0.62	887.01	576.10	0.63	889.31	570.74	-	419.99	225.88
ΔA	0.24	361.41	179.37	0.25	361.32	177.63	-	301.91	134.14
$\Delta \mathcal{H} $	0.34	21.74	11.95	0.34	21.74	11.89	-	19.40	9.96

 Table 7.3.
 Model performance summary

To give a better intuition about the model performance, the predictions are plotted as a function of the true corresponding target variable value in Figure 7.14. Note that the two linear models behaved similarly in all tasks, so predictions from the forward selection linear regression is not shown.



Figure 7.14. Predictions (\hat{y}) from the LASSO regularized linear regression model and from a XGBoost regressor, plotted as the corresponding true target variable (y). The training and test data was split randomly following a 8 : 2 ratio.

7.3 Anisotropy of grain face area change

Grain face crystallographic information is not captured efficiently by the features we designed. Seven crystallographic features have been designed but the correlation with other features are generally uninformative (Figure 7.7). One feature, $Dist_{\Sigma}3$, was fed into the machine learning models but did not play an obviously important role in any of the models. The misorientation feature can probably be improved if some compression techniques, like principle component analysis (PCA), has been applied instead of the misorientation distance to twin.

However, as for the plane normal parameters, we do not see a straightforward way to construct good one-dimensional features for the grain faces, which contain many different plane normal directions within each one of it. As a result, we returned to individual grain boundaries for the plane normal related anisotropy analyses and plotted the evolution features, such as area change and curvature change, as a function of the grain boundary plane normal direction.

7.3.1 Grain face area change distribution of some low Σ CSL misorientations

Several possibly interesting misorientations are identified following the coincident site lattice (CSL) model [123], [147]. Specifically, the target misorientations include $\Sigma 3$, $\Sigma 5$, $\Sigma 7$, $\Sigma 9$, $\Sigma 27a$, and $\Sigma 27b$, which correspond to the twin related misorientations ($\Sigma 3$, $\Sigma 9$, $\Sigma 27a$, and $\Sigma 27b$) plus the next two lowest Σ misorientations ($\Sigma 5$ and $\Sigma 7$) (Equation 2.6). A grain face is identified to have a target misorientation if the misorientation distance β (Equation 6.1), between this grain face and the corresponding target misorientation, is smaller than the Brandon criterion (15 ° $\times \Sigma^{-0.5}$) [148]. The distribution of ΔA is plotted as a function of the misorientation type in Figure 7.15. Grain faces with general misorientations, namely those that do not belong to any of these low Σ target misorientations, are gathered in the Others type. Note only tracked complete grain faces are included.

The grain face populations, indicated in the upper axis of Figure 7.15a, are consistent with our expectation for Ni (FCC material) [85]. Among the target misorientation types, Σ 3 has the largest population. Σ 9 has approximately 1/3 population of Σ 3 and is the second most common misorientation. Σ 5 and Σ 7, which are not related to Σ 3, have relatively few observations. A distribution of ΔA exists in every misorientation class and the median ΔA of all classes are not far from zero. Σ 3 grain faces are more likely to be associated with substantial area changes, while ΔA distributions of rest misorientation classes are relatively similar.



Figure 7.15. Distributions of ΔA for several misorientation classes, given in (a) box plot, and (b) empirical cumulative distribution function (CDF).

7.3.2 Face-averaged grain face area change as a function of plane normal direction

It has been seen in Figure 7.7 that plane normal distance features averaged over a given grain face are not informative, so we decided to focus back to the individual grain boundary triangles to study plane normal related anisotropies. However, analyzing the evolution of individual grain boundaries, like grain boundary area or curvature change, requires a successful tracking for every piece of each grain boundary, which is very tricky as discussed in Sections 6.6 and 7.1.6.

This problem needs to be simplified by some reasonable assumptions, and we took a faceaveraged approach. For example, the face-averaged grain boundary (unsigned mean) curvature in anneal-state-4 can be calculated as $|\overline{\mathcal{H}}| = |\mathcal{H}| / A$, in which $|\mathcal{H}|$ is the grain face integral absolute curvature as before (Table 7.2) and A is the grain face area. Note that $|\mathcal{H}|$ is a grain face property and $|\overline{\mathcal{H}}|$ is a grain boundary property. In other words, we assume that every grain boundary, or mesh triangle, on a given grain face has the same curvature.

The validity of this assumption is not apparent, so we tested it by calculating $|\mathcal{H}|$ for every non-outlier grain boundary (Section 6.2.3) and plotted it as a function of plane normal following the GBPD routine. The result is presented in Figure 7.16c, in which the true grain boundary (unsigned) curvature distribution (Figure 7.16b) and the relative grain boundary area distribution (Figure 7.16a) are also shown for reference. Note that all non-outlier tracked grain boundaries, not just those on the complete grain faces, were used in Figure 7.16c to keep the data consistent with Figure 7.16 a and b.



Figure 7.16. The distribution of grain boundary (a) area, (b) unsigned mean curvature, and (c) face-averaged unsigned mean curvature, as a function of grain boundary plane orientation (ignoring the grain boundary misorientation).

It can be seen that the values in the face-averaged curvature distribution (Figure 7.16c) are generally smaller than the values in the true curvature distribution (Figure 7.16b) and the amount of anisotropy in Figure 7.16c is smaller than that in Figure 7.16b. The reason is probably that high curvature triangles tend to have small area and are preferentially smoothed in the face average procedure. However, note that the trends in Figure 7.16 b and c are very similar, suggesting that the face-averaged distribution provides a good reference for the true distribution.

We then applied this face-averaged method to evolution features and calculated the faceaveraged grain boundary area change $(\Delta \bar{A})$ and the face-averaged grain boundary (unsigned integral) curvature change $(\Delta |\bar{\mathcal{H}}|)$, in which $\Delta \bar{A} = \Delta A / n$ and $\Delta |\bar{\mathcal{H}}| = \Delta |\mathcal{H}| / A$. The results are presented in Figure 7.17.



Figure 7.17. The distribution of grain boundary (a) face-averaged area change and (b) faceaveraged (unsigned mean) curvature change, as a function of grain boundary plane orientation (ignoring the grain boundary misorientation).

Figure 7.17a shows that $\Delta \bar{A}$ varies with the grain boundary plane normal. The values lie in a range between $-0.010 \,\mu m^2$ and $0.025 \,\mu m^2$, covering both positive and negative numbers. The peak sits at the (111) position. The (100) orientations are associated with positive $\Delta \bar{A}$ and the (101) orientations are associated with negative $\Delta \bar{A}$.

The change in grain boundary curvature shows a different trend (Figure 7.17b). Note that there are no positive values in Figure 7.17b, so the interpretation of the red color at (111) position is different from that in Figure 7.17a. In Figure 7.17b, the red color indicates that the (111) position corresponds to the smallest, nearly zero, change in the curvature magnitude.

The zero curvature change at the (111) position (Figure 7.17b) is interesting. Note that both flattening grain faces (negative $\Delta |\overline{\mathcal{H}}|$) and sharpening grain faces (positive $\Delta |\overline{\mathcal{H}}|$) are included in Figure 7.17b. Does the zero change arise because (111) boundaries really do not change in curvature, or because the negative component from the flattening faces and the positive component from the sharpening faces cancels each other? To answer this question, we plotted $\Delta |\overline{\mathcal{H}}|$ for grain boundaries on the flattening and sharpening faces separately (Figure 7.18).



Figure 7.18. The distribution of grain boundary face-averaged unsigned mean curvature change as a function of grain boundary plane orientation for (a) flattening grain faces with negative $\Delta |\overline{\mathcal{H}}|$ and (b) sharpening grain faces with positive $\Delta |\overline{\mathcal{H}}|$.

It can be seen that $\Delta |\overline{\mathcal{H}}|$ is not zero at the (111) positions in Figure 7.18. Nevertheless, the (111) position still corresponds to the slightest curvature decrease on the flattening faces and the least curvature increase on the sharpening grain faces.

7.4 Discussion

The engineering of geometric features is straightforward since the elementary data has been provided by DREAM.3D in a well-structured form. The out-of-plane migration data is most

tricky. No distinct pattern has been discovered in the data, probably because the out-of-plane migration distances are too small (Section 7.1.6), thus overshadowed by the various noises introduced in the data collection procedures (Section 6.6). The topological features are also non-trivial, as the simple concepts of edge and corner are ambiguous in the context of discrete 3D microstructures. It is also difficult to quantify the quality of measurements directly for the same reason.

We measured grain face edges (*E*) as triple lines from mesh triangles, and corners (*C*) as quadruple, or quintuple, nodes from voxels (Section 6.4.2). The two features match for the majority grain faces (Figure 7.2a), indicating that the two features are highly correlated and both measurement approaches are approximately correct. This high correlation is confirmed in Figure 7.7, with a 0.84 correlation coefficient. Note that zero-corner, and zero-edge, grain faces are observed. Zero corners usually happen for twins, where a grain face is only connected to a total of three grains. Zero edges usually happen for small faces whose boundary is defined a few quadruple lines. Quadruple lines are not counted as edges in this research so they appear to have zero edges. It has come to our notice that the edge measurements are usually better than corner measurements according some visual checks, though the exact reason is unclear. Note that the correlation coefficient between *A* and *E* (0.64) is also more significant than that between *A* and *C* (0.55).

The correlation between *E* and \sqrt{A} is even more clear, and approximately linear (Figure 7.2b). Note that \sqrt{A} can be considered as a linear measurement of grain face size, and *E* plays the role of a primary topological feature. Very similar correlations have also observed for grains, between the number of faces (*F*) and equivalent grain diameters (*D*) (Figure 7.2b).

Dihedral angles were measure from mesh triangles groups sitting on triple lines, and then integrated over all triple lines of each grain face. It is interesting to note that DA_L and DA_R are highly correlated with quasi-curvature gradient features (Figure 7.7). One possible reason is that low energy boundaries are preferentially found on big grains. Let us walk through an example of DA_L and V_Diff with the simplified 2D illustration in Figure 6.4c. DA_L is negatively correlated with V_Diff ($V_{left} - V_{right}$), which means the larger V_Diff , the smaller DA_L (labeled as DA_left in the Figure 6.4c). The smaller DA_L the higher energy GB_right_NN , according to the triple line equilibrium condition (Section 2.2.4). DA_R is positively correlated with V_Diff , for which the same reasoning applies. DA_O is inversely correlated with $Dist_\Sigma \Sigma$

and the correlation coefficient is -0.36, meaning a grain face with a near $\Sigma 3$ misorientation generally has a large DA_O thus low energy. This is consistent with the expectation that $\Sigma 3$ grain faces have relatively low energy [45]. We have also expected DA_O to be correlated with A and ΔA , since some 2D measurements have shown that the length of a grain boundary is inversely correlated to its energy [149]. However, though the correlation between DA_O and A is positive, the correlation coefficient is marginally small (0.08).

Various mean-field features are designed, from topological and geometric features, to capture the influence of nearest neighbor faces. For grains, a mean-field defined as $F - \langle F_{NN} \rangle$ is highly correlated with G', the normalized integral curvature of grains faces (Figure 4.3 and Figure 5.5b), and possibly the change of grain size [88]. We see that similar mean-fields of grain faces, like $E - \langle E_{NN} \rangle$ and $|\mathcal{H}| - \langle |\mathcal{H}|_{NN} \rangle$ are also likely to be informational. For example, the correlation between A and $|\mathcal{H}| - \langle |\mathcal{H}|_{NN} \rangle$ is remarkably high (0.70). However, the correlation between $E - \langle E_{NN} \rangle$ and ΔA , the change of grain face area, is meager, as shown in Figure 7.5 and Figure 7.7.

Figure 7.7 suggests that ΔA is much more difficult to predict than A. A is highly correlated with $E - \langle E_{NN} \rangle$ but ΔA is not. The correlation between ΔA and A is also weak (- 0.16 from Figure 7.7), though big faces generally have a slight tendency to shrink (Figure 7.4a). Another possible guess is that ΔA may be correlated with E, since the "n - 6" predicts that the growth of an isotropic 2D grain, which is comparable to 3D grain faces, is completely determined by its number of edges. However, we see the correlation between ΔA and E is neither positive nor strong (- 0.10 from Figure 7.7). This conclusion is confirmed in the machine learning models. The achievable R^2 score is obviously higher in the task of A (Table 7.3) and the predictions (\hat{y}) are closer to the true target values (y) (Figure 7.14).

A curvature informed grain face shape change, like $\Delta |\mathcal{H}|$, is easier to predict than the simple grain face area change (ΔA). Figure 7.4b shows that $|\mathcal{H}|$ may serve as a useful predictor for $\Delta |\mathcal{H}|$ and the correlation is inverse. This inverse correlation can be interpreted following the ideal of Equation 2.27 [59], which is simplified to Equation 7.1 in this research.

$$\frac{dV}{dt} = -2 \int_{Faces} M\gamma H dS = -2M\gamma \int_{Faces} H dS$$
(7.1)

H is the grain boundary local mean curvature and *S* is the grain boundary area. Equation 7.1 is defined for grains. It suggests that the volume change of a grain is proportional to $\int_{Faces} HdS$, its integral curvature of grain faces, if grain boundary mobility *M* and grain boundary energy γ are approximately constant for the general boundaries. Note $|\mathcal{H}|$ is the grain face version of $\int_{Faces} HdS$, with *H* replaced by |H|, the unsigned mean curvature of grain boundary, and the integral confined to be within the grain face of interest. Following this idea, we see that $|\mathcal{H}|$ is proportional to the velocity of the corresponding grain face grows slower and slower, while a shrinking face shrinks faster and faster. We also note that the majority grain faces are associated with negative $\Delta |\mathcal{H}|$ (Figure 7.4b), which agrees with the common experimental observation that the migration of grain faces slows down as the heat treatment goes on. When machine learning models are fitted with $|\mathcal{H}|$ and other features, a 0.34 R^2 score can be achieved for the prediction of $\Delta |\mathcal{H}|$, slightly larger than that of ΔA but still much smaller than A.

In all three prediction tasks, the non-linear model XGBoost performs better than the linear models, suggesting that high-order correlations exist among the various grain face features (Table 7.3 and Figure 7.14). One example of such high-order correlations is illustrated in Figure 7.2, in which a linear correlation between *E* and \sqrt{A} , thus a 2nd order correlation between *E* and *A*, is suggested.

The relative feature importance has been interpreted in four ways in this research, including the correlation coefficient, the selection order in the forward selection model, the slope coefficients in the LASSO regularized linear regression, and the feature gains in XGBoost. Note that these different models generally agree on a similar set of important features for each task. For example, $|\mathcal{H}| - \langle |\mathcal{H}|_{NN} \rangle$ and *E* are identified to be the most important features by all three models in the prediction of *A*. Similarly, $|\mathcal{H}|$ is marked to be important in the prediction of ΔA and $\Delta |\mathcal{H}|$ by all models. The correlation coefficients between these predictor and target feature pairs are also significant. This agreement confirms the significance of these features.

However, the exact feature importance ranks generally do not match perfectly. We note that one should not rely on the rank of a single model too much. The relative importance from correlation coefficients and the linear models are inherently limited to linear relationships. The slope coefficient interpretation, as in the LASSO linear regression model, is also prone to another problem known as multicollinearity [140], [141]. Multicollinearity exists when predictors of a linear regression model are not independent. The existence of multicollinearity is usually harmless to model performance, as long as the predictor correlations are not too serious, but may invalidate the interpretation of slope coefficients because the model may assign slope coefficients among the correlated predictors in an ungrounded manner. An example is seen in this research. In the prediction of A, $E - \langle E_{NN} \rangle$ is assigned a negative slope coefficient by the LASSO regularized linear regression model (Figure 7.9a) though the two are positively correlated (Figure 7.7). We have tried to predict A with $E - \langle E_{NN} \rangle$ being the only predictor. In that case, the model assigns a positive slope coefficient to $E - \langle E_{NN} \rangle$. The other methods are more robust to the correlation between predictors, but it is always worth remembering that the relative importance is more likely to be reliable if it is consistent among different models.

In summary, three major conclusions can be drawn from the results of machine learning models. First, mean-field features, defined following a logic similar to the $F - \langle F_{NN} \rangle$ of grains [88], serve as useful predictors of grain face properties. For example, $|\mathcal{H}| - \langle |\mathcal{H}|_{NN} \rangle$ has been assigned as one of the most significant predictors by at least one model in all tasks. Second, curvature does play an indispensable role in the evolution of grain faces. This is supported by several consistent observations, including that $\Delta |\mathcal{H}|$ can be predicted better than ΔA , and that $|\mathcal{H}|$ plays an important role in the prediction of ΔA . However, the grain face area change cannot be predicted with high accuracy given curvature and topological information. The R^2 score achieved for the prediction of A (0.63) is much better than that for ΔA (0.25), leading us to the third conclusion that the role of curvature is not deterministic and the correlation between grain face geometric and topologic changes is not perfect.

There are several possible factors contributing to the poor prediction of ΔA . First, the magnitude of A is generally much larger than the magnitude of ΔA , so ΔA is likely to be more sensitive to whatever measurement noises within the dataset. The second possible reason is that there may exist some solutes within our dataset, dragging the grain faces and deviating their behaviors from ideal and continuous, since our sample is not of ultra-high purity (99.999 %) [115]. It is also possible that grain boundary evolution is not a continuous process by nature. Note that our ΔA is confined to the 25 minutes experiment time window while A contains the entire life-time information of a grain face, in which a much longer time period is covered. The worse prediction of ΔA might have originated from some critical events, whose effects are more

significant in shorter time intervals. Possible examples of such critical events include grain boundary disconnection pile and stress accumulation [55]. Finally, note that grain boundary anisotropy may also affect the behavior of grain faces and grain boundaries.

The misorientation dependent anisotropy in grain face area change is obvious in Figure 7.15, which shows that the Σ 3 misorientation grain faces are generally more aggressive than other grain faces in terms of area change. This observation is interesting because it does not match our expectation exactly. It is known that the Σ 3 misorientation is associated with low energy [45] so we expected it to have generally positive ΔA . Figure 7.15 shows that though some Σ 3 grain faces are indeed associated with large area increase, there are also many Σ 3 grain faces with significant area decrease, and the median ΔA is slightly negative. We note that the negative median ΔA of Σ 3 grain faces is probably not representative, since it is close to zero and only complete grain faces are included in Figure 7.15. In other words, large grain faces have been preferentially removed (Section 7.3.1).

The plane normal dependent anisotropy of grain boundaries is studied following a faceaveraged method, in which the tricky process of individual grain boundary tracking is circumvented by assigning a face-averaged value to all grain boundaries on that grain face. The face-averaged method works probably because we have a large number (10913) of tracked grain faces so that each grain boundary normal direction is observed multiple grain faces. Note that the effectiveness of this method would be undermined if the number of tracked grain faces is small.

The grain boundary face-averaged evolution distributions show that the (111) orientations are associated with the largest increase in area (Figure 7.17a) and the smallest change in curvature magnitude (Figure 7.17b and Figure 7.18). These observations are probably related to the large population of coherent twins within Ni [85]. Remember that coherent twins with the (111) orientations may decrease their energy by rotating to the (111) orientation, thus contributing to the (111) peak in Figure 7.17a. The small magnitude of curvature change at the (111) orientation can also be explained by coherent twins, which cover a considerable population at the (111) position and are likely to be resistant to curvature change because of their relatively flat shape and low curvature (Figure 4.4).

While significant anisotropy is noticed in the grain boundary population change and the grain boundary curvature change, the exact effect of grain boundary anisotropy is not clear. It is possible that curvature and topology would have played a more important role if the anisotropy was less significant. There are two ways to test this hypothesis. First, one can conduct another HEDM experiment for high purity Ni at a higher temperature, at which the amount of grain boundary anisotropy should be smaller, and compare the results with this research. Alternatively, one can also repeat the measurements and predictions with a material that is known to be less anisotropic, like the ones with BCC structure. The effect of solutes can be tested similarly, by repeating the measurements with various sample purity.

7.5 Conclusion

The majority tracked grain faces go through a decrease in the integral unsigned curvature, suggesting a deceleration in the evolution process. Face integral dihedral angles are negatively correlated with the local grain size gradient, indicating that low energy boundaries are preferentially found on big grains. However, the face integral dihedral angles are not obvious correlated with the face area change.

The grain face area change is generally weakly correlated to other features and is difficult to predict, while a closely related curvature informed feature, the grain face integral unsigned curvature change, is easier to predict. The R^2 score of linear models and the visualization of prediction results show that the grain face area can be predicted much better than the grain face area change and the grain face integral unsigned curvature change. One possible reason is that the evolution of grain faces is a noncontinuous process and is not entirely dominated by curvature. The relative feature importance from machine learning models shows that the most important predictor for grain face area is a mean-field feature defined from the excess face integral unsigned curvature.

A face-averaged method is designed to calculate the grain boundary area change and the grain boundary curvature change without tracking individual grain boundaries. The method is applied to plot the face-averaged grain boundary curvature distribution (GBHD) and is validated by the fact that the face-averaged GBHD shows a very similar trend as in the true GBHD. When the face-averaged grain boundary area change and the face-averaged grain boundary curvature change is plotted as a function of plane normal direction, the (111) orientations show the largest area change and the smallest curvature magnitude change. This observation is probably related

to the large population of coherent twins within the material and provides evidence that anisotropy plays an important role in microstructure evolution.

8. Conclusions

This thesis focused on the study of experimentally measured three-dimensional microstructures, including an EBSD collected austenite dataset, an EBSD collected ferrite dataset, an EBSD collected 1470 °C annealed $SrTiO_3$ dataset, and two HEDM collected Ni datasets. The two HEDM Ni datasets record the orientations of the same sample, before and after a 25-minute annealing at 800 °C. Each dataset contains more than 1000 grains, and the grain boundaries were approximated by continuous meshes of triangles.

Grains within the two steel datasets (austenite and ferrite) and the ceramic dataset ($SrTiO_3$) showed similar topological and geometric characteristics. The integral mean curvature of grain faces varies such that small grains with few sides have positive curvatures and large grains with many sides have negative curvatures. The number of excess neighbors correlates strongly with the normalized integral mean curvature. The curvature is positive (negative) if a grain has fewer (more) neighbors than the average of its nearest neighbors. The results suggest that the grain boundary mean curvature is influenced by the grain size and by the number of nearest neighbors.

We also measured the grain boundary mean curvature as a function of lattice, misorientation and grain boundary plane orientation. The grain boundary mean curvature shows significant anisotropy and is correlated with the boundary area and energy. The grain boundary mean curvature is inversely correlated to the grain boundary area in all three EBSD samples, such that flat boundaries make up a relatively larger portion of the grain boundary area. In the steel samples, the lowest curvature grain boundaries also have the lowest grain boundary energies, while the curvature and energy of more general grain boundaries are on average inversely correlated. In the SrTiO₃ sample, the grain boundary mean curvature is on average correlated to the grain boundary energy. Note that the correlation between curvature and energy is expected to be different for singular boundaries and general boundaries. The observation suggests that the grain boundary network of 1470 °C annealed SrTiO₃ is dominated by singular boundaries.

Grain faces were tracked between the two Ni datasets. Most grain faces are associated with a negative integral curvature change during the annealing, suggesting that the evolution of grain faces slows down as annealing goes on. Other types of features were also engineered to capture different grain face characteristics, and machine learning models were trained to analyze feature correlations efficiently. The results show that the grain face integral unsigned mean curvature

plays an important role in the prediction of grain face area change, validating the importance of mean curvature. However, it is also noticed that the grain face area is much better predicted than the grain face area change, indicating that microstructure evolution is probably a discontinuous process and mean curvature alone does not determine the evolution of grain faces.

The grain boundary area and the grain boundary curvature change were calculated following a face-averaged method, which has been shown to be credible by the grain boundary mean curvature distribution (GBHD) and the face-averaged GBHD of the same dataset. It was found that both the grain boundary area change and the grain boundary curvature change vary with the plane normal directions. The (111) direction is associated with the largest net area increase and the smallest curvature magnitude change. This observation agrees with the large population of coherent twins within the material and suggests that coherent twins gain area and have relatively stable shapes during annealing.

9. References

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