Topological Analysis of Local Structure in Atomic Systems

Emanuel A. Lazar and David J. Srolovitz

May 28, 2017

1 Introduction

Increasingly powerful experimental and computational resources have made possible large-scale studies of an enormously broad range of physical systems on the atomic scale. A central challenge in analyzing atomic systems is the automated characterization, visualization, and analysis of structure, so that meaningful results can be extracted from massive sets of raw data. Given only atomic coordinates, what can be said about the underlying structure of the sample? In what crystalline phases, if any, are atoms arranged? What types of defects appear in the sample and where are they located?

Such questions are easy to ask and surprisingly difficult to answer. The last several decades have witnessed the development of numerous automated approaches for characterizing, visualizing, and analyzing structure in atomic systems [1, 2]. Despite much progress in this area, conventional methods tend to be ineffective in analyzing high-temperature systems without quenching or time-averaging atomic coordinates. This chapter describes a topological approach for automated structure analysis in atomic systems which is substantially more robust than conventional approaches, especially for high-temperature and imperfect systems.

This chapter begins by detailing the related problems of structure characterization and defect identification, considers several conventional approaches and their limitations, and then explains how Voronoi topology can be used to analyze structure in atomic systems. We provide several examples of applications that benefit from this approach. We conclude with a brief discussion of *VoroTop*, a new set of open-source tools built to automate this analysis.

1.1 Local structure in atomic systems

Molecular dynamics simulation techniques are now widely applied to investigate material properties in systems with billions of atoms, often over the course of many millions of time-steps. Molecular statics and Monte Carlo methods are also routinely employed in studies of large systems with atomic resolution. More recently, experimental methods such as atom probe tomography have been



Figure 1: A typical two-dimensional atomic system [4].

introduced that provide three-dimensional atomic coordinate data sets directly from physical samples [3]. To a large degree, these enormous data sets must be substantially simplified to allow for the extraction of interesting conclusions from a vast sea of mostly uninteresting data. Countless terabytes of data might be ultimately distilled into a short statement such as: "The migration of point defects is inhibited by grain boundaries." The task of the scientist – as distinct from that of the programmer – is to understand how to properly reduce and interpret the massive data generated by experiment or simulation. Without proper tools to help with this task, many atomic coordinate data sets look almost identical.

Consider the two-dimensional system illustrated in Figure 1. Although the sample is primarily crystalline, it contains defects of various types, including grain boundaries and vacancies. Although many of these defects can be seen with our eyes, defining them precisely enough to make them amenable to automated analysis can be difficult. A simple exercise helps illustrate some of the underlying complexities. Look again at Figure 1 and choose an arbitrary atom. Now think about the following two questions. First, does the chosen atom belong to a crystal or to a defect? Second, how can the answer to the first question be made precise? Even brief reflection on these questions will persuade most readers that answers are neither simple nor unambiguous.

Although Figure 1 may be analyzed with only an intuitive idea of what it means for an atom to "belong to a crystal", making this intuition precise is necessary for automating the analysis of larger systems, especially threedimensional ones. For example, while studying phase transitions containing billions of atoms, determining which atoms belong to which phases will depend on precise definitions of what it means for an atom to belong to one phase or another. Without precise definitions, quantitative analysis of such systems is not possible.

1.2 Conventional characterization approaches

The characterization considered in this chapter is a form of *local* structure analysis, as its objective is to describe the local environment around each atom by considering how its neighbors are arranged relative to it. Only after local structure is characterized can larger-scale structure be determined.

Conventional approaches to local structure characterization can be classified as either *physical* or *aphysical*. Physical approaches take into account physical properties of a system, such as energy and stress, in addition to atomic coordinates. As atoms belonging to defects often have higher energies than those belonging to bulk crystals, or different stress patterns, such quantities can be helpful in identifying structural defects.

In physical approaches, a threshold value is typically chosen, and atoms with property values above or below that threshold are identified as defects. In high-temperature systems, choosing a threshold can be difficult because the variance in energy, stress, or other physical quantities associated with thermal fluctuations is typically of the same order of magnitude as that associated with structural defects. In practice, physical quantities are rarely useful in directly studying high-temperature atomic systems [2].

Aphysical approaches, in contrast, consider only atomic coordinate data, and not the underlying energetics. In coordination number analysis, perhaps the simplest example of an aphysical method, each atom is assigned a number counting atoms within a specified radius. The expected number of neighbors in many crystalline systems is known *a priori*, and atoms with different coordination numbers are associated with defects. For example, for a properly chosen threshold, most atoms in Figure 1 will have a coordination number of 6, while those belonging to defects will have coordination numbers other than 6.

More sophisticated aphysical approaches consider not only the number of neighbors of an atom, but also the manner in which those neighbors are arranged. In an ideal triangular lattice, for example, every atom is surrounded by six equally-spaced neighbors; adjacent pairs of neighbors make identical angles $\alpha = \pi/3$; see Figure 2. Centroysymmetry analysis [5] and bond-angle analysis [6] are but two examples of widely-used methods that measure deviation from this ideal structure. Centrosymmetry measures the extent to which neighbors of an atom can be matched in equally-spaced but oppositely-directed pairs, so that their displacement vectors cancel. Bond-angle analysis measures the extent to which angles between "bonds" from a central atom to neighboring atoms remain close to an idealized value, $\pi/3$ in the example of Figure 2.

Several other aphysical approaches, including bond-order analysis [7] and neighbor distance analysis [1], have been developed and applied, sometimes



Figure 2: A central particle and neighbors in (a) an unperturbed triangularlattice crystal, and (b) a perturbed triangular-lattice crystal.

at greater computational cost. As with physical approaches, most aphysical approaches tend to be ineffective in analyzing high-temperature systems, in which deviations from ideal values are affected by thermal fluctuation as much as by structural defects. In a sense that can be made mathematically precise, this problem is a necessary limitation of all continuous structure-characterization methods [8]. To circumvent this problem, systems must be quenched or time-averaged before analysis [2]. It is unknown whether this preconditioning of the data results in changes to its meaning. Consider, for example, the effect of quenching on a material that has different high- and low-temperature polytypes and a displacive transition between them.

1.3 Voronoi analysis

Voronoi analysis traces its history to the mathematical study of crystal lattices [9], and in recent decades has been used to analyze many physical and biological systems [10, 11]. In this section we introduce the central ideas of Voronoi analysis and consider how they can be used to characterize local structure in atomic systems. We do this first in the context of two-dimensional systems, and defer discussion of the conceptually similar, but practically more complex, three-dimensional case to Section 2.

The Voronoi cell of an atom is the region of space closer to that atom than to any other; Voronoi cells which meet along a boundary are called **neighbors**. Voronoi cells of atoms are always convex polygons (in two dimensions) or polyhedra (in three dimensions), though not necessarily regular. Figure 3(a) shows several atoms in an unperturbed triangular lattice along with their Voronoi cells. Figure 3(b) shows a finite-temperature version of the same system, in which atoms are slightly perturbed from their perfect lattice sites. Although cell perimeters and areas have slightly changed, the topology of each Voronoi cell has not; in particular, all cells remain six-sided. This stability in the presence of small perturbations is a powerful feature of Voronoi analysis, and is the source of its robustness in analyzing high temperature systems.

The Voronoi cell of an atom can be characterized both geometrically and topologically. Its area, for example, can be used to calculate the "free volume" of an atom or to estimate local atomic density. These geometric characterizations



Figure 3: (a) atoms in a zero-temperature crystal with regular six-sided Voronoi cells; (b) atoms in finite-temperature crystal with slightly irregular six-sided Voronoi cells.

of Voronoi cells tend to be sensitive to small distortions of atomic coordinates. In contrast, topological descriptions of the Voronoi cell tend to be robust under such distortions. In particular, the number of sides of a Voronoi cell, equivalently its number of neighbors, is generally invariant under small perturbations of atomic coordinates. For reasons that will be explained in Section 2.2, we use the word topology to refer to the number of sides of a two-dimensional Voronoi cell.

In defect-free crystals with triangular lattice structure, the Voronoi cell of every atom has six sides [12]. Atoms whose Voronoi cells have more or fewer than six sides can be considered as belonging to defects. Local structure near an atom in a two-dimensional system can thus be characterized and analyzed according to its number of Voronoi neighbors. Figure 4 illustrates the same polycrystal shown in Figure 1, this time with each atom colored according to the number of sides of its Voronoi cell. Most atoms have six sides and are colored yellow; other Voronoi cells have five or seven sides and are colored blue and red, respectively.

Characterizing local structure through Voronoi cell topology facilitates the visualization and analysis of defect structure in polycrystalline materials. In Figure 4, for example, atoms whose Voronoi cells have six sides can be classified as belonging to crystals, whereas those with more or fewer sides can be classified as belonging to defects. After we have identified defects at the single-atom level, we can identify larger-scale defects as contiguous regions of defect atoms. Notice, for example, a ring of 3 red and 3 blue atoms on the left side of Figure 4. This ring identifies the presence of a vacancy. Similarly, a chain of alternating red and blue atoms indicates the presence of a high-angle grain boundary. This analysis requires no choice of threshold or preconditioning of the data, and is robust against thermal vibrations and elastic strains.

In the following section, we present a similar analysis for studying threedimensional systems. The topology of Voronoi cells in three dimensions is more complicated, yet can be approached in much the same way.



Figure 4: The two-dimensional polycrystal from Figure 1 with Voronoi cells shown and atoms colored by the number of sides of their Voronoi cells.

2 Voronoi Topology Structure Analysis

2.1 Topology basics

Topology is the mathematical study of properties of objects that do not change under continuous deformations; these properties are often related to the manner in which objects are connected to themselves and to other objects. To illustrate this idea, consider the shapes shown in Figure 5. While the sphere can be continuously deformed into the ellipsoid without cutting or gluing, the torus cannot. In the language of topology, the sphere and ellipsoid are *isomorphic* with one another, whereas the torus is not isomorphic to either.

Many properties of these shapes do not change when they are continuously deformed. For example, imagine taking a pair of scissors and cutting a closed loop in the three shapes, as illustrated in Figure 5. This procedure inevitably divides each of the sphere and ellipsoid into two disconnected pieces. In contrast, the same procedure can leave the torus connected as one piece. This type of "connectedness" is a topological property of a shape, and if two shapes are isomorphic then they either both have this property or both do not.

This brief exercise illustrates one property that is preserved under continuous deformations; the field of topology develops powerful tools to study shapes and other topological invariants [13].

As topology focuses on studying the connectivity of shapes such as spheres and tori, it is not immediately clear that it would have much relevance to study-



Figure 5: The sphere and ellipsoid can be deformed into one another without cutting or gluing, while the torus cannot. Cutting a loop in the first two shapes necessarily divides them into two pieces; a loop cut in the third shape can leave it connected.



Figure 6: The Voronoi cell of a central blue atom (blue), surrounded by neighboring atoms (gold).

ing sets of discrete points, such as those encountered in studying atomic systems. In what meaningful way can points in space be considered connected? Over the last decade or so, however, powerful tools such as discrete Morse theory and persistent homology [14, 15] have been developed to analyze data of diverse kinds [16]. Voronoi topology continues in this spirit. In what follows we show how considering the topology of a Voronoi cell can provide keen insight into the manner in which a set of points are arranged in space. In this sense, Voronoi topology forms a bridge between the discrete and continuous, and enables the application of ideas from topology to the study of atomic systems.

2.2 Voronoi topology

In atomic systems, small perturbations resulting from thermal noise or small strains are often unimportant for understanding crystal structure and defects. Whereas geometrical characterizations of local structure are generally sensitive to such perturbations, topological ones are generally not. Figure 6 illustrates the three-dimensional Voronoi cell of a central atom surrounded by neighbors. When atomic positions are perturbed, geometrical properties of this Voronoi cell, including edge lengths and face areas, almost always change. In contrast,



Figure 7: Three topologically distinct Voronoi cells, each with 4 four-sided, 4 five-sided, and 2 six-sided faces.

the manner in which edges and faces are connected does not. Such topological properties are thus naturally suited for studying atomic systems when we wish to ignore small perturbations.

In the remainder of this chapter, we use the term **topology** of a Voronoi cell to refer to the manner in which neighboring Voronoi cells are connected to a central Voronoi cell and to each another. In two dimensions, neighbors of a central Voronoi cell can be connected in only one manner – cyclically, with each neighbor connected to two others – and so a count of sides of a Voronoi cell completely describes its topology. In three dimensions, however, completely describes its number of all neighboring cells is more complicated. Consider, for example, that while a count of faces of a Voronoi cell indicates its number of neighbors, it says nothing about how those neighbors are arranged.

Additional topological information about a Voronoi cell is provided through consideration of the number of sides of its faces. This additional data provides a more refined description of the manner in which neighbors are connected to a central cell and to each other, as the number of sides of a face indicates the number of neighbors shared in common between two Voronoi cells.

Even this additional information, however, does not completely describe the manner in which neighbors of a Voronoi cell are connected, as seen through the examples in Figure 7. While all three Voronoi cells have 4 four-sided faces, 4 five-sided faces, and 2 six-sided faces, these faces are arranged differently in the three examples. For example, a pair of six-sided faces are adjacent in (b), but not in (a) or (c). Differences in the arrangements of faces indicate differences in the manner in which neighboring Voronoi cells are connected to one another and, consequently, the manner in which neighboring atoms are arranged. Our desire to completely describe the arrangement of neighbors motivates the development of a method to record all information about the topology of a Voronoi cell.

2.3 Recording Voronoi topology

The language and tools of graph theory can be used to record complete topological information of a Voronoi cell by looking at it as a planar graph. Briefly, a graph is a set of points called vertices, and a set of connections between those vertices called edges. A planar graph is one whose vertices and edges can be drawn



Figure 8: Planar edge graphs of the three Voronoi cells shown in Figure 7.

in the plane without any edges crossing. Two graphs are *isomorphic* if there is a correspondence between their vertices so that two vertices are connected by an edge in one graph if and only if corresponding vertices are connected by an edge in the other graph [17]. Mathematical theorems from the early twentieth century [18, 19] guarantee that every Voronoi cell can be uniquely represented as a planar graph, thus allowing us to make precise statements about Voronoi cells using the language of graph theory. Figure 8 illustrates planar graphs corresponding to the three Voronoi cells of Figure 7.

We employ an algorithm introduced by Weinberg [20, 21] to calculate a unique "code" for each planar graph that completely describes the manner in which its edges and faces are connected. Equivalently, this code captures complete information about the manner in which neighbors of a Voronoi cell are arranged relative to a central cell and to each other. Determining whether two atoms have the same local structure then reduces to comparing codes of two Voronoi cell graphs [22].

The algorithm of Weinberg is as follows: (a) An initial vertex is chosen and assigned the label 1. (b) An edge incident with that vertex is chosen and travel begins along it. (c) If an unlabeled vertex is reached, it is labeled with the next unused integer and we "turn right" and continue. (d) If a labeled vertex is reached after traveling along an untraversed edge, we return to the last vertex along the same edge but in the opposite direction. (e) If a labeled vertex is reached after traveling along an edge previously traversed in the opposite direction, we "turn right" and continue; if that right-turn edge has also been traversed in that direction, we instead continue along the next right-turn edge available; if all outgoing edges have been traversed, we stop.

Throughout this procedure, the list of the vertices in the order in which they are visited, including multiplicities, is recorded; we call this ordered list a *code*. Figure 9 illustrates the process of constructing a code. Codes are then produced for each choice of initial vertex and edge, and for each of two possible orientations of the graph; the lexicographically smallest code is used as the canonical code for the graph.

Constructing canonical codes allows us to capture complete information about the topology of a Voronoi cell, and hence about the manner in which neighboring atoms are arranged. After determining the Voronoi topologies that are associated with a particular crystal structure we can identify which atoms belong to the bulk, and which ones are associated with defects.



Figure 9: Vertices are labeled as they are initially encountered while traversing the graph following the rules described in the text. The code lists all vertices in the order in which they have been visited.

2.4 Topological instability and families of topologies

Although many Voronoi cells are topologically stable under small perturbations, many are not. Consider, for example, the Voronoi cells in a two-dimensional square lattice, illustrated in Figure 10(a). When unperturbed, the Voronoi cell of each atom has exactly four edges, and exactly four Voronoi cells meet at every corner. These corners are unstable in the sense that small perturbations of the atomic coordinates transform them into pairs of corners at which only three cells meet; examples of these transformation can be seen in Figures 10(b) and (c).

A consequence of these instabilities is that Voronoi cells in finite-temperature square-lattice crystals can have between 4 and 8 edges. Voronoi cells with fewer than 4 or more than 8 edges cannot be obtained through small perturbations of the atomic coordinates and should thus be considered defects. We use the term **family** to refer to a set of Voronoi cell topologies that can be obtained from a perfect structure through infinitesimal perturbations of atomic coordinates; topologies that cannot be obtained in this manner are classified as defects.

This approach is directly applicable to analyzing three-dimensional systems. Consider, for example, the Voronoi cell of an atom in an unperturbed FCC



Figure 10: (a) atoms in an unperturbed square lattice; (b-c) atoms in finite-temperature square-lattice crystals.



Figure 11: Voronoi cells of atoms in unperturbed BCC, FCC, and HCP crystals [23]; red circles indicate unstable corners.



Figure 12: Voronoi cells of atoms in a finite-temperature FCC crystal; each unstable corner has transformed into one of the stable configurations illustrated in Figure 13.

crystal, illustrated in Figure 11. Many of its corners are topologically unstable, and small perturbations of the atomic coordinates result in topological changes [23]; Voronoi cells of several atoms in a finite-temperature FCC crystal are illustrated in Figure 12. We refer to the set of Voronoi cell topologies that can be obtained in this manner as the family of FCC topologies; Voronoi cells that cannot be obtained in this manner are classified as defects in FCC crystals. We can likewise associate to any structure a family of topologies which can be obtained through infinitesimal perturbations. In the following section we outline a method by which these families can be determined.

2.5 Determination of families of topologies

Determination of families of topologies associated with particular structures enables us to anticipate which topologies will appear in finite-temperature systems, and consequently identify and characterize defects in those systems. We briefly consider both analytic and Monte Carlo approaches.

The unique Voronoi cells of atoms in perfect crystalline systems are easily determined and well known; Figure 11 shows several such Voronoi cells. In three dimensions, Voronoi cell corners that are adjacent to more than four Voronoi cells are topologically unstable, and random perturbations of nearby atomic coordinates will change the manner in which neighboring Voronoi cells are connected. For example, Voronoi cells of atoms in perfect FCC crystals have six



Figure 13: Unstable corner in an FCC Voronoi cell and seven possible ways in which it can transform under small perturbations of atomic positions.

corners which are each adjacent to six different cells; these can be seen in Figure 11 as corners at which four edges meet. When atomic positions are perturbed, each of these topologically-unstable vertices can resolve in one of seven ways, illustrated in Figure 13. Unstable corners that appear in other systems can resolve in different manners, and each system must be analyzed independently.

To enumerate all topologies associated with FCC, we must consider all permutations of these resolutions over all unstable corners. Since each of the six unstable vertices can resolve in one of seven ways, or remain unstable, we must check a total of $8^6 = 262,144$ possible permutations. We compute canonical codes, as described in Section 2.3, for each of these, and find 6250 unique topologies in the family associated with FCC; due to symmetries, many topologies appear multiple times in the initial analysis. Similar analysis for other crystalline systems proceeds in a similar fashion.

The analytic approach described here is not practical for analyzing all systems. For example, the unique Voronoi cell associated with the diamond cubic crystal has 12 topologically-unstable corners, each of which can resolve in one of 7 possible manners, or remain unstable. Enumerating all possible topologies associated with diamond cubic crystal would thus require consideration of $8^{12} = 68,719,476,736$ topologies, the determination and storage of which can be computationally restrictive. In these cases, Monte Carlo sampling allows us to determine Voronoi topologies that occur with significant probability within finite-temperature versions of a particular structure. In particular, atoms in a perfect structure are randomly displaced to simulate the effects of temperature, and the resulting Voronoi topologies are recorded. This is repeated for a large number of atoms in order to sample the set of expected topologies. Care must be taken in choosing appropriate perturbations and sample size.

2.6 Ambiguous topologies and their disambiguation

One complication of the topological classification approach results from individual Voronoi topologies belonging to multiple families. Consider for example a two-dimensional Voronoi cell with six sides. We have previously observed that such Voronoi cells can appear both in triangular and perturbed square-lattice crystals. Thus, knowledge that the Voronoi cell of an atom has six sides is insufficient to unambiguously identify its local structure. Similar ambiguities arise in three-dimensional structures, as many Voronoi topologies that belong to the FCC family also belong to the HCP family [23].

Such ambiguities can be resolved by reconsidering topological instabilities under small perturbations as follows. We first consider the case of the ambiguous two-dimensional six-sided Voronoi cell; similar analysis for three-dimensional systems will be described below. We have noted before that Voronoi cells in triangular-lattice crystals are topologically stable under small perturbations; in contrast, Voronoi cells in square-lattice crystals are not. Therefore, if we slightly perturb atoms near a six-sided Voronoi cell, its topology will unlikely change if it belongs to a triangular lattice. In contrast, if it belongs to a square-lattice crystal, then the topology will be more likely to change. Notice, for example, that the six-sided Voronoi cell in the center of Figure 10(b) changes upon the small perturbation illustrated in Figure 10(c). Observing whether the topology of a Voronoi cell changes when atomic positions are perturbed can thus help disambiguate ambiguous topologies.

Similar analysis is both necessary and effective in studying three-dimensional systems. For example, many Voronoi topologies belong both to the families of FCC and HCP crystals. When neighboring atoms are slightly perturbed, topologies of such Voronoi cells will often change. If small perturbations of neighboring atoms result in unambiguous FCC topologies then we can identify these atoms as belonging to FCC crystals; similarly, if small perturbations of neighboring atoms result in unambiguous HCP topologies then we can identify these atoms as belonging to HCP crystals. Understanding how small perturbations of atomic coordinates change the topology of a Voronoi cell thus helps resolve ambiguous topologies. An example in which this method of resolving ambiguous topologies improves the identification of defect structure is described in Section 3.1.

2.7 Alloys

The topological approach described so far does not distinguish between atoms of different element types, but can be generalized to do so. Each code described in Section 2.3 records an implicit ordering of the faces. In particular, since each code "travels" along each edge of every face exactly once in a particular direction, faces can be ordered by the point along the path at which all of their directed edges have been traversed. Then, in addition to the code which describes the Voronoi topology, we can also record the element types associated with each face in that order. Figure 14 shows three different colorings of a Voronoi cell with BCC structure. If red faces indicate neighbors with element types R and blue faces indicate neighbors with element types B, then lists of the corresponding element types are: RRRRRRRRRRRR, BRBRBRBRBRBRBRBRBRR, and RBRBRRRBRRRBRR. This additional information about element types distinguishes between different arrangements of neighbors in alloys, even



Figure 14: Voronoi cells of atoms in binary alloys, with faces colored according to neighboring element.

when the geometry and topology of the Voronoi cells are identical.

3 Applications

Voronoi topology enables the analysis of complex systems in ways not possible using convention methods. In this section we consider two primary applications of this approach. First we consider its utility in identifying defects in high-temperature systems, something that is difficult to do using conventional approaches. We then consider how Voronoi topology can be used to characterize complex grain boundary structures, and subsequently be used to analyze their evolution.

3.1 Defect identification in high-temperature crystals

The first step in studying defect structure evolution in high-temperature systems is the accurate identification of defect structure. We consider here how the topological approach, and its extension described in Section 2.6, can be used to precisely identify a stacking-fault tetrahedron in a high-temperature FCC copper crystal; we also contrast it with two popular conventional methods. A stacking-fault tetrahedron (SFT) is a three-dimensional defect consisting of four stacking faults that form faces of a tetrahedron. The interior and exterior of an SFT are FCC crystals, bounded by stacking-fault planes with a local structure resembling HCP, and edges which are stair-rod dislocations [24]. Figure 15 illustrates a cross-section through the center of an SFT and parallel to one of its faces; the intersection of the SFT with the viewing plane is an equilateral triangle. This SFT was constructed in an FCC copper crystal and then thermalized at 85% of its melting temperature.

Figure 15 illustrates the SFT visualized using two conventional approaches, and the topological methods described in this chapter. Figure 15(a) shows atoms colored using the centrosymmetry order parameter [5]. In this coloring, atoms belonging to faces of the SFT have higher centrosymmetry values than those in the FCC crystal, as expected. However, many atoms inside and outside the



Figure 15: Cross-section of a stacking-fault tetrahedron in copper at 85% of its melting temperature, colored using (a) centrosymmetry, (b) bond-angle analysis, (c) Voronoi topology, and (d) Voronoi topology with perturbation disambiguation. In (a), colors represent the centrosymmetry parameter as per the color bar; in (b-d) dark blue, yellow and red indicate atoms with FCC, HCP, and other local structures, respectively.

SFT also have high centrosymmetry values, making the automated location of the SFT difficult at the simulation temperature.

Figure 15(b) shows atoms colored using bond-angle analysis [6]. Many atoms belonging to the SFT faces are classified as having HCP local structure, as expected. However, many atoms away from the SFT are also erroneously classified as structural defects, despite the absence of other defects in the crystal. Moreover, bond-angle analysis incorrectly identifies many atoms in the bulk as having HCP local structure. Although the general shape of the SFT can be discerned, its structural details are ambiguous, restricting automated analysis.

These figures should be contrasted with the pictures produced using the approaches discussed above. Figure 15(c) illustrates the same sample colored using Voronoi topology. Atoms whose Voronoi cell topologies belong to FCC are colored dark blue. Atoms whose Voronoi topologies are unambiguously HCP are colored yellow; all remaining atoms are colored red. Every atom characterized as have an HCP local structure is on an SFT face. Moreover, all atoms not at the surface of the SFT are correctly identified as belonging to an FCC crystal. Finally, atoms lying at the corners of the triangular cross-section through the SFT triangle are identified as having a local structure that is distinct from the bulk crystal and the stacking-fault faces; these are the stair-rod dislocation cores. The sole weakness of this visualization procedure results from Voronoi topologies which belong to both FCC and HCP families and whose local structure identified as FCC rather than HCP.

Figure 15(d) shows the clearest picture of the SFT using the extension of the Voronoi analysis method described in Section 2.6. To resolve the ambiguous topologies, we perturbed the system 50 times using a random Gaussian perturbation with standard deviation 1% of the average interatomic distance. Atoms which transform into exclusively HCP topologies are characterized as having HCP local structure, while those that occasionally transform into unambiguously FCC topologies, or which always remained ambiguous, are charactered as FCC. Here many more atoms belonging to the stacking fault faces are correctly identified as having HCP-like local structure. In [23], we further demonstrated the successful application of the Voronoi topology method to the identification of grain boundaries, twins, stacking faults, vacancies, and dislocations in a high temperature, plastically deformed nanocrystalline metal.

The correct identification of atoms as belonging to bulk or defect structure allows for a wide range of possible applications in studying many physical mechanisms. We briefly consider the analysis of heterogeneous melting in superheated metals.

3.2 Melting

The melting of crystals is one of the most ubiquitous and also least-understood phase transformations. Due to its intrinsic high-temperature nature, and because one of the two phases involved in the process is amorphous, melting has been notoriously difficult to study at the atomic level, even through simulation. We provide here a brief description of how Voronoi topology analysis can be



Figure 16: A single (111) plane in an FCC single crystal, heated to 120% of the bulk melting temperature, and annealed for 200 ps at this temperature. Blue atoms are those with local FCC structure; gold atoms belong to a single liquid nucleus; all other atoms are not shown.

used to identify liquid phases in a superheated crystal matrix.

Even at temperatures just below the bulk melting point, the Voronoi topologies of over 98% of atoms in a single copper crystal belong to the FCC family [23]. This suggests identifying liquid phases as contiguous regions of atoms with Voronoi topologies that do not belong to the FCC family. To study melting, a liquid nucleus was constructed inside a large copper crystal. The size of the liquid nucleus was large enough so that it would grow when the copper crystal was thermalized at 120% of its bulk melting temperature. Figure 16 shows a single (111) plane inside this system at several times. Every atom in the system is first identified as FCC or not, based on whether its Voronoi topology is in the FCC family. Next, atoms with non-FCC topologies are clustered so that any pair of neighboring non-FCC Voronoi cells belong to the same "cluster". Figure 16 shows all atoms with Voronoi topologies belonging to the FCC family in dark blue, and atoms in the largest cluster of non-FCC topologies in gold. Other atoms with non-FCC topologies, belonging to smaller liquid nuclei, are not shown.

Although the system is heated to well above its melting point, the crystalline and liquid phases in the system are correctly identified without quenching or time-averaging, as validated by visual inspection. This ability to precisely identify the two phases allows for quantitative analysis of the rate at which the supercritical liquid nucleus grows. Figure 17 shows the volume of the largest liquid nucleus, measured in number of atoms, as a function of time. While a de-



Figure 17: The volume of a liquid nucleus as a function of time in a crystal heated to 120% of its bulk melting temperature.

tailed analysis of this phase transformation is beyond the scope of this chapter, this example shows the potential of the Voronoi topology approach for studying questions inaccessible to conventional analysis methods.

3.3 Grain boundary characterization

In addition to accurately identifying known defects, Voronoi topology can also be used to characterize structure in complex systems and automate their analysis.

At 0 K, a $\Sigma 5$ [001] (310) symmetric tilt boundary in BCC tungsten has three metastable states. The atomic structure of each state can be characterized as a pattern of several Voronoi cell topologies. This can be seen in Figure 18, where each atom is assigned a color according to its Voronoi topology. Phase I consists of three distinct Voronoi topologies, and its atoms are colored in three shades of blue. Phase II consists of two Voronoi topologies, and its atoms are colored in two shades of green. Phases III consists of six Voronoi topologies, and its atoms are colored in shades of red, orange, and yellow. These Voronoi topologies are stable under small perturbations of the atomic coordinates, suggesting Voronoi topology as a robust method for characterizing, and subsequently identifying, grain boundary structure.

In one study, Voronoi topology was used to study the evolution of grain boundaries under irradiation conditions [23]. In particular, a $\Sigma 5$ [001] (310) symmetric tilt boundary was constructed in the Phase I state of body-centered cubic tungsten and equilibrated at 1500 K, or roughly 40% of its melting temperature. Self-interstitial atoms were inserted in random locations in the grain boundary at a constant rate to mimic the effects of radiation damage. The insertion of these atoms transformed the grain boundary from a Phase I state



Figure 18: Three meta-stable phases of the $\Sigma 5 [001]$ (310) symmetric tilt boundary in BCC tungsten. Each Voronoi topology is assigned a distinct color. In the profile view, atoms with BCC topologies are shown in grey; in the planar view, these atoms are not shown.

to a mixture of Phases I, II, and III states. By characterizing atoms using their Voronoi topologies, domains of different grain boundary phases can be readily observed in the irradiated grain boundary, illustrated in Figure 19. This automated identification of complex structure allows for further automated analysis of the manner in which this grain boundary changes over time [23]. Although a complete analysis of grain boundary evolution under irradiation is beyond the scope of this chapter, this example highlights the potential of Voronoi topology to automate analysis of complex defect structures.

4 Automation Through Software

The analysis described in this chapter can be automated through publiclyavailable computer software. *VoroTop* is an open-source software package that characterizes local structure in atomistic data sets based on Voronoi cell topology. *VoroTop* was developed and is maintained by the first author with generous support of the NSF under grant DMR-1507013; both the software and source code are available at http://www.vorotop.org.

VoroTop reads atomistic data in several standard formats, including those of LAMMPS [25] and AtomEye [26], and then uses the **Voro++** software library [27] to compute the Voronoi cell of each atom. Using algorithms described in Section 2.3, *VoroTop* computes the topology of each Voronoi cell and then compares it against a precomputed family of topologies associated with a user-chosen structure, such as BCC, FCC, or HCP crystals. The program also enables users to create new families of topologies, with techniques described in Section



Figure 19: Grain boundary, initially of Phase I state, transformed under irradiation conditions; atoms are colored by Voronoi topology.

2.5, and then use those user-generated families to analyze other data sets.

After characterizing atoms through their Voronoi cell topology, *VoroTop* outputs data in standard formats, including those of LAMMPS and AtomEye; these and other programs can then be used for visualization and further analysis. *VoroTop* can also output the topology of each atom (through codes described in Section 2.3), and calculate distributions of Voronoi topologies; these capabilities allow for further independent analysis. Much of the analysis described in this chapter has also been integrated into the popular OVITO visualization and analysis software package [28] for convenient use. Additional documentation about *VoroTop*, and information about other functionality, are available on the website.

The use of Voronoi topology for structure identification is computationally efficient, and its runtime scales linearly with the number of atoms in a system. In preliminary tests, the Voronoi topology of one million atoms could be calculated on a single core of a desktop computer in under one minute. Although this is slower than most conventional methods, Voronoi topology obviates the need for quenching, a step otherwise necessary for analysis of high-temperature systems. Furthermore, Voronoi analysis also provides more accurate characterization of structure even in quenched systems; see Supporting Information of [23].

Extensions of the basic topological approach, such as those described in Sections 2.6 and 2.7, and the clustering method described in Section 3.2 are currently being developed for future implementation.

References

- A. Stukowski, "Structure identification methods for atomistic simulations of crystalline materials," *Modelling Simul. Mater. Sci. Eng.*, vol. 20, no. 4, p. 045021, 2012.
- [2] D. Li, F. Wang, Z. Yang, and Y. Zhao, "How to identify dislocations in molecular dynamics simulations?," *Science China Physics, Mechanics & Astronomy*, vol. 57, no. 12, pp. 2177–2187, 2014.
- [3] M. K. Miller, T. F. Kelly, K. Rajan, and S. P. Ringer, "The future of atom probe tomography," *Materials Today*, vol. 15, no. 4, pp. 158–165, 2012.
- [4] E. A. Lazar, "Molecular dynamic studies of the fracture of metals." Yeshiva University, 2005. Undergraduate Honors Thesis.
- [5] C. L. Kelchner, S. Plimpton, and J. Hamilton, "Dislocation nucleation and defect structure during surface indentation," *Phys. Rev. B*, vol. 58, no. 17, p. 11085, 1998.
- [6] G. J. Ackland and A. P. Jones, "Applications of local crystal structure measures in experiment and simulation," *Phys. Rev. B*, vol. 73, no. 5, p. 054104, 2006.
- [7] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, "Bond-orientational order in liquids and glasses," *Phys. Rev. B*, vol. 28, no. 2, p. 784, 1983.
- [8] P. S. Landweber, E. A. Lazar, and N. Patel, "On fiber diameters of continuous maps," *American Mathematical Monthly*, vol. 123, no. 4, pp. 392–397, 2016.
- [9] G. Voronoï, "Nouvelles applications des paramètres continus à la théorie des formes quadratiques. Deuxième mémoire. Recherches sur les parallélloèdres primitifs.," J. Reine Angew. Math., vol. 134, pp. 198–287, 1908.
- [10] A. Okabe, B. Boots, K. Sugihara, and S. N. Chiu, Spatial tessellations: concepts and applications of Voronoi diagrams, vol. 501. John Wiley & Sons, 2009.
- [11] D. Stoyan, W. S. Kendall, J. Mecke, and L. Ruschendorf, Stochastic Geometry and Its Applications. Wiley Chichester, 1995.
- [12] H. Leipold, E. A. Lazar, K. A. Brakke, and D. J. Srolovitz, "Statistical topology of perturbed two-dimensional lattices," J. Stat. Mech., no. 4, p. 043103, 2016.
- [13] J. R. Munkres, Topology. Prentice Hall, 2000.
- [14] H. Edelsbrunner and J. Harer, "Persistent homology-a survey," Contemporary mathematics, vol. 453, pp. 257–282, 2008.

- [15] S. Weinberger, "What is... persistent homology?," Notices of the AMS, vol. 58, no. 1, pp. 36–39, 2011.
- [16] R. Ghrist, Elementary Applied Topology. Createspace, 2014.
- [17] R. J. Trudeau, Introduction to graph theory. Courier Corporation, 2013.
- [18] E. Steinitz, Polyeder und raumeinteilungen. Teubner, 1916.
- [19] H. Whitney, "A set of topological invariants for graphs," American Journal of Mathematics, vol. 55, no. 1, pp. 231–235, 1933.
- [20] L. Weinberg, "A simple and efficient algorithm for determining isomorphism of planar triply connected graphs," *IEEE Trans. Circuit Theory*, vol. CT13, no. 2, pp. 142–148, 1966.
- [21] L. Weinberg, "On the maximum order of the automorphism group of a planar triply connected graph," SIAM J. on Applied Math., vol. 14, no. 4, pp. 729–738, 1966.
- [22] E. A. Lazar, J. K. Mason, R. D. MacPherson, and D. J. Srolovitz, "Complete topology of cells, grains, and bubbles in three-dimensional microstructures," *Phys. Rev. Lett.*, vol. 109, no. 9, p. 95505, 2012.
- [23] E. A. Lazar, J. Han, and D. J. Srolovitz, "Topological framework for local structure analysis in condensed matter," *Proceedings of the National Academy of Sciences*, vol. 112, no. 43, pp. E5769–E5776, 2015.
- [24] J. P. Hirth and J. Lothe, *Theory of Dislocations*. John Wiley & Sons, 1982.
- [25] S. Plimpton, P. Crozier, and A. Thompson, "Lammps-large-scale atomic/molecular massively parallel simulator," *Sandia National Labora*tories, vol. 18, 2007.
- [26] J. Li, "Atomeye: an efficient atomistic configuration viewer," Modelling and Simulation in Materials Science and Engineering, vol. 11, no. 2, p. 173, 2003.
- [27] C. Rycroft, "Voro++: A three-dimensional Voronoi cell library in C++," Chaos, vol. 19, p. 041111, 2009.
- [28] A. Stukowski, "Visualization and analysis of atomistic simulation data with ovito-the open visualization tool," *Modelling and Simulation in Materials Science and Engineering*, vol. 18, no. 1, p. 015012, 2009.