Development of Physically Based Atomistic Microstructures: The Effect on the Mechanical Response of Polycrystals

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Abstract

A method for the generation of atomistic realizations of polycrystalline aggregates from a phase field grain growth model is presented. Topologies of computational microstructures constructed from the proposed method as well as conventional Poisson Voronoi tessellation are quantitatively compared. While little difference is exhibited in the macroscale mechanical response, substantial differences in the resolved contribution to strain of deformation mechanisms of the structures under uniaxial tension are uncovered using post-processing kinematic metrics. These differences in the fundamental strain accommodation processes suggest that grain topology and grain boundary character significantly affect local responses of polycrystals in molecular dynamics simulations and that significant attention should be paid to the chosen starting microstructure.

Keywords: polycrystalline microstructure generation, molecular dynamics, mechanical properties

1. Introduction

Polycrystalline materials are agglomerations of many crystals, or grains, with mean grain size typically in the micron range for conventional metals and a few nanometers for nanocrystalline materials. The volume fraction of interfaces, i.e., grain boundaries (GBs), scales inversely with grain size [1] and therefore in nanocrystalline materials, a significant fraction of atoms reside in interfaces, driving a change in behavior and properties [2, 3, 4, 5]. The onset of interface-mediated physics drives divergent behavior from coarse-grained systems, including enhanced strength and ductility [6, 7, 8, 9, 10, 11, 12], improved fatigue resistance [13, 14, 15, 16], capacity for superplasticity [17, 18, 19, 20], and greater radiation tolerance [21, 22, 23], which has produced

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10 interest in nanocrystalline materials for a variety of applications [24, 25, 26]. The mechanical behavior of these systems is of particular interest; the conventional Hall-Petch model predicts increases in strength and hardness with decreasing grain size [27, 28], but recent findings suggest that nanocrystalline systems become softer [29, 30] due to a change in the dominant deformation mechanism from dislocation plasticity to grain boundary mediated deformation as grain size
15 decreases below 10-20nm [31, 32].

In nano-grained materials, interfaces such as GBs begin to fundamentally govern material behavior. As such, significant effort has been made to better correlate structure to properties in nanoscale interfaces. However, the behavior of nanoscale interfaces is difficult to directly probe experimentally, but can be efficiently studied using atomistic simulations techniques such as
20 molecular dynamics (MD). This computational method, in particular, has been used to investigate and provide pivotal insight into plasticity [33, 34, 35, 36, 37, 38], shock response [39, 40, 41], radiation tolerance [42, 43], solute segregation behavior [44, 45], and thermal conductivity [46, 47] both at isolated interfaces and in nanocrystalline systems.

Both atomistic and continuum scale simulation methods require the creation of computational
25 microstructures. Polycrystals are commonly constructed using Voronoi tessellation methods [48, 49]. The Voronoi diagram [50] is constructed for a distribution of grain centers, and the resulting polyhedra are taken as grains. The most common form of this method is Poisson Voronoi (PV) where grain centers are placed following a uniform distribution. Microstructures appear superficially similar to nanocrystalline structures produced in experiment (Fig 1), but
30 differ in several critical regards. Voronoi constructions can produce grains with sharp points, wedge-shaped grains, or planar prismatic grains that are not observed experimentally. The grain topology of microstructures generated using PV has been shown to be significantly different than grain growth simulations and real systems [51]. Voronoi constructions also produce planar grain boundaries, while curved boundaries are common in experimentally observed microstructures.
35 Triple junction morphology is also not accurately reproduced; thermodynamic theory predicts that triple junctions ought to have a dihedral angle of $2\pi/3$ [52, 53] in isotropic media, but is not consistently reproduced by Voronoi constructions. Properties of nanocrystalline systems have been found to heavily depend on interface character [54, 55, 56, 57], therefore it is critical that realistic representations of grains and GBs are used as the initial conditions for simulations to
40 more accurately predict the behavior of the microstructure under load.

Attempts have been made to improve Voronoi constructions to avoid some of these problems. So-called inverse Monte Carlo methods have been implemented to tune grain size distributions

and misorientation angle distributions for use in molecular dynamics simulations [32, 58, 59].

Hardcore Voronoi tessellation, in which a minimum distance between grains is enforced, [60] reduces the number of unphysical grains. Neither of these methods resolves all problems associated with the Voronoi construction. Idealized microstructures are often annealed to allow the relaxation of GBs, but this method is unreliable, computationally expensive and growth during annealing prevents direct control of grain size. Other methods of producing initial microstructures include the solidification of melts [61] and the sintering of finite sized particles [62]. The solidification method requires a very rapid quenching rate (10^{12} K/s), which produces an unrealistic concentration of twin boundaries; the sintering method often leaves a significant fraction of voids in the microstructure.

Phase field grain growth models, on the other hand, have been used to produce realistic microstructures, with curved boundaries and the correct triple junction dihedral angle [63]. In this framework, different phases of a material are designated by one or multiple ‘order parameters’ which evolve in time following thermodynamic and physical constraints. Phase field models have been shown to reproduce many aspects of real nanocrystalline microstructures, including grain boundary morphology and grain topology [63, 64, 58, 65].

In this paper, we present a method for discretizing microstructures from voxelated representations to atomistic resolution and quantitatively compare this structure to those produced by a PV method. While this work focuses on voxelated structures produced through phase field modeling, other methods such as Potts models or even experimental data from electron backscatter diffraction may be used. The mechanical properties, strain accommodation and deformation mechanisms are investigated with the aim of quantifying the differences produced by divergent GB morphology and grain topology.

2. Methods

2.1. Phase Field Grain Growth Model

A recently developed phase field model of grain growth is employed to generate polycrystalline aggregates [66, 65]. Order parameters (OPs), $\phi_i(\mathbf{r}, t)$, $i = 1 \dots n$, define individual grain orientations, where $\mathbf{r}$ and t are the positions in space and time and n is then number of OPs. The free energy functional, $\mathcal{F}_{tot}$, is defined as

$$\mathcal{F}_{tot} = \int d\mathbf{r} \left[W_{\phi} f_{grain}(\phi_i, \dots, \phi_n) + \sum_i^{n_{\phi}} \frac{\epsilon^2}{2} |\nabla \phi_i|^2 \right], \quad (1)$$

Figure 1: **(a)** A typical nanocrystalline structure created by the Poisson Voronoi method and examples of **(b)** grains with sharp points **(c)** wedge-shaped grains and **(d)** planar prismatic and taken from this structure.

where f_{grain} is the free energy density, W_ϕ is a scaling factor and ϵ is an isotropic GB energy scaling factor. The free energy density is defined as

$$f_{grain} = \frac{4}{3} \left[1 - 4 \sum_{i=1}^{n_\phi} \phi_i^3 + 3 \left(\sum_{i=1}^{n_\phi} \phi_i^2 \right)^2 \right]. \quad (2)$$

Minima of f_{grain} are conveniently located where $\phi_i = 1, \phi_j = 0 \forall i \neq j$. The spatial and temporal evolution of OPs is defined by the Allen-Cahn equation [67]:

$$\frac{\partial \phi_i}{\partial t} = -L \left(\frac{\delta \mathcal{F}_{tot}}{\delta \phi_i} \right), \quad (3)$$

where L is a grain boundary mobility factor. In this work, simulations were performed on a $120 \times 120 \times 120$ voxel cube with 100 order parameters with an initial seed of uniformly distributed random noise. Snapshots were taken within the topologically self-similar regime.

2.2. Atomistic Structure Generation

Phase field simulation data was converted to atomistic structures, here called Discrete Phase Field (DPF) structures. Individual grains were extracted from each order parameter using a

cluster labelling algorithm [68]. The atomistic grains within the microstructure were then created by processing each grain order parameter using the following algorithm:

1. Replicate the order parameter in any direction where it crosses a periodic boundary.
- 85 2. Identify contiguous regions using a burn algorithm.
3. Choose a contiguous region that contains voxels in the original box and fill this region with atoms by enumerating integer multiples of lattice vectors. Lattice orientations are assigned randomly according to a uniform distribution.
4. Check that each atom is in a position with $\phi > \phi_{cutoff}$ where $\phi \in [0, 1]$ is the interpolated value of the order parameter at the atom position and ϕ_{cutoff} is a tunable parameter.
- 90 Interpolation is necessary for the production of smooth grain boundaries.

This algorithm allows for lattice orientation to be separately defined for grains that originally shared an order parameter, while also ensuring that assigned lattices are contiguous across periodic boundaries. A three-dimensional microstructure generated from the phase field model and
 95 corresponding atomistic microstructure are presented in Figure 2.

The order parameter cutoff, ϕ_{cutoff} , allows for the control of the density of the structure. At $\phi_{cutoff} = 0.5$, ellipsoid grains with common tangents are formed, leaving voids at triple junctions and vertex nodes, which are not removed through low temperature equilibration. Reducing ϕ_{cutoff} inflates the grains which results in overlap at grain boundaries and fills triple junctions.
 100 Deleting atoms within 90% of the first nearest neighbor distance produces structures with stable density after 10ps equilibration at 10K. $\phi_{cutoff} = 0.35$ was found to be the highest cutoff that produced structure with total density equivalent to those produced by the PV method after short, low temperature, equilibration suggesting that both triple junctions and grain boundaries had relaxed to reasonably dense configurations.

105 Five realizations of atomistic microstructures were generated using the DPF and PV methods in order to obtain a more statistical sense of the results. Generated microstructures had simulation box sizes of $(50\text{nm})^3 \pm 1\%$, composed of around 10 million atoms. Microstructures were generated with an average grain diameter of 10nm using the spherical grain approximation.

Due to the diffuse nature of interfaces within the phase field framework, faces were counted
 110 by identifying voxels with multiple non-zero order parameters. It was assumed that these order parameters must then be connected by faces. Isosurfaces at $\phi = \phi_{cutoff}$ were extracted for each grain, from which the surface area and volume were calculated. Since some atoms are deleted from each grain, this overestimates the volume and surface area of each grain, but remains a useful first order approximation.

Figure 2: Microstructures generated from **(a)** Phase Field and **(b)** Discrete Phase Field. In all images GBs are white while grains are blue. GBs are identified by $\sum \phi_i^2(1 - \phi_i)^2$ in (a) and by common neighbor analysis in (b).

115 The volume and surface area of the five structures created using the PV tessellation were computed using the Voro++ Library [69]. Calculated values were found to be consistent with the surface extraction method performed on blurred digital Voronoi structures.

2.3. Molecular Dynamics Simulation

MD simulations were performed using an embedded atom method (EAM) interatomic potential for nickel [70] using the LAMMPS MD package [71]. All simulations employed three-dimensional periodic boundary conditions. For each structure a conjugate gradient minimization was performed, allowing the simulation box to relax to a target pressure of zero in each dimension, followed by equilibration for 20ps at 10K and at 300K with zero pressure maintained using the isothermal-isobaric (NPT) ensemble. Uniaxial tension up to 10% was performed along the x-axis of each sample at a strain rate of 10^9 s^{-1} at 300K, while the normal pressure was maintained at zero in the transverse directions.

2.4. Kinematic Metrics

To analyze the deformation behavior of the system, the continuum strain field is approximated at each atom using the method described by Tucker et al. [72, 73, 74, 75]. The deformation gradient tensor, $\mathbf{F}$, is approximated at each atom by computing the change of its initial neighborhood. The strain tensor is obtained from the deformation gradient tensor as

$$\mathbf{E} = \frac{1}{2}(\mathbf{F}^T \mathbf{F} - \mathbf{I}),$$

where $\mathbf{I}$ is the identity tensor. The strain tensor is transformed into two scalar metrics: dilatation, δ , and von Mises strain, ϵ_{vm} , defined by:

$$\delta = E_{ii}$$

$$\epsilon_{vm} = \sqrt{\frac{3}{2} \mathbf{E}_{ij} \mathbf{E}_{ij}}$$

The microrotation vector, φ_k , is also computed from the deformation gradient as the skew part of the rotation matrix, $\mathbf{R}$ obtained from the polar decomposition of $\mathbf{F}$:

$$\mathbf{F} = \mathbf{R}\mathbf{U}$$

$$\varphi_k = \epsilon_{ijk} \text{skew}(\mathbf{R})_{ij}$$

130 where $\mathbf{U}$ is the right stretch tensor and ϵ_{ijk} is the Levi-Civita permutation tensor. The magnitude of the microrotation vector, $|\varphi|$, is the angle of rotation about axis $\vec{\varphi}$ for infinitesimal rotations.

Using these metrics, common neighbor analysis and slip vector [76, 77, 78], each atom was assigned to one of four groups: twin, dislocation, bulk and GB, corresponding to deformation mechanisms of twinning, dislocation plasticity, elastic strain and GB sliding and restructuring. 135 The twin group is defined by all atoms belonging to a twin boundary and those FCC atoms that have been traversed by a migrating twin boundary [75]. The dislocation group is defined by FCC coordinated atoms with a slip vector magnitude near the theoretical Burgers vector magnitude for perfect slip and all HCP coordinated atoms within stacking faults that have a slip 140 vector magnitude near the theoretical Burgers vector magnitude for partial dislocation slip. It is important to note that this method includes all atoms that have been deformed by dislocation in previous states, not only those that are components of dislocations in the current state. The bulk group consists of all FCC coordinated atoms that have not been included in either the dislocation or twin group. Finally, the GB group consists of all other atoms. After dividing the 145 atoms into these four groups, the fraction of each kinematic metric accommodated by a given deformation mechanism can be computed [74, 75].

3. Results and Discussion

Statistical analysis of the grain topology was performed to quantify the differences in the microstructures produced using the DPF and PV methods. Figure 3 illustrates the grain volume 150 distribution and surface area distribution for the structures generated using both methods. As expected, the DPF structures follow an exponential decay-like distribution of grain volumes, matching other thermodynamically driven grain growth methods [79], while the PV method produces a lognormal-like distribution. The surface area distribution is notably different for the

Figure 3: Characterization of grain topology in Poisson Voronoi (PV) and Discrete Phase Fields (DPF) by (a) normalized grain volume distribution (b) surface area distribution, where SA_0 is the surface area of a 10nm diameter sphere. Error bars are the standard error of the mean across the five instances. The dotted line in panel (b) indicates the surface area of a 10nm diameter sphere.

Figure 4: Per-atom properties of defect atoms (a) Atomic energy histogram (b) Voronoi volume histogram (c) Normalized radial distribution function

Figure 5: Mean mechanical response under uniaxial tension for structures produced by the three methods. Compared to the Discrete Phase Field, the Poisson Voronoi over estimates tensile strength. Lighter areas indicate a single standard deviation from the mean stress. The inset table shows common values associated with each stress strain curve: elastic modulus, ultimate tensile stress (UTS) and 0.02% offset yield strain.

DPF structures; the large number of small grains results in a peak below the spherical 10nm grain average, while the PV structure has a peak at a larger surface area. To quantify the difference in grain boundary structure, the distributions of the per-atom potential energy and volume of the resultant cells created by Voronoi tessellation, or Voronoi volume, were computed for defect atoms, in addition to the radial distribution function (Fig. 4). All profiles were quite similar, but some small differences were noted. The energy profile of the DPF structures is slightly more narrow and the PV structures contain significantly more atoms at the high end of the distribution, though still a very small fraction of total atoms. The Voronoi volume profile shows the opposite trend; the PV distribution is more narrow. The radial distribution function for both structures is exactly identical. Based on this analysis, the distribution of local atomic structure does not appear to differ significantly between the two methods.

Despite these differences in structure, the mean mechanical response of structures generating using the two methods is similar (Figure 5). While there are substantial differences in both the grain volume and surface area distributions produced by the two methods, these differences do not have a significant effect on elastic modulus, ultimate tensile strength and 0.2% offset yield strain (Figure 5 inset table). While macroscopic mechanical responses of polycrystals obtained from two approaches agree relatively well, significantly different local responses are observed. Figure 6 shows development of dislocation and twin groups upon 6% deformation. Qualitatively,

Figure 6: Paths of dislocations (red) and twins (blue) in the grain boundary network (gray) in single instances of (a) DPF and (b) PV Structures at 6% uniaxial tensile strain. A significantly higher number of both dislocations and twins have been generated in DPF compared to PV, suggesting the fundamental role of GB structure on deformation behavior.

Figure 7: Fraction of atoms that have undergone (a) partial slip and (b) perfect slip as a function of imposed tensile strain for DPF (blue) and PV (red) microstructures.

a much higher number of dislocations appear to be present in the DPF structures. This disparity is confirmed through quantitative analysis of dislocation slip. Figure 7 shows the fraction of atoms that have undergone partial or perfect slip during deformation. In both cases, while dislocation activity increases during deformation, the DPF structure shows a higher fraction of slipped atoms at a given strain. This suggests that in PV structures, the nucleation of dislocations is inhibited relative to the DPF structure, requiring either a higher dislocation nucleation energy or the presence of a lower-cost path, such as GB sliding, in the PV structure.

Differences in the operative GB and dislocation mechanisms at a given strain can be directly linked to the fundamentally different atomic structure of interfaces generated by the two methods. PV methods tend to create perfectly flat GBs, while the DPF methods creates more realistic

curved GBs. It is likely that the planar nature of interfaces and unrealistic geometric constraints within the microstructures from PV facilitates GB sliding and reordering, while the curved GBs inhibit this strain accommodation mechanism. Furthermore, the increased volume fraction of GBs induced by curvature in the DPF structures may result in an increased number of sites for dislocation nucleation, leading to higher dislocation concentrations at lower strains compared to PV structures. Finally, dislocations occasionally nucleate at triple junctions in the DPF structures, but this behavior is rarely observed in the PV structures, suggesting that the character of triple junctions may also play a role in dislocation plasticity. Further study of these systems is required to quantitatively resolve the contributions of these additional intercrystalline effects.

Figure 8 shows the fraction of strain metrics accommodated by each of four deformation mechanisms: elastic strain in the bulk, grain boundary sliding and restructuring, dislocation slip and twinning. The strain is quantified according to three kinematic metrics (a) E_{11} , the strain component parallel to the axis of loading, (b) absolute dilatation, and (c) Von Mises Equivalent strain. The data shown in Figure 8 is obtained by summing the relevant kinematic metric for every atom within each group (or mechanism) and then normalizing by the total strain tensor of all atoms in the simulation. As such, E_{11} for the GB group in Figure ?? is found by summing the E_{11} strain tensor component from each atom in the GB group to obtain a total E_{11} value and then normalizing by the total E_{11} summing over all atoms in the simulation cell, as detailed earlier. In all cases, strain is initially dominated by elastic deformation in the bulk which gradually gives way to GB-mediated deformation at higher strains. Beyond approximately 4% strain, dislocations and twins become the dominant deformation modes, further decreasing the amount of strain accommodated in the bulk.

Figure 8: (left) The fraction of total strain accommodated by bulk elastic deformation, GB-mediated deformation, dislocation plasticity and twinning, and (right) the difference in fraction between the DPF and PV structures for each mechanism, with strain quantified using (a,b) E_{11} (c,d) Absolute Dilatation and (e,f) Von Mises Equivalent strain.

The differences between DPF and PV structures show that, for all three metrics, a higher
 205 fraction of strain is accommodated by GBs in PV structures, while DPF structures exhibit a
 larger contribution from dislocation plasticity. The differences in GB structure outlined previ-
 ously and their corresponding effect on dislocation nucleation and GB sliding produce significant
 differences in the competition of operative deformation mechanisms. In all three metrics, the
 DPF structures show a significantly higher fraction of strain accommodated by dislocations off-
 210 set primarily by a decreased contribution from GBs, supporting the idea that GB deformations
 are inhibited in the DPF structures. While the fraction of strain accommodated by twinning is
 stable, that accommodated by bulk atoms is not. As more atoms slip due to passing dislocations,
 they move from the bulk group to the dislocation group, giving rise to a disparity in calculated
 elastic strain accommodation between the two sets of structures. Future work should resolve the
 215 elastic and plastic components of individual atomic strain, rather than assuming all deformation
 is either one or the other.

The distribution of strain mechanisms raises some other interesting questions. Figure ??
 exhibits a small transient effect in the first time step that is not present in other kinematic
 metrics. This is likely the result of strain-induced restructured of unstable GBs. It is unclear,
 220 however, why only E_{11} captures this effect. All metrics also show a peak in the difference of strain
 accommodation of twins near 6% strain, which suggests that GB character also plays a role in
 twin nucleation. Also present are significant changes in the difference in strain accommodation
 by bulk atoms, which in all kinematic metrics shows significant trends towards the DPF structure
 beyond 6% strain. This may be the result of differences in GB migration, which is not individually
 225 resolved in this study.

4. Conclusion

Molecular dynamics simulations of nanocrystalline solids typically employ Poisson Voronoi
 methods to create interfaces and grains, commonly used to study the mechanical properties of
 nanocrystalline systems. In this work, we present a novel method for the creation of nanocrys-
 230 talline structures from phase field simulations. This method has numerous advantages over
 Voronoi methods in that it produces curved, rather than flat boundaries, recovers the correct
 triple junction angle with greater accuracy and produces grain size and surface area distributions
 more consistent with other grain growth models. The mean mechanical response of structures
 generated using both methods is similar despite differences in grain size and surface area dis-
 235 tributions, however, probing the deformation mechanisms of both structures reveals significant

differences. Structures generated using the phase field based method displayed a greater tendency towards dislocation slip rather than grain boundary sliding. Extensive study has been performed on the transition from Hall-Petch behavior in coarse-grained structures to grain boundary mediated deformation in nanocrystalline structures, however, that work has relied on the Voronoi tessellation method to produce microstructures. The work presented here demonstrates that the dislocation plasticity in these systems is sensitive to interface character. Therefore, grain size quantifications of the Hall-Petch breakdown performed on microstructures generated using Voronoi tessellation method are likely inaccurate and must be reevaluated with greater consideration of interface character.

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