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An efficient Monte Carlo algorithm for determining the minimum energy structures of metallic grain boundaries

Arash Dehghan Banadaki[a], Mark A. Tschopp[b], Srikanth Patala[a,*]

[a] Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, 27617, USA
[b] U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA

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ABSTRACT

Sampling minimum energy grain boundary (GB) structures in the five-dimensional crystallographic phase space can provide much-needed insight into how GB crystallography affects various interfacial properties. However, the complexity and number of parameters involved often limits the extent of this exploration to a small set of interfaces. In this article, we present a fast Monte Carlo scheme for generating zero-Kelvin, low energy GB structures in the five-dimensional crystallographic phase space. The Monte Carlo trial moves include removal and insertion of atoms in the GB region, which create a diverse set of GB configurations and result in a rapid convergence to the low energy structure. We have validated the robustness of this approach by simulating over 1184 tilt, twist, and mixed character GBs in both fcc (Aluminum and Nickel) and bcc (α-Iron) metallic systems.

1. Introduction

Grain boundaries (GBs) influence a wide array of mechanical [1–7], chemical [8–10] and functional [11,12] properties in polycrystalline materials. However, they are also among the least understood defect types due to the vast and topologically complex five-dimensional (5-D) crystallographic phase-space of interfaces [13,14]. In other words, the GB properties are functions of, at the least, five macroscopic crystallographic degrees of freedom (DOF).

In general, for single component metallic systems, there exist *nine* crystallographic parameters that uniquely define the structure of a GB [15]. These parameters are classified into macroscopic and microscopic DOF—five parameters specifying the misorientation and boundary plane orientation and the additional four representing the microscopic relative displacements between the adjoining lattices and the translation of the boundary plane along its normal vector. However, under conditions of thermodynamic equilibrium, it is generally accepted that the five macroscopic DOF are sufficient for representing the properties of interfaces [16].

For developing reliable GB structure-property relationships, the lowest energy GB structures, computed at 0 K, are essential. The energy landscape and the structure of a GB with fixed crystallography (the five macroscopic parameters) depends on the microscopic DOF and the atomic density λ [17] (traditionally controlled by tuning the allowed extent of overlap between atoms). In the past few decades, several, reasonably successful efforts have been made to predict the low-energy GB structures [18–23]. While the implementation varies slightly, these techniques generally rely on generating a large number of initial GB configurations by varying the microscopic DOF of an interface, which can be considered as a brute-force approach for determining the minima in the energy landscape. While such a brute-force approach might suffice for simulating GBs with low Σ-number [24], the computational cost usually increases as the symmetry of the GB is reduced.

Monte Carlo (MC) based algorithms have been routinely utilized for finding minima in energy landscapes in a variety of complex systems in condensed-matter physics [25]. However, such a technique has never been applied to computing the minimum energy structures for GBs in single component systems. This is primarily due to the fact that atoms along the interface are not constrained to lie on a fixed lattice [25]. For example, hybrid Monte-Carlo/Molecular-Dynamics simulations have been utilized to compute low energy GB structures in binary alloy systems [26,27]. These alloys have at least two components and the trial moves correspond to swapping the positions of *unlike* atoms. Unfortunately, in single component systems, atom swapping does not change the configuration of the bicrystal. In this article, we introduce a Monte Carlo based GB energy minimization algorithm applicable for single component systems. The advantage of a MC framework is that, when the acceptance probabilities are devised appropriately [28], it can be utilized to compute thermodynamic equilibrium properties in a variety of relevant statistical ensembles.

* Corresponding author.
E-mail address: spatala@ncsu.edu (S. Patala).

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As will be discussed in the next section, the trial perturbations that facilitate the MC-based approach involve both atom removal and, more importantly, atom insertions in the GB region. These two Monte-Carlo moves change the density of the GBs and are likely the most important perturbations for sampling the energy landscape of the microscopic DOF of an interface. There have been recent studies where atom removal and insertions were utilized to compute minimum energy structures or to investigate phase transitions in GB structures. For example, in [29], the atomic density was allowed to vary by removing periodic boundary conditions in the GB plane. The free surfaces act as sources and sinks for atoms. This facilitated the required changes in grain boundary density and a structural phase transition was observed. In [30,31], low energy GB structures were obtained using a genetic algorithm where, among others, atom removal and insertion were used to perturb the GB structure. The insertions were made by constructing a uniform grid in the GB region and filling the unoccupied grid points at random.

For a Monte-Carlo simulation to work in an efficient manner, it is important that the increase in energy due to the perturbations are not always too large. However, if atoms are inserted randomly, the Monte-Carlo simulations will take a long time to converge due to low acceptance rates. In this article, we introduce a geometric construction to identify voids for atom insertion in the GB region, which alleviates the large increases in energy. This technique is similar to the cavity based MC method developed for the simulation of dense fluids [32]. Inserting atoms in these voids and minimizing the structure dramatically improves the acceptance probability of the atom-insertion move. As far as the authors are aware, there has been only one previous report that utilized atom insertions and removals in a Monte-Carlo framework for defects in crystalline systems. Phillpot and Rickman [33] proposed a grand canonical framework, where *sites* with fractional occupancies instead of atoms are used, to obtain ground state structures in the presence of defects. In [33], a simple Lennard-Jones potential is used to compute the minimum energy structure of (110) twist GB. However, in this technique, the sites for insertion are determined *a priori* and are fixed during the MC simulation. Our algorithm builds on these ideas and shows that low-energy configurations for GBs can be obtained for a diverse set of GB crystallographic characters in both fcc (Aluminum and Nickel) and bcc (α-Iron) metallic systems.

The MC approach, introduced in this article, is also very efficient in generating the low energy GB structures. The biggest obstacle for generating large GB databases that are well-sampled in the 5-D crystallographic phase-space is the massive number of simulations required to obtain the lowest-energy GB structure. For example, determining the lowest energy structure for a typical GB using such brute force algorithms requires anywhere between 1000 and 150 000 unique energy-minimization simulations. In this article, we also show that the proposed Monte Carlo scheme is more efficient in generating the low-energy GB structures when compared to such traditional brute-force simulations. In the following sections, we describe the Monte Carlo algorithm, the trial moves and the test cases, involving the three GB databases, in greater detail.

2. Methodology

Our Monte Carlo algorithm starts with an initial GB configuration and applies random perturbations (trial moves), which are then evaluated using a Metropolis-like criterion [34]: accepted if the energy is reduced, accepted or rejected by a Boltzmann-weighted probability if the energy increases. At each step of the simulation, the following perturbations may be introduced: (a) removal of an atom from the GB and (b) insertion of an atom in the GB region.

The trial move involving *atom removal* (or creation of a vacancy) is inspired by investigations of von Alfthan et al. [35], Yu and Demkowicz [36], and Tschopp et al. [37]. Initially, we only considered trial moves involving atom removal and realized that applying just this perturbation does not result in the low-energy structure in many of the test cases (described in the later part of the article). We observed that an efficient convergence to the low energy GB structure is obtained by also considering perturbations that involve *atom insertions* at GB interstitial sites.

The algorithm starts with an initial random GB configuration, which is created using a random set of microscopic DOF for the interface. The next step involves choosing one of the two trial moves stochastically (i.e., the removal and insertion moves are chosen with a probability of p_{rm} and $p_{\text{in}} = 1-p_{\text{rm}}$, respectively). Once the decision for removal or insertion has been made, the atom to remove or the interstitial site for atom insertion is also chosen stochastically to facilitate the possibility of generating a diverse set of GB structures. For example, to determine the GB atom to remove,[1] we first assign a removal probability $p_{rm,i}$, for each atom i in the GB, which is given by:

$$p_{\text{rm},i} = \begin{cases} (E_i - E_o) \Big/ \left(\sum_{j=1}^{N_{\text{GB}}} (E_j - E_o) \right), & \text{if} E_i \geqslant E_o \\ 0, & \text{otherwise} \end{cases} \quad (1)$$

where E_i is the energy of the i^{th} GB atom, E_o is the cohesive energy of the atom in the single crystal configuration at 0 K, N_{GB} is the number of GB atoms, and $\sum p_{\text{rm},i} = 1$. According to this equation, the probability of removing an atom is proportional to its excess energy. In principle, we are interested in removing an atom that lowers the GB energy. Such an atom can be determined by computing the minimum GB vacancy formation energy defined in [36]. However, to determine the atom that corresponds to the minimum vacancy formation energy, one would have to remove a GB atom, relax the structure, compute the vacancy formation energy, and then repeat this procedure for all the atoms in the GB. This is computationally very expensive. Instead, we simply choose to remove atoms based on their excess energies. The excess energies can be directly determined from the GB configuration and no further simulations are required. This choice is further motivated by prior studies that have shown, for example, that the excess energy is positively correlated with the formation energy of certain GB defects (e.g., He and He_2 in a monovacancy in Ref. [37]). In Fig. 1(a), the atomistic structure of a $\Sigma5(0\bar{2}1)$ GB is shown, where the atoms are colored according to their energy. Corresponding removal probabilities for the atoms are shown in Fig. 1(b).

Similarly, the sites for atom insertion are also chosen stochastically within the GB. The importance of the insertion step has been highlighted in a Cu-Al binary alloy system [39], where the copper atoms preferentially segregate to the interstitial sites in the $\Sigma5(310)$ Aluminum GB. This result underscores the importance of considering atom insertion steps during the Monte-Carlo simulation for achieving faster energy convergence.

The potential interstitial sites for inserting an atom in the GB region are determined through a Delaunay triangulation [40] of the GB atomistic structure. The circumcenters of the Delaunay tetrahedra provide the locations of the interstitial voids. For example, Fig. 2(a) shows the voids that are identified at the circumcenters of the Delaunay tetrahedra of the $\Sigma3(10\bar{1})$ GB.[2] To simplify presentation, we show only one Delaunay tetrahedron within the GB. A magnified version of this tetrahedron and the void is shown in Fig. 2(b). The radius of the interstitial void is given by $r_{in} = r_s - r_a$, where r_s is the radius of the circumsphere of the Delaunay tetrahedron and r_a is the radius of the atom.

In a recent study, we showed that the interstitial voids, determined

[1] In FCC and BCC bicrystals, the centrosymmetry parameter [38], as computed by LAMMPS, is used to identify GB atoms (with the criterion of CSP > 0.1).

[2] We chose this asymmetric tilt GB to simply illustrate the algorithm for computing voids in the GB structure. The same concept can be utilized for any complex GB structure.