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Exploring grain boundary energy landscapes with the activation-relaxation technique

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Abstract

To develop a structure-kinetic property mapping for grain boundaries requires an understanding of their energy landscapes, i.e., the energy basins and nearby saddle points separating adjacent structures. We implement the activation-relaxation technique to obtain a first view of grain boundary energy landscapes for the $\Sigma 5$ (130), $\Sigma 5$ (210), and $\Sigma 3$ (111) grain boundaries in copper. The energy landscapes of these boundaries are very different, which supports a focus on energy landscapes, rather than absolute boundary energy, to understand boundary properties.

Keywords: grain boundary energy, grain boundary migration, grain boundary sliding, energy landscape, simulation

Grain boundaries (GBs) govern many materials properties such as plasticity, intergranular and fatigue cracking, corrosion, creep, and thermal coarsening [1–6]. The kinetic properties of individual GBs that drive such macroscopic behavior can vary by orders of magnitude from one GB to the next [7–10], and, as such, materials' macroscopic properties are significantly impacted by the collection of individual grain boundaries in a specimen [7,11,12]; the practice of “grain boundary engineering” relies heavily on this concept and has led to some remarkable property enhancements [7,11–13]. However, predictive relationships between GB structure and kinetic properties remain elusive. This is at least in part because the number of possible GB configurations across the full 5-parameter GB crystallographic space is vast [14]. Over the years, a number of investigations of GB properties across the 5-parameter space have been undertaken [15–18]. However, the major focus of most such work has been on the absolute excess energy of GBs, while the kinetic properties of GBs across the space are substantially less studied.

It is the premise of our investigation that grain boundary engineering, by virtue of its dependence upon GB kinetic properties, does not necessarily require information about the excess energy of GBs, but rather needs input on the shape and structures of GB energy landscapes—the series of local stable and metastable GB configurations and the pathways and activated states between them. It is the depth or shallowness of the potential well that an individual GB sits in relative to other nearby configurations, rather than the absolute position of that well on the energy scale, that will determine the stability and evolution of a GB. Yet to our knowledge, there are no prior studies revealing the energy landscape of any given GB. It is our purpose here to do so for a few coincidence boundaries to establish the importance of such data for grain boundary engineering.

An illustration of the concept of the GB energy landscape is shown in Figure 1. The atomic

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configurations of a GB in its absolute minimum energy (ground state) configuration, at a transition state, and at an adjacent minimum are shown, mapped to a schematic potential energy landscape plotted on two arbitrary axes denoting the configuration space. A transition state corresponds to the point of highest energy on a pathway of lowest energy connecting two adjacent minima. While transition states have negative curvature in one direction, minima (or basins) have positive curvature in every direction.

GB potential energy landscapes in this study were investigated using the activation-relaxation technique (ART) [19,20]. ART is an efficient saddle point finding algorithm consisting of three phases: perturbation, convergence, and relaxation. The initial grain boundary configurations were generated, using the LAMMPS molecular dynamics simulation package [21,22], from two individual grains oriented according to the desired final configuration and separated by a small distance of ~ 1 Å. Using the embedded atom method (EAM) [23] potential developed by Mishin et al. [24,25], a conjugate gradient minimization was performed on the two-grain system, resulting in a minimum energy GB configuration. The conjugate gradient relaxation was performed at zero pressure in a region within a cutoff distance of the boundary. In some cases, numerous initial configurations were required in order to generate the ground state structure. Three symmetric tilt GBs were investigated here:

- $\Sigma 5$ (130) (905 mJ/m^2 , 3232 atoms)
- $\Sigma 5$ (210) (952 mJ/m^2 , 2040 atoms)
- $\Sigma 3$ (111) coherent twin (23 mJ/m^2 , 5850 atoms)

System size and GB-region cutoff were optimized in the initial stages of the investigation by considering systems ranging from less than 1,000 atoms to greater than 10,000, and varying the GB-region cutoff distance.

Figure 1. Schematic of a potential energy landscape of a grain boundary. Atomic configurations of the $\Sigma 3$ (111) grain boundary modeled in copper are shown as examples of grain boundary configurations at the indicated points of interest. The potential energy surface shown here is intended as a visual aide and is plotted as energy vs. a two dimensional projection of configuration space. Atomic configuration images were generated with AtomEye [30].

The present implementation of ART was initiated by perturbing a random GB atom, identified as one with a centrosymmetry parameter greater than 4.0 [22,26], by a distance $\alpha_0 = 1.3$ Å in a random direction. The perturbation phase followed Ref. [27], with $N_R = 2$ steps of modified conjugate gradient relaxation for each perturbation and $\lambda_c = -1.0$, the cutoff value the minimum eigenvalue had to be less than in order to proceed to the convergence phase of the algorithm. The lowest eigenvalue of the system was calculated using the Lanczos algorithm with $L_N = 15$ Lanczos iterations, where the product of the Hessian matrix with the j^{th} vector of the Krylov subspace was calculated using a second order finite difference approximation. If, after L_N Lanczos iterations, the residual (i.e., the difference

for a matrix $\mathbf{H}$, eigenvalue λ , and approximate eigenvector $\mathbf{v}$) was greater than 0.1, the Lanczos algorithm was implicitly restarted using the most recently approximated eigenvector as the initial guess until the residual was less than 0.1 or the Lanczos method had been attempted L_N times [28]. The convergence phase again followed Ref. [27] with $\alpha_{\max} = 0.5$ Å, the largest distance any atom could move for a given convergence step, $f_{\text{tol}} = 0.005$ eV/Å, the maximum value any component of the force vector could have for a transition state to be identified, and $N_{\max} = 50\text{--}75$, the maximum number of convergence steps.

The requirements for successful saddle point identification were $\lambda_{\min} \leq \lambda_{\text{cf}} = -0.001$ and $f_{\max} \leq f_{\text{tol}}$. If these were satisfied, the connectivity checking phase of the algorithm was entered. Following Ref. [27], connectivity was verified if a constant strain conjugate gradient minimization of the saddle point configuration resulted in a maximum deviation from the initial configuration, $\Delta x_{\max} \leq \Delta x_{\text{tol}} = 0.5$ Å. The adjacent minima to connected saddle points were identified using a conjugate gradient minimization in LAMMPS with all stress components zero. Transitions for which the adjacent minimum was sufficiently similar to the saddle point (within 0.05 eV of the saddle point energy and with $\Delta x_{\max} \leq \Delta x_{\text{tol}}$) were excluded as these are not kinetically viable pathways.

As the algorithm ran, saddle points were binned into groups of 5 according to the order in which they were found, and frequencies and standard deviations of their occurrence were determined. The t -statistic was then used to calculate the total number of saddle points required to achieve a desired confidence interval (95%, two-sided, within 10% of the true mean) for the frequency of each saddle point. If the number of saddle points found was greater than what was required for the confidence interval for the most frequently occurring saddle point, the program was stopped, and the space was deemed sufficiently explored.

It should be noted that the choice of parameters used in ART, most importantly α_0 and λ_c , can affect the distribution of saddle points found in the search; however, we have found that the specific transitions revealed are independent of these parameters, with the exception of very extreme choices. For this reason, parameters that minimized the time required to find a saddle point were used.

The present implementation of ART was validated through investigation of vacancy migration in copper, yielding excellent agreement with expectations (i.e., a single prominent event with activation energy of 0.68 eV, compared to 0.71 eV from experiments and within 0.01 eV of other simulation results for copper [24]). The precision of the saddle points found by the algorithm was thus taken to be 0.01 eV, limited by f_{tol} , while the accuracy was limited by the potential used and was taken to be 0.03 eV. As our interest is in energy differences rather than absolute energies, the precision drives the uncertainty in this investigation.

From the output of ART, the energy landscapes governing the kinetic behavior of GBs are obtained, and a graphical representation of this data is shown in Figure 2 for the three GBs in this study. The nodes of each graph correspond to accessible states (minima and transition states) and are positioned with respect to the vertical energy axis shown. Multiple nodes with very similar energy were combined together to generate the pictorial representation in Figure 2 and are larger in size than uncombined nodes. The edges connecting the nodes correspond to the trajectories (initial configuration to transition state to adjacent minimum) found for each GB and are shown as curved arrows. Examples of the atomic configurations of a transition are shown in the figure and correspond to the shaded nodes.

Several noteworthy features of these energy landscapes can be observed directly from Figure 2.

Figure 2. Graphs of the energy landscape of grain boundaries in copper. The nodes show accessible states to each GB, ranging from the equilibrium configuration (left) over activated states (middle) to adjacent basins (right). For clarity, nodes of very similar energy are shown as single large nodes. The black lines correspond to the lowest energy symmetric transition. Atomic configurations corresponding to the shaded nodes are shown in the figure. Atomic configuration images were generated with AtomEye [30] and are colored according to centrosymmetry. Only non-fcc-coordinated atoms are shown. The largest eigenvalue of the adjacency matrix, λ , and the normalized degree heterogeneity, Δ , of each graph are shown in the subcaptions.

First, Figure 2 provides an intuitive illustration of the kinetic transitions accessible to each GB. A discrete set of transitions are accessible to each GB which lead to a final structure that is either locally perturbed from the ground state or structurally identical to the ground state but atomically distinct. For both of the $\Sigma 5$ GBs, locally perturbed transitions disrupted the order in the plane of the GB and used the GB free volume to accommodate the disturbance. However, for the $\Sigma 3$ (111) GB, for which there is no excess free volume in the GB, the perturbation was out of the plane of the GB and resembled the formation of a Frenkel pair, which is why these transitions are so much higher in energy than those in the two $\Sigma 5$ GBs. Additionally, it can be seen from Figure 2 that the transitions with activation energy less than 1.0 eV in the $\Sigma 5$ (130) GB have very low energy barriers for the reverse process (0.04–0.08 eV). These transitions will be frequent, but primarily transient as the reverse transition energy barrier is so low. Conversely, similar low-energy transitions in the $\Sigma 5$ (210) GB have relatively higher barriers for the reverse process (0.1–0.25 eV), so it is expected that these low energy transitions will have a greater impact on the kinetic behavior of this GB.

Another interesting feature of these energy landscapes is that in all three cases, “symmetric” transitions were found that returned the GB to a ground state configuration, but one distinct from the initial state; the lowest energy symmetric transition for each GB is designated by black curved arrows in Figure 2. For the $\Sigma 5$ GBs, these events correspond to the shear sliding of the two grains past one another along the plane of the GB. The minimum activation energy for sliding for the $\Sigma 5$ (130) GB is 1.70 eV and is 2.10 eV for the $\Sigma 5$ (210) GB (in the absence of biasing stress, which could lower this value). This disparity is particularly noteworthy as the ground state energies of these two GBs differ by only about 5% and they have the same misorientation. Only the plane inclination of these boundaries is different, and whereas the plane has little effect on the GB energy, it has a remarkable effect on the

kinetic properties. If we consider the symmetric transitions for these two GBs at 200 °C, transition state theory would suggest that sliding in the $\Sigma 5$ (210) GB would be 4 orders of magnitude slower (i.e. 10^4 , with $E_a = 0.40$ eV, the difference in activation energies, T , the temperature, and k_B , Boltzmann's constant). Similarly, the relative sliding rates would be expected to differ by more than 6 orders of magnitude at room temperature.

Another noteworthy result from Figure 2 is that the lowest energy transition observed for the $\Sigma 3$ (111) coherent twin is ~ 6 times higher than either of the $\Sigma 5$ GBs. The symmetric transition in the $\Sigma 3$ (111) GB does not lead to macroscopic sliding, but rather consists of the local interchange of several atoms in the GB plane without sliding. Nevertheless, if we follow the kinetic analysis above for $T = 200$ °C, we find the rate of the symmetric transition in the $\Sigma 3$ (111) GB is expected to be 27 orders of magnitude slower than in the $\Sigma 5$ (130) GB and 23 orders of magnitude slower than in the $\Sigma 5$ (210) GB. Although the much lower energy of the coherent twin is its most well-known distinguishing feature (roughly 0.5% of the energy of the $\Sigma 5$ GBs), we view the very dramatic difference in the energy landscape and its effect on kinetic properties as being of primary importance.

The graphs in Figure 2 offer a unique description for the energy landscape about the minima of each GB; they can be regarded as kinetic fingerprints for the GBs they correspond to, and their properties as graphs may also be worthy of analysis. In an initial characterization of these graphs, we consider the largest eigenvalue of the adjacency matrix, λ , and the normalized degree heterogeneity, Δ , of each graph (unweighted and undirected in this analysis), as shown in the subcaptions of Figure 2. λ , also called the spectral radius, is important in calculating graph invariants and scales with network size; it is largest for the $\Sigma 5$ (210) GB and decreases slightly for the $\Sigma 5$ (130) GB and again for the $\Sigma 3$ (111) GB. The degree heterogeneity, Δ , is a metric that varies from zero, for a regular graph, to one, for a star graph, and is calculated by normalizing the Randić index [29]. It is largest for the $\Sigma 3$ (111) GB and is very similar for the two $\Sigma 5$ GBs. Together, these metrics indicate that the energy landscape networks for the $\Sigma 5$ GBs are larger and more regular than the network of the $\Sigma 3$ (111) GB, features which may correlate with the formation of complex dynamic GB structures during GB evolution.

In summary, the activation-relaxation technique has been employed to determine a first view of grain boundary energy landscapes in fcc copper. Each GB has a characteristic energy landscape with a unique, relatively small set of transitions available to it. We suggest that this energy landscape, rather than absolute energy, will play a primary role in governing GB properties. For the few select coincidence boundaries examined here, we have found activation energy differences for symmetric transitions ranging from 0.40 to 2.56 eV with GB plane and misorientation, which corresponds to differences in kinetic activation rates of up to 27 orders of magnitude at 200° C.

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