Supporting Information

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Quantized Grain Boundary States Promote Nanoparticle Alignment During Imperfect Oriented Attachment

Andrew P. Lange, Amit Samanta, Tammy Y. Olson, and Selim Elhadj*
Supplementary Materials for

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A.P. Lange, A. Samanta, T.Y. Olson, S. Elhadj*

Correspondence to: *elhadj2@llnl.gov

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Extended Materials and Methods

Calculation of melting point for nanoparticle sintering mechanism map (Fig. 4)

The melting point of metal nanoparticles decreases with particle size. To calculate the melting point for Fig. 4, the string method\textsuperscript{[64]} in the space of collective variables was used. To this end, the bond orientation order parameter\textsuperscript{[65-67]} $Q_i$, $i = 6, 4$, was used which is commonly utilized to identify and distinguish common crystal phases - bcc, fcc, hcp, simple cubic, etc. The global order parameters used as collective variables in the study took the form:

$$Q_i = \left[ \frac{4\pi}{2l + 1} \sum_{m=-l}^{l} |Q_{lm}|^2 \right]^{1/2}, \quad Q_{lm} = \frac{1}{N} \sum_{b=1}^{N_b} f_c(r_b)Y_{lm}(\hat{r}_b).$$

Here, $N_b$ is the total number of atom pairs separated by a distance $r_{\text{max}}$ and $N$ is the total number of atoms. $Y_{lm}$ are the spherical harmonics, $\hat{r}_b$ is the unit vector along the direction $r_b$. While the normalization factor in Eq. 2 should be $N_b$, the quantity $N_b$ varies as the structure changes, which will cause discontinuities in the function $Q_i$. For this reason, $N$ was chosen as the normalization factor for convenience, however, in principle, it can be any fixed number. $f_c(r)$ is a smooth switching function defined in Ref.\textsuperscript{[66]} that is used to remove discontinuities in the original definition of the Steinhardt parameters\textsuperscript{[65]} that occur when each bond is switched off at a specific radius $r_{\text{max}}$. The value of $r_{\text{max}}$ was determined from the end of the first peak in the radial distribution function. Copper nanoparticles were used as a representative fcc metal for our analysis. The interatomic interactions were modeled using the same EAM potential mentioned above developed by Mishin et al.\textsuperscript{[55]} The details of the procedure used to calculate the melting temperature is described below:

(i) The AFED sampling technique\textsuperscript{[68,69]} was used to obtain trajectory joining the solid and liquid basins. The AFED equations of motion were integrated using the algorithm of Yu et al.\textsuperscript{[70]}, and the two temperatures were maintained using the generalized Gaussian moment thermostating scheme of Liu and Tuckerman\textsuperscript{[69]}. The values of the coupling constants for collective variables $Q_6$ and $Q_4$ were set to $1 \times 10^8$ K, $2 \times 10^8$ K, respectively, and the temperature of the coarse-grained
variables was set to $T_s = 1 \times 10^7$ K. The time-constants for the thermostats on the atoms and the $s$ variables were set to 100 and 3500 time-steps, respectively.

(iii) Thirty structures were selected from the sampling trajectory to obtain an initial guess path joining the solid and liquid basins.

(iii) Restrained molecular dynamics simulations were performed by keeping the values of the collective variables fixed.

(iv) These simulations were analyzed and forces acting on the collective variables were obtained as detailed in Ref. [70] and free energy profile along the path was obtained.

(v) The path in the collective variable space was evolved using a dimensionless time-step of 0.005.

(vi) Steps (iii)-(v) were repeated until convergence.

(vii) Simulations were performed at different temperatures and melting point of 1210 K was identified as the temperature at which the solid and liquid basins have same free energy.

Supplementary Figures
Movie S1

Movie showing molecular dynamics simulation of 10 initially misoriented gold nanoparticles during aggregation. Salient features are called out during movie which show dislocation-mediated alignment process of small particles on perimeter then slow disintegration of grain boundary in interior of aggregate. Simulation run using potential developed by Ackland et al.\textsuperscript{[50]}

Additional plots of non-twin boundaries (NTBs) and twin boundaries (TBs) as a function of sintering are provided in Fig. S2. Similar trends observed in all simulations:

- The number of NTBs rapidly decreased during the early part of the simulation
- The number of NTBs then slowly decreased as more stable GBs were removed
- The number of TBs rapidly increased due to the formation of twins from surface shearing events and the evolution of NTBs to TBs
- The number of TBs then slowly decreased
- The final structures generally had GB junctions with multiple stable TBs and at least one stable NTB
Supplementary figure S3 shows the attachment and GB disintegration process in greater detail for the particles marked A and B in Fig. 1A. As the \{111\} planes of the two particles bond together the smaller particle rotates relative to the larger particle. During this process, local atomic shuffling at the interface facilitates the formation of edge dislocations with Burgers vectors of a[111]. The edge dislocations then climbed as the GB continued to form. Finally, the top particle sheared which left a TB at the interface. This presumably occurred by the dissociation and glide of GB dislocations to the surface.
**Fig. S3.**

Intermediate structures during the coalescence of two nanoparticles marked A and B in Fig. 2A. Local atomic arrangement at the interface aided by surface diffusion led to the formation of a well-defined
GB, shown in (c), consisting of three dislocations. Since lattice planes in the GB contained tens of atoms, diffusion and local atomic shuffling helped these dislocations climb, leading to the structure in (d). Subsequently, the dislocations glided through the top particle (particle B) and exited at the surface as shown in (e).

Beam heating of small, 5-20 nm particles was carried using citrate-coated particles provided by BBI Solutions as well as synthesized in-house. These particles were heavily twinned, which made it difficult to track grain evolution. However, two notable observations were made during these experiments. The first was the relative rotation between two particles after attachment which led to grain boundary disintegration. Particle rotation after attachment was observed previously, but in this case, the grain boundary was eliminated which necessitates a concurrent evolution of the grain boundary character.

In movie S4, the lattice planes at the interface of the two, initially misoriented gold nanoparticles became aligned within seconds. The particles rotated after neck formation, which was followed by neck growth, then shape evolution. The neck grew until its width was roughly equal to the diameter of the smaller of the two particles. While neck growth was completed within minutes, subsequent shape evolution continued for a few more minutes. These observations qualitatively illustrate the sequence and relative time scales of these different aggregation processes under beam-heating conditions. Specifically, the alignment of lattice planes occurs during neck growth followed by shape evolution which is thought to be rate-limited by surface diffusion in nanoparticle systems. Another example of particle alignment during neck growth is shown in movie S5. In this case, crystallographic alignment across the interface is easier to discern.
Movie S4.

Movie showing 2-particle coalescence during in-situ TEM electron-beam heating experiment. This observation highlights the relative timescales of the coalescence process where particle rotation occurs during attachment, followed by neck growth, then finally shape evolution.
Movie S5.

Movie showing 2-particle coalescence during in-situ TEM electron-beam heating experiment. This observation highlights particle rotation during neck growth. As the neck grows, evident from successive lines at interface, the particle on the right rotates, evident from successive traces of atomic planes in left-hand particle.
Kinetics of surface shearing

The energy barriers for shearing small surface islands, described in the methods section and shown in Fig. S6, are less than 1 eV which is significantly lower than barriers to nucleate dislocations in the bulk shown in Fig. S7. This suggests that such events can happen frequently even at room temperature, especially if strain is present near grain boundaries due to surface tension. For example, using the Arrhenius relationship \( f = f_0 \exp(E/k_B T) \), taking \( f_0 = 1 \times 10^{13} \text{ sec}^{-1} \) (rough oscillation frequency of surface atoms in potential well), \( T = 300 \text{ K} \), \( k_B = 8.617 \times 10^{-5} \), \( E = 0.75 \text{ eV} \), it is found \( f \sim 2.5 \text{ sec}^{-1} \). If the barrier is reduced to 0.5 eV, the frequency of surface shearing is found to be \( \sim 4 \times 10^4 \text{ sec}^{-1} \). At higher temperatures (~1000 K), the frequency of such events increases to \( \sim 1 \times 10^9 \text{ sec}^{-1} \), comparable to the timescale of molecular dynamics simulations. The calculations shown in Fig. S6 represent only a couple ways in which dislocations can nucleate from the surface of a nanoparticle. A movie showing only atoms with hcp coordination during a simulation of a 5 nm particle annealed at 1100 K is provided in movie S8. This visualization scheme was used as bulk atoms have fcc coordination while hcp-coordinated atoms only arise in the plane below sheared domains on the surface. It is clear from this video that the lifetime of stacking faults near the surface varied considerably for the Ackland MD potential; some remain for hundreds of picoseconds, while others disappear after less than ten picoseconds.
(a) shows the energy barrier to shear two rows of atoms (containing 5 atoms in total) in a 12 atom island (marked Path 1) is 0.70 eV. The blue curve (marked Path 2) shows the energy barrier to further shear the 5 atoms further away from the remaining 7 atoms is 1.03 eV. (b) shows the saddle point (i.e. the transition state) along Path 1. (c) shows the energy barrier to shear one island (marked Path 3) and top three layers (marked Path 4) in the Cu nanoparticle shown in (d).
Fig. S7.

Shown here is the activation energy for homogeneous nucleation of a dislocation in bulk Cu as a function of the shear stress resolved on a (111) plane and along [112] direction.
Movie S8.

Movie of molecular dynamics simulations over 1 nanosecond showing a single particle annealed at 1100 K. Only atoms with hcp coordination are shown corresponding to layers under sheared surface domains and each frame in the video corresponds to a snapshot after 100 femtoseconds. It is clear from this video that the surface of the spherical particles here, under the chosen MD potential, are very active providing a rich source and sink of particle dislocations across the neck-groove in agglomerated particles.
Grain boundary potential energy surfaces

The grain boundary energy profiles shown in Fig. 2(b) and (c) were calculated at fixed y and z, y = z = 0, with x being the direction normal to the grain boundary. In the case of 10 nm particles, this position corresponded to a grain boundary energy minimum (Fig. 2(g)). However, this position did not correspond to a minimum in the case of 5 nm particles as shown in Fig. 2F.

Many GB energy minima with respect to lateral translations within the GB plane are evident in Fig. 2(f) and (g). These minima are associated with low energy dislocation network configurations. The potential energy surfaces differed significantly for systems with the same misorientation but different particle size. This indicates that particle size influences the way dislocation networks “tile” the grain boundary. The potential energy surfaces for systems with the same particle size but different misorientations had the same overall pattern, or symmetry, while the number of minima increased for higher misorientation angles. Thus, particle misorientation determines the dislocation separation while translations in the grain boundary plane determine how the dislocation network sits on the grain boundary. The latter is expected to be more significant for smaller particles for which a larger fraction of the grain boundary is near the grain boundary perimeter.

Model to describe discrete grain boundary energy levels

The discrete nature of grain boundary energy profiles can also be explained by considering the GB schematic below. Imagine the distance between dislocations corresponds to that determined by the Read-Shockley model for a given misorientation (blue lines in figure below).
If the misorientation increases, the separation between dislocation segments (in an infinite boundary) should decrease as shown by the dotted black lines. Although the total dislocation length, and therefore grain boundary energy, will increase slightly in this case due to the curvature of the boundary perimeter, it will increase much more abruptly when the dislocation separation is such that new additional dislocation line segments are introduced at the edges of the GB. It should be noted this simple model does not account for dislocation interactions which will play a more dominant role as the misorientation angle increases and the separation decreases. However, it highlights one cause of the observed discretization. When particle diameters are very small (say, 2.5 nm), the number of dislocations at the GB, even at large misorientation angles, may only equal one or two. In calculations of GB energy with twist misorientation, it was found that particles rotated during minimization so that there is only one stable dislocation array (or GB structure) corresponding to the addition of each new dislocation line segment. This effectively eliminates the continuity in GB energy with misorientation as results in the formation of one stable misorientation “state” for each misorientation “band”, or range of angles.

If translations within the GB plane are also considered, the number of states for a given misorientation angle would increase. Changes in lateral translations of particles are equivalent to changes in the way the dislocation arrays “tile” the GB. Therefore, for a given misorientation, there should be one (or more) dislocation configurations which correspond to minimum energy states (dictated by the way the dislocations intersect the GB perimeter).

The total energy of dislocations present at the interface between two nanoparticles consists of four different contributions:

(i) self-energy of all dislocations in the grain boundary,

(ii) energy due to interaction between dislocations in the grain boundary,
(iii) energy due to interaction between dislocations and their surface images, and
(iv) energy of dislocation junctions.

The self-energy of a straight dislocation line (ignoring the end effects) is \( E_s = 0.5 \mu b^2 L \), where 
\( \mu \) is the shear modulus on the glide plane and along the Burgers vector direction, \( b \) is the magnitude of the Burgers vector of the dislocation and \( L \) is the length of the dislocation. The interaction energy between two dislocations is \( E_i = \mu b^2 L \log (r/r_o) \). Here, \( r \ll L \) is the separation between dislocations and \( r_o \) is the core-cutoff radius. The interaction between two parallel dislocations with same Burgers vector is repulsive while the interaction between a dislocation and its surface image is attractive. Within the Read-Shockley theory, the separation between parallel dislocations in a grain boundary with twist misorientation \( \theta \) is \( \delta \theta = b/2 \sin(\theta/2) \). For small \( \theta \), \( 2 \sin(\theta/2) \sim \theta \) and \( \delta \theta = b/\theta \). A calculation for the total energy of a GB dislocation within a GB of radius \( R \), considering only (i) and assuming a dislocation separation predicted by Read-Shockley about the GB center, is shown in Fig. S9. This is accurate for small angles when \( r/r_o \) is much greater than 1 (i.e. \( r/r_o \gg 1 \)) as \( \log (r/r_o) \) changes very slowly with changes in \( \theta \) and can be approximated to be a constant, eliminating the influence of (ii) and (iii). Figure S9 shows that the self-energy of dislocations vs misorientation agrees well with the simulation results for low angle grain boundaries (< 15 degrees) when the separation between dislocations is large. For high misorientation angles, dislocation separation is small and which can lead to the formation of alternative high angle GB structures, such as coincident site lattices. This reduces the overall energy of the GB (as seen in Fig. S9 at larger misorientations), however the discrete nature of misorientation states was still observed for these more complex GB structures. It should be emphasized again here that the GB energy for the MD calculations is plotted against the starting misorientation between particles in Fig. S9. After minimization, the relative misorientation was always different (e.g. going to 0° for all misorientations below 5°). Therefore, a more accurate representation of this data would be discrete lines similar to what was plotted in Figs. 2(b), (c), and (h).
Fig. S9

The total self-energy of dislocations in a model symmetric tilt grain boundary in a nanoparticle shows discrete jumps as the misorientation changes.
The 4 clusters monitored during the heating experiments are labeled in Fig. S11(A). Additional low magnification images of the clusters after the first and second heating cycles are provided in Figs. S11 (B), (C), respectively. Higher magnification images of the two clusters not discussed in the manuscript, clusters 1 and 2, are shown in Fig. S12. The clusters are shown both before annealing (left) and after both annealing cycles (right).

The two most remarkable results from the holder heating experiments were the formation of a nearly single crystal agglomerate (cluster 3) and the presence of a remnant twin after a particle rotated to align itself with a neighboring grain. These two observations are highlighted in Fig. 1 of the manuscript.
**Fig. S10.**

Bright field TEM images of as-synthesized nanoparticles after drop-casting (A and B), and after drop casting followed by oxygen plasma cleaning for 15 seconds (C). Evidence of residual carbon on particle clusters evident in energy filtered TEM image tuned to the carbon K-edge in (D).
Particle clusters observed during two annealing cycles. Nanoparticles in clusters, labeled 1-4 in (A), were in contact but misoriented prior to annealing. Nanoparticles in each cluster underwent densification and alignment during \(\sim 1.5\) hour anneal cycle at \(450\) °C (B) and during \(\sim 1\) hour anneal cycle at \(570\) °C (C). The actual temperature experienced by the clusters depends on its proximity to the SiNx grid. So, it is possible that some of the clusters were at a much lower physical temperature and hence received only a small fraction of the supplied thermal energy.
Figure S12.

Particle cluster 1 (top) and 2 (bottom), as labeled in Fig. S11, before (left) and after (right) heating at \( \sim 450 \, ^\circ\text{C} \) for \( \sim 1.5 \) hours and \( \sim 570 \, ^\circ\text{C} \) for \( \sim 1 \) hour. The actual temperature experienced by the clusters depends on its proximity to the SiN\(_x\) grid. So, it is possible that some of the clusters were at a much lower physical temperature and hence received only a small fraction of the total supplied thermal energy.
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