



Editor's Choice

Bridging time-scales: Grain boundary sliding constitutive law from atomistics

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ABSTRACT

Grain boundary sliding is the key deformation and damage mechanism for high temperature deformation of crystalline materials impacting, thus, applications ranging from nuclear reactors to aircrafts. Despite decades of research—theoretical and experimental—a definitive atomistic understanding of this phenomenon has been elusive. The primary bottleneck is the fact that conventional molecular dynamics can only address pico-to-nano seconds of material physics while the characteristic relaxation times for creep phenomena (including grain boundary sliding) are several orders of magnitude slower. In this letter, we use a fresh approach based on a recently developed potential energy surface sampling method that allows us to bridge long time scales and, for the first time, develop a physically reasonable constitutive law. Our results show a dramatic improvement over what can be gleaned from conventional molecular dynamics and provide insights on the relative merits of existing theories of grain boundary sliding. Our simulations (based on a prototypical metal, Al) answer important questions such as (i) is there a threshold stress for grain boundary sliding?, (ii) what is the form of constitutive law for grain boundary sliding? and others.

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At low enough temperatures—low compared to half the homologous temperature—crystalline materials exhibit irrecoverable deformation provided the imposed mechanical stresses exceed the so-called yield threshold [1]. For all practical purposes, this deformation is considered to occur instantaneously. At high temperatures, however, even at stresses below the yield stress, irrecoverable deformation occurs gradually over an extended period of time. At the micro scale, this time-dependent deformation is predicated on several viscous processes such as grain boundary and volume diffusion, grain boundary sliding, dislocation glide-climb, void nucleation, void growth and others [2–5]. These micro mechanisms exhibit characteristic relaxation times that range from seconds to years (depending on the level of applied stress and temperature). This “creeping” deformation behavior is the predominant cause of failure in materials that are subject to high temperature environment: ice glaciers, nuclear reactors, air crafts, electronics among others [6–8]. For example, Sn–Pb alloys (solders) are extensively used in electronics and the melting temperature of this class of alloys is low enough that at even room

temperature, creep eventually (in conjunction with other factors) leads to failure [8].

It is now well recognized that grain boundary sliding (GBS) is a key deformation and damage mechanism in creep [9]. Grain boundary sliding is the phenomenon of relative sliding of crystalline interfaces or grains in a slow viscous manner upon application of a macroscopic shear stress. The sliding is accommodated by grain boundary diffusion, volume diffusion and in the case of metals, dislocation glide-climb within the adjacent grains (i.e. grain plasticity).

Although work on grain boundary sliding dates back more than sixty years, some of the first quantitative studies on this are those by Raj and Ashby [11] who presented an analytical study of this phenomenon based on accommodation by grain boundary and volume diffusion. Raj and Ashby's work – the most widely used paradigm of this phenomenon – proposed a linear dependence between the imposed shear stress on the grain boundary and the consequent sliding rate; and an absence of any threshold stress. Extensive theoretical and experimental literature now exists which outline a number of (sometimes) contradictory observations. For example, Chauhan et al. [12] studied the problem from an experimental viewpoint and qualitatively observed a threshold stress for grain boundary sliding in ultra-fine grained Al alloy (300 nm grain

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size). The proposed value of threshold was found to be about 10 MPa (23 times lower than the experimentally determined yield stress). For further details, the reader is referred to the review article by Langdon and references therein [10]. Despite the extensive focus on this phenomenon, several issues still remain open, or at least, relatively unsettled, e.g. (i) in the case of diffusion dominated creep, is the stress-sliding rate relation linear, as predicted by Raj and Ashby [11]? (ii) is there a threshold stress for grain boundary sliding? (iii) what is the qualitative form of the constitutive law for grain boundary sliding?

Given the advent of computational power and the concomitant development in atomistic simulation methods, the latter is a logical route to answer the aforementioned questions and in general to obtain insights into the atomistics of grain boundary sliding. To that end, Qi and Krajewski [13], in a nice work, carried out a molecular dynamics study of a shear test on an Al bicrystal. This study was carried out at 750 K to investigate the effect of applied force and grain boundary mis-orientation on sliding. A linear relationship between constant sliding velocity and applied stress was observed, although the linear fit had positive intercepts indicating a critical value of applied stress below which no sliding was perceived. In other words, their work appears to confirm the linear relation between stress-sliding albeit a sharp threshold stress is predicted—around 0.2 GPa for the material simulated, which is about 10 times lower than the yield strength for the 6 nm grain size used in the simulation [14].

While the work by Qi and Krajewski provided important insights, there is a fundamental limitation of classical molecular dynamics methodology that has prompted us to reexamine this problem with alternative approaches. As is well known, classical molecular dynamics can only handle time-scales of the order of a few pico to nano-seconds. While this is sufficient for several classes of problems, it is a serious deficiency when it comes to the study of creep related phenomena, where the relaxation times are in seconds and sometimes years. In other words, in classical molecular dynamics, the applied strain rate is several orders of magnitude faster than typical grain boundary sliding rates thus preventing conventional molecular dynamics to truly capture the time-dependent nature of the irreversible creep deformation process.

In this communication, we employ a sequence of methods to extract a realistic constitutive law for grain boundary sliding and answer some of the questions raised in the preceding paragraphs. We choose Al bi-crystal as a model material system albeit our approach can be repeated for any material. One motivation for choosing this particular system is that conventional molecular dynamics based results by Qi and Krajewski [13] are already available, thus facilitating a comparison. Our work is paved by the recent success of the potential energy surface sampling approach (the so-called autonomous basin climbing algorithm [15]). Yip and co-workers have confirmed its applications to several time-dependent problems such as viscosity of supercooled liquids, creep relaxation of metals, and void nucleation rates [16–18]. We note here the recent work by Pattamatta et al. [19] that also shows promise for time-scaling applications.

The simulation layout is as follows (consistent with [13]): An Al bi-crystal was generated by juxtaposing two grains separated initially by a 3 Å gap. The two grains, approximately 60 Å × 40 Å × 20 Å in dimension each, have parallel $\langle 110 \rangle$ axis about which a 25.2° miss-orientation angle is introduced. The simulation cell is periodic along y and z directions to make an infinite grain boundary surface, while non-periodicity in x direction is artificially created by adding a 30 Å vacuum to the two extremes of the bi-crystal (see Fig. 1).

The system was then equilibrated at 300 K under NPT conditions to relax the stresses arising due of the incompatibility of atomic arrangement along the interface. During the course of the

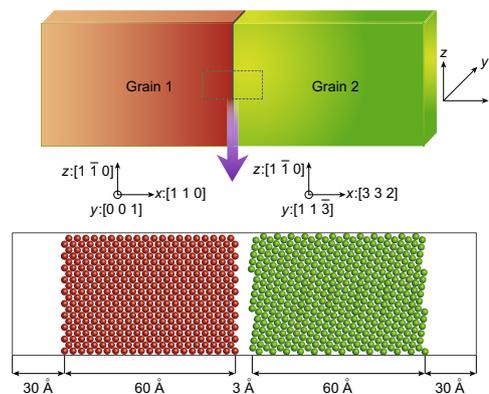


Fig. 1. Orientations of the grains used in the present analysis. Schematics show the convention used to rotate the grain with respect to the other one.

simulation, the interfacial gap between the two grains gets filled to form the grain boundary. The correctness of the GB formation was confirmed by calculating the grain boundary energy (0.58 J/m²), which compares well with Qi et al. [13] (0.548 J/m²). Our subsequent simulations were carried out at 750 K which is 0.8 homologous temperature; thus well into creep deformation regime. Accordingly, the temperature of the bi-crystal was raised slowly from 300 K to 750 K and subsequently relaxed at 750 K for 50 ps under NPT conditions. The whole structure is subsequently minimized using conjugate gradient iterations. The initial structure of grain boundary interface before commencement of the sliding (computer) experiment is shown in Fig. 2. The GBS can in general be initiated by a strain [17,20] or stress controlled process. Although controlling the strain is a commonly used approach in atomistics, to us it is not the most appropriate to study grain boundary sliding. A strain-controlled simulation would be more appropriate to study creep-stress relaxation, however, sliding (as understood in most creep experiments) appears most clearly via an applied resolved shear stress. Under the application of a shear stress along the grain boundary, we sample the potential energy surface using the Autonomous Basin Climb (ABC) algorithm. This algorithm developed by Kushima and Yip et al. [15,17,16,21] is a modified version of meta-dynamics introduced by Laio and Parinello [22]. The algorithm outputs a list of stable configurations that the system visits successively under given boundary conditions (e.g. an imposed shear stress in the present case). The algorithm moves the system from one energy basin to the other through a series of small activation and relaxation steps. The process starts from a minimum energy configuration, where an activation is introduced by adding a 3 N gaussian penalty function $\Phi_p^k(r)$, centered at the minimum configuration, to the total potential energy of the system:

$$\Phi_p^k(r) = W \exp \left[-\frac{(r - r_{min}^k)^2}{2\sigma^2} \right] \quad (1)$$

where r and r_{min}^k are the atomic configuration at any point and at the k th minimized configuration. The parameters W and σ are constants and determine, respectively, the amplitude (in eV) and width (in \AA^2) of the gaussian penalty function. The choice of these parameters is crucial, and should be carefully adjusted in accordance with the physics of the problem under consideration. For instance, a small W can lead the system to remain in the same well for thousands of iterations, while a large W can lead the system to overcome small barriers without “seeing” them. Once the penalty function is added, the minimum configuration transforms into a saddle point because of the penalty energy (Fig. 3), the system is again relaxed and an activation energy centered at current position is added. This process

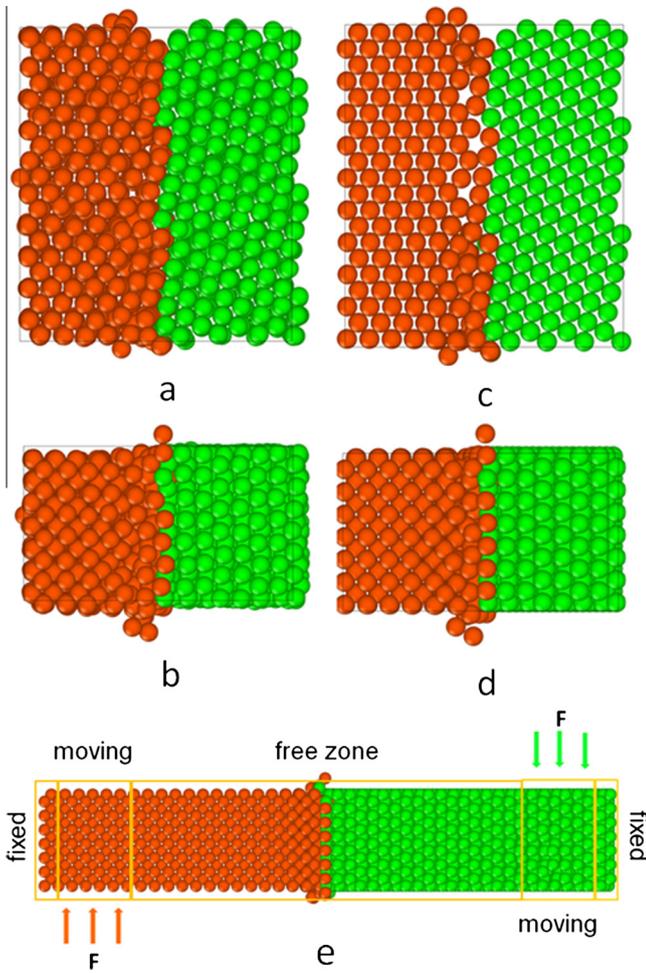


Fig. 2. Aluminum bicrystal with a misorientation of 25.2° , relaxed under constant stress and temperature at 750 K and minimized subsequently using the conjugate gradient approach: (a) x - y projection of GB region relaxed at 750 K under NPT condition (b) x - z projection of GB region relaxed at 750 K under NPT (c) x - y projection of GB region after minimization (d) x - z projection of bicrystal after minimization. (e) The projection of the bicrystal on x - z plane shows the boundary conditions for the present simulation.

continues till the accumulation of the penalty energies is enough to coax the system to cross the lowest neighbor barrier and reach a new basin. The energy penalty function added in each step is not removed from the energy during this potential energy topography exploration to ensure that the system is prevented from reverting back to a previous energy minimum. It is worthwhile mentioning here that Park and co-workers [23,24] have recently modified the ABC approach so that the system adapts the penalty function parameters through a *self-learning* process. However, in these works they do not employ KMC to circumvent the artifact that the ABC algorithm finds the saddle points in a sequence that is not physically relevant.

To carry out the ABC simulation on the Aluminum bi-crystal, we have divided the sample into three zones. A fixed zone consisting of 140 atoms on each extreme of the model along x direction, where atoms are only allowed to move in the shear direction z , (Fig. 2(e)). A moving zone consisting of 700 atoms adjacent to the fixed zone in each grain, where a force f is applied on each atom, but in opposite direction for two grains to produce a shear effect on the grain boundary. The remaining 4084 atoms in both the grains makeup the free zone, where no constraints are imposed. The corresponding shear stress along the grain boundary is obtained by Eq. (2).

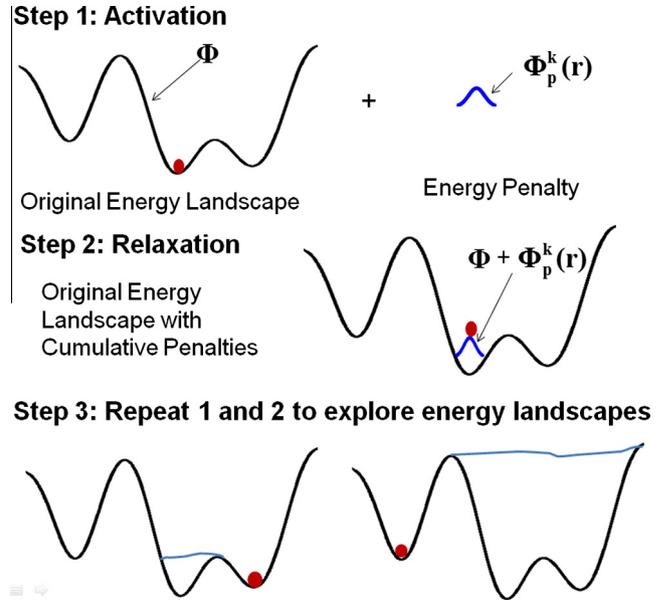


Fig. 3. The Autonomous Basin Climbing approach (Adapted from [15]): an energy minimized initial structure is activated by adding a gaussian penalty energy $\Phi_p^k(r)$ (centered at the original configuration) on the potential energy landscape Φ and followed by subsequent relaxation, which pushes the system to climb up the basin to a higher energy configuration. Repeated activation by penalty energy and relaxation drives the system to explore new minima in adjacent basins.

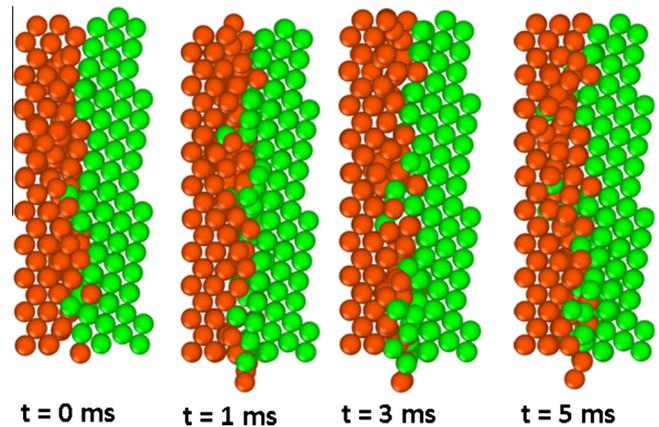


Fig. 4. At 173 MPa, a plot of grain boundary diffusion at different instants of time.

$$\tau = \frac{f \times n}{A} \quad (2)$$

where τ is the shear stress, f is the applied force per atom, and n is then number of atoms in the moving zone. The parameters used for the simulations are $W = 0.5$ and $\sigma^2 = 0.1$.

At an applied stress of 170 MPa, the mechanism for accommodation of grain boundary sliding appears to be grain boundary diffusion at 750 K as evident from the atomistic pictures of the grain boundary interface as shown in Fig. 4.

We observe no evidence of dislocation based accommodation and this may be anticipated given the extremely small sizes of the grains. The used ABC algorithm is combined with two other algorithms to relax some of its assumptions and to increase its accuracy. On the one hand, since the penalty energies added to the system are cumulative, the potential topography might be biased in some areas, which can lead to a lack of accuracy in the configurations of the obtained minima. The obtained barriers are in general over estimated because of the nature of the algorithm.

To increase the accuracy of the transitions barriers, the structures of the bi-crystal corresponding to the obtained minima are extracted and then minimized individually using conjugate gradient iteration technique. Nudged Elastic Band (NEB) [25] simulation between these minima is performed with 24 replicas between each of the two minima. The energy barriers are then obtained accurately. Unlike the ABC method, where the output is in sequential form, the output of the NEB simulation is a matrix containing the exact barrier between each two explored minima regardless of their order of appearance.

The second algorithm used in accordance with the ABC is Kinetic Monte Carlo (KMC) [26]. The sequential order of the visited minima does not mimic the real physics of the problem and does overrule the Boltzmann distribution for the jump probabilities. In fact, the transition from a potential well to the other is probabilistic: The system might go one step back or oscillate between two or more states before moving to the next configuration if the energy barriers dictate so.

Subsequent to the application of KMC, the time corresponding to each transition event is calculated using the harmonic transition state theory (HTST) Eq. (3) [27]

$$t_{(A \rightarrow B)} = \left(\nu \exp \left[-\frac{\Delta E_{(A \rightarrow B)}}{K_B T} \right] \right)^{-1} \quad (3)$$

where ΔE is the energy barrier between A and B , ν is the characteristic frequency factor approximated to 10^{13} Hz, T is temperature, and K_B is the Boltzmanns Constant. Having the transition time needed to cross each barrier on the path (Fig. 7), and the sliding distance at each configuration (Fig. 6) the sliding rate can be obtained by mean of a linear interpolation of the time dependent sliding (Fig. 8).

The points i and j correspond to the same pair of minima in all the plots. Fig. 6 shows non-uniform sliding for different transitions and this is due to non-continuous sliding of the grain boundary. Larger obstacles can make the system deform slower over many transitions and there may be “sudden” sliding after the obstacle is overcome.

In the current study a comparison between our constitutive equation and that found by Qi et al. [13] is made in Fig. 9.

Based on the obtained numerical results shown in Fig. 9, we find that a hyperbolic sine function bests fits the results. The resulting constitutive equation relating the dependence of sliding rate on applied stress is given in Eq. (4).

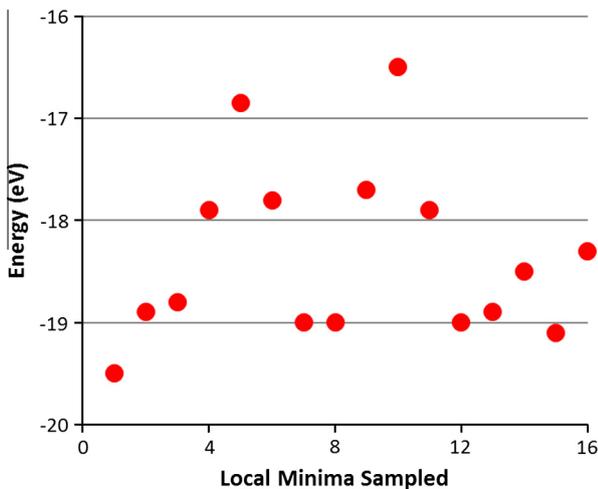


Fig. 5. For 130 MPa and 0.3 Å displacement: energy of transition between local minima obtained from NEB.

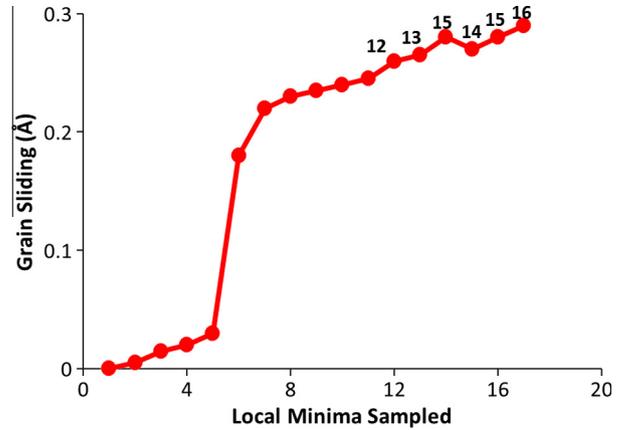


Fig. 6. For 130 MPa and 0.3 Å displacement: GB sliding for every transition between successive minima.

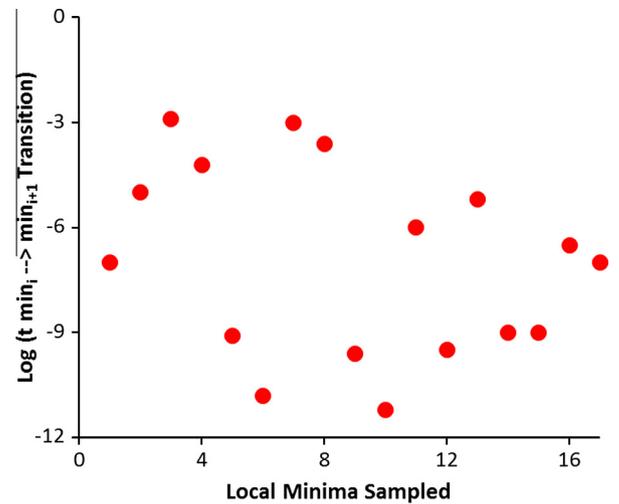


Fig. 7. For 130 MPa and 0.3 Å displacement: time for barrier transition is calculated using Eq. (3). Energy from Fig. 5 is used in the calculation of time by the Harmonic Transition State Theory.

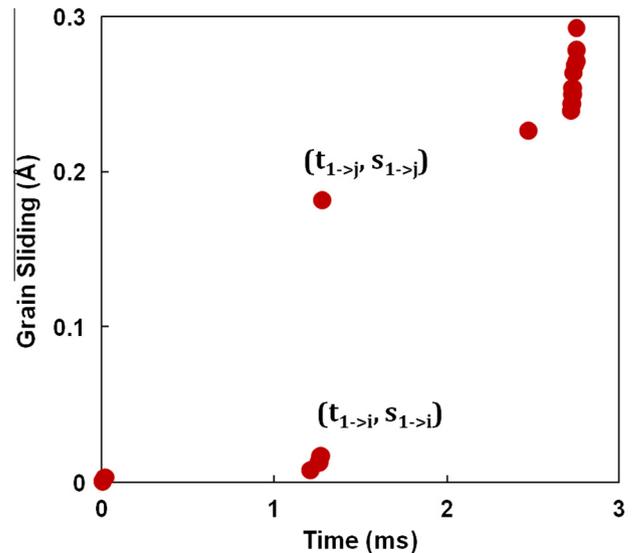


Fig. 8. A plot of grain boundary displacement as a function of time: obtained by correlating sliding produced from Fig. 6 to time for transition from Fig. 7.

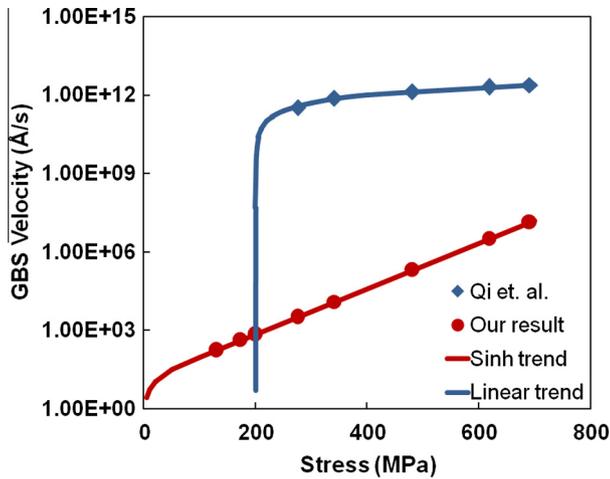


Fig. 9. GBS Constitutive Law (y-axis is in logarithmic scale): a plot of grain boundary velocity against corresponding applied shear stress. Our results are compared with the conventional molecular dynamics results of Qi and Krajewski [13].

$$\dot{\gamma} = C \sinh \left[\frac{A\tau}{\tau_{yield}} \right] \quad (4)$$

where $\dot{\gamma}$ is grain boundary velocity in $\text{\AA}/\text{s}$, and τ is the shear stress in MPa. Here 'A' is a material constant and τ_{yield} is a normalizing stress taken to be the yield strength of material for the simulated grain size (2 GPa). For the present case, we found $C = 27$ and $A = 40$. Fig. 9 suggests that a meaningful threshold does *not* exist for grain boundary sliding (at least in the present configuration). For getting an exact value of threshold stress ABC simulation needs to be done at much lower stresses which is not computationally expedient at this point. Nevertheless, given the trend, we propose that practically speaking, the threshold stress in this particular case is indeed negligible. Although the combination of the used algorithms (ABC, NEB, KMC and HTST) is surely an improvement against conventional MD, our results may be improved further. The accuracy of barrier estimation can be improved by using the finite temperature string method [28]. The assumptions inherent in simple harmonic

approximation for transition state theory may be relaxed as well [29]. However, for the specific purpose of this paper, where no complex dislocation motion or grain rotation is observed, we believe that, certainly qualitatively, our results are reasonable. Future work is anticipated that will employ some of these aforementioned refinements and investigate cases where dislocation accommodation is evident.

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