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Elucidating the atomistic mechanisms underpinning plasticity in Li-Si nano-structures

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Amorphous Lithium-Silicon (a-Li-Si), especially in nanostructure form, is an attractive high-capacity anode material for next-generation Li-ion batteries. During cycles of charging and discharging, a-Li-Si undergoes substantive inelastic deformation and exhibits micro-cracking. The mechanical response to repeated lithiation-delithiation eventually results in the loss of electrical contact and consequent decrease of capacity; thus underscoring the importance of studying the plasticity of a-Li-Si nanostructures. In recent years, a variety of phenomenological continuum theories have been introduced that purport to model plasticity and the electro-chemo-mechanical behavior of a-Li-Si. Unfortunately, the micro-mechanisms and atomistic considerations underlying plasticity in Li-Si material are not yet fully understood and this impedes the development of physics-based constitutive models. Conventional molecular dynamics, although extensively used to study this material, is grossly inadequate to resolve this matter. As is well known, conventional molecular dynamics simulations can only address phenomena with characteristic times scales of (at most) a microsecond. Accordingly, in such simulations, the mechanical behavior is deduced under conditions of very high strain rates (usually $10^8 s^{-1}$ or even higher). This limitation severely impacts a realistic assessment of rate-dependent effects. In this work, we attempt to circumvent the time-scale bottleneck of conventional molecular dynamics and provide novel insights into the mechanisms underpinning plastic deformation of Li-Si nanostructures. We utilize an approach that allows imposition of slow strain rates and involves the employment of a new and recently developed potential energy surface sampling method—the so-called autonomous basin climbing—to identify the local minima in the potential energy surface. Combined with other techniques, such as nudged elastic band, kinetic Monte Carlo and transition state theory, we assess the behavior of a-Li-Si nanostructures under tensile strain rates ranging from $10^3 s^{-1}$ to $10^8 s^{-1}$. We find significant differences in the deformation behavior across the strain rates and discover that the well-known shear transformation zones (widely discussed in the context of amorphous materials) are formed by a “diffusion-like” process. We identify the *rotation* of the shear transformation zone as a key dissipation mechanism.

I. INTRODUCTION

Rechargeable lithium-ion batteries find applications in portable electronics, electric vehicles and many other contexts where a compact energy storage system is required¹⁻³. Due to the critical role batteries are likely to play in the future energy storage needs, intense efforts are being dedicated to both understand the basic science underlying the pertinent materials as well to engineer higher energy density, improve safety, and prevent the progressive loss of capacity due to chemical and mechanical degradation⁴⁻⁷. Silicon is an important candidate material for anodes due to the potential of high specific charge capacity—more than ten times that of carbon based materials⁸. However, during the charging and discharging processes,

silicon electrodes experience remarkably large volumetric changes (as much as 300%, Fig. 1) and the concomitant stresses lead to nucleation of defects, and eventually, mechanical failure of the system⁹. As a result, the effective charge capacity often sharply reduces after just a few charging and discharging cycles¹⁰⁻¹².

The use of amorphous silicon (a-Si), instead of its crystalline counterpart, is considered to offer several advantages. Experiments have shown that the amorphous alloys tend to cycle better than the corresponding crystalline phases¹³⁻¹⁵. Crystalline Si, in fact, converts to amorphous Li-Si alloy phase during lithiation¹⁶⁻¹⁸. Finally, there is increasing evidence to indicate that the mechanical degradation of Si electrodes under electrochemical

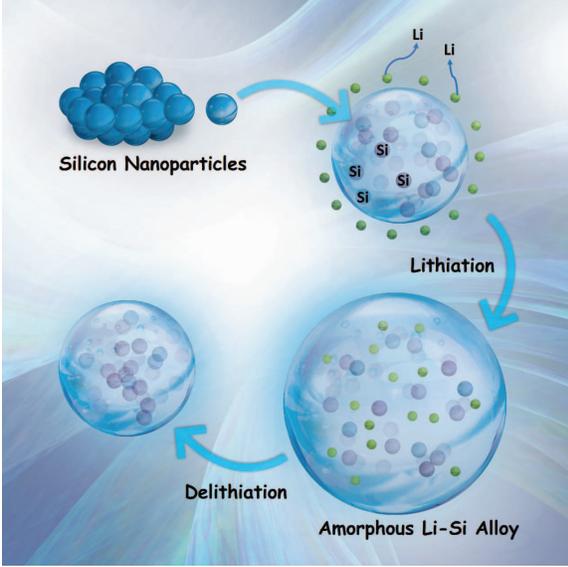


Figure 1. Schematic of the lithiation and delithiation processes in Si nanoparticles. Lithiation dramatically enlarges the volume of the nanoparticle and alters the position of the host Si atoms. During delithiation, while some of the deformation is reversed (elastic deformation), the original microstructure is irreversibly altered (plastic deformation).

cycling may be mitigated by reducing their feature size i.e. by using nanoscale configurations such as nanowires, nanoparticles among others^{5,19}. Accordingly, this work is focused on understanding the atomistic mechanisms underpinning plasticity in a-Li-Si *nanostuctures*.

Over the past decade or so, a variety of phenomenological (and increasingly sophisticated) continuum theories have been proposed to describe the elastic-plastic behavior of lithiated Si electrode^{11,20,21}. For example, earlier work by Sastry²² focussed on using linearized elasticity and simple thermodynamic considerations for the stress analysis of lithiated electrodes, while subsequent ones have addressed fracture^{23,24}, importance of large deformation and plasticity^{20,25,26}, rigorous continuum framework²⁷⁻²⁹, proper consideration of the interplay between electrochemistry and mechanics³⁰, design of optimal motifs³¹ among others³². However, the atomistic and micro-mechanisms underpinning the observed plastic behavior of Li-Si alloys, to date, remain unclear.

In parallel and complementary to continuum models, empirical force-field based molecular dynamics (MD), as well as more fundamental approaches such as quantum-based Density Functional

Theory (DFT) calculations^{33,34}, have been used to obtain atomistic insights into the electro-chemical and mechanical behavior of lithium-ion battery materials—from electrodes^{35,36} to electrolytes^{37,38}. While these atomistic modeling works have provided interesting and valuable insights, there is a fundamental limitation of conventional MD methodology that precludes an assessment of material behavior over realistic laboratory-timescales. MD can only handle time-scales of the order of, at best, a few microseconds. Even though this is adequate for understanding several physical, chemical, and mechanical phenomena in materials, the inability to address long timescales prevents an assessment of slow-strain rate mechanical behavior that is the norm in laboratory experiments and real-life applications. We hardly need to emphasize that strain rate has a profound impact on plastic deformation behavior of materials³⁹. In this research we employ a time-scaling atomistic approach to understand the fundamental mechanisms underpinning plasticity in amorphous fully lithiated nanostructures at room temperature. Our approach allows us to consider strain rates as low as 10^3 s^{-1} which is several orders of magnitude beyond the reach of conventional molecular dynamics.

II. APPROACH

Our 3-dimensional model system is depicted in Fig. 2 which is a fully lithiated amorphous silicon ($\text{Li}_{15}\text{Si}_4$) nanostructure at room temperature and consists of 4864 atoms. Fully lithiated silicon is the most severe case as far as mechanical deformation is concerned. The amorphous structure is created *via* a melting and quenching process. We increase the temperature of an initial crystalline structure to 4000K, relax the structure for 1000ps and decrease the temperature with the quenching rate of 3.7 K/ps to room temperature. An external pressure of 50 bar is applied during the annealing process. After the temperature is decreased to room temperature, the system is equilibrated using NPT (zero pressure) ensemble for another 1000 ps. The top and bottom layers are constrained to allow the application of a constant tensile strain rate in the z-direction while the lateral surfaces in x and y directions are kept free⁴⁰. The modified embedded-atom method (MEAM) potential is used in all of the calculations presented in this work⁴¹. This potential has been widely used in the study of amorphous and crystalline Li-Si alloy and appears to provide a reasonable description of its mechanical properties^{35,42,43}.

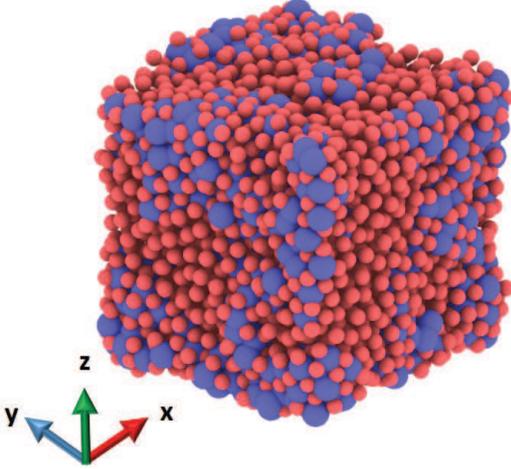


Figure 2. Initial amorphous $Li_{15}Si_4$ alloy nanostructure. Red small balls represent Li atoms and large blue balls represent Si atoms.

We consider two imposed strain rates—the benchmark high strain rate of $10^8 s^{-1}$ which is accessible with conventional MD and the low strain rate of $10^3 s^{-1}$. We briefly summarize the approach used for time-scaling. Since this approach has been described in detail elsewhere^{43–48}, including in a recent review article⁴⁹, we avoid an elaborate discussion regarding the method. In this approach, the desired strain rate ($\dot{\epsilon}$) is first fixed and then the strain is imposed on the system in small incremental steps. The Potential Energy Surface (PES) during each small strain increment is identified by using the so-called autonomous basin climbing (ABC) algorithm^{44,50} which is implemented by us through an in-house code utilizing the LAMMPS software⁵¹. The ABC algorithm therefore yields as output the minima and saddle points of the PES (and therefore also the energy barriers between different local minima). The aforementioned PES sampling approach has been successfully applied in the study of the mechanical behavior of both crystalline⁵² and amorphous systems^{53,54}. The 3N-dimensional PES is quite complex and the use of the ABC algorithm for even a few hundred atoms is computationally very demanding^{44,55}.

The energy barriers obtained from ABC are approximate since the determination of the saddle points can be in error based on the resolution of the sampling approach. Accordingly, to extract accurate energy barriers, the Nudged Elastic Band method (NEB) is applied to refine the barriers from the initial state to all possible final minima identified in the sampling process. With the energy barriers

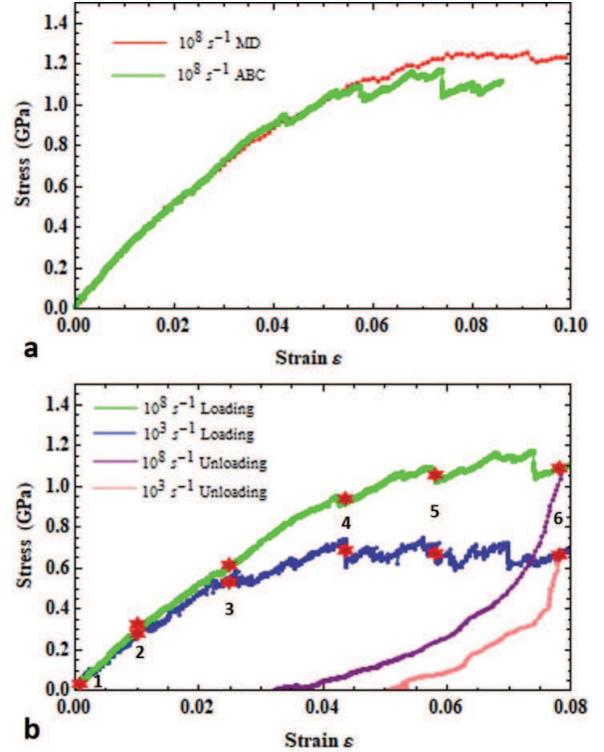


Figure 3. a) Stress-strain curves of the tensile test using averaged MD data (red curve) and the time-scaling approach (green curve) with imposed strain rate of $10^8 s^{-1}$. b) Stress-strain curves of loading and unloading for both slow and high strain rates. Red stars represent stages corresponding to 1) $\epsilon = 0$, 2) $\epsilon = 0.01$, 3) $\epsilon = 0.025$, 4) $\epsilon = 0.044$, 5) $\epsilon = 0.058$ and 6) $\epsilon = 0.079$ and these snapshots are analyzed in detail in the main text.

in hand, Kinetic Monte Carlo (KMC) is used to find the most probable pathway based on the relative probability⁵⁶. From the barrier energy of this selected transition, transition state theory is used to evaluate the time: $\Delta t = (\nu \exp[-\Delta E/k_b T])^{-1}$, ν is the hopping frequency⁵⁷, T is temperature. Finally, the transition time multiplied by pre-defined strain rate ($\dot{\epsilon}$) yields the strain increment for the next iteration through $\Delta \epsilon = \dot{\epsilon} \Delta t$. The calculated strain increment ($\Delta \epsilon$) is applied to the system and a new round of ABC sampling, NEB, KMC (i.e. the entire aforementioned process) is repeated. In the recent aforementioned process) a detailed comparison of the various ABC-based approaches has been made including how the one used in the present work (proposed by Fan et. al.⁵⁸) differs from what was outlined in the earlier papers^{44,59,60}.

III. RESULTS AND DISCUSSION

We first compare our time-scaling based simulation of high strain rate (10^8 s^{-1}) with MD results (Fig. 3 a). MD simulation is performed on the same structure initially equilibrated at 300K, but deformed at a temperature close to zero under a strain rate of 10^8 s^{-1} . Seven independent MD simulation runs were carried out and the average stress-strain response is used for comparison. As evident, as far as this high strain rate case is concerned, ABC-based calculations and MD results are in *reasonable* accord⁶¹. For the high strain rate of 10^8 s^{-1} the nanostructure appears to yield “roughly” around 1.0 GPa⁶². Based on this benchmark comparison, we conclude that the present time-scaling method can reasonably capture high strain rate deformation behavior of amorphous $\text{Li}_{15}\text{Si}_4$ nano-structures or, at least, agrees with conventional MD. We note that the yield stress for *bulk* Li-Si is less than 0.5 GPa⁴¹.

We now turn to the key objective of this work—imposition of low-strain rates that are inaccessible by conventional MD. The resulting stress-strain curves are shown in Fig 3 b. The two different stress-strain curves correspond to the two tensile rates, 10^8 s^{-1} and 10^3 s^{-1} . We remark here that the simplicity of the results depicted in Fig 3 b is deceptive. For example, the MD result shown in Fig. 3 needs merely 20 hours (12 processors), while, the curve shown in Fig.3 b requires 4500 computational hours to obtain. Before we examine the mechanisms for plasticity, it is instructive to compare the emergent stress-strain behavior of the nanostructure plastic response for the two different strain rates. Not only is the yield strength highly rate dependent (as expected), the difference between the rates is quite significant—the high strain rate yield stress is nearly 80 % larger which implies that conventional MD simulations are certainly inadequate to predict the key macroscopic parameter that dictates the plastic response of $\text{Li}_{15}\text{Si}_4$ nanostructure. The slow loading process that the time-scaling approach enables, allows longer time for structural relaxation and self-adjustment. As a result, the yielding occurs at lower stresses at slower strain rate. Plastic deformation, as deduced by merely examining the stress-strain curve, initiates much sooner at slow strain rate—at $\varepsilon = 0.025$ for slow strain rate and at $\varepsilon = 0.044$ for the faster strain rate. We also note the higher frequency of the stress-drops (signifying microscopic dissipation events) during the slow loading process. It is also of interest to examine how different the rate behavior is as far as accumulated plastic strain is

concerned—once the load is removed. For both the slow and fast rates, we unload from the strain value of $\varepsilon = 0.079$. The residual plastic strain, after complete unloading, is 0.032 for the high strain rate case and 0.05 for the low strain rate case—again, a rather significant difference. Further discussion regarding the unloading behavior may be found in the Appendix.

We now turn to an investigation into the atomistic mechanisms that lead to the emergent plasticity behavior shown in Fig 3 b. To quantify the plastic deformation at the atomic level, we use the approach laid out in Ref.^{63,64} to study amorphous systems. For that, two quantities: the local shear strain (η_i^s) and non-affine squared displacement (D_{min}^2), are evaluated. The index i labels the atom. Evaluation of η_i^s requires two configurations, the reference one and the current one. To facilitate a subsequent comparison between the two loading rates, we take the initial configuration as the reference (corresponding to label 1 in Fig. 3 b) and all the labeled points as “current” configurations corresponding to different strain values. The local Lagrangian strain matrix $\boldsymbol{\eta}_i$ can then be calculated from:

$$\boldsymbol{\eta}_i = \frac{1}{2} (\mathbf{J}_i^T \mathbf{J}_i - \mathbf{I}) \quad (1)$$

where \mathbf{I} is identity matrix and \mathbf{J}_i is an affine transformation matrix which transforms the initial configuration to the current configuration. The dilatational component is:

$$\eta_m = \frac{1}{3} \text{Tr}(\boldsymbol{\eta}_i). \quad (2)$$

and the scalar measure of the local shear strain content η_i^s is defined as:

$$\eta_i^s = \sqrt{\frac{1}{2} \text{Tr}(\boldsymbol{\eta}_i - \eta_m \mathbf{I})^2}. \quad (3)$$

As shown in Fig. 4a, with the increase of the applied strain, both the high strain rate and low strain rate cases exhibit increasing local shear strain. Comparison between top line (high strain rate) and bottom line (low strain rate) in Fig. 4a reveals that atoms with higher shear strain under high strain rate loading are localized at the center of the nanostructure, while the high shear strained in the low strain rate case are more evenly distributed in the specimen ($\varepsilon = 0.058$ and $\varepsilon = 0.079$). In other words, more localization becomes evident under high strain rates.

To systematically analyze the plastic deforma-

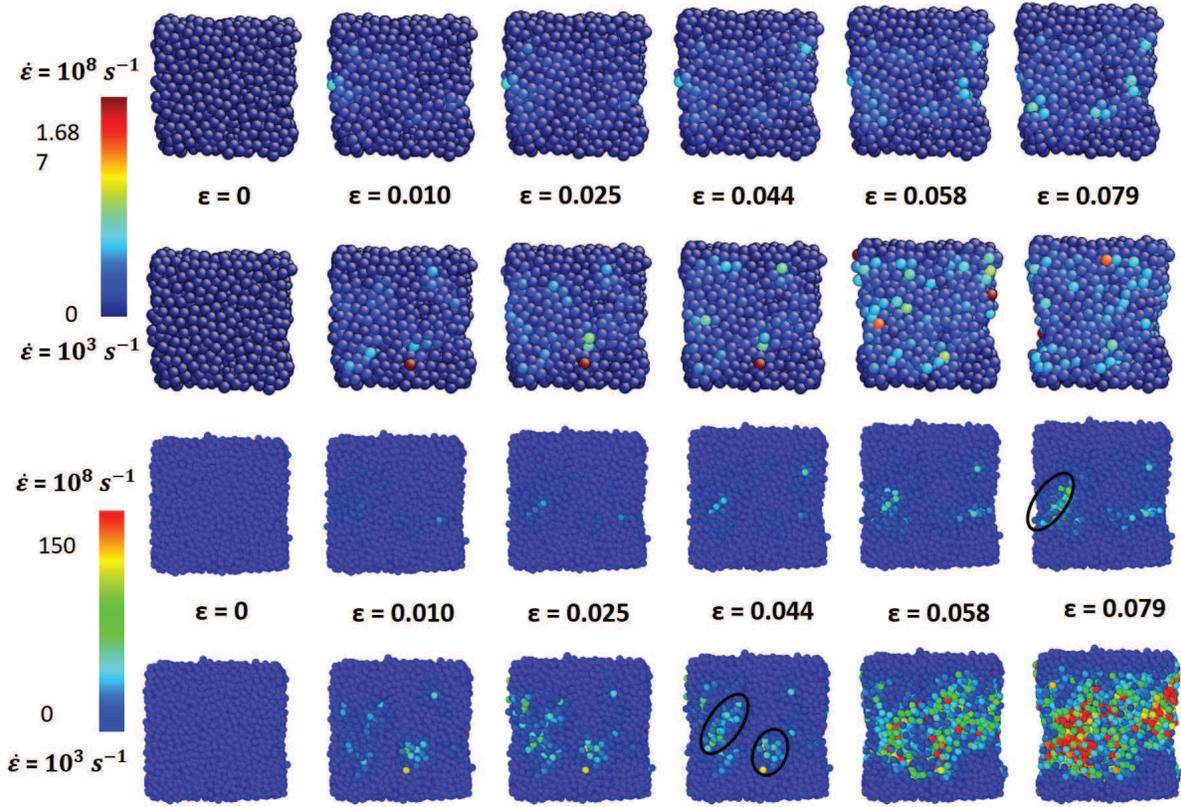


Figure 4. (a) Local shear strain (η_i^s) visualization of high strain rate case (top line) and the low strain rate case (bottom line) corresponding to different strain values. (b) Non-affine squared displacement visualization of $\{010\}$ free surface for the high strain rate case (top line) and low strain rate case (bottom line) for different strain values. Black circles highlight a few examples of shear transformation zones.

tion and identify the exact region where the irreversible plastic rearrangements are occurring—the so-called shear transformation zones (STZs)⁶⁵ need to be identified. The concept of STZ’s has been extensively invoked in the study of plasticity of amorphous materials (—see for example, Ref.⁶⁶ and references therein). Besides analyzing local shear strain, which represents the shear content of the multi-axial deformation field correspond to an affine shape change, non-affine squared displacement (D_{min}^2) is calculated to pinpoint the location of the STZs^{64,65}. Similar to local shear strain, the calculation of non-affine squared displacement also require two configurations. We take the initial structure as the reference configuration and all the labeled points in Fig. 3 b as current configurations. First, we apply an affine transformation to the distance vector between neighboring particle (j) within the cutoff distance r_c (assume there are N_i atoms within r_c and $j \in N_i$) and the center particle (i) at reference time^{63,64}:

$$\mathbf{r}_{ji}^a(0) = \mathbf{J}_i \mathbf{r}_{ji}(0), \quad (4)$$

where the distance vector $\mathbf{r}_{ji}(0)$ is defined as:

$$\mathbf{r}_{ji}(0) = \mathbf{r}_j(0) - \mathbf{r}_i(0). \quad (5)$$

Analogous to the way mean square displacement (MSD) is defined, D^2 for each single atom can be expressed as:

$$D^2 = \frac{1}{N_i} \sum_{j \in N_i} [\mathbf{r}_{ji}(t) - \mathbf{r}_{ji}^a(0)]^2. \quad (6)$$

The difference between MSD and D^2 is that MSD ($MSD = \frac{1}{N} \sum_{n=1}^N [\mathbf{x}(t) - \mathbf{x}(0)]^2$) is an evaluation based on atom position vectors \mathbf{x} , while D^2 is a measure of the non-affine deformation content. From Equation 6 and 4, D^2 depends on both distance vec-

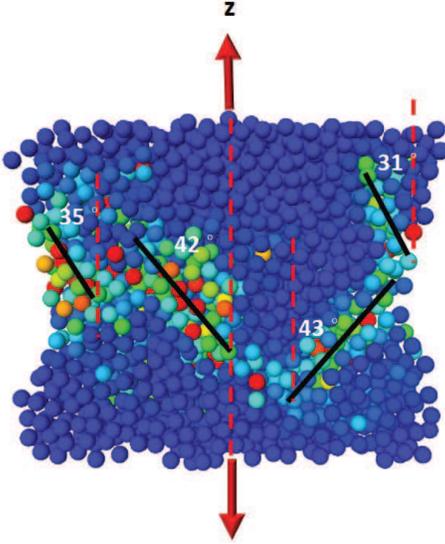


Figure 5. Snapshot for $\{110\}$ surface of low strain rate case with $\varepsilon = 0.079$. Atoms are colored according to their values of D_{min}^2 using the same scale as in Fig. 4 b. Red arrows represent the loading direction and black lines represent the “shear bands”.

tors as well as affine matrix \mathbf{J}_i . To minimize the error of deformation mapping, best affine transformation matrix need to be used and the non-affine squared displacement D_{min}^2 is defined as^{63,64}:

$$D_{min}^2 = \frac{1}{N_i} \min_{\mathbf{J}_i} \sum_{j \in N_i} [\mathbf{r}_{ji}(t) - \mathbf{r}_{ji}^a(0)]^2. \quad (7)$$

The results for the computed non-affine squared displacement for the labeled points in Fig. 3 b on the $\{010\}$ surface are shown in Fig.4b. The top row constitute the snapshots for the high strain rate case and the bottom row contains the snapshots for the low strain rate case. The nucleation of STZs (black circles in Fig.4 b) are shown for both cases. The low strain rate loading process nucleate STZs at an earlier stage compared to high strain rate loading. The STZs can be observed at the strain of 0.025 or even earlier during slower loading while they appear around $\varepsilon = 0.058$ in high strain rate situation. Furthermore, the size of STZs in the low strain rate case is larger than for the high strain rate case and the latter exhibit higher values of D_{min}^2 (atoms in red color). Comparison of the snapshots shown in Fig.4a and Fig. 4b reveals that the larger values of η_i^s appear in the same region as the larger values of D_{min}^2 . The correlated relation of η_i^s and D_{min}^2 is because the plastic deformation from shape change (represented by η_i^s) will introduce local particle

rearrangement in the neighborhood (represented by D_{min}^2). Massive atomistic rearrangement is notable for slow strain rate case—which allows neighboring atoms the sufficient time and “luxury” to rearrange themselves. These self-rearrangements can involve the participation of more neighboring atoms and generate denser STZs with higher D_{min}^2 values.

Theoretical models reported in Ref.^{67–69} indicate that for a strained amorphous solid, it is energetically favorable to have localized non-affine plastic flow in a shear band which lies at 45° to the principal stress axis (loading direction of uni-axial tension). We attempt to visualize this interesting phenomenon from an atomistic viewpoint using our simulation results, thus we focus on $\{110\}$ section which is parallel to the loading direction (Fig. 5). We find that the atoms with high D_{min}^2 lie along lines (black lines) which are roughly 45° with the loading direction (z direction shown in red arrows). While the theoretical predictions are for a bulk system, it is interesting to note that even for a nanostructure, the shear band orientation is close to the predicted value of 45° .

As it is well known, dislocations are the microscopic plasticity carriers for crystalline materials, however, for amorphous system, the unit plasticity events have been a matter of much debate—see Ref.⁷⁰ and references therein. While we certainly cannot resolve that issue in this work, we hope to critically examine the deformation in the STZs of LiSi nanostructure to see if we can ascertain the major dissipative mechanisms. In order to better visualize the evolution of STZs we focus on the $\{1\bar{1}0\}$ section which is also parallel to the loading direction (Fig. 6). On this surface, the effect of maximum shear stress (in principle, along the directions having 45° angle with the loading direction) on STZs should be most relevant. In Fig. 6, clear differences between high strain rate case (top line) and low strain rate case (bottom line) are observed on this section. At every strain value, except $\varepsilon = 0$, STZs in low strain rate case are larger in size and exhibit higher value of D_{min}^2 compared with the STZs under high strain rate snapshots. We also note that STZs appear in similar regions across both fast and slow rate cases. The snapshots at $\varepsilon = 0.079$ are good examples of this observation. For the low strain rate case, the STZs (circled in black) are formed with very high D_{min}^2 (atoms with red color) while in the same region for sample loading with low strain rate, less dense STZs with lower D_{min}^2 appear. Regardless of the strain rate, local atomic re-arrangements or micro-adjustments appear to be the key stress-accommodation process. However, in the case of fast

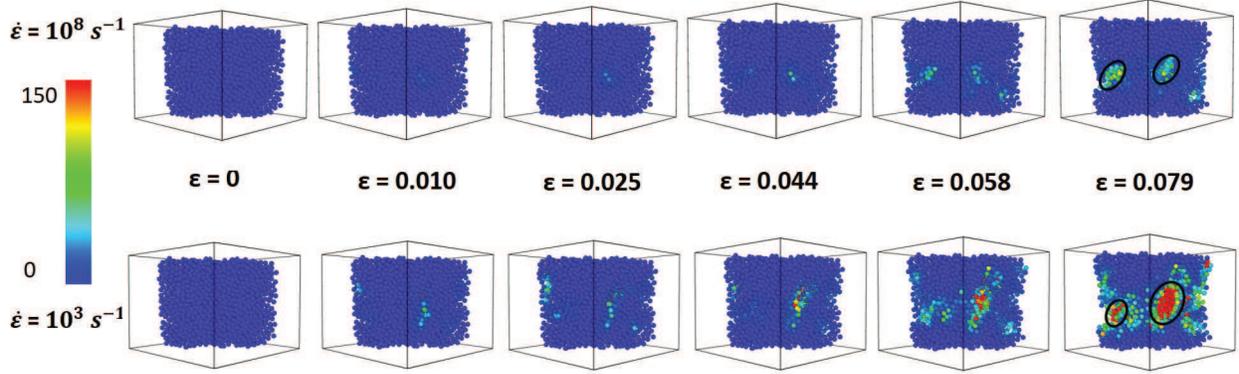


Figure 6. Non-affine squared displacement visualization of $\{1\bar{1}0\}$ surface with high strain rate stretching (top line) and low strain rate stretching (bottom line) at different strain values. Black circles highlight two examples of STZs.

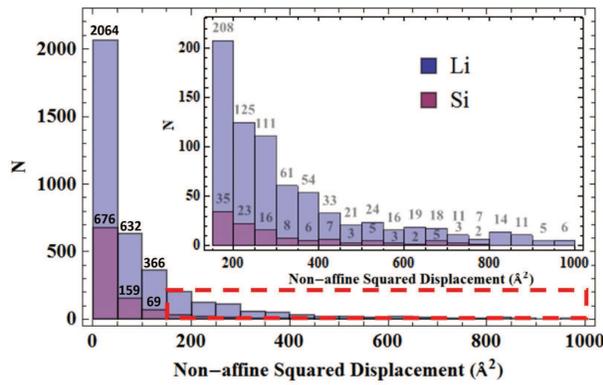


Figure 7. Non-affine squared displacement of Li and Si atoms. The subset (a zoomed view of red dashed box) shows the distribution and numbers of atoms for both Li and Si atoms at higher value of D_{min}^2 .

loading, there is not enough “time” for the atoms to dissipate energy and the corresponding stress-strain curve (green) shown in Fig. 3 b is smoother with only a few drops. Slow loading process, however, allows the neighboring atoms to adjust themselves corresponding to the shape change so that the stresses on the atoms are relieved much more efficiently. Due to the longer relaxation time, frequent energy dissipation events yield multiple successive bursts evident in the blue curve of (Fig.3 b).

In the charging and discharging process, Li-ions migrate from one electrode *via* the intervening electrolyte and insert and diffuse in the opposite electrode. The insertion and diffusion of Li ions is accompanied by a rather large volumetric swelling and the consequent generation of mechanical stresses. Li and Si play different roles in the

battery system. Thus, it is worthwhile to assess the behavior and contribution of these two types of atoms to the plastic deformation of the alloy.

As shown in Fig. 7, we plot the distributions of non-affine squared displacement (D_{min}^2) of Li and Si separately. In this figure, the horizontal axis is the value of non-affine squared displacement and the vertical axis represents the corresponding number of atoms. The distribution of Li atoms is shown in blue and the distribution of Si atoms is shown in purple. The inset (the zoomed-in view of the red dashed box) shows the distribution and numbers of atoms with higher value of D_{min}^2 (red atoms in Fig. 4 and Fig. 6). We note that for higher values of D_{min}^2 ($D_{min}^2 > 50$), the ratio between the number of Li atoms and Si atoms is much higher than the average atom ratio (the average ratio is 3.75 for $Li_{15}Si_4$). On the other hand, the ratio between Li atoms and Si atoms is lower than 3.75 for lower values of D_{min}^2 (3.05 for the first bar in Fig. 7 which represents $D_{min}^2 < 50$). This observation, in our opinion, signifies that Li is more active in the plastic deformation. In other words, more Li atoms, compared with Si atoms play the role of plasticity carriers. Interesting, a similar conclusion was reached in Ref.⁷¹ using an entirely different approach where they argue that Si forms the skeleton of the structure and the Li atoms are the “flowing defects” of the system.

To further understand what happens during slow strain rate deformation, we also tracked the movement of a group of atoms in a STZ during the deformation process. As shown in Fig. 8, we track the atoms inside of the STZs shown in Fig. 6 (snapshot of slow strain rate case at $\epsilon = 0.079$). Fig. 8a and b illustrate deformation which mainly

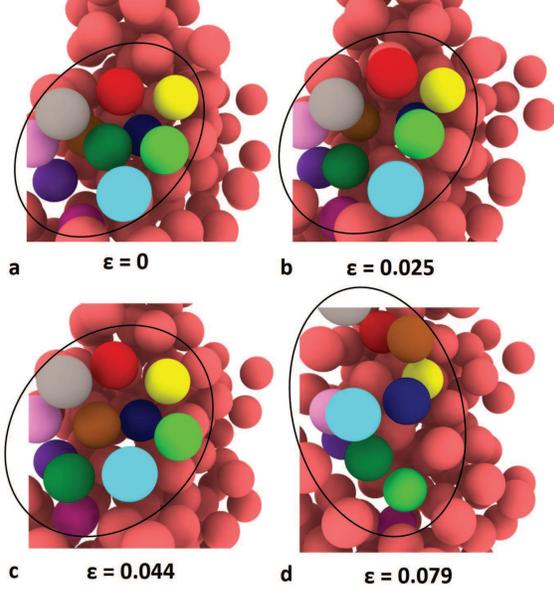


Figure 8. Tracing map of the positions of a few atoms (in different colors) inside the big STZ in the snapshot of low strain rate case at $\varepsilon = 0.079$ in Fig. 6. The snapshots are taken at a) $\varepsilon = 0$, b) $\varepsilon = 0.025$, c) $\varepsilon = 0.044$ and d) $\varepsilon = 0.079$.

occurs in elastic regime (points 1 and 3 in Fig. 3 b). Here there is no significant variation of the relative positions (colored atoms in ellipsoid). With the larger amount of deformation ($\Delta\varepsilon = 0.035$ from Fig. 8 c to d and $\Delta\varepsilon = 0.025$ from Fig. 8 a to b), in the plastic deformation region (point 4 and 6 in Fig. 3 b), the STZ in Fig. 8 c rotates clockwise and becomes the shape shown in Fig. 8d. Additional rotation also occurs in the out-of-plane direction, however we don't emphasize this part because it shares the same physics as what we observed from Fig. 8. This type of rotation is in our opinion an important dissipation mechanism for plasticity in LiSi amorphous nanostructures. During elastic deformation, because of stretching, atoms are subjected to increasing stress. Correspondingly, in Fig. 3 b, the stress difference between point 1 and 3 is 0.5 GPa. For plastic deformation, due to the aforementioned relative rotation of a group of atoms, with larger amount of strain increment, the stresses at point 4 and 6 in Fig. 3 b are almost the same.

IV. SUMMARY

In summary, with the help of a time-scaling atomistic simulation approach, we have provided insights

into the key atomistic mechanisms underpinning plasticity in Silicon-Lithium nanostructures. Due to its inability to handle lower strain rates, conventional molecular dynamics overestimates the yield stress, underestimate the accumulated plastic strain and misses important microscopic events underlying the plasticity response of LiSi. In this research, we were able to simulate a slow strain rate to 10^3 s^{-1} and compared the atomistic behavior with the system under high strain rate loading. Our simulations show reduced yield stress for slow loading process with more frequent dissipation events in comparison with the high strain rate loading process. Direct atomistic visualization reveal a plethora of insights into the microscopic dissipation processes underlying plastic deformation and we conclude that rotation of localized regions in the shear transformation zones is likely an important dissipation mechanism for amorphous Li-Si alloy.

ACKNOWLEDGMENTS

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Appendix: Atomistic analysis of unloading

During the unloading process, the constraints are removed from the system and the system undergoes a recovery process. From Fig. 2b, as evident, the unloading process is not linear. We first visualize the non-affine squared displacement (D_{min}^2) on the $\{1\bar{1}0\}$ surface (Fig. 9). In general, the length in z direction (loading direction) is reduced. Comparison between the snapshots before and after unloading for both high strain rate loading process and low strain rate loading process reveals that the shape and location of the shear transformation zones (STZs) remain unaltered.

The zoomed-in view of the STZs are shown in Fig. 10. In the top row of this figure, colored atoms are selected from the black circle shown in Fig. 9 b. Fig. 10 a and b demonstrate the elastic recovery—reduction of the distance between atoms. Similar (less significant) observations can be found in the snapshots in the bottom row (Fig. 10 c and d) and they display the tracked atoms for the unloading process in the slow strain rate deformation case. The colored atoms are the same as Fig. 6.

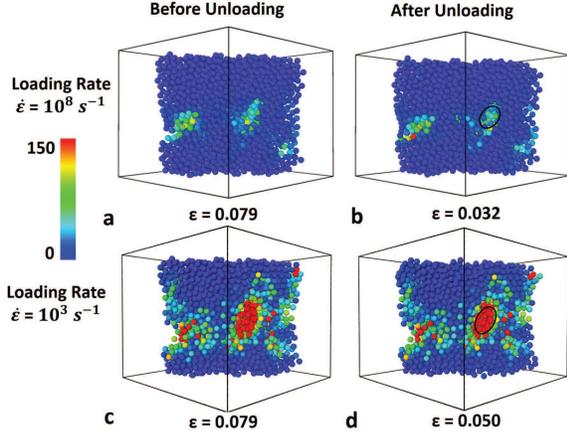


Figure 9. Non-affine squared displacement visualization of $\{1\bar{1}0\}$ surface with snapshots of a) before unloading from high strain rate deformation, b) after unloading from high strain rate deformation, c) before unloading from low strain rate deformation and d) after unloading from low strain rate deformation. The reference configuration is the initial configuration before loading ($\epsilon = 0$).

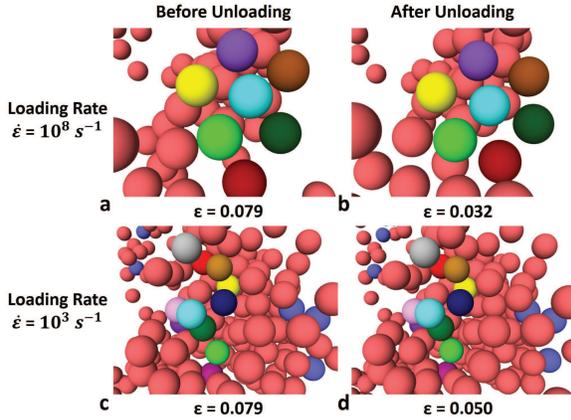


Figure 10. Tracking map of the positions of a few atoms (rendered in different color) inside the STZ. The snapshots of a) before unloading from high strain rate deformation, b) after unloading from high strain rate deformation, c) before unloading from low strain rate deformation and d) after unloading from low strain rate deformation. Colored atoms for low strain rate case (c and d) are same as the ones in Fig. 6.

From the unloading curves in Fig. 3, reverse plastic deformation also occurs during the unload-

ing process. However, this is difficult to observe from the atomistic snapshots in Fig. 9 and Fig. 10. To facilitate a quantitative evaluation of the reverse plastic deformation, we calculate non-affine squared displacement with the configuration before

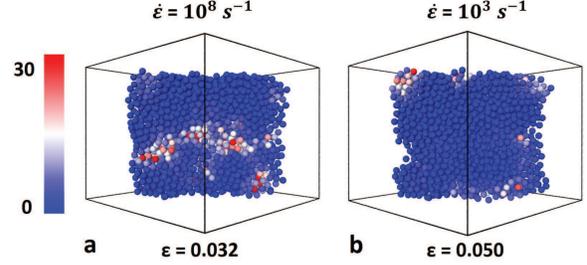


Figure 11. Non-affine squared displacement visualization of $\{1\bar{1}0\}$ surface with snapshots of unloading from high strain rate deformation (left) and low strain rate deformation (right). The reference configuration is the one before unloading ($\epsilon = 0.079$).

unloading as the reference configuration and the results are shown in Fig. 11. In the snapshot for high strain rate loading process (Fig. 11 a), the zone of the reverse plastic deformation is in the center of the system. We remark that different coloring system is adapted in this figure from Fig. 4 and 6 since the value of D_{min}^2 is much smaller as compared to the loading process. As shown in Fig. 3 b, during unloading (for the high strain rate case), roughly 0.01 plastic strain is reversed (there is 0.04 plastic strain accumulated in loading process for high strain rate loading case). Thus, we adjusted the coloring scale to yield better visualization. The reverse plastic deformation for low strain rate deformation is even smaller (0.005) and the distribution of D_{min}^2 is shown in Fig. 11 b. Such difference between unloading process for high strain rate and low strain rate deformation is due to fact that the self-rearrangement is irreversible and atoms are “locked ” after this type of self-adjustments. For the slow loading process, more atoms are involved in this irreversible rearrangement and the plastic deformation accumulated during loading remains even after unloading. We speculate that for the high strain rate loading process, atoms are unable to access entropically favorable states and there is therefore more scope for reverse plastic deformation can happen in the unloading process.

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