An Atomistic Method for Slow Structural Deformations

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Abstract. We investigate the feasibility of applying a recent algorithm for sampling activation barriers in supercooled liquids to probe activated kinetics of solid-state deformation under stress. The basis for exploring this isomorphism is that the elementary processes of activation and relaxation in potential energy space are valid for any bulk system. Since the method is able to explain shear relaxation over a range of temperatures, it seems reasonable to expect the approach also can be useful for studying structural deformation over a range of applied stresses. We present preliminary results on time-dependent deformation of nano-grained structures to suggest a new way to probe structural relaxation at slow strain rates that retains atomistic details of individual and collective rearrangements.

1. Introduction

In a 2002 paper on creep at very low rates [1], F. R. N. Nabarro wrote in the abstract, "The creep rate in a land-based power station must be less than 10^{-11} s^{-1}.", and concluded at the end, "The present state of knowledge reveals specific questions that call for experimental investigation. Theory will contribute, but atomic computation, with a time scale of 10^{-11} s, will not handle processes that take 10^{11} s.". One can readily sympathize with this assessment given that molecular dynamics simulation is typically constrained to a time-step size of 10^{-14} s. On the other hand, such a point of view seems to preclude the possibility that methods can be found to simulate slow dynamical processes without explicitly following all the atomic rearrangements all the time, which is in fact the spirit of multiscale modeling. Here we describe a potential energy surface sampling method which shows promise of reaching the kind of time scale called out by Nabarro. The method, like molecular dynamics, requires the input of an interatomic interaction potential for the constituent particles in the system, and retains full information on the particles along the trajectory of the sampling. However, the system does not evolve by allowing the particles to move according to Newtonian dynamics, instead it evolves by a series of activation and relaxation in the space of its potential energy.

We first summarize the activation-relaxation approach which allows the system to climb out of any potential well. We have shown this enables the determination of effective temperature-dependent activation barriers that account for the observed shear viscosity of supercooled liquids [2]. Then we discuss using the method to characterize the deformational responses of two models of nano-crystal under tensile loading. Results are presented to indicate the feasibility of probing strain rates ranging from 10^4 s^{-1} to 10^{-11} s^{-1}. Although very preliminary, these results point to the feasibility of probing the atomic-level mechanisms of creep by atomistic simulations.

2. Autonomous Basin Climbing Method

We have formulated a method consisting of a series of elementary steps of alternating activation and relaxation the effects of which are to allow a system to climb up an arbitrary potential well. On the potential energy surface (PES) where there are many local minima and saddle points, having the ability to climb out of any potential well means that one can then sample the topography of the PES by generating an explicit transition state pathway (TSP) trajectory. The system evolution, on an energy scale, is therefore described by this trajectory. At every point on the trajectory one also has complete information of the atomic degrees of freedom of the system so that any part of the system evolution can be studied in full atomistic details, if desired. Since this method has been presented previously [2] we summarize here only the essential ideas.

Figure 1(a) shows the two elementary steps of activation and relaxation that move the system up a particular potential well. A $3N$ dimensional Gaussian penalty function (N is the number of atoms in the system) is first added to an initial energy minimized configuration. This has the effect that, upon minimization of the combined energy (sum of penalty and the original potential energy of the system), the system is pushed away from the initial minimized configuration into a higher energy state. With sufficient energy penalties accumulated after a series of such steps, the system will cross an energy saddle point during a relaxation step and enter into an adjacent well. Starting at the bottom of this well the activation-relaxation series is repeated until the system is able to escape from the second well. Notice that the energy penalty functions imposed in the previous activation steps are not removed during the entire sampling, so that the system is always discouraged from returning to any previous potential minima. Thus with this method one is not sampling a fixed PES, rather the PES evolves along with the sampling such that the system is always encouraged to sample new regions of the PES. This method, in contrast to saddle point sampling techniques such as the nudged elastic band method [3], does not require *a priori* knowledge of the final state. This is particularly useful for the system where the structure is too complex to generate such an input.
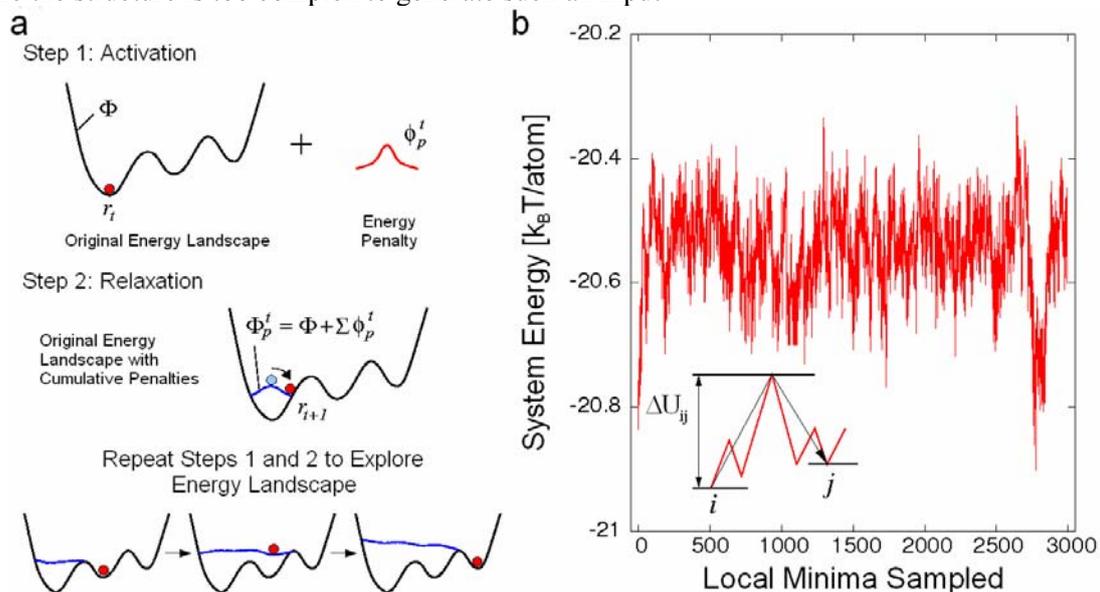

Figure 1. The Autonomous Basin Climbing Technique: (a), a schematic of the method – an energy minimized initial structure is activated by imposing on the energy landscape a Gaussian energy penalty ϕ_p^t (centered at the original configuration), which causes the system to climb up the basin into a higher energy configuration. Repeated application of the energy penalties will eventually cause the system to move to another energy minimum; and (b), an illustration of the results obtained from ABC, where a series of interconnected energy minima and saddle point transition between them is obtained. Activation barrier between two minima i and j, ΔU_{ij}, is defined by the highest saddle energy between the two as shown in the inset.
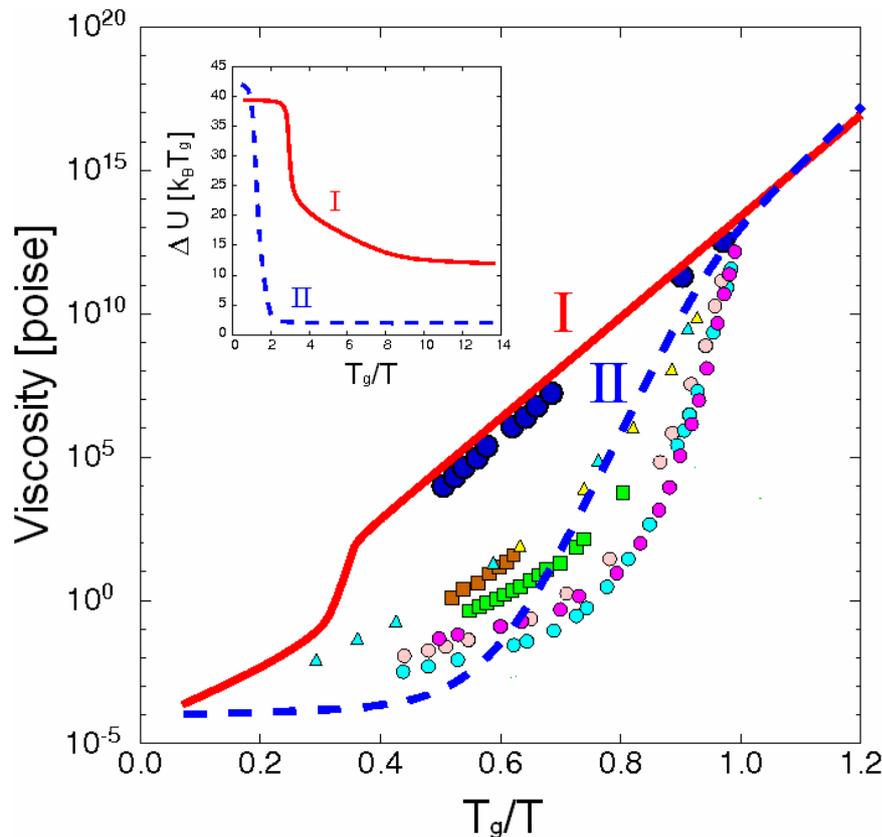
Figure 2. The viscosity of supercooled liquids as calculated using the ABC method (solid and dashed curves) [2] in comparison with experimental measurements (symbols [4]). I and II denote SiO_2 [5] and binary Lennard-Jones model [6], respectively. The inset shows the extracted activation barriers as a function of temperature. T_g is the glass transition temperature where the viscosity is 10^{13} poise.

We have used this method to obtain transition state pathway trajectories in supercooled liquids, an example is shown in figure 1(b). The trajectory is an alternating sequence of energy minima (potential wells) and maxima (saddle points) that allow the system to evolve along a particular PES pathway. From such data we can extract an effective temperature-dependent activation barrier, shown in the inset in Figure 2, which in turn determines the temperature variation of the shear viscosity through the application of transition state theory [2]. Figure 2 shows the atomistic results for SiO_2 and a model of binary Lennard-Jones interaction have the same behavior as existing viscosity data. We regard this agreement as confirmation that our method is able to probe the activated state kinetics of shear relaxation over a wide temperature and temporal range.

3. Creep in Fe Nano-Grains

To apply the basin climbing algorithm to deformation in solids under an applied load, we consider the process of strain production in two BCC models of nano-grain structures, a 2-D columnar system (model A) and a 3-D system of spherical grains (model B). Model A is constructed by creating 4 grains of random orientation arranged in a 2 dimensional close packed lattice. The overall periodic box at zero stress is $39.0 \times 39.0 \times 19.1$ Å containing 2408 atoms, with the columns oriented along the short axis. Model B is constructed by creating 2 grains of random orientation, each 29.8 Å in diameter, with 3456 atoms in total. A Finnis-Sinclair type empirical potential for Fe is used [7]. Both structures are studied at room temperature under uniaxial tension, model A at 0.2 GPa, and model B at 0.2 and 0.7 GPa**.**

Figure 3 shows the system set up and trajectory results for model A. Figure 3(a) shows the system energy evolving toward a lower-energy region during the sampling, while figure 3(c) gives the corresponding evolution in system strain (defined by the deformation of the simulation cell). From the activation energy required for the system to go from one energy minimum to the next, given in figure 3(a), we can estimate the time required for each activation process using transition-state theory [8]
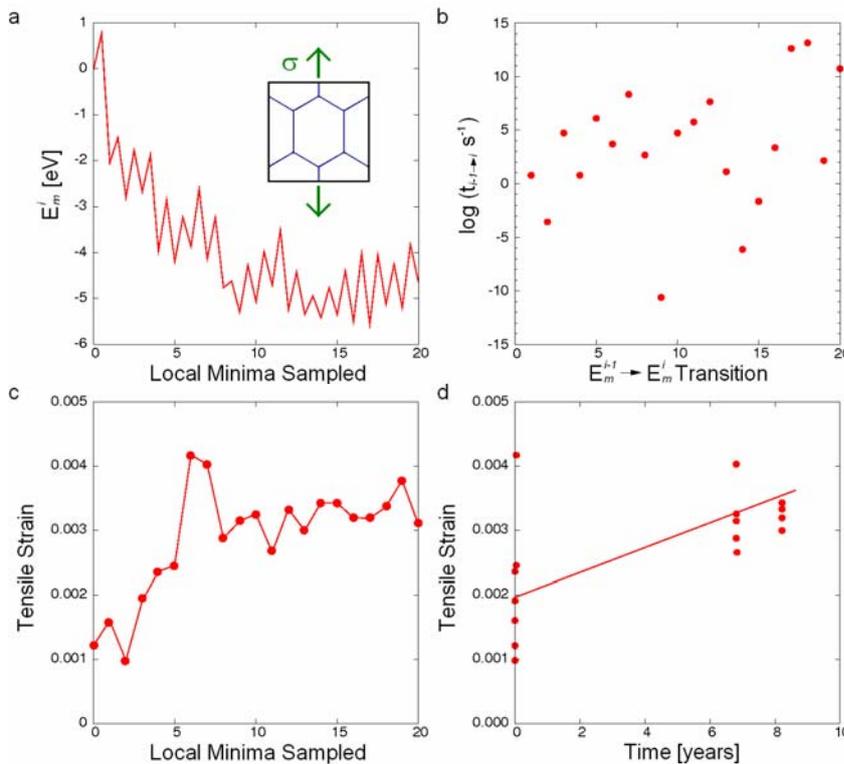
Figure 3. The strain rate of the columnar grains at 0.2 GPa and 300 K: from (a), the energy of transition between the energy minima as we sample the energy landscape; we are able to obtain the time needed to transition from one minima to another (b) using equation 1 and an assumed frequency factor of 10 THz. Combining this time information with the cell dimensions of the atomic configurations at the different minima (c), we obtain (d), a plot of the strain as a function of time. Fitting a line to (d) yields the strain rate of 0.52×10^{-11} s^{-1}.

$$t_{A \rightarrow B} = \left(\nu_{\circ} \exp \left(-\frac{\Delta U_{A \rightarrow B}}{k_B T} \right) \right)^{-1} \tag{1}$$

By correlating the strain produced with the time required, figure 3(b), we arrive at figure 3(d) where we have assumed a frequency factor $_{\circ}$ of 10 THz. Fitting a line to figure 3(d) yields the strain rate, 0.52×10^{-11} s^{-1}.

Figure 3(d) indicates that the deformations sampled undergo "fast" transitions (too rapid to resolve on the scale of this figure), except for two slower events, both on the scale of years. Within any short time interval the data are too scattered to reveal any trend. However, on the long time scale (years) an overall positive trend leads to a strain rate of the order of magnitude mentioned by Nabarro.

Figure 4 shows the corresponding results obtained for model B. A distinctive feature of figure 4(a) is that the transition state pathway trajectory takes the form of a series of oscillations, "saw-tooths",
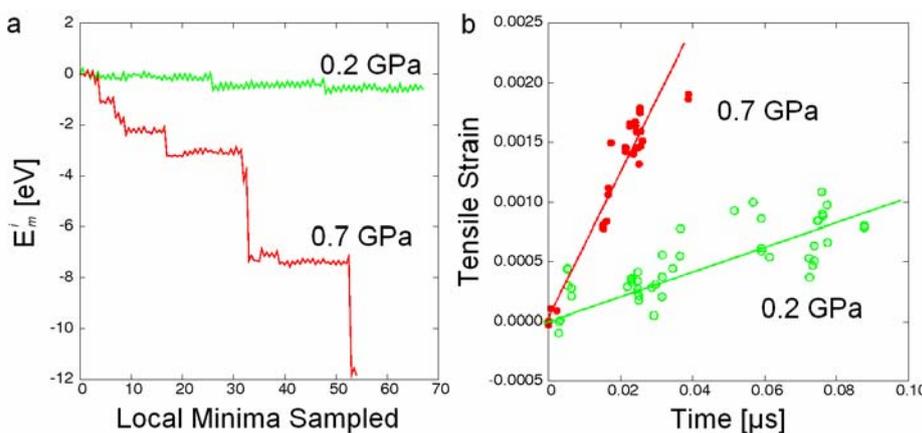

Figure 4. The energy evolution of the spherical nanograins, obtained at 0.2 GPa and 0.7 GPa: (a) the energy evolution as the system traverses different energy minima; and (b) the strain as a function of time for the two stresses at 300K.
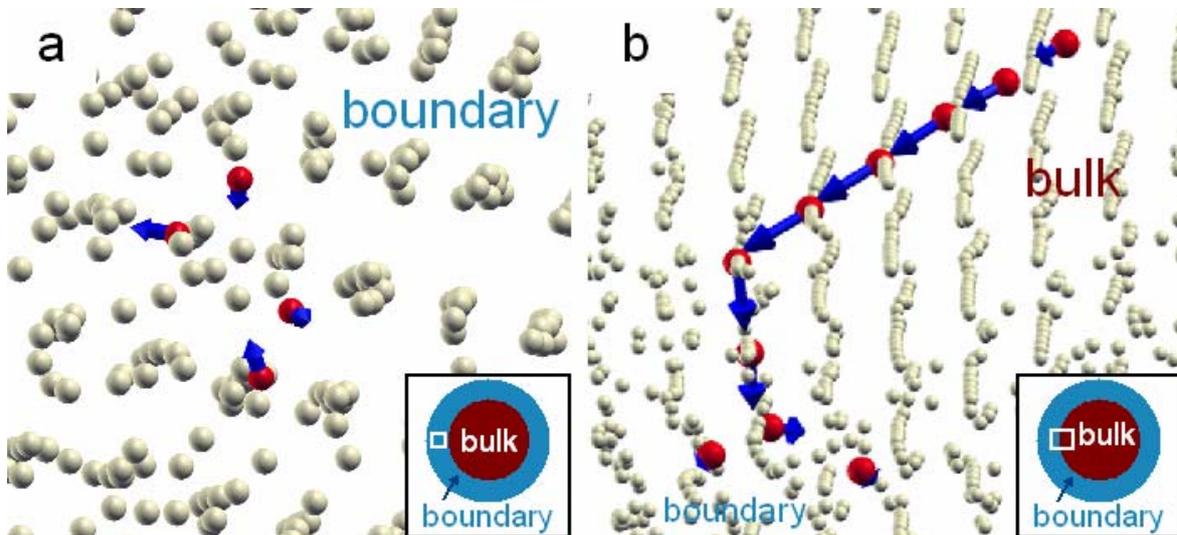
Figure 5. Depicting atomic displacements during creep: (a), localized grain boundary response, obtained from a comparison of 2 atomic configurations separated by an energy "saw-tooth"; and (b), injection of an interstitial atom into the grain boundary by the collective displacements of atoms along <111> direction which is the nearest neighbour direction in the BCC lattice, obtained from a comparison of 2 atomic configurations at the end of two successive energy drops and separated by a series of "saw-tooth" and one energy drop. Atoms that have displaced more than 0.1 Å or more are marked in red/dark shade. The arrows mark the direction and relative magnitude of displacement. Each inset shows the enlarged area (small rectangle) relative to the bulk (spherical grain) and surrounding boundary in each case. Thus displacements in (a) occur entirely in the boundary, whereas displacements in (b) start in the grain (bulk) and end up in the boundary region. Figure generated with XCrysDen [9].

punctuated by sudden energy relaxations, particularly pronounced at the higher stress. Figure 4(b) shows the time evolution of the tensile strain at 300K. From the data we obtain estimates of strain rate of 1×10^4 s^{-1} at 0.2 GPa and 7×10^4 s^{-1} at 0.7 GPa.

Figure 5 shows the atomistic mechanisms that one can deduce from the atomic configurations at various points along the generated trajectory. Inspection of the atomic configurations associated with the energy minima on each side of a "saw-tooth" indicates "minor", local rearrangements within the grain. An example of this type of displacements is seen in figure 5(a).

In contrast inspection of the atomic configurations immediately after each sudden relaxation indicates coordinated atomic motions that could be regarded as an extended interstitialcy mechanism which results in the injection of atoms into the grain boundary, as seen in figure 5(b). This also can be interpreted as an incorporation of atoms from the grain boundary into the grain leading to a form of grain growth.

Our preliminary findings support the interpretation that the atomistic precursors to creep in the conventional sense consist of a series of localized "adjustments" in the grain boundary, manifesting as "saw-tooth" in the TSP trajectory. These rearrangements then enable the coordinated displacements that lead to the removal or addition of atoms in the grain which in turn result in changing the grain shapes. Furthermore, we associate this mechanism with the sharp drops in the energy as the microstructure evolves, changes which are irreversible.

It should be noted that within this basic mechanism there are possibilities of variation where external factors (e.g. stress) can play a significant role. As seen in Figure 4, we find that at higher stresses, the drops in energies due to the collective motion are significantly larger. This provides some degree of confirmation for the proposed mechanism as the actual creep mechanism, as the energetic penalty for "backwards" microstructural evolution should be higher at higher stresses.

4. Discussions

We have described an attempt to replace molecular dynamics simulation by a method based on activated state kinetics in the study the atomistic aspects of structural deformation in condensed matter, motivated by the desire to reach longer time scales. The method, which we call autonomous basin climbing, thus far has allowed us to tackle the longstanding problem of computing, using interatomic potentials, the temperature dependence of shear relaxation in supercooled liquids, with implications for understanding the nature of glass transition. When this approach is extended to the response of nanostructures, in the form of 2-D columnar and 3-D spherical grains under tensile loading, we find the results sensitive to the structural characteristics of each system in ways that are rather reasonable. In the case of spherical grains, we feel a useful connection can be made with the extensive MD study of grain-boundary diffusion creep by Yamakov and co-workers at strain rates in the range $10^7 - 10^8$ s^{-1} and elevated temperatures [10]. Our estimate of significantly higher strain rates in the spherical-grain system, relative to the columnar system, is in the right direction toward the range accessible by MD. Also the characteristic sudden relaxations we have observed in figure 4(a) have connections with the intermittent plastic deformation events in amorphous matter investigated by Argon and Demkowicz [11], with mechanistic implications concerning localized shear transformations. While we are at a very early stage where much work lies ahead and a number of computational and conceptual issues still need to be addressed, we nevertheless see a possibility of atomistic simulations contributing to the physical insights into deformation processes at strain rates of practical interest.

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