



Exploring structural mechanisms in disordered materials using the activation-relaxation technique

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Abstract

Structural mechanisms in disordered materials like amorphous semi-conductors and glasses can be explored with the activation-relaxation technique (ART). The application of a sequence of such mechanisms allows for the generation of well-relaxed structures. The method and its application in the study of the microscopic changes in amorphous silicon and silica glass are reviewed, and two recent improvements are presented. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

While the smallest relevant time scale in atomic systems is that belonging to atomistic oscillations, around a tenth of a pico-second, the microscopic dynamics of glassy and complex materials at low temperature can proceed at time scales that are easily ten orders of magnitude larger, seconds or hours. Approaches based on the atomic oscillation time scales, such as molecular dynamics, will not be able to bridge this gap in the foreseeable future: alternative approaches have to be explored.

The nature of the discrepancy between these time scales is best understood from the configurational energy landscape: the system finds itself in a deep minimum surrounded by energy barriers which are many times larger than its temperature. Only rare fluctuations of thermal energies allow the system to jump over a barrier and move to a new minimum.

In this paper, we review the activation-relaxation technique [1,2] which proposes one avenue for the exploration of such systems. We first discuss the algorithm in some detail, including some new algorithmic improvements, and then briefly present its application to amorphous silicon and vitreous silica.

2. The activation-relaxation technique

The activation-relaxation technique consists of two parts: a path from a local energy minimum to a nearby saddle point – the activation; and a trajectory from this new point to a new minimum – the relaxation.

The relaxation to a local energy minimum is a well-defined and well-behaved operation for which a number of efficient algorithms are available (see, for example, Ref. [3]). We use an adaptive algorithm that uses a steepest descent close to the saddle point and a conjugate-gradient algorithm as the configuration converges to the new minimum.

The activation from a minimum to a saddle point poses a bigger challenge. While previous work con-

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centrated on low-dimensional problems for which, often, the minima were known, ART is aimed at finding saddle points in high-dimensional energy landscapes, knowing the location of one minimum only.

At the saddle point, all eigenvalues of the Hessian but one are positive. In the energy landscape, this negative eigenvalue sets the direction of a valley going down on both sides. Starting somewhere in this valley, convergence to the saddle point can be obtained by keeping the configuration at the energy minimum along all directions but the one corresponding to the lowest eigenvalue, which is assimilated with the local bottom of the valley, and pushing upward along that one direction. This is in essence Cerjan and Miller's approach for locating transition states in low-dimensional energy surfaces [4].

This approach is too computer intensive for realistic bulk systems with hundreds to thousands of atoms, since the time required for the diagonalization of the Hessian grows as $\mathcal{O}(N^3)$. By approximating the Hessian, ART proposes an $\mathcal{O}(N)$ algorithm. Its standard implementation follows a modified force vector \vec{G} , obtained by *inverting* the component of the force *parallel* to the displacement from the current position to the local minimum $\vec{r} = \vec{x} - \vec{x}_m$ while minimizing all other $3N - 1$ directions:

$$\vec{G} = \vec{F} - (1 + \alpha)(\vec{F} \cdot \hat{r})\hat{r}, \quad (1)$$

where \hat{r} is the normalized vector parallel to \vec{r} , \vec{F} is the total force on the configuration as calculated using an interaction potential, and α is a control parameter. Iteratively, this redefined force is followed until $\vec{F} \cdot \hat{r}$ changes sign.

Because of this projection, the standard algorithm fails for valleys perpendicular to \vec{r} . We now introduce a trailing position \vec{x}_t , that initially is located in the old minimum, but is moved in the direction of the position as soon as it is more than a trailing distance r_t behind. The direction in which we invert the force is now chosen according to $\vec{r} = \vec{x} - \vec{x}_t$, thus avoiding the limitation mentioned above. This improvement is particularly helpful in the simulation of systems with strong short-range potentials, like metallic glasses.

Since the force \vec{G} as redefined in Eq. (1) is not curl-free, it cannot be written as the gradient of a redefined energy function. For the convergence to the saddle point we therefore have to modify the standard conjugate gradient method as for instance in [3]: the

line minimization in direction \hat{h} is replaced by a root-finding algorithm of $\vec{G} \cdot \hat{h}$.

In non-degenerate disordered materials, only two valleys start at the minimum: the ones corresponding to the softest vibration mode around the minimum. To explore other valleys leading to other saddle points, we must therefore leave the harmonic well before starting the search for valleys. We discuss separately the direction of the initial displacement and its size.

Any random escape direction overlaps with the softest elastic modes. While following the redefined force, they tend to dominate exponentially rapidly. The softest modes should therefore be eliminated from the initial displacement. Starting with an initially random direction \vec{r}_0 , we suppress the softest modes by n iterations of

$$\vec{r}_{i+1} = -\vec{F}(\vec{r}_i),$$

a series of very small steps, mathematically equivalent to multiple applications of the Hessian.

This suppression of the softest modes in the initial displacement has the side-effect that it boosts the strongest modes exponentially. The result is that the initial displacement points to a very stiff direction, and the energy raises rapidly along this direction. We propose here a modification: the stiffest directions are removed from this vector \vec{r}_n by simply making it orthogonal to directions $\vec{r}_{n+1}, \dots, \vec{r}_{n+m}$, with n and m depending on the details of the system studied. This leaves us following a random vector from which the softest and stiffest modes have been removed.

This initial direction is then followed until the ratio of the perpendicular to the parallel component of the force, as projected on the displacement from the minimum, reaches some ratio, indicating that the harmonic region has been left.

3. Applications

The activation-relaxation technique is well suited to identify atomistic mechanisms for diffusion and relaxation in disordered systems, since the events that are created follow closely the physical activation paths. The method was recently used for the identification of microscopic relaxation and diffusion mechanisms in two materials: amorphous silicon and vitreous silica.

3.1. Amorphous silicon

In a simulation study of amorphous silicon, we generated more than 8000 events from three independent runs on 1000-atom samples [5] using the empirical Stillinger–Weber potential [6] with an increased three-body term. The activation barriers for the events range from 0 to 15 eV, peaking at 4 eV. The number of atoms that are displaced significantly in these events (0.1 Å or more) lies typically around 40, but there are usually only a few bonds broken or created. A typical event, showing only atoms rearranging their topology and their near-neighbors, is shown in Fig. 1.

Since in this material the list of neighbors is well-defined, we can identify three classes of events: in *perfect events* four-fold atoms exchange bonds but keep their total coordination; in *conserved events*, coordination defects diffuse around, while the overall

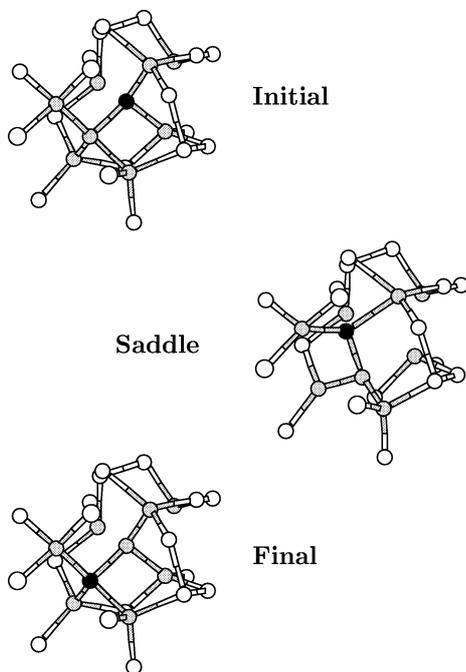


Fig. 1. A perfect event in amorphous silicon, corresponding to the concerted-exchange mechanisms proposed by Pandey for self-diffusion in crystalline silicon. From top to bottom: the initial, saddle point, and final configurations. The dark atoms participate directly into the event while the white ones are their nearest neighbors. The activation barrier is 5.12 eV, with no asymmetry since the initial and final configuration have exactly the same topology.

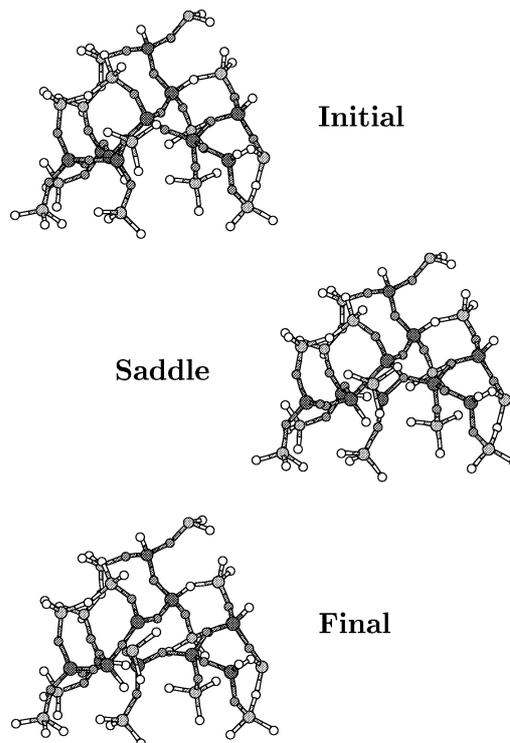


Fig. 2. A small event in SiO_2 . Shown here are the atoms that move more than 0.1 Å during activation and relaxation, plus their nearest neighbors. Large circles are Si atoms, small ones O. This particular event is the creation of a dangling bond on an O. The activation barrier and asymmetry are 3.64 and 1.35 eV, respectively.

coordination is preserved; *annealing events*, finally, involve the creation or the annihilation of defects.

For the class of perfect events, we label the atoms that change their bonding, and construct a loop consisting of all created and broken bonds, visited in the loop in alternating order. The sequence of the atoms visited by this loop gives a classification of the topological change in the bonded network. To avoid having many labels for the same topological reordering, all possible loops are generated, and the alphabetically lowest classification is chosen. Three types of perfect rearrangements dominate the dynamics. They correspond in order of likelihood to (a) an exchange of neighbors between two nearby atoms, corresponding to the Wooten–Winer–Weaire bond-exchange mechanism introduced initially as an artificial move, (b) the exchange of two atoms, similar to the concerted exchange mechanism introduced by Pandey [8] and il-

lustrated in Fig. 1, and (c) a step in between where two nearest neighbors are exchanged, giving a “double” Wooten–Winer–Weaire mechanism, with a shared backbone. We are still working on the classification of also the conserved and annealing events.

3.2. *Vitreous silica*

In a study of the mechanisms occurring in silica glass, we generated a database of 5645 events in well-relaxed 1200-atom samples of silica, in which the interactions were described by the screened-Coulomb potential of Nakano et al. [9]. This study has revealed a completely different dynamics for this material [10] than in amorphous silicon. In particular, because of the need to maintain chemical ordering, the perfect mechanisms of *a*-Si do not have a direct counterpart. One frequently observed mechanism is depicted in Fig. 2.

4. Conclusion

The activation relaxation technique provides a unique tool for identifying the microscopic mechanisms responsible for relaxation and diffusion in disordered materials. It avoids imposing pre-defined atomic moves, by working in the configurational energy landscape, and allows for real-space rearrangements of any size. With ART, we have been able to provide the first

analysis of relaxation and diffusion mechanisms taking place below melting in *a*-Si and *g*-SiO₂ and show that their respective dynamics is qualitatively different. The activation relaxation technique promises to be a powerful tool in the investigation of a wide range complex materials.

Acknowledgements

Part of the work reviewed here was performed in collaboration with Simon W. de Leeuw. NM wishes to acknowledge partial support by the NSF under Grant No. DMR 9805848.

References

- [1] G.T. Barkema, N. Mousseau, *Phys. Rev. Lett.* 77 (1996) 4358.
- [2] N. Mousseau, G.T. Barkema, *Phys. Rev. E* 57 (1998) 2419.
- [3] W.H. Press et al., *Numerical Recipes* (Cambridge University Press, Cambridge, 1988).
- [4] C.J. Cerjan, W.H. Miller, *J. Chem. Phys.* 75 (1981) 2800.
- [5] G.T. Barkema, N. Mousseau, *Phys. Rev. Lett.* 81 (1998) 1865.
- [6] F.H. Stillinger, T.A. Weber, *Phys. Rev. B* 31 (1985) 5262.
- [7] F. Wooten, K. Winer, D. Weaire, *Phys. Rev. Lett.* 54 (1985) 1392.
- [8] K.C. Pandey, *Phys. Rev. Lett.* 57 (1986) 2287.
- [9] A. Nakano, L. Bi, R.K. Kalia, P. Vashishta, *Phys. Rev. B* 49 (1994) 9441.
- [10] N. Mousseau, G.T. Barkema, S.W. de Leeuw (1998), to be published.