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.

2. The activation-relaxation technique

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.
centrated on low-dimensional problems for which, of- 
ten, 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 re-
alistic 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 stan-
standard implementation follows a modified force vector 
\( \tilde{G} \), obtained by inverting the component of the force 
parallel to the displacement from the current position 
to the local minimum \( \tilde{r} = \bar{x} - \bar{x}_m \) while minimizing all 
other \( 3N - 1 \) directions:

\[
\tilde{G} = \tilde{F} - (1 + \alpha)(\tilde{F} \cdot \tilde{r})\tilde{r},
\tag{1}
\]

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

Because of this projection, the standard algorithm 
fails for valleys perpendicular to \( \tilde{r} \). We now introduce 
a trailing position \( \bar{x}_t \), 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 \( \tilde{r} = \bar{x} - \bar{x}_t \), 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 \( \tilde{G} \) 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 \( \tilde{h} \) is replaced by a root-
finding algorithm of \( \tilde{G} \cdot \tilde{h} \).

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 \( \tilde{r}_0 \), we suppress the softest modes by \( n \) 
iterrations of

\[
\tilde{r}_{i+1} = -\tilde{F}(\tilde{r}_i),
\]

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 \( \tilde{r}_n \) by simply making it 
orthogonal to directions \( \tilde{r}_{n+1}, \ldots, \tilde{r}_{n+m} \), 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 relax-
ation in disordered systems, since the events that are 
created follow closely the physical activation paths. 
The method was recently used for the identification of 
mesoscopic 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 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-
illustrated 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.

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References