Numerical Studies Of The Dynamics Of Silicon: Relaxation, Nucleation And Energy Landscape

Normand Mousseau* and Philippe Beaucage and Francis Valiquette

Département de physique and Groupe de recherche en science et technologie des couches minces,
Université de Montréal, C.P. 6128 succ. Centre-ville, Montréal (Québec), Canada, H3T 1J7

ABSTRACT

Using various simulation techniques, such as molecular dynamics and the activation-relaxation technique, we are slowly developing a consistent picture of the dynamical properties of amorphous silicon. For example, results of an extensive search for the activated events surrounding a single minimum, in a well-relaxed model represented by a modified Stillinger-Weber potential, confirm that barrier height at the transition point, for activated mechanisms, is determined essentially by the binding energy of a single bond and not the details of the mechanism. We will discuss these results in some detail as well as recent simulations of nucleation in liquid and amorphous silicon.

INTRODUCTION

It is commonplace to affirm that the most studied element of all time, silicon, still deserves our attention. Amazingly, though, this affirmation holds true: although we have mapped in great details many of the properties of this material, a number of fundamental questions continue to elude us. This is particularly so of dynamical properties, which are difficult to study both experimentally and theoretically. In this paper, we present the results of simulations attempting to draw a first sketch of two dynamical processes that have received relatively little attention until now: the dynamics of nucleation from the liquid phase and the dynamics of relaxation and diffusion in the amorphous state.

Within the last five years, our group and collaborators have spent considerable efforts trying to obtain a reasonably clear picture of the structural and dynamical properties of the amorphous phase of silicon. For example, Barkema and one of us, NM, have developed various methods to generate high-quality a-Si models which can serve as a basis for further structural, dynamical or electronic studies. [1] One of these methods is an optimized version of the Wooten-Winer-Weaire bond-switching algorithm which generates an amorphous network starting from a perfectly 4-fold-coordinated random network. [2, 3] This is achieved using a rather artificial but remarkably satisfactory harmonic Keating potential. Although producing the best models available, this method is essentially static in nature, providing no information as to how real a-Si is produced or how defects relax and diffuse.

To look at these aspects of a-Si, we have used another method, the activation-relaxation

*Electronic address: normand.mousseau@umontreal.ca
technique (ART and ART nouveau). [4, 5] This method, which was used with a slightly modified Stillinger-Weber potential [6, 7] to generate good quality models of a-Si, can also explore the energy landscape of complex materials, jumping literally over activation barriers of all heights and complexity. [8, 9] With ART nouveau, it is possible to characterize the energy landscape and the basic mechanisms responsible for relaxation and diffusion in a wide range of systems. In the next section, we discuss an application of this technique to sample the energy landscape surrounding a single energy minimum of a well-relaxed 1000-atom cell of a-Si.

Much less work has been done on another fundamental dynamical property of this material: the nucleation process. The study of this process can help us understand the origin of the amorphous phase as well as the rapid crystallization, from the amorphous state, that takes place at temperatures much below melting. In section III, we present some preliminary results on this process to indicate the feasibility of such a theoretical study. Almost everything remains to be done on this problem.

Together these two themes offer just a glimpse of the complexity of the dynamical processes taking place in such a simple material. Much more experimental and theoretical will be needed before we can claim to understand them.

DIFFUSION AND RELAXATION IN AMORPHOUS SILICON

Dynamics through the energy landscape

In the last ten years, the concept of energy landscape has gained considerable importance [10]. This places the dynamics of diffusion in complex systems such as disordered materials into a global point of view, where the whole configuration can be seen as jumping from one local minimum to another, through the energy landscape, instead of being just something happening somewhere in the lattice (see Fig. 1). This conceptual change has no impact on the mechanisms as such, of course, but help us understand diffusion and relaxation as the configuration moves from one macroscopic state to another.

The energy landscape representation has many advantages. This is particularly so when designing accelerated algorithms. The time scale associated with activated relaxation or diffusion in many materials, such as semiconductors, is many orders of magnitude larger than the typical phonon frequency, and might involve some rather complex atomistic rearrangements. This often goes beyond the limits of standard simulation techniques such as molecular dynamics or real-space Monte-Carlo — where atoms are moved one by one by a small amount.

To circumvent these limitations it is preferable to define moves directly in the energy landscape, where activation can be seen as a jump from one local energy minimum to a nearby one, going through a first-order saddle point. In this picture, the real-space complexity of the move, which might involve many tens or hundreds of atoms, is completely set aside, simplifying considerably the simulation. It is such an approach that we selected for our study of the energy landscape around a local energy minimum in a 1000-atom model of a-Si. We use the activation-relaxation technique (ART nouveau), which has been described in details in Ref. 5 and represents an improved version of the original algorithm of Barkema and Mousseau [4, 11].

But the energy landscape picture has its limits. In particular, it hides the fundamentally
FIG. 1: The energy surface as a function of a generalized coordinate for a generic system. The circle represents a 3N-dimensional conformation oscillating in a local minimum at a temperature $T$.

localized nature of the dynamics in bulk materials: in these systems, all activated events always involve a finite number of atoms except at a phase transition. The 1+1 dimensional picture presented in Fig. 1 can therefore be very misleading. For example, much has been made recently of the barrier energy associated with higher-order saddle points implying some complex correlations between various levels of the energy landscape in disordered systems. [12] Analyzing these events in real space, we discover that these higher-order saddles correspond simply to a series of normal local events, each at the transition point and characterized by a direction of negative curvature in the energy landscape.

**Details of the simulation**

We study the energy landscape around a well-relaxed 1000-atom $\alpha$-Si unit cell prepared using ART nouveau. The configuration is described by a modified Stillinger-Weber potential, where the 3-body force constant has been increased by 50% in order to lead to the correct amorphous structure. [4, 7] The radial distribution function for this initial configuration is in excellent agreement with a recently measured high-quality RDF, as shown in Fig. 2. The initial configuration has only 26 three-fold and 20 five-fold coordinated defects at a cut-off of 2.8 Å, with more than 95% perfectly coordinated. The energy of the configuration is -4.000 eV/atom, compared to -4.137 for the crystalline state at zero pressure.

In previous work, our group and others studied the relaxation and diffusion process, as the configuration walked through the energy landscape, relaxing from a high-energy configuration to a well-relaxed one. [8, 9, 14] We are interested here in the characterization of the energy landscape in the **immediate surrounding** of a single minimum. Following a similar study of the landscape around local minimum in Lennard-Jones clusters, we want to evaluate, among others: (1) the structure and energy distributions of the barriers, (2) the number of escape routes, (3) the bias of the sampling method (ART nouveau). We present
FIG. 2: Radial distribution function (RDF) of the 1000-atom α-Si configuration used as the initial minimum (solid line). The dashed line represents the experimental RDF measured by Laaziri et al.[13].

Here results for a sampling of more than 42,000 events around the minimum described in the previous paragraph. Each event is started from the initial minimum by selecting an atom, $i$, at random and drawing a random direction in the subspace of the atom $i$ and its near neighbors. However, the activation to the saddle point is done without spatial restriction: all atoms are treated in exactly the same way. At this point, this technique represents the best way to ensure that no class of event is missed. [5] We have checked that these results are generic by sampling around a second minimum of similar structural quality and found that the results are independent of the fine details of the structure and topology of the network studied.

An event is characterized by an initial state and a final state, both representing local energy minima, and an intermediate state measured at the saddle point, defining the reaction state. As discussed in Ref. [5], these ART events are fully reversible, in the sense that a long-enough search at the final minimum will be able to find the saddle point and the original minimum. Although not guaranteeing detailed balance, this ensures that the search is ergodic.

Properties of the energy landscape

By construction, the initial direction for leaving the minimum is selected uniformly throughout the configuration. However, because there is no limitation on the number of atoms involved in the event, we could expect that a few atoms or regions of the 1000-atom configuration dominate in terms of events. Fig. 3 shows that the probability for each atom to participate into an event is equivalent, within a factor three or so. The dynamics of relaxation and diffusion in a well-relaxed model of α-Si is therefore uniform, confirming its local nature.

Because the search for events is random, the same event can occur many times. This
FIG. 3: Probability of participation to an event for each of the 1000 atoms in the model, computed over all generated events using displacement and change in coordination, as described in the text. The top panel shows that probability for at the saddle point and the bottom panel, at the final minimum. For this graph, an atom is involved in an event if it changes coordination or if its displacement is more than 0.1 Å. Results do not depend qualitatively on the exact value of the threshold selected.

helps us answer the fundamental question as to how many saddle points and minima surround any given local minimum in α-Si. Fig. 5 shows the number of unique saddle points, minima and overall events as a function of the number of generated events; even 42 000 events are not sufficient to ensure a complete sampling of the landscape surrounding a local minimum in a 1000-atom cell. We find 6519 different minima, 8799 different saddles and 11014 different events, yet the curve do not seem to converge to any specific value. Because moves are defined in the continuous space, the identification of unique events is not perfect and the exact number depend on the criteria we use. Although the convergence criterion for the saddle point and the minimum can be fixed with any desired accuracy, it has a finite precision. To decrease the impact of this finite precision, we label an event using only atoms that have moved significantly: only atoms moving by at least \( \delta r_{\text{threshold}} = 0.4 \) and 0.2 Å, respectively, at the saddle point and the final minimum, are used to label a specific event. We consider that two events are identical if they have the same list of participating atoms and their respective energy barriers is the same within a precision of 0.2 eV. The exact value of these thresholds affects the quantitative number of unique events but not the overall conclusion.

Although the number of unique events as a function of trial event is not converged, we have enough information to try to assess the total number of activated paths around a
single minimum in configuration space. First, we need to identify the bias of ART nouveau in its selection of events. To do so, we compare the energy distribution of the all events to that of the unique events (top panel of Fig. 4). Similarly to what we had found for Lennard-Jones clusters, it seems that ART selects events with an exponential bias on the energy barrier. Here, we find that the bias is well fitted by \( \exp\left(-\frac{E}{E_0}\right) \) with \( E_0 = 4.0 \) eV. The origin of this bias is not understood at this point but it is likely related to the width of the valley leading to the saddle point.

We can now try to assess the total number of different events surrounding a given minimum in \( \alpha \)-Si. If we suppose a random selection of events, drawn with an exponential preference for low energy events and taken from a distribution of energy such as that already calculated here, we find that the growth in the number of different events can be reproduced with a bias function \( \exp\left(-\frac{E}{A}\right) \) with \( 0.4 \leq A \leq 0.6 \) and a total number of different events between 30 000 and 60 000, or 30 to 60 different events per atom.

Because of the approximation needed, the estimation of the total number of paths surrounding a minimum has to be taken as an order of magnitude. From the above result, this number is more than one order of magnitude greater than the number of degrees of freedom, but remains finite, as one could have expected. These results are not expected to be qualitatively affected by the use of better interaction potential or less relaxed configurations. [15] The main challenge now will be to connect these results with experiment.

**NUCLEATION OF SI**

Amorphous silicon is known to re-crystallize well below the melting point of Si. The mechanisms underlying this transition are not clear, however, and we do not know what this implies regarding the structural and dynamical properties of Si. As a first step to-
FIG. 5: Number of unique events (solid line), unique final minima (dashed line) and unique saddle points (dotted line) as a function of the number of events generated. The distribution remains the same if we recreate this curve by drawing events at random in the sequence generated. There is therefore no bias in the order of the events selected.

wards trying to answer this question, we consider the crystallization process from the liquid phase, which is more easily accessible in computer simulations as it happens at a higher temperature.

Numerical research on the nucleation process started with hard spheres and Lennard-Jones models [16–18]. For covalent material like silicon, crystallization was studied either from a liquid/crystal interface [19] or an amorphous/liquid interface [20]. In the first case, the interest was to the planar front crystallization was studied as a function of the orientation of the crystal. In the second case, the stability of amorphous clusters imbedded in a crystalline matrix was studied as a function of the size of these clusters.

In previous work, we have shown that it is possible to crystallize a 1000-atom cell of liquid silicon described by a modified version of the Stillinger-Weber potential used in the previous section without having to introduce seed clusters artificially. [21] The set of parameters used had been developed by Vink and collaborators [7] in order to obtain the right structural and vibrationnal properties in the amorphous phase. Although excellent in the amorphous phase, this potential, which includes a three-body term 50 percent larger than the original Stillinger-Weber potential, does not get the right density relation between the crystalline and the liquid silicon: contrary to experiment, this potential generates a $c$-Si denser than $l$-Si.

After toying with the potential, the results we present here are for a Stillinger-Weber potential with a three-body term strengthened by 12.5% only, ensuring the crystallization of a 1000-atom cell while providing the proper phase diagram. This slight increase in the angular force with respect to the initial parameter set for the Stillinger-Weber potential seems to be necessary in order to crystallize a 1000-atom cell on a timescale reachable by molecular dynamics. Some problems still seem to remain much below the melting point and we are currently trying to address them. [22]
Before discussing the nucleation process, we must establish the melting transition temperature with this set of parameters. Because crystal-liquid melting is a first-order, there is strong hysteresis and one cannot simply identify the temperature at which a cell is melting as the melting transition temperature. The standard procedure to measure this quantity is to use thermodynamical integration, a numerical method which can give the free energy as a function of temperature for both the crystalline and the liquid phase as a function of temperature. The intersection of these two curves is the melting transition temperature. Although well established, this procedure is heavy and requires extensive sets of simulations.

Here, we follow instead the elegant technique of Keblinski and collaborators, [23] which can identify the melting transition temperature with precision without having to resort to thermodynamical integration. A crystalline and a liquid slabs are first equilibrated near the melting temperature and then put in contact in an NPE MD simulation. As shown in Fig. 6, the crystalline or the liquid phase grow until equilibrium is reached, at the melting temperature. This procedure, which is much simpler than thermodynamical integration, gives the right melting transition temperature for the Stillinger-Weber potential and 1767 ± 16 K for the potential used here.

Crystallization from the liquid phase

To limit size effects, we simulate the crystallization process in a 10648-atom cell with periodic boundary conditions. After equilibrating the liquid well above the melting temperature, we bring at once the system at a temperature 25 % below the melting temperature and pursue the simulation in the NVT ensemble, in a box corresponding to the crystalline density. This degree of undercooling is similar to what is used experimentally for the crystallization of a wide variety of materials [24] and also numerically for Lennard-Jones systems [17]. We select a NVT ensemble for numerical convenience. We have checked that crystallization also occurs in a NPT ensemble but found that it did so only after a
FIG. 7: Left panel: Radial distribution function at T=0, 2.4, 3.8 ns for the run described in the right panel. The sharp peaks correspond to crystalline distances. Right panel: Pressure as a function of time for the 10648-atom cell, during the crystallization process. The clock is started as the system is brought to 0.75 $T_m$.

FIG. 8: Left panel: Evolution of the size of the largest cluster in the model as a function of time. Right: Number of atoms member of a Wurtzite, Diamond and both building block as a function of time. The total number of atoms part of a crystalline network is smaller than the sum of the two since some atoms might be member of both a Wurtzite and a Diamond local structure.

considerably longer simulation time. The analysis of the crystallization process does not show qualitative differences between the two trajectories so we use constant volume for the simulations.

In the NVT ensemble, the crystallization process of the 10648-atom cell starts typically between 1 and 3 ns from the time the system is brought at its final temperature. Comparing with smaller simulation cells, we find that this time seems to decrease with an increasing cell, in agreement with standard nucleation theory. For a 1000-atom cell, the typical nucleation time is between 5 to 15 ns. As can be seen in Fig. 7, once nucleation starts, the crystallization is rapid, overtaking the model in slightly less than 1 ns.

**Characterization of the crystallization process**
In order to characterize better the process of crystallization, we identify two basic blocks, representing the smallest rigid structures that can be extracted from tetrahedral structure. The first, counting 12 atoms, is made up of two 6-fold rings, placed on top of each other and connected by three bonds, is extracted from a Wurtzite (hexagonal) structure. The second, from the tetrahedral network, consists of 10 atoms assembled as four 6-fold rings back to back. Both structures appear with a very low incidence in high quality amorphous silicon networks and are therefore good indicators of crystallization.

Figure 8 shows the evolution of the nucleation process analyzed in terms of these building blocks. For simplicity, we plot only the evolution of the size of the largest crystallite as a function of time. We see that, in the metastable equilibrium of the supercooled liquid, the fluctuations are sizable. From another simulation that did not crystallize in 5 ns, we plot Fig. 9 the distribution of size for the largest cluster in the supercooled liquid region sampled every 1 ps. The distribution is smooth and asymmetrical, with a peak at about 40 atoms and a tail reaching 180. The critical size for nucleation, at a temperature 25% below melting, seems therefore to be around 200. In Lennard-Jones systems, the critical size is 170 atoms [17].

At the end of the nucleation process about 95% of all atoms are part of at least one of the two building blocks. Given the size of the system the final configuration is clearly affected by the periodic boundary conditions: there is a single crystallite which forms grain boundaries with itself as it wraps around the box. These grain boundaries contain a significant fraction of the Wurtzite conformation, which does not correspond to the crystalline symmetry of silicon. At 0 K, the Stillinger-Weber potential is cut-off before the third shell of atoms and cannot, therefore, differentiate between the two phases. However, thermal fluctuation are sufficient and allow the potential to distinguish them. We expect, therefore, that the Wurtzite phase is only a result of the rapid crystallization process and that it would anneal into a tetrahedral conformation with further relaxation.

Much remains done in the analysis of the nucleation process in silicon. These results indicate however that this process is achievable on simulation time scale, which should allow
us to make predictions that will need to be confirmed experimentally.

CONCLUSIONS

In this short paper, we described two sets of simulations that attempt to describe some of the dynamical properties of silicon. In order to go much beyond these simulations, it will be necessary to establish ways to compare the results we obtain with experiment. This, in itself, represents a considerable challenge. Although the activation barrier distribution we generate with ART is in agreement with the barrier measured experimentally, we do not know if the wide distribution of mechanisms we see is occurring in real samples. Similarly, the nucleation process in silicon has been very little studied experimentally. It would be of great interest to have more experimental results on this transition.

ACKNOWLEDGEMENTS

We thank Frédéric van Wijland for his help in analyzing the trend in the number of unique events as a function of sampled ones. This work is funded in part by NSERC (Canada) and NATEQ (Québec). Most of the simulations were run on the computers of the Réseau québécois de calcul de haute performance (RQCHP) whose support is gratefully acknowledged. NM is a Cottrell Scholar of the Research Corporation.