

Investigation of the order continuum in the evolution of quenched Silicon using accelerated Molecular Dynamics techniques

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ABSTRACT

The thermodynamic, electronic and structural properties of silicon phases are inextricably linked to the underlying order in the material. While the crystalline and amorphous phases are well characterized, the existence of a glassy silicon phase is unknown as the quench rate ‘window’ available to experiments is too low to observe this material, except perhaps transiently. Our interest lies in characterizing order in the various solid phases of Si, looking in particular at phases with partial order. In traditional Molecular Dynamics (MD) studies, the accessible timeframe is too small, and the underlying kinetics too sluggish, to be confident that the MD results represent complete equilibrium. We have implemented accelerated MD methods like Hyper-MD (HMD) and Self-Guided MD (SGMD) for a system of atoms interacting via a Stillinger-Weber (SW) potential to reduce the effects of frequent, but non-essential, events. We have used these approaches to study the evolution of glassy and amorphous silicon from the relaxation of an ultra-rapidly quenched liquid and investigated the inherent structural order and its relationship to key system properties.

Keywords: Accelerated Molecular Dynamics, Silicon, Order, Amorphous

1 INTRODUCTION

Molecular Dynamics (MD) is a commonly used computational tool to study structural, thermodynamic and kinetic properties of a wide variety of molecular systems from simple fluids to large biological molecules. In molecular systems, motions take place over a wide range of time scales. Vibrations of the covalent bond take place in 10^{-14} s, whereas infrequent processes often take place over the course of microseconds or longer. Examples of processes undergoing long-term evolution

include large-scale conformational changes such as protein folding, evolution of surface morphology during crystal growth, diffusion of extended defects in solids and the migration of grain boundaries during plastic strain. In spite of the availability of inexpensive, powerful computers, the time scales accessible to traditional MD simulations remain on the order of nanoseconds. Recent advances in parallel computing hardware have dramatically increased the number of atoms that may be simulated, but it has had little impact on the time scales accessible to MD, due to the sequential nature of the integration of the equations of motion.

The limitation of traditional Molecular Dynamics timescales has been a long-standing obstacle to studying problems such as the evolution of amorphous silicon from the relaxation of a rapidly quenched liquid. Recent activity in accelerated MD schemes has provoked considerable interest in the community: Two algorithms, differing in philosophy, the Self-Guided Algorithm [1] and Hyper Molecular Dynamics [2] have been demonstrated to accelerate infrequent or slowly occurring events.

In a multidimensional space, the path of a conformational search is often complicated, resembling a random walk. The presence of local minima further reduces the efficiency of a conformational search as the system gets easily trapped in these energy basins. In the context of conformational search, the motion of particles can be divided into random and systematic motions. While the random vibrational motion is important to the detailed conformational distribution, the slower systematic motions are often the bottlenecks that limit the efficiency of conformational searching.

In order to boost the systematic conformational changes taking place, Wu and Wang, proposed the Self-Guiding MD algorithm (SGMD) [1] in which an extra force is added to the instantaneous forces derived from the potential. This additional guiding force is estimated from the force information

experienced by the system in the past and is an indicator of the local structural rearrangements taking place [For a detailed theoretical basis for the self-guided algorithm, the reader is referred to Ref 1]. The guiding force, $\mathbf{g}_i(t)$, is calculated as a time average of the instantaneous forces, $\mathbf{f}_i(t)$, that have acted on atom i during the last t_1 time steps. The addition of this guiding force results in a smoother energy profile, leading to lower energy barriers and fewer energy minima.

The only difference between the SGMD algorithm and the equations of motion used in a conventional MD simulation is the guiding force term, which nudges the system to the energy landscape minimum in a shorter amount of computational time. The properties of the guiding force only depend on two tunable parameters in the equation, t_1 and λ , where λ is the proportionality factor used for the guiding force.

Alternatively, the long-term evolution of a molecular system can be thought to be a sequence of infrequent transitions from one potential basin (“state”) to another. These infrequent transitions are typically not accessible to the trajectories mapped out by conventional MD schemes due to the prohibitive costs involved in long run times. The Hyper-MD (HMD) scheme reduces the time spent by systems trapped in these potential minima basin states. This is done by the modification or ‘biasing’ of the potential surface such that the simulations of the modified potential surface exhibit the correct relative probabilities of escape from the current state of the system to the various adjacent states, but with enhanced overall escape rates. This results in an undistorted long-term evolution of the system at the loss of the detailed short time vibrational information.

The key to implementing HMD is to design a computationally tractable bias potential that does not require advance knowledge of the potential surface. It is difficult to define a bias potential that does not introduce any TST-violating correlations, but a good approximation suffices. Voter [2] proposed a scheme which involved the computation of the eigenvalues of the Hessian matrix. The bias potential fills the minima, and is required to go to zero smoothly near a saddle point so that the evolution of the system through the saddle points is unaffected. Steiner and co-workers forgo the calculation of the smooth bias potential completely and used the following simple approximation [3]: If, in any region, $V(\mathbf{R})$ falls below a carefully chosen

‘boost energy’, E_b , $V(\mathbf{R})$ is replaced by the constant E_b . In order to give a smooth crossover and, at the same time, restrict the range of the smoothing region, the *bias* potential is defined as

$$\Delta V_b = f(\chi) + E_b - V = \chi g(\chi) + h(\chi) + E_b - V \quad (1)$$

where $\chi(\mathbf{R}) = V(\mathbf{R}) - E_b$ and $g(\chi) = 1/(1 + \exp(-\alpha\chi))$ and $h(\chi) = \exp(-\gamma^2 \alpha^2 \chi^2)/\alpha$.

The choice of $\gamma = 1/3$ and α between 10 and 50 achieves the goals of a restricted yet smooth crossover. The forces due to V^* are related to those on V by a simple chain rule and the *boost* factor of the computational time over the conventional MD scheme can be calculated as

$$\text{Boost factor} = \langle \exp[\beta \Delta V_b(\mathbf{R})] \rangle_{V^*} \quad (2)$$

The extent of the code change from a normal MD scheme is nominal. However, since the bias potential is not zero on the surface of the configuration space, this scheme may introduce substantial errors in the calculations if too aggressive a choice of the *bias* potential is employed.

2 METHOD

This study involves a comparison of the properties of disordered phases of silicon (amorphous, glassy and liquid) and how the extent of disordering affects the mechanical, thermodynamic and electric properties of these substances. We investigate this by tracking the change in order in the system as a sample of liquid silicon is quenched hard (10^{11}Ks^{-1}) and subsequently evolves using Molecular Dynamics techniques. While the terms ‘glassy’ and ‘amorphous’ are often used interchangeably in the literature, we define a ‘glass’ to refer to a material with the structure of a “frozen liquid” but the diffusional characteristics of a solid. We reserve the term “amorphous Si” for the enigmatic material produced experimentally by self ionization of crystalline silicon [4], which is known to have tetrahedral short-range order but little long-range order. Whether amorphous Si (*a*-Si) is a special kind of glass is an open and intriguing question. This study is intended to help address some of the issues raised by this question. Experimental attempts to produce a glassy Si have failed, largely due to their inability to cool the liquid Si fast enough [5], and partly, perhaps, because it is unclear how rapidly

the glass transforms to the amorphous (*a*-Si) state. Computational studies, however, has the opposite problem: the slowest cooling rates possible in a reasonable MD time frame is still extremely high (greater than 10^{10} K/s) due to the small time step of integration. As a result, the supercooled liquid gets trapped in deep energy wells and the transformation to less disordered phases takes a long amount of time (many *ns*) and is computationally prohibitive to study. This makes it an ideal candidate for a study using accelerated MD techniques to unlock the structural evolution of a glassy, as quenched, Si solid into whatever more ordered state may arise. With this goal in mind, we have implemented both the SGMD and HMD techniques in a study of structural evolution in a system of Stillinger-Weber (SW) particles [6].

From a liquid state at 2300K, silicon was quenched at 10^{11} K/s to a temperature of 700 K and allowed to evolve in a NPT (isobaric-isothermal) ensemble for a period of several ns, observing the structural changes that occurred. The order in the system was determined using traditional parameters such as bond angle and dihedral angle distributions, ring statistics and co-ordination number. Important new insight was also provided by a new order parameter [7] based on a pattern recognition technique. Determination of the electronic and thermodynamic properties throughout this evolution, obtained using quantum mechanical methods, showed that these properties are closely linked with the structural changes taking place.

3 RESULTS AND DISCUSSION

Figure 1 shows the evolution of the coordination number for the same initial configuration of glassy silicon using a conventional MD scheme and the two accelerated schemes: SGMD and HMD. The relaxation using a conventional MD scheme gets mired in kinetic traps, as a result of which the evolution is sluggish. The accelerated MD schemes are however able to overcome such barriers and evolve to a more ordered phase at a quicker rate. The effect of the SGMD scheme on the evolution is more gradual as it guides the system by smoothing out the energy surface. The effect of the HMD scheme is more dramatic and can be seen in the quick drop in coordination number achieved over the first few thousand steps. Boost factors of 4-5000 were observed in our HMD runs depending on how aggressively we biased the system.

Most of the final structural properties using HMD and SGMD were found to be identical. The average coordination number of the final structure fluctuates around 4.10 (c.f. experimental value: 3.88 and continuous random network (CRN) [8] model: 4.0). The CRN is an idealized random network produced with the coordination number set exactly to be 4 using a set of Monte Carlo moves. Since it does not incorporate any dynamic information and is, instead, a form of energy minimization, to make an appropriate comparison of the properties of our virtual amorphous silicon with it, we carry out the minimization of the final SW configuration using a tight-binding algorithm. This shall be referred from now on as the SGMD-TB structure. This sample has a coordination number of 3.97 with structural and electronic properties very similar to that of the CRN model and experiment.

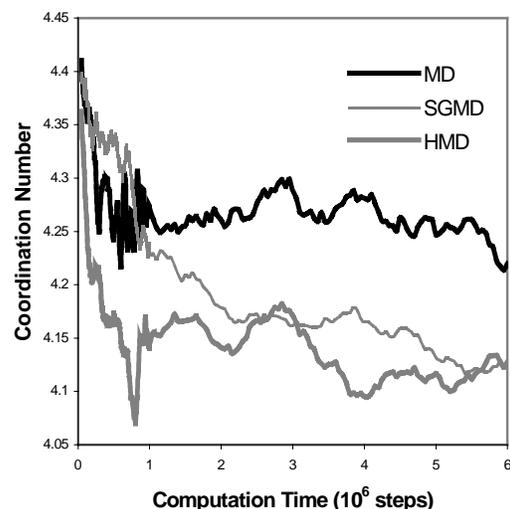


Figure 1: Evolution of coordination number

	N	Z	θ (deg)	σ_{θ} (deg)
Crystal	512	4	109.39	3.85
Exptl. <i>a</i> -Si		3.88-3.97	108.6	9.0-11.3
CRN model	1000	4	109.3	9.03
SGMD-TB	512	3.97	109.01	11.31
SGMD (31ns)	512	4.05	108.51	13.54
HMD(11 ns)	512	4.11	108.25	15.23
Liquid	512	4.45	104.17	26.79

Table 1: Comparison of properties of various silicon phases.

Table 1 provides a comparative description of the various phases of silicon. Here N stands for the computational system size, Z the average coordination number, θ the average bond angle and σ_θ the deviation from the average bond angle. Disorder in the system increases as we descend the table (from crystal to liquid phases), as observed in the increased distribution of bond angles, for example. The SGMD and HMD samples are snapshots taken at arbitrary times during the runs.

Conventional order parameters like coordination number, average bond angle, ring statistics are difficult to use on a *per atom* basis, for example in characterizing order in a small cluster of atoms. The use of a new Skeletal Order parameter based on recognizing patterns or signatures, developed by our collaborators, Shetty and Escobedo, is helping us to get a better quantitative grasp of the extent of ordering in materials [7]. On a scale of order from 0 to 1, where 0 represents complete disorder (as seen in a dilute gas) and 1 the complete order represented by a perfect crystal, the SGMD-TB and CRN samples have an average order of 0.75 and 0.79 respectively. The small difference between the two samples is seen to originate from certain atoms in our virtual amorphous silicon, which display a local order signature typical to that observed in a liquid sample. This shows that a few of the atoms retain the structural memory of the quenched liquid form from which they originated.

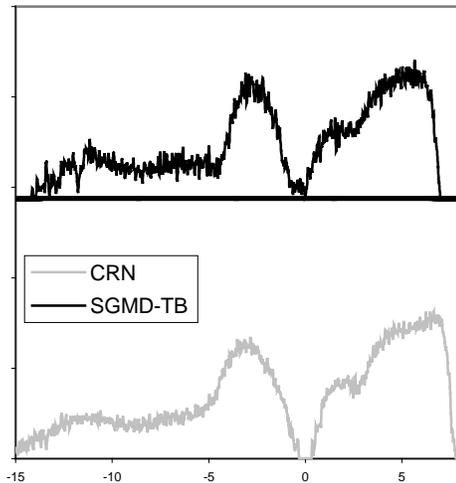


Figure 2: Electronic Density of States for the SGMD-TB and CRN samples

We compared the electronic properties of our virtual amorphous sample with that of

CRN, as shown in the Electronic Density of States (EDOS) plots in Figure 2. The two curves are similar but for the presence of a few gap states in our virtual a-Si. These again point out to small remnants of metallic liquid ‘pockets’ present in our samples. Another confirmatory test that can be used to distinguish between a glassy phase and an amorphous phase is the melting profile. Disordered phases, which are glassy, exhibit a second-order transformation to a liquid phase. In contrast, a first-order phase transition to a liquid state was observed for both the CRN sample ($1205 \pm 5K$) and our virtual a-Si ($1212.5 \pm 12.5K$). This is significantly less than the experimental value reported in literature ($1450 \pm 50K$) because of an inherent inadequacy in the SW potential to accurately describe disordered phases of silicon.

4 CONCLUSIONS

Accelerated MD schemes have allowed us to investigate the continuum of order that exists from the glassy, “frozen liquid”, obtained by quenching the liquid, to an a-Si-like material that evolves over timescales difficult to study using conventional MD. The interrelationship between structural, electronic and thermodynamic changes along this continuum has become clearer, including the nature of the phase transition between a-Si and the molten phase. A new order parameter has provided us with a better ‘vocabulary’ with which to discuss the extent of order in disordered material

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