Generation of amorphous-silicon structures with use of molecular-dynamics simulations

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Amorphous-silicon states have been generated in a computationally efficient manner by quenching liquid silicon configurations using a molecular-dynamics simulation. Classical two- and three-body interatomic Si potentials have been used. We present results for the radial distribution functions, bond-angle distributions, vibrational densities of states, and neutron scattering functions for the theoretically generated *a*-Si states. The molecular-dynamics simulations generate threefold- and fivefold-coordinated defects in the *a*-Si structures.

INTRODUCTION

Amorphous solids have been a subject of extensive experimental and theoretical studies. Much of this interest has focused on the amorphous tetrahedral solids (*a*-Si, *a*-Ge) which have important microelectronics applications. A major problem in theoretical studies of these materials has been to generate physically reasonable amorphous structures and to compare properties of these structures with experimental measurements. Continuous random-network models[1,2] have achieved considerable success in generating *a*-Si structures, but these models are not easily generalizable to other glassy materials or systems with different species of atoms. Recently, Wooten, Winer, and Weaire[3] (W3) have developed a Monte Carlo scheme for the computer generation of amorphous tetrahedral structures. In their approach, local atomic rearrangements are introduced into a tetrahedral structure that preserve distorted tetrahedral bonding but introduce fivefold and sevenfold rings. These local rearrangements were accepted according to a Metropolis Monte Carlo algorithm[4] with a Keating[5] model for the strain energy. A steepest-descent relaxation was needed after each Monte Carlo move. A very large number of such moves were found to effectively randomize the structure and produce radial distribution functions (RDF's) for the final state that compared very well with experiment for *a*-Si.

In this paper we present an alternative approach for the computer generation of amorphous structures with molecular dynamics (MD). We start with the separable two- and three-body Si potentials recently developed by Biswas and Hamann.[6,7] These classical models were developed by fitting to first-principles total-energy calculations for bulk, surface, and defect Si configurations. We emphasize at the outset that none of the several classical models developed for Si (Refs. 6–10) to date can model all the known structural properties for Si. The present model,[7] for example, describes energies of surface geometries and defect configurations in tetrahedral Si reasonably. It, however, does much less well on the energies of bulk Si phases—particularly the high-pressure metallic Si phases. Alternatively a longer-range Si potential[6] very accurately describes the bulk Si phases, but has serious shortcomings for defect-formation energies (particularly the tetrahedral interstitial defect in diamond Si). In a similar spirit, Ding and Andersen[11] found that the classical Stillinger-Weber[8] Si potential fits liquid and crystalline diamond Si reasonably well but is not satisfactory for *a*-Si. Ding and Andersen[11] concluded that any classical potential can describe two of the three condensed phases well, but not all three. They modified the Si potential to describe the *a*-Si structure and the crystalline diamond phase well at the expense of describing the liquid-Si state less well.

Our goal, in this paper, is to develop an efficient computational strategy for generating amorphous-silicon states, and then study the structural and vibrational properties of the generated *a*-Si states. We recognize the inherent deficiencies of the underlying classical potential models for silicon. We do not aim to improve on these potentials in this paper. We instead aim to use these models to extract the relevant physics of the *a*-Si states and a computational molecular-dynamics (MD) scheme that can be easily generalized to other systems. We are interested in determining how the *a*-Si configurations generated using MD methods compare with that generated by W3.

COMPUTATIONAL METHODS

Our computational strategy is to equilibrate a melt of bulk Si and then form a glass by cooling the system from the melt. Cooling the liquid configuration on the com-

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puter is physically equivalent to a quench, since it is several orders of magnitude faster than usual experimental cooling rates for bulk materials. Annealing back to the crystalline ground state is highly improbable in the relatively short annealing times. Our MD calculations allow the system to explore a wide range of configurations, rather than a restrictive set of bonding configurations that are sampled in previous *a*-Si generation schemes. Recently, similar MD calculations have been used to generate an *a*-Ge structure.[11]

Our calculations were performed for a system of N atoms in a cubic supercell with periodic boundary conditions, similar to those used by W3. We have made *a*-Si structures with $N=216$, 512, and 2000, whereas the published results from W3 are for $N=216$. In this paper we will confine mostly our analysis to the 216- and 512-atom structures in order to compare our results with W3. Our MD simulations were performed by immersing the atoms in a heat bath, providing a random fluctuating force. The temperature of the system can be controlled easily using this Langevin approach. A time step (Δt) of 0.00129 ps was used, with damping constants $\gamma \sim 0.02(\Delta t)^{-1} - 0.04(\Delta t)^{-1}$.

RESULTS

We melted the Si crystal and equilibrated the melt at a temperature of 0.26 eV. The melt was annealed by reducing the temperature by 0.01 eV every 750 steps (1500 steps for the 512-atom system) to a final temperature of 0.08 eV. The atomic positions were then locally relaxed with a steepest descent algorithm. This resulted in an amorphous state, for an $N=216$ system, characterized by a peaked pair distribution function $g(r)$, labeled 1.0 in Fig. 1, and a double-peaked bond-angle distribution, labeled 1.0 in Fig. 2. The atoms in this glass have an average of 5.5–6 nearest neighbors and exhibited bond angles (of $\approx 60°$) that were very different from tetrahedral. This glass represented an amorphous metallic configuration rather than an amorphous tetrahedral

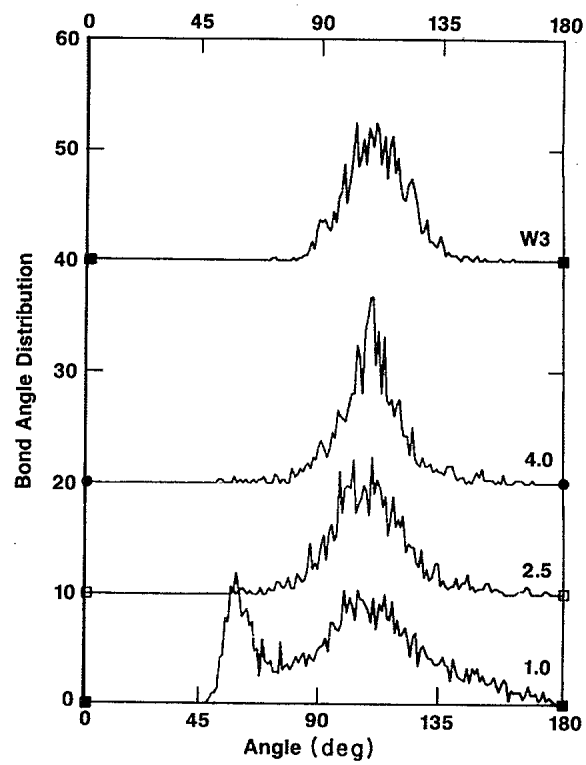

FIG. 2. Bond-angle distributions for quenched amorphous Si configurations using the original Si potential (1.0) and models with the three-body potential scaled by 2.5 and 4.0 (2.5 and 4.0), compared with that from Ref. 3 (W3). Bonds are defined by neighbors within the first peak of the pair distribution function. All of these results are for $N=216$.

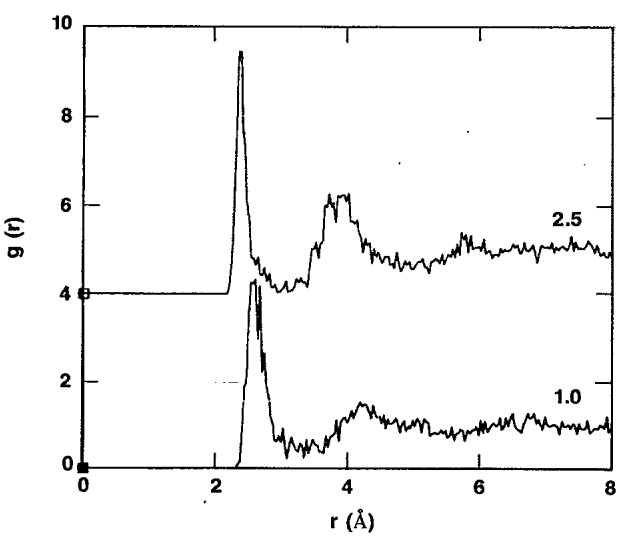

FIG. 1. Pair distribution functions $g(r)$ for the as-quenched amorphous states with the original Si potential (1.0) and with the three-body potential scaled by 2.5 (2.5) for an $N=216$ glass.

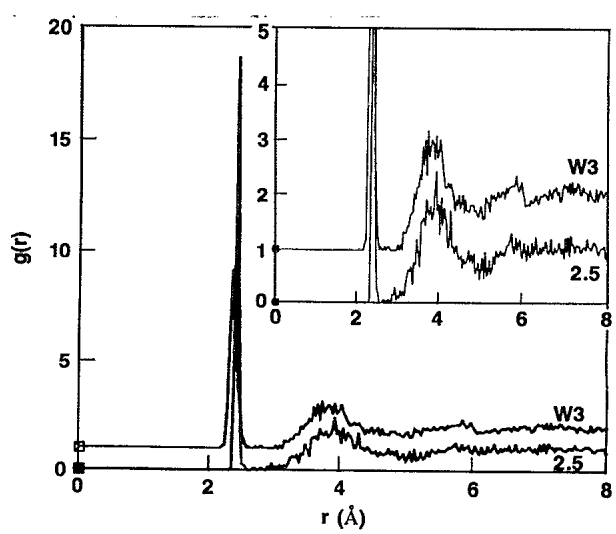

FIG. 3. Pair distribution function for the amorphous state produced after quenching and Monte Carlo relaxations with the present Si potential (2.5), compared with that from Ref. 3 (W3). An offset of 1.0 unit has been used.

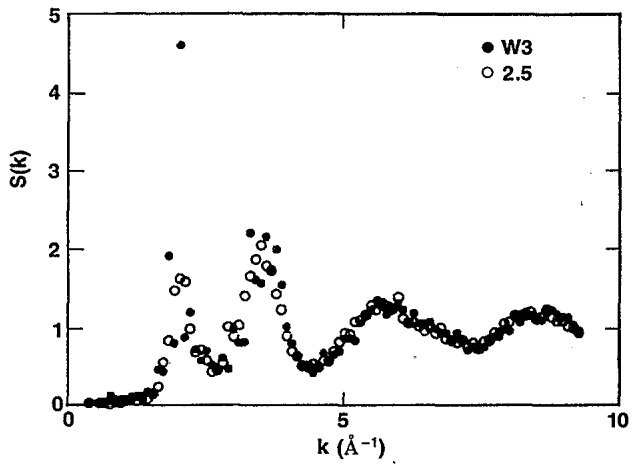

FIG. 4. The static structure factor $S(k)$ for the amorphous-Si configurations in the present work (2.5) compared with that of Ref. 3 (W3) for $N=216$.

configuration. In fact, the energy of the quenched state (0.18 eV/atom above that of crystalline diamond Si) was actually lower than the energy of the representative W3 amorphous tetrahedral state (0.25 eV/atom) with this Si potential.[6]

General improvements to the Si model involve the computationally difficult task of exploring the large parameter space of the Si model. We found that a simpler solution was to implement a one-parameter scaling, where the strength of the three-body potential was increased by a factor of $\approx 2.0-4.0$. This scaling generates a larger energy penalty for bond-angle distortions from the tetrahedral. This modified Si potential energetically favors an amorphous tetrahedral state over an amorphous metallic one. The modified Si potential provides a larger energy difference between the diamond and the more dense-packed crystal phases. The liquid Si phase has an average coordination between 4.5–5, in comparison to 5.5–6 with the original Si model.[6]

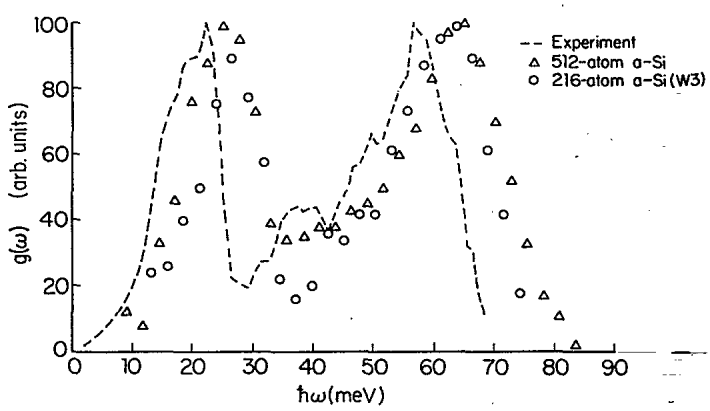

FIG. 5. Vibrational densities of states for the a-Si states in the present work ($N=512$) and that from Ref. 3 ($N=216$) compared with experiment (dashed line).

The modified Si potentials have a larger equilibrium lattice constant than the original model, e.g., the scaling of 2.5 increases the equilibrium lattice constant by 5.3%. However to facilitate comparisons between the glasses made with different potentials, we have kept the density of all the glasses at the equilibrium crystal density with the original Si model.

We repeated the above procedure of melting, annealing, and relaxation, using the Si model of Ref. 6 with a three-body potential scaled by 2.5, and produced a quenched amorphous state with $g(r)$ displayed in Fig. 1 as 2.5. This amorphous state had a sharp nearest-neighbor peak with strength of $\simeq 5.5$ and an average coordination of 4.0–4.05.

The bond-angle distribution (labeled 2.5 in Fig. 2) is peaked around the tetrahedral angle, and is very similar to that of the W3 amorphous state (see Fig. 2). Similar amorphous structures were also generated by scaling the three-body potential strength by 4.0 (with the slightly narrower bond-angle distribution 4.0 in Fig. 2). We made one run for the 216-atom system with a cooling rate that was slower by a factor of 10. This led to an amorphous structure with very similar statistical properties.

The present Si potentials have not been fitted to the diamond-Si phonon frequencies and are consequently not accurate for most vibrational modes. Instead, the vibrational properties are more accurately described by the Keating model with the interaction cutoff at $r=2.84$ Å, near the first minimum in $g(r)$.[5] To calculate the vibrational densities of states and to compare to experimental data, we further relaxed the 2.5 glass at $T\approx 0$ using a Monte Carlo simulation[3] and a Keating model for the strain energy. The resulting amorphous configuration had a significantly narrower and sharper pair correlation function $g(r)$ (Fig. 3) but had only a small change in the bond-angle distributions of Fig. 2. The pair distribution function $g(r)$ is identically zero between the first- and second-neighbor peaks, allowing an unambiguous definition of the coordination number. The radial and bond-angle distributions for the 2.5 glass compare very well with that of the W3 glass.[12] The short-range order exhibited by the static structure factor $S(k)$ is very similar for both the 2.5 and W3 amorphous states (Fig. 4). The height of the first peak is significantly higher for the W3 state, indicating a somewhat greater long-range order for the W3 glass. Similar conclusions were found for the 4.0 glass.

An essential difference of our glasses from the W3 glass and amorphous structures from continuous random network models is the presence of defect sites in the present glasses. These defect sites are either threefold-coordinated dangling-bond sites or sites with five neighbors that are present in approximately equal number. The number of twofold-, threefold-, and fivefold-coordinated sites were (i) 0, 14, and 18 for the $N=216$ 2.5 glass; (ii) 0, 12, and 12 for the $N=216$ 4.0 glass; and (iii) 1, 34, and 52 for the $N=512$ 2.5 glass. For comparison, when the $N=216$ system was cooled ten times slower, the defect counts were 0, 23, and 9, respectively—similar in number to the faster cooled sys-

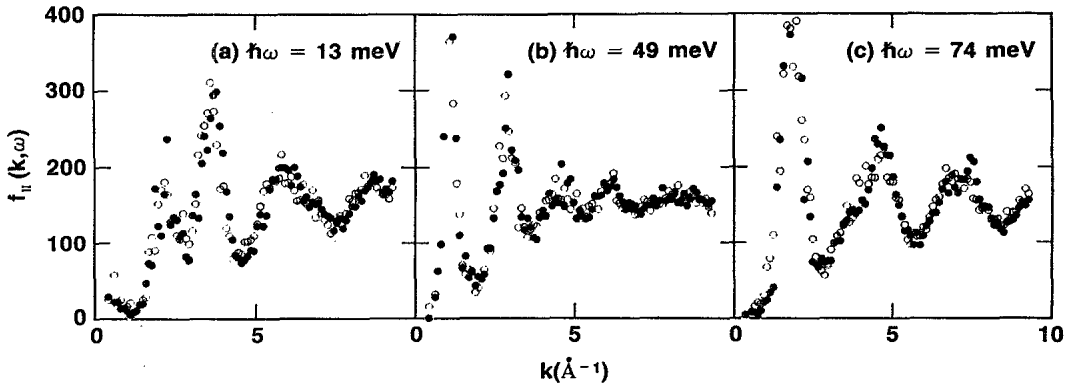

FIG. 6. The reduced structure factor $f_{\parallel}(k,\omega)$ vs k for the present 216-atom a-Si configurations (2.5) (open circles) and the state of Ref. 3 (W3) (closed circles) plotted for the three modes.

tems. Sixfold-coordinated sites were not found. Generally about equal numbers of fivefold-coordinated and threefold-coordinated defects were produced. For the fivefold-coordinated sites at least one, and usually two or three bond lengths were longer—representing only weak bonds. Fivefold-coordinated sites have been proposed as an intrinsic defect in a-Si.[13] The defects have an atomic density of 10–15% that are clearly larger than in experimental a-Si samples, but are consistent with H concentrations of up to 25% in a-Si:H materials.

We have made the major comparison between experiment and theory by comparing the vibrational properties of our glass with results from neutron scattering measurements on a-Si.[12] A straightforward diagonalization of the dynamical matrix led to the vibrational densities of states (DOS) for our 512-atom 2.5 glass that we have compared with experiment[12] and the DOS for the W3 state in Fig. 5.

The results for the two theoretical a-Si states show general overall agreement. However, the larger 512-atom system has a considerably smoother DOS at lower frequencies, than the 216-atom configuration. This indicates the importance of large system sizes for theoretical amorphous structures. The presence of defects gives rise to a high-frequency tail in the 2.5 glass, compared to the W3 state, but has little effect at other frequencies. Compared to experiment both a-Si states model well the high-frequency peak in the DOS—which represent a broadening of the TO- and LO-phonon peaks of the crystal. This indicates physically reasonable bond-length distributions for the a-Si states.

There is discrepancy between theory and experiment[9] in the low-frequency region, where the theoretical density-of-states (DOS) peak is at higher frequency than experiment. This disagreement is not any worse for our 2.5 glass than for the W3 state. The computer-generated a-Si states may be more strained, in terms of a wider bond-angle distribution, than in experiment leading to stiffer bond-bending modes. Keating model parameters appropriate to the crystal have been used here. An alternative interpretation may be that a good description of the vibrational DOS of a-Si requires bond-bending force constants that are softer than in the crystal.

A further comparison between our structures and those of W3 can be made by comparing the neutron scattering functions $f_{\parallel}(k,\omega)$ and $f_{\perp}(k,\omega)$ which is given by[14]

$$f_{\parallel}(k,\omega)=\left\langle \left| \sum_i \hat{\mathbf{k}}\cdot\mathbf{P}_i^{\omega} \exp(i\mathbf{k}\cdot\mathbf{R}_i) \right|^2 \right\rangle ,$$
$$f_{\perp}(k,\omega)=\left\langle \left| \sum_i \hat{\mathbf{k}}\times\mathbf{P}_i^{\omega} \exp(i\mathbf{k}\cdot\mathbf{R}_i) \right|^2 \right\rangle , \quad (1)$$

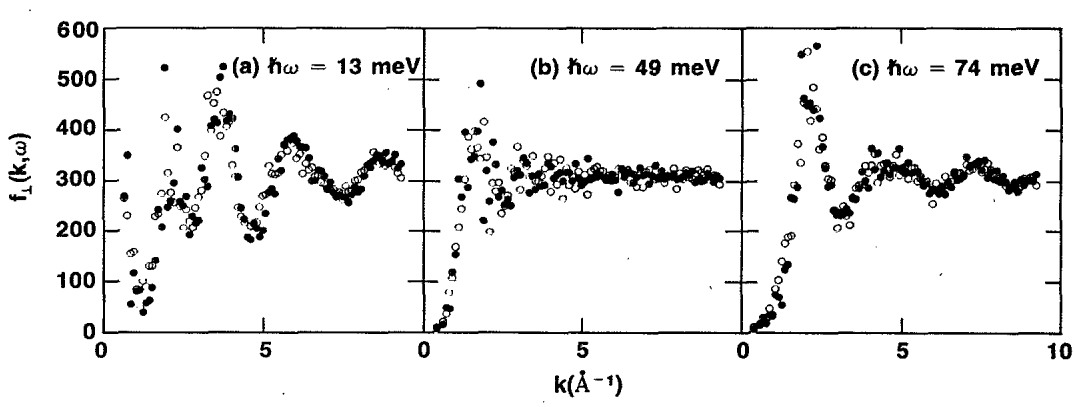

FIG. 7. $f_{\perp}(k,\omega)$ vs k for the three modes shown in Fig. 6.

$\mathbf{P}_i^{\omega}$, the polarization vector, is the maximum displacement of the ith atom ($\mathbf{R}_i$) vibrating in that mode. The average is performed over all k of the same magnitude. In the one-phonon approximation $f_{\parallel}(k,\omega)$ is directly proportional to the structure factor $S(k,\omega)$ that is observed in neutron scattering. Results for the lowest nonzero-frequency mode (13 meV) for our 216-atom 2.5 glass and the W3 glass are shown in Figs. 6 and 7. Also shown in Figs. 6 and 7 are results for intermediate-frequency (49 meV) and a high-frequency mode (74 meV). The scattering functions are very similar for both a-Si states, indicating that the presence of defects do not affect the scattering properties of the system. The presence of the defects generate a higher frequency tail in the densities of states. We have studied the dependence of the inverse participation ratio on frequency and find the higher-frequency tail modes to be localized in character. Generally there are 3–4 times more localized modes in our MD glasses than in the MC. However, these localized modes only consist of 1–2 % of the total phonon modes.

We have presented results for $N=216$ and 512 systems, which describe well the static structural properties and many aspects of the vibrational DOS. We are performing further studies on a $N=2000$-atom system, which will be reported in a separate paper. This large system will provide new low-frequency vibrational modes whose DOS and scattering cross sections can be compared to experiment.[12]

CONCLUSIONS

In conclusion, we have presented a scheme for making glasses that is computationally more efficient than the Monte Carlo procedure. We require a modest 1–2 CRAY-XMP hours per 216-atom glass, for anneal times of $(12-24)\times 10^3$ MD time steps. We estimate that the Monte Carlo procedure may require at least an order of magnitude more computer time. The cooling method generates defects unlike the Monte Carlo method. We did not know *a priori* how many defects would be generated. There is little distinction in the vibrational frequencies of the MD and MC glasses, except at high frequencies where there are $\approx 1-2$ % of extra modes. The defects do not alter the bond-angle distributions in the glass. The neutron scattering functions are very similar for both MD and MC glasses and compare well with experiment. The structural defects and disorder can be studied as a function of the anneal rate with MD calculations. Furthermore, the present MD procedure can be easily extended to larger systems and to other glass forming materials, including materials with different species of atoms, particularly with recent progress with interatomic potential models.

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