Glassy Quasithermal Distribution of Local Geometries and Defects in Quenched Amorphous Silicon

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Simulations of amorphous silicon formed by quenching of the liquid indicate that *a*-Si has a Boltzmann-like distribution of local geometries, corresponding to a "glass temperature" of roughly 700 K. The resulting tetrahedral network exhibits native defects, threefold- and fivefold-coordinated atoms, which have mean formation energies of 0.6 and 0.3 eV, respectively, and which are apparently mobile even at fairly low temperatures. These results are obtained by a novel approach to the analysis, and are relatively insensitive to the empirical interatomic potential used in the simulations.

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Interest in the fundamental properties of glassy and amorphous systems has grown steadily over the years, both because of their ubiquity and practical importance, and because of the subtle and fascinating questions to which they give rise. However, the quantitative description of disordered materials is intrinsically difficult. Often their microscopic properties can only be inferred indirectly by the comparison of measurements of average statistical properties with results of theoretical models.

Here, we present results of simulations of a prototypical disordered system, amorphous silicon (*a*-Si), formed by rapid quenching of the liquid. We use two very different empirical potentials to model the atomic interactions, in order to ensure that the results do not depend upon the choice of potential.

By introducing a novel technique for analyzing the results, we are able to extract important quantities which have not previously been accessible in such calculations. We find that *a*-Si formed by quenching is a glass, in the sense that it exhibits a thermal distribution of local geometries, corresponding to the temperature at which the undercooled liquid becomes effectively a solid. We infer this "glass temperature" to be $T^* \simeq 700$ K. However, "defects" in the tetrahedral network remain mobile down to somewhat lower temperatures, "freezing" at roughly 500 K. We are also able to address the somewhat subtle issue of defect formation energies in *a*-Si. We find that fivefold-coordinated atoms, viewed as native defects in *a*-Si, have a mean formation energy of 0.3 eV, half that of threefold-coordinated atoms, and that the fivefold-coordinated atoms are correspondingly more numerous.

a-Si represents an ideal system for studies of disorder, since it is particularly simple, consisting of a one-component tetrahedrally bonded network. Moreover, *a*-Si is of great technological importance. It is therefore natural that several theoretical studies of its structural properties have recently been reported.[1-6] (We do not address electronic properties here.)

Wooten, Winer, and Weaire[1] introduced a discrete Monte Carlo bond-switching algorithm for generating a continuous tetrahedral amorphous network. More recently, Ding and Anderson[2] generated a structural model for *a*-Ge (which is quite similar to *a*-Si) by performing a molecular-dynamics (MD) simulation of Ge, adapting an empirical interatomic potential[7] developed for Si. The Ge was melted and quenched, forming an amorphous tetrahedral network. A similar procedure has been followed in studies of *a*-Si by at least three other groups,[3-5] with considerable success.

These studies, though illuminating, naturally have certain limitations. The model of Wooten, Winer, and Weaire cannot address issues of defects in *a*-Si. Two of the dynamically generated models[2,4] used interatomic potentials which had been adjusted *ad hoc* to give a good amorphous structure upon quenching, and so it cannot be assumed that energies are quantitatively described. This could affect the number and type of defects or highly strained bonds.

Two recent studies[3,5] used the potential of Stillinger and Weber[7] (which we hereafter call SW). This potential has been relatively well tested, and gives reasonable energies for point defects in Si.[8] However, SW does not result in a tetrahedral structure upon simple quenching of the melt,[2,3] and so tricks had to be used during the cooling to ensure that a tetrahedral structure was reached. Thus the kinetics of quenching may not be realistically described.

Finally, in a radically different and, in principle, fundamentally superior approach, Car and Parrinello[6] have performed MD simulations of quenching of Si using a fully quantum mechanical calculation of the energies and forces. However, this approach is so numerically intensive that, at present, it is restricted to very short simulated times and small numbers of atoms.

The present work differs from previous studies in several ways. By far the most important of these is the manner in which we analyze results of the simulation, which permits us to extract the glass temperature T^*, and to infer the formation energies of defects in the tetrahedral network. In addition, the interatomic potential and simulation techniques used here differ from previous work.

We use a new potential developed recently by one of us.[9] This potential, hereafter referred to as T2, is similar to one presented earlier[10] (T1), but has been improved to avoid certain pathologies[11] of T1. T2 has been extensively tested,[9] and is particularly appropriate in the present context because it describes the energies of point defects in crystalline silicon rather well.

However, all the important results have been checked by our repeating the analysis with SW. SW is complementary to T2 in having very different strengths and weaknesses,[12] so that the quantitative similarity of results obtained with the two potentials provides strong evidence for the reliability of the conclusions.

We use a continuous-space Monte Carlo (MC) algorithm instead of molecular dynamics. We begin with 216 atoms in the diamond structure at the equilibrium lattice constant, with periodic boundary conditions. The sample is heated at fixed volume to 3000 K, and permitted to melt and equilibrate. The melt is then cooled at inverse rates ranging from 1 to 16 MC steps/atom-K, with the maximum length of the random steps continually updated to maintain a success rate of approximately 0.5 (subject to an absolute maximum step length of 0.3 Å to maintain some connection with real-time kinetics). After reaching 300 K, we equilibrate and take statistics to obtain sample properties.

The radial distribution function obtained in this way for T2 gives a first-neighbor distance and coordination number in excellent agreement with experiment, but shows too sharp a first-neighbor peak, and very weak subsequent peaks, which we attribute to the weak bond-angle forces in the present model, which permit a more distorted topology than in real *a*-Si. Because of the very local nature of the properties studied here, this does not seem to represent a significant problem, especially in view of the comparison with another very different sample and potential.

A central step in our analysis is the partitioning of the cohesive energy of the sample among the atoms. While such a partitioning is not unique, it has proven to be a very powerful tool. For T2, the energy is partitioned as described in Ref. 9. For SW, the two-body interactions are divided equally between the two atoms. The three-body terms each involve a vertex atom, rather than treating general three-atom interactions, and so we assign the corresponding energy to the vertex atoms.

The solid line in Fig. 1(a) shows the distribution of atom energies obtained in this way, for a sample formed by a relative fast quench. $P(E)$ is defined as the probability of finding an atom in the sample at energy E. The distribution has a low-energy cutoff around the crystal energy (-4.6 eV), a peak about 0.15 eV higher, and a high-energy tail.

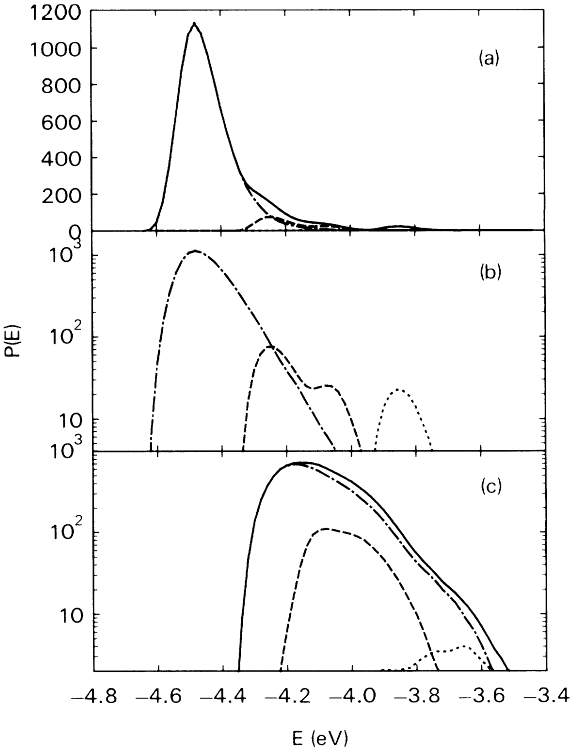

FIG. 1. Energy distribution $P(E)$ of atom energies at 300 K. (a) $P(E)$ for one T2 sample. Solid line: total distribution. Dashed, dot-dashed, and dotted lines are projected distributions for fivefold-, fourfold-, and threefold-coordinated atoms, respectively. (b) Same data on a logarithmic scale. The solid curve is omitted for clarity. Double-peaked structure in the fivefold distribution was not seen in most samples. (c) $P(E)$ for SW sample of Ref. 3.

We can characterize the individual atoms as threefold-, fourfold-, or fivefold-coordinated, and consider their separate contributions to $P(E)$. (To define coordination, we count the number of neighbors within 2.75 Å, the position of the dip in the radial distribution function between the first- and second-neighbor peaks. For the SW sample the corresponding distance is[3] 2.9 Å.) The broken lines in Fig. 1(a) show $P(E)$ decomposed in this way. Distinct peaks are seen for each type of atom, illustrating the higher energy of nontetrahedral atoms.

Figure 1(b) shows the same data on a logarithmic scale. The high-energy tail for the fourfold-coordinated atoms closely obeys an exponential Maxwell-Boltzmann distribution over nearly 3 orders of magnitude. However, an analysis of the slope gives an effective temperature T^* of about 750 K, much higher than the actual 300-K temperature of the sample.

Evidently, during quenching the sample undercools to about 750 K while maintaining a thermal quasiequilibrium among the kinetically accessible liquidlike states. At that point it falls out of quasiequilibrium and becomes a supercooled liquid, i.e., a glass. While not all runs show such perfectly exponential behavior, the value inferred for T^* is a monotonically increasing function of quench rate, as expected. For the slowest quenches attempted, T^* approaches 650 K.

Experimentally, T^* can be readily measured for materials which are good glass formers, i.e., which remain disordered even at the slowest laboratory cooling rates. But this quantity is relatively inaccessible for materials such as *a*-Si, which are formed by processes which are extremely fast, or which are highly nonequilibrated at all temperatures. Yet T^* is a crucial parameter determining the properties of the material. For example, Bar-Yam, Adler, and Joannopoulos[13] have stressed the importance of T^* in determining band tails and the number and type of defects in amorphous semiconductors. Thus a theoretical determination of T^* is of considerable interest, but has not been feasible with traditional techniques.

The tails of the projected distributions of threefold- and fivefold-coordinated atoms can also be analyzed to yield effective temperatures T_3^* and T_5^*. Because of the much worse statistics, such an analysis must be somewhat crude, especially for the few threefold-coordinated atoms. However, we have analyzed several samples in this manner, and consistently obtained values of $T_5^* \simeq 500$ K, much lower than T^*. (T_3^* appears to be as much as 100 K lower than T_5^*, but we cannot place much reliance in this result because of the poor statistics.)

We interpret this to mean that, below T^*, the amorphous network is essentially frozen, except for the defects, which remain mobile down to much lower temperatures. Such mobility presumably involves bond switching,[14,15] rather than substantial motion of the actual atoms. The low values of T_5^* and T_3^* mean that coordination defects in *a*-Si can be very effectively annealed in the intermediate temperature range, and these temperatures may be related to the threshold temperature of about 425 K for annealing found by Lang, Cohen, and Harbison.[16] We stress that, in view of the significant difference between T^* and T_5^*, the fivefold-coordinated atoms must be viewed as defects in the glass, and not as part of the inherent glassy disorder.

While the partitioning of energy among individual atoms is, strictly speaking, nonunique, we believe that there cannot exist two different partitionings which both give an exponential tail in the energy distribution, but with different exponents corresponding to different values of T^*. As an independent check, we have confirmed that T^* is fairly close to the temperature at which self-diffusion becomes negligible on the scale of the simulation.

To test dependence of the results upon the empirical potential used, we repeat the above calculation using the SW potential, taking statistics as before at 300 K on the sample generated and characterized by Kluge, Ray, and Rahman.[3] The results are shown in Fig. 1(c). From the exponential tails, we infer a value of $T^* \simeq 1000$ K and $T_5^* \simeq 670$ K.

While the precise values of T^* obtained with the two potentials are somewhat different, the similar overall behavior and semiquantitative agreement are striking. For both models, the quenched samples exhibit a quasithermal distribution of local geometries at a temperature T^* well below the melting temperatures, with defects remaining in equilibrium down to a temperature T_5^* roughly 30% lower than T^*.

We now discuss the defects in the tetrahedral network, in particular their number and formation energies. Traditionally, only threefold-coordinated atoms have been considered as possible intrinsic defects in *a*-Si. Recently, however, Pantelides proposed[14] that fivefold-coordinated atoms should be considered on an equal footing with threefold-coordinated atoms as possible intrinsic defects, and offered arguments[15] suggesting that fivefold-coordinated atoms could in fact be the predominant defect.

In these simulations, the fraction of threefold-coordinated atoms ranges from 0% to 2%, while fivefold-coordinated atoms represent from 3% to 6% of the sample, with fewer defects at slower quench rates. In every sample we find *at least* 3 times as many fivefold-coordinated atoms as threefold. Kluge, Ray, and Rahman also found fivefold-coordinated atoms to dominate in earlier simulations.[3] Thus, regardless of the quantitative accuracy of these results, the outright neglect of fivefold-coordinated atoms as a possible native defect in *a*-Si is clearly unjustified.

The most crucial property of a defect is its formation energy. However, it is not clear in general even how to define the formation energy of a defect in a disordered system. In particular, if the defect is present as the material passes through the glass transition, the surrounding material may be expected to accommodate the defect, giving a much lower energy than for a defect inserted into the cold material. This problem does not arise in crystalline materials, where the geometry of the surrounding material is more constrained. Thus in the present case it is necessary to study "native" defects, which are present in the as-formed sample, rather than inserting defects by hand. (The latter procedure might, however, be appropriate for the study of, e.g., radiation-induced damage in cold *a*-Si.)

If the density of defects is low, we can obtain a reasonable measure of the formation energies in the following way. For each N-fold-coordinated atom we calculate the energy of the cluster of $N+1$ atoms consisting of the atom and its neighbors. We then subtract our best estimate of the energy of $N+1$ atoms in the ideal tetrahedral amorphous network, estimated from the peak of the energy distribution for fourfold-coordinated atoms. The results for the T2 sample are shown in Fig. 2(a).

The distribution of "formation energies" for fourfold-coordinated atoms in Fig. 2(a) is peaked at zero energy,

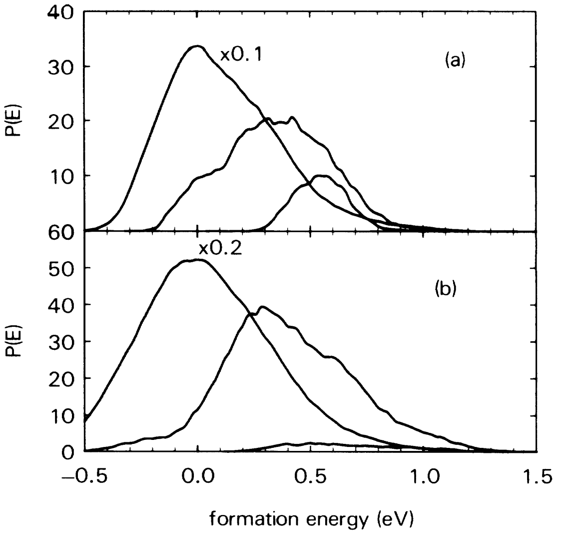

FIG. 2. Distribution of "formation energies" for atoms of a given coordination, defined relative to the ideal tetrahedral amorphous network as described in the text. From upper left to lower right, lines are fourfold-, fivefold-, and threefold-coordinated atoms, respectively. (a) For the same T2 sample as in Fig. 1(a). (b) For the SW sample of Ref. 3.

consistent with the definition used here. We obtain average formation energies for threefold- and fivefold-coordinated defects of 0.6 and 0.3 eV, where the sample-to-sample reproducibility is about 0.05 eV. It is important, though, to notice that the width of the distributions is comparable to their separation. Thus while the formation energies are well defined in a statistical sense, any quantitative analysis of activated processes should integrate over the entire distribution.

The threefold energy is slightly under one-fourth the vacancy formation energy in the crystal (2.8 eV with this potential), as expected. In addition, a naive estimate of the formation energies can be obtained directly from Fig. 1(a). The energy peaks for threefold- and fivefold-coordinated atoms are displaced from the fourfold peak by about 0.25 and 0.65 eV, respectively, in good agreement with the more careful estimate. However, this simpler approach only works because of the very short range of the potential, and is not applicable to the SW results.

No experimental values are available for these formation energies. However, Pantelides suggested that a variety of data are consistent with formation energies of 0.8 and 0.6 eV for threefold- and fivefold-coordinated defects.[15] Similarly, Bar-Yam, Adler, and Joannopoulos[13] inferred a formation energy of 0.7 eV for the paramagnetic defect (which they assumed to be threefold).

Figure 2(b) shows the corresponding analysis for the SW sample. We obtain a formation energy of 0.3 eV for the fivefold-, and 0.6 eV for the threefold-coordinated defects, in extremely good agreement with the T2 values. However, the SW sample contains only one threefold-coordinated defect, making it risky to draw general conclusions about the threefold case. The energy per dangling bond for SW, in the absence of strain or of second neighbors closer than in the crystal, is much higher: 1.1 eV per dangling bond.

Finally, we note that the detailed analysis which permitted us to extract glass temperatures and defect formation energies would not be possible in an *ab initio* calculation, where there is no convention at present for spatially partitioning contributions to the total energy. Thus the sacrifice in accuracy involved in the use of empirical interatomic potentials is compensated in part, not only by the added convenience and the possibility of greater statistical precision, but also by the opportunities for additional insight. Such heuristic analysis is particularly helpful in the study of disordered systems, where a rigorous treatment of defect energies and glass temperatures for real materials is not generally feasible.

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