

Molecular-dynamics simulations of amorphous Si

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A new procedure for generating networks of Si atoms with the properties of amorphous Si is presented. We have used *ab initio* molecular-dynamics simulations and a simple simulation procedure to produce cells with radial distribution functions, coordination defect concentrations, and vibrational densities of states in excellent agreement with experiment. A comparison of our method is made with other techniques and the conditions under which specific kinds of defects occur in simulations (e.g., floating or dangling bonds) is discussed. Implications to calculations using semiempirical angle-dependent potentials is briefly discussed. We have found that Brillouin-zone sampling significantly affects interatomic forces, and that the final amorphous structures obtained are dependent upon the sampling scheme used.

I. INTRODUCTION

An outstanding problem of solid-state physics is a reliable description of short-range order (SRO) in amorphous and glassy semiconductors. Much effort has been devoted to this area, but there is still considerable doubt about many details of the structure of these important materials. Ideally, one would like to possess coordinates of atoms making up an amorphous structure. Such knowledge is useful for many calculations of properties of the amorphous matrix: a detailed theory of doping and transport requires such detailed microscopic information, for example. A route to improving our theoretical understanding of SRO is to employ careful molecular-dynamics (MD) simulations which are to be related to specific types of experimentally practical methods of fabrication of the amorphous semiconductors. Also, since there are several experimental approaches to making *a*-Si of high quality (with few coordination defects), it is also likely that a theoretical approach may produce networks much like true *a*-Si, though the simulation procedure may not be experimentally realizable. At present, experimental information about the microstructure is rather limited. Frequently, amorphous samples are characterized by a radial distribution function¹ (which as the name suggests, contains no angular information about structure) obtained from x-ray diffraction² or other techniques. Some other information is provided by probes like electron spin resonance (ESR).³ Of course the basic difficulty with each of these methods is that detailed local information is

averaged over the entire sample, and much of the information concerning the local environment of atoms is lost in this process. Here, we hope to enhance the understanding of these issues with a new efficient *ab initio* MD technique,^{4-6,7} and a new approach to simulating the fabrication of *a*-Si. In this paper we restrict our attention to Si, though the methods are applicable to any covalently bonded system.

Many investigators have considered MD simulations with angle-dependent interatomic potentials⁷ (ADP). Here, a semiempirical potential is constructed by fitting a functional form to a selected database of experimental data or *ab initio* calculations. Such potentials are convenient in part because the calculation of interatomic forces is very efficient. This allows for the simulation of hundreds or even thousands of atoms. In another study,⁸ we have recently examined several of these potentials, and compared them to accurate interatomic forces obtained from the *ab initio* total-energy-MD scheme of Sankey and Niklewski. It was found that all of the ADP's studied were only qualitatively accurate: forces were often discrepant by amounts comparable to the magnitude of the exact interatomic force. The size of the errors is not surprising. Most ADP's are constructed by fitting assumed functional forms to a limited amount of data: usually there is an emphasis on the crystalline phase. The relevance of this input to complicated disordered structures is not obvious. Also, it is clear that the physical origin of the interatomic interactions is many body and quantum mechanical. There is no "representability theorem" that the true interatomic interactions can be

expressed by moderately simple functional forms with parameters determined from a small database.⁹ How the ADP errors manifest themselves in terms of the final structures obtained from a simulation is an important question. We have found that small differences in forces can lead to qualitative changes in structure. To explain the scale of discrepancies in forces among the different techniques, we note that the characteristic force scale of a highly disordered, nonequilibrium cell is of order 5 eV/Å. For the several ADP methods investigated, it was found that for such cells, typical errors were comparable in magnitude to the exact force. In a more ordered environment the absolute errors between ADP's and the exact forces was only a few tenths eV/Å. However, based upon our experience⁸ with *ab initio* simulations, it is clear that such errors are large enough to lead to spurious minima in the total energy, and more coordination defects than the more accurate MD methods. This is relevant to one of the central problems of *a*-Si simulations: the question of why investigators¹⁰ tend to obtain structures with defect concentrations much higher than the few percent experimentally observed in electronically acceptable *a*-Si.³

The first *ab initio* study of SRO in *a*-Si was performed by Car and Parrinello (CP), using their plane-wave MD method.¹¹ The forces obtained by these authors were undoubtedly more accurate than the ADP-derived forces. CP found a radial distribution function and vibrational density of states in good agreement with experiment. As CP point out, however, care must be exercised in the comparison of their structures to experiment because of the large (but unspecified) number of defects found in their simulations. Finally, the simulation "algorithm" introduced by CP is rather complex. It would be desirable to develop a simpler method if possible.

An interesting general aspect of band-structure-based MD studies is the question of the effects of Brillouin-zone (BZ) sampling on interatomic forces which are expressible as an integral over the BZ. In Sec. IV we find that forces are significantly dependent upon the BZ sampling scheme to approximate this integral.

From the foregoing considerations, we believe that the basic problems of performing MD simulations of *a*-Si are (1) all existing calculations have employed forces which are inaccurate to some degree, and (2) all investigators performing simulations get far too many coordination defects in their proposed structures. In Sec. IV we will demonstrate that this is of crucial importance to the electronic properties of the simulated structure. We will demonstrate that the use of *ab initio* MD in conjunction with a new algorithm for simulating *a*-Si can yield networks with only (i) a few percent coordination defects and (ii) radial distribution functions and (iii) vibrational spectra in agreement with experiment. As to our knowledge, this is the first simulation scheme which simultaneously satisfies these three conditions.

The rest of this paper will be organized as follows. Section II will present a new simulation scheme for producing networks with the properties of *a*-Si. In Sec. III we analyze the results of this procedure and in Sec. IV compare our work with other simulations.

II. METHOD

All the simulations performed in this paper have used the MD scheme of Ref. 4. Four major approximations are used in this method: (1) Norm-conserving nonlocal pseudopotentials of the Hamann-Schlüter-Chiang class.¹² (2) The Harris total-energy functional¹³ within the Hohenberg-Kohn-Sham local-density approximation,¹⁴ (3) a basis set of four orbitals per site. These consist of one *s* orbital and three *p* orbitals. The basis functions are solutions of the free atom pseudo-Schrödinger equation with the additional boundary condition that the orbitals vanish beyond a radial distance r_c from the atom. This procedure can be thought of as slightly exciting the orbital from the free atomic ground state. In all applications of the method, r_c is chosen so that only atoms up to and including third neighbors (in the diamond structure) are included. For Si, this corresponds to an interaction range of 10.6 Å.⁴ (4) Real-space matrix elements of the Hamiltonian and overlap are obtained from Lagrangian interpolation over finely spaced lookup tables which are calculated once and for all. For some of the three center matrix elements, an angular momentum expansion is used to approximate the matrix elements. These approximations are both accurate and efficient.^{4,5} This MD scheme has been tested in a wide range of bonding environments, ranging from small molecules to bulk Si. Excellent agreement has been obtained with more sophisticated quantum-chemical calculations¹⁵ for microclusters and their vibrational spectra,¹⁶ and the phase diagram of Yin and Cohen¹⁷ for several phases of Si. Details of the method and comparisons to other calculations can be found in the literature.^{4,5} We emphasize that the MD scheme we employ is entirely first principles: no experimental input or adjustable parameters are used.

Our approach to simulating *a*-Si is motivated by two facts. In a typical "liquid-quench" simulation an investigator starts with a "sample" of *l*-Si with some amount of disorder. If the sample is truly representative of a liquid phase, it must naturally be highly disordered. It is well known that a rapid simulated quench from such a structure (rearrangement of atoms to obtain a local minimum in the total energy) yields a disordered structure with more than 15% coordination defects. On the other hand, it is also clear that if one starts with a "small" amount of disorder (relative to *c*-Si), that a quench to find a total-energy minimum must yield *c*-Si (with no defects). An obvious procedure to investigate is thus the intermediate regime, for which the sample we quench from is sufficiently disordered that an energy minimization does not lead to *c*-Si, but yields a sample with a reasonable number of defects (a few percent). We have found that the quenching of "incompletely melted" samples can yield disordered networks with radial distribution functions close to experiment and defect concentrations consistent with ESR data. Since our *ab initio* method is very efficient we have been able to try several approaches to simulating *a*-Si. After examining these different approaches, we have fixed upon a procedure in which we begin with a supercell in the diamond structure with one vacancy, simulate heating this structure to a high kinetic

temperature, and then let the system freely evolve under Newton's equation until the cell is very disordered. This single MD run provides us with structures ranging continuously from the starting (diamond plus vacancy) cell to a highly disordered configuration. Let "preparation time" τ denote the time (in fs) from the initial "heating" of the ordered cell. We study metastable minima in the total energy as a function of τ by performing "dynamical quenching"^{4,5} to find local minima in the cell's electronic total energy for each of several τ . This procedure enables us to understand the effects of the disorder of a given starting structure on the local minimum that is discovered by dynamical quenching. We start from a cell with a vacancy to assure that the system does not quench into the diamond structure. In detail, our procedure is outlined in the following: (1) We start with a large supercell (for the results discussed in this paper a 64-atom simple cubic cell in the diamond structure with one vacancy). The volume chosen is that of crystalline Si. (2) At a constant volume, we simulate heating this cell to a high kinetic temperature T , where T is defined by

$$\frac{3}{2}k_B T = \langle p^2/2m_{\text{Si}} \rangle, \quad (1)$$

where the right-hand side is the average kinetic energy of the Si atoms in the cell. This heating is accomplished by assigning each atom in the cell a velocity sampled at random from the Maxwell-Boltzmann distribution, and requiring the average kinetic temperature to be T at the beginning of the free evolution. In these simulations we use $T=8000$ K. (3) We allow the free evolution of the cell for a time sufficient for the cell to acquire a highly disordered liquidlike structure. (4) We use dynamical quenching to find a local minimum in the configurational energy for several different steps (τ) in the cell's evolution from crystal to liquid. The efficacy of this method is discussed in Sec. III.

III. RESULTS

To illustrate the results of this approach, we begin by analyzing the behavior of $R^2(\tau)$, the mean-square deviation of the atoms from their initial positions averaged over the cell. As defined above, τ is the time in fs from the initial heating of the starting (diamond) cell. As one expects for a diffusive process, R^2 is found to be quite linear, as we illustrate in Fig. 1.

A standard (though incomplete) way of characterizing structural disorder is to use the number density function $n(r) = 4\pi\rho r^2 g(r)$, where $g(r)$ is the usual radial distribution function, ρ is the average number density, and

$$\int_0^R n(r) dr = N(R), \quad (2)$$

where $N(R)$ is the sample-average number of atoms enclosed in a sphere of radius R centered on an atom. It is well known that amorphous silicon possess a $n(r)$ with a broadened second-neighbor peak, and either a weak or nonexistent third-neighbor feature.^{2,18} We note the insensitivity of $n(r)$ to structural details: structures with a surprisingly wide variety of microstructure have similar $n(r)$. To illustrate the increasing disorder associated

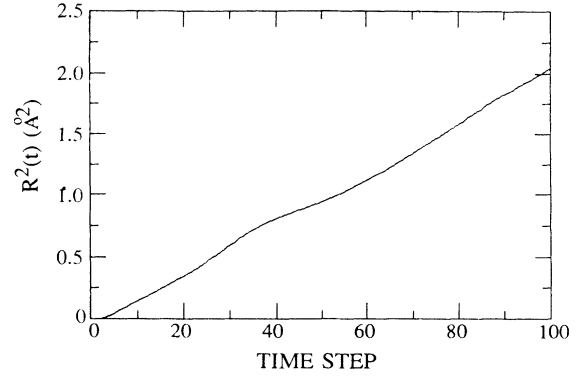


FIG. 1. $R^2(t)$ plotted against time step. This is the sample averaged expected-squared deviation of the Si atoms from their initial positions in a diamond lattice. Each time step is 2.07 fs.

with the melting process, in Figs. 2(a), 2(c), and 2(e) we present $n(r)$ for several different preparation times τ in the crystal to liquid evolution. Note that even after only 50 preparation time steps ($\tau \approx 104$ fs), the main structures of $n(r)$ are weak or eliminated. The results of simulated quenching to convergence for three different τ are indicated in Figs. 2(b), 2(d), and 2(f).

It is interesting to observe how sharp the changes are in the quenched $n(r)$ as a function of τ . Figure 2(b) clearly indicates that for quenching after $\tau=104$ fs, the structure obtained is rather ordered (we do not call it crystalline because the sample possesses four dangling bonds, and many odd-membered rings). Certainly this structure

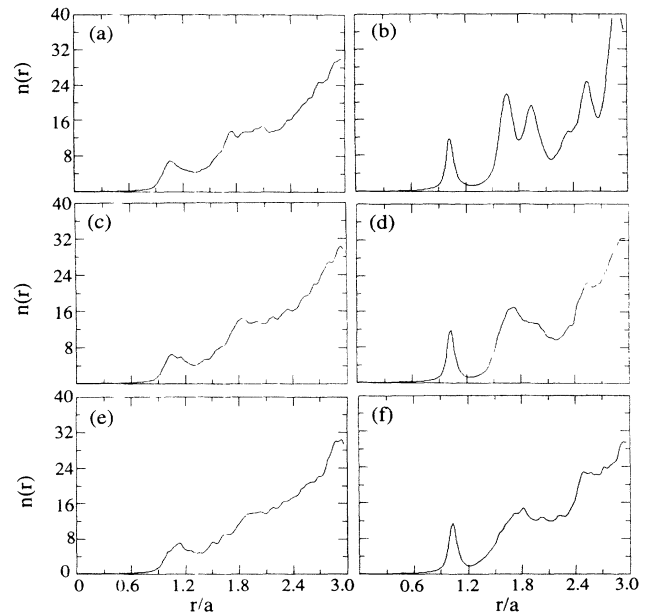


FIG. 2. Number density function $n(r)$ for nonequilibrium cells (a), (c), and (e) with preparation time τ of 104, 124, and 207 fs, respectively, and corresponding n for cells dynamically quenched from structures (a), (c), and (e) illustrated in (b), (d), and (f), respectively. The abscissa is in reduced units of $a = 2.35$ Å.

cannot be described as amorphous because of the very strong third-neighbor peak in $n(r)$. Remarkably, quenching after only 20 fs of further time evolution produces a $n(r)$ with the properties expected of *a*-Si [Fig. 2(d)]. This sample has four coordination defects: two dangling and two floating bonds. Quenching from a yet larger τ leads to $n(r)$ showing more disorder than is observed experimentally (even the second-neighbor peak is weak for quenching after $\tau=207$ fs [Fig. 2(f)]). Also, in contrast to acceptable samples of real *a*-Si, there are far too many defects for this sample (five dangling bonds and nine floating bonds). Of course, all of the statements we make depend upon the choice of $T=8000$ K. A lower temperature (but still well above the melting point) would yield less diffusion, for example. A detailed study of the T dependence of diffusion and implications to structures is beyond the scope of the present paper.

In Table I we show the number of coordination defects as a function of τ for the quenched cells. The number of coordination defects (with coordination defined by a distance of 2.7 Å) increases monotonically with τ . Floating bonds (associated with fivefold coordinated atoms) are not observed until there is considerable disorder present ($\tau=124$ fs). This is not surprising: in a rapid quench of an overcoordinated system (such as a liquid), fivefold configurations would be easily attainable. For a more crystalline system, where most atoms are fourfold coordinated, undercoordination (dangling) defects are more likely. We also note that for the most disordered sample studied ($\tau=207$ fs), that there are almost twice as many floating bonds as dangling bonds.

It is apparent from the radial distribution functions that dynamical quenching after preparation time $\tau=124$ fs yields a network in good agreement with experiment [Fig. 2(d)]. In addition to the satisfactory radial distribution function, this sample has only four defects. This is somewhat higher than the concentrations measured in ESR experiments, but much better than the ≈ 15 –25 % observed for other simulations. Examination of the bond-angle distribution for this cell shows that 67% of the atoms have bond angles within 20° ($\pm 10^\circ$) of the tetrahedral angle, and 83% were within 30° . The average number of fivefold, sixfold, and sevenfold rings was found to be 2.5, 16.5, and 32.0, respectively.

In an attempt to reduce the defect concentration further, we simulated heating the four defect cell (two floating and two dangling bonds) to an equilibrated kinetic

temperature of about 300 K. After 320 fs we observed that the average kinetic energy of the cell was rising above 400 K. This suggests that some configurational energy was converted into kinetic energy—which one might expect from the “conversion” of a defect into a tetrahedral site. After 320 fs of free evolution, simulated quenching was again applied to find a near local minimum in the total energy. We found that two defects had disappeared: we were left with a two defect (dangling bonds) cell, with a corresponding defect concentration of about 3% (Fig. 3). The procedure of heating the four defect sample is somewhat analogous to the procedure of “annealing” a real sample though, as usual, care must be taken in using this interpretation because of the difference in time scales between experiment and simulation. In the two defect sample 73% of the atoms are in a 20° spread about the tetrahedral angle, and 86% are within a 30° range. Here, the average number of fivefold, sixfold, and sevenfold rings was found to be 1.8, 17.5, and 25.1, respectively. It is clear from the larger number of sixfold rings and the reduced number of seven-member rings that the two defect sample is somewhat less disordered than the four defect sample. This is also evidenced by the presence of a third-neighbor shoulder on the broad second-neighbor peak in $n(r)$ for this sample (Fig. 3).

As a further test of the two defect sample we have calculated the vibrational density of states (VDOS) by Fourier transforming the velocity-velocity autocorrelation function for a 400 fs MD simulation at an average kinetic temperature of ≈ 300 K. The width of the structures in Fig. 4 is primarily an artifact of finite-time sampling on the discrete Fourier transform.¹⁹ We note that the calculated VDOS is in outstanding agreement with the experimental data of Ref. 20. In particular, we observe that both the peak locations and structure are in closer agreement with experiment than the VDOS obtained by CP. This is due both to the difference in structure and to the CP use of the Γ point in calculating interatomic forces. Another contrast to the work of CP is that we find seven-member rings to be much preferred to the five-member rings, as one can conclude from the ring statistics presented above. It is interesting to observe that our VDOS is nonzero at $\omega=0$. This is, in part, an artifact of the Fourier transform; it is also a consequence

TABLE I. Coordination defects in quenched cells after preparation time τ . Coordination is defined by a distance of 2.7 Å.

τ (fs)	Threefold	Fivefold
100	4 ^a	0
120	2	2
160	5	4
200	5	9

^a The cell started with four dangling bonds because of the vacancy in the starting configuration.

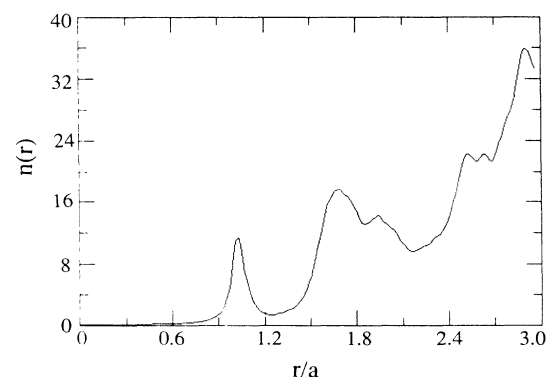


FIG. 3. $n(r)$ for the two defect cell, as discussed in the text.

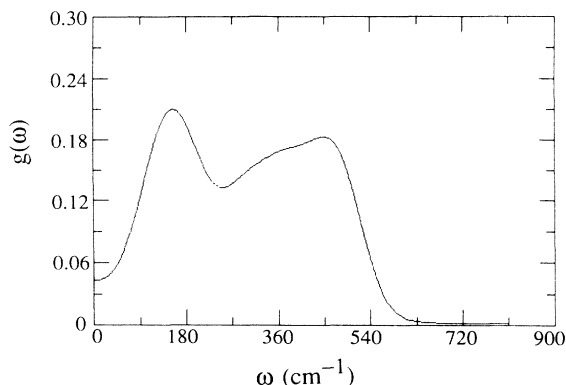


FIG. 4. The vibrational density of states for the two defect cell obtained by Fourier transforming the velocity autocorrelation function.

of some finite-temperature rearrangement and/or diffusion of weak bonds and/or defects. For a sufficiently long MD simulation, it is clear that the VDOS would vanish at $\omega=0$.

In order to accurately investigate the electronic density of states in the region of the gap, it is necessary to use a method which produces more accurate conduction bands than the LDA. Provided that we restrict our attention to structures that are not very distorted, an adequate tool is an empirical tight-binding technique²¹ along the lines discussed by Fedders and Carlsson in their studies of defects in *a*-Si.²² In this method, the overlap integrals vanish at the second-neighbor distance in *c*-Si, and a Bethe-lattice truncation is used to eliminate surface effects.²³

The two defect sample has a band gap of 1.3 eV after about 0.2 eV was lost to band tailing of the valence band and another 0.2 eV to band tailing of the conduction band. Surprisingly, this (two defect) sample had *three* states in the gap. Two of these states were normal three-fold coordinated dangling-bond states with more than 50% localization on the back bonded site (that site missing a neighbor). The third defect state consisted of a central atom with two normal neighbors and two other neighbors at the quite large distances of 2.62 and 2.67 Å. The angle subtended by the neighbors was a surprising 164°. This state had about 25% of the charge on each of the three atoms. These defects were reasonably well separated spatially, and there was no difficulty defining the spectral width of each of the defects.

The discovery of a structure such as this raises an important point: It seems quite possible that for true *a*-Si many of the spectral features "in the gap" may be due not to threefold or fivefold atoms, but to badly strained fourfold coordinated atoms. Such defects would not give rise to an ESR signal, but would still significantly influence the electronic properties of *a*-Si. Determination of the frequency of occurrence of such structures, and an analysis of their implications to electronic structure are underway.

For samples more disordered than the two defect cell, we found that it was difficult even to define a gap. In the case of the four defect sample [$n(r)$ of Fig. 2(d)] with two floating and two dangling bonds, we find more than four

defect states in the region of "the gap." None of these defects were very well localized, and the floating-bond states merged into the conduction band. The nonexistence of an obvious gap raises serious questions about the experimental relevance of the many proposed disordered structures with 15–20 % defects.¹⁰

The agreement we have observed between the two defect cell and experiment leads us to tentatively conclude that the 64-atom simple cubic geometry is adequately large to characterize the important features of real *a*-Si. Thus, it seems that the supposed "tradeoff" between *ab initio* methods (with a small cell but accurate forces) and ADP calculations (with much larger cell, but somewhat inaccurate forces) is not relevant for simulating a quench from a disordered cell. Of course, direct simulations of epitaxial growth are another matter, and seem to present a formidable challenge to *ab initio* methods at present.

IV. DISCUSSION

In this section we discuss some general features of band-structure-based MD techniques, and compare to some other simulations of *a*-Si. We first turn our attention to the *ab initio* methodology.

In order to simulate an infinite system, band-structure-based schemes use supercells. Here, one chooses a particular large unit cell with the geometry of one of the Bravais lattices, and performs calculations for the infinite system composed of the unit cell repeated through the lattice vectors of the Bravais net. To do this properly, one needs to choose a cell large enough that local microstructures of a disordered system may be studied without intercell correlations being a significant factor. Also, there are energy bands associated with the "artificial periodicity" of the supercells. In a MD simulation, interatomic forces depend upon an integration throughout the BZ of the supercell bands. Despite this, it is common practice to approximate the bands as flat. This is the effect of the Γ -point approximation, in which total energies and interatomic forces are calculated with a sampling of only the Γ point in the BZ. The rationale underlying this approximation is that for a large enough supercell (for supercell dimensions greatly exceeding interatomic spacings), the band curvature is negligible. This is certainly true asymptotically. However, we have recently shown that significant errors in forces may be attributed to inadequate treatment of band curvature.⁸ For a highly disordered 54-atom cell (cell "L" discussed in Ref. 8), a bandwidth of ≈ 0.1 eV was found for the supercell bands. We expect that the discrepancy in forces found for the 54-atom cell should be somewhat larger than for the 63-atom geometry we employ. In order to assure the accuracy of forces for the 63-atom cell we have used four Monkhorst-Pack²⁴ (MP) special points in the BZ for computing total energies and forces. Earlier experience with the 54-atom cell⁸ suggests that this leads to small ($\approx 2\%$) errors in the highly disordered cell L. This is to be compared to 10–12 % errors for the use of the Γ point. The differences between the Γ -point method and the use of special points can also be viewed as evidence that finite-size effects are relevant, since, for a large

enough cell, the Γ point must be adequate.

To illustrate the effect of using one special MP point (four, taking the star of k into account as we must for a system with no point-group symmetry) versus the Γ point, consider a simple s -only tight-binding model with nearest neighbor (NN) interactions. The dispersion $E(\mathbf{k})$ is well known to have the form²⁵

$$E(\mathbf{k}) = E_0 + \sum_{\text{NN cell}} \cos(\mathbf{k} \cdot \mathbf{R}) T(\mathbf{R}), \quad (3)$$

where the first term can be regarded as a “single-cell” term, and the second arises from nearest-neighbor-cell correlations. It is obvious that the use of $\mathbf{k}^* = \mathbf{0}$ in a BZ average *maximizes* the intercell correlation part of the dispersion, whereas, by construction, a single MP special point *minimizes* this contribution (giving zero in this case). Thus, at least for this simplified case, it seems that in addition to estimating BZ averages more accurately, the use of a single MP point minimizes intercell correlations which is presumably desirable for extracting properties of the “infinite system.”

The effect of the Γ -point approximation on the melting of c -Si is also revealing: examination of $R^2(t)$ using the Γ -point scheme shows a super-linear behavior, characteristic of partially ballistic trajectories of the atoms. The same calculation for four special points gave a more linear R^2 . To explain this, we note that for small deviations from the diamond structure, there should be a force which tends to restore the atoms to their initial positions. Thus, the difference in diffusion can be understood: the energetically favorable nature of the diamond structure is due entirely to the “band-structure” term in the total interatomic force. If this force is calculated without proper regard for the k dependence of the bands, there is an inaccurately small restoring force acting on the atoms, and the diffusion is therefore erroneously large. Related conclusions on the importance of k sampling have recently been reached by Jank and Hafner²⁶ using the linear muffin-tin orbitals method.²⁷ Fernando *et al.*²⁸ have studied the effects of partial occupancy of electronic state near the Fermi level in Na and also observed that the Γ -point approximation needs to be interpreted with care in metallic systems.

As we briefly reported elsewhere,⁸ the importance of proper BZ sampling was strikingly indicated in simulations involving a 32-atom (bcc) cell. Rapid quenching of a partly melted sample using only the Γ point yielded a structure with a radial distribution function resembling experimental a -Si, and two dangling bonds. This structure proved to be unstable, however: When further simulated quenching was performed with four MP special points, the sample became *crystalline*. From this we conclude that the Γ -point method can lead to a spurious minimum in the configurational potential energy of the system. As expected, these effects are more drastic in the smaller supercell. This is a rather explicit demonstration that inadequate sampling of the BZ can lead to a “false disorder.” Since the errors in forces for the ADP’s are much larger than the error from Γ -point sampling, we expect that such false disorder should be an even greater difficulty for the ADP-based simulations.

In order to examine the finite-temperature effects of BZ

sampling further, we “heated” the two defect cell to a moderate kinetic temperature (≈ 300 K), and let the cell freely evolve from identical initial conditions for the Γ point and MP sampling schemes. For both cells we monitored the type and number of nontetrahedral sites as a function of time step. Results for the two cells were significantly different: in the cell using MP sampling it was found that instantaneous floating defects were quite rare; the dominant defect was always of dangling type. In the Γ -point cell floating defects were much more common. This result suggests that more accurate forces tend to favor threefold defects. It also implies that the small differences in interatomic forces calculated with the MP and Γ -point method lead to significant differences in finite-temperature properties of the amorphous matrix.

We also stress that the effects we describe here depend upon the geometry of the supercell: since the Γ -point approximation is better for a larger cell, it is hard to completely decouple the pure “size” effects from BZ sampling artifacts. At this point, all we can say about cell size is that to make intercell correlations negligible, we have to choose the cell size much larger than the size of structures we want to examine. For the simulations we present here for the 64-atom simple cubic geometry, we note that there are no direct interactions between an atom in one cell and its image in another, as the image of any given atom is at a distance exceeding $2r_c$, the maximum interaction range of the pseudoatomic orbitals.

In general we note that there are difficulties in comparing experiment and simulation for the systems we study. Other authors¹⁰ have rightly pointed out that the relevant time scale for epitaxial growth or other methods of fabricating a -Si is a time scale which is several orders of magnitude longer than the MD time step. Since many atoms need to be included to gain a realistic description of a structure, it is clearly impossible to run a simulation long enough to truly simulate the growth process. The situation for quenching l -Si is every more murky. It is difficult or impossible to experimentally fabricate a -Si with acceptable electronic properties in this way. In agreement with others,¹⁰ we have found a large number (≈ 15 – 25 %) of defects in quenches from the liquid. We therefore conclude that the high defect concentration for liquid quenches is primarily a consequence of the quench rate, and not necessarily the inaccuracies of the ADP forces.

Newly developed methods for making a -Si, including laser annealing and ion implantation may be much closer to the time scale we are compelled to work with. In ion implantation, for example, c -Si is bombarded with energetic Si ions which disturb the crystalline matrix. The “lattice” then rapidly “cools” the cascading atoms. This experimental method of making a -Si is perhaps closest to the simulation scheme we use, where a few atoms (with particularly large initial velocities) quickly diffuse away from their equilibrium (crystal) positions, and the system is then suddenly “cooled” with the dynamical-quenching method.

V. CONCLUSION

We have provided a simple recipe for generating networks of Si atoms with the known experimental proper-

ties of α -Si. Throughout the calculation we used accurate forces calculated from the MD scheme of Sankey and Niklewski, and always included a reasonable treatment of the curvature of supercell bands with four MP special points in the BZ. We observe that for the initial conditions indicated in Sec. II, there is a sharp transition from a rather ordered structure to an amorphous structure for a quench from preparation time $\tau=124$ fs. Annealing of our best sample so obtained led to a two defect sample which is, to the best of our knowledge, unique in satisfying structural information from experiments [$n(r)$], the VDOS and defect concentrations (from spin resonance). We find a new weakly bonded fourfold defect in α -Si which produces a level in the gap.

Future developments on this approach should include the use of larger supercells to verify that intercell correlations are unimportant, the study of microvoids (which are very important in real α -Si), and further examination of the relationship of our method to experimentally accessible techniques for making α -Si. It would also be useful to examine the effects of ensemble averaging on our results.

All cells discussed in this paper are available upon request.²⁹

Note added in proof. Since this paper was accepted, we have performed additional calculations relevant to the interpretation of BZ sampling artifacts. Briefly, we found that much of the error in the Γ -point sampling method derived forces was due to the treatment of bands crossing at the Fermi surface. A complete discussion is given in Ref. 8. This observation in no way affects the results of this paper, except for the interpretation of why the Γ point and special point schemes differ.

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