Radial distribution functions of *ab initio* generated amorphous covalent networks

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A thermal procedure and an *ab initio* molecular-dynamics method based on the Harris functional, applied to originally crystalline, periodically continued 64-atom cubic cells, is used to generate random networks of four different materials of varying degrees of covalency: C, Si, Ge, and a nearly stoichiometric sample of Si-N. We obtain their radial distribution functions (RDF's) for four different time steps, one for each material, using densities dictated by experiment. The simulated RDF's for amorphous C, Si, and Ge show the four characteristic radial peaks observed experimentally. For the nearly stoichiometric $SiN_{1.29}$ sample two runs were performed and averaged. The agreement between simulated and experimental RDF's is very good.

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In the last 15 years Car-Parrinello molecular dynamics[1] and quenching from the melt of no more than 125-atom periodically continued supercells have been the standard procedure to *ab initio* generate amorphous structures of tetrahedral covalent semiconductors. Car, and Parrinello and collaborators applied their first-principles plane-wave molecular dynamics (CPMD) method to C, Si, and Ge; their simulations were done starting from the corresponding liquid phases and, after cooling, radial distribution functions (RDF's) were calculated for the range $0 \leqslant r \leqslant l/2$, where l is the length of the cell edge used and, generally, includes the first two radial peaks. Even though the RDF's obtained reproduce the first two peaks of the experimental results, the overall agreement with experiment varies from material to material. Quenching from the melt produces an excess of defects, both dangling and floating bonds, and the electronic and/or optical gaps are difficult to observe. However, the pioneering work of Car and Parrinello, no doubt, has been a landmark in the development of the field, and has permeated all efforts up to date. *Ab initio* methods are in principle widely applicable, without adjustment of parameters, and they are the subject of the present work.

Of the four materials considered here, carbon is the most versatile, since the variety of chemical bonds that it displays has no counterpart. For this reason it is very difficult to produce a unique amorphous material and to generate random networks that reproduce the totality of the experimental results. Due to this versatility a variety of terms have been developed to describe the different amorphous phases. One talks of tetrahedral (*ta*-C), diamond like, graphitic, and plain amorphous carbon (*a*-C), to mention those most frequently used.[2] The existence of four well-defined radial peaks in the RDF's for $0 \leqslant r \leqslant 6.00$ Å is nevertheless experimentally observed, particularly in high-density samples. Several experimental RDF's were obtained for amorphous carbon at various densities,[3–7] but only that of Gilkes *et al.*[7] is considered here.

The CPMD method was applied to amorphous C.[8–10] The simulations were done starting from liquid phases and, after cooling, RDF's were calculated for $0 \leqslant r \leqslant l/2$, where l is the length of the cell edge used. The maximum number of atoms in the largest supercell used is 125 and pseudopotentials are utilized within the local-density approximation (LDA) or the generalized gradient approximation (GGA). The system studied by Galli *et al.*[8] corresponds to a low-density material of 2.0 g/cm^3, whereas Marks *et al.*[9] studied a *ta*-C with a density close to 3 g/cm^3. So far the work of McCulloch *et al.*[10] is the most complete *ab initio* study of amorphous carbon for five different densities using 125-atom supercells and the GGA approximation. RDF's were reported by all of them, and they compare favorably with existing data.

Amorphous silicon, *a*-Si, was studied intensively and extensively for the last three decades, both experimentally and theoretically. It exists at densities comparable to those of crystalline silicon. Experimentally, RDF's also show four peaks for $0 \leqslant r \leqslant 8.00$ Å; the position of the first and second amorphous peaks coincide with the corresponding crystalline ones, thereby emphazising the relevance of the short-range order.[11] Only the experimental results from Refs. 12–18 are used in this work. They are plotted so that their uppermost values are given in the upper experimental curve, and their lowermost data in the lower experimental curve of the figures.

The first application of CPMD was to amorphous Si,[19,20] and Lee and Chang[21] also studied it using a decoupled Car-Parrinello scheme. Recently, CPMD was applied to *a*-Si by Cooper *et al.*[22] using the GGA. The RDF is plotted up to the second peak, and the LDA calculation from Ref. 20 gives a better agreement with experiment than the GGA. As expected, a large number of overcoordinated atoms are found, essentially due to the melting of the supercells, since some of the liquid phases are overcoordinated; e.g., liquid silicon and liquid germanium have average coordination numbers between 6 and 7, and quenching preserves some of this overcoordination.

The behavior of *a*-Ge is quite similar to *a*-Si. Four peaks are also experimentally observed for $0 \leqslant r \leqslant 9.00$ Å. Amorphous germanium exists at densities 10% lower than those of the crystalline material. Here the work of Refs. 23–25 is considered, and the experimental plots of the RDF's were

made in a way similar to those of *a*-Si. The CPMD method,[26] and a variant of it,[27] are applied to study Ge; the reported RDFs (first two peaks) barely resemble the experimental ones. Again, a large number of overcoordinated atoms are found.

From the applicational point of view amorphous silicon nitride, a-Si_3N_4 or a-$SiN_{1.33}$, is an important material, since it is preferred over the crystalline counterpart due to its uniformity and electrical properties. Experimental reports are scarce, but the results found[28] offer the possibility of studying the role of the *partial* RDF's in the total RDF, and is our point of comparison. As far as we know, SiN alloys have not been the subject of CPMD, and therefore the results herein are likely the first *ab initio* study of this material.

Another *ab initio* approach to this subject is a molecular dynamics (MD) method due to Sankey *et al.*[29] based on the Harris functional,[30] and pseudoatomic orbitals per site. Drabold *et al.*[31] used this method within the LDA; starting with a 64-atom cubic cell of Si in a diamond structure, with one vacancy, they generated an ''incompletely melted'' sample by heating it up to 8000 K. The system acquires a highly disordered liquidlike structure before final quenching to a solid. They stated that their results for the RDF agree well with experiment, without making a direct comparison. Posterior work[32] applied this method to ''hand-made'' amorphous structures[33] with 216 atoms in a periodic supercell and to other cells. Diamondlike amorphous carbon is also studied using this MD method and 64-atom diamond cubic cells;[34] the first two peaks of the RDF were given, but were not compared to experiment.

In this work we report the generation of random networks using a code and a thermal process that lead to RDF's that are in very good agreement with experiment. The code is FASTSTRUCTURE,[35] a density-functional code based on the Harris functional[30] that allows simulated annealing/molecular dynamics studies with quantum force calculations.[36] The LDA parameterization of Vosko, Wilk, and Nusair[37] was used in all simulations. The core is taken as full, except for amorphous germanium, which means that all-electron calculations are carried out. For *a*-Ge the frozen-core approximation was invoked, due to finite computational resources. Minimal basis sets of atomic orbitals were chosen for the molecular dynamics processes, except for C, where the standard *sp* set was used since the role of the *p* states is decisive. Cutoff radii of 3 Å for C and 5 Å for Si, Ge and for $SiN_{1.29}$ were used, a compromise between computational cost and accuracy. For the geometry optimization of the final structures, a cutoff radius of 3 Å was used. In order to better reproduce the amorphous networks experimentally found, time steps of 4 fs for C, 10 fs for Si, 15 fs for Ge, and 6 fs for $SiN_{1.29}$ were utilized. The forces are calculated using rigorous formal derivatives of the expression for the energy in the Harris functional.[38]

The thermal procedure used was as follows. We amorphisized crystalline diamondlike cells with 64 atoms (36 N and 28 Si for Si-N) by heating them in 100 steps from 300 K up to just below their respective melting points—4100 K for C, 1685 K for Si, 1210 K for Ge and 2175 for $SiN_{1.29}$—and immediately cooling them down to 0 K in 108, 122, 133, and 116 steps, respectively, in order to reproduce the heating rates. It was established[39] that the melting temperature of *a*-Si is 250 K, lower than the melting temperature of *c*-Si; therefore, we always expect to be above the melting temperatures of the respective amorphous phases by staying just below the melting temperatures of the crystalline counterparts. We then subjected each cell to annealing cycles at the following temperatures: 700 K for C, 300 K for Si, 300 K for Ge, and 300 K for a-$SiN_{1.29}$, with intermediate quenching processes. For a-$SiN_{1.29}$ two runs were performed and averaged, to assure the adequacy of our procedure for this material. Samples with the following densities were studied: 2.6 g/cm^3 for C; the crystalline density 2.33 g/cm^3 for Si; 4.79 g/cm^3 for Ge, 10% below the crystalline one; and 3.115 g/cm^3 for the nearly stoichiometric a-$SiN_{1.29}$.

The heating/cooling rates for C, Si, Ge, and $SiN_{1.29}$ were 9.25, 1.38, 0.60, and 3.11×10^{15} K/s, respectively. The at-

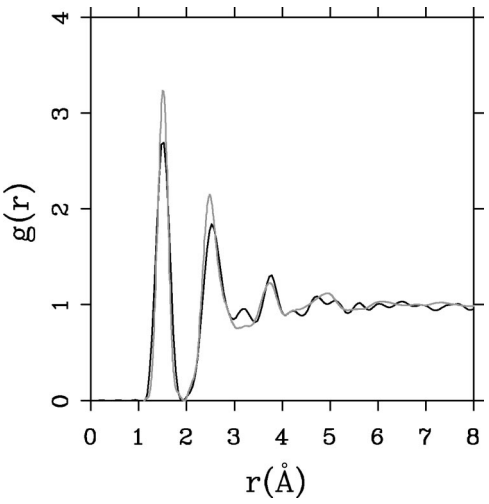

FIG. 1. RDF's for amorphous carbon. The dark line is our simulation for $\rho=2.6$ g/cm^3, with a 3.0-Å cutoff and a 4-fs time step. The lighter experimental line is taken from Ref. 7.

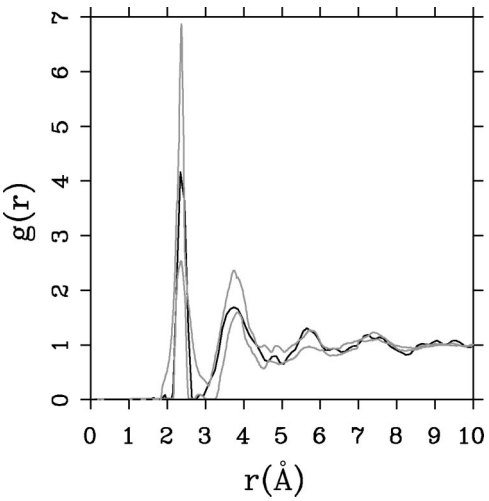

FIG. 2. RDF's for *a*-Si. The lighter lines are the experimental upper and lower bounds. The dark line is our result with $\rho=2.33$ g/cm^3, a 10-fs time step, and a 5-Å cutoff.

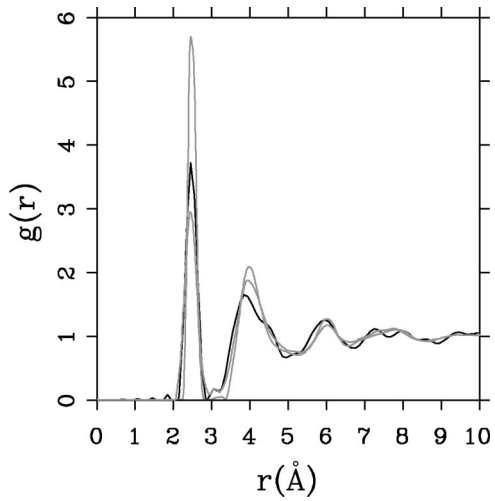

FIG. 3. RDF's for *a*-Ge. The lighter lines are the experimental upper and lower bounds. The dark line is our simulation with $\rho = 4.79$ g/cm^3, a 15-fs time step, and a 5-Å cutoff.

oms were allowed to move within cells of volumes $(7.8889\ \text{Å})^3$ for C, $(10.8614\ \text{Å})^3$ for Si, $(11.7194\ \text{Å})^3$ for Ge, and $(8.8280\ \text{Å})^3$ for $SiN_{1.29}$, always with periodic boundary conditions. Our processes do *not* pretend to mimic the production of such materials, but only to generate random networks, using *ab initio* techniques, that agree with the experimental RDF's in order to be able to study their topological, electronic and optical properties.

The simulated RDFs for the various samples are plotted in Figs. 1–4 where a comparison is made with the upper and lower experimental bounds, where appropiate. In particular, the radial features for the pure elements all show four prominent peaks for $0 \leqslant r \leqslant l$, where l is the length of the cell edge used, in agreement with experiment. Since the number of atoms in the cells leads to statistical fluctuations that are not representative of the bulk, we have Fourier-smoothed the RDF's to have adequate curves to allow comparison with experiment.

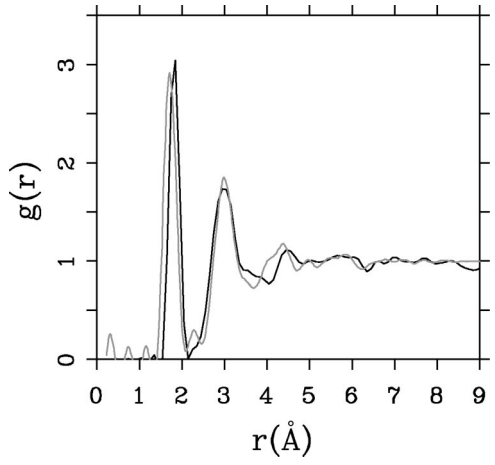

FIG. 4. RDF's for silicon nitride. The lighter line is the experimental curve (Ref. 28, a-$SiN_{1.33}$). The dark line is our averaged results (a-$SiN_{1.29}$) for $\rho = 3.115$ g/cm^3, a 6-fs time step, and a 5-Å cutoff.

TABLE I. Height and position of the maxima of radial peaks and $\langle nn \rangle$.

	First peak		Second peak		
Material	Position	Height	Position	Height	$\langle nn \rangle$
C	1.52	2.69	2.52	1.84	3.41
Si	2.35	4.16	3.75	1.69	4.00
Ge	2.45	3.72	3.85	1.65	3.94
$SiN_{1.29}$	1.85	3.04	2.95	1.73	3.47

Table I shows the positions and maximum values of the first and second peaks, and the average nearest neighbors $\langle nn \rangle$. The carbon peak at 1.52 Å is similar to the experimental value given in Ref. 7 for a 3.0 g/cm^3 density sample, and agrees with the simulations of Ref. 10 for a sample with the same density as ours. The first peak for silicon, located at 2.35 Å, and for germanium located at 2.45 Å, are in agreement with experiment. The peak at 1.85 Å for silicon nitride may be compared to Ref. 28 and to 1.71–1.76 Å for the crystalline β phase.[40] The average number of nearest neighbors, is 3.41 for C, in agreement with Ref. 7 for the corresponding sample; 4.00 for Si, 3.94 for Ge and 3.47 for Si-N. All our RDF's have well defined minima between the first and the second peaks and these values are used to obtain $\langle nn \rangle$: 1.95 Å for C, 2.70 for Si, 2.80 for Ge, and 2.15 for $SiN_{1.29}$.

The carbon samples studied experimentally correspond to densities from 2.00 to 3.00 g/cm^3; therefore, we decided to study a sample with an intermediate density, $\rho = 2.6$ g/cm^3 (Fig. 1); the agreement is very good although the densities are slightly different. Figure 2 shows a comparison of our simulated RDF with experiment for *a*-Si; the four peaks are well reproduced, and some of the experimental fine structural features appear in the simulation as can be seen in the features between the second and third peaks. Similar observations apply to Fig. 3 for *a*-Ge and to Fig. 4 for a-$SiN_{1.29}$.

In conclusion, we have devised a thermal process and used a density-functional theory LDA computer code to generate *ab initio* random networks for covalent materials, both for pure elements and alloys, that lead to RDF's in excellent agreement with experiment. Our simulated results are also in agreement with some theoretical work for corresponding densities, as for carbon. The thermal process used to generate these structures is different from those found in the literature; it consists of heating crystalline samples of 64 atoms just *below* their respective melting temperatures, and then cooling them to 0 K with subsequent annealing and quenching cycles at temperatures dictated by experiment. This thermal process seems adequate both for pure elements and alloys, has the advantage of involving well-defined procedures, and is based on the fact that, at least for silicon, the melting temperature of the amorphous phase is well below the melting temperature of the crystalline phase.[39]

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