

Ab initio generation of amorphous carbon structures

Fernando Alvarez^a, C.C. Díaz^a, R.M. Valladares^b, Ariel A. Valladares^{a,*}

^aInstituto de Investigaciones en Materiales-UNAM, Apartado Postal 70-360, México, D.F. 04510, Mexico

^bFacultad de Ciencias-UNAM, Apartado Postal 70-542, México, D.F., 04510, Mexico

Abstract

Using a new thermal process and an ab initio molecular dynamics method based on the Harris functional on original crystalline, periodically continued 64-atom diamond-like cells, we generated amorphous carbon for two different densities: 1.8 and 2.6 g/cm³, with a 4.0-fs time step. The radial distribution functions (RDF) show the four characteristic experimental peaks. Bond angle distributions are also obtained, as well as the number of *n*-atom rings. The low-density sample has a larger quantity of sp² bonds but the high-density sample agrees better with experiment. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Car–Parrinello molecular dynamics and quenching from the melt of no more than 64-atom periodically-continued supercells have been the standard procedures for producing amorphous structures of semiconductors from first principles. They have the generic shortcomings of radial distribution functions (RDFs) that reproduce, at best, the first two peaks of the experimental results and that only agree with some of them. However, the pioneering ab initio work of Car and Parrinello has been a landmark and has permeated all efforts during the last 15 years.

These methods were applied first to amorphous silicon (a-Si) [1], a semiconductor that has been studied intensively and extensively for the last three decades, both experimentally and theoretically [2]. They were next used to generate amorphous carbon [3]. Carbon is versatile due to the multiplicity of its bonding since it ranges from sp¹ to sp³. Hybridizations of the sp² type lead to graphite-like carbon, whereas the sp³ type generates diamond-like, or tetrahedral carbon; combinations thereof lead to bucky balls, nanotubes, etc. This implies that the type of atomic structure depends on the percentage of sp¹, sp² and sp³ bonds. Equivalently, since

the density of amorphous carbon depends on the percentage of their content [4], the atomic random network of amorphous carbon should depend on the density.

Several experimental radial distribution functions (RDFs) were obtained for pure amorphous carbon, a-C. The experimental work of several authors [5–9] is considered in this paper, and represented in the corresponding figures as two curves that are the upper and lower bounds.

On the theoretical side the original ab initio calculation, described in Car and Parrinello [1] has been extended by posterior work along the same lines [10,11]. Another approach, very similar to ours since it also uses the Harris functional, is due to Sankey and collaborators [12,13], and has been applied to amorphous carbon by Drabold et al. [14]. All of these consider the structural problem by generating amorphous supercells using first-principles quantum methods. The questions of how generally can an ab initio method that uses a reasonably sized supercell be applied, and how accurate one can expect the results to be, are addressed in this work.

2. Method

We use FastStructure [15], a DFT code based on the Harris functional [16], and optimization techniques based on a fast force generator to allow simulated annealing/molecular dynamics studies with quantum

*Corresponding author.

E-mail address: valladar@servidor.unam.mx (A.A. Valladares).

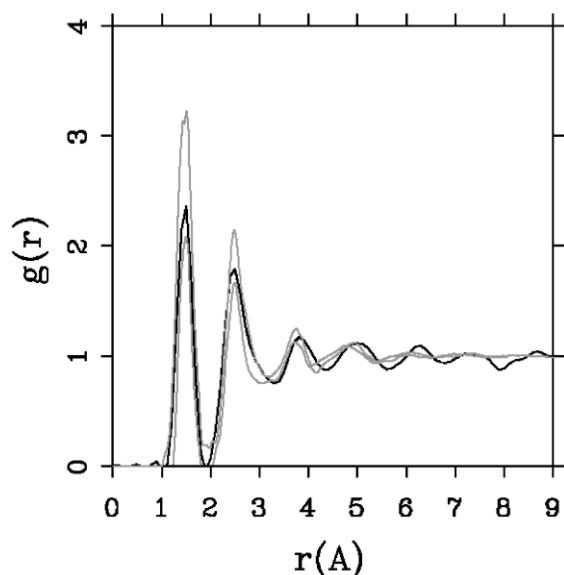


Fig. 1. RDFs for a-C. The lighter lines are the experimental upper and lower bounds and the dark line is our simulation for $\rho = 2.6 \text{ g/cm}^3$.

force calculations [17]. We use the LDA parameterization due to Vosko et al. [18]. The core is taken as full which means that an all electron calculation is carried out, and for the amorphization process a minimal basis set of atomic orbitals was chosen with a cutoff radius of 3 Å. The physical default time step is given by $(m_{\min}/5)^{1/2}$, where m_{\min} is the value of the smallest mass in the system, i.e. 1.6 fs. However, in order to increase the dynamical processes that occur in the amorphization in reasonable computer time, a time step of 4 fs was used. The forces are calculated using rigorous formal derivatives of the expression for the energy in the Harris functional, as discussed by Lin and Harris [19].

Our process is not designed to reproduce the way an amorphous material is grown, but has the objective of generating an amorphous sample that adequately represents those obtained experimentally. We amorphized the crystalline diamond structure, with 64 carbon atoms in the cell, and two different densities: 1.8 and 2.6 g/cm^3 . We slowly heated them from 300 to 4000 K, just below the melting point, in 100 steps of 4 fs, and immediately cooled them to 0 K in 108 steps. The heating/cooling rate was $9.25 \times 10^{15} \text{ K/s}$. The atoms were allowed to move freely within each cell of volume $(8.9176 \text{ Å})^3$ and $(7.8889 \text{ Å})^3$, respectively, with periodic boundary conditions. We next subjected them to annealing cycles at 700 K, with intermediate quenching processes. At the end a geometry optimization was carried out to find the local energy minimum of the amorphous structures.

3. Results and discussion

Experimentally the samples studied correspond to densities given by 2.44 and 3.00 g/cm^3 . For example, Li and Lannin [5,6] consider samples with $\rho = 2.44 \text{ g/cm}^3$, Gaskell et al. [7] and Jungnickel et al. [8] with $\rho = 3.0 \text{ g/cm}^3$, and Gilkes et al. [9] with $\rho = 2.9862 \text{ g/cm}^3$. So we decided to undertake the study of a sample with $\rho = 2.6 \text{ g/cm}^3$ to compare with experiments, and of another sample with low density, 1.8 g/cm^3 , to observe the structural consequences. McCulloch et al. [11] consider several densities from 2.0 to 3.2 g/cm^3 , and the density of one of their samples coincides with ours, 2.6 g/cm^3 .

In Fig. 1 we present a direct comparison of our high-density simulation with the upper and lower experimental bounds taken from the literature [5–9] and the agreement is very good, including the existence and position of the third and fourth amorphous peaks. We forced the first peak to fully coincide with the first experimental peak to study the fine structural behavior of both simulations. The RDF obtained from our low-density simulation (Fig. 2), shows a very interesting behavior: even though we also forced the first amorphous peak to coincide with experiment, the remaining peaks are displaced towards higher distances. This is an indication of the presence of sp^2 bonds.

In Fig. 3 a comparison of the two simulated RDFs is presented and it can be clearly seen that the low-density simulation is systematically displaced towards the high end of the interatomic distances. Fig. 4 is a comparison of our two simulations normalized to the highest density and it can be seen that the number of average nearest

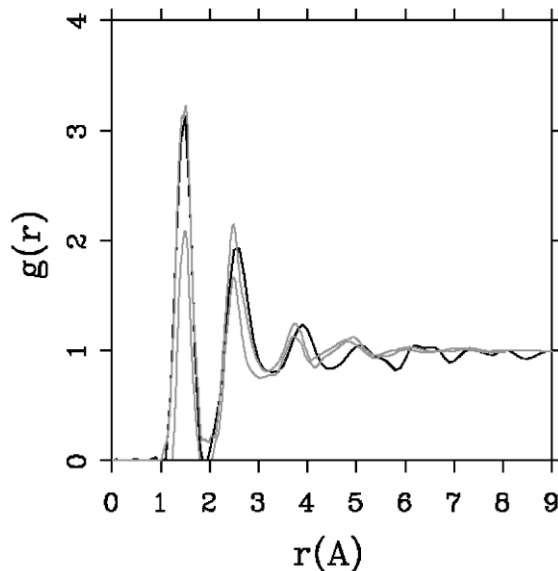


Fig. 2. RDFs for a-C. The lighter lines are the experimental upper and lower bounds and the dark line is our simulation for $\rho = 1.8 \text{ g/cm}^3$.

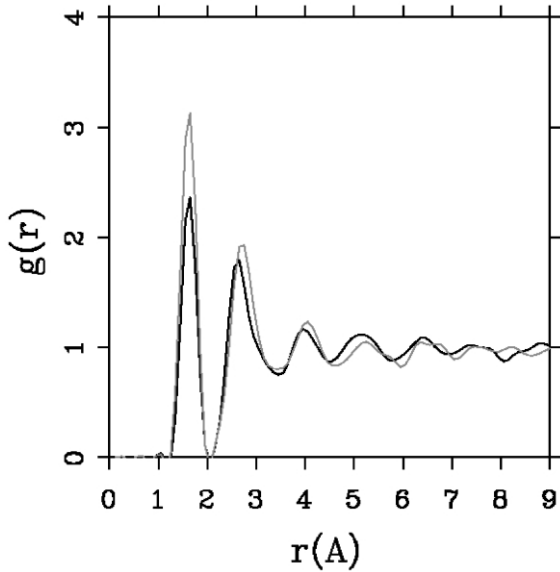


Fig. 3. Simulated RDFs for a-C. The lighter line is the low-density result and the displacement of the amorphous peaks towards higher interatomic distances can be observed.

neighbors is larger for the high-density sample than for the low density one: 3.75 vs. 3.47. A cut-off radius of 2.0 Å, the minimum between the first and the second amorphous peaks, is used throughout.

The bond angle distribution is given in Fig. 5 for the high-density sample. The crystalline bond angle is 109.47°. There are 48 fourfold coordinated atoms and their distribution shows a peak at approximately 105°, and represents the main contribution to the graph. The

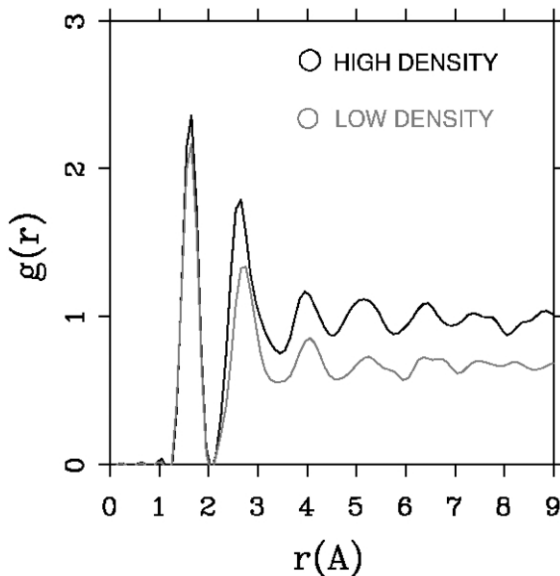


Fig. 4. Simulated RDFs for a-C normalized to $\rho = 2.6 \text{ g/cm}^3$. The lighter line is the low-density result and the area under the first peak is larger for the high-density sample.

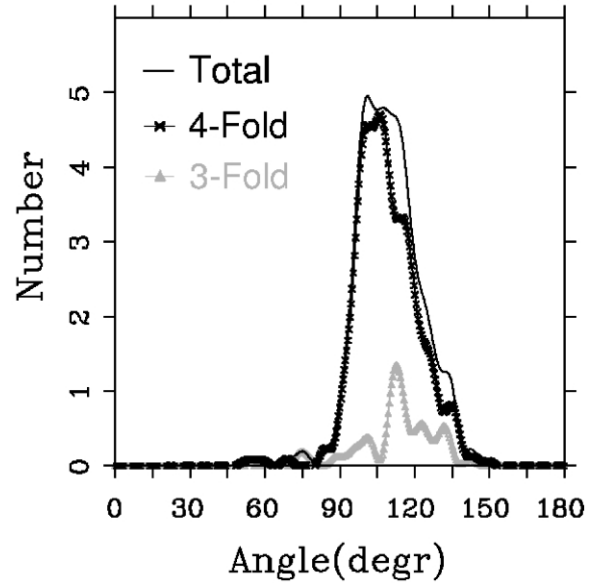


Fig. 5. The bond angle distribution for the high-density sample is shown. Tetrahedral coordination is predominant and the maximum is at approximately 105°.

16 threefold coordinated atoms show a minor peak at 115°.

Fig. 6 is the bond angle distribution for the low-density sample. The number of four-, three- and two-fold coordinated atoms is 33, 30 and 1, respectively. The contribution of threefold coordinated atoms is prominent and presents a double peak centered at 120°, the

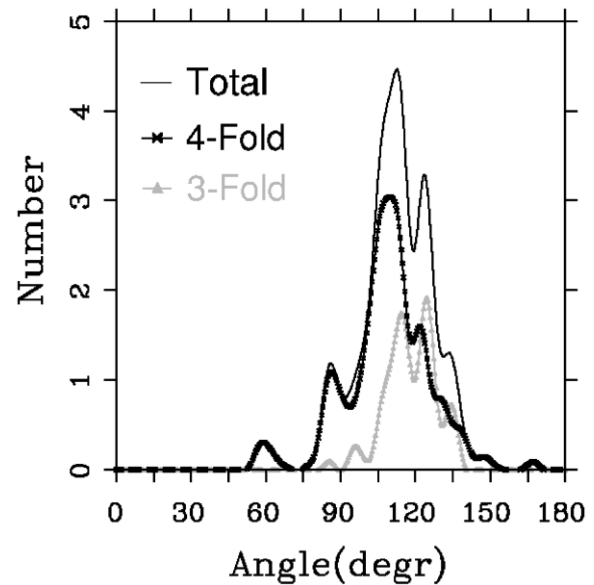


Fig. 6. The bond angle distribution for the low-density sample is shown. Tetrahedral and trihedral coordination is important. The four-fold maximum is at approximately 110°, the threefold has a double peak centered at approximately 120°.

Table 1
Density and sp-hybridization for several ab initio density functional simulations

	Galli et al. [3]	Drabold et al. [13]	Marks et al. [10]	McCulloch et al. [11]				This work	
ρ (g/cm ³)	2.0	3.0	2.9	2.0	2.6	2.9	3.2	2.6	1.8
sp ³	15%	91%	66%	6%	43%	58%	79%	75%	51%
sp ²	85%	9%	34%	79%	56%	41%	21%	25%	47%
sp ¹	–	–	–	15%	1%	1%	–	–	2%

graphite planar bond angle. The tetrahedral contribution shows a peak at approximately 110°, very close to the crystalline value. No five-bonded carbon atoms were observed in either sample.

The high-density sample contains the following distribution of simple atomic rings: one ring of three atoms, no rings of four, 29 of five, 18 of six, 18 of seven and seven rings of eight atoms. The low-density sample contains two rings of three atoms, seven rings of four, seven of five, 29 of six, nine of seven, six of eight and six rings of nine atoms.

4. Conclusions

We were able to generate, from first principles, random structures that have features in agreement with experiment. For the high-density sample the RDF agrees well with experiment; it has 75% of fourfold atoms and 25% of threefold atoms, as in ta-C for these densities. The maximum number of rings corresponds to those with five atoms, 29; six- and seven-atom rings have equal contributions, 18. The bond angle distribution has a maximum at 105°, which indicates a homogeneity typical of ta-C.

For the low-density sample the RDF is displaced with respect to the experimental results; it has 51.5% of fourfold atoms, 46.9% of three-fold atoms and 1.6% of two-fold atoms, as in graphitic amorphous carbon. Table 1 compares the results of various ab initio calculations with our work. The maximum number of rings corresponds to those with six atoms, 29; all others are much lower and evenly distributed. The bond angle distribution due to the tetrahedral contribution shows a peak at approximately 110°, whereas the threefold atoms have a double peak centered at approximately 120°, the sp² planar angle in graphite. This indicates that for this density the amorphous sample is a juxtaposition of three- and four-fold crystalline-like regions.

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