

Amorphizing non-cubic structures of carbon. The case of rhombohedral and hexagonal crystalline supercells

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Abstract

We have recently developed a procedure to amorphize structures of some semiconducting elements starting from cubic supercells. This procedure includes the use of an ab initio computer code based on the Harris functional, 64 or 216 atoms in the originally crystalline supercells, and a thermal procedure that heats the samples to just below their corresponding melting temperature. Here we report the use of non-cubic supercells: the graphitic hexagonal (72 atoms) and rhombohedral (108 atoms) supercells, both with a density $\rho = 2.239 \text{ g/cm}^3$. The rhombohedral form is metastable whereas the hexagonal form is stable. We find that the radial distribution functions as well as the atomic topologies are similar in both cases, indicating that the symmetry of the initial crystalline structure does not affect the final amorphized samples.

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1. Introduction

Car–Parrinello molecular dynamics and quenching from the melt of no more than 125-atom periodically-continued cubic supercells have been the standard procedures for producing amorphous structures of semiconductors from first principles. These have the generic shortcomings of radial distribution functions (RDFs) that reproduce, at best, the first two peaks of the experimental results; structures with an excess of defects, both dangling and floating bonds; and samples without electronic and/or optical gaps, when expected, just to mention the most relevant. However, the pioneering ab initio work of Car and Parrinello has been a landmark, has permeated all efforts during the last 17 years and, no doubt, has furthered the development of the field.

These methods were applied first to amorphous silicon [1], a-Si, that has been studied thoroughly 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 sp^1 to sp^3 . Hybridizations of the sp^2 type lead to graphite-like carbon, whereas the sp^3 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 sp^1 , sp^2 and sp^3 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) have been obtained for pure amorphous carbon, a-C. In this paper the work of Refs. [5–9] is considered, and represented in the corresponding figures as two curves that are the upper and lower bounds of the experimentally obtained RDFs.

Theoretically, the original ab initio simulation of a-Si [1] has been extended by posterior work along the same lines [10] and recently applied to several samples of

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carbon, with varying densities [11]. Another approach, similar to ours since it also uses the Harris functional, is due to Sankey and collaborators [12] and has been applied to amorphous carbon by Drabold et al. [13]. All of them consider the structural problem by generating amorphous *cubic* supercells using first-principles quantum methods. The questions of whether *non-cubic* supercells can be used as starting cells to generate amorphous networks, and how difficult it is to reliably amorphize them, are addressed in this work.

2. Method

We use FASTSTRUCTURE [14], a DFT code based on the Harris functional [15], and optimization techniques based on a fast force generator to allow simulated annealing/molecular dynamics studies with quantum force calculations [16]. We use the LDA parameterization due to Vosko et al. [17]. The carbon core is taken as full which means that an all electron calculation is carried out, and for the amorphization process a *standard* basis set of carbon atomic orbitals was chosen with a cutoff radius of 5 Å. The reason for using a standard set is that, within our approximations, these orbitals give the correct position of the first peak of the resulting amorphous structure [18]. The *minimal* basis sets do not reproduce this position adequately [19]. 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 better simulate the dynamical processes that occur in the amorphization in reasonable computer time, a time step of 4.1 fs for the hexagonal supercell and 4.2 fs for the rhombohedral supercell were 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 [20].

In this occasion we amorphize graphitic hexagonal and rhombohedral supercells. The hexagonal supercell has 72 atoms with a density $\rho = 2.239 \text{ g/cm}^3$. The rhombohedral supercell has 108 atoms and the same density as the hexagonal supercell. We slowly heated the hexagonal samples from 300 to 4800 K in 100 steps of 4.1 fs, and immediately cooled them down to 0 K in 107 steps. A similar process was carried out for the rhombohedral samples: heating up from 300 to 4800 K, in 100 steps of 4.2 fs, and immediately cooling down to 0 K in 107 steps. The atoms were allowed to move within each cell of volume $(7.38 \times 7.38 \times 13.6 \text{ Å}^3)$ for the hexagonal cell, and $(7.38 \times 7.38 \times 20.4 \text{ Å}^3)$ for the rhombohedral cell, with periodic boundary conditions. We next subjected them to annealing cycles at 300 K, with intermediate quenching processes. At the end, a geometry optimization was carried out to find the structure with a local energy minimum for the amorphous cells.

3. Results and discussion

Experimentally, the samples studied correspond to densities of 2.44 and 3.00 g/cm^3 . For example, Refs. [5,6] consider samples with $\rho = 2.44 \text{ g/cm}^3$, Refs. [7,8] with $\rho = 3.0 \text{ g/cm}^3$, and Ref. [9] with $\rho = 2.9862 \text{ g/cm}^3$. The graphitic samples studied here correspond to densities $\rho = 2.239 \text{ g/cm}^3$ and our results are compared with experiments considering the upper and lower bounds. McCulloch et al. [11] do simulations for several densities: 2.0, 2.6, 2.9 and 3.2 g/cm^3 .

In Fig. 1 we present a direct comparison of the RDF of our amorphized hexagonal graphitic supercell with the upper and lower experimental bounds taken from Refs. [5–9]. In Fig. 2 we present a direct comparison of the RDF of the amorphized rhombohedral graphitic supercell also against the upper and lower experimental bounds taken from Refs. [5–9]. The fact that the RDFs

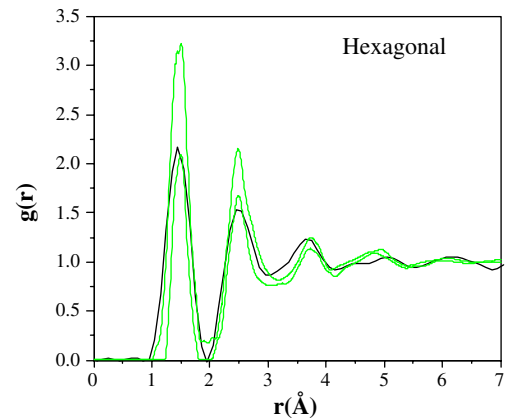


Fig. 1. RDFs for a-C. The lighter lines are the experimental upper and lower bounds and the dark line is our simulation for the graphitic *hexagonal* supercell, with $\rho = 2.239 \text{ g/cm}^3$, using a standard basis set.

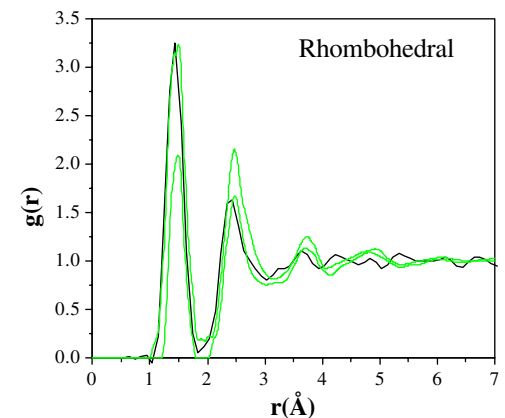


Fig. 2. RDFs for a-C. The lighter lines are the experimental upper and lower bounds and the dark line is our simulation for the graphitic *rhombohedral* supercell, with $\rho = 2.239 \text{ g/cm}^3$, using a standard basis set.

compare favorably with the experimental results gives us confidence that the amorphous samples adequately represent the atomic topology of low density a-C. This means that we were able to amorphize these non-cubic structures with success. However it must be said that we encountered more difficulties amorphizing the graphitic structures using standard basis sets than the cubic structures using standard basis sets. The amorphizing process for the graphitic structures using minimal basis sets was also more difficult than using these same basis sets in the cubic structures. For example, it was common to find the graphitic layers displaced with respect to one another in some of our runs, or that some of the layers became ‘amorphous’ while others remained ‘crystalline’.

Figs. 3 and 4 show the atomic structure of the amorphized samples corresponding to the, originally, hexagonal and rhombohedral supercells, respectively. In order to plot these structures we used a bond length of 1.95 Å for both samples; this value corresponds to the minimum value of their RDFs between the first and the second peaks, which we believe to be the natural way to establish the extent of the bonding in amorphous materials.

4. Conclusions

As part of our program to generate, from first principles, amorphous networks of covalent materials by amorphizing crystalline supercells, we studied the amorphization of hexagonal and rhombohedral gra-

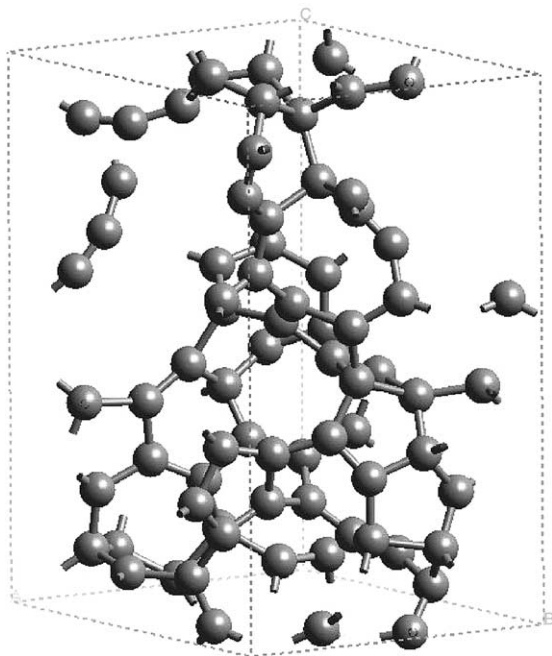


Fig. 3. The atomic structure of the *hexagonal* supercell amorphized with a standard basis set.

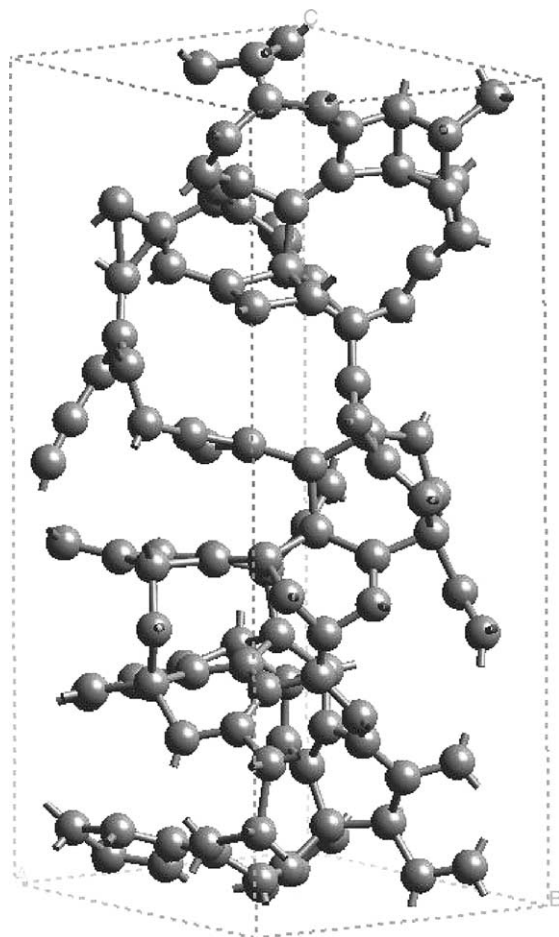


Fig. 4. The atomic structure of the *rhombohedral* supercell amorphized with a standard basis set.

phitic structures with 72 and 108 atoms, respectively, to see if the final results are similar to those obtained from amorphizing cubic supercells. The thermal processes utilized are similar to those previously reported; i.e., we heat our graphitic supercells from 300 to 4800 K in 100 steps of 4.1 fs for the hexagonal and 4.2 fs for the rhombohedral. Afterwards each sample is cooled down to 0 K in 107 steps. Further processes have the objective of annealing the structures, and a final optimization of geometry is performed to bring the samples to a local energy minimum.

We have encountered more difficulties amorphizing the graphitic-like cells than the cubic ones and this may have to do with the fact that the hexagonal structure is more stable than the cubic ones (see also Ref. [21] for some of these tendencies when carbon growth is simulated). It is a well known fact that graphite is the stable form of solid carbon and this may be why the difficulties appear. Nevertheless we were able to amorphize the graphitic supercells and the atomic structures and RDFs obtained compare well with previous results [18,19] and with experiment.

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