



# Amorphous carbon at low densities: An *ab initio* study



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## ARTICLE INFO

### Article history:

Received 29 September 2016

Received in revised form

4 January 2017

Accepted 10 January 2017

Available online 12 January 2017

### Keywords:

*Ab initio*

Low density

Amorphous carbon

Phonons

Specific heat

## ABSTRACT

In this paper, we present new computer models of low-density amorphous carbon, and study the structural, electronic and vibrational properties all based upon plane-wave density functional methods. The static structure factor and real space pair-correlation function is in agreement with available experimental data. We observe chains of  $sp$  bonded carbon in the models, along with  $sp^2$  and  $sp^3$  structures in varying concentrations. These models provide atomistic insight into the microstructure of the system, delineating variation in bonding ( $sp^2$ ,  $sp^3$  and  $sp$ ) preferences as a function of density. For these low densities, the vibrational density of states is computed for the first time, along with localization of modes and the specific heat with comparison to experiments. We contrast the amorphous three dimensional networks with amorphous graphene, which bears a striking similarity in the radial distribution functions, but shows a distinct signature in the vibrational density of states. The vibrational modes are analyzed and discussed, and animations of particularly interesting modes are provided as Supplementary Material. The modes are generally well extended, but are more complex than simple molecular pictures that are sometimes invoked, in some cases even revealing mixing among modes of different type.

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## 1. Introduction

Amorphous carbon has been an important research topic both for its many technological applications, and its scientific interest due to its remarkable ability to form an array of microstructures. Carbon forms bonds of  $sp$ ,  $sp^2$  and  $sp^3$  type [1], and these tend to be surprisingly energy-degenerate. An interesting question we will explore is the concentration of these three types of bonds as a function of density. Experimentally, non-hydrogenated amorphous carbons are challenging [2], which further justifies a new theoretical study. The variation in low density carbon samples arise in part from the method of preparation of the sample and the heat-treatment [3]. Furthermore, glassy carbon may be extracted from various polymers, which may leave a residue of bonded H. The presence of hydrogen significantly impacts the inelastic neutron scattering spectrum [4].

Some earlier research on amorphous carbon was been focused on tetrahedral (ta-c) or diamond-like carbon [5,6], along with amorphous graphene [7] and its applications. ta-C was explored

mostly in the hope of devising a dopable substitute for diamond for electronic applications. To date, there have been few modeling studies of low-density ( $1.0 - 1.5 \text{ g/cm}^3$ ) amorphous carbon phases [8–10]. Such calculations are based on MD simulations, albeit with tight-binding [11], and Reverse Monte Carlo (RMC), respectively. An alternative scheme for modeling amorphous carbon, more reliable than RMC, is to use experimental information and a force field, along the lines of Opletal and coworkers [12] and in more recent related approaches [13–16].

In this paper, we present new models for low density carbon. We have used state of the art *ab initio* interactions for our calculations. This approach provides a benchmark, as we obtain the atomistic models without any *a priori* assumptions of the system and accurate interatomic forces. Further, this paper will be an extension of the previous *ab initio* method based theoretical work done for higher densities of amorphous carbon [17].

The paper is organized as follows, In section 2 we discuss the computational methodology. In section 3, we report our models and the methods of preparation. Section 4, mainly focuses on the structural properties of the models and comparisons to experiments. Section 5 is devoted to the vibrational properties of the system, localization, identification of the vibrational states and the low-temperature specific heat. Section 7 gives a brief description of electronic properties of these low density carbons by evaluation the

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**Table 1**

Nomenclature and details of our models: density of the models ( $\rho$ ), position of first ( $r_1$ ) and second ( $r_2$ ) peak of RDF, Mean co-ordination number ( $n$ ), percentage of  $sp^3$ ,  $sp^2$  and  $sp$ , cooling time/cooling rate and the Free Energy per atom of the relaxed models ( $E_0$ ).

Model	$\rho$ (g/cm <sup>3</sup> )	$r_1$ (Å)	$r_2$ (Å)	$n$	% of $sp^3$	% of $sp^2$	% of $sp$	cooling time (ps)/rate (K/ps) <sup>a</sup>	$E_0$ (eV/atom) <sup>b</sup>
c64_4ps	1.50	1.43	2.45	2.90	6.25	78.12	15.63	4.0/1850.0	0.13
c120_15ps	1.50	1.45	2.49	2.90	4.17	81.67	14.16	15.0/493.3	0.15
c120_20ps	1.50	1.44	2.48	2.93	9.17	75.00	15.83	20.0/370.0	0.11
c72_16ps	0.92	1.41	2.48	2.67	0.00	66.67	33.33	16.0/462.5	0.35
c72_20ps	1.40	1.43	2.46	2.89	7.00	75.00	18.00	20.0/370.0	0.00
c72_20ps <sup>†</sup>	1.60	1.43	2.47	2.86	4.17	77.78	18.05	20.0/370.0	0.02

<sup>a</sup> Refers to cooling time or cooling rate from 8000 K to 600 K.

<sup>b</sup> After subtraction from lowest value of  $E_0$ .

electronic density of states and the electronic localization. In section 6, we summarize our findings and discuss the effectiveness of our approach by comparing it to the other known results. In section 8, we also describe animations of representative vibrational modes of interest.

## 2. Computational methodology

We have prepared models of glassy carbon [18] with densities ranging from (0.923 g/cm<sup>3</sup>–1.6 g/cm<sup>3</sup>). The models were prepared by using the *ab initio* Package “Vienna *Ab initio* Simulation Package” (VASP), a molecular dynamics package with a plane-wave basis and using the local-density approximation. The electron-ion interactions for the plane wave basis or VASP models were described by the Projector Augmented-Wave (PAW) [19,20] method with Ceperley-Alder exchange correlation functional. A liquid phase at each density was equilibrated and then “cooled” as described below yielding an arrested solid phase, which was then fully relaxed using the conjugate gradient (CG) method. All simulations were performed at constant volume, employing only the  $\Gamma(\vec{k} = 0)$  point to compute the forces and total energies.

## 3. Models

We have prepared models with system size ranging from 64 atoms to 120 atoms.<sup>1</sup> We have chosen densities varying between (0.923 g/cm<sup>3</sup> - 1.6 g/cm<sup>3</sup>). We began with random coordinates, these were “heated” to 8000 K, equilibrated at 8000 K and then cooled to 300 K in multiple steps (see Table 1). Finally, a well-equilibrated model at 300 K was relaxed using the conjugate gradient (CG) scheme.

The resulting six models provide us with a reasonable selection of low density regime in amorphous carbon. These models will hereafter be identified as (c64\_4ps, c120\_15ps, c120\_20ps, c72\_16ps, c72\_20ps and c72\_20ps<sup>†</sup>). These assigned nomenclatures indicate: the number of atoms in the cell, and the cooling time used for each model. We summarize our models in Table 1.

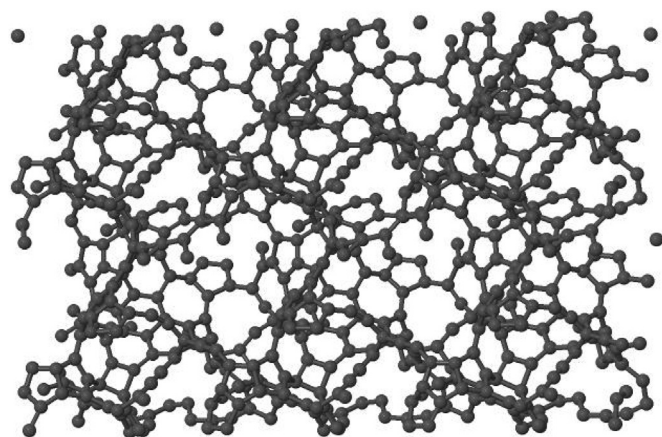
## 4. Structural properties

A visual representation of these models has been provided in Figs. 1 and 2. We have used periodic boundary conditions to replicate the (c120\_15ps) model and show 720 atoms in Fig. 1. Meanwhile, in Fig. 2, the various bonding environments have been assigned different colors. These reveal that  $sp^3$  bonding mainly inter-connects the  $sp^2$  bonding networks and that  $sp^2$  bonding

dominates for lower density. Interestingly, a significant fraction of  $sp$  bonded atoms are also formed in low density carbon, providing a chain-like topology, familiar from a-Se [22]. In particular, our model (c72\_16ps) at a density of 0.923 g/cm<sup>3</sup> has 33%  $sp$  bonded atoms. To our surprise this model has the same final free energy per atom ( $E_0$ ), as the other model with much less  $sp$  content, which suggests that at low concentration the  $sp$  bonding is to be expected [23] and justifies the common assertion that the three hybridizations yield similar local energetics. The  $sp$  bonded model is shown in Fig. 2. These  $sp$  chains were first conjectured in the work of McCulloch et al., we show that their conclusions were valid. We have also compared our results (see Fig. 3) with the amorphous graphene network [24]. To our surprise, despite the fact that our amorphous carbon is three dimensional in nature (see Fig. 1), structurally it resembles strictly the two dimensional amorphous graphene (albeit puckered around pentagonal structures) [7].

The structure of low density carbon has been controversial as different heat treatment protocols yields different structural features [10]. Further, there has also been a debate about the bonding present in these structures. Mildner and Carpenter [3] suggested that the concentration of  $sp^3$  bonding in these materials is less than 10 %. Our models are in agreement with this claim, as all of our models have  $sp^3$  fraction below 10 %.

Structurally, glassy carbon can be described with the help of the Static Structure Factor in reciprocal space or its real space counterpart the Radial Distribution function (RDF). The RDF obtained for the models are plotted in Fig. 3 and also for a model of amorphous graphene. The position of the first and second peak from the RDF is similar for the different models irrespective of the different carbon bonding environments and the method used for making the models. The peak positions and the coordination number are in good agreement with previous calculations [8,10,26] and with



**Fig. 1.** Visualization of model (c120\_15ps), 720 atoms are shown (replicated by using periodic boundary condition).

<sup>1</sup> We also prepared a larger model (with 216 atoms) using SIESTA [21], with (Harris Functional). The non-self consistent scheme resulted in slightly larger fraction of  $sp^3$  and a minor shift in RDF was observed, with almost no change in other properties.

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