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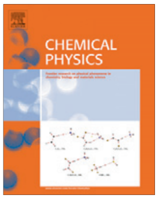

Amorphous carbon and its surfaces

Charles W. Bauschlicher Jr. [a,*], John W. Lawson [b]

[a] Mail Stop 230-3, NASA Ames Research Center, Moffett Field, CA 94035, USA
[b] Mail Stop 234-1, NASA Ames Research Center, Moffett Field, CA 94035, USA

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ABSTRACT

We have investigated bulk amorphous carbon at three densities (3.2, 2.6, and 2.0 g/cm^3) using density functional theory (DFT). The variation in the structure with density is discussed. The bulk structures are used to create surface structures. If the surfaces are relaxed at 700 K, the surface structures, as a function of density, are more similar than the analogous bulk structures. The relaxed surfaces appear to be graphene sheets with defects, sizable distortions, and have covalently bonded carbon chains holding the sheets together.

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1. Introduction

Amorphous carbon is a general term, covering a large range of densities, structures, and compositions [1]. One form of amorphous carbon that is of great interest to NASA is the char that forms on the surface of carbon based ablative heat shields during reentry. The heat shield includes a polymer, which under the heat and radiation of reentry is converted into a low density amorphous carbon char. The chemical and physical properties of the char have significant implications on the performance of the heat shield. For example, the absorption of visible and ultraviolet radiation heats the char, while infared emission cools it. Oxygen molecules are dissociated in the shock in front of the heat shield and arrive at the surface of the heat shield. The oxygen atoms can react with the surface of the char, which can bond with the surface or etch the surface. The energy released in these reactions can heat the surface. The oxygen atoms can recombine on the surface and some of the O_2 binding energy can be transfered to the surface, which can also heat the surface. The migration of the O atoms along and into the char are also of interest, since this could have implications on where and how fast the O atoms react.

Understanding the chemical and physical properties of the surface of heat shield char could help design more efficient shields, either by reducing the safety margins and hence saving weight or by designing a better shield material. Before one can tackle the chemical and physical properties of the char surface, one must have confidence that one can describe the surface and especially describe the surface as a function of density. In this manuscript we discuss generating models for bulk char at densities from 3.2 to 2.0 g/cm^3, and then extend these bulk models to models of the surface.

2. Methods

In the simulations of the bulk, the number of atoms and the density determine the cell size, which, for convenience, was chosen to be a cube. In all of the reported calculations, 64 carbon atoms were used. The positions of the atoms within the cell were fully optimized, while the size and shape of the cell were fixed for each density. For the studies of the surfaces, we start from the geometries obtained in the bulk calculations, change one dimension of the cell, center the slab in the expanded cell direction, and optimize the atomic positions in the slab calculations. Thus two of the dimensions were taken from the bulk, while the third dimension was made sufficiently large such that the neighboring slabs did not interact. We computed the density in the surface calculations using the positions of the upper and lower most atom in the surface direction and the cell sizes in the periodic directions. This was perhaps a bit simplistic because the upper and lower atoms were not given any size and shape of the surface was not accounted for. However, we believe that it is sufficiently consistent that we can compare different surfaces and look for trends.

We should note that we did test an additional approach to model the surface, where we consider one side of the slab to be the surface and the other side to be the bulk. Hydrogen atoms were added to the terminate the dangling bonds on the "bulk" side of the model. This approach was applied to the study of diamond (111) surfaces [2], and might appear to be straight forward to apply to amorphous surfaces as well, but it is not. Consider the carbon atoms on the "bulk" side of the slab. Two neighboring carbon in

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* Corresponding author. Tel.: +1 650 604 6231; fax: +1 650 604 0350.
E-mail addresses: Charles.W.Bauschlicher@nasa.gov (C.W. Bauschlicher Jr.), John.W.Lawson@nasa.gov (J.W. Lawson).

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the slab might have been connected in the bulk by a bridging carbon atom that was eliminated when the slab was formed. If two H atoms are added, they will be very close together and result in a strain on the “bulk” side of the slab. An optimization will reduce the strain, but this distorts the atoms away from their positions in the bulk, which partly defeats the object of tying off the dangling bonds to make one surface more bulk like. The problem can be over come if a CH_2 group is used to tie off the dangling bonds that previously had a bridging C atom. Clearly adding multiple CH_2 groups can lead to complications if adjacent CH_2 groups were bonded together in the bulk. Thus trying to tie off the dangling bonds for amorphous structures, especially at higher densities, results in a very tedious process that required multiple passes to create a stable “bulk” without dangling bonds. Given the somewhat arbitrary nature of tying off bonds, we adopted the approach of creating two surfaces. This approach not only has the advantage of simplicity, it creates twice as many surfaces for study.

The calculations were performed using the Vienna ab initio simulation package (VASP), version 4.6.34 [3–5]. The generalized gradient corrected functional of Perdew and Wang [6] was used. We used a plane wave basis set in conjunction with the projector augmented wave method [7] (PAW). Two different types of studies were performed, namely 0 K geometry optimizations and molecular dynamics (MD) with a finite temperature. In the 0 K calculations, a plane wave cutoff of 400 eV was used, while for the molecular dynamics calculations, a lower cutoff of 300 eV was used. A time step of 2 fs is used in all of the molecular dynamics calculations. A $1 \times 1 \times 1$ grid of k points was used; several test calculations using a $4 \times 4 \times 4$ grid yielded very similar results.

3. Results and discussion

3.1. Bulk systems

Preliminary calculations were performed for a density of 3.2 g/cm^3 to determine how to generate bulk models in the best manner. We added 64 carbon atoms in the cell at random coordinates; the addition of an atom was rejected if it was within 1.1 Å of any of the existing atoms. From this starting point, the structure was optimized in several ways. In the first test, the carbon positions were optimized at 0 K. Because ESR experiments show [1,8] a density of unpaired electrons of 10^{20} cm^{-3} or less, which translates into only one unpaired electron per 1000 or more carbon atoms, we discarded all systems where any carbon atom had a dangling bond, which we denote as a defect. The dangling bonds were detected by counting the number of σ and π bonds each carbon has. Two of the twenty runs produced systems with no defects, see Table 1. One had 69% sp^3 carbons and 31% sp^2 carbons, which appears to be a little low for a system that should correspond to diamond like carbon (DLC), while the other had 81% sp^3 carbons, which is more consistent with DLC [1]. However despite the change in number of sp^3 carbons, the total energies of the two structures were similar.

Table 1
Summary of the 3.2 g/cm^3 tests.

Test	Temp[a]	Time[b]	0 def[c]	E (eV)	% sp^2	%sp^3
1	0	0/0	2	−528.485	25.0	75.0
2	1000	0.6/2	3	−528.664	24.0	76.0
3	2000	0.6/2	1	−531.299	18.8	81.3
4	5000	0.6/2	4	−543.161	14.8	85.2
5	5000	0.6/0.2	0			
6	5000	0.6/4	4	−546.841	13.3	86.7
7	5000	4/4	5	−546.373	15.0	85.0
8	5000	0.6/1/2/0.6[d]	1	−542.422	9.4	90.6

[a] Highest temperature use to relax the atomic positions.

[b] Time in ps at highest temperature/quench time.

[c] Number of simulations with zero defects.

[d] 0.6 ps at 5000 K, 1 ps for the 5000 K to 2000 K quench, 2 ps for 2000 K to 300 K quench, 0.6 ps at 300 K, followed by 0 K optimization.

In the second test, a molecular dynamics calculations was performed to equilibrate the system for 0.6 ps (using a 2 fs time step as noted above) at 1000 K starting from the same random geometries as used in the 0 K optimizations. This was followed by a 2 ps quench from 1000 to 0 K using a linear schedule and then a 0 K optimization. This approach lead to three out of twenty structures with no defects. The energy of one was almost 3 eV less stable than found using the 0 K approach, while one had about the same stability and the third was about 3 eV more stable. The average sp^2 and sp^3 percentages were similar to test 1, see Table 1. The third test was similar to the second, except that the starting temperature was 2000 K. This approach yielded only one structure out of twenty tries with zero defects; its energy was very similar to the best run at 1000 K. The fourth test involved raising the initial temperature to 5000 K. This resulted in a melting of the carbon and a loss of the initial geometrical information. A 2 ps quench followed by a 0 K optimization resulted in four structures out of 20 starting geometries with no defects. The total energies of all four were lower than the results from the 0, 1000, or 2000 K calculations, with three of the four being about 15 eV more stable than the 0 K optimization results. The four simulations in test 4 had between 75% and 90% sp^3 carbon atoms.

Four additional tests (five, six, seven, and eight) were performed for an initial temperature of 5000 K. In the fifth test, the quench was reduced to 0.2 ps, which resulted in no structures with zero defects. The sixth test used 4 ps to quench and the results were similar to the 2 ps quench, namely there were four defect free structures that had total energies and percentages of sp^3 carbons that were very similar to the three more stable structures from test four. The seventh test ran the 5000 K molecular dynamics for 4 ps instead of only 0.6 ps. The quench was 4 ps as in test six. The sp^3 percentage and total energies of tests seven and six were very similar, suggesting that 0.6 ps at 5000 K was sufficient. In the eighth test, 1 ps were used to quench from 5000 to 2000 K and 2 ps to quench from 2000 to 300 K. This was followed by 0.6 ps at 300 K and finally 0 K optimization. This approach yielded only one defect free structure in twenty tries. This structure had an energy similar to the average energy for 5000 K with 2 ps quench and high percentage of sp^3 carbons. In this calculation, the quench from 5000 to 2000 K occured in 0.2 ps shorter time than test 4, while the quench from 2000 to 0 K was significantly slower. Apparently the slower quench from 5000 to 2000 K reduced the number of defects. It is perhaps a bit surprising that changing the quench slightly between tests 4 and 8 would significantly reduce the number of zero defect results, while increasing the quench time from 2 to 4 ps between tests 4 and 6 would have a much smaller effect. We would not be surprised if one could develop a method that used less computer time by breaking the quench into subranges, but to simplify our calculations we use a linear quench from 5000 to 0 K with a minimum of 2 ps.

On the basis of these test calculations, our bulk structures for all densities were generated by: (1) initial geometry was generated by randomly placing the atoms in the cube, (2) molecular dynamics were performed for 0.6 ps at 5000 K, (3) the cell was quenched to 0 K in 2 or 4 ps, and (4) a 0 K optimization with a tighter threshold was performed.

We adopted this procedure since 5000 K calculations yield total energies that are lower than those for 0, 1000, and 2000 K, suggesting that the positions of the carbons need to be randomized to obtain the lowest energies. However, the 0, 1000, and 2000 K structures are local minima, and should any experimental information become available that suggests the structure of heat shield