Microscopic Structure of Tetrahedral Amorphous Carbon

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Simulations are reported of a highly tetrahedral amorphous carbon network at a density of 3 g/cc using Car-Parrinello first principles molecular dynamics. The simulated structure consists of 65% fourfold and 35% threefold coordinated carbon sites, in good agreement with experiment. The structure is also in good agreement with recent neutron diffraction data. An unexpected observation was the presence of small carbon rings in the structure containing as few as three atoms. These carbon triangles and quadrilaterals, which resemble the organic compounds cyclopropane and cyclobutane, give the network a topology unique among tetrahedrally bonded amorphous materials.

The existence of an amorphous carbon network in which the coordination of carbon is close to four has been established by neutron [1,2] and electron diffraction studies [3,4]. This material, termed tetrahedral amorphous carbon *ta*-C [4], has a density of approximately 3 g/cc, is extremely hard, and is a weak *p*-type semiconductor. Potential applications for *ta*-C include wear-resistant coatings and thin-film semiconductor devices. Electron energy loss spectroscopy [5] has shown the fraction of threefold coordinated (sp^2) atoms to be (15–20)%. This is in contrast to amorphous silicon which contains only sp^3 atoms in a disordered network, a structure known as a "random tetrahedral network" [6]. Defects in the random tetrahedral network of silicon are believed to consist of threefold coordinated atoms still in the sp^3 configuration, giving rise to dangling bonds [6]. Thus *ta*-C can be viewed as a random tetrahedral network with a "contamination" of sp^2 bonding. However, despite progress in establishing the basic structure of *ta*-C, an accurate structural model has yet to be found.

Previous attempts to calculate the structure of *ta*-C using molecular dynamics (MD) simulations have been limited by the quality of the interatomic potentials. Recently, more sophisticated simulations based on the tight-binding approximation [7,8] and non-self-consistent *ab initio* method [9] have been presented. Although these schemes have had some success describing other forms of carbon, it has yet to be shown they have sufficient transferability to model the wide variety of bonding environments present in *ta*-C. This paper presents the results of the first fully *ab initio* MD calculation of a *ta*-C network in the scheme developed by Car and Parrinello [10,11].

The application of *ab initio* MD in this work has revealed a new and at first surprising result: The *ta*-C network has a significant number of three-membered sp^3 bonded rings, well known to organic chemistry in cyclopropane (C_3H_6), and four-membered rings as in cyclobu-

tane (C_4H_8). A comparison of the simulated structure with experimental neutron diffraction data shows good agreement and confirms the validity of the simulation.

The simulation system contained 64 atoms at a density of 3 g/cc in a simple cubic supercell whose volume remained constant throughout the simulation. Recent electron spin resonance measurements of *ta*-C [12] have shown that the density of unpaired spins is less than one unpaired spin for every 50 sp^2 atoms. Therefore no unpaired spins are expected in the sample, and the use of the local density approximation [13] instead of the local spin density approximation is justified. A Car–von Barth norm-conserving pseudopotential in the Kleinman-Bylander form was used [14]. The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 35 Ry and an integration timestep Δt of 3 atomic units (0.072 fs) was used. Nosé thermostats on both ions [15] and electrons [16] were used to control the ion temperature and fictitious kinetic energy, respectively.

A simple cubic lattice was chosen as the initial configuration of the atoms as this structure is highly unstable for carbon. Once molten, the sample was equilibrated at 5000 K for 0.36 ps where the liquid was highly diffusive with a diffusion constant of 7×10^{-5} cm^2/s. The liquid sample was then cooled to 300 K over 0.5 ps, and, following this, the system was equilibrated for a further 0.5 ps to gain temporal averages. The cooling rate of 10^{16} K/s is similar to that used in other simulations of carbon [9,17]. To verify that this cooling rate was appropriate we performed a second simulation in which the liquid took twice as long to cool to the solid. The second structure was structurally very similar to the first structure and contained both three- and four-membered rings.

The final annealed structure is shown in Fig. 1 using three different visualization schemes. As shown in Fig. 1(a), the structure consists of 22 threefold coordinated atoms, which we shall refer to as sp^2 hybridized, and
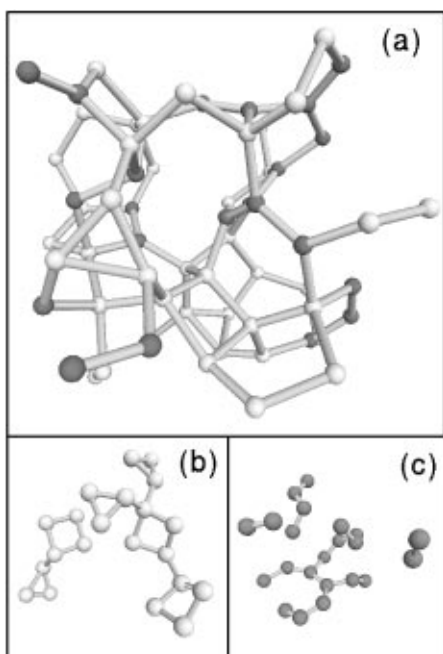
FIG. 1. Snapshot of the 64 atom *ta*-C network. The heavy lines show the network of bonds; the 22 dark spheres depict threefold coordinated atoms (sp^2 hybridized) and the 42 light spheres show the fourfold coordinated atoms (sp^3 hybridized). (a) The complete 64 atom structure. (b) The three- and four-membered rings present in the structure. (c) The 22 sp^2 hybridized carbon atoms showing how they group into clusters.

42 fourfold coordinated atoms, which we refer to as sp^3 hybridized. A significant feature of the structure is the frequent occurrence of three-, four-, and five-membered rings which give the network an unusual topology.

Some of the basic structural parameters of the network are shown in Table I. For comparison, experimental results for *ta*-C prepared by cathodic arc deposition [3] are included in the table. The simulated structure is in good agreement with experiment at this density, particularly with regard to the nearest neighbor distances r_1 and r_2. The sp^3 fraction is also in satisfactory agreement with

TABLE I. Comparison between structural parameters of simulated *ta*-C (this work), and experimentally prepared *ta*-C.

Quantity	Simulated network	Experiment	Ref.
First nearest neighbor distance r_1 (Å)	1.52	1.52	[3]
		1.53	[1]
Second nearest neighbor distance r_2 (Å)	2.50	2.50	[1]
First coordination number N_1	3.65	3.93	[1]
Second coordination number N_2	9.65	7.7–11.3	[2]
sp^3 fraction	0.65	0.80	[4]

experiment as the experimental uncertainty is of the order of 10%. The present structure has the highest sp^3 content of any carbon network simulated with the Car-Parrinello technique. Previous work [17], using a density of 2 g/cc, produced a pure carbon network with a sp^3 fraction of 15%, and more recently a hydrogenated carbon network at a density of 2.6 g/cc was found to have an sp^3 fraction of 56% [18]. Our results at a density of 3 g/cc confirm that *ab initio* simulations reproduce the experimentally known increase in sp^3 fraction with density.

Figure 1(b) shows just the three- and four-membered rings present in the structure of Fig. 1(a). Although the presence of such small rings seems at first surprising, the hydrogenated analogs of these rings (cycloalkanes) are well known and stable. Cyclopropane (C_3H_6) contains a ring of three sp^3 bonded carbon atoms, and cyclobutane (C_4H_8) contains a ring of four. Through the presence of these structures even the tetrahedrally bonded part of the network differs substantially from the silicon tetrahedral network inferred from experimental data [6] as well as from *ab initio* simulations [19]. Figure 1(c) shows only the sp^2 atoms in the structure. The sp^2 atoms occur in a variety of bonding environments ranging from pairs of sp^2 atoms with ethylenelike double bonds to extended structures containing some graphitelike sp^2 atoms.

The radial distribution function $G(r)$ provides a useful means of comparison of the simulated structure with experiment. $G(r)$ is defined by

$$G(r) = 4\pi r[\rho(r) - \rho_0],$$

where $\rho(r)$ is the density of atom centers at a distance r from an atom, averaged over the network, and ρ_0 is the average density. We show in Fig. 2 the $G(r)$ calculated from the simulation and a recent neutron diffraction result [2]. The agreement is good in both the position and shape of the first two coordination peaks. The third principal peak (near 3.7 Å) shows some discrepancies which are
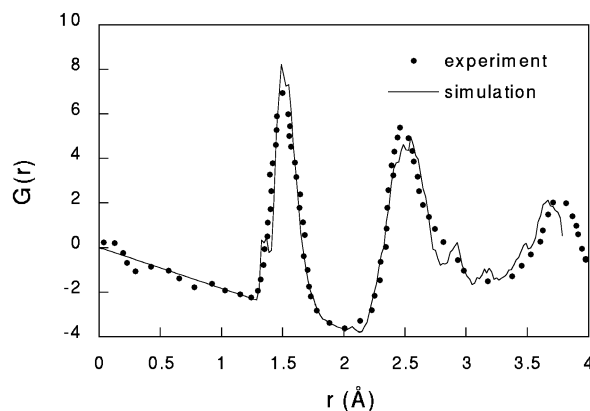

FIG. 2. The radial distribution function $G(r)$ calculated for the simulated *ta*-C structure shown as a solid curve, compared with neutron diffraction results [2] (dotted curve). The simulated $G(r)$ is a temporal average over 0.5 ps at 300 K.

probably due to the finite size of the simulation cell. The strong asymmetry observed experimentally for the second peak agrees well with the presence of subsidiary features in the $G(r)$ for the simulated network at large r. When subject to experimental broadening these features should give rise to the observed asymmetry.

Looking at the topology of the simulated structure, it is possible to resolve an experimental discrepancy raised by Gilkes, Gaskell, and Robertson [2] concerning the coordination of ta-C. They reported that the number of second nearest neighbors N_2 was too small relative to the first coordination number N_1 by approximately 20%. This conclusion was based on the relation $N_2 = N_1(N_1 - 1)$, which is expected for a fully bonded network with a minimum ring size of 5. However, the presence of the three- and four-membered rings, not taken into account in the Gilkes analysis, changes the topology and reduces the second coordination number. Furthermore, the bond length distribution of the second nearest neighbors is too broad to be deconvoluted from $G(r)$, preventing the calculation of N_2 from $G(r)$ alone. The range of values reported for the experimental N_2 in Table I reflects the uncertainty in the procedure for extracting N_2 from $G(r)$.

Figure 3 shows the distribution of bond angles subtended by the nearest neighbors at both sp^2 and sp^3 bonded atoms. Although the most common bond angle at an sp^3 site is close to the tetrahedral value of 109.5°, three- and four-membered rings also make clear contributions to the distribution near 60° and 90°. It is interesting to note that the sp^2 distribution is a maximum near 110°, rather than at 120°, which is the sp^2 minimum energy angle. This reflects the distortion caused by immersing the sp^2 atoms into an sp^3 environment, particularly into pentagons where the bond angle is constrained to be near 108°.

The distribution of ring sizes provides a useful means of comparing networks, and Table II shows the ring statistics for this work and the 3 g/cc simulations of Wang and Ho [7] and Frauenheim et al. [8]. It is evident that

TABLE II. Ring statistics for this work and other simulations of ta-C performed at a density of 3 g/cc. The ring statistics for the 128 and 216 atom structures have been normalized to 64 atoms for the purposes of comparison.

	Number of atoms	% sp^3	Number of rings				
			3	4	5	6	7
This work	64	65	3	3	21	19	9
Frauenheim et al. [8]	64	53	0	0	20	21	20
	128	64	0	3	18	27	16
Wang and Ho [7]	216	33	0	0	10	15	10

the structure presented in this work differs considerably from previous simulations of ta, particularly with regard to the number of three- and seven-membered rings. In the simulation of Wang and Ho, no three- and four-membered rings are present and the number of five- and six-membered rings is lower than in this work due to the underestimation of the sp^3 fraction. While the simulations of Frauenheim et al. have more reasonable sp^3 fractions, no three-membered rings are present and the number of seven-membered rings is nearly double that of this work. We note that while the 128-atom structure contains four-membered rings as observed in this simulation, no rings of this type are present in the 64-atom structure.

The computed electronic density of states (EDOS) of the simulated structure is shown in Fig. 4. As would be expected, the π and π^* peaks, which reflect the amount of sp^2 bonding, are not as pronounced as in the amorphous carbon sample of Galli et al. [17], and this has the effect of widening the band gap. As is typical for amorphous materials, it is difficult to measure the band gap from the EDOS due to the presence of states near the Fermi energy (0 eV). A useful measure of the gap can be obtained by calculating the "Tauc band gap" [20] using the imaginary part of the dielectric permittivity $\epsilon_2(\omega)$. The process of calculating $\epsilon_2(\omega)$ for the simulated structure is a straightforward one [21]
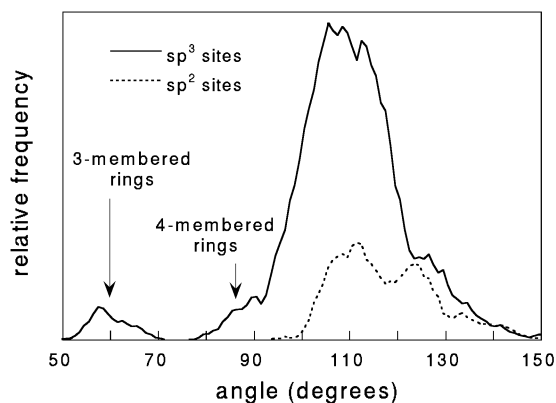

FIG. 3. The distribution of bond angles in the simulated structure. The solid curve is for angles subtended at an sp^3 bonded atom and the dashed curve is for angles at an sp^2 bonded atom.
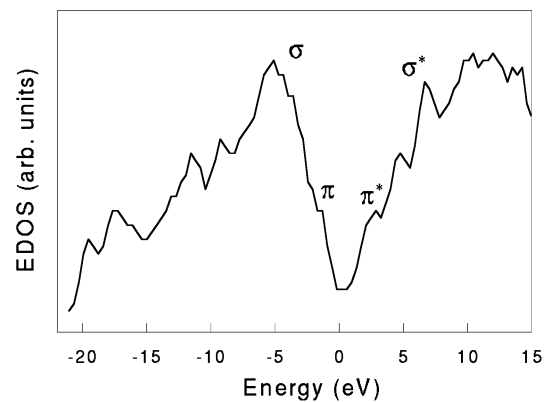

FIG. 4. The electronic density of states (EDOS) of the simulated ta-C structure. Only the Γ point of the supercell is used. A Gaussian has been used to smooth the data.

involving a convolution of the occupied and unoccupied density of states, provided one makes the assumption that the matrix elements for dipole transitions are independent of energy. The calculation yielded a Tauc band gap of 0.5 eV, which is an underestimate because of finite cell size effects which overweight the defect contributions and the use of the local density approximation. The experimental value of 2.5 eV [22] is somewhat uncertain because the experimental Tauc plot for *ta*-C shows deviations from the linear behavior typical of amorphous semiconductors.

In summary, this work shows that the *ab initio* method used here to simulate a dense carbon network is in good agreement with available structural measurements. The predicted network shows substantial departures from the idealized tetrahedral network and from the amorphous structures shown by the other group IV semiconductors.

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