Structural Study of Amorphous Carbon using Adaptive Interatomic Reactive Empirical Bond-order Potential Model

M. Todd Knippenberg, Oyeon Kum, and Steven J. Stuart

Department of Chemistry, Clemson University, Clemson SC 29634 USA

ABSTRACT

The structural properties of amorphous carbon (a-C) systems with densities of 2.0, 2.6, and 3.0 g/cm^3 were studied using classical molecular dynamics with the adaptive interatomic reactive empirical bond-order (AIREBO) potential model. The AIREBO model enhances the locally reactive bond-order REBO potential for covalent materials to include long range van der Waals and torsional interactions that are quite important in an a-C system. The shape and position of the first peak of the pair-correlation function were found to be quite sensitive to the density, with the peak position shifting towards shorter distances as the density increases. However, the simulated structure showed predominantly threefold coordination at the highest density of 3.0 g/cm^3, with higher sp^2 fractions than observed in ab initio models. The distribution of sp^2 and sp^3 carbons was visible in the pair correlation functions at 3.0 g/cm^3. Ring statistics showed relatively little density dependence up to five-membered rings and a significant number of larger rings. We observed that the AIREBO model demonstrates structural properties for a-C that differ from those obtained from ab initio and tight-binding models.

Keywords: structural study, amorphous carbon, AIREBO potential, coordination numbers, ring statistics

1 INTRODUCTION

Carbon has the ability to exist in a remarkable variety of nonequilbrium crystalline and noncrystalline structures at a wide range of temperatures and pressures. From both the scientific and application points of view, amorphous carbon (a-C) is one of the more important of these, and the microscopic structural properties of this noncrystalline form of solid carbon are quite intriguing and useful. For example, diamondlike a-C films are found to be hard, optically transparent, and chemically inert, which makes them important for applications in coating technology.

In the last couple of decades, extensive experimental investigations [1]–[3] and theoretical studies using computer simulations [4]–[9] have been devoted to elucidating the microstructure and bonding nature of this disordered form of carbon. While these studies have provided useful data about the structure of a-C, the microscopic bonding details are still not well understood. Many properties such as the relative concentration of atoms with various coordination nubmers in a-C are still controversial in the literature [6]–[8].

The a-C structure is stable in a wide range of densities varying from lower than 2.0 g/cm^3 up to higher than 3.0 g/cm^3. The physical properties are quite different for different densities. For example, at a low density of approximately 2.0 g/cm^3, it is an electrically conductive, optically absorbing material with a majority of atoms bonded in a graphitelike (sp^2) configuration. On the other hand, at densities of approximately 3.0 g/cm^3, the material becomes electrically insulating with the properties of a wide-band-gap semiconductor, including an optical band gap giving significant visible light transmission. The hardness at this density is very high, with a majority of atoms in the diamondlike (sp^3) configuration.

Thus the a-C system is a challenging system for simulation study because the carbon atoms can show bonding states ranging from sp up to sp^3. For an accurate computational model, it is therefore necessary to have a framework that can describe all bonding possibilities simultaneously. The system size may affect the results because of the wide heterogeneity in coordination number and chemical environments. In this study, we investigated structural properties of a-C using the adaptive interatomic reactive empirical bond-order (AIREBO) potential model [10], which treats both covalent bonding as well as long-range non-bonded interactions. We chose three systems with densities of 2.0, 2.6, and 3.0 g/cm^3 spanning a wide range of properties. This work addresses the structural trends in different a-C samples by comparing radial distribution functions, coordination numbers, and ring statistics [11] against existing experiments and other simulation models.

2 THE MODELS

The accuracy of atomistic molecular dynamics simulations depends directly on the use of appropriate interatomic energies and forces. These interactions are generally described using either analytical potential en-

ergy expressions or semi-empirical electronic structure methods, or obtained from a total-energy first principles theory. Though the last approach is not (as) subject to errors that can arise from assumed functional forms and parameter fitting usually required in the first two methods, there are still clear advantages to classical potentials for large systems and long simulation times.

The AIREBO potential [10] is an enhanced classical potential model for reactive covalent systems that includes both long range interaction forces and covalent bond breaking and forming. Chemical bonds vary in strength depending on the local bonding environment, via a bond-order potential. It has appropriately fitted parameters to describe the attenuation of the Lennard-Jones repulsive barrier at short distances, which would otherwise cause problems when modeling van der Waals interactions in condensed phases such as a-C. However, to date there have been no simulations of a-C using the AIREBO potential.

The simulation systems contained 2048 atoms for each density, in a simulation cell of constant volume. These systems were heated to 5000 K with a Langevin thermostat, under which conditions they were liquid and diffusive. Once molten, the samples are equilibrated at 5000 K for 100 ps. The liquid samples were then cooled down to 300 K over 10 ps for a cooling rate of 5×10^{14} K/s, comparable to previous stidues [6]. Following this, the systems were equilibrated for a further 50 ps to anneal away any transient structures. Finally, we calculated the temporal averages over another 50 ps. The final structures are shown in Fig. 1 for each density with color coding indicating the different coordination numbers.

3 RESULTS AND DISCUSSION

Figure 2 shows the radial distribution functions for the three different densities of 2.0, 2.6, and 3.0 g/cm^3 at a temperature of 300 K for the 2048-atom a-C systems. Each distribution was averaged over 50 ps after the systems were equilibrated at ambient temperature. The most interesting feature in this plot is that the positions of the first peaks of the radial distributions shift systematically towards smaller distances as the density of the system is increased. This is the reverse of the result observed in Wang and Ho's tight-binding model [5]. This result occurs because the sp^3 fraction increases to only 17% at 3.0 g/cm^3 in these studies, in contrast to Wang and Ho's results shown in Table 1. As seen in Fig. 1, the majority of the bonding topology observed here is sp^2 (threefold) at all densities. Thus, the position of the first peak of the radial distribution function results primarily from the increase in density. The small shoulder in the radial distribution function at distances slightly beyond 1.5 Å indicates the growing sp^3 fraction with increasing density (cf. Table 1). Table 1 com-
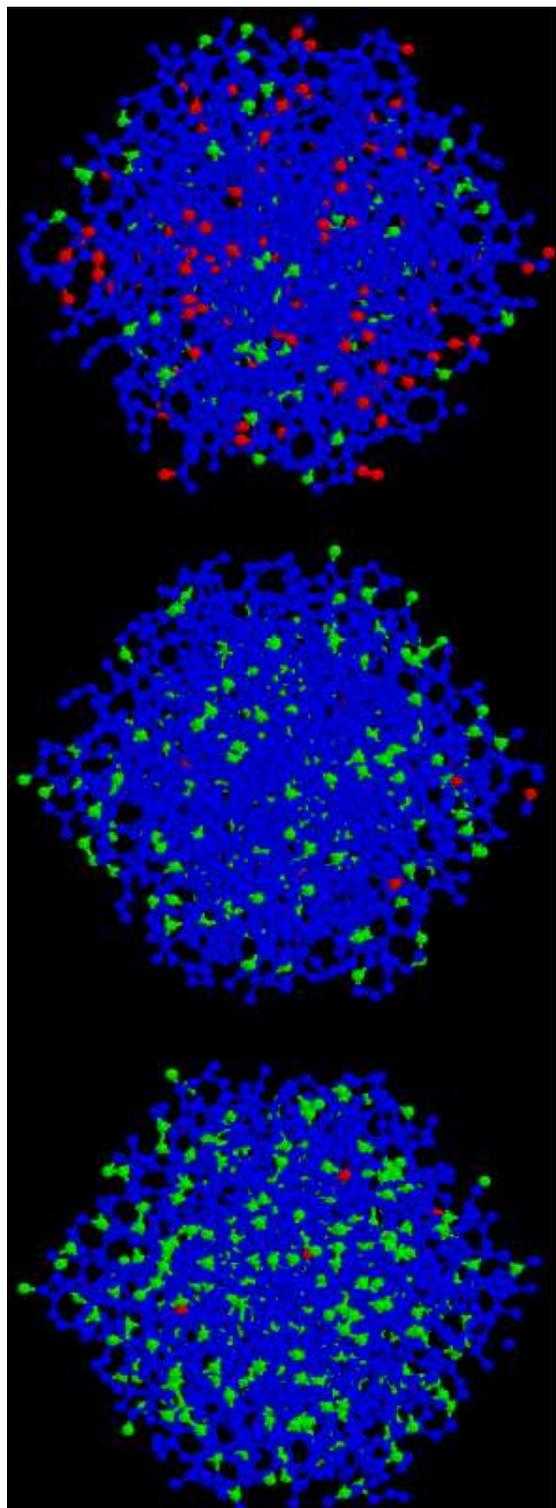

Figure 1: (Color) The annealed a-C samples. From top to bottom, the densities are 2.0, 2.6, and 3.0 g/cm^3. Colors show the coordination numbers: red for two-fold coordinated sp atoms, blue for three-fold coordinated sp^2, and green for four-fold sp^3 bonding. While the densities vary in a wide range from 2.0 to 3.0 g/cm^3, the blue sp^2 coordination dominates at all densities.
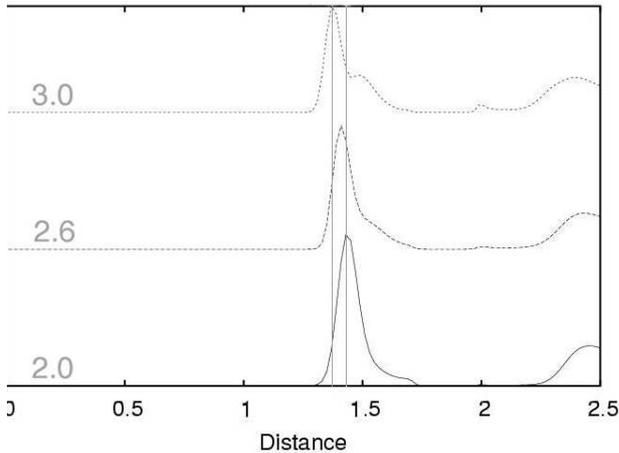
Figure 2: The radial distribution functions for densities of 2.0, 2.6, and 3.0 g/cm^3. The first peak (sp^2-bonded carbons) moves to progressively shorter distances with increasing density, as a shoulder grows in representing sp^3-bonded carbons.

pares the concentration of various coordinated atoms in a-C network with those from ab initio, tight-binding, and experiments. The chemical bonding between carbon atoms is an inherently quantum mechanical process. While the AIREBO potential includes parameters that describe the variation in covalent bonding in an average way, it does not explicitly treat electronic effects. Thus, the discrepancy between the AIREBO and other results may reflect an inability of bond-order models to capture subtle electronic effects. Simulations with the reactive empirical bond-order (REBO) model (not presented here) also show similar results. Also, the a-C is a metastable, nonequilibrium structure that is formed kinetically. Although other simulation studies have followed similar quenching procedures to generate a-C structures, these differ markedly from experimental deposition methods; the variations could be due to kinetic effects in how the structures were produced.

Ring statistics are a useful tool to investigate physical properties of amorphous solids and have become the generally accepted measure of medium-range order. However, there is unfortunately no general theory that explains which rings are relevant to the physical properties of the solid represented. In this study, we calculated the shortest-path rings, which exclude all rings with bridges that reduce their length, while preserving at least half of the original ring as defined in Ref. 11. Figure 3 shows two of the larger rings observed.

Figure 4 shows the distribution of the ring sizes for each of the three densities. For hydrocarbon systems, the ring size that exhibits the smallest strain energy for both sp^2 and sp^3 carbon is a six-membered ring. However, in this amorphous environment, there is a substantial population of rings at a wide range of sizes.

Table 1: Percentage of atoms with various coordination in the amorphous carbon networks. The density is in units of g/cm^3. KKS is this work.

ρ	Coords.	KKS	MM[1]	WH[2]	HA[3]	FE[4]
2.0	sp	6.69				
	sp^2	88.96			78.0	
	sp^3	4.3			22.0	
2.6	sp	0.44				
	sp^2	89.35			31.0	
	sp^3	10.2			67.0	
3.0	sp	0.34		2.3		
	sp^2	82.42		64.7	6.0	
	sp^3	17.23	65.0	33.0	94.0	81.0

1. Ref. 6;   2. Ref. 5;   3. Ref. 3;   4. Ref. 2.

Small 3-, 4- and 5-membered rings exist in low numbers, due to their higher strain energy. There is little dependence on density for these small rings. A higher-than-expected population of 3-membered rings indicates that the AIREBO potential underestimates the strain energy for cyclopropyl systems. The rings that occur in the highest numbers are 7-membered rings. This differs slightly from previous studies [5]–[9], [11], which found primarily 5- and 6-membered rings. We find a non-negligible number of larger rings, especially at the lowest density. In the low-density system, these represent traversals around small pockets or voids in the a-C. There are fewer voids, and thus fewer large rings, in the denser systems. This effect has also been observed in previous simulations at low densities. There is some even-odd alternation, in which rings with an odd number of members are more prevalent than even rings of about the same size. This phenomenon persists for all ring sizes and densities, and is a side effect of the method by which the shortest-path rings are defined [11]. The requirement that a shorter ring contain at least half of the atoms in a longer ring in order to disqualify it has a different effect on even and odd rings: rings of length $2N$ and $2N - 1$ both need a shorter ring with at least N atoms in common in order to be disqualified. Thus a higher proportion of the even rings are disqualified, leaving a population slightly enriched in odd rings.

4   CONCLUSIONS

We have studied structural properties of a-C systems as modeled with a classical bond-order potential at three densities of 2.0, 2.6, and 3.0 g/cm^3. We used the AIREBO potential model including long range van der Waals interactions, which has computational advantages for the large 2048-atom system size, but relies on a fitted functional form.

We calculated pair distribution functions, coordination number ratios, and ring statistics. The AIREBO model showed quantitatively different results from those
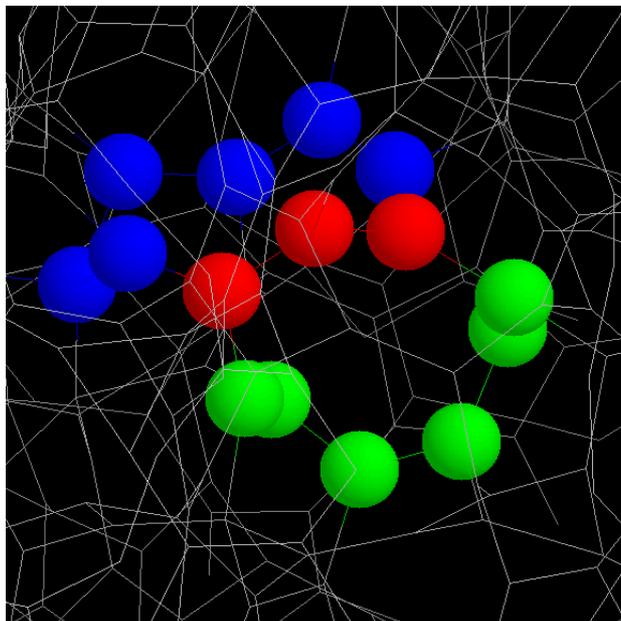
Figure 3: (Color) An example of two nine-membered (shortest-path) rings at a density of 2.0. Three atoms (red color) are common to both rings. Both rings satisfy the shortest-path condition of Ref. 11.

of experiments and other simulations such as ab initio and tight-binding models. The first peak of the radial distribution moved to shorter distances as the system density increases, in contrast to previous studies. This phenomenon is explained by the small fraction of sp^3 coordination generated by the AIREBO model. With this model, even at the highest density of 3.0 g/cm^3, the fraction of sp^3 coordination was below 20%, while values from other studies ranged from 33% to 94%.

The ring statistics showed a peak for moderate ring sizes of 7 atoms, slightly different from previous results which favored 5- and 6-membered rings. This likely indicates a different quantitative treatment of strain energy in the classical, tight-binding, and ab initio models. It is also worth noting that in previous studies, larger rings are found more commonly in studies that utilized larger numbers of atoms, so there is possibly some system size effect that has not been fully acknowledged. Small rings were not favored due to their higher strain energy, and larger rings were not favored due to the high cost of introducing voids into the a-C. The larger rings were less common in the denser systems.

It is not clear whether the differences between this study and earlier studies arose from the inability of the classical model to account for electronic effects treated in the ab initio and semi-empirical models, or whether there are differences in the kinetic pathway by which the systems were formed, or whether there are system size effects that affected earlier studies, most of which used
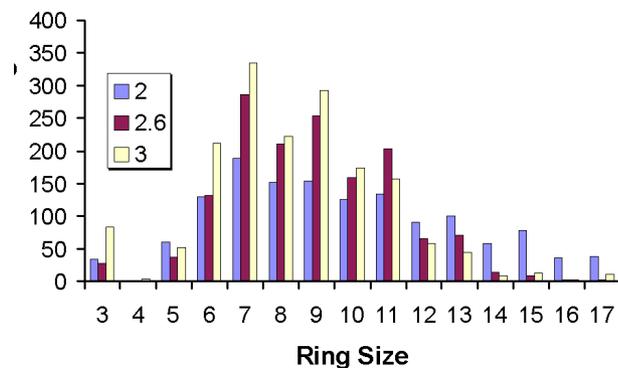

Figure 4: (Color) : Distribution of shortest-path ring sizes for each of the three densities in the AIREBO a-C systems.

216 or fewer atoms. The ability to use a classical model to study this important system would represent a significant advance, so a detailed understanding of these issues is crucial. Further study to elucidate the dependence on potential model, system size, and kinetic pathway are currently underway.

REFERENCES

[1] K. W. R. Gilkes, P. H. Gaskell, and J. Robertson, Phys. Rev B. **51**, 12303 , 1995.

[2] A. C, Ferrari, Libassi, A, Tanner, B. K, Stolojan, V, Yuan, J, Brown, L. M, Rodil, S. E, Kleinsorge, and J. Robertson, Phys. Rev. B. **62**, 11089, 2000.

[3] R. Haerle, E. Riedo, A. Pasquarello, and A. Baldereschi,Phys. Rev. B, **65**, 045101, 2001.

[4] J. Tersoff, Phys Rev. B. **37**, 6991, 1988.

[5] C. Z. Wang and K. M. Ho, Phys. Rev. B **50**, 12429, 1994.

[6] N. A. Marks, D. R. McKenzie, B. A. Pailthorpe, M. Bernasconi, and M. Parrinello, Phys. Rev. Lett. **76**, 768, 1996.

[7] D. G. McCulloch, D. R. McKenzie, and C. M. Goringe, Phys. Rev. B, **67**, 2349, 2000.

[8] G. Opletal, T. Petersen, B. O'Malley, I. Snook, D. G. McCulloch, N. A. Marks, and I. Yarovsky, Molecular Simulation, **28**, 927, 2002.

[9] C. Mathioudakis, G. Kopidakis, P. C. Kelires, C. Z. Wang, and K. M. Ho, Phys. Rev. B **70**, 125202, 2004.

[10] S. J. Stuart, A. B. Tutain, and J. A. Harrison, J. Chem. Phys. **112**, 6472, 2000.

[11] D. S. Franzblau, Phys. Rev. **44**, 4925, 1991.