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The Application of Car-Parrinello Molecular Dynamics to the Study of Tetrahedral Amorphous Carbon

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The Car-Parrinello method for carrying out molecular dynamics enables the forces between atoms to be calculated by solving Schrodinger's equation for the valence electrons using Density Functional Theory. The method is capable of giving good structural predictions for amorphous network solids by quenching from the melt, even in situations where the bonding changes from one site to another. In amorphous carbon where, depending on its environment, carbon may show sp^2 or sp^3 bonds. The method is applied here to the study of network solids using the example of tetrahedral amorphous carbon.

INTRODUCTION

Tetrahedral amorphous carbon (ta-C) is a high density amorphous carbon with properties which reflect its relatively high fraction of tetrahedral bonding[1]. In this paper, the details of the structure of ta-C are explored using the Car Parrinello Molecular Dynamics method[2].

Various computer generated structures of amorphous carbon are available in the literature using molecular dynamics techniques. These are valuable in giving us insight into the details of the structure, but the usefulness of the result is dependent on the accuracy of the method used. Carbon is a difficult atom to describe with an empirical potential owing to the possibility of its hybridization states varying between the trigonal sp^2 state and the tetrahedral sp^3 state. Consequently, the so called *ab initio* methods are the most useful, as they make no assumptions about the hybridization states. This is important since one of the issues we would like to study is the detailed distribution between these states, including the degree to which the atoms are separated into well defined sp^2 and sp^3 states.

Marks et al[3] applied the Car-Parrinello method to a carbon network at a density of 2.9 g/cm^3 in a 64 atom simulation. The Car-Parrinello method treats the atom as a positively charged core surrounded by four valence electrons whose wavefunction is expressed in terms of a plane wave expansion. The atom core is described by a pseudopotential and the electrons are assumed to adapt to ionic motion quickly enough that at each atom configuration the electrons are in a minimum energy state (the Born-Oppenheimer approximation). The simulation of Marks reveals some expected and some unexpected features. First, the structure did have distinct sp^2 and sp^3 as judged by their coordination. The sp^2 atoms formed into rings containing most commonly five members, but with occasional three and four membered rings. The occurrence of such small rings is surprising at first sight, but their existence in nature is already known in such molecules as cyclopropane and cyclobutane.

COMPUTATIONAL DETAILS

We have now implemented the Car-Parrinello program at the University of Sydney and have repeated the 64 atom carbon simulation of Marks et al[3]. The exchange contribution was described by the Becke functional[4] with correlation contribution described by the functional of Lee, Yang and Parr[5]. Carbon and nitrogen atom cores were described by pseudopotentials due to Goedecker[6]. These pseudopotentials have given good agreement with experimental values of the formation energies of several compounds.

The simulation was performed by melting 64 atoms of carbon at a density of 2.9 g/cm^3 and the equilibrating at 5000 K, followed by quenching to 300 K in 500 fs. This time scale is consistent with an estimate of the quenching time for a thermal spike at incident ion energies used during the formation of ta-C experimentally in a vacuum arc.

RESULTS

Figure 1 shows the resulting network with atoms coded according to the coordination. This network is essentially the same as that of Marks et al[3]. In particular, three and four memebered rings are present. The fraction of sp^3 atoms was 59% which compares with 65% in the previous simulation[3].

An alternative way of visualising the structure is to plot the valence electron charge density isosurface. This is shown in figure 2. Note that the valence charge density vanishes at the atom core giving rise to a low density hole (pseudo-core) in the charge density.

A valence charge density slice through a three memebered ring consisting of sp^3 atoms is shown in figure 3. Such rings are known to exist in such molecules as cyclopropane and therefore their existence in this network in not unreasonable.

CONCLUSION

We have implemented the Car Parrinello molecular dynamics code at the University of Sydney. We have confirmed that the existence of three and four membered rings in dense carbon networks is robust against the choose of pseudopotential and exchange correlation functionals.

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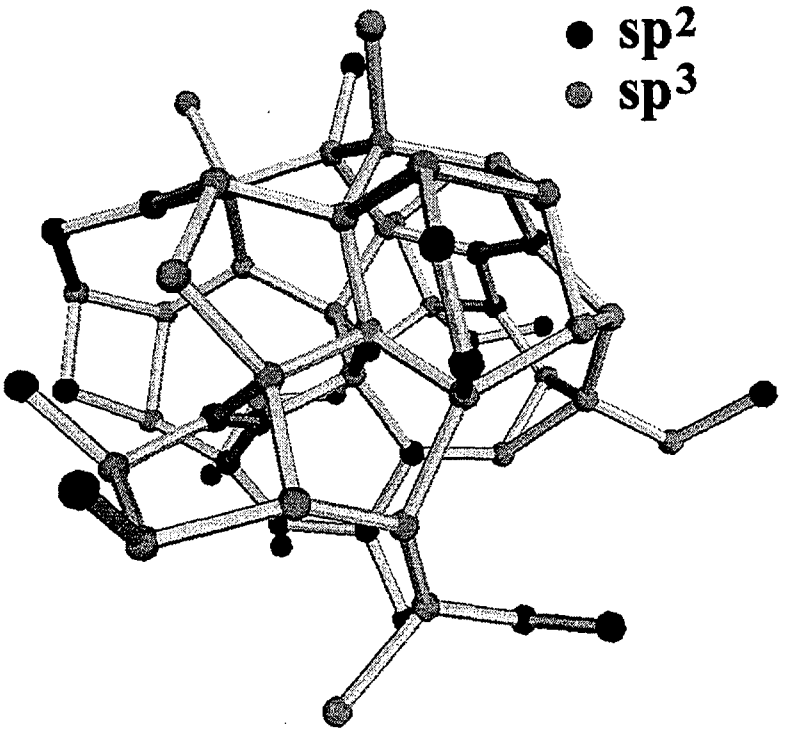

Figure 1 - The 64 atom carbon network calculated using the Car Parrinello molecular dynamics technique.

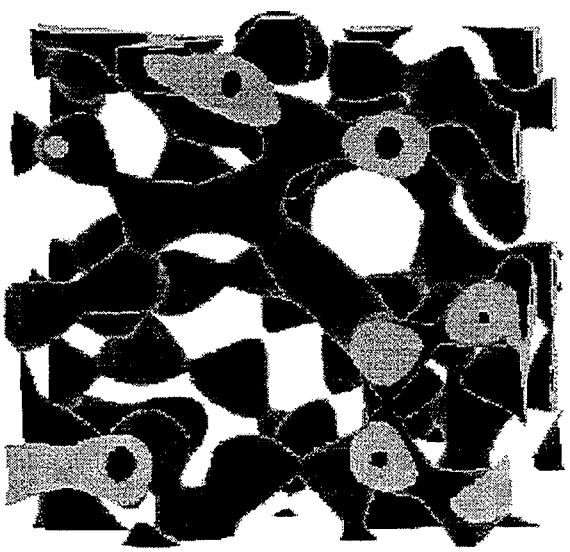

Figure 2 - The valence charge density isosurface plot for the 64 atom carbon network of figure 1 calculated using the Car Parrinello molecular dynamics technique.

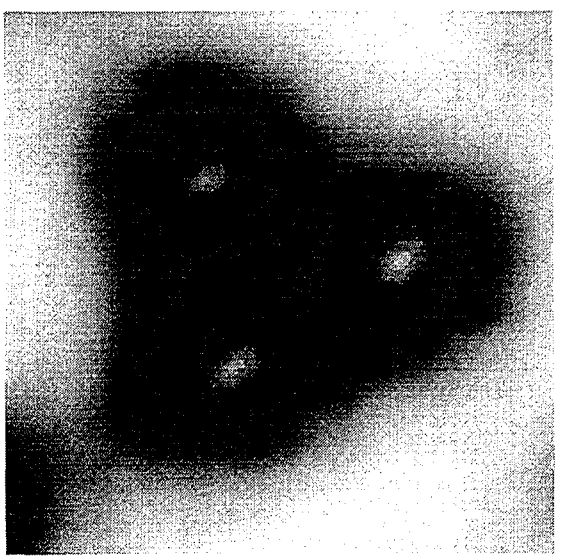

Figure 3 - Valence charge density slice through a three membered ring from the 64 atom carbon network.