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LETTER TO THE EDITOR

A new approach to modelling tetrahedral amorphous carbonJ K Walters[†], K W R Gilkes[‡], J D Wicks[§] and R J Newport^{||}[†] Department of Physics and Astronomy, University College, Gower Street, London WC1E 6BT, UK[‡] School of Physics, University of East Anglia, Norwich NR4 7TJ, UK[§] Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK^{||} Physics Laboratory, The University, Canterbury, Kent CT2 7NR, UK

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Abstract. We have generated a new model for the structure of tetrahedral amorphous carbon using a modified reverse Monte Carlo modelling method. The novel feature of this approach is the definition of three different types of carbon atom, corresponding to tetrahedral, planar and linear bonding conformations. The particular strengths of the method are the large model size (3000 atoms), that all the possible arrangements of sp^3 and sp^2 bonds are allowed, and that no interatomic potential is required. For the first time we have determined the distribution of sp^2 bonded sites within the predominantly disordered tetrahedral structure, and we find that they form polymer-like chains and small clusters which connect the sp^3 bonded regions.

Tetrahedral amorphous carbon (ta-C) is a particular form of amorphous carbon (a-C) which has a high proportion (>80%) of fourfold coordinated tetrahedral sp^3 sites. Experimental studies [1, 2] have concluded that the structure of ta-C consists predominantly of a disordered tetrahedral network with a small contamination of sp^2 bonding and no discernible sp^1 bonds, but, as yet, no satisfactory model for the structure of ta-C has been found [3–9]. a-C is difficult to model because of the variety of local bonding environments that the carbon atom can adopt. Indeed, until this work, no model has permitted fourfold, threefold and twofold coordinated bonding configurations whilst still maintaining a physically reasonable structure. Many existing models demand 100% fourfold coordination [3, 10, 11]; however, the interesting electronic properties of ta-C are completely determined by the distribution of sp^2 sites and their associated π bonds. It is therefore of crucial importance to establish a model for their atomic-scale structure which includes both sp^3 and sp^2 bonds.

The reverse Monte Carlo (RMC) [12] technique produces three-dimensional models of the structure of disordered materials that agree quantitatively with the available experimental data, usually diffraction data. RMC is also a particularly appealing method because interatomic potentials, which are often difficult to define for amorphous networks but are essential to molecular dynamics and other Monte Carlo based simulations, are not required. RMC has already been applied, with varying degrees of success, to modelling a-Si [3], a-Ge [3, 13] and even a-C [3, 5], although we believe that the results presented here for ta-C represent significant progress in the application of RMC to amorphous networks.

Neutron diffraction data were obtained by Gilkes *et al* [5] in an experiment carried out at the ISIS pulsed neutron source (Rutherford Appleton Laboratory, UK) using the LAD diffractometer [14]. The quantity obtained from a diffraction experiment is the structure

factor, $S(Q)$ [15], which is directly related to the measured neutron scattering intensity and can be Fourier transformed to obtain the real-space pair distribution function, $g(r)$.

The basic RMC algorithm has been described elsewhere [12, 16]. In essence, ‘atoms’ in a box are moved until the derived structure factor, $S_{mod}(Q)$, and/or the associated pair correlation function, $g_{mod}(r)$, matches the experimentally measured data, $S_{expt}(Q)$ or $g_{expt}(r)$. For each attempted move the quantity χ^2 is calculated, where $\chi^2 = \sum_i [S_{expt}(Q_i) - S_{mod}(Q_i)]^2 / \sigma_i$, and σ_i is the experimental error. The new configuration is accepted if the associated χ^2 has been reduced, and rejection is subject to a probability function dependent on the experimental error, σ_i . The process is repeated until $S_{mod}(Q)$ reproduces the experiment, $S_{expt}(Q)$, to within the experimental errors. Where more than one data set, or any additional imposed constraints, are used, the χ^2 calculations and the acceptance–rejection criteria are applied to each.

For the model presented here, a simulation box of length 27.14 Å was used, containing 3000 atoms placed initially at random sites, subject only to the criterion that the defined distances of closest approach were not violated. Compare this to the models of Polk and Boudreaux [11], Wooten *et al* [10] and Marks *et al* [4], where the largest consists of only 216 atoms. The larger box size significantly reduces truncation errors, and allows the generation of reliable ensemble average values for bond distances, coordination numbers, ring size statistics, etc. Neutron diffraction $S(Q)$ and $g(r)$ data were modelled simultaneously using a modified version of the original RMC code supplied by R L McGreevy [12] until ~330 moves per atom were made. Note that the $S(Q)$ data set was fitted preferentially as this is obtained directly from the experiment and has not undergone any further manipulation.

In our previous work using RMC [13, 17], we have come across several problems intrinsic to applying the RMC method to covalently bonded amorphous systems which are not built up from simple molecular units. To overcome these problems we have developed a number of constraints which are applied to the model to avoid chemically and physically unreasonable features. This has been critical in the generation of models for structures containing carbon–carbon bonds because of the variety of bond types that can be formed (sp^1 , sp^2 and sp^3), and the associated range of first-neighbour coordination numbers.

For the model presented here, three different types of C atom have been defined. Using the upper and lower limits of the first peak in the experimental $g(r)$ data and prior chemical knowledge, a single bond is defined by a near-neighbour distance $1.40 \text{ \AA} < r_s < 1.80 \text{ \AA}$, and a double bond by the range $1.28 \text{ \AA} < r_d < 1.42 \text{ \AA}$. The three C atom types are type 1 (C1)—a C atom with four near neighbours at r_s , i.e. an sp^3 tetrahedral site; type 2 (C2)—a C atom with three near neighbours, two at r_s and one at r_d , i.e. a mixed sp^3 – sp^2 planar site; and type 3 (C3)—a C atom with two near neighbours at r_d , i.e. an sp^2 linear site.

In accordance with the 84% ($\pm 10\%$) sp^3 sites estimated directly from electron energy loss spectroscopy measurements [5] and the requirement that all double bonds are saturated, we assign the 3000 atoms in the model as follows: 2520 are C1, 320 are C2 and 160 are C3. A novel method of evaluating and applying coordination number constraints was implemented. In this method an sp^3 site is defined as having four near neighbours of C1 or C2 at r_s , and no C3 near neighbours. Similarly, an sp^3 – sp^2 mixed site will have two near neighbours of C1 or C2 at r_s , and one near neighbour of C2 or C3 at r_d , and an sp^2 site will have two near neighbours of C2 or C3 at r_d . Using this type of constraint, all 14 possible configurations of the three C atom types are explicitly allowed.

A further constraint was applied to remove ‘triplets’, i.e. three atoms forming an equilateral triangle with side length equal to the CC near-neighbour distance. The existence of these is typified by a sharp peak in the bond angle distribution at 60° [3, 18, 19] and they form very readily when using the RMC algorithm because they result in a relatively large

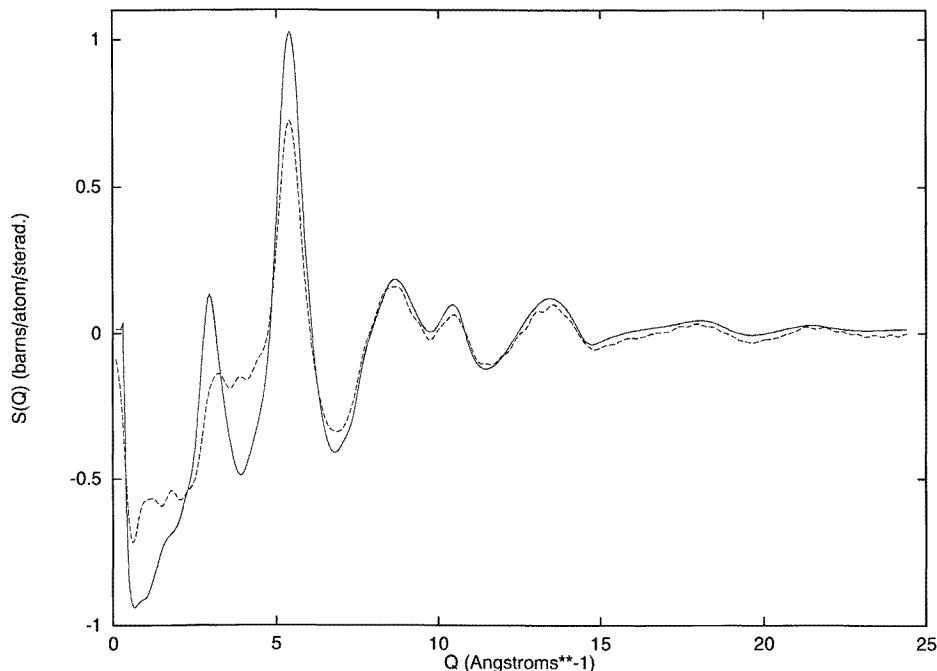


Figure 1. The fit to the experimental structure factor, $S(Q)$ (solid line), generated from the RMC model (broken line).

fall in the value of χ^2 . Recent work by Marks *et al* [4] argues for the possibility of a small number of three- and four-membered rings, using evidence from organic chemistry (namely cyclobutane and cyclopentane molecular configurations), but given the strong distorting effect of the RMC computer algorithm in the present study we have chosen to eliminate three-membered rings altogether.

Figure 1 shows the fit to the neutron diffraction $S(Q)$, and the corresponding one for $g(r)$ is shown in figure 2. The RMC model fits the $S(Q)$ well beyond $\sim 6 \text{ \AA}^{-1}$, although there is a small offset which most probably results from a small H contamination of the sample. There may also be a small discrepancy arising from the subtraction of the Bragg peaks due to crystalline graphite present in the sample. In the low- Q region, below $\sim 6 \text{ \AA}^{-1}$, there is a greater difference between the data and the fit. Features in this region of the $S(Q)$ are generally determined by intermediate-range order in the network, whereas features at higher Q values arise from the short-range order i.e. the near-neighbour correlations. Starting from a random initial configuration, and using RMC in the way we have for this model, the short-range order has been very well defined by the coordination and triplet constraints; however, we have imposed no constraints over longer-range order in the RMC generated structure, which will tend to be as disordered as the data allows within errors. This may well lead to a model which, although consistent with the data and other constraints, is 'too disordered' i.e. too far from a tetrahedral arrangement—something which is also supported in part by the ring distribution obtained. It is therefore to be expected that the fit in this low- Q region will not be as good as that at higher Q values. Even so, the fit is better than that achieved by Djordjevic *et al* [20]. Also, the fact that the model $g(r)$ fits the experimental data well, particularly for the second-neighbour and higher correlations, indicates that we should not

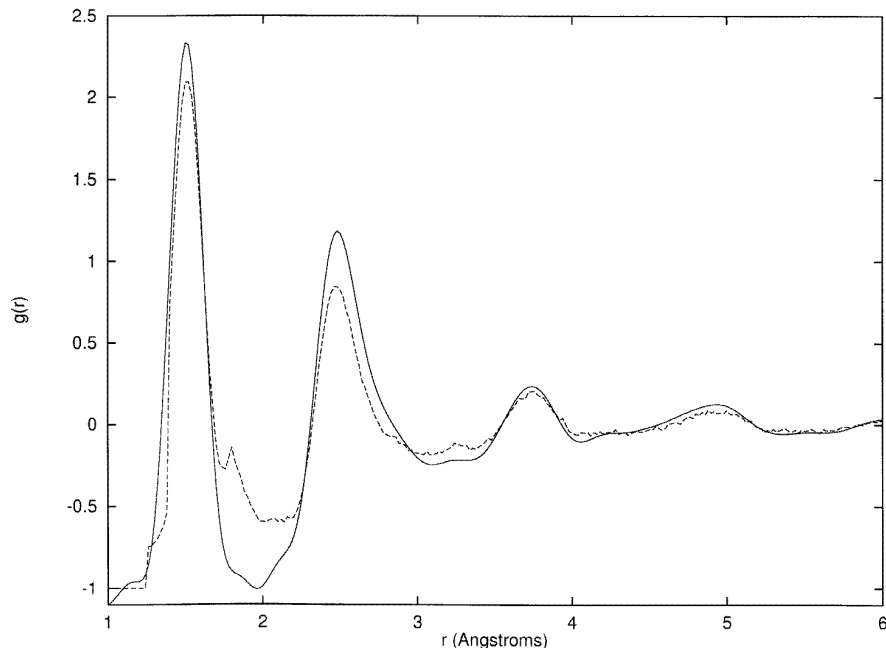


Figure 2. The fit to the experimental correlation factor, $g(r)$ (solid line), generated from the RMC model (broken line).

attach too much significance to the poorer fit in the low- Q region of $S(Q)$.

It is also possible that differences between the model and the experimental data are caused by inaccurate measurement of the density. The RMC method requires the microscopic density (rather than the bulk, or macroscopic, density), which is very difficult to determine accurately by experimental methods: our work uses the measured macroscopic value for the density, i.e. 2.98 g cm^{-3} , which is comparable to other measured densities for ta-C [21]: other workers have used a range of densities from 2.9 [4] to 1.58 [20] g cm^{-3} .

It is difficult to assess the quality of the fit to $S(Q)$ which we have obtained here against other models, as almost all other published results show only fit the $g(r)$ data. Our fit to $g(r)$ is comparable to that achieved by other models [3, 5] and shows that the discrepancy in the low- Q fit does not have a large effect on the fit to $g(r)$. The small peak in the RMC generated $g(r)$ (figure 2) at $\sim 1.8 \text{ \AA}$ is due to the triplet constraint, where 1.8 \AA is the defined maximum distance for near-neighbour bond lengths.

It is important to emphasize here that a good fit to the experimental data is not necessarily a good measure of the quality of the model produced using the RMC algorithm. It is relatively easy to fit experimental diffraction data with a model which is chemically and physically unrealistic (see for example [3], [17] and [19]). Indeed, it is for this reason that we have developed the RMC method and the constraints presented in this letter.

The bond angle distribution obtained from the RMC model is shown in figure 3. The main, broad peak occurs at $\sim 100^\circ$, but there is also a small peak at $\sim 80^\circ$ which arises from the exclusion of 60° (this effect was also observed in our earlier models of a-Ge [13]). The average bond angle for this RMC generated model of ta-C is 109.0° .

Table 1 gives the average coordination numbers for the three atom types together with the total average coordination numbers for the first and second coordination shells. For C1

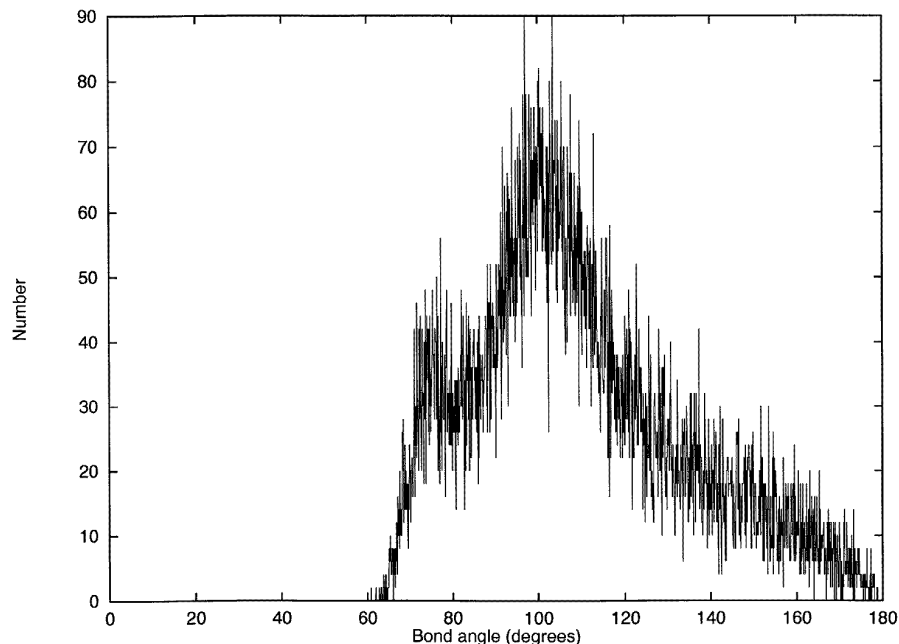


Figure 3. The bond angle distribution obtained from the RMC model configuration.

and C2 atoms 98% fourfold coordination is achieved, and C3 atoms achieve 93% twofold coordination, giving an average total coordination number for the model of 3.79, which must be compared to the experimentally determined value of 3.84 [5]. Considering the chemically intuitive nature of the present approach to producing a network, it has been very successful in generating the expected level of coordination in the structure.

Table 1. Average coordination numbers for the three defined atom types and the total average coordination numbers.

	Coordination number (atoms)	Comparative physical value
C1	3.93	4.0 (diamond)
C2	2.95	3.0 (graphite)
C3	1.91	2.0 (methylallene)
Average for 1st shell	3.79	
Average for 2nd shell	9.17	

Further analysis of the coordination in the model shows that, out of a total of 480 double bonds, only 88 are isolated i.e. have no neighbouring double bonds. The number of these isolated double bonds is important in determining the electrical conduction of the material, specifically the size of the electronic band gap: the larger the number of isolated sp^2 bonds, the larger the band gap. In addition, dangling bonds will give rise to defect states in the band gap unless they occur in pairs, creating two sp^2 sites and a double bond. In our new model the problem of controlling the number of dangling bonds does not arise because sp^3 and sp^2 sites are defined separately and the constraints are such that there are

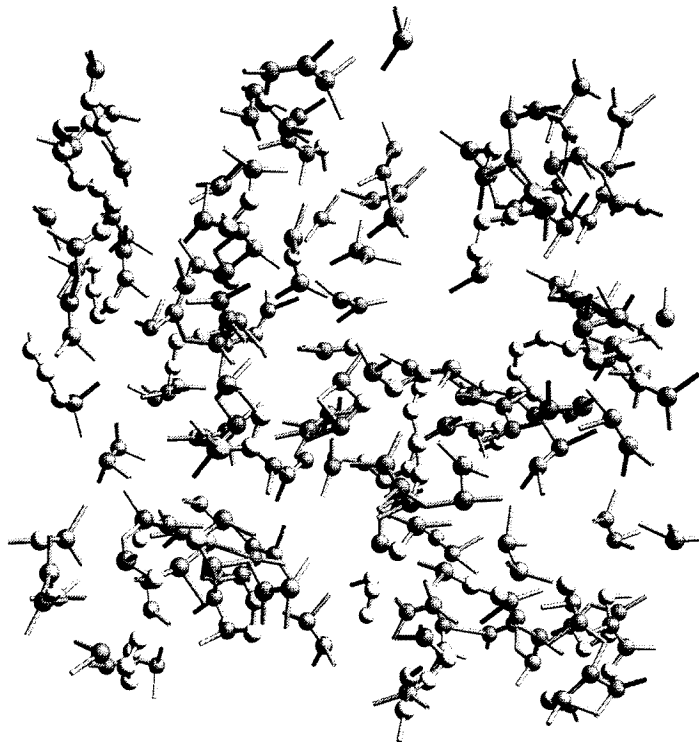


Figure 4. A $27 \text{ \AA} \times 27 \text{ \AA} \times 15 \text{ \AA}$ slice taken through the RMC model configuration showing the chains and small clusters formed by atoms of types C2 and C3.

an insignificant number of dangling bonds. This supports the low defect density of states in the band gap observed in the experimental data.

The ring-size distribution for the RMC model of ta-C indicates that the probability of finding different ring sizes decreases in the order $4 > 5 > 6 > 7 > 8$; however, the distribution is distorted by excluding three-membered rings. In other cases, the problem of three-membered rings has been overcome by constraining the bond angle distribution [18], or by demanding 100% fourfold coordination [3]. In the case of ta-C, requiring 100% fourfold coordination would not be feasible because it would exclude sp^2 bonds, which are definitely present as a small but significant fraction. Also, constraining the bond angle distribution is very expensive on computer time and is difficult to implement simply; our present results show that it is unnecessary.

A slice taken through the RMC box showing only the C2 and C3 atoms (i.e. those with sp^2 bonds) is presented in figure 4. The model structure is consistent with the diamond-like properties of the material, where the disordered tetrahedral regions of C1 atoms result in a high hardness, which is complemented by strong cross-linking of these areas by polymer-like chains and small clusters containing sp^2 bonds. These chains and small clusters can be seen clearly in figure 4, where we can also see that the sp^2 bonds do not form graphitic–aromatic rings, but act like a polymer ‘glue’ holding the sp^3 regions together. The polymeric regions are also associated with small pores; forming a pore in a higher-density sp^3 tetrahedral region would introduce a much larger strain into the network and is therefore intrinsically less likely.

Further studies will involve exploring the effects of changing the density and the fraction of tetrahedrally bonded C atoms in the model. There is also the possibility that fitting the ring-size distribution could be included, so that the complete exclusion of three-membered rings is avoided, and additional constraints on the MRO could be introduced, e.g. constraints on second-neighbour correlations. We are already working on a model which includes 5 at.% H to look at its effect on the structure. All these options should be examined in trying to improve the fit to the experimental data, whilst maintaining a physically and chemically sensible structure.

In conclusion, a new approach to modelling ta-C has been implemented, and, considering its relatively simple basis, has been extremely successful in producing a physically realistic model for ta-C. Starting from a random configuration of 3000 atoms, and using only hard-sphere cut-offs and coordination constraints to achieve the correct bonding configurations for three different types of carbon atom, we have produced a model which, overall, is at least as good as those generated using sophisticated MD methods applied to relatively few atoms. For the first time, we are able to demonstrate that in ta-C there are regions of disordered tetrahedral sp^3 atoms, which are connected via polymer-like chains of sp^2 atoms. These chains give rise to less dense areas of the network and lead to the formation of small pores.

The large size of the network produced using this new method opens up the possibilities for modelling other experimental data, particularly the vibrational density of states, as measured by Raman and infrared spectroscopy [22] and inelastic neutron scattering.

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