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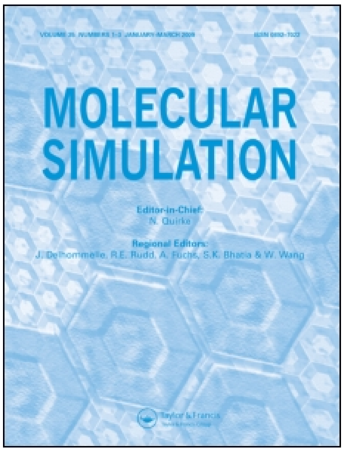

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Simulating nano-carbon materials

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Simulating nano-carbon materials

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The structure of carbon based nano-scale materials is extremely diverse at the molecular level and is very important in determining the properties and potential uses of these materials. *Ab initio* quantum mechanical methods have proved to be successful in giving insight into this structure. This is especially so, for nano-diamond clusters, -wires and -tubes. Here, we apply *ab initio* DFT based simulations to study some aspects of the structure and properties of graphene layers and graphene tubes to compare and contrast some of their properties such as energy, interconversion and X-ray spectra.

Keywords: Molecular level; Nano-tubes; DFT; Interconversion

1. Introduction

Carbon based materials promise to be one of the most significant classes of nano-scale materials due to the variety of bonding types that can co-exist in carbon materials resulting in a very large range of theoretically possible solids [1], especially at the nanoscale. Many of these have been produced experimentally [1], such as nano-diamonds in 0-D (nano-diamond crystals) [2], nano-diamond in 1-D (nano-diamond wires and bucky wires) [3,4], fullerenes ("bucky balls") [5], bucky-diamonds [4], carbon onions [4], carbon nano-tubes [6] and nano-graphene [7]. Theoretical predictions of the stability and properties of these new materials are extremely valuable, as often the structure and properties of such systems are difficult to measure experimentally [1,8,9].

If one looks at the equilibrium phase diagram of carbon [10] in bulk we deduce that under ambient conditions graphite is the thermodynamically stable phase of solid carbon, requiring high temperatures and pressures for diamond to become the thermodynamically stable phase. However, it is well known that diamond may be produced under non-equilibrium conditions such as those typically used for the chemical vapour deposition (CVD) growth of diamond thin films [11]. An experimental example of this is shown in figure 1, showing small diamond particles grown on graphite by microwave irradiation of a mixture of CH_4 and H_2 gases in the presence of a graphite substrate. This illustrates that under non-equilibrium conditions one can grow the thermodynamically metastable form of carbon (diamond) on the surface of the thermodynamically stable solid (graphite). In general it is possible to grow many non-equilibrium phases using kinetics rather than thermodynamics. Once a metastable phase is formed energy must be supplied to convert it into the thermodynamically stable form. The growth of metastable solids is of interest since they may have many desirable properties. For example, although metastable, diamond is extremely hard and has the highest thermal conductivity known [12].

Furthermore, in many cases it has been found that the (long lived) metastablity is size dependent, with the metastable phase becoming thermodynamically stable at the nano-scale [1]. We then have an even larger number of possibilities for new materials.

In order to investigate the phase stability of small systems we have previously used both *ab initio* quantum based simulations and semi-empirical models to calculate the total energies of carbon systems. Predictions of the geometry and stability nano-diamond crystals [1,2] and nano-diamond wires have been previously made [1,3]. Although these calculations show that for large enough numbers of atoms (or for systems stabilized by surface hetero-atoms) the small diamond-like particles are thermodynamically stable [1,13], it should be noted that the structures reported in these studies may only be locally stable, due to the computational techniques used. Nano-carbon particles may however be obtained from

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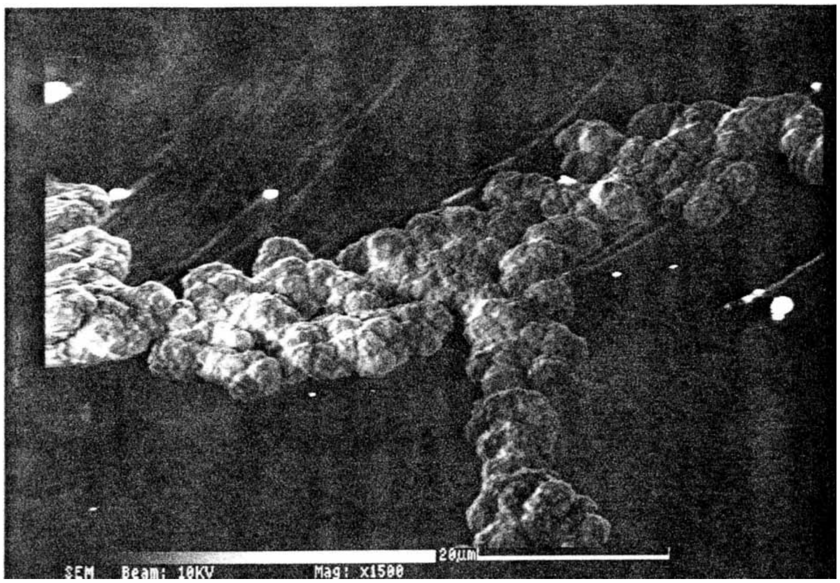

Figure 1. Diamond particles (light colour) grown on a graphite substrate (dark background) by microwave irradiation of CH_4 and H_2 in the presence of graphite. (Work courtesy of Debbie Hill, Department of Applied Physics, RMIT, 1993).

commercial sources[†] showing distinct crystalline features. Examples are shown in figure 2, where typical samples of these particles give transmission electron microscopy (TEM) lattice images and electron energy loss spectroscopy (EELS) spectra which indicate both the crystallinity and the diamond-like structure.

This paper will present an extension of our previous theoretical work investigating some aspects of the structure and properties of graphene layers and graphene tubes. We will also highlight some problems with these structures which cannot be solved by conventional theoretical techniques.

2. Theoretical techniques

Two program suites were used to carry out these studies.

The structural relaxations and electronic structure calculations have been performed with the Vienna *ab initio* simulation package (VASP) [14,15] using ultra-soft, gradient corrected Vanderbilt-type pseudopotentials (US-PP) [16] as supplied by Kresse and Hafner with outermost core radii of 1.810 and 1.250 a.u. for C and H, respectively. The calculations were performed using density functional theory (DFT) within the generalized-gradient approximation (GGA), with the exchange-correlation functional of Perdew and Wang [17].

All structures were initially optimized using an efficient matrix-diagonalization routine based on a sequential band-by-band residual minimization method of single-electron energies with direct inversion in the iterative subspace [18]. Both the ionic positions and super-cell volume have been relaxed to a convergence threshold of 10^{-4}eV. The same procedure was also used to quench the structures following annealing using *ab initio* molecular dynamics (MD). The MD simulations were performed in the canonical ensemble using the Nosé thermostat for temperature control. All calculations were performed with the valence orbitals expanded in a plane-wave basis up to a kinetic energy of 290 eV. The linear tetrahedron method (LTM) with Blöchl corrections was used for the reciprocal space Brillouin zone integrations, with $4 \times 4 \times 4$ Monkhorst-Pack [19] *k*-point mesh. Although this choice of *k*-mesh results in superfluous *k*-points in the non-periodic directions, it was found that the inclusion of these *k*-points is more consistent with the LTM.

Molecular orbital calculations were also performed within the CRYSTAL98 *ab initio* software package [20], which uses a periodic, linear combination of atomic orbitals (LCAO) formalism where the Bloch orbitals of the crystals are expanded using atom centered Gaussians orbitals with *s*, *p* or *d* symmetry. The carbon basis set used here was a 6-111G* type which we optimized for graphite. Once again, the DFT calculations were performed using the Perdew-Wang exchange and correlation. The Coulomb and exchange series are evaluated in direct space and truncated at long range using Gaussian overlap criteria. The details of this procedure have been described elsewhere [20]. The criteria are determined by five cut-off tolerances which in the current study were set to 10^{-7}, 10^{-7}, 10^{-7}, 10^{-7} and 10^{-14} which, (typically) converge the total energy differences between related structures to less than 0.1 mHa. The reciprocal space integration was performed by sampling the Brillouin zone using an $8 \times 8 \times 8$ Monkhorst-Pack mesh [19]. The electron density of states (EDOS) were calculated using

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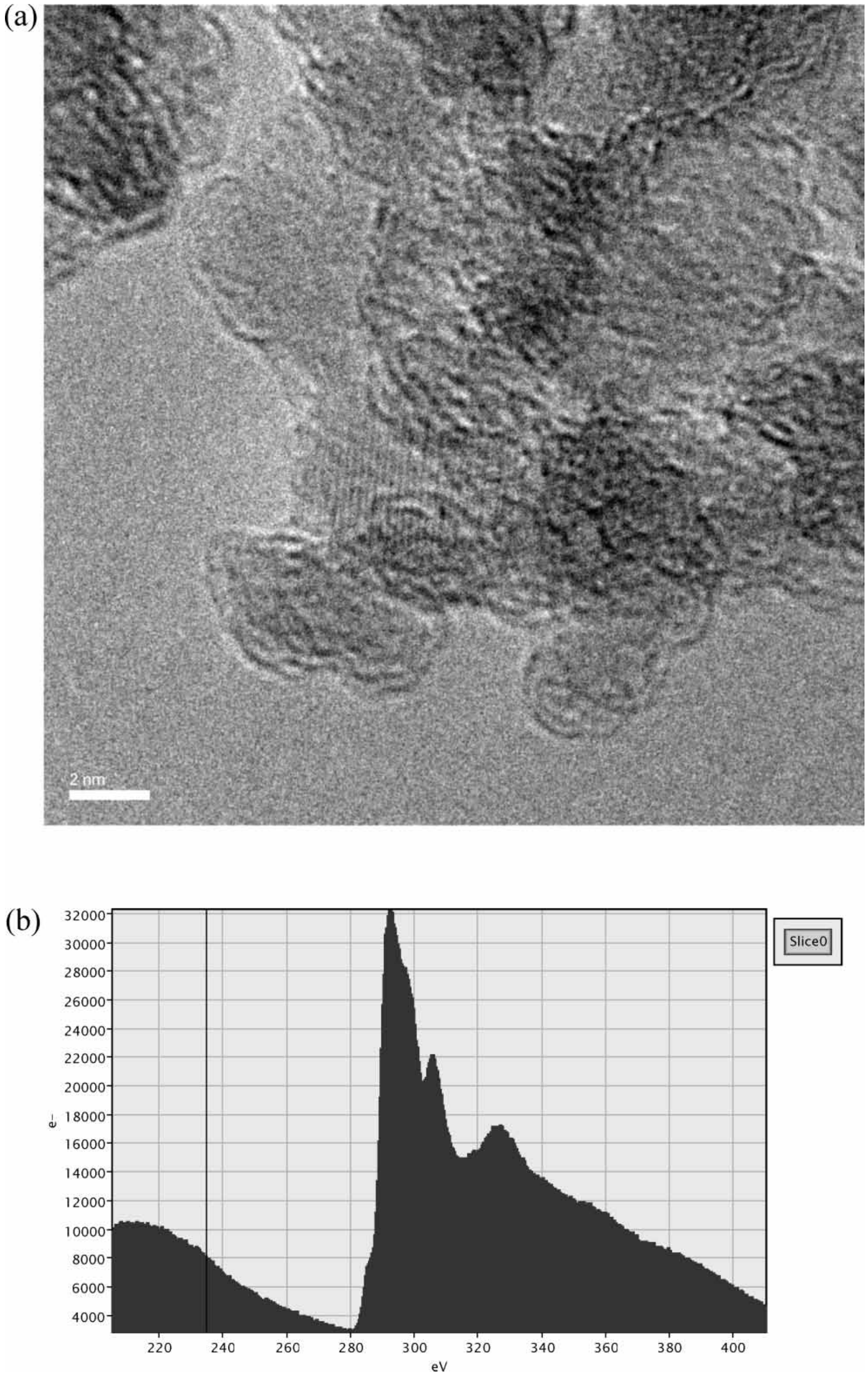

Figure 2. (a) TEM lattice image and (b) EELS spectrum of commercial nano-diamonds [14] which show that they are crystalline and diamond-like. Results courtesy of Dougal McCulloch and Luke Simpson, Applied Physics, RMIT University, 2003.

the Fourier-Legendre technique as implemented in the CRYSTAL software [20].

3. *Ab initio* studies of stability of graphenes

Our previous studies have used *ab initio* DFT [1], semi-empirical estimates of energy [1] and classical MD [13] to investigate possible structures of nano-diamond and hydrogenated nano-diamond in 0- and 1-D. This work showed that one can obtain a variety of structures starting from diamond-like structures, which are at least locally (if not globally) stable. Some of these structures were already known to exist experimentally, such as bucky-diamonds and carbon onions [1], whilst at least one predicted structure, (involving a long 1-D linear C chain encapsulated within a carbon nano-tube), has subsequently been observed [1,21]. This establishes that such methods can give very useful insights into the structure and properties of these 0- and 1-D diamond-like systems. Here, we extend our *ab initio* DFT studied to investigate some of the properties of nano-carbon materials based on graphene sheets.

3.1 The stability of flat nano-graphene sheets

At the nanoscale, a variety of carbon based structures also exist with the bonding structure attributed macroscopically to graphene. It is very well established that curved graphene structures exist, such as fullerenes and carbon nano-tubes [6]; and that these structures are extremely stable. However, it is also known that flat nano-carbon graphene layers can be prepared experimentally, such as large polycyclic aromatic hydrocarbons [22] and sub-nanometer graphene sheets [7], although there seems to be less examples of these. Therefore, it is interesting to determine if an initially flat graphene structure can be transformed into a curved form via *ab initio* DFT simulations.

With this goal in mind we constructed a series of both centro-symmetric structures consisting of 24, 54, 96, 150 and 216 carbon atoms and a series of non-centro symmetric structure consisting of 32, 50, 72, 98 and 128 carbon atoms. The geometry of these structures were fully relaxed using VASP, as was done previously for nano-diamonds in 0- and 1-D [1]. After this geometry optimization the centro-symmetric structure remained unaltered and the non centro-symmetric structure altered only marginally as can be seen from a typical example shown in figure 3. Thus these calculations indicate that nano-graphene sheets of this size (once formed) at low temperature show no tendency to transform to fullerenes nor to form small sections of single walled nanotubes (SWNTs).

As this relaxation procedure is essentially equivalent to $T = 0\,\mathrm{K}$, the smallest structures of both types i.e. the centro-symmetric C_{24} and the asymmetric C_{32} were also subjected to temperatures of 300, 600, 900, 1200, 1500, 1800 and 2100 K ("annealing"). The C_{24} sheet curled during this heating but the curling was not constant, but occurred at various regions of the sheet at different times. The transition from one curled configuration to another also passes through an almost planar configuration at each temperature. There was only a structural oscillation between opposing saddle-like structures (a type of "flapping" mode) but there was no transformation to a fullerene or a SWNT. The C_{32} structure behaved very similarly but with larger distortions. However, once again it did not transform to a fullerene or a section of SWNT.

To see if this is a size dependent effect a larger asymmetric sheet of 128 carbon atoms (that showed some change at $T = 0\,\mathrm{K}$) was annealed at $T = 300\,\mathrm{K}$ for 673 fs. This sheet buckled slightly but also failed to transform to a fullerene or a SWNT (see figure 4).

Since the annealing of the structures shown above did not produce fullerenes (or nanotubes), as a final step all the annealed structures were "quenched" from high temperature to $T = 0\,\mathrm{K}$ to see if the barrier to a lower energy fullerenic structure could be overcome, or if some other metastable structure would form.

The instantaneous quenching nanographene sheets was simulated by relaxing the annealed structure at $T = 0\,\mathrm{K}$,

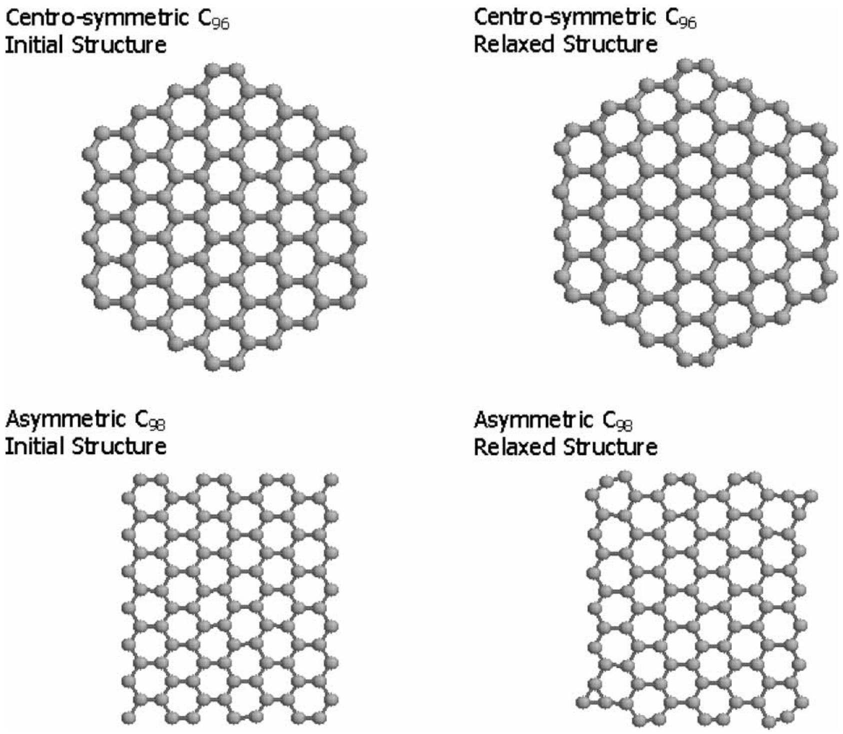

Figure 3. Initial and final structures of C_{96} and C_{98} graphene sheets. No out-of-plane distortions were observed upon relaxation at $T = 0\,\mathrm{K}$.

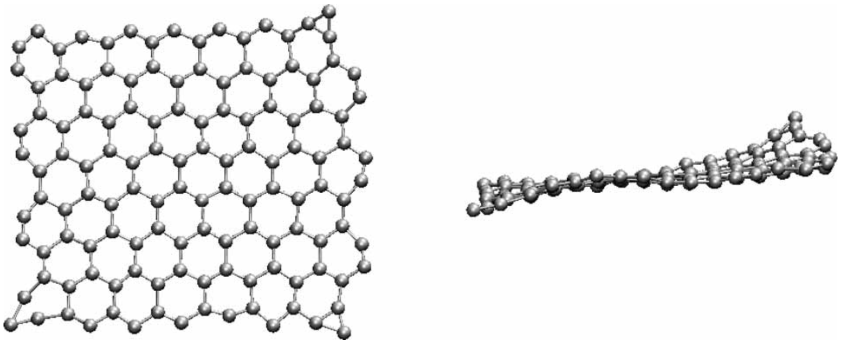

Figure 4. Final relaxed C_{128} asymmetric nanographene sheet following annealing for 673 ps at 300 K.

using the procedure applied in the case of the initial relaxations of the structures described above. The results of the quenching of the annealed C_{24} centro-symmetric sheets lead in all cases the annealed structures which almost completely reverted to the original structure. In some cases (e.g. the structure annealed at 2400 K) a slightly curved surface was retained, but overall the quenching did not assist in the formation of lower energy structures.

Similarly, the quenching of the annealed asymmetric C_{32} sheet also resulted in structures closer to ideal graphene. Here, the quenching reduced the out-of-plane distortions and restored some of the in-plane symmetry to the structures. In some cases, a minor amount of curling has been retained, but it is clear that the significant in-plane distortions such as broken rings introduced during the annealing process could not be mended. The quenched sheets are, therefore, metastable clusters formed as the structures became trapped in a local energy minimium during the relaxation.

Thus, we may conclude that there must exist a substantial barrier to conversion of small graphene sheets to curved structures under ambient conditions. In the next section, we investigate the energetics of a variety of related candidate structures based on graphene sheets.

3.2 Comparative energetics of flat and curved structures

To further explore the relative energies of some typical flat and curved structures, and the likely energy barriers to their interconversion, we performed DFT calculations using CRYSTAL98 [20] for a variety of different (but related) geometries. These structures ranged from planar sheets which were periodic in two dimensions to fully curved structures which were periodic in one dimension these structures were: undistorted bulk graphite, bulk graphite with one slightly displaced atom, a single planar layer of graphene, a single planar graphene sheet of 50 atoms, and a planar graphene sheet of 50 atoms with one atom displaced by 0.8 Å in the *z* direction. In addition, more significant distortions were considered, represented by a planar graphite sheet of 50 atoms buckled with a sinusoidal displacement covering the unit cell (but with no broken bonds) approximating random buckling, and a buckled alkane buckled as if being bent into a SWNT chosen

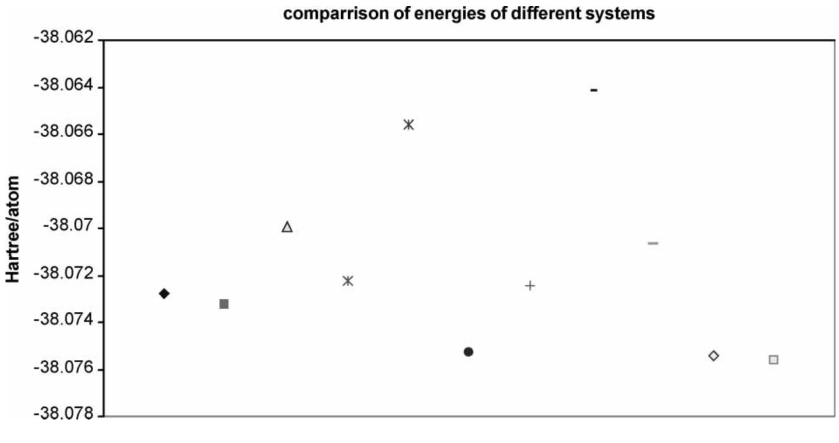

Figure 5. The energy of various carbon structures in calculated by DFT. The results shown on the right hand side are based on graphite and those on the left hand side are carbon nanotubes. In detail, undistorted bulk graphite (◇), bulk graphite with a slightly displaced atom (□), an alkane distorted towards a nanotube (–), randomly buckled graphite (—), graphite with one displaced carbon atom (+), single plane of graphite (■), (8,0) nt (✳), (15,0) nt (✳), (10,0) nt (△), (10,10) nt (▪) and (9,9) nt (◆).

in an attempt to simulate an intermediate state. These results were compared with (9,9), (10,10), (8,0), (10,0) and (15,0) carbon nano-tubes. The optimized energies per atom of these structures are given in figure 5. From this figure it may be seen that the most stable structures are bulk graphite, graphite with one atom displaced, a single planar graphite layer, and the (9,9) and (10,10) SWNTs. These structures are all very similar in energy. The figure indicates that at $T = 0$ K there is a reasonably large energy barrier which must be overcome to interconvert these structures.

3.3 Electron density of states of flat and curved structures

Therefore, assuming that some of these alternative structures based on graphene may be produced experimentally (under non-equilibrium conditions), it may be expected that different structures or a mixture of them, may be produced by varying the experimental conditions.

Scanning and transmission electron microscopy and X-ray diffraction may be used to give information about these structures and their alignment. Spectroscopy can also be used to study orientational effects, such as K_α X-ray spectra, [23,24] and may, therefore, yield some useful information regarding the structure of these various forms of graphene based solids. The K_α X-ray line in carbon is generated by an electron transition from $2p$ to $1s$ orbitals which reflects the chemical state of the carbon atom. It has been shown that the K_α X-ray line shape is directly related to the shape of the $2p$ electronic density of states (EDOS) since the EDOS corresponding to the 1s orbitals can be well approximated by a delta function [23]. Hence, we have calculated the EDOS corresponding to the $2p$ orbitals in the x, y and z directions for the structures described above, in order to see if there are any clear features in the K_α X-ray line shapes which could be used to differentiate the various structures. The results are shown in figures 6, 7, 8 and 9 where the energies are in eV and the red, blue and black lines indicating the x, y and z directions, respectively. Where, only a blue or red line is evident the results for the x and y directions completely overlap.

As can be seen from figure 6(a) for bulk graphite (and described in more detail in ref. [24]), and for slightly buckled bulk graphite (figure 6(b)), there is no anisotropy in the EDOS for the x and y directions. These EDOS do

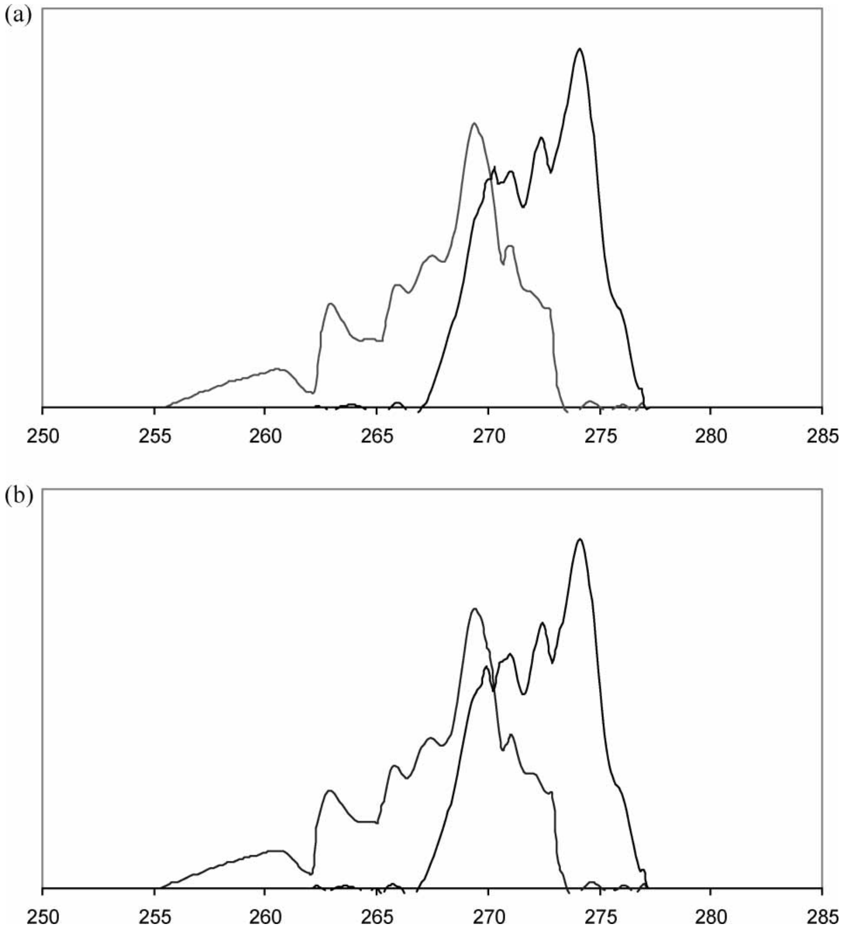

Figure 6. EDOS for (a) bulk graphite (unbuckled) and (b) bulk graphite, buckled as per experimental observation i.e. one atom out of plane by 0.005 Å i.e. < 1/20 of c parameter (distance between layers). In this figure and figures 7, 8 and 9 the planes are in x,y plane and energies are in eV. Red = x, blue = y and black = z directions where there is only blue or red it shows that x and y directions completely overlap.

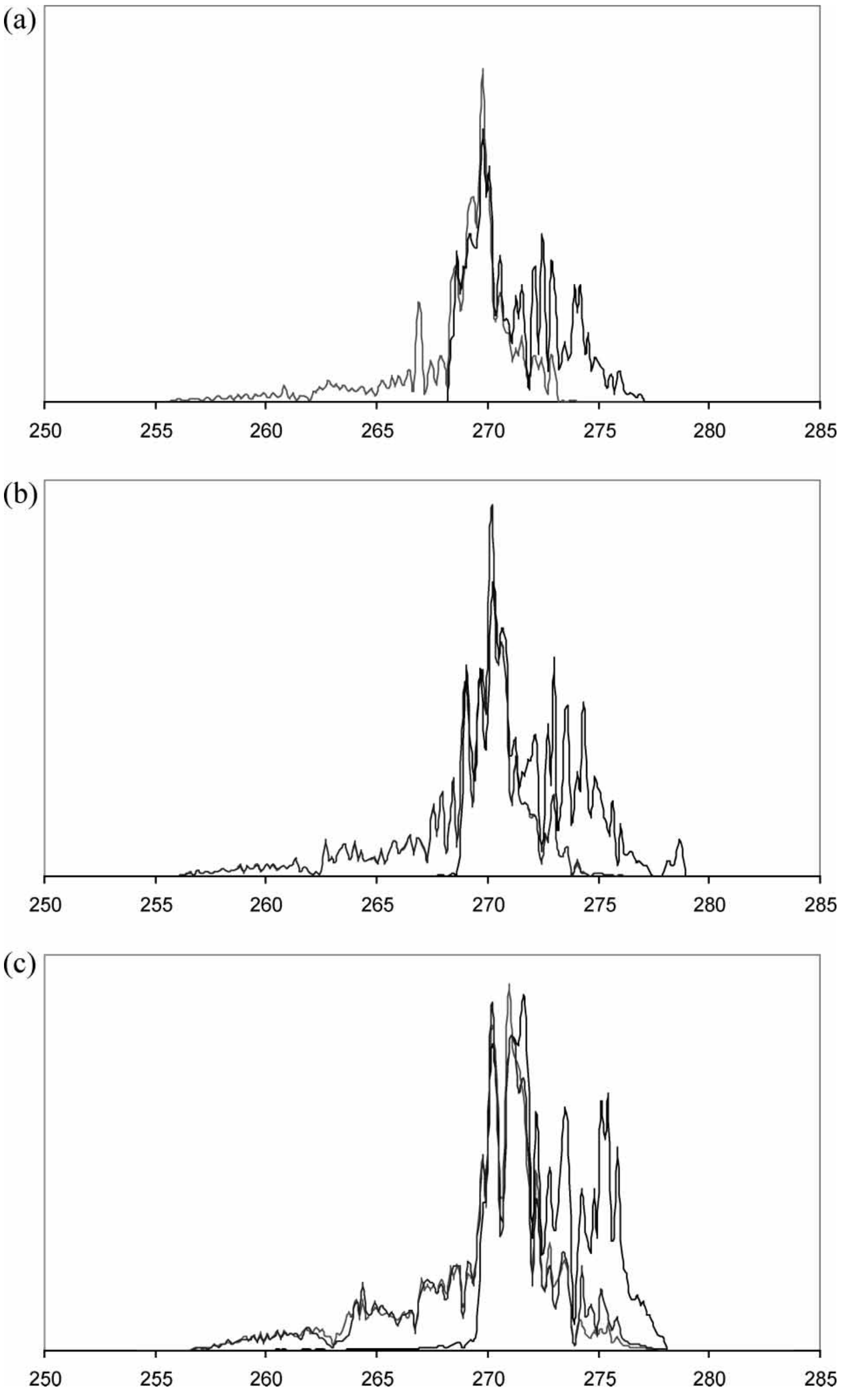

Figure 7. EDOS for (a) Planar sheet of graphite with supercell size of 50 atoms. (b) Planar sheet of graphite with supercell size of 50 atoms with 1 atom displaced from equilibrium by ~ 0.8 Å in z direction. c) Planar sheet of graphite with supercell size of 50 atoms, buckled with sinusoidal displacement covering the unit cell to mimic severe (almost random) buckling while maintaining some degree of symmetry so that chemical bonds were not completely broken.

differ however, from that in the z direction. This is similar to the result for a single sheet of graphene, except that random buckling induces a slight difference in the EDOS for the x and y directions, (see figure 7). The EDOS for the planar systems shows considerably more fine structure than that of bulk graphite, and the EDOS in the x and y directions are non zero at lower energies than that in the z direction. Thus, experimental spectra will be expected to show more features for planar graphenes than for bulk graphite if sufficient energy resolution can be achieved to resolve these features.

For the nanotubes the EDOS also shows more fine structure than that of bulk graphite, (see figures 8 and 9), but all the directional components of the spectra span an energy range comparable with that of a planar sheet. Referring to figure 8, the EDOS for the (8,0), (10,0) and (15,0) nanotubes also shows a difference in magnitude between the x, y and z directions especially with regard to

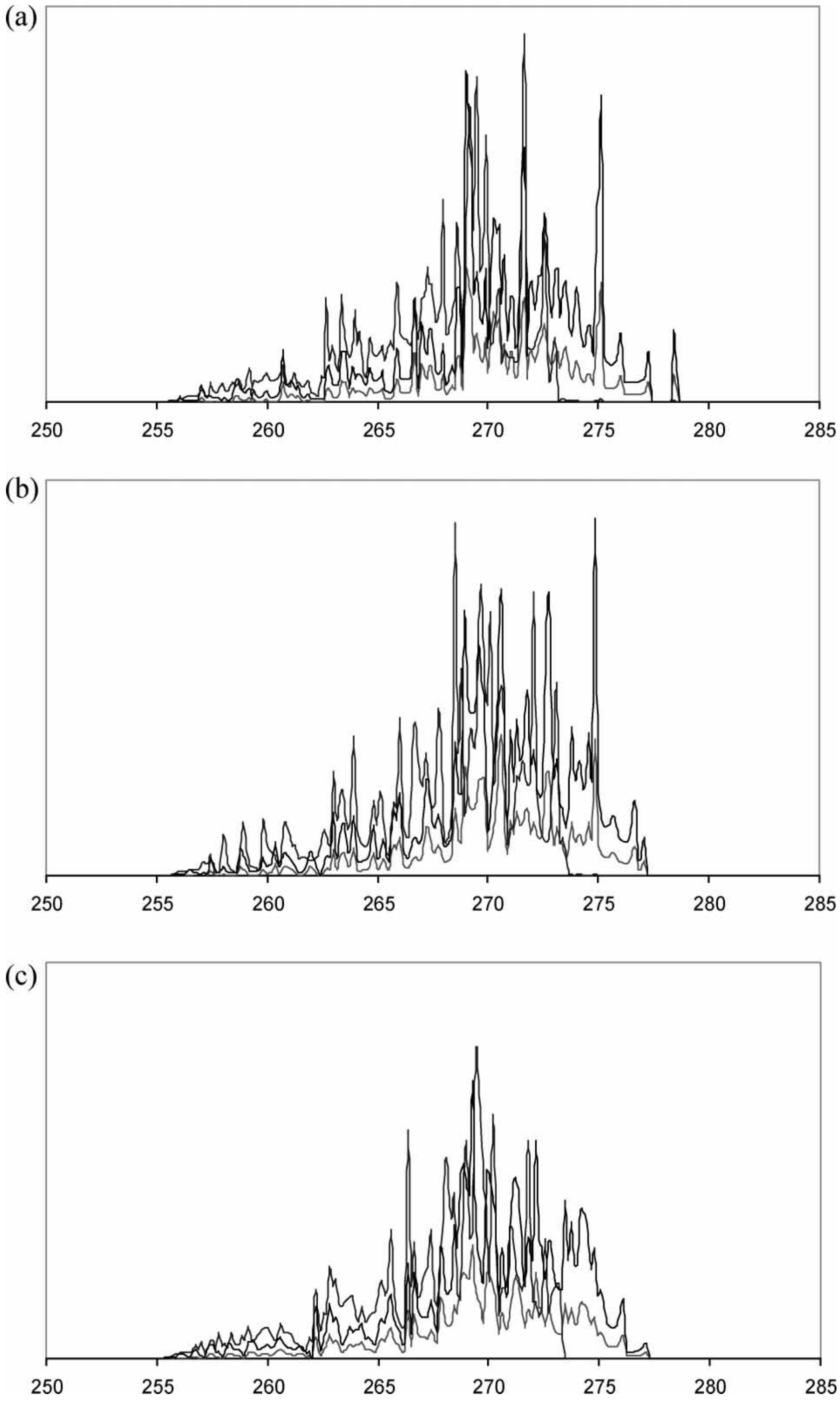

Figure 8. EDOS of (a) (8,0) nano-tube, (b) (10,0) nano-tube and (c) (15,0) nanotube.

intensities of some of the peaks. The results are somewhat similar for the (9,9) and (10,10) nanotubes (as shown in figure 9), except that the EDOS in the x and y directions for the (9,9) nanotube are identical. This indicates that angle resolved spectra should be able to distinguish between these two structures, given sufficient energy resolution.

3.4 Necessary refinement of ab initio methods

Currently available DFT implementations such as are available in the packages VASP and CRYSTAL provide a very good description of many bonding situations. There is, however, one type of atomic interaction which is treated rather poorly that is, van der Waals (or dispersion) interactions [25,26]. Some structures which are observed or predicted to exist involve long bonds which are often weak bonds which are likely to be of the van der Waals type. Currently, the actual values of the bond lengths (and other properties of these bonds) may be only qualitatively predicted by DFT. In order to illustrate this we have simulated graphite using CRYSTAL98 and calculated the bond lengths and

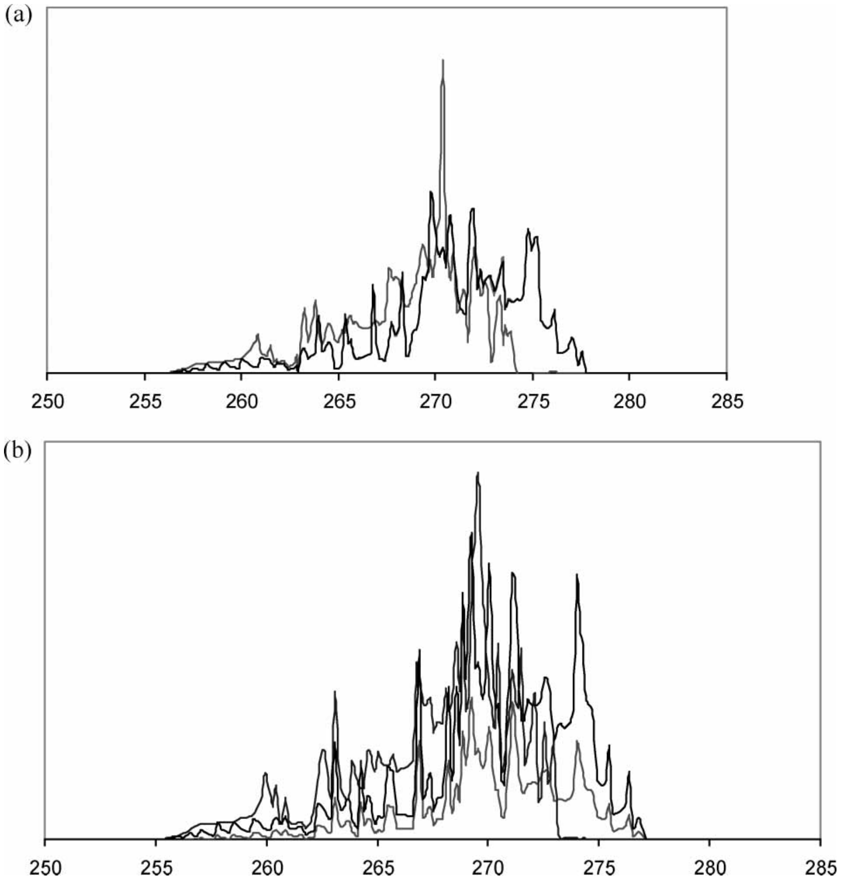

Figure 9. EDOS of (a) (9,9) nano-tube and (b) (10,10) nano-tube.

elastic constants. The values of the intra-layer spacing *a*, the inter-layer spacing *c* and the elastic constants C11 + C12 and C33 for graphite calculated by the PBE, BLYP and B3LYP density functional calculations compared with experimental values are listed in table 1. From this it may be seen that the quantities characterizing the in-plane strong interatomic interactions (*a* and C11 + C12) are well reproduced, but those dependent on the inter-planar van der Waals interactions (*c* and C33) are very poorly represented. This is a clear illustration of the inadequacy of commonly used DFT approximations to describe van der Waals interactions. Thus, an active area of research should be to develop new DFT functionals which can accurately describe such important interactions.

Table 1. The intra-layer spacing *a*, the inter-layer spacing *c* and the elastic constants C11 + C12 and C33 for graphite calculated by the PBE, BLYP and B3LYP density functional calculations compared with experimental values.

Property	*PBE*	*BLYP*	*B3LYP*	*Experiment*
a [Å]	2.472	2.481	2.482	2.46
c [Å]	6.307	6.474	6.468	6.71
C11 + C12 [GPa]	13.01	12.92	12.90	13.3
C33 [GPa]	1.6	1.78	1.9	0.41

4. Conclusions

The application of *ab initio* DFT based simulations to some aspects of the structure and properties of graphene layers and graphene tubes shows the following:

- Both flat and curved structures based on graphene exist which are energetically stable and are similar in energy
- There exists a substantial barrier to conversion of small graphene sheets to curved structures under ambient conditions. Thus, direct simulation of this transition is difficult.
- At low temperatures there are likely to be a variety of structures based on graphene sheets which may be produced under non-equilibrium conditions and their interconversion will require a considerable input of energy.
- Angle resolved X-ray spectra should be able to distinguish between some of these structures, given sufficient energy resolution and angular resolution.

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