

Computer Simulations of Carbon Nanostructures under Pressure

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Abstract: Several interesting phenomena are observed when materials are put under pressure. The goal is to achieve modification and control over their mechanical and electronic (conduction) properties. Within this spirit, we have recently focused our attention into how carbon nanostructures respond to hydrostatic pressure. We performed Monte Carlo simulations with the Tersoff potential of various free-standing carbon nanostructures. These range from fullerenes, onions, and carbon spheres to nanotubes and nanodiamonds. Our simulations show that the nanostructures undergo some notable structural modifications.

Keywords: Monte Carlo simulations, carbon nanostructures, hydrostatic pressure, structural modifications

INTRODUCTION

In recent years, novel carbon materials have been studied intensively because of their enormous potential utility. They display unique structural, mechanical, and electronic properties. Much research has been done since the mid-80s when C_{60} was discovered (1). New perspectives conjured after finding the 4th form of carbon: nanotubes (2). These structures have inspired interesting advances in science and guided the visualization and production of similar other stable structures such as peapods (C_{60} s inside CNT) (3) and a whole

family of fullerenes. In these categories of carbon forms, carbon onions (4) and carbon spheres (5) are also included.

Carbon nanotubes (CNT) display a unique structure, can be metals or semi-conductors, and exhibit exceptional properties such as high stiffness and flexibility. Fullerenes, on the other hand, are ideal for manipulating materials on a molecular scale in order to form or tailor structures of this size. Regarding the hybrid forms of CNT and fullerenes, namely peapods, their tunable electronic properties must be underlined, since they exhibit electronic features additional to that of CNT, which are strongly dependent on the location of fullerenes along the tube. In addition, carbon onions can be used as fuel cells or immensely tiny ball bearings that may be applied in nanomachines built on the scale of molecules. Carbon spheres (5), which consist of an amorphous carbon (a-C) core and graphine (fullerene-like) shells, might find potential application such as catalyst carriers, lubricants, and hydrogen storage materials.

On the other hand, a hybrid $sp^2 - sp^3$ carbon nanocluster is a bucky diamond. These are carbon nanoparticles with a diamond core of a few nm and a fullerene-like surface (6). Bucky diamonds are expected to be present at meteorites in residues of detonation as well as inclusions of diamond-like films. Quantum confinement effects are present if these bucky diamonds become smaller than 2 nm. However, it is not yet clear what their behaviour is if they are coalesced, suspended, or interconnected.

All of the preceding nanostructures are potential building blocks of nanotechnology. Many of them have been extensively investigated theoretically and experimentally to discover their properties. An open question, though is how these properties are altered or can be manipulated if the structures are compressed.

In the current study, we examine how carbon nanostructures respond under pressure and reveal a transformation path that may guide to the answer of the preceding question. Hydrostatic pressure is thus applied and the structural deformations are examined. Estimations on critical values of pressure at which shape transformations occur will also be presented. An intimation, finally, of the coalescence of bucky diamonds under pressure will be made as it is essential to know the way that nanoscale units join. These issues are interesting as they can lead to different configurations and provide ways of modification and control of the electronic properties of the carbon nanostructures (7).

METHODOLOGY

Computer simulations using empirical potentials are effective methods for the analysis of structural and mechanical properties of complex systems. The Monte-Carlo (MC) technique, more specifically, is able to handle large systems and is preferable for statistical accuracy. Within the MC approach,

a canonical (N,P,T) ensemble was employed in order to apply pressure to the system and Tersoff's (8) empirical potential was used to model the atomic interactions.

In addition to these interactions, the Lennard-Jones potential was also implemented into the calculations to simulate the long-range van der Waals forces wherever they exist (e.g., between the walls of a mwnt or a carbon onion or between the atoms of the amorphous carbon core and that of the fullerene shell). The parameters of this potential were given by Lu and Wang (9): $\varepsilon = 2.964$ meV, $\sigma = 3.407$ Å, and have been used successfully to describe the bulk properties of solid C_{60} and multiwall nanotubes (9, 10).

RESULTS AND DISCUSSION

Hydrostatic pressures ranging from 0 to 100 GPa were applied on Carbon nanostructures. As a first step we use only one nanostructure per simulation cell. The simulation temperatures are in the range of 300–500 K, while calculations for 1,500 K and 2,000 K in the case of nanodiamond coalescence were also carried out.

The effect of pressure on single wall nanotubes (swnt) has already been studied, although in most cases the pressure was axial (11, 12) or it was applied to swnt bundles (13). The resulting structures consist of a series of segments resembling deformed ellipsoids, connected with narrowed junctions and are actually buckled. This buckling is noticeable for pressures higher than 3 GPa and range up to 5–7 Gpa. Some sp^3 sites at the approaching shells are also formed. These sp^3 atoms are mostly clustered and are located on the narrowed junctions. An elastic recovery of these buckled swnts upon decompression was found, although as the pressure increases some defects still exist.

Multi-wall nanotubes (mwnts) under pressure show similar trends, where sp^3 hybridization is again visible. These results coincide with another study published while we were analyzing our result (14). We find that the buckling of mwnts occurs at relatively high pressures. The critical pressure is about one order of magnitude higher than in the case of swnts and it is calculated around 30–50 GPa. The long range van der Waals (vdW) forces that are present between the adjacent walls of a mwnt may play a role in the significant increase of the buckling pressure.

An analogous increase of this pressure was evident also in the case of compressed peapods. Another point here is that as pressure continues to rise, the surrounding swnt may bond to the inner array of C_{60} s. Focusing at this inner array shows a coalescence of the fullerene molecules while buckling takes place. This bonding is actually favored through the exertion of pressure event at low temperatures. An example of a compressed (12, 12)

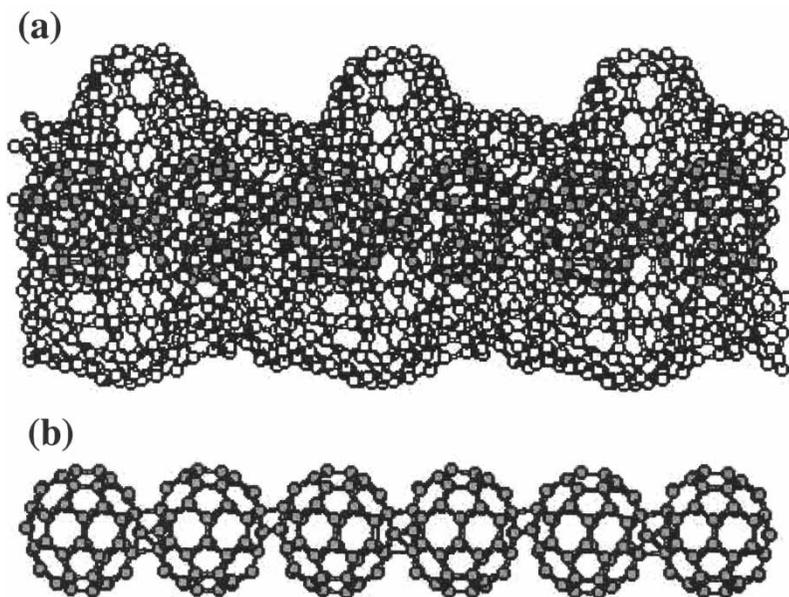


Figure 1. Peapod under a pressure of 100 GPa (a). The coalesced array of the internal C_{60} s is shown in (b).

peapod at a pressure of 70 GPa, is shown in Fig. 1a. The inner coalesced C_{60} s at this pressure is shown in Fig. 1b.

Fullerenes, on the other hand, spherical-and oval-shaped were also put under pressure. The former obtain a shape similar to a buckled star, while the latter a more rectangular one. An initially spherical- (C_{540}) and an oval-shaped (C_{100}) fullerene with diameters of about 21 and 11.6 Å, correspondingly are shown in Fig. 2. Their transformation takes place at modest pressures close to $\approx 5-6$ GPa.

The effect of hydrostatic pressure on carbon onions is similar to that of spherical fullerenes although a higher pressure around 50 GPa is needed. The shape transformation in this case propagates through the shells, leaving almost unaffected the last inner shell, which in our simulations corresponds to small fullerenes of approximately 0.8–1 nm size, like C_{60} or C_{70} . Slight distortions, though, of their bonds were seen (these are slightly elongated), but the shape is actually not changed. An example of a three shell carbon onion compressed at 50 GPa is presented in Fig. 3. The insets (a) and (b) show the internal two shells. It is clearly shown that the shape of the inner C_{60} is not deformed.

One remark concerning the configuration of carbon spheres is that the internal amorphous carbon (a-C) forms a shell resembling that of the fullerene, having a high percentage of six fold rings. When the carbon

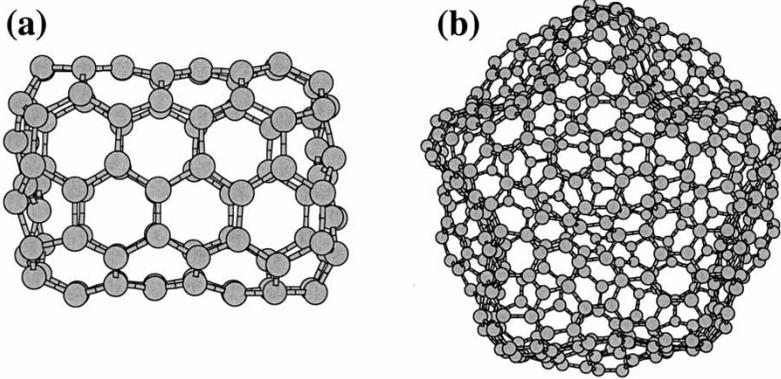


Figure 2. Figures of C_{100} and C_{540} after their compression at 5 GPa. Their initial shape was oval and spherical, correspondingly.

sphere is compressed, the fullerene shell firstly obtains a polygonized shape, while the a-C core remains spherical. As the pressure increases over 200–300 GPa, the spheres—both the fullerene shell and the a-C core—flatten at their edges and turn into cubes. This is clearly shown in a cross-view of such a structure in Fig. 4. The different walls are now more evident, as three concentric squares are shown. The outer one corresponds

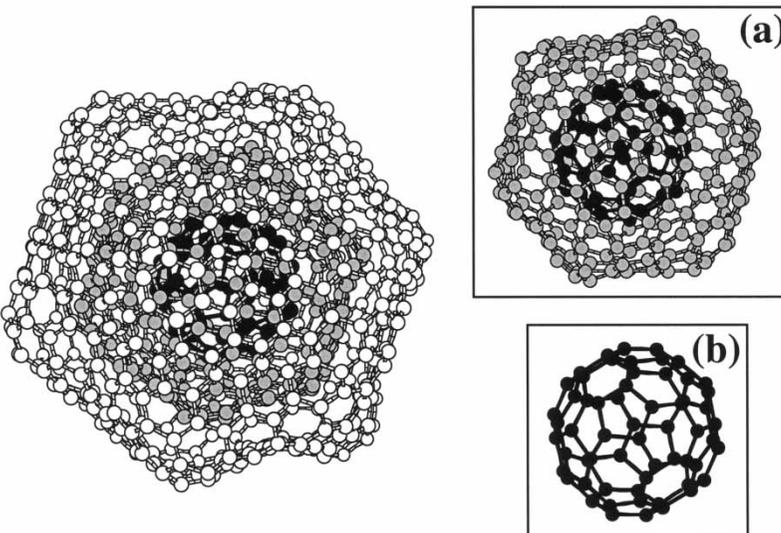


Figure 3. $C_{60}@C_{240}@C_{540}$ onion under a pressure of GPa. The insets (a), (b) show the internal shells C_{240} and C_{60} , correspondingly.

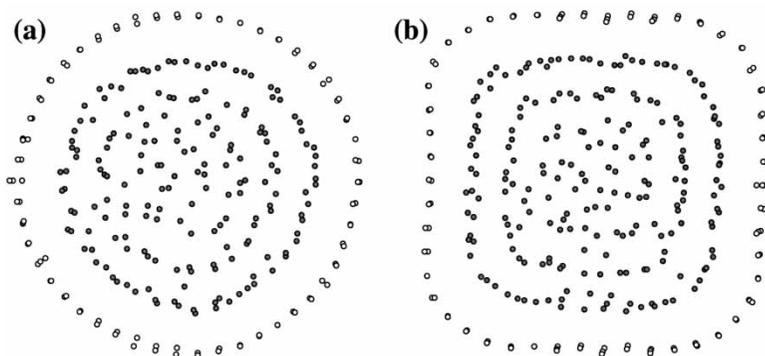


Figure 4. Cross views of highly compressed carbon spheres (a) before and (b). The internal grey atoms correspond to the a-C core, the white ones to the fullerene shell.

to the external fullerene, while the two internal to the amorphous carbon core. No bonding takes place among the two outer shells even at high pressures, as they are held apart at distances close to 3 \AA (Fig. 5).

A final preliminary result is the coalescence of diamond nanocrystals. The open question is whether they develop a reconstructed surface (and become bucky diamonds) even if they are compressed. In order to give an answer, we first compressed under various pressures a free-standing spherical nanodiamond with a 6.8 \AA radius. As we raised the temperature up to $1,500 \text{ K}$, the

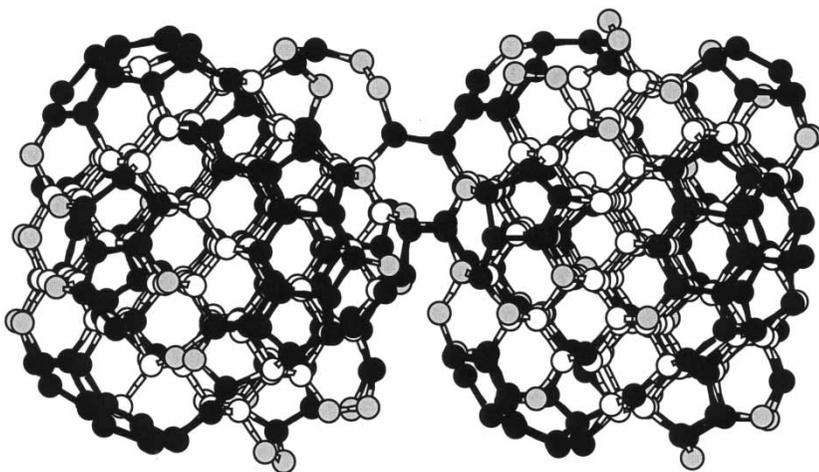


Figure 5. Coalescing of 2 nanodiamonds (each with a radius of 6.8 \AA) at $1,500 \text{ K}$ under a pressure of 20 GPa . White atoms correspond to sp^3 bonding, while the black ones to sp^2 . Bonds close to $1.4\text{--}1.5 \text{ \AA}$ are formed.

fullerene-like reconstruction occurred even under the effect of pressures up to 50–70 GPa. The same procedures was carried out for two diamond nanocrystals put aside at various small distances of 3–10 Å. The reconstruction again occurred at similar to the preceding conditions. An example is given in Fig. 4, where two nanodiamonds with a 6.8 Å radius are compressed and their coalescence is promoted. In the final case of relatively small temperatures close to 300–500 K, the bonding among the two nanostructures is visible, but no reconstruction occurs.

CONCLUSIONS

Results regarding the effect of hydrostatic pressure on different free-standing carbon structures of the nanometer scale were presented. Their structural transformations were studied, which may reveal a path to the modification of their electronic properties. A modest buckling pressure for single wall nanotubes was found, which increased significantly for structures that included van der Waals bonding. Finally, a preliminary study on the coalescence of nanodiamonds showed that at an adequate temperature they develop a fullerene-like reconstructed surface even under compression.

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