Theory and Modeling
On the Unzipping Mechanisms of Carbon Nanotubes: Insights from Reactive Molecular Dynamics Simulations

Ricardo P. dos Santos1, Pedro A. Autreto2, Eric Perim2, Gustavo Brunetto2, and Douglas S. Galvão2

1Physics Department, IGCE, Universidade Estadual Paulista, UNESP, 13506-900, Rio Claro, SP, Brazil.
2Applied Physics, State University of Campinas, 13083-970, Campinas, São Paulo, Brazil.

ABSTRACT

Unzipping carbon nanotubes (CNTs) is considered one of the most promising approaches for the controlled and large-scale production of graphene nanoribbons (GNR). These structures are considered of great importance for the development of nanoelectronics because of its dimensions and intrinsic nonzero band gap value. Despite many years of investigations some details on the dynamics of the CNT fracture/unzipping processes remain unclear. In this work we have investigated some of these process through molecular dynamics simulations using reactive force fields (ReaxFF), as implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code. We considered multi-walled CNTs of different dimensions and chiralities and under induced mechanical stretching. Our preliminary results show that the unzipping mechanisms are highly dependent on CNT chirality. Well-defined and distinct fracture patterns were observed for the different chiralities. Armchair CNTs favor the creation of GNRs with well-defined armchair edges, while zigzag and chiral ones produce GNRs with less defined and defective edges.

INTRODUCTION

The unique and unusual electronic properties of graphene make it a very promising material for the creation of new nanodevices [1-3]. However, its zero band gap value hinders many possible technological applications making band gap engineering an important issue in order to overcome these limitations [4, 5]. Many different approaches have been tried to create, in a controllable way, a nonzero band gap value in graphene-like structures. These approaches included hydrogenation [6], fluorination [7] and/or other chemical and physical functionalizations. These methods have achieved only limited successes.

Another possibility it is to use the so-called graphene nanoribbons (GNRs). GNRs are basically long thin graphene strips [8]. Due to their small dimensions and active electronic edge states, GNRs can exhibit finite (nonzero) band gap values, which can be easily tuned depending on the their geometric features [8]. However, the controlled GNR synthesis remains a challenge up to the present.

A new and very promising approach is to obtain GNRs from the unzipping of carbon nanotubes (CNTs), in which CNTs are fractured (unzipped) along their longitudinal axis in a way that the obtained fractured structures are the GNRs. This can be experimentally realized by chemical [9] or physical methods [10].
Figure 1. Scheme of the atomistic model used in the molecular dynamics simulations. Defective external tube atoms (cyan) are free to move. Inner CNT atoms (purple) are held fixed. Red bands represent "clamped" atoms, which are moved along the direction indicated by the arrows at constant velocity.

Another advantage in using CNTs as starting materials to produce GNRs resides in the fact that the vast existing knowledge on CNT synthesis and purification methods can be easily applied to control and to optimize GNR fabrication.

However, despite many years of investigations some details on the dynamics of the CNT fracture/unzipping processes remain unclear. Recently, several theoretical studies have produced new and valuable information towards improving our understanding of the unzipping processes [11, 12]. However, studies considering large multi-walled structures of different dimensions and chiralities and addressing how these aspects affect the general features of the unzipping processes have not been carried out yet. In this work we report preliminary results from fully atomistic reactive potential molecular dynamics simulations along these lines.

MODELING

In Figure 1 we present the general scheme of the models used in our simulations. From the experimental works [9,10] it was identified that two essential features are associated with the multi-walled CNT unzipping processes; the presence of defective regions (chemical or physically induced) and the internal stress created as the many tubes start to unzip. Our used model mimics these experimental conditions. We used two-concentric CNTs in which the internal tube was held fixed (purple in Figure 1), while the external one is set completely free to move and contains defects (vacancies, divacancies, and similar) randomly distributed. Part of this external tube is then submitted to an induced mechanical stress, through the application of an external force on the small bands of "clamped" atoms (red region in Figure 1). These regions are then moved along the directions indicated by the arrows in Figure 1, at constant rate (v=0.001Å/fs), until the process results in a completely unzipped tube. This specific value for the pulling
velocity was chosen to be consistent with the estimated stress/strain values at the experimental conditions [9,10].

We have considered several CNTs of different diameters and chiralities. Typical structures consist of (112,0), (65,65) and (95,35) external CNTs, with lengths of ~150Å.

All calculations were carried using the reactive force field ReaxFF [13], as implemented on the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [14]. ReaxFF is a force field that employs a bond length/bond order relationship, updating the bond orders at each interaction [13]. It allows, in contrast with many other force fields, the creation and/or break of chemical bonds, which are essential in our present problem. This potential has been proved to be very effective on the study of dynamical aspects of a great number of carbon-based structures, including CNTs and graphene-related systems [11,12].

For the unzipping (fracture and/or crack propagation) analysis, the temperature of the system was set at ~10K and controlled by a Langevin thermostat imposing a canonical ensemble with constant number of atoms, temperature and volume (NVT ensemble). The use of low temperature in the simulations allows to filter thermal fluctuations and to obtain a more precise analysis of the stress profiles. The simulations were carried out until a complete unzipped tube is obtained. Typical simulation times were on the range of 10-20 ps.

The determination of stress values was carried out using the force per atom calculated at each step of the simulations and then obtaining the stress tensor. Since we are interested in the CNT fracturing processes, we subtracted the hydrostatic components of the tensor, obtaining the deviatoric stress and then we computed one of its invariants, sometimes called the von Mises stress [15] or equivalent stress. This quantity describes the distortion stress state of the structure and plays an important role in the understanding of the fracturing process.

**DISCUSSION**

In Figures 2 and 3 we present representative snapshots of the unzipping processes and the corresponding von Mises stress profiles, respectively.

As we can see from Figure 2, the fracture/unzipping patterns are quite distinct for the armchair, zigzag and chiral tubes. These results show that the tube chirality plays an important role on how the unzipping (crack propagation) occurs and also on the resulting fractured structures.

For the armchair tubes, the crack propagation has a linear character and exposes mainly zigzag edges (Figures 2a-2c). In general and under similar conditions (tube length and diameter, applied external forces, etc.), the unzipping of zigzag tubes occurs faster than for the cases of armchair and chiral ones. For the zigzag tubes the obtained fractured tubes exhibit zigzag, as well as, small armchair edge regions. Also, the fracture line is in general along a tilted direction in relation to the nanotube axis (Figures 2d-2f). For the chiral tubes the unzipped structures exhibit mainly armchair edges but some small zigzag edge regions are also present (Figures 2g-2i).

Another interesting result from the simulations was the observation of formation of Linear Atomic Chains (LACs) during the unzipping processes. LACs were frequently observed during the unzipping of zigzag and chiral nanotubes, but less often in the case of armchair ones. LAC structures were experimentally observed in the fracture of carbon-based materials [16].
A better understanding on the unzipping processes can be obtained analyzing how the stress accumulates and is released as the fracture cracks propagate. In Figure 3 we present the von Mises stress profiles for the corresponding structures presented in Figure 2. As we can see from Figure 3, the stress profile distribution is strongly chirality dependent. When we compare the stress distribution during the process of pulling the clamped atoms (red region in Figure 1), the zigzag tubes present higher concentration of distortion stress then the other ones and the structure cracks earlier. It is followed by the chiral and later by the armchair tubes, respectively. These results helps us to understand the temporal ordering of tube unzipping, as well as, why in some cases we have a more well defined fracture lines (the cases where the accumulated stress is exactly at the region of bond breaking sequences (see Figures 2 and 3). These fracture patterns are consistent with the available experimental data [9,10]. Considering the recent advances in the experimental techniques of separation different types of CNTs [17], our results could be helpful in selecting the best CNTs in order to produce better and more well-defined GNRs. Works along these lines are in progress.

Despite the lack of extensive theoretical studies regarding the complete analysis of the CNT unzipping processes, our main results are in good agreement with some recent investigations [18,19] which point out that, for armchair tubes, the energetically preferred unzipping path is...
parallel to the tube axis while for zigzag tubes there are two energetically equivalent unzipping directions. These results also corroborate the straight zigzag-edges formed in unzipped armchair tubes.

CONCLUSIONS

In summary, we report here preliminary results for the process of the unzipping of defective multi-walled nanotubes induced by mechanical stress [9,10]. We have investigated different CNT tubes (diameter, chirality, length, etc.) through reactive force field (ReaxFF) [13] molecular dynamics simulations. These simulations were carried out using the LAMMPS code [14].

Our results show that the unzipping process is strongly chirality dependent, not only in terms of the fracture time but also, and more important, in the resulting edge topology of the fractured structures. Zigzag tubes cracks earlier, followed by chiral and later by armchair ones. Armchair CNTs favor the creation of graphene nanoribbons (GNRs) with well-defined armchair edges, while zigzag and chiral ones produce GNRs with less defined and defective edges. How this information can be used to fabricate better and more well-defined GNRs is also addressed.

Figure 3. Equivalent Stress (von Mises) profile distribution for representative snapshots from the molecular dynamics simulations for each corresponding cases presented in Figure 2. The color scale goes from blue (low stress) through white (moderate stress) to red (high stress). See text for discussions.
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REFERENCES

Redesign of Carbon Materials for Novel Storage, Mechanical and Optical Properties

Stefano Leoni1, Igor A. Baburin1, S. E. Boulfelfel2, D. Selli1

1 Technische Universität Dresden, Institut für Physikalische Chemie, 01062 Dresden, Germany
2 Stony Brook University, Department of Geosciences, New York 11794-2100, USA

ABSTRACT

We revisit the polymorphism of carbon along two directions. First, we discover novel polymorphs in the vicinity of graphite, with outstanding optical and mechanical properties. Using numerical methods and graph-theoretical tools, we find as many as 4 novel superhard and transparent polymorphs, with great technological potential. Second, scaling up a model of rod packing to carbon nanotube (CNT) scaffoldings, we discover that such complex assemblies of CNTs are outstanding adsorbers of hydrogen, capable of reaching the DOE target (~6.0 wt% at ambient conditions). Along this line, we highlight novel paradigms for revisiting carbon, in view of remarkable qualities and superior properties.

INTRODUCTION

Carbon remains the most versatile material. In the era of energy efficiency and reversible storage, carbon has the potential of providing clean and very effective solutions within an upcoming hydrogen economy. The polymorphism of carbon has been the object of repeated surprise over the years. Novel forms, ranging from extended (graphene) to finite (nanotubes and fullerenes) have appeared, with outstanding properties [1]. In this work we review recent results on the polymorphism of carbon along two lines: a) novel superhard and transparent sp3 carbon materials [2, 3], b) carbon nanotubes assemblies with superior hydrogen storage properties [4].

The quest for carbon materials with enhanced mechanical properties and a modified optical gap is a topic of high priority. Property engineering is tightly connected with the ability to predict crystal structures, which remains a central issue in both basic solid-state research and modern materials science. In the effort of achieving superior materials for hydrogen storage and gas segregation, structure prediction stands out for its capacity to efficiently indicate viable target compounds. The identification of metastable modifications that can exhibit interesting physical and chemical properties is the central challenge of numerical approaches to predicting materials.

A recent scientific challenge consists in identifying the crystalline product of cold graphite compression. At high pressures and high temperatures graphite is transformed into diamond. Cold compression on the contrary produces a hard and transparent product, which is nonetheless different either from cubic or hexagonal diamond [5]. Recent works deal with the nature of this product of cold graphite compression [6]. The two energetically most preferable candidates so far, M- and W-carbon, can be considered as parallel sets of corrugated graphene sheets interconnected by odd rings fused into characteristic ‘5+7’ patterns. Following this structural principle, other possibilities may arise.
Carbon-based materials proposed so far for hydrogen storage (graphite intercalated with fullerene, carbon foams, nanotube bundles, etc.) perform only modestly [7]. Hydrogen uptake usually amounts up to $\sim 3.0–7.0 \text{ wt.}\%$ at 77 K, quite far from the target value set by the US Department of Energy (6 wt.\% at ambient conditions). Nowadays the focus is shifted to other more capable materials such as metal–organic frameworks (MOFs) or covalent–organic frameworks (COFs) [8]. Arrangements of nanotubes held together by van der Waals forces were also considered [9], however the choice was restricted to so-called nanotube bundles. In experiments tubes are usually obtained as mixtures of tubes (often of different sizes and orientations). This suggested a different way of looking at arrangement of CNTs, namely as entangled assemblies (which we refer to as CNT matrices) [4], like it is presented here.

In the following, four novel hard sp$^3$ carbons are presented, together with a mechanistic investigation on the growth of $M$- and $W$-carbons from compressed graphite. In the second part, the great potential of CNT matrices in hydrogen adsorption is illustrated.

**THEORY**

**Superhard Carbons.** To systematically include known and find new carbon forms, plain metadynamics runs [10] were performed on simulation boxes comprising three, four, six, eight, 12, and 16 carbon atoms, respectively. Quasirandom four-connected nets were used as starting configurations. Each run typically consisted of $\sim 25'000$ metasteps. Within each metastep MD was performed in the $NVT$ ensemble for at least 0.5 ps at 300 K. In these preliminary scans the

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**Figure 1.** Polymorphs and allotropes of carbon. a) diamonds, b) graphite, c) hexagonal diamond (lonsdaleite), d) $C_{60}$, e) $C_{540}$, f) $C_{70}$, g) carbon sponge (amorphous), h) carbon nanotube. Source: http://de.wikipedia.org/wiki/Kohlenstoff.