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Computational studies of carbon nanotube structures

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Abstract

Here we continue our previous exploratory work [Huhtala et al., Comput. Phys. Commun. 146 (2002) 30] in investigating carbon nanotube structures under different bending strain conditions by using large-scale molecular dynamics simulations. On the one hand bending strain is obtained by forcing nanotubes of different chirality to a closed toroidal configuration and on the other hand by bending a straight nanotube along a semicircle. Our previous work has indicated that the toroidal form buckles at a critical radius without changes in the local hexagonal bonding structure when the temperature is relatively low. Here this work has been continued by studying buckled tori at very high temperatures, where bond breakages in the form of pentagon–heptagon pair creation have been observed. These thermally excited defects seem to settle mainly in the unbuckled regions of the torus. The buckling phenomenon was also found to take place when straight single-walled nanotubes were bent along a semicircle. For a small and moderate amount of bending buckling behaviour seems similar to that observed in nanotori while for large bendings large structural deformations of the tube are observed. These include bond breakages and rupture, being dependent on the chirality of the tube. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Since the discovery of carbon nanotubes ten years ago by Iijima [2], these tubular all-carbon molecules have roused a lot of interest. This is because they show ideal and novel mechanical and electronic properties, which in turn are intimately related to the atomic configuration of the tube structure. Changes in the atomic configuration can manifest themselves as local structural deformations in the bonding angles and lengths or as local defects through bond breakages and reorganisations. Such structural changes can be induced by various chemical treatments or by mechanical means such as exerting stress or bending strain on the tube, which can be seen as very a promising way to engineer locally and globally the mechanical and electronic properties of carbon nanotube structures.

In this work we have concentrated on looking at the bending strain induced deformations and defects in single-walled carbon nanotube structures at the atomic level. This is a continuation of our earlier work [1], in which we studied local structural changes induced by the toroidal shape through molecular dynamics simulations of nanotori 22, 220, and 700 nm in diameter. There we estimated the critical buckling diameters of nanotori built from tubes of different chirality. In the present work our intention is to study in more detail the accommodation of strain

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by structural changes and defect formation in small nanotori and in straight nanotubes forced to bend. The toroidal configuration is used in order to obtain uniform bending strain.

2. Simulation method

In our study of the carbon nanotube structures we have employed classical molecular dynamics simulations, where the interatomic interactions are described by using the semiempirical potential developed by Brenner [3]. The minimum energy configuration of the model system is obtained by using the gradient cooling method. A more detailed description of the simulation methods used is found in our previous article [1].

3. Minimum energy configurations of nanotori

The initial atomic configurations of nanotubes are obtained by creating a planar hexagonal network of carbon atoms corresponding to an (n, m)-nanotube cut open axially. The nearest neighbor distance between carbon atoms is set to that of graphite, 1.421 Å. This plane is then mapped onto a 3D-cylindrical surface to form the tube, from which it is further mapped onto a torus.

We have chosen to generate the initial toroidal configurations by mapping the straight tube configuration in space so that the tube ends come next to each other in order to form a closed torus. This choice is based on the observations of Refs. [4,5], in which the torus configuration with uniformly distributed strain is more stable for large toroidal structures than the configuration with strain localized to defects. This is supported by the experimental observations of Liu et al. [6] and Martel et al. [7], because the size of the observed rings is restricted to a well-defined diameter range—the ring formation appears to be a thermally controlled process.

The toroidal structures that have been studied in this work are of (n, n)- and $(n, 0)$-chirality with tube diameters ranging from 0.71 to 1.88 mn and torus diameters of approximately 12.5 and 22 nm. Minimum energy configurations of the tori were obtained by using the gradient cooling method, and the initial temperature of the system was set to 100 K.

In Fig. 1(a) the strain energy of a torus—i.e. the difference in the potential energy between the relaxed torus and the corresponding straight tube—is plotted for the (n, n)- and $(n, 0)$-chirality tori 22 nm in diameter as a function of the tube diameter. The observed kinks in the potential energy curves correspond to a

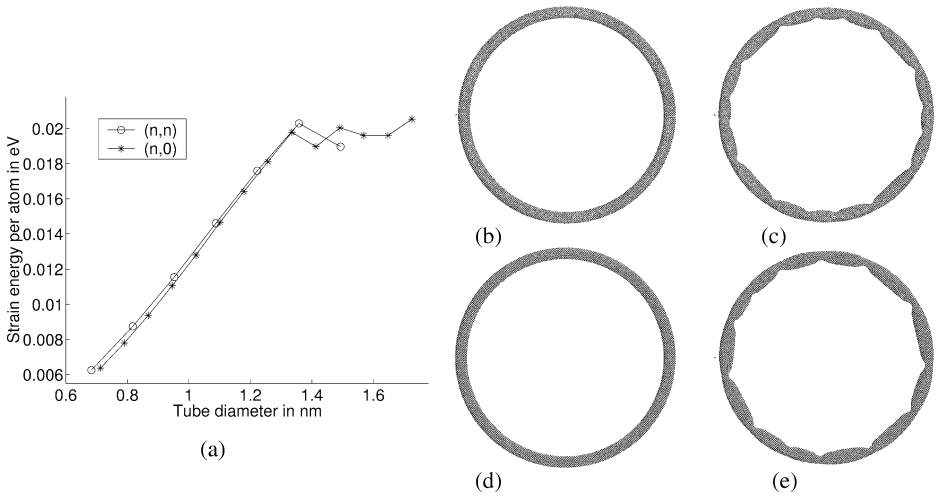

Fig. 1. (a) Potential energy difference per atom between the nanotorus and the corresponding straight tube plotted as a function of the tube diameter for the torus 22 nm in diameter. The structural change in the tori appears as an irregularity in the potential energy curves near 1.35 nm. (b)–(e) Minimum energy configurations of nanotori 22 nm in diameter for tube diameters d just below and above the buckling transition. (b) $(17, 0)$-tube, $d = 1.33517$ nm; (c) $(18, 0)$, 1.41328 nm; (d) $(10, 10)$, 1.35828 nm; (e) $(11, 11)$, 1.49344 nm.

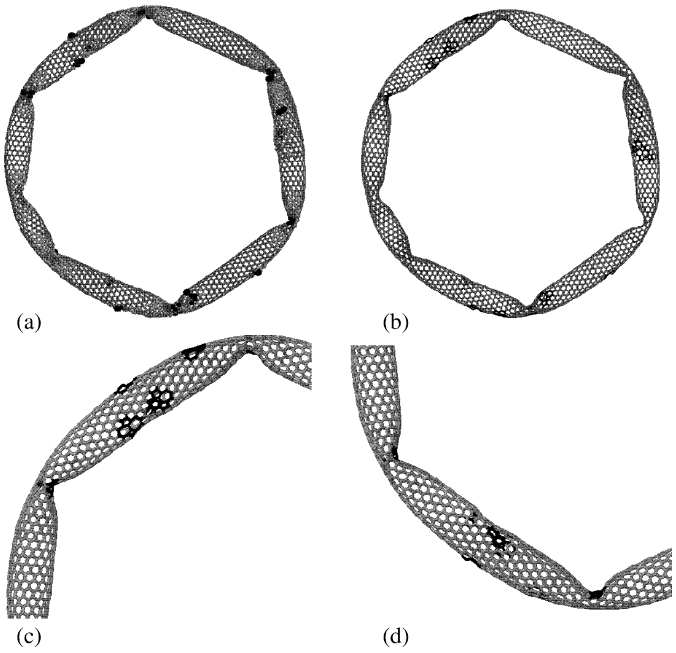

Fig. 2. Results of simulating a $(14, 0)$-torus of a diameter of 12.5 nm (5208 atoms) at the temperature of 5000 K for 3000 fs and then cooling the structure down. In (a) the larger the atom is drawn, the higher is its potential energy. In (b)–(d) bonds in pentagon–heptagon defects are drawn darker. (c) and (d) are portions of the ring depicted in (a) and (b).

structural change in the minimum energy configuration of the torus. This is caused by the torus becoming buckled, as depicted in Figs. 1(b)–1(e).

Our results of the relaxation calculations of the buckled tori show that the strain is localized to the corners of the folds. The hexagonal bonding configuration is deformed but no actual bond breakages were observed. However, if the torus diameter is decreased local strain becomes large enough to eventually cause bond breakages. Previous studies have indicated that it becomes energetically favorable to induce the curvature by pentagons and heptagons when the torus diameter becomes smaller [5]. However, due to large energy barriers, these defects were not observed in the minimum energy configurations determined by the gradient cooling method.

In order to study the formation of these defects we have heated a torus very close to the melting temperature. Fig. 2 shows the results for a $(14, 0)$-torus of 5208 atoms (diameter 12.5 nm), which was simulated at the temperature of 5000 K for 3 ps and then let to cool down. In the beginning of the simulation bond breakages occur everywhere in the torus but when the cooling has begun, the bonds seem to recombine more easily in the immediate vicinity of the folds. The dominating defect type is a pentagon–heptagon pair or several adjacent pairs. These defects seem to settle mainly in the non-buckled regions of the torus. This can be understood by the fact that two adjacent pentagon–heptagon pairs can alter the nanotube length locally and thus relax the strain in the torus [8]. In the buckled sections, the functionality of the defects as a strain release mechanism is not as clear.

4. Bending of straight tubes

Recently there have appeared studies of carbon nanotubes with bends [9,10]. In them buckling was observed, which together with defect formation alters the properties of the tubes, thus making them interesting from the application point of view. A uniformly bent nanotube is under straining conditions similar to the above-discussed toroidal structures, which also

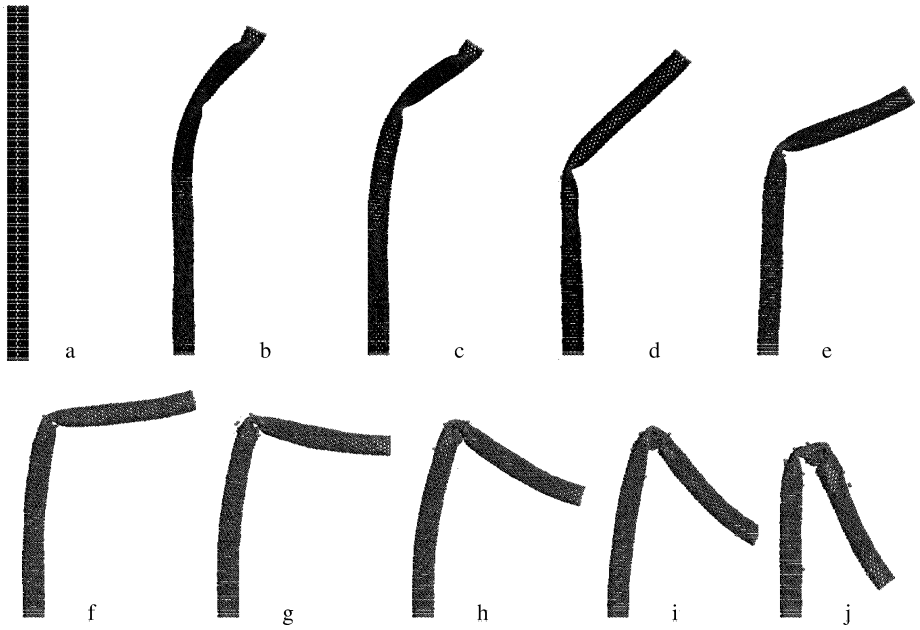

Fig. 3. Bending of a (14, 0) nanotube.

showed buckling and defect formation. We also expect the strain in a non-uniformly bent nanotube to be locally similar to the corresponding uniform bending. Thus we expect that these discussions can be extended and generalized to bent nanotubes.

The bending strain in a toroidal nanotube structure —when non-buckled—is evenly distributed and can be thought to describe the situation in a locally uniformly bent nanotube. We have performed bending studies on an (8, 8)- and a (14, 0)-tube of 2688 and 2744 atoms, about equal in length and tube diameters differing only 1% in favor of the (14, 0)-tube. In the simulations we fixed a portion of $2.5 \cdot a_0$, where a_0 is the graphite lattice constant 2.46 Å, from both ends of the simulated structure and forced one of these ends to move on a half-circular path at a constant rate. The radius of the circular path was a half of the tube length, in order to eliminate phenomena due to stretching of the tube as much as possible. The bending was performed in 250 ps and the simulation temperature was kept at 300 K.

At first, with a small amount of bending the overall tube form stayed intact although a change in the tube cross section from circular to oval shape was observed in the curved section of the tube near the moving end. When the local strain grew large enough the tube formed a buckle. For tubes of both chiralities this corresponded to the average local potential energy per atom rising to approximately -7.31 eV with the maximum potential energy values being -7.28 eV for the (14, 0)-tube and -7.27 eV for the (8, 8)-tube. This is in excellent agreement with our earlier results for nanotorus structures [1]. The corresponding toroidal nanotubes buckle when the average potential energy per particle in the torus is -7.318 eV for the (14, 0)-torus and -7.310 eV for the (8, 8)-torus. The current work does not show strong chirality dependence in the initial formation of a buckle but in the bending process spatial fluctuations occur in the structure, which in turn can facilitate the buckle forming process.

After the first buckle was formed various structural changes were observed as the bending proceeded. The buckle moved, oscillated, atoms were forcibly shooting off the structure and bond breakages, and even serious fracture in the case of the (14, 0)-tube occurred. The behaviour of the bent tubes can be seen in Figs. 3 and 4. In Fig. 5 the average potential energy in the structures is plotted against bending,

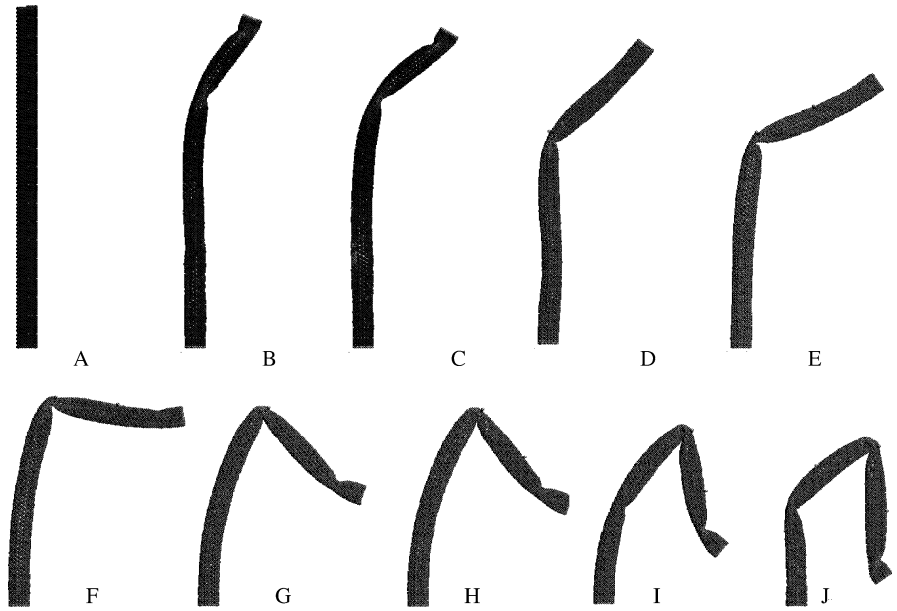

Fig. 4. Bending of a $(8, 8)$ nanotube.

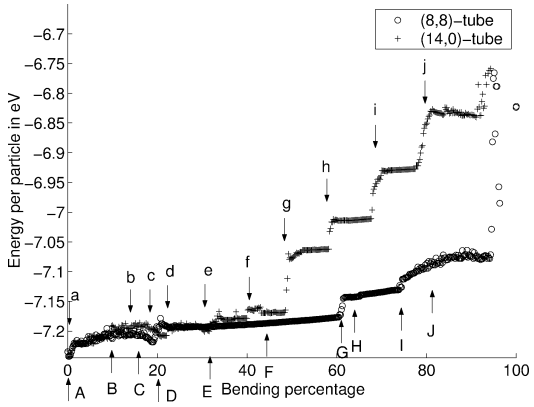

Fig. 5. Potential energy of nanotubes during bending simulation. Lower case and upper case letters refer to frames in Figs. 3 and 4, respectively.

where 100% corresponds to a semicircle. Arrows with small and capital letters indicate the corresponding configurations of Figs. 3 and 4. From these curves it is seen that in the beginning the potential energy rises slowly due to the curvature of the tube increasing smoothly. At (b) and (B) the tube buckles and the potential energy does not rise for a while. This corresponds to the buckle becoming steeper. Arrows (c) and (C) correspond to the buckle starting to move, that is, the tube relaxes the strain by repositioning the buckle. The average potential energy goes down as a better position is found. At (d) and (D) the buckle stops moving. The $(8, 8)$-tube also shoots out a few atoms. So far, except for the atom emission, the two tubes have behaved very analogously but arrows (e) and (f) correspond to bond breakage while (E) and (F) show a smoothly bending tube with the bending being compensated by the buckle becoming steeper and steeper. Arrows (g) and (h) correspond to severe bond damage and atoms being emitted while (G) and (H) have less bond damage but atoms are emitted from the area of the kink. Arrow (i) corresponds to a second buckle forming next to the previous one and a fracture-like rupture of the graphite bonds near the buckled area. The arrow (I) on the other hand corresponds to another buckle forming but for this tube further away from the first one. Bonds are also broken in the process and that contributes to the rise in the potential energy although forming a buckle should lower the energy. Arrows (j) and (J) and the corresponding images of Figs. 3 and 4 show the final configurations. In configuration (j) much more bonds have broken

and atoms have been emitted than in configuration (J), which shows a more or less intact structure. Hence it appears that the $(14, 0)$-tube has experienced more severe damage than the $(8, 8)$-tube. However, in order to draw a more definite conclusion about how chirality affects the bending process, a larger set of simulations is needed.

5. Conclusions

We have studied toroidal carbon nanotubes and nanotube bending for two different chiralities using molecular dynamics simulations. Our previous work [1] indicated that there exists a critical tube radius, below which the torus buckles, but the buckling does not change the hexagonal bonding configuration although the bonding angles change to account for the buckles. In this work we report the formation of pentagon–heptagon defect pairs when the buckled nanotori have been heated up to very high temperatures. These defects were found to settle mainly at the non-buckled low-strain sections of the torus.

In the bending simulations we observed buckling for sufficiently large local curvature, buckle propagation, bond breakage, single atoms and atom clusters shooting forcefully away from the structure and fracture depending on the local strain in the structure. Our simulations seem to indicate that the nanotube chirality affects at which stage of bending these different processes occur. It can also be concluded that in many ways the behaviour of the tube under constant bending strain seems to be locally similar to the behaviour found in toroidal structures. It should be noted that in the extreme case the bending configurations are far from equilibrium, and that the interatomic model potential used in this work might not be able to describe such a situation accurately.

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