Dynamics of the Formation of Carbon Nanotube Serpentines

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Recently, Geblinger *et al.* [Nat. Nanotechnol. **3**, 195 (2008)] reported the experimental realization of carbon nanotube *S*-like shaped nanostructures, the so-called carbon nanotube serpentines. We report here results from multimillion fully atomistic molecular dynamics simulations of their formation. We consider one-μm-long carbon nanotubes placed on stepped substrates with and without a catalyst nanoparticle on the top free end of the tube. A force is applied to the upper part of the tube during a short period of time and turned off; then the system is set free to evolve in time. Our results show that these conditions are sufficient to form robust serpentines and validates the general features of the "falling spaghetti model" proposed to explain their formation.

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Carbon nanotubes (CNTs) have been the subject of intense research, mainly due to their unique mechanical, electronic, optical, and thermal properties. In particular, these structures may have important applications in nanoelectronics [1–5]. However, some of these applications would require arrays of nanotubes of high quality and uniformity (identical chirality). The synthesis of a large amount of CNTs with specific chirality remains an unsolved problem [6]. One possible solution to overcome these limitations could be the use of carbon nanotube serpentines (CNSs). CNSs are *S*-like shaped nanostructures, composed of a series of straight, parallel, and regularly spaced segments, connected by alternating *U*-shaped turns (Fig. 1). CNSs were synthesized in 2008 by Joselevich's group [6–8], and recently other groups have reported similar results [9–11]. A recent resonance Raman spectroscopy study showed the potential for tube-substrate engineering using such systems [8].

CNS formation has been qualitatively explained based on the "falling spaghetti mechanism" [6,7]. The serpentines would be formed in a two-step process, where the isolated nanotubes are grown standing up from the silicon dioxide stepped substrates under the influence of a gas flux and, at a second stage, the tube would fall down preferentially along the steps, creating the oscillatory patterns (that propagate along the gas flow direction), like spaghetti falling on a tilted bamboo mat [6]. The force that would be primarily responsible for the tube fall is supposed to be the result of the strong nanotube-surface van der Waals interactions.

In this Letter we present the first modeling of the dynamics of formation of carbon nanotube serpentines. We have carried out multimillion fully atomistic molecular dynamics simulations with the CHARMM molecular force field [12], using the well-known high-performance parallel molecular dynamics NAMD code [13] in its CUDA implementation [14]. We have used quartz stepped substrates (see inset Fig. 1), which were used in the experiments [6–11]. For comparison purposes we have also considered graphite substrates. For the quartz substrate (alpha type with a miscut angle of 10.3 degrees, in order to mimic the experimental conditions), $h = 0.54$ nm and $L = 2.98$ nm, while for the graphite one, $h = 0.68$ nm and $L = 3.0$ nm, respectively. We did not use periodic boundary conditions and considered the substrates in vacuum. More detailed structural information is provided in the Supplemental Material [15]. For the serpentine structures we considered long tubes (about 1 micron in length), with and without a catalyst nanoparticle present on the free tube end. An external forward force (mimicking the flow gas in the experiments) was applied to the suspended part of the tube only during a certain period of time and then turn off. The system is then set to freely evolve in time. A continuous applied force would generate a larger kinetic energy to the tube and for the same time of the simulations the serpentine length, as well as the *S*-shaped segment separation values, would be larger. Consequently, longer tubes and larger substrates are needed, which make the simulations cost prohibitive or even impossible. There is a limit to the size of the structure the NAMD code [13] can handle, and the structures we used here are very close to this limit. Tests showed that the main qualitative aspects of serpentine formation are not affected by this procedure, the main differences being the length and *S*-shape separation values.

In all simulations, the following protocols were used in order to analyze the dynamics of serpentine formation. A stepped substrate is created from large graphite or quartz slabs (see inset Fig. 1 and Supplemental Material [15]). Typical models contain about 1.5–2.0 million atoms. Next, a long single walled carbon nanotube is generated.

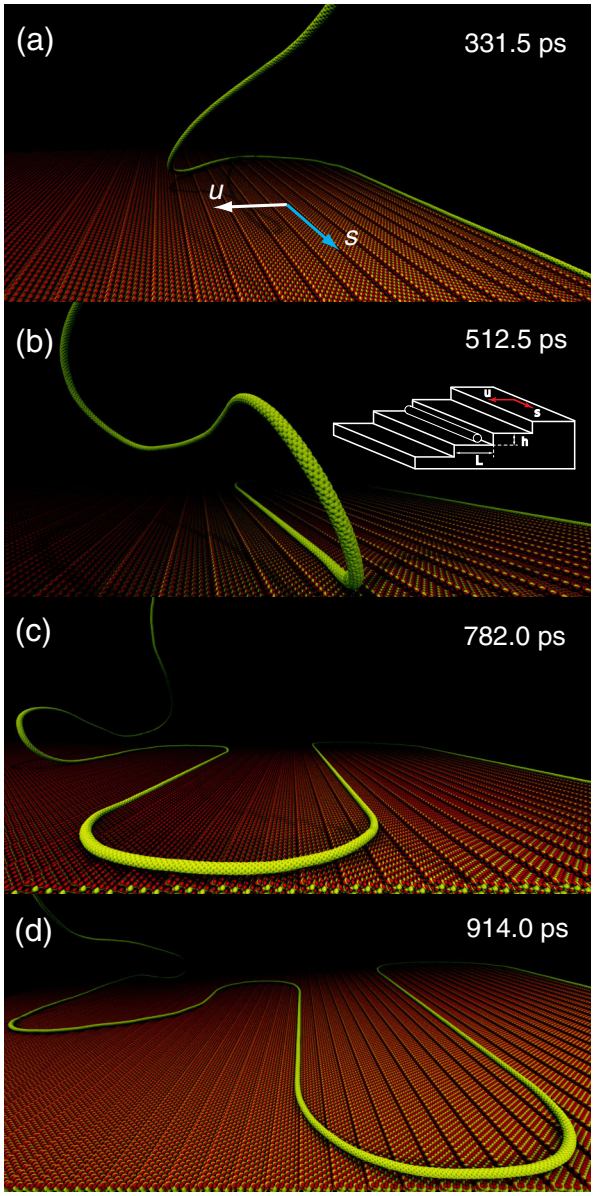

FIG. 1 (color online). Typical snapshots from molecular dynamics simulations of the CNS formation on a stepped quartz substrate. In Fig. 1(a) the **s** and **u** vectors refer to the step orientation and direction of the applied forward force, respectively. The indicated values of time (in picoseconds) are relative to the initial application of the force. In the inset a schematic view of the used stepped substrates is shown. The atoms are displayed with their atomic radius. The equilibrium distance between CNT and the substrate is 0.34 nm. See text for discussions. See also video 01 in the Supplemental Material [15] for the whole serpentine formation.

For comparison, we have considered (6,0) and (12,0) nanotubes, with diameter values of 4.70 and 9.40 Å, respectively. The tubes are bent at an angle of 90° resulting in two straight sections of ~350.0 and ~9, 650.0 Å, (see Supplemental Material [15]). Then, the tubes are placed on the substrates in such a way that their short section is along a step (see Fig. 1). We have considered cases with and without the presence of a catalyst particle placed at the top free end of the suspended CNT. The used mass particle was about 5500 amu, in order to mimic the experimental conditions [6,7], and consisted of a cluster of 96 iron atoms placed in the same carbon atom positions on the free end serpentine tube, bonded with each other and with the carbon atoms through sp^2 bonds. We ran simulations with different particles of different sizes and shapes, and although the degree of damping changes somewhat, the main conclusions are not dependent on this. We ran the simulations with and without the catalytic particle in order to determine whether its presence would significantly affect the dynamics of serpentine formation. In all the simulations we kept the substrate atomic positions frozen. Before running the MD simulations the CNT geometries were optimized and the system equilibrated in the canonical ensemble ($T = 300$ K).

For the equilibration processes in the molecular dynamics simulations, we used the Langevin thermostat [12] and the Brunger-Brooks-Karplus integration algorithm. After this necessary step, the simulations were carried out on the microcanonical ensemble, and the time integration was performed with the velocity Verlet algorithm. An external forward force (along **u** direction, see Fig. 1) was applied to the suspended part of the tube (value 0.001 kcal/mol/Å/atom, ~0.7 pN/atom) during 36.0 ps. Then the force was turned off, the system was set free to evolve in time, and the tube dynamics were recorded. These specific sets of values were chosen after some exploratory simulations and found to be effective to produce well-formed serpentines. We observed that, without the use of the external force, the tube falls on the substrate and on itself, in an irregular form, and no serpentine is formed.

In Fig. 1, we show typical snapshot sequences from molecular dynamics simulations of a serpentine formation on a quartz substrate. The indicated time (in pico seconds) is in relation to the elapsed time due to the application of the external force. As the process starts, the strong surface-nanotube (van der Waals) interactions cause the tube to fall down, initially perpendicular [Fig. 1(a)] and then along the steps [Fig. 1(b)], exhibiting rapid oscillatory movements, while part of it simultaneously keeps going on forward due to the initial applied force. When the tube reaches a critical inclination angle, it makes a U-turn. This repeated process leads to the formation of the serpentine with multiple U-turns [(Fig. 1(c) and 1(d)], while the remaining suspended part of the tube continues to exhibit random motion. These processes are better visualized in the video 01 of the Supplemental Material [15]. The obtained serpentine structures reproduce quite well the general structural features observed in the experiments [6–11]. It should be stressed that this critical inclination angle is very important and it contributes to determine the morphology and quality of the formed serpentines. In the simulations and in the experiments, this angle value depends on many factors,

such as the tube size and diameter, flux flow values, substrate quality, etc.

For the same type of tube, the separation between U-turn segments can, in principle, be controlled by varying the applied force (larger force values would generate larger segment separations). The obtained nonuniformity of these segments (again consistent with what is observed in the experiments) is a consequence of the kinetic or thermal fluctuations at nanoscale and more difficult to control. In the experiments the nonuniformity can be attributed, among other factors, to the fluctuations in the gas flux (intensity and directions) [6–11].

We have also investigated whether the nanoparticle (present in the experiments) can have an active role in the serpentine formation. We ran simulations with and without a particle at the top of the tube. Our results showed that the particle plays indeed an active role. It helps to damp large amplitude tube oscillations. These oscillations significantly contribute to prevent the formation of more uniformly shaped serpentines.

The serpentine stability is in great part due to the surface adhesion. In order to investigate whether serpentines could also be formed on different substrates, we created an idealized stepped substrate made of graphite. Our results (Fig. 2) showed that well-formed serpentines are also possible on graphite substrates (see video 02 in the Supplemental Materials [15]).

The main differences in the dynamics of serpentine formation for the different substrates are that, while for quartz once formed the U-turn structures remain virtually motionless, on graphite they remain moving for a long time. Also, on quartz, in some cases, the tube lies on the middle of the steps, while on graphite the tube always lies at the corners of the steps (see video 01 and video 02 in the Supplemental Material [15]). These aspects can be understood in terms of the different energy profiles experienced by the tube on quartz and graphite substrates. In Figs. 3 and 4 we present the energy profiles for a straight and U-turn tube segments on quartz and graphite. As we can conclude from these figures, the quartz substrate is "stickier" (deeper energy valleys) than graphite; thus, it more efficiently damps the tube oscillations and traps the tube, which can occur at any part of the steps. The graphite substrate is too "smooth," thus allowing the tube to oscillate for a longer time and with a well-defined energy minima only at the corners of the steps. In spite of these aspects, it is also possible to have well-formed serpentines on graphite substrates. It seems that the steps are much more important to induce serpentine formation than the materials of the substrates.

It should be stressed that the crystal structure by itself contributes to make it stickier depending on the surface topography. This effect goes beyond the different nonbond interactions between the nanotube and the different substrates (quartz and graphite). The existence of the energy valleys contribute to trap the nanotube on these related regions, increasing the friction and consequently making it stickier.

In order to better understand the nanotube structural changes, during the processes leading to serpentine formation, we calculated the temporal evolution of the tube internal strain forces between pairs of neighboring atoms over a specific nanotube region. Typical results, for the case of a (6,0) tube, are presented in slide 16 of the Supplemental Material [15]. Topologically, this carbon nanotube can be considered as formed by a series of six-atom rings interconnected by sp^2 bonds. The forces acting on the atoms exhibit great fluctuations, due mainly to elastic deformations (as a consequence of the interactions

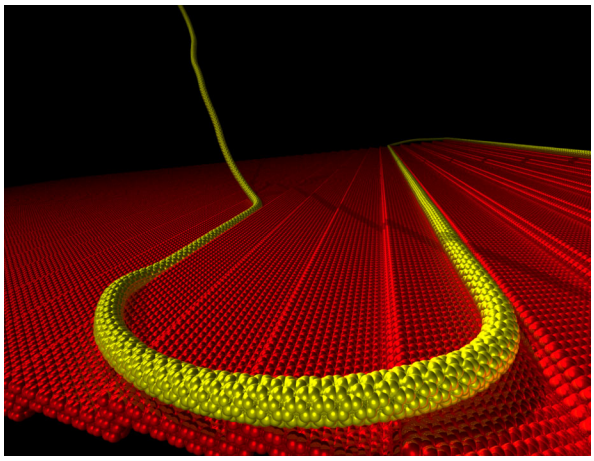

FIG. 2 (color online). Typical snapshot from molecular dynamics simulations of the serpentine formation on a stepped graphite substrate. The atoms are displayed with their atomic radius. The equilibrium distance between CNT and the substrate is 0.34 nm. See text for discussions. See also video 02 in the Supplemental Material [15] for the serpentine formation on this substrate.

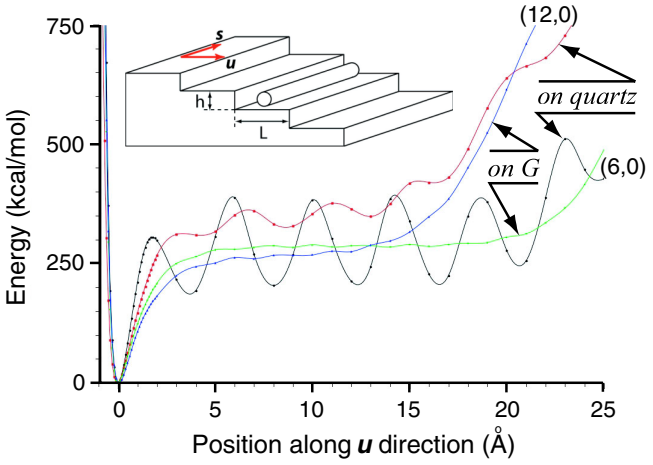

FIG. 3 (color online). Energy profiles for (6,0) and (12,0) zigzag nanotube segments placed parallel to a step on quartz and graphite (G) substrates, when shifted along the **u** direction of the steps.

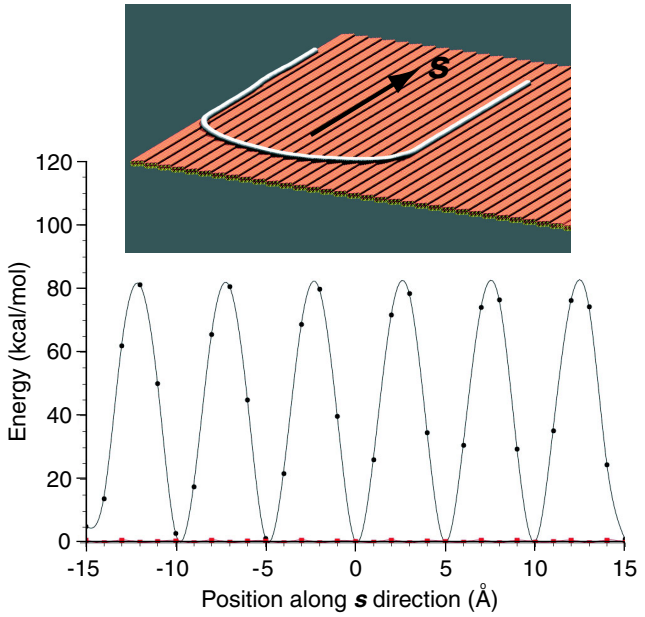

FIG. 4 (color online). Energy profiles for U-shaped nanotubes placed on quartz and graphite stepped substrates, when shifted along the **s** step direction. The curve in black (red) represents the interaction energy of the tube with the quartz (graphite) substrate.

with the substrate) and thermal fluctuations. At the moments just before the formation of a given U-turn, the forces on certain atoms can substantially increase [greater than 30 kcal/mol/Å (> 2 nN)]. It should be remarked that these specific force values are dependent on the serpentine geometries. For structures with large U-turn separations it is expected that these force values will be smaller.

A more comprehensive view of the force profiles of the first U-turn formation on a graphite substrate (the critical process for serpentine formation) is presented in slide 17 of the Supplemental Material [15], where the results displayed in slide 16 [15] are presented for three different tube regions at different times. Initially, the external forward force is applied to the tube, and 360 ps later the first U-turn is formed. The force on each of the six atoms of the analyzed rings varies ~10 kcal/mol/Å. However, between ~90 and ~190 ps, the forces increase on all the atoms up to ~35 kcal/mol/Å, at the moments of U-turn formation. This same behavior is observed in the other rings at different times. As the tube falls on the substrate, an elastic deformation wave is created and it propagates along the tube [Figs. (b) and (c) of slide 17 [15]]. The stress values of the tube segments, parallel to the steps and in contact with it, return to their previous values after the U-turn formation. The process is repeated at each U-turn structure, leading to the serpentine formation.

From the simulations and force profile analysis, it is possible to explain how the serpentines are formed. The process involves a balance of different kind of forces, elastic deformations, stress-strain force distributions modulated by the materials and format of the substrate steps. As the forward force is applied, the tube starts to move forward, but at the same time the interactions with the substrate (mainly van der Waals forces) pulls it down toward the substrate. As the tube segments start to interact with the substrate, elastic waves (deformations) are generated and propagate through the tube which tends to align it with the substrate steps. This continues until the elastic limit (maximum stress) is reached (which depends on multiple factors, such as kind of substrate, temperature, applied external force, catalytic particle, etc.) and the forward tube force or velocity overcomes the elastic deformation, leading to an U-turn formation. The repetition of these processes leads to serpentine formation. From the simulations we observed that, as far as the top part of the tube continues to be ahead of its main body, serpentinelike structures can be formed. When this condition is not satisfied, the tube falls on itself, producing looped or ill-formed serpentines. Interestingly, the simulations showed that, although complex and involving many factors, the qualitative general trends of the serpentine formation are basically the ones of the proposed "falling spaghetti mechanisms" [6].

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[15] See Document No. E-PRLTAO-XX-XXXX for a Powerpoint presentation contaning Supplemental Material and videos of the structural evolution and formation of carbon serpentines on different substrates. A direct link to this document may be found in the online articles HTML reference section. The document may also be reached via the Supplemental Material homepage (http://link.aps.org/supplemental/10.1103/PhysRevLett.110.105502) or from ftp.aip.org in the directory /epaps/. See the Supplemental Material homepage for more information.