On the Formation of Carbon Nanotube Serpentines: A Multi-Million Fully Atomistic Molecular Dynamics Investigation

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Abstract

Carbon nanotubes (CNTs) have been subject of intense research in the last decades, mainly due to their unique mechanical and electronic properties. However, their disseminated use in many different applications has been limited by the experimental difficulties in producing large amounts of CNTs with specific diameters and chiralities.

One possible solution to overcome these limitations could be the use of carbon nanotube serpentines (CNSs) [1]. CNSs are S-like shaped nanostructures, composed of a series of straight, parallel, and regularly spaced segments, connected by U-shaped turns (Figure 1).

CNS formation has been qualitatively explained based on the "falling spaghetti mechanism"[1,2]. The serpentines would be formed in a two-step process, where the isolated nanotubes are grown standing up from the stepped substrates. The tube would then fall down, preferentially along the steps, as a result of the van der Waals interactions between the tubes and the substrates. These movements can create oscillatory patterns, like spaghetti falling on a tilted bamboo mat [1.2], thus leading to the spontaneous formation of the serpentines.

In this work we present the first modeling of the dynamics of CNS formation. We have carried out multi-million fully atomistic molecular dynamics simulations (MD) using the well-known and tested CHARMM force field, as implemented in the NAMD computer code [3]. We have considered long carbon tubes (about 1 micron in length) and stepped substrates of silicon oxide (used in the experiments [1,2]) and graphite. The graphite substrates were also used to test the dependence of the dynamics of CNS formation on the type and composition of the substrates. Typical systems (nanotube plus substrate) contain up to 2 million atoms.

In order to simulate the formation of the CNSs we considered a CNT placed over the substrate with a significant part of the tube initially perpendicular to the substrate. An external forward force (mimicking the gas flow used in the experiments) was applied to the suspended part of the tube and the system is then set to freely evolve in time.

Our results [4] show that these conditions are sufficient to form robust serpentines. 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, and 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 a 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'' [1-2], thus validating the general features of this model. A typical snapshot from MD simulations, showing a well-formed CNS is shown in Figure 2.

References

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Figures

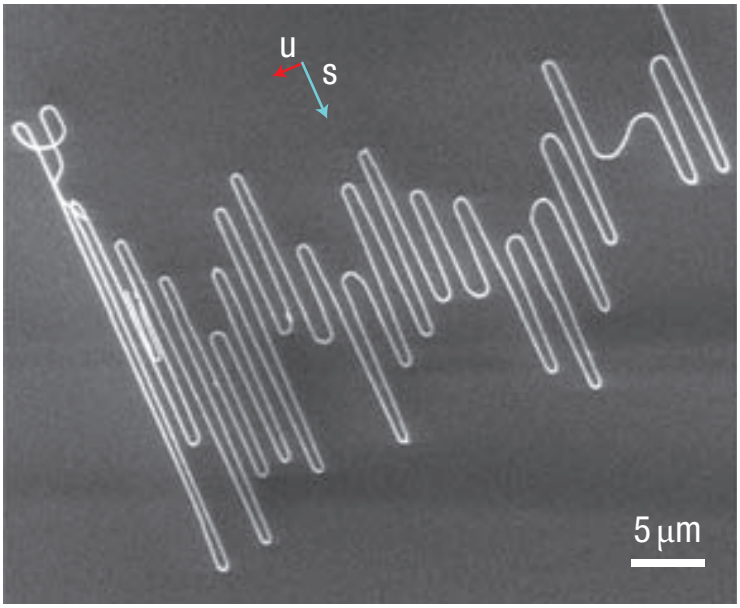

Figure 1. Example of a carbon nanotube serpentine formed on silicon oxide substrate. Figure adapted from reference [1].

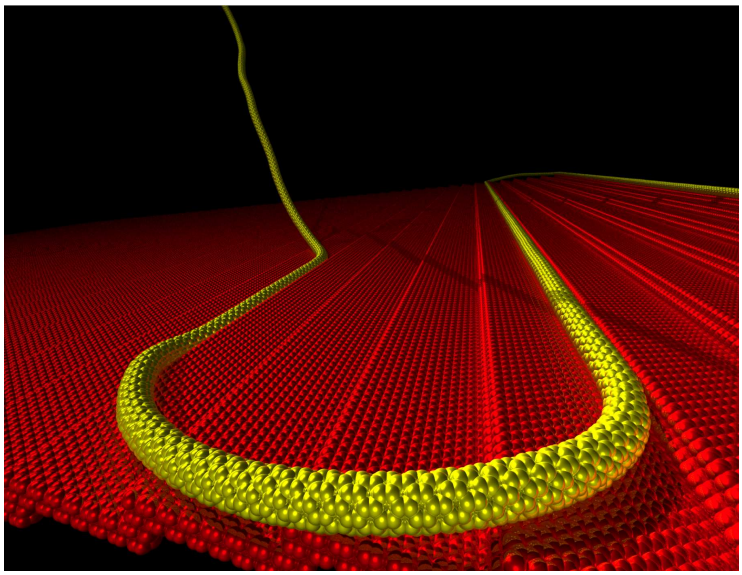

Figure 2. Typical snapshot from molecular dynamics simulations showing a well-formed carbon nanotube serpentine. Figure adapted from reference [4].