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Graphene nanoribbon winding around carbon nanotube

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ABSTRACT

Graphene is a one-atom thick carbon sheet with unique combination of physical and mechanical properties promising for many applications. Bending rigidity of graphene is very small and that is why weak van der Waals forces can create secondary structures such as folds, scrolls, etc. Recently the authors offered a model of a chain with particles moving in a plane to simulate properties of such secondary structures. In the present work the model is modified to enable the study of structure and properties of graphene nanoribbon scrolls (GNS) around carbon nanotubes (CNT). With the help of this model possible equilibrium structures are found and their energies are compared. Particularly it is shown that relatively short graphene nanoribbons wrap CNT without a cavity, producing a dense structure. For nanoribbons with larger length there always appears a cavity between GNS and CNT. Then the temperature effect on the GNS-CNT complex is studied. It is found that the dense complexes at elevated temperatures undergo a phase transition to the states with a cavity. This transition is characterized by a sharp increase in the outer radius of GNS. This finding opens a way to design materials with a huge thermal expansion coefficient in a specific temperature range as well as temperature sensors with a great sensitivity.

1. Introduction

Carbon atoms are able to create a huge variety of structures, including linear strings of sp^1-hybridized atoms called carbyne [1,2], structures composed of sp^2-hybridized atoms, such as fullerenes [3], carbon nanotubes [4], graphene [5–9] and crumpled graphene [10,11], as well as crystalline diamond or diamond-like nanostructures composed of sp^3-hybridized atoms [12,13], and amorphous structures with mixed sp^2 and sp^3 carbon [14]. Relatively weak van der Waals interactions between carbon atoms in sp^2 structures provide stability of secondary structures such as folded and scrolled graphene [15,16], collapsed carbon nanotubes (CNT) [17,18], crumpled graphene [10,11] and other. These structures exist due to the balance between energy reduction with increasing area between graphene sheets interacting via van der Waals forces and increase of energy due to the sheet bending. Bending stiffness of graphene is very small that is why it tends to wrinkle under stress [19–21].

Graphene scrolls have been reported already in 1960 in relation to the abrasion of the graphite lubricant [22]. Mechanism of macroscopic superlubricity has been revealed as follows: graphene patches at a sliding interface wrap around nanodiamonds to form CNS with reduced contact area that slide against the diamond-like carbon surface, achieving an incommensurate contact and substantially reduced coefficient of friction [23].

To date a number of experimental methods for synthesis of scrolled graphene nanoribbons and the study of their structure and properties have been developed [24–31]. Structure and properties of graphene nanoscrolls (GNS), apart from experimental methods, have been extensively studied with the help of first-principles calculations [32–34], molecular dynamics [35–46] molecular mechanics [47] and using the spiral elastic rod model [35,40,48,49]. Theoretical band structure analysis of zigzag (16,0) graphene nanoscroll has been performed [50,51] in frame of the theoretical model developed by the authors. Well-defined CNSs can be formed by single-side hydrogenation and fluorination of graphene, according to the molecular dynamics simulations reported in [52]. GNS can be single-layer or multilayer, the latter are produced by rolling up the multilayer graphene [53,54]. For such multilayer scrolls low-frequency vibrations were measured by Raman scattering [53]. GNS with a polygonal cross-section have

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been observed by high resolution transmission electron microscopy in films synthesized by chemical vapor deposition [30].

Another interesting configuration stabilized by the van der Waals interactions is a graphene scroll around CNT [39,55–58]. Molecular dynamics method has been used to model self-winding of graphene nanoribbon around CNT at low temperatures [39,55–57] and unwinding at elevated temperatures [58]. Nanowires with sufficiently large diameter can also initiate graphene nanoribbon self-scrolling and formation of the core/shell composite nanowires [37,59–62]. Properties of graphene and GNS subject to various levels of vacancy concentrations have been studied to show that addition of vacancies to graphene can lower or eliminate the potential energy barrier that must be overcome to form a stable GNS [63]. A stiff CNT inside GNS increases quality of nanomotor proposed in Ref. [64] by reducing the damping coefficient and increasing the oscillating frequency.

The presence of a cavity in GNS allows their use for storage and transportation of hydrogen [65–67], for gas sorption, storage and separation [68], as an ion channel [69], nanopumps [65,66] or nanofilters [49,70]. An approach has been developed for highly efficient transformation of 2D graphene oxide sheet into 1D GNS with high specific surface area to utilize as a porous cathode scaffold for encapsulating sulfur with a high loading, and also as a conductive skeleton for assembling MnO2 nanowires into a flexible free-standing hybrid interlayer, both enabling high-rate and long-life Li-S battery [71]. The effect of gas adsorption on GNS surface makes the changes in GNS conductance which leads to the changes in the current of sensor consequently [72,73]. GNS are promising for making high-quality supercapacitors [74–76]. It has been found that graphene oxide-based nanocomposites, that include carbon nanoscrolls filled with silver nanoparticles, possess enhanced and lengthened antifungal activity due to the slow release of silver ions [77,78]. Molecular dynamics simulations have been done to examine the gas adsorption properties of nanoscrolls made from various materials, including GNS [79]. In particular, adsorption kinetics for post-combustion CO_2 capture by GNS has been investigated. The simulations have demonstrated that an empty GNS with a roll length of 200 Å adsorbs CO_2 into the center of the roll within 10 ns. Electrical measurements of the transport and breakdown behavior of catalytically grown, multi-turn single-layer GNS having 30–65 nm outer diameter have been undertaken to demonstrate promising nature of such carbon nanostructures for a number of electronic device applications [80]. Optical properties of suspended self-scrolled and aggregated GNS have been investigated in Ref. [81]. Transport properties of GNS in a uniform electric field have been investigated theoretically [82]. It has been found that variations in the electronic structures with the geometry of GNS or the field strength are reflected in their conductance. The possibility of the assembly of 2D carbon nanosheets into 1D nanostructures and their potential applications in energy storage, electronic devices, and sensors have been discussed in a recent review [83]. Formation of nanoscroll bundles can be explained by van der Waals intertubular interaction or/and the incomplete separation and scrolling of graphene sheets.

Three stages of evolution of the system composed of graphene nanoribbon and CNT have been revealed in the molecular dynamics study of a nanomotor [84]. CNS unwinding from CNT due to the CNT rotation has been studied numerically to demonstrate that the unwinding of CNS happens earlier when the CNT has a higher rotational speed or the system is at a higher temperature [85].

It is clear that CNS winding around CNT is a structure promising for many applications and further investigations are needed to uncover all the peculiarities of this structure. It has been proved that molecular dynamics is a powerful tool in the study of the structure and properties of carbon nanopolymorphs. The main difficulty in the use of this method is the necessity to deal with a huge number of degrees of freedom. Under certain physically motivated assumptions the number of degrees of freedom can be greatly decreased allowing to study more efficiently particular modes of atomic motion.

When modeling the folds and scrolls of graphene nanoribbons, until recently full-atomic models were used [35–46,55–62,72]. Such models demand considerable computational resources and do not allow to investigate dynamics of relatively long nanoribbons at long time intervals. To overcome these difficulties, the authors proposed a chain model of graphene nanoribbon, which takes into account its longitudinal and flexural deformation, as well as van der Waals interactions [54,86,87]. In the frame of this model, the possible stationary structures that can be formed by graphene nanoribbon (flat, folded and scrolled configurations, as well as collapsed scrolls) were described, their energy characteristics were compared, low frequency vibrational modes were found, and anomalously high coefficient of radial thermal expansion was detected [86,87]. Later this model was extended to analyze the multilayer GNS [54]. In this work, the model is modified to make it applicable to the analysis of GNS around CNT and to reveal new interesting features of these structures.

2. Simulation details

Firstly, we modify the original chain model of graphene nanoribbon [86] to make it applicable to the analysis of structural and mechanical properties of GNS around CNT.

Single layer graphene nanoribbon of constant width is cut out from a flat graphene sheet. Graphene is an elastically isotropic material whose longitudinal and bending rigidities, for small strain, do not depend on the direction of the applied stress [88]. For definiteness, let us consider the nanoribbon with zigzag edges shown in Fig. 1(a) since all other orientations have nearly same

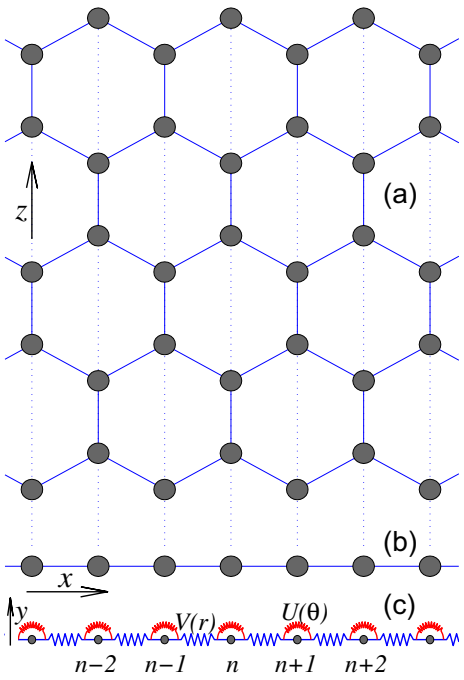

Fig. 1. (a) Flat graphene nanoribbon in *xz* plane with zigzag edges parallel to *x* axis and (b) its chain model with particles able to move only in *xy* plane, each representing a rigid atomic row parallel to *z* axis. Translational cells of the nanoribbon are indexed by *n*. (c) The atomic chain model with particles moving in the *xy* plane describing longitudinal and bending deformation of graphene nanoribbon. The potential $V(r)$ describes the longitudinal rigidity, while the angular potential $U(\theta)$ defines the bending rigidity of the chain.