ELASTIC PROPERTIES OF GRAPHENE-GRAFTHANE NANORIBBONS

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Abstract: The results of theoretical investigation of the atomic structure, deformations, and elastic properties of graphene-graphane nanoribbons (GGN) are represented here. To study the properties of GGN we applied the empirical method based on the bond-order potential developed by Brenner and the tight-binding method. We calculated the Young’s pseudo-modulus of GGN and the strain energy of GGN subject to axial tension and compression. The curve of the strain energy collapse occurs at the axial compression of 0.03-0.04. Plane atomic network subject to axial compression becomes wave-like. This is a so-called phase transition. Elasticity of armchair-graphene nanoribbons is greater than elasticity of armchair nanotubes and graphene nanoribbons with the same width and length.

Introduction

Discovery of new materials leads obligatory to discovery of their new applications and properties. Synthesis of graphene-graphane nanoribbons (GGN) has stimulated very broad and intense research both of theoretical investigation of GGN and their applications. This is due to their unique properties. Graphene is the simplest organic compound made only of carbon and hydrogen atoms. All the known hydrocarbons, until now, are molecules that consist of a carbon backbone with hydrogen atoms attached. Graphane is a semiconductor and it provides a playground for fundamental science and technological applications. The first-principles total energy calculations show that this compound has a very favorable formation energy, quite comparable with other hydrocarbons.

As it is known, carbon nanotubes demonstrate excellent mechanical properties. So it is possible that the other carbon nanostructures such as GGN may also be of high elasticity.

In the present work two methods were used to investigate the elastic properties: the empirical method based on the bond-order potential developed by Brenner and the tight-binding method. To describe the interactions between bonded and non-bonded atoms a multiscale topological network around each atom was introduced.
1. Empirical study

1.1. Computational method

To study the elastic properties and deformations of GGN we applied the empirical method based on the bond-order potential developed by Brenner [1]. The entire system energy is described by the sum of the binding energy $E_b$, the torsional energy $E_{\text{tors}}$, and the van der Waals energy $E_{\text{vdW}}$:

$$E_{\text{tot}} = E_b + E_{\text{tors}} + E_{\text{vdW}}.$$  \hspace{1cm} (1)

To describe the interaction between the atom and its environment we introduce three different regions in the topological network (see figure 1).

As shown in figure 1, there are three regions around atom $i$: the first (near), the second (intermediate) and the third (far). Atoms from the near region are covalently bonded with atom $i$, atoms from the other regions are non-bonded with atom $i$. The far region has no borders.

Each pair of covalently bonded atoms interacts via potential-energy:

$$E_b = \frac{1}{2} \sum_{i=1}^{Nat} \left( \sum_{\langle j \neq i \rangle} \left( V_R(r_j) - B_{ij} V_A(r_j) \right) \right)$$  \hspace{1cm} (2)

This is binding energy. Here $V_R$ is the repulsive pair term, $V_A$ is the attractive pair term, $r_j$ is the distance between the atom with number $i$ and atom $j$ from the near region. The function $B_{ij}$ is a many-body term. This term was introduced to describe the specificity of $\sigma$–$\pi$ interaction. So, the value of the binding energy depends on the position and chemical identity of atoms.

The original bond-order potential by Brenner lacked any torsional interactions around a single bond. To describe the non-bonded interaction between the atoms we introduce the torsional interaction energy to the entire system energy. The torsional potential is given by

$$E_{\text{tors}} = \frac{1}{2} \sum_{i=1}^{Nat} \left( \sum_{k=1}^{Nat} \left( \sum_{l=1}^{Nat} V_{\text{tors}}(\omega_{ijkl}) \right) \right)$$  \hspace{1cm} (3)

The torsional potential $V_{\text{tors}}(\omega_{ijkl})$ is given as a function of dihedral angle $\omega$. The torsion angle $\omega_{ijkl}$ is defined in the usual way as the angle between the plane defined by the vectors $r_k$ and $r_j$ and that of defined by $r_j$ and $r_{kl}$. Here atoms $j$ and $k$ are given from the intermediate region (second) and atom $l$ is given from the third (far) region.

The van der Waals energy $E_{\text{vdW}}$ defines the interaction between non-bonded atoms:

$$E_{\text{vdW}} = \frac{1}{2} \sum_{i=1}^{Nat} \left( \sum_{\langle j \neq i \rangle} V_{\text{vdW}}(r_{ij}) \right)$$  \hspace{1cm} (4)
As known, it is advisable to incorporate the van der Waals potential only if the short-distance potential becomes zero. This is to prevent an artificial reaction barrier from forming due to the steep repulsive wall of the van der Waals potential. To achieve a seamless coupling between a short-distance potential and a long-distance potential we apply our multiscale definition of the topological network around the atom.

The van der Waals interaction energy may be described by the Lennard-Jones, Morse, Buckingham potentials and so on. We use the Morse potential that is given by

\[
V_{\text{Morse}}(r_{ij}) = D_e \left( (1 - \exp(-\beta (r_{ij} - r_e)))^2 - 1 \right) + E_r \cdot \exp(-\beta' r_{ij}), \tag{5}
\]

where \(D_e\) is the average bond energy, \(E_r\) is the repulsion nucleus energy, \(\beta, \beta'\) [2]. The interatomic distance in graphite calculated by the empirical method is equal to 0.1421 nm.

Using the empirical method we studied some GGN with length-to-width ratio \(L / D\) from 2 to 3.22. Nanostructures with ratio \(L / D\) less than 3 are classified as nanoparticles, nanostructures with ratio greater than 3 are classified as nanoribbons. The study of deformations and elastic properties of nanoparticles and nanoribbons was implemented with the help of the following algorithm:

1) Optimization of atomic structure by entire system energy minimization (see equation (1)) on atomic coordinates (the atomic structure obtained from the previous optimization);
2) Tension or compression of the atomic network of a nanoribbon and reoptimization of atomic structure with fixed atoms on the nanoribbon ends;
3) Calculation of the Young’s pseudo-modulus for the elastic tension of a nanoribbon by 1% according to the formula:

\[
Y_p = \frac{F}{D \Delta L}, \tag{6}
\]

where a deformation force is given by \(F = 2\Delta E / \Delta L\). Here \(\Delta E\) is the strain energy, namely, the total energy at a given axial strain minus the total.

1.2. Results of empirical study
We calculated the Young’s pseudo-moduli of the armchair- and zigzag-nanoribbons with different length and width. The dependences of the Young’s pseudo-modulus are shown in figure 2. We can see that the pseudo-modulus increases with the length and decreases with the width. When the length-to-width ratio \(L / D\) becomes 3 and greater than 3 the value of the Young’s pseudo-modulus stops to increase.

We also studied the axial tension and compression of nanoribbons. At first the length is increased or decreased by 1-10 %, then the entire energy is minimized but without affecting the atoms at the both ends. Strain energy of nanoribbons subject to axial tension is presented in figure 3.

The reported results show that the stress-strain curve may be fitted by a parabola. So, at the respective strains from 0 to 0.12 we have the region of elastic deformation. We studied nanoribbons subject to axial compression. The strain energy collapse occurs at the respective strain 0.04.

We compared the elastic properties of the carbon nanotube and the nanoribbon of the same width. We calculated the Young’s pseudo-modulus of the nanotube (5,5) with the perimeter about 2.1 nm and
one of the armchair-nanoribbon with the width 2.3 nm. The Young’s pseudo-modulus of the armchair-nanoribbon is greater than the modulus of the nanotube by 27%.

The dependences of the strain energy and the Young’s pseudo-modulus for graphane-nanostructures are given in figure 4.

![Figure 2. The Young’s pseudo-moduli of nanoribbons](image1)

![Figure 3. Strain energy of nanoribbons subject to axial tension](image2)
2. Quantum-mechanical study

2.1. Computational scheme

Let us consider the unusual process of the axial compression of the nanoribbon. In this work TB was applied to study this process. To study stability of carbon nanoclusters the TB method was earlier presented in [3] and it was successfully implemented. The energy of a system of ion cores and valence electrons is written as

$$E_{\text{tot}} = E_{\text{bond}} + E_{\text{rep}}$$  (7)

Here the term $E_{\text{bond}}$ is the bond structure energy that is calculated as the sum of energies of the single-particle occupied states. Those single-particle energies become known by solving the following equation

$$H |\psi_n\rangle = \varepsilon_n |\psi_n\rangle,$$  (8)

where $H$ is the one-electron Hamiltonian, $\varepsilon_n$ is the energy of the $n$th single-particle state. The wave functions $|\psi_n\rangle$ can be approximated by linear combination

$$|\psi_n\rangle = \sum_{l\alpha} C^n_{l\alpha} |\varphi_{l\alpha}\rangle,$$  (9)

where $\{|\varphi_{l\alpha}\rangle\}$ is an orthogonal basis set, $l$ is the quantum number index and $\alpha$ labels the ions. The matrix elements in equation (8) are calculated after fitting a suitable database obtained from the experiments and were presented in [3]. For carbon compounds the matrix elements are calculated by

$$V_{ab}^{\alpha\beta}(r) = V_{ab}^{\alpha\beta}\left(\frac{p_3}{r}\right)^{p_4} \exp\left\{ p_4 \left[ \left(\frac{r}{P_2}\right)^{p_4} + \left(\frac{P_3}{P_2}\right)^{p_4} \right] \right\},$$  (10)

where $r$ is the distance between atoms.

Term $E_{\text{rep}}$ in equation (9) is phenomenon energy that is a repulsive potential. It can be expressed as a sum of two-body potentials as

$$E_{\text{rep}} = \sum_{a,\beta:|a\rangle} V_{\text{rep}}^{\alpha\beta}(r_{ab}),$$  (11)
where $V_{rep}$ is a pair potential between atoms at $\alpha$ and $\beta$. This two-body potential describes an interaction between bonded and non-bonded atoms and is presented in [3]

$$V_{rep}(r) = p_3 \left( \frac{p_3}{r} \right)^{\rho_3} \exp \left\{ \rho_6 \left[ -\left( \frac{r}{p_2} \right)^{\rho_2} + \left( \frac{p_3}{p_2} \right)^{\rho_2} \right] \right\},$$  \quad (12)

where $i$ and $j$ are orbital moments of wave function, $\gamma$ presents the bond type ($\sigma$ or $\pi$). The values of the parameters $V_{\alpha\beta}^0$, the atomic terms and $p_\alpha$ for carbon compounds are given in table 1 [3].

Optimization of atomic structure is implemented by entire system energy minimization on atomic coordinates (see equation (9)). The study of the compression process was implemented with the algorithm presented earlier. The parameters were fitted from the experimental data for fullerenes and carbon nanotubes. Transferability to other carbon compounds was tested by comparison with *ab initio* calculations and experiments.

Our transferable tight-binding potential can reproduce changes correctly in the electronic configuration as a function of the local bonding geometry around each carbon atom.

**Table 1.** Values of the parameters

| $\varepsilon_s$, $\varepsilon_B$ | $\varepsilon_p$, $\varepsilon_B$ | $V_{ss\sigma}^0$, $\varepsilon_B$ | $V_{sp\sigma}^0$, $\varepsilon_B$ | $V_{pp\sigma}^0$, $\varepsilon_B$ | $V_{pp\pi}^0$, $\varepsilon_B$ |
|-------------------------------|-------------------------------|------------------|-----------------|-----------------|-----------------|
| -10,932                       | -5,991                        | -4,344           | 3,969           | 5,457           | -1,938          |
| $p_1$                         | $p_2$, Å                       | $p_3$, Å         | $p_4$           | $p_5$, $\varepsilon_B$ | $p_6$           |
| 2,796                         | 2,32                          | 1,54             | 22              | 10,92           | 4,455           |

**Figure 5.** Schematic representation of the interaction of $P_z$- and $P_x$-orbital.

All $S$- and $P$-orbitals are given in the real Cartesian coordinates system. To reproduce changes in the electronic configuration of the local bonding geometry around each atom correctly we defined $P_z$-orbital as an axial vector (see figure 5). Each axial vector makes the angle with direction $R_\beta (\alpha, \beta, \theta)$ and it may be written as the geometrical sum of the two vectors:

$$\vec{P}_x = \vec{P}_{xD} + \vec{P}_{x\perp}, \quad \vec{P}_y = \vec{P}_{yD} + \vec{P}_{y\perp}, \quad \vec{P}_z = \vec{P}_{zD} + \vec{P}_{z\perp}$$ \quad (13)
Here $\vec{P}_D$, $\vec{P}_D$, $\vec{P}_D$ are projections to an interatomic direction, $\vec{P}_{\perp}$, etc are projections to an orthogonal direction.

So, to describe the interaction between $P_z$ and $P_x$ (see figure 5) we must write:

$$\vec{P}_x \cdot \vec{P}_z = \vec{P}_D \cdot \vec{P}_D + \vec{P}_{\perp} \cdot \vec{P}_{\perp}$$

(14)

The angle between projections $\vec{P}_D$ and $\vec{P}_D$ is equal to zero, but the other angle between projections to an orthogonal direction is not zero and it is equal to $\gamma$ (see figure 5). As a result of some mathematical transformations we can write the expressions for $\cos \gamma$ and the energy of the interaction between $P_z$ and $P_x$ in the following way:

$$\cos \gamma = \frac{\cos \alpha \cdot \cos \theta}{\sin \alpha \cdot \sin \theta},$$

$$V_{P_xP_z}(r_j) = \cos \alpha \cdot \cos \theta \left(V_{r_{\perp}r_{\perp}}(r_j) - V_{r_{\perp}r_{\perp}}(r_j)\right)$$

(15)

As well known, the expression for the energy of the interaction between $S$ and $P$-orbitals can be defined simply:

$$V_{SP}(r_j) = V_{SP}(r_j) \cdot \cos \theta$$

The presented scheme provides the consideration and calculation of the rehybridization between $\sigma$- and $\pi$-orbitals to reproduce the electronic configuration and the local bonding geometry around each atom. In figure 6 we can see that the atom in $sp^2$ hybridization becomes one in $sp^2\Delta$ hybridization because of a curvature of the topological network. The degree of rehybridization is defined by the pyramidalization angle. This angle is calculated by the following formula:

$$\theta_p = \theta_{\sigma\pi} - \frac{\pi}{2}$$

(16)

Our own program was used to research the nanoribbons with the help of the tight-binding method. It provides the calculation of the total energy of nanostructures, which consist of 50-5000 atoms. We adapted our TB method to be able to run the algorithm on a parallel computing machine (a computer cluster).

So, the presented transferable tight-binding method and the described scheme to reproduce the electronic configuration and the local bonding geometry around each atom are well suited for computer simulations. We tested our scheme by comparison with the experiments for fullerene and some carbon nanotubes.

2.2. Results of quantum-mechanical study

To simulate axial compression the atoms on the ends were fixed on the plates (see figure 7). The plates were moved towards each other to decrease the length by some percent.

The plane atomic network subject to axial compression becomes wave-like. It is a so-called phase transition. The calculation of density of states demonstrates the absence of changes in the electronic structure. However, the topology has nonzero pyramidalization angles. The amplitude of a wave and its period are not constant and they change along the length (see figure 8a). The strain energy collapse occurs at the strain of axial compression 0.03-0.04.
3. Conclusions

- Elasticity of armchair-graphene nanoribbons is greater than elasticity of armchair nanotubes and graphane nanoribbons with the same width and length.
- The curve of the strain energy collapse occurs at the axial compression of 0.03-0.04. Plane atomic network subject to axial compression becomes wave-like. This is a so-called phase transition.
- The curvature of the atomic network because of its compression is suggested to increase the reactivity of the nanoribbon.

References

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