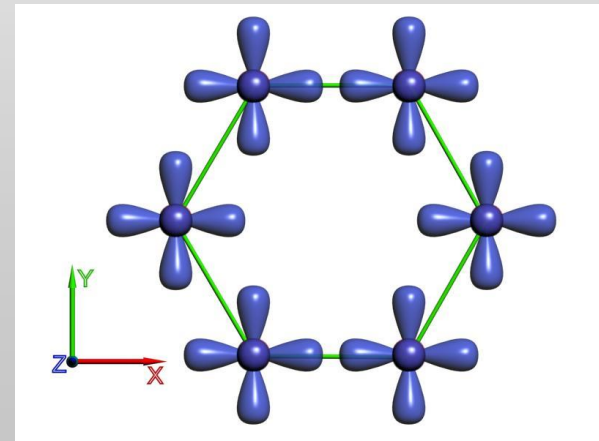


Theoretical research of crooked graphene

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The energy of a system of ion cores and valence electrons is written as

$$E_{tot} = E_{bond} + E_{rep} \quad (1)$$

Here the term E_{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

$$\mathbf{H} |\psi_n\rangle = \varepsilon_n |\psi_n\rangle, \quad (2)$$

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

$$|\psi_n\rangle = \sum_{l\alpha} C_{l\alpha}^n |\varphi_{l\alpha}\rangle, \quad (3)$$

where $\{\varphi_{l\alpha}\}$ is an orthogonal basis set, l is the quantum number index and α labels the ions.

The matrix elements in equation (2) are calculated after fitting a suitable database obtained from the. The overlap matrix elements, which takes into account four types of interaction $ss\sigma$, $sp\sigma$, $pp\sigma$ u $pp\pi$ and the pair repulsive potential are calculated by the formulas:

$$V_{ij\alpha}(r) = V_{\alpha\beta}^0 \left(\frac{p_3}{r} \right)^{p_1} \exp \left\{ p_1 \left[- \left(\frac{r}{p_2} \right)^{p_4} + \left(\frac{p_3}{p_2} \right)^{p_4} \right] \right\}, \quad (4)$$

where i and j are orbital moments of a wave function, α presents the bond type (σ or π).

The bond structure energy is determined by the formula

$$E_{bond} = 2 \sum_n \varepsilon_n \quad (5)$$

This expression is the sum of the energies of molecular orbitals obtained by diagonalization of the Hamiltonian. The parameter n is the number of occupied orbitals, and ε_n is the energy of single-particle orbitals.

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

$$E_{rep} = \sum_{\alpha, \beta \neq \alpha} V_{rep}(r_{\alpha\beta}), \quad (6)$$

where V_{rep} is a pair potential between atoms at α and β . This two-body potential describes an interaction between bonded and non-bonded atoms.

$$V_{rep}(r) = p_5 \left(\frac{p_3}{r} \right)^{p_6} \exp \left\{ p_6 \left[- \left(\frac{r}{p_2} \right)^{p_4} + \left(\frac{p_3}{p_2} \right)^{p_4} \right] \right\}, \quad (7)$$

where i and j are orbital moments of wave function, γ presents the bond type (σ or π). The values of the parameters $V_{\alpha\beta}^0$, the atomic terms and p_n for carbon compounds are given in table 1.

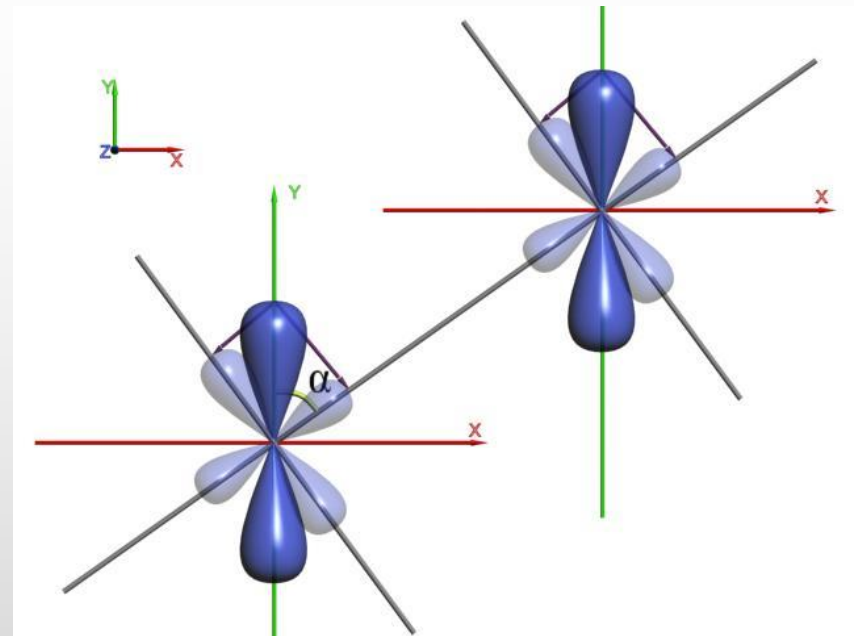
The phenomenon energy (феноменологическая энергия)

Table 1. Values of the parameters

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

Optimization of atomic structure is implemented by entire system energy minimization on atomic coordinates. 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.

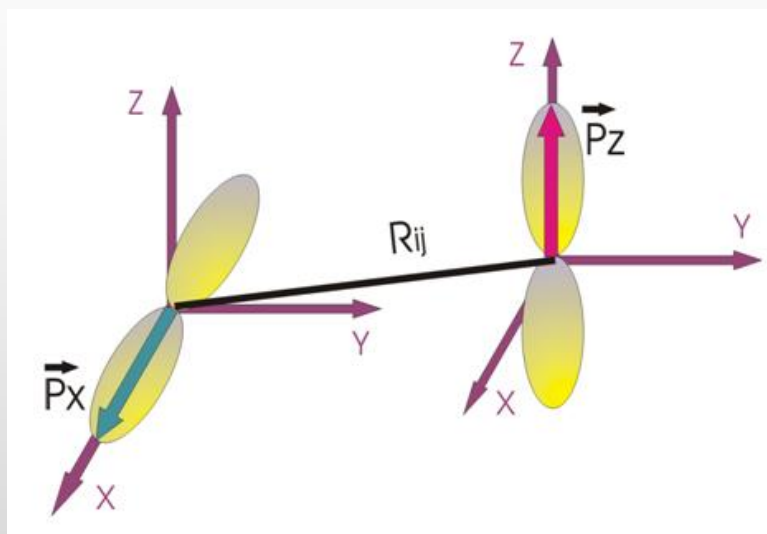
The TB parameters for carbon nanoclusters



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.

	S_1	S_2	S_3	P_{x1}	P_{x2}	P_{x3}	P_{y1}	...	P_{z3}
S_1	ϵ_s	$V_{ss\sigma}^0$	$V_{ss\sigma}^0$	0	$V_{sp\sigma}$	$V_{sp\sigma}$	0	...	$V_{sp\sigma}$
S_2	$V_{ss\sigma}^0$	ϵ_s	$V_{ss\sigma}^0$	$V_{sp\sigma}$	0	$V_{sp\sigma}$	$V_{sp\sigma}$...	$V_{sp\sigma}$
S_3	$V_{ss\sigma}^0$	$V_{ss\sigma}^0$	ϵ_s	$V_{sp\sigma}$	$V_{sp\sigma}$	0	$V_{sp\sigma}$...	0
P_{x1}	0	$V_{sp\sigma}$	$V_{sp\sigma}$	ϵ_p	V_{pp}	V_{pp}	0	...	V_{pp}
P_{x2}	$V_{sp\sigma}$	0	$V_{sp\sigma}$	V_{pp}	ϵ_p	V_{pp}	V_{pp}	...	V_{pp}
P_{x3}	$V_{sp\sigma}$	$V_{sp\sigma}$	0	V_{pp}	V_{pp}	ϵ_p	V_{pp}	...	0
P_{y1}	0	$V_{sp\sigma}$	$V_{sp\sigma}$	0	V_{pp}	V_{pp}	ϵ_p	...	V_{pp}
...
P_{z3}	$V_{sp\sigma}$	$V_{sp\sigma}$	0	V_{pp}	V_{pp}	0	V_{pp}	...	ϵ_p

The Hamiltonian



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*-orbital as an axial vector. Each axial vector makes the angle with direction R_{ij} (α, β, θ) and it may be written as the geometrical sum of the two vectors:

$$\vec{P}_x = \vec{P}_{xD} + \vec{P}_{x\perp},$$

$$\vec{P}_y = \vec{P}_{yD} + \vec{P}_{y\perp}, \quad \vec{P}_z = \vec{P}_{zD} + \vec{P}_{z\perp}$$

Here \vec{P}_{xD} , \vec{P}_{yD} , \vec{P}_{zD} are projections to an interatomic direction, $\vec{P}_{x\perp}$, etc are projections to an orthogonal direction.

So, to describe the interaction between P_z and P_x we must write:

$$\vec{P}_x \cdot \vec{P}_z = \vec{P}_{xD} \cdot \vec{P}_{zD} + \vec{P}_{x\perp} \cdot \vec{P}_{z\perp}$$

σ - bonding π - bonding

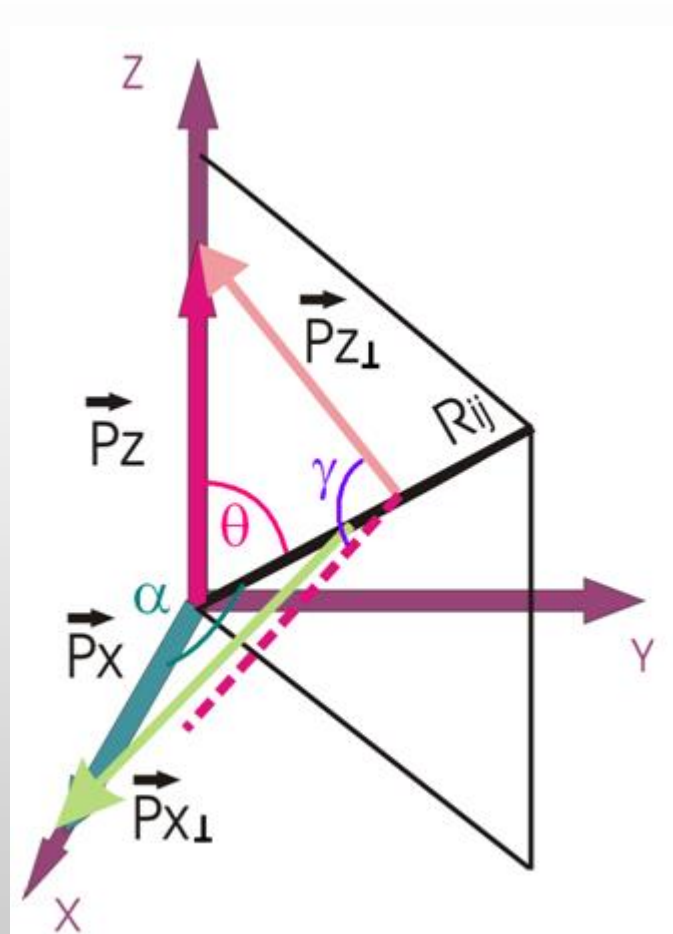
The interaction of π -orbitals

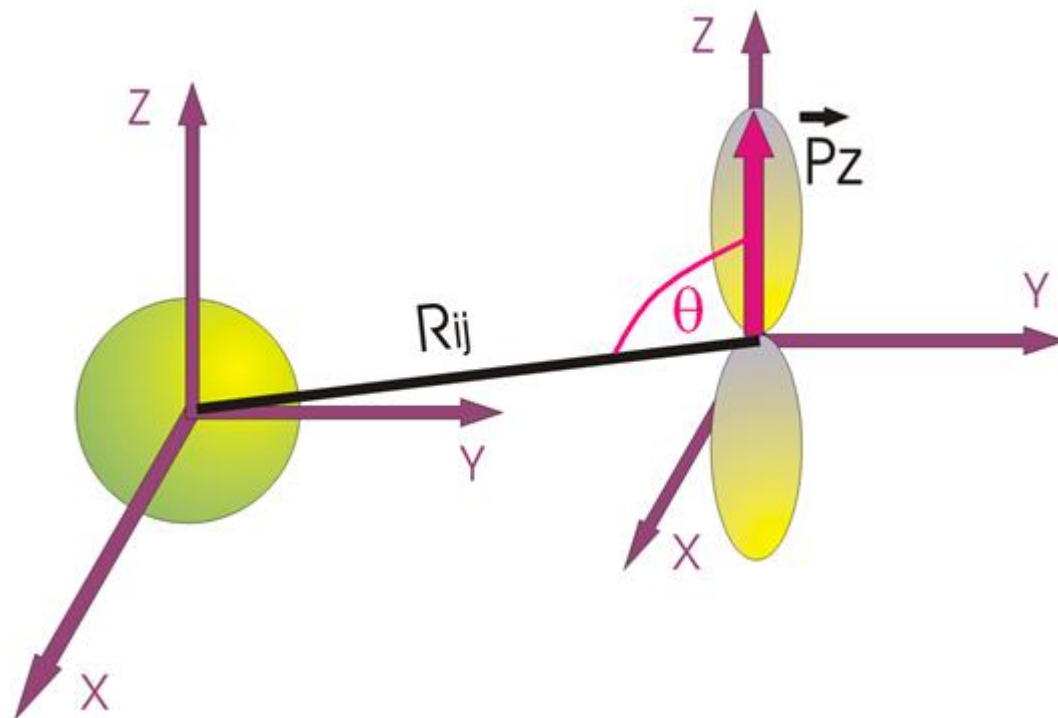
The angle between projections \vec{P}_{xD} and \vec{P}_{zD} is equal to zero, but the other angle between projections to an orthogonal direction is not zero and it is equal to γ .

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:

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

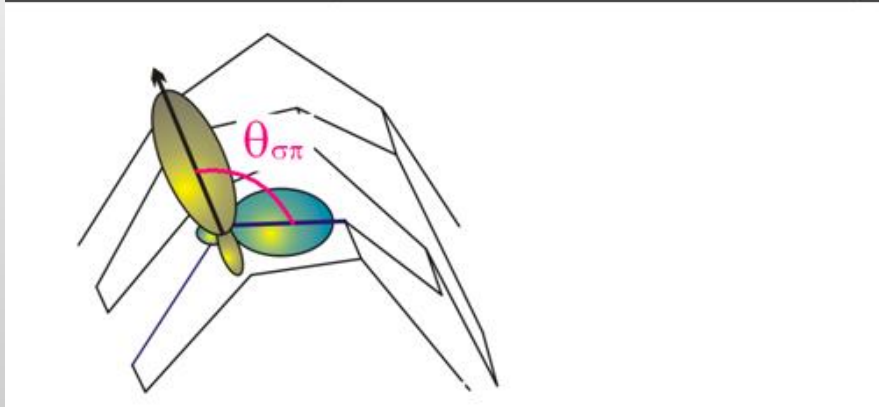
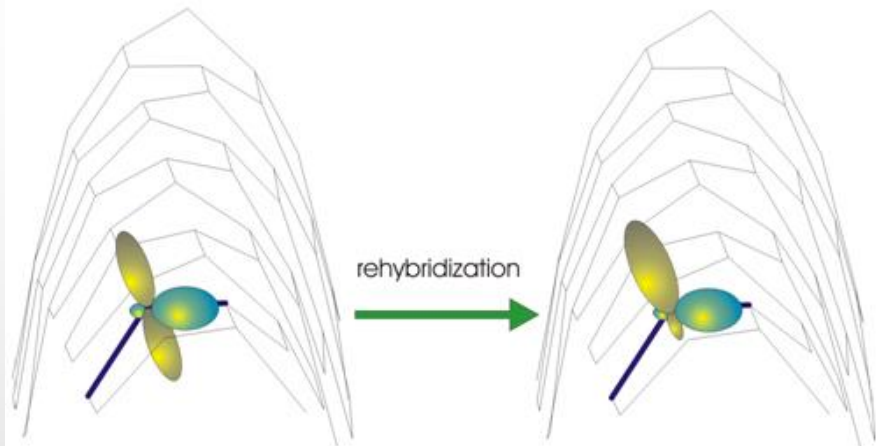
$$V_{P_x P_z}(r_{ij}) = \cos \alpha \cdot \cos \theta \left(V_{P_x P_z}^{\sigma}(r_{ij}) - V_{P_x P_z}^{\pi}(r_{ij}) \right)$$





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

$$V_{SP_z}(r_{ij}) = V_{SP_z}^{\sigma}(r_{ij}) \cdot \cos \theta$$



The presented scheme provides the consideration and calculation of the rehybridization between σ - and π -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+d} 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:

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

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).

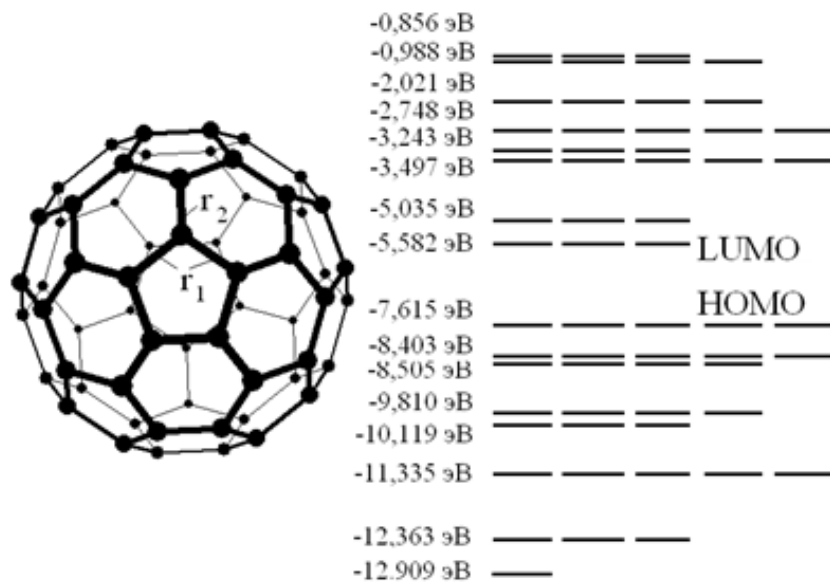
The rehybridization

The electron spectra

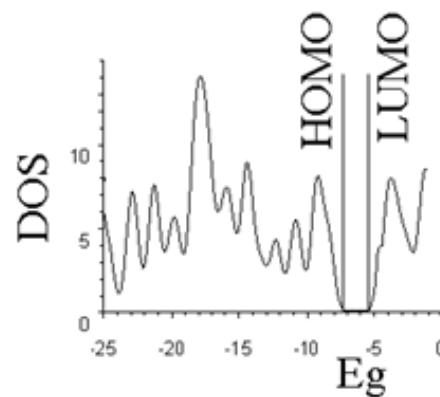
So, the presented transferable tight-binding potential and the described scheme to reproduce the electronic configuration and the local bonding geometry around each atom are well suited for computer simulations of covalently bonded systems in both gas-phase and condensed-phase systems.

We have tested our scheme by comparison with experiments for fullerene and some carbon nanotubes. In the table the spectra of the π -orbitals and density of states are presented.

Results are in reasonable agreement with experimental data.

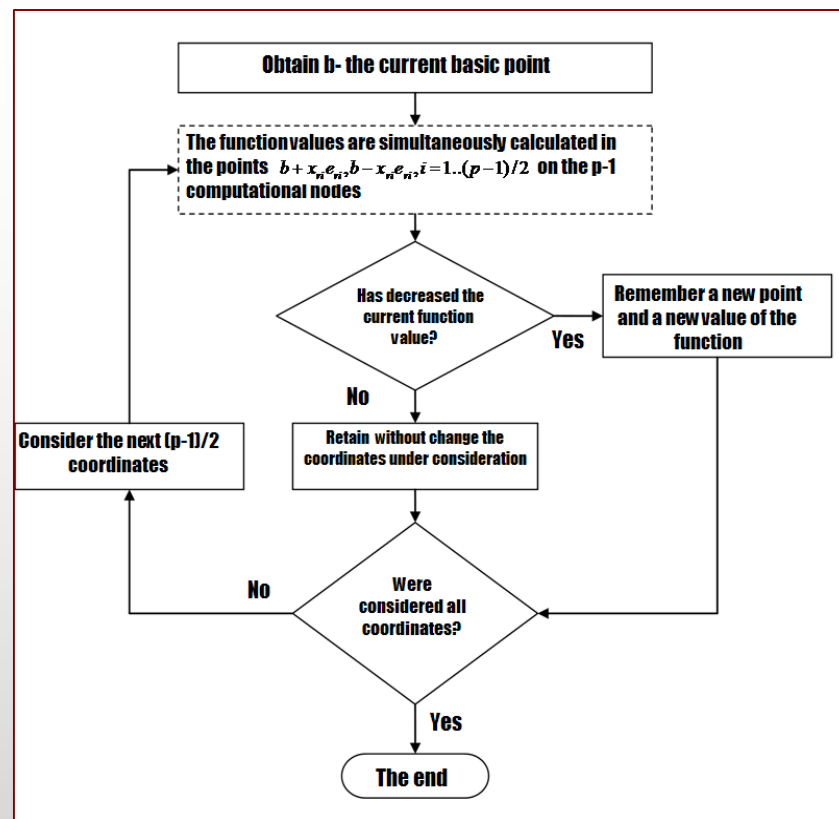
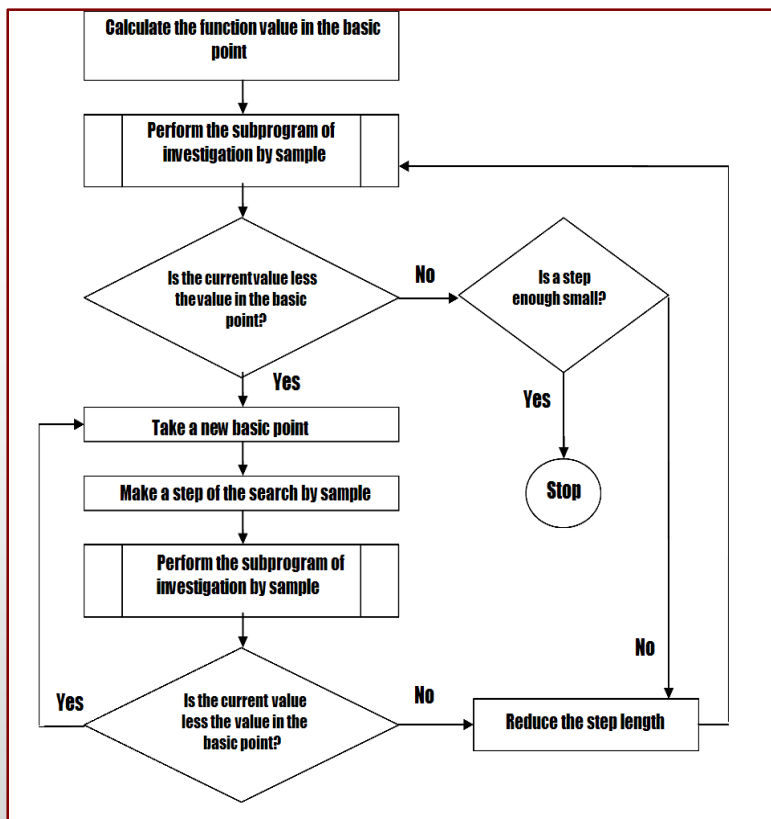


Fullerene C₆₀ and the spectra of π -orbitals



IP = 7.61 eV, E_g = 2 eV

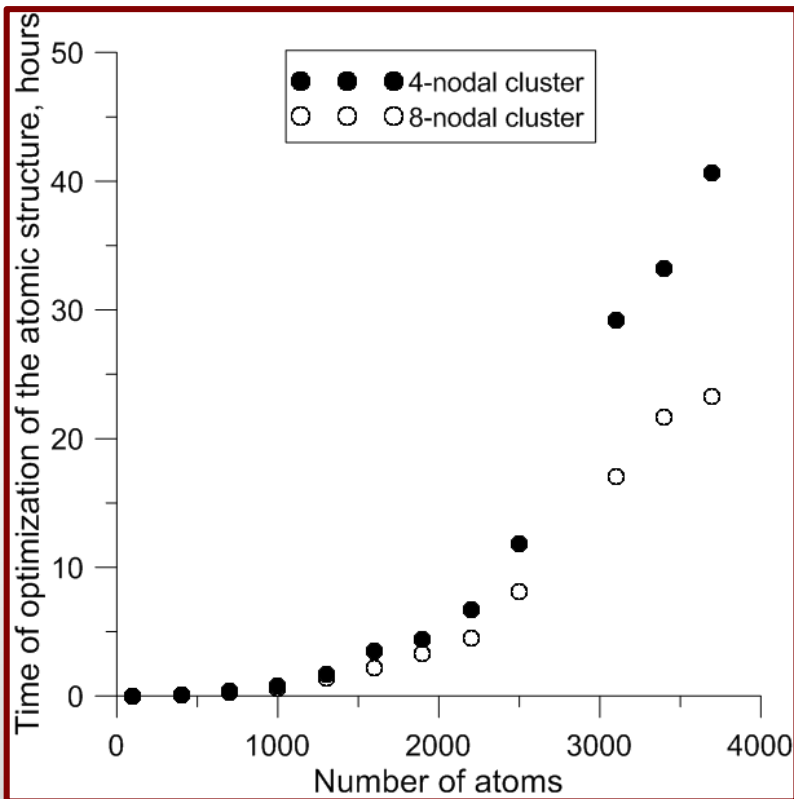
r_1 = 1.45 Å, r_2 = 1.40 Å.



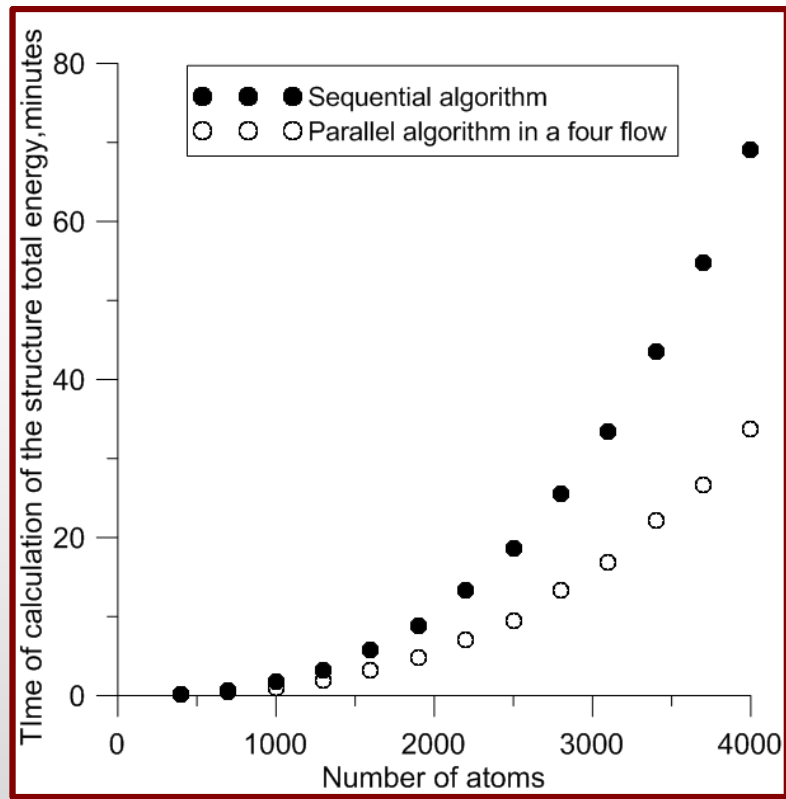
Block scheme of the modified Hooke-Jeeves method

Block scheme of the subprogram of investigation by sample

1. Optimization of the initial atomic structure (Optimized Hooke-Jeeves method)



At optimization of the structure with transition from four block cluster on eight block cluster the efficiency of calculations increases in 1.4 times.



At carrying out of calculations by means of the parallel manner in four flow the efficiency of calculations increases in average of 1.8 times in comparison with sequential method.

Efficiency of the parallel calculations

Research of the local stress field of the atomic grid of graphene nanoribbons and prediction of the appearance of defects in compression process

The method of the calculation of the local stress of atomic network include following steps:

1. the optimization of the atomic structure of the stable unstrained graphene sheet by the minimization of the total energy by the coordinates of atoms;
2. the calculation of distribution of the bulk energy density on atoms of the stable unstrained graphene;
3. the optimization of the atomic network of the deformed structure;
4. the calculation of distribution of the bulk energy density on atoms;
5. the calculation of the local stress field of atomic.

The bulk energy density of the bamboo-like nanotube was calculated by formula:

$$w_i = \left(\sum_{j(\neq i)} (V_R(r_{ij}) - B_{ij}V_A(r_{ij})) + \sum_{j(\neq i)} \left(\sum_{k \neq i, j} \left(\sum_{l \neq i, j, k} V_{tors}(\omega_{ijkl}) \right) \right) + \sum_{j(\neq i)} V_{vdW}(r_{ij}) \right) / V_i \quad (8)$$

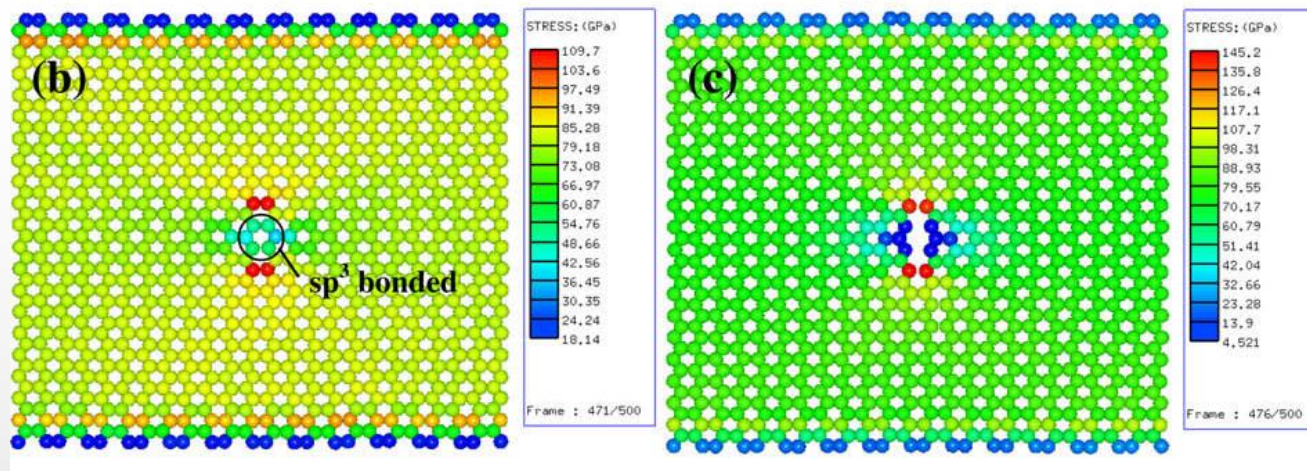
where $V_R(r_{ij})$ and $V_A(r_{ij})$ - the pair potentials of repulsion and attraction between chemically bonded atoms which are determined by the atoms type and the distance between them. r_{ij} is the distance between atoms i and j , i and j - are the numbers of interaction atoms; B_{ij} is the multiparticle term correcting interaction energy of the atoms pair $i - j$ considering specificity of interaction of σ -and π -electron clouds; $V_{tors}(\omega_{ijkl})$ is the torsional potential which is the function of the linear dihedral angle ω_{ijkl} constructed on the basis of atoms with an edge on bond $i - j$ (k, l are the atoms forming chemical bonds with i, j). $V_{vdW}(r_{ij})$ is the van der Waals interaction potential between the chemically unbounded atoms; $V_i = \frac{4}{3}\pi r_0^3$ is the occupancy volume of the atom i , r_0 is the Van der Waals radius of the carbon atoms which is equal of 1.7 Å

The strain of the atomic framework near the atom with number i is calculated as:

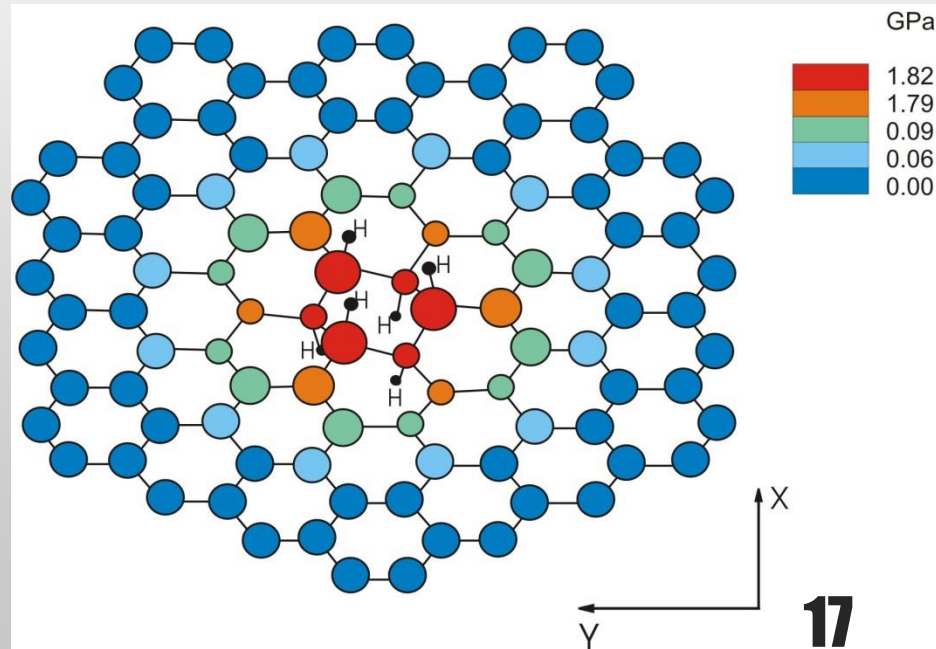
$$\sigma_i = |w_i - w_i^0|$$

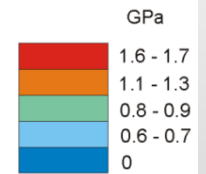
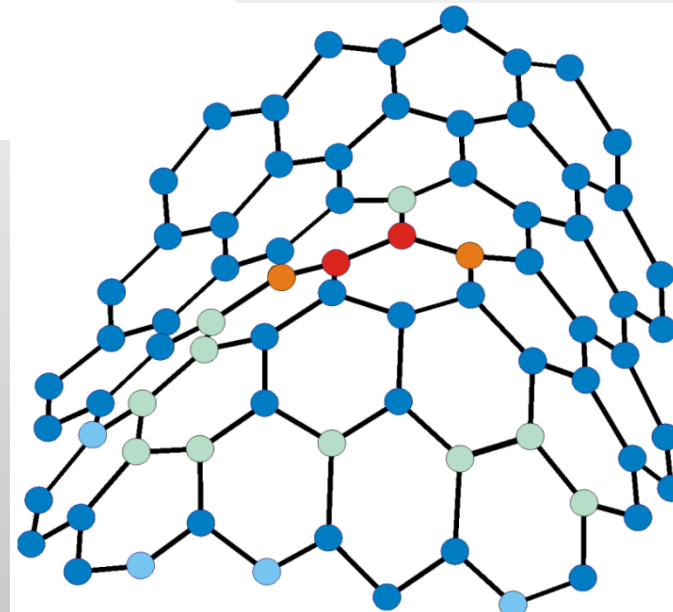
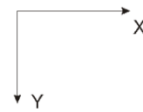
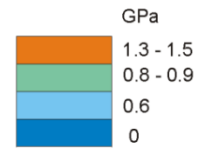
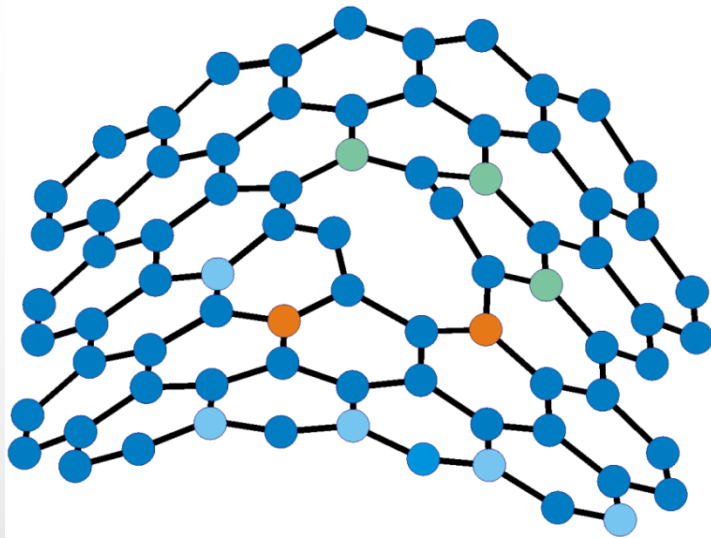
where w_i^0 is the bulk energy density of atom i of the graphene sheet which is in equilibrium; w_i is the bulk energy density of the CBNT. The value of the bulk energy density w_i^0 in the centre of the graphene sheet is equal of -58.609 GPa. At the edges of the graphene sheet the bulk energy density is more because the atoms of the edges have only two links with other carbon atoms. It is equal -41.546 GPa. It is suggested that stress is equal to zero on the atoms in center and on edges.

Q.X. Pei Y.W. Zhang,
V.B. Shenoy,
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(2010) 898–904



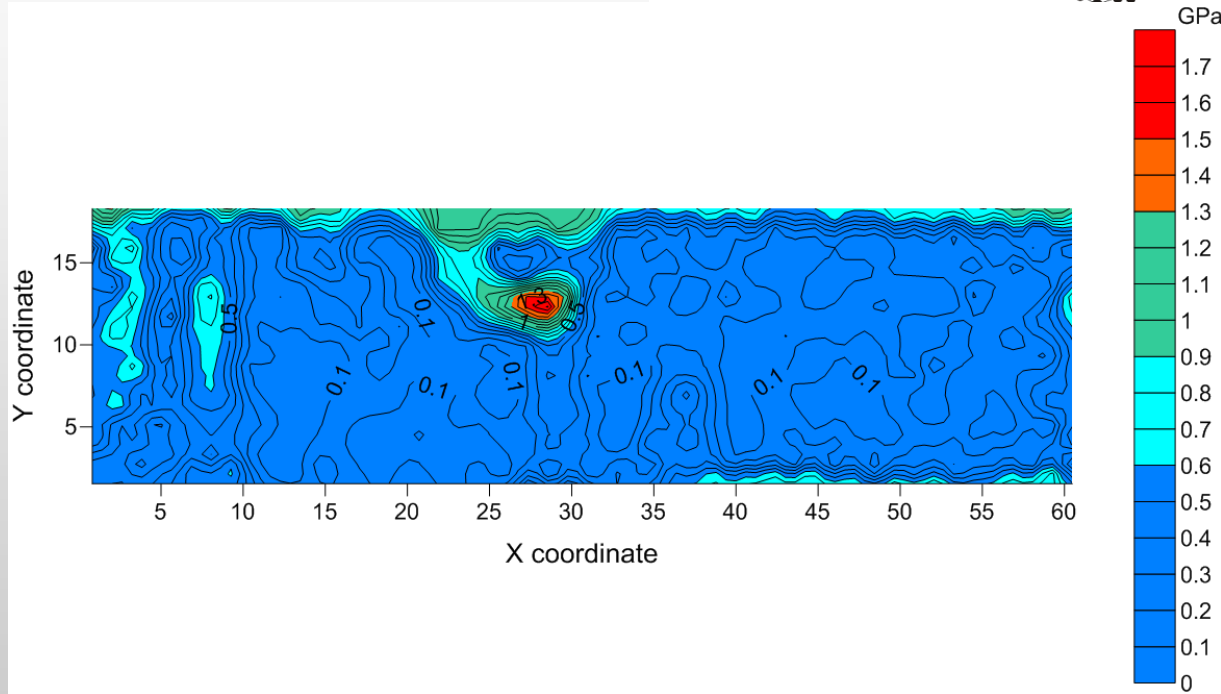
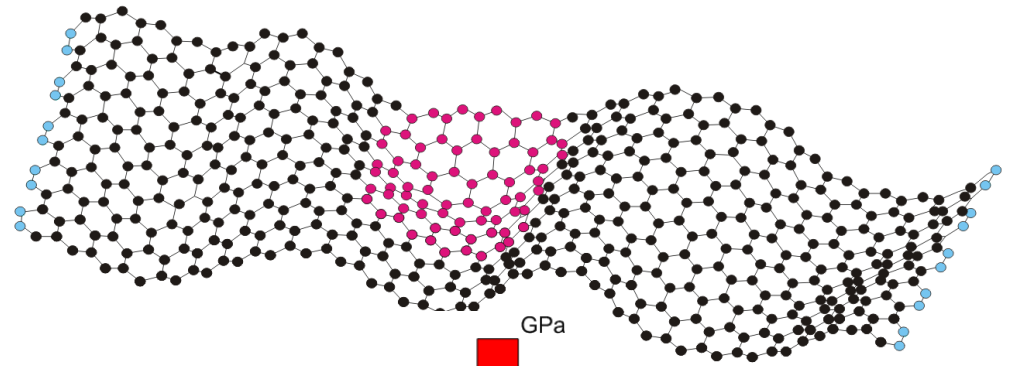
Approbation of method (prediction of the graphene destruction with defect of hydrogenation)





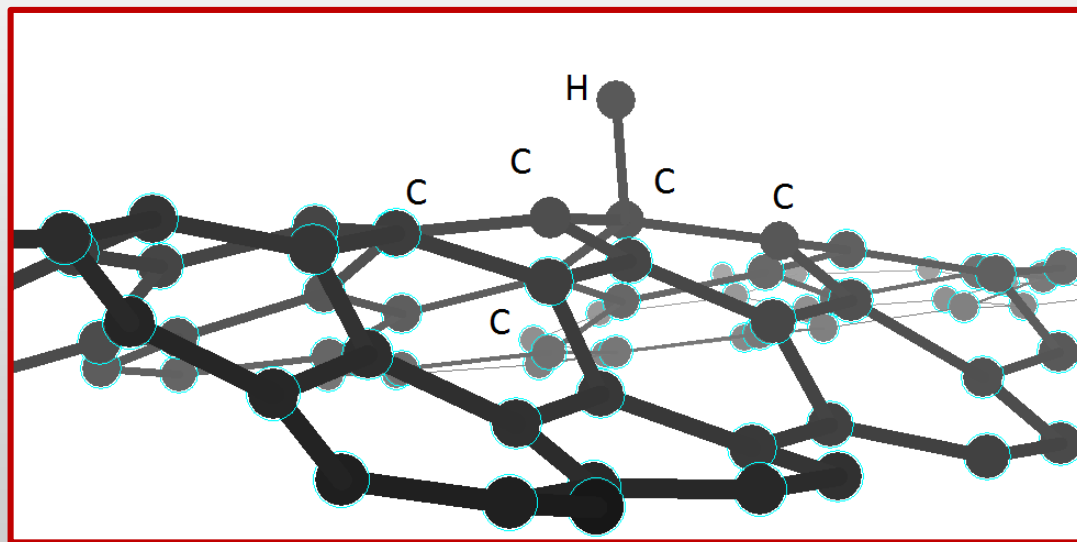
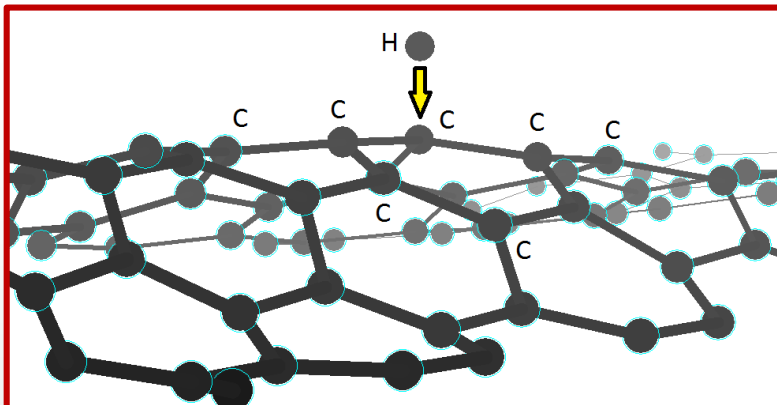
Occurrence of the defect

18



Prediction of the defects occurrence at strain of the atomic grid

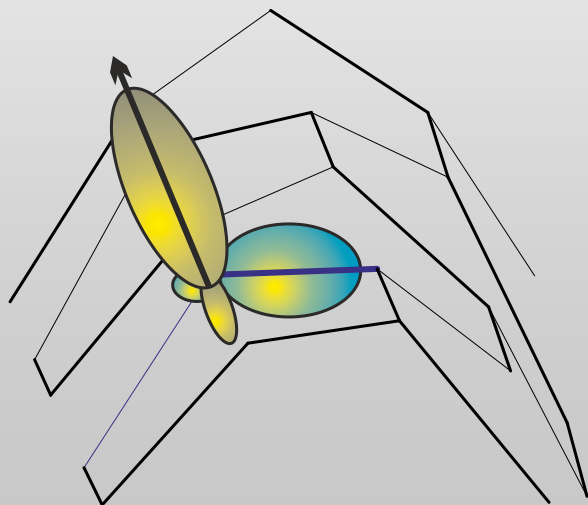
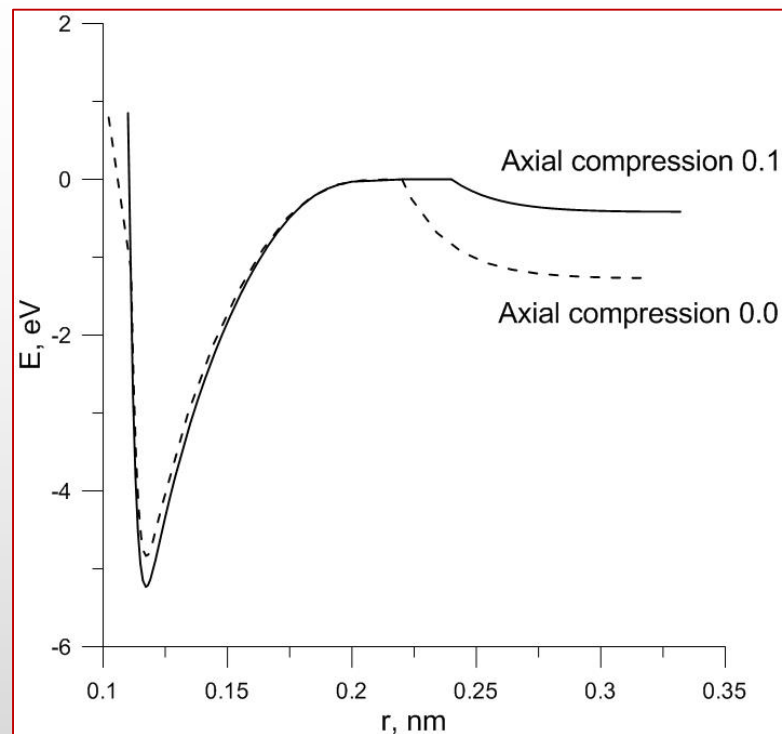
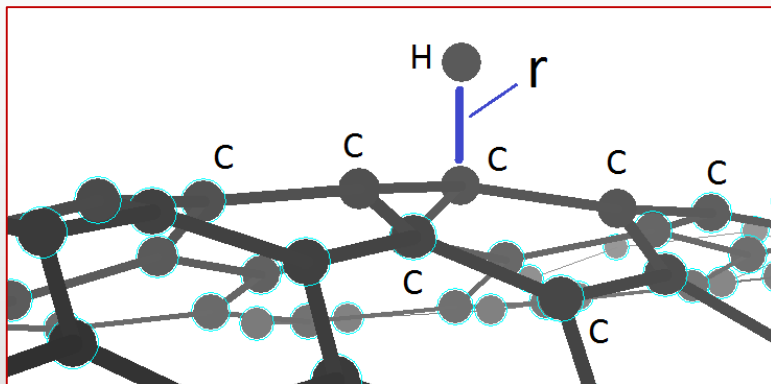
19



The absorption of H-atom on the atomic network

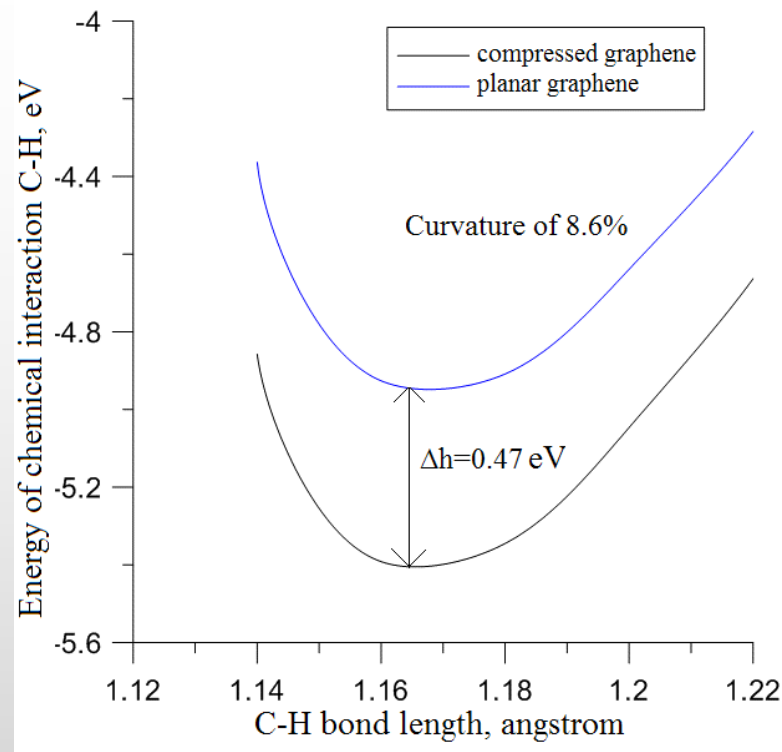
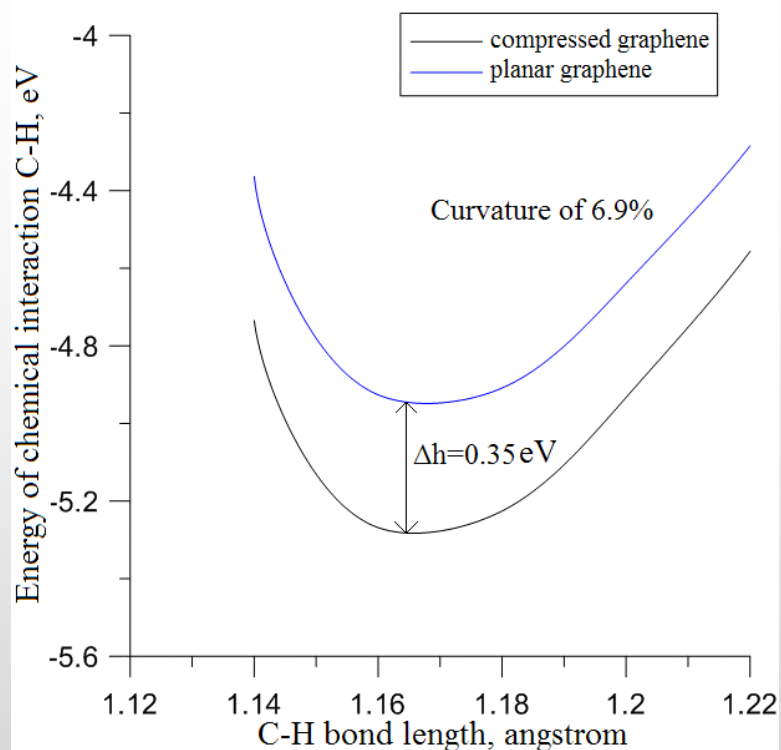
20

The total energy of the structure depends on the distance between the hydrogen atom and the carbon atom



Кривизна

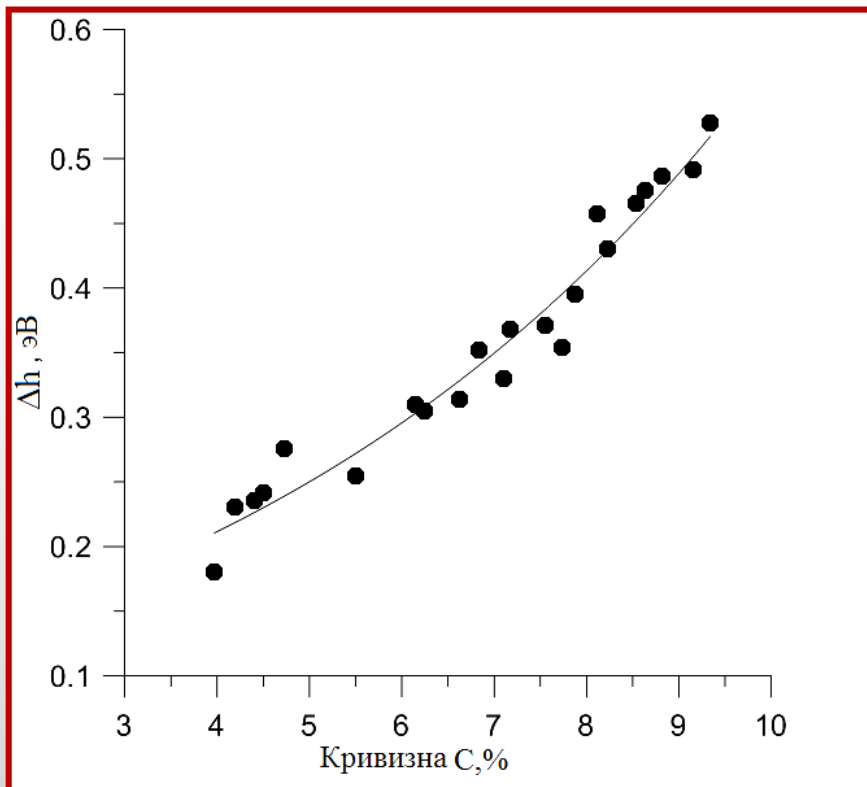
$$C_i = \frac{\theta_i}{90}$$



Graphene	Enthalpy of reaction
The planar	-23.31 kcal/mol
Curvature of 6,9 %	-28.13 kcal/mol
Curvature of 8,6 %	-31.59 kcal/mol

Investigation of the atomic grid curvature influence on the adsorption properties

22



Approximation formula:

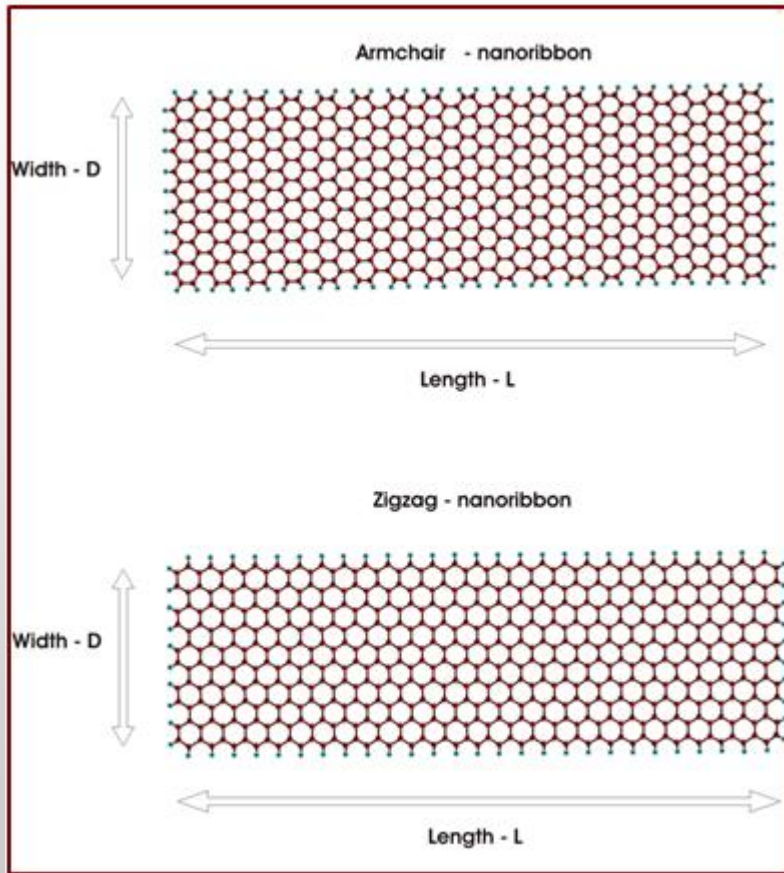
$$\Delta h = 0.1 \exp(0.16C)$$

Dependence of the difference between potential energy minima for the planar and strained graphene nanoribbon from the surface curvature

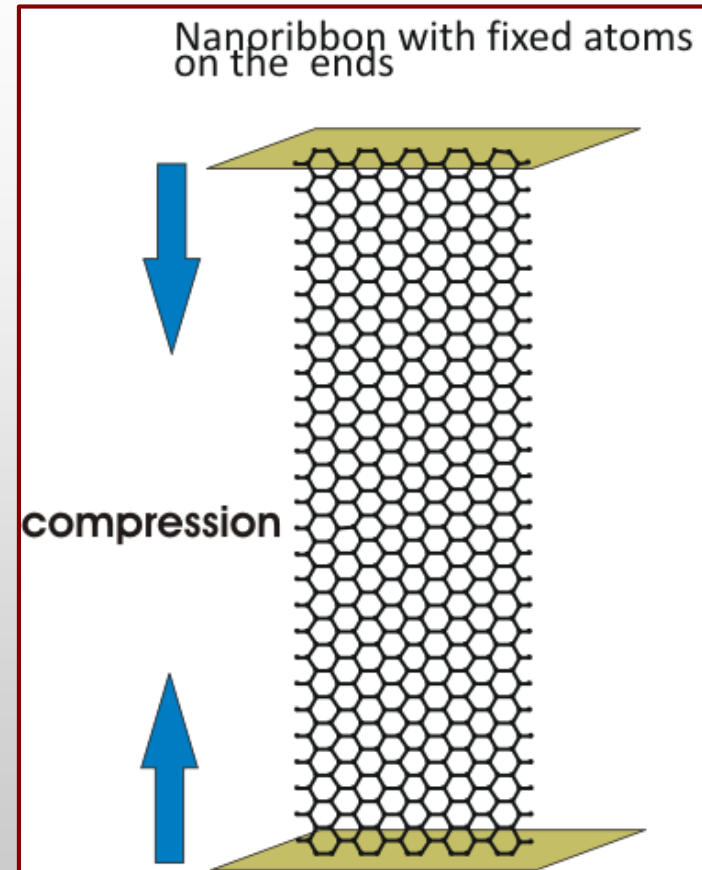
Influence of the curvature on the potential barrier depth

23

Graphene nanoribbons

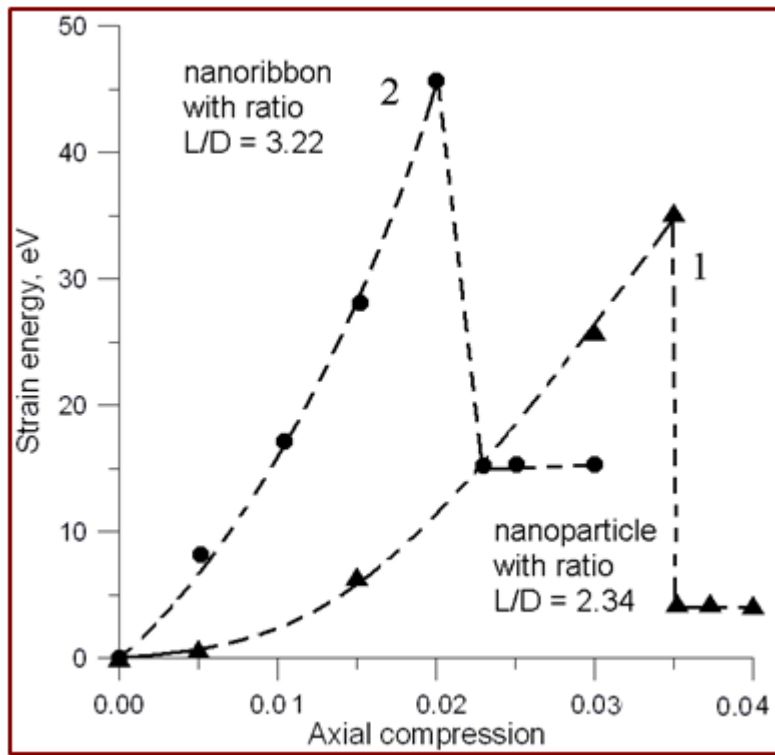


Modeling of the compression process

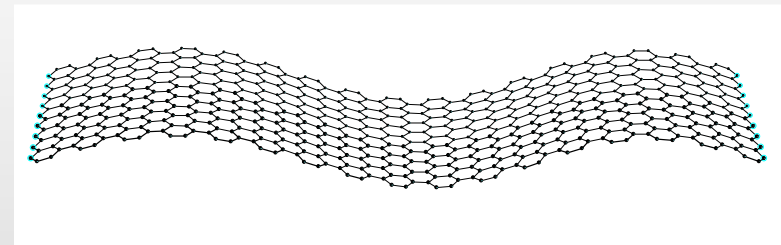


Compression of graphene nanoribbons 24

Nanoribbons and nanoparticles



**Compressed nanoribbon:
96% of initial length**

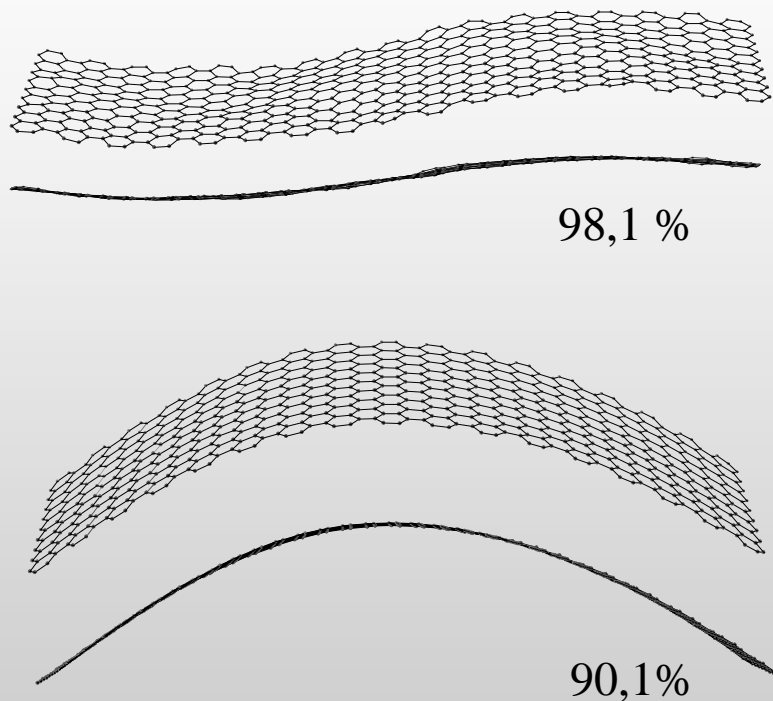


Velocity of the compression 10 m/sec

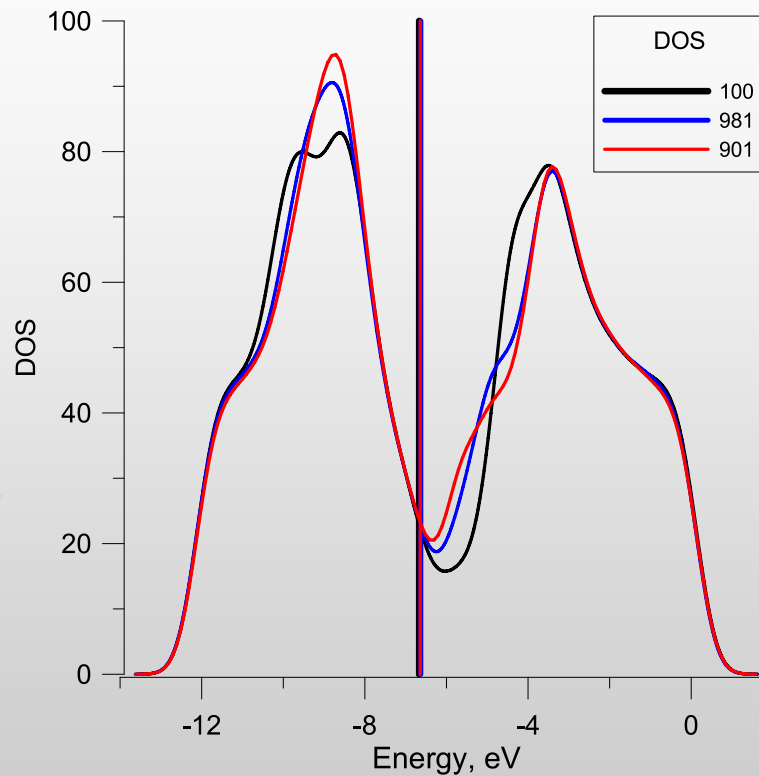
Compression of graphene nanoribbons

25

Compression of armchair ribbon (646 atoms)



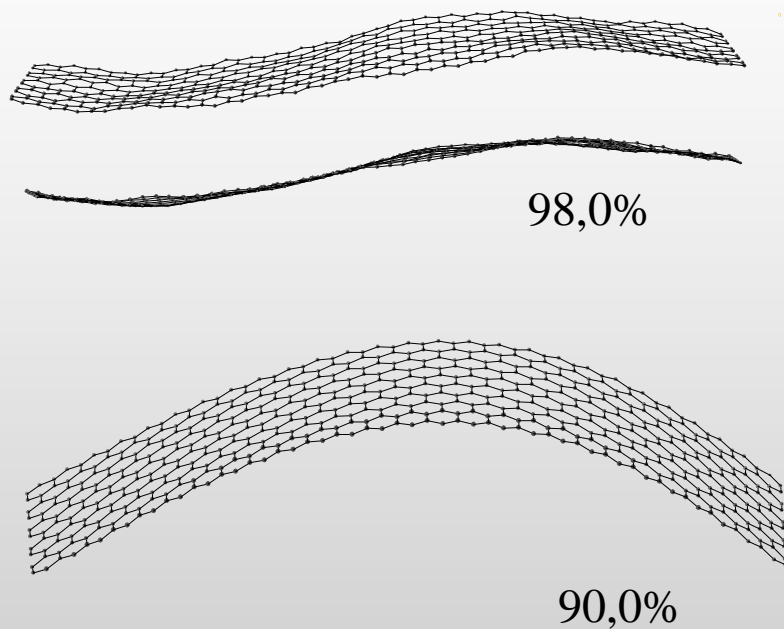
DOS of π -electron system



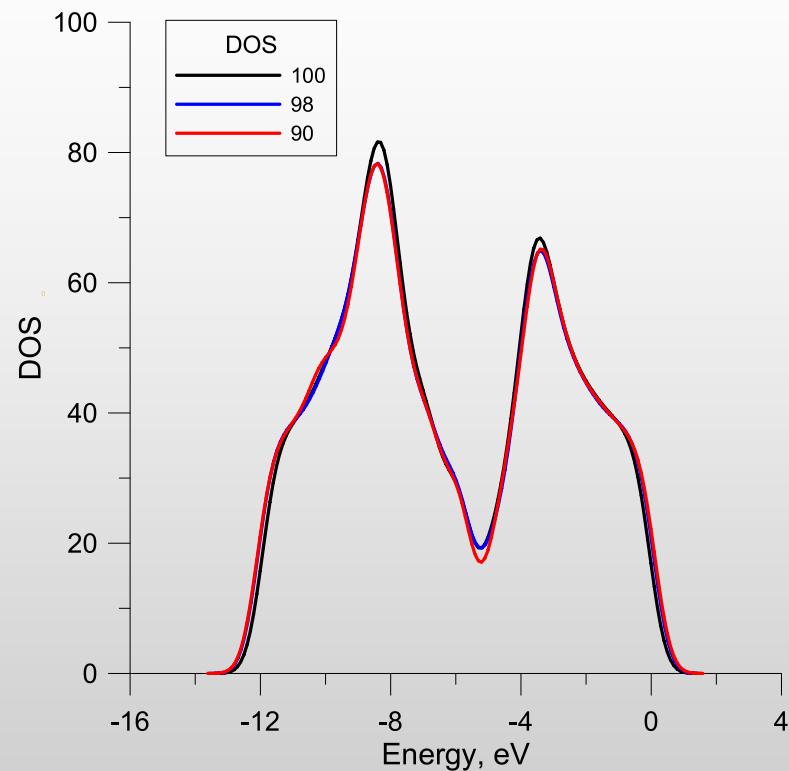
Change of electron structure at an axial compression

26

Compression of zigzag ribbon (550 atoms)



DOS of π -electron system



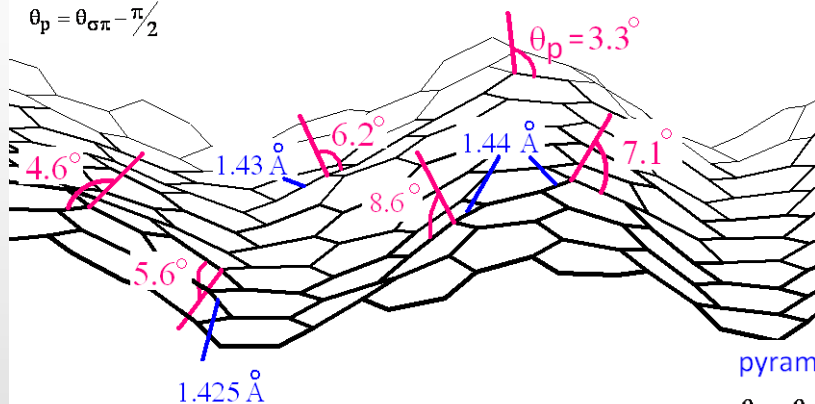
Change of electron structure at an axial compression

27

Compression of ribbon

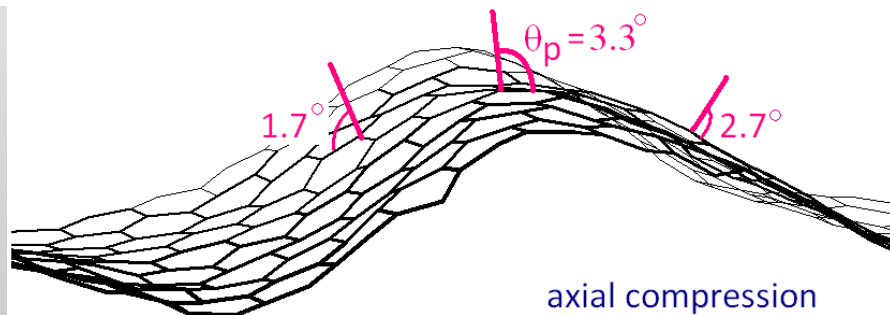
pyramidalization angles

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



pyramidalization angles

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



Change of the pyramidalization angle along the strained atomic framework

28

Compression of armchair ribbon: 98%

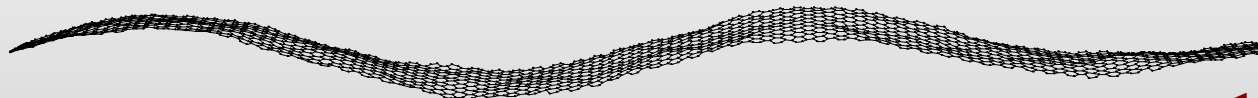
L – length of nanoribbon , $\lambda/2$ – length of half-wave, A – amplitude of half-wave



$$L=71\text{Å}, \lambda/2=35.5\text{Å}, A=2.2\text{Å} \quad \mathbf{9 \text{ hexagons}}$$



$$L=181.7\text{Å}, \lambda/2=60.5\text{Å}, A=5.3\text{Å}$$



$$L=258.4\text{Å}, \lambda/2=64.6\text{Å}, A=5.65\text{Å}$$

14-15 hexagons



$$L=335.12\text{Å}, \lambda/2=66.2\text{Å}, A=5.4\text{Å}$$

**Change of the half-waves quantity at compression
(molecular dynamics, tight-binding method)**

29

Compression of zigzag ribbon: 98%

L – length of nanoribbon, $\lambda/2$ – length of half-wave, A – amplitude of half-wave

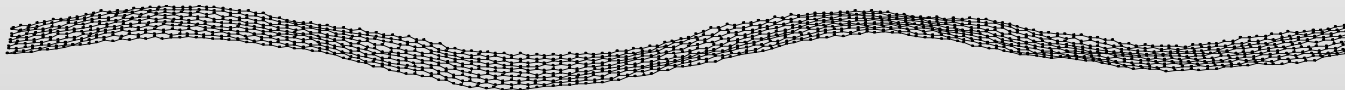


$$L=65\text{\AA}, \lambda/2=32.5\text{\AA}, A=2.8\text{\AA}$$

12 hexagons



$$L=165.18\text{\AA}, \lambda/2=55.06\text{\AA}, A=5.4\text{\AA}$$

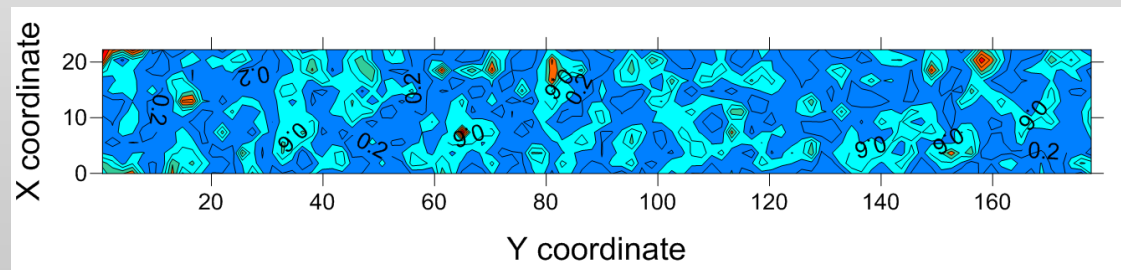
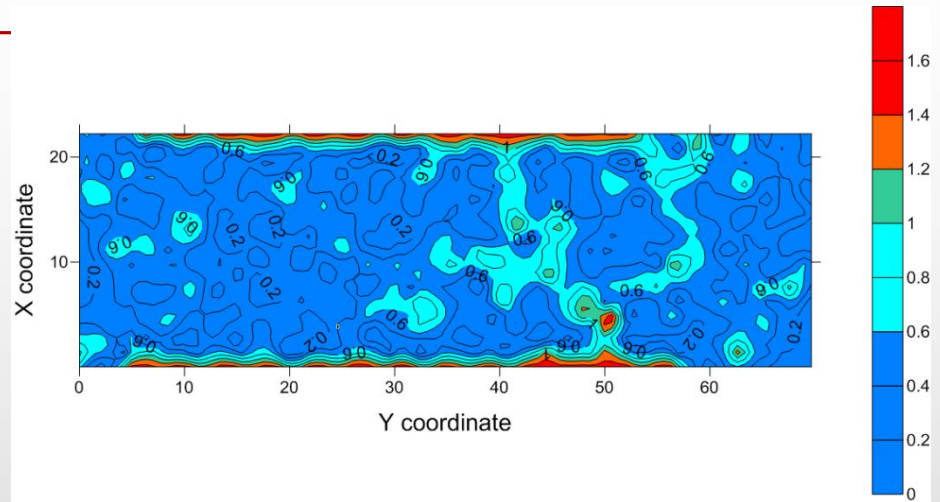
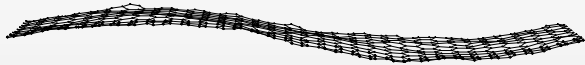


$$L=198.7\text{\AA}, \lambda/2=49.6\text{\AA}, A=5.6\text{\AA}$$

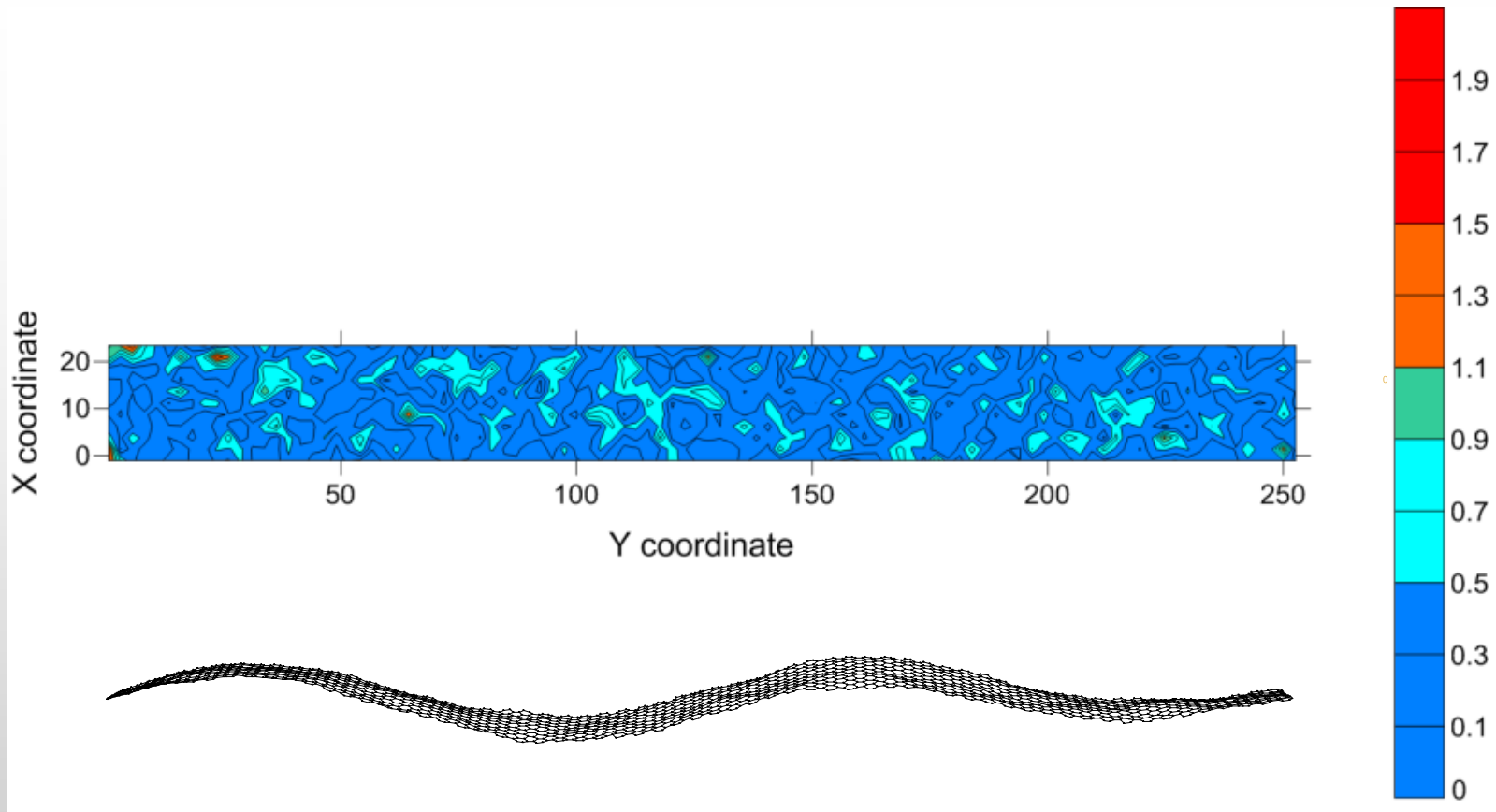
20 hexagons

**Change of the half-waves quantity at compression
(molecular dynamics, tight-binding method)**

30



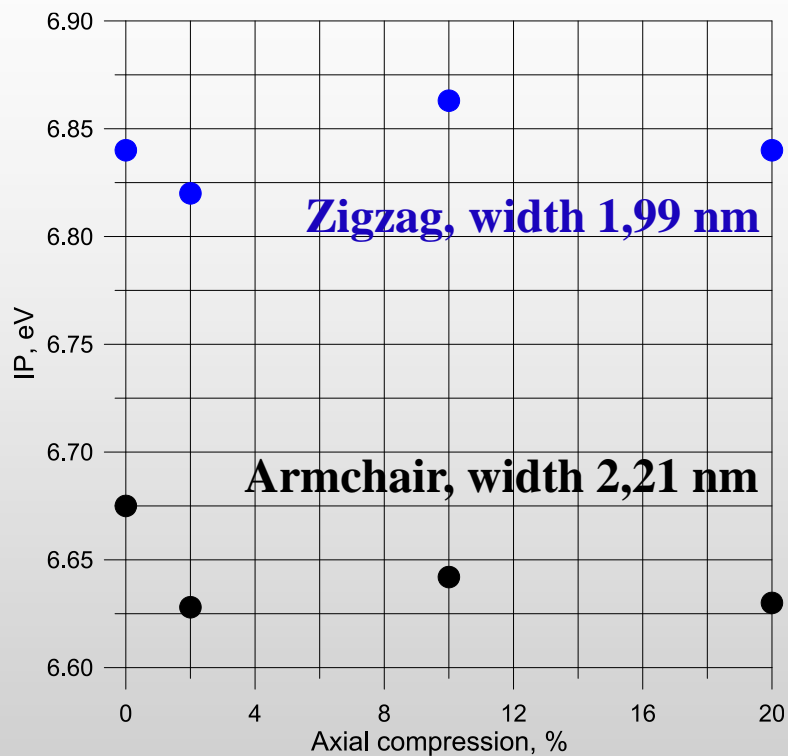
Maps of stress



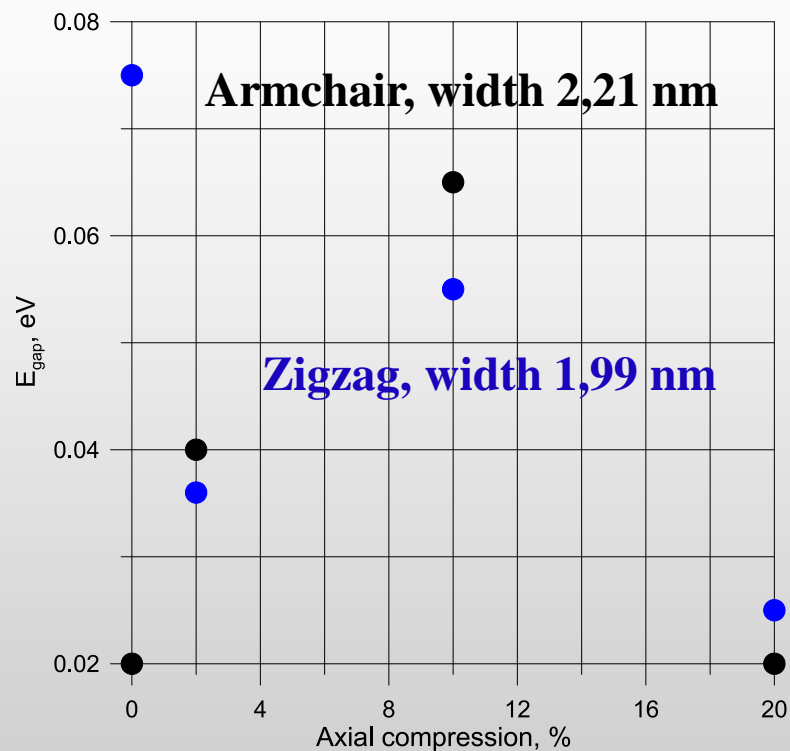
Map of stress

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Ionization potential

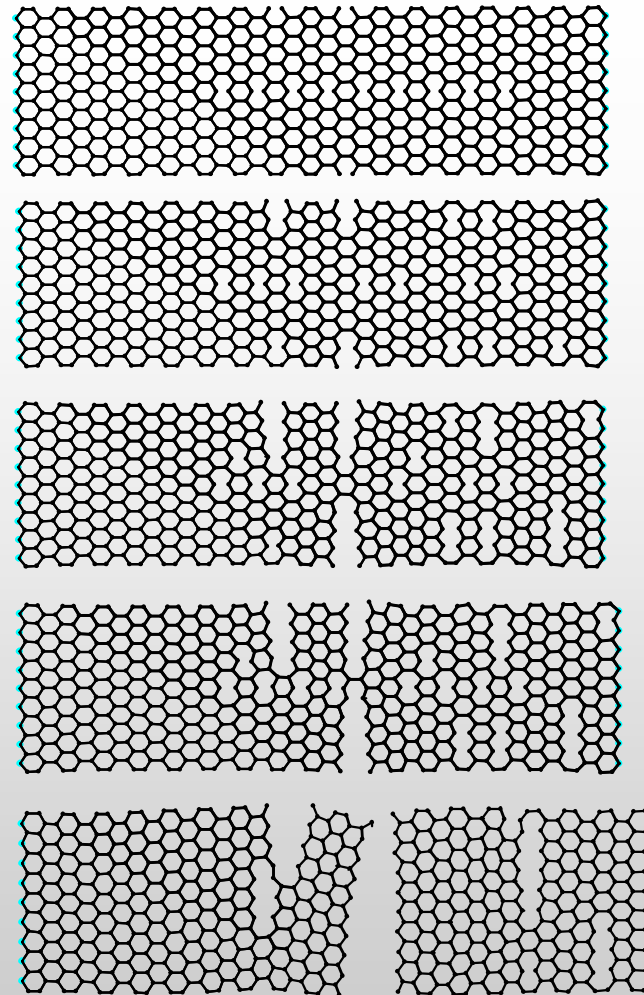
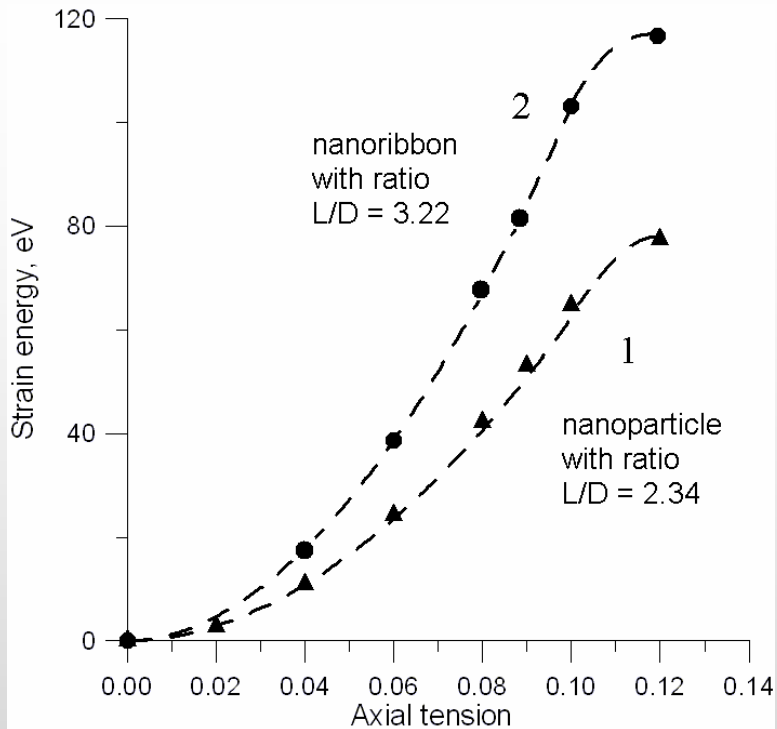


Energy gap



Nanoribbons armchair (552 atoms), zigzag (646 atoms)

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Tension of graphene nanoribbon

Investigation of the strain and prediction of the defects formation and destruction of graphen nanoribbon



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Спасибо за внимание!

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