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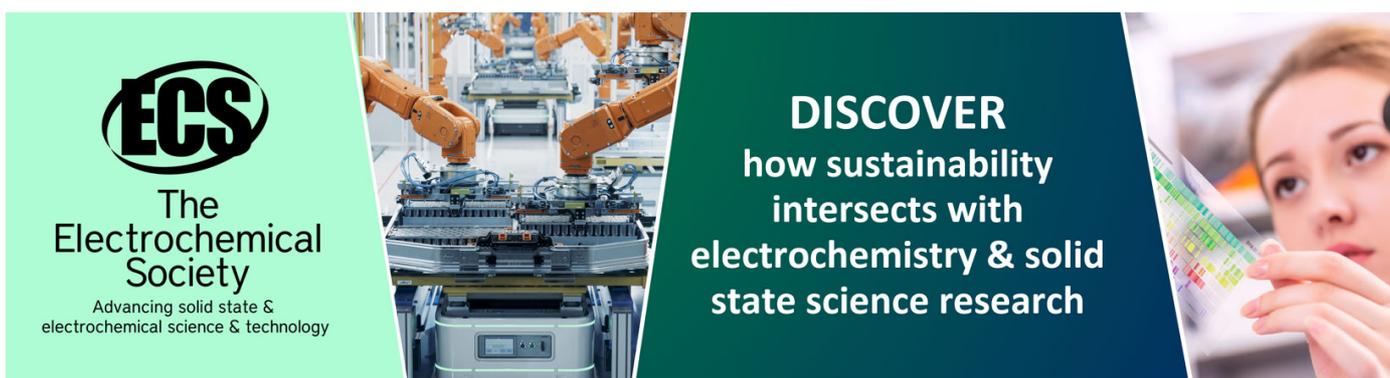
Numerical simulation of multi-layer graphene structures based on quantum-chemical model

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Numerical simulation of multi-layer graphene structures based on quantum-chemical model

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Abstract. The electronic structure of the multi-layer graphene has been studied using the density functional theory (DFT). The dependence of the average interlayer distance on the number of layers ($n = 2 \div 6$) has been determined. The analysis of the charge redistribution and the electron density of the bi- and three-layer graphene under the external pressure up to 50 GPa has been performed. The model of the interlayer conductivity of compressed multi-graphene was offered

1. Introduction

A multi-layer graphene (MG) is a two-dimensional allotropic modification of carbon, formed by several layers of the graphene [1–3]. MG combines exceptional properties of graphene, such as low resistivity, high thermal conductivity, transparency and surpasses it in stability and stiffness [4, 5]. The valence band and the conduction band touches or are close to the corners of the hexagonal Brillouin zone, so the MG is a semimetals or narrow-gap semiconductor [5–7]. The control of the band overlap is achieved by the virtue of external influences, in particular by the electric field [8]. The band gap modulation in the range $E_g = 0-250$ meV in MG with the application of an electric field directed perpendicular to layers have been shown experimentally [9]. Zhang et al. [6] created transistors based on the MG. Scientists are intensively pursuing research and development activities to develop a variety of techniques for syntheses of multi-layer graphene of the large area [4, 9]. The violation of the boundary conditions is the reason of the increase of interlayer distances in MG with compare to the graphite, this is an important practical value [10–12]. Lee et al. [11] received a stable multi-layer graphene suspension in the water and organic solvents without the chemical modification of MG. The precipitate is not dropped within 6 months. This simplifies the deposition on the substrate as opposed to the insoluble graphene substantially. Yoo et al. [13] replaced the graphite to the multi-layer graphene, that allowed to increase the capacity of lithium-ion batteries by 50%. The pressure dependences of the electrical resistance of MG are actively researched. The interlayer distance dependence on the definition of the pressure is an important task in the development of nanoelectromechanical devices, high-capacity batteries, hydrogen cells etc. [14]. For this purpose, pressure dependences of electro physical properties of MG are actively investigated. Interlayer distances and dependences of the effective charge and electron density distribution on layer numbers of the MG under external pressure is the aim of the present work.



2. Computational details

A quantum-chemical modelling is an effective way for the carbon nanomaterials research. All electron simulations of the electronic structure of the multi-layer graphene were performed using the density functional theory (DFT) computational method with a local spin density approximation (LSDA) [15] with the help of the Gaussian09 software in the Supercomputing Centre of Voronezh State University. The initial MG geometry is a ABABA package and the interlayer distance $r_{sh} = c/2 = 3.35 \text{ \AA}$ (c - graphite lattice parameter). The interlayer distance was determined after the optimization of the MG geometry. An impact of the external pressure on the electronic structure of MG was determined for bi- and three-layer structures. At the first, the distance between the boundary layers decreases in optimized early structures. Then, the interaction force between layers is defined as $F = -dE_{tot} / dr_{sh}$, where E_{tot} – the total energy of the MG elementary cell. The shift of layers caused by the pressure P defined as $P = F / S$, where S is a twice area of the graphene elementary cell. An upper pressure limit is 50 GPa, that is usual value for experimental works [16].

3. Results and discussion

Let us to present the results of the investigation of the interlayer distance on the number of layer of uncompressed MG. It was found, that the average interlayer distance is a monotonically decreasing function on the number of layers (figure 1). In the range of layer numbers $n = 2, \dots, 6$ the interlayer distance decreases from 3.61 \AA to 3.49 \AA , which is more by 7.8% and 4.2% than in graphite.

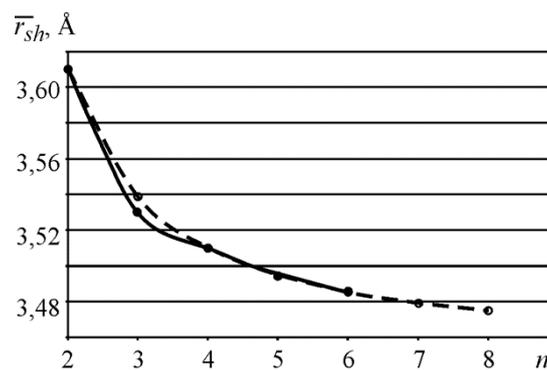


Figure 1. (a) The averaged multi-layer graphene distance, calculated by DFT (solid line) and by the equation (1) (dotted line).

Based on the result of the numerical simulation an analytic dependence of the interlayer distance on the number of layer was installed:

$$r_{sh} = \frac{c}{2} + k \left(\frac{2}{n^2} + \frac{1}{n} \right) + a, \quad (1)$$

where $k = 0.16 \text{ \AA}$; $a = 0.1 \text{ \AA}$.

A maximum absolute error between the numerical calculations and by the equation (1) is 0.01 \AA for three-layer MG. Yoo et al. [13] using transmission electron microscopy defined the average interlayer distance $r_{sh} = 3.650 \text{ \AA}$ of MG obtained by mechanical graphite cleavage. Agrinskaya et al. [12] experimentally defined the average interlayer distance of eight-layer MG $r_{sh} = 3.39 \pm 0.02 \text{ \AA}$ that is less than calculated values according to the equation (1) on 1.9-3.1% $r_{sh} = 3.475 \text{ \AA}$ ($n = 8$) (figure 1). It should be noted, that in [12] MG was obtained by the thermal graphitization of SiC. The substrate effect may cause a decrease of the interlayer distance in the relation to simulated free MG.

In this way the interlayer distance is sensitive to the layer number. The layer structure defines the sense to the external pressure. It was found that in the pressure range $P = 0\text{--}50$ GPa the interlayer distance for bi- and three-layer MG is reduced by 47% (from 3.61 to 1.90 Å) and 36% (from 3.56 to 2.28 Å) respectively (figure 2). It is commonly thought that interlayer interaction in the graphite and MG is Van-der-Waals. Consequently, the force and pressure are proportional to r_{sh}^{-7} . With the aim to investigate the features of the interlayer interaction of the MG under the external pressure the dependence of $P(r_{sh}^{-7})$ was calculated. At the pressure $P < 20$ GPa the dependence $P(r_{sh}^{-7})$ of bi-layer MG is close to linear (figure 2a). It was revealed that at the pressure $P > 20$ GPa the dependence becomes steeper, that indicates the interlayer additional attraction. The deviation from the Van-der-Waals interlayer interaction for three-layer MG is occurs at the pressure $P > 30$ GPa. That point out to the stiffness increase of MG with the rice of layer numbers.

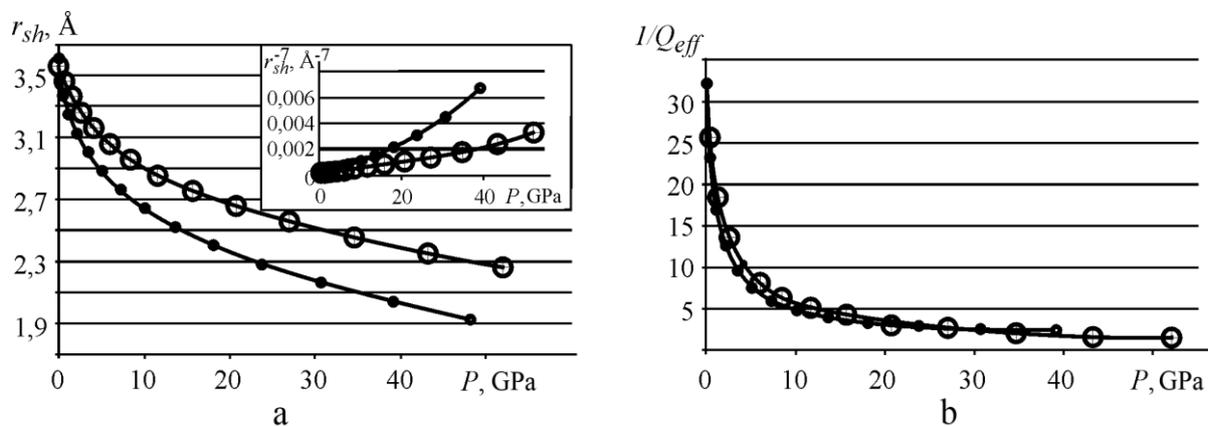


Figure 2(a, b). (a) The interlayer distance versus the pressure value for bi- (○) and three-layer (●) multi-graphene ($r_{sh}^{-7}(P)$ dependence is represented in the inset); (b) the reverse module of the induced effective charge versus the pressure value.

The electron density redistribution was analysed to determine the mechanism of the interlayer additional attraction. The evolution of the electron density distribution of the highest occupied crystal orbital (HOCO) and lowest unoccupied crystal orbital (LUCO) of bi- and three-layer MG is shown in the figure 3.

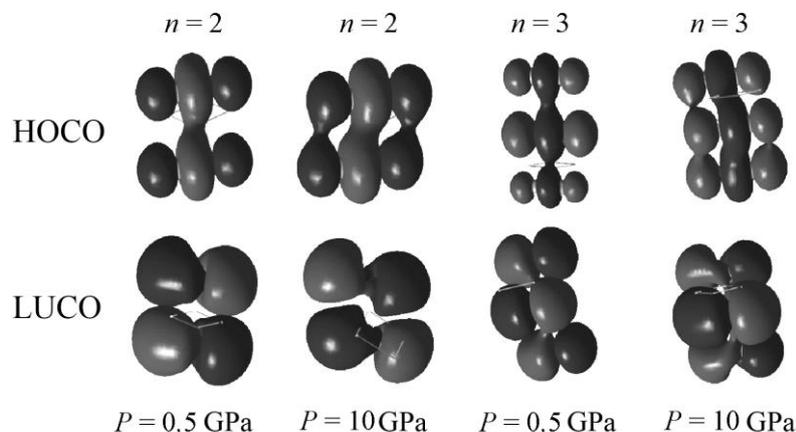


Figure 3. Electron density redistribution for bi- and three-layer MG at 0.5 GPa to 10 GPa pressure.

LUCO is the antibonding orbital, the electron density distribution is weakly depends on the pressure value. At the pressure to $P \sim 10$ GPa HOCO is weakly binding in the interlayer direction. The electron density is localized in the interatomic and interlayer space. It was found, that at the pressure $P \sim 10$ GPa interlayer π -bonds are beginning to form, that has two consequences. At the first, the addition binding leads to the deviation of the interlayer interaction from the Van-der Waals. Secondly, in the direction perpendicular to the layers forms the electron transfer channels, this reduce the anisotropy of the MG electrical conductivity. At the pressure $P \sim 10$ GPa conduction channels are not fully formed, so it can be concluded that the critical pressure of the conductivity channels formation increases with the number of layers.

Based on the results of the visualization of HOCO and LUCO of compressed MG the model of MG conductivity was offered (figure 4). In the case of uncompressed MG the p_z orbitals of MG directed perpendicular to the layers. Probabilities of the finding of electrons above and below of each graphene layer are equal (figure 4). At the external pressure orbitals are deformed as a result of rapprochement layers that lead to the increase of the electrons finding probability on external sides of MG. At the critical value of the pressure (pressure of the conductivity channel formation P_{cf}) interlayer covalent bonds are formed that is the reason of the direct electron transfer in the direction perpendicular to layers.

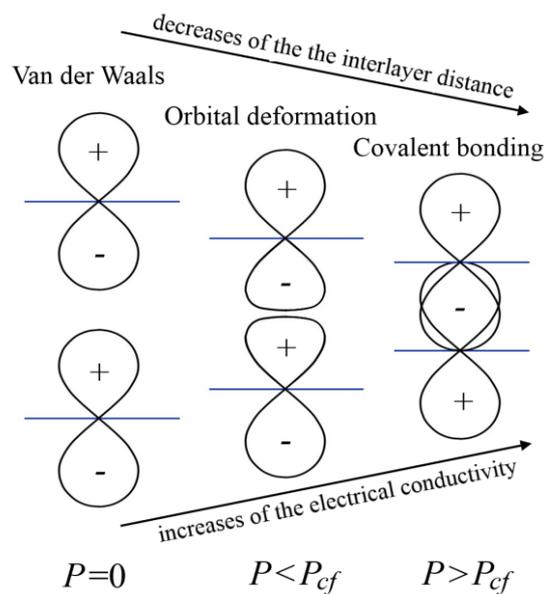


Figure 4. The model of conductivity channels formation for bi- layer MG under an external pressure P (P_{cf} – pressure of the channel forming). A sign plus and minus indicates a positive and negative part of the wave function.

The effective charge Q_{eff} of carbon atoms is a quantitative measure of the electron density redistribution. The ppressure dependence of the effective charge for bi- and three–layer MG is linear. Hence, the hyperbolically dependence of $1/Q_{eff}(P)$ (figure 2b) should diatremes an analogic dependence of the electro resistivity of MG versus the pressure value. This has been demonstrated experimentally by Petrosyan et al [14].

4. Conclusion

The numerical investigation of the electronic structure of MG under external pressure was performed using the density functional theory. For MG with the number of layers $n=2-6$ was found that the

interlayer distance is greater of 4.2–7.8% than the corresponding value in the graphite. The decreasing dependence of the interlayer distance on the layers number n was established $r_{sh} \sim (2+n)/n^2$. The calculated interlayer distances are in a good agreement with experimental works. The π -bonds interlayer formation was detected at the critical pressure value 10 GPa and 30 GPa for bi- and three-layer MG. Interlayer π -bonds serve as channels of the electron transfer in the direction perpendicular to layers, that causes the reduce of the electrical conductivity anisotropy of MG. It was revealed that the critical pressure of the conductivity channel formation increases with the number of graphene layers in the MG. The research results extend the knowledge about the electronic structure and phase transitions in the compressed graphene-like structures and can be used for the development of nanoelectromechanical devices.

Acknowledgments

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