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TOPOLOGICAL MECHANOCHEMISTRY OF GRAPHENE

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The current paper describes the effects caused by uniaxial tension of a graphene molecule in the course of the mechanochemical reaction. Basing on the molecular theory of graphene, the effects are attributed to both mechanical loading and chemical modification of the edge atoms of the molecule. The mechanical behavior is shown to be not only highly anisotropic with respect to the direction of the load application, but greatly dependent on the chemical modification of the molecule edge atoms, thus revealing the topological character of the graphene deformation.

Keywords: graphene, molecular theory, electron correlation, mechanochemical reaction; chemical modification; strength characteristics, Young's moduli.

1. Introduction

Topochemical reactions have been studied since the nineteenth century (see [1] and references therein). The first stage of the study was completed in the late 1920's [2] and then, a renewed interest in them appeared after the 1970 publication of the Woodward and Hoffmann monograph devoted to the conservation of orbital symmetry [3]. Since then, topochemical reactions have become an inherent part of not only organic, but inorganic chemistry, as well. Readers interested in this topic are referred to a set of comprehensive reviews [1, 4-7]. The current state of the art in this field can be exemplified by the direct structural understanding of the topochemical solid state photopolymerization reaction [8].

Currently, we are witnessing the next pulse, stimulating investigations in the field, which should be attributed to the appearance of a new class of spatially extended molecular materials, such as sp^2 hybridized carbon nanostructures. Obviously, the main members of the class such as fullerenes, nanotubes, and numerous graphene-based species are absolutely different from a formal topology viewpoint. Thus, fullerenes exist in the form of a hollow sphere, ellipsoid, or tube consisting of differently packed benzenoid units. Carbon nanotubes are present predominantly in cylindrically packed units. In graphene, the benzenoid units form one-atom-thick planar honeycomb structure. If we address the common terms of the formal topology, namely, connectivity and adjacency, we have to intuitively accept their different amounts in the three species listed above. In turn, the connectivity and adjacency determine the 'quality' of the C-C bond structure of these species, thus, differentiating them by this mark. Since non-saturated C-C bonds are the main target for chemical reactions of any type, one must assume that identical reactions, involving the bonds, will occur differently for different sp^2-hybridized carbon-based nanostructures. Therefore, one may conclude that the spatially extended sp^2-hybridized carbon-based nanostructures present not only peculiar structural chemicals, but a class of species for which the formal and empirical topologies overlap. For the first time, results, presented in [9, 10], have revealed this tight interconnection in terms of molecular quantum theory. Not only fullerenes, but carbon nanotubes and graphene (their fragments) have been considered at the molecular level. The obtained results are related to the computational study of the intermolecular interaction between fullerene C_{60} and one of the other addends, among which there are both sp^2-hybridized carbon nanostructures and monoatomic species. The intermolecular interaction lays the foundation of any reaction so that its topological peculiarities may evidence a topochemical character of the reaction being studied. However, since the 'quality' of the C-C bonds is the most sensitive point of the inherent topology of the sp^2-hybridized carbons, external actions, such as mechanical deformation, on the bonds should obviously result in particular topological effects that accompany the relevant intramolecular reactions. The current paper is devoted to the discussion of such reactions that are represented by the mechanochemical one related to the uniaxial tension of a graphene molecule.

2. Uniaxial tension of graphene as a mechanochemical reaction

Below we will consider a particular topological effect caused by the influence of both the loading direction and the graphene molecule edge termination on the inherited topology of the molecule. Graphene deformation, under external mechanical loading, is extremely sensitive to the state of the edge atoms and makes it possible to disclose the topological nature of this sensitivity.

Recently, a new approach has been suggested to describe graphene deformation, based on considering the failure and rupture process of graphene as the result of a mechanochemical reaction [11-14]. A similarity between the mechanically induced reaction and the initial chemical ones, first pointed out by Tobolski and Eyring seventy years ago [15], suggested the use of a well developed quantum-chemical approach of the reaction coordinate [16] in the study of atomic structure transformation under deformation. First applied to the deformation of poly(dimethylsiloxane) oligomers [17], the approach has revealed a high efficacy in exhibiting elastic, plastic, and superplastic regions of the oligomer uniaxial tension, disclosing the mechanism of its failure and rupture. This has been successfully applied recently for the description of the uniaxial tension of both graphene [11, 12] and graphane [13] molecules, thus positioning itself as a significant part of the molecular theory of graphene [18].

The main point of the approach concerns reaction coordinate definition. When dealing with chemical reactions, the coordinate is usually selected among internal ones (valence bond, bond angle or torsion angle) or is presented as a linear combination of the latter. Similarly, mechanochemical internal coordinates (MICs) are introduced as modified internal coordinates, defined in such a way as to be able to specify the considered deformational modes [17, 19]. Thus, uniaxial tension and contraction are described by linear MICs similar to valence bonds. In the case of tensile deformation, the benzenoid pattern of graphene sheets and a regular packing of the units predetermined the choice of either parallel or normal MICs orientation with respect to the chain of C-C bonds. In rectangular nanographene sheets and nanoribbons, the former orientation corresponds to tensile deformation applied to the zigzag edges (*zigzag* mode) while the latter is attributed to the armchair edges (*armchair* mode). The MIC configurations of the two tensile modes of the (5,5) nanographene (NGr) molecule are presented in Fig.1. The molecule lays the foundation for previously performed computational experiments [11-14] and presents a rectangular fragment of a graphene sheet that is cut along zigzag and armchair edges and contains 5 benzenoid units along each direction. The deformation proceeds as a stepwise elongation of the MICs with increments of δL=0.1Å, so that the current MIC length constitutes $L = L_0 + n\delta L$, where L_0 is the initial length of the MIC and n counts the number of the deformation steps. The right ends of all the MICs are fixed so that these dark colored atoms are immobilized while the atoms on the left ends of MICs move along the arrows providing the MIC successive elongation, once excluded from the optimization, as well. The relevant response force is calculated as the energy gradient along the MIC, while the atomic configuration is optimized over all of the other coordinates under the MIC constant-pitch elongation. The results presented in the paper were obtained in the framework of the Hartree-Fock unrestricted (UHF) version of the DYQUAMECH codes [20] exploiting advanced semiempirical QCh methods (PM3 version [21]).

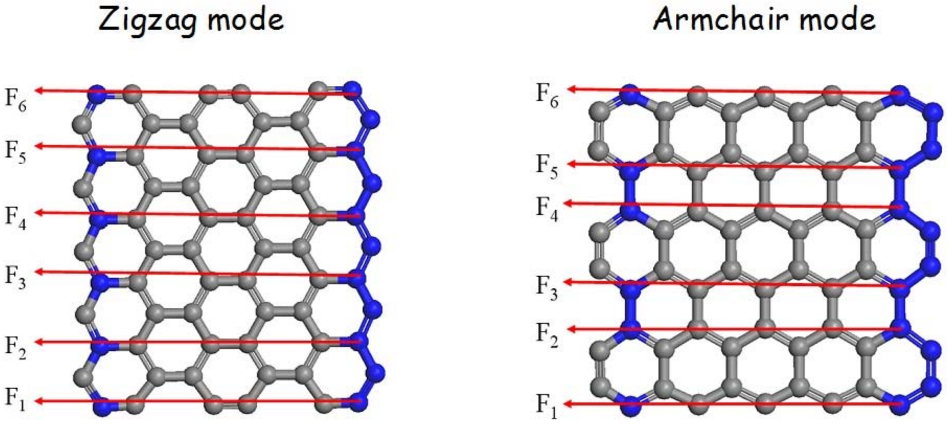

FIG. 1. Six mechanochemical internal coordinates of uniaxial tension of the (5,5) NGr molecule for two deformation modes. F_1, F_2, F_3, F_4, F_5 F_6 are forces of response along these coordinates. Dark atoms fix the coordinates ends

The corresponding forces of response F_i applied along the i^{th} MICs are the first derivatives of the total energy $E(R)$ over the Cartesian coordinates [17]. When the force calculation is completed, the gradients are re-determined in the system of internal coordinates in order to proceed further in seeking the total energy minimum by the atomic structure optimization. Forces F_i are used afterwards for determining all the required micro-macroscopic mechanical characteristics, which are relevant to the uniaxial tension, such as the total force of response $F = \sum_i F_i$, the stress $\sigma = F/S = \left(\sum_i F_i\right)/S$, where S is the loading area, the Young's modulus $E = \sigma/\varepsilon$, where both stress σ and the strain ε are determined within the elastic region of deformation.

3. Computational results

Thus arranged computations have revealed that a high stiffness of the graphene body is provided by that one of the benzenoid units. The anisotropy of the unit mechanical behavior in combination with different packing of the units either normally or parallel to the C-C bond chains lays the ground for the structure-sensitive mechanism of the mechanical behavior of the object that drastically depends on the deformation modes [11-13]. The elastic regions of tensile deformation for both (5, 5) NGr and nanographane (NGra) molecules are extremely narrow and correspond to the first few steps of the deformation. The deformation, as a whole, is predominantly plastic and dependent on many parameters, among which, the most important is the chemical composition of the molecule edge atoms [14].

The equilibrium structures of the (5, 5) NGr molecule before and after uniaxial tension, which was terminated by the rupture of the last C-C bond coupling two fragments of the molecule, are shown in Fig. 2. Looking at the picture, two main peculiarities of the molecule deformation should be notified. The first concerns the anisotropy of the deformation with respect to two deformational modes. The second exhibits a strong dependence of the deformation on the chemical composition of the molecule edge atoms. As mentioned above, the deformation anisotropy of graphene has been attributed to the mechanical anisotropy of the constituent benzenoid units [11, 12]. The dependence of the deformation on the chemical modification of the framing edge atoms has been revealed for the first time.

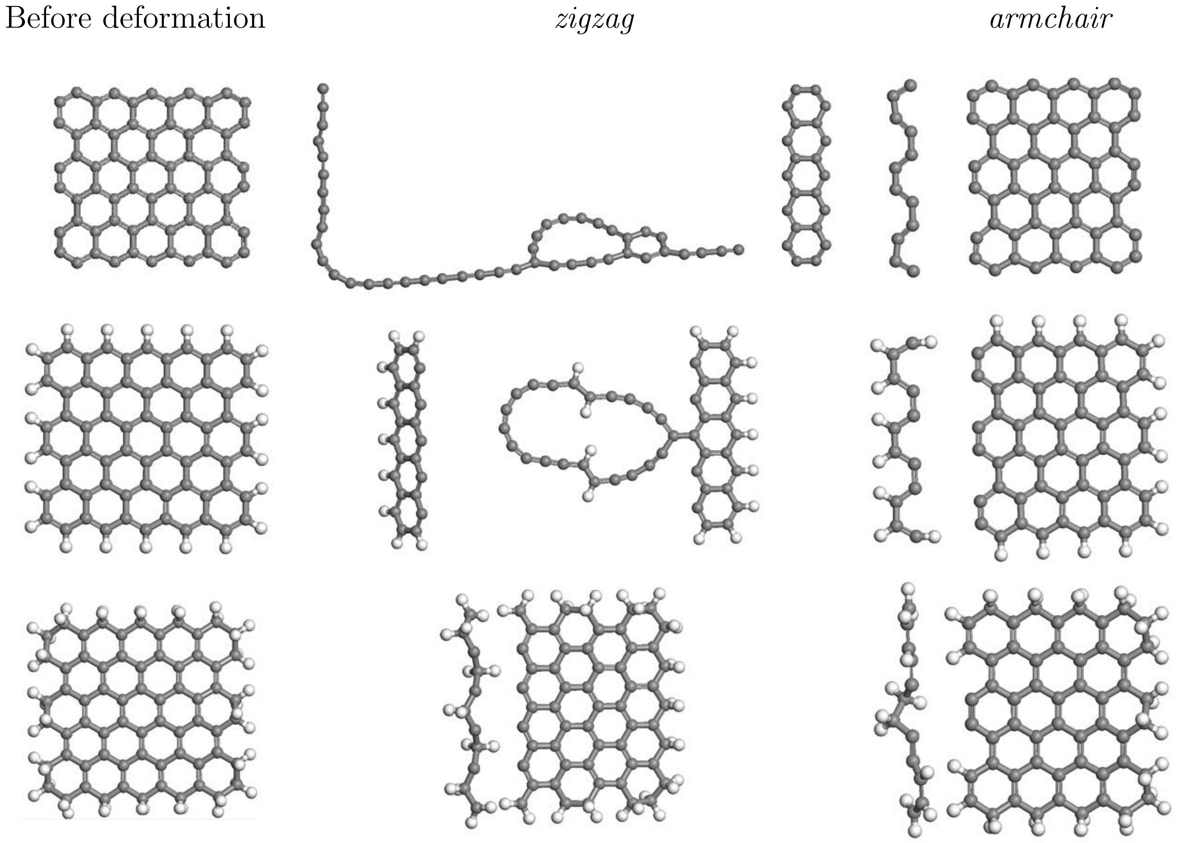

FIG. 2. Equilibrium structures of the (5,5) NGr with different chemical modification of edge atoms before and after completing tensile deformation in two modes of deformation. Bare edges (top); H_1-terminated edges (middle); H_2-terminated edges (bottom)

As seen in Fig. 2, the deformation behavior is the most complex for the naked molecule. The mechanical behavior of the (5, 5) NGr molecule is similar to that of a tricotage sheet when either the sheet rupture has both commenced and been completed by the rupture of a single stitch row (*armchair* mode) or the rupture of one stitch is ‘tugging at thread’ the other stitches that are replaced by still elongated one-atom chain of the carbon atoms (*zigzag* mode). In the former case, the deformation is one-stage and is terminated on the 17^{th} step of the deformation. In contrast, the deformational mode *zigzag* is multi-stage and consists of 250 consecutive steps with an elongation of 0.1Å at each step [11, 12]. The formation of the one-atom chain under zizgzag-mode tension of the naked graphene piece has been supported experimentally [22].

Quite unexpectedly, the character of the deformation seems to be strongly dependent upon the chemical substitution at the molecule edges. As seen in Fig. 2, the addition of one hydrogen atom to each of the molecule edge atoms does not change the general character of the deformation: it remains a tricotage-like one, so that there is still a large difference between the behavior of *zigzag* and *armchair* modes. At the same time, the number of the deformation steps of the *zigzag* mode reduces to 125.

Even more drastic changes for this mode are caused by the addition of a second hydrogen atom to the edge (Fig. 2). Still, the *armchair* mode is quite conservative while the *zigzag* one becomes practically identical to the former. The tricotage-like character of the deformation is completely lost and rupture occurs at the 20^{th} step.

Figure 3 presents a set of the ‘stress-strain’ relations that fairly well highlight the differences in the mechanical behaviors of all the three molecules. Table 1 presents the Young’s moduli that were defined in the region of the elastic deformation. As seen from the table, the Young’s moduli depend on the character of the edge atom chemical modification. As shown in [13], elastic properties of extended molecules such as polymers [17, 23] and nanographenes [13] are determined by dynamic characteristics of the objects, namely, by force constants of the related internal vibrations. Since benzenoid units provide the determining resistance to any deformation of the graphene molecules, the dynamic parameters of the stretching C-C vibrations of the units are mainly responsible in the case of the uniaxial tension. Changes in the Young’s moduli mean that there are changes in the force constants (and, consequently, frequencies) for these vibrations. The latter are attributed to the G-band of graphene that lays the foundation of a mandatory testing of any graphenium system by the Raman spectroscopy. In numerous cases, the relevant band is quite wide which might indicate the chemical modification of the edge zone of the graphene objects under investigation.

Since the deformation-induced molecule distortion mainly concerns basal atoms, such drastic changes in the deformation behavior point to a significant influence of the chemical state of the edge atoms on the electronic properties in the basal plane. The observed phenomenon can be understood if it is suggested that: 1) both the deformation and rupture of the molecule is a collective event that involves the electron system of the molecule as a whole; 2) the electron system of the graphene molecule is highly delocalized due to valuable correlation of the odd electrons; and 3) the electrons correlation is topologically sensitive because the chemical termination of the edge atoms so strongly influences the behavior of the entire molecule. The latter has turned out to be the reality, indeed. The topography of the atomic chemical susceptibility transformation over the molecule’s atoms is presented elsewhere [25].

4. Topological character of the odd electron correlation in graphene

The performed computations have revealed that the correlation of the studied molecules’ odd electrons changes quite remarkably in the course of the deformation. This result can be illustrated by the evolution of the total number of effectively unpaired electrons N_D during the deformation. The N_D value is a direct characteristic of the extent of the electron correlation [18], on one hand, and the presents molecular chemical susceptibility [24], on the other. Changes in N_D reveal deformation-induced changes in the molecule chemical activity induced by deformation.

Figure 4 presents the evolution of N_D for the three studied molecules. Since breaking each C-C bond causes an abrupt change in N_D, a tooth-like character of the relevant dependences related to the *zigzag* mode of the molecule with the naked and H-terminated

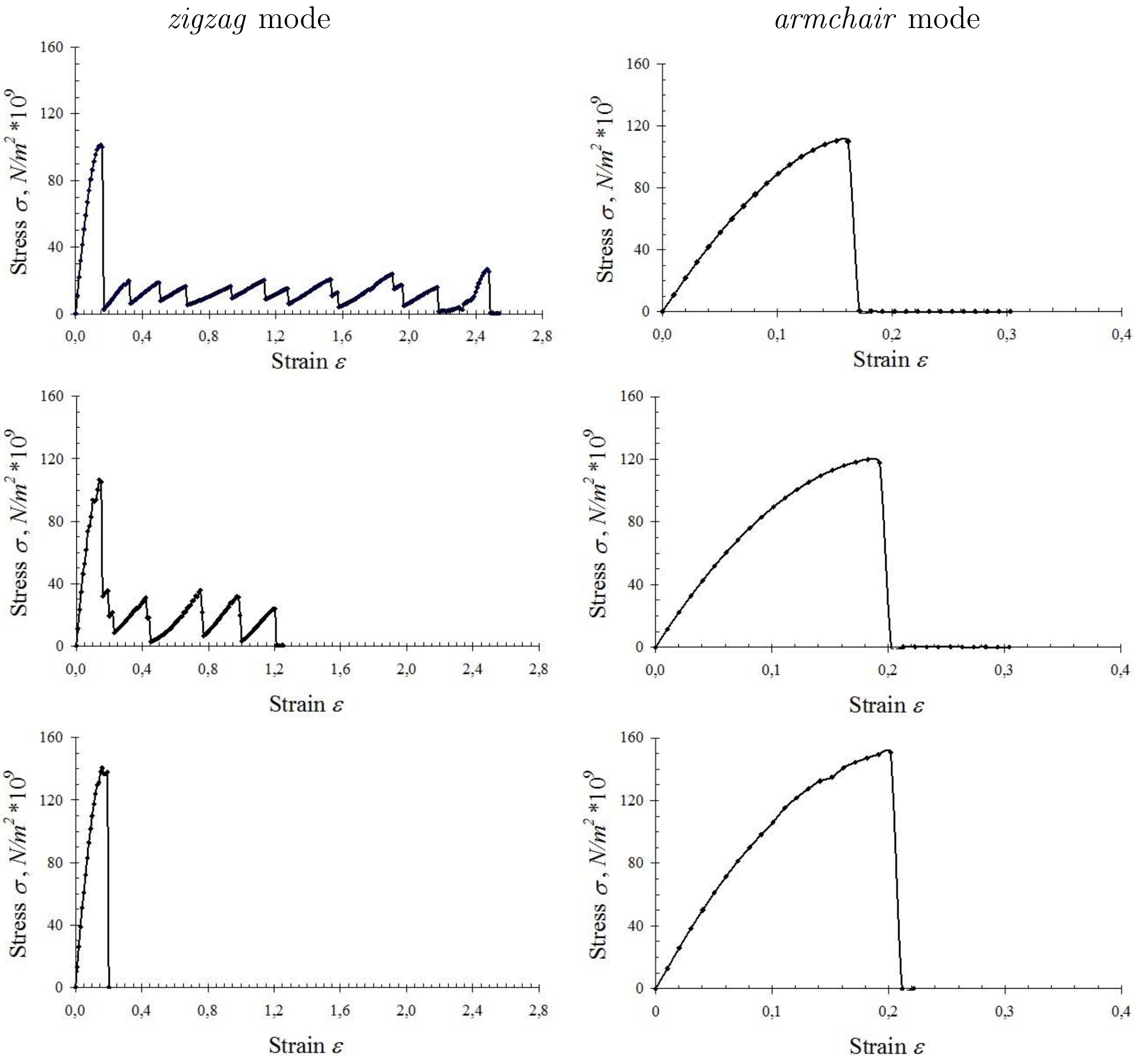

Fig. 3. Stress-versus-strain dependences of tensile deformation of the (5, 5) NGr molecule with different edge-atom chemical modification in two deformation modes. Nake molecule (top); H_1-terminated edges (middle); H_2-terminated edges (bottom)

edges is quite evident. One should draw attention to the N_D absolute values as well as to their dependence on both the chemical modification of the edge atoms and the deformational modes. Evidently, the chemical activity of the molecules drastically changes in the course of the mechanically induced transformation. This changing is provided by the redistribution of the C-C bond lengths caused by the mechanical action. This action combines the positions of both basal plane and edge atoms into the a single whole and is topologically sensitive. Therefore, the redistribution of the C-C bonds over their lengths causes changes in the topological 'quality' of individual bonds.

5. Conclusion

Data presented in the current paper undoubtedly show that chemical modification of the graphene molecule's edge atoms has a great impact on its mechanical behavior. This feature results from the significant correlation of the molecule's odd electrons followed by

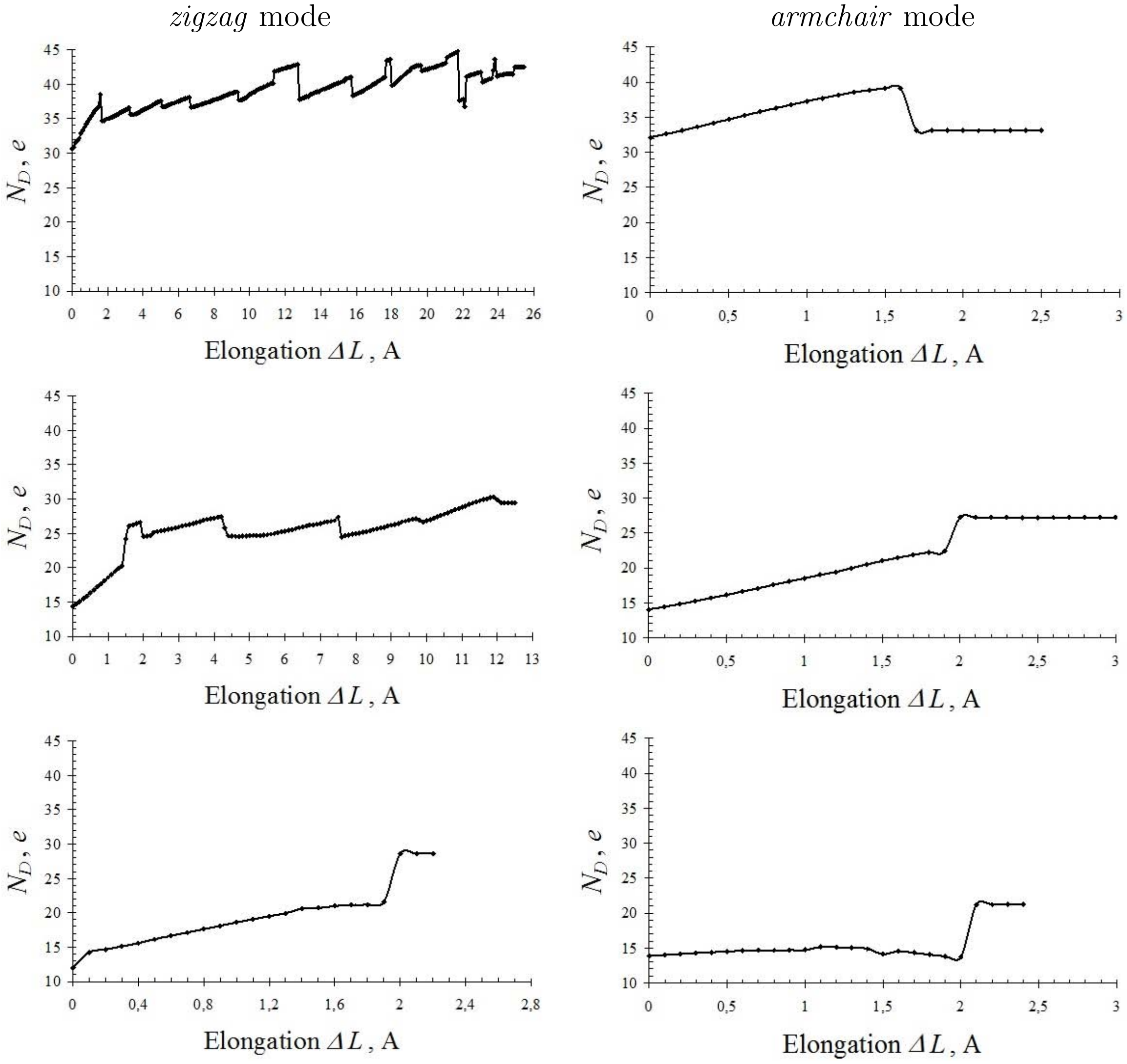

FIG. 4. Evolution of the odd electrons correlation in terms of the total numbers of effectively unpaired electrons under tensile deformation of the (5, 5) NGr at two deformation modes. Bare edges (top); H_1-terminated edges (middle); H_2-terminated edges (bottom)

their conjugation over the molecule. Thus, the transition from the naked molecule, characterized by the maximal correlation of the odd electrons, to the molecule with the single- and double-hydrogen-terminated edges is followed by a considerable suppression of the correlation related to the edge atoms in the former case and a complete zeroing of the latter in the second case. As it turns out, the changes are not local and strongly influence the electronic structure in the basal plane, where the main deformation process occurs, causing a redistribution of the C-C bonds over their lengths, thus, changing ‘the quality’ of the bonds and providing the topological character of the deformation processes in graphene.

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