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STRUCTURE AND ENERGY OF INTERCRYSTALLITE BOUNDARIES IN GRAPHENE

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Abstract. A systematic approach to constructing intercrystallite boundaries (IBs) in graphene is developed based on the structural units (SUs) model of grain boundaries (GBs). The approach operates with SUs composed of carbon octagons, heptagons, pentagons and squares, which correspond to six-member carbon rings of an ideal hexagonal graphene lattice altered by wedge disclinations of different strength. A linear periodic arrangement of SUs containing disclination dipoles and quadrupoles is used to construct IBs in graphene. The energies of symmetric IBs are calculated in molecular dynamics simulations and are used for evaluation of the feasibility of experimental fabrication of the IBs in graphene.

1. INTRODUCTION

Graphene is a two dimensional allotrope of carbon with outstanding mechanical, thermal, optical and electronic properties, see, e.g. [1]. It is considered to be a very promising material for electronics, sensors, membranes, composites and coatings [2]. Graphene produced by chemical vapor deposition (CVD) is normally polycrystalline [3] and, hence, it contains intrinsic linear defects in the form of intercrystallite boundaries (IBs). By now, a considerable experimental and theoretical evidence has been obtained that such IBs may significantly affect the mechanical [4-6], thermal [7-9], and electrical [10-13] properties of graphene. A good example is a boundary named by authors of Ref. [12] as "one-dimensional linear 5-8-5 defect" (the chain of 8- and 5-member carbon atom rings) in graphene, which acts as a quasi-one-dimensional metallic wire.

Experimental data on the real structure of IBs in graphene, including boundaries with misorientation between two adjacent grains, also known as grain boundaries (GBs), are rather limited. Scanning transmission electron microscopy (STEM) studies [10,14] showed that the GBs in graphene are usually made up of pairs of pentagonal and heptagonal (i.e. 5- and 7-member) carbon rings in the graphene lattice and are arranged along a serpentine path. Other atomic configurations of graphene GBs were also observed, including structures containing distorted hexagons [15,16] and vacancies in various ratios and arrangements [15].

An important parameter characterizing a graphene GB is its energy. The GB structure

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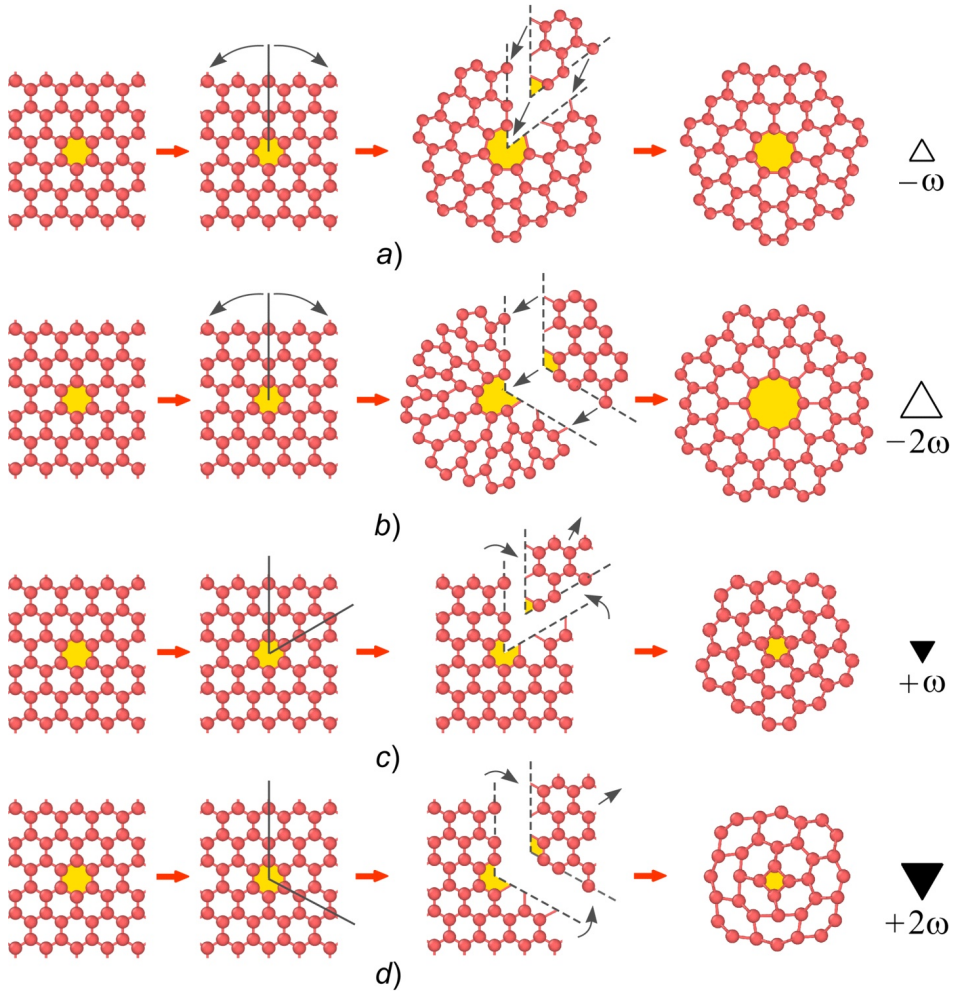

Fig. 1. Volterra's procedure for the formation of wedge disclinations in 2D hexagonal crystal lattice: (a) negative disclination and associated 7-member ring; (b) negative disclination and associated 8-member ring; (c) positive disclination and associated 5-member ring; (d) positive disclination and associated 4-member ring. Minimal magnitude of disclination strength in hexagonal lattice is $\omega = \pi/3$. Negative and positive disclinations are denoted by empty and black triangles, respectively.

models as well as their energies have been studied in a number of theoretical works [17-22]. In particular, authors of Ref. [19] considered symmetrical and nonsymmetrical GBs containing 5- and 7- member carbon rings in detail, subdivided them in several classes, calculated their energies and discussed their electronic properties. Recently, several research groups introduced models for graphene GBs incorporating carbon rings with four to nine members [19-26]. In our previous work, e.g. in Ref. [20,26], we developed a disclination approach [27,28] to the analysis of the structure and properties of IBs in graphene.

In the present study, we utilize the disclination approach to construct and analyze new types of IBs in graphene. The description of 2D carbon structures containing 8- (octagon), 7- (heptagon), 5- (pentagon), and 4- (square) atomic rings in terms of disclinations as well as the advantages of this description are discussed in Section 2. The structural units containing disclination dipoles and quadrupoles are then considered in Section 3 and are used for construction of IBs in graphene in Sections 4. In Section 5, the energies of IBs are calculated and the IBs with the lowest formation energies (hence, the most feasible to observe experimentally) are identified. Finally, the main findings of this study are summarized in Section 6.

2. DISCLINATIONS IN TWO-DIMENSIONAL (2D) HEXAGONAL CRYSTAL LATTICE

Individual defects and their ensembles occurring in the 2D lattice of graphene can be well described in terms of wedge disclinations [26,29,30]. Pioneer-

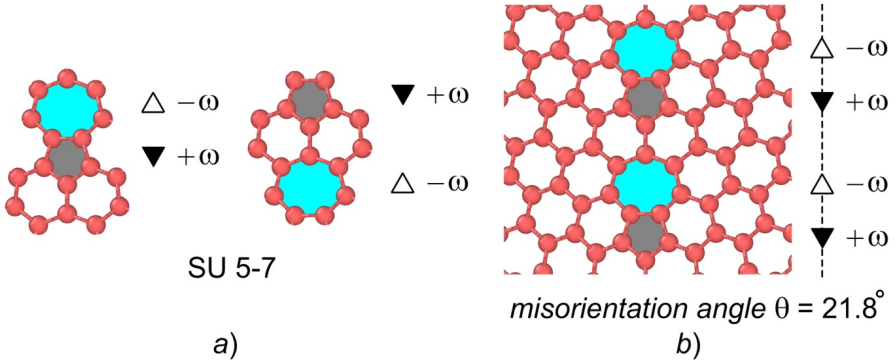

Fig. 2. Structural units (SUs) and favorable symmetrical grain boundary (GB) in graphene: (a) two variants of SU 5-7 and (b) favorable GB with misorientation angle $\theta = 21.8°$, constructed with SUs 5-7. The corresponding disclination schematics are shown to the right of atomic configurations. Disclination strength magnitude is $\omega = \pi/3$.

ing ideas on the disclinations in 2D crystals have been outlined four decades ago by Harris [31].

Fig. 1 shows the geometrical Volterra's procedure [27,28] of wedge disclination formation in a 2D hexagonal crystal lattice, which leads to the appearance of 8-, 7-, 5- and 4-member rings. For example, disclinations that are formed by inserting or removing a 60-degree wedge have minimal strength (or "charge") of $\omega = -\pi/3$ or $\omega = +\pi/3$, and cause the formation of isolated 7- or 5-member rings in the otherwise defect-free hexagonal lattice, respectively (Figs. 1a and 1c). In a similar manner, 8- and 4-member rings are associated with the formation of disclinations of double strength $-2\pi/3$ or $+2\pi/3$, respectively (Figs. 1b and 1d).

It is known that a single disclination introduces global elastic distortions in the crystal lattice (Fig. 1) and has stored elastic energy that scales quadratically with the size of the 2D crystal [27]. For example, the elastic energy of a wedge disclination in a thin disk made of isotropic material is expressed as $E = (1/8)D\omega^2 R_0^2$ [27], where ω is the strength or charge of the disclination, R_0 is the radius of the disc, $D = G(1+\nu)/2\pi$ for a two-dimensional disc [30], G is the shear modulus in units *Force/Length*, and ν is Poisson ratio. As a result of the strong size dependence of the elastic energy, single disclinations or ensembles of disclinations of the same sign can be found only in nanoscale objects, such as atomic clusters and nanoparticles with pentagonal symmetry [32,33] and fullerenes [34].

Another possibility to diminish the stored energy in disclinated solids is to form self-screened configurations [27,35], i.e. dipoles, quadrupoles, and multipoles of higher order. It has been demonstrated [27] that the energy of the dipole depends logariphmically on the external screening parameter, i.e., the size of the crystal. The energeis of the quadrupoles do not depend on the external parameter, see, e.g., Refs. [27,28,35]. This means that disclination quadrupoles are fully self-screened systems. Therefore, in our search for low-energy IBs in graphene described in the following sections we focus our attention on configurations containing disclination quadrupoles.

3. CONCEPT OF DISCLINATED STRUCTURAL UNITS IN GRAPHENE

For the first time, the concept of structural units (SUs) was applied to the modeling of GBs in graphene in our earlier work [20]. The structural unit 5-7 (SU 5-7) and the preferred symmetrical tilt grain boundary that consists of 5-7 SUs only are shown in Fig. 2. It was found that with the help of SUs 5-7 mixed with 6-membered carbon rings it is possible to construct the symmetrical GBs with arbitrary misorientation angle in the whole diapason from 0 to 60 degrees [31].

Experiments demonstrate the existence of IBs in graphene composed of SUs with pentagon-octagon-pentagon (5-8-5) ring configurations [12]. The boundary 5-8-5 was found in CVD graphene grown on Ni (111). This boundary does not contribute to the lattice misorientation of neighboring crystallites. We assume that under certain conditions, for example, for a particularly chosen substrate or growth mode, IBs can be formed from not only SUs 5-7, but also from SUs containing 5-8-5, 4-8 and 7-4-7 carbon ring configurations.

We propose two principles for selecting SUs for building low-energy symmetrical IBs in graphene:

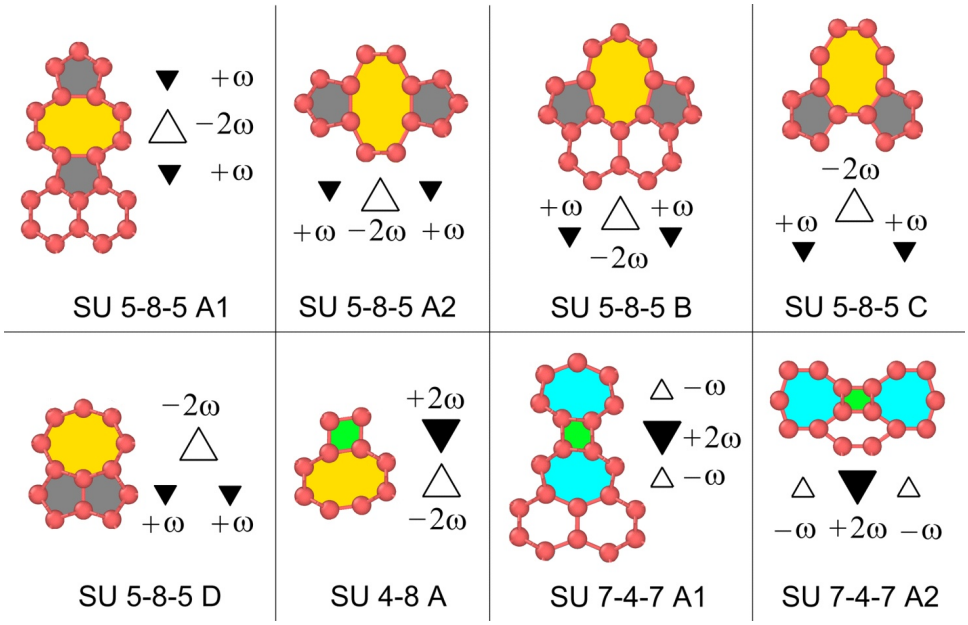

Fig. 3. Structural units (SUs) of symmetrical intercrystallite boundaries (IBs) containing 8- and 4- member carbon rings and the corresponding disclination schematics. Minimal disclination strength magnitude is $\omega = \pi/3$.

(i) the total strength of disclinations within a SU should be zero, which corresponds to a screened dipole or quadrupole configuration;
(ii) each SU should include no more than one negative and (or) positive disclination of highest strength.

For examples, in SU 5-7 the highest disclination strength magnitude is $\pi/3$, and we have one positive $+\pi/3$-disclination and one negative $-\pi/3$-disclination. In SUs 5-8-5 or 7-4-7 the highest magnitude of disclination strength is $2\pi/3$, and we have one negative $-2\pi/3$- or one positive $+2\pi/3$-disclination and two compensating disclinations of strength $+\pi/3$ or $-\pi/3$, correspondingly. In Fig. 3, all possible SUs with octagons and squares for building symmetrical IBs are presented. In some SUs, six-member carbon rings are added in order to connect them into symmetrical GBs.

4. GENERATION OF INTERCTYSTALLITE BOUNDARIES FOR MD SIMULATIONS

Using the SUs shown in Figs. 2a and Fig. 3, a series of atomic configurations containing symmetrical IBs are generated using three different routes illustrated in Fig. 4:
(i) Joining two mutually rotated crystallites (Fig. 4a). In this way, the GBs with SUs 5-7 (Fig. 2a) are obtained, including the energetically favorable GB 5-7 with misorientation angle of $\theta = 21.8°$ (Fig. 2b), consisting only of 5-7 SUs.
(ii) Attaching two crystallites to a chain of SUs (Fig. 4b). In this case, one obtains boundaries with SUs 5-8-5 and 7-4-7.
(iii) Joining mutually shifted crystallites (Fig. 4c). In this case, one gets boundaries with SUs 4-8.

As noted above, some of IBs are tilt GBs with misorientation of adjacent graphene crystal regions, while the others are linear defects in 2D crystals with zero misorientation angle.

5. SYMMETRICAL INTERCRYSTALLITE BOUNDARIES 5-8-5, 4-8, AND 7-4-7 AND THEIR ENERGIES

The energies of the atomic configurations with IBs generated as discussed above were evaluated in molecular dynamics (MD) simulations performed with LAMMPS software package [36]. The interatomic interactions were described by the adaptive intermolecular AIREBO potential developed for simulation of different phases of hydrocarbons [37] and commonly used in simulations of GBs in graphene [21,22]. The images of equilibrium structures were produced with software package OVITO [38]. The MD simulations were performed at zero temperature, and Polak-Ribiere version of the conjugate gradient algorithm for energy minimization was used [39].

The simulations are done for symmetrical IBs composed of SUs 5-8-5, 4-8, and 7-4-7 (Fig. 5). Al-

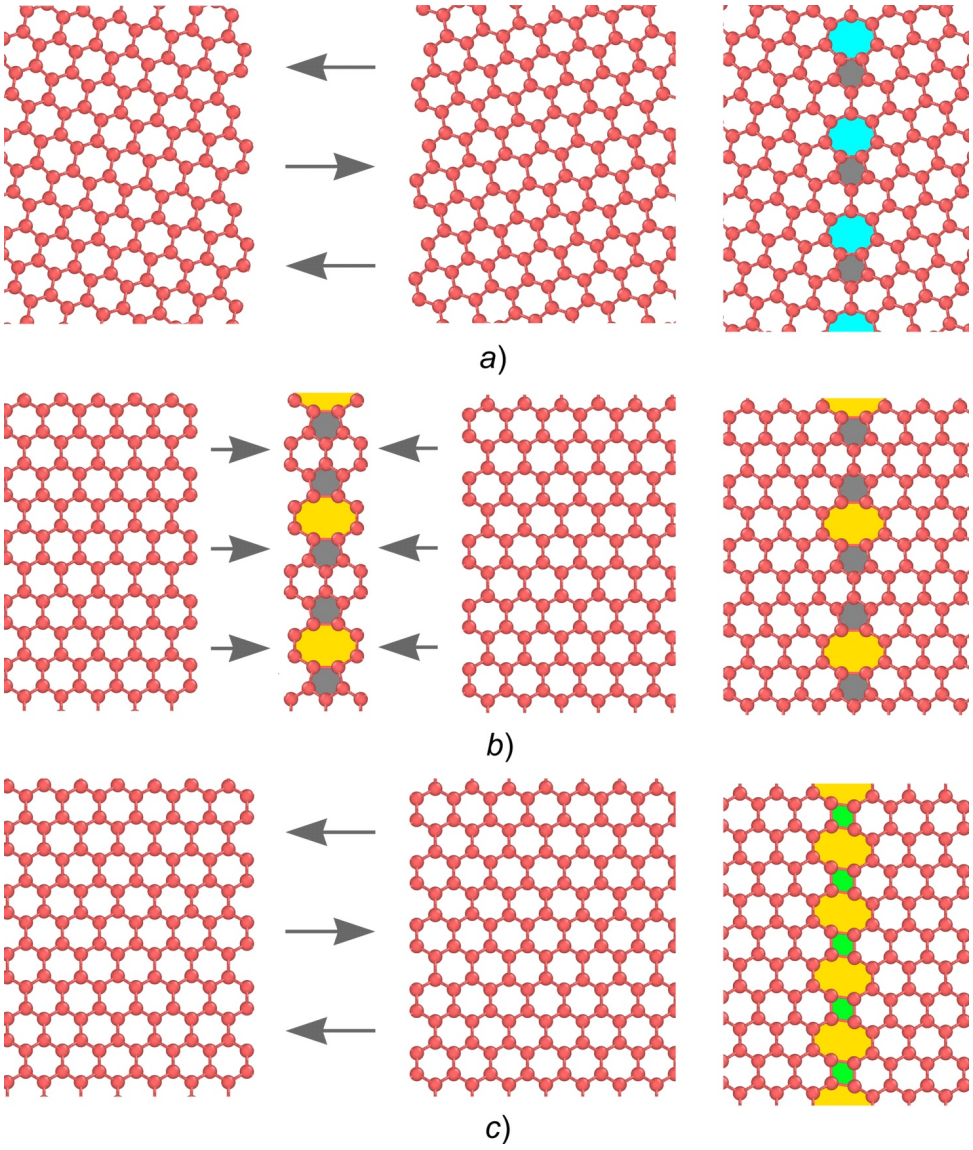

Fig. 4. Three routes of IB generation in graphene used in the present study: (a) joining mutually misoriented crystallites; (b) joining crystallites to a chain of SUs; (c) joining mutually shifted crystallites.

though it is possible to construct IBs by combining different types of SUs, only *mono-boundaries*, constructed with a single type of SUs are considered in the simulations. In Fig. 5, possible mono-GBs with octagons and squares, i.e., with $\pm\pi/3$ disclinations, are shown. GB of type 7-4-7 A2 is also simulated but not presented in Fig. 5 because of its large distortions and high energy.

Disclination schematics in Fig. 5 helps explaining the distortions of the carbon rings within the boundaries, as well as the presence or absence of misorientation between crystallites that the boundary separates. For example, the elongation of the octagons along the axis within GBs 5-8-5 of types A2, B, and C (Fig. 5) can be explained by considering the elastic field produced by the disclinations.

In the MD simulations, the excess IB energy, E_{IB}, was calculated using the relation [29] $E_{IB} = (E_{Gr+IB}\text{-}NE_{Gr})/L$, where E_{Gr+IB} is the total potential energy of the sample with IB, E_{Gr} is the energy per atom in perfect graphene, N is the number of atoms in the sample with IB, and L is the total length of the IB. The method for the calculation of IB energy E_{IB} in MD simulations eliminating the effect of the boundary conditions applied at the edges of the computational system has been described in detail in Ref. [26].

The results of the energy calculation are shown in the form of a diagram in Fig. 6 and are listed in Table 1. The values of the IB energies can be used as indicators of the feasibility of finding or fabricating an IB of a particular type in graphene. Indeed,

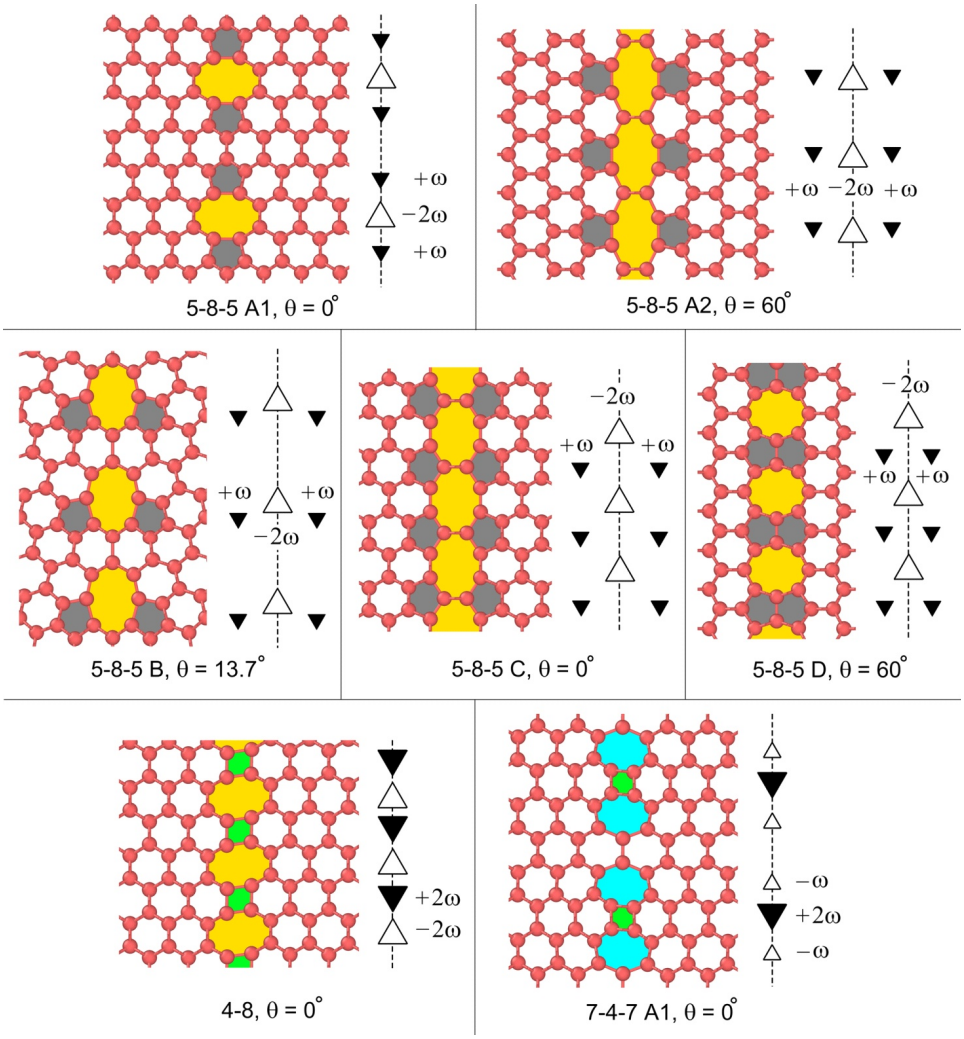

Fig. 5. Intercrystallite boundaries (IBs) constructed with structural units (SUs) shown in Fig. 3 and the corresponding disclination schematics. Minimal disclination strength magnitude is $\omega = \pi/3$.

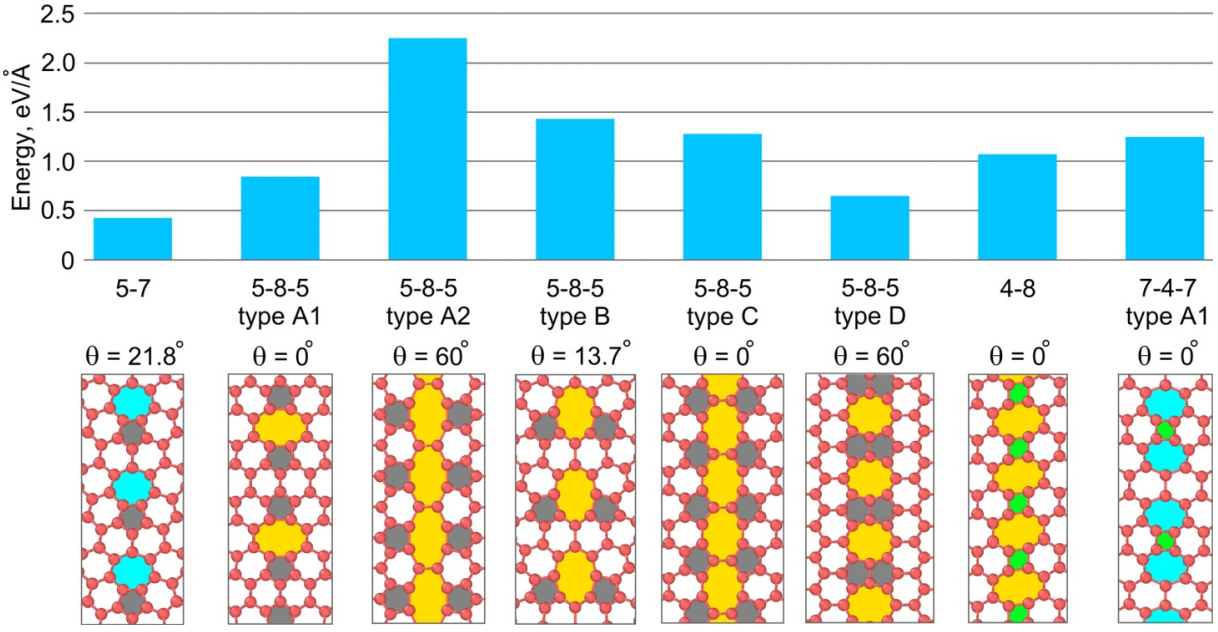

Fig. 6. Energies, misorientations, and atomic structures of intercrystallite boundaries (IBs) in graphene.

Table 1. Energies of symmetrical *mono-boundaries* in graphene, i.e. intercrystallite boundaries (IBs) constructed with structural units (SUs) of a single type. The entries for boundaries that have been observed in experiments are highlighted by color.

Type of boundary	Angle of misorientation	Energy per unit length, eV/Å	MD simulation and observation	Possibility of formation in graphene
5-7	21.8°	0.439	generated by joining mutually misoriented crystallites; observed, see Refs. [10,14]	possible
5-8-5 A1	0°	0.886	generated by joining crystallites to a chain of SUs	possible using special substrate
5-8-5 A2	60°	2.253	generated by joining crystallites to a chain of SUs	unlikely
5-8-5 B	13.7°	1.408	generated by joining crystallites to a chain of SUs	unlikely
5-8-5 C	60°	1.292	generated by joining crystallites to a chain of SUs	unlikely
5-8-5 D	60°	0.639	generated by joining crystallites to a chain of SUs; observed, see Ref. [18]	possible using special substrate
4-8	0°	1.051	generated by joining mutually shifted crystallites	unlikely
7-4-7 A1	0°	1.247	generated by joining crystallites to a chain of SUs	unlikely

the two configurations with the lowest energies, 5-7 and 5-8-5 D, have been experimentally observed [10,14,18]. The simulations suggest IB 5-8-5 A1, which is characterized by energy below the level of 1 eV/Å, as an additional configuration that may exist in graphene crystals.

6. CONCLUSIONS

We summarize the results of the study as follows.
(i) Structural units (SUs) containing disclinated carbon rings are identified.
(ii) A set of symmetrical intercrystallite boundaries (IBs) with and without misorientation between adjacent crystallites in graphene is constructed based on the SUs.
(iii) The energies of intercrystallite boundaries in graphene containing 8- and 4-member carbon rings are evaluated in molecular dynamic simulations, and several energetically favorable IBs with energies less than 1 eV/Å are identified.

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