DISCLINATED RINGS AS STRUCTURAL UNITS
IN MD SIMULATION OF INTERCRYSTALLITE BOUNDARIES
IN GRAPHENE

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Abstract. In this paper, we present a method of assembling intercrystallite boundaries in graphene from well-defined structural units containing the multipoles of non-hexagonal carbon rings (disclinations). We demonstrate that two types of intercrystallite boundaries are possible in graphene: those with misorientation between neighboring regions of the crystal and the others with a zero angle of misorientation. The misorientation is controlled by the type of disclination multipoles composing the intercrystallite boundaries. The energies of "5-8-5" boundaries, consisting of pentagonal and octagonal carbon rings, are calculated by molecular dynamics simulations.

1. Introduction
Graphene is a two-dimensional (2D) carbon crystal with a hexagonal lattice, which has unique properties: high strength, extraordinary electrical conductivity and high thermal conductivity [1-7]. Modification of graphene properties can be achieved by introducing various defects in 2D graphene lattice [8-11]: point defects, i.e. interstitial and substitutional atoms and vacancies, or imperfect carbon rings in the form of squares, pentagons, heptagons, octagons, etc. [10, 12-15]. One-dimensional (1D) defects in the form on intercrystallite boundaries can also strongly affect functional properties of graphene [16-18].

The present work is devoted to the analysis of representation of intercrystallite boundaries in graphene as chains of structural elements containing the pentagons and the octagons, and the calculation of energy of the boundaries by molecular dynamics (MD) simulation technique.

2. Intercrystallite boundaries in graphene
At the junctions of crystal grains in polycrystalline materials, including 2D ones, the boundaries are formed, and their atomic structures depend on the relative misorientations of the contacting grains [10, 12, 16-19]. However, in graphene, in addition to the conventional grain boundaries, the boundaries (i.e. 1D defects) with zero misorientation have been observed [16]. Such boundaries can be initiated by substrate, on which the graphene is grown [16], and cannot be modeled by relative rotations of adjacent regions of the crystal.

We propose the following approach to modeling of 1D defects in graphene both with and without misorientation: (i) identification of structural units on the basis of disclination multipoles, (ii) construction of a boundary using the structural units, and (iii) the subsequent addition of the crystalline regions to it.

First, structural units consisting of a pair "heptagon + pentagon" and two hexagons (Fig. 1a) were identified in the study of symmetric tilt boundaries in graphene [19]. With these structural units, the favorable grain boundary with misorientation angle 21.8° was constructed. The pentagonal and the heptagonal rings can be considered as the cores of positive and negative wedge disclinations with strength $\omega = \pi/3$ introduced in the hexagonal crystal lattice [20]. From the energy considerations, it follows that in a flat 2D crystal disclinations can exist in the form of dipoles, quadrupoles, etc., with a zero total disclination strength (magnitude of Frank vector) [21]. For that reason, it is expected that in graphene, rings associated with disclinations are present in the form of combinations, such as "heptagon + pentagon", "octagon + two pentagons", and "square + octagon", In this paper, the combinations of disclinated rings are designated as "5-7", "5-8-5", and "4-8.", respectively.

The structural units of intercrystallite boundaries in graphene are shown in Fig. 1. Note that the grain boundaries with units "5-7" have been studied in details [17, 18], and boundaries with units "5-8-5", type D, have been observed in experiment [16].
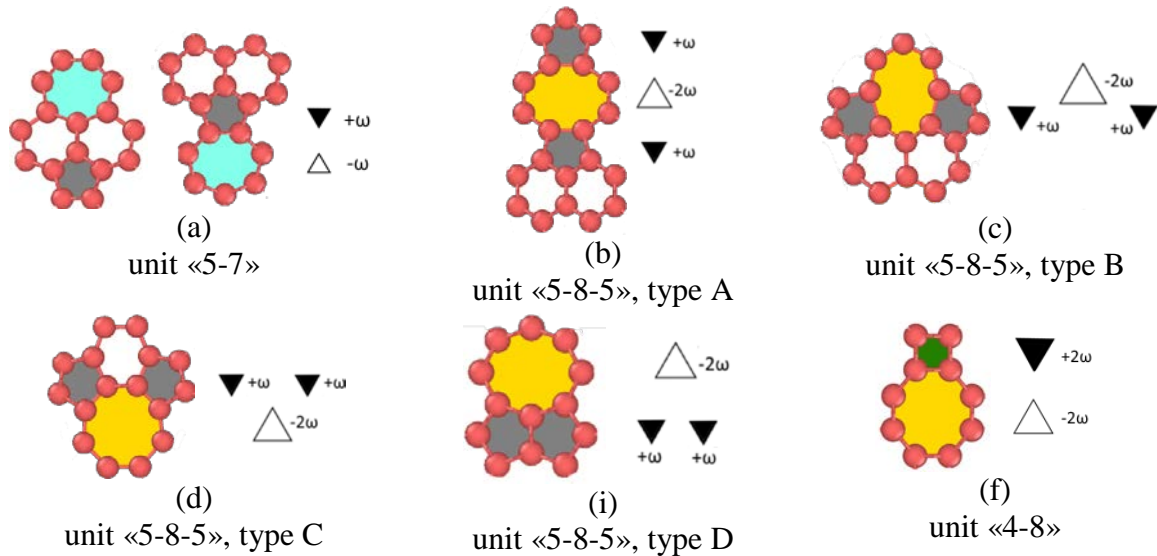

(a)
unit «5-7»

(b)
unit «5-8-5», type A

(c)
unit «5-8-5», type B

(d)
unit «5-8-5», type C

(i)
unit «5-8-5», type D

(f)
unit «4-8»

Fig. 1. Structural units of the boundaries in graphene and their disclination models. Filled and empty triangles indicate the positive and negative disclinations, correspondingly.

The structural units in Fig. 1 correspond to disclination dipoles (a,f) or quadrupoles (b-i), as schematically shown to the right of the atomic structures. The presence of the hexagons in the structural units "5-7" and "5-8-5", types A, B, C, is caused by geometrical necessity of the connection of the structural units in a continuous boundary.

3. Description of the calculation model of intecrystallite boundary

The real graphene crystals are not flat but exhibit intrinsic ripples that form spontaneously due to thermal fluctuations [22-24]. Moreover, the introduction of disclinated rings can be expected to result in the appearance of local buckling of the graphene sheet, which provides an additional channel of the elastic energy relaxation. Indeed, 2D carbon crystals with a single pentagonal ring are known to acquire a strong curvature as also occurs in fullerene [20]. In this paper, however, as the first step in the analysis of the disclination model of intercrystallite boundaries, the buckling of the graphene sheets is not allowed and perfectly flat systems are considered.

The main indicator of the boundary stability is the minimization of its energy, which in the framework of MD simulation can be calculated with the following equation [25]:

$$E_{form} = \left(E_{graph.b} - N\, E_{perf.graph} \right) / L \,, \tag{1}$$

where E_{form} is the energy of boundary formation [eV/nm], $E_{graph.b}$ is the total potential energy of the sample with the boundary [eV], $E_{perf.graph}$ is the energy per atom in a perfect graphene [eV/atom], N is the number of atoms in the sample with the boundary, and L is the total length of the boundary in the computational system [nm].

In this work, the MD simulation of intercrystallite boundaries was performed with LAMMPS software package [26]. The interatomic interactions were described by the adaptive intermolecular reactive empirical bond-order (AIREBO) potential developed for simulations of different phases of hydrocarbons [27] and commonly used in investigations of grain boundary properties in graphene [10, 28]. The images of equilibrated structures were produced with software package OVITO [29].

4. The algorithm for calculation of intercrystallite boundary energy

The first step in the calculation of the intercrystallite boundary energy is to generate an atomic configuration of a graphene sheet containing the boundary. The finite size of the systems that can be considered in MD simulations makes it necessary to ensure that the edges of the computational system do not affect the predicted values of the boundary energies. Two approaches for the elimination of graphene sheet edge influence were considered in this work, namely:
- application of periodic boundary conditions;
- elimination of the energy contributions of graphene sheet edges by considering an internal part of a sufficiently large system.

In the first approach, the periodic boundary conditions are applied in both directions in the plane of the graphene sheet. This approach eliminates the free edges of the system and, for sufficiently large systems, allows for reliable evaluation of the boundary energies. In the case of grain boundaries, however, the application of periodic boundary conditions in the direction normal to the boundary is not possible because of the misorientation of the grains. To solve this problem, it is possible to analyze atomic configurations that include two anti-parallel boundaries well separated from each other. As examples of this technique, two grain boundaries are demonstrated in Fig. 2a and Fig. 3a. The length L in Eq. (1) in this case is the total length of the two boundaries. For intercrystallite boundary with zero misorientation there is no need to create a second boundary, see Fig. 2b.

The second way of finding the energy of the boundary in graphene is to perform calculations for several increasingly large regions around the boundary and check when the energy per length starts to converge. The scheme of this approach is shown in Fig. 3b. Here, the geometry of the sheet is not important. Consequently, there is no need to consider the specifics of graphene edges and to apply periodic conditions.

After choosing the calculation method and creating the corresponding initial atomic configurations (with free or periodic boundary conditions), all structures were thoroughly equilibrated in MD simulations prior to the energy calculations. The MD simulation was performed at zero temperature, and Polak-Ribiere version of the conjugate gradient (CG) algorithm for energy minimization was used [31].

To compare the predictions of the two approaches described above we applied them to the boundary composed of structural units "5-8-5", type B (Fig. 1c, Fig. 3). Misorientation angle corresponding to this boundary was $\theta = 13.7°$. The energy of the boundary calculated using the periodic boundary conditions was 1.42 eV/Å. The energy of the same boundary found with free boundaries, within the second approach for sufficiently large calculation region, was 1.4 eV/Å. The difference in the energy values obtained by two methods is small.

For boundaries shown in Fig. 2a ($\theta = 21.8°$) and Fig. 2b ($\theta = 0°$), the energies were 0.44 eV/Å and 0.88 eV/Å, respectively.
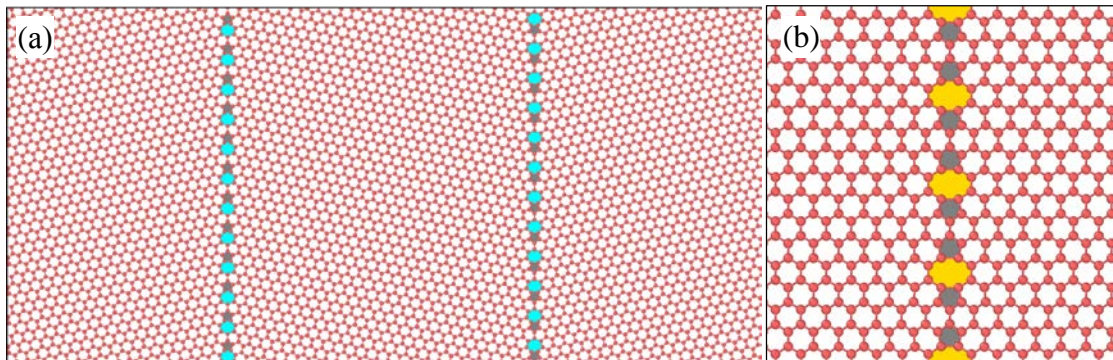

Fig. 2. Graphene configurations with intercrystallite boundaries built for calculation of boundary energies with periodic boundary conditions.
(a) The sheet with boundaries composed of "5-7" structural units; (b) sheet with boundary composed of "5-8-5", type A structural units.
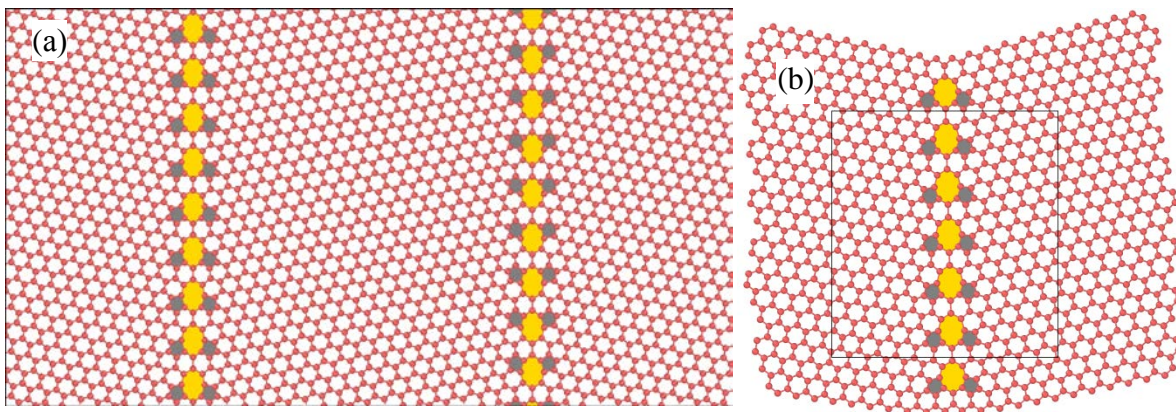

Fig. 3. Schematics of graphene configurations used for calculating the energy of intercrystallite boundaries with structural units of "5-8-5", type B for
(a) technique with application of periodic boundary conditions;
(b) technique with a selected region.

5. Summary and conclusions

This short paper presents a method of constructing intercrystallite boundaries in graphene on the basis of structural units (Fig. 1). Disclination content of structural units has been defined. It has been noted that some boundaries are real tilt boundaries with misorientation of adjacent graphene crystal regions, while the others are linear defects in 2D crystals with zero misorientation angle.

Two methods of the calculation of the energy of the intercrystallite boundaries in MD simulation have been developed with the focus on the elimination of the effect of the boundary conditions at the edges of the computational system. The two methods have been applied to boundaries constructed of "5-8-5" structural units and have been demonstrated to provide consistent energy values.

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