Condensed Matter Physics.
Physics of Low-Dimensional Structures and Nanostructures

UDC 547.022.1/.4 DOI: 10.33910/2687-153X-2020-1-4-129-134

On mesoscopic description of interfaces in graphene

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For citation: Kolesnikova, A. L., Rozhkov, M. A., Abramenko, N. D., Romanov, A. E. (2020) On mesoscopic description of interfaces in graphene. *Physics of Complex Systems*, 1 (4), 129–134. DOI: 10.33910/2687-153X-2020-1-4-129-134

Received 13 October 2020; reviewed 6 November 2020; accepted 7 November 2020.

Funding: The work was supported by the Russian Foundation for Basic Research (grant No. 18-01-00884 A).

Abstract. The article discusses a mesoscopic approach to the description of interfaces (IFs) in graphene. The approach is based on the representation of defective carbon rings with broken six-fold symmetry in hexagonal lattice of graphene as singular defects, i.e. wedge disclinations, in an elastic continuum. The angle of the sector inserted into or removed from the hexagonal lattice that results in the formation of localized quadrate, pentagon, heptagon, and octagon carbon rings, defines the strength (charge) of disclinations. The mesoscopic approach views IF in graphene as an ensemble of disclinations distributed along a line. Elementary building blocks for IFs with periodic motives of carbon atoms are structural units (SUs) containing disclination sets with zero total disclination charge. The junction of SUs of different type is considered as a virtual disclination. The approach works well in graphene when analyzing elastic fields and stored energies of IFs of two types: grain boundaries (GBs) that induce misorientation of neighboring domains of graphene lattice, and zero misorientation interfaces (ZMIs) that do not possess such a property.

Keywords: graphene, crystal lattice defects, elastic continuum, disclinations, interfaces, structural units.

Introduction

One of the most important scientific discoveries of the early 21st century is the successful production of graphene, a two-dimensional carbon crystal with a hexagonal lattice (Geim, Novoselov 2010). This fact, as well as the unique properties of graphene, gave rise to works on the synthesis, analysis and modelling of new two-dimensional materials with desired properties, see, for example, recent publications in Nature Communications (Tang et al. 2019) and Scientific Reports (Bravo et al. 2019; Wang et al. 2019). Graphene has high strength and plasticity (Frank et al. 2007; Lee et al. 2008), special electronic properties due to the presence of a Dirac cone in its band structure (Avouris 2010; Castro Neto et al. 2009), and a record high thermal conductivity (Balandin et al. 2008). These characteristics allow to consider graphene as a material for next-generation electronics and optoelectronics.

Physical and mechanical properties of graphene are significantly affected by defects in its crystal lattice, in particular, linear defects—interfaces (IFs), see Ref. (Bagri et al. 2011; Ovid'ko 2013; Romanov et al. 2018). At present, there are well-developed atomistic methods for studying defects in graphene: molecular dynamics (MD) simulation technique operating with empirical interatomic potentials, and

the density functional theory (DFT) approach based on first principle calculations for atomic systems. The other methods known as mesoscopic ones consider defects in a continuum with prescribed effective properties of graphene.

In our previous studies of defects in graphene we used both atomistic modelling methods and tools of the continuum theory of solids (Kolesnikova et al. 2017; 2020; Romanov et al. 2018; Rozhkov et al. 2016; Rozhkov, Kolesnikova, Hussainova et al 2018; Rozhkov, Kolesnikova, Yasnikov et al. 2018). In this work, based on the theory of disclinations in an isotropic elastic continuum, we use a mesoscopic approach to analyze graphene IFs.

Disclinations in graphene

In the framework of mesoscopic approach, a single carbon pentagon (five-member carbon ring) in otherwise hexagonal graphene lattice points to the core of a positive 60-degree wedge disclination. Indeed, the removal of the 60-degree wedge from the graphene lattice consisting of six-member carbon rings leads to the appearance of a wedge disclination with a strength of $\omega = 60^\circ = +\pi/3$. The atoms nearest to the disclination point form a pentagon, and the entire graphene lattice is elastically distorted (Fig. 1). In a similar manner, one can imagine carbon quadrate (Fig. 1). Unlike the pentagon, the heptagon serves as the core of a negative 60-degree disclination, as its appearance is a consequence of the insertion of the 60-degree wedge into the hexagonal graphene lattice (Fig. 1). Embedding of $60n$-degree wedge (n = 2, 3, ...) into graphene lattice leads to the negative wedge disclination of the corresponding strength with a core in the form of an octagon, a nonagon, etc. (Fig. 1) (Kolesnikova et al. 2017; Romanov et al. 2018; Rozhkov et al. 2016; Rozhkov, Kolesnikova, Yasnikov et al. 2018; Harris 1977).

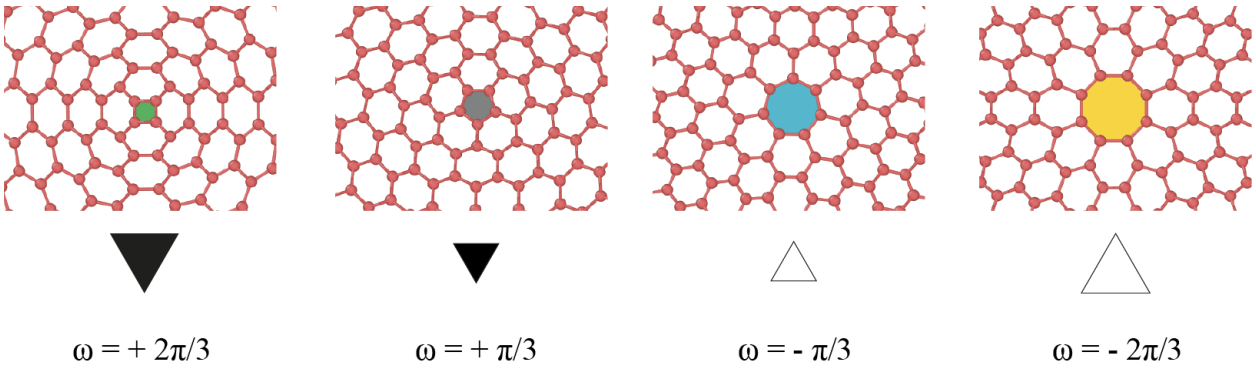

Fig. 1. Defective carbon polygons in graphene lattice and their relation to disclinations.
The strength ω of positive and negative disclinations is denoted below the corresponding schematics

Single isolated wedge disclinations cause enormous elastic distortions that scale logarithmically with the distance from their cores and have their energies proportional to R^2, where R is the crystallite size (Romanov, Vladimirov 1992). In case of graphene sheets, the elastic energy diminishes when disclination approaches to the edge of the sheet that is similar to the screening of disclination elastic fields by a free surface in case of 3D-crystals (Romanov, Vladimirov 1992). Changing the geometry of the graphene sheet, i.e. the formation of a curved carbon shell, provides the release of disclination elastic energy. In the extreme case, closed spherical-alike carbon shell with twelve positive wedge disclinations of strength $\omega = +\pi/3$ each form fullerene macromolecule (Kolesnikova, Romanov 1998).

In the flat graphene sheet, disclinations of opposite sign can form self-screened configurations, whose energies do not depend on the crystallite size. Such configurations have zero disclination charge and zero dipole moment (Romanov, Vladimirov 1992):

$$\sum_i \omega_i = 0, \tag{1a}$$

$$\sum_i \omega_i \boldsymbol{r}_i = 0, \tag{1b}$$

where ω_i is the strength of the i-th disclination in the ensemble, $\boldsymbol{r}_i$ is the radius-vector from the coordinate origin to the i-th disclination.

 DOI: 10.33910/2687-153X-2020-1-4-129-134

Important examples of screened disclination configurations are disclination quadrupoles and their ensembles, for which the conditions (1a, b) are fulfilled, see, e.g. Ref. (Rozhkov, Kolesnikova, Yasnikov et al. 2018). Interfaces in graphene consisting of periodic chains of disclinated carbon polygons (Ovid'ko 2013; Romanov et al. 2018) give other examples of screened disclination ensembles satisfying Eqs. (1a, b).

Interfaces in graphene

In our earlier work, see Ref. (Romanov et al. 2015), it was established that the grain boundaries (GBs) in graphene consist of structural units (SUs), which are well-defined motives (or combinations) of disclinated and regular carbon rings. Then the concept of SUs was extended to all periodic straight-linear IFs in graphene (Kolesnikova et al. 2017; Romanov et al. 2018; Rozhkov et al. 2016).

Structural units of periodic interfaces in graphene

Figure 2 shows selected SUs from a wide range of possible SUs and their disclination schematics. The nomenclature for a SU includes numbers that denote the types of disclinated carbon rings, e.g. 4—quadrat, 5—pentagon, 7—heptagon etc., and letters (sometimes with a number) denoting a modification for combining these carbon rings into a SU.

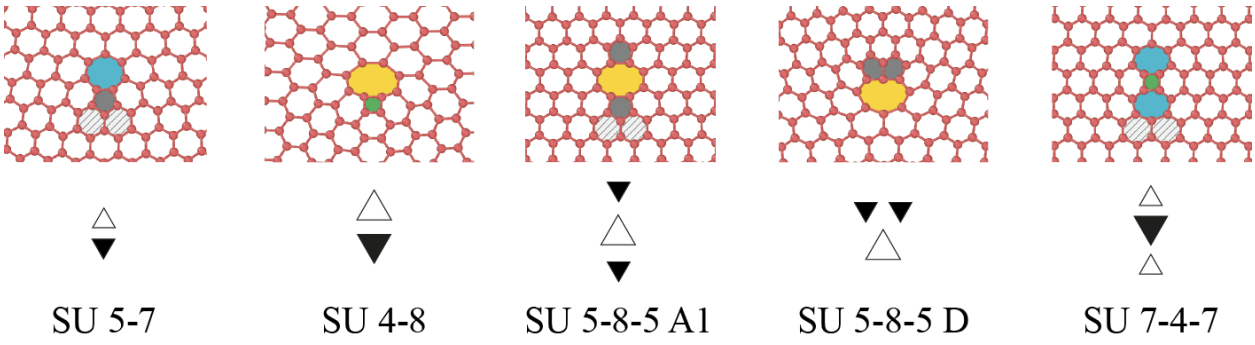

Fig. 2. Typical structural units (SUs) of interfaces in graphene and their disclination schematics. The filled carbon rings belong to the shown SUs

Structural units that may construct interfaces in graphene meet two major requirements:

(a) SUs have to form the interface without breaking the bonds and without changing the type of the bond (sp^2 hybridization for graphene) when joining. Some SUs contain additional hexagonal carbon rings typical for the defect-free graphene crystal lattice, see SU 5—7, SU 5—8—5 A1, SU 7—4—7 with the shaded hexagons in Fig. 2. This allows to construct straight-linear interfaces.

(b) SUs have to obey the rule of Eq. (1a), i.e. they must have zero disclination charge.

We note that the condition (1b) is not required for a single SU. This condition has to be satisfied when connecting SUs into the linear periodic chain—the interface. For example, SU 5—8—5 A1 and SU 7—4—7, according to their disclination schematics, are the disclination quadrupoles and, therefore, have both properties (1a, b) (Romanov, Vladimirov 1992; Rozhkov, Kolesnikova, Yasnikov et al. 2018), while SU 5-7, SU 4—8 and SU 5—8—5 D have property (1a), only.

Disclination schematics for interfaces in graphene

Figure 3 shows typical straight-linear IFs in graphene. These interfaces are composed of closely packed SUs shown in Fig. 2, they are marked correspondingly. Interface 5—7 is the so-called "favorite" grain boundary (GB) with misorientation angle $\theta = 21.8^\circ$, see, e.g. Refs. (Romanov et al. 2015; Zhang, Zhao 2013). All other IFs in Fig. 3 are zero misorientation IFs.

For each atomistic IF configuration, its disclination scheme is given. The splitting of IF disclination content into disclination quadrupoles is highlighted with dashed ellipses in the same Fig. 3. As a result of such subdivision, IF structure can be modelled with a set of periodically distributed disclination quadrupoles. Therefore, we conclude that in addition to the property defined by Eq. (1a) straight-linear IFs in graphene possess the property given by Eq. (1b). Note that SUs are not necessarily equivalent to the defined disclination quadrupoles in IFs, they are just building blocks for an IF atomistic structure whereas quadrupoles relate to the mesoscopic description of IFs.

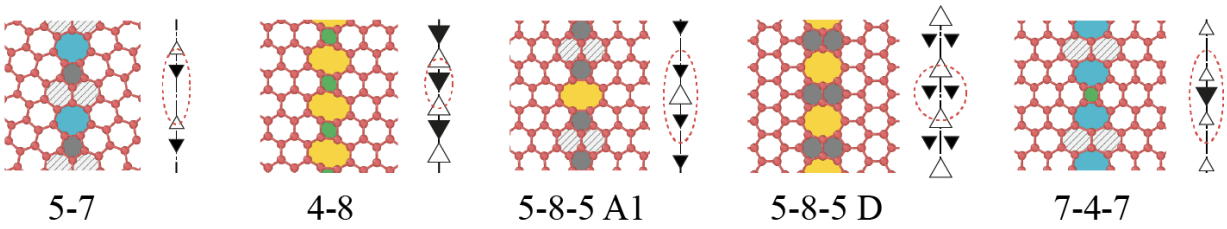

Fig. 3. Straight-linear interfaces in graphene and their disclination content. In disclination schematics, quadrupole configurations are highlighted with dashed-line ellipses

Elastic fields and elastic energy of interfaces in graphene

Figure 3a gives mesoscopic disclination description of IFs. It allows to calculate their elastic fields: displacements, strains and stresses using analytical relationships of disclination theory (Kolesnikova et al. 2014; Romanov, Vladimirov 1992). For such calculations graphene elastic constants, i. e. Poisson's ratio ν and shear modulus G have to be determined in experiments or be extracted from the atomistic simulations.

Defining disclination quadrupole content of IFs we estimate their elastic energies with the help of analytical formulas for quadrupole energies (Romanov, Vladimirov 1992). Starting with the energy of a single quadrupole one gets a rough approximate value for the energy per unit length of the interface, which can be then refined by accounting for the interactions of neighboring quadrupoles, next to the neighboring ones, etc. For example, IF 5—8—5 D energy per unit length will be $E_{5-8-5D} = 1.032$ eV/Å when accounting for the energy of a single quadrupole, and $E_{5-8-5D} = 0.757$ eV/Å when considering pair interactions among disclinations quadrupoles. In this mesoscopic analysis we used Poisson ratio ν and shear modulus G found by the MD simulation with AIREBO potential of defect-free graphene: ν = 0.367 and G = 367 GPa, respectively. Atomistic MD modelling for the same interface gives the value $E_{5-8-5D} = 0.626$ eV/Å. The above example demonstrates that the mesoscopic approach works quite well for the analysis of elastic properties of IFs in graphene.

Grain boundaries in graphene as the walls of virtual disclination dipoles

According to the approach developed for metals (Gertsman et al. 1989; Nazarov et al. 1993) and applied to graphene (Romanov et al. 2015), each favored grain boundary (GB) consists of only one type of SUs; each arbitrary GB with a misorientation angle θ consists of only two types of SUs belonging to the two nearest favored GBs, denoted as "r" and "r + 1", with misorientations θ_r and θ_{r+1} (r = 1, 2…). Since the junctions of SUs with different misorientations by definition form disclinations, the structure of arbitrary GB is described as a wall of *virtual* disclination dipoles, in which the arm of the dipoles depends on θ , and it is equal or multiples to d_A or d_B , where d_A and d_B are the lengths of SUs A and B corresponding to GB_r and GB_{r+1}, respectively (Gertsman et al. 1989).

In the mesoscopic disclination-structural unit model of the structure of arbitrary GB, disclination dipoles will be distributed periodically with the shortest period $H = md_A + nd_B$, where m and n are the numbers of SUs forming the period, or the larger period $H_k = kH$, where k is an integer. Inside the period the distribution of the disclination dipoles is nonuniform. The average misorientation angle can be determined with good accuracy from a simple expression:

$$\theta \cong \frac{md_A\theta_r + nd_B\theta_{r+1}}{H}. \quad (3)$$

In the framework of the disclination-structural unit model, the total energy E per unit length of the GB in 2D crystal is calculated as the sum of three terms (Nazarov et al. 1993):

$$E = E_0 + E_{elastic} + E_{core}, \quad (4)$$

where E_0 is the GB average interface energy, $E_{elastic}$ is the elastic energy of the disclination ensemble, and E_{core} is the energy of disclination cores. All energies are considered as the energies per unit length of GB.

 DOI: 10.33910/2687-153X-2020-1-4-129-134

Shown in left column in Fig. 3 and in Fig. 4 GB 5–7 is composed of SU 5–7 only, hence the description "favorite". Using SU 5–7 of the two modifications *B* (*B'*), and structural units of the degenerate type, consisting of hexagons only, *A* and *C*, any geometrical configuration for arbitrary GB can be constructed, see examples of GBs with $\theta = 13.2^\circ$ and $\theta = 26.1^\circ$ in Fig. 4. Following this procedure we find the distribution of SUs and the disclination dipoles for GBs in graphene with the misorientation in the range $0–60^\circ$, which is divided by the favored GB into two intervals $0^\circ < \theta < 21.8^\circ$ and $21.8^\circ < \theta < 60^\circ$, see Fig. 4.

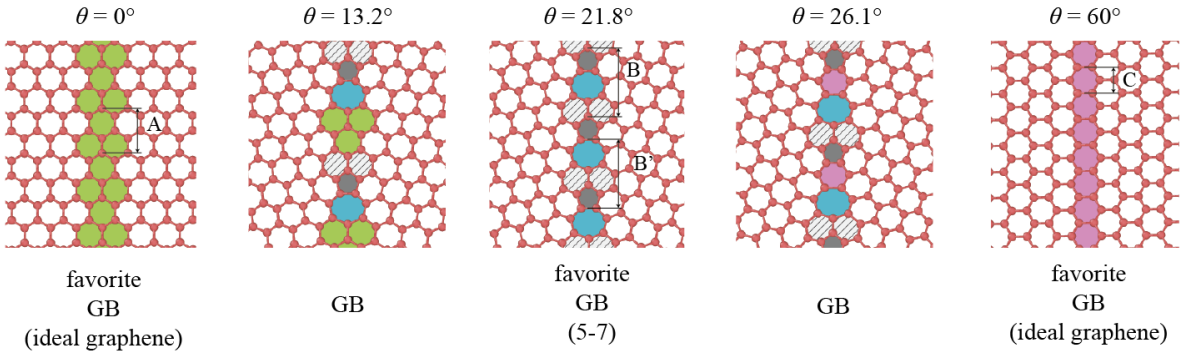

Fig. 4. Symmetrical tilt GBs in graphene, composed with structural units A, B (B'), and C. Favored GBs made of SUs of a single type with misorientation angles $\theta = 0°$, 21.8°, and 60°; arbitrary GBs made of SUs of two types with misorientation angles $\theta = 13.2°$ and 26.1°

Misorientation angle for any arbitrary GB is calculated using Eq. (3):

$$\theta \cong \frac{md_A\theta_A + nd_B\theta_B}{md_A + nd_B}, \quad 0^\circ < \theta < 21.8^\circ, \tag{5a}$$

$$\theta \cong \frac{md_B\theta_B + nd_C\theta_C}{md_B + nd_C}, \quad 21.8^\circ < \theta < 60^\circ, \tag{5b}$$

where m and n are the numbers of the structural units in the period $H = md_A + nd_B$ (or $H = md_B + nd_C$) of GB, $\theta_A = 0^\circ$, $\theta_B = 21.8^\circ$, and $\theta_C = 60^\circ$; $d_A \approx 3a$, $d_B \approx \sqrt{21}a$, and $d_c \approx \sqrt{3}a$, where a is the side size of a hexagon.

The following simple relations for the contributions E_0 to the total energy for GBs with misorientation angle θ in graphene can be proposed:

$$E_0 \cong \frac{md_Ae_A + nd_Be_B}{md_A + nd_B}, \quad 0^\circ < \theta < 21.8^\circ, \tag{6a}$$

$$E_0 \cong \frac{md_Be_B + nd_Ce_C}{md_B + nd_C}, \quad 21.8^\circ < \theta < 60^\circ, \tag{6b}$$

where interface energies per unit length $e_A = e_C = 0$ and $e_B = E_{5-7}$. Other designations are the same as in Eqs. (5a, b). Energy E_{5-7} is found from atomistic modelling.

As the final step the contributions $E_{elastic}$ and E_{core} are found with the help of analytical formulas of the disclination theory by considering a GB structure as the wall of the virtual disclination dipoles, see Ref. (Romanov et al. 2015) for detail.

Conclusions

We can conclude that the tools and techniques for the mesoscopic disclination description of IFs in graphene are effective both for determining the potential types of IFs and for calculating their elastic fields and energies. The continual theory of disclinations is especially effective in combination with atomistic modelling, when such parameters as the elastic moduli, IF period, etc. are found by MD simulation and used in the analytical formulas of the mesoscopic approach.

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