

Dislocation dipole in graphene at finite temperatures

A I Klyavlina¹, L Kh Rysaeva², R T Murzaev²

¹Bashkir State University, Validy Str. 32, Ufa 450076, Russia

²Institute for Metals Superplasticity Problems of the Russian Academy of Sciences, Khalturina 39, Ufa 450001, Russia

E-mail: A. I. Klyavlina alsou1961@yandex.ru

Abstract. In the present work, the evolution of defect structure of graphene with dislocation dipole of three types in thermal equilibrium is studied by molecular dynamics simulations. The presence of defects can considerably reduce the temperature at which graphene remains stable in thermal equilibrium. It is found, that at elevated temperatures, there is a movement of dislocations in a dipole with arm equal to 7 Å, so that a new dipole with the arm 3 Å is formed with the further transformation to the Stone–Wales defect. This reveals that dipole arm is less than annihilation distance for dislocation dipole. Again, the Stone–Wales defect at elevated temperatures disappears as a result of the rotation of the C–C bond. The obtained results will allow describing the dynamics of defects in graphene in thermal equilibrium, which can be helpful to analytically describe dislocation dynamics in graphene.

1. Introduction

Crystal defects formed intentionally, caused by external effects or during the synthesis have a great influence on the thermal, electrical, and mechanical properties of any materials [1, 2, 3, 4, 5, 6, 7, 8]. Currently, graphene is one of the most actively studied nanomaterials due to its unique mechanical, physical, and optical properties, which open up the possibilities of its use in electronics, optics, spintronics, and in many other areas. Especially for two-dimensional materials, such as graphene and silicene, their properties can strongly depend on structural features, for example, the presence of vacancies or dislocations. Graphene has a high strength, which can be reduced by the presence of defects [2, 9]. Thus, the study of defects in graphene is of crucial importance. One of the defects in graphene lattice, commonly observed in experiments, is Stone-Wales defect which is composed of two pentagon-heptagon pairs and can be formed by rotating a sp^2 bond by 90 degrees. SW defects are stable and commonly present in graphene, fullerenes and carbon nanotubes [2, 3, 4]. Such multiple 5-7 (SW) defects very often can relax to the original unperturbed lattice by reverse rotation of sp^2 bond [10, 7]. The 5–7 pair defect formation can be interpreted as the nucleation core of dislocations in the planar hexagonal network of the graphene layer.

A dislocation dipole is formed by two dislocations with opposite Burgers vectors $\pm a$ separated by the arm distance. Thus, SW defect can be considered as the dislocation dipole with zero arm. In [7] separation of SW into two dislocations was studied in carbon nanotubes at high temperatures. However, the dynamics of defects in a core-shell structure as fullerenes and nanotubes is considerably different from that in planar graphene.

In the present work, three types of dislocation dipoles differ by its arm are studied in graphene in thermal equilibrium by classical molecular dynamics simulation. History of the structural



changes during exposure at elevated temperature is described.

2. Simulation details

The initial simulation cell with a defect in the center is presented in Fig. 1a. The x and y axes are oriented along with the armchair and the zigzag directions, respectively. Size of the computational cell is $a=106$ Å and $b=75$ Å. Periodic boundary conditions are applied along x and y . Comparison of the results obtained for simulation cells of different sizes has shown that the chosen size is large enough that defects in the image cells do not interact. Three types of dipoles with different arm are introduced to the system: with $l_1=0$ Å (SW defect), $l_2=7$ Å and $l_3=27$ Å.

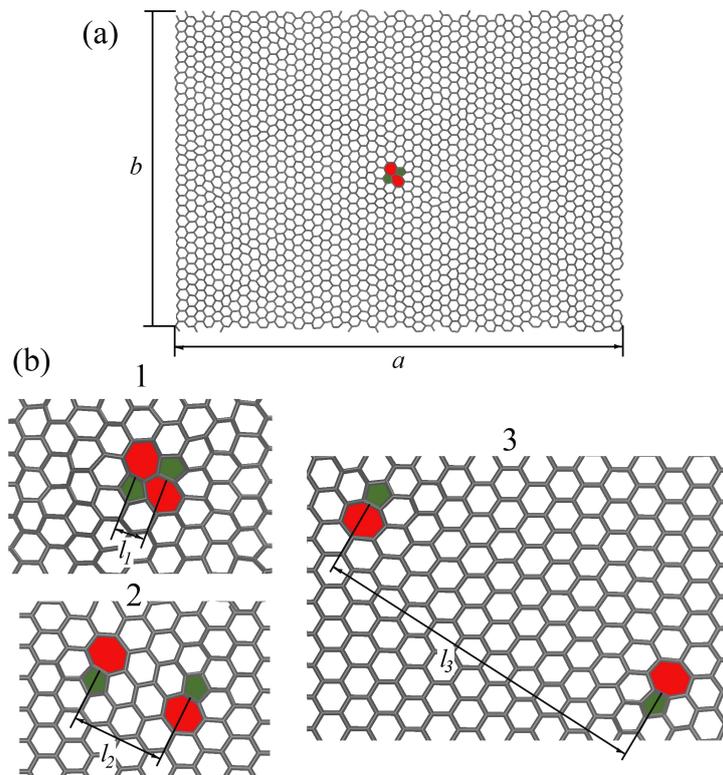


Figure 1. (a) Simulation cell. (b) Three types of dislocation dipoles.

The simulations are carried out by molecular dynamics using the LAMMPS free simulation package, with the well-known interatomic interaction potential AIREBO [11]. This potential was successfully used for calculation of various properties of carbon structures including graphene, fullerenes, and nanotubes with the defects [12, 13, 14, 15, 16, 17, 18, 19]. AIREBO potential can accurately demonstrate the breaking or formation of new carbon bonds.

The process of thermalization of carbon structures can lead to bond breaking and other structural transformation [20, 21, 22, 23]. When the dipole is introduced into the simulation cell, relaxation of the structure is conducted. After that, graphene with defects subjected to exposure at different temperatures (from 300 to 4000 K) in order to study the stability of graphene with a defect in thermal equilibrium and reveal the possible defect dynamics. The temperature stability in the system was maintained using the Nose-Hoover thermostat. Since the process at elevated temperatures is statistical, fifty numerical experiments were performed at each temperature.

3. Results and discussion

Estimation of the melting temperature gives value 5000 K (5100 K in [24], 4900 K in [25], 4510 K in [26]) for defect-free undeformed graphene, and 3950 K [2] for undeformed graphene with SW defect. The melting temperature is estimated as the temperature at which bonds were broken during 5 ps from the averaging on all numerical experiments with randomly set initial conditions. It should be noted, that in the present model, the structure is not considered during melting from room or zero to high temperatures, but just exposed and thermally equilibrated at different temperatures.

Since the process of thermalization is crucially important, relaxed structure thermalized at room temperature to check the stability of the system. During thermalization, the potential energy E_{pot} and the kinetic energy E_k oscillate around a certain equilibrium value. In Fig. 2 potential (a) and kinetic (b) energy during thermalization of the structure with dipole $l_2=7 \text{ \AA}$ at $T=300 \text{ K}$ as example. As can be seen, the structure is in thermal equilibrium. The same parameters are controlled for all the considered temperatures.

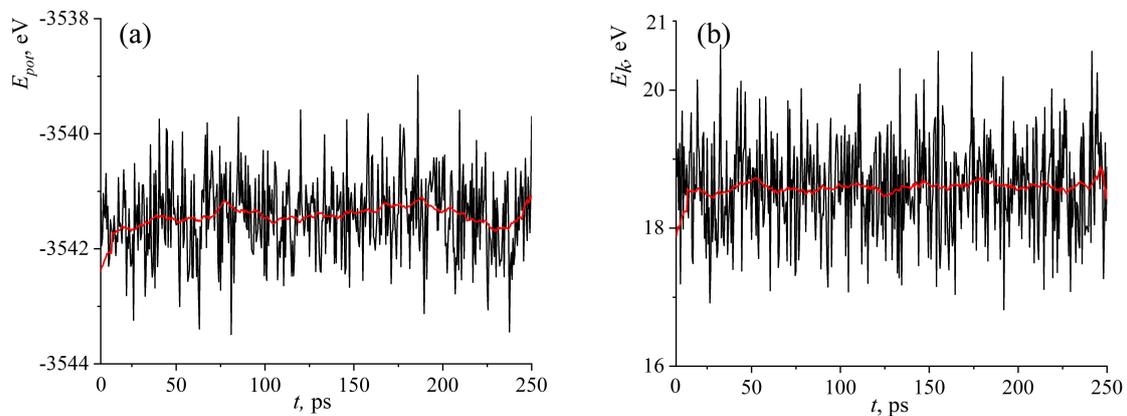


Figure 2. Potential (a) and kinetic (b) energy as the function of equilibration time at 300 K. Average value is shown by red curves.

The evolution of configurations comprising three dislocation dipoles with different arms is studied based on fifty numerical runs. In Fig. 3 different types of structural transformations which took place at high temperatures are presented: 5-atom carbon rings shown in dark green, 7-atom rings are shown in red, 6-atom rings, which replacing defects, shown in light green. As it can be seen, for SW defect just one type of structural transformations can be observed: disappearance of a defect by rotation of C-C bond (highlighted by the blue color in Fig. 3a). Obviously, the reverse transformation also took place. One of the dislocations in a dipole begins to move already at a temperature of 1400 K. For higher temperatures, the event of movement became more frequent.

For dislocation dipole with $l_2=7 \text{ \AA}$, several basic scenarios can be realized: movement of one or both dislocations; a transformation to 2 SW defects; a transformation to one SW defect. This can be followed by the disappearance of a defect, like in Fig. 3a and transformation to the ideal graphene lattice. In case I, bond breaking took place due to thermal fluctuations. After that, four 6-atom rings between two dislocations transform to SW defect. Such configuration can leave for a quite long time or immediately transform to defect-free lattice or graphene with SW defect. However, such a scenario is rare in comparison with the simple movement of dislocation towards each other which took place in case II and III. All possible variants are observed: simultaneous movement of dislocation towards each other or movement of one dislocation. The direction of motion in Fig. 3b is shown by arrows. The configuration is shown in Fig. 3b, left part of III,

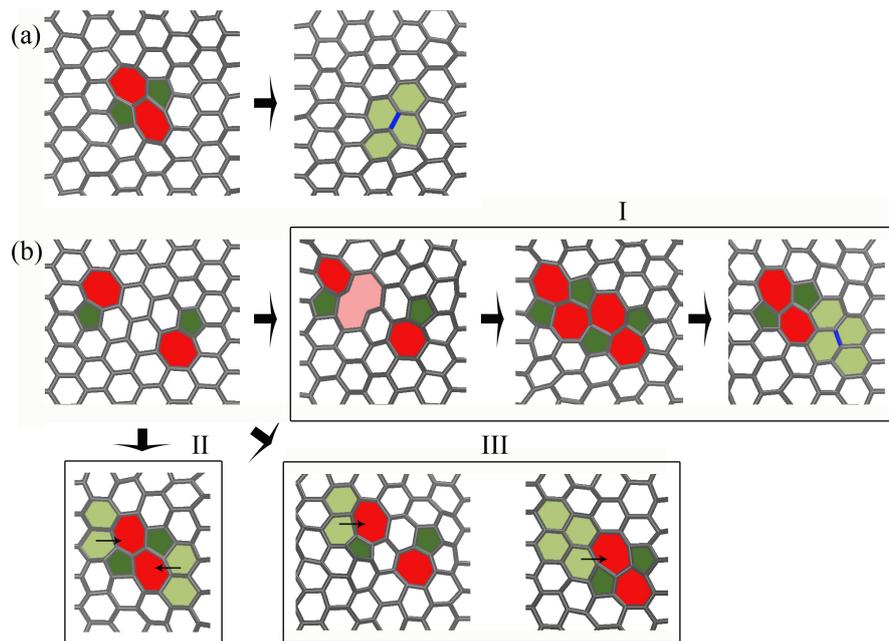


Figure 3. Scenario of defect movement for (a) SW defect and (b) dislocation dipole with $l_2=7 \text{ \AA}$.

can be considered as the dislocation dipole with the arm equal to 3 \AA .

Dislocation dipole with the arm $l_3=27 \text{ \AA}$ is stable and cannot move even at temperature 3500 K .

4. Conclusions

In summary, molecular dynamics simulation is used to study the stability of graphene with three types of dislocation dipole under thermodynamic equilibrium, and dipole dynamics. Different types of structural transformations took place – from movement of dislocations to transformation to the totally ideal lattice.

The results showed that graphene with dipoles remains stable up to high temperatures. In this case, an increase in temperature leads to dislocation sliding, the formation of a new dipole with a different arm length, or the dis-appearance of a defect from the graphene lattice due to a simple rotation of the C–C bond. The main mechanism of dislocation sliding is bond breaking which can lead to appearance of 5-7 defect on the new site. However, thermal fluctuations can also lead to the formation of 6-atom rings again. Movement of two dislocations towards each other can be considered as annihilation of dislocations and distance between dislocations $l_2=7 \text{ \AA}$ less than critical annihilation distance. However, search for equilibrium dipole distance at which no annihilation is observed should be the goal of further studies.

Dislocation dynamics in metals is well-studied and can explain numerous mechanical properties of crystalline materials. Thus, search for rules of sliding or climbing of dislocations in such new materials as graphene is an interesting and non-trivial task. At elevated temperatures, active structural transformations occur, the patterns of which can be described within the framework of molecular dynamics and then transferred to phenomenological models.

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