(Two page abstract format: including figures and references. Please follow the model below.)

Stability and kinetics of the butterfly defect in bilayer graphene from first principles

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Abstract (Arial 10)
Graphene is a very promising material for a large variety of applications due to its singular properties. These properties can be modified by defect formation in the sample; therefore, the study of these formations could help to control the properties of graphene[1].

Andrey Chuvilin has observed by TEM that in bilayer graphene under electron radiation one type of divacancy defect is formed for lower electronic energies than the displacement threshold energy for monolayer graphene (personal communication). This defect, known as the butterfly defect, is shown in figure 1 and figure.

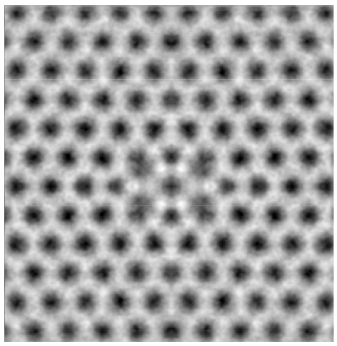

Figure 1. Experimental TEM image where the butterfly defect can be clearly observed. (Image obtained by Andrey Chuvilin, unpublished).

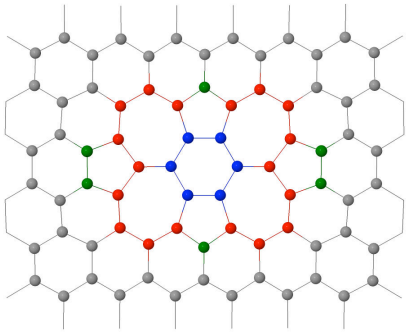

Figure 2. Relaxed DFT simulation of the butterfly defect. Four pentagons (green), four heptagons (red) and one central hexagon (blue) are created. The central hexagon is 30° rotated compared to the original configuration

In order to observe the influence that the addition of the second layer has on the creation and stabilization of the butterfly defect, we have studied the change in stability of the defect between monolayer and bilayer graphene and the kinetic process of its creation. We have used the SIESTA method[2], based on first principles DFT calculations to carry out the calculations.

In order to analyze the stability of the butterfly defect in monolayer and bilayer graphene we have calculated its formation energy. The obtained values are shown in table 1. The difference between the formation energies is very small (0.14 eV) compared with the maximum kinetic energy that an atom can obtain (15-20 eV) for typical experimental energies of the incoming electrons (80-100 keV)[3].

Type of system	Formation energy (eV)
Monolayer	7.079
Bilayer	6.939

Table 1.

As the stability of the defect does not explain the experimentally-observed effect, it appears possible that the second layer catalyzes the creation of the butterfly defect, or at least, that of the vacancy. In order to verify this hypothesis, we have simulated the electron-atom collision by giving an initial velocity to one atom. Then, we let the system evolve in time by *ab initio* molecular dynamics (AIMD).

In order to know if any atom is expulsed due to the collision with the electron, we determine the emission threshold energy, which, by definition, is the minimum kinetic energy, required to expulse an atom from the system. We observe that the atoms need at least the same amount of energy to be removed in the bilayer system as in the monolayer one. We conclude that no atom can be expulsed to create the butterfly defect. Instead, we consider the formation of a Frenkel defect that could be energetically more favorable: in this case, an atom is expulsed from one layer to create a vacancy,

remaining trapped between the two layers and thereby creating an interstitial defect. The relaxed structure can be observed in the figure 3. We obtained a formation energy of 10.4 eV for the Frenkel defect. The stacking that was used is the one that minimizes its formation energy[4].

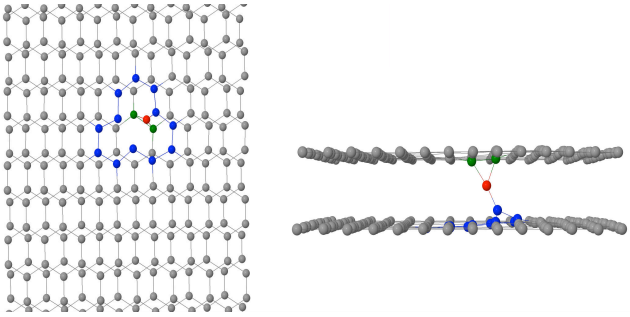

Figure 3. Two different views of the relaxed Frenkel defect, where an interstitial defect (red) and a vacancy (blue) have been created

For the AIMD simulations, we started from the pristine system and gave 6 different kinetic energy values between 22 and 16 eV for 11 different emission angles. We do not observe the stabilization of the defect in any of them: in all cases, the displaced atom eventually returns to its original position.

In order to find a possible structure that could promote the formation of the Frenkel defect, we repeated the simulations from a system in which a Stone-Wales defect has been created in the bottom layer.

The two central atoms of the Stone-Wales defect are the most promising ones since they have the largest displacement from their original positions. We 'kicked' one central atom with a collision energy of 18 eV (which corresponds to 90 keV of incoming electronic energy) at a given emission angle, and we observed that a Frenkel defect was stabilized. The figure 4 shows the initial system with the Stone-Wales defect, and the final system in which the Frenkel defect is stabilized.

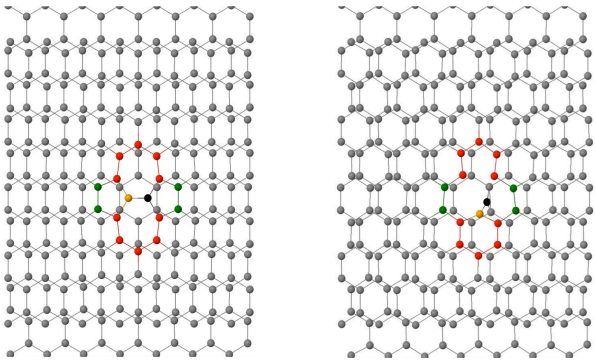

Figure 4. Initial system with Stones-Wales defect (left) and the final system which contains a Frenkel defect.

In conclusion, we have observed that the butterfly defect is not noticeably more stable in bilayer graphene than in monolayer and that preexisting defects (e.g. Stones-Wales) could help the creation of the Frenkel defect in bilayer graphene.
The next step in the investigation of Chuvilin's experiments would be to analyze if it is possible to create a divacancy in the system once the Frenkel defect is created.

References

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[4]Rob. H. Telling *et al.*, Nat. Mater. **2**, (2003) 333