A large scale molecular dynamics study of the
divacancy defect in graphene

Jean-Marc Leyssale*,† and Gérard L. Vignoles‡

CNRS, Laboratoire des Composites Thermostructuraux, UMR 5801:
CNRS-Herakles-CEA-Université de Bordeaux, 3 allée de la Boetie, 33600 Pessac, France, and
Université de Bordeaux, Laboratoire des Composites Thermostructuraux, UMR 5801:
CNRS-Herakles-CEA-Université de Bordeaux, 3 allée de la Boetie, 33600 Pessac, France

E-mail: leyssale@lcts.u-bordeaux1.fr

*To whom correspondence should be addressed
†CNRS, Laboratoire des Composites Thermostructuraux, UMR 5801: CNRS-Herakles-CEA-Université de Bordeaux, 3 allée de la Boetie, 33600 Pessac, France
‡Université de Bordeaux, Laboratoire des Composites Thermostructuraux, UMR 5801: CNRS-Herakles-CEA-Université de Bordeaux, 3 allée de la Boetie, 33600 Pessac, France
Abstract

We report on the dynamical behavior of single divacancy defects in large graphene sheets as studied by extensive classical molecular dynamics (MD) simulations at high temperatures and static calculations. In the first part of the paper, the ability of the used interatomic potential to properly render the stability and dynamics (energy barriers) of such defects is validated against electronic structure calculations from the literature. Then, results from MD simulations are presented. In agreement with recent TEM studies, some mobility is observed through series of Stone-Wales-like bond rotations involving the 5-8-5, 555-777 and 5555-6-7777 reconstructions. Although these three structures are by far the most probable structures of the DV defect, not less than 18 other full reconstructions, including the experimentally observed 55-66-77 defect, were occasionally observed in the $\approx 1.5 \, \mu s$ of MD trajectories analyzed in this work. Most of these additional reconstructions have moderate formation energies and can be formed by a bond rotation mechanism from one of the aforementioned structures, with a lower activation energy than the one required to form a Stone-Wales defect in graphene. Therefore their future experimental observation is highly probable. The results presented here also suggest that the barrier to a conventional Stone-Wales transformation (the formation of two pentagon/heptagon pairs from four hexagons) can be significantly reduced in the vicinity of an existing defect, strengthening a recently proposed melting mechanism for graphene based on the aggregation of Stone-Wales defects. On a structural point of view, in addition to pentagons, heptagons and octagons, these new DV reconstructions can also contain four- and nine-member rings and show a particularly large spatial extent of up to 13 rings (42 atoms) against three (14 atoms) for the original 5-8-5 defect.

Introduction

The topic of point defects formation and migration in graphite has been a long subject of debate in carbon science as, for instance, it is of key importance in understanding radiation damages in nuclear graphites or structure-property relationships in carbon/carbon composites, especially when exposed to high temperatures. Even if their concentration may be very low in single crystals...
under equilibrium conditions, a particular attention has been given to single vacancies (SV) due to their possibly higher concentrations in more disordered or irradiated materials. In 1978, reviewing earlier experimental works, Thrower and Mayer have proposed values of $7.0 \pm 0.5$ and $3.1 \pm 0.2$ eV for respectively the formation and the migration (in the basal plane) energies of SVs. Later on, and before its actual experimental realization, electronic structure calculations (ESC) of SVs were performed on single graphene sheets used as model graphite. Kaxiras and Pandey obtained a formation energy of 7.6 eV for a bare SV and a migration energy $E_m$ of 1.6 eV, involving a saddle point with a fourfold atom in the center of the vacancy (55-66, or split-monovacancy, configuration). These results were revisited by a few authors and it was shown that SVs reconstruct by closure of two of the three dangling bonds to form a pentagon (noted 5-db), lowering the formation energy by 0.2 eV. The migration energies were also calculated using DFT methods and the most recent results indicate values of around 1.1 and 1.4 eV for the migration in graphite and graphene respectively. These values being significantly lower than the one previously hypothesized by Thrower and Mayer, indicate that self-diffusion in graphite cannot be accounted for by SVs only. The case of divacancies (DV) was also studied and a fully sp$^2$ reconstruction made of two pentagons and a central octagon (5-8-5) was found with a formation energy of 8.7 eV and a migration energy of around 7 eV was obtained, turning DVs almost immobile at low temperatures.

The facile synthesis of single graphene sheets together with the development of atomic resolution microscopy techniques like Scanning Tunneling Microscopy (STM) or aberration corrected Transmission Electron Microscopy (ac-TEM) have opened a new era in the characterization of point defects in carbon materials. Using ac-TEM Hashimoto et al. were the first to create and image in situ some atomic defects in graphene. More precisely they were able to detect a bare SV, a bare DV, a reconstructed DV (5-8-5) and an adatom on a very tiny surface of a few tens of nm$^2$ only. In the following years many kinds of defects were imaged ranging from point defects — SVs, DVs and other topologies composed of 4 to 8-member rings — to delocalized and pseudo-amorphous defect areas. These experimental results have considerably renewed
the interest in DVs by showing that, in addition to being abundant, they can display a significant mobility under an electron beam. Density-Functional Theory (DFT) calculations have shown that mobility is achieved through series of Stone-Wales bond rotations, involving several defect topologies.\textsuperscript{13,14,18–20}

Using tight-binding molecular dynamics (TBMD) at elevated temperatures Lee \textit{et al.}\textsuperscript{18} have shown that the 5-8-5 reconstruction (noted here form A) spontaneously transforms into a more stable form composed of three pentagon/heptagon pairs, the 555-777 defect (noted form B). Local Density Approximation (LDA) DFT calculations presented in the same paper have shown that the latter has a formation energy 0.9 eV lower than the former. Later on, Kim \textit{et al.}\textsuperscript{20} have reported that the energy barrier computed by Generalized Gradient Approximation (GGA) DFT of the rotation transforming form A into form B is of around 5.3 eV. In the same paper, another reconstruction made of two pentagon/heptagon pairs, the 55-66-77 defect (form D) was considered as a stable intermediate for the translation or rotation of the 5-8-5 defect. Its formation energy is however much higher than the former two (4.37 eV above form B). From the experimental viewpoint, form D was first observed in reduced graphene oxide by Gómez-Navarro \textit{et al.},\textsuperscript{21} then in graphene by Kotakoski \textit{et al.}\textsuperscript{13} Finally, another stable form, the 5555-6-7777 (form C), was recently observed in a few TEM experiments.\textsuperscript{13,14,19} It consists of four pentagons, four heptagons and a central hexagon rotated 30 degrees with respect to the graphene lattice and is formed by a bond rotation from the 555-777 defect. Calculations by Cretu \textit{et al.} have shown that its formation energy lies in between those of forms A and B and the rotation barrier is around 6 eV.\textsuperscript{19} All these migration steps are certainly of great interest in understanding the behavior of defects in graphene but the picture is still probably quite incomplete.

Owing to the extremely high computational cost associated to ESC, these techniques have been limited so far to the study of small time and length scales (typically on the order of one or two nm and for a few ps). Molecular dynamics (MD) simulations with empirical interatomic potentials (EIP), although supposedly less accurate, allow bypassing these limitations. Many EIPs for carbon have been developed in the past decades starting with the Tersoff potential,\textsuperscript{22} the Bren-
ner potential (REBO)\textsuperscript{23} and its different improvements (REBO\textsc{ii}\textsuperscript{24} and AIREBO\textsuperscript{25}), to the most sophisticated EDIP,\textsuperscript{26} ReaxFF,\textsuperscript{27} LCBOP,\textsuperscript{28} LCBOP\textsc{ii}\textsuperscript{29} and SED-REBO\textsuperscript{30} potentials. The last developed ones, thanks to having a proper treatment of middle-range interactions (bonding interactions in REBOs are generally cut off around 2 Å), are often more suited for some particular applications. For instance, EDIP and LCBOP\textsc{ii} potentials have been shown to better reproduce the structure of tetrahedral amorphous carbon\textsuperscript{26,29,31} and the energy barrier of the graphite/diamond transformation.\textsuperscript{32} LCBOP\textsc{ii} has shown a great improvement over REBO in reproducing intrinsic ripples\textsuperscript{33} and the phonon density of states of graphene.\textsuperscript{34,35} Also, the SED-REBO, thanks to its extended interaction cutoff, has been shown to properly reproduce the correct brittle fracture behavior of graphene while ductile fracture is usually obtained with REBOs.\textsuperscript{30} Nevertheless, apart from the above-mentioned cases and a few others, the family of REBO potentials has given excellent results for graphitic carbon and nanocarbon systems and these potentials are used in most published studies on such systems. This includes many papers on the structure and energetics of defect-containing graphene or nanotubes\textsuperscript{36–45} as well as on their mechanical and thermal properties.\textsuperscript{46–56} In the case of SW and vacancy defects in graphene (or nanotubes), it has been shown that these potentials give a rather fair account of the formation energies, including bare and reconstructed (5-db) SV as well as the A, B and C reconstructions of the DV defect.\textsuperscript{38,43–45} However, it has also been shown that the second generation REBOs (including REBO\textsc{ii} and AIREBO) predict the 55-66 reconstruction to be the ground state of the SV defect instead of the 5-db defect.\textsuperscript{43–45} Although REBOI is more accurate for the SV defect, REBO\textsc{ii} and AIREBO, considered as more advanced potentials, are generally used. They also benefit from being implemented in some widely used simulation software packages like GULP\textsuperscript{57} and LAMMPS.\textsuperscript{58}

Finally, another domain for which atomistic simulations have recently shown some great interest is the melting of graphene.\textsuperscript{59} Indeed, melting experiments for materials with such high melting temperatures (>4000 K) are difficult to carry out with accuracy - experimental values for the melting temperature ($T_m$) of graphite have been reported with a 1000 degrees variability (in the range [4000:5000 K])\textsuperscript{60} - and such experiments would be particularly challenging technically to achieve.
for a 2D crystal like graphene. However, using Monte Carlo simulations with the LCBOPII potential Zakharchenko et al.\textsuperscript{59} have been able to determine a reasonable estimate of $T_m$ for graphene (4900 K) which turned out to be significantly higher than the 4250 K computed for graphite with the same interatomic potential by Colonna et al.\textsuperscript{61} These simulations have also unraveled that melting in graphene is preceded by the clustering of SW defects into larger topological defects and the special role played by octagonal rings in initiating the melting process. Divacancies which have shown the ability to easily migrate and reconstruct into different topologies - including some based on octagonal rings - at high temperatures, are certainly important to consider in a model for graphene melting. In the same context, melting of small graphene clusters and hydrogen-passivated graphene clusters was studied using MD by Kumar Singh et al. who have shown that their melting properties are equally obtained by DFTB and the REBOII potential.\textsuperscript{62}

In this paper, we use MD simulations with the AIREBO potential to study the dynamical behavior of an already formed isolated DV defect in graphene, at high temperatures, yet significantly lower than $T_m$. After a short description of our methods, we first thoroughly evaluate the validity of the AIREBO potential to describe DV defects in graphene by comparing their formation and migration energies to ESC values from the literature and give an account of possible size-effects. We then present results from MD simulations at temperatures in the range [3000:4000 K], allowing characterizing the equilibrium distribution of the different reconstructions of DVs and their dynamical properties. These simulations also show the occasional formation of many other reconstructions with interesting topologies. In the last part of the paper we discuss the possibility of having some of these new structures observed in a real experiment.

**Systems and Methods**

**General information**

Calculations are performed on single graphene sheets containing a unique DV defect. Pristine graphene, SV and a few other well-known point defects like the Stone-Wales (SW)\textsuperscript{63} and inverse
Stone-Wales (ISW)\textsuperscript{64} are also considered, for comparison. The adaptive interatomic reactive empirical bond order (AIREBO) potential of Stuart et al.\textsuperscript{25} is used to describe carbon-carbon interactions in all the calculations reported in this paper. As in former work,\textsuperscript{41} the Lennard-Jones component of the potential is discarded as we are only concerned with single isolated carbon sheets. For practical reasons we have been working with orthorhombic cells with periodic boundary conditions (PBCs). A large cell dimension (z axis) is taken perpendicular to the sheets (xy plane) to avoid artificial interactions due to PBCs. The number of unit cells in the x and y directions are chosen to obtain graphene sheets with geometries as close as possible to a square. The different kinds of calculations performed in this work are described in what follows.

**Static energy calculations**

Geometry optimizations including cell relaxation have been performed with a simulated annealing scheme using a hybrid Monte-Carlo (HMC) simulation procedure.\textsuperscript{41} In these simulations, pure canonical HMC\textsuperscript{65} moves (with a 70\% probability) were complemented by attempts to increase or decrease the cell parameters in x or y (30\% probability) with an acceptance probability derived to fix the diagonal elements of the stress tensor to zero.\textsuperscript{41} Maximum volume changes attempts as well as the lengths of the MD runs in terms of step length (0.1 to 1 fs) and number of steps (5 to 20 steps) are adjusted along the runs to roughly get a 50\% acceptance rate. Starting from a high temperature the system is slowly quenched down to $10^{-3}$ K, a sufficient value for the convergence of energy, forces and geometries, by multiplying the temperature by 0.9 every $10^5$ steps. Most of the calculations are performed with an initial temperature of 2000 K apart for some unstable structures (bare SV or DV defects essentially) that would undergo a quick reconstruction at such a high temperature and for which the simulations were initiated at 500 K. In most calculations a perfectly flat initial structure was used. We have realized that in some cases, those showing significant out-of-plane distortions close to the defect (see the $C_{2v}$ forms of the ISW and 5-8-5 defects for instance), this can lead to a metastable structure with respect to the buckling of the sheet. For that reason, the calculations on many systems were also performed with buckled initial
configurations.

Formation energies were computed according to

\[ E_f = E(N) - Ne_0 \]  

(1)

where \( E(N) \) is the energy of the optimized sheet of \( N \) atoms and \( e_0 \) is the energy per atom in a perfect graphene sheet (optimized in the same way). Most of the static calculations reported in this paper have been performed on sheets based on a 3840-atom (\( \approx 10 \times 10 \text{ nm}^2 \)) graphene. In order to look for possible finite size effects when smaller sheets are considered, some calculations were also performed on 640-atom graphene (\( \approx 4 \times 4 \text{ nm}^2 \)). This size can be considered as an upper limit for ESC calculations as most of them, reported so far, deal with systems of around 100 atoms. For the same concern, calculations on the 5-8-5 reconstruction of the DV defect have been performed either with the pentagon-octagon-pentagon axis parallel to a simulation cell edge or rotated by 30° with respect to the latter. Indeed, PBCs can induce interactions between the defect and its periodic images when small system sizes are used; these interactions, if any, should depend on the defect orientation.

Static energy calculations were also used to characterize the energy barriers connecting different forms of defects between themselves and graphene through SW-like bond rotations. These barriers were computed by series of simulated annealing runs at increasing (or decreasing) values, by steps of 2.5°, of the orientation in the \( xy \) plane of a rotating dimer. In each of these simulations the dimer orientation was held fixed in plane and move attempts were performed to increase or decrease its length (15 %), to move the other N-2 atoms using HMC (70%) or to change the cell dimensions (15 %). In these runs the simulations were initiated at 10 K, the temperature was decreased by a factor 0.75 every 2000 steps and stopped at \( 10^{-2} \) K. This procedure is similar to the one adopted by Kim et al. with DFT calculations.\(^{20}\)
Series of molecular dynamics simulations were performed to study both the mobility (diffusion) and the relative importance of the different possible forms of the DV defect (some simulations have been also carried out on the SV defect for comparison), at different elevated temperatures. The general setup of the simulations is shown in Figure 1. In each case the simulation is initiated with a unique bare defect (either SV or DV) located in the center of a large, almost square, ideal graphene sheet (the lattice parameters of the sheet are obtained from a HMC simulation on a pristine graphene sheet at the suited temperature). In a circled area surrounding the defect, of radius close to half the square edge, atoms are allowed to move using unperturbed Newtonian equations. On the square corners, on the contrary, some atoms are fixed to their lattice positions avoiding global translational motions of the sheet, while in the intermediate area a simple Andersen thermostat is applied to set the working temperature. This particular setup ensures that the defect can diffuse up to half the box length before entering the thermostated area: in practice the simulations were much too short for this to happen. Avoiding the translation of the box, which would naturally occur with a stochastic thermostat, by clamping the atoms close to the box corners essentially aims at facilitating the calculation of the defect’s diffusivity with respect to the sheet. The existence, and thus the width, of the thermostated area is not essential as the thermostat is mainly used here to avoid temperature (energy) drifts that would occur for such long timescale simulations if purely newtonian (NVE) MD were used.

Details of the molecular dynamics simulations are as follows: initial velocities on moving atoms are drawn from a Maxwell-Boltzmann distribution. Equations of motion are integrated using a velocity Verlet algorithm with a 0.2 fs time step. The collision frequency of the thermostat is set to a low value, typically $1 \text{ ps}^{-1}$ per thermostatted atom, in order to perturb as less as possible the Newtonian dynamics. Simulations are performed at temperatures ranging from 3000 K to 4000 K (from 2000 to 3000 K for SVs) and different numbers of runs, with different run lengths and system sizes, are used for different temperatures. These details are summarized in Table 1. During most of these runs, configurations were stored every 2 ps for analysis. In some cases and for shorter
The principal element of the analysis consists in determining the evolution of the defect location and morphology with time. A programmable analysis of the DV localization is difficult to achieve because of the different fully sp² structures under which they can reconstruct. Also at the highest temperatures studied in this work some overlap can exist between first and second neighbor shells in graphene making difficult the determination of the bonding structure. To avoid such problems, DVs are identified by visual inspection (using the VMD visualization software⁶⁸) of every
configuration and their location defined by the center of mass of the four atoms lying closest to the vacancy center. Localizing SV is much easier as the latter are simulated at lower temperatures and can easily be identified by the presence of three twofold of fourfold atoms.

From these analyzed trajectories, equilibrium distributions of the different forms of the DV defect are simply obtained by averaging over the different trajectories performed at a given temperature. In order to characterize their mobility, the average mean square "in-plane" displacements (MSD) of the defects are computed according to:

\[
MSD(t) = \left\langle (x_I(t + t_0) - x_I(t_0))^2 + (y_I(t + t_0) - y_I(t_0))^2 \right\rangle_{t_0} \tag{2}
\]

where \(x_I(t)\) and \(y_I(t)\) are the positions of the vacancy at time \(t\) on the x and y axes respectively and \(\langle \ldots \rangle_{t_0}\) indicates averaging on different time origins \(t_0\). In our calculations each configuration is used as a time origin and the MSD\((t)\) are computed up to different times ranging from 500 ps to 20 ns, depending on the defect mobility. The defects "in-plane" self-diffusivities \(D_s\) are then computed from MSD\((t)\) according to Einstein’s equation:

\[
D_s = \frac{1}{4} \lim_{t \to \infty} \frac{d(MSD(t))}{dt} \tag{3}
\]

In these calculations only the second half part of the MSD\((t)\) curves (the high \(t\) linear part) is considered. It is also worth noting that prior to these equilibrium and dynamic property calculations, the initial parts of the trajectories (up to at least five mobility events) are discarded. Error bars on the MD results, when computed, are given as one standard deviation on the average properties computed from different MD runs performed with the same conditions.
Figure 2: Optimized geometries of SW, ISW, SV (bare, 5-db and 55-66 configurations) and DV (bare, 5-db2, 5-8-5, 555-777, 5555-6-7777 and 55-66-77 configurations) defects in a 3840-atom graphene sheet as computed with the AIREBO potential. (the color scale indicates the out-of-plane positions from -1.5Å(red) to 1.5Å(blue)).
Results

Energetics of vacancy defects in graphene

The geometries of several point defects, as optimized using the AIREBO potential in a $\approx 10 \times 10$ nm$^2$ graphene sheet, are shown in Figure 2. Included are the bare SV and DV defects and their known reconstructed forms: 5-db and 55-66 configurations for SV; 5-8-5 (A) 555-777 (B), 5555-6-7777 (C) and 55-66-77 (D) configurations for DV. The hypothetical partial reconstruction $5$-$db_2$ of DV, the Stone-Wales (SW) and Inverse Stone-Wales (ISW) defects and graphene are also given for comparison. For some defects (SW, ISW, 5-8-5 DV) two different conformations differing in their out-of-plane features were obtained, only the ones of lowest energies are shown in Figure 2, snapshots of the metastable forms can be found in the supporting information (SI). The formation energies of these different defects with respect to graphene, as computed using Eq. (1), are compared to ESC values from the literature, when available, in Table 2. In this table only values regarding pristine free standing graphene are reported as it was shown that the corresponding values in 3D graphite$^9$ or in metal supported graphene$^{69,70}$ can differ significantly from the latter.

Table 2: Formation energies of SW, ISW, SV and DV defects in graphene. Results from simulated annealing calculations using the AIREBO potential on a 3840-atom graphene sheet are compared to ESC from the literature.

<table>
<thead>
<tr>
<th>Vacancies</th>
<th>Name</th>
<th>Configuration</th>
<th>$E_{f}^{\text{AIROBO}}$ (eV)</th>
<th>$E_{f}^{\text{ESC}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>SW</td>
<td>55-77 ($C_{2h}$)</td>
<td>5.13</td>
<td>4.6-5.9$^{71-74}$</td>
</tr>
<tr>
<td>-</td>
<td>SW</td>
<td>55-77 ($C_{2v}$)</td>
<td>5.38</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>ISW</td>
<td>55-77 ($C_{2v}$)</td>
<td>5.86</td>
<td>6.22$^{64}$</td>
</tr>
<tr>
<td>-</td>
<td>ISW</td>
<td>55-77 ($C_{2h}$)</td>
<td>6.75</td>
<td></td>
</tr>
<tr>
<td>SV</td>
<td>bare</td>
<td>$db_3$</td>
<td>7.55</td>
<td>7.6$^{3,6}$</td>
</tr>
<tr>
<td>SV</td>
<td>reconstructed</td>
<td>5-db</td>
<td>7.02</td>
<td>7.4$^{6}$</td>
</tr>
<tr>
<td>SV</td>
<td>reconstructed</td>
<td>55-66</td>
<td>5.34</td>
<td>7.6$^{6}$</td>
</tr>
<tr>
<td>DV</td>
<td>bare</td>
<td>$db_4$</td>
<td>10.08</td>
<td></td>
</tr>
<tr>
<td>DV</td>
<td>1/2 reconstr.</td>
<td>5-$db_2$</td>
<td>9.47</td>
<td></td>
</tr>
<tr>
<td>DV</td>
<td>A</td>
<td>5-8-5 ($C_{2v}$)</td>
<td>7.35</td>
<td>7.5,$^{38}$ 8.25,$^{74}$8.7$^{6}$</td>
</tr>
<tr>
<td>DV</td>
<td>A</td>
<td>5-8-5 ($C_{2h}$)</td>
<td>7.70</td>
<td></td>
</tr>
<tr>
<td>DV</td>
<td>B</td>
<td>555-777</td>
<td>7.29</td>
<td>6.8,$^{38}$ 7.25-7.8$^{75}$</td>
</tr>
<tr>
<td>DV</td>
<td>C</td>
<td>5555-6-7777</td>
<td>7.87</td>
<td>7.5,$^{38}$ 7.65-8.2$^{76}$</td>
</tr>
<tr>
<td>DV</td>
<td>D</td>
<td>55-66-77</td>
<td>9.78</td>
<td>10.8-11.9$^{20}$</td>
</tr>
</tbody>
</table>
With the AIREBO potential, the energy per atom in a relaxed graphene sheet, $e_0$ in Eq. (1), is -7.408 eV, corresponding to a CC bond length of 1.398 Å. The Stone-Wales defect in graphene has been the subject of numerous studies and formation energies in the range [4.6-5.8 eV] were obtained using DFT calculations.\textsuperscript{71–73} While earlier studies were reporting a planar geometry, Ma \textit{et al.}\textsuperscript{73} have shown that the latter counts two imaginary frequencies and that the stable state for the SW defect ($\approx 200$ meV lower in energy than the flat form) is an antisymmetric defect of $C_{2h}$ symmetry with a buckling parameter (BP) of $\approx 1.7$ Å (defined as the difference between the maximum and minimum out-of-plane values). Its formation energy was found in the range [4.7-5.6 eV] depending on the functional (PBE, LDA, PBE0), system size (50-260 atoms) and geometry of the unit cell (hexagonal or orthorhombic). Using simulated annealing simulations with the AIREBO potential and starting from a perfectly flat structure and an initial temperature of 2000 K we converged to the correct $C_{2h}$ symmetry displayed in Figure 2 and a formation energy of 5.14 eV, in excellent agreement with the DFT values. The obtained BP, 2.5 Å, is close to the DFT value (1.7 Å) keeping in mind the difference in supercell size. In an attempt to obtain a flat structure for the SW defect, by lowering the initial temperature of the simulated annealing simulations we arrived at a $C_{2v}$ symmetry with $E_f = 5.38$ eV. The buckling parameter obtained (1.4 Å) confirms that the geometry is not planar. Ma \textit{et al.} have also reported a $C_{2v}$ form for the SW defect with exactly the same BP (without giving any value for $E_f$) and have shown that it is a transition state (one imaginary frequency).\textsuperscript{73}

The ISW defect is an interesting test for the AIREBO potential as it is a good check of the ability of the potential to describe the energetics of paired pentagons in graphene. According to the DFT calculations of Lusk \textit{et al.}, the ISW defect has a formation energy of 5.86 eV, a $C_{2v}$ symmetry and a BP of 2.1 Å.\textsuperscript{64} Using AIREBO we found two variants of this defect: a metastable $C_{2h}$ form with $E_f = 6.75$ eV (obtained from a flat initial structure) and a stable $C_{2v}$ form (obtained from a buckled initial structure) with $E_f$ (5.86 eV) and BP (2.87 Å) in very fair agreement with DFT values.

The formation energy of a bare SV was used in the fitting process of REBO potentials so that
the obtained value of 7.55 eV is almost equal to the one (7.6 eV) found with DFT.\textsuperscript{5,6} Also in agreement with DFT, the formation energy of the 5-db SV defect is slightly lower than the one of the bare SV (0.5 eV lower with AIREBO against 0.2 with DFT\textsuperscript{6}). However, as observed by Krasheninnikov \textit{et al.} for the REBOII potential,\textsuperscript{44,45} the AIREBO potential fails in reproducing the energetics of the 55-66 SV. While it should be a low energy transition state ($E_f = 7.6$ eV) according to DFT, AIREBO finds it as the ground state of the SV defect ($E_f = 5.34$ eV).

Formation energies for the DV defects are also reported in Table 2. Reconstructions A, B and C show $E_f$ values around 2-3 eV below the bare (db\textsubscript{4}) defect while form D is almost iso-energetic to the latter (we could not find in literature any ESC value for db\textsubscript{4} and 5-db\textsubscript{2} defects). Formation energies obtained with AIREBO for the three commonly observed DV reconstructions (A, B and C) are found in the range of DFT values published in the literature (they are also very close to those obtained with the REBOI potential\textsuperscript{38}); $E_f$ of form D is slightly underestimated with AIREBO. In agreement with DFT, form B (555-777) is the most stable.

![Figure 3: Optimized geometry of a 5-8-5 defect in a 3838-atom sheet; (a) stable ($C_{2v}$) form; (b) metastable ($C_{2h}$) form (same color scale as is Figure 2).](image)

As can be seen in Table 2, and as for the SW and ISW defects, two $E_f$ values are reported for the 5-8-5 defect. Indeed, doing our simulated annealing calculation starting from a perfectly flat
structure, the $C_{2h}$ geometry displayed in Figure 3b was obtained with $E_f = 7.70$ eV. Repeating the calculation on a much smaller system (638 atom), a more buckled $C_{2v}$ form came out with $E_f = 7.26$ eV; the $C_{2h}$ geometry being only recovered in this small system by initiating the calculation at a much lower temperature (10 K). The formation energy of the latter (7.68 eV) was close, though slightly lower than the one of the corresponding form for the large system. By initiating the calculation on the large system with a curvature compatible with the $C_{2v}$ geometry we were able to obtain the structure shown in Figure 3a, which with $E_f = 7.35$ eV is the AIREBO ground state for the 5-8-5 defect.

![Figure 4: Root mean square deviation (RMSD) of the CC bond length with respect to pristine graphene as a function of the radial distance to the 5-8-5 defect center (circles: $C_{2v}$; squares: $C_{2h}$).](image)

The evolutions of the deviation of the C – C bond length with respect to its value in pristine graphene as a function of the distance from the defect center are shown in Figure 4 for the two geometries of Figure 3. It shows that buckling in the $C_{2v}$ structure allows reducing the strain on the C – C bond length, thus reducing elastic energy. Considering elastic energy also explains the slight increase of $E_f$ with the system size for a given geometry: the smaller the size, the smaller the number of strained bonds and so the lower the elastic energy (more data regarding size effects are given as SI). Finally, in Figure 4 we can see that the RMSD of the C – C bond length reaches a plateau at distances from the defect core above 3 nm, justifying the use of $8 \times 8$ nm$^2$ sheets in the MD simulations. Very little is said in literature regarding buckling induced by the 5-8-5 defect.
El-Barbary et al.\textsuperscript{6} described it as flat; yet the formation energy reported by these authors (8.7 eV) is the highest among reported values for this defect. With AIREBO we have obtained BP of 2.53 and 4.94 Å for respectively the $C_{2h}$ and $C_{2v}$ forms of the 5-8-5 defect (the complete list of BP values are given in the SI), however, the maximum out-of-plane value for the latter was not obtained close to the defect but at the border of the simulation box. In agreement with former studies,\textsuperscript{18–20,38} defects B and C were found to have rather flat geometries for both system sizes (638 and 3838 atoms) with little size effects on the energies as well ($E_f$ on 638-atom systems were found 0.05 and 0.14 eV lower than in 3838-atom systems for respectively B and C reconstructions). As for form A, form D is a highly buckled defect. Our calculations have converged to an $S_i$ symmetry structure for both system sizes with the smaller one stabilized by 0.3 eV with respect to the larger one.

Table 3: Migration energies $E_m$ of DV through SW-like bond rotations (the case of SW defect formation in graphene is given for comparison).

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$E^{\text{AIREBO}}_{m,\alpha\beta}$ (eV)</th>
<th>$E^{\text{DFT}}_{m,\alpha\beta}$ (eV)</th>
<th>$E^{\text{DFT}}_{m,\beta\alpha}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene</td>
<td>Stone-Wales</td>
<td>9.4</td>
<td>4.0</td>
<td>9.2,\textsuperscript{71,10,11} 10.3-11\textsuperscript{72}</td>
</tr>
<tr>
<td>5-8-5 (A:$C_{2h}$)</td>
<td>555-777 (B)</td>
<td>5.8</td>
<td>6.2</td>
<td>5.3\textsuperscript{20}</td>
</tr>
<tr>
<td>5-8-5 (A:$C_{2h}$)</td>
<td>55-66-77 (D)</td>
<td>5.0</td>
<td>2.6</td>
<td>5.3\textsuperscript{20}</td>
</tr>
<tr>
<td>55-777 (B)</td>
<td>5555-6-7777 (C)</td>
<td>6.6</td>
<td>6.0</td>
<td>6.0\textsuperscript{19}</td>
</tr>
</tbody>
</table>

In Table 3 we compare the energy barriers of the SW transformations connecting different reconstructions to DFT data from the literature. The $C_{2h}$ form of the 5-8-5 defect was chosen as it is the one with closest $E_f$ to DFT calculations. Again, AIREBO performs almost equally with DFT, especially when looking at the large range of values obtained by different authors for the SW defect.\textsuperscript{71,72,77} Note that because we lock the rotating dimer in the $xy$ plane in our barrier calculations the difference in the energy barriers from reactant to product and from product to reactant is not strictly equal to the difference in the formation energies reported in Table 2. This is especially the case for curved structures like forms A and D for which $E_f$ can significantly be affected (a few tenths of eV) by such a constraint.

To summarize, we have shown in this section, that apart for the split SV (55-66), the AIREBO
potential gives a very fair account of the formation energies of the most common point defects in graphene. In addition, we provide in the SI section some results on the formation energies of graphene allotropes based on respectively the SW, 5-8-5, 78 55-7-77781 and 555-6-777741 defects and on the $I_h$ and $C_{2v}$ isomers of the $C_{60}$ molecule. 63, 82 For these structures also, a good agreement between AIREBO and DFT is observed. Furthermore, we have shown that AIREBO also reproduces extremely well the energy barriers associated to SW-like bond rotations in these systems. This gives us confidence in using this potential to characterize the static and dynamic properties of the DV defect in graphene which we attempt, using MD, in the next section.

**Molecular Dynamics**

**Description of trajectories**

![MD simulations snapshots](image)

Figure 5: Initial steps of MD simulations of a SV defect at 2000 K (a-d) and a DV defect at 3000 K (e-h) in $8 \times 8$ nm$^2$ graphene sheets.

Figure 5 shows some snapshots characterizing the early steps of MD simulations initiated with a bare SV (Figure 5(a-d)) and a bare DV (Figure 5(e-h)) defects simulated at respectively 2000 and 3000 K. As expected from the formation energies (Table 2), the bare SV ((Figure 5a) quickly reconstructs into the erroneous split monovacency defect (55-66) after 64 ps (Figure 5c). The
Correct stable configuration (5-db) is only obtained for a few ps as an intermediate state between the bare and 55-66 defects (Figure 5b). The remaining of the trajectory shows the diffusion of the 55-66 defect from a lattice position to another (Figure 5d). This behaviour is clearly an artifact due to the AIREBO potential and we will not comment further on the dynamics of SV defects in the remaining of the paper. At 3000 K, a bare DV (Figure 5e) evolves to a 5-8-5 reconstruction after 228 ps (Figure 5f) by the successive closure of the four dangling bonds (an intermediate 5-db2 structure, not shown, is observed between \( t = 224 \) and \( t = 228 \) ps). It then remains unchanged for more than 3.5 ns before the 555-777 (Figure 5g) reconstruction gets formed at \( t = 3746 \) ps, survives for \( \approx 2.7 \) ns and transforms into the 5555-6-7777 (Figure 5h) defect. This succession of 5-8-5, 555-777 and 5555-6-7777 configurations was observed in a recent TEM experiment by Kotakoski et al. (see Fig. 2 in Ref. 13). The sequence of configurations displayed in Figure 5(e-h) is typical of what we have observed in our simulations: DVs acquire mobility through series of bond rotations involving different fully reconstructed forms. In all these simulations the transient times (time required to actually perform the transition between two configurations) can be estimated to be of the order of 2 ps. No clear dependence on the temperature could be estimated for the transient time.

Another point worth mentioning is that at 3000 K, lattice vibrations are such that no distinction can be made any more between the \( C_{2v} \) and \( C_{2h} \) forms of the 5-8-5 defect.

Equilibrium distributions and dynamical properties

We comment now on average properties computed from the different trajectories performed in this work (see Table 1). The self-diffusivity coefficients \( D_s \), computed from the simulations, are plotted with respect to the temperature in Figure 6. Data collected at 3000 K for DV defects were not sufficient to obtain a reasonable estimate of \( D_s \) at this temperature. Linear fit to the data were computed according to the Arrhenius equation \( \ln(D_s) = \ln(k_0) + \frac{E_a}{k_B T} \) where \( k_0 \) is the pre-exponential factor, \( E_a \) the activation energy, \( k_B \) the Boltzmann constant and \( T \) the temperature. It is interesting to note that while the AIREBO potential poorly describes the geometry and energetics of the SV defect, the activation energy obtained from the Arrhenius plot of the self-diffusivity coefficients
As can be seen in Figure 6, and as expected from both experiments and calculations, the mobility of the DV defect is much lower and the error bars larger. Fitting the complete set of data we found an $E_a$ value of 4.55 eV which is significantly lower than what is expected from the calculated migration barrier (around 6 eV). This difference is possibly due to large error bars on the $D_s$ values, especially at the lower temperatures. For instance repeating the fit while excluding the 3250 K (the less accurate) data leads to a more satisfactory value of 5.17 eV. In all cases the kinetic prefactors $k_0$ are in satisfactory agreement (i.e. within two orders of magnitude) with the commonly assumed values derived from the Debye frequency of graphite.

In Figure 7 we plot the relative fractions of time spent by a DV defect in respectively the 5-8-5 (A), the 555-777 (B) and the 5555-6-7777 (C) reconstructions. For simplicity the bare DV and 5-db$_2$ defects as well as a few other structures with dangling bonds obtained by the breaking of a bond in the A form were counted as part of the latter (they amount for around 2% of the time spent in A form at 3000 K up to 15% at 4000 K, where they are certainly stabilized by entropic effects).
Figure 7: Distribution of the relative probabilities of the three main DV reconstructions: A (circles), B (squares), C (diamonds). Data computed from MD simulations performed on an 8 × 8 nm$^2$ sheet for $T \geq 3250$ K and a 5 × 5 nm$^2$ sheet for $T = 3000$ K. The inset shows $\ln \left( \frac{P_\beta}{P_\alpha} \right)$ vs. $1/T$ (symbols) and $(H_\alpha - H_\beta) / (k_B T) + \text{cst}$ plots for different ($\alpha, \beta$) couples; circles & full lines (A,B); squares & dashed lines (C,B); triangles & dotted lines: (C,A).
In agreement with the formation energies reported in Table 2, the B defect is the most encountered configuration with around 60% of the simulated time spent in this form. The A and C forms both account for around 20% of the time. This, however, is in apparent contradiction with the formation energies: form A should have a significantly larger weight than form C. To further investigate this point we have computed the relative enthalpies of the three forms (assuming the pressure is zero) by averaging the potential energy obtained for each form over the 60 ns of simulations performed at 3000 K on the large system. We found out that at this temperature forms A and C have very close excess enthalpies of respectively 0.55 ± 0.23 eV and 0.57 ± 0.45 eV relatively to form B. According to basic statistical mechanics, the equilibrium respective probabilities \( P_\alpha \) and \( P_\beta \) of being in state (configuration) \( \alpha \) or \( \beta \) should follow \( \ln \left( \frac{P_\beta}{P_\alpha} \right) = \frac{H_\alpha - H_\beta}{k_B T} - \frac{S_\alpha - S_\beta}{k_B} \) where \( H_i \) and \( S_i \) are respectively the enthalpy and entropy of form \( i \). Measured \( \ln \left( \frac{P_\beta}{P_\alpha} \right) \) data are shown in the inset of Figure 7 for AB, CB and CA couples together with the corresponding predictions by considering the above mentioned enthalpies (the entropic terms being adjusted). The agreement is very good, keeping in mind the width of the error bars. This Figure also shows that these probabilities do not evolve much in the temperature range considered here. Note that, not considering the out-of-plane features, the 555-777 defect can be arranged in two ways (up and down) for a given lattice position of the DV while the 5-8-5 and 5555-6-7777 defects can both be found under three orientations: horizontal and rotated by 30° clockwise and counter-clockwise for 5-8-5, vertical and rotated by 30° clockwise and counter-clockwise for 5555-6-7777. These different numbers of possible ways to arrange each defects should act on their relative entropies and increase (slightly) the statistical importance of 5-8-5 and 5555-6-7777 forms with respect to 555-777 as temperature increase. The main panel in Figure 7 shows that this effect is too subtle to be observed, especially when compared to error bars.

The evolution with temperature of the average residence times (or lifetimes) \( \langle \tau \rangle \), where \( \tau \) is the time lap between the appearance of the defect and its annihilation, are given in Figure 8 for reconstructions A, B and C. These results quantify two facts that were clearly observed in our trajectories. First, the lifetimes of the different forms diminish by around two order of magnitudes.
Figure 8: Average residence time with respect to temperature for the three main reconstructions of the DV defect. Error bars for form C at $T = 3000$ K and $3250$ K were not computed due to insufficient data. The escape rates ($1/\tau$) are plotted with respect to $1/T$ in the inset together with their Arrhenius fit.
when the temperature is increased from 3000 to 4000 K. Second, although having similar equilibrium distributions, forms A and C show completely different lifetimes: $\langle \tau \rangle$ for the latter being one order of magnitude larger than for the former. In other words, form A is often encountered yet for short times while form C is rarely encountered but survives for longer times when it is formed. Lifetimes values for form B have intermediate values between these two. Remembering that the lifetime $\tau$ of a given form is actually the inverse of the escape rate from this form, we show in the inset of Figure 8 an Arrhenius plot of the escape rates from these three defect forms.

![Potential energy surface and apparent enthalpy surface](image)

Figure 9: Schematic of the potential energy surface (left) compared to the apparent enthalpy surface (right) deduced from MD simulations (side numbers correspond to the barrier heights in eV).

From the data collected in the MD simulations we can thus propose an apparent enthalpy surface (AES) for the DV defect that we compare in Figure 9 to the calculated potential energy surface (PES). To build this diagram we have considered the enthalpies computed at 3000 K for the three forms. The barriers from one form to another were based on the activation energies $E_a$ obtained in fitting the escape rates vs. temperature (see the inset in Figure 8). Indeed if the previously described bond rotation schemes are the dominant migration mechanism, the activation energy obtained for the disappearance of forms A and C can be identified in both cases to the
enthalpy barrier towards form B. Similarly the $E_a$ value for the disappearance of form B can be attributed to the formation of form A, as it should have a higher rate than the formation of form C. As can be seen in Figure 9 the AES is in qualitative agreement with the PES; however, the barriers are underestimated by around 1 eV with respect to the PES, which is certainly too large a difference to be attributed to the thermal energy only.\textsuperscript{83} We will come back to that point later on, in the discussion section.

In addition to forms A, B, and C the MD trajectories gathered in this work have also revealed the occasional appearance of the already described form D and of not less than 17 additional fully reconstructed forms of DV. In what follows we briefly enumerate these structures, then highlight some observed reaction mechanisms.

**Seventeen more full reconstructions of the DV defect**

Figure 10 shows snapshots of DV reconstructions E-U after geometry optimization. Their formation energies with respect to their number of atoms in non-hexagonal rings, as a measure of the defect size, are plotted in Figure 11 (numerical values are given in the SI). As can be seen in Figure 10, DV reconstructions can contain up to 42 atoms (form U) in non-hexagonal rings, against 14 for form A. Apart from form Q ($E_f = 15.06$ eV), all their formation energies are in the range [7:13] eV. If globally the formation energy tends to increase with the defect size, the data appear very scattered. Based on Figure 11 the reconstructions can be classified into two groups: a low energy group consisting of forms A, B, C and E, and a high-energy group with all the other forms. Also, no correlation can be derived between the formation energy and the out-of-plane distortion. Indeed, with buckling parameters of respectively 1.06 and 4.94 Å, forms B and A are the full DV reconstructions showing respectively the lowest and highest out-of-plane components (see the SI for the complete list of buckling parameters); they are also the two most stable configurations.

Among the structures presented in Figure 10, all but two (L and Q) can be transformed into at least another one by a single bond rotation. Numerical values of the rotation barriers (migration energies) for all possible SW transformations between these structures are given in the SI. Their
Figure 10: Seventeen other full reconstructions of the DV defect obtained in MD simulations. The geometries were optimized using simulated annealing with the AIREBO potential in a 3838-atom sheet (same color code as in Figure 2).
average lifetimes $\langle \tau \rangle$ (including those shown in Figure 8 for forms A, B and C) are given in Table 4. Tables for the number of occurrences and the longest-lived event of each of these forms are also given in the SI. We now briefly enumerate these different defects.

Form D was obtained in simulations run at 3250 K and higher. It is a particularly unstable defect with lifetimes of only 1-4 ps due to a very low barrier (2.6 eV) for the migration back to the 5-8-5 defect (form A). At the same temperature were also obtained forms I and J. Among these 17 structures, form I has the most numerous occurrences and non-negligible lifetimes (up to 86 ps at 3250 K) while form J was extremely rarely encountered and never survived more than a few ps. Form I was most of the time obtained from form B, form J from form I. Increasing the temperature to 3500 K we were able to observe forms F and G with lifetimes up to 180 ps for both structures. These two defects are particularly interesting as they are both obtained by a true SW (TSW) rotation, transforming four hexagons into two pentagons and two adjacent heptagons, in the immediate neighborhood of a 5-8-5 (A) defect. The rotation barriers of 7.4 and 7.6 eV
to respectively form defects F and G from the 5-8-5 defect, 2 eV lower than the barrier to SW defect formation in graphene, clearly show that the presence of tensile strain close to the 5-8-5 defect strongly facilitates the bond rotation mechanism. F and G defects are only two of the many possibilities to extend the size of the 5-8-5 defect by a TSW transformation. In the SI we consider all the other possibilities involving rotations around the first and second neighbor bonds. Among 11 possible such structures, forms N and O were also obtained in MD simulations performed at 4000 K. Interestingly, forms F, G, N and O are those combining rather low formation energies (below 12 eV) and low rotation barriers (from 7.4 to 7.7 eV). Also, these four structures show lower buckling parameters than the seven other possible 5-8-5+SW defects (see the SI) even though the BP of form (N), 4.08 Å, is almost equal to the one of the hypothetical form AA (4.10 Å). In addition to be connected to form A, form F is also connected to forms C and G to form I. Three structures containing a four-member ring, P, R and S, were also observed at 3500 K although with very short lifetimes of 2-3 ps. According to our calculations, both static and dynamic, form P is a metastable intermediate for the rotation of form D, obtained from the latter by the $30^\circ$ rotation and destruction of the central bond. This structure possesses two fourfold atoms in an almost planar geometry and can be considered as two merged split-monovacancies (55-66 SV). As for the latter, this defect is certainly an artifact arising from the AIREBO potential. Forms R and S are obtained by an SW rotation of a bond shared by a pentagon and a hexagon in respectively the 555-777 and the 5-8-5 defects. Form M is another short-lived structure obtained at 3750 K from form A.

Rising the temperature to 4000 K, seven more structures were identified in addition to the already presented forms N and O. Form E belongs to the low energy structures in Figure 11, despite its 38 atoms in non-hexagonal rings. It is formed from form C by exactly the same process by which form C is obtained from form B. As for form C, it is a very long-lived structure with $\langle \tau \rangle = 304$ ps at this temperature. Form H is also a rather long-lived defect with $\langle \tau \rangle = 88$ ps (to be compared with 108 ps for form A at this temperature). It can either be formed by a TSW rotation from form B, or by a bond rotation from form E. As for forms E and H, forms K, L and U are three of the largest full reconstructions observed in this work (U even being the largest of
Table 4: Average lifetimes $\langle \tau \rangle$ (ns) of the different reconstructions of the DV defect as obtained from MD simulations on 3838-atom system (error bars are given in parentheses when sufficient data were available for their evaluation).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>3000</th>
<th>3250</th>
<th>3500</th>
<th>3750</th>
<th>4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.94 (1.45)</td>
<td>1.82 (0.40)</td>
<td>0.694 (0.026)</td>
<td>0.255 (0.045)</td>
<td>0.108 (0.021)</td>
</tr>
<tr>
<td>B</td>
<td>21.75 (6.64)</td>
<td>4.40 (1.15)</td>
<td>1.81 (0.20)</td>
<td>0.568 (0.038)</td>
<td>0.222 (0.030)</td>
</tr>
<tr>
<td>C</td>
<td>52.66</td>
<td>13.68</td>
<td>3.12 (1.64)</td>
<td>1.24 (0.23)</td>
<td>0.364 (0.075)</td>
</tr>
<tr>
<td>D</td>
<td>0.005</td>
<td>0.004</td>
<td>0.004</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td></td>
<td>0.304</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>0.186</td>
<td>0.010</td>
<td>0.024</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td></td>
<td>0.089</td>
<td>0.026</td>
<td>0.110</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td>0.088</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td></td>
<td>0.047</td>
<td>0.043</td>
<td>0.011</td>
<td>0.014</td>
</tr>
<tr>
<td>J</td>
<td></td>
<td>0.008</td>
<td></td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>K</td>
<td></td>
<td></td>
<td></td>
<td>0.030</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td></td>
<td></td>
<td></td>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.009</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>R</td>
<td></td>
<td></td>
<td></td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td>0.003</td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>T</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>U</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.010</td>
</tr>
</tbody>
</table>
all with 42 atoms in non-hexagonal rings). Their lifetimes range from 10 (U) to 40 (L) ps. Forms K and U were both obtained from form E: by a bond rotation for form K and by a TSW rotation for form U. The formation of form L involves two simultaneous bond rotations from form C (see below). Finally, forms Q and T are two short-lived four-member ring containing structures. With a 15.06 eV formation energy, form Q is by far the reconstruction of highest energy observed in this work. Form T, in addition to a four member-ring, also contains a nine-member ring. This defect is obtained by a bond rotation from A. An unsaturated variant of this form, with the bond connecting the 4- and 9-member rings broken, was often encountered in transient states between fully reconstructed structures (see below).

Transition mechanisms

In what follows the transformation mechanisms are further investigated by looking at some sequences of configurations extracted from the MD trajectories. It will actually show that the Stone-Wales like bond rotation mechanism considered so far is far from being the only one involved in the dynamics of the DV defect. Five typical kinds of mechanisms are shown in Figure 12. In the sequence of Figure 12a, taken from an MD simulation run at 3000 K, form A is transformed into B in around 2 ps by the usual SW-like bond rotation mechanism. Conversely, Figure 12b illustrates the rotation of a B defect at 3000 K. As can be seen, this transition is obtained through a completely different mechanism involving the successive rotation of three atoms around the central atom. The third mechanism (Figure 12c) shows the rotation and translation of form A at 3250 K. It involves (i) the formation of form D through the rotation of the red bond; (ii) the isomerization of D defect through the rotation of the bond between a red and a green atoms, and eventually (iii) the rotation of the bond between the upper red and green atoms. In Figure 12d are shown a single atom (yellow) migration mechanism transforming form B into form J, immediately followed by a bond rotation (orange-yellow) mechanism transforming form J into form I (also taken from an MD run at 3250 K). Finally in Figure 12e is shown a concerted rotation mechanism of two bonds, observed at 4000 K, transforming form C into form L in less than 2 ps. Unfortunately, we can not
Figure 12: Typical migration mechanisms of the DV defect observed in MD simulations. a: A → B transition with a bond rotation mechanism (3000 K); b: rotation of the 555-777 defect (B) with a concerted three-atom rotation mechanism (3000 K); c: migration-rotation of the 5-8-5 (A) defect (3250 K); d: B → J transition with an atom translation mechanism immediately followed by a J → I transition using a bond rotation (3250 K); e: C → L transition using two concerted bond rotations (4000 K). (colored atoms and bonds are guides to the eyes).
provide yet the energy barriers associated to the three-atom rotation mechanism (Figure 12b), the single-atom translation mechanism (Figure 12d) and the two-bond concerted rotation mechanism (Figure 12e).

![Figure 13: Three reactive sequences of configurations taken from a 92 ps long part of a DV trajectory obtained at 3500 K (the color code is redefined at the beginning of each sequence).](image)

In Figure 13 we show a sequence of snapshots characterizing 92 ps of MD performed at 3500 K. Starting from form C, the 4-555-77777 (R) configuration is obtained after 4 ps by a three-atom rotation mechanism. As for the rotation of the B defect (see Figure 12b) it proceeds by the successive counter-clockwise rotation of the red, green and orange atoms around the central blue atom. This structure quickly evolves towards form G (t = 8 ps) by the rotation of the bond between the blue and orange atoms. Form G survives for around 30 ps until a long sequence of configurations with unsaturated bonds is observed. As can be seen, this sequence corresponds to the 180° rotation of the bond between a red atom and an orange atom; defect G is recovered at t = 52 ps with only these two atoms inverted. At t = 90 ps this configuration then evolves to form I (t = 92 ps) by the rotation of the red bond.

Finally, in Figure 14 we show some snapshots of a particularly disordered and reactive se-
Figure 14: Snapshots of a MD simulation of a DV defect at 4000 K (the simulation time is indicated in the bottom right corner of the images; the color code is a guide to the eyes).

sequence taken from an MD simulation run at 4000 K. Starting from a 5555-6-7777 (C) defect a structure containing four dangling bonds is obtained at $t = 6$ ps by (i) the insertion of a blue atom in between the two orange atoms ($t = 4$ ps); and (ii) the rotation of the bond between a green and an orange atoms ($t = 6$ ps). This structure is actually an open form of the 4-55-77-8 (S) defect obtained by creating two bonds between the four unsaturated atoms (compare to the structural relationship between the 5-8-5 and the bare DV defects). It survives for more than 10 ps until the bond shared by the remaining five- and seven-member rings breaks up ($t = 18$ ps). At this point starts a complex series of transformations involving either a four-member ring bonded to a twofold atom (see the snapshots at $t = 18$ or 26 ps) or a chain of two twofold atoms ($t = 20$ or 28 ps) which eventually evolves toward a T defect at $t = 34$ ps. Form T does not survive for more than 2 ps and is transformed to form S ($t = 46$ ps) through another complex series of disordered unsaturated configurations. Among them, one contains a planar fourfold atom (at $t = 36$ ps), certainly over stabilized by the AIREBO potential. More interestingly, the structures observed on the snapshots at $t = 42$ and 48 ps differ only from form S ($t = 46$ ps) by the breaking of the bond shared by the four- and eight-member rings in the latter, this time in close analogy with the 5-db$_2$ partial reconstruction of the DV defect. This structure eventually gets transformed into form A at $t = 54$ ps.
Discussion

In this work we have used the AIREBO potential to study the energetics and dynamics of isolated single and di-vacancies in graphene. In the first part of the paper we have shown that, in agreement with former studies, potentials based on REBOII considerably overestimate the stability of the 55-66 reconstruction of the SV defect. This is also certainly the case for other structures possessing a fourfold carbon atom in a close to planar geometry. Such structures have been indeed very occasionally encountered in this work (form P of the DV defect for instance). However our dynamical results have shown that the migration kinetics of the SV defect is pretty well reproduced by the AIREBO potential with an activation energy of 1.7 eV, very close to estimations based on DFT, somehow minoring the wrong behaviour on SVs as, with such an $E_a$ value, they should quickly collapse into larger defects. More interestingly, we have shown that AIREBO performs extremely well in describing the energies of the most common point defects in graphene, apart from the already mentioned split-SV. Indeed, formation energies of the four DV reconstructions identified experimentally A, B, C and D as well as those of the SW and ISW defects are close to the values reported earlier from DFT calculations; and so are the migration barriers through the well-known SW-like bond rotation mechanism. We have also shown (see the SI) that this potential is extremely accurate for the description of most graphene allotropes reported so far.

In the second part of the paper we have carefully analyzed the results of long MD trajectories of a graphene sheet with a DV simulated at high temperatures to enhance the mobility of the defect. Although MD simulations at such high temperatures should only be compared with caution to observations made in TEM experiments - thermal annealing on the one side and electron irradiation on the other side could indeed affect in different ways the relative stabilities of the different defects - we have been able to reproduce the behavior observed in recent TEM studies, showing a series of transformations (bond rotations) between forms A, B and C leading to the diffusion of the defect’s location. Quantitative equilibrium and dynamical descriptors were computed from the MD data including the self-diffusion coefficients of the defect as well as the statistical importance of the different reconstructions, their average lifetimes and escape rates. The results have shown that
a DV defect spend around 60% of the time in form B against around 20% for both forms A and C, whatever the temperature (in the range [3000 K:4000 K]). Also, it was found that form C is the one with the lowest occurrences but the longest lifetimes while form A, the shortest-lived of these three structures, is formed much more often than the former. The activation energy for the diffusion of the defect (around 5 eV), calculated from the Arrhenius plot of self-diffusion coefficients has appeared slightly lower that what would have been expected from the rotation barriers (≈ 6 eV according to Table 3). Similarly, the apparent enthalpy surface (Figure 9) derived from the computed enthalpies (at 3000 K) and escape rates seems to present slightly shorter barriers than those computed in the static calculations. This discrepancy between static calculations and MD calculations could stem from several sources of errors that we attempt to enumerate in what follows.

First, the rotation barriers have been computed with a "circle" method, similar to the one adopted by Kim et al., which does not ensure that the minimum energy path is followed between the reactant and the product. Furthermore, in our calculations the rotating dimer was constrained in the main plane of the sheet: this can have a significant effect on the energy. Note that it is possible that the energy barriers published by Kim et al. are slightly overestimated for the same reason. The DFT reference value for the $B \rightarrow C$ transition, by Cretu et al. should be more accurate, however, as these authors used a Nudged Elastic Band approach. Another possible explanation for the discrepancy reported here could simply be the large error bars on the data inferred from the MD simulations, due to poor statistical convergence arising for the limited timescale accessible to MD simulations: see for instance the change of 0.6 eV obtained on the activation energy derived from the $D_s$ values (Figure 6) by excluding the 3250 K data from the fitting procedure. Nevertheless, other possible explanations can also be considered like for instance i) the thermal contribution to the enthalpy and the appearance of dangling-bond containing structures like the bare DV and the 5-db$_2$ structures from the 5-8-5 defect or ii) the possibility of other mechanisms with similar or slightly lower energy barriers. Looking closely at the simulations these two scenarios cannot be neglected. The formation of the 5-db$_2$ defect, whose contribution to the time spent in form A (where
the 5-8-5, 5-db$_2$, and 5-db$_4$ defects are considered as form A) has been found to be up to 15% at 4000 K, could diminish the rotation barrier of the A $\rightarrow$ B transition. Also, the rotation-translation of form A through the mechanism described in Figure 12c, involving form D as an intermediate, has a barrier almost 1 eV lower than the direct rotation mechanism. Another important mechanism is the three-atom rotation mechanism of form B displayed in Figure 12b. In their interesting paper Kim et al.\textsuperscript{20} have considered such a three-atom rotation mechanism for the rotation of the 555-777 defect. They have obtained a rather large barrier - 1.7 eV higher than for the indirect way involving the successive formation of form A, D, A (rotated) and finally B - for the simultaneous rotation of the three atoms, without giving further details on the calculation methodology. It is possible that considering the successive rotation of the three atoms, as is observed in the MD simulations would reduce the overall energy barrier. Unfortunately we do not dispose of the adequate numerical tools to investigate the energy barrier of such a complex mechanism, neither with AIREBO, nor with DFT.

Figure 15: Distribution of the residence time $\tau$ of the 5-8-5 (blue-dashed) and 555-777 (red-empty) defects computed from the MD simulations at $T=4000$ K (truncated at 500 ps for clarity).

Finally, a last, worth-mentioning, possible explanations for this apparent discrepancy between static and dynamic results is given in Figure 15 showing the normalized distributions of the residence times of forms A and B computed at 4000 K (this temperature was chosen as it is the one
with the larger data sets). As can be seen the distributions reach their maxima at much lower times than the $\langle \tau \rangle$ values (108 and 222 ps for respectively forms A and B). More interestingly the very first bin of both distributions, corresponding to a time interval of 16 ps, show high values while it should be close to 0 under the transition state theory (TST), assuming the proper separation of successive reactive events. This might indicate that at such high temperatures some reactions could immediately follow a preceding one, without re-thermalization of the system (the deactivation step in TST). As a result, activation energies inferred from MD simulations (either from diffusivity or escape rates calculations) might show apparent lower values than the computed barrier heights.

In addition to the four experimentally observed DV reconstructions A, B, C and D, our MD simulations have revealed the occasional appearance of 17 new fully reconstructed forms. Apart from form P, certainly artificially stabilized by the AIREBO potential, and form Q, having a much higher formation energy than the others, all these reconstructions have formation energies in the range [7.13 eV], i.e. significantly lower than two isolated SVs. Also, this work has shown that, apart from form L, they can all be obtained from another one by a bond rotation mechanism for which the activation energy is significantly lower than the one required to form an SW defect in graphene. Indeed, SW defects have been occasionally observed away from the DVs in our simulations, yet with a rather low frequency compared to the appearance of the DV reconstructions, especially if we take into account the many possible sites for the formation of an SW defect in an 8 × 8 nm$^2$ sheet. Therefore, most of the new DV reconstructions reported in this paper could certainly be formed under the electron beam of a TEM. Among these structures, forms E, F, G and I are often found in the MD simulations (see the occurrence table in the SI) and have relatively high lifetimes. Form E is certainly the best candidate to bet on for an experimental observation. As already said, defects B, C and E have closely related structures and seem to represent a lower energy limit for the data cloud of Figure 11. Similarly to form C, form E is rarely encountered with only eight occurrences at 4000 K over approximately 400 events observed during the 72 ns simulated. However, after forms A, B and C, form E is the fourth most encountered configuration at 4000 K (with 3.5 % of the time spent in this configuration) due to a long average lifetime of 316 ps, larger than those of
forms A and B (86 and 256 ps respectively) and only slightly lower than the one of form C (450 ps). Indeed, the three longest-lived events observed in MD runs at 4000 K were a 555-777 form (1200 ps), a 5555-6-7777 form (1182 ps) and a 55555-66-77777 (E) form (1144 ps).

It is also interesting to notice that some of the reconstructions discovered in this work are extremely extended defects compared to the bare DV or to its 5-8-5 reconstruction. For instance the five largest of them (H, K, L, E and U) count between 34 and 42 atoms in non-hexagonal rings against 14 in the 5-8-5 defect and from two to four bond rotations are necessary to obtain them from the latter. Some of these defects actually closely resemble the extended defect areas obtained in MD simulations of graphene at temperatures slightly below the melting point. As we have seen however, the formation energies of these structures are rather moderate. These extended point defects deriving from localized vacancy defects have been observed long ago in metals and termed "relaxions" by Nachtrieb and Handler. In this paper we have shown that graphene is a particularly favorable material for the formation of such relaxions, despite its 2D nature which should in principle limit the possibility of stress relaxation through delocalization.

Such a possibility for a point defect to considerably extend its size was also characterized very recently in hexagonal bilayer silica, another 2D crystal.

Figure 16: Optimized geometry (AIREBO) of the ISW+SW defect in a 3840-atom graphene sheet (same color code as Figure 2).
Another important result from this study concerns the lowering (up to 2 eV) of the barrier to a TSW rotation, transforming four hexagons into two pentagon/heptagon pairs, in the immediate neighborhood of a reconstructed DV. This can have a significant effect in the melting transition mechanism for graphene as it was pointed out by Zakharchenko et al. that the latter is initiated by the clustering of SW defects. In this work, forms F, G, N and O were obtained from form A, form H from form B and from U from form C through TSW transformations. Some six years ago Meyer et al. published one of the first papers on the direct imaging of topological defects in graphene. By closely looking at Figure 3i in Ref. 12 we can see that the defect they imaged is actually the combination of a SW and a ISW defect. Figure 16 gives a snapshot of this ISW+SW defect after geometry optimization with AIREBO. The formation energy of this experimentally observed defect is of 9.03 eV. Interestingly, the energy difference between this defect and the ISW defect (slightly higher than 3 eV), is of the same order than the difference in $E_f$ between many of the new DV reconstructions reported here and their parent A, B, or C reconstructions. This gives us further confidence that some of them will eventually be observed. Furthermore, even though it is difficult to know whether the SW or ISW defect was created first in the aforementioned experiment, we have calculated the barrier of the TSW rotation transforming a ISW into a ISW+SW defect. In agreement with the results presented above on the 5-8-5+SW, 555-777+SW and 5555-6-7777+SW cases, the obtained barrier of 8.2 eV, is significantly lower than the one for TSW rotation in pristine graphene.

To conclude this discussion we would like to add a few comments on structures counting four-member rings. Four-member rings have been often observed in recent TEM experiments, essentially under the form of reconstructed vacancies $V_n$ where the number of vacancies $n \geq 4$. A typical structure of this type is the 5-8-4-8-5 reconstruction of the quadruple vacancy ($V_4$) defect formed by the coalescence of two aligned neighboring DVs. In this work we have shown that structures containing 4-member rings can possibly be formed from DVs. However, all these structures (Q, R, S and T) are found on the high-energy side of the data cloud in Figure 11. Also, the MD simulations have shown that some of these structures (S and T particularly) are easily prone to ring
opening (see Figure 14) during the dynamics. In the SI section we show that with the AIREBO potential unreconstructed forms of the 5-8-4-8-5, S and T defects are very close in energy to the fully reconstructed variants. In the case of the 5-8-4-8-5 defect, the structure obtained by opening a bond joining a 4-member ring and an octagonal ring has a lower formation energy than the reconstructed defect. Similarly, the partial reconstruction of form S observed in Figure 14 is stabilized by around 0.2 eV with respect to the full reconstruction. These results agree with the usual underestimation of the fraction of 4-member rings obtained in atomistic models of amorphous carbons or graphitic carbons prepared using the liquid quench MD method and EIPs based on the REBOII parameterization with respect to quenches performed with ab-initio (DFT) MD. Therefore one can expect that the statistical importance of 4-member ring containing structures is slightly underestimated in this paper.

Acknowledgement

Access to the computer resources of the Mesocentre de Calcul Intensif en Aquitaine (MCIA) is gratefully acknowledged. This work was supported by the Agence Nationale de la Recherche through the PyroMaN (Pyrocabon Matrices at the Nanoscale) project (Grant ANR 2010 BLAN 0929 01) and by the Aerospace Valley Foundation.

Supporting Information Available

Available as supporting information are: 1) Results on graphene allotropes and C\textsubscript{60} isomers; 2) Snapshots of metastable forms of the SW, ISW and 5-8-5 defects; 3) discussion on the size effects on the formation energy of the 5-8-5 reconstruction; 4) tables of the formation energies (AIREBO) of all the structures studied in this work and of all the rotation barriers; 5) snapshots of the optimized structures and discussion of hypothetical defects based on TSW rotations in the immediate neighborhood of the 5-8-5 defect; 6) Discussion on the stability of 4-member rings in reconstructed vacancy defects; 7) tables for the number of occurrences and longest-lived events of each DV reconstruction. This material is available free of charge via the Internet at
Notes and References


(56) Han, J.; Ryu, S.; Sohn, D.; Im, S. Mechanical strength characteristics of asymmetric tilt grain boundaries in graphene. Carbon 2014, 68, 250–257.


(75) This range of values is obtained by considering the relative formation energy with respect to the 5-8-5 defect (-0.9 (Ref. 18) and -1 (Ref. 19) eV), and the different absolute values published for the 5-8-5 defect.6,74

(76) Obtained by adding 0.4 eV to the formation energy of the 555-777 defect.19


(83) Here also, there can be different numbers of equivalent ways to connect two given forms. This would have an impact on the entropy barrier to the reaction and so the constant term of the Arrhenius fit (Figure 8), not on the activation energy.


Graphical TOC Entry