

Real-time evolution of the buckled Stone-Wales defect in graphene



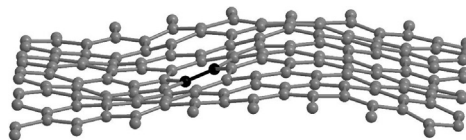
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HIGHLIGHTS

- Dynamics of the buckled Stone-Wales defect in graphene is simulated.
- Thermally activated switching between sine-like defect structures is demonstrated.
- There are two types of switching, "fast" and "slow".
- At high temperatures, switching times satisfy the Arrhenius law only on the average.
- At low temperatures, there is a strong departure from the Arrhenius law.

GRAPHICAL ABSTRACT



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ABSTRACT

Dynamics of the buckled Stone-Wales defect in graphene is studied by means of computer simulation. Thermally activated switching between two degenerate sine-wave-like configurations of the defect is traced in real time. Transition trajectory is found to be rather complex and pass through a multitude of near-planar, wave-like, and irregular configurations. Surprisingly, the switching time fluctuates strongly and can be up to an order of magnitude longer or shorter than the value given by the Arrhenius formula. This is due to a peculiar shape of the potential relief in the neighborhood of sine-wave-like configurations and, as a result, the occurrence of two radically different characteristic times.

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1. Introduction

Graphene, a hexagonal carbon monolayer [1], is in the focus of the modern condensed matter physics because of both its unique electronic characteristics (Dirac fermions) and potential for practical use [2–4]. As in the case with three-dimensional crystals, the physical properties of graphene are strongly affected by structural imperfections, such as vacancies, substitutional impurities, etc., which are either spontaneously produced at the stage of preparation or generated intentionally (e.g., under particle

irradiation). Being two-dimensional, graphene can hold the so called topological defects that are absent in bulk materials. These are intrinsic defects formed upon rearrangement of interatomic bonds. The simplest defect of this kind is the Stone-Wales (SW) defect. It is obtained by in-plane rotating one of the C–C bonds by 90° (SW transformation [5]), so that four hexagons are transformed in a pair of pentagons and a pair of heptagons, see Fig. 1. SW defects in graphene have been observed experimentally [6] and predicted to modify its electronic properties and chemical reactivity [7,8].

For a long time, SW defects in graphene were thought to be two-dimensional [9,10] (Fig. 1). However recently Ma et al. [11] have shown with first principles calculations that the flat SW defect is not a local minimum on the potential-energy surface (PES),

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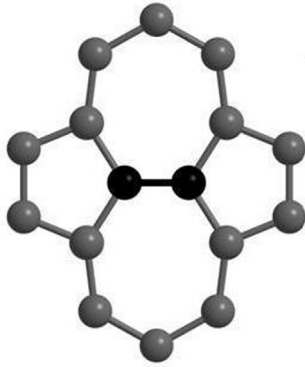


Fig. 1. Top view of the flat SW defect in graphene. The rotated C–C bond is shown in black.

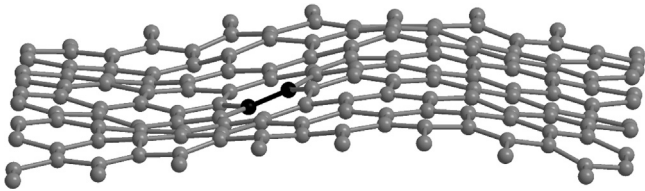


Fig. 2. Perspective view of the sine-wave-like SW defect in graphene. The rotated C–C bond is shown in black.

but a saddle point. The lowest-energy atomic configuration of the SW defect has been shown [11] to have a sine-wave-like form. In this buckled structure, the atoms of the rotated C–C bond (the defect core) move out of plane in the opposite direction, giving rise to the long-range out-of-plane displacement field (Fig. 2). Such buckled SW defects can be responsible (at least partly) for the rippling behavior of graphene [12].

Since there are two degenerate sine-wave-like configurations (differing in sign of out-of-plane atomic co-ordinates, i. e., in phase) the switching between them can hinder the observation of the buckled defect structure by means of scanning tunneling microscopy and atomic force microscopy. According to Ref. [11], in order to attain the switching time ~ 1 min sufficient for implementation of the local probe techniques, one should cool the sample down to ~ 70 K. This conclusion rests on the assumption that switching of the SW defect occurs through a cosine-wave-like configuration in which the core atoms are displaced out of plane in the same direction. Note however that in the neighborhood of the sine-wave-like configuration, the PES is rather complex and bears three saddle points with similar energies. One of those saddle points relates to the flat configuration, and two other arise from the cosine-wave-like configurations considered as transition states in Ref. [11]. In such a situation, evaluation of the switching time with the Arrhenius formula is questionable.

The main objective of this work is to study the thermally activated evolution of the SW defect by means of molecular dynamics (MD) simulation, to find the transition paths, and to determine the switching times at several selected temperatures. Since the first principles MD is extremely time-consuming, in our calculations we make use of the tight-binding model. The paper is organized as follows. The computational details are briefly described in Section 2. The results of MD simulation and PES analysis accompanied by discussion are presented in Section 3. We summarize and conclude in Section 4.

2. Computational details

We modeled graphene by a 160-atom supercell composed of 8×5 rectangular 4-atom cells. Periodic boundary conditions along

two in-plane directions were employed. To compute the supercell energy at given atomic co-ordinates, we made use of the non-orthogonal tight-binding potential [13]. Such an approach is much less computer time demanding as compared with first principles methods and provides a possibility to examine the evolution of a system consisting of ~ 100 atoms for a sufficiently long (on the atomic scale) time 1–10 ns [14], the characteristic times for *ab initio* MD being 1–10 ps [15]. For the structure and energetics of carbon clusters (including fullerenes) and bulks (diamond, graphene) this model gives the results in a good agreement with experimental data and first principles calculations [13]. Previously, we successfully used it to study the static and dynamic characteristics of various carbon-based nanostructures [14,16–18].

MD simulations have been carried out using the velocity Verlet method with the time step 0.272 fs, about two orders of magnitude shorter than the period of the graphene's highest frequency vibrations (see Refs. [14,16] for details). We recorded the co-ordinates of all atoms in the supercell every ten MD steps and then visualized the system evolution as a “computer animation”. To explore the PES, we employed techniques described in Refs. [19,20].

3. Results and discussion

First, to validate the applicability of our tight-binding model to the structure and energetics of the SW defect in graphene, we calculated several basic characteristics of the defect and compared them with available density functional theory (DFT) data. For the energy barrier to the formation of a flat SW defect we obtained $E_b = 8.6$ eV, close to the DFT value $E_b = 9.2$ eV [10]. The formation energy of this defect (the difference in energies of the supercell with and without defect) was found to be $E_{\text{flat}} = 4.96$ eV, in agreement with the DFT result $E_{\text{flat}} = 5.02$ eV [11]. The formation energy of the sine-wave-like SW defect $E_{\text{sine}} = 4.51$ eV appeared to be little less than the DFT energy $E_{\text{sine}} = 4.66$ eV computed for the supercell of the same size [11]. For the sine-wave-like configurations, the out-of-plane co-ordinates of atoms in the rotated C–C bond are $z_{1,2} = \pm 0.28$ Å or ∓ 0.28 Å, while the height between the highest and lowest atom in the supercell is $\Delta z = 1.84$ Å ($\Delta z = 1.51$ Å in DFT [11]). In the cosine-wave-like configurations, both z_1 and z_2 are equal to 0.63 Å or -0.63 Å, and $\Delta z = 1.44$ Å ($\Delta z \approx 1.4$ Å in DFT [11]).

Taking the energy of the sine-wave-like configurations as zero, we have for the energy of the cosine-wave-like configurations (first order saddle points of PES) $E_{S1} = 0.28$ eV, and for the energy of the flat configuration (second order saddle point of PES) $E_{S2} = 0.45$ eV. These values agree with the DFT results $E_{S1} \approx 0.2$ eV and $E_{S2} \approx 0.4$ eV [11]. If one assumes that the switching between sine-wave-like configurations occurs via either of cosine-wave-like configurations as transition states, then the temperature dependence of the switching time τ is given by the Arrhenius law

$$\frac{1}{\tau(T)} = A \exp \left[-\frac{U}{k_B T} \right], \quad (1)$$

where k_B is the Boltzmann constant, $U = E_{S1}$ is the switching activation energy, and A is the frequency factor. The value of A can be computed from the Vineyard formula [21] whose validity has been explicitly demonstrated in Ref. [22] by the example of several typical thermally activated processes in carbon clusters and nanostructures. In the case under consideration, this formula reads

$$A = 2 \frac{\prod_{i=1}^{3N-3} \nu_i}{\prod_{i=1}^{3N-4} \nu'_i}, \quad (2)$$

where ν_i are the eigenfrequencies of vibrations of the supercell in

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