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Transition state and formation process of Stone–Wales defects in graphene

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Stone–Wales (SW) defects are possibly formed in graphene and other two-dimensional materials, and have multiple influence on their physical and chemical properties. In this study, the transition state of SW defects in graphene is determined with the fully discrete Peierls theory. Furthermore, the atomic formation process is investigated by means of *ab-initio* simulations. The atomic structure change and energetics of the SW transformation are revealed. It is found that the transition state is at the SW bond rotation of 34.5° and the activation energy barrier is about 12 eV. This work provides a new method to investigate SW transformations in graphene-like materials and to explore unknown SW-type defects in other 2D materials.

Keywords: graphene, Stone–Wales (SW) defect, transition state, fully discrete Peierls theory

PACS: 61.72.Lk, 61.48.Gh, 61.72.Bb **DOI:** 10.1088/1674-1056/ac20c5

1. Introduction

Since graphene was synthesized and characterized a decade ago,[1,2] two-dimensional (2D) materials with extraordinary properties have stimulated intensive investigations.[3–7] A variety of lattice defects are inevitably formed in stage of synthesis. Stone–Wales (SW) defects are the simplest topological defects, which are stable at room temperature and can be experimentally observed using transmission electron microscopy (TEM).[8–10] A SW defect consists of a dipole of a dislocation and an anti-dislocation, whose Burgers' vector is 0. It can be simply realized by a 90° rotation of two bonded carbon atoms in a perfect graphene.[11] SW defects exist in not only graphene but also other 2D materials, e.g., phosphorene and h-BN.[12,13] The SW transformation in 2D materials plays an important role in their plastic deformation,[14,15] and is significant to result in modification of their thermal, electronic, optical and magnetic properties.[16–20]

Recent studies devoted to atomic structure changes in graphene were reviewed in Ref. [21], including the formation of SW defects. The activation energy of the SW transformation calculated by DFT was in the range of 9–11 eV, while the threshold energy for irradiation-induced process was 19 eV.[22] The SW transition state was expected to possess approximately midway geometry.[15] Later, DFT calculations showed a similar result, i.e., the SW transition state is roughly at a rotation angle of 45°.[23] However, there are some restrictions in the previous DFT calculations, e.g., underestimate of energy induced by the bond length change during the rotation and the boundary effect. The transition state of SW defects in monolayer hexagonal boron nitride was shown at a B–N bond rotation of 60°, in which calculation of the bond length was optimized during the rotation.[19] Although the SW bond rotation involves only minor structure distortion of the surrounding lattice, the long-range field is still vital to determine the energetics of the transformation.

The main objective of this work is the direct determination of the lattice structure of SW defect transition state in the framework of the fully discrete Peierls theory,[24,25] and the first-principles simulation of SW defect transformation process. The fully discrete Peierls theory was developed firstly to describe dislocations in graphene, in that case this elasto-plastic model is comparable with the *ab initio* simulation. Recently, the movement of a single dislocation in graphene and the intermediate states were discussed in the accuracy of first principles.[26] The *ab initio* simulation was started at the saddle point on the energy surface of dislocation's motion. The saddle point corresponds to the unstable equilibrium configuration, which was determined by the fully discrete Peierls theory. For the SW transformation, the transition state with the highest energy is at the saddle point on energy surface of SW formation. Therefore, it is reasonable to determine the transition state of SW defects in the framework of the fully discrete Peierls theory.

2. Theoretical method

By adopting the fully discrete Peierls theory, the free energy functional of an SW defect is in the form of discrete summation, instead of continuum integration. The transition state of SW defect (SW-TS) is the unstable equilibrium configura-

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tion of the disregistry field, which satisfies the energy functional as well. The SW-TS was determined through the variational principle. Then the formation process of the SW defect was simulated atomistically, in which the transition state was set to be the initio state.

First-principles atomic simulation of the SW formation process was performed in the frame work of density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP).[27] The exchange-correlation functional is described by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) approach.[28] The plane-wave kinetic-energy cutoff is 480 eV. A finite rectangle supercell of 8×6 hexagonal cells (108 atoms) is chosen. Periodic boundary conditions and a 10 Å vacuum spacing vertical to the plane are employed to simulate the monolayer graphene. The boundary atoms are fixed during the simulation. The Brillouin zone is sampled with a $3\times3\times1$ k-point mesh generated by the Monkhorst–Pack scheme for the supercell.[29]

For normal *ab initio* molecular dynamics, the time is very short. It is assumed that the kinetic path of the transformation process can be approximated as the quasi-static path, i.e., the kinetic energy is quickly dissipated and the system state falls from the saddle point to the energy bottom along the steepest decent path in the energy landscape. Therefore, the atomic simulation is performed by the conjugate gradient algorithm. To control the reaction direction, different disturbance is employed as a trigger, i.e., the SW bond rotation is set to be slightly larger than that of the transition state to simulate the formation from SW-TS to stable SW, while the bond rotation is set to be slightly smaller to simulate the transformation from perfect lattice to SW-TS.

3. Results and discussion

The SW defect in graphene does not cause out-of-plane buckling due to its strong interaction between extrusion and stretching, and its small internal stress.[30] The transition state is assumed to have a planar geometry as well. An SW defect is a dipole consisting of a dislocation and an anti-dislocaiton. And an SW defect shares the same free energy functional with a dislocation. In the fully discrete Peierls theory, the free energy functional of an SW defect in graphene reads

$$\begin{aligned} F \;=\; & \frac{\mu(1+\nu)}{16\sqrt{3}(1+3\nu)}\sum_{l}\rho_x(l)^2 \\ & -\frac{\mu(1+\nu)}{4\pi}\sum_{l}\sum_{l'}[\rho_x(l)\rho_x(l')+\rho_y(l)\rho_y(l')]\varphi(|l-l'|) \\ & +\sum_{l}\phi(\rho_x)+\sum_{l}\gamma(u_x,u_y)a, \end{aligned} \tag{1}$$

where u is the mismatch field, ρ is the density distribution; x denotes the edge direction along a zigzag chain in graphene, while y denotes the vertical direction perpendicular to the zigzag chain. In comparison with metals, the nonlinear bond interaction ϕ is necessary to describe dislocations in graphene. Details of the parameters in the energy functional can be seen in Ref. [4].

The edge component and vertical component of the mismatch field are, respectively, expressed as

$$u_x=\frac{c_x\zeta^2 a}{l^2+\zeta^2},\quad u_y=\frac{c_y\xi^2 a}{l^2+\xi^2}. \tag{2}$$

The dislocation solution is obtained by virtue of the Ritz variational method. We can find two sets of solutions corresponding to two related equilibrium configurations of dislocation: the stable one that has minimum energy, and the unstable one that has maximum energy. The SW defect is the stable defect which localizes at the energy valley. The unstable equilibrium configuration localizes at the top of energy surface during the formation process of an SW defect, that is, the transition state of SW defect. The difference of the SW-TS solution and SW solution is shown in Table 1. The total Burger's vector of an SW defect is zero. The lattice distortion mainly occurs in the dislocation core area. It is a intrinsic property that is remained during the whole formation process. The characteristic distribution parameter in the edge direction (ζ) and that in the vertical direction (ξ) are almost the same for both SW defect and SW-TS. Surprisingly, the distribution parameters remain nearly unchanged from the SW-TS to the stable SW defect. The change of amplitude parameters (c_x, c_y) shows that the SW-TS has a larger distortion vertical to the glide line and a smaller edge distortion than SW.

Table 1. Parameters of SW and SW-TS solutions. Here, c_x and c_y represent the amplitude of distortion; ζ and ξ control the distribution of distortion field in x and y directions, respectively.

	c_x	ζ	c_y	ξ
SW[24]	0.730	0.286	0.154	0.286
SW-TS	0.532	0.285	0.193	0.286

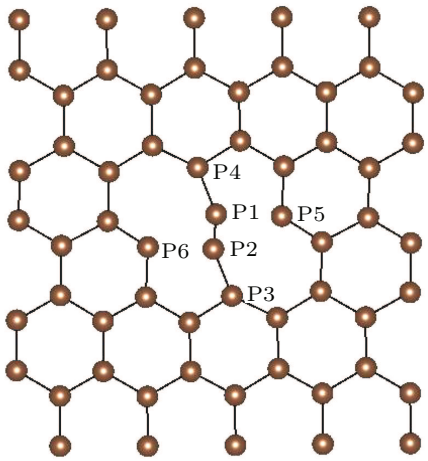


Fig. 1. Atomic structure of the SW transition state in graphene. The central SW bond P1–P2 rotates clockwise through 34.5°.

The displacement field produced by the SW-TS is directly obtained in the context of the elastic continuum theory.[24] The

atomic configuration of SW-TS is shown in Fig. 1. The bond length and bond angle in the core are calculated and listed in Table 2. The bonds in the core of dislocation change from sp^2 to sp. It is found that the SW bond (P1–P2) rotates through 34.5° for the SW-TS. The SW bond length is only 1.02 Å, which is much shorter than a C–C bond in a perfect graphene lattice. The distance between atom P2 and atom P5 is 1.8 Å, which indicates a bond break. The calculation shows that the dilation of SW-TS in graphene is very small. In the theory of elasticity, internal strain is the main factor when considering about buckling of materials, and the strain becomes larger, the buckling is bigger. Hence, the buckling of SW-TS is tiny enough so as to assume being unchanged. The result of first-principles optimization is about 0.3 Å. The buckling of SW-TS is almost the same as that of normal dislocation in graphene.[30]

Table 2. The bond length and angle in the core area of SW-TS.

Bond length	P1–P2	P1–P4	P2–P3
	1.02 Å	1.44 Å	1.44 Å
Bond angle	∠P4P1P2	∠P1P2P3	
	153.1°	153.1°	

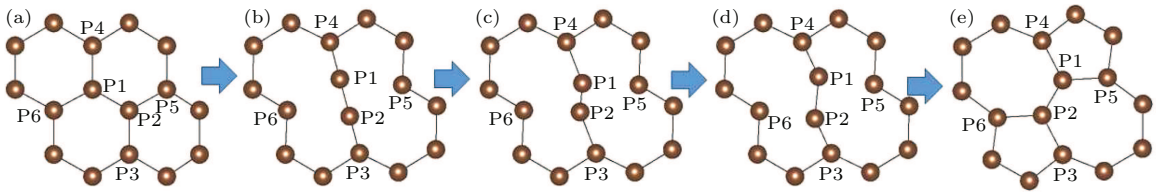


Fig. 2. The formation process of SW defect in graphene.

The quasi-static formation process of SW defect in graphene and the corresponding energy landscape are shown in Figs. 2 and 3, respectively. The energy difference between the SW defect and the perfect graphene is 4.56 eV, and the activation energy barrier to create an SW defect is about 12 eV, which is very high. The formation of SW defect can be divided into four stages. The first one is the chaos of perfect graphene lattice, in which the displacement field is irregular and the energy change is small. The second one mainly contains bond breaking. In this stage, the SW bond (P1–P2) firstly rotates 34.5° to reach the transition state (SW-TS), along with breaking of bonds P1–P6 and P2–P5, and the SW bond is compressed by nearly 30%. Then in the third stage, the SW bond continues to rotate and the bond formation of P2–P6 and P1–P5 takes place. In the meantime, the SW bond returns to normal length. In the second and third stages, the energy changes dramatically. The last one is the adjustment of defect lattice surrounding the core.

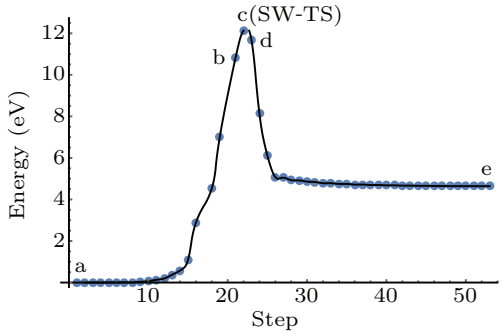


Fig. 3. The energy landscape of SW formation in graphene.

4. Conclusion

In summary, we have proposed a new method to investigate the formation of SW defects in graphene. The transition state of SW defects in graphene is determined with the fully discrete Peierls theory. Furthermore, the atomic formation process is investigated by means of *ab-initio* simulations. For the transition state of SW defects, the SW bond is of 34.5° rotation, and contraction by nearly 30%. It has to overcome a high activation energy of 12 eV for the formation of an SW defect in graphene. In addition, this research provides a method for in-depth study of SW defects in graphene-like materials and to explore unknown SW type of defects in other 2D materials.

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