Bending the rules: Contrasting vacancy energetics and migration in graphite and carbon nanotubes

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Abstract

The traditional picture of a carbon nanotube as a rolled graphene sheet implies that the mechanisms of intra-layer atomic processes in the two systems should be qualitatively similar. Using density-functional theory and tight-binding methods we show that the mechanism of single vacancy migration in nanotubes is different from that in graphite, as the curvature of the nanotube atomic network breaks the trigonal symmetry of a perfect graphene sheet, making the diffusion anisotropic, and strongly influencing the migration barrier. We further demonstrate that the formation energy of a double vacancy in nanotubes is smaller than that for a single vacancy, a behavior different from most monatomic solids, including graphite.
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1. Introduction

Understanding the formation and migration of point defects – particularly vacancies, adatoms and interstitials – in carbon nanotubes [1] is indispensable for improving nanotube growth methods [2,3], tailoring their electronic properties [4,5] and controlling irradiation-induced transformations in these systems [6–9]. Due to similarities in the atomic structure, the properties of these defects in nanotubes have been traditionally considered to be qualitatively the same as those in graphite [2,3].

As graphite is an important moderator material in fusion reactors, point defects in graphite have repeatedly been studied both experimentally [10–12] and theoretically by density-functional theory (DFT)-based methods [13–18], which have proven to be a very powerful tool for understanding the properties of defects in materials. Based on the results of early experiments on defect migration in graphite, it was argued that the carbon interstitial forms no bonds with the atoms in the lattice, and it can easily migrate in the hollow regions between the graphene layers with an activation barrier of 0.1 eV [10]. Contrary to the above, theoretical calculations predicted that carbon adatoms form covalent bonds with atoms in graphene planes [2,14,17] and diffuse with a migration barrier of around 0.4 eV [17]. For vacancies, the interpretation of indirect experiments carried out mostly in the 1960s assigned single vacancies a migration barrier of around 3 eV [10]. Again, the results of calculations differ, predicting a barrier of around 1.6 eV [13,16], much less than the experimental value. Thus, even if the assumption about the similarities in defect behavior in graphite and nanotubes is correct, there is no reliable data on point defect migration in graphite.

The best way to determine the migration energies of point defects in nanotubes could be direct experimental probing of individual point defects by transmission electron or scanning tunneling microscope (TEM/STM). Very recently, by creating defects in nanotubes with energetic electrons in a TEM and monitoring defect evolution in situ at room [19] and elevated [20] temperatures, the first direct information on the mobility of point defects in nanotubes was obtained. In principle, similar experiments can be carried out by STM [21].

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In this Letter, we study theoretically the migration of vacancies in single-walled carbon nanotubes (SWNTs). We show that the mechanism of single vacancy (SV) diffusion in nanotubes is different from that in graphite, as the curvature of the nanotube atomic network breaks the trigonal symmetry of a perfect graphene sheet. We further demonstrate that the formation energy of a divacancy (DV) is smaller than that for a SV, a behavior different from most monatomic solids, including graphite.

2. Computational details

To study the mechanism of SV migration in SWNTs, we employ two computational techniques. In the majority of calculations, we use the non-orthogonal DFT-based tight-binding (DFTB) method [22]. We also use *first principles* DFT implemented in the plane wave (PW) basis set VASP [23] code. Although the PW DFT method has higher accuracy and more predictive power than DFTB, we were unable to carry out all simulations using this method due to computational limitations. However, as shown below, the results for the two limiting cases – vacancies in nanotubes with small diameters and graphite – obtained through both methods are in excellent agreement, which provides strong evidence for the adequacy of the DFTB method.

In our DFT calculations, we used projector augmented wave (PAW) potentials [24] to describe the core electrons and the generalized gradient approximation (GGA) [25] for exchange and correlation. A kinetic energy cutoff of 400 eV was found to converge the total energy of the system to within meV. The same accuracy was also achieved with respect to the k-point sampling of the Brillouin zone.

We calculated the migration barriers using three different methods: the 'drag method' [26], the nudged elastic band method [27], and, if the path is known, by generating a series of atomic configurations between the initial and final states and relaxing the system with constraints. By comparing the migration paths and energies we were able to calculate the barriers with an accuracy of at least 0.1 eV or better.

3. Results and discussion

To establish a link with the already published results [13,15,16], we first studied the migration of a SV in graphite modeled as a single graphene sheet. In complete agreement with the previous studies, both DFTB and PW DFT showed that when an atom is removed from the graphene sheet, the ideal vacancy reconstructs due to a Jahn–Teller distortion. A long bond (around 2 Å) is formed between two atoms near the vacancy, and the system can easily switch between three degenerate structures. The SV formation energy E_{sv}, as calculated by DFTB/PW DFT was $E_{sv} = 7.6/7.7$ eV, respectively, which is in good agreement with the experimental value of 7.0 ± 0.5 eV [10]. We found that SV migrates via the path outlined in [16], with a migration barrier of 1.3/1.4 eV (PW DFT/DFTB). These values

are very close to the results of previous calculations: 1.6 eV [13] and 1.7 eV [16]. Thus, all the DFT methods give the migration energy for SV much less than the experimental value.

Having calculated the migration energy of a SV in graphite, we move to vacancies in SWNTs. Simulations were carried out for armchair and zigzag SWNTs composed of 80–336 atoms, with diameters of 4–17 Å and length of 17.3 (armchair) and 12.3 (zigzag) Å. Test calculations for longer nanotubes gave essentially the same results.

Similar to graphite, SVs in nanotubes reconstruct by saturating two dangling bonds [28,29] and forming a pentagon. The atomic networks of (5,5) nanotubes with SVs are shown in Fig. 1. The reconstruction is much stronger due to the curvature and inherent nanosize of the system: it is easier for the tube to contract locally to 'heal' the hole and thus saturate energetically unfavorable dangling bonds. The curvature gives rise to a shorter bond (bonds between atoms labeled 'A'–'B' and 'A'–'C' in Fig. 1a) and a drop in E_{sv}, see Fig. 2. Similar results were reported earlier, [28] but the dependence has never been checked with first principles methods. Note the good agreement between the DFTB and PW DFT results for zigzag tubes. To have another reference point for a strongly curved system, we calculated E_{sv} for a (4,4) nanotube with both methods.
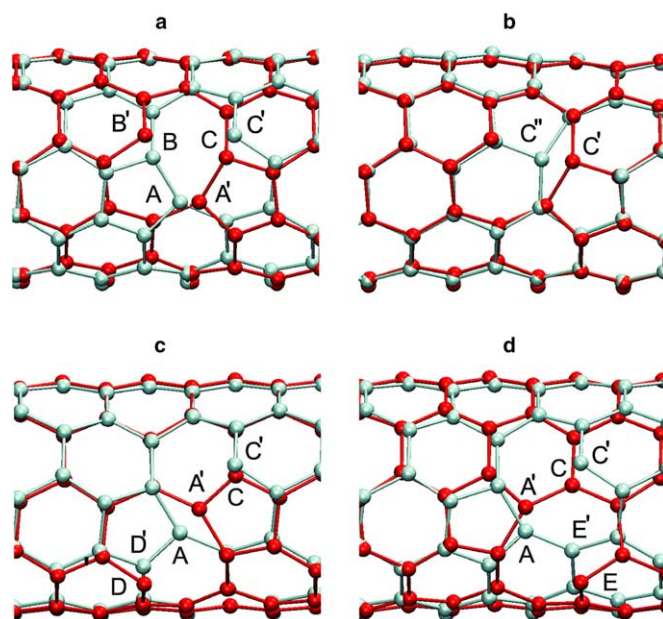

Fig. 1. Atomic networks of (5,5) nanotubes with single vacancies in a ball-and-stick representation illustrating all non-equivalent 'elementary' migrations/bond switching for a single vacancy. Atoms in the back part of the tube are not shown for the sake of clarity. Each panel depicts the initial and the final configurations (shown in different colors) for every migration event. Atoms in the final configurations are labeled by letters with primes. (a) Horizontal switching of the dangling bond on atom B to atom C. Atom A moves along the tube axis. (b) Horizontal and (c) diagonal migration of atom C. (d) Vertical switching of the dangling bond on atom B to atom C. Atom A moves perpendicular to the tube axis. (For interpretation of the references in colour in this figure legend, the reader is referred to the Web version of this article.)
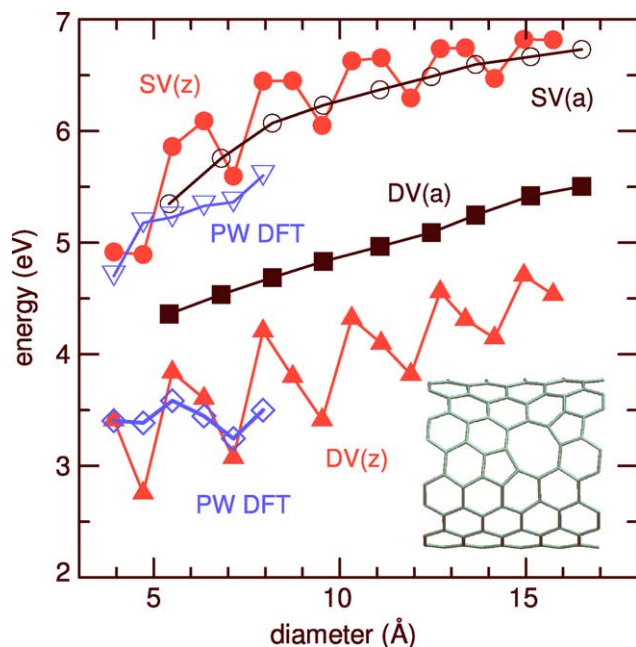
Fig. 2. Formation energies of single vacancies (SV) and double vacancies (DV) in armchair (a) and zigzag (z) SWNTs as functions of nanotube diameter as calculated through the DFTB and PW DFT methods. The inset shows the atomic network of a $(8,8)$ armchair SWNT with a double vacancy.
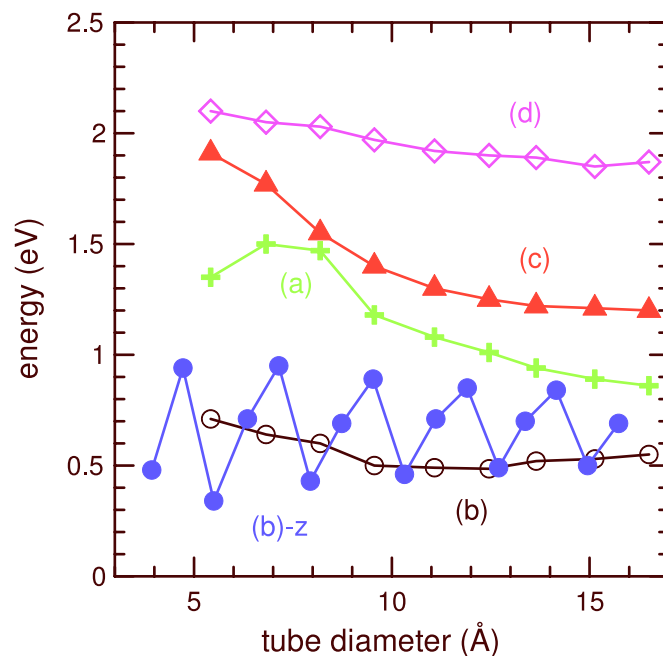

Fig. 3. Migration barriers (barriers for switching the dangling bond) between the configurations shown in Fig. 1 for armchair nanotubes. The curves are labeled corresponding to the migrations shown in Fig. 1. The migration barrier for process (b) is also presented for zigzag nanotubes ((b)-z). The curve maxima correspond to $(6,0)$, $(9,0),...,(3m,0),...$ metallic nanotubes.

The results are also in excellent agreement: 5.34 vs. 5.31 eV (DFTB/PW DFT).

As curvature breaks the trigonal symmetry of the graphene sheet, the configuration when a bond is formed between atoms 'B' and 'C' (parallel to the tube axis) is higher in energy as compared to the case when the bond is perpendicular to the axis (configurations 'A'–'B' and 'A'–'C'). This strongly influences the migration, as the motion along and perpendicular to the tube axis is different. We found that the diffusion of a single vacancy in armchair tubes can be represented by four non-equivalent 'elementary' migration/bond switching events depicted in Fig. 1. Both the initial and the final configurations for every migration event are shown. We stress that all the initial and final configurations in Fig. 1 have exactly the same energy.

Fig. 1a shows the switching of the dangling bond between atoms B and C accompanied by the motion of atom A to a new position A′. The vacancy site does not move. Although this process costs very little energy for graphite (about 0.1 eV, [16]), we found that the curvature of the nanotube gives rise to an increase in the barrier for switching the bond. The dependence of the barrier on the tube diameter is shown in Fig. 3. The curve labels correspond to the events shown in Fig. 1. The switching costs around 1.5 eV for a $(5,5)$ nanotube, and the energy decreases to ~1 eV for a $(15,15)$ SWNT. One can expect that with increasing diameter, the energy eventually saturates toward the value for graphite. The high energies can be understood in the context of a very strong deformation of the nanotube atomic network. The dangling bond

atoms are strongly displaced outward from the tube, so that one should invest lots of energy to move the atoms to the transition state – note the difference in the positions of atoms B/B′ and C/C′.

The curvature of the atomic network and the associated strong reconstructions also result in an increase in the barriers associated with the actual motion of a vacancy to an equivalent site in the atomic network [30]. In particular, the 'diagonal' and 'vertical' migration barriers, panels (c) and (d) in Fig. 1, respectively, are higher than the SV migration barrier in graphite. Again, the barriers decrease with the diameter, and the 'diagonal' migration barrier is very close to the value for graphite already for $(15,15)$ SWNT. Thus, the migration barrier of vacancies along the tube circumference is higher than in graphite. Strong distortion of the atomic network and shorter bonds at the pentagons facilitate the process shown in Fig. 1(b). This involves the motion of atom C′ to a new position C″, and corresponds to bond stretching and dynamical re-bonding of the moving atom, so that it costs relatively little energy, 0.6–0.7 eV, as shown in Fig. 3, curve (b). As a further check on the methods employed we also calculated this process for a $(4,4)$ nanotube within PW DFT, giving a barrier of 0.52 eV – in good agreement with the DFTB value of 0.71 eV.

The diffusion of the vacancy along the tube axis can be represented as a combination of processes (a), (b) and those for the equivalent (with the mirror symmetry) configurations. As the diffusion is governed by the process with

highest activation energy, the switching (a) determines the barrier of SV migration in SWNTs. In graphite the situation is different, as switching the bond costs much less. Thus, one can expect a critical tube diameter, apparently around 25 Å, corresponding to the cross-over from the nanotube to the graphite vacancy migration mechanism.

We obtained qualitatively similar results for zigzag nanotubes. The barrier corresponding to the vacancy motion along the tube circumference was always higher than in graphite, while the barrier for process (a) governed the diffusion along the tube axis. The difference from armchair tubes was a sawtooth-like dependence of the barrier on the diameter, curve labeled '(b)-z' in Fig. 3. The maxima correspond to $(3m, 0)$ tubes which are metallic in the DFTB picture. Similar oscillations can be seen in Fig. 2, and have been reported for vacancy formation energy in zigzag tubes [28] and carbon adatom adsorption energies [31]. It reflects the increase in electron density available for bonding due to electron density delocalization in the metallic tubes. This results in increased formation energies, and correspondingly increased migration barriers. As armchair and zigzag tubes can be viewed as the limiting cases for SWNTs with all possible chiralities, one can conclude that for SWNTs with typical diameters of 12–15 Å, the vacancy migration barrier is around 1 eV. This means that carbon adatoms on the outer surface have roughly the same mobility as vacancies (although the adatoms inside nanotubes have a higher diffusivity [9]).

A barrier of 1 eV implies that a SV will be mobile already at temperatures of 100–200 °C. SVs can migrate toward nanotube ends, which work as sinks for vacancies. They can also form vacancy clusters, and in particular, DVs. One can expect the DV formation energy in nanotubes to be smaller than the formation energy of *two* SVs, as there are no dangling bonds in the system – see the inset in Fig. 2. The DV formation energy $E_{dv} = 8.7$ eV in graphite [16] is indeed lower than twice $E_{sv} = 7.7$ eV. We calculated E_{dv} for armchair and zigzag nanotubes as a function of nanotube diameters (see Fig. 2). We found that, similar to SVs, E_{dv} decreases when the diameter becomes smaller, which can be understood in terms of the easier reconstructions of the nanotube atomic network. The diameter locally decreases, so no dangling bond or strongly strained bonds (typical for the case of graphite) are present. However, the most surprising finding was that E_{dv} is smaller than the formation energy of *one* SVs. Such behavior is inherently related to the nanosize and the unique atomic structure of SWNTs, and is fundamentally different from most monatomic solids [32], including graphite [16].

The thermodynamic concentration of DVs at room temperature will be still very low, but the high mobility of SVs and the big gain in energy when a DV is formed due to coalescence of two SVs imply that DVs can be particularly prolific in SWNTs irradiated with energetic electrons or ions. We found that DVs are practically immobile in SWNTs, as the barrier for migration is more than 5 eV. Such a picture is consistent with recent experiments on

the dependence of the SWNT conductance on Ar$^+$ ion irradiation dose [4]. The exact knowledge of the relation between SV and DV concentration is highly important for understanding the mechanical properties of defected nanotubes [33].

As discussed previously, high resolution TEM and STM images of defect migration in nanotubes offer important insights into the diffusion process. However, the correlation of the monitored changes in the TEM and STM images to particular types of defects and the extrapolation of the results for nanotubes to graphite is not straightforward. As the TEM/STM experiments make it possible to measure the diameter of SWNTs and monitor formation and diffusion of individual defects in situ [19,20], such experiments, combined with our results, should be able to shed light on point defect behavior in low- dimensional systems, and also unequivocally answer a 40-year-old question if the energy of 3.1 eV, associated with vacancies, should be associated with other types of defect [15], or if indeed there is a real contradiction between the DFT and experimental results.

4. Conclusions

To conclude, we have shown that the mechanism of vacancy diffusion in nanotubes is different from that in graphite, as the curvature of nanotube atomic network breaks the trigonal symmetry of a perfect graphene sheet. Contrary to graphite, the migration barriers of SVs and exohedral adatoms which play the role of interstitials in these system are roughly the same. We further demonstrate that the formation energy of a divacancy (DV) is smaller than that for a SV, a behavior different from most monatomic solids, including graphite. These unique properties are directly related to the nanotube low dimensionality and inherent nanosize.

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