J. Phys.: Condens. Matter 26 (2014) 125301 (9pp)

Transforming graphene nanoribbons into nanotubes by use of point defects

A Sgouros¹, M M Sigalas¹, K Papagelis^{1,2} and G Kalosakas^{1,2,3}

¹ Department of Materials Science, University of Patras, 26504 Patras, Greece

² Institute of Chemical Engineering Sciences—Foundation of Research and Technology Hellas (FORTH/ICE-HT), 26504 Patras, Greece

³ Crete Center for Quantum Complexity and Nanotechnology (CCQCN), Physics Department, University of Crete, 71003 Heraklion, Greece

E-mail: georgek@upatras.gr

Received 4 October 2013, revised 24 January 2014 Accepted for publication 30 January 2014 Published 4 March 2014

Abstract

Using molecular dynamics simulations with semi-empirical potentials, we demonstrate a method to fabricate carbon nanotubes (CNTs) from graphene nanoribbons (GNRs), by periodically inserting appropriate structural defects into the GNR crystal structure. We have found that various defect types initiate the bending of GNRs and eventually lead to the formation of CNTs. All kinds of carbon nanotubes (armchair, zigzag, chiral) can be produced with this method. The structural characteristics of the resulting CNTs, and the dependence on the different type and distribution of the defects, were examined. The smallest (largest) CNT obtained had a diameter of \sim 5 Å (\sim 39 Å). Proper manipulation of ribbon edges controls the chirality of the CNTs formed. Finally, the effect of randomly distributed defects on the ability of GNRs to transform into CNTs is considered.

Keywords: graphene nanoribbbons, nanotubes, molecular dynamics simulations

S Online supplementary data available from stacks.iop.org/JPhysCM/26/125301/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Carbon nanotubes (CNTs) and more recently graphene are two carbon allotropes that have attracted a lot of interest due to many possible applications they can offer [1-3]. Graphene nanoribbons (GNRs) are now able to be produced in a well-controllable manner [4]. Different fabrication methods have been reported to produce GNRs, such as reduction of graphite oxide [5], chemical vapor deposition [6], lithographic methods, and plasma etching [7-10]. More recently, it was demonstrated that GNRs with submicrometer precision can be fully manufactured in a controlled reproducible fashion inside a transmission electron microscope [11]. Also, a scalable method based on chemical vapor deposition for the direct growth of well-defined graphene nanoribbons of width ~ 20 nm on SiO₂ substrates has been reported [12]. The width of the graphene nanoribbons is defined by the thickness of the catalyst film, therefore avoiding the diffraction limit of conventional optical lithographic methods. Finally, a bottomup approach based on thermally induced polymerization of suitable precursor molecules has succeeded in fabricating atomically precise nanoribbons [13, 14].

Alternatively, the fabrication of GNRs from CNTs has been studied [15]. The possibility of forming CNTs from GNRs has recently been explored. In a computational study, carbon nanotubes were fabricated directly from graphene nanoribbons by means of twisting [16]. The authors found that the CNTs produced were pristine, provided that the twisted nanoribbons had smooth edges. The experimental realization of thermally induced synthesis of carbon nanotubes through the twisting of GNRs has been reported very recently [17]. Here, we examine the possibility of creating CNTs from GNRs with artificially made defects. By inserting defects into specific sites of the GNR, an inflection process is initiated, transforming the GNRs into CNTs.

Defects in graphene have been investigated both theoretically and experimentally. Different defect types, such as Stone-Wales defects and bivacancies, have been studied with density functional calculations, focusing on their chemical activity [18]. The electronic properties and the out-of-plane deformation of topological defects in graphene have been explored with *ab initio* calculations [19]. The effect of grain boundaries, made with pentagon-heptagon defects, on the strength of graphene was studied using molecular dynamic simulations [20]. In another computational study, four fundamental dimer manipulations were used to produce a variety of defect structures in graphene [21]. Experimentally, alternating Stone-Wales and bivacancy defects were introduced in an epitaxial layer of graphene on a nickel substrate [22], to create an extended defect made of paired pentagons and octagons (inverse Stone-Wales defects). Moreover, by using an aberration-corrected transmission electron microscope, bivacancies and larger disordered structures were produced and imaged within a $10 \times 10 \text{ nm}^2$ region of graphene [23].

2. Methods

2.1. Molecular dynamics simulation details

Molecular dynamics simulations at T = 300 K were mainly performed with the XMD code [24] using the Tersoff potential [25, 26] for the C–C interactions. The same method with XMD has been used in a previous study for calculation of the phonon density of states of graphene structures [27]. Many of the results obtained have also been reproduced with the LAMMPS code [28] using either the Tersoff potential [25, 26] for the C–C interactions or the adaptive intermolecular reactive empirical bond order (AIREBO) potential [29] for the C–H and C–C interactions. The results produced by LAMMPS were visualized with the VMD code [30]. Whenever we present results produced in LAMMPS, it will be explicitly mentioned.

A box containing a graphene nanoribbon with up to ~ 3000 atoms has been used, and periodic boundary conditions have been applied at the edges of the box. In the direction perpendicular to the graphene nanoribbon (z-axis), there is a 50 nm thick layer of empty space. Between the edges of the graphene nanoribbon and the edges of the simulation box (x-axis and y-axis) there was a 50 nm empty space as well. Therefore, essentially the GNR could move freely within the box. This allowed us to observe the behavior of the GNR's edges. Our simulations took place in the canonical ensemble (NVT) in both XMD and LAMMPS codes. In XMD, the temperature was held constant with a velocity rescaling algorithm, using the software's thermostat with the recommended settings. For more details see [24]. In LAMMPS, the Nose-Hoover thermostat was considered, with the atom velocities being rescaled every 0.1 ps (\sim 167 time steps).

In order to stabilize the engineered defects within the GNR, initially we performed an energy minimization procedure for 1500 time steps with a time step of 0.6 fs. After the minimization we performed molecular dynamics simulations for about 10^5 time steps (60 ps), at a temperature equal to 300 K. Typically in our simulations the CNTs obtained are formed in a timescale ranging from a few picoseconds up to 25 ps, depending on the width of the GNRs. We also performed simulations for many of our results using different realizations (random seeds of velocity distribution) to check their reproducibility. For convenience, the various coordinates and lengths in our simulations are measured in units of L_0 . L_0 is equal to the distance between two neighboring carbon atoms, so it is effectively 1.421 Å, as in pristine graphene. It should be noted that the Tersoff potential overestimates L_0 by ~2.6% while the AIREBO potential underestimates L_0 by ~1.8%.

2.2. Types of defects

In this study, we examined defects formed either within or outside the graphene plane. The 'in-plane' defects (like Stone–Wales defects [31], bivacancies, and impregnation with Si dopants [27]) were not able to inflect the graphene layer; thus they could not form CNTs. On the other hand, 'out-of-plane' defects such as adatoms [32, 33], inverse Stone–Wales defects, and blisters [21, 34], could controllably inflect the GNRs, thus forming CNTs. From now on, the three aforementioned out-of-plane types of defect will be referred as type-A, type-B, and type-C defects, respectively.

The type-A engineered defects represent a category of adatoms and molecules which form bonds in between neighboring carbon atoms (figure 1(a)) [32, 33]. In order to computationally design such defects, initially, two neighboring carbon atoms (green, in figure 1(a)) were moved apart by $0.2L_0$ each and $\pm 0.4L_0$ perpendicularly to the graphene plane. Then an additional carbon adatom (orange, in figure 1(a)) was placed in the middle of the neighboring atoms, at $\pm 1.3L_0$ from the graphene plane. The ' \pm ' sign signifies whether the defect is engineered on the top or the bottom side of the graphene lattice; thus there are two possible configurations, 'up' and 'down', with equal energy. After the adatom was inserted, the distance between the two initial carbon neighbors was measured to $\sim 1.6L_0$, indicating that the bond was broken. We have also reproduced the same effect with the AIREBO potential with LAMMPS, by adding C-H molecules instead of plain C atoms at the defect sites. Other elements or molecules might be able to show similar phenomena.

Type-B defects are quite similar to type-A defects, where now, instead of single atoms, carbon dimers were added to each defect site, as shown in figure 1(b), resulting in inverse Stone–Wales (ISTW) defects. ISTW defects have been studied extensively [21, 35], and they have also been observed experimentally [22, 23]. The method we used to computationally design such defects is similar to that of type A. The distance between the initial carbon neighbors was measured to be $\sim 1.8L_0$ after the defect was inserted, indicating that the C–C bonds were broken.

In order to construct type-C defects (see figure 1(c)), we replaced four neighboring carbon atoms (black atoms) with a carbon ring having six atoms (orange atoms), at $\pm 1L_0$ from the lattice. Before the addition of the carbon ring, the atoms shown in figure 1(c) in green were moved by $\pm 0.3L_0$ perpendicularly to the GNR plane. Such defects can equivalently be formed by combining a single and an inverse Stone–Wales defect [21].



Figure 1. Engineered defects of (a) type-A (adatoms), (b) type-B (inverse Stone–Wales defects), and (c) type-C (blisters) defects. The left panels show the initial configuration before the addition of the carbon atoms of the defect (orange), and the right panels display the graphene layer after their addition. Neighboring atoms (green) to the defect site are displaced before the insertion of the atoms of the defect (see text). (d) The three possible orientations of the type-A and type-B defects are shown by the lines denoted as 'ZZ'. Type-C defects exhibit neutral orientation when they are isolated. The defects shown on panels (a) and (b) share the same orientation with the green line of panel (d).

As in the case of type-A defects, there are two possible configurations, 'up' and 'down', with equal energy for type-B and type-C defects as well.

Defects of type A and type B can have three different orientations, as shown in figure 1(d), since, from any hexagonal center, one can draw three discrete lines parallel to zigzag directions in graphene. In contrast, type-C defects exhibit no orientation when they are isolated, as they are symmetrical along every zigzag direction. In order to produce a notable inflection to the graphene layer, the engineered defects should share the same orientation. Most of the simulations presented below display GNRs with inflection of the GNR layers along the armchair direction (y-axis of figure 1(d)), thus producing armchair and sometimes chiral CNTs. In this case, the defects were designed to have their orientation parallel to the x-axis of the GNR in the zigzag direction (see figure 1(d), green line). However, it is also possible to inflect GNRs along the zigzag direction, as is showcased by two example cases (see figure 5), thus producing zigzag CNTs. Finally, it should be noted that all kinds of defect (types A, B, and C) were found to be stable at higher temperatures; this was checked by additional simulations performing thermal annealing at 1100 K.

2.3. Characterization of defect distribution

The defects are regularly placed and their periodic distribution in each case is characterized by three parameters: (dx, dy, n) as



Figure 2. Graphene nanoribbon with type-A defects placed in a periodic distribution characterized by (dx, dy, n) = (3, 6, 4). dx is normalized to $\sqrt{3}L_0$ (second-neighbor distance) while dy is in units of L_0 (first-neighbor distance). The parameter *n* represents the number of defect lines along the *y*-axis.

shown in figure 2. The parameter dx represents the separation distance between the defects along the x-axis in units of $\sqrt{3}L_0$ (second-neighbor distance in graphene), and dy is the separation distance of the defects along the y-axis, in units of



Figure 3. GNR with just one line of (a) type-A and (b) type-B defects with a separation distance of dx = 3. (c) The angle of inflection as a function of the separation distance between the defects (dx) for defects of type A (squares) and type B (circles). The separation distance dx is in units of $\sqrt{3}L_0$. The error bars represent the standard deviation from the mean value with respect to time calculated over a very long run. Single lines with type-C defects were unable to inflect the CNT. These results were produced using LAMMPS with the Tersoff potential.

 L_0 (first-neighbor distance). The parameter *n* represents the number of defect lines along the *y*-axis. It should be noted that the perimeter of the obtained CNTs is equal to the width of the initial GNRs.

Since the graphene nanoribbons contain *n* lines with engineered defects, separated by dy, the width of each graphene nanoribbon (W_{GNR}) and the perimeter of each obtained CNT (P_{CNT}) are given by $P_{\text{CNT}} = W_{\text{GNR}} = \text{d}y * n$ (apart from some specific cases considered in section 3.5, with a slightly different width explicitly mentioned therein). The longitudinal dimension of the starting nanoribbons and the resulting nanotubes is parallel to the *x*-axis of the simulation box and has a length of about $50L_0$ by default. The same assignment will be used for all defect types in the present study. We note that for type-A and type-B defects the surface coverage is less than 8% (concentration $3.2 \times 10^{18} \text{ cm}^{-2}$), for all structures discussed here.

3. Results and discussion

3.1. Inflection angle induced by a single defect line

Initially, one line of type-A and type-B defects along the x'x direction of the GNR is considered. To calculate the inflection angle produced by a single line with defects we used a nanoribbon with a width equal to $36L_0$ along the y-axis. This line of defects causes an inflection of the graphene layer along the y'y direction, as is shown in figures 3(a) and (b). The closer the distance between those defects in the line, the higher the inflection. This is quantitatively presented in figure 3(c), where the angle of inflection of the graphene ribbons is plotted as a function of the separation distance between the defects, dx, in units of $\sqrt{3}L_0$. These results were obtained using the LAMMPS code with the Tersoff potential. The inflection angle was measured at the area near the center of the GNRs, and it reached values of $\sim 75^{\circ}$ and $\sim 65^{\circ}$ for type-B and type-A defects, respectively, which is the maximum inflection for each case. For a separation distance of dx = 2, type-B defects would slightly inflect the GNR towards the x'x direction instead of the y'y direction, due to the fact that the defect sites heavily interact with each other in this case. This structure is similar to a minimal ribbon of Octite M2 within graphene according to [21] or a 'metallic wire' [22]. Similar results were obtained using the AIREBO potential implemented in the LAMMPS code, presenting exactly the same distance dependence as in figure 3(c). The only difference was that the inflection angle was shifted to lower values, by 5°–10° in the case of type-A defects and 15°–20° in the case of type-B defects.

In contrast to the cases of type-A and type-B defects, a single line of type-C defects showed no significant inflection of the GNR. However, by applying two or more lines of type-C defects separated by $dy = 3L_0$ along the *y*-axis, the GNR was inflected along the *y*'*y* direction. By increasing the number of lines of any type of defect along the *y*-axis, one can construct nanotubes with different diameters.

3.2. Type-A defects

Figure 4 shows cases with type-A engineered defects having different values of (dx, dy, n). An interesting characteristic of the resulting CNTs is their polygon-like cross-section. The inflection of the CNT occurs at the defect's lines so the cross-section of a CNT with 4, 5, ..., n lines of defects should resemble a square, pentagon, ..., n-gon, respectively, with the number of sides equal to n and the length of each side equal to dy. The average diameter D_{CNT} of the nanotube, when successfully formed, can be calculated as the average of the diameter of circumscribed circle and the diameter of the inscribed circle:

$$D_{\text{CNT}} \approx \frac{1}{2} \left[\frac{\mathrm{d}y}{\sin\left(\frac{\pi}{n}\right)} + \frac{\mathrm{d}y}{\tan\left(\frac{\pi}{n}\right)} \right]$$
$$= \frac{\mathrm{d}y}{2} \left[\csc\left(\frac{\pi}{n}\right) + \cot\left(\frac{\pi}{n}\right) \right]. \tag{1}$$

The smallest-diameter CNT produced in this case, shown in figure 4(a), was for (dx, dy, n) = (3, 3, 4), with a diameter of ~ 5 Å (equation (1)), just 2 Å larger than the smallest-possible





(3, 3, 4), an armchair CNT with a diameter of ~5 Å was produced. (b) For (dx, dy, n) = (3, 6, 13), the edges of the graphene ribbon would not match, due to over-inflection. (c) For (dx, dy, n) = (5, 6, 13), a CNT with a diameter of ~35 Å was formed. (d) An armchair CNT formed with hydrogen-passivated adatoms for (dx, dy, n) = (3, 6, 5), having a diameter of ~13 Å. (a), (b), and (c) were obtained using XMD with the Tersoff potential, while (d) was obtained using LAMMPS with the AIREBO potential. For clarity, the scale in each panel is not the same, as indicated in the corresponding scaling bars.

CNT that can be formed [36]. By increasing n and dy, nanotubes with larger diameters were obtained. Figure 4(b) shows a case of (dx, dy, n) = (3, 6, 13), where the edges of the graphene layer along the y-axis do not match upon closing. Instead, the defects in the last lines before the edges are bonded together, resulting in a scroll-like structure. This failure is due to the over-inflection of the graphene layer. One way to overcome this fabrication drawback is to increase dx (from 3 to 5), thus decreasing the inflection angle. According to figure 3(c), the angle of inflection for each line of defects would be $\sim 30^{\circ}$ for dx = 5, instead of $\sim 50^{\circ}$ for dx = 3, corresponding to significantly smaller bending of the graphene layer. Simulations for n = 13, dx = 5, and dy = 6, indeed show that a nanotube can be formed, with a diameter of \sim 35 Å (see figure 4(c)). Note that the CNT in figure 4(c) is slightly chiral. The largest-diameter CNT that we have produced with type-A defects was for (dx, dy, n) = (3, 18, 5), with its diameter equal to \sim 39 Å (not shown). It should be possible to construct larger CNTs as well.

Similar results were produced using different realizations with different initial velocity distributions. Small-diameter CNTs are quite reproducible, while in the case of larger ones sometimes the GNR's edges may shift slightly, like in the case of figure 4(c) (see the red boxes as well as the relevant discussion in section 3.5). Simulating the structures for lower



Figure 5. Zigzag nanotubes produced by graphene nanoribbons with type-A defects. (a) and (d) are the initial configurations of the GNRs that resulted in zigzag CNTs at (b) and (e) respectively. Panels (c) and (f) display the cross-sections for the final configurations at panels (b) and (e) respectively.

temperatures (as was checked at T = 150 K) can sometimes improve the reproducibility.

These phenomena were also observed using the AIREBO interatomic potential for the C–C interactions in LAMMPS. In this case we also ran simulations with much longer GNRs (with length around 200 nm, consisting of about 33 000 atoms), and we found that CNTs can be successfully formed as well (see figure S1 in supplementary material available at stacks.iop. org/JPhysCM/26/125301/mmedia). Also, simulations starting from GNRs with non-ideal edges have shown that CNTs could be formed even in this case, although they exhibit holes in the places where they close (see figure S2 in supplementary material available at stacks.iop.org/JPhysCM/26/125301/mm edia).

A difference between the CNTs obtained with type-A defects and conventional CNTs is the large number of dangling bonds due to adatoms. Those carbon atoms can easily create bonds with other substances, resulting in rather sticky CNTs. This property could be eliminated by passivating the CNT with hydrogen atoms. Indeed calculations with the AIREBO potential show that CNTs with hydrogen-passivated type-A adatoms are stable. In figure 4(d), a CNT formed with type-A C–H molecules is displayed, with a diameter of ~ 13 Å. The dangling atoms are hydrogen atoms.

As has already been mentioned, with this method it is also possible to inflect the GNRs along the zigzag direction, thus producing zigzag CNTs. This is showcased at figure 5 by two example cases with type-A defects. In the case of figure 5(a), the configuration of the defects followed an alternating pattern along the x-axis, similar to the red and blue lines at figure 1(d). This pattern was then repeated along the y-axis every $6L_0$



Figure 6. The final configurations of GNRs with type-B defects for (dx, dy, n) equal to (a) (3, 6, 3), (b) (3, 6, 4), (c) (4, 6, 6), (d) (5, 6, 6), and (e) (4, 12, 5). In cases (a), (b), (d), and (e) the GNRs were transformed successfully into CNTs. In case (c), the GNR was over-inflected, so instead of a CNT a scroll-like structure was formed. On the right, cross-sections of the corresponding CNTs are displayed. The scale in each panel is indicated in the corresponding scaling bar.

units (this can be seen clearly in the zoomed area), resulting in a zigzag CNT with a diameter of ~16 Å. In the case shown in figure 5(d), the configurations were alternated along the y-axis, and then the same pattern was repeated along x-axis every $3\sqrt{3}L_0$ units. This case then resulted in a zigzag CNT, and the diameter was ~16 Å.

3.3. Type-B defects

Figure 6 presents the final structures for some of the studied cases with type-B defects (as shown in figure 1(b)). The smallest-diameter CNT produced in this case (see figure 6(a)) was for (dx, dy, n) = (3, 6, 3), having a diameter of ~8 Å (equation (1)). On increasing the value of n to 4 and 5 for the same values of dx and dy, CNTs were also formed (figure 6(b)). By increasing *n* even more, for dx = 3 as well as for dx = 4, the GNR is over-inflected (see figure 6(c) for the case (dx, dy, n) = (4, 6, 6), similar to the case of figure 4(b), resulting in a scroll-like structure. As with type-A defects, increasing the value of the parameter dx (from 4 to 5) lowers the inflection angle (see figure 3(c)), so for (dx, dy, n) = (5, 6, 6) a CNT was successfully formed, as shown in figure 6(d). The largest CNT obtained in this case was for (dx, dy, n) = (4, 12, 5), around 26 Å in diameter (figure 6(e)).

As discussed earlier, these kinds of defects have two possible configurations with equal energy. In the first configuration the two additional carbon atoms are on the top, and in the other they are on the bottom surface of the graphene sheet. In this case the energy required to shift between the



two configurations is relatively small, so the defects would sometimes be transferred to the opposite side of the lattice during the simulation. This may disrupt the successful formation of CNT, resulting in lower reproducibility of the simulations with these types of defect. There is clear evidence of the existence of regions with outwards inflection as in the (dx, dy, n) = (3, 6, 4) case (see red boxes in figure 6(b)). It should be mentioned that two configurations ('up' and 'down') with the same energy exist for the type-A defects as well. However, similar phenomena do not appear in the case of type-A defects, indicating that the energy barrier between those equal energy configurations is much higher. Therefore, if the type-A adatoms were all placed at the top surface of graphene, they would stay on the same side.

It has also been found that, for type-B defects, dy must be higher than or equal to 6; otherwise, the GNRs cannot form CNTs. For dy equal to 3, the neighboring defects along the y'ydirection tend to stay on opposite sides of the graphene layer, effectively canceling the inflection tendency of each other, thus making the folding of the GNR impossible. As already mentioned, producing CNTs with type-B defects shows lower reproducibility due to that configuration shift between the two sides of the graphene layer (especially for higher diameters). In some cases the reproducibility can be improved by lowering the temperature, as was checked for 150 K.

3.4. Type-C defects

Examined cases with type-C defects (see figure 1(c)) are presented in figure 7. We observe that for dy > 3 CNTs were unable to form using these defects. As we discussed earlier (see section 3.1) single lines with type-C defects would not inflect the GNRs. By placing the lines of defects at small separation distances along the y-axis (dy = 3), the GNRs would inflect towards the y'y-axis; thus CNTs were able to form. Also, for dy = 3, the barrier between the two type-C configurations ('up' and 'down') is sufficiently high enough that defects with



Figure 8. Graphene nanoribbons with (a) symmetrical and (b) asymmetrical edges (see atoms in red boxes). For the same dy and n, the asymmetrical GNR has a width longer by $1.5L_0$ than the corresponding symmetrical GNR. (c) CNT formed by a GNR with symmetrical type-A defects for (dx, dy, n) = (3, 6, 5). (d) CNT formed by a similar GNR as in case (c), with the exception that it now has asymmetrical edges; thus the resulting CNT exhibits a chirality $\theta_c = 28.43^\circ$.

added atoms in the top surface of the graphene layer would not be transferred to the bottom.

The smallest fabricated CNT that we got in this case was for (dx, dy, n) = (3, 3, 6), having a diameter of ~8 Å (figure 7(a)). The CNT obtained for (dx, dy, n) = (3, 3, 15)exhibits an elliptical cross-section (see figure 7(b)), having an approximate diameter of ~21 Å. For higher values of *n*, the GNRs started to over-inflect, as is shown in the cross-section of figure 7(c), for n = 17. CNTs obtained with type-C defects exhibit an interesting structure, as they are composed of pentagons, hexagons, and heptagons. A shortcoming of type-C defects is that the CNTs produced are limited to relatively small diameters due to the small value of dy needed for the stable formation of the nanotube.

3.5. Chirality control

The chirality of the fabricated CNTs can be controlled to some extent by manipulating the edges of the original graphene layer. If the edges of the original GNR are symmetrical (compare the edge atoms in red boxes in figure 8(a)) as in all previous cases, then usually no chirality is observed (apart from some realizations in cases of ribbons with large widths; see below). On the other hand, if the edges of the GNR are asymmetrical (compare the edge atoms in red boxes in figure 8(b)), then they need to shift along the x-axis by $\sqrt{3}/2L_0$ in order to match, thus providing chirality to the fabricated CNT. For example, in the case of figure 8(a) (GNR with symmetrical edges) the green atom labeled as (1) will most likely form a bond with the other green atom labeled as (2), while in the case of figure 8(b) (GNR with asymmetrical edges) the atom labeled as (1) will bond either with atom (2) or atom (3), thus shifting the GNR edge by $\Delta x = \pm \sqrt{3/2L_0}$. The chirality θ_c of the corresponding CNT can be given by the expression

$$\theta_{\rm c} = \frac{\pi}{6} - a \tan\left[\frac{\Delta x}{W_{\rm GNR}}\right],$$
(2)

where Δx is equal to $\sqrt{3}/2L_0$, and W_{GNR} is the width of the initial GNR. A chirality of $\theta_c = \frac{\pi}{6}$ corresponds to armchair CNTs, while $\theta_c = 0$ corresponds to zigzag CNTs.

In figures 8(c) and (d) we present CNTs produced by nanoribbons with the same (dx, dy, n) = (3, 6, 5), but with symmetric and asymmetric edges, respectively. In the former

case, the width of the starting nanoribbon is $W_{\text{GNR}} = 5 * 6L_0 = 30L_0$, while in the latter one it is $W_{\text{GNR}} = 5 * 6L_0 + 1.5L_0 = 31.5L_0$. The CNT shown in figure 8(c) has a chirality of $\theta_c = \frac{\pi}{6}$ (armchair CNT). However, figure 8(d) clearly shows a chiral pattern, and the CNT has a chirality of $\theta_c = 28.43^{\circ}$ (equation (2)).

It should be noted that some realizations, in cases of GNRs with symmetrical edges (especially when their width is large), show that the ribbon's edges can spontaneously shift by $\Delta x = \sqrt{3}L_0$, leading thus to chiral CNTs. This was the case of figure 4(c), where the resulting CNT has a chirality of 28.73°, in agreement with equation (2) for $\Delta x = \sqrt{3}L_0$ and $W_{\text{GNR}} = 6 * 13L_0$.

3.6. Randomly distributed defects of type A

Besides periodically induced defects, we have also examined cases where x'x-oriented defects of type A (see section 2.2) were randomly distributed in the lattice, as shown in the example of figure 9(a). Each case was simulated several times with differently distributed random positions of defects of GNR lattice. The reproducibility of each case depends on two parameters: the density of the engineered defects and the width of the initial GNR. It was found that the inflection of the GNR increases with the concentration of the engineered defects; thus a high concentration of defects is needed in order to fabricate small-diameter CNTs. The opposite is true for larger-diameter CNTs.

Figures 9(b)-(d) demonstrate results for the cases of GNRs with $W_{GNR} = 30L_0$ and various concentrations of type-A defects. For defects with surface coverage up to 3%, the GNRs are under-inflected in most realizations, so they could not close into CNTs (see figure 9(b)). For defects with surface coverage between 4 and 8%, the GNRs were transformed into CNTs with high reproducibility (see figure 9(c)), while for surface coverage of 9% and more the GNRs were over-inflected (see figure 9(d)); thus scroll-like structures were usually formed (similar to the cases of figures 4(b) and 6(c)). The smallest-diameter CNT produced in this way was of ~8 Å in diameter, with W_{GNR} equal to $18L_0$ and 9.5% surface coverage of type-A adatoms, while the largest-diameter CNT was of ~ 24 Å in diameter, with $W_{\rm GNR}$ equal to $54L_0$ and 2.7% surface coverage of adatoms. Since the cross-sections of the CNTs were circular in this case,



Figure 9. (a) An example of a GNR with $W_{\text{GNR}} = 12L_0$ and 6% surface coverage of randomly distributed type-A adatoms (the initial configuration is shown). Final configurations of GNRs with $W_{\text{GNR}} = 30L_0$ and a surface coverage of randomly distributed type-A adatoms equal to (b) 3%, (c) 5%, and (d) 9%. In case (b), the inflection was not sufficient to form a CNT. In case (c), an armchair CNT was formed. In case (d), the GNR was over-inflected, so, instead of a CNT, a scroll-like structure was formed.

the diameters of the CNTs were simply calculated using the relation $D_{\text{CNT}} = \frac{W_{\text{GNR}}}{\pi}$.

Similar effects were observed with randomly distributed type-B defects as well (see figure S3 in supplementary material available at stacks.iop.org/JPhysCM/26/125301/mmedia). In contrast, GNRs with randomly placed type-C defects cannot be transformed into CNTs. This is expected since, as mentioned above (see section 2.2), type-C defects do not present any preferential orientation when they are isolated.

4. Conclusions

Using molecular dynamics calculations, the formation of CNTs obtained through GNRs with engineered structural defects was studied. Both in-plane and out-of-plane defects were examined, but only the out-of-plane ones led to the formation of CNTs. Armchair, zigzag, and chiral CNTs can be produced in this way.

Just one line of type-A or type-B defects along the *x*-axis of a GNR produced a stable controllable inflection of the nanoribbon along the armchair direction. It was found that type-B defects inflect the graphene layer more than type-A defects, while for both kinds the inflection angle increases as the density of the defects along the line increases.

By adding more lines of periodically engineered defects, the GNRs were transformed into CNTs. On changing the parameters of the defect distribution, CNTs with various structural characteristics were produced. Chiral CNTs were also formed by manipulating the edges of the original graphene sheet.

Type-A defects were able to form stable CNTs, with the largest one obtained here having a diameter of ~39 Å, and the smaller one a diameter of ~5 Å. CNTs formed with type-B defects had a diameter between ~8–26 Å, though they were less likely to form due to the existence of two configuration states ('up' and 'down') with low barrier energy. The last type of defect studied (type C), was also able to form CNTs, with diameters of ~8–24 Å. GNRs with random distribution of x'x oriented type-A defects were also able to produce CNTs of ~8–20 Å in diameter, with their reproducibility depending on the density of the randomly inserted adatoms and the width of the initial GNR.

Acknowledgments

This work has been partially supported by the Thales Project 'GRAPHENECOMP', co-financed by the European Union (ESF) and the Greek Ministry of Education (through $E\Sigma\Pi A$ program) and by the European Union's Seventh Framework Program (FP7-REGPOT-2012-2013-1) under grant agreement no 316165.

References

- Novoselov K S, Fal'ko V I, Colombo L, Gellert P R, Schwab M G and Kim K 2012 A roadmap for graphene *Nature* 490 192
- [2] Tielrooij K J, Song J C W, Jensen S A, Centeno A, Pesquera A, Elorza A Z, Bonn M, Levitov L S and Koppens F H L 2013 Photoexcitation cascade and multiple hot-carrier generation in graphene *Nature Phys.* 9 248
- [3] Schnorr J M and Swager T M 2011 Emerging applications of carbon nanotubes *Chem. Mater.* 23 646
- [4] Mohanty N, Moore D, Xu Z, Sreeprasad T S, Nagaraja A, Rodriguez A A and Berry V 2012 Nanotomy-based production of transferable and dispersible graphene nanostructures of controlled shape and size *Nature Commun.* 3 844
- [5] Lee W H, Park J, Sim S H, Jo S B, Kim K S, Hong B H and Cho K 2011 Transparent flexible organic transistors based on monolayer graphene electrodes on plastic *Adv. Mater.* 23 1752
- [6] Campos-Delgado J *et al* 2009 Bulk production of a new form of sp² carbon: crystalline graphene nanoribbons *Nano Lett.* 8 2773
- [7] Bai J, Duan X and Huang Y 2009 Rational fabrication of graphene nanoribbons using a nanowire etch mask *Nano Lett.* 9 2083
- [8] Wang X and Dai J 2010 Etching and narrowing of graphene from the edges *Nature Chem.* 2 661
- [9] Han M Y, Özyilmaz B, Zhang Y and Kim P 2007 Energy band-gap engineering of graphene nanoribbons *Phys. Rev. Lett.* 98 206805
- [10] Ryu S, Maultzsch J, Han M, Kim P and Brus L 2011 Raman spectroscopy of lithographically patterned graphene nanoribbons ACS Nano 5 4123
- [11] Börrnert F, Fu L, Gorantla S, Knupfer M, Büchner B and Rümmeli M H 2012 Programmable sub-nanometer sculpting of graphene with electron beams ACS Nano 6 10327

- [12] Martin-Fernandez I, Wang D and Zhang Y 2012 Direct growth of graphene nanoribbons for large-scale device fabrication *Nano Lett.* 12 6175
- [13] Cai J et al 2010 Atomically precise bottom-up fabrication of graphene nanoribbons Nature 466 470
- [14] Talirz L et al 2013 Termini of bottom-up fabricated graphene nanoribbons J. Am. Chem. Soc. 135 2060
- [15] Kosynkin D V, Higginbotham A L, Sinitskii A, Lomeda J R, Dimiev A, Price B K and Tour J M 2009 Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons *Nature* 458 872
- [16] Kit O O, Tallinen T, Mahadevan L, Timonen J and Koskinen P 2012 Twisting graphene nanoribbons into carbon nanotubes *Phys. Rev.* B 85 085428
- [17] Lim H E, Miyata Y, Kitaura R, Nishimura Y, Nishimoto Y, Irle S, Warner J H, Kataura H and Shinohara H 2013 Growth of carbon nanotubes via twisted graphene nanoribbons *Nature Commun.* 4 2548
- [18] Boukhvalov D W and Katsnelson M I 2008 Chemical functionalization of graphene with defects *Nano Lett.* 8 4373
- [19] Yazyev O V and Louie S G 2010 Topological defects in graphene: dislocations and grain boundaries *Phys. Rev.* B 81 195420
- [20] Wei Y, Wu J, Yin H, Shi X, Yang R and Dresselhaus M 2012 The nature of strength enhancement and weakening by pentagon–heptagon defects in graphene *Nature Mater*. 11 759
- [21] Appelhans D J, Carr L D and Lusk M T 2010 Embedded ribbons of graphene allotropes: an extended defect perspective *New J. Phys.* **12** 125006
- [22] Lahiri J, Lin Y, Bozkurt P, Oleynik I I and Batzill M 2010 An extended defect in graphene as a metallic wire *Nature Nanotechnol.* 5 326
- [23] Robertson A W, Allen C S, Wu Y A, He K, Olivier J, Neethling J, Kirkland A I and Warner J H 2012 Spatial control of defect creation in graphene at the nanoscale *Nature Commun.* 3 1144

- [24] 2002 See http://xmd.sourceforge.net/ for J. Rifkin, XMD Molecular Dynamics Program, University of Connecticut
- [25] Tersoff J 1988 New empirical approach for the structure and energy of covalent systems *Phys. Rev.* B 37 6991
- [26] Tersoff J 1989 Modeling solid-state chemistry: interatomic potentials for multicomponent systems *Phys. Rev. B* 39 5566
- [27] Sgouros A, Sigalas M M, Kalosakas G, Papagelis K and Papanicolaou N I 2012 Phononic band gap engineering in graphene J. Appl. Phys. 112 094307
- [28] Plimpton S 1995 Fast parallel algorithms for short-range molecular dynamics J. Comput. Phys. 117 1
- [29] Stuart S J, Tutein A B and Harrison J A 2000 A reactive potential for hydrocarbons with intermolecular interactions *J. Chem. Phys.* **112** 6472
- [30] Humphrey W, Dalke A and Schulten K 1996 VMD—visual molecular dynamics J. Mol. Graph. 14 33
- [31] Stone A J and Wales D J 1986 Theoretical studies of icosahedral C₆₀ and some related species *Chem. Phys. Lett.* 128 501
- [32] Amara H, Latil S, Meunier V, Lambin Ph and Charlie J C 2007 Scanning tunneling microscopy fingerprints of point defects in graphene: a theoretical prediction *Phys. Rev.* B 76 115423
- [33] Nakada K and Ishii A 2011 Migration of adatom adsorption on graphene using DFT calculation *Solid State Commun.* 151 13
- [34] Lusk M T, Wu D T and Carr L D 2010 Graphene nanoengineering and the inverse-stone-thrower-wales defect *Phys. Rev. B* 81 155444
- [35] Sternberg M, Curtiss L A, Gruen D M, Kedziora G, Horner D A, Redfern P C and Zapol P 2006 Carbon ad-dimer defects in carbon nanotubes *Phys. Rev. Lett.* 96 075506
- [36] Zhao X, Liu Y, Inoue S, Suzuki T, Jones R O and Ando Y 2004 Smallest carbon nanotube is 3 Å in diameter *Phys. Rev. Lett.* 92 125502