Defect-induced carbon nanoscroll formation

Joseph Wallace and Lin Shao*

Department of Nuclear Engineering, Texas A&M University, College Station, TX 77843

ABSTRACT

Carbon nanoscrolls (CNSs), a graphitic structure formed by rolling of a graphene plane, must overcome an energy barrier in order to form. This energy barrier is the result of competing interactions between the van der Waals force, which wants to cause overlap of the graphene and the torsional or bending force which resists bending of the graphene plane. In this study we used molecular dynamics simulation to examine the effect of vacancies on the CNS formation dynamics. We found that the energy barrier, which must be overcome to obtain a stable scroll structure, can be lowered or completely eliminated by introducing vacancies. Individual vacancy and divacancy configurations are studied and found to reduce the torsional bending energy by allowing local stress relaxation around the defect site. A structural transition diagram is created in which we show the energy barrier height for a range of vacancy concentrations and CNS rolling widths. These results provide the theoretical backing for a new method of fabricating CNSs using a focused ion beam and shed new light on the self-rolling phenomenon in graphene.

*Corresponding author at: Department of Nuclear Engineering, Texas A&M University, College Station, Texas 77843, USA. Fax: +01 9798456443, Phone: +01 9798454107.

E-mail address: lshao@tamu.edu (L. Shao)

1. Introduction

Graphitic systems, including graphene, carbon nanotubes (CNTs) and fullerenes have been at the forefront of nanotechnology since the field's inception in the mid-1980s. With the discovery of each of these graphitic systems intensive research ultimately led to a number of potential technological applications [1-3]. Another promising graphitic system that has received significantly less attention is carbon nanoscrolls (CNSs). Similar in some ways to multiwalled carbon nanotubes, a CNS is formed by rolling up a sheet of graphene creating a tube-like structure. CNSs are expected to share a number of properties with other graphitic systems such as high mechanical strength, high thermal conductivity and high electrical conductivity [4-7]. In contrast, the novel topology in CNSs exposes a number of unique properties. For example, electron transport in CNSs occurs throughout the entire system as opposed to MWCNT structures in which the current is confined to each layer. Additionally, CNSs will more easily accept intercalation of compounds due to the open structure as opposed to CNTs which will strongly resist lattice expansion [8,9]. These properties have led to a number of proposed applications including hydrogen storage [8], super capacitors [10] and nanoactuators [11-14].

Despite these promising applications, how to fabricate these structures controllably remains a great challenge. Carbon nanoscrolls were first produced by the arc discharge method by Bacon in 1960 [15]. Synthesis methods have since greatly improved. One method for synthesizing carbon nanoscrolls involves the use of an isopropyl alcohol solution to rollup graphene on SiO₂/Si wafers [14]. Other methods include sonochemical [16] and ultrasonication [9]. Braga et al. used molecular dynamics simulation to show that the formation and stability of CNSs results from a competing interaction between the torsional or bending force which wants the graphene to lay flat, and the van der Waals force which pulls the layers together [17]. Furthermore, Braga et al. showed that these competing interactions result in a potential energy barrier which can be overcome by bending the graphene layer to the point of overlap. Regardless of synthesis method, this potential energy barrier must be overcome to form a CNS.

Herein we report the first results that show local structural relaxation via vacancy introduction can significantly lower the potential energy barrier. Beyond a certain vacancy concentration, the potential energy barrier is completely removed, meaning the sheet could roll up without the need for external energy. A number of CNS systems of varying width and

vacancy concentration are modeled such that a map of stability as a function of two controllable parameters, dimensions and defect numbers, could be created.

2. Modeling

The classical molecular dynamics code, LAMMPS [18] along with the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) [19] potential were used to model the CNS systems. The AIREBO potential is capable of describing graphene systems by including bond stretching, bond angles, dihedral angles, van der Waals force, and electrostatic forces. All CNS systems were created by rolling a sheet of graphene into a truncated archimedean spiral [20] such that the interatomic bond spacing is maintained constant. Figure 1a shows the flat plane of graphene in which the width is defined to be perpendicular to the rolling axis and the length is defined to be parallel. We define the inner radius to be the distance from the center of the CNS to the inner most atomic row as indicated by the red arrow in Figure 1b. The interplanar spacing in all CNS

Figure 1. (a) Graphene plane showing the rolling axis with width defined perpendicular to the axis and length defined parallel, (b) carbon nanoscroll conforming to the shape of an Archimedean spiral [20] with the red arrow indicating the inner radius and (c) perspective view of the a CNS with width of 91.8 Angstroms.

systems is 3.354 Angstroms, which agrees well with experimentally determined interplanar spacing of 3.5 [14]. For sake of simplicity, all CNS systems considered have zigzag chirality.

Starting from a flat plane of graphene, 0.25% of carbon atoms are randomly removed, which accurately simulates the vacancy creation process upon particle irradiation. Under particle irradiation from electrons, light ions, and high energy heavy ions, damage cascade creation is less likely due to the relatively small nuclear stopping power compared to the electronic stopping power [21]. Thus, the defect creation is dominated by point defects. In addition, the ease of sputtering atoms from graphene suggests vacancies are the dominant point defect type [22,23]. Therefore, randomly introducing vacancies represents the defect morphology likely created in practical ion irradiation conditions. After defect loading, the system is annealed at 3000K for 40ps. The high temperature annealing provides a means for quickly reaching stable defect configurations expected in an experiment. This defect loading and relaxation process is repeated until the desired vacancy concentration is obtained. Next, the defective graphene sheet is rolled into a CNS with the desired inner radius. Then, the edge atoms are fixed in place while all other atoms are allowed to evolve in time at a temperature of 0.15K with a timestep of 0.1fs for 2ps.

3. Results and discussion

Figure 2a shows the per-mol change in potential energy relative to a flat plane of graphene for three vacancy concentrations in a CNS of width 91.8Å and length of 418.8Å. To allow for the comparison among the curves each system reference energy or zero energy was chosen as the energy of the system at infinite inner radius. It should be noted that the system energies increase with increasing defect levels, going from 2.51Kcal/mol to 4.62Kcal/mol (above the defect free level) for 1.5% and 5 5% defect levels respectively. We further compare the energies of different systems to check consistency. In a comparison with a defect-free graphene, the energy of defect-free bi-layer graphene is about 0.35Kcal/mol below, and that of graphite is about 1.1Kcal/mol below. As previously shown by Braga et al. the potential energy of the vacancy free CNS will initially increase due to the bending of the graphene plane. This energy increase arises due to the three and four body angle, dihedral angle and improper dihedral angles formed in the graphene plane. The change in energy due to the changing bond angles is described by the AIREBO potential. Once the graphene reaches a critical overlap, the van der Waals force takes over and a

self-sustaining rollup process begins. The potential energy barrier is defined to be the energy difference between a flat plane of graphene and a CNS at the point of initial overlap. The potential energy barrier height for the vacancy free case is 0.112Kcal/mol. Introducing 1.5% vacancy concentration lowers the barrier to -0.025Kcal/mol. At 5% vacancy concentration the barrier is -0.2Kcal/mol with a slope tending towards the scroll configuration, indicating the graphene sheet could spontaneously roll into a CNS.

Figure 2. (a) The absolute potential energy change as a function of inner radius for several vacancy concentrations and (b) the torsional and van der Waals components of the potential energy curves shown in (a). The reference or zero energy for each system is the systems energy at infinite inner radius.

Figure 2b shows the torsional and van der Waals components of the potential energy. The van der Waals interaction is described solely by the Lennard-Jones term in the AIREBO potential, whereas the torsional component includes all other contributions to the potential energy. In the unirradiated case, the van der Waals component of the potential energy is seen to be nearly zero until the graphene plane starts to overlap itself. In contrast, the torsional component is seen to increase exponentially as the inner radius decreases. Introduction of vacancies results in a slight drop in the van der Waals interaction which is comparable to the drop in effective interaction area between the overlapping regions. The torsional interaction shows a much more significant change in energy. Prior to overlap, the van der Waals force is

nearly zero. As such, the torsional component dominates any changes in potential energy, and by consequence, the energy barrier encountered during the transition from a flat plane to the point at which overlap begins. Thus, introducing single vacancy point defects causes a decrease in the torsional component of energy, and by relation, a drop in the potential energy barrier.

To understand why vacancies are effective at lowering the potential energy barrier, we studied isolated vacancy and divacancy structures under bending strain and compared these structures to defect free systems at a similar bending strain (Fig. 3). The calculation details are the following: First we calculate the energy change of a given atom after rolling from a flat defect-free graphene plane into a defect-free scroll. This energy change reflects the energy barrier required for rolling. Then we calculate the potential energy change of the same atom after rolling from a defective graphene plane into a defective scroll. Next we calculate the difference of these two potential energy changes, which corresponds to the efficiency to lower down the energy barrier in rolling process due to unique structural relaxation associated with defect presence. In Fig. 3, atoms are colored according to this energy barrier difference. The figures were created using Ovito [24]. The red color refers to an increase in the energy barrier for rolling while the blue color refers to a decrease. The plot is helpful to understand the contributions from individual atoms surrounding a vacancy defect to lower the overall energy barrier for scroll formation, due to the defect presence. In other words, Fig. 3 is a measure of how much the potential energy barrier is decreased by introducing a vacancy defect. The modeling considers several representative single vacancy and double vacancy configurations, including non-reconstructed vacancy, asymmetric 5-7 vacancy, symmetric 5-7 vacancy, asymmetric 5-8-5 di-vacancy and symmetric 5-8-5 di-vacancy. The modeling does not include much more complex vacancy structures, but we believe the consistent trend observed here applies to other vacancy defect types, due to the nature of strain relaxation around the defects.

Figure 3. (a) The change in absolute energy relative to a vacancy free CNS as a function of curvature for several commonly observed defect structures: non-reconstructed vacancy(b), asymmetric 5-7 (c), symmetric 5-7(d), asymmetric 5-8-5(e) and symmetric 5-8-5(f). Defect structures (b)-(f) are shown at the curvature indicated in (a) by the red line. Atoms are color coded according to the change in absolute potential energy relative to a defect free system.

For the case of the unannealed vacancy shown in Figure 3b, the energy drop is found to decrease linearly with curvature. Additionally, the local curvature increases at the site of the vacancy and decreases above and below the vacancy relative to a defect free system. This redistribution of curvature leads to a drop in the strain energy above and below the defect and an increase in the strain energy to the left and right of the defect. In this case, the structural relaxation is due simply to the absence of bonds at the vacancy leading to lower bending resistance in the defect region. In contrast, each of the annealed bond configurations has additional local stress resulting from the newly formed bonds. The 5-7 defect structure is formed by creating a bond between atoms on one of the three corners of the unannealed vacancy while the 5-8-5 defect structures are similarly created by annealing a divacancy system. When the new

bond(s) are formed it causes a strain inwards in the atoms parallel with the bonding direction(s). When a curvature is applied to the system, the initially strained region experiences a drop in energy. Thus in the annealed case the structural relaxation is due to both a dissipation of the local strain energy present before rolling and lower bending resistance at the defect site. Both of these factors contribute to the local curvature increase at the defect site and a decrease in curvature above and below the defect. If the strain direction is perpendicular to the rolling axis, as in the symmetrical cases, then the structural relaxation will be at a maximum (Figure 3d and 3f). In this case the desired strain relaxation direction aligns with the direction of increased strain due to rolling causing a net cancelation of strain energy. However, if the strain direction is not perpendicular to the rolling axis the structural relaxation will be significantly reduced as in the case of the asymmetric 5-7 and asymmetric 5-8-5 defects (Fig. 3c and 3e). Regardless of strain direction, the structural relaxation will be greater in the annealed cases. Comparing the various defect structures, the symmetric 5-7 defect is seen to be the most efficient per vacancy at decreasing the potential energy barrier. In contrast, the asymmetric 5-8-5 defect is seen to be the most inefficient per vacancy at lowering the potential energy barrier. The depth with which the structural relaxation stretches outwards from the defect location is determined by both the curvature and the defect structure. For the symmetric 5-8-5 defect the relaxation can reach 6-7 atoms outwards. This set of simulations has revealed the atomic scale details of how vacancies are able to lower the torsional energy and enhance CNS formation.

It should be noted that the existence of unreconstructed vacancies is somewhat controversial. Experimentally Robertson et al. observed such vacancies under transmission electron microscopy [25]. But various modeling studies suggest a zero energy or small energy barrier for Jann-Teller reconstruction [26,27]. In the present study, we include unreconstructed vacancies for a complete discussion on the effects from vacancies of various configurations, and will leave verification of stability of unreconstructed vacancies to the future study. **The consideration of non-reconstructed vacancies is one of the approximations made in this study.**

To see how this knowledge could be applied to fabricate CNSs, over 600 simulations were run varying the vacancy concentration in a graphene plane from 0% to 5% and the width from 30 to 180 angstroms. To dampen statistical variations a large length of 418.7Å was used.

The total number of atoms varied between 4,000 to over 30,000. The resulting potential energy barrier obtained from each system is plotted in Figure 4.

The transition from stable flat sheet of graphene to a sheet which can spontaneously rollup occurs at around 1.5% vacancy concentration for all widths larger than approximately 80Å. For smaller structures the necessary vacancy concentration to eliminate the potential barrier sharply increases. It should be noted that crossing the zero energy barrier transition does not ensure free-standing graphene will instantly form a CNS. Though no energy barrier may exist to rolling, there still exists an entropic barrier that must be overcome. This entropic barrier can be overcome given a sufficiently long time.

One feasible way of realizing the CNS fabrication technique modeled here is to use a focused ion beam (FIB). Initially, the low energy gallium beam is used to cut a graphene plane of specific dimensions from a large flat sample. Next, a CNS is fabricated by using in situ electron irradiation to create vacancy defects. However, comparing this model to experiment would bring into question several differences between the two: (1) “How will different geometries and sizes of graphene sheets other than those considered undergo CNS formation?” (2) “Is the modeled vacancy creation process actually representative of that seen in experiment?” and (3) “Given that the vacancy creation process is accurate, will the experimental system amorphize before reaching the necessary vacancy concentration?”.

First, we address the question of graphene plane geometry and size. The present study uses a rectangular graphene strip as the model system, but the findings are expected to be applicable to irregularly shaped small graphene flakes. However, the shape will affect the final CNS configuration.

For a large graphene flake, complexity arises. There are two possible paths to form a CNS from a large graphene strip/flake: one is to start bending the entire system until the edges of graphene begin to touch and van der Waals forces begin to play a role. This mechanism, however, is difficult considering the entropic cost required to reach the point of overlap. The other path is to start rolling from one of the edges. In this case, the CNS core is formed first from the edge. In this case, the CNS size increases as the rolling process continues. This path is entropically favorable since it requires only a subset of the material to obtain a specific shape at which point the van der Waals force causes a self-sustaining rolling process. In fact, this could

explain the experimentally observed self-rolling of suspended few-layer graphene. The rolling of edges creates specific interface patterns which are observable under transmission electron

Figure 4. Structural transition diagram showing the absolute potential barrier height as a function of vacancy concentration and width of the graphene plane.

microscopy [28,29]. Rolling at the edge does not occur for every graphene edge. According to the present study, edge rolling is unlikely to occur below a specific defect concentration.

Second, we address the question of vacancy creation in modeling vs. experiment. Our modeling considered effects from isolated vacancies only, which can be justified by the following facts: (1) irradiation induced C displacements are unlikely to stay on a graphene surface to form interstitial type defects such as adatoms, meaning vacancy defects are dominant after irradiation; (2) under electron or monomer ion irradiations, it is unlikely that a two dimensional damage cascade will be created on a graphene plane, thus, individual vacancies instead of vacancy clusters, are dominant.

Third, we address the question of whether the system will amorphize before reaching the desired vacancy concentration. The vacancy concentrations required to remove energy barriers

for CNS formation are relatively low. Therefore, the proposed defect engineering technique is feasible considering that the corresponding displacement per atom values are much lower than that required for amorphization. Recent studies suggest that structures of low dimensional carbon system collapse when one of every six-fold ring atoms is displaced. This corresponds to a vacancy concentration of about 15% [30]. In comparison, 5% vacancy concentration is needed to roll up a 5 nm wide graphene strip and less than 1% vacancy concentration is required for strips wider than 10 nm.

Early studies by Krashennnikov et al. show that formation energies of single vacancies and double vacancies decrease with decreasing diameters in single-walled nanotubes. [31]. Although their systems are single-walled nanotubes and ours are scrolls, our studies agree with their findings in the principle that curvature and local structural relaxation lower down the defect formation energies. On the other hand, scrolls are more complicated since their formation energies are determined by defect formation energies, the stress energies associated with curvature changes and van de Waals interactions associated with interacting graphene planes. Thus the lowest energy states or final stable configurations of scrolls are determined by the competing effects from the above three major energy contributions.

The present study considers only a self-suspended graphene sheet and ignores the effect by the van der Waals interactions with an underlying substrate. Furthermore, the modeling does not consider possible metastable configurations due to inter-layer covalent bonds mediated by defects [32-34]. If these complexities are considered, the barrier to roll a defective graphene sheet deposited on a substrate may be higher. It should also be noted that all CNS systems are not hydrogen capped at the edges, which would make small differences when compared with experiments due to the reactivity of dangling bonds. In our modeling, reconstruction happens before scrolling, based on the assumption that such reconstruction occurs fast once vacancies are created. We do not consider the case that both reconstruction and scrolling occur simultaneously, due to computational cost and time scale limits.

4. Conclusions

In summary, we have studied the properties of graphene and CNSs subject to various levels of vacancy concentrations. The findings showed that addition of vacancies to graphene can lower or eliminate the potential energy barrier that must be overcome to form a stable CNS. The

mechanisms responsible for lowering of the potential energy barrier were a concentration of the curvature at the location of the defect and dissipation of the local strain energy present prior to rolling. The local strain energy was a result of reconfiguration of the bonds at the defect site and was thus only present in annealed defect structures. Of the vacancy configurations studied, the symmetric 5-8-5 defect structure was found to lower the potential barrier by the largest amount while the symmetric 5-7 defect was found to be the most efficient at lowering the potential barrier. Finally, a diagram showing the absolute potential barrier height as a function of vacancy concentration and width of the plane was produced. This diagram shows the point at which the potential barrier drops to zero, which represents the eventual structural transition of a flat plane of free-standing graphene to a rolled CNS system. The ease with which the CNS will rollup is highly dependent on the size of this potential energy barrier. These results were used to propose a defect engineering technique to fabricate CNSs of predictable and controllable radii. As a result, these findings could be of importance to researchers attempting to fabricate CNSs.

Acknowledgements

This work was supported by the US Department of Energy, Office of Basic Energy Sciences, under Grant No. DE-SC0006725.

References

- (1) Geim, A. K.; Novoselov, K. S. The rise of graphene, *Nature Mater.* **2007**, 6, 183. doi:10.1038/nmat1849
- (2) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; et al. Graphene-based composite materials, *Nature* **2006**, 442, 282. doi:10.1038/nature04969
- (3) Novoselov, K. S.; Fal'ko, V. I.; Colombo, L.; Gellert, P. R.; Schwab, M. G.; Kim, K. A roadmap for graphene, *Nature* **2012**, 490, 192. doi:10.1038/nature11458
- (4) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene, *Science* **2008**, 321, 385. doi:10.1126/science.1157996

- (5) Berber, S.; Kwon, Y.; Tomanek, D. Unusually high thermal conductivity of carbon nanotubes, *Phys. Rev. Lett.* **2000**, 84, 4613. doi: 10.1103/PhysRevLett.84.4613
- (6) Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; et al. Superior thermal conductivity of single-layer graphene, *Nano Lett.* **2008**, 8, 902. doi:10.1021/nl0731872
- (7) Ebbesen, T.; Lezec, H.; Hiura, H. Electrical conductivity of individual carbon nanotubes, *Nature* **1996**, 382, 54. doi:10.1038/381678a0
- (8) Mpourmpakis, G.; Tylianakis, E.; Froudakis, G. E. Carbon nanoscrolls: a promising material for hydrogen storage, *Nano Lett.* **2007**, 7, 1893. doi:10.1021/nl070530u
- (9) Savoskin, M. V.; Mochalin, V. N.; Yaroshenko, A. P.; Lazareva, N. I.; Konstantinova, T. E.; Barsukov, I. V.; et al. Carbon nanoscrolls produced from acceptor-type graphite intercalation compounds, *Carbon* **2007**, 45, 2797. doi:10.1016/j.carbon.2007.09.031
- (10) Zeng, F.; Kuang, Y.; Liu, G.; Liu, R.; Huang, Z.; Fu, C.; Zhou, H. Supercapacitors based on high-quality graphene scrolls, *Nanoscale* **2012**, 4, 3997. doi:10.1039/c2nr30779k
- (11) Shi, X.; Cheng, Y.; Pugno, N. M.; Gao, H. A translational nanoactuator based on carbon nanoscrolls on substrates, *Appl. Phys. Lett.* **2010**, 96, 053115. doi:10.1063/1.3302284
- (12) Shi, X.; Pugno, N. M.; Cheng, Y.; Gao, H. Gigahertz breathing oscillators based on carbon nanoscrolls, *Appl. Phys. Lett.* **2009**, 95, 163113. doi:10.1063/1.3253423
- (13) Rurali, R.; Coluci, V.; Galvão, D. Prediction of giant electroactuation for papyruslike carbon nanoscroll structures: first-principles calculations, *Phys. Rev. B* **2006**, 74, 085414. doi:10.1103/PhysRevB.74.085414
- (14) Xie, X.; Ju, L.; Feng, X.; Sun, Y.; Zhou, R.; Liu, K.; et al. Controlled fabrication of high-quality carbon nanoscrolls from monolayer graphene, *Nano Lett.* **2009**, 9, 2565. doi:10.1021/nl900677y
- (15) Bacon, R. Growth, structure and properties of graphite whiskers, *J. Appl. Phys.* **1960**, 31, 283. doi:10.1063/1.1735559

- (16) Viculis, L. M.; Mack, J. J.; Kaner, R. B. A chemical route to carbon nanoscrolls, *Science* **2003**, 299, 1361. doi: 10.1126/science.1078842
- (17) Braga, S. F.; Coluci, V. R.; Legoas, S. B.; Giro, R.; Galva, D. S.; Baughman, R. H. Structure and dynamics of carbon nanoscrolls, *Nano Lett.* **2004**, 4, 881. doi: 10.1021/nl0497272
- (18) Plimpton, S. J. Fast parallel algorithms for short-range molecular dynamics, *Comput. Phys.* **1995**, 117, 1. doi: 10.1006/jcph.1995.1039
- (19) Stuart, S. J.; Tutein, A. B.; Harrison, J. A. A reactive potential for hydrocarbons with intermolecular interactions, *J. Chem. Phys.* 2000, 112, 6472. doi:10.1063/1.481208
- (20) The truncated archimedean spiral is described the formula $r = a\varphi + a_o$, where the interplanar spacing is $d = 2\pi a$ of 3.354Å and a_o is the inner radius.
- (21) Northcliffe, L.; Schilling, R. Range and stopping-power tables for heavy ions, *Nucl. Data Tables* **1970**, 7, 233. doi: 10.1016/S0092-640X(70)80016-X
- (22) Warner, J. H.; Rümmele, M. H.; Ge, L.; Gemming, T.; Montanari, B.; Harrison, N. M.; et al. Structural transformations in graphene studied with high spatial and temporal resolution, *Nature Nanotech.* **2009**, 4, 500. doi:10.1038/nnano.2009.194
- (23) Dimiev, A.; Kosynkin, D. V.; Sinitskii, A.; Slesarev, A.; Sun, Z.; Tour, J. M. Layer-by-layer removal of graphene for device patterning, *Science* **2011**, 331, 1168. doi:10.1126/science.1199183
- (24) Stukowski, A. Visualization and analysis of atomistic simulation data with OVITO-the open visualization tool, *Modell. Simul. Mater. Sci. Eng.* **2010**, 18, 015012. doi:10.1088/0965-0393/18/1/015012
- (25) Robertson, A.W.; Montanari, B.; He, K.; Allen, C.S.; Wu, Y.A.; Harrison, N.M.; Kirkland, A.I.; Warner, J.H.; Structural reconstruction of the graphene monovacancy, *ACS Nano* **2013**, 7, 4495.
- (26) El-Barbary, A.A.; Telling, R.H.; Ewels, C.P.; Heggie, M.I.; Briddon, P.R.; *Phys. Rev. B* **2003**, 68, 144107.

- (27) Casartelli, M.; Casolo, S.; Tantardini, G.F.; Martinazzo, R.; *Phys. Rev. B* **2013**, 88, 195424.
- (28) Zhang, J.; Xiao, J.; Meng, X.; Monroe, C.; Huang, Y.; Zuo, J.M. Free folding of suspended graphene sheets by random mechanical stimulation, *Phys. Rev. Lett.* **2010**, 104, 66805. doi:10.1103/PhysRevLett.104.166805
- (29) Liu, Z.; Suenaga, K.; Harris, P.; Iijima, S. Open and closed edges of graphene layer, *Phys. Rev. Lett.* **2009**, 102, 015501. doi:10.1103/PhysRevLett.102.015501
- (30) Aitkaliyeva, A.; Martin, M.S.; Harriman, T.A.; Hildebrand, D.S.; Lucca, D.A.; Wang, J.; et al. Radiation effects on the D to G Raman intensities of carbon nanotubes, *Phys. Rev. B* **2014**, 89, 235437
- (31) Krasheninnikov, A.V.; Lehtinen P.O.; Foster A.S.; Nieminen R.M.; Bending the rules: Contrasting vacancy energetics and migration in graphite and carbon nanotubes, *Chem. Phys. Lett.* **2006**, 418, 132.
- (32) Telling, R.H.; Ewels, C.P.; El-Barbary A.A.; Heggie, M.I.; Wigner Defects bridge the graphite gap, *Nat. Mat.* **2003**, 2, 333.
- (33) Gulans, A.; Krasheninnikov, A.V.; Puska, M.J.; Nieminen, R.M.; Bound and free self-interstitial defects in graphite and bilayer graphene: A computational study, *Phys. Rev. B* **2011**, 84, 024114.
- (34) Li, L.; Reich, S.; Robertson, J.; Defect energies of graphite: Density-functional calculations, *Phys. Rev. B* **2005**, 72, 184109.

Captions:

Figure 1. (a) Graphene plane showing the rolling axis with width defined perpendicular to the axis and length defined parallel, (b) carbon nanoscroll conforming to the shape of an Archimedean spiral [20] with the red arrow indicating the inner radius and (c) perspective view of the a CNS with width of 91.8 Angstroms (same width used in the CNSs of Figure 2).

Figure 2. (a) The absolute potential energy change as a function of inner radius for several vacancy concentrations and (b) the torsional and van der Waals components of the potential energy curves shown in (a). The reference or zero energy for each system is the systems energy at infinite inner radius.

Figure 3. (a) The change in absolute energy relative to a vacancy free CNS as a function of curvature for several commonly observed defect structures: unannealed vacancy(b), asymmetric 5-7 (c), symmetric 5-7(d), asymmetric 5-8-5(e) and symmetric 5-8-5(f). Defect structures (b)-(f) are shown at the curvature indicated in (a) by the red line. Atoms are color coded according to the change in absolute potential energy relative to a defect free system. Atomistic figures were created using Ovito [24].

Figure 4. Structural transition diagram showing the absolute potential barrier height as a function of vacancy concentration and width of the graphene plane.

Figure 1

Figure 2

Figure 3

Figure 4