Analysis of band-gap formation in squashed arm-chair CNT

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The electronic properties of squashed arm-chair carbon nanotubes are modeled using constraint free density functional tight binding molecular dynamics simulations. Independent from CNT diameter, squashing path can be divided into three regimes. In the first regime, the nanotube deforms with negligible force. In the second one, there is significantly more resistance to squashing with the force being \(\sim 40 - 100 \text{ nN/per CNT unit cell}\). In the last regime, the CNT loosens its hexagonal structure resulting in force drop-off followed by substantial force enhancement upon squashing. We compute the change in band-gap as a function of squashing and our main results are: (i) A band-gap initially opens due to interaction between atoms at the top and bottom sides of CNT. The \(\pi-\sigma\) orbital approximation is successful in modeling the band-gap opening at this stage. (ii) In the second regime of squashing, large \(\pi-\sigma\) interaction at the edges becomes important, which can lead to band-gap oscillation. (iii) Contrary to a common perception, nanotubes with broken mirror symmetry can have zero band-gap. (iv) All armchair nanotubes become metallic in the third regime of squashing. Finally, we discuss both differences and similarities obtained from the tight binding and density functional approaches.

I. INTRODUCTION

Experiments probing the electromechanical response of carbon nanotubes have been the most interesting recent work in nanotubes.\(^1\)\(^2\)\(^3\)\(^4\)\(^5\) These experiments involve nanotubes interacting electrically with contacts and mechanically with an atomic force microscope (AFM) tip. Apart from the fundamental physics governing the electromechanical response, these experiments are also important for future use of carbon nanotubes as actuators and nano-electromechnical devices.\(^6\) There are two categories of experiments exploring the electromechanical properties. The first category involves deformation of a suspended nanotube with an AFM tip.\(^7\)\(^8\)\(^9\)\(^10\) The electrical conductance was found to decrease by two orders of magnitude upon modest deformation due to bond stretching which results in band-gap opening at Fermi energy.\(^8\)\(^9\)\(^10\)\(^11\)\(^12\) The second category of experiments involves the squashing of nanotubes lying on a hard substrate.\(^12\)\(^13\)\(^14\) In the experiment of Gomez et al., a metal to semiconductor transition has been demonstrated in squashed metallic nanotube. Theoretically, there have been several studies that modeled the electro-mechanical properties of squashed carbon nanotubes.\(^8\)\(^9\)\(^10\)\(^11\)\(^12\) It was found that mirror symmetry breaking and formation of bonds between atoms at the top-bottom sides of CNT are necessary to open a band-gap in an arm-chair nanotube. While reference \(^12\) performed energy relaxation by enforcing specific symmetries during deformation, reference \(^11\) modeled squashing by a tip whose width was \(5.8 \text{ Å}\), which is smaller than even a \((6,6)\) nanotube diameter.

In this study, we model the tip-nanotube interaction more realistically by performing constraint free density functional tight binding (DF-TB) molecular dynamics (MD) simulations. Our calculations differ from prior work in that we do not impose specific symmetry conditions and allow for the nanotube to change symmetry during deformation. Further, our tip diameter is larger than the nanotube diameter, as in the experiments of Ref.\(^11\). The aim of our work is to investigate: (i) the magnitude of the force required to squash CNT, (ii) dependence of band-gap formation on the initial conditions of the MD simulations, (iii) applicability of \(\pi-\sigma\) orbital theories to find the band-gap upon deformation, (iv) relative roles of interactions between atoms at the top-bottom sides and atoms at the edges on the band-gap, (v) the electronic properties of a CNT squashed beyond the reversible regime, (vi) diameter dependence on the band-gap opening upon squashing, and (vii) effect of self consistent calculations on band-gap formation.

We will address the aforementioned issues in the rest of the paper. Initially we describe our method to simulate the experiment. Following this we present the mechanical properties of squashed CNT in Section III. In Section IV various aspects on the electronic properties of squashed CNT will be investigated. Finally, the conclusion will be given in Section V.

II. METHODOLOGY

An \((n,n)\) CNT is generated from a planar rolled graphene strip, where \(n \in \{6, 7, 8, 9, 10, 11, 12\}\). The corresponding diameters of these CNTs are in the range of \(\sim 8 - 16 \text{ Å}\). If such tubes are squashed in an AFM set-up, the tip radius is at least one order of magnitude larger than the CNT diameter. Hence we approximate the tip as a rigid graphene sheet where the atoms do not relax. The substrate is also modeled as a rigid graphene sheet. The distance between the graphene sheets and
CNT edges is at least 4.5 Å at the beginning of the MD simulations, so that CNT is not deformed in the first step. A snap shot of the atomic configuration of a squashed CNT between tip and sample is shown in the inset of Fig.1b. To model squashing of CNT we adopt two different methods: the first method consists of moving both the tip and substrate symmetrically towards the nanotube and the second one consists of moving only the tip towards the nanotube. We do not employ any further constraint on CNT atoms.

The MD simulations are performed using DFTB, which is a density functional theory-based tight binding approach. At each MD step of squashing, forces are calculated using Hellmann-Feynman theorem and CNT atoms are fully relaxed by the conjugate gradient method. Convergence criteria on the relaxed CNT structure is set such that the maximum force of on each CNT atom is < \(10^{-4}\)au. We have squashed the nanotubes all the way to irreversible regime. That is, the CNT structure is lost at the end of the simulation and cannot be recovered if the graphene sheets are removed. Since CNTs are constraint free, both “tank treading” (motion of atoms along circumference) and translational motion at various stages of squashing are possible if the energetics is favorable to such movement. We have also found that the symmetry of squashed CNT depends on the initial conformation of the CNT with respect to tip and substrate as well as the method adopted to squash CNT.

As CNT is being squashed, atoms follow various trajectories depending on the details of initial and ambient conditions. This would affect the conformation of the CNT with respect to the AFM tip as well as the symmetry of the CNT itself during squashing. To model this experiment faithfully and to draw more general conclusions on the electro-mechanical properties of squashed arm-chair CNTs, various simulations are required. In our work, constraint free squashing of more than fifteen paths have been performed on various CNTs and this represents substantial improvement over previous simulations.

III. MECHANICAL PROPERTIES

Our MD simulations reveal three different regimes of a squashed nanotube. These regimes can be clearly resolved by plotting the distance between top and bottom sides of the nanotube \((d_{TB})\) vs. tip-substrate separation distance \((d_{Tip-Sub})\) as shown in Fig.1a as well as the force on the tip vs. \(d_{Tip-Sub}\) as shown in Fig.1b. In the first regime, \(d_{TB}\) is larger than 3.8 Å and the nanotube is compressed relatively easily. This is reflected in the rather large slope \(\Delta d_{TB}/\Delta d_{TIP-Sub} \sim 0.88 \pm 0.07\) as seen in Fig.1a, and small force of less than 10 nN/per CNT unit cell on the tip as seen in Fig.1b. The second regime of squashing corresponds to \(d_{TB} \sim 2.3 - 3.8\) Å. Here the nanotube is more rigid to compression as seen by the moderate value of \(\Delta d_{TB}/\Delta d_{TIP-Sub} \sim 0.6 \pm 0.05\), and the relatively large value of force on the tip, 40 – 100 nN/per CNT unit-cell. These two regimes are reversible, i.e. retracting the tip and substrate results in a reversible change of the nanotube. The third regime corresponds to \(d_{TB} < 2.3\) Å and is characterized by an irreversible change, where the honeycomb structure of the nanotube is lost. The nanotube undergoes major atomic rearrangements so that total energy of the system is reduced. The CNT structural relaxation is also accompanied by force drop-off on the tip. However, this is substantially enhanced upon further squashing as seen in Fig.1b. An interesting feature of this regime is that atoms at the top and bottom sides of CNT are no longer planar. They form a sawtooth structure and results in an increase of \(d_{TB}\) with decrease in \(d_{TIP-Sub}\) as shown in Fig.1a.

In Fig.1b,c we present the force curves on the tip for all CNTs as a function of \(d_{TIP-Sub}\) and \(d_{TB}\), respectively. The curves corresponding to (6,6) and (12,12) nanotubes are shown as thick dotted and dashed lines, respectively. Comparison of the two curves indicates that, in general the force on the tip increases with increase in nanotube diameter. However, we find that the force required to squash an (11,11) nanotube (shown as thin lines) is larger than the one needed for a (12,12) nanotube when \(d_{TB} > 2.3\) Å. The underlying reason for this discrepancy is that the mirror symmetry is preserved during this simulation of the (11,11) nanotube while broken in the (12,12) CNT. If the nanotube mirror symmetry is preserved, atoms at the top-bottom sides of the nanotube are aligned. This results in a “more robust” structure, which offers resistance to squashing. Over all, our results indicate that the force required to squash nanotubes increases with increase in diameter, and is larger for conformation which preserves mirror symmetry.

IV. ELECTRONIC PROPERTIES

(6,6) arm-chair CNT has been investigated substantially and we start our discussion on the electronic properties of this tube. Depending on the initial orientation of the tube with respect to the graphene sheets and the manner of squashing, structural deformation may proceed along different paths. At each step of these paths and when the CNT atoms are fully relaxed, we compute the band structure and find the band-gap. Fig.2 shows an evolution of the band-gap as a function of \(d_{TB}\) for different paths. Qualitatively, one can see common features corresponding to the three regimes of squashing.

In the first regime, when \(d_{TB} > 3.8\) Å, initially metallic (6,6) CNT shows a zero band-gap. The transition to the second regime is manifested by the opening of the band-gap at \(d_{TB} = 3.8\) Å. It is at this deformation that atoms at the top and bottom sides of the CNT start to interact, which leads to the stiffening of the tube and to the modification of the band structure. The interaction between top and bottom sides of the CNT induces a perturbation term to ideal CNT Hamiltonian \(H_0\). We define this additional term as \(\Delta H_{TB}\) and it cor-
responds to the interaction between atoms shown as grey and dark grey atoms in the insets of each panel of Fig.2.

We note, that the opening of the band-gap may occur only when the mirror symmetry of the tube is broken, which is not the case in Fig.2a.

In the second regime, where CNT is squashed such that 2.3 Å < dTB < 3.8 Å, major changes to the band-gap occur. The most striking feature is that while the band structure is qualitatively similar to that of the undeformed nanotube, the band-gap oscillates, becoming zero, as in Fig.2b,c at dTB = 2.90 Å. Another important observation is that the symmetry of the tube is constantly changing in the course of deformation. Sudden changes of symmetry are accompanied by steep changes of band-gap, as in Fig.2d at dTB = 3.0 Å. The galore of various scenarios of band-gap behavior under squashing raises a question about the robustness and universality of the conductance modulation in such experiments. There are two sources of uncertainty. The first one is the constantly changing symmetry of the tube which leads to an “on-off” behavior of conductance as discussed in Subsection IV A. The second one is due to a collective effect of top-bottom and edge atomic interactions. As will be shown in Subsection IV B, the curvature at the edges induces large π − σ interactions, which may enhance or cancel the band-gap due to π − π∗ interactions between top and bottom atoms. This edge interaction, ΔHED, is defined such that the squashed CNT Hamiltonian is

\[ H_0 = H_0 + \Delta H_{TB} + \Delta H_{ED} \]

In this regime ΔHED induces π − σ interaction and band gap cannot be deduced within π-orbital model.

Finally, in the third regime, where dTB < 2.3 Å, we find that the band-gap vanishes in all the simulations. At this stage the CNT undergoes irreversible structural transformation where the honey-comb geometry is lost. The electronic band structure of a completely squashed nanotube resembles that of a metal, with multiple sub-bands passing through EF. Previous studies[2],[10] predicted that the nanotube will always become semiconducting in the course of squashing due to a spontaneous symmetry breaking. However, we find that it is possible for a structure to remain mirror symmetrical all the way till the irreversible regime as in the case of Fig.2a. Although mirror symmetry is broken in the irreversible regime, this does not lead to the band-gap opening.

A. The role of symmetry breaking in the formation of the band-gap

One can understand the band-gap opening in the first regime within a simple model[11]. In this model only a single π-orbital/atom is taken into account. In addition to this, squashing is treated as a first order degenerate perturbation of the crossing sub-bands, π and π∗ of an ideal arm-chair CNT. At the crossing point, the energy eigenstates are determined by diagonalizing the perturbation Hamiltonian

\[ H^p = \begin{pmatrix} V_{\pi\pi} & V_{\pi\pi^*} \\ V_{\pi^*\pi} & V_{\pi^*\pi^*} \end{pmatrix} \]

where \( H^p = H_s - H_0 + H_A \), \( H_0 \) and \( H_s \) are the Hamiltonians of squashed and ideal CNTs, respectively. The diagonal term in Eq.1 results in energy shift of π and π∗ bands by \( V_{\pi\pi} \) and \( V_{\pi^*\pi^*} \), respectively. This shifts the sub-bands crossing point but does not lead to a band-gap. If the off-diagonal term is applied a band gap \( E_g \) opens at Fermi energy \( E_F \), such that \( E_g = 2|V_{\pi\pi^*}| \).

In Fig.3a(b) we show that this approximation describes well the band-gap opening in the first regime (dTB > 3.8 Å) for results presented in Fig.2c(d). However, at slightly higher deformations both the π-orbital representation and the perturbation approach fail, as elaborated in the next sub-section.

A band-gap opening in arm-chair nanotubes has been correlated to the mirror symmetry breaking[21,12], where the mirror symmetry is broken and bonds between top and bottom atoms are formed, \( V_{\pi\pi^*} \) becomes non zero and the band-gap opens up. The underlying mechanism is to make the two originally equivalent sub-lattices A and B of the CNT distinguishable. To investigate the rigor of the correlation between the band-gap and mirror symmetry breaking, we have analyzed CNT atomic positions as a function of squashing. In each panel of Fig.2 we display a snap-shot of one (6,6) CNT ring at \( d_{TB} = 2.90 \pm 0.05 \) Å. It is clear from Fig.2a, that mirror symmetry is preserved and indeed the band-gap does not develop in the course of squashing. However, mirror symmetry is broken for the other simulations as indicated by the rest of the insets of Fig.2. Yet, our calculations, which include 4-orbitals/atom, show that the band-gap vanishes at \( d_{TB} \sim 2.9 \) Å for panels (b) and (c) of Fig.2. These results indicate clearly that the degree to which sub-lattices A and B are distinguishable is not the main factor in determining the magnitude of the band-gap upon deformation. We conclude that mirror symmetry breaking is necessary, but not sufficient for the band-gap opening, and thus can’t be used as a general guide to the metal-to-semiconductor transition.

B. Failure of π-orbital representation and perturbation approach

We now check the validity of the above model for the description of the band-gap. The sp2 (4 orbitals/atom) representation of a CNT Hamiltonian (\( H_0 \) or \( H_s \)) can be transformed into two sub-blocks \( H_{sp2} \) and \( H_{s\pi} \). The band structure of an undeformed carbon nanotube in the vicinity of the Fermi energy \( E_F \), can be described using only the π-orbital Hamiltonian, \( H_s \). The band-gap derived using the single π-orbital/atom model for these systems is shown in Fig.9a,b as dashed lines. It is clear from Fig.5a that, for \( d_{TB} < 3.5 \) Å, the single π-orbital/atom model overestimates the band-gap and does not predict...
the dip at $d_{TB} \sim 2.9$ Å. Similarly, it fails to determine band-gap $E_g$ for $d_{TB} < 4.5$ Å in Fig 3b. These results show that the band structure is determined by interactions between all orbitals, rather than $\pi$-orbitals alone.

We have also tested the rigor of perturbation theory, i.e., whether the band-gap $E_g$ can be estimated as $2|V_{\pi\pi}|$. In Fig 4 we display the value of $2|V_{\pi\pi}|$ calculated using the full Hamiltonian (triangle down symbols) and the $\pi$-orbital Hamiltonian (triangle up). It is clear that within $sp^3$ model perturbation theory results do not match $E_g$ for $d_{TB} < 3.5$ (3.7) Å in Fig 3a(b). Even if a single $\pi$-orbital/atom model is employed, perturbation theory results fail to describe $E_g$ for $d_{TB} < 2.8$ (3.0) Å in Fig 3a(b). Hence we conclude that neither the single $\pi$-orbital/atom model nor perturbation theory, assumed in $\pi$ Fig.3-a(b). Hence we conclude that neither the single theory results fail to describe $E_g$ for $d_{TB} < 2.8$ (3.0) Å in Fig 3a(b). Hence we conclude that neither the single $\pi$-orbital/atom model nor perturbation theory, assumed in Eq 4 is able to describe the electronic band structure of a squashed arm-chair carbon nanotube.

To determine the origin of single $\pi$-orbital/atom failure to describe the electronic properties of squashed arm-chair CNT in the vicinity of $E_F$, we decompose the perturbation Hamiltonian, $H_{\pi} = H_0$, to a sum of top-bottom and edge interaction, $\Delta H_{TB}$ and $\Delta H_{ED}$. We define $H_{TB} = H_0 + \Delta H_{TB}$ and use this Hamiltonian to find the band-gap, shown in Fig 3a(b), for the structures discussed in Fig 3a(b). We note that single $\pi$-orbital/atom model describes $E_g$ due to all top-bottom interaction Hamiltonian accurately. Moreover, this band-gap can be modeled within perturbation theory between $\pi$ and $\pi^*$ states for $d_{TB} \geq 2.7$ Å. If CNT is squashed such that $d_{TB} \leq 2.7$ Å, top-bottom interaction is substantially enhanced and perturbation theory fails to predict the band-gap.

When similar analysis is applied to the interactions at the edges, $H_{ED} = H_0 + \Delta H_{ED}$, we find that the single $\pi$-orbital/atom model as well as perturbation theory fail to reproduce full model calculations, as shown in Fig 3a’(b’). We see that a single $\pi$-orbital/atom model underestimates the true band-gap $E_g$ computed using 4 orbitals/atom, while the perturbation theory result $2|V_{\pi\pi}|$ predicts a much smaller value. These graphs indicate that at the high curvature edge regions, $\pi-\sigma$ interaction is large compared to $\pi-\pi^*$ interaction and cannot be neglected.

The degree of sophistication required to describe the band-gap of a squashed CNT in the second regime can be summarized by the following steps: (i) if the mirror symmetry is broken, top bottom interaction induces a band-gap opening, which can be predicted within the single $\pi$-orbital/atom model and a perturbation theory; (ii) Further squashing increases $\pi-\sigma$ interaction at the edges due to large curvature. This interaction necessitates the use of full calculation within $sp^3$ model. It is also important to note that neither top-bottom nor edge interactions alone can explain the dips of the band-gap. Only cancellation effect of both interactions leads to the oscillations of the band-gap in Fig 3b,c.

C. Effect of CNT diameter

In this subsection we highlight the most important results for arm-chair CNTs with larger diameters. In Fig 5 we show the band-gap of $(n,n)$ nanotubes as a function of squashing, where $n \in \{7,8,9,10,11,12\}$.

In each panel of Fig 5 we display a snapshot of the atomic configuration of the corresponding CNT. These insets indicate that when mirror symmetry is strongly broken, larger band-gap is formed. The origin of this gap is of the same nature as in the (6,6) CNT. It is due to top-bottom interactions as well as edge effects. In Fig 5 we present the gap results when including only interactions up-to second nearest neighbor as continuous lines while dashed lines include all Hamiltonian except top-bottom interactions. We note that the Hamiltonian which takes into account only first and second nearest neighbors is similar to edge interaction Hamiltonian $H_{ED}$. These results indicate that edge effect on the band-gap formation is relevant only for $d_{TB} \leq 3.5$ Å. The initiation of the gap at large separation distance, $d_{TB}$, is solely due to top-bottom interactions as found for (6,6) CNTs.

Our simulations also show that there is no preference for mirror symmetry breaking during CNT squashing. This is clearly seen for (7,7) and (8,8) CNTs whose gap results are shown in Fig 5a,b, respectively. In the course of squashing of these tubes, mirror symmetry is broken at $d_{TB} \sim 3.4$ Å and a gap is formed around $E_F$. After 1–2 steps mirror symmetry is recovered and the gap closes at an early stage, as seen in the graphs of Fig 5a,b.

The major differences of the larger diameter nanotubes are (i) the initiation of the band-gap at smaller deformation when mirror symmetry is broken, and (ii) the increased stability of the system in the course of squashing. This stability is due to robustness of the CNT conformation with respect to the tip: larger tubes have more atoms at the surface interacting with graphene layers. Hence “tank-treading” as well as translational motion is less significant. Therefore, we expect that for CNTs with large diameters, the band-gap opening is more reproducible.

D. Effect of self consistency

All our calculations are based on DF-TB parameterization. However, such empirical potentials may suffer from transferability problems, especially for largely deformed structures. Hence we need to check the validity of our conclusions using better models. To test our results, we consider the calculations of (6,6) CNT structures displayed in Fig 2a,b,d. Band-gap calculation using DF-TB model is compared to calculations within self consistent density functional tight binding model (SCTB)12 and density functional theory calculations (DFT). The latter is performed using Gaussian03 framework within BPW91 exchange-correlation functional parameterization and 6-31G basis set.

In Fig 6 we show the band-gap calculation results for
the three different simulations using different models. When the CNT conserves its mirror symmetry a band-gap cannot develop at \( E_F \). The three models agree and the results are identical as shown in Fig 4a. When mirror symmetry is broken, the three models predict a band-gap opening, non monotonic behavior and closure in the same region of deformation, but the magnitude depends strongly on the description of the interaction. In particular, DF-TB results which are shown as dotted lines with open circles in Fig 4 do not incorporate charge redistribution. Such a description is reasonable for small deformation. However as \( d_{TB} \) decreases below 3.3 Å, charge can redistribute between carbon atoms and this may result in different electronic properties. The importance of charge transfer revealed in the SCTB calculations is shown as continuous line in Fig 4b. It diverges from DF-TB model only under strong deformation, \( d_{TB} < 3.3 \text{ Å} \).

The band-gap calculated within DFT is different from DF-TB model. The origin of this difference is two fold: DFT underestimates the band-gap and DF-TB model fails to describe long range interaction. When mirror symmetry is broken, both DF-TB and DFT predict mismatch between sub-lattices A and B, but the strength of the mismatch depends on the interaction. Within DFT parameterization, the exchange correlation functional is underestimated and hence the band-gap is smaller than DF-TB results under large deformations. However, at \( d_{TB} \geq 3.5 \text{ Å} \), DF-TB fails to describe long range interaction due to an imposed cut-off radius of 5.2 Å. This causes DFT results to be larger than those of DF-TB. Therefore, for large diameter squashed CNTs with broken mirror symmetry a band-gap can develop at much earlier stage, i.e at \( d_{TB} > 5.0 \text{ Å} \).

Finally we note that our results derived from the three models are in qualitative agreement, and our conclusion deduced from DF-TB calculations are valid. Quantitatively \( E_g \) depends on the model and some differences emerge. In particular, within DFT model conductance oscillations are less pronounced and disappear in Fig 4b. However, this model predicts \( E_g \) oscillations in Fig 4c and the band-gap vanishes \( d_{TB} \sim 2.8 \text{ Å} \).

V. CONCLUSION

We have performed the state of the art DF-TB MD simulations of squashing arm-chair CNT. Our analyses have been carried out on tubes with diameters in the range of 8 – 16 Å. Such a large number of simulations enable to have more conclusive analysis on these systems and we find that:

- Force required to squash CNT increases with tube diameter and is larger for conformations with mirror symmetry preserved. The path for squashing an arm-chair CNT can be split into three different regimes. For \( d_{TB} > 3.8 \text{ Å} \), the force exerted on the AFM tip is small (\(< 10 \text{nN/per CNT unit cell}\) and the CNT undergoes most of the compression. In the intermediate regime, \( d_{TB} \sim 2.3 - 3.8 \text{ Å} \), force is substantially enhanced and reaches \( 40-100 \text{nN/per CNT unit cell} \). Finally, for \( d_{TB} < 2.3 \text{ Å} \), CNT is under strong deformation. It undergoes atomic relaxation and looses its hexagonal shape, resulting in force drop-off.

- If CNT mirror symmetry is broken, \( E_g \) can develop due to mismatch between sub-lattices A and B. However, this distinguishability between the sublattices is due to top-bottom interactions as well as edge effects. The former can be modeled within single \( \pi \)-orbital/atom while the latter has strong \( \pi - \sigma \) interaction and cannot be represented within single \( \pi \)-orbital/atom.

- The band-gap is initiated primarily due to the top-bottom interactions, but for \( d_{TB} \leq 3.5 \text{ Å} \) mismatch at the edges becomes important and can lead to cancellation of the band-gap formed. This can result in band-gap oscillation as a function of squashing. However this effect depends on the exact atomic position at the edges. Hence we do not expect smooth variation of the conductance as a function of squashing.

- Under strong deformation CNT looses its honeycomb structure and becomes metallic.

- Large diameter CNTs have more contact area with AFM tip during squashing. Hence, their conformation with respect to the tip is more robust. Their squashing results are expected to be more reproducible in an AFM experiment performed in the reversible regime of the CNT structure.

- Band-gap formation of squashed arm-chair CNT described by DF-TB, SCTB and DFT models are in qualitative agreement. However, quantitatively the value of the band-gap is model dependent. Under large deformation, \( d_{TB} < 3.5 \text{ Å} \), charge transfer is important and band-gap is over estimated within DF-TB model. In addition to this, DF-TB model under estimates long range interaction. Hence interaction between top and bottom sides of CNT are under estimated and this results in smaller gap compared to DFT for \( d_{TB} > 3.5 \text{ Å} \). Hence large diameter squashed CNTs with broken mirror symmetry, are expected to develop a band-gap even for \( d_{TB} \geq 5.0 \text{ Å} \).

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To determine unit vector $\vec{U}$ corresponding to the $\pi$-direction at every Carbon atom, we initially find the unit vectors $\vec{C}_1, \vec{C}_2$ and $\vec{C}_3$ in the direction of the three nearest neighbors of the Carbon atom. Three vectors, $\vec{V}_1, \vec{V}_2$ and $\vec{V}_3$ are defined such that $\vec{V}_i = \epsilon_{ijk}(\vec{C}_j, \vec{C}_k)\vec{C}_l + \epsilon_{ijk}(\vec{C}_l, \vec{C}_k)\vec{C}_j$. $\vec{U}$ should be orthogonal to the three vectors, $\vec{V}_1, \vec{V}_2$ and $\vec{V}_3$; hence $\vec{U}$ is determined such that $[\vec{V}_1 \vec{V}_2 \vec{V}_3].\vec{U}$ has negligible elements.

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19. Two Carbon atoms define a graphene unit cell. Hence graphene can be viewed as a superposition of two sublattices each composed of a single atom. This defines sublattices A and B which have identical interactions for ideal CNT.
20. To determine unit vector $\vec{U}$ corresponding to the $\pi$-direction at every Carbon atom, we initially find the unit vectors $\vec{C}_1, \vec{C}_2$ and $\vec{C}_3$ in the direction of the three nearest neighbors of the Carbon atom. Three vectors, $\vec{V}_1, \vec{V}_2$ and $\vec{V}_3$ are defined such that $\vec{V}_i = \epsilon_{ijk}(\vec{C}_j, \vec{C}_k)\vec{C}_l + \epsilon_{ijk}(\vec{C}_l, \vec{C}_k)\vec{C}_j$. $\vec{U}$ should be orthogonal to the three vectors, $\vec{V}_1, \vec{V}_2$ and $\vec{V}_3$; hence $\vec{U}$ is determined such that $[\vec{V}_1 \vec{V}_2 \vec{V}_3].\vec{U}$ has negligible elements.
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FIG. 1: The inset in (b) displays the atomic configuration of a squashed CNT between tip and sample. $d_{\text{tip-sample}}$ and $d_{\text{sub}}$ are the tip-sample separation distance and the distance between top and bottom sides of CNT, respectively. (a) $d_{\text{sub}}$ vs. $d_{\text{tip-sub}}$: CNT squashing undergoes three regimes, $d_{\text{sub}} > 3.8 \text{ Å}, 3.8 \text{ Å} > d_{\text{sub}} > 2.3 \text{ Å}$, and $d_{\text{sub}} < 2.3 \text{ Å}$. These regimes are separated by the horizontal dashed lines. In the first regime, the slope of $d_{\text{sub}}$ vs. $d_{\text{tip-sub}}$ is $\sim 0.88 \pm 0.07$ while in the second regime the slope is $\sim 0.6 \pm 0.05$, where the corresponding fits are represented as thick solid lines. At $d_{\text{sub}} < 2.3 \text{ Å}$, CNT undergoes structural transformation and the honey-comb structure cannot be identified. (b),(c) Force exerted on the tip (top graphene sheet) as a function of $d_{\text{tip-sub}}$ and $d_{\text{sub}}$, respectively. In all panels, every thin line corresponds to one simulation and results for (6,6) and (12,12) CNT are highlighted as thick dotted lines and dashed lines respectively.

FIG. 2: $E_g$ of (6,6) CNT at $E_F$ as a function of $d_{\text{sub}}$ for different simulations. In (a) and (b) only top graphene layer is displaced, while in (c) and (d) both layers are moved to squash CNT. The insets in each panel show the atomic configuration of the corresponding CNT unit cell for $d_{\text{sub}} = 2.90 \pm 0.05 \text{ Å}$ where grey atoms and dark grey atoms indicate top and bottom sides of CNT, respectively.

FIG. 3: (a) and (b) show band-gap at $E_F$ and $2|V_{\pi\pi}|$ of (6,6) CNT for simulation results shown in Fig 2c,d, respectively. Continuous lines and dashed lines correspond to $E_g$ using 4 orbitals/atom and a single $\pi$-orbital/atom, respectively. Thin lines with triangle down symbols and dashed lines with triangle-up symbols represent $2|V_{\pi\pi}|$ using 4 orbitals/atom and a single $\pi$-orbital/atom, respectively.
FIG. 4: (a,b) and (a’,b’) show band-gap at $E_F$ and $2|V_{\pi\pi^*}|$ of (6,6) CNT for simulation results shown in Fig.2c,d due to top-bottom interactions ($H_{TB}$) and edge effects ($H_{EB}$), respectively. Top and bottom of CNT are shown in the insets of Fig.2 with grey and dark grey atoms. In these panels, continuous and dashed lines correspond to $E_g$ using 4 orbitals/atom and a single $\pi$-orbital/atom, respectively. Thin lines with triangle down symbols and dashed lines with triangle-up symbols represent $2|V_{\pi\pi^*}|$ using 4 orbitals/atom and a single $\pi$-orbital/atom, respectively.

FIG. 5: Band-gap of arm-chair CNTs as a function of squashing. (a), (b), (c), (d), (e) and (f) correspond to (7,7), (8,8), (9,9), (10,10), (11,11) and (12,12) tubes, respectively. Dotted lines with open circles correspond to all interactions, continuous lines are interactions up-to the second nearest neighbor and dashed lines correspond to results when top-bottom interactions are omitted. The insets in each panel show the atomic configuration of the corresponding CNT unit cell for $d_{TB}$ closest to 3.2 Å where grey atoms and dark grey atoms indicate top and bottom sides of CNT, respectively.

FIG. 6: Energy gap of (6,6) CNT at $E_F$ as a function of separation distance between top and bottom sides of CNT ($d_{TB}$) for simulations shown in Fig.2a,b,d. Dotted lines with open circles are the original calculations within DF-TB model. Solid and dashed lines correspond to calculations using SCTB and DFT, respectively.