The Unravelling of Open-Ended Single Walled Carbon Nanotubes Using Molecular Dynamics Simulations

The unravelling of (10, 10) and (18, 0) single-walled carbon nanotubes (SWCNTs) is simulated using molecular dynamics simulations at different temperatures. Two different schemes are proposed to simulate the unravelling: completely restraining the last atom in the chain and only restraining it in the axial direction. The forces on the terminal atom in the unravelled chain in the axial and radial directions are reported till the separation of the atomic chain from the carbon nanotube structure. The force-displacement relation for a chain structure at different temperatures is calculated and is compared to the unravelling forces. The axial stresses in the body of the carbon nanotube are calculated and are compared to the failure stresses of that specific nanotube. Results show that the scheme used to unravel the nanotube and the temperature can only effect the duration needed before the separation of some or all of the atomic chain from the nanotube, but does not affect the unravelling forces. The separation of the atomic chain from the nanotube is mainly due to the impulsive excessive stresses in the chain due to the addition of a new atom and rarely due to the steady stresses in the chain. From the simulations, it is clear that the separation of the chain will eventually happen due to the closing structure occurring at the end of the nanotube that would not be possible in multiwalled nanotubes.

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1 Introduction

Since 1991 [1] when carbon nanotubes were re-identified experimentally, they have attracted considerable curiosity to investigate their electrical [2–5] and thermomechanical behavior [6–9] as well as the electromechanical behavior [10,11]. Experiments show that carbon nanotubes have extraordinary electrical and mechanical properties. Mechanically, carbon nanotubes (CNTs) have a tensile strength that is 20 times that of high strength steel [12] and a Young’s modulus in the order of a terapascal [13]. These extraordinary mechanical properties can easily be explained by the strong hybrid sp² carbon–carbon bond, which is considered to be the strongest bond in nature [14]. Geometrically, CNTs can be classified into single-walled carbon nanotubes (SWCNTs) formed from folding a single sheet of graphite or multiwalled carbon nanotubes (MWCNTs) that is formed of SWCNTs that are concentrically aligned inside each other. The direction of folding the graphite sheet is defined by the chiral vector \( C_0(n,m) \) [15], where CNTs can be classified into armchair nanotubes \((n,n)\) and zigzag nanotubes \((n,0)\) or chiral nanotubes \((n,m)\). Both the mechanical and the electrical properties of CNTs depend on the chirality of the nanotube. Mechanically, it was found that armchair nanotubes can sustain higher stresses than zigzag nanotubes [12].

After the first proposals of the usage of MWCNT as field emitters in 1995 [16,17], a lot of research was directed to study their applicability [18–20], and showed a lot of success. In Ref. [16], the enhanced field emission of a single MWCNT was attributed to the unravelled atomic chain from the open-ended nanotube. It was proposed that the electric field generated the forces that caused the unravelling process. In 1997 [21], ab initio density functional formalism was used to simulate the unravelling process in double-walled CNTs as proposed in Ref. [16].

In this paper, molecular dynamics (MD) Simulation is used to investigate the mechanical unravelling of (10, 10) armchair and (18, 0) zigzag SWCNT till failure, using different mechanical schemes at different temperatures. MD simulations can serve as a powerful tool for studying CNTs in different applications [22–25] that allows for the investigation of the applied atomic forces and stresses as well as the atomic trajectories during the course of the simulation.

2 Molecular Dynamics Simulation

The second generation, reactive empirical bond order (REBO) potential [26,27] based on the Abell–Tersoff potential [28,29] is used to represent the covalent bonding between the carbon atoms (taking into account different possible hybridizations). Mylvaganam and Zhang [12] have shown that for CNTs Tersoff–Brenner potential is more accurate and cost effective. The potential energy of a set of covalently bonded carbon atoms is given by

\[
U = \sum_{i=1}^{N} \sum_{j \neq i} \left[ U^R(r_{ij}) + U^A(r_{ij}) \right]
\]

(1)

where \(r_{ij}\) is the distance between atom \(i\) and atom \(j\), \(U^R\) and \(U^A\) are the pair-additive interactions that represent the interatomic repulsions and attractions, respectively, and \(b_{ij}\) is the bond order between atom \(i\) and atom \(j\), which takes into account the effect of the many-body interactions between the carbon atoms. When the distance between two carbon atoms exceeds the maximum bond
length of 2 Å (the equilibrium unstrained sp² bond length is 1.42 Å), Lennard–Jones potential [30,31] is used to represent the interaction between those carbon atoms [32].

The simulations were performed in the canonical (NVT) ensemble (Constant number of atoms, volume and temperature) where the temperature was kept constant at 300, 600, 900, and 1200 K using Brendsen thermostat technique [33] for all moving atoms. The integration time step in the simulations is 0.5 fs, which is less than 10% of the vibration period of a carbon atom [12]. The third order predictor-corrector Nordsieck algorithm is used for integrating the equations of motion.

In this paper, MD simulations were performed on a single carbon atomic structure and CNTs. Displacement was applied on one side of the simulated structure and the stresses and the forces were calculated due to the inscribed displacement. The displacement is applied in increments every 50 simulation time steps, and the forces and the stresses were calculated as the average value over these 50 time steps. The value of the displacement increment is proven to be crucial and has a major effect on the kinematic behavior of the atoms at failure [34]. In a previous study [34], we have shown that a value of 0.025 Å or less is required for the displacement increment to avoid any error in the simulated behavior of a carbon nanostructure, thus throughout this paper we use a displacement increment of 0.0125 Å.

When calculating the stresses in CNTs the total forces at the end atoms is divided by the cross-sectional area in the direction required. For calculating the cross-sectional area, a wide range of nanotube wall thickness values are used in the literature ranging from 0.617 Å to 3.4 Å ([12,35–38]). In this paper, the thickness of the nanotube was taken as 0.617 Å as this was the only value that its calculation was Referenced [39].

3 Behavior of Single Atomic Chain

The behavior of a single atomic chain and its force-displacement relation is required to fully understand and explain the behavior of the unravelling of CNTs. In this section, we calculate the force-strain relation of a single atomic chain of carbon using MD simulations till the failure of the chain at different temperatures. Due to the difference in the hybridization between a single atomic chain structure and CNTs (sp² in a single atomic chain with two π bonds per atom versus sp² in CNT with one π bond per atom), the equilibrium bond length used in CNTs (1.42 Å) cannot be used. For calculating the equilibrium bond length, a 0 K molecular mechanics simulation for a 105 atoms long chain is run for 100,000 time steps. The first and the last atoms in the chain were restrained in the two directions perpendicular to the axial direction of the chain to insure the straightness of the chain and free to move in the axial direction. The rest of the atoms were free to move in all three directions. For the first half of the simulation time, atoms were left to relax to their equilibrium position without any trajectory tracked. In the second half of the simulation, the distance between the atoms were averaged over all the time steps used for the calculation and yielded an equilibrium interatomic distance of 1.292 Å, which is expected compared to that of CNTs due to the stronger bond.

For calculating the force-strain relation for the atomic chain, the same structure used for the energy minimization was used but with fully restraining four atoms at one end of the chain and using the last atom on the other end of the chain for the application of the displacement increments as described in Sec. 2 (Fig. 1). The force-strain relation is plotted in Fig. 2. It is clear from the figure that the thermal fluctuation in the calculated axial force at 1200 K increases significantly compared to that calculated at 300 K and is the reason for the change of the maximum average force that can be sustained in the chain from 16.7 eV/Å at 300 K to 14 eV/Å at 1200 K. But it is clear from the figure that the absolute maximum force is the same at both temperatures with a value of 18.6 eV/Å.

4 Unravelling of Nanotubes

4.1 Restrained Scheme. In this section, simulations are performed for two types of CNTs; (10, 10) armchair SWCNTs of diameter 13.6 Å and 40 atoms per unit cell with 52 unit cells resulting in a total length of 128 Å and (18, 0) zigzag SWCNTs of diameter 14.1 Å and 72 atoms per unit cell with 32 unit cells resulting in a total length of 136.4 Å. These two selected CNTs are always metallic [14]. As a boundary condition, all the atoms in the two unit cells on one side of the CNT are completely fixed in all three directions. In both (10, 10) and (18, 0) CNTs the geometry of the CNT was designed to have one dangling atom on the free end of the nanotube. The coordinates of this atom is kept fixed throughout the simulation time in the directions perpendicular to axial direction of the nanotube and used for applying the prescribed displacements in the axial direction by changing its axial coordinate every 50 time steps as described earlier. The rest of the atoms are allowed to move freely (but with keeping the temperature constant) under the effect of the forces that result from the interatomic potential.

The force acting on the terminal atom of the chain is calculated and is averaged every 50 time steps. The absolute resultant of the
two forces acting in the plane perpendicular to the axial direction is also calculated. The axial force and the absolute resultant force for (10, 10) CNT are plotted against the displacement at the end of the chain in Fig. 3. The axial stress at the fixed end of the nanotube is plotted against the displacement in Fig. 4. Figure 5 shows a schematic of the steps of the unraveling in SWCNTs. In Fig. 3(a) for the (10, 10) CNT at 300 K, the axial force builds up till reaching a value of 16 eV/A with a displacement of 5.2 Å then an atom unravels from the tube to the chain causing part of the force to relax immediately as shown in the figure. This is also accompanied with a peak in the in-plan force, which raises the question of whether restraining the terminal atom in the in-plan direction has any effect on the mechanism of the unraveling, thus, leading us to use another scheme to study this effect in Sec. 4.2. After the unravelling of the first atom, stresses build up again with increasing the displacement and relax several times, but not all of these relaxations are due to the addition of new atom to the chain; some of them are only due to an internal relaxation at the end of the
nanotube itself by the formation and breakage of several bonds. These are in contrast to the simple continuous radial unravelling of the end atoms without any change in the structure of the nanotube itself suggested earlier [16,21]. It is also important to note that the force required to unravel more atoms or cause the internal relaxation is independent of the force required to start the unravelling and can sometimes be larger or smaller than the initial unravelling force. At a displacement of 12.7 Å two hexagons from the body of the nanotube unravel together and the end of the nanotube at the position of its connection to the atomic chain starts to have some curvature similar to that in closed-ended nanotubes. The force required to start the unravelling process decreases slightly with the increase of the simulation temperature and it is clear from Fig. 3 that at temperatures of 300 K and 600 K the failure of unravelled chain only occurs when the direct force at the end of the chain exceeds the maximum force allowed in an atomic chain calculated in Sec. 3, but at higher temperatures the plotted value of the force at failure is less than these values. This can be attributed to a local instantaneous indirect increase in the stress in the atomic chain near the nanotube during the addition of a new atom to the chain assisted by the thermal fluctuations. It is important to note that in all the simulations, the direction of the unravelling from the end of the nanotube is not radial as suggested earlier [16,21] and that the source of the atoms feeding the chain does not rotate around the circumference of the nanotube. At 900 K and 1200 K, initially, the unravelling starts in the radial direction but soon tends to stop. This is the reason for the delay of the failure at those temperatures to displacements of 26–33 Å as we observed that the failure happens only after the formation of a partial cap at the end of the nanotube, which will not happen if the unravelling continues radially. The formation of the partial cap is also a result of the pulling force causing the walls of the nanotube to fold onto itself. In Fig. 4, the maximum axial stresses built in the body of the (10, 10) nanotube at 300 K due to the unravelling is 150 GPa, which is about 10% of the capacity of the perfect nanotubes [34], and thus failure in the body of the nanotube can never happen under these loading conditions. In the figure, it is clear that there is a time lag between the actions taking place in the force-displacement diagram and the stress-displacement diagram as it take a few time steps for the effect to reach the fixed end of the nanotube. The same level of stresses is also generated at the other temperatures simulated.

Figure 6 shows the force-displacement relation for the simulated (18, 0) zigzag nanotubes at different temperatures. Unlike the (10, 10) CNTs, the force required to start the unravelling in (18, 0) CNT is in the order of 10 eV/Å with a slight decrease with the increase in the simulation temperature but after the unravelling of the first atom, the force required to unravel more atoms is in the same range as the (10, 10) CNTs (Fig. 6). This is in agreement with the density functional calculations carried out by Lee and his colleagues [21], where they found that unravelling happens in zigzag nanotubes at an electric field of 2 eV/Å while armchair nanotubes unravel at an electric field of 3 eV/Å, which is the same ratio in this work. The same ratio also holds for the maximum stress in perfect CNT and thus the lower unravelling force in the zigzag nanotubes is due to the easier to break zigzag oriented bonds. For 600 K, it appears in the figure that the force required to start the unravelling is larger than that at 300 K. Actually, the force causing the unravelling is not larger as the unravelling in both simulations happens at the same displacement level and the extra force is a reflex force after the unravelling already started. Regarding the failure of the atomic chain, at 300 K, although the start of the curvature of the end of the nanotube and the formation of the partial cap happens as early as a displacement of 12.8 Å, but the
Fig. 7 Force-displacement diagram for (10, 10) CNTs at different temperatures using the unrestrained scheme

Fig. 8 Force-displacement diagram for (18, 0) CNTs at different temperatures using the unrestrained scheme
unravelling continues till a displacement value of around 35 Å. This is due to that the location of the connection between the atomic chain and the end of the nanotube is not at the center of the cap as in the previous simulations but moves the edge of the cap. The same behavior is observed at 600 K delaying the failure to a displacement value beyond the maximum displacement value simulated of 50 Å. This also happens at 1200 K, and the delay is increased by the delay of the formation of the cap itself due to a few radial unravelling at the beginning of the simulation.

4.2 Unrestrained Scheme. In this section, the same CNTs simulated in Sec. 4.1 are simulated with exactly the same details except for the boundary conditions of the terminal atom of the atomic chain used to apply the displacement. The terminal atom is allowed to move freely in the two directions perpendicular to the axial direction of the tube. This can be more close to the case of unravelling during field emission where there are no restraints on the end of the tube.

For the (18, 0) CNT, as shown in Fig. 7, the displacement to failure generally increased compared to the restrained scheme except for the 600 K simulation. In the 600 K simulation, a special failure occurred, where the failure is not due to the curvature of the end of the nanotube, as no curvature was observed till failure in this simulation due to the unravelling being in the radial direction for the first few atoms. In this simulation, failure happened due to the separation of the whole atomic chain from the tube end assisted by an increased indirect reflex force, and not due to the breakage in the atomic chain itself. At 1200 K, the duration of the unravelling is even extended more by the change of the position of the connection between the end of the tube and the atomic chain to the end of the cap instead of its center.

For the (18, 0) CNT, as shown in Fig. 8, at 300 K, increases a little bit to 12 eV/Å due to the change of the restraining condition. At 300 K, 600 K, and 1200 K the failure happens due to the increase of the direct force in the chain above its maximum capacity without the availability of a relaxation mechanism. At 900 K, two different random phenomena occurred. First, unravelling started at a smaller displacement value corresponding to a force of 5.6 eV/Å. This is due to an internal change in the structure near the unravelling atom assisted by the thermal fluctuations, before reaching the force required for unravelling. Second, failure was delayed beyond the simulation time by a repetitive movement of the connection of the chain to the tube to the side of the partial cap at displacements of 35 and 42 Å.

Generally, comparing the kinematics of the atomic systems in the restrained scheme with the unrestrained scheme, it is observed that the radial force is not strong enough to force the unravelling to the radial direction. It can be concluded that the jumps in the radial force is not due to the restraining of the unravelling atom in the radial direction; as it is present in both schemes, but rather can be attributed to the stress trying to force the unravelling toward the radial direction, and since it is not strong enough to cause that change in the unravelling direction, it relax through the atomic movements immediately.

5 Conclusions

Two molecular dynamics simulation procedures have been proposed to simulate the unravelling of single-walled (10, 10) and (18, 0) carbon nanotubes (SWCNTs) till failure of the atomic chain and compared to the capacity of an atomic chain structure. From the simulations the following can be concluded:

—The maximum force that can be supported in a single atomic chain structure is 18.6 eV/Å.
—Generally, using the unrestrained scheme delays, the failure of the atomic chain especially in the armchair carbon nanotubes, but has no significant effect on the magnitude of the unravelling forces.

—The unravelling force is in the order of 15 eV/Å for armchair nanotubes and 10 eV/Å for zigzag nanotubes. The start of the unravelling can rarely start at a lower force if an internal mutation forms near the unravelling atom like a sudden movement of an atom in the body of the nanotube itself (for example, Fig. 8(c)).
—The force required to continue the unravelling changes according to the evolution of the atomic coordinates after the unravelling of the first atom and can be higher or lower than the force required to unravel the first atom, thus it is recommended to apply a force level only 1 eV/Å less than the failure force to insure a maximum level of unravelling for the best field emission behavior.
—Failure of the unravelling structure is redundant and can be due to the (listed according to the probability of occurrence) indirect failure of the atomic chain due to a reflex force generated during the addition of an additional atom to the chain, direct failure of the atomic chain due to the exceedance of the force in the chain.
—Failure usually happens after the formation of a partial cap at the end of the nanotube, which would not happen in a MWCNT due to the presence of internal walls, and thus failure in MWCNTs is expected to be delayed compared to SWCNTs.

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References


