Channeling on Carbon Nanotubes: A Molecular Dynamics Approach

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We have performed classical molecular dynamics on different kinds of carbon nanotubes in order to examine their response to self-irradiation nearly parallel to the tube axis. We have found that the critical angle for channeling decays as a power law. Following the energy loss along the projectile path, we have determined the maximum range as a function of energy at the critical angle. Narrower tubes seem to be more adequate for transporting particles to longer distances.

1. Introduction

Carbon nanotubes (CNTs) are one of the most promising research topics nowadays. Several applications have been proposed, as semiconducting devices,[1] association with atomic force microscope,[2] nanoengines,[3] and even a biped walking device.[4] A tool commonly used to tailor nanodevices is irradiation and a recent review on the subject can be found on ref 5. Oblique irradiation of CNTs can produce a large variety of different kinds of geometry. Terrones et al.[6] have shown that neighboring nanotubes under electron irradiation can coalesce following a zipper-like mechanism. Pillboxlike[7] or onionlike[8] compartments can be created in a multiwall carbon nanotube under electron irradiation. CNTs can also be welded together under electron irradiation.[9] Despite the huge effort spent on the investigation of oblique irradiation of CNTs, only a few works can be found considering irradiation on the axial direction.[10] Probably, the application that would come at first to someone's imagination would be channeling of energetic particles, which could be used in radiation therapy, where particle transport in a nanotube could be used to drive particles to a cancerous region. So far, glass capillary structures have been shown to be effective in transporting, focusing and deflecting beams of X-rays and neutrons.[2] There are several drawbacks in these glass artifacts; e.g., they are very brittle and inflexible and have too large dimensions for medical use. Dedkov[2] claims that CNTs would reduce the system size up to 10^4 times; moreover, CNTs are quite flexible and resistant.

High energy physics could use CNT for the production of quasi-monochromatic X-ray and γ-beams by channeled electrons.[11] Charged particles propagating along the nanotube axis could interact with their walls and generate coherent electromagnetic radiation, as was shown by the theoretical work of Klimov and Letokhov.[12] Those authors even consider the possibility of producing a laser out of a CNT. Gevorian[11] demonstrated that if a particle beam enter a nanotube rope at constant velocity and small angle with respect to the main axis, the fraction of channeled particles would be 91%. This fraction corresponds to the tubes cross section in a dense pack of nanotubes.[12] Moreover, the dechanneling length could reach a value of 1 m for energies greater than 100 GeV. So far, such a long CNT has not been synthesized, but nanotube strands of several centimeters in length have already been reported.[13]

2. Computational Details

In this work we have performed computer simulations of self-irradiation of (4,4) and (10,10) single (SWCNT) and (4,4)@-(10,10) double wall carbon nanotubes (DWCNT). The code used is a standard classical molecular dynamics which has already been successful for the simulation of silicon nanostructures.[14] To scale the simulation time linearly with the number of particles, we use time saving techniques such as neighbor list and cutoff radius. The interaction between carbon atoms at distances near the equilibrium position was ruled by the Tersoff potential, which has given an accurate description of structural properties and energetics of carbon in graphite and diamond structures.[15] During particle collisions, the distances between atoms can be very small and then the Tersoff potential becomes inaccurate. In our code, every time two particles get closer than 0.2 Å, the interaction potential switches to the universal ZBL potential.[16] The connection between both potentials at the crossover region must be done by a mathematical expression that guarantees the continuity of the energy and its derivative, the force. We have chosen a combination of exponentials which has already been used successfully.[17,18]

Belucci et al.[19] state that in order to steer efficiently the beam trajectory a sufficiently narrow nanotube must be used. They affirm that its diameter should be on the order of 5−20 Å. Hence, we have chosen to work with two armchair nanotubes: (4,4) and (10,10), which have diameters of 5.6 and 13.7 Å, respectively. To ensure the free entrance of particles into the channel, the tube tip was kept open, instead of adding a closing fullerene cap. This kind of geometry has already been detected experimentally.[9,20]

Before proceeding with irradiation, a relaxation process is followed. The atoms are placed near equilibrium positions, their velocities are set to zero and then the coupled equations of motion are solved for some hundreds of time steps. Usually, temperature raises during the initial stage of relaxation. Therefore, the velocities are brought down to zero and the system is let to evolve again. This procedure is repeated until there is no temperature increase, except for statistical fluctuations. The (4,4)

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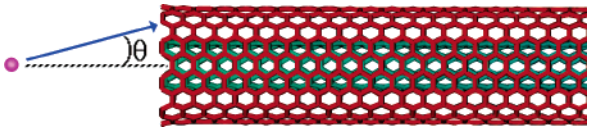

Figure 1. Relaxed DWCNT and an incoming projectile. θ is the incidence angle.

and (10,10) nanotubes lengths are 754 and 487 Å, respectively. The DWCNT was constructed placing a (4,4) tube inside a (10,-10) tube. Figure 1 shows the geometry presented by the DWCNT after a relaxation process. The whole tube has a total length of 487 Å, nonetheless only one end is shown in the picture. Despite the high chemical activity of the tube tips, only small distortion could be observed. No periodic boundary conditions were used. A fixed time step was set to 0.05 fs for incidence energies bellow 50 keV and 0.01 fs for energies above this value.

When a projectile impinges a nanotube from the inside, basically two things can happen: either it keeps moving within the tube or either it leaves the tube. To leave the tube, the projectile must have enough kinetic energy to break the bonding between the tube atoms and hence create defects on the system. Sometimes the collisions create defects, but the projectile keeps moving within the tube and the just created defects could interfere with the next incoming atom and dechannel it. Less frequently, the projectile may sneak between neighboring atoms and leave the tube creating no defects at all. We will call θ the incidence angle and define the critical angle θ_c as the maximum angle of incidence at which the projectile remains inside the tube and there is no defect creation. Therefore, every time a projectile hits the internal surface at an angle bellow θ_c, it will channel. For the DWCNT case, only incidence between both tubes was analyzed, for the interaction of an atom inside the inner tube with an atom on the outer tube can be neglected, and therefore this kind of event could be described by a (4,4) SWCNT only. To determine the critical angle as a function of energy, we have varied the incidence angle from zero up to the limit value where either the projectile leaves the tube or a defect is created. All the simulations have been performed at 0 K, which causes an expected underestimation of the critical angle because, at higher temperatures, the created defects may anneal and improve channeling.

3. Results and Discussion

When projecting a device based on ion channeling through nanotubes, aside from the critical angle, one must have an estimate of the maximum ion range. For low incidence angles the ion range can be very large, but for higher angles, it becomes significantly reduced. Dedkov[2] has also observed this phenomenon. It happens because the projectile loses most of its energy at the collisions and is allowed to move nearly free between the consecutive reflections at the tube wall.

Energy also plays a role on the projectile range. In our simulations, for energies bellow 500 eV, the projectile could not reach the other end getting stuck somewhere within the tube. This fact confirms the theoretical predictions of Wang and Miscovic,[21] which give higher energy losses for low velocity particles traveling through a cylindrical cavity. Hence, for low energy, the maximum range can be easily obtained keeping track of the projectile axial position. On the other hand, a highly energetic projectile quickly leaves our simulation cell. Longer systems having a larger amount of particles become impracticable due to computing time. To circumvent this problem, we estimated the tube stopping power at the critical angle, as

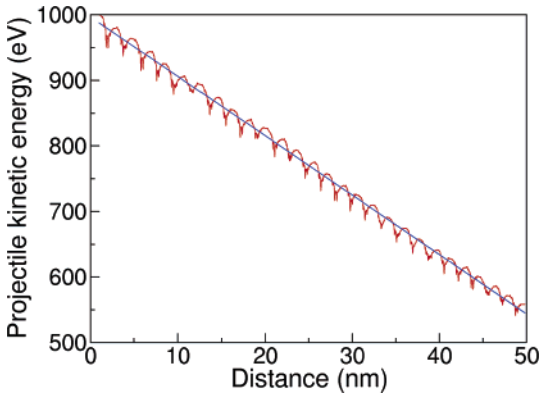

Figure 2. Energy loss plot of a 1 keV projectile striking a DWCNT at an angle of 10° degrees. The straight line is a linear regression fitted to the calculated projectile energy. Each step on the energy curve indicates a glancing collision at the tube surface.

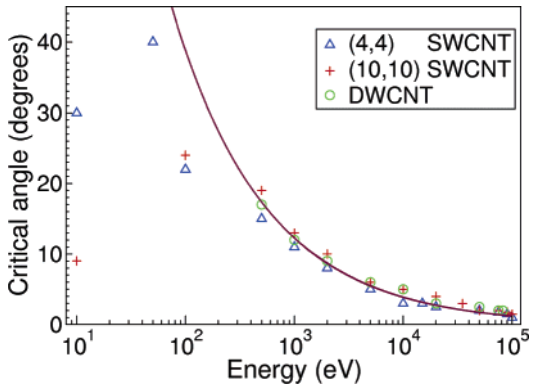

Figure 3. Critical angle as a function of energy for the SWCNTs and DWCNT. The line represents a theoretical prediction (see the text).

follows. Figure 2 shows a typical energy loss plot of a 1 keV projectile striking a DWCNT at an angle of 10°. The horizontal axis shows the axial position of the projectile along the tube. At every collision, the moving atom loses energy to the tube, causing only thermal heating but no defects creation. An approximate stopping power can be calculated fitting a straight line to the curve. The slope in the case of Figure 2 provides a stopping power of roughly 17 eV/(mg/cm^2). Extrapolating the straight line down to zero energy, we obtain the maximum range of the projectile at this energy and geometry.

The critical angle was determined for the three tube geometries studied in this work. The results are shown in Figure 3. The symbols represent the numerical results from our calculations. As one can see, the (4,4) SWCNT has a trend to have smaller critical angles than the other two geometries. A CNT can be imagined as a rolled sheet of carbon. The (4,4) CNT has a smaller radius than the (10,10) CNT, and then it has an excess of mechanical tension with respect to the latter one. Therefore, it becomes easier to displace permanently an atom from the thinner tube than from the larger one. The (10,10) SWCNT and the DWCNT have quite similar critical angle values. It seems easier to cross a tube wall from the inside to the outside than the other way around. Therefore, in most cases in which dechanneling happened, it occurred when the projectile hit the DWCNT outer wall instead of the inner one.

Dedkov[2] predicted through theoretical calculations the dependence of the critical angle as given by

$$\theta_c = \text{const}/E^{1/2} \qquad (1)$$

where E is the projectile kinetic energy. This result has been

recently confirmed by Krasheninnikov and Nordlund[10] for heavy ions channeling through multiwalled carbon nanotubes. The bold line depicted in Figure 3 represents a function given by eq 1. As one can see, our results are in accordance with the prediction from medium to high energies. Nevertheless, for very low energies, the critical angle is below the values given by eq 1. Dedkov has used eq 1 for light particles, e.g., neutrons. It is well-known that in a classical binary collision, when the mass difference between projectile and target is large, the projectile delivers only a small fraction of its energy to the target and its trajectory suffers only a minor deviation. On the other hand, when the projectile has the same mass as the target, the energy transfer is maximized. At high energies, the critical angle is quite small, implying a glancing collision, and then the mass effect becomes weak. Nonetheless, at low energies the mass effect becomes important because then the critical angle increases which implies on a head-on collision. As the projectile energy is decreased bellow 100 eV, the discrepancy becomes more evident. Moreover, at energies lower than 10 eV, the projectile energy becomes comparable to the covalent bonding energy of carbon in a nanotube structure implying that chemical effects should be considered. Hence, we conclude that low-energy self-irradiation of CNTs is less efficient when compared to light ion irradiation, due to the high energy transfer between particles of the same mass.

The projectile kinetic energy can be separated in two components: one given by the velocity parallel to the tube axis and the other one, perpendicular to this direction. We have observed that the perpendicular kinetic energy needed to eject atoms from the tube surface has only a minor dependency on incidence angle or total kinetic energy. Typically, its value is around 100 eV. Naturally, not all this energy is used to create only one vacancy, and sometimes several vacancies are created, besides thermal agitation. Rossato et al.,[22] using first principles calculations, have shown recently that in a (8,8) SWCNT one needs to exert a work of approximately 20 eV in order to detach one atom from the tube surface to the tube hollow. This value is consistent with the results presented in the current work.

So far we have seen that as the projectile energy increases, the critical angle decreases following a power law. On the other hand, we have observed that the energy increase provides a larger projectile range. For practical applications it would be interesting to obtain the maximum range possible. Therefore, we analyzed the worst case possible, i.e., channeling at the critical angle. Smaller incidence angles would provide a deeper penetration and a range that could reach macroscopic scales. In Figure 4, we show a log−log plot of the range R that a projectile would reach after striking different nanotubes at the critical angle. For medium and high energies, it is possible to fit the data through a simple equation like

$$R = aE^b \tag{2}$$

The empirical coefficients for eq 2 are given in Table 1. Once again we observe similarities between the behavior of a (10,-10) SWCNT and a (4,4)@(10,10) DWCNT, when the particle travels between the tubes on the latter case. The coefficients are very closer to each other, indicating that intertube channeling is ruled out by the outermost tube. The inner tube plays only a minor role in the process. In both cases, the projected range deviates from the fitted curve for energies bellow 500 eV. Nevertheless, we must consider that in the case a DWCNT is used for particle transport, channeling may happen within the inner tube as if there was no outer tube. Therefore, in a real situation, the particle transport between the tubes must be added to the transport within the inner tube, improving its efficiency. We observe that the present results are valid for straight and aligned tubes at 0 K. More work is under way in order to check if this conclusion is valid for bent tubes and at nonzero temperatures.

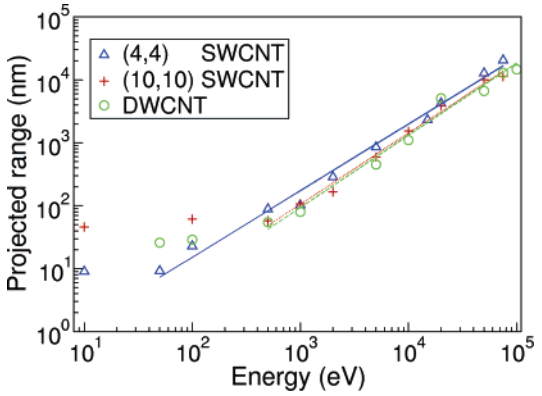

Figure 4. Projected range for a carbon atom striking different kinds of nanotubes at the critical angle. The symbols show the projectile range for each of the tubes studied. The lines represent a power law function fitted to the data: (−) (4,4) SWCNT; (···) (10,10) SWCNT; (- -) DWCT.

TABLE 1: Numerical Coefficients for Equation 2

	a (nm)	b
(4,4) SWCNT	0.116	1.06
(10,10) SWCNT	0.044	1.13
DWCNT	0.034	1.15

The empirical fit given by eq 2 to the (4,4) SWCNT is in good agreement to the simulation results over a larger range than the other two cases, particularly down to 50 eV. At medium energies, the (4,4) SWCNT presented higher range than the wider tube. It agrees with the statement of Belluci et al.,[19] in which the narrower the tube the larger the dechanneling length. However, extrapolating our findings to very high energies, the (4,4) SWCNT could become less efficient than the (10,10) SWCNT, since the exponent in eq 2 is closer to unity in the former case compared to the latter one.

4. Summary

In this work, we have studied the behavior of different types of carbon nanotubes under self-irradiation along the axial direction. We have observed that under certain conditions projectile channeling can take place. It is favored by small incidence angle and high energies. For medium and high energies the dependence of critical angle and projected range follow power laws on the energy. Small incidence energy presents a deviation from the theoretical prediction, indicating the need to consider other effects. A (10,10) SWCNT has similar behavior to a DWCNT consisting in a (4,4) SWCNT enclosed by a (10,10) SWCNT, which demonstrates that the most external tube rules out intertube channeling. A narrow nanotube seems more adequate to transport energetic particles than nanotubes having larger diameters. We have also done a rough estimate of the stopping power of a carbon atom traveling within a CNT. Comparison to prior analytical calculations showed good agreement.

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