



## Field-induced unraveling of carbon nanotubes

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Received 31 October 1996

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### Abstract

We investigate the disintegration mechanism of carbon nanotubes in strong electric fields using the ab initio density functional formalism. We find that nanotubes withstand fields up to  $2 \text{ V}/\text{\AA}$  before they start unraveling carbon chains from the exposed edge, followed by field-induced fragmentation. We find this unraveling to be facilitated in negatively charged tubes, which have been shown to be efficient nano-scale electron emitters. We demonstrate that unraveling terminates at sites where adjacent walls are bridged by a covalent bond. © 1997 Published by Elsevier Science B.V.

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Carbon nanotubes [1–4] have recently been established as ultimate field electron emitters [5,6] with potential applications in flat panel displays [7]. When exposed to a high electric field, individually mounted multi-wall nanotubes have been demonstrated to emit electron currents of up to several microamperes [5]. Based on these experimental data, Rinzler et al. conjectured that such large emission currents originate from “atomically sharp” structures that evolve at the tube tip in high fields [5]. These structures were proposed to consist of monatomic carbon chains that unravel from the exposed tube edge, being taught by the electric field. Even though this proposed field disintegration scenario is very appealing, it has so far not been confirmed by independent experiments or calculations. There is no information available about the critical field needed for a nanotube to decay or about the detailed disintegration mechanism. It remains questionable whether a nanotube will start disintegrating before evaporating charged fragments from the edge, and whether the exotic unraveling mechanism is at all viable. In particular, it is not clear whether the postulated chains at the exposed edge could possibly withstand the high fields before breaking up or detaching as a whole.

In this Letter, we address these questions rigorously by investigating the microscopic mechanism of field disintegration using an ab initio formalism. We show that “zig-zag” nanotubes preferentially decay by unraveling carbon chains from the exposed edge in applied fields exceeding  $2 \text{ V}/\text{\AA}$ , whereas “armchair” nanotubes do not disintegrate in this way. Unraveling chains not only withstand fields up to  $3 \text{ V}/\text{\AA}$ , but also increase the field locally near their end, thus enhancing electron emission. We further propose this unraveling process to be facilitated by the excess electrons accumulated at the exposed tube end that fill antibonding orbitals and lead to evaporation of ions from the exposed chain end. Our simulations show that covalent bonds between adjacent wall edges, mediated by bridging atoms acting as “spot-welds” [5,8], are strong enough to terminate the unraveling process at these field values.

In our study we considered a double-wall (9,0)@ (18,0) [9] zig-zag nanotube with an open edge<sup>1</sup>, shown in Fig. 1. The diameters of the inner and outer

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<sup>1</sup> We do not consider capped nanotubes, where all the atoms are strongly bound in the defect-free graphitic structure, since they do not disintegrate under the experimental conditions of Ref. [5].

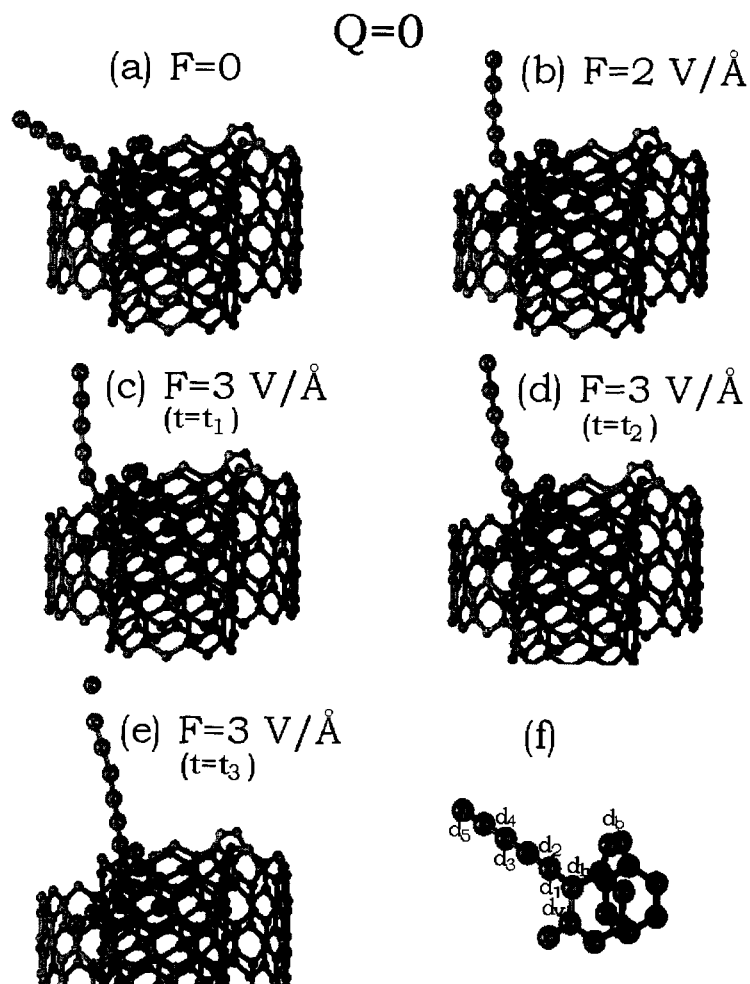


Fig. 1. Fully relaxed geometry of a neutral carbon nanotube with an attached chain for (a)  $F=0 \text{ V/\AA}$  and (b)  $F=2 \text{ V/\AA}$ . Snap shots of the unraveling dynamics for  $F=3 \text{ V/\AA}$  are presented in (c)–(e). Bond labeling in the center cluster is given in (f).

walls are  $7 \text{ \AA}$  and  $14 \text{ \AA}$ , respectively. The exposed tube edges are locally stabilized by covalent “spot-welds” consisting of two carbon atoms connecting the adjacent walls. Such “spot-welds” have recently been postulated in Refs. [5,8,10,11], and are believed to stabilize the open edge of multi-wall tubes<sup>2</sup>. Our results do not depend significantly on the particular choice of the nanotube diameter since the bonding

nature near “spot-weld” sites does not change with diameter. To represent sharp structures emerging under the experimental conditions of Ref. [5] we considered a  $C_5$  chain attached to the open edge near the “spot-weld” site.

Our model geometry, including the evolving chain, leaves the answer open, whether the nanotube will start disintegrating by first field evaporating atoms from the exposed edge or the “spot-weld”, by vertical “unzipping”, or by horizontal unraveling. The preferential disintegration mechanism is governed by the competition between the energy loss in breaking bonds and the polarization energy gain of the system. It can be

<sup>2</sup> When comparing the energetics of different carbon adsorption sites on the nanotube edge, we have found an energy gain of  $\approx 0.5 \text{ eV}$  per adatom connecting the inner and outer tube (in the way shown in Fig. 1) over their adsorption at the exposed edge of the inner tube.

best discussed in terms of the changing length of important bonds that are labeled in Fig. 1f. Tube disintegration by horizontal unraveling would be indicated by  $d_v$  exceeding significantly the graphite bond length  $d_{C-C} = 1.42 \text{ \AA}$ . Similarly, vertical unzipping would be signaled by a large value of  $d_h$ , and breaking the “spot-weld” by a large value of  $d_b$ . Should the chain not be stable enough to unravel and prefer to detach, we would expect any of the five chain bonds, labeled  $d_1 - d_5$ , to break first.

The actual calculation was performed on a twenty-atom fragment<sup>3</sup>, shown by the large atoms in Fig. 1. Embedding of this cluster in the large nanotube is described by saturating the corresponding dangling bonds with hydrogen atoms. Since these hydrogen atoms are at least second neighbors to the exposed bonds at the nanotube edge, their effect on such bond lengths and orbital population will be negligible. Neither these hydrogen atoms nor their carbon neighbors are allowed to move in the conjugate gradient relaxations described below.

Our total energy and structure optimization calculations are based on the ab initio local density functional (LDA) formalism, as implemented in the DMOL code [12]<sup>4</sup>. We use the von Barth and Hedin parameterization [13] of the exchange-correlation energy, and expand the all-electron Kohn–Sham wavefunctions in a local atomic orbital basis. In the double-numerical basis set [12], the C2s and C2p orbitals are represented by two wave functions each, and a 3d type wave function on each carbon atom is used to describe polarization. We do not make use of the frozen core approximation. Our energies are converged to  $10^{-4}$  eV.

The optimized geometry of a neutral nanotube in zero field, presented in Fig. 1a, indicates that the direction of the attached chain is determined by the local graphitic  $sp^2$  bonding at the anchor point of the chain. Also the chain bond length closest to the anchor point,  $d_1 = 1.36 \text{ \AA}$ , is half-way between the bond lengths of graphite and the rest of the chain. The other bond lengths in the chain,  $d_2 = 1.27 \text{ \AA}$ ,  $d_3 = 1.29 \text{ \AA}$ ,  $d_4 = 1.29 \text{ \AA}$ , and  $d_5 = 1.30 \text{ \AA}$ , are shorter and do not show length alternation as they do in free odd-numbered

chains [14,15]. The bond length between the bridging adatoms at the “spot-weld” site,  $d_b = 1.24 \text{ \AA}$ , is indicative of a strong double bond. We also find that the two unpaired valence electrons of the adatoms are engaged in forming a strong double bond with the edge sites. Also the values  $d_v = 1.47 \text{ \AA}$  and  $d_h = 1.44 \text{ \AA}$ , even though somewhat larger than the graphite bond length, indicate that the bonds which anchor the chain in the tube are all intact.

Next we apply a homogeneous electric field  $F \lesssim 2 \text{ V/\AA}$  along the tube axis<sup>5</sup>. This field polarizes the fragment, accumulating a negative charge of up to  $-0.98 e$  near the chain end. The resulting electrostatic force pulls on this end and aligns the chain with the field. Even though the chain remains intact in fields  $F \lesssim 2 \text{ V/\AA}$  [14], the individual chain bonds are stretched by  $\delta d_i \approx 2\text{--}6\%$ , as shown in Fig. 1b. While the horizontal chain anchor bond is stretched by only  $\delta d_h = 0.4\%$ , the most substantial elongation  $\delta d_v = 13\%$  occurs in the vertical chain anchor bond that appears to be most prone to fracture.

This bond indeed breaks in the stronger field  $F = 3 \text{ V/\AA}$ , as illustrated in Figs. 1c–e by consecutive snap shots depicting the structure evolution during the optimization process. In the initial stage of this process, shown in Fig. 1c, the last chain bond competes in strength with the vertical anchor bond of the chain. The bond lengths  $d_1 = 1.57 \text{ \AA}$  and  $d_v = 1.65 \text{ \AA}$  suggest the vertical anchor bond to be the weakest. The larger strain in the latter bond, that leads to fracture shown in Fig. 1d, results from its better alignment with the field direction than the first chain bond. Following the fracture, the original horizontal anchor bond assumes the role of the first chain bond and aligns with the field. The second chain bond relaxes to  $d_1 = 1.46 \text{ \AA}$ , close to the expanded bond lengths found in the rest of the chain. At this point, the chain attempts to detach at its anchor in the tube. That site, however, is stabilized by the strong covalent “spot-weld”. As shown in Fig. 1e, even the base of the chain aligns now with the strong field. Due to the decreasing distance between the chain and the “spot-weld”, a new bond forms between the base atoms of the chain and one of the adatoms. Subsequently, the chain switches its anchor point from the outer wall to one of the “spot-

<sup>3</sup> We confirmed the adequacy of our finite-size system by calculating its ionization potential. This quantity, which is most sensitive to the size, was found to change by only  $\lesssim 0.1$  eV when increasing the system size.

<sup>4</sup> DMOL is a registered software product of Biosym Technologies.

<sup>5</sup> In order to avoid confusion with energy, we label the electric field  $F$ .

weld” adatoms. The new bond between the chain base and the “spot-weld” appears to be very stable at the graphite-like value  $d = 1.46 \text{ \AA}$ , while the largest stress shifts to the “spot-weld”. This bond stretches to  $d_b = 1.52 \text{ \AA}$  without breaking, thus inhibiting further unraveling. In the meantime, significant negative charge  $Q \approx -2.2 e$  has accumulated at the chain end, where it fills antibonding orbitals and leads to a spontaneous detachment of the last chain atom, shown in Fig. 1e.

Our finding that the vertical chain anchor bond breaks first, well before any other bonds within the chain or the tube, is the first solid evidence for the unraveling process as the preferential disintegration mechanism of carbon nanotubes in electric fields of few  $\text{V/\AA}$ . Similarly, these results have established that covalent “spot-welds” between shells can stop the otherwise unconstrained unraveling of a nanotube. Once anchored in the stable “spot-weld” site, the chain continues to field evaporate down to its base.

Field-induced disintegration has been observed while the nanotube was under a high negative bias [5]. Therefore, we investigate in the following the effect of excess negative charge on the unraveling process. Fig. 2a summarizes our results for the binding energy of the nanotube fragment as a function of the external electric field and excess charge. The equilibrium excess charge  $Q_{\text{eq}}$ , listed in Table 1 for zero and nonzero fields, accumulates preferably at the chain end. We reported earlier that while the equilibrium excess charge increases only slightly with increasing chain length, its dependence on the external field is much more significant [14]. Based on Fig. 2a, we find that the system is most stable with an excess charge  $Q_{\text{eq}} = -1 e$  in fields below  $1 \text{ V/\AA}$ . In the field range  $1 \text{ V/\AA} \lesssim F \lesssim 3 \text{ V/\AA}$  the equilibrium charge increases to  $Q_{\text{eq}} = -2 e$ . A further increase would occur at  $3 \text{ V/\AA}$ . In such a high field, however, spontaneous unraveling has been shown to occur even in the neutral system.

Figs. 2b,c show snapshots of equilibrated nanotubes, carrying two extra electrons, at different field strengths. As shown in Fig. 2b, the nanotube with the attached chain is still stable in  $F = 1 \text{ V/\AA}$ , but the bonds in the chain and at the anchor point are strained with respect to the neutral system due to the larger charge accumulated at the tip. In the higher field  $F = 2 \text{ V/\AA}$ , depicted in Fig. 2c, the charged system is

Table 1

Ionization potential  $I$  of charged carbon nanotube fragments  $C_n$  as a function of the electric field  $F$  that is applied along the tube direction (see footnote on page 671).  $Q_{\text{eq}}$  is the equilibrium charge of the system

$F$ ( $\text{V/\AA}$ )	$Q_{\text{eq}}$	$I(C_n^{Q_{\text{eq}}-})$ (eV)
0	-1 e	3.02
1	-2 e	0.13
2	-2 e	1.87
3	-1 e	0.11

no longer stable, in stark contrast to the neutral system shown in Fig. 1b. We find a significant increase of  $d_v$ , corresponding to breaking the vertical chain anchor bond first, mainly due to the stronger force pulling at the higher charged chain. The charged tube begins to unravel in this field in much the same way as the neutral system in the higher field  $F = 3 \text{ V/\AA}$ . The polarization of the chain (which behaves as the square of the applied field) is much less pronounced than for  $F = 3 \text{ V/\AA}$  and the excess negative charge is distributed more evenly along the chain. Unlike the neutral system exposed to  $F = 3 \text{ V/\AA}$ , the chain remains intact, with the largest elongation  $\delta d_5 = 6\%$  occurring at the tip. Under these conditions, we would expect continuing unraveling without field evaporation, resulting in a long chain attached to the nanotube. Such conducting chains may enhance the local electric field by many orders of magnitude and consequently lead to strong field emission currents. As in the neutral tube exposed to  $F = 2 \text{ V/\AA}$ , we expect the unraveling process in the charged system to stop at the “spot-weld site” that is still very stable.

Finally, we have compared the disintegration dynamics of a neutral and a charged system in the strong field  $F = 3 \text{ V/\AA}$ . We found that even a small negative excess charge  $Q = -1 e$  changes the disintegration behavior qualitatively. The excess charge accumulates at the chain tip and stretches the chain and its tube anchor more strongly than in the neutral case. We find the bond length  $d_1$  at the chain base to increase more than the vertical anchor bond length  $d_v$ . The former bond eventually breaks, causing the charged chain to detach well before any unraveling and reattachment to the “spot-weld” site could occur. The accumulation of negative charge at the tip of the detached chain causes further fragmentation of the charged chain.

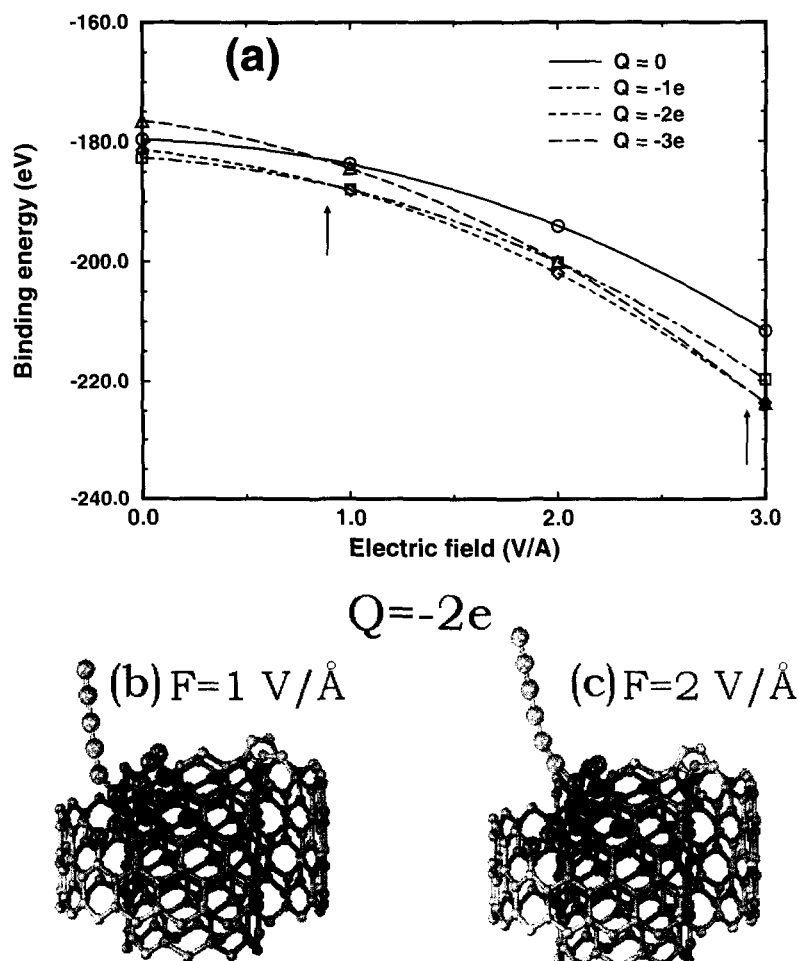


Fig. 2. (a) The binding energy of a nanotube carrying a charge  $Q$ , as a function of the applied electric field  $F$ . Fully relaxed geometries of carbon nanotubes charged with  $Q = -2e$ , for (b)  $F = 1 \text{ V/Å}$  and (c)  $F = 2 \text{ V/Å}$ .

The observation of large field emission currents from individually mounted nanotubes [5] appears first somewhat surprising in view of the high work function of graphite  $\phi = 5 \text{ eV}$  [16]. Yet as we show in Table 1 and discuss below, the energy  $I$  to detach an electron from nanotubes turns out to be much lower than the graphite value. The most important reason for this fact is that finite nanotubes, which are attached to a cathode, prefer to carry a net negative charge  $Q_{\text{eq}}$  that increases with the field. This charge fills unoccupied molecular orbitals and hence is less bound than any valence electron of the neutral system. Secondly, there is no reason for the electronic structure of nanotubes and chains to resemble that of graphite. Our

currently used definition of the ionization potential in a nonzero field <sup>6</sup> also implies that the values given in Table 1 are an upper bound on the barrier relevant in the field emission process, suggestive of high emission currents.

We have argued above that the preferential disintegration mechanism of carbon nanotubes is comparable to the unraveling of a sleeve in a sweater. Since

<sup>6</sup> When determining the ionization potential in a field, we consider the energy to detach and move an electron to infinity along virtual trajectories that are perpendicular to the external field and hence involve no work by the field. This is equivalent to placing the tube in an inhomogeneous field that is zero far from the tube, but homogeneous in its vicinity.

the unraveling process depends primarily on the local bonding geometry at the chain anchor in the tube, we expect our results to hold for both chiral and achiral nanotubes with an exposed zig-zag edge. In a chiral nanotube, one could imagine a continuous unraveling process in fields exceeding  $2 \text{ V}/\text{\AA}$ , that was possibly observed in the “catastrophic burnback” event [5].

In most cases, the unraveling process stops at the covalent “spot-weld” sites. Once anchored at such a site, the chain continues to field evaporate down to its base, thus temporarily suppressing the emission current [5]. We expect such unraveling to repeat itself over and over again, preferably starting at the outermost shell, due to the effective shielding of the electric field by the conducting outer tubes.

The bonds that are most prone to fracture in strong fields are those that are weak and parallel to the field. For this reason, we argue that the unraveling process discussed here will likely occur only in zig-zag nanotubes. There, the two initially unpaired electrons of the doubly coordinated edge atoms attempt to convert single bonds at the edge to stronger double bonds. In this process, the double bonds which connect the edge atoms to the rest of the graphene sheet, get depleted of electrons and consequently weakened. This favors the detachment and unraveling of a zig-zag chain, formed by the strongly connected edge atoms, from the nanotube.

In the armchair tube, on the other hand, all the atoms at the edge are tetravalent and strongly bound, resulting in a lower edge energy than in the zig-zag tube. The single bonds adjacent to the “seat” at the edge close an angle of  $30^\circ$  with the field and do not experience as large a pulling force as the double bonds in zig-zag tubes that are parallel to the field. For this reason, we expect the armchair edge to be stable up to higher electric fields and to disintegrate preferably by field evaporation, not unraveling.

In summary, we have investigated the disintegration of double-wall zig-zag nanotubes of carbon in strong electric fields. We have found that such nanotubes withstand fields up to  $2 \text{ V}/\text{\AA}$  before they start unraveling carbon chains from the exposed edge, followed by field-induced fragmentation of the chains. We have found this unraveling to be facilitated in negatively charged tubes, which have been shown to be efficient nano-scale electron emitters. We have also demonstrated that unraveling terminates at sites where

adjacent walls are connected by bridging atoms that establish strong covalent “spot-welds” stabilizing the tube edges.

We acknowledge financial support by the National Science Foundation under Grant No. PHY-92-24745 and the Office of Naval Research under Grant No. N00014-90-J-1396. We acknowledge useful discussions with R.E. Smalley, P. Nordlander and M. Dykman. One of us (YHL) acknowledges financial support by the LG Yonam Foundation and the Korea Science and Engineering Foundation (KOSEF) (Grant No. KOSEF94-0501-11) and partial support by the Semiconductor Physics Research Center at Jeonbuk National University.

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