Bond-breaking bifurcation states in carbon nanotube fracture

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Fullerene nanotubes yield to tension in two basic ways. At high temperature (or in the long time limit) a single bond rotation creates a dislocation-dipole favored thermodynamically under large stress. However, at low temperature (or limited time range) this process remains prohibitively slow until further increase of tension causes direct bond-breaking and brittle crack nucleation. This instability proceeds through the formation of a distinct series of virtual defects that only exist at larger tension and correspond to a set of shallow energy minima. The quantum mechanical computations of the intermediate atomic structures and charge density distributions clearly indicate a certain number of broken bonds. © 2003 American Institute of Physics.

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Strength of solids at given conditions (load, temperature) originates from the nature of chemical bonds. Microcracks or flaws reduce the material strength, ultimately determined by nucleation process. Theory of nucleation of failure remains an important topic studied for model ideal solids (see, for example, Refs. 1, 2). While macroscopic samples usually contain imperfections, an important example of well-defined ideal structure is naturally offered by carbon nanotubes (CNT).

The strength of nanotubes has been a subject of intense experimental4–9 and theoretical9–15 studies. This interest is further stimulated by the recent advances in CNT-fiber making7, where mechanical properties remain in the focus. While various causes might downgrade the moduli and strength in a particular measurement, as better care is exercised in sample preparation, the measured strength tends to higher values (~150 GPa in the very recent reports8). Understanding of atomistic relaxation and the theoretical strength benchmarks is a challenge for physics of fracture and for CNT research.

In hexagonal lattice of CNT a recognized possibility is a dislocation yield11–14 by a Stone–Wales (SW) bond rotation.16 This rearrangement of chemical bonds has a high activation barrier of 6–9 eV (Refs. 17–19), and therefore requires high temperature (or irradiation). Accordingly, the yield point lowers with temperature,19 similar to the early Monte Carlo and molecular dynamics findings for generic Lennard-Jones crystals.1,2 While the thermally-activated bond-rotation mechanism has been extensively studied11–14 the failure at more realistic room temperature remains unexplored and is the focus of present work. Below we describe such an alternative failure path that becomes possible at high tension, while requiring no thermal activation. It proceeds by direct bond-breaking, through a sequence of metastable states corresponding to “lattice trapping,” discussed in the phenomenology of fracture.20 Such primary states of nucleation are revealed here for the first time with accurate quantum-chemical description of a covalently-bonded material.21 Near the failure threshold these structures are metastable and correspond to one, two, three, etc. broken bonds (b=1,2,3,…). Their energies are almost degenerate and the separating barriers are low (in contrast with the still high SW barrier). Probabilistic analysis unequivocally shows the dominance of the brittle bond-breaking path b=0→1→2→3→… as CNT failure mechanism at room temperature in a tensile test experiment.

Our calculations employed the AM1 model22 of GAUSSIAN 98 package,23 which is well suited for the present problem since it includes electron correlation effects, is self-consistent, and practical in finding equilibrium geometries involving a large number of atoms and especially a variety of initial trial conditions. In addition, key features were repeated with the density functional theory (DFT) with the exchange-correlation functional of Perdew, Burke, and Ernzerhof24 and a STO-3G basis set.

We applied incremental 3% tensile strain, aiming for failure of both (10,0) and (5,5) CNT samples. The geometries (C_{120}H_{20} and C_{130}H_{20} in AM1, C_{160}H_{20} and C_{180}H_{20} in DFT) were optimized under the constraint of fixed distances between pairs of atoms located at opposite ends, so that the equilibrium geometries are local minima on the potential energy surfaces (PES). For the analysis of structural defects the cluster approach was preferred over the periodic boundary conditions since the latter causes unwanted long-range (via lattice strain) defect-image interactions. We choose the H-terminated clusters to be large enough to reproduce the bulk C–C bond properties. We also verify that AM1 and DFT methods yield close C–C bond lengths (1.43 Å), binding energy, and elastic properties. (The differences in values of the in-plane stiffness d²E/dσ² are within 1%).

The strength of C–C bonding is quantified by Fig. 1 where it is shown that the nanotubes sustain high elongations, while the energy follows a Hooke’s parabola. The failure only occurs at ε ~16% for zigzag and above 24% for...
armchair CNT. (As expected, since in the zigzag type the axially oriented bonds incur a higher strain.)

In order to see the details of fracture nucleation from our microscopic model, with the perfect CNT system at a near-threshold strain, we have carried systematic relaxed PES scans under perturbation of a single central bond with increments of .02 Å or smaller. In the vicinity of threshold we have found a series of metastable configurations and Fig. 2(a) presents the geometries of the first states in a (10,0) CNT around 16% strain. Visually, they correspond to one, two, and three axial broken bonds (b = 1, 2, 3), respectively. Similar configurations have been found in the (5,5) type and the emerged b = 1 state is also shown.

The lattice-trapped states do not exist in the strain-free material and we further studied their stability ranges. The strain level is varied until the tiny crack either falls over into a longer one by further bond breakage, or heals by bond restoration, b − 1 → b + 1. Fig. 2(b) plots the computed formation energies as measured with respect to the perfect CNT, \( \Delta E_b(\varepsilon) = E_b(\varepsilon) - E_0(\varepsilon) \). One can see that the obtained ranges of existence increase with the number of broken bonds, from a very narrow interval in the b = 1 case to \( \Delta \varepsilon \sim 1\% \) for b = 5. The following states b = 4 and 5, although less important in crack nucleation, are also included.

Due to their bifurcation nature, the trapped state energies are quite close to the ideal strained lattice. For a physical interpretation, one can formally determine the “free” formation energies (without strained lattice contribution) of these defects by extrapolating them into the lower strain region.

For this purpose, for each set of states we reconstructed a parabola which employs the stiffness of ideal CNT, as shown in Fig. 1. Remarkably, we found that the near-minima energies of these virtual defects approximately correspond to multiples of cohesive energy (per bond), which justifies the broken-bonds association. The dilatation nature of trapped lattice states becomes also apparent in Fig. 1 where the positions of zero-strain minima are marked. Analysis for the armchair case finds a similar picture where the \( E_b(\varepsilon) \) curves must be shifted toward smaller dilatation values, in order to prolong the \( E_0(\varepsilon) \) crossover to higher strains.

Figure 2(b) shows several important regularities. The range of existence begins earlier, at lower strains, for the larger defects (greater b). At lower \( \varepsilon \) their formation energies \( \Delta E_b(\varepsilon) \) are higher, but due to greater slopes the energies of these “longer cracks” turn into lowest on the larger strain side. In other words, the lattice trapped states formally emerge in reverse order, and the shortest of them (b = 1) requires the highest tension. We note that by the time the crossover of b = 1 state with \( E_0(\varepsilon) \) curve occurs, all following crack defects would be lower in energy. This allows for a simple interpretation of the CNT fracture mechanism: Upon

![FIG. 1. Energy vs strain for ideal (10,0) CNT (thick solid line) is intersected by SW defect (thin solid line, small arrow near 8%) or by the virtual defects (dashed lines, large arrow near 16%). Vertical spacing (3.7 eV) and the minima shifts (circles) for the parabolas show the energy and dilatation added to the lattice due to these defects corresponding to the 1, 2, or 3 broken bonds, and vanishing at lower strain. Analogous fit for the armchair tube yields another set of parabolas with higher crossover range and smaller dilatation shift.](Image 1)

![FIG. 2. (a) Relaxed atomic structures of lattice-trapped states in a 16.1% strained (10,0) CNT display b = 1, 2, and 3 broken bonds (right) with central interatomic separations of 1.9, 2.0, and 2.3 Å while, the nearest intact bonds retain about 1.6 Å length. In (5,5) CNT a single broken bond emerges at above 24% strain, with 1.9 Å separation while the surrounding bonds remain shorter than 1.7 Å (left). (b) Formation energies \( \Delta E_b(\varepsilon) = E_b(\varepsilon) - E_0(\varepsilon) \) for defect-states b = 1 - 5 are shown as functions of strain, to detail the crossover in Fig. 1: three gray levels indicate the ranges of stability, with b = 1 being the darkest, and b = 4,5 ranges (and some actual data points) extending beyond the scope of the plot. Vertical arrows illustrate the possibility of transition between the states in real space (a) or in the energy scale (b).](Image 2)
breaking of one bond, lattice can easily slide down through a series of lattice-trapped defect states toward global failure, as suggested by the vertical arrow in Fig. 2(b).

The absence of virtual defects in free lattice and the obtained order of emergence as local minima can be explained in terms of a standard phenomenological model of a nucleating crack. In the continuum Griffith theory, the free energy of the crack is a superposition of its surface energy, nucleating crack. In the continuum Griffith theory, the free energy of the crack is a superposition of its surface energy, nucleating crack. 

In both energy curves (at 15.8% and 16.1% strain) show presence of \( b = 2 \) metastable states, whereas the shoulder around 1.8 Å develops into the \( b = 1 \) minimum only at the higher load.

An inspection of Fig. 3(b) shows that the barriers for transition from perfect lattice to \( b = 1 \) and then 2 are quite insignificant (10–15 meV shown) and thus there is no need for thermal activation at the failure strain level. This observation brings the discussion to the comparison with the SW yield. As mentioned above, SW transformation becomes thermodynamically favorable at lower tension, but retains the intrinsic activation barriers \( E^* \) even at the \( \varepsilon = 15\%–20\% \) strain values. Therefore, at high temperature \( (T) \) or long time \( (\Delta t \rightarrow \infty) \) limit SW mechanism dominates, whereas in a finite duration test at lower temperature the dislocation threshold rises (cf. Refs. 1, 2) and the brittle bond breaking sequence must prevail. At what load-experiment duration \( \Delta t \) or rate \( \varepsilon \) is the SW relaxation more likely to occur? What then is the primary yield event in a typical laboratory experiment? To answer these questions we assume an experimental situation in which the applied tension grows from zero to the critical bond-breaking \( \varepsilon_c \). During this interval, a cumulative probability of SW flip can be expressed as an integral of the Arrhenius rate

\[
P = R \int_0^{\varepsilon_c} \exp \left( -\frac{E^*(\varepsilon, \chi)}{k_B T} \right) \frac{d\varepsilon}{\varepsilon}
\]

where \( R = 10^{15} Ld \text{ nm}^{-2} \text{s}^{-1} \). As an example-approximation we choose a CNT length \( L = 1 \mu \text{m} \), diameter \( d = 1 \text{ nm} \), chirality \( \chi = 0 \), and the classical potential-based activation energy strain dependence \( E^*(\varepsilon) = (6–28\varepsilon) \text{ eV} \). One obtains that in near-zigzag CNTs (\( \varepsilon_c = 16.1\% \)) SW becomes kinetically favorable \((P \sim 1)\) at high \( T \) or large \( \Delta t \), e.g., in a month-long load at room temperature. Therefore, in a room temperature experiment with a few seconds duration, the critical \( \varepsilon_c \) is being reached without SW rotation and, due to the negligible bond-breaking barriers, the brittle failure occurs.

The competition between dislocation- and bond-breaking channels can in principle be verified by comparing MD simulations at high (where SW rotation occurs) and low \( T \), where particular caution should be observed in describing the interatomic forces (cf. Ref. 21). Simulations with nonorthogonal tight-binding indeed show dislocation yield at \( T > 2000 \text{ K} \), while at \( T < 500 \text{ K} \) the lattice undergoes brittle bond breaking. In comparing different temperature regimes one should keep in mind the refractory nature of graphite (in-plane Debye temperature \( \sim 2500 \text{ K} \), melting point \( \sim 4500 \text{ K} \), binding energy 7.4 eV/atom), which essentially renders room temperature as “low.”

Finally, the association of the found local minima with broken-bond states becomes more evident from the picture of electronic charge density (Fig. 4), which shows a lack of...
bonding charge around the $b=3$ crack, as opposed to the perfect strained lattice. The two shown configurations have nearly equal energies, which underlines the bifurcation nature of the broken-bond states. As well visible is an increase in electronic charge density at the crack edge, suggesting localization of nonbonding electrons, analogous with the electronic distribution of open-ended CNTs.\textsuperscript{27}

In summary, we have presented a brittle bond-breaking CNT failure mechanism, which generally competes with the extensively discussed\textsuperscript{11–19} Stone–Wales bond rotation dislocation path. Remarkably, the proposed failure path dominates at low temperatures, and is more probable to take place in a tensile-test experiment. The failure mechanism involves a series of shallow energy minima in the highly strained CNT lattice which can be associated with broken-bond states. These states cease to exist in a free lattice, where they are “virtual.” However, at high strains these defects have well defined structure, and their energy ranking fully overturns at the failure threshold. The potential barriers between them are shallow and so the lattice quickly evolves toward the energy descend, $b=0 \rightarrow 1 \rightarrow 2 \rightarrow 3 \rightarrow \ldots$, therefore giving rise to a brittle crack and failure. Described lattice-trapped crack states could be stabilized in bent nanotubes, creating an electronic structure similar to an open-end,\textsuperscript{27} of interest for field emission study. The emerging cleave may additionally be stabilized by termination with other chemical species (e.g., H); their presence, conversely, must reduce the breaking strain—a possible explanation of important sonication-chemical cutting process.\textsuperscript{28}

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\textsuperscript{25} The dilatation for $b=1$ states is less than 0.5% which ensures that the present results obtained within the constant-length condition hold also if the constant-stress condition would be employed.

