Supplementary Materials for

Fatigue in assemblies of indefatigable carbon nanotubes

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Other Supplementary Material for this manuscript includes the following:

Movies S1 and S2
S1. System representations and methods

![Diagram of system representations and methods](image)

Figure S1: Schematics of system representations and methods. The diagram illustrates the relations between length-, time-scales, the representations of the studied systems, and the employed methods.

Multiple approaches have been utilized to investigate the fatigue mechanism not only inside the nanotube $sp^2$-C lattice, but also on a larger scale when they assemble into a fiber with a distribution in their lengths. The energetics and kinetics of defect formation in the walls of an individual nanotube are evaluated using both the density-functional theory based tight-binding (DFTB) as well as the large-scale atomic/molecular massively parallel simulator (LAMMPS) together with the long-range carbon bond-order potential (LCBOP) \((15,43,47)\). Through DFTB calculations the initial stages of plastic deformation in a nanotube and its brittle failure is explored. However, for the complete tube failure due to the plastic route, LCBOP is used, which although less accurate is more computationally efficient, making this possible. On the other hand, nanotube assemblies, consisting of 100’s of tubes, with the length of the simulation box around 2 $\mu$m, is difficult to model atomistically even if empirical potentials are used. Therefore, a coarse-grained approach is adopted where a segment of a (5,5) nanotube consisting of 20 atoms is replaced by a single bead. This allows for representative modelling of these assemblies, which can be loaded cyclically to extract their fatigue mechanism. These methods are schematically illustrated in Fig. S1.

S2. Energetics and Kinetics of Stone–Wales (SW) Defects

S2.1 Interaction of two SW defects in unstrained graphene

The formation energy of a single Stone–Wales (SW) defect is 5.654 eV in unstrained pristine graphene. As shown previously \((24,25)\), given an existing SW defect, the favorability of the pres-
Figure S2: Formation energy of a SW pair. (A–C) Colored maps showing DFTB computed formation energies of structures formed after 90° bond rotation, in the presence of a bond already 90° rotated (i.e., a preexisting SW defect, center). The energies are calculated relative to the total energy of 2 isolated SW defects (or $2E_{SW}^f$), where $E_{SW}^f = 5.654$ eV is the formation energy of a single SW defect. (A) and (B) show only the horizontal and slant bonds, respectively, while (C) shows the map for all the bonds. The gray bonds are not computed. (D–H) show the selected structures marked in (C), in which bonds are colored by their bond length to indicate local stress concentration.

ence of another SW defect in its vicinity can be evaluated by finding the total energy of the configuration as compared to when the 2 SW defects are far-away from each other. In Fig. S2 (A to C) these maps are shown for the 90° rotation of the bonds around the first SW defect. These results are obtained for unstrained graphene, and present drastically different results as compared to the condition when the graphene lattice is strained. This is demonstrated in Fig. S2 (D to H), where the two most favorable configurations (identical under rotation) shown in Fig. S2 (D and E) are rather different from Fig. S2 (F to H), the so-called “split”, “octagonal” and “sheared” configurations, respectively (see main text, Fig. 2B), which are the most favorable at non-zero strain.

These maps indicate the complexity involved in calculating potential energy maps for even 2 SW defects since the results not only will depend on the uniaxial strain level $\varepsilon$, but also on the chirality ($\chi$) of the tube (which translates into the direction of uniaxial strain in graphene). If, for a CNT of diameter $d$, the number of bonds is $N$ ($\simeq 100$), then the number of computations will be $\sim n_\varepsilon n_\chi N$, where $n_\varepsilon$ is number of strain values, and $n_\chi$ is number of chiral-angle values. Other multiplicative factors may also accompany when more than 2 SW defects are being considered, making this approach unmanageable. Therefore a better way to tackle this problem is through Monte Carlo based techniques adopted in this work.
Table S1: Fitted parameters from equations S1 and S2.

| Structure     | C (eV)   | D (eV Å\(^{-3}\)) | a (Å)   | b (Å)   |
|---------------|----------|--------------------|---------|---------|
| 0 SW (pristine)| 23942.3  | 0.225267           | 51.8203 | 60.6919 |
| 1 SW          | 24762.0  | 0.229354           | 51.9427 | 60.6261 |
| 2 SW          | 24790.4  | 0.228238           | 52.0689 | 60.7248 |
| 3 SW          | 26217.2  | 0.236010           | 52.2019 | 60.5670 |
| 4 SW          | 28405.7  | 0.248265           | 52.3428 | 60.3288 |
| 5 SW          | 29445.5  | 0.253263           | 52.4793 | 60.2843 |

S2.2 Strain-dependent SW Formation Energies and Enthalpies

The plot in Fig. 2A of the main text is obtained by using a (6,6) armchair nanotube of length \( L = 5.18 \) nm in a simulation cell with periodic boundary conditions in \( z \) direction and non-periodic in \( x-y \). It is common to express the elastic response of a nanotube as a quadratic stress-strain relation (or equivalently, stress vs length, \( \sigma(l) \)). In doing so, once the stress reaches its maximum, instead of going down (as a quadratic function would) we expect that the stress \( \sigma(l) \) should saturate. Hence a piece-wise formulation is adopted as listed below:

\[
\sigma(l) = \begin{cases} 
\frac{3}{4} D [(a - b)^2 - (l - b)^2], & l \leq b \\
\frac{3}{4} D (a - b)^2, & l > b 
\end{cases}
\]  

(S1)

The energy \( E(l) \) of this system is obtained through integration and results in the following expression.

\[
E(l) = \begin{cases} 
C - D [3l(a - b)^2 - b^3 - (l - b)^3], & l \leq b \\
C - D [3l(a - b)^2 - b^3], & l > b 
\end{cases}
\]  

(S2)

Here \( a \) is the value of \( l \) when \( \sigma(a) = 0 \) and \( b \) is the value of \( l \) at which the stress saturates or \( \sigma'(b) = 0 \). \( C \) and \( D \) are the coefficients in the energy expression. These four parameters can then be fitted for each configuration starting from pristine, up to 5 SW defects (see Table S1). Note that fitting is performed of the DFTB data points for both axial stress and energy simultaneously, using their respective equations (S1 and S2), and are plotted in Fig. S3. Here \( A \) is defined as the cross-sectional area of the nanotube, and for the plot in Fig. S3A \( A \) is taken as its cylindrical area, \( \pi d^2/4 = 0.523 \) nm\(^2\).

These fits are then used to find the enthalpy change at constant stress (or pressure) with respect to pristine nanotube loaded to axial stress \( \sigma_0 \) to obtain the plots in Fig. 2A (main text). This is achieved by inverting equation S1 to obtain \( l \) at which \( \sigma(l) = \sigma_0 \) for all the configurations. Each such value of \( l \) is then also used to evaluate \( E(l) \) of the corresponding configuration (at the same stress level). Subsequently, \( \Delta E \) and \( \Delta l \) are obtained as the differences in the energy and length at \( \sigma_0 \) with respect to the pristine tube. Finally, the enthalpy change is obtained: \( \Delta H = \Delta E - \sigma_0 A \Delta l \).
Figure S3: **Stress and energy of the shear band configurations.** Plots of (A) $\sigma(l)$ and (B) $E(l)$ according to equations S1 and S2 for a (6,6) nanotube with 0–5 SW defects. The solid curves indicate that the nanotube remained stable and did not fail, while the dashed curves are extrapolations, somewhere along which the nanotube may already have failed.

### S3. DFTB-based corrections to LCBOP-computed defect energies

Although DFTB computations are reasonably accurate, they are computationally intensive and pose a challenge for the kinetic Monte Carlo simulations, both in terms of the total number of computations needed, but also the length of the tube in periodic boundary conditions. Ideally, tube length should be long enough that at the boundaries the strain remains relatively constant as the simulation progresses.

Empirical potentials like AIREBO and LCBOP are very efficient in computational speed, and are expected to represent material properties of carbon nanoforms reasonably well, as evidenced by their common usage in many aspects of nanotubes and graphene (48). However, these potentials suffer from numerical inaccuracies, especially when directly compared to DFTB, which is a major hindrance in their effective usage.

In Fig. S4 (A to D) a direct comparison of the defect energy is made using DFTB and the LCBOP potential. Here AIREBO was not chosen because in addition to inaccuracies in energy, the lattice parameter of graphene when relaxed using the AIREBO potential is too small ($\approx 2.42$ Å). It is observed that although both DFTB and LCBOP demonstrate a linear trend in the defect energy with respect to tube strain, the slopes of the linear fit differ significantly. To correct for this mismatch in slope, the coefficients of the linear models are averaged for all 4 configurations to obtain $E_{\text{DFTB}} = -105.67 \varepsilon + 5.7630$ and $E_{\text{LCBOP}} = -82.597 \varepsilon + 4.9346$. This gives correction a factor $A = (-105.67)/(-82.597) = 1.27938$ and a correction offset $B = -0.5502$ eV. These are then used as stated below:

- The structure of interest with tube length $l$ is relaxed (with LCBOP) to obtain energy $E_1$. 
Figure S4: **Correction to the LCBOP potential.** (A–D) Linear fits to the defect energy of configurations from Fig. 2B, providing coefficients for the correction scheme. (E) Comparison of defect energies obtained from DFTB and LCBOP, with and without correction.

- A pristine tube (with same number of atoms) is stretched to the same length $l$ to obtain the strain energy $E_0$.

- The corrected energy is then obtained as: $(E_1 - E_0)A + B$

Figure S4E demonstrates that after correction the energies become very similar to DFTB computed energies.

**S4. Strain-life curves of an already defective tube**

Figure S5 shows the strain-life curves of all trajectories in Fig. 3H, but reevaluated from a different starting configuration to represent an already defective tube (as indicated in the caption). As can be expected with more defects, the strength of the tube decreases, as is indicated by the top-most point in the curves above which the tube has already failed. The time to failure also drops as the initial number of defects increases. It is however important to note that the configurations at the 30th kMC steps do not necessarily have 20 more defects than the configuration at the 10th kMC step, since many intermediate bond rotations may already heal prior defects leaving only a few visible defects (as indicated by arrows) in addition to diameter reduction.
Figure S5: **Strain life curves of already defective tubes.** Plots for (6,6) tube with preexisting defects, i.e., the configuration of tubes at the (A) 10th, (B) 20th and (C) 30th kMC step in Fig. 3G (main text).

**S5. Atomistic kinetic Monte Carlo simulation in LAMMPS**

The implemented kMC protocol is shown in Fig. S6. The main steps of kMC include building a list of all possible transformations, i.e., bond rotations, from the current system state, evaluation of the corresponding rates $r_i$ based on transition state theory, with $\nu = k_B T / h \sim 10^{13} \text{s}^{-1}$, calculation of the cumulative rate $R$, executing a transformation selected in accordance with reaction rates, and updating the simulation clock.

**S6. Basic coarse grained model of a CNT**

The coarse grained (CG) model uses linear harmonic and harmonic angular terms for the interactions of beads of the same CNTs.

$$E_r = k (r - r_0)^2, \quad E_\theta = k_\theta (\theta - \theta_0)^2.$$  \hspace{1cm} (S3)

The energy of a linear harmonic interaction, $E_r$, is characterized by $k_r$, the linear stiffness, $r$, the distance between two adjacent beads of the same CNT, and $r_0$, the equilibrium separation distance of two adjacent beads of the same CNTs. Similarly, energy of an angular harmonic interaction, $E_\theta$, is characterized by $k_\theta$, the angular stiffness, $\theta$, the angle between three adjacent beads of the same CNT, and $\theta_0 = \pi$, the equilibrium angle of three beads of the same CNTs.

For beads of different CNTs, the interaction is a 12-6 Lennard-Jones (LJ) potential with shifted argument,

$$E_{\text{LJ}}(r; d) = 4\epsilon \left[ \left( \frac{\sigma_0}{r - d} \right)^{12} - \left( \frac{\sigma_0}{r - d} \right)^6 \right].$$  \hspace{1cm} (S4)

Collectively, for a given CNT diameter $d$ and chosen $r_0$, the $\{k, k_\theta, \epsilon, \sigma_0\}$ parameters are fit to reproduce the elastic modulus, bending stiffness, and dispersion interaction of CNTs. The quality
Figure S6: **General flowchart of the rejection-free kinetic Monte Carlo algorithm.** On each step, a list of all possible transformations is built, the rate $r_i$ of each individual transformation is computed as well as the cumulative rate $R$. Based on these, a process (bond rotation) is executed, and the simulation clock is updated.

of the CG procedure/model largely depends on the choice of $r_0$, which is discussed in detail in (10). The parameterization of the CG model is summarized in Table S2.

| $r_0$ | $k_r$ | $k_\theta$ | $\epsilon$ | $\sigma_0$ |
|-------|-------|-------------|------------|------------|
| Å | kcal/molÅ² | kcal/mol rad² | kcal/mol | Å |
| 2 | 2500 | 35750 | 9.323 | 0.4205 |

Additionally, friction is introduced via a granular-type interaction potential (49) which enables force exchange between two bead spheres when they establish a “contact”. Detailed description (including parameterization and tests) is provided in the Supporting Information of (10). The complete model is implemented in LAMMPS and the script in the next section demonstrates the key settings.

**S7. Cyclic loading simulation in LAMMPS**

Below we provide the actual script used to simulate the tensile cyclic loading whose $\sigma$-$\varepsilon$ curve is shown in Fig. 5A in the main text. This is a representative example of all simulations performed.

```
# in.cyclic

LAMMPS (27 May 2021)
# usage: lammps -v xlinkdens <real> -in in.cyclic
```
variable prefix string f${xlinkdens}_cl_sm16635
log log.{prefix}

† Model parameters: Gupta et al, ACS Nano 15, 1342-1350 (2021)
variable r0 equal 2.0 # bead-bead eq bondlength [Ang]
variable d_b equal 11.5 # bead diameter [Ang]
variable m_b equal 195.3 # bead mass [g/mol]
variable kr_b equal 103.9743427 # bead-bead bond spring const [eV/Ang^2]
variable kt_b equal 597.4700198 # ... angular spring const [eV/rad^2]
variable Temp equal 10
variable vpull equal 0.1
variable dumpfreq equal 200000
variable thermofreq equal 10000
variable avefreq equal 10000
†
variable optsteps equal 1000

† Parameters for granular Hookean friction
variable kn equal 1
† friction (estimate based on DFT for C2 dimer cross-link)
variable kt equal 0.0208575 *2*${xlinkdens} # D=11.5 A

----------------------------------------------------------------
processors 1 1 *
units metal
atom_style hybrid molecular sphere
bond_style harmonic
angle_style harmonic
neighbor 1.0 bin
neigh_modify every 10
neigh_modify exclude molecule/intra all
boundary f f p
read_data data

† Parameters for Lennard-Jones Expand (modified)
† (5,5) CNT
variable sig equal 2.9377272992133148
variable eps equal 0.033320425155318655
variable d_cnt equal 6.85776404
variable cutoff equal 2.5*${sig}

----------------------------------------------------------------
newton off on
comm_modify vel yes
pair_style hybrid/overlay lj/expand/gran $(v_cutoff) gran/hooke/history $(v_kn) $(v_kt) 0 0 1e4 0
pair_coeff * * lj/expand/gran $(v_eps) $(v_sig) $(v_d_cnt) $(v_kn) $(v_d_b)
pair_coeff * * gran/hooke/history
variable Lz equal lz
dump 1 all custom $(dumpfreq) rlx_${prefix}.dump id mol type x y z
balance 1.0 z uniform

†--->>> initial relaxation
min_style cg
minimize 1.0e-8 1.0e-8 1000 1000

# Fixes
fix _boxrlx all box/relax z 0.0
minimize 1.0e-8 1.0e-8 10000 10000
unfix _boxrlx
velocity all create ${Temp} 3141592 dist gaussian loop local

# need only T-control, integration is done by 'fix nph' below
fix _tstat all temp/rescale 500 ${Temp} ${Temp} 0.1 1

timestep 0.001
run ${optsteps}
undump 1

#<<<--- initial relaxation done ----------------------------------------------------
reset_timestep 0

# stress
compute stot all stress/atom NULL
fix _stress all ave/atom 1 ${avefreq} ${avefreq} c_stot[3]

# strain
dump 1 all custom ${dumpfreq} trj_${prefix}.dump id mol type x y z f__stress
variable Lz0 equal ${Lz}
variable ezz equal v_Lz/${Lz0}-1

thermo ${thermofreq}
thermo_style custom step temp ke pe ebond eangle epair lz vol pzz v_ezz
thermo_modify flush yes
fix _ptensor all ave/time 1 ${avefreq} ${avefreq} &
v_ezz c_thermo_press[3] file stress_${prefix}.dat
restart ${dumpfreq} restart.${prefix}.1 restart.${prefix}.2

#=============== cyclic loading, stress-controlled mode ===============
variable Pmin equal 0.0
variable Pmax equal -16635.0 # 99% of ultimate tensile strength
variable time equal 335000
next cycle
label _cycle
#--- load
fix _tens all nph z ${Pmin} ${Pmax} 1.0
run ${time}
#--- unload
fix _tens all nph z ${Pmax} ${Pmin} 1.0
run ${time}

next cycle
jump SELF _cycle

#<<<---
write_restart restart.${prefix}
Supplementary Movies

Movie S1
Animation of representative CNT geometry evolution during the kMC simulation for the stress- and strain-controlled loading with initial strains in the range 6–14% at 1000 K. The kMC step number is indicated on the top of each geometry, indicating the number of bond rotations executed. In some instances, these numbers stop updating which indicates that the corresponding CNT has already failed. The simulation is only conducted up to 100 bond rotations.

Movie S2
Animated strain evolution, $\varepsilon(t)$, curves for a bulk bundle element subjected to cyclic (black) and static (blue) loading, with the same maximum stress (amplitude) demonstrating differences in strain accumulation. The inset shows animated coarse-grained trajectories of mechanical simulation with color indicating the stress distribution inside the nanotubes.