Comment on "Mechanism for Superelongation of Carbon Nanotubes at High Temperatures"

Recently Tang *et al.* [1] reported a molecular dynamics (MD) simulation of carbon nanotube (CNT) elongation, with numerous topological defects generated. They interpret this as a more realistic superplasticity mechanism than the pentagon-heptagon pair (5|7) glide and climb [2,3]. Although the extensive MD computations do display some interesting detail, it is important to explain how the conditions and the physics of simulated relaxation are rather different than observed in reality [4,5].

In experiments, the length L increased by 100%–280% nearly uniformly and flawlessly, which was justly called superplasticity [4,5]: except a few moving kinks, no disorder was observed. In contrast, in MD simulations [1] "Hundreds of defects are activated and widely distributed over almost the entire tube," which soon necks off and fails.

The structural relaxation consists mainly of C-C bond rotation flips [Stone-Wales (SW) transformations] known to dominate the formation and mobility of defects in the sp^2 carbon network [6]. In a pristine unstrained CNT or graphene, the SW defect has positive formation energy E_{SW}. Under tension, E_{SW} lowers as the bond flip reduces the elastic strain. This lattice strain ε and the initial bond orientation angle χ control the E_{SW} [7]:

$$E_{\mathrm{SW}}(\chi, \varepsilon) = 2.7 - 3.9\varepsilon - 32\varepsilon\cos(2\chi). \quad (1)$$

(Henceforth all energies are expressed in numbers of eV.) Equation (1) shows that only under high strain ($\varepsilon > 7.6\%$ makes the SW defect exothermic, $E_{\mathrm{SW}} < 0$) the topological defects can proliferate via SW flips, although the SW barrier may still remain high (8–9 eV at $\varepsilon = 0$ [6]).

In contrast to other structural rearrangements, a glide (gl) of an edge dislocation—a pentagon-heptagon pair 5|7 in a sp^2 network—creates no new disorder and at $\varepsilon = 0$ has zero formation energy [2]. Tension ε affects its formation energy $E_{5|7\ \mathrm{gl}}$ and barrier $E^*_{5|7\ \mathrm{gl}}$ (computed here):

$$E_{5|7\ \mathrm{gl}}(\beta, \varepsilon) = -64\varepsilon\sin(2\beta), \quad (2)$$

$$E^*_{5|7\ \mathrm{gl}}(\beta, \varepsilon) = -6.8 - 45\varepsilon\sin(2\beta), \quad (3)$$

where β is the 5|7 orientation angle [3].

According to Eqs. (1) and (2), the CNT elongation can proceed via clean 5|7 glide, without multiple topological defects, if the tension is not too great ($E_{5|7\ \mathrm{gl}} < 0$, but still $E_{\mathrm{SW}} > 0$). In experiments, the low stretching speed u ($\sim$0.01 nm/s) and high temperature T ensure that tension remains low enough. In the tube of nominal diameter d_0, length L_0, and 5|7 concentration $n_{5|7}$, the total number of 5|7 in the wall is $N_{5|7} = \pi d_0 L_0 n_{5|7}$. Each 5|7 glide step changes the tube length by $\Delta L = (b^2/2\pi d)\sin(2\beta)$, where $b = 0.246$ nm is the length of Burgers vector [2,3]. According to Eq. (3), the gross frequency of such steps is controlled by the elastic strain ε, $f_{5|7} = N_{5|7}(kT/h) \times \exp(-E^*_{5|7\ \mathrm{gl}}/kT)$, and in the steady state it just keeps up with the stretching, $\Delta L f_{5|7} = u$.

From this, the elastic tensile strain is found,

$$\varepsilon \approx \frac{1}{45.3}\left[6.8 - kT\ln\left(\frac{L}{u}\frac{kT}{h}b^2 n_{5|7}\right)\right], \quad (4)$$

where k and h are the Boltzmann and Planck constants. In Eq. (4), we consider orientations of 5|7 close to the most energetically favorable, $\beta \approx 45°$.

Typically, in the experiments $L_0 \approx 40$ nm and $d_0 = 12$ nm [4], the concentration of visible kinks is low $n_{5|7} \sim 0.01\ \mathrm{nm}^{-2}$, elongation rate $u/L = 2.8/4000 = 7 \times 10^{-4}\ \mathrm{s}^{-1}$, and $T = 2273$ K. The estimated elastic strain is then only $\varepsilon \sim 1.7\%$, significantly lower than required to generate many topological defects (7.6%, above). In contrast, in a typical MD simulation [1] $L_0 = 10.6$ nm, $d_0 = 2.43$ nm, $T = 2000$ K, $u = 2$ nm/ns (faster than in experiments by a factor of 10^{11}). Then the estimated $\varepsilon \approx 13\%$ is much higher than needed to activate numerous defects. It is not surprising that complicated defects have appeared in the MD, but not in real experiments.

The above analysis shows that in experiments the CNT superplasticity occurs at rather low internal elastic strain, $\sim$2%. This low strain is important for preventing the disorder of the lattice. In contrast, in the reported [1] MD simulations, 11 orders of magnitude faster stretching results in a high strain, e.g., $\varepsilon > 10\%$, and activates large amount of topological defects. Their random motion and interactions lead to amorphization, tube necking, and failure, prior to substantial elongation. The MD simulations [1,8] represent the CNT plastic failure, not the superplasticity, which is better understood as the mobility of a few 5|7 dislocation kinks through a relatively clean lattice.

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