Pseudoclimb and Dislocation Dynamics in Superplastic Nanotubes

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(Received 28 March 2006; published 13 February 2007)

Plastic relaxation of carbon nanotubes under tension and at high temperature is described in terms of dislocation theory and with atomistic computer simulations. It is shown how the glide of pentagon-heptagon defects and a particular type of their pseudoclimb, with the atoms directly breaking out of the lattice, work concurrently to maintain the tube perfection. Derived force diagram quantifies the balance between these mechanisms, while simulations show both helical and longitudinal movement of the kinks, in agreement with the forces and with experimental observations.

DOI: 10.1103/PhysRevLett.98.075503 PACS numbers: 62.20.Fe, 61.46.Fg, 62.25.+g

The mechanics of carbon nanotubes has recognizable milestones that motivated great theoretical interest: observation and conjuncture of their perfect cylindrical lattice [1], evidence of highly bent and buckled structures [2,3], first measurements of the modulus [4,5], and continuing attempts to identify their ''true strength'' [6,7]. The initial surprise with the nanotube resilience has led to challenging strength measurements which in turn motivated conceptual development of the plastic [8–11] and brittle failure [12] mechanisms. Recent studies show that both brittle and ductile (plastic) yield to external load are concurrent [13] and the failure mechanism can follow either of the paths: an abrupt cleavage of bonds or a relatively gradual dislocation movement, with the resulting necking and failure. Naturally, the brittle mechanism dominates at lower temperatures, while plasticity becomes possible at high temperatures.

The theoretical possibility of plasticity in nanotubes [8–10] predicted almost a decade ago and described in some detail by the research that followed, has very recently found a growing experimental support [14–19]. First, significant elongation and thinning of nanotube structures, observed by several workers [15,19], suggests clearly nonbrittle behavior. Furthermore, reports of a more controllable, deliberately guided plastic deformation have appeared over the past months independently from several laboratories [14,16–18]. Recent compelling evidence [16,17] of greatly elongated yet unbroken nanotubes shows general behavior in good agreement with ''intramolecular plasticity'' theory [9], yet other important features certainly call for further development of the theoretical views.

Early theory was based on the notion of a 5|7 dislocation core—a pentagon and adjacent heptagon, surrounded by the perfect network of hexagons. Under great external tension, it can glide by bond flips (Stone-Wales isomerization, SW [20]) causing stepwise reduction of the diameter and overall elongation of the tube. Wall lattice warping near the 5|7 topological defect results in a visible kink [21]. It should propagate along the helical path [9] (i.e., a glide plane wrapped around the CNT cylinder), but cannot move in a purely axial direction since the longitudinal driving force is zero [9]. Recent high resolution microscopy shows this clearly: the kinks propagate along the tube, occasionally appearing and disappearing from the field of view [16,17], likely as a result of revolving around the axis. On the other hand, there are features that cannot be explained by the glide of a 5|7 core. In particular, a direct longitudinal kink propagation clearly seen [16,17] in several cases cannot be attributed to the glide. Furthermore, significant (multifold) loss of the mass [16,17] cannot be accounted for: dislocation glide or the underlying SW bond flips are mass conserving. A simple assumption of additional diffusion transport towards the tube end-attachments or into the atmosphere faces serious qualitative difficulties. Any noticeable concentration of the vacancies or interstitials should result in their aggregation (a mobile vacancy would encounter other vacancies sooner than it might reach the remote ends), causing the formation of voids, failure, and possible amorphization.

What else, besides the glide, goes on in the course of great plastic elongation? To understand it, here we approach the dynamics of kinks from both atomistic and dislocation theory viewpoints. We derive the main degrees of freedom for the movement of the 5|7 core in the lattice (which also reveals the main nucleation mechanisms, if the 5|7 defect is to be generated in a pristine lattice). We further analyze the origin and calculate the magnitudes of the driving forces controlling the kink dynamics, and present a convenient and general driving force diagram. This allows one to predict the preferred kink trajectory at different conditions. An atomistic step of the climb process is shown to consist of the removal of two atoms from a particular location, which is indeed favored at sublimation temperature. This eliminates the necessity of diffusion transport through the lattice, a process both too slow and detrimental to the lattice integrity. After describing the two complementary mechanisms, their driving forces, and atomistic detail, we demonstrate how they operate in the long-time simulations. Upon changing conditions, the atomic dynamics illustrates the change from glide to pure

climb, the diameter reduction and elongation, and even the trend in the chirality change, in accord with the analytical theory. The obtained comprehensive model is able to describe all major features observed in the experiments [16,17].

The key role of 5|7 dislocation in nanotube relaxation has been recognized, and how its glide [22] can occur is also known. Indeed, a single 90° rotation of a "shoulder" bond [Fig. 1(a)] causes lateral displacement of the whole 5|7 core by one lattice parameter b (Burgers vector $\boldsymbol{b}$), while a series of such SW bond flips constitutes its glide along the strictly defined crystallographic direction. Applied strain can bias such a process to the right or left, but cannot move the defect away from the glide plane (here, a line). For a nanotube under axial stress σ (N/m) the Peach-Koehler force causing such bias is shown [9] to be along the circumference, while its magnitude is proportional to the axial component of the Burgers vector [Fig. 1(b)]: $F_s = \sigma b \sin\beta$.

The activation barrier for the SW bond flip is high, yet it is the lowest energy atomic rearrangement to arise at very high temperatures [14–19]. Moreover, sublimation conditions mean that the removal of C_2 dimers (known in fullerene fragmentation [20]) become frequent, and therefore the movement of the 5|7 core perpendicular to its glide plane can in principle occur by means of a different mechanism. If some atoms are removed (or added), the extra plane terminated by the 5|7 core shortens (or extends), while the 5|7 core "climbs" [22] up in the "5" direction (or down in the "7" direction). It is easy to see that the climb displacement must be $\pm\frac{3}{4}$ of a bond length a, per each removed/added atom, Fig. 1(a). Therefore the driving force should be proportional to the drop of free energy (chemical potential, μ) as carbon diffuses away from the dislocation core elsewhere, say to the gas or cold amorphous form at the ends, $F_{\text{chem}} = 4\Delta\mu/3a$. Obviously this force is directed along the extra plane that is perpendicular to the Burgers vector $\boldsymbol{b}$, Fig. 1(b).

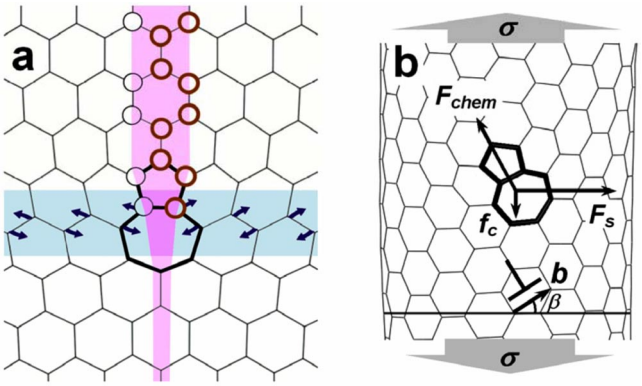

FIG. 1 (color online). (a) A pentagon-heptagon defect represents a core of edge dislocation in the all-hexagons lattice of the nanotube wall. Such a 5|7 defect can glide left or right horizontally by 90° bond flips (SW isomerizations, shown by arrows), or it can climb vertically, shortening the extra plane (shaded) by sequential removal of the atoms, e.g., those marked as thick circles. (b) The movement of 5|7 core is governed by a reduction in total thermodynamic potential, as reflected by three driving forces. $\mathbf{F_s}$ is due to the work by applied tensile stress, σ. $\mathbf{F_{chem}}$ is due to a reduction of free energy of carbon as it diffuses away into another state (e.g., sublimates into gas). Usually small $\mathbf{f_c}$ is due to a reduction in the internal elastic energy caused by the tube widening. Burgers vector $\mathbf{b}$ is at the angle β with respect to tube circumference.

The third force is due to the change of tube curvature caused by the 5|7 defect. Since the tube roll-up vector (chiral vector [20]) $\boldsymbol{c}$ changes exactly by the Burgers vector $\boldsymbol{c}' - \boldsymbol{c} = \boldsymbol{b}$, the radius change is proportional to the circumferential component of $\boldsymbol{b}$, $b \times \cos\beta$. The elastic energy per unit length of the cylinder is proportional to $1/d$, its increment leads to the estimate of a small force, $f_{\text{curv}} \sim 1\ (\text{eV}) b \cos\beta/d^2$, directed along the tube axis, towards its wider section in the Fig. 1(b). The three forces in such a diagram clearly indicate two major factors governing kink dynamics: mechanical stress σ and chemical nonequilibrium $\Delta\mu$. High temperature boosts mobility by facilitating SW flips and the diffusion of atoms, as well as increasing $\Delta\mu$, if carbon is moved to the entropy-rich gas phase, as in sublimation.

Movement of 5|7 dislocations eventually brings them to the sample boundaries, where they stop or vanish. A fresh supply is required for maintaining the extensive plastic deformations. Common Frank-Reed sources [22] cannot exist in two-dimensional graphene. However, the very same bond flip responsible for the glide can also serve as a nucleation mechanism in a perfect lattice: a bond rotation transforms any four adjacent hexagons into a dipole of 5|7/7|5, which then can split by the glide, providing a pair of new dislocations: $0 \leftrightarrow 5|7 + 7|5$.

Uniquely for the sublimation conditions, there is another source of dislocations when some atoms inevitably break out even from perfect lattice. Formation of a divacancy is the lowest energy route [23]. It is instructive to see that such removal of the two atoms is equivalent to a disruption of crystal plane, although by just a short missing segment, Fig. 2. This obviously is identical to having two "extra"

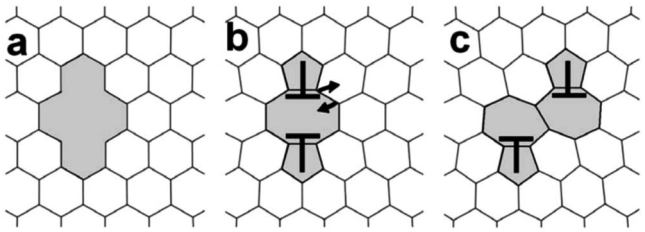

FIG. 2. Removal of two atoms creates a divacancy (a), (b), and can also be viewed as a removal of a small segment of a full crystal plane, leaving the two extra planes, that is two edge dislocations (b) able to glide away (b → c).

planes with their edges viewed as dislocation lines, that is a pair of head-to-head edge dislocations. In other words, the identity $0 \leftrightarrow 5|8|5 + C^2 \uparrow = 5|7|\ldots|7|5 + C^2 \uparrow$ can be made obvious by inspection of the bond reconstruction upon removal of two adjacent atoms from the lattice, and by further possible bond flip, Fig. 2. (Similarly, adding C_2 in the form of addimer [20] structure 7|5|5|7 essentially inserts a tiny segment of an extra plane, a pair of edge dislocations also serving as a source; however, at sublimation conditions [18] in vacuum, such addition is less likely.)

This observation leads one to its next logical extension: if removing a pair of atoms disrupts a crystal plane into two semi-infinite extra planes, then a breakout of more C atoms should further shorten an extra plane, thus moving the corresponding 5|7 dislocation, which constitutes a step of climb [22]. This unambiguously suggests a new mechanism of climb at sublimation conditions. The presence of the sublimation channel permits the bypassing of slow transport through the lattice (either diffusion of vacancies or interstitials such as addimers, etc., inherent to and rate limiting for the climb in three-dimensional solids) and opens a rapid pseudoclimb mechanism. Calculations show that indeed the energy of C_2 removal from the side of the pentagon in the 5|7 core is lower than from anywhere else in the lattice, because it does not create additional dangling bonds or topological defects [23]. The driving force $\mathbf{F}_{\mathbf{chem}}$ in Fig. 1(b) is proportional to the $\Delta\mu$ between the solid lattice and the gas vapor.

It is important to realize that the pure glide (mass-conserving movement in the $\pm\boldsymbol{b}$ directions) and pure climb (movement perpendicular to $\boldsymbol{b}$, accompanied by the mass loss or accretion) form an orthogonal basis, so that their linear combination can transfer a 5|7 defect to an arbitrary position around the lattice. This easily explains how the 5|7 kinks, stacked as a dislocation line through the layers of multiwall tube, can move together, [16,17] although their individual glide planes might diverge due to different chiralities of the walls. The mixture of glide and climb permits such 5|7 cores to migrate as a group, retaining together the lowest energy configuration. For a single 5|7 core, its most probable trajectory can be tuned by the change of conditions of tension and temperature, according to the diagram of Fig. 1(b), possibly with the addition of external force.

The discussion above identifies two constituent mechanisms of superplastic behavior, SW bond flips and C_2 removal. Molecular dynamics (MD) also clearly show these concurrent possibilities, but are prohibitively expensive for simulating an extensive process. A more affordable Monte Carlo (MC) method was modified to incorporate the bond flips (for glide) and C_2 breakouts (for pseudoclimb); at each MC step the transformation is selected to ensure the lowest possible energy of the next configuration. To simulate large systems (~1000 atoms) over extensive progression (~1000 transformations), the classical force field of Tersoff-Brenner potential [24] was used. For pure glide, its initial stages show [Fig. 3(a)] the defect helical propagation and the incurred chirality change in complete agreement with early MD simulations [11] and theoretical prediction [8,9]. Beyond that, Figs. 3(b)–3(e) show an example of significant stretching (~ 250%) achieved by a glide movement (210 SW steps total) of a few 5|7 defects. Note that the reduction of diameter is inversely proportional to the elongation, $d \sim 1/\ell$ as it should be for the mass-conserving glide process (neglecting small 3% elastic strain). A more subtle effect is the change of chirality: starting from almost an armchair tube [e.g., (12,10) in Fig. 3(b)] it gradually changes into a nearly zigzag type (11,2) in Fig. 3(c), later to (9,1)|(9,0) in Fig. 3(d), and (7,1) in Fig. 3(e), that is remains nearly zigzag upon further glide relaxation, in accord with theory [8,9].

Pure pseudoclimb, in contrast, causes a reduction of the area $(d \times \ell)$ due to mass loss, as the lattice lines (crystal planes) are being seamlessly removed by the sequence of C_2 breakouts, Figs. 4(a)–4(d). As the 5|7 core continues shuttling back and forth [Figs. 4(e)–4(h)] the

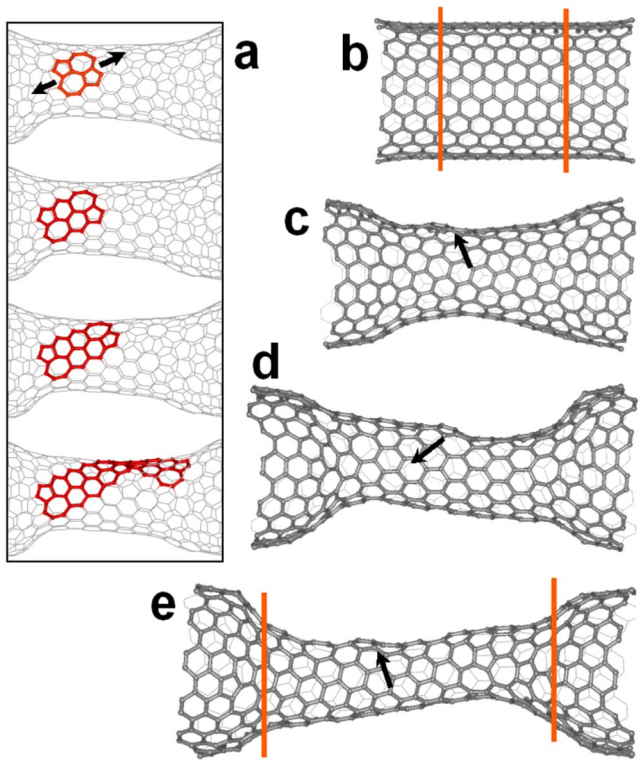

FIG. 3 (color online). (a) Glide of the 5|7's through sequential bond flips moves the associated kink along helical path, as in MD simulations [11]. Extensive simulations (b)–(e) demonstrate significant elongation, diameter reduction, and a systematic change of chirality, here from (12,10) to (7,1). Starting from an ideal structure (b), the snapshots (c), (d), and (e) show the structures after 84, 162, and 210 of SW steps, respectively. Arrows mark the positions and glide directions of the kinks.

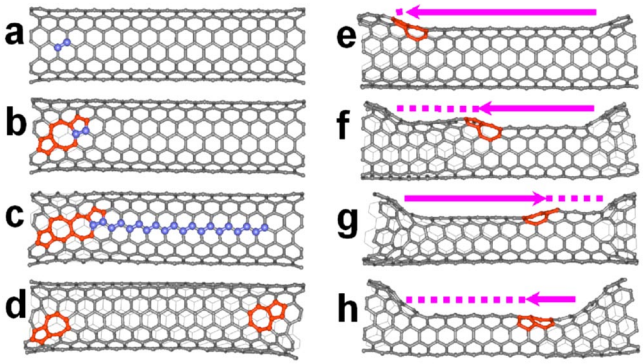

FIG. 4 (color online). The removal of atom pairs causes translational displacement of 5|7 defect complimentary to its possible glide, (a)–(d). Purely longitudinal motion can always be achieved by the mixture of climb and glide mechanisms, guided by the force diagram in Fig. 1(b), and is clearly observed in the simulations. Solid arrows mark the path traveled, and the dashed line shows its projected direction. Snapshots in (b)–(h) are the structures after the removal of 1, 2, 12, 24, 45, 58, and 72 (respectively) C_2 molecules.

tube gets thinner. Generally, a helical trajectory changes the tube length, since it has a nonzero circumferential component along the force $\mathbf{F}_s$ [Fig. 1(b)]. Then tension σ increases (if the ends are clamped) and thus greater force will bend the trajectory towards the longitudinal direction, which is always attainable by a proper mixture of climb and glide mechanisms.

A comprehensive relaxation model discussed here includes a combination of glide of the 5|7 dislocation cores and their pseudoclimb, where the atoms of the extra plane are removed directly into the gas phase. The mixture of these two mechanisms permits any direction of the kink movement. The proposed driving force diagram quantifies the balance between the mechanisms and allows one to predict the relaxation dynamics at specific conditions. Performed atomistic simulations illustrate the plasticity process in agreement with theory and with available experimental observations [14,16,17]. For example, the change of chirality, preferentially from armchair to zigzag, as observed in simulations, can determine the limits of plastic elongation: zigzag configuration is more brittle [13] and the tube is more prone to failure. It can be noted that the tube reconstruction and plasticity observed at temperatures well below the sublimation [25,26] must be greatly enhanced by the irradiation: a knock out of individual atom forms a monovacancy, able to diffuse towards the 5|7 defect and to switch this sessile dislocation into a highly mobile radical state [23], via reaction $v + 5|7 = 5|7^{\cdot}$. The $5|7^{\cdot}$ core contains extra atom with a dangling bond, and has much lower glide barrier than the 5|7 defect, thus adding significantly to the plastic flow at reduced temperatures.

This work was supported by the Office of Naval Research (DURINT), the National Science Foundation (CBEN), and the Robert Welch Foundation.

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